Selective Alkylation of Phenols Using Solid Catalysts

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for the Degree of Doctor of Philosophy

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Abstract

Alkylphenols are important industrial chemicals used in a wide range of applications. In particular, 2,6-di*tert*butylphenol is an indispensable building block for anti-oxidants and light protective agents. A new solid catalyst was prepared, characterised and tested for the alkylation of phenols with alkenes in an attempt to reduce the environmental hazards associated with the aqueous wastes generated by the homogeneously catalysed alkylation reactions.

The new silica gel supported aluminium phenolate catalyst was prepared by a two steps procedure, first grafting of an aluminium precursor such as aluminium trichloride or triethyl aluminium onto silica mainly through reaction with the support silanol groups, then exchange of the aluminium ligand with phenol. Catalysts exhibited mainly Lewis acidity and two types of active sites were detected.

The new catalyst was successfully applied in the phenol – isobutene alkylation system. Catalysts exhibited an *ortho-* selectivity for the introduction of the first *tert*butyl group. The selectivity of the second alkylation could be tuned by varying reaction conditions (reaction temperature, catalyst amount, alkene addition methods) and catalyst characteristics (support surface pre-treatment temperature, aluminium precursor and loading). Hence high yields of 2,4-di*tert*butylphenol or moderated yields of 2,6-di*tert*butylphenol were obtained.

Alkylation of phenol with other alkenes and cresols alkylations were successfully catalysed by the new silica gel supported aluminium phenolate catalyst with the same selectivity. However, the di*ortho*propylphenol was the main dialkyl products when using propene as alkylating agent.

"Greening" of the catalyst preparation by reducing the amount of solvent used was carried out without changing the selectivity and the activity of the catalyst. Reusability of the catalyst was investigated and a decrease of activity was observed. Storage of the catalyst was possible for a long time but activity and selectivity were affected.

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Declaration

Some of the results presented in this thesis have been obtained by or with the assistance of other workers. Where this is the case, the contribution of these workers has been acknowledged in the text. All other results are the work of the author.

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Abbreviations and Acronyms

+I and -I	Inductive effect
+M and -M	Electron field effect
ACS	American Chemical Society
$AlCl_3$	Aluminium trichloride
Å	Angstrom (10^{-10}m)
BET	Brunauer, Emet and Teller
BF_3	Boron trifluoride
BHT	Butylhydroxybenzene
BJH	Barrett, Joyner and Halenda
CCPA	Canadian Chemical Producer's Association
CEFIC	European Chemical Industry Council
CN	Coordination Number
COSY	Correlated Spectroscopy
δ	NMR chemical shift
DDT	Dichlorodiphenyltrichloroethane or 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane
DIB	Diisobutene
DRIFT	Diffuse Reflectance Infra Red Fourrier Transform
DRIFTS	Diffuse Reflectance Infra Red Fourrier Transform Spectroscopy
2,6-DTBP	2,6-di*tert*butylphenol
2,4-DTBP	2,4-di*tert*butylphenol
2,5-DTBP	2,5-di*tert*butylphenol
EPA	US Environment Protection Agency
eq.	Equivalent
eV	Electron Volt
FID	Flame Ionisation Detector
FTIR	Fourier Transform InfraRed
GC	Gas Chromatography
GC-MS	Gas Chromatography-Mass Spectroscopy
HCl	Hydrochloric acid
HF	Hydrofluoric acid

H_3PO_4	Phosphoric acid
H_2SO_4	Sulfuric acid
HS&E	Health, safety and environment
IPC-OEC	Inductively Coupled Plasma-Optical Emission Spectroscopy
IUPAC	International Union for Pure and Applied Chemistry
K100	Silica gel Kieselguhr 100
K60	Silica gel Kieselguhr 60
KBr	Potassium bromide
MAS-NMR	Magic Angle Spinning Nuclear-Magnetic Resonance
MCT	Mercury-Cadnium-Telluride
MS	Mass Spectroscopy
NMR	Nuclear Magnetic Resonance
OTBP	Mono-*ortho tert*butylphenol
PC	Personal computer
PhOH	Phenol
ppm	Part per million
PTBP	mono-*para tert*butylphenol
py	Pyridine
rpm	Round per minute
SM	Starting Material
2-TBP	2-*tert*butylphenol
3-TBP	3-*tert*butylphenol
4-TBP	4-*tert*butylphenol
TEAL	Triethyl aluminium
TEPO	Triethyl phosphine oxide
THF	Tetrahydrofurane
TMPO	Trimethyl phosphine oxide
TBOTBPE	*tert*butyl-(2-*tert*butylphenyl)ether
TBPTBPE	*tert*butyl-(4-*tert*butylphenyl)ether
TTBP	2,4,6-tri*tert*butylphenol
UV	Ultra Violet
XPES	X-Ray PhotoElectron Spectroscopy

Chapter 1

Introduction

1.1 Introduction

Alkylphenols are important industrial chemicals. They are used as building blocks for a wide range of applications, such as anti-oxidants, surfactants and disinfectants.

Alkyl- phenols are prepared homogeneously with Brønsted type catalysts, such as sulfuric acid, or Lewis type catalysts, based for example on boron or aluminium. The separation of the reaction mixture is carried out by distillation, requiring all traces acidic species to be removed by aqueous washes. In the case of aluminium based catalyst, the disposal of phenol and aluminium contaminated aqueous wastes leads to environment concerns. To overcome these problems and as part of the growth of interest to Green Chemistry, many new catalysts have been developed to convert the homogeneous process into a heterogeneous method, which offers many advantages: ease of separation and reusability, better yields due to enhanced selectivities, milder reaction conditions and waste minimisation.

After the description of the Green Chemistry concept, the Friedel-Crafts alkylation reaction and its mechanism are briefly described. Alkyl- phenols in general will be discussed followed by the description of their preparation method and uses. Finally a brief overview of the area of supported reagents and catalysts will be presented.

1.2 Green chemistry: history and concepts

The growing scientific knowledge of our world helped increases the quality of life to the present level. Chemists, among other scientists, have helped to fulfill all the society's needs by designing and producing things, such as for example pharmaceutical chemicals, pesticides or plastics, that we use everyday and that we take for granted[1, 2].

However, if the scientists were considered as heros for all their achievements, today the feeling regarding their work is not as bright anymore. Some outcomes were not foreseen at the time of discovery, as for example the side effect of using dichlorodiphenyltrichloroethane (DDT or 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane) as insecticide[3] or appearance of drug-resistant illnesses.

Several accidents did shake up the industries like a tsunami, of which probably the most well known, thanks to the media, are Seveso[4], Bhopal[4, 5], Chernobyl[6–10], Amoco Cadiz[11] or the Exxon Valdez[12]. These examples have contributed to the growing feeling of mistrust felt by people towards the chemical industry[4].

Following the growing pressure from the public to be less secret about their activities and a self-consciousness about safety, environment and health, initiatives were launched worldwide. 'Responsible Care' was launched by the Canadian Chemical Producer's Association (CCPA)[13]. This commitment to continuous improvement in all aspects of health, safety and environment (HS&E) was gradually adopted across the world. Guidelines for the protection of the environment were compiled and adopted by the European Chemical Industry Council (CEFIC) in 1987[14]. During the same year, the UN Commission on Environment and Development (also known as Bruntland Commission) defined the concept of 'sustainable development' as[15]:

> "Development which meets the needs of the present without compromising the ability of future generations to meet their own needs."

When applied to chemistry, this concept leads the way to the 'Green Chemistry'. The Green Chemistry Mission was first defined by the US Environment Protection Agency (EPA) as[16]:

> "To promote innovative chemical technologies that reduce or eliminate the use or generation of hazardous substances in the design, manufacture and use of chemical products."

The EPA, in conjunction with the American Chemical Society (ACS), compiled all these ideas into a set of 'Twelves Principles of Green Chemistry'(Table 1.1). The understanding and the practice of these principles when designing a new process involve a multidisciplinary approach. The researchers goal has to be the design of a new product, which is 'green' from the first atom, through the production to the final use and disposal, including the social impact of their discoveries and works[17].

These also imply the development of the so-called green-metrics, to be able to

1. Waste prevention is better than treatment or clean-up
2. Chemical synthesis should maximise the incorporation of all, starting materials
3. Chemical synthesis ideally should use and generate non-hazardous substances
4. Chemical products should be designed to be non-toxic
5. Catalysts are superior to reagents
6. The use of auxiliaries should me minimised
7. Energy demands in chemical syntheses should be minimised
8. Raw materials increasingly should be renewable
9. Derivations should be minimised
10. Chemical products should break down into innocuous products
11. Chemical processes require better control
12. Substances should have minimum potential for accidents

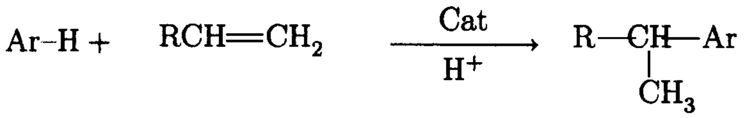
Table 1.1: The twelve Principles of Green Chemistry[2].

compare processes, and decide which one is the greenest. The atom efficiency (ratio of molecular weights of desired product to the sum of the molecular weights of all materials produced) or E-factor (ratio of the weight of 'non-useful' products to the weight of 'useful' products)[18, 19] are some examples of such green metrics. Hence, in practice, if chemists want to become green chemists, they have to change the way they think about a reaction and find the path towards the achievement of the ideal synthesis (Table 1.2).

1. Environmentally acceptable
2. Use of readily available materials
3. Simple and safe
4. One step with 100% yield
5. Atom efficient and no wasted reagents

Table 1.2: The ideal synthesis[20].

$$\text{Ar–H} + \text{RX} \xrightarrow{\text{Cat}} \text{Ar–R} + \text{HX} \tag{1.1}$$



$$\text{Ar–H} + \text{RCH}{=}\text{CH}_2 \xrightarrow[\text{H}^+]{\text{Cat}} \text{R—}\underset{\displaystyle \text{CH}_3}{\underset{|}{\text{CH}}}\text{—Ar} \tag{1.2}$$

Table 1.3: General Friedel-Crafts alkylation reactions.

1.3 Friedel-Crafts aromatic alkylation

1.3.1 The Friedel-Crafts reactions

The discovery of the action of aluminium chloride on aromatic compounds opened a door in the chemistry world. Charles Friedel and James Mason Crafts were the first, in 1877, to recognise the role and the need of only a catalytic quantity of the metal halide in the reaction between an aromatic compound and an alkyl halide[21, 22]. The scope of this discovery was then extended to other affiliated reactions and is now known as the Friedel-Crafts reaction, one of the most important 'named' reactions in chemistry.

Friedel-Crafts reactions were originally related to the formation of a carbon – carbon bond between two organic molecules, one of them being an aromatic compound, in the presence of an acidic metal halide catalyst. The scope of the reaction today is much wider, and includes any reaction between two molecules in the presence of a so-called "Lewis acid" acidic halide, a proton acid or a solid acid catalyst. These reactions are part of the electrophilic family of reactions. These include any addition, substitution, isomerisation, elimination, cracking, or polymerisation reaction.

Different classifications of Friedel-Crafts reactions have been proposed[21, 22], the most common being the classification into 'alkylation' and 'acylation' reactions. For the purpose of this discussion, alkylation reactions catalysed by Lewis acids will be of major interest.

An alkylation reaction involves introducing alkyl groups into aromatic or aliphatic compounds. The general reaction scheme is represented in Table 1.3[21]: in presence of a Lewis acid catalyst, an aromatic compound reacts with an alkylating agent to yield the alkylated aromatic product. Three types of alkylating agents are used, alkyl halides, alcohols (RX, Equation 1.1) or alkenes (for example $RCH=CH_2$, Equation 1.2).

The alkylation reaction proceeds following the generally accepted mechanism: the alkylating agent interacts with the catalyst (with the help of a co-catalyst in the case of an alkene) yielding an alkyl-metal-halide complex. The resulting carbocation reacts with the aromatic ring to form the alkylated aromatic product by the substitution of one hydrogen from the ring by the alkyl group.

The following discussion will now focus on the use of alkenes as alkylating agents.

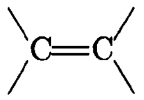
1.3.2 Alkenes as alkylating agents

The first alkylation using alkenes as alkylating agents was carried out by Balsohn in 1879[23]. Since then, they have become the most used alkylating agents as they are inexpensively available from petroleum cracking[21, Chapter 2].
The use of alkenes requires that the reaction conditions are finely controlled:

- alkenes have a tendency to polymerise when in presence of an acid catalyst, the reaction is therefore often carried out with an excess of aromatic substrate and with a small amount of catalyst,

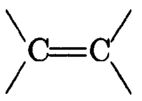
- Brønsted catalysts are active as such for the alkylation of aromatics with alkenes; however a co-catalyst is required in the case of an Lewis acid catalyst to activate the alkenes (traces of water, for example, can be sufficient to act as proton source).

The mechanism of the alkylation reaction with alkenes involves the formation of a reactive intermediate, a carbocation or a polarised complex, which then reacts with the aromatic ring. The reactive intermediate is formed *via* protonation of the double bond (Equations 1.3 and 1.4).



$$+\,\mathrm{HA} \longrightarrow \mathrm{R}^{\delta^{+}}\mathrm{A}^{\delta^{-}} \qquad (1.3)$$

Brønsted acids as catalyst



$$+\,\mathrm{HX} + \mathrm{MX}_{n} \longrightarrow \mathrm{R}^{\delta^{+}}\mathrm{MX}_{n+1}^{\delta^{-}} \qquad (1.4)$$

promoted Lewis acids as catalyst

From all the Lewis acids used as catalysts for the alkylation of aromatic compounds with alkenes, aluminium trichloride with hydrogen chloride as co-catalyst is still the preferred catalyst; although not as effective as an initial alkylating catalyst such as the Brønsted acids sulfuric acid; aluminium chloride is much more active in de- and trans-alkylation of unwanted poly-alkyl products. Alkylations of phenol with alkenes have been carried out with these catalysts and other Lewis and Brønsted acids, but also with pure metal, mostly aluminium. This aspect will be discussed in details in the section 1.6.

1.3.3 Mechanism of the Friedel-Crafts alkylation

1.3.3.1 The arenium ion mechanism

The Friedel-Crafts alkylation of aromatic substrates proceeds *via* the electrophilic substitution of a ring hydrogen (or group) by an electrophile (for simplicity during the discussion about the mechanism, the carbocation will be noted E^{+}, and the leaving group R) formed from the interaction between the alkylating agent and the catalyst. This reaction takes place *via* an arenium ion mechanism, in which the first step is aromatic ring electrophilic attack, forming a positively charged intermediate (arenium ion). This ion regains aromaticity by the departure of the hydrogen (or group). The existence of arenium ions (also called Wheland intermediates or σ-complexes)[24, Chapter 11] has been confirmed and details can be found in the literature[21, 22, 25]. However, the question is still open as to how the arenium ion is itself formed: either by direct addition of the electrophile to the aromatic ring to form the σ-complex, or formation *via* a π-complex, as described by the Figure 1.1[26].

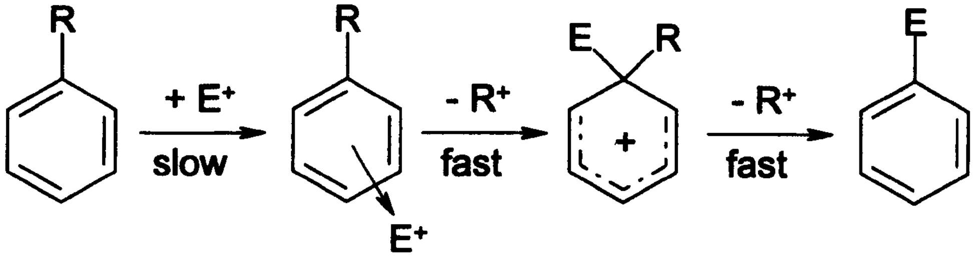


Figure 1.1: Arenium ion mechanism: *via* a π-complex.

1.3.3.2 Electrophilic Substitution of mono-substituted aromatic substrates

The mechanism so far has been described for non-substituted aromatic ring (benzene). In the case of the mono-substituted substrates, the position of the electrophilic attack and the reaction rate will be affected by the substituent 'R', due to its electronic influence on the electron density of the aromatic ring.

The substituent R can have two effects on the electron density of the ring: either it activates the ring, when the substituent has an electron-donating field effect (noted *+I*), or it deactivates the ring, when the substituent has an electron-withdrawing field effect (noted *-I*). In many cases, another effect can interfere with, and even overcome, the electron field effect: the resonance interaction between the substituent and the ring (noted *+M* or *-M*). The effect *+M* occurs when the substituent can share a pair of electron with the ring, the effect *-M* occurs when the substituent can accept such a pair of electron. This effect can either contribute in the same direction as the field effect or opposes it.

These substituents effects affect the electronic density of the aromatic ring of the aromatic compound, and so all the reaction intermediates. Table 1.4 illustrates the three possible arenium ions formed by the electrophilic attack of a mono-substituted aromatic substrate, along with the resonance hybrids. The resonance forms drawn in the fourth column are only possible if the substituent does have a *+M* effect. The position of the attack of the electrophile 'E' will depend mainly from the relative stability of these intermediates. An empirical rule can be drawn, regarding the effect of the substituent R on the orientation of the electrophilic substitution, called the "Holleman" rule [27, Chapître 12]. The group R can be put into three categories:

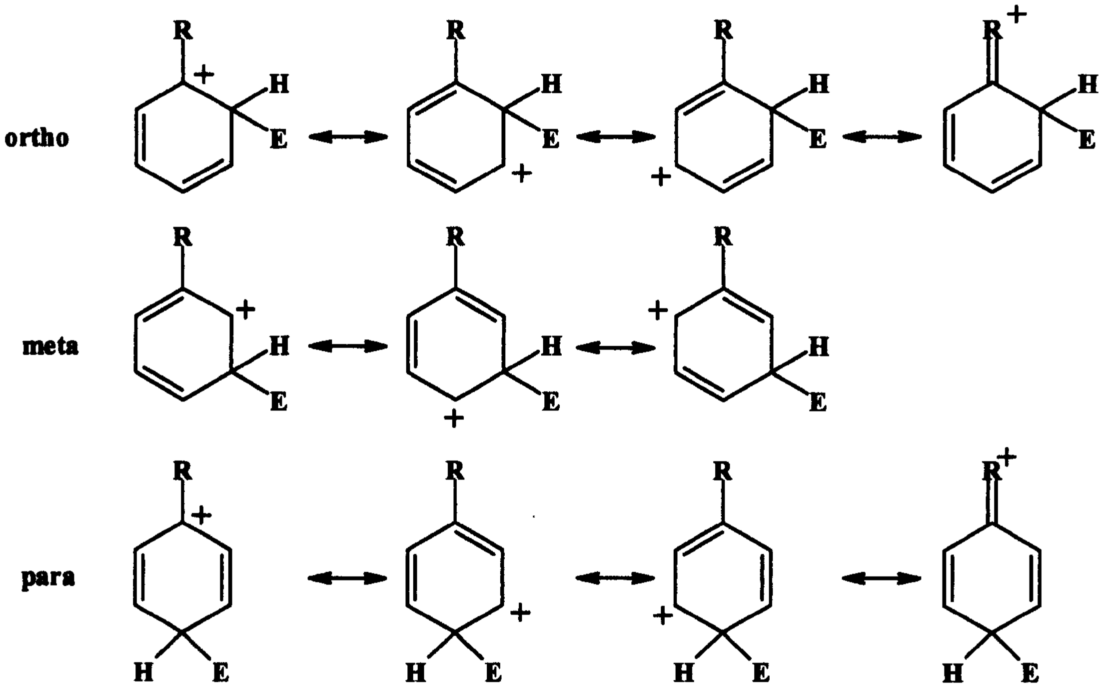


Table 1.4: Resonance structures for the three positional isomers of the arenium ion. The fourth column reproduces additional resonance structures for activating substituent (*+M* effect).

- *+I* or *+M* (with *-I* negligible): *ortho-* and *para-* directing, activating, (such as –OH, –NH_2, –R, –OR)
- *-I* or *-M* : *meta-* directing, deactivating, (such as –NO_2, –SO_3H, –COOH, –CHO, –COR, –CN)
- *-I* (strong) and *+M* : *ortho-* and *para-* directing, deactivating (halides).

No examples of a substituent, which would activate the ring and directs to the *meta-* position, are known[28].

In the case of phenol, the substituent 'OH' exhibits a *+I* effect as well as a small *+M* effect, the electrophilic attack can then be predicted to be directing to the *ortho-* and the *para-* position. The ratio *ortho-* / *para-* is more difficult to predict. Statistically, there should be twice as much *ortho-* than *para-* products. It is often not the case. The relative approximate charge distribution on the two positions, steric hindrance induced by the substituent or the catalyst, or reaction conditions will influence the direction of the electrophilic attack [24, Chapter 11].

In the case of poly-substituted substrates, in order to predict to a certain extent, the position of electrophilic attack and the reaction rate, the various resonance structures of the arenium ion have to be drawn and the relative stability of the intermediates and the electronic density of the ring accessed. Then other parameters such as steric hindrance have to be taken into account[29].

1.4 The alkyl-phenols: facts and figures

1.4.1 Phenols

The New Penguin English Dictionary[30] defines 'phenol' as follows:

1. A caustic poisonous acidic chemical compound present in coal tar, a derivative of benzene containing a hydroxyl (OH) group in place of a hydrogen atom. It is used in dilute solution as a disinfectant.
2. Any of various acidic chemical compounds analogous to phenol in that they contain one or more hydroxyl groups attached to a ring of atoms similar to a benzene ring.

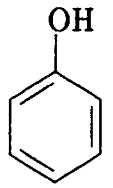


Figure 1.2: Phenol, the simplest member of the aryl alcohol family.

Phenol (Figure 1.2) is the simplest member of the family, with a chemical formula of 'C_6H_5OH'[31]. Chemists first isolated this chemical as a natural compound by stirring coal tar medium range oils with concentrated sodium hydroxide solution. The aqueous layer was separated and acidified with a mineral acid, leading to an oil layer formation. The first compound, obtained by fractional distillation of this oil, had a boiling point of about 175°C, crystalised on cooling and had a melting point of 40°C. Due to the extraction method, the compound was considered as an acid, and called 'carbolic acid' by F.F. Runge in 1834, then 'phenic acid' by A. Laurent[31]. Soon, the absence of the carboxylic acid function was established (in contradiction with all organic acid compounds then known) and called in 1841 by A. Laurent and C. F. Gerhardt "phenol"[32]. The name of phenol conforms to the IUPAC nomenclature: phenol results from

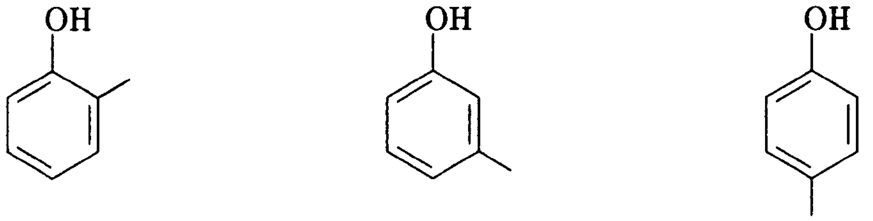


Figure 1.3: *ortho-*, *meta-*, and *para-* Cresol.

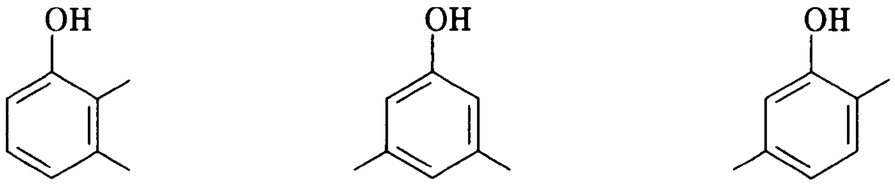


Figure 1.4: Examples of xylenols (dimethylphenols).

the substitution of a hydrogen from the benzene ring (the official but unused name is 'phene') by an hydroxyl group[31].

As defined by the New Penguin Dictionary, phenols is also a generic name used to name various compounds, where a hydroxyl group is bonded directly to the aromatic ring, such as cresols (figure 1.3), xylenols (figure 1.4). These phenols were also historically extracted from coal tar *via* the same method used for phenol itself.

Phenols are powerful antiseptics, they were used as such by Joseph Lister as early as 1865[33]. But in general, phenols are corrosive and highly toxic. They are nevertheless still used for disinfection and in veterinary surgery. However, the main interests of the natural or synthetic phenols are their uses as intermediates for various products. The uses of alkylphenols will be presented in the section 1.4.6.

1.4.2 Reactivity of the phenol

Because of the presence of the chain C–O–H, phenol seems similar to an alcohol. But the interaction between the hydroxyl group and the aromatic ring alters both reactivity of the C–OH group (compared to alcohol) and the aromatic ring (compared to the benzene derivatives)[27, Chapître 12].

Regarding the function reactivity: the O–H bond can be easily broken, due to

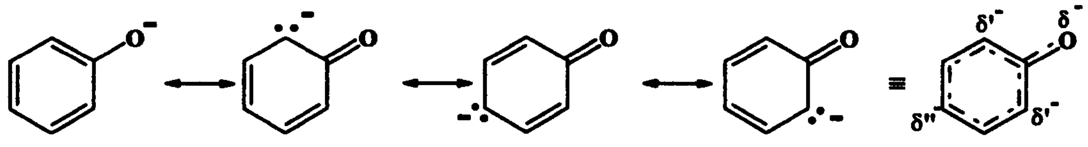


Figure 1.5: Canonical forms of the stabilisation of the phenolate ion.

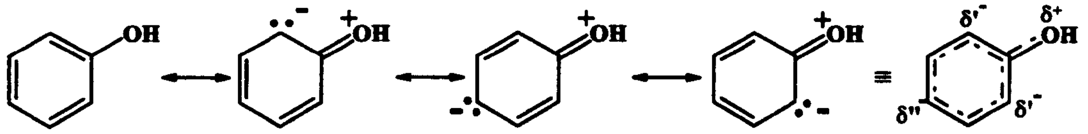


Figure 1.6: Electronic density repartition in the phenol molecule.

the partial positive polarisation of the oxygen (which increases the polarisation of the O–H bond compared to alcohol) and the stabilisation by resonance of the conjugated base, as shown in Figure 1.5. The C–O bond is stronger compared to the alcohol analogs, due to the delocalisation of the electron pairs of the oxygen with the electrons of the aromatic ring, as shown in Figure 1.6[27, Chapître 12]. Compared to the alcohols, phenols are more acidic and less nucleophilic.

Regarding the ring reactivity: the ring is activated by the OH group, therefore, substitution reactions will be facilitated (oriented in *ortho-* and *para-* positions, as described in the section 1.3.3.2).

1.4.3 General preparation methods of phenols

Coal tar is today a small source of pure phenols. If phenol, the most volatile one, can be easily extracted, the separation of the derivatives are more difficult, due to the similar boiling point of the isomers. Pure phenols are today synthesised from an aromatic substrate.

1.4.3.1 Preparation of the phenol itself[31, 34–36]

Historically, phenol was prepared industrially from benzene. Three different methods (2 to 4) were employed, all of them were replaced by the methods developed by Hock (method 5) and by Dow (method 6).

Method 1: Historical isolation of the phenol, by distillation of coal tar oils.

Method 2: After the mono-nitration of benzene, the nitrobenzene was then reduced into aniline, which was then converted into the diazonium counterpart (sodium nitrite in sulfuric medium). The hydrolysis of the diazonium ion led to the phenol.

$$\begin{aligned}
C_6H_6 + HNO_3 &\xrightarrow{H_2SO_4} C_6H_5NO_2 + H_2O \\
C_6H_5NO_2 + 3H_2 &\xrightarrow{[cat]} C_6H_5NH_2 + 2H_2O \\
C_6H_5NH_2 + HNO_2 + HCl &\xrightarrow{0°C} C_6H_5N_2^+Cl^- + 2H_2O \\
C_6H_5N_2^+Cl^- + H_2O &\xrightarrow{100°C} C_6H_5OH + N_2 + HCl \qquad (1.5)
\end{aligned}$$

Method 3: The initial step involved the sulfonation of the benzene. The resulting acid was first, neutralised, then converted into the phenolate. The phenol was finally generated by acidic hydrolysis.

$$\begin{aligned}
C_6H_6 + H_2SO_4 &\xrightleftharpoons{oleum} C_6H_5SO_3H + H_2O \\
C_6H_5SO_3H + NaOH &\longrightarrow C_6H_5SO_3Na + H_2O \\
C_6H_5SO_3Na + 2NaOH &\longrightarrow C_6H_5ONa + Na_2SO_3 + H_2O \\
C_6H_5ONa + HCl &\longrightarrow C_6H_5OH + NaCl \qquad (1.6)
\end{aligned}$$

Method 4: The benzene was first chlorinated. The chlorobenzene was then hydrolysed (acidic medium) or saponified (basic medium) at 350°C.

$$\begin{aligned}
C_6H_6 + Cl_2 &\xrightarrow{AlCl_3} C_6H_5Cl + HCl \\
C_6H_5Cl + OH^- &\xrightarrow{base} C_6H_5OH + Cl^- \qquad (1.7)
\end{aligned}$$

Method 5: This method, also called cumene process, was developed by Hock in 1945. The first step is the synthesis of cumene from benzene and propylene in presence of a catalyst (H_3PO_4 or zeolite). The cumene is then oxidised by the air into the hydroperoxide, which decomposes with heat in presence of an acidic catalyst into phenol and acetone. The interest of this method arises from the increase of value of the two hydrocarbon compounds, and the combined preparation of two interesting chemicals.

$$
\begin{aligned}
C_6H_6 + CH_2 = CHCH_3 &\xrightarrow{H^+} C_6H_5CH(CH_3)_2 \\
C_6H_5CH(CH_3)_2 &\xrightarrow{\text{air}} C_6H_5C(CH_3)_2OOH \\
C_6H_5C(CH_3)_2OOH &\xrightarrow{\text{air}} C_6H_5OH + CH_3COCH_3 \qquad (1.8)
\end{aligned}
$$

Method 6: The Dow process involves the radical oxidation of toluene to benzoic acid as first step. The second step is oxidising decarboxylation to phenol.

$$
\begin{aligned}
C_6H_5 - CH_3 + O_2(\text{air}) &\xrightarrow[\text{-}H_2O]{\text{cat}} C_6H_5 - COOH \\
C_6H_5 - COOH + O_2(\text{air}) &\xrightarrow[\text{-}CO_2]{\text{cat}} C_6H_5OH \qquad (1.9)
\end{aligned}
$$

1.4.3.2 Preparation of other phenols

Other members of the phenol family may be extracted or prepared following the same methods. This is the case of cresols, xylenols or naphthols.
But as phenol is an aromatic compound itself, derivatives can be prepared by reactions involving aromatic substrates, such as for example Friedel-Crafts reactions. March gives a list of 28 different reactions with phenols as products, such as Fries or Claisen rearrangements or cleavage of phenolic ethers[24].

The discussion will now be focussed on the alkylphenols, some of which are the target product of the work introduced in this thesis.

1.4.4 General physical and chemical properties of alkylphenols[37, 38]

Alkylphenols are defined as a derivative of benzene, in which one ring hydrogen has been replaced by an OH group, and one or more other ring hydrogens have been replaced by a substituent being either an alkyl, alkenyl, cycloalkyl, cycloalkenyl or aralkyl group only.

Extensive descriptions of the phenols physical and chemical properties can be found in the literature[34]. The main properties of the alkyl-phenols are summarised in this section.

1.4.4.1 Physical properties of the alkylphenols

In general, pure alkylphenols are either colourless liquids or low-melting crystals. The *para-* isomer has the highest melting point. Their boiling points are above 200°C at normal pressure. The difference between the boiling point of the *meta-* and the *para-* isomers is very small; but the *ortho-* isomer boils at a temperature 10-20°C lower than the *para-* isomer.

Alkylphenols are soluble in polar organic solvents and their solubilities in hydrocarbon solvents increase with the number and size of their ring substituents. In water, the opposite trend is observed. The water solubility decreases with the proximity of the alkyl group, as the hydroxyl group is shielded from the water.

1.4.4.2 Chemical properties of the alkylphenols

Compared to phenol itself, the chemical behaviour of the alkylphenols deviate with the number, the size and branching of the alkyl groups. The more the hydroxyl group is sterically hindered, the less "phenolic" is the behaviour of the alkylphenol. This is explained by the difficulty to access the hydroxyl group.

Alkylphenols are less acidic than phenol. In general, alkyl groups exhibit a *+I* effect. They therefore tend to push the electron density back to the oxygen, destabilising the conjugate base PhO^-. The trend in the acidity decrease is from the *meta-* isomer, then the *para-* to the *ortho-*. Within the *ortho-* isomers, the branching in their α-position decreases furthermore the acidity, by hindering the solvation of the phenolate anion. These properties can be used to separate alkylphenols by solubilising them selectively in alkali solutions or Claisen solution (potassium hydroxide in a mixture of water and methanol).

Organic reactions, breaking the O–H bond, can be performed with alkylphenols, such as etherification and esterifications. As the electron density on the oxygen is

lower compared to their alcohol counterparts, these reactions require either activated reagents or activation of the alkylphenols to alkylphenolates. For example, esterification with carboxylic acids is slow and limited, while esterification with acid chlorides or anhydrides and etherification in alkali medium are easy[31]. As for other properties, bulky alkyl groups in the *ortho-* position reduce the reactivity and special reaction conditions are required.
Ipso attacks are also possible but are difficult. At high temperature in presence of a palladium-based catalyst, alkylaniline can be prepared from alkylphenols.

Hydrogenation of the aromatic ring is possible catalytically. Alkylcyclohexanols and alkylcyclohexanones are the reaction products. Ketones are preferably formed in case of sterically hindered alkylphenols.

Phenols in general are sensitive to oxidation; colouring is often observed when phenols are exposed to air. Depending on oxidation conditions and oxidising agents, various types of chemicals are formed, such as, for example, quinones, aldehydes or linked products. Stronger oxidising agents decompose the aromatic rings and yield fatty acids.

As aromatic substrates, alkylphenols can undergo electrophilic aromatic substitution (Friedel-Crafts type reactions). Hydroxyl group exhibits a *+I* and a *+M* effect, therefore, the electrophilic substitution is easier compared to benzene (activated ring) and will preferably take place on the available *ortho-* and *para-* positions. However, particularly with nitration or halogenation reactions, substitution or displacement of alkyl groups by the electrophile can also occur, when several bulky alkyl groups are present.
Alkylphenols can also be further alkylated in presence of Friedel-Crafts type catalysts. However, care in the reaction conditions has to be taken to avoid side reactions, such as positional isomerisation, transalkylation or dealkylation. The tendency to undergo these types of reactions follows the order: primary, then secondary, then tertiary alkyl groups. The *meta-* isomer is the most thermodynamically stable, and is the product of isomerisation equilibrium. Alkyl groups attached to the phenol ring at this position are also less prone to cleavage than those attached to *ortho-* and *para-* position. Dealkylation occurs in presence of an acid or acid-forming substances, also for example during purification by distillation.

*tert*butylphenols(total)	128000
2,6-di*tert*butylphenol	25000
2,4-di*tert*butylphenol	15000
Butylhydroxytoluene (BHT)	~ 40000
Higher alkylphenols(total)	540000

Table 1.5: Worldwide productions of some alkylphenols. Values are given in tons per annum.

1.4.5 Industrial production of alkylphenols

Alkylphenols are found in various natural sources, such as various coal, wood, lignin or petroleum oils. They are also present in many natural essential oils and fragrances or used by natural species as defensive secretions.

Alkylphenols can be extracted by various cracking processes, but the main actual industrial production process is the catalytic Friedel-Crafts alkylation of phenol cresols and xylenols by olefins. Olefins are readily available and cheap alkylating agents. Alkyl halides and alcohols are used only if they are more readily available (for example, cyclohexanol) or the corresponding alkene does not exist (for example methanol or benzyl chloride).

Table 1.5 gives production levels of *tert*butylphenols and higher alkylphenols (alkylphenol when at least one alkyl group with 8 or more carbons) in 1999[38]. Butylhydroxytoluene (BHT) and 2,6-di*tert*butylphenol are alkylphenols of particular importance industrially, accounting for around half the worldwide production of *tert*butylphenols.

In the sections 1.5 and 1.6, the Friedel-Crafts alkylation of phenol with alkenes as alkylating agents will be presented. The first section will discuss the reactions generally, while the second will focus particularly on the selective *ortho-* alkylation of phenol.

1.4.6 Use of alkylphenols

Examples of alkylphenols, their use and the main industrial production methods are listed in Table 1.6. More examples and details can be found in the literature[37].

Table 1.6: The industrial uses of alkyl-phenols, some examples. They are used either as is or as starting materials (indicated by SM).

Phenol	Uses	Examples of production methods and catalysts used
tri-methyl-	Vitamin E synthesis, herbicides, acaricides, insecticides (SM).	By-products of cresol production, gas phase phenol, cresol or xylenol methylation (metal oxides).
2-, 3-ethyl-	Photochemicals (SM).	Alkylation of phenol (aluminium triphenolate), sulfonation of ethylbenzene and alkali fusion.
4-ethyl-	Antioxidants (SM), intermediates for pharmaceuticals or dyes.	Sulfonation of ethylbenzene and alkali fusion.
3-methyl-6-isopropyl- (thymol)	Antiseptics (SM).	Alkylation of *meta*-cresol with propene (activated alumina), gas phase alkylation (zeolites).
2-*sec*-butyl	Herbicides, acaricides, insecticides (SM).	Alkylation of phenol with *n*-butene (metal oxides or aluminium triphenolate).
2-TBP	Antioxidants (SM).	Alkylation of phenol with isobutene (metal oxides or aluminium triphenolate).

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Phenol	Uses	Examples of production methods and catalysts used
3-TBP	Few industrial applications.	Isomerisation of TBP or dealkylation of TTBP(acid-activated clays, zeolites, trifluoromethanesulfonic acid).
4-TBP	Co-monomer for phenolic resins, antioxidants (SM), flagrances (SM), UV stabilisers (SM).	Alkylation of phenol with isobutene (clays, zeolites, ion-exchange resins or strong Brønsted acids).
2,4-DTBP	UV stabilisers (SM).	Alkylation of phenol with isobutene (ion-exchange resins).
2,6-DTBP	Light stabilisers and protection agents, antioxidants (important SM).	Alkylation of phenol or OTBP with isobutene (aluminium triphenolate).
TTBP	Antioxidants (SM).	By-products of alkylation of phenol with isobutene.
*tert*butyl of *m*- or *p*- cresol	Light stabilisers and protection agents, antioxidants (SM).	Alkylation of cresols with isobutene (sulfuric acid), trans-alkylation (acid-activated clays), debutylation of cresol (aluminium triphenolate or zirconium phenolate).

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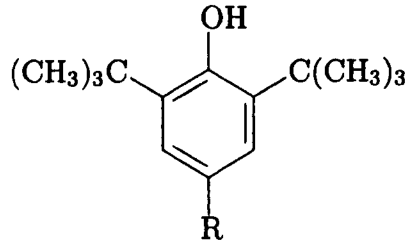
Phenol	Uses	Examples of production methods and catalysts used
BHT	Antioxidants.	Alkylation of *para*-cresol (sulfuric acid).
2,4-*tert*pentyl-	Light stabilisers (SM), photographic color developers (SM).	Alkylation of phenol with methylbutenes (acid-activated clays).
Higher alkyl- (mainly *4-octyl-* *4-nonyl-* *4-dodecyl-*)	Light stabilisers (SM), co-monomers for phenolic resins, surfactants (SM), antioxidants (SM), lubricant oil additives (SM), dispersants (SM).	Alkylation of phenol with higher alkenes (ion-exchange resins, acid-activated clays or aluminosilicates).
2-cyclopentyl-	Toner components.	Alkylation of phenol with cyclopentene (metal oxides, aluminium triphenolate,boron trifluoride or clays).
2-, 4-cyclohexyl-	Intermediates for pharmaceuticals, agrochemicals (SM).	Alkylation of phenol with cyclohexene or cyclohexanol (same as for cyclopentylphenol, and phosphoric acid).
2-, 4-benzyl-	Disinfectants.	Alkylation of phenol with benzyl chloride without catalyst, or in presence of a Lewis acid.



a: R = CH_2OH
b: R = CH_2Cl
c: R = $CH_2CH_2COOCH_3$
d: R = $COOH$

Table 1.7: Industrially important derivatives of 2,6-DTBP.

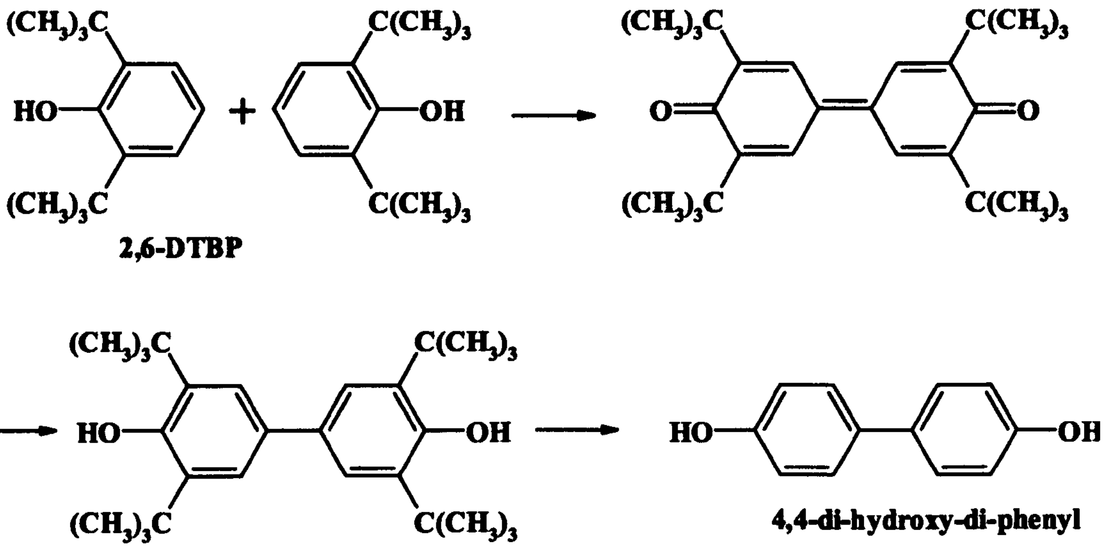


Table 1.8: Preparation of the 4,4-dihydroxydiphenyl from 2,6-DTBP.

From the examples listed in Table 1.6, several phenols of industrial importance are still produced with homogeneous aluminium triphenolate, including the 2,6-DTBP. This particular alkylphenol is a necessary building block of high molecular mass anti-oxidants and light-protection agents for plastics. Table 1.7 provides examples of such derivatives. Another important use of 2,6-DTBP is the synthesis of the building block for thermo-resistant polymers, 4,4-dihydroxydiphenyl (Table 1.8)[38].

1.5 Phenol alkylation with alkenes[21, 22, 37]

In regard of the wide range of applications of the alkylphenols, the Friedel-Crafts phenol alkylation reactions are very important industrially, in particular, with alkenes as alkylating agents.

As presented earlier in this chapter, the electrophilic substitution of the phenol is facilitated by the nucleophilic activity of the phenol (increased electron density induced by the hydroxyl group); therefore, compared to other aromatic hydrocarbon substrates, the alkylation of phenol requires milder conditions.

Also, the hydroxyl group is directing the electrophile to the *ortho-* and *para-*positions. Therefore mono-*ortho-*, or *para-*alkyl, 2,4- or 2,6-dialkyl and 2,4,6-trialkylphenols are formed. The more thermodynamically stable *meta-*isomer can be prepared with stronger conditions, *via* isomerisation.

However complications can be encountered during the alkylation reaction:

- formation of aryl-ethers occurs, when very mild conditions are used,
- in presence of certain catalysts, the phenol ring is readily attacked,
- the hydroxyl group has a tendency to complex to the catalyst (in some cases, it can be in the favour of the reaction, see section 1.6).

Catalysts used depend on the substrate, the alkenes and the reaction conditions[21, 38]. Lewis acids such as $AlCl_3$, BF_3, or Brønsted acids such as HF, H_2SO_4 or H_3PO_4 are used. The selective *ortho-* alkylation of phenols is achieved with aluminium triphenolate ($Al(OPh)_3$). Solid catalysts are also suitable, examples are acidic ion-exchange resins or sulfonated polystyrenes, γ-aluminium oxide or zeolites. More detailed examples can be found in the literature[21, 37, 39]. Solid catalysts present the advantages to avoid aqueous washes at the end of the reaction, but only to a certain extent. The reaction has to be carried out carefully to avoid any formation of acidic abrasive particles, which have to be filtered off (this is satisfactory) or neutralised by aqueous washes (which cancels the advantages of the use of solids).

Industrially, three main processes are used: liquid-phase alkylation, without solvent, where the alkene is added to a mixture of catalyst / phenol, or fixed-bed liquid or vapour phase. In most cases, the product has to be recovered by distillation, with recycling of unreacted substrates, after complete removal of all traces of acidic compounds or abrasive particles by aqueous washes (water or sodium hydroxide solutions), to avoid side reactions during the purification process[38]. Unwanted products can be recycled as well, by trans- or de-alkylation using the same catalyst as for the alkylation reaction. But often only the starting materials are separated and the products are used as a mixture.

Regio-selectivity control is possible[40]. Most of the Brønsted type catalysts lead to *para-* substituted phenols. Lewis type catalyst, such as $AlCl_3$, BF_3, also lead firstly to *para-* substituted phenols. In contrast, aluminium triphenolate leads nearly exclusively to *ortho-* and di*ortho-* substituted phenols. γ-Aluminium oxide is used, when *mono- ortho-* phenols are desired. The *ortho-* selectivity will be discussed in more detailed in the section 1.6.

The mechanism of the alkylation of phenol is not entirely defined. If very mild reaction conditions, such as mild catalysts or low temperature, formation of ethers are observed. These ethers were believed to be intermediate to the alkylation in the following way: the ether is formed and then undergoes rearrangement into the alkylphenol[41–43]. Shortly after, other studies ruled out this pathway[44], but did not rule out the role of the ether, in the following way: ether is formed, then the ether undergoes a Friedel-Crafts alkylation, the resulting alkyl-phenol-ether is splited into alkene and alkylphenol[29]. It is now generally accepted that the alkylation proceeds *via* an electrophilic attack on the *para-* position of the phenol itself or its ether counterpart. The mechanism of the *ortho-* alkylation of phenol will be detailed in the next section (Section 1.6).

The stability of the alkylphenols depend on the reaction conditions. Heating them in presence of acidic catalysts (the same as those used to synthesise them) leads to side reactions, such as dealkylation (sometimes followed by realkylation), trans-alkylation and isomerisation[45]. The more branched the alkyl group is, the more likely the products will undergo side reactions, and therefore in the case several alkyl groups are to be inserted into the ring, the last one to be introduced has to be the most branched. Methyl groups are very stable once attached to the ring and can be moved only with great difficulty. As the *meta-* isomer is the most stable thermodynamically, de-alkylation reactions are occurring more easily in the *ortho-* and the *para-* position, and isomerisation leads to an equilibrium where the isomers 3- and 3,5- are predominant. Finally, regarding the trans-alkylation, the major isomers depend on the nature of the catalyst, *para-* isomer for *para-*directing and *ortho-* isomer for *ortho-* directing catalysts.

As the discussion shows, the optimal product distribution can be achieved by careful reaction condition control. The discussion in the next section will focus on the selective *ortho-* alkylation of phenol with alkenes.

1.6 The *ortho*-alkylation of phenol with alkenes[21, 38, 40, 46]

The *ortho*-alkylation of phenol with alkenes requires the selective introduction an alkyl group on the *ortho-* position without substituting the *para-* position, using alkenes as alkylating agents. This section will first present the discovery of this reaction, then detail the different parameters influencing, and catalysts used to carry out, this reaction. Finally, the mechanism will be detailed.

1.6.1 The discovery of the *ortho*-alkylation of phenols with alkenes

The first synthesis of an *ortho*-alkylated phenol was reported in 1924 by von Auers and Wittig[47]. Since then, several examples of *ortho-* alkylation of phenol *via* a Friedel-Crafts reaction were reported[see for examples 48, 49]. But none of them were economically viable: the method involved the protection of the *para-*position, the alkylation in the only available *ortho-* positions, and finally, the de-protection of the *para-* position.

The first selective *ortho-* alkylation of phenol with alkenes were discovered in 1954 independently by two research groups from Ethyl Corp.[50, 51] and Bayer A.G.[52, 53]. Both groups achieved the *ortho-* alkylation by using aluminium triphenolate as catalyst. This discovery allowed the studies of the *ortho*-phenols, as they became easily available.
Since these reactions discovery, many studies have dealt with the introduction of

alkyl groups into the *ortho-* position relative to the hydroxyl group. A wide range of alkenes were tested, as well as a wide number of substituted phenols[29]. The role of the steric hindrance was acknowledged, as for example, if the introduction of ethyl and propyl groups is allowed between the hydroxyl and a methyl group, the introduction of isobutene in this position is forbidden. Most alkenes gave the mono- *ortho-* or the 2,6-dialkyl products, but in certain cases, as for example with α-methylstyrene as alkylating agent, isomerisation to the *para-* position occurred.

1.6.2 Catalysts and reaction conditions

Ortho- alkylation of phenols without catalyst were carried out, called the thermal *ortho-* alkylation. Harsh conditions were required, temperature above 250°C and pressure between 40 and 320bar[54], up to 3000bar in some cases[55]. Conversions were moderate and yields based on alkenes were very low. No *para-* substitutions were observed at all and, if α-long chain alkenes were used, chains were introduced mostly at the second carbons, some at the first, none at the middle carbons.
A mechanism *via* a 6-membered cyclic transition state was suggested[54, 56].

The original catalyst to achieve the *ortho-* alkylation of phenols with alkenes was aluminium triphenolate. The Bayer A.G. group also reported the use of several other metal phenolates, such as magnesium, zinc, iron, zirconium, hafnium, niobium, tantalum, gallium, boron and in certain cases titanium[38]. But the aluminium triphenolate remained the preferred compound[38, 51, 57].

Several types of catalysts based on aluminium were reported, as diphenoxyaluminium chloride or diphenoxyaluminium hydroxide[46]. The chloride catalyst appeared to accelerate the reaction, but as some alkyl chloride was isolated, the increase in the reaction rate was due to the formation of this intermediate. Alkylation with aluminium triphenolate and alkyl chloride exhibited the same rates. The hydroxide catalyst was, however, much slower than the original aluminium triphenolate.

To prepare the aluminium triphenolate, aluminium sand, powder or turnings is mixed with dry phenol at a temperature set between 120°C and 180°C. Hydrogen is formed. Other aluminium derivatives, such as trialkyl, dialkyl chloride, trichloride or alkoxide of aluminium can be used. Usually, alkyl derivatives, such as triethylaluminium, are preferred, as they evolve gas, and not HCl, which is a Brønsted acid directing to the *para-* position.

All those catalysts are soluble in phenol. As discussed previously, complete removal of the catalyst, often by aqueous washes, is required to avoid side reactions during products purification. To avoid these additional steps, attempts to insolubilise the catalyst or to attach it to a solid support were taken. *Ortho*-phenolsulfonic acid aluminium salts can be filtered off the reaction mixture and reused[58]. Aluminium phenolate-bonded to phenol-formaldehyde resins have also been used as a catalyst for the *ortho-* alkylation of phenol[59].

Several reaction parameters were studied. The best results for the alkylation of phenol requires an optimal concentration of the catalyst[60, see for example]. The concentration of water is also crucial. No reaction occurs between phenol and isobutene, in the presence of aluminium chloride with a complete absence of water. Traces are beneficial, but high water level slows or stops the reaction, by hydrolysing the catalyst[61]. Water also contributes to the formation of the aluminium phenolate dimer complex at a temperature above 130°C, which is also insoluble in phenol. However if the reaction mixture is stirred above 130°C at high speed, an equilibrium is quickly reached between the dimer and the aluminium triphenolate[62].

Catalyst preparation temperature affects in some cases the yields of dialkylproducts. High temperature is preferred when preparing aluminium triphenolate from phenol and aluminium chloride[63].

Reaction temperature affects the product distribution and the control of side-reactions. At low temperature, ethers of phenol are observed. The formation of the ethers is reversible when increasing the temperature. At higher temperature, the formation of ether is in some cases unobserved, but de-alkylations and formation of *para-* isomers take place.

The alkylation of phenols has been carried out since its discovery with the starting material as solvent. The lack of a solvent gives to this reaction a "green" aspect: no solvent recycling and emission control (for this particular chemical) are required.

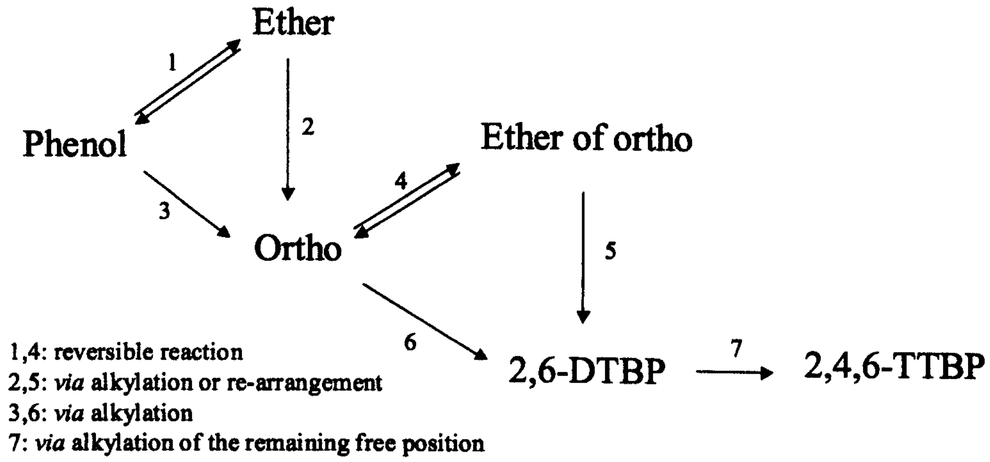


Figure 1.7: Possible pathways of the selective *ortho*-alkylation of phenol with alkenes.

Solid catalysts are also used for the alkylation of phenol. γ-Alumina, and in certain cases other forms of aluminium oxide (but the α- form) exhibit high selectivity toward the *ortho*- alkylation of phenol[64, 65]. The advantage over the aluminium triphenolate is the higher selectivity at a ratio phenol / alkene of 1:1 to the *mono*- *ortho*-alkylphenol, and the possibility to filter off the catalyst and thus reuse it, without any washing step.

1.6.3 Reaction mechanism

The mechanism of the reaction is not completely understood. Figure 1.7 shows the different pathways proposed and Figure 1.8 gives more details of the mechanism of each possible path. The reversibility of the reaction phenol – ether (1) was shown by Kozlikovskii et al.[66]. The mono- *ortho*-alkylphenol can be obtained *via* either direct alkylation (3) or *via* alkylation of the ether and de-etherification or *via* rearrangement of the ether (2). Similar mechanisms lead to the 2,6-di*tert*butylphenol. Then the free *para*- position is alkylated *via* a 'normal' Friedel-Crafts mechanism. Knapp et al. suggested that the ether was a necessary intermediate to the synthesis[46]. Ether was observed only at low temperature and was stable to the catalyst up to a critical temperature, above which it was converted into the alkylphenol. Also, when the reaction of alkylation of a particular substrate proceeded slowly, little or no ether was found. They also looked for a similar intermediate regarding the second alkylation, but were not able to

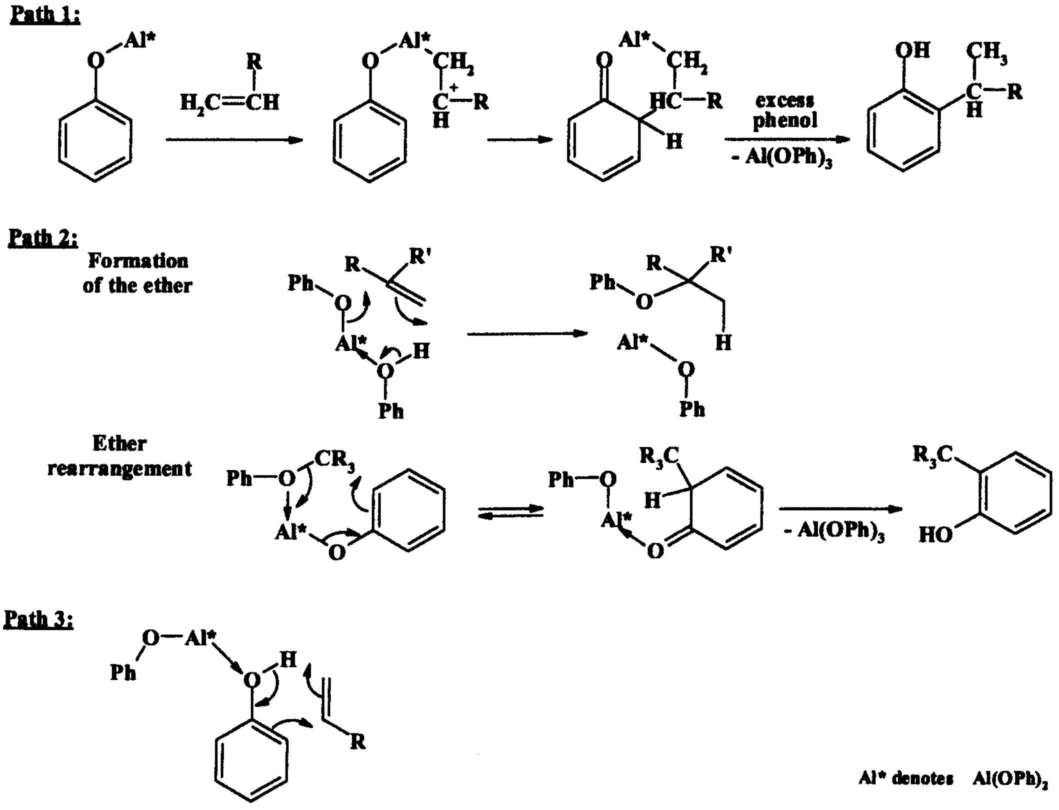


Figure 1.8: Possible mechanisms for the selective *ortho*-alkylation of phenol with alkenes.

isolate any alkyl mono-*ortho*alkylphenyl ether. Stroh et al. however suggested that the reaction proceeded either directly or *via* the ether by two different 6-membered intermediates[53], as shown in Figure 1.8. Kozlikovskii et al. studied the alkylation of phenol by cyclohexene with aluminium triphenolate as catalyst (Figure 1.9)[66]. They showed that the reaction proceeds first by formation of the acid $HAl(OC_6H_5)_4$, which reacts with a molecule of alkene. The complex is surrounded by a solvent cage (phenol) and reacts intramolecularly to form either ether or the mono- *ortho-* product. But the alkyl ion can escape the solvent cage and then reacts following the 'normal' Friedel-Crafts mechanism, yielding *para-* substituted products.

Three pathways are assumed to be possible, all of them involving the acidic $HAl(OC_6H_5)_4$ complex: either *via* direct electrophilic attack of the alkene to the sterically more favourable *ortho-* position (Figure 1.8,path 1)[67] followed by proton exchange with excess substrate, or *via* ether formation and its rearrangement by complexation with the catalyst to the *ortho*-alkyl product (Figure 1.8, path 2), or by direct alkylation by complexation of phenol and alkene with the catalyst (Figure 1.8, path 3).

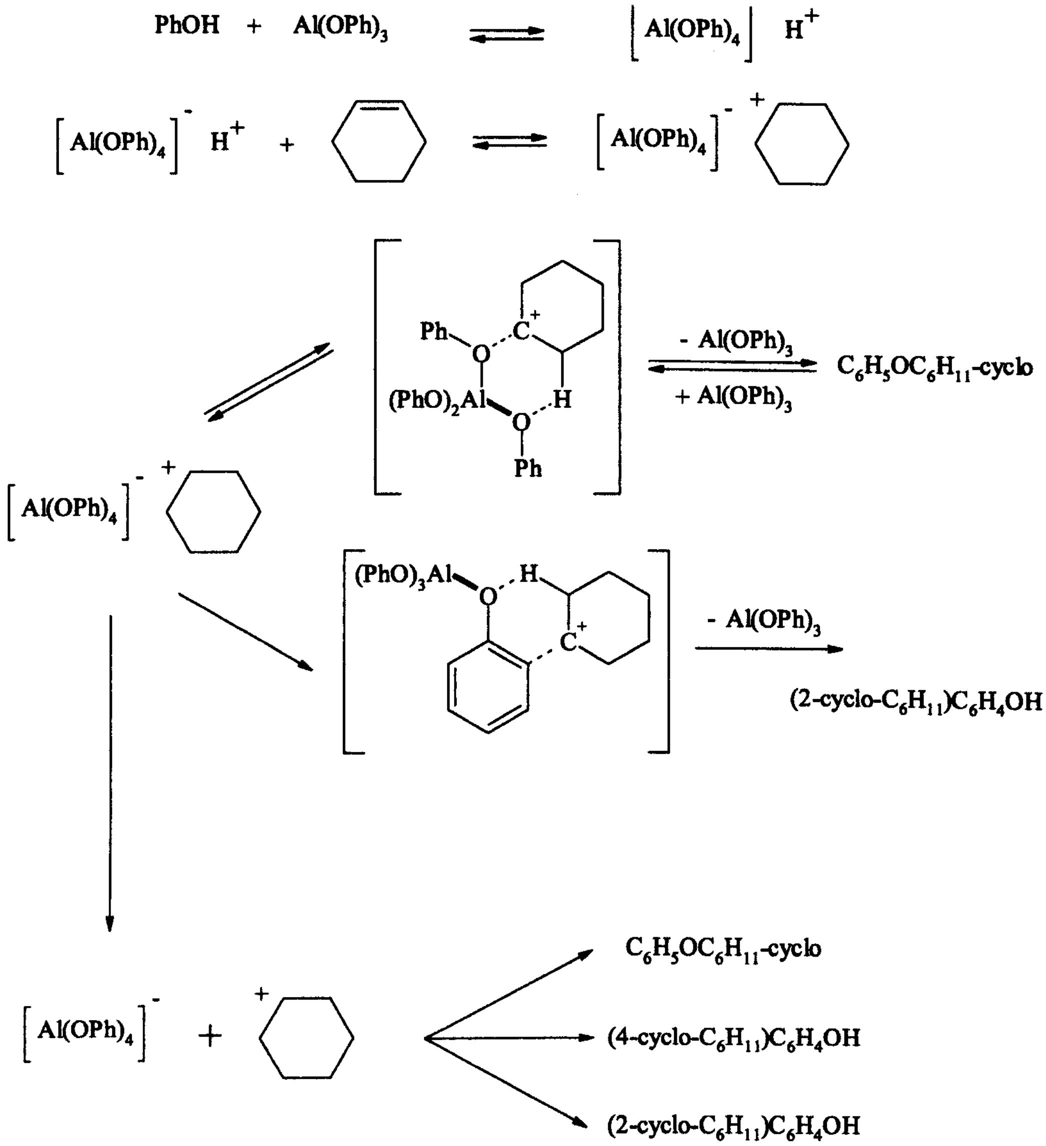


Figure 1.9: Mechanism alkylation of phenol by cyclohexene with aluminium triphenolate as catalyst (reproduced from [66]).

The proposed mechanisms are not similar to the classical Friedel-Crafts arenium ion mechanism, but explain the selectivity observed. However, the reactivity of the alkenes is similar to those observed for alkylations reaction in presence of Friedel-Crafts catalysts: the reactivity increases from the ethene, to the R-CH=CH-R, to the R-CH=CH$_2$, finally to the R$_2$C=CH$_2$. Also, the major product is with the most branched alkyl group.

Figure 1.10 shows a typical phenol / alkene alkylation reaction profile. The alkylation of phenol with isobutene was carried out with diphenolatealuminium chloride as catalyst at 120°C. The ether of phenol and the *ortho*- products appeared at the same time, the ether reached a maximum first then decreased. The

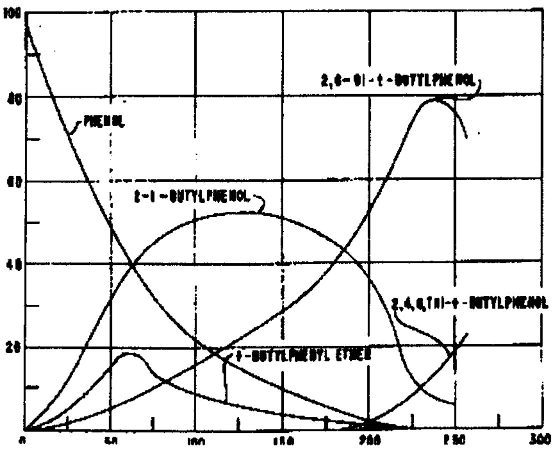


Figure 1.10: Typical reaction profile of an *ortho-* alkylation of phenol with alkenes and aluminium triphenolate as catalyst (reproduced from [60]).

mono- *ortho-* alkyl product reached a maximum then decreased when the di*ortho-* product became the major product. Some 2,4,6-trialkyl product was also observed. If a lower temperature was used, the maximum of the ether would have been the same but the curve representing the yield of the mono-*ortho-* would have been below the curve of the ether, and its maximum would have been delayed, as the other. If the temperature was even lower, either only ether would be formed, or no further reaction would occur.

Therefore, depending on the desired *ortho-* product, the lowest possible temperature, but sufficiently high for rapid cleavage of the ether, has to be chosen and the reaction can be stopped at the optimum time by removing the heat and the catalyst quenched or separated.

1.7 Supported reagents, supported catalysts and solid acids

Solids are used as catalysts in a heterogeneous manner, as for example alumina for the alkylation of phenols, since as early as the middle of last century. Solid catalysts are very suitable for heterogeneous reactions in gas phase in fixed or fluidised bed reactors. In 1968, Fetizon and Golfier defined the term 'supported reagents', when they used silver carbonate supported on celite as a reagent for alcohols oxidations[68]. The idea was to increase the surface area of a useful insoluble inorganic reagent by dispersing it on a high surface area material. In

1979, McKillop and Young gave a general definition of 'supported reagents' , as a material formed by adsorption on, dispersion over or intercalation in an insoluble support material of a chemical reagent[69].

The original use of these materials was to enhance the reactivity of insoluble reagents, hence used in stoichiometric manner. However, under the impulsion of the Green Chemistry movement, the focus has turned to the development of supported catalysts, thus to link chemically or physically the catalytic species used for a reaction on an insoluble inorganic or organic support. Supported catalyst, being insoluble, is easily recovered from the reaction mixture, and can be reused[70].

Supported catalysts are becoming more and more widely used for all types of chemistry. Some are commercially available, e.g. as Envirocats™[71].

1.7.1 Advantages and disadvantages of the use of supported catalysts

Apart from being recoverable and reusable, supported catalysts often exhibit lower toxicity, higher reactivity and selectivity, thanks to their inner structure (pore shape and size), and are less corrosive and easier to handle than liquids or gases. In some cases, supported catalysts can be inert to moisture, when the homogeneous version of the catalyst is not. They also help reducing effluents and waste production by removing the need of any separation step, or by allowing the reaction to be carried out under solvent-free conditions.

The new types of catalysts would be the panacea if some inconveniences were not induced. First of all, their preparation can be expensive, as several new reaction steps are required, and does require new plant technology. During their use, leaching, fouling, thermal and mechanical degradation or poisoning deactivates the catalyst and results in product contamination[72–74].

However from an environmental point-of-view, the advantages overweight the inconveniences. Various works were and are published in the literature, on understanding and finding new preparation methods or completely new catalysts to overcome these catalyst drawbacks[72–76].

1.7.2 Methods of preparation

In order to design an efficient supported catalyst, many parameters have to be considered. The first parameter is the support itself; its choice will be discussed in the next section. Then four preparation parameters have to be taken into account: the pre-treatment of the support, the method employed to fix the catalyst active species onto the surface, the loading and finally the post-treatment if applicable. Another preparation method is to build the support around the catalyst active species.

Pre-treatments are related to either modify thermally on purpose the structure of the support, to remove the physisorbed water or to modify on purpose the nature of the surface.

The support exhibits a certain thermal stability, therefore the temperature should not be raised over the critical stability temperature to avoid any degradation; in some cases, for example with silica, the support shows high thermal resistance, but the nature of the surface (silanol giving water and siloxane) and the structure of support are modified.

Water is always physisorbed on any support materials. The presence of water can either be beneficial or affect the preparation, the stability and the efficiency of the supported catalyst.

Surface can be treated in order to ease the fixing of the active catalyst species. In the case of silica, for example, treatment with aqueous HCl hydrolysed siloxane bridges, liberating surface silanols, which can be useful for supporting some metals or ligands.

Table 1.9 lists all common methods for the preparation of supported catalysts used today. Early methods (methods 1 to 4) used to prepare supported reagents and catalysts were simple. Recently, efforts were and continue to be taken to prepare more stable supported catalysts towards deactivation and leaching (methods 5 to 8). Much more details can be found in various references[69, 77–81].

Post-treatment is in some cases required. For example, removal or control of the amount of of physisorbed water might be required to obtain an efficient catalyst or to avoid side reactions such as hydrolysis. But changes in the support structure or final formation step of the catalyst active species may also be carried out

Evaporation: Mixing of the support with a solution of the reagent in a solvent, latter evaporated. Good dispersion control and also, good loading control, as all the reagent is forced to adsorb.

Precipitation: Precipitation of a soluble form of the active catalyst species on a insoluble support, which is in suspension in a solvent.

Adsorption: Mixing and/or refluxing of the support with the reagent in a solvent, followed by filtration and washing. Chemisorption occurs selectively or not on surface sites, but the loading is more difficultly controlled compared to the evaporation method.

Mixing/grinding: Mixing or grounding of the support and the reagent together, without the need of a solvent. Simple and sometimes efficient preparation method, but does not produce necessarily a supported reagent.

Ion exchange: Exchange of ions between a support and a well stirred solution, followed by centrifugation and washings.

Framework substitution: Incorporation of metal ions in the framework of the catalyst, by mixing the ions with a gel containing building units elements and a template, followed by crystallisation. The template is then removed by extraction or calcination.

Encapsulation: Building of the catalyst complex inside the support pores, complex too big to allow exit, or building of the support (for example zeolite crystallisation) around the catalyst species (ship in the bottle method). The catalyst ought to be thermally stable, regarding the required harsh conditions during the synthesis.

Grafting/post-synthesis: Chemical reaction between the catalyst species or reagent and some chemical functions available at the support surface, such as for example silanol function at the surface of silica. These available functions can be generated beforehand during a pre-treatment step. The sol-gel method even allows both the grafting and the framework incorporation of metal ions, with better control of the loading and the dispersion without loss of stability.

Table 1.9: Preparation methods of supported catalysts.

by thermal activation at temperature higher than those required for the water removal[see for example 77]. Finally further reactions can be carried out on the chemisorbed species to end the formation of complex catalyst active species not accessible directly, such as ligand exchange.

	Pore diameter (nm)
Micropores	0 - 2
Mesopores	2 - 50
Macropores	50 - 7500

Table 1.10: IUPAC classification of pores, according to their diameter.

Support/Catalysts	BET area (m^2g^{-1})	Volume (cm^3g^{-1})	Pore diameter (nm)
Activated carbon	500 - 1500	0.6 - 0.8	0.6 - 2
Zeolites (molecular sieves)	500 - 1000	0.5 - 0.8	0.4 - 1.8
Silica gels	200 - 600	0.4	3 - 20
Activated clays	150 - 225	0.4 - 0.52	20
Activated alumina	100 - 300	0.4 - 0.5	6 - 40
Kieselguhr (celite 296)	2200	1.14	4.2

Table 1.11: Physical properties of various inorganic supports, used as such or as catalyst by themselves.

1.7.3 Types of support materials

The support, with which the catalyst has to be associated, has to be chosen carefully, as it will be an important 'companion' of the catalyst. Catalyst affects the nature of the surface, but this surface will in return modify the activity of the catalyst.

Various organic and inorganic materials have been used as supports; they are chosen for their stabilities, rigidities and prices. Organic polymers, zeolites, clays, alumina and silica are some examples used for the alkylation of phenols with alkenes, which will be discussed in this section.

Supports are also chosen from various parameters, such as specific surface area, pore shape and size and the presence of anchoring sites. Table 1.10 shows the IUPAC classification of pores according to their diameters[82], when Table 1.11 gives some physical properties of various supports.

Many reviews and books can be found in the literature about the use and the surface studies of supports. Some key references are given within the text.

1.7.3.1 Organic polymers[2, 80]

Organic polymers of various types have been used as supports. Their properties depend on the monomer or co-monomers and on the employed polymerisation or co-polymerisation method. Porous polymer supports can be generated *via* a small degree of cross-linking and the use of diluent during the preparation. Functionality can also be introduction either by co-polymerisation of functionalised monomer. The choice of the polymer is governed by the resistance requirement under the reactions conditions.

Goins et al. reported the alkylation of phenols with alkenes using supported aluminium triphenolate on polymeric resins and phenol-formaldehyde resins[59]. With polymeric resins, bearing sulfuric or phosphoric acid functions on a styrene-divinylbenzene copolymer, 2,4-disubstituted phenols are prepared from phenol and olefins, with the advantages of catalyst recycling and canceling all phenol-bearing wastes[58]. Using phenol-formaldehyde resins instead, 2,6-disubstituted phenols could be prepared from the mono-*ortho*- substrate[83]. Unfortunately, if the first use led to high yields and required short reaction time, catalyst activity dropped after some reuses. In general, reactions using solid acid catalysts proceed preferentially in the *para*- position or decrease the *ortho* / *para* ratio[84, 85].

1.7.3.2 Zeolites[78–80]

Zeolites are originally microporous crystalline oxides, also known as molecular sieves or aluminosilicates, with molecular-sized intracrystalline channels and cages. The intracrystalline pore structure of zeolite is based on three-dimensional cages linked *via* faces and/or interconnecting channels. The cages are built from SiO_4^{4-} and AlO_4^{3-} tetrahedra, sharing oxygen atoms. The negative charge is compensated by exchangeable solvated, usually by water, cations.
Properties of zeolites depend on several parameters: the framework structure, as the shape, size, connectivity between channels and cages, the framework composition, the intracrystalline cations as type, charge, concentration or location, and the presence of additional phases, as non-framework guest molecules or metals. The acidity of zeolites can be tuned by controlling the amount of Si / Al ratio and the cation exchange. The nature of the acidity, Brønsted or Lewis, can also

be controlled, by the modification of the zeolite framework.

Studies of the structure and the catalytic activity of zeolites have been published [86, 87].

1.7.3.3 Clays

Clays have been used for a thousand years for their high surface area, sorption and ion exchange properties. During the twentieth century, clays were used for catalytic properties, for example in petroleum industry before being replaced by thermically more stable catalysts[80].

Clays are natural hydrous aluminosilicates minerals. They exhibit crystal and layered structure. Layers are usually formed either of SiO_4^{4-} tetrahedra units or cation (Al^{3+}, Fe^{3+}, Mg^{2+}) octahedral units. A variety of synthetic clays are prepared by substitution of the silicon ion or, more frequently, substitution of the cation. Layer spacing can also be controlled by hydration (swelling). However, clays exhibit poor thermal stability, as the structure starts to collapse above 200°C.

If the cations, which are part of the layer structure, are substituted by ones of lower charge, the layer becomes electronegative and exchangeable cations are required in the inter-layer space to counterbalance charges. This process has been extended to the preparation of more stable clays, the pillared inter-layer clays[88]. Clays are swelled and cations are exchanged by polyoxocations (pillar agents), followed by calcination, which leaves oxide entities holding the layers, thus preventing collapsing.

Clays have been used for the alkylation of phenols with alkenes. Chitnis and Sharma summarised works carried out in this area with α-methyl styrene, cyclohexene or long chain alkenes[89]. Due to the type of acidity that clays exhibit and a pore shape effect, the alkylation preferentially takes place in the *para-* position, with highly selective formation of ether if the reaction temperature is low (between 45°C and 60°C). Leston reported the use of acid activated silica-alumina clays for the preparation of the most stable *meta-* isomer of *meta-* cresol, by a one-pot alkylation–isomerisation procedure at high temperature[90]. *Ortho-* alkylations of phenols were also carried out using clays, but with alcohols. Velu and Swamy obtained high yields of a mixture of mono*ortho* and di*ortho* phenols[91].

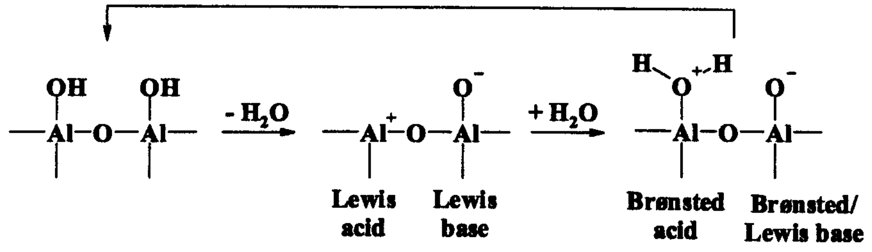


Figure 1.11: Action of water on the generation of the different active sites: amphoteric nature of the alumina surface.

1.7.3.4 Alumina

The name 'alumina' refers to a wide range of aluminium oxides (Al_2O_3). Alumina can be found under the non-hydrated or the hydrated form, either monohydrate (AlO(OH)) or trihydrate ($Al(OH)_3$). Each of the hydrated aluminas can be found under various polymorphic forms[78–80]. The natural non-hydrated form, α-alumina, can also be prepared by high temperature calcination of any other forms of alumina (usually 1200°C). α-Alumina exhibits high density, and good mechanical and thermal stability. Unfortunately, the surface area and the porosity are low, making it a poor choice as support for supported reagents or catalysts. γ-Alumina, however, exhibits high surface area, large pore volume and good thermal stability. The surface of γ-alumina also exhibits strong surface acidity and basicity. The amphoteric nature and the strength of the active sites can be tuned by careful thermal post-treatment (calcination). Figure 1.11 shows the role of water in the generation of the different active sites, bearing Brønsted and Lewis acidity or basicity[80].

γ-Alumina has been used, either as such or prepared in-situ from other forms, for the alkylation of phenols with alkenes. For small alkenes (below C_4), this catalyst leads to mono- and di*ortho* alkylated products. However for higher alkenes, the mono*ortho* alkylated product is selectively obtained. Hahn[64] and Napolitano[65] also reported the use of various forms of alumina for the alkylation of phenols with alkenes, but also functionalised alkenes, such as for example allylamine or vinyl chloride.

Alumina has also been used as support for supported heteropoly acid catalysts. But in this case, the alkylation of phenols occurs mainly in the *para*- position[92].

1.7.3.5 Silica

The name 'silica' refers to a wide range of silicon dioxide, SiO_2. Silica can be found under various forms, such as hydrated and anhydrous crystalline, microcrystalline and amorphous forms. Crystalline forms, with their high density and low porosity, are, as for alumina, of little use as supports. Amorphous silicas can be under the high-density vitreous form or the low-density form. This low-density amorphous silicas exhibit high surface area and high porosity, and thus are very suitable as sorbents and supports for supported reagents and catalysts.

The structure of silica is constructed by assembly of structural units, consisting in tetrahedron SiO_4^{4-}, corner linked (siloxane bridges: Si–O–Si) in chains, rings, sheets or three-dimensional assembly (for example, zeolites). When unshared, the oxygen yields a silanol function, which can be either isolated (silicon bonded thrice with the bulk structure and once with a free OH group), vicinal (isolated silanol type closed enough to interact *via* hydrogen bond) or geminal (two OH groups attached to the same silicon).

These silanol functions are useful when using silica as supports, as they allow reagents or catalyst species to be attached to the surface either *via* physisorption (hydrogen bonding interactions) or chemisorption (direct reactions). At room temperature and without any thermal treatment, silicas are highly hydrated (they can be used as desiccants). This physisorbed water can be removed by heating at a temperature slightly above 100°C. Higher temperatures cause the surface silanol groups conversion into siloxane bridges with water removal. This process, depending on the silica type, becomes irreversible at temperature over 400°C. More details regarding this support are discussed in the chapter 2.

Alkylation of phenol with cyclohexene using supported boron trifluoride on silica has been reported[93, 94]. As the supported boron fluoride is a mild solid acid, the main products were the ether and the mono- alkyl phenols.

1.8 Introduction to the work in the thesis: the idea of the new catalyst

Alkylations of phenol derivatives with alkenes were carried out with solid catalysts. For most of the cases however, either *para-* substituted phenols are major products, or the reaction stopped at the mono- alkylation.

In the case of the alkylation of phenol with isobutene, in order to prepare the 2,6-di*tert*butylphenol, the best catalyst remains the homogeneous aluminium triphenolate[38]. The use of this catalyst is efficient and highly selective, but leads to environmental concerns. In order to separate the reaction product mixtures, all traces of acidic reagents have to be removed by aqueous washes. These aqueous wastes, contaminated with aluminium and phenols have to be treated before disposal[40].

The use of supported reagents, easily separated from the reaction mixture and reusable, could help the preparation of 2,6-di*tert*butylphenol without the need for aqueous washes[77–80].

The aims of the work described in this thesis were to develop a new type of solid catalyst to allow the selective synthesis of di*ortho*alkylphenols from phenol and alkene, in particular the selective synthesis of 2,6-di*tert*butylphenol from phenol and isobutene which does not require any aqueous washes before the purification of the reaction mixture.

One aim of the work was to find a suitable catalyst and to optimise its preparation. Characterisation of the solid catalyst was carried out, and the new catalyst tested. Various parameters, related to the catalyst or to the reaction conditions, were studied and attempts were taken to optimise the yield and selectivity towards the 2,6-di*tert*butylphenol in particular. Applications of this new catalyst to other phenol alkylation with alkenes were also briefly investigated.

Chapter 2

Catalyst preparation and characterisation

2.1 Introduction

The preparation and the characterisation of a new type of supported catalyst, the aluminium phenolate supported on silica gel, is described in this chapter. The techniques used for its characterisation, such as nitrogen adsorption, solid Nuclear Magnetic Resonance (NMR), X-Ray Photoelectron Spectroscopy (XPES) and Diffuse Reflectance Infra-Red Fourier Transform (DRIFT) are first briefly outlined. The silica gel used as a support is subsequently described and characterised.

The general preparation method of supported Lewis acids is discussed and applied to the preparation of supported aluminium phenolate. The structural properties of the catalyst were studied by porosimetry techniques and the nature of the active species was investigated using spectroscopic methods. The determination of the Brønsted or Lewis nature of acid sites was attempted and is presented. All the characterisations allow a better understanding of the possible active sites on the surface of the silica gel supported aluminium phenolate.

2.2 Techniques used for the characterisation of the solid catalysts

In this section, techniques used for the characterisation of the catalysts are briefly presented. Various books and reviews can be found in the literature if need be the reader desires more details.

2.2.1 Nitrogen adsorption: surface area, pore size and volume[76, 95–97]

Specific surface area, pore size and pore volume distribution of a porous material may be determined by gas adsorption. At a definite pressure and temperature, any solid adsorbs gas. The volume of adsorbed gas can be monitored by exposing a solid to a known volume of gas. Once the equilibrium is reached, the relative pressure (pressure 'p' of the gas the sample is exposed to divided by the saturation pressure 'p_0') and temperature are recorded and subsequent calculations lead to the adsorbed gas volume. The practice of this technique has standardised the use of nitrogen as adsorbant. In this case, the measurement is carried out at a constant temperature of 77K. The process can be repeated for various relative pressures and the plot of adsorbed volume against the relative pressure produces an adsorption isotherm. Similar measurements are performed during desorption of the gas from the solid surface and pores. The plot of both adsorption and desorption curves gives an isotherm plot exhibiting a certain shape, from which information on pores can be obtained.

Before proceeding to the analysis, the solid sample has to be cleaned of any adsorbed gas. This is usually done by heating under vacuum. Care has to be taken when choosing the so-called 'outgas' temperature in order to induce no structural changes. Once the surface is cleaned, the sample is exposed to nitrogen. For relative pressures between 0.005 and 0.2, nitrogen first adsorbs as a monolayer, each molecule of nitrogen occupying its cross-sectional area. For higher relative pressure, formation of a multilayer of nitrogen is observed, filling the small pores first, by capillary condensation, then the large ones. At the saturation point ($p/p_0 = 1$), all pores are filled as well as all voids and interparticle spaces. The emptying of the pores by the desorption process is then recorded.

Isotherm plots have been classified into six categories (IUPAC classification[98]) and are shown in Figure 2.1. By analysing the shapes of these curves and that of the hysteresis loops when present, nature and structure of the pores as well as the specific surface area and the total pore volume distribution can be evaluated. Type IV isotherms are characteristic of mesoporous solids, where formation of a monolayer is observed for low relative pressure, then followed by the filling of the pores until saturation.

A characteristic feature of this type of isotherm is the hysteresis loop. Figure 2.2 shows the different types of hysteresis loops (IUPAC classification). Complete modelisations of pore shapes and associated isotherm and hysteresis loops can be found in the literature[95, 96]. H1 hysteresis is characteristic of a narrow distribution of uniform mesopores.

Several models for the calculation of the surface area have been developed[76]. The Langmuir model is adequate when only a monolayer is adsorbed. The Brunauer, Emmet and Teller (BET) model, despite implied simplifications, is the most widely used. The model extends the Langmuir model to a multilayer system.

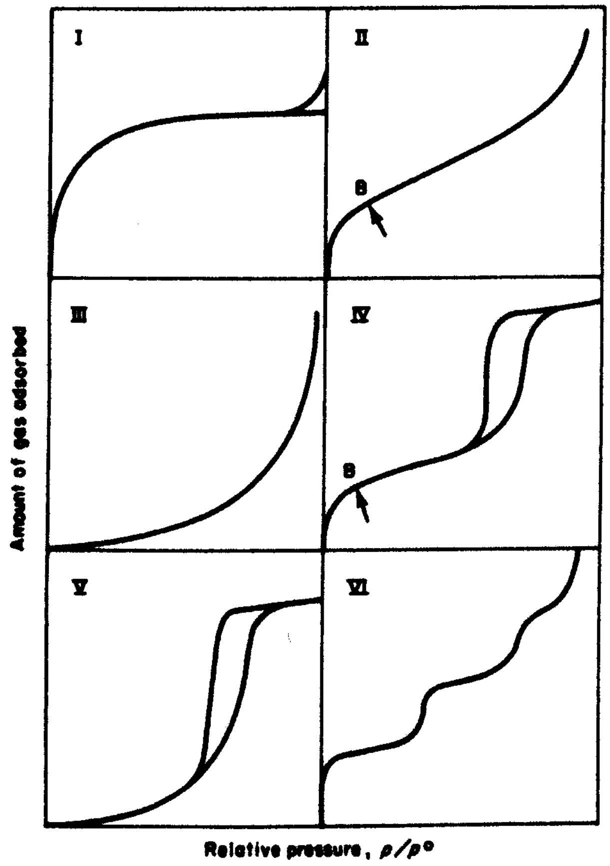


Figure 2.1: Gas adsorption on the solid surface: types of isotherm (IUPAC classification)

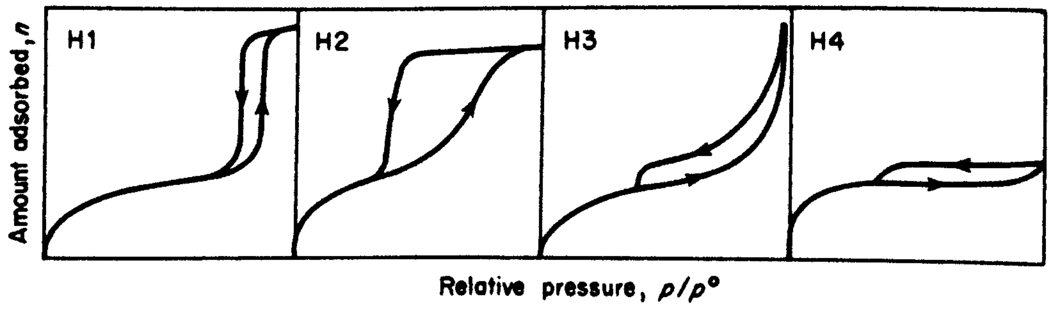


Figure 2.2: Gas adsorption on the solid surface: types of hysteresis (IUPAC classification).

Subsequent calculations give the volume of the monolayer layer, and knowing the cross-sectional area of nitrogen, the specific surface area.

Models have been developed to link the shape of the hysteresis loop with the shape of the pores[76]. Pore size distribution models have also been developed. The Barrett, Joyner and Halenda (BJH) model allows the determination of the pore size distribution and the calculation of the total pore volume using the desorption branch of the isotherm[95]. This model is based on the assumption that the mesoporous pore exhibits a cylindrical pore shape, open at one or both ends, and on the use of the Kelvin equation 2.1 (relation between the equilibrium vapor pressure p of a curved surface to the equilibrium pressure p_0 of the same liquid on a plane surface)

$$\ln \frac{p}{p_0} = -\frac{2\gamma \bar{V}}{rRT} \cos \theta, \tag{2.1}$$

where γ is the surface tension of liquid nitrogen at its boiling point, $\bar{V}$ is the molar volume of liquid nitrogen at its boiling point (T), R is the ideal gas constant, θ is the contact angle with which the liquid meets the pore wall and r is the narrow pore radius.

The average pore diameter $\bar{d}$ is calculated, also assuming that the pores exhibit a cylindrical shape, by the Weeler's formula (Equation 2.2)

$$\bar{d}(nm) = \frac{4.10^3 V_t}{S_{BET}} \tag{2.2}$$

where V_t is the total pore volume given in $\mathrm{cm^3g^{-1}}$ and S_{BET} is the BET surface area given in $\mathrm{m^2g^{-1}}$.

2.2.2 Solid Nuclear Magnetic Resonance[99–106]

Nuclear Magnetic Resonance (NMR) is a powerful technique looking at an element nucleus and its closed environment. The magnetic moment of the element, which we desire to study, placed in a permanent magnetic field $\vec{B}_0$, is excited by one, or several, electromagnetic pulses $\vec{B}_1$. The element magnetic moment relaxation, back to the equilibrium position, is recorded. Subsequent calculations yield the NMR spectra.

Investigations of chemical structure in the liquid phase are carried out by analysing chemical shifts, couplings, and relatives intensities of the resonances in their

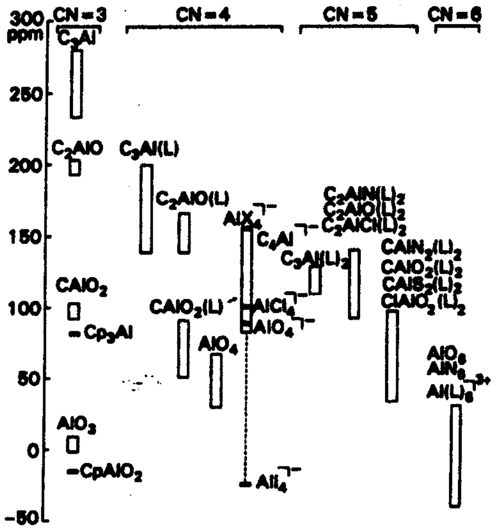


Figure 2.3: ^{27}Al chemical shifts ranges of various aluminium compounds, showing the relation between the coordination number (CN) of the aluminium atom and the substituents nature. L: monodentate ligand, neutral chelating bidentate ligand or bridging alkoxide oxygen atoms. X: ligand carrying a negative charge. Reproduced from [107].

spectra. 2D experiments are also powerful NMR techniques to help the elucidation of structures by a better understanding of the coupling of separate atoms. One of these techniques, called Correlated Spectroscopy (COSY), looks at the ^{1}H-^{1}H interaction, giving information on which hydrogen atoms are neighbours of each other.

Solid NMR however presents a challenge due to the solid state of the sample, which induces new interactions, broadening resonance signals. Techniques have been developed to enhance the signal and retrieve the chemical shift and other characteristics observed in liquid phase. One of these methods is the Magic Angle Spinning NMR (MAS-NMR) spectroscopy. This technique cancels the dipolar interaction by rotating at high speed the solid sample around an axis inclined at the so-called magical angle (54°44') to the magnetic field.

The ^{27}Al MAS-NMR is a powerful tool to investigate the nature of the substituents and the aluminium coordination number[87, 108–110]. However, the Al spectra still pose interpretational difficulties, as the chemical shift cannot be linked with the coordination number without understanding of the substituent nature[107, 111]. Figure 2.3 shows graphically some aluminium chemical shift ranges in function of substituents, recorded in the liquid phase with an Al^{3+} compound, such as an acidic solution of Al^{III} salts or $Al(acac)_3$, as reference.

2.2.3 X-Ray Photoelectron Spectroscopy[76, 101, 112]

X-Ray Photoelectron Spectroscopy (XPS or XPES) is also a powerful technique to identify atoms at a solid surface by probing atomic and molecular electronic energy levels. The sample is exposed to a X-Ray beam, which excites core electrons. If the incident energy is higher than the binding energy, the inner core electron is ionised and its kinetic energy is measured. The difference between the energy of the X-Ray beam and the electron kinetic energy gives the binding energy of this particular electron, which is characteristic of an orbital of a particular atom. By scanning all kinetic energy (wide scan), an elemental analysis of the surface can be obtained.

The X-Ray beam can penetrate the sample to excite electrons of atoms belonging to inner layers. These electrons have to escape through these layers without any collision before being detected. Therefore XPS can only give information on the few layers closed to the surface. In the case of the analysis of a powder, care has to be taken concerning the results of the 'elemental analysis'. Indeed, the inside of some pores may be inaccessible to the X-Ray beam and electrons may have difficulty to escape in the direction of the detector.

2.2.4 Diffuse Reflectance Infra-Red Fourier Transform Spectroscopy (DRIFT)[76, 101, 113]

Infra-Red spectroscopy is a powerful technique, which looks at the bond vibration modes of a molecule. Therefore functional groups are easily identified. The sample is exposed to infra-red radiation. When energy corresponding to a specific wavelength is absorbed by the sample, the detector will record a decrease of the radiation intensity for that particular wavelength. Several techniques were developed to record spectra of chemical species, either diluted in solvents, pressed into a transparent disc of potassium bromide, or grounded in oil slurry (Nujol). These spectra are recorded by transmission. Solid samples, being opaque to the infra-red radiation, are investigated using the diffuse reflectance technique, called 'DRIFT'.

2.2.5 Surface acidity measurements using probe molecules

Assessing the nature and the strength of the acidity of a solid catalyst surface is challenging. Two methods will be described here, DRIFT measurement using pyridine as a probe molecule and ^{31}P MAS-NMR using triethyl-phosphine oxide (TEPO) as a probe molecule.

The qualitative measurement of the acidity of the solid surface may be investigated by adsorbing a basic probe molecule and studying its interaction with the surface solid acid sites by Infra-Red or DRIFT. A large range of chemicals are available[114, 115], for example nitriles and amines. The choice of the probe molecules depends mainly on the ability to differentiate Brønsted and Lewis acid sites as well as their strengths[116]. Commonly used probe molecules are acetonitrile[117–119] and pyridine[120, 121].
The sample, whose surface acidity properties are to be investigated, is exposed to the probe molecule, which bonds differently to the various acid sites. The nature and the strength of these acid sites can then be evaluated as specific IR vibration bands shifts depending on the coordination mode between the probe molecule and the Brønsted acid, Lewis acid or hydrogen bonding sites are induced. When using pyridine as probe molecule (Figure 2.4), interaction with Lewis acid sites leads to a coordinate bond increasing the $p\pi$-$p\pi$ interaction between the nitrogen atom and the ring carbons, therefore increasing the frequency of the ring bending mode; interaction with a Brønsted acid site can lead to a pyridinium ion produced by proton transfer from the Brønsted acid site to the probe molecule; the probe molecule can also be simply physisorbed to the surface *via* hydrogen bonding. Table 2.1 summarises the adsorption bands value ranges of pyridine interacting with different acid sites, as well as the relative intensities of the bands. Among these peaks, the one in the 1447 - 1460cm^{-1} range can be used to determine Lewis acidity, while Brønsted acidity is determined using the peak at 1540cm^{-1}.

The adsorption of small basic probe molecules on a solid surface exhibiting acid sites can also be studied by solid NMR. The initial works in this field involved the use of an amine[122] or acetone[123] as probe analysed, respectively, by ^{15}N or ^{13}C MAS-NMR. However, these nuclei present the disadvantages of being seen with great difficulty with the NMR technique, due to their low natural abundance and

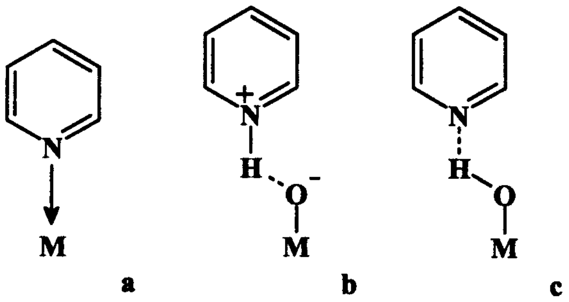


Figure 2.4: Pyridine adsorption on Lewis (a) or Brønsted (b) catalyst surface acid sites or free hydrogen bonded pyridine (c) on the catalyst surface.

Lewis site		Brønsted site		Free Py.	
1445 - 1460	(v.s.)			1440 - 1447	(v.s.)
1488 - 1503	(v)	1485 - 1500	(v.s.)	1485 - 1490	(w)
		1540	(s)		
~ 1580	(v)			1580 - 1600	(s)
1600 - 1633	(s)	1620	(s)		
		1640	(s)		

Band intensities: v.s.: very strong, s.: strong; w.: weak; v.: variable.

Table 2.1: IR pyridine (Py.) adsorption bands values, in cm^{-1}, of coordinatively-bonded pyridine (Lewis site), pyridinium ion (Brønsted site) and hydrogen-bonded pyridine (Free Py.)

gyromagnetic ratio. Focus was turned to the use of phosphorus-containing probe molecules, such as phosphine, since phosphorus offers a greater NMR sensitivity, due to a high gyromagnetic ratio and a 100% natural abundance of the spin $\frac{1}{2}$ isotope[124].

Probe molecules, as trialkyl-phosphines[125, 126] and trialkyl-phosphine oxides [124, 127], have been reported for the identification of various acid sites, such as silica-alumina surfaces, and attempts were also made to identify the nature of the acid sites. The phosphine oxides, as for example tri-methyl phosphine oxide (TMPO) or tri-ethyl-phosphine oxide (TEPO), are more stable and easier to handle than the phosphines and they offer a larger variation of chemical shifts, which is more convenient for the analysis of solids exhibiting wide acidity ranges. The adsorption of the phosphorus probe on an acidic site leads to a complex, where the phosphorus electron density is shifted toward the acid site. This shift yields a change of the ^{31}P isotropic chemical shift, which is proportional to the strength of the acid site. As such, overall acidity of the solid surface can be determined. However, problems arise about the distinction between Lewis and Brønsted acidity, and controversy about the capacity of this method to achieve this discrimination is still taking place. For instance, different chemical shifts area are assigned to Lewis chemisorbed probes when using TMPO[124, 127, 128]. TEPO is an efficient probe for measuring the overall acidity of a solid surface without discrimination between the two acidity types[129, 130], and is used in our laboratory to study various solid acid materials.

Comparisons between different solids are made by evaluating the difference in chemical shifts, $\Delta\delta$, between the ^{31}P chemical shift of the adsorbed probe on a surface acid site and the one of physisorbed TEPO estimated at 50ppm (Equation 2.3).

$$\Delta\delta(\text{ppm}) = \delta^{31}\text{P}(\text{ppm}) - 50.0 \tag{2.3}$$

2.3 Silica as support

As described in chapter 1, silica is a cheap easily available inorganic material, which can be found under various forms. Amorphous forms of silica are the most suitable as support, due to the porosity and the high surface area they exhibit. Furthermore, silanol and siloxane groups present on the silica surface allow reactions to be carried out as well as modification of the surface and catalyst binding.

2.3.1 Silica silanol groups

On the silica surface, three types of silanol groups, shown in Figure 2.5, are present at various concentrations: isolated or single (A), geminal (B) and triple or tertiary (C) silanol groups[131]. Sindorf and Maciel showed that the single hydroxyl groups are likely to be the more prolific[132, 133]. The next most common is the geminal silanol group, followed by the tertiary silanol group. When the concentration of silanol groups is high, hydrogen bonding between two hydroxyl groups close enough occurs. These types of silanol groups are called vicinal silanol groups (D, Figure 2.5).

These silanol groups are weak Brønsted acids, and they rarely affect catalytic activity directly. However they can transfer protons and initiate further reactions. They can react and undergo chemisorption with various molecules.

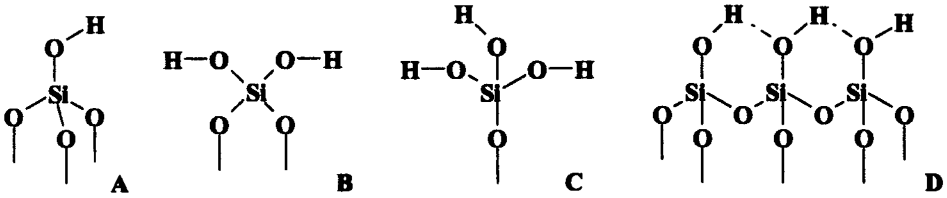


Figure 2.5: Types of silanol groups: A: isolated, B: geminal, C: triple, D: vicinal (hydrogen bonded).

They can also participate to the physisorption of many chemicals *via* hydrogen bonding, the most important being water[131]. Figure 2.6 shows some possibilities of how water can be physisorbed by silanol groups at the silica surface, as a monolayer from the less stable to the most stable complex (three first, from the left), but also as a multilayered system (last, on the right). As the different systems have different energy of formation, the drying of the silica surface by heating will not be a one step process. Single bonded water is removed at temperature below 200°C, simultaneously to the formation of vicinal silanol groups; between 200 and 400°C, more strongly held water is removed as well as the condensation of the silanol groups into siloxane bridges. Complete condensation of silanol groups is not reached until temperature in excess of 900°C (at these temperatures, the structure of silica changes to relieve the strain, altering the surface acidity properties). After thermal treatment of the surface at a temperature around 600°C, only isolated hydroxyl groups exist, but the surface is still very hydrophilic. If high temperature (900°C) is applied, the silica surface becomes hydrophobic[134]. This is due to the nearly complete formation of hydrophobic siloxane bridges, which preclude rehydration of the surface. These siloxane functions are nevertheless highly reactive and participate to the chemisorption of chemicals, as do the silanol groups.

Various methods for the measurement of the concentration of silanol groups were developed and can be found in the literature[131]. For the fully hydrated silica surface, the concentration of silanol groups varies between 4 and $6.5 \mathrm{OHnm}^{-2}$[135]. However, thermal treatment of silica changes the nature of the surface (as discussed below) and the concentration drops to $1 \mathrm{OHnm}^{-2}$ when the silica is heated above 800°C. Vasant et al. have also reviewed models and estimated average silanol distributions: 4.6 OHnm^{-2} for pre-heated silica at 200°C, down to 1.5 at 600°C, and only 0.7 at 800°C[136]. Vicinal silanol groups represent 60% of the

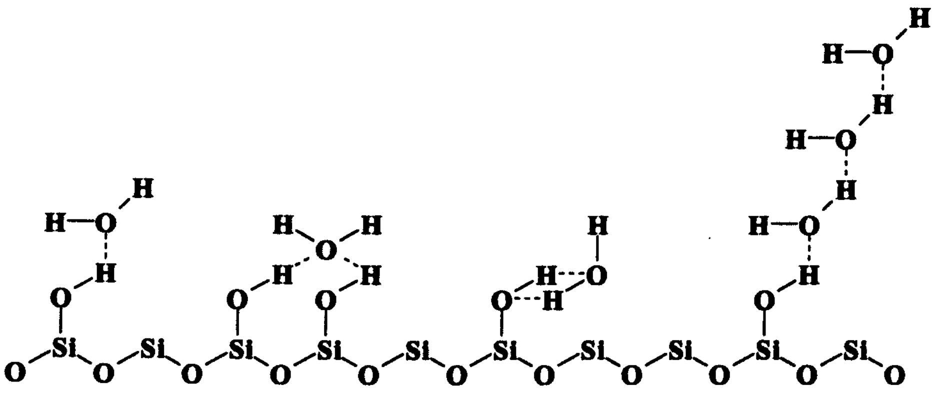


Figure 2.6: Various types of hydrogen bonded water on a silica surface.

total silanol groups at 200°C. Above 400°C, none are left and 85% of the silanol groups are isolated groups.

The silica gel Kieselguhr 100 (K100) from Merck was chosen as main support for this work. K100 is available in two particle sizes: 0.063 - 0.2mm and 0.2 - 0.5mm. For convenience through this thesis, the small size will be named either K100 or K100Small when the big size will be named K100Big. Some catalysts were also prepared using Kieselguhr 60 (K60) (particle size of 0.2 - 0.5mm) from Merck. The following section deals with the characterisation of these supports.

2.3.2 Characterisation of the K100 silica support

K100 silica gel has been used in our laboratory for various applications. Shorrock and Sage used supported aluminium chloride on K100 silica to catalyse polymerisation reactions[137, 138]. Supported Boron Fluoride on K100 was developed in our laboratory by Wilson et al.[94]. This catalyst was used for the alkylation of phenol with alkenes. It is also used for polymerisation reactions.

2.3.2.1 Characterisation by Nitrogen adsorption

K100 and K60 silica gels were analysed by nitrogen adsorption. Nitrogen adsorp tion - desorption isotherm and the pore size distribution is presented for each set of supports.

Figure 2.7 shows the surface area and pore size distribution of the K100 silica gel as purchased and pre-treated at 200, 600, 750 and 900°C. K100 silica gel exhibits type IV isotherms, which are characteristic of mesoporous materials, with cylindrical pores. The isotherm also exhibits an H1 type hysteresis loop, which is characteristic of a relatively narrow distribution of uniform pores. This can be seen on the plot of the pore size distribution, where all pores exhibit a diameter between 3 and 15Å. The pre-treatment of K100 silica gel at high temperature does not affect the isotherm shape, therefore the pores retain their shape. However the total adsorbed volume decreases to half its original value, when 900°C is the pre-treatment temperature. The amount of large diameter pores also decreases, while the pore size distribution for small pores (3 to 7Å) remains similar to the non-treated K100 silica gel. This reflects either the rearrangement of the silica particles or the partial structure collapse of the large pores of silica gel when treated to high temperature, when the small pores retain their shape. A consequence of this collapse is the increase in ratio of the external surface area with the pre-treatment temperature, as the contribution of the pore walls to the total surface area decreases.

Figure 2.8 shows the isotherm and pore size distribution of the two different particle sizes of K100 silica gel without thermal pre-treatment. Both isotherms are of type IV with an H1 hysteresis and similar pore size range. The total adsorbed volume is slightly higher for the K100Big, probably due to bigger inter-particle spaces.

K60 nitrogen adsorption – desorption studies are shown in the figure 2.9. K60 also exhibits a type IV isotherm with an H1 hysteresis loop, characteristic of a mesoporous material with cylindrical shaped pores. The pore size range is very narrow, between 3 and 10Å, narrower than for the K100 silica gel, as expected from the manufacturer's specification. High temperature pre-treatment also affects the physical properties of the solid: drying of the surface at 200°C does not decrease the total volume adsorbed, but pre-treatment of the K60 silica gel at 750°C induces a partial structure collapse, as observed for the K100 silica gel.

The BET surface areas, pore volumes and average pore diameters are summarised in Table 2.2. The effect of pre-treatment of the silica gel by high temperature is again illustrated here with a decrease in surface area and pore volume at high

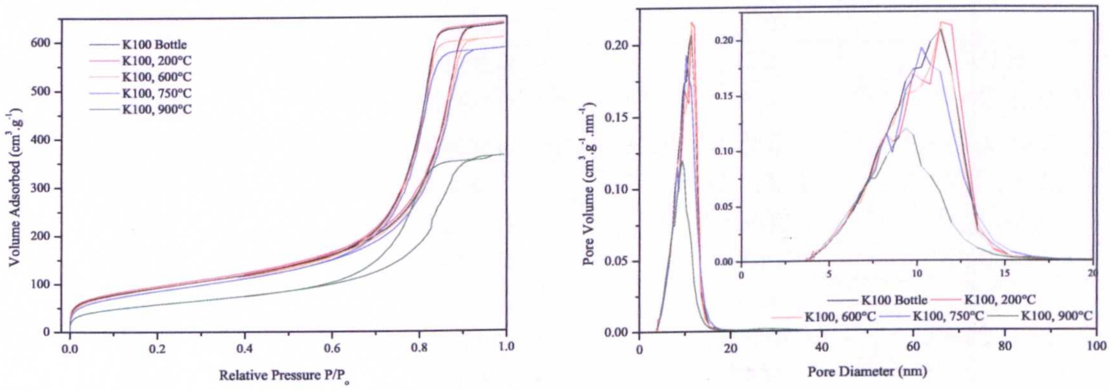


Figure 2.7: Nitrogen adsorption (left) and desorption isotherm and pore size distribution (from the desorption curve)(right) of the K100 silica gel calcined at different temperatures. The analysis of the K100 pre-treated at 200 and 600°C were carried out by Sage[138].*(Original in colour)*

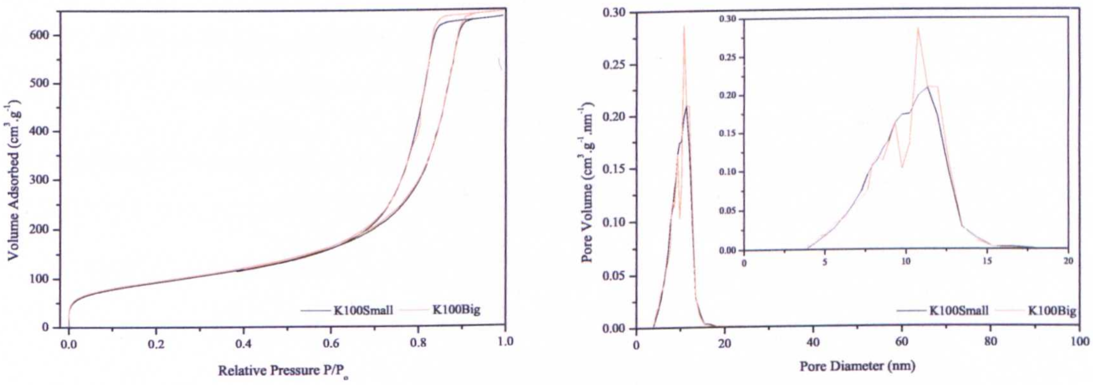


Figure 2.8: Nitrogen adsorption and desorption isotherm (left) and pore size distribution (from the desorption curve)(right) of the K100 silica gel, comparison between the two particle sizes.*(Original in colour)*

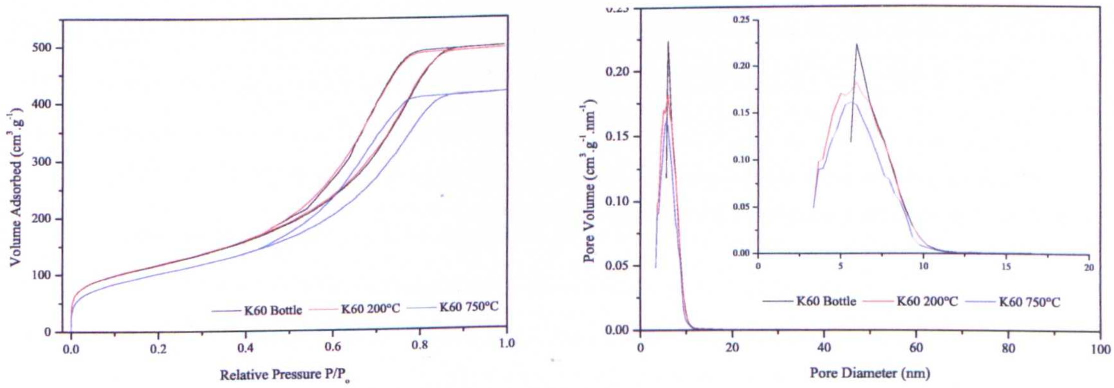


Figure 2.9: Nitrogen adsorption and desorption isotherm (left) and pore size distribution (from the desorption curve)(right) of the K60 silica gel calcined at different temperatures.*(Original in colour)*

Support	BET surface area m^2g^{-1}	Total pore volume cm^3g^{-1}	Average pore diameter† nm
K100	333.2	0.9812	11.78
K100, 200°C‡	345.7	0.9858	11.41
K100, 600°C‡	333.5	0.9389	11.26
K100, 750°C	311.3	0.9054	11.63
K100, 900°C	208.82	0.5624	10.77
K100Big	340.45	0.9983	11.73
K60	424.4	0.7718	7.27
K60, 200°C	428.99	0.7655	7.14
K60, 750°C	374.37	0.6441	6.88

†: based on the assumption that the pores are cylindrically shaped.

‡: results obtained by Sage[138].

Table 2.2: Surface area, pore volume and average pore diameter of the different K100 and 60, as purchased and pre-treated at high temperature.

Wavenumber (cm^{-1})	Vibration mode
3745	Isolated O–H, stretching
3700-3100	Hydrogen bonded O–H, stretching
1870	Overtone skeleton vibrations
1630	Molecular water, bending
1250-1000	Si–O–Si, symmetric and asymmetric stretching
970	Si–OH, stretching
810	Si–O–Si, bending

Table 2.3: Assignments of bands in the DRIFT spectra of the K100 and K60 silica gel.

temperature. The BET surface area of the 900°C pre-treated K100 silica gel is about a third lower compared to the K100 purchased silica gel.

K100Big exhibits similar surface area and pore characteristics compared to the K100 of smaller particle size. K60 exhibits a higher surface area, which could be advantageous when used as support, as the contact surface with the reagent will be higher. The pore size is however smaller compared to the K100 silica gel.

2.3.2.2 Characterisation using DRIFT

K100 and K60 silica gels were analysed by DRIFT spectroscopy. Figure 2.10 presents the spectra of K100 silica recorded following two procedures. The curve labelled 'K100 Bottle' (black) presents the spectra recorded under vacuum at room temperature of K100 silica as purchased. The three next curves present the same silica sample, heated inside the IR vacuum cell at the temperature of

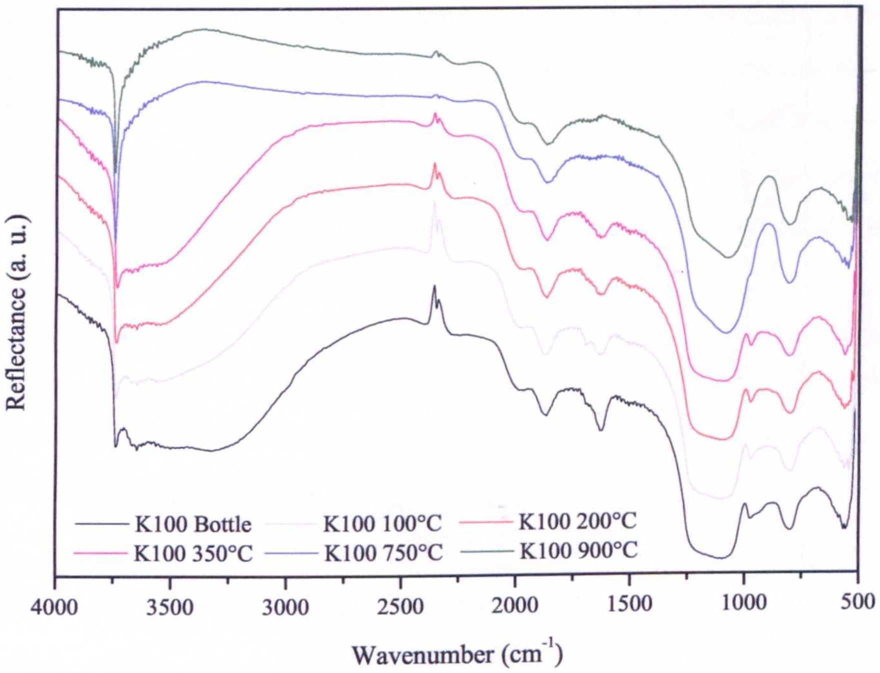


Figure 2.10: DRIFT spectra of K100 silica gel; upward: the four first curves are the spectra of K100 silica calcined inside the IR vacuum cell, the two last ones are the spectra recorded at 150°C of K100 at the given temperature in a muffle furnace. *(Original in colour)*

100°C (grey), 200°C (red) and 350°C (magenta). The curves K100 750°C (blue) and K100 900°C (green) present the spectra recorded under vacuum at 150°C of a K100 silica sample calcined beforehand at 750 or 900°C in a muffle furnace and stored without care regarding exposure to moisture.

The bands can be attributed to various vibration modes of the silanol and siloxane groups of the silica gel and are summarised in Table 2.3. The two most prominent bands for all spectra obtained from silica calcined at different temperatures are seen at 1090 and 1200cm^{-1}, they are assigned respectively to the asymmetric and the symmetric stretching mode of bulk silica (siloxane, $\equiv$Si–O–Si$\equiv$).
The band at 1630cm^{-1} is assigned to adsorbed water (O–H). As expected, this band decreases when the calcination temperature is increased and disappears at temperature above 700°C. The absence of this band for the support calcined at temperature above 700°C and stored without care regarding moisture exposure shows that this calcined silica support is and remains for a reasonable long time hydrophobic. Sage has also shown that this band nearly disappears for K100 silica calcined beforehand at 600°C[138].
The sharp band at 3745cm^{-1} corresponds to isolated silanol groups. This band is still present for the silica calcined at 900°C, therefore isolated silanol groups

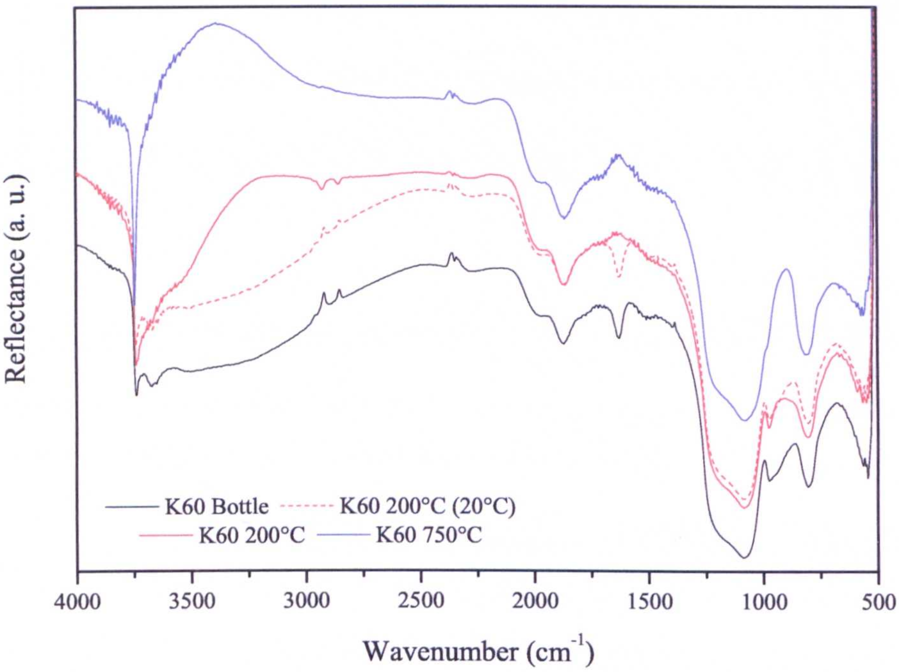


Figure 2.11: DRIFT spectra of K60 silica gel, as purchase, or calcined at the given temperature in a muffle furnace. The spectra were recorded under vacuum at 20°C (K60 Bottle) or at 150°C (K60 750°C and 900°C).*(Original in colour)*

still exist on the silica surface.

The broad band between 3700 to 3100cm^{-1} is characteristic of hydrogen bonded OH groups, this corresponds to the vicinal silanol groups and physisorbed water. As expected, this band decreases as the temperature is raised and completely disappears at high calcination temperature. This intensity decrease corresponds to the removal of physisorbed water and also shows the condensation of silanol groups into siloxane bridges. The intensity of the band at 970cm^{-1}, assigned to the stretching mode of the vicinal silanol groups, also decreases with the temperature and completely disappears for silica calcined at high temperature, indicating complete dehydroxylation of the silica surface.

This dehydroxylation process is also confirmed by the intensity increase of the band at 810cm^{-1}, assigned to the bending mode of the siloxane groups.

The same bands assignments can be made for the spectra of K60 silica gel (Figure 2.11). The 'K60 Bottle' curve presents the spectrum recorded under vacuum at room temperature of the K60 silica gel as purchased.

The red lines present the spectra of the K60 silica gel dried in an oven at 200°C, recorded at room temperature (dashed red) and at 150°C (solid red). The bands corresponding to physisorbed water are not present when the spectrum is recorded at 150°C, which confirms that a significant amount of physisorbed water was removed when dried in the oven at 200°C. Some vicinal silanol groups are still present on the surface. However, the surface of a 200°C dried K60 silica gel remains highly hydrophilic, as shown by the reappearance of the bands corresponding to the physisorbed water, when a sample of the same batch is exposed for a short time to air moisture.

The blue line presents the spectrum of the K60 silica gel calcined in a furnace at 750°C recorded under vacuum at 150°C. A sample from the same batch recorded at room temperature would show the same bands (not plotted), which shows that the surface became hydrophobic.

2.3.2.3 Characterisation using ^{29}Si solid NMR

Shorrock recorded ^{29}Si MAS-NMR of K100 silica gel, pre-treated at 300°C[137]. The spectrum exhibited one main peak at -110ppm (Q^4, bulk silicon linked to four other silicon atoms *via* oxygen atoms) with two shoulders at -100 (Q^3, silicon bearing a silanol group) and -90ppm (Q^2, silicon bearing two geminal silanol groups). The intensities of these two peaks were expected to vary with the pre-treatment temperature, as pre-treatment modifies the silanol concentration on the silica gel surface[139, 140].

2.4 Supported aluminium phenolate

2.4.1 Supported Lewis acids on silica

Immobilised Lewis acids on silica support have been prepared for use in organic reactions to help reducing chemical wastes and product contaminations by improving reactivity and / or selectivity, avoiding aqueous quenching steps and favouring catalyst reuse. Various examples of supported Lewis acids can be found in the literature[86, 141–144].

Figure 2.12 summarises the different steps of the preparation of supported Lewis acids. The support can be used as obtained or prepared and can be pre-treated in order to modify or control some of its characteristics, such as structure or nature

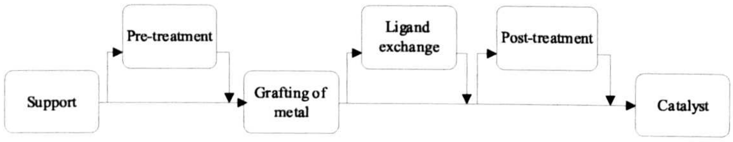


Figure 2.12: Preparation steps of supported Lewis acids by grafting of the metal on the support surface.

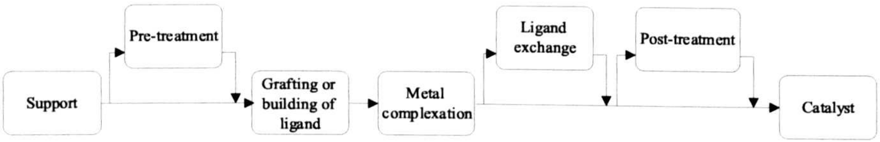


Figure 2.13: Preparation steps of supported Lewis acids by grafting or building of a ligand of the catalyst complex on the support surface.

of the surface. The metal of the catalyst complex is then grafted to the surface, *via* several means, for example by mixing the metal reagent with the solid in a solvent or by vapour deposition[135]. If the chosen metal complex is the desired catalyst, then the supported catalyst is ready. If the metal reagent was chosen to facilitate the grafting of the metal on the support surface but the ligand is not the desired one, ligand exchange can then be carried out. Finally, a post-treatment may be necessary to fine tune the final properties of the catalyst, for example partial poisoning or surface modification.
One example of the preparation of a supported catalyst using this method will be described in section 2.4.3.

Another method of preparation is summarised in Figure 2.13. In this case, one of the ligands of the catalyst complex is first grafted or built on the surface of the support. The metal reagent then is reacted with this modified support to form the catalyst complex or its precursor[145].

The two methods described here, as for other, involve the grafting of a reagent by the means of "handling" groups available at or on the surface of the support. The choice of the support and the control of the nature of its "handling" groups are therefore of prime importance. In the case of silica gel, these "handling" groups are the silanol and the siloxane groups. These react with a chemical reagent forming either physisorbed or chemisorbed species. Figure 2.14 shows the three different pathways. Reaction between silanol group and the reagent can lead either to physisorbed species involving secondary bonds (path 1), or to chemisorbed species involving covalent bonds (path 2). Reaction with siloxane

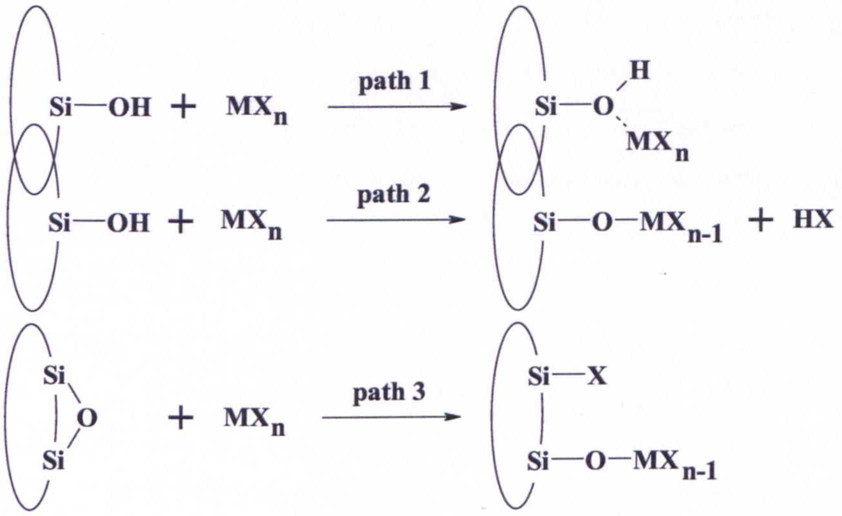


Figure 2.14: Possible reactions between handling groups at the surface of the silica with a chemical: paths 1 and 2, reactions with the silanol groups; path 3, reaction with the siloxane groups.

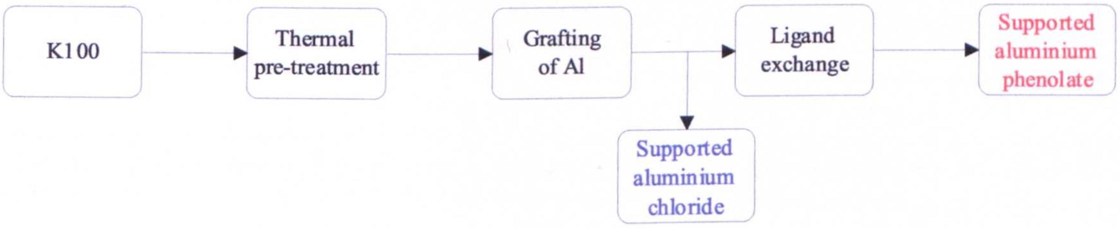


Figure 2.15: Preparation steps of the supported aluminium phenolate. *(Original in colour)*

groups lead to the same chemisorbed groups as previously described and a silicon based function (path 3). The chemical reagent can be a metal reagent, such as a Lewis acid, or a silane, which will allow the grafting of an organic group on the surface.

2.4.2 New supported catalyst: supported aluminium phenolate on K100 silica gel

Selective *ortho-* alkylation of phenols with alkenes is carried out using a metal phenolate as catalyst. As described in chapter 1, the *ortho-tert*butylphenols are prepared with aluminium phenolate as catalyst, requiring aqueous quenching steps. One of the aims of this work is to avoid these quenching steps by immobilising the catalyst on a silica support. More precisely, the goal is to obtain a diphenolate aluminium species attached to the silica surface *via* an oxygen atom.

The preparation steps of such a new supported catalyst are shown in Figure 2.15. The support, silica gel K100, is first thermally pre-treated to control the hydration level and the surface properties. The metal is then grafted on the silica surface. The material obtained is a supported aluminium material, and in the case aluminium chloride is used as metal reagent, is a silica supported aluminium chloride. The preparation of such catalyst is described in the literature and will be summarised in section 2.4.3. Using this material and exchanging the chloride ligand with a phenol leads to the desired supported catalyst.

In the work described here, the support is the K100 silica gel (both particle sizes are used) and K60, treated at various temperatures (200, 600, 750 and 900°C). The metal reagent (which will also be referred to as "metal precursor" throughout the thesis) used to produce the desired material will be mainly aluminium trichloride (ATC). Triethyl aluminium (TEAL) and aluminium phenolate were also investigated and will be described, respectively, in sections 2.4.6 and 2.4.7.

2.4.3 Preparation of supported aluminium chloride on silica

At room temperature, pure aluminium trichloride is a colourless, crystalline and very moisture-sensitive chemical[146]. The presence of impurities, excess of metal, chlorine, iron or traces of organic matter, gives to aluminium trichloride a colour, either pale orange to yellow, or green to gray. The solid presents a dimeric structure, Al_2Cl_6, with an aluminium coordination number of 4, which prevails up to 440°C. Between 440°C and 880°C, an equilibrium between the monomer and the dimer exits. Above 880°C, only the monomer subsists. At high temperature (above 1000°C), ionic dissociation can take place[147].

In solution, various coordinations are observed. In inert solvent, the major form is the dimer form with a coordination number of 4. Aluminium trichloride reacts violently with water generating hydrochloric acid and ill-defined oxychloride aluminium species. Fumes are evolved when the aluminium trichloride is in a moist atmosphere[146].

Aluminium trichloride finds its main use as catalyst for Friedel-Crafts reactions [146]. It has to be noted that the active catalytic species for this reaction is the monomeric form of aluminium trichloride[148].

Due to toxicity, corrosion and waste problems attached to its use[2], numerous publications on the immobilisation or grafting of aluminium chloride on a variety of supports, such as polymers[149], alumina[150] or silica, can be found. Silica being the chosen support for this work, the preparation of supported aluminium chloride on this support is shortly reviewed here.

The first reported immobilisation of aluminium trichloride on silica was carried out using the vapour deposition method. The aluminium chloride is vaporised above 200°C and the dimeric species reacts with the silanol groups to form Si–O–Al bonds in either a chloro or a dichloro aluminium species[151]. Drago and Getty immobilised aluminium chloride in the liquid phase using chlorinated solvents[152–154]. Clark et al. improved the 'greenness' of the catalyst by using alternative (non-chlorinated solvents such as toluene) solvents and supports[155]. More recently the use of Micelle Templated Silica (MTS)[156] as support was also reported[157, 158]. All these various catalysts are active in a subsequent number of reactions and help to improve their greenness by reducing waste and allowing the reuse of the aluminium chloride[See for examples 157–161].

From all these studies, several critical parameters emerged. The kind and structure of the support, more particularly the pore size, the surface acidity and hydration level, the solvent used for the preparation, influenced the activity and selectivity. The loading of the catalyst is also important. Below 2mmolg^{-1}, the Si–O–Al bond stability was confirmed as no leaching of active species was observed in the reaction products. Above this level, aluminium trichloride starts to aggregate with aluminium trichloride already bonded to the surface. On the other hand, low loading leaves some uncovered surface, which can initiate side reactions.

Different possible aluminium species grafted on the surface are summarised in Figure 2.16. Reaction between aluminium trichloride and siloxane groups of the silica surface lead to a very reactive Si–Cl bond (path 3, figure 2.14) and a dichloro aluminium species (structure 1). A dichloro aluminium species may also react with a siloxane group and generate a monochloro species and a Si–Cl group. The Si–Cl bond, being very reactive, would be readily hydrolysed by any trace of water present in the reaction mixture. Structure 2 and 3 are the results of reaction between aluminium trichloride and surface silanol groups. The dichloro species is a strong Lewis acid site while the monochloro is a weak Lewis acid site.

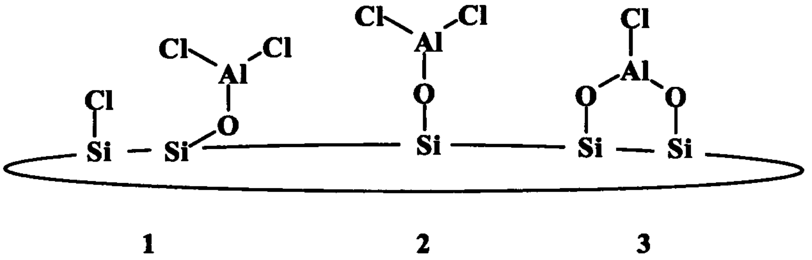


Figure 2.16: Aluminium sites on the silica gel surface, following reactions between aluminium trichloride and siloxane groups (1) and silanol groups (2 and 3).

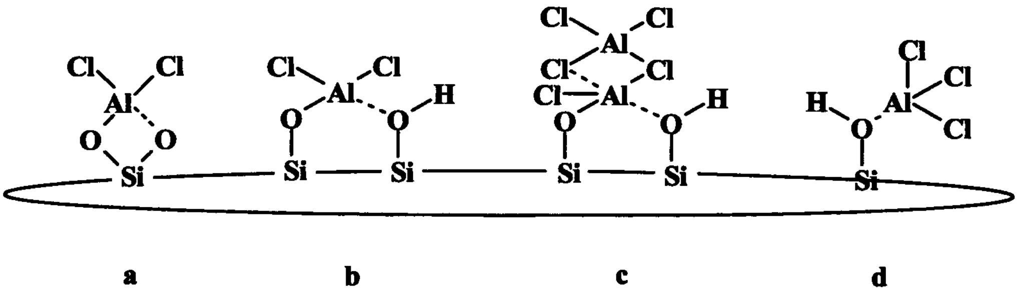


Figure 2.17: Other possible aluminium sites on the silica gel surface, involving secondary bonds.

Other possibilities, involving secondary interactions, are shown in Figure 2.17, where the aluminium trichloride reacts with geminal or vicinal silanol groups (respectively structure a and b), or where the dimer reacts or forms at the surface (structure c). Aluminium trichloride may also interact with a silanol group and form an acid site exhibiting both Brønsted and Lewis acidities (structure d).

MAS-NMR spectra of ^{29}Si and ^{27}Al were recorded by Shorrock and Sage in our group[137, 138]. The ^{29}Si MAS-NMR spectrum of the supported aluminium chloride showed that the main peak was shifted downfield to -105ppm and was attributed to silicon atoms bonded to aluminate and three other silicon atoms *via* oxygen atoms[140]. The intensities of the two shoulder peaks at -100 and -90ppm observed on the support spectrum (Section 2.3.2.3) decreased, consistently to the grafting of aluminium trichloride *via* reaction with surface silanol groups.

Figure 2.18 summarises the aluminium centre with associated aluminium chemical shift. For a catalyst prepared with a loading of 0.8mmolg^{-1}, four peaks were observed at 87, 62, 35 and 2ppm. These peaks correspond respectively to 4-coordinated AlCl–(OSi)$_2$ interacting with a silanol, 4-coordinated AlCl$_2$–(OSi) interacting weakly with a silanol, 5-coordinated aluminium atom with two chlorine atoms and three oxygen atoms, and 6-coordinated aluminium atom corresponding

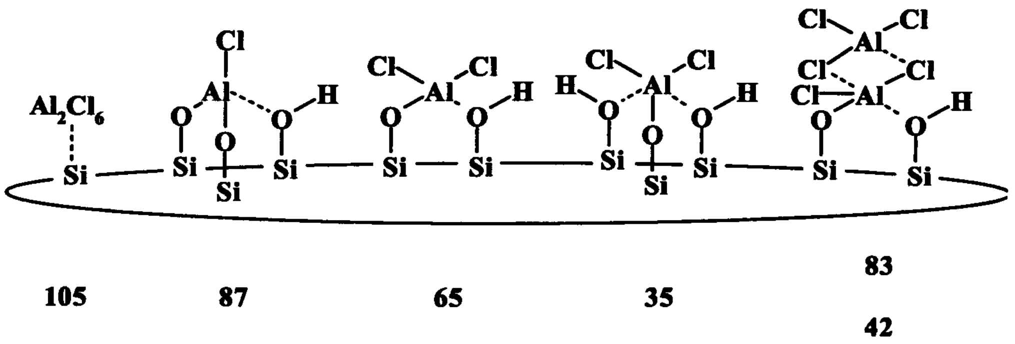


Figure 2.18: ^{27}Al MAS-NMR chemical shifts (ppm) of aluminium sites on the surface of the supported aluminium chloride.

to octahedral species formed with water. At higher loading, aluminium trichloride aggregates leading to two new aluminium centres, one 4-coordinated $AlCl_4$ at 83ppm, and one 5-coordinated $AlCl_3(OSi)_2$ at 42ppm. No peak corresponding to physisorbed aluminium trichloride dimer (around 100ppm) was observed. The relative intensities of these peaks varied with the silanol concentration on the silica gel surface, hence the pre-treatment temperatures[139, 154].

Acidities measurements were also reported by Shorrock and Sage[137, 138]. Studies, using the adsorption of pyridine and DRIFT method, showed that both Lewis and Brønsted acid sites were present at the surface of the $AlCl_x$K100 material. Studies, using the ^{31}P MAS NMR method, showed that two mains peaks were observed ($\Delta\delta = 17, 29$), as well as the peak corresponding to the coordinated TEPO with the silica surface ($\Delta\delta = 6$). The authors explained these two peaks by the presence of two aluminium species on the silica gel surface, the dichloro $AlCl_2$–OSi and the monochloro AlCl–$(OSi)_2$ species.

Supported aluminium chloride exhibits a yellow colour, which intensity depends on the silica surface and the loading. Once exposed to air and moisture, the colour of the material turns from yellow to pink at a speed depending also on the silica pre-treatment temperature and the loading. The pink colour becomes then lighter and lighter and finally turns grey. These pink and grey supported aluminium materials were not active in the reactions investigated by Sage and Shorrock[137, 138].

For convenience throughout the thesis, the supported aluminium chloride on K100 silica gel will be named $AlCl_x$K100. More details regarding the catalyst will be

Method 'is': By refluxing the AlCl$_x$K100 in phenol in the reaction flask

Method 'ishf': By refluxing the AlCl$_x$K100 in phenol, followed by hot-filtration

Method 'hf': Hot-filtration of the AlCl$_x$K100 with a phenol-toluene solution

Method 'jc': In a hot jacket-column with a phenol-toluene solution

Method 'tp': By refluxing the AlCl$_x$K100 in a phenol-toluene solution, in two steps (tp1) or in a one-pot (tp2).

Table 2.4: Preparation methods of the supported aluminium phenolate from the AlCl$_x$K100.

noted as follows:

$$\mathrm{AlCl}_x\mathrm{Support}\begin{pmatrix}\text{Pre-treatment}\\ \text{temperature}\end{pmatrix}\begin{pmatrix}\textit{Theoretical}\\ \textit{loading}\end{pmatrix}$$

For example, the supported aluminium chloride on K100 silica gel as support, pre-treated at 600°C, with a theoretical loading of 0.8mmolg^{-1} will be noted as:

AlCl$_x$K100(600)(*0.8*).

2.4.4 Preparation of the supported aluminium phenolate

2.4.4.1 Preparation methods

As described in section 2.4.2, the last step of the preparation of the supported aluminium phenolate is the ligand exchange from chlorine to phenol of the aluminium site of the supported aluminium chloride. Five different methods were developed to achieve this goal and are listed in Table 2.4.

Method 'is' involves the preparation and isolation of the AlCl$_x$K100. The ligand exchange step is then carried out in the flask in phenol at reflux temperature. The mixture is subsequently cooled down and the phenol is then alkylated. The ligand exchange step generates hydrogen chloride, which has to be removed from the mixture by a flow of nitrogen to avoid side alkylation in *para-* position. If this method is easily carried out in a flask mounted with a condenser, the removal of the hydrogen chloride when the reaction is carried out in the pressure reactor is not complete, therefore leading to *para-* substitution.

Method ‘ishf’ involves the mixing of AlCl_xK100 in phenol at reflux temperature under a nitrogen atmosphere. When the exchange is complete, the slurry is filtered above the melting point of phenol and washed with dried toluene. If the catalyst is kept wet at all time, the catalyst is active in the alkylation reaction. Unfortunately, characterisation is difficult due to the presence of physisorbed phenol filling the pores, which is not removed by toluene washing.

Methods ‘hf’ and ‘jc’ involve the ligand exchange step in the hot filter or in a column by a toluene-phenol solution. These were not satisfactory practically and were not further investigated.

Method ‘tp’ is the easiest and most efficient. The two steps are either separated or carried out in a one-pot method. Once the AlCl_xK100 is prepared, the slurry is cooled down, then either separated, dried and placed in fresh dry solvent with the phenol, or the phenol added with the material kept in its own solvent. By this means, the solvent used to prepare the AlCl_xK100 is recycled. The separation of the final catalyst is facilitated and the characterisation of the surface is possible. Another difference between the two methods ‘tp’ is that a washing step between the aluminium trichloride grafting and the ligand exchange step removes all unreacted aluminium trichloride, when with the reuse of the grafting step solvent allows unreacted aluminium trichloride to form with phenol chlorophenoxo aluminium species, which can then further be attached to the silica surface.

Unless stated, all the results presented in this chapter and in chapter 3 were obtained with catalysts prepared using this last method.

For convenience throughout the thesis, the supported aluminium phenolate will be named as follows:

$$\mathrm{Al(OPh)}_x\mathrm{Support}\begin{pmatrix}\text{Pre-treatment}\\ \text{temperature}\end{pmatrix}\begin{pmatrix}\text{Al}\\ \text{origin}\end{pmatrix}yy\begin{pmatrix}\textit{Theoretical}\\ \textit{loading}\end{pmatrix}$$

where ‘Support’ is the abbreviation of the support, ‘Al origin’ is the chemical reagent used to graft the aluminium on the silica gel surface and ‘yy’ are the abbreviations naming the catalyst preparation method given in Table 2.4. For example, the supported aluminium phenolate on 200°C pre-treated K60 silica gel prepared from aluminium trichloride with a loading of $1.7\mathrm{mmolg}^{-1}$ using the method ‘tp’ (Table 2.4) is named:

$Al(OPh)_xK60(200)(ATC)tp(1.7)$.

2.4.4.2 Possible active sites

In this section, a list of possible active sites, which may exist on the catalyst surface, will be presented. For the $Al(OPh)_x$Silica, being prepared by ligand exchange from the $AlCl_x$Silica, some active sites of the new catalyst may be proposed (Figure 2.19). These are the monochloro and the dichloro aluminium species. Depending on the nature of the silica surface, the sites may be isolated or complexed with silanol groups.

Beside these main sites, side reactions may occur. Physisorbed water, which could be present as traces despite the precautions taken, may hydrolyse the Al–O–C bond, generating aluminium hydroxide species. Besides, the ligand exchange also generates hydrogen chloride. During the catalyst preparation, a constant flow of nitrogen was then applied through the stirred refluxing mixture, to remove this Brønsted acid. However, hydrogen chloride can complex to aluminium sites or be physisorbed on the surface *via* secondary bonds with a silanol group.

It also should be borne in mind that the exchange may not be complete and that sites with only chloride or with chloride and phenolate attached to the aluminium may exist, as shown in Figure 2.19. The presence of mixed ligands will change the acidity of the aluminium centre and modify the complexation effect of the phenolate group.

During the preparation of the supported aluminium chloride, Si–Cl group may be generated (Section 2.4.3). This group can react with phenol and generate silicon phenolate group. However the concentration of this function is expected to be low, since the Si–Cl concentration on the surface of the supported aluminium chloride is low[138] and as the very reactive group has to survive until the ligand

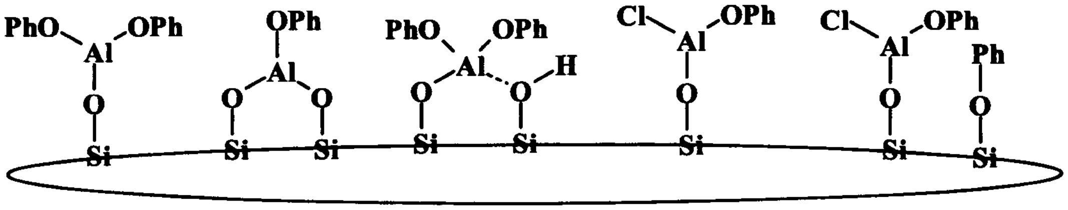


Figure 2.19: Some possible aluminium sites on the silica gel surface of the supported aluminium phenolate.

exchange step.

However, silanol and phenol may react together and generate the silicon phenolate function.

2.4.5 Characterisation of the supported aluminium phenolate

The following section will present the characterisation of the supported aluminium phenolate, prepared with aluminium trichloride as aluminium precursor, using several techniques.

2.4.5.1 Elemental analysis

Theoretical and found weight percents are summarised in Table 2.5 for various catalysts. The column "Catalyst" gives the catalyst type and the parameters regarding respectively the support pre-treatment temperature and the amount (theoretical loading) of aluminium trichloride in mmol per g of silica used for the preparation of the $AlCl_xK100$. The theoretical and found weight percentages are given in mmol per g of analysed catalyst. Hypotheses have to be drawn to correctly link the theoretical loading (given in $mmolg_{silica}^{-1}$) and the expected weight percent and theoretical loading (given in $mmolg_{catalyst}^{-1}$). Two assumptions are made, each leading to a different calculation. The first one, assumption A1, consists in assuming that all the aluminium trichloride reacts only once with a silanol group on the silica surface, therefore with a loss of one hydrogen chloride molecule, leading to the dichloro aluminium species $(SiO)\text{–}AlCl_2$. The second one, assumption A2, is to assume that all aluminium trichloride reacts twice with silanol groups on the silica surface, hence with a loss of two hydrogen chloride molecules, leading to the monochloro aluminium species $(SiO)_2\text{–}AlCl$. These two assumptions lead to a range of weight percent values. As described in section 2.4.3, these two species are the main aluminium species at the surface of the supported aluminium chloride $AlCl_xK100$ material. For the supported aluminium phenolate, all chloride ligands are assumed to have been exchanged into phenolate.

Catalyst $Al(X)_xK100$	Th. Al cnt. wt%	Th. Ld. $mmol.g^{-1}$	Fd. Al cnt. wt%	Fd. Ld. $mmol.g^{-1}$	Fd./Th. %
X=Cl, 200°C, 1.7	3.95 - 4.10	1.46 - 1.54	3.6	1.38	94.5
X=OPh, 200°C, 1.7	3.31 - 3.82	1.25 - 1.42	2.9	1.11	88.8
X=OPh, 200°C, 0.8	1.85 - 1.97	0.68 - 0.73	1.5	0.56	82.4
X=OPh, 750°C, 0.8	1.85 - 1.97	0.68 - 0.73	1.03	0.39	57.4
X=OPh, 900°C, 0.8	1.85 - 1.97	0.68 - 0.73	0.58	0.22	32.3

Table 2.5: Aluminium content by elemental analysis of different catalysts. (Fd.: Found, Ld.: Loading in $mmolg^{-1}_{catalyst}$, cnt.: Content)

The assumption A1 can be written as follows:

$$SiOH + AlCl_3 - HCl \longrightarrow SiO\text{-}AlCl_2 \quad \text{which is a gain of } 97g.mol^{-1}.$$

Therefore, if 1.7mmol of aluminium trichloride is used for 1g of silica, the final weight of the $AlCl_xK100$ assuming A1 is 1.1649g, and 0.0459g of aluminium is present. The theoretical weight percent is therefore $\frac{0.0459}{1.1649} = 3.95\%$, which corresponds to a theoretical loading of $\frac{1.7}{1.1649} = 1.46 mmolg^{-1}_{catalyst}$. All other calculations were done following the same method with equations:

$$\begin{array}{lcll} 2\ SiOH + AlCl_3 - 2\ HCl & \longrightarrow & (SiO)_2\text{-}AlCl & \text{gain of } 60.5g.mol^{-1} \\ 2\ SiOH + Al(OPh)_3 - 1\ HOPh & \longrightarrow & SiO\text{-}Al(OPh)_2 & \text{gain of } 212g.mol^{-1} \\ 2\ SiOH + Al(OPh)_3 - 2\ HOPh & \longrightarrow & (SiO)_2\text{-}AlOPh & \text{gain of } 97g.mol^{-1} \end{array}$$

The found aluminium contents in weight percent of the different catalysts are given in the fourth column of Table 2.5 and the calculated loading in $mmolg^{-1}_{catalyst}$. All values are lower than the theoretical loading range. In the case of the $AlCl_xK100$, catalyst, the found loading represents 94.5% of the theoretical loading, which shows that nearly all the aluminium trichloride did graft on the silica surface. The corresponding phenolate exhibits a loading, which represents 88.8% of the expected loading, ratio lower than for the $AlCl_xK100$. One possible explanation could be a leaching of the aluminium during the ligand exchange step or the vaporisation of aluminium species during the drying step. However, during the ligand exchange step, an excess of phenol is used and may not have been completely removed by washings, therefore decreasing the weight percent of the aluminium, as this amount of remaining phenol is not taken into account in the calculations.

The found loadings for the catalyst prepared with 0.8mmol per g of silica, which was thermally pre-treated at different temperatures, show that not all the aluminium trichloride was grafted on the silica surface, and as the ratio is 32.3% for the catalyst prepared with silica treated at 900°C, the surface seems to be saturated. Due to the simplifying assumptions taken during the calculations, the real values are not exactly determined. However, these studies show the effect of the pre-treatment temperature on the loading of the final catalyst. The real loading is much lower than the expected one and the trend, 61% decrease from 0.56 to 0.22 (column 5 in Table 2.5), is higher than the decrease in surface area of the corresponding silica gel used as support, 37% 333.2 to 208.8m^{2}g^{-1} (Table 2.2, page 76).

For convenience through this thesis, the given loading of Al(OPh)$_x$K100 will be the amount of aluminium trichloride used in mmol per g of silica gel to prepare the AlCl$_x$K100 material. However, all catalyst amounts used experimentally were determined assuming that for a theoretical loading of $1.7 mmolg_{silica}^{-1}$ used for the preparation of the AlCl$_x$K100 material, the final theoretical loading of the Al(OPh)$_x$K100 catalyst was 1.35mmolg^{-1}, which is an average value of the theoretical loading in $mmolg_{catalyst}^{-1}$ (column 3 in Table 2.5).

2.4.5.2 X-Ray Photoelectron Spectroscopy (XPES)

Catalysts were analysed by XPES. Table 2.6 summarises the atomic concentration of oxygen, silicon, carbon, chlorine and aluminium, as well as some ratios. The two first rows compare results obtained for catalysts with the same parameters but prepared by two different methods, method 'ishf' (refluxing of AlCl$_x$K100 material in neat phenol followed by an hot filtration) and method 'tp 1' (isolation of the AlCl$_x$K100 material, then refluxing in a toluene-phenol solution). The catalyst prepared with method 'ishf' exhibits a much higher chlorine content than all the other catalysts and the higher Cl/Al ratio, showing that the exchange of the chlorine ligand is far from complete. Method 'tp' allows a more complete ligand exchange. The aluminium loading of the surface seems however to be in the same order.

The two next rows in the table compare results obtained from catalysts prepared by the methods 'tp': 'tp 1' or 'two steps'and 'tp 2' or 'one-pot'. These results show that the washing step between the aluminium trichloride grafting step and the ligand exchange step do not affect the atomic concentrations of the five ana-

S. Pre-T. Temp. °C	Th. Ld. mmolg^{-1}	%O	%C	%Cl	%Si	%Al	Cl/Al	C/Al	Si/O	Si/C
200†	1.7	37.12	19.74	26.45	4.89	11.83	2.24	1.67	0.13	0.25
200§	1.7	43.01	33.69	6.38	3.61	13.32	0.48	2.53	0.08	0.11
600§	0.8	57.43	19.18	0.16	21.7	1.54	0.1	12.5	0.38	1.13
600	0.8	56.11	21.74	0.16	20.4	1.54	0.11	14.14	0.36	0.94
200	0.8	57.87	19.15	0.16	21.26	1.57	0.1	12.2	0.37	1.11
600	0.8	56.92	20.56	0.24	20.66	1.61	0.15	12.74	0.36	1.0
750	0.8	56.47	19.77	0.26	22.05	1.45	0.18	13.6	0.39	1.11
900	0.8	58.83	16.83	1.17	19.73	3.44	0.34	4.89	0.34	1.17

S. Pre-T. Temp.: Surface pre-treatment temperature, Th. Ld.: Theoretical loading.
†: prepared using the method 'ishf'; §: prepared using the 'two steps' method (tp 1). All other samples were prepared using the 'one-pot' preparation method (tp 2).

Table 2.6: Atomic concentrations of Al(OPh)$_x$K100()(ATC)tp() catalysts measured by XPES.

lysed elements.

The four next rows compare catalysts prepared with K100 silica gel pre-treated at different temperature. The atomic concentration of Cl increases with the pre-treatment temperature, when the atomic concentration of Al increases significantly between 750 and 900°C. However, from the elemental analysis results, we know that the aluminium loading decreases with the pre-treatment temperature. Since the XPES analysis concerns the first layers of the catalyst surface, and as it will be shown by the nitrogen analysis that the pore size distribution shifts toward lower pore diameter values with the pre-treatment temperature, these results suggest that the aluminium is more and more grafted outside the pores when the high temperature pre-treated silica gel is used. The Cl/Al ratio, staying almost constant up to a pre-treatment temperature of 750°C, increases for a temperature of 900°C, showing that the ligand exchange is less complete when using this support. This is confirmed also by the sharp decrease of the C/Al ratio between 750 and 900°C.

Catalysts prepared with a theoretical loading of 1.7mmolg^{-1} show a low Si content, this is explained by the fact that for this loading, the surface is well covered by aluminium species hiding the silica from the XPES beam. For a theoretical loading of 0.8mmolg^{-1}, the surface is less covered by aluminium species, and the silicon is more visible.

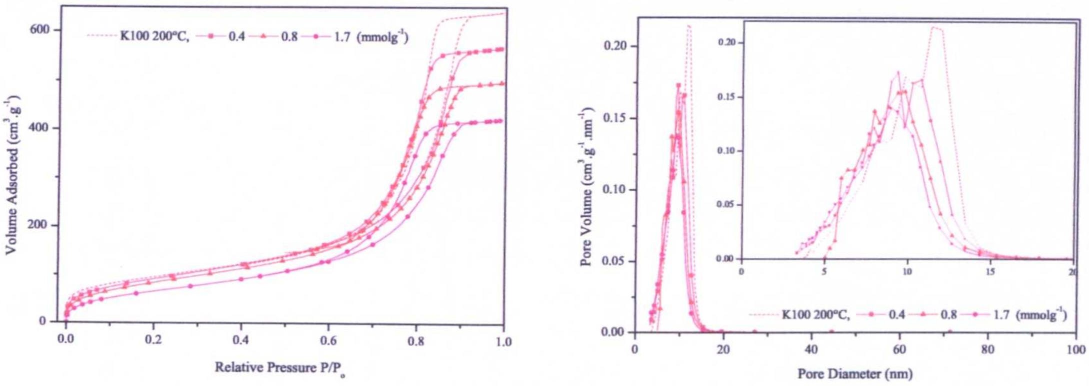


Figure 2.20: Nitrogen adsorption – desorption isotherm (left) and pore size distribution (from the desorption curve) (right) of Al(OPh)$_x$K100 catalysts prepared with thermally pre-treated at 200°C silica gel and different aluminium loadings. The analysis of the support itself, K100 pre-treated at 200°C represented by the dashed line, were carried out by Sage[138]. *(Original in colour)*

2.4.5.3 Nitrogen adsorption

Effects of the support pre-treatment temperature and the theoretical aluminium loading were studied using the nitrogen adsorption technique. Figure 2.20 shows the adsorption – desorption isotherm and the pore size distribution of catalysts prepared with thermally pre-treated at 200°C silica gel and different aluminium loadings (Al(OPh)$_x$K100).

The isotherm shape of the catalysts plots remains sensibly similar to that of the support, indicating that the grafting of the aluminium species on K100 silica gel surface did not affect its structure. The decrease of the total adsorbed volume at saturation relative pressure following the increase of the theoretical aluminium loading indicates that the grafting took place inside the pores. This is also confirmed by the shifting of the pore size distribution towards the smaller diameter values when the theoretical loading is increased.

Figure 2.21 shows the adsorption – desorption isotherm and the pore size distribution of Al(OPh)$_x$K100 catalysts prepared at an aluminium loading of 0.8mmolg^{-1} on silica thermally pre-treated at different temperatures. The solid lines correspond to the catalyst, when the dashed lines reproduce, for comparison, the data of the silica supports, already discussed in the section 2.3.2.1.

The grafting of the aluminium species on the silica surface, pre-treated thermally at high temperature, did not affect its structure. The decrease of the total

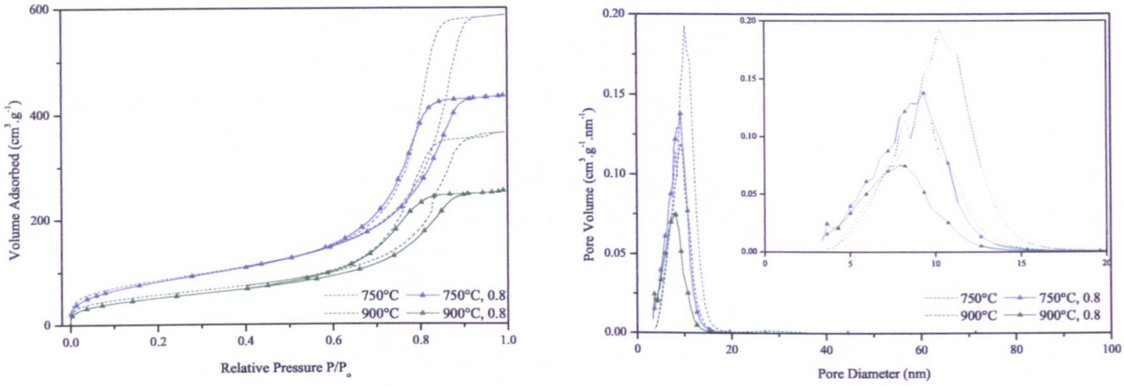


Figure 2.21: Adsorption – desorption isotherm (left) and pore size distribution (from the desorption curve)(right) of Al(OPh)$_x$K100 catalysts prepared with an aluminium loading of 0.8mmolg^{-1} on silica thermally pre-treated at different temperatures. (The solid lines correspond to the catalyst, while the dashed lines reproduce, for comparison, the data of the silica supports) *(Original in colour)*

adsorbed volume at saturation relative pressure between the support itself and the catalyst material, and the shifting of the pore size distribution towards the smaller diameters, show that some grafting took place inside the pores.

Table 2.7 shows the BET surface area, the total pore volume and the average pore volume of supported aluminium phenolate on K100 silica gel.

For catalyst prepared using a support pre-treated at the same temperature (200°C), the surface area and the total pore volume decreased as the theoretical aluminium loading was increased. This indicates that aluminium species have been successfully grafted on the surface of the silica gel, filling the smallest pores (micropores), hence reducing the surface area.

For catalyst prepared with a loading of 0.8mmolg^{-1}, the surface area and the total pore volume of the catalysts were in every case lower than that of their corresponding silica support. This also indicates that aluminium species were successfully grafted on the silica surface.

The lower average pore volume of the catalyst compared to the corresponding silica support is also consistent with the grafting of aluminium species inside the pores, filling the micropores and reducing the size of the larger ones.

Support pre-treatment temperature (°C)	Aluminium loading (mmol.g^{-1})	BET s.a. ($m^2.g^{-1}$)	Tot. p. vol. ($cm^3.g^{-1}$)	Av. p. diameter (nm)
200	0†	345.0	1.001	11.5
200	0.4	340.1	0.874	10.3
200	0.8	320.7	0.767	9.6
200	1.7	253.2	0.650	10.3
600	0†	333.5	0.939	11.3
600	0.8	328.9	0.767	9.3
750	0.0	311.3	0.905	11.6
750	0.8	309.2	0.671	8.7
900	0.0	208.8	0.562	10.8
900	0.8	192.1	0.390	8.1

†: reproduced from [138]

Table 2.7: BET surface area (BET s. a.), total pore volume (Tot. p. vol.) and average pore diameter (Av. p. diameter) of supported aluminium phenolate prepared with different support pre-treatment temperature and aluminium loading. A nil value of loading indicates that the results are for the thermally pre-treated support itself, for comparison.

2.4.5.4 DRIFT

$Al(OPh)_x$K100(200)(ATC)tp(*1.7*) catalyst was analysed using DRIFT. All assignments corresponding to a chemical function were confirmed by the literature[162]. Figure 2.22 shows the DRIFT spectra of a supported aluminium phenolate recorded at different temperatures.

All the bands assigned to the K100 silica support (Table 2.3 on page 76) but the band corresponding to isolated O-H stretching are observed. The absence of this band indicates that the silanol groups reacted with the aluminium trichloride to form Si-O-Al bonds. The decrease of the intensity of the broad band between 3700 and 3000cm^{-1} corresponding to O-H stretching is assigned to the silica surface modification, as discussed in the section 2.3.2.2. The decrease of this band allows the peak corresponding to the aromatic C-H bond (between 3100 and 3000cm^{-1}) to be more observable. The substitution of the aromatic ring, mono-substituted or five hydrogen adjacent, is deduced from the two bands at 690 and 754cm^{-1}, which are shifted to respectively 692 and 756cm^{-1} above 150°C.

In the 1700-1400cm^{-1} region (zoomed in the inset), three peaks are observed at 1597cm^{-1}, with a weak shoulder at 1581cm^{-1}, 1498 and 1473cm^{-1} on the spectrum recorded at 50°C. The peak at 1473cm^{-1} disappears and the band at

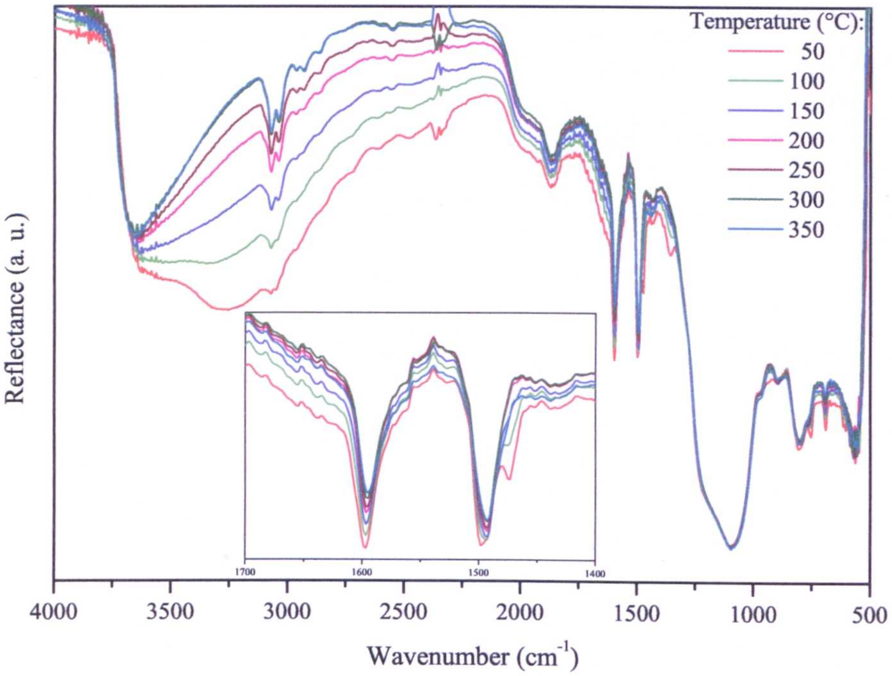


Figure 2.22: DRIFT spectra of Al(OPh)$_x$K100(200)(ATC)tp(*1.7*) catalyst, recorded at different temperatures. *(Original in colour)*

1498cm^{-1} is shifted to 1492cm^{-1}, when the sample is heated above 150°C.

To assign correctly these bands, spectra of pure sodium phenolate, commercial aluminium phenolate and phenol adsorbed on K100 silica gel were recorded and are shown in Figures 2.23 and 2.24. As the band at 1473cm^{-1} is present below and absent above 150°C, the spectra of these three chemicals and materials were recorded at room temperature and at 150°C only.

The spectrum of sodium phenolate exhibits three characteristic bands in the 1700-1400cm^{-1} region corresponding to the aromatic C-C bond: 1585, 1560 and 1479cm^{-1}. The substitution of the ring is confirmed by the bands at 767 and 698cm^{-1}. The band corresponding to the C-O bond is in the same region as the Si-O-Si stretching (by comparison with the silica gel spectrum reproduced in section 2.3.2), therefore it is not available for the identification of the phenolate function for the catalysts.

Phenol physisorbed on K100 silica gel exhibits at 20°C three bands, at 1599, 1500 and 1473cm^{-1}. The second band is shifted to 1496cm^{-1} at 150°C, when at the same time the third band disappears.

The commercial aluminium phenolate also exhibits three bands in the same region at 20°C, 1595, 1493 and 1473cm^{-1} as a shoulder of the second band. Another small shoulder is observed at 1579cm^{-1}. Bands at 1595, 1579 and 1493cm^{-1}

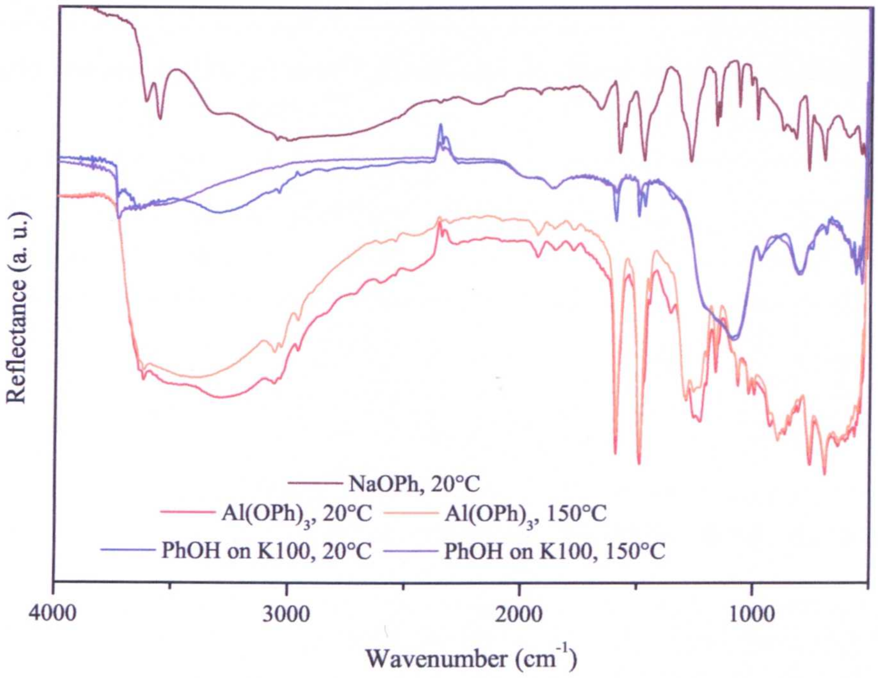


Figure 2.23: DRIFT spectra of sodium phenolate recorded at 20°C, commercial aluminium phenolate and phenol physisorbed on K100 thermally pre-treated at 200°C, recorded at 20 and 150°C. *(Original in colour)*

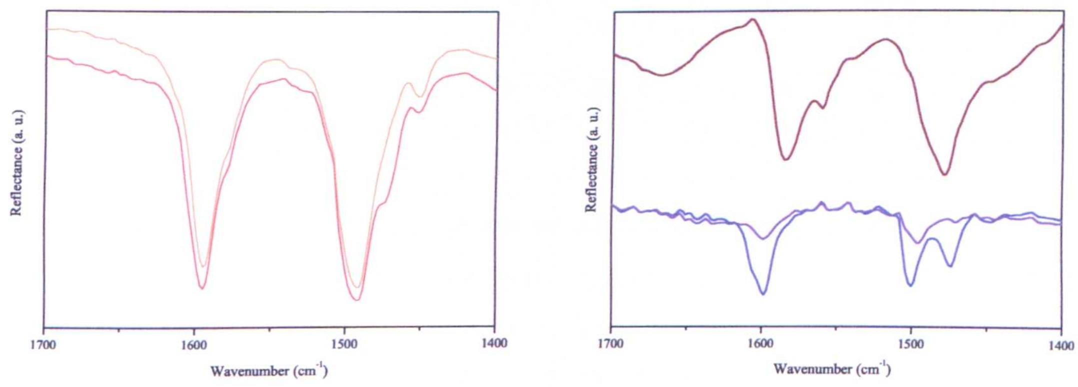


Figure 2.24: DRIFT spectra of sodium phenolate, commercial aluminium phenolate and phenol physisorbed on K100 thermally pre-treated at 200°C, recorded at 20 and 150°C: zoom to the 1700-1400cm^{-1} region. The legend is the same as for the figure 2.23. *(Original in colour)*

Wavenumber (cm^{-1})	Vibration mode
3100 - 3000	Aromatic C-H, stretching
1600 - 1450	Aromatic C-C, stretching
770 - 690	Aromatic C-H, ring substitution paterns

Table 2.8: Assignments of bands in the DRIFT spectra of supported aluminium phenolate.

Material	Band 1	Band 2	Band 3
Phenol[†]	1595	1498	1473
Phenol on K100	1599	1500 → 1496	1473*
Sodium phenolate	1585	1560 1479	
Commercial aluminium phenolate	1595 (1579sh)	1492	1473*
Al(OPh)xK100(200)(ATC)tp(*1.7*)	1597 (1581sh)	1498 → 1492	1473*

†: DRIFT spectrum not plotted. * indicates band, which disappears when the spectra is recorded at 150°C. 'sh' stands for shoulder.

Table 2.9: Assignments of bands in the DRIFT spectra of supported aluminium phenolate in the 1700 - 1400cm^{-1} region.

correspond to the aromatic C-C. These observations are similar to the bands observed for the sodium phenolate, the wavenumber being shifted due to the interaction with a different metal. The band at 1579cm^{-1} being weaker than the band at 1595cm^{-1} the aromatic ring is not further conjugated. The band at 1473cm^{-1} is the only one, which is not present at 150°C. This band being observed only in the spectrum of phenol physisorbed on K100 silica gel at low temperature, the shift towards lower wavenumber of the band around 1500cm^{-1} can therefore be used to trace the presence of physisorbed phenol.
The bands at 1599 and 1500cm^{-1} in the spectrum of phenol physisorbed on K100 silica gel are also observed at 150°C, and the second band is shifted to 1496cm^{-1}. This observation suggests that phenol does react with the silanol group to form a silicon phenolate Si-O-Ph bond.

Tables 2.8 and 2.9 summarise respectively bands assignments in the whole spectrum wavenumber range and values in the 1700-1400cm^{-1} region. Band assignments corresponding to the silica gel support can be found in section 2.3.2.

2.4.5.5 MAS-NMR

The aluminium environment of supported aluminium phenolate were analysed by ^{27}Al MAS-NMR. Figure 2.25 shows the ^{27}Al MAS-NMR spectra of four cata-

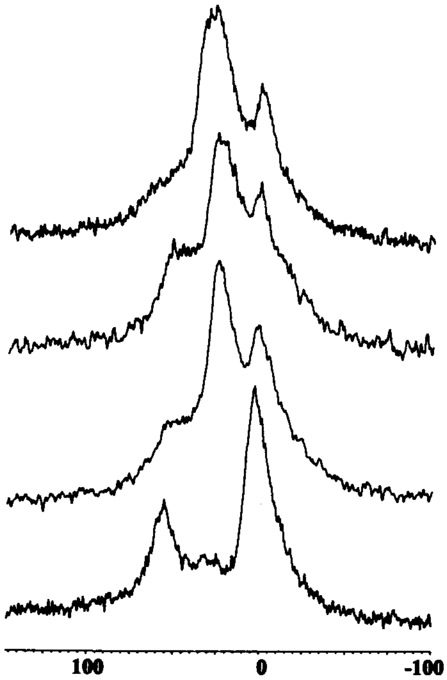


Figure 2.25: ^{27}Al MAS-NMR spectra of catalysts corresponding to, from top to bottom, Al(OPh)$_x$K100(200)(ATC)tp(*1.7*), Al(OPh)$_x$K100(200)(ATC)tp(*0.8*), Al(OPh)$_x$K100(600)(ATC)tp(*0.8*) and to the previous catalyst exposed deliberately to air and moisture (Chemical shifts in ppm).

lysts corresponding to, from top to bottom, Al(OPh)$_x$K100(200)(ATC)tp(*1.7*), Al(OPh)$_x$K100(200)(ATC)tp(*0.8*), Al(OPh)$_x$K100(600)(ATC)tp(*0.8*) and to the previous catalyst exposed deliberately to air and moisture.

In the cases of the three catalysts protected from "on-purpose" exposure, three main peaks are observed, at 2, 25 and 52ppm. No peak around 85ppm is observed, which indicates that no Al(Cl)(OSi)$_2$ species from the AlCl$_x$K100 remains (Section 2.4.3) and that all the chlorine from these aluminium chloride species were exchanged. The peak at 62ppm for the AlCl$_x$K100, which corresponds to AlCl$_2$(OSi), seems also to have been exchanged, but the peak at 52ppm of the Al(OPh)$_x$K100 is broad, therefore it is not possible to confirm the complete exchange of these AlCl$_2$(OSi) aluminium chloride species.

The peak at 2ppm can be assigned to either a 6-coordinated aluminium species or a 3-coordinated AlO$_3$ species[107]. The 6-coordinated aluminium species could be due to exposure to moisture or hydrolysis of aluminium species during loading of the sample for analysis or during the catalyst preparation. The 3-coordinated aluminium species AlO$_3$ could be the di-phenolate aluminium bonded to the silica gel surface *via* an oxygen atom, which is the desired aluminium configuration.

The assignment of the two other peaks are not definitive.

Once the catalyst has been exposed to air, and therefore to moisture, the peak at 25ppm nearly disappears and the peak at 2ppm becomes the major one. We can therefore deduce that the peak at 25ppm corresponds to an aluminium atom with a coordination number of 4 or 5, and that this aluminium centre is either further complexed or hydrolysed into a 6-coordinated species. However, the peak at 52ppm remains. Benn et al. studied the ^{27}Al liquid NMR of aryloxyaluminium compounds[110] and reported the chemical shift of tri-(2,6-di-methyl-phenyl) oxyaluminium at 51ppm, the compound being under the dimer form with an aluminium coordination number of 4. They also showed that the aluminium chemical shift of the dimer complex does not change dramatically (47ppm) when recorded in tetrahydroxyfuran (THF). However, the study showed that tri-(2,6-di-methyl-phenyl) oxyaluminium is not under a dimer form and is not a un-complexed monomer AlO_3 type species. All the compound is under the form of an adduct with THF, with a coordination number of 4. The peak at 52ppm could therefore correspond to a 4-coordinated AlO_4 species, which once hydrolysed, retains its coordination number. It could also be AlO_4 species, which were already hydrolysed during the catalyst preparation despite all the precautions taken to avoid water in the preparation mixture, and therefore not subject to further hydrolysis.

So far, the discussion focussed on the supported aluminium phenolate prepared with aluminium trichloride as metal precursor. Catalysts prepared with TEAL and aluminium triphenolate as aluminium precursor were also prepared and some characterisations were carried out. These results are discussed in the sections 2.4.6 and 2.4.7 respectively.

2.4.6 Preparation of supported aluminium phenolate using TEAL as metal precursor

Triethyl aluminium (TEAL), diluted in toluene, was used instead of aluminium trichloride as metal precursor for the grafting of aluminium on the silica surface. TEAL was chosen as metal precursor in order to avoid the formation of any Brønsted acid during the catalyst preparation, which could affect the alkylation

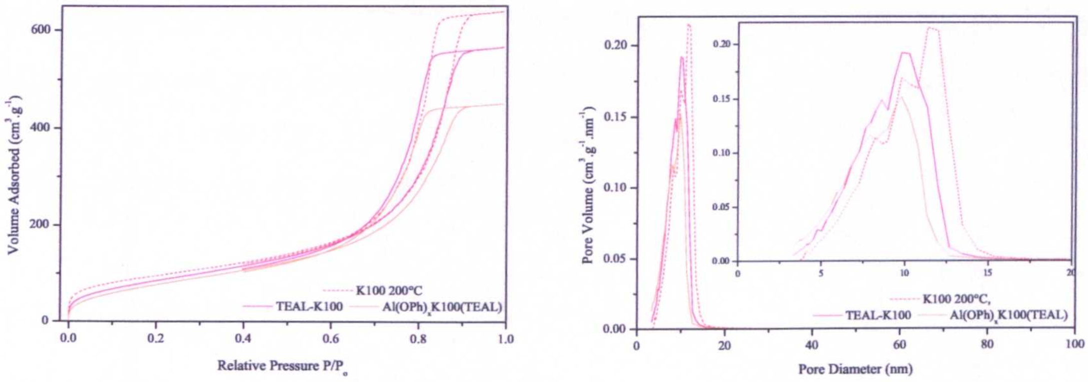


Figure 2.26: Adsorption – desorption isotherm (left) and the pore size distribution (from the desorption curve)(right) of TEAL-K100(200)tp(*1.7*) and the corresponding Al(OPh)$_x$K100(200)(TEAL)tp(*1.7*) catalyst. The dashed line corresponds to the analysis of the support itself, as discussed previously in the section 2.3.2.1.*(Original in colour)*

ortho – *para* selectivity. TEAL reacts with silanol or siloxane groups generating ethyl-aluminium bonded to the surface *via* oxygen atoms and ethane, which evolves. The supported ethyl aluminium on K100 silica gel, which for convenience will be named throughout the thesis 'TEAL-K100', is expected, if isolated and dried, to be very air and moisture sensitive, as TEAL itself violently is. Indeed even handled in a glove bag flushed with nitrogen, the material evolved smoke.

Once the grafting of TEAL on the K100 silica gel took place, the toluene mixture was cooled down and phenol added to preform the ligand exchange. The final material, Al(OPh)$_x$K100()(TEAL)tp() was isolated dried and stored under argon. The colour of the supported aluminium phenolate prepared from TEAL was creamy white, compared to the purple pink of the same material prepared from aluminium trichloride.

2.4.6.1 Characterisation by nitrogen adsorption

Supported TEAL on K100 silica gel and supported aluminium phenolate prepared from TEAL were analysed using nitrogen adsorption. Figure 2.26 shows the adsorption – desorption isotherm and the pore size distribution of TEAL-K100(200)tp(*1.7*) and the corresponding Al(OPh)$_x$K100(200)(TEAL)tp(*1.7*) catalyst. The grafting also takes place inside the pores, as the surface area at relative saturation pressure decreases after the grafting of TEAL on the K100 silica gel surface and that the pore

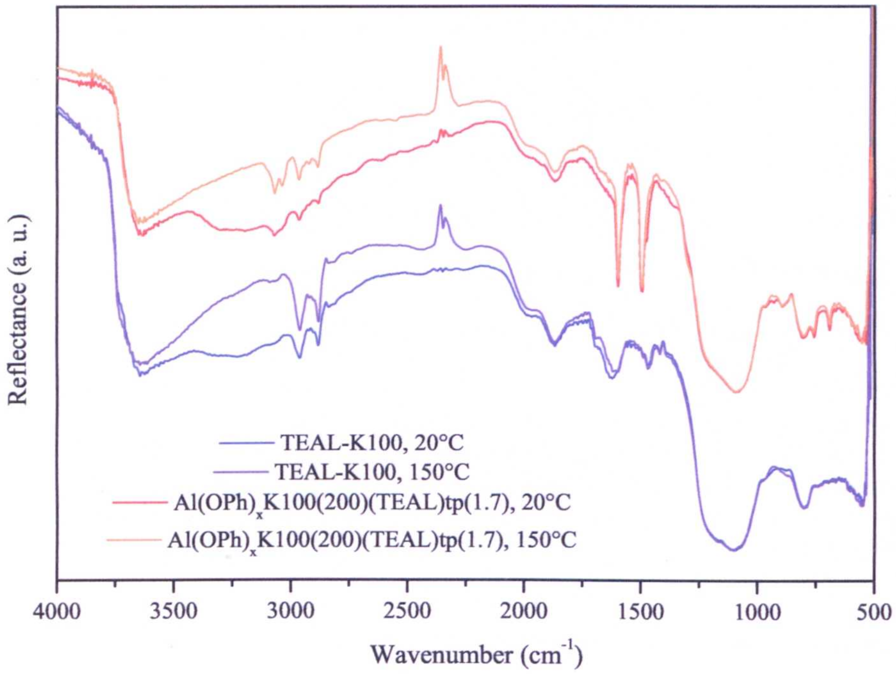


Figure 2.27: DRIFT spectra of TEAL-K100 material and Al(OPh)$_x$K100(200)(TEAL)tp(*1.7*), recorded at 20 and 150°C under vacuum.*(Original in colour)*

size distribution is shifted toward the low pore diameters. The ligand exchange of ethyl by phenol does also occur as the previously described effects are accentuated. Finally, the structure of the support is not affected by grafting of the aluminium species as the isotherm shape remains similar after each preparation step.

2.4.6.2 Characterisation by DRIFT

Supported TEAL on K100 silica gel and supported aluminium phenolate prepared from TEAL were analysed using DRIFT. Figure 2.27 shows the DRIFT spectra of the TEAL-K100 material and Al(OPh)$_x$K100(200)(TEAL)tp(*1.7*) recorded at room temperature and at 150°C under vacuum.

The DRIFT spectrum of the TEAL-K100 material exhibits the peaks characteristic of the K100 silica gel (Table 2.3). Beside these peaks, bands corresponding to the C-H bonds are observed between 3000 and 2850cm^{-1}, which shows that some ethyl groups are present on the surface of the material. The grafting of aluminium is also confirmed by the disappearance of the bands associated with isolated silanol groups (3745cm^{-1}).

The spectra of $Al(OPh)_xK100(200)(TEAL)tp(\mathit{1.7})$ is similar to that of the catalyst prepared with aluminium trichloride. However, bands corresponding to aliphatic C-H bonds are still observed, indicating that the exchange of the ethyl group by phenol is not complete.

2.4.6.3 Characterisation by ^{27}Al MAS-NMR

Figure 2.28 shows the ^{27}Al MAS-NMR of, from top to bottom, TEAL-K100(200)(1.7) and the corresponding $Al(OPh)_xK100(200)(TEAL)tp(\mathit{1.7})$. The silica surface was only thermally treated at 200°C, hence a high silanol surface concentration. It is then likely that the main aluminium species will contain only one Al–C bond, as for example in $EtAl(OSi)_2$ species, complexed with close silanol groups.

No peaks are observed above 80ppm, therefore no aluminium species with two carbons attached to it are present at the surface of the catalyst support (see Figure 2.3[107]).

The peak at 4ppm for the TEAL-K100 material and at 3ppm for the $Al(OPh)_xK100(TEAL)$ material can be assigned to 6-coordinated aluminium species, which are generated by exposure to moisture or hydrolysis of the aluminium complexes.

The two other peaks at 29ppm and 54ppm are similar to those observed for the catalyst prepared from aluminium trichloride but are slightly shifted toward higher chemical shifts values. However, the ratio between these two peaks is different compared to the spectra obtained with the $Al(OPh)_xK100(ATC)$ catalyst, thus the relative ratio between the different types of aluminium species at the surface is different.

Some care has to be taken when analysing this ratio between the different species. For the catalyst prepared from aluminium trichloride, exposure to moisture induced disappearance of the peak corresponding an aluminium coordination number of 5, and increase of the peaks corresponding to an aluminium coordination number of 4 and 6. As the material prepared from TEAL is much sensitive to moisture, the ratio observed might have been disturbed during the loading of the MAS-NMR rotor, even that has been done in a glove bag under nitrogen.

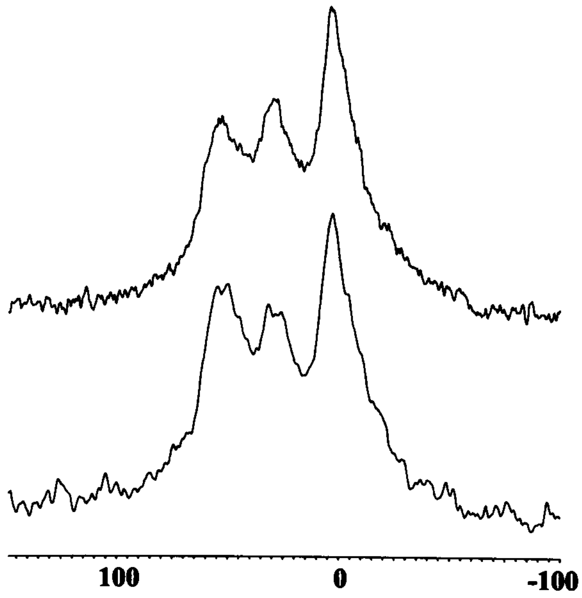


Figure 2.28: ^{27}Al MAS-NMR spectra of, top, TEAL-K100(200)(1.7) and, bottom, the corresponding Al(OPh)$_x$K100(200)(TEAL)tp(*1.7*) (Chemical shifts in ppm).

Regarding the nature of those two species, some suggestions can be made. The silica surface, as shown earlier in this chapter, when thermally pre-treated at 200°C exhibits a high concentration of silanol groups at its surface. One of the peaks, in the spectrum of the TEAL-K100 material could correspond to an EtAl(OSi)$_2$ complexed *via* secondary bonding with one silanol group. The other one could correspond to an EtAl(OSi)$_2$ complexed with two silanol groups. Once the material is reacted with phenol, the ethyl group is exchanged to a phenolate and both aluminium become respectively 4- and 5-coordinated species with respectively 4 and 5 oxygen atoms, the signals for which are in the same chemical shifts range. It is however not confirmed whether these species exist and that no other are present at the surface of the catalyst, as we know from the DRIFT analysis that some ethyl groups are still present in the final catalyst.

2.4.7 Preparation of supported aluminium phenolate using aluminium triphenolate as metal precursor

Direct grafting of aluminium phenolate on K100 silica gel was attempted. Aluminium phenolate, of a metallic grey colour, was used as purchased. The K100 silica gel was refluxed in toluene with aluminium phenolate and a grey material was isolated, named $Al(OPh)_xK100(Al(OPh)_3)()tp()$.

Aluminium phenolate can be physisorbed to the silica surface by interaction with a silanol group, or can react with the silanol group and yield a diphenolate aluminium species.

2.4.7.1 Characterisation by nitrogen adsorption

The catalyst prepared by grafting the aluminium phenolate on the K100 silica gel was studied by nitrogen adsorption. The surface area is $289.0m^2g^{-1}$ and the total pore volume is $0.6151cm^3g^{-1}$, which corresponds to an average pore diameter of 8.5nm. These values are lower than the characteristics of the support and show that, as for all the catalysts discussed previously, some species did get chemisorbed or physisorbed inside the pores and that the support structure is not affected by the grafting reaction.

2.4.7.2 Characterisation by DRIFT

The $Al(OPh)_xK100(Al(OPh)_3)(600)tp($*1.6*$)$ catalyst was analysed using DRIFT (Figure 2.29). Bands corresponding to aromatic C–H, aromatic rings C–C and C–H substitution modes are observed. Bands corresponding to the support are also observed (see Table 2.3 on 76). The broad band between 3750 and $3300cm^{-1}$ is assigned to hydroxyl groups. Sage showed that the DRIFT spectrum of the K100 silica gel thermally pre-treated at 600°C exhibits only a sharp peak at $3745cm^{-1}$[138]. The presence of the broad band for the catalyst shows that the $Al(OPh)_xK100(Al(OPh)_3)(600)tp($*1.6*$)$ is highly moisture sensitive. However, no band at $3745cm^{-1}$ is observed, indicating that no isolated silanol group remains at the surface.

2.4.7.3 Characterisation by ^{27}Al MAS-NMR

The $Al(OPh)_xK100(600)(Al(OPh)_3)tp($*1.7*$)$ catalyst and the purchased aluminium phenolate were analysed by ^{27}Al MAS-NMR (Figure 2.30). The purchased aluminium phenolate had a purity of 95% with aluminium oxide as main impurity.

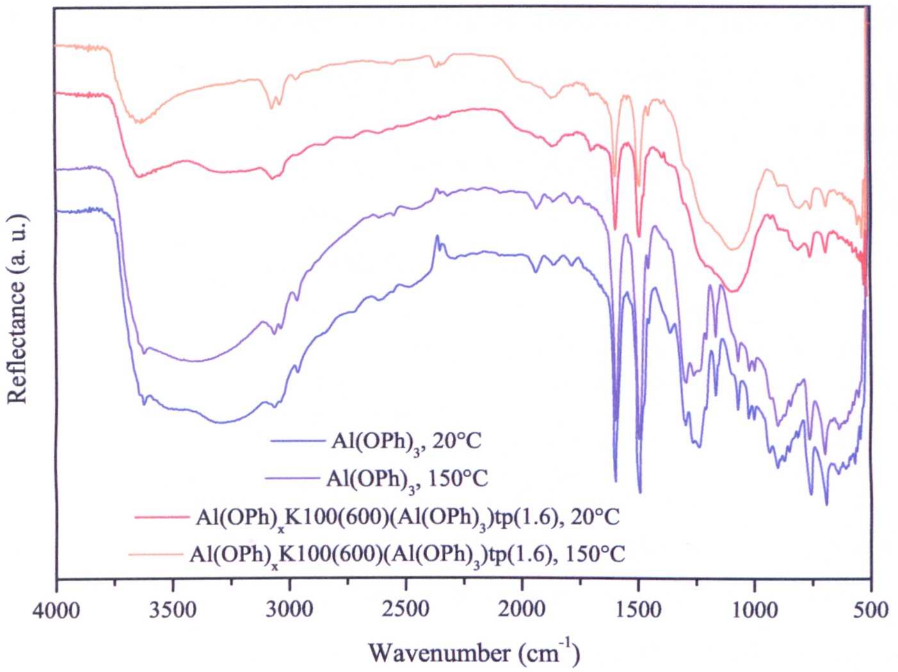


Figure 2.29: DRIFT spectra of the aluminium phenolate and Al(OPh)$_x$K100(600)(Al(OPh)$_3$)tp(*1.7*), recorded at 20 and 150°C under vacuum. *(Original in colour)*

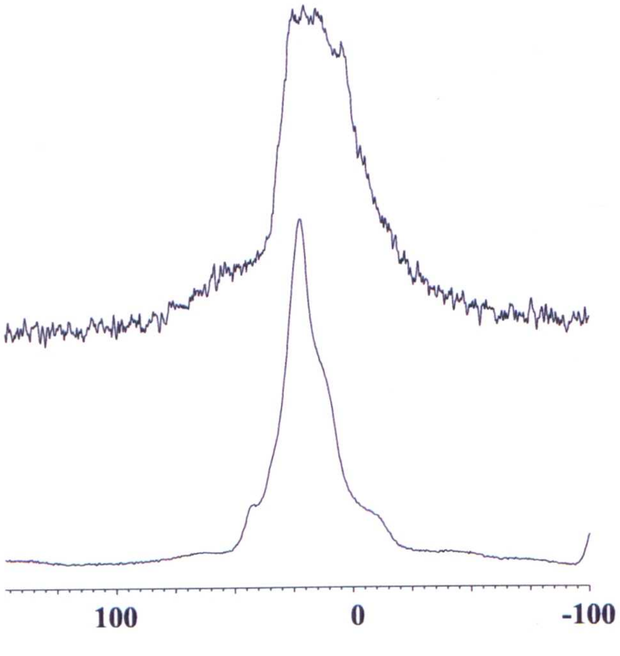


Figure 2.30: ^{27}Al MAS-NMR spectra of, top, the material Al(OPh)$_x$K100(600)(Al(OPh)$_3$)tp(*1.7*) and, bottom, the purchased aluminium phenolate (Chemical shifts in ppm).

The spectrum of aluminium phenolate exhibits five peaks, at -8, 11, 23, 35 and 42ppm. These peaks show that aluminium species have coordination numbers of 4, 5 or 6.

The spectrum of the catalyst exhibits mainly two peaks, at 1 and a broad peak between 5 and 35ppm. Another broad peak centered on 52ppm is also observed, but the relative height of this peak with the broad peak centered on 20ppm is much less intense compared to the catalysts prepared previously. This peak was proposed to correspond to a 4-coordinated aluminium species arising from isolated physisorbed aluminium phenolate or to hydrolysed species.

The peak at 1ppm is assigned to 6-coordinated aluminium species due to hydrolysis during the sample loading or by water traces during the catalyst preparation. The peak centered on 20ppm could be aluminium species with coordination number of 4, 5 or 6. As the NMR resolution is low, the broad peak may be due to overlapping unresolved peaks.

2.4.8 Surface acidity measurements

2.4.8.1 by DRIFT of pyridine loaded catalyst

Shorrock showed that pyridine adsorbed on the K100 silica gel only *via* hydrogen bonding, hence that the silanol groups are not acidic enough to protonate pyridine[137].

Figure 2.31 shows the DRIFT spectra of pyridine adsorbed on four different aluminium phenolate catalysts. Difficulties in identifying correctly peaks belonging to the pyridine complexes arise due to the presence in this area of bands corresponding to the aluminium phenolate itself. However, by comparison with the unloaded catalyst (represented by the dashed line in the same colour), peaks at 1445, 1490, and a weak band at 1540cm^{-1} and a shoulder at 1606cm^{-1} are observed. In the case of the catalyst prepared with K100 silica gel pre-treated at 200°C ($Al(OPh)_x$K100(200)(ATC)(*1.7*)), a strong peak at 1592cm^{-1} is observed. This peak corresponds to free pyridine bonded to silanol groups *via* hydrogen bonds. Therefore, the $Al(OPh)_x$K100(200)(ATC)(*1.7*) catalyst surface exhibits free silanol groups, as expected by the low temperature used to pre-treat the silica gel.

In all the cases, peaks at 1444, 1490 and 1577cm^{-1} can correspond either to

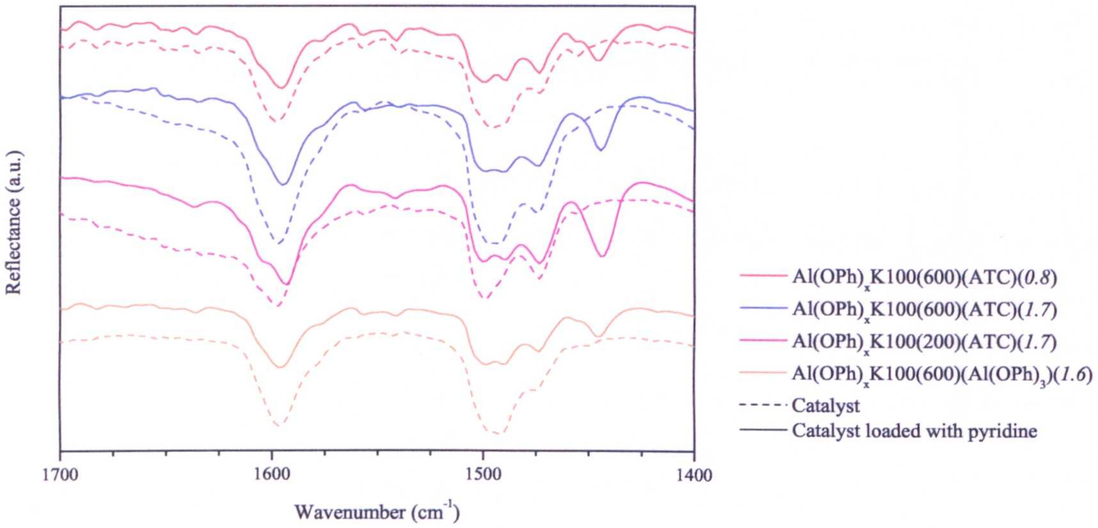


Figure 2.31: DRIFT spectra of pyridine adsorbed on aluminium phenolate catalysts. The spectra were recorded at room temperature.*(Original in colour)*

free pyridine or to Lewis acid sites. However, the spectra were recorded under vacuum, hence most of the free pyridine was expected to be removed, therefore these peaks are assigned to the pyridine-Lewis acid site complex. The presence of the shoulder at 1606cm^{-1} confirms the presence of the coordinately bonded pyridine to Lewis acid sites. The very weak peak at 1540cm^{-1}and the lack of observable peaks at 1620 and 1640cm^{-1}, all three expected to be strong for the pyridinium ion, shows that very few pyridinium ions are formed. Thus few if any acid sites exhibit Brønsted acidity.

2.4.8.2 ^{31}P MAS-NMR of TEPO loaded catalyst

Table 2.10 presents ^{31}P chemical shift differences $\Delta\delta$, in ppm (see Section 2.2.5), for various supports and Al(OPh)$_x$Silica()(ATC)() catalysts. The support type, the pre-treatment temperature and the theoretical loading are given in the table. Regarding the different pre-treated K100 silica supports, one peak is observed for each of them at a $\Delta\delta$ value between 5 and 7. This peak is assigned to the coordination of TEPO with the silica surface[130]. The $\Delta\delta$ value increases with the pre-treatment temperature, corresponding to a slightly acidity increase of the silanol groups. Indeed, at low pre-treatment temperature, the concentration of the silanol groups is high and they are linked together by hydrogen bonding (vicinal silanols). At high pre-treatment temperature, the concentration of silanol decreases and they are more isolated, hence not stabilised by hydrogen bonding.

Support	Support pre-treatment temperature	Loading	$\Delta\delta$
	°C	mmolg^{-1}	ppm ±1ppm
K100	300	0	4.9†
	200	1.7	7, 15, 23
	750	0	6
	750	0.8	7, 17, 25
	900	0	7
	900	0.8	7, 16, 25
K60	Bottle	0	10
	200	0	8
	200	0.8	8, 13, 25
	750	0	5, 6
	750	0.8	8, 14, 25

†: results obtained by Shorrock[137].

Table 2.10: ^{31}P chemical shift differences $\Delta\delta$ in ppm for various supports and Al(OPh)$_x$Silica()(ATC)() catalysts.

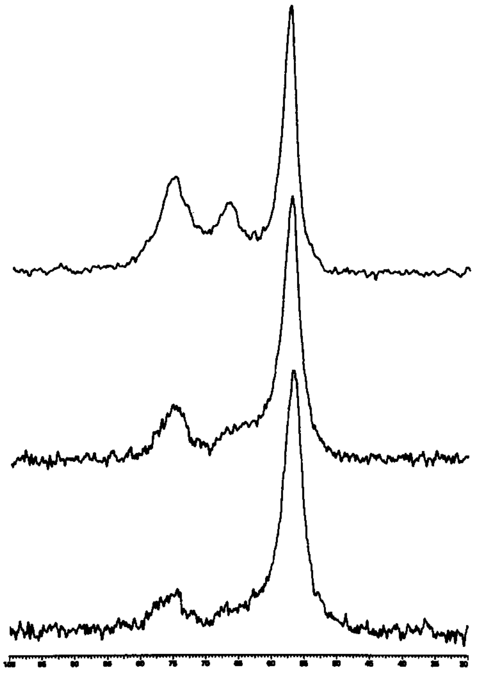


Figure 2.32: ^{31}P MAS-NMR spectra of some TEPO loaded catalysts (Chemical shifts in ppm).

However, concerning the K60 silica gel, the effect is the opposite. The acidity of the surface of the silica gel unexpectedly seems to decrease, and a second acid site appears when the silica gel is pre-treated at 750°C. This behaviour is not understood and further investigations would be required.

Regarding the catalysts, in all cases, regardless the silica pre-treatment temperature, three peaks are observed, at around 7, 16 and 25ppm, when the support is K100 silica gel, and at around 8, 13 and 25ppm, when K60 silica gel is the support. The peak at 7 or 8ppm respectively is accounted for the coordinated TEPO with the silica surface. The two other peaks are assigned to two different acid sites. This could confirm the $Al(OPh)_2$–OSi and the Al(OPh)–$(OSi)_2$ species, results consistent with those discussed earlier in this chapter. Figure 2.32 reproduces some of the ^{31}P MAS-NMR spectra obtained. The peak corresponding to a $\Delta\delta$ of 25 is always larger than the peak corresponding to a $\Delta\delta$ value of 15 when the pre-treatment temperature is increased. This could confirm that, when increasing the pre-treatment temperature of the silica gel, the concentration of the silanol groups decreases favouring the formation of diphenoxy aluminium species.

Compared to the results obtained when analysing by this method $AlCl_x$K100 material, the acidity of the most acidic sites are slightly lower (30 down to 25 and 17 to 15). This shift in values could also confirm that the ligand exchange from chlorine to phenol has taken place, as alkoxide aluminium species are less acidic than halide aluminium species.

2.5 Conclusion

The preparation of silica gel supported aluminium phenolate materials have been described in this chapter. The main preparation method implied the use of silica gel supported aluminium chloride as intermediate, which preparation description and characterisation of the $AlCl_x$K100 material is described in the literature[137, 163]. Alternative preparation routes were also investigated. They involved the grafting of triethyl aluminium on silica gel followed by a ligand exchange step, or the direct grafting of the aluminium phenolate on the silica gel surface.

In total, five methods of preparation were attempted but only two were efficient for the preparation of the silica gel supported aluminium phenolate. However among these, the 'in-situ' method does not allow proper characterisation due to partial removal of phenol filling pores, as shown by XPES. The method involving the ligand exchange step in a toluene solution is the most efficient and yields the most active and selective catalyst, as it will be shown in the chapter 3.

Physical characterisation by nitrogen adsorption of the different materials showed that the structure of the silica gel support is not affected by the grafting of aluminium species on its surface, retaining its mesoporous structure with a narrow cylindrical pore size distribution. However, the specific surface area and the pore size distribution both expectedly decrease subsequently to the grafting. This also shows that the grafting of the aluminium species occurs successfully on the surface of silica gel and that it does at least partly occur inside the pores.

Elemental analysis of catalysts showed that not all the aluminium is grafted on the surface during the preparation of the intermediate $AlCl_x$K100. The pre-treatment temperature of the silica gel also affects the grafting level, the concentration of aluminium decreasing by more than 50% when increasing the pre-treatment temperature from 200 to 900°C.

XPES analysis of the catalyst, prepared from aluminium trichloride, showed that the ligand exchange step is either not complete or that chlorine does remain in the bulk material. Catalysts prepared from triethylaluminium also show a non-complete exchange of ethyl groups into phenolate, as IR bands corresponding to ethyl are still observed in the final material. DRIFT analysis of the various catalysts also showed that the phenolate groups are present on the catalyst surface.

Solid NMR analyses showed that mainly two aluminium species are on the catalyst surface, aluminium mono- and diphenolate. The NMR data confirmed that all monochloro aluminium from the $AlCl_x$K100 material are converted into the corresponding phenolate. The concentration of the different species varies with the silica gel pre-treatment temperature and the metal precursor. Aluminium trichloride and aluminium phenolate yield a material exhibiting more 5-coordinated aluminium species and triethyl aluminium leads to a material with more 4-coordinated aluminium species.

Acidity measurements were also carried out. Analysing pyridine loaded catalysts by DRIFT showed that the catalyst exhibits mainly Lewis acidity, whereas the analysis by ^{31}P NMR of TEPO loaded catalyst showed that two acid sites are present on the surface of the catalyst, which strength is in overall lower than of the $AlCl_x$K100 material.

Chapter 3

Alkylation of phenol with isobutene

3.1 Introduction

The direct di*ortho*- alkylation of phenols with isobutene is almost exclusively carried out in neat starting phenols. Since its discovery[50–53], the starting reagent is reacted with the alkene in the presence of the catalyst in a homogeneous manner. From the solvent point-of-view, this reaction is already a very "green" one, as no solvent is required and the excess of starting reagent is recovered by distillation. However, the most efficient catalyst for the direct di*ortho*- alkylation of phenols and cresols is the aluminium triphenolate[38]. Recovering the catalyst is almost impossible and it has to be quenched by aqueous washings, generating wastes.

The use of a solid catalyst would overcome the needs for aqueous washings, hence decreasing the costs of production and the production time, as well as the cost of catalyst disposal.

The aim of this chapter is to present the results of the alkylation reactions of phenol with isobutene using the new supported aluminium phenolate material. Investigations of catalyst preparation parameters, such as support pre-treatment temperature, aluminium precursor and loading, and reaction conditions, such as reaction temperature, amount of catalyst or alkene addition methods, are reported. To ease the reading of this chapter, products of the alkylation reaction of phenol with isobutene are each respectively associated with an abbreviation and a colour. The product list and their associated abbreviations and colour can be found in the appendix.

3.2 Homogeneous alkylation of phenol with isobutene

The alkylation of phenol (PhOH) with isobutene was carried out homogeneously using two kinds of aluminium triphenolate as catalyst. In one, the reaction was carried out using commercial aluminium triphenolate purchased from Aldrich, in order to check the activity of this material. In the other one, the catalyst was prepared '*in-situ*' from the aluminium metal in the starting material solution.

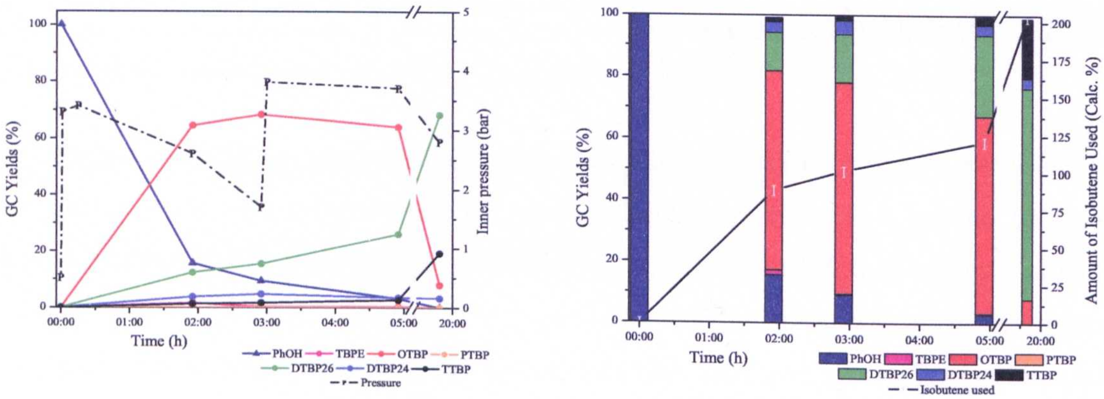


Figure 3.1: Alkylation of phenol with isobutene (1.93eq.) and commercial aluminium triphenolate as catalyst (1%) carried out at 100°C: reaction profile, reactor inner pressure and isobutene consumption estimation.*(Original in colour)*

3.2.1 Homogeneous alkylation using commercial aluminium triphenolate

The alkylation of phenol with isobutene was carried out in the pressure reactor with the commercial aluminium triphenolate from Aldrich. Figure 3.1 shows the reaction profile, the reactor inner pressure and the isobutene consumption estimation.

Along with the product yields and the isobutene consumption, the inner pressure of the pressure reactor during the reaction is also given. As described in chapter 6, isobutene is added as a liquid *via* a pressure reservoir. The volume of this reservoir corresponds to one equivalent of isobutene based on the starting amount of phenol. The connection of the reservoir with the inner reactor (beginning of the isobutene addition) induced a pressure rise. The pressure, then, decreased with the consumption of isobutene, which followed the rate of the alkylation reaction. Once the pressure dropped, which corresponded to the end of the first alkylation (end of the addition of the first equivalent), the reservoir was then disconnected, refilled and reconnected, which induced the second pressure rise, showing when the second phenol alkylation started (addition of the second equivalent of isobutene). The pressure, then, decreased again following the consumption of the isobutene. This method of addition of the alkene can also be named a "kinetically controlled addition" as the isobutene is added following the kinetics of its consumption.

It can already be noticed that the consumption of the isobutene is slower during the second alkylation step than during the first as the isobutene consumption

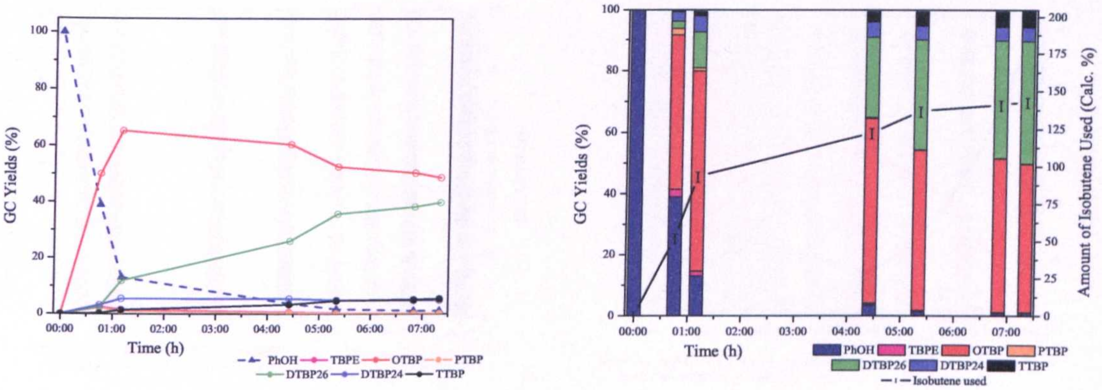


Figure 3.2: Alkylation of phenol with isobutene (1.5eq.) and aluminium triphenolate prepared *in-situ* as catalyst (1%) carried out at 100°C at atmospheric pressure: reaction profile and isobutene consumption estimation. *(Original in colour)*

rate is lower (showed by the pressure drop rate).

The reaction profile is similar to the alkylation of phenol with isobutene carried out with '*in-situ*' prepared aluminium triphenolate[60]. This profile corresponds to successive reaction steps, here PhOH followed by mono-*ortho**tert*butylphenol (OTBP) then 2,6-di*tert*butylphenol (2,6-DTBP) and 2,4,6-tri*tert*butylphenol (TTBP).

3.2.2 Homogeneous alkylation using '*in-situ*' prepared aluminium triphenolate

The catalyst was prepared from aluminium metal in the starting material. Once the catalyst was ready, the isobutene was added as a liquid in such a way that all the isobutene added was consumed (no gas was entering or leaving the system). This way of addition could also be named a "kinetically controlled addition" as the isobutene is added following the kinetics of its consumption.

The main mono *tert*butyl phenol was the OTBP and the main di*tert*butylphenol was the 2,6-DTBP (Figure 3.2). Low levels of 2,4-di*tert*butylphenol (2,4-DTBP), 2,5-di*tert*butylphenol (2,5-DTBP) and TTBP were detected. The rate of alkylation was slower compared to the reaction carried out with the commercial aluminium triphenolate, or reactions reported in the literature. This illustrated the need of pressure to speed up the reaction and to obtain a high yield of 2,6-DTBP.

The commercial aluminium triphenolate reagent behaves in a similar way as the '*in-situ*' prepared aluminium triphenolate. The profile of these reactions gives an

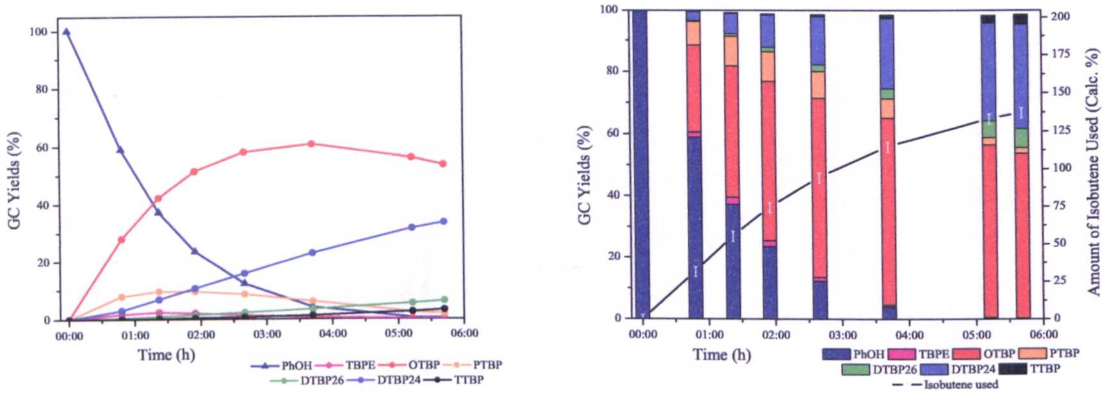


Figure 3.3: Alkylation of phenol with isobutene (1.5eq.) and silica supported aluminium phenolate prepared *in-situ* (Method 'is') as catalyst (1%) carried out at 100°C and at atmospheric pressure: reaction profile and isobutene consumption estimation. *(Original in colour)*

idea of the reaction rate of the alkylation of phenol with isobutene when carried out using this "kinetically controlled addition" method.

The next section will discuss the first experiments carried out with the silica supported aluminium phenolate and investigate its activity, selectivity and the importance of the pressure.

3.3 First experiments with the new catalyst

The first phenol alkylation reaction with isobutene and the new solid catalyst was carried out at atmospheric pressure using the silica supported aluminium phenolate prepared '*in-situ*' (Preparation Method 'is', Table 2.4 on page 86). The reaction was carried out in the laboratory of Schenectady GmbH, Pratteln in Switzerland, the isobutene was added following the consumption rate. Figure 3.3 shows the reaction profile and the isobutene consumption estimation.

Phenol was completely converted into products. The major mono-alkyl product was the OTBP, PTBP was also observed along with *tert*butylphenylether(TBPE). The major di-alkyl product was the 2,4-DTBP. The isobutene consumption estimation shows that 1.35eq. was converted into products. The difference with the total added amount (1.5eq.) can be explained by the change of atmosphere from nitrogen to isobutene of the reaction flask at the beginning of the reaction.

To ease the reading of the plots, some products are not plotted and therefore the product distribution is not always equal to 100%. Four of these products were

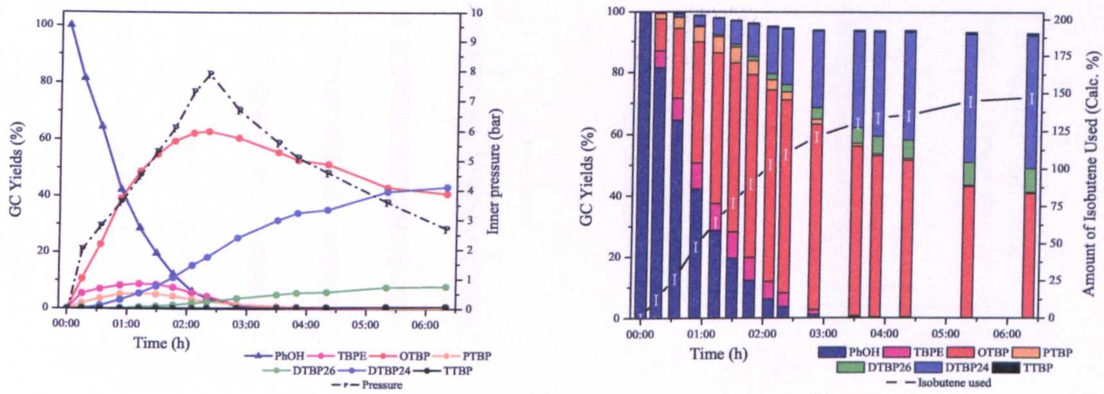


Figure 3.4: Alkylation of phenol with isobutene (2eq., added by the mean of a pressure pump) and silica supported aluminium phenolate prepared by hot-filtration (Method 'ishf') as catalyst (1%) carried out at 100°C and under pressure: reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

identified by GC-MS as *tert*butyl-(2-*tert*butylphenyl)ether (TBOTBPE), *tert*-butyl-(4-*tert*butylphenyl)ether (TBPTBPE), 2,5-DTBP and 4-(C_8H_{15})-phenol. The remaining products were assigned by GC-MS to heavy products with a molecular weight of, or more than, 262gmol^{-1}. In this experiment, these products accounted for 1.45%. As the peak corresponding to TTBP was identified separately, these heavy products could be ethers of DTBP or derivatives exhibiting C_8-alkyl groups. Throughout the thesis, these products will be referred as the "non-plotted" products. Their relative amounts will be detailed in the text.

The second phenol alkylation reaction with isobutene and the new solid catalyst was carried out under pressure using the silica supported aluminium phenolate prepared by hot-filtration (Preparation Method 'ishf', table 2.4 on page 86). The reaction was carried out in the laboratory of Schenectady GmbH, Pratteln, Switzerland, the isobutene was added by the means of a pressure pump at the rate of one equivalent per hour. Figure 3.4 shows the reaction profile, the reactor inner pressure and the isobutene consumption estimation.
Compared to the previous experiment, a similar reaction profile was observed with complete conversion of phenol, OTBP then 2,4-DTBP as the major products. However, the 'non-plotted' products accounted for 7% at the end of the reaction, 73% of that being heavy products, the remaining being ethers of mono-*tert*butylphenols. On the other hand, the reaction rate seems faster when carried out under pressure: at the time of 6 hours, the OTBP yield was down to 40% (compared to 53%) and the 2,4-DTBP yield was up to 43% (compared to 33%).

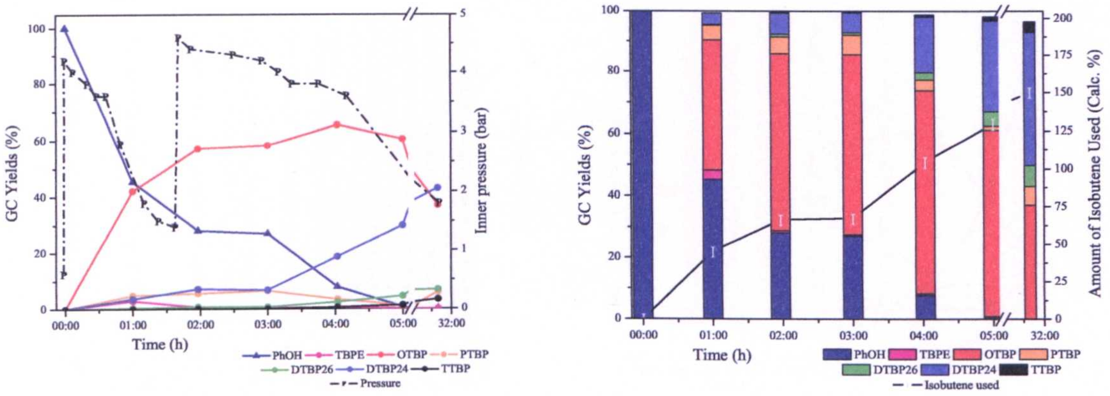


Figure 3.5: Alkylation of phenol with isobutene (1.45eq.) and $Al(OPh)_xK100(200)(ATC)$ishf(*1.7*) as catalyst (1%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

These two first experiments show that the new catalyst, the K100 silica gel supported aluminium phenolate, is active in the alkylation of phenol with isobutene. Complete conversion of phenol is obtained. The catalyst is *ortho-* selective for the first alkylation, then *para-* selective for the second alkylation. The third alkylation, in the second *ortho-* position, is also allowed as some TTBP was observed.

3.4 Comparison between the different catalyst preparation methods

The different preparation methods of the silica gel supported aluminium phenolate were described in section 2.4.4. Methods 'hf' and 'jc' were never tested as the preparation was not successful. Methods 'is', 'ishf' and 'tp' were tested. The difference between method 'tp1' and 'tp2' will be discussed in more details in chapter 5.

Figure 3.3, on page 118, shows the alkylation reaction carried out with the catalyst $Al(OPh)_xK100(200)(ATC)$is(*1.7*). Figure 3.5 and figure 3.6 shows the reactions carried out respectively with the $Al(OPh)_xK100(200)(ATC)$ishf(*1.7*) material and the $Al(OPh)_xK100(200)(ATC)$tp(*1.7*) material as catalysts.

All three reactions exhibited the same general product profile, the major mono-TBP being the OTBP, and the major DTBP being the 2,4-DTBP. However, at the reaction time of 6 hours, the product distribution is different, the yield (exact

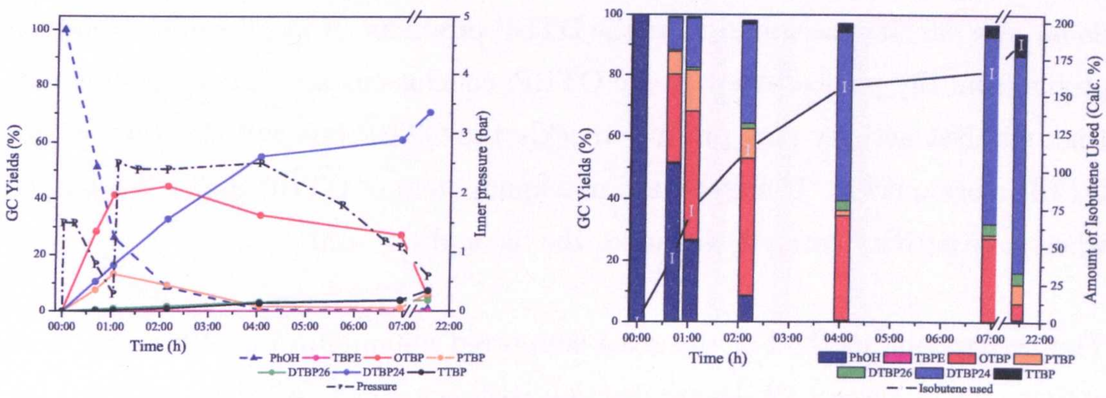


Figure 3.6: Alkylation of phenol with isobutene (1.95eq.) and Al(OPh)$_x$K100(200)(ATC)tp(*1.7*) as catalyst (1%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

or estimated) of 2,4-DTBP increases. In other words, the yield of 2,4-DTBP reached, for example, 30% at the reaction time of 5h15 when the reaction was carried out with the catalyst prepared '*in-situ*' at 5h00 with the catalyst prepared by hot-filtration and 2h00 with the catalyst prepared by the 'tp' method (Method E). The final yield of DTBP products after more than 20h of reaction was much higher (70%) with the 'tp' prepared catalyst then with the 'ishf' one.

The fact that the difference between the preparation method 'is' and 'ishf' is not as important as the difference between them and the 'tp' preparation method, may be due to the refluxing step at the phenol boiling point, which is higher than the toluene boiling point. This higher temperature may induce rearrangement of the aluminium species, for example from the di-ligand species into the mono-ligand species, by reaction of the aluminium with silanol groups of the silica surface. The ratio between the different aluminium species may induce different behaviour of the various catalysts towards the *ortho-* selectivity.

Para- phenol synthesis is generally catalysed by Brønsted species. Elemental analysis (Section 2.4.5.1 on page 91) showed that catalysts prepared with the 'ishf' method contained more chlorine than the catalyst prepared with the 'tp' method. However, more mono-*para* product is observed in the products of the reaction carried out with the 'tp' catalyst. Therefore, it may not be, or not only, the chloro- species by itself present on the catalyst surface, which induces the *para-* substitution of the phenol. More details on the role of chlorine will be discussed in the section 3.6.3.

So far, the interest was focussed on the DTBP products. If we look at the reaction profile from the point-of-view of the OTBP, conclusions are somewhat different. High catalyst activity may produce quickly the OTBP but will also turn it into DTBP more quickly. Therefore, the maximum yield of OTBP (65%) is obtained when slow activity catalyst was used, the 'is' and the 'ishf'.

The preparation method of the silica supported aluminium phenolate affects its activity in the phenol alkylation reaction with isobutene. All three catalysts are *ortho-* directing for the first alkylation then *para-* directing for the second. The 'is' preparation method may lead to residual chlorine in the catalyst leading to *para-* selective catalyst species. The 'ishf' preparation method leads to more handling difficulties to avoid air exposure and therefore to decomposition. The 'tp' preparation method is the easiest and yields a catalyst with a higher activity.

3.5 Comparison of the isobutene addition methods

Figure 3.4 (on page 119) shows the profile, reactor inner pressure and the isobutene consumption estimation of the alkylation reaction carried out with the isobutene being added as a liquid using a pressure pump, hence the alkene was added against the reactor inner pressure. This addition method will be called in this discussion 'by pump addition' method. The addition of the isobutene was carried out at the fastest achievable rate. The reaction profile, regarding the two major products, is similar to the previously described experiments. However, the TBPE is now observed at the beginning of the reaction. The pressure profile exhibits a sharp point up to when the addition of the two equivalents of isobutene was finished. The alkene continued to be consumed and therefore the pressure decreased. The pressure profile induced by this 'by pump addition' method is different to the one observed with the 'kinetically controlled addition' method described previously, as the addition does not follow the kinetics of the alkene consumption.

Figure 3.7 shows the profile, the reactor inner pressure and the isobutene consumption estimation of the alkylation reaction carried out with the isobutene

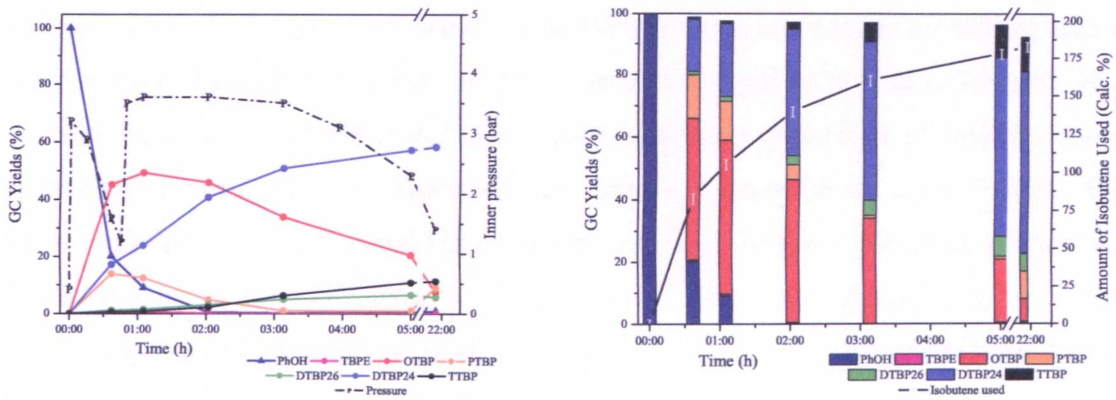


Figure 3.7: Alkylation of phenol with isobutene (1.95eq.) and Al(OPh)$_x$K100(200)(ATC)tp(*1.7*) as catalyst (1%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation. The isobutene was added following the 'kinetically controlled addition' method.*(Original in colour)*

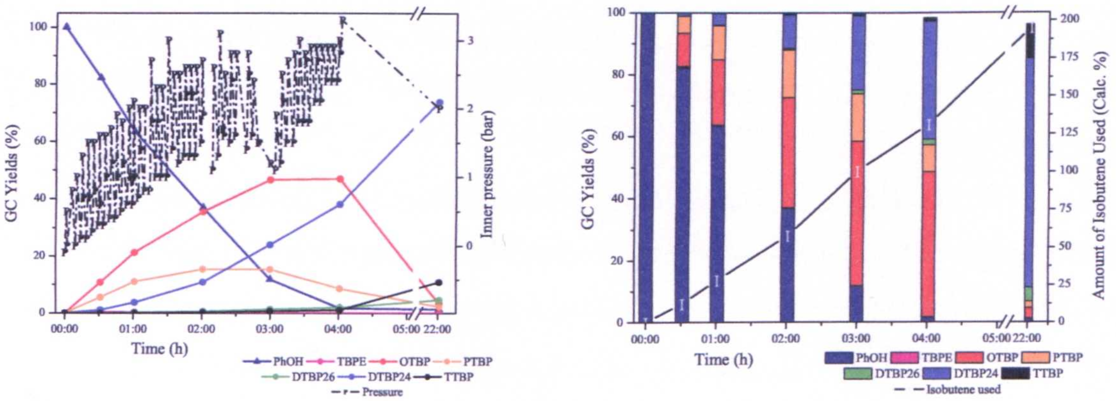


Figure 3.8: Alkylation of phenol with isobutene (1.93eq.) and Al(OPh)$_x$K100(200)(ATC)tp(*1.7*) as catalyst (1%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation. The first equivalent of the isobutene was added gradually.*(Original in colour)*

being added using the 'kinetically controlled addition' method. The general product profile is similar, regarding the major mono- and the major dialkyl products. PTBP was observed at the beginning of the reaction, but not TBPE. The yield of the 2,6-DTBP was however in the same range, slightly less than 10%.

Figure 3.8 shows the profile, the reactor inner pressure and the isobutene consumption estimation of the alkylation reaction carried out with the first equivalent of isobutene being added gradually. This was achieved by adding every five minutes a known volume of liquid isobutene. This experiment was carried out with the same batch of catalyst as for the experiment shown in Figure 3.7.

The two reaction profiles are very similar, giving the same selectivity regarding the first alkylation (*ortho-*) and the second one (2,4-DTBP), the same maximum OTBP yield and the same PTBP yield. However, two differences emerged. The gradual addition leads to a cleaner reaction, regarding the non-plotted products, 3% of the thermodynamically more stable 2,5-DTBP, compared to 2.5% of 2,5-DTBP and 5.3% of heavier products for the reaction carried out with the 'kinetically controlled addition' method. Less 2,6-DTBP and more 2,4-DTBP were observed when using the gradual addition of isobutene. This could be explained as follows: the gradual addition of isobutene induces a lower concentration of the alkene in the reaction medium, the alkyl- phenols are therefore more prone to side reactions, such as rearrangements or trans-alkylation. Stability studies of the *tert*butylphenols will be discussed in the section 3.6.5.

The choice of the addition method between the 'by pump addition' method and the other two was a more geographical one, the equipments required for the 'pump' method being available only in the laboratory of Schenectady GmbH in Pratteln, Switzerland.

The choice between the gradual addition method and the 'kinetically controlled addition' method was based on the yield of the main target molecule, the 2,6-DTBP. Hence, for results reported in the following of this work, all experiments were carried out using the 'kinetically controlled addition' method.

3.6 Selectivity: why 2,4- and not 2,6-?

The new silica supported aluminium phenolate catalyst is active in the alkylation reaction of phenol with isobutene, and as will be presented in chapter 4, with other phenol derivatives and other alkenes. The first alkyl group is introduced in the *ortho-* position, which is promising for a desired *ortho-* directing catalyst. The second alkyl group is, unfortunately, introduced in the *para-* position. 2,4-DTBP is a commercial chemical, however, better catalysts for their synthesis exist and they exhibit higher selectivity[38]. Furthermore, the goal of this work is the synthesis, using solid catalysts, of the di*ortho-* alkylphenols products.

As discussed in the introduction chapter, *para-* C- alkylation occurs with both Brønsted and Lewis acid catalysts, such as aluminium trichloride. *Ortho-* C-alkylation occurs either when γ-alumina (for the selective mono-*ortho-* alkylation) or metal phenolates are used as catalysts. The new silica supported aluminium phenolate catalyst does direct to the *ortho-* position for the first, but to the *para-* position for the second alkylation. As the metal precursor is the aluminium trichloride, remaining chlorine in the catalyst as physisorbed hydrochloric acid, or under aluminium chloride species on the surface or as mixed aluminium chloride phenolate species may induce this selectivity. Water can also induce a Brønsted character to the catalyst surface.

Another parameter is the steric hindrance on the surface, which can forbid or hinder some intermediate configurations.

3.6.1 K100 silica gel as catalyst by itself

Kamitori et al. used dried silica gel as catalyst by itself in the alkylation of phenol with *tert*-butyl chloride as alkylating agent, under mild conditions (in dichloromethane (DCM) as solvent at 30°C)[164]. A mixture of OTBP (58%), PTBP (32%) and 2,4-DTBP (10%) was obtained, with a phenol conversion of 41%. However, wet silica gel did not allow the reaction to proceed and all the starting material was recovered.

Following these results, the role of our chosen support was then checked in our system. K100 silica gel dried in an oven at 200°C was used as such as a catalyst for the alkylation of phenol with isobutene, carried out under pressure at 100°C. Table 3.1 shows the product distribution at the time of 21 hours. The conversion of phenol was very low and the main product was the TBPE. However, some alkyl products are also observed, with the *ortho-* product being the main monoalkyl phenol, and the 2,4-DTBP being the major dialkylphenol. The positional selectivity exhibited with isobutene as alkylating agent is similar as the selectivity observed by Kamitori et al. with *tert*butyl chloride. However, with the alkene, the K100 silica gel by itself was far from being as active in the phenol alkylation reaction as the silica gel used by Kamitori et al. for the phenol alkylation with *tert*butyl chloride. These observations show that the support itself was not responsible for the results we have obtained.

Product	GC yields %
PhOH	96.2
TBPE	2.4
OTBP	1.17
PTBP	0.13
2,6-DTBP	0.01
2,4-DTBP	0.06
TTBP	0.01

Table 3.1: Product distribution of the phenol with isobutene alkylation mixture carried out at 100°C under pressure using K100(200) silica gel as catalyst, sample taken at the time of 21 hours.

3.6.2 Does steric hindrance forbid the second *ortho*-alkylation?

2,6-DTBP was observed at low levels during the first experiments using silica supported aluminium triphenolate as catalyst. To check if this low level of di*ortho*-products was due to steric hindrance, *para*- cresol was used as starting material. The *para*- position being occupied by a methyl group, only the *ortho*- positions are available for the alkylation. Methyl groups exhibit a +I effect, therefore the cresol aromatic ring is slightly more activated than the phenol aromatic ring. However, if the steric hindrance forbids the second *ortho*- alkylation, only the 2-*tert*butyl-4-methylphenol should be observed and a very low level of 2,6-di*tert*butyl-4-methylphenol, also called ButylHydroxyToluene (BHT).
The experiment will be discussed in more details in the chapter 4 (Section 4.3 on page 176). The conclusion is that more than 30.2% of BHT were obtained when 1.5eq. of isobutene were consumed, which is more than the yield of 2,6-DTBP observed so far. At that reaction time, the 2-*tert*butyl-4-methylphenol yield was decreasing from its maximum of 82%, showing that the second alkylation step had started.

This result shows that steric hindrance, if relevant, is not the only factor explaining the observed selectivity in our system.

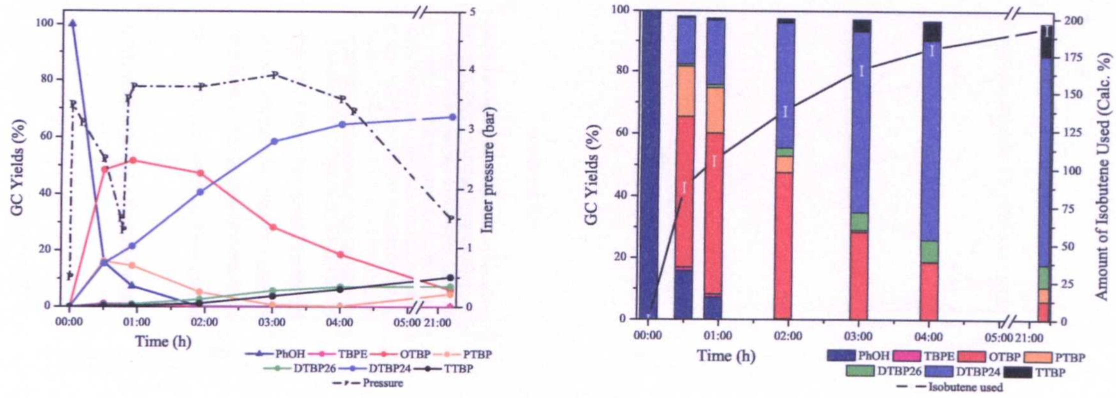


Figure 3.9: Alkylation of phenol with isobutene (1.95eq., 'kinetically controlled' addition method) and Al(OPh)$_x$K100(200)(TEAL)tp(*1.7*) as catalyst (1%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation.*(Original in colour)*

3.6.3 Role of the chlorine

As explained earlier, chlorine is present in the final material. It can be in various forms, physisorbed hydrochloric acid, aluminium species with mixed chloro and phenolate ligands, or Si-Cl species from the aluminium grafting step. Since the latter is very reactive, it seems reasonable to expect it to react with phenol or any moisture traces during the catalyst ligand exchange step.

The role of hydrochloric acid was ruled out by carrying out an experiment with a 37% aqueous solution of hydrochloric acid as catalyst. The only product observed was the ether and the addition of HCl on the double bond. Homogeneous catalysis by hydrochloric acid, which could have been released from the bulk of the solid catalyst could not explain the observed results and selectivity.

To check the role of mixed aluminium species, a catalyst prepared with a non chlorine containing aluminium precursor was prepared and tested. Triethyl aluminium (TEAL), chosen as the precursor, is available as a solution in toluene, which is the chosen solvent for the catalyst synthesis. Its characterisation has been presented in section 2.4.6 on page 100. The analysis of the final material showed that aluminium species were grafted on the surface and inside the pores of the silica gel support, and that phenolate functions were present. However, the exchange of ethyl groups was not complete.

Figures 3.9 and 3.10 show the alkylation reactions of phenol with isobutene carried out at 100°C with 1mol% of catalyst, respectively, in York and using the 'kineti-

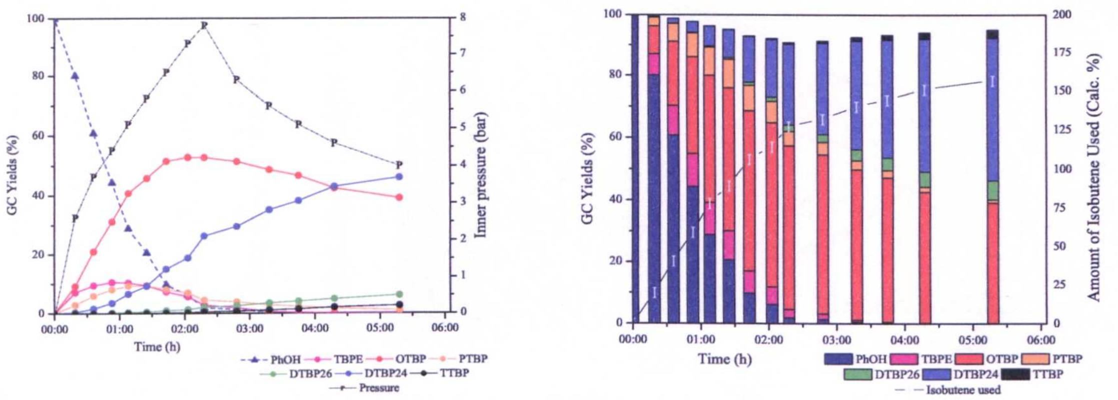


Figure 3.10: Alkylation of phenol with isobutene (2eq., 'by pump' addition method) and Al(OPh)$_x$K100(200)(TEAL)tp(*1.7*) as catalyst (1%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation.*(Original in colour)*

cally controlled addition' method, and at the Schenectady laboratory, Pratteln, Switzerland, using the 'by pump addition' method. Both reactions were carried out with the Al(OPh)$_x$K100(200)(TEAL)tp(*1.7*) material as catalyst.

Both reactions exhibited the same general product profile, hence the same general selectivity. Phenol was completely converted, the major products were OTBP and 2,4-DTBP. The difference between the two ways of addition of the isobutene was the observable amount of ether and the slower rate of alkylation when the 'by pump addition' method was used.

Another way of comparison is to look at the profile of reactions carried out with all the same parameters but the aluminium precursor. Figures 3.7 and 3.9 shows the data from reactions carried out respectively with Al(OPh)$_x$K100(200)(ATC)tp(*1.7*) and Al(OPh)$_x$K100(200)(TEAL)tp(*1.7*) using the 'kinetically controlled addition' method. No ether was observed in either experiments and the OTBP maximum yield was the same. However the reaction with the catalyst prepared from TEAL exhibits a higher activity as the rate of the second alkylation was higher. The reaction profile was cleaner with the catalyst prepared from TEAL, as there were less heavy products (2% compared to 5%). Figures 3.4 and 3.5 shows the data from reactions carried out respectively with Al(OPh)$_x$K100(200)(ATC)tp(*1.7*) and Al(OPh)$_x$K100(200)(TEAL)tp(*1.7*) using the 'by pump addition ' method. The same conclusions can be drawn. But also, more ether products were observed with this isobutene addition method, TBPE (maximum at 10%) and the non-plotted products TBOTBPE (maximum at 2%, at the time of 2h20) and TBPTBPE (maximum at 6%, at the time of 2h20).

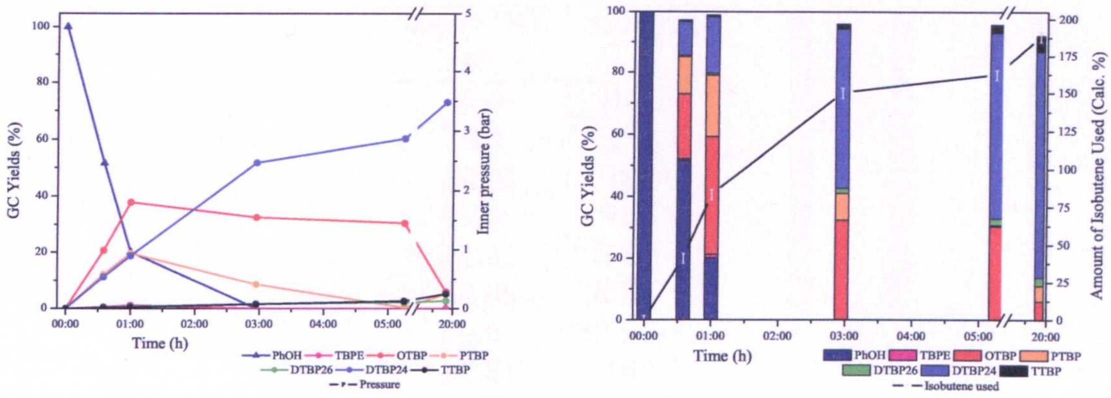


Figure 3.11: Alkylation of phenol with isobutene (1.94eq.) and Al(OPh)K100(200)(ClAl(OPh)$_2$)tp(*1.7*) as catalyst (1%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

The use of TEAL as aluminium precursor did not change the general selectivity of the catalyst, the major mono-TBP was OTBP, and the major di*tert*butylphenol was the 2,4-DTBP. Little 2,6-DTBP was observed.

From these experiments, the chlorine, which could have been remaining in the final material, seems not to be the reason for the observed selectivity.

3.6.4 Aluminium configuration on the surface

The industrial homogeneous alkylation of phenol is carried out using the aluminium triphenolate[38]. The proposed mechanisms involve the formation of an acidic complex HAl(OPh)$_4$[66]. If we want to favour the formation of a similar species on the support surface, we need to design a catalyst preparation method, which leads to the formation of either the chemisorbed (Si-O)$_1$Al(OPh)$_2$ species, isolated or complexed with silanol group(s), or to the physisorbed species Si-OH$\cdots$Al(OPh)$_3$.

To obtain a catalyst, which exhibits mainly (Si-O)$_1$Al(OPh)$_2$ species, aluminium chloro- diphenolate ClAl(OPh)$_2$ was prepared from aluminium trichloride and 2eq. of phenol in toluene and reacted with the K100 silica gel. The results of alkylation reaction of phenol with isobutene carried out with this new material, Al(OPh)K100(200)(ClAl(OPh)$_2$)tp(*1.7*), are presented in Figure 3.11.
Unfortunately, the general selectivity remained the same. Phenol was totally converted into alkylphenols. The major mono- alkylphenol was OTBP and the

Product	GC yields %
PhOH	0.0
TBPE	0.0
OTBP	30.52
PTBP	0.34
2,6-DTBP	15.15
2,4-DTBP	36.34
2,5-DTBP	0.98
TTBP	13.74
Heavy	2.74

Table 3.2: Product distribution of the phenol with isobutene (1.94eq.) alkylation mixture carried out at 100°C under pressure using Al(OPh)K100(200)(Al(OPh)$_3$)tp(*1.7*) as catalyst, sample taken at the time of 21 hours.

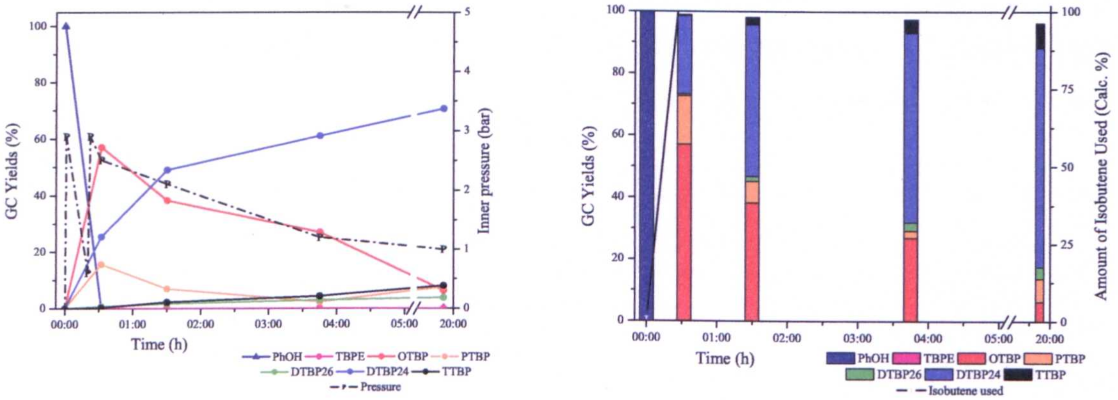


Figure 3.12: Alkylation of phenol with isobutene (1.96eq.) and Al(OPh)K100(200)(Al(OPh)$_3$)tp(*0.8*) as catalyst (1%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

major dialkyl phenol was the 2,4-DTBP. Regarding the non-plotted products, 2% of 2,5-DTBP and 5.8% of heavy products were detected.

To obtain a catalyst, which exhibits mainly Si-OH$\cdots$Al(OPh)$_3$ species, aluminium triphenolate was reacted with K100 silica gel in toluene. The first attempt was to load the surface at 1.7mmolg^{-1}, but this catalyst leached during the test reaction. The samples were grey as is the aluminium triphenolate starting material, hence the increase of 2,6-DTBP yields, as shown by the product distribution in Table 3.2, was suspected to be due to leached homogeneous catalysis from aluminium triphenolate. A new batch of this material was prepared at a theoretical loading of 0.8mmolg^{-1}. Leaching was again observed (grey samples), but to a less extent. The results of alkylation reaction of phenol with isobutene carried

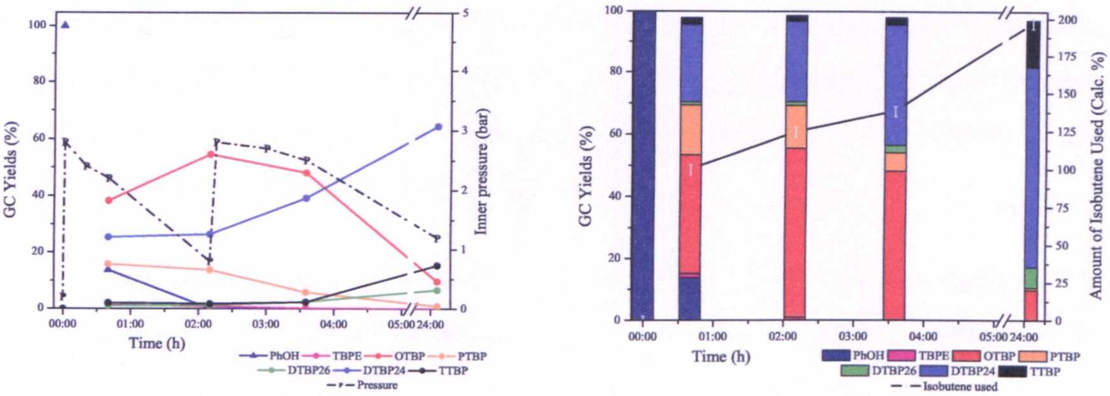


Figure 3.13: Alkylation of phenol with isobutene (1.96eq.) and Al(OPh)K100(200)(Al(OPh)$_3$)tp(*0.8*) as catalyst (<1%, reuse) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

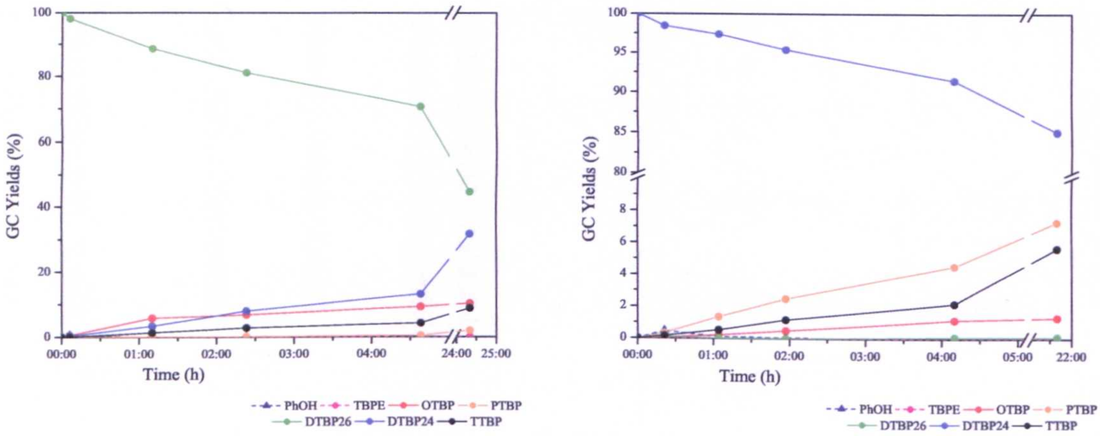
out with the new material, Al(OPh)K100(200)(Al(OPh)$_3$)tp(*0.8*), are presented in Figure 3.12. To check the effect of the leaching on the yield of 2,6-DTBP, the catalyst was reused, assuming that all leaching occured during the first use and that nearly all leached species were removed when taking out the 'first use' reaction mixture out of the pressure reactor. The results obtained when reusing this material are shown in Figure 3.13.

In both cases, even for the first use where leaching was observed, the selectivity was the same as observed for other experiments, the major products were first OTBP then 2,4-DTBP. However, a dramatic decrease of activity was observed, 20min for the first isobutene equivalent addition during the first use reaction, more than two hours for the reuse reaction. The reusability of the catalyst will be presented in chapter 5.

The aluminium configuration seems not to be the reason for the observed selectivity. However, the desired product, the 2,6-DTBP, might not be stable and undergo rearrangement or trans-alkylation reactions leading to the more thermodynamically stable 2,4-DTBP product. The next section will discuss the stability studies of the various *tert*butylphenols.

3.6.5 Product stability studies

2,6-DTBP and 2,4-DTBP were stirred under a pressure of an inert atmosphere of nitrogen with the Al(OPh)$_x$K100(200)(ATC)hf(*1.7*) catalyst at 100°C. Figure 3.14 shows the GC yields of each stability study. To check the effect of the



Product	GC yields %
OTBP	0.34
2,6-DTBP	98.84
2,4-DTBP	0.27
Heavy	0.55

Figure 3.14: Product stability studies at 100°C, left to right, top to bottom, 2,6-DTBP and 2,4-DTBP with Al(OPh)$_x$K100(200)(ATC)hf(*1.7*), and product distribution at the time of 24 hours of the stability study of 2,6-DTBP with K100(200).

silica support on its stability, 2,6-DTBP was stirred with K100(200) under argon at 100°C for 24 hours. The product distribution is also given in Figure 3.14.

2,6-DTBP was mainly rearranged into 2,4-DTBP, which is thermodynamically more stable. Trans-alkylation also happened, as mono-*tert*butylphenol and TTBP were observed. However the yield of TTBP was lower than the yield of the mono-*tert*butylphenols, which suggests that some isobutene was in the reaction medium and the reactor atmosphere, and that the reaction might have occurred *via* a de-alkylation – re-alkylation mechanism. The stability problem of 2,6-DTBP in presence of the catalyst is not due to the silica support itself, as no transformation of the 2,6-DTBP was observed when stirred under the same condition with K100(200) alone (GC percentages corresponding to a 99% purity of the OTBP, in correlation with the product specifications).

2,4-DTBP was not stable in presence of the catalyst, although only 15% was transformed compared to 55% of 2,6-DTBP both after the same time. As expected, 2,4-DTBP underwent mainly trans-alkylation into PTBP and TTBP. PTBP is thermodynamically more stable than OTBP, therefore it is not surprising that the *tert*butyl group at the *ortho*- position of the 2,4-DTBP is removed preferentially. However, some OTBP was observed during the reaction at a non-negligible level, showing that the catalyst can also remove the *tert*butyl group at the *para*- position. As for the 2,6-DTBP stability study, the yield of the mono-*tert*butylphenols was higher than the yield of TTBP, showing that isobutene was present in the reaction medium and in the reactor atmosphere.

From these studies, we may conclude that the 2,6-DTBP was not stable in the presence of the new solid catalyst and underwent side reactions to the thermodynamically more stable 2,4-DTBP, mainly. These side reactions, rearrangement or trans-alkylation, may be induced by Brønsted acid sites or "classic" Lewis acid sites[38].

Residual Brønsted acidity may be caused by traces of water, which could either hydrolyse the aluminium species or interact with the silica gel surface generating mobile proton sites. Water content was measured by the Karl-Fischer method for the experiments carried out at the Schenectady laboratory, Pratteln, Switzerland, and shows that the water content was lower than 0.1%. At York, Karl-Fischer equipment was not available. However, experiments were reproduced with freshly purchased chemicals, for which specifications show that they were either water free or the water level was below 0.3%, and exhibited the same general selectivity.

The rest of this chapter will discuss a more systematic study of various parameters affecting the reaction, such as temperature, amount of catalyst, and the final nature of the solid material itself, such as aluminium loading, silica gel pretreatment temperature, nature of the silica support and nature of the aluminium ligand.

3.7 Effect of the reaction temperature

The first reaction parameter studied was the reaction temperature. Figures 3.15 and 3.16 show the reaction profile, the reactor inner pressure and the isobutene consumption estimation of reactions carried out respectively at 60 and 100°C and with 1% of the same batch of the catalyst Al(OPh)$_x$K100(200)(ATC)hf(*1.7*). Decreasing the reaction temperature affects the reaction profile. The rate of the reaction was much slower at 60 than at 100°C. However *tert*butylphenyl ether, TBPE, which was so far not observed or at low level during experiments carried out at 100°C, was observed at 60°C at high level. Unfortunately, the major

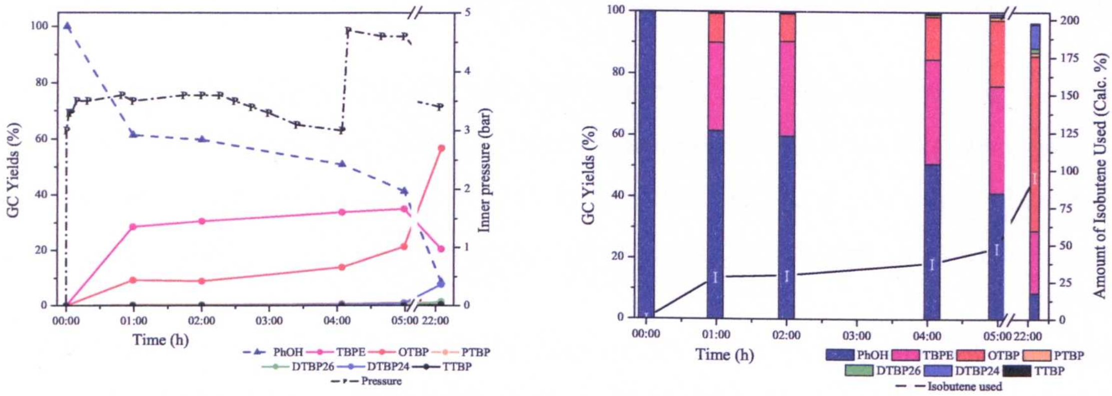


Figure 3.15: Alkylation of phenol with isobutene (1.33eq.) and Al(OPh)$_x$K100(200)(ATC)hf(*1.7*) as catalyst (1%) carried out at 60°C: reaction and reactor inner pressure profiles and isobutene consumption estimation.*(Original in colour)*

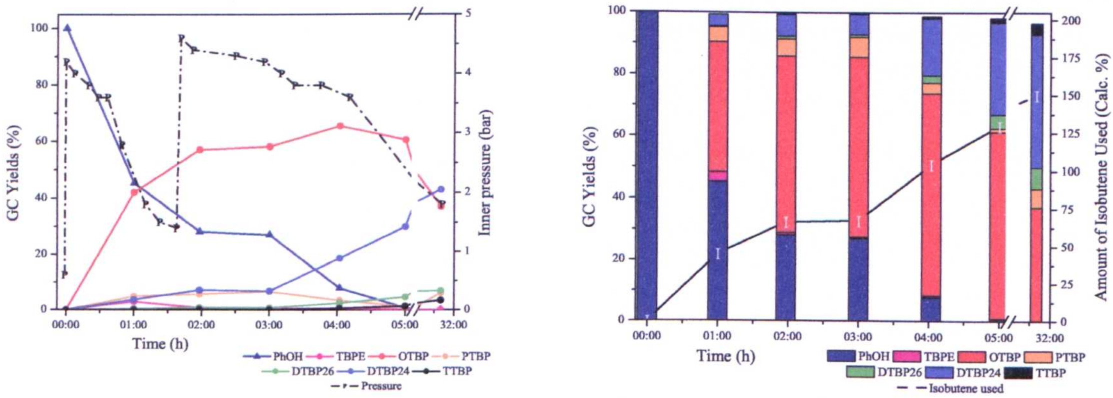


Figure 3.16: Alkylation of phenol with isobutene (1.45eq.) and Al(OPh)$_x$K100(200)(ATC)hf(*1.7*) as catalyst (1%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation.*(Original in colour)*

product, di*tert*butylphenol, which appeared at low level at the time of 22hours, was the 2,4-DTBP. The reaction temperature seems to stretch in time the profile, with the ether of phenol being produced at low temperature. The observation of the formation of the ether at low temperature and its non-observation at higher temperature has been reported in the literature[46, 66, 165, 166].

Effect of the reaction temperature (Figures 3.17 to 3.19, respectively at 60°C, 100°C and 140°C) was studied using Al(OPh)$_x$K100(300)(TEAL)is(*1.7*) as catalyst. These experiments were carried out at the Schenectady laboratory, Pratteln, Switzerland and the isobutene was added following the 'by pump addition' method; the alkene addition time can be deduced from the time when the pressure reached its maximum. These three experiments presented here, and the next one (Figure 3.20) were carried out with the same batch of catalyst, but some being carried out reusing the catalyst from previous variable temperature experiments (details are given in the figure captions).
The general selectivity observed is similar to the one reported so far. The major mono*tert*butylphenol was the OTBP, the major di*tert*butylphenol was the 2,4-DTBP. The rate of the reaction increased as expected with temperature, the OTBP maximum yield being reached earlier, respectively at the reaction time of 6hours, about 2hours and about 1hour and a half when the temperature is increased from 60 to 100 to 140°C, and the maximum yield of 2,4-DTBP at the time of 5 hours increasing from about 20% to about 65%. Ethers of phenols are observed at low temperature and disappeared when increasing the reaction temperature. At 60°C, TBPE up to 35.6%, and also up to (at the reaction time of 6hour) 2.7% of TBOTBPE, 8.8% of TBPTBPE were observed. At 100°C, only up to 10.6% of TBPE, 1.9% of TBOTBPE and 5.8% of TBPTBPE were detected. At 140°C, less than 0.7% of each ether were observed. However, as the temperature was increased, the yield of the thermodynamically most stable di*tert*butylphenol, 2,5-DTBP, increased from 0.3 to 1 to 2.6%, and more PTBP was observed.

As ethers are unstable at high temperature in the presence of catalyst[21], and as we learned that *ortho- tert*butylphenols are less stable than their *para-* counterparts in presence of the new catalyst (Section 3.6.5), it is not surprising that increasing the temperature decreases the formation of ethers and favours the production of *para-* products.

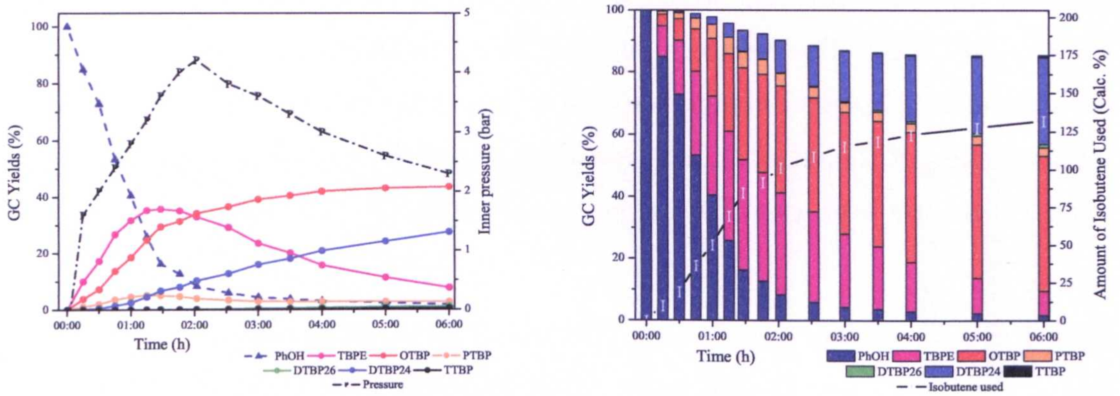


Figure 3.17: Alkylation of phenol with isobutene (2eq., added by the mean of a pressure pump) and Al(OPh)$_x$K100(300)(TEAL)is(*1.7*) as catalyst (1%) carried out at 60°C: reaction and reactor inner pressure profiles and isobutene consumption estimation.*(Original in colour)*

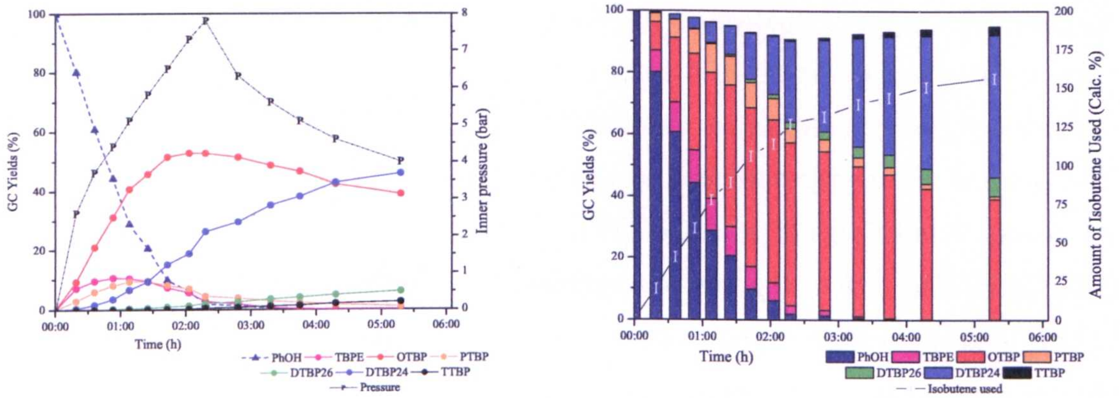


Figure 3.18: Alkylation of phenol with isobutene (2eq., added by the mean of a pressure pump) and Al(OPh)$_x$K100(300)(TEAL)is(*1.7*) as catalyst (1%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation.*(Original in colour)*

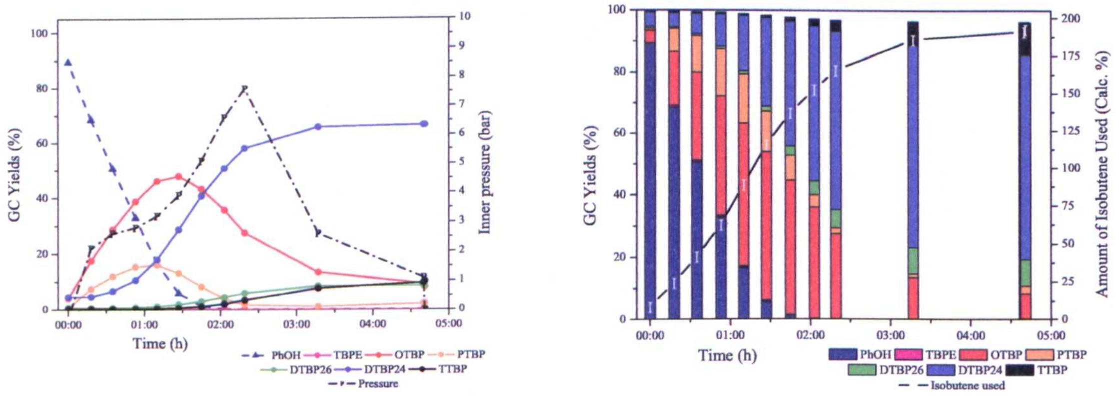


Figure 3.19: Alkylation of phenol with isobutene (2eq., added by the mean of a pressure pump) and Al(OPh)$_x$K100(300)(TEAL)is(*1.7*) as catalyst (1%, reuse from the reaction at 140°C) carried out at °C: reaction and reactor inner pressure profiles and isobutene consumption estimation.*(Original in colour)*

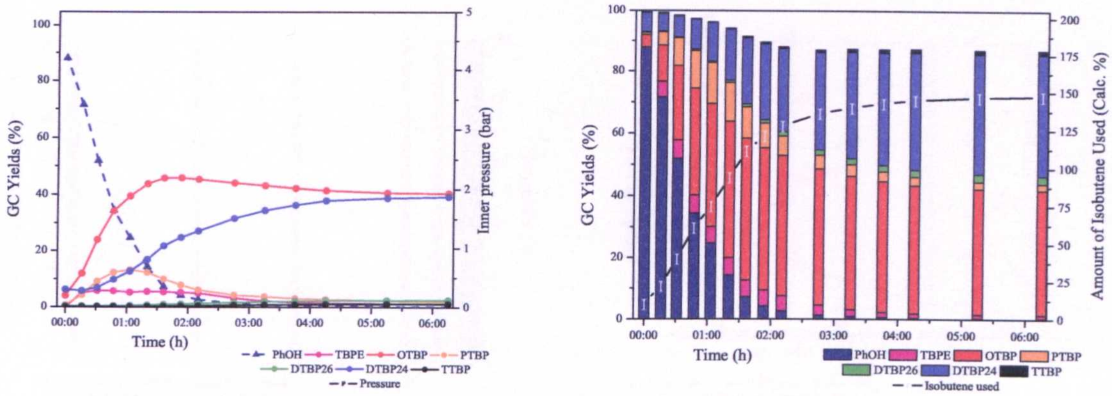


Figure 3.20: Alkylation of phenol with isobutene (2eq., added by the mean of a pressure pump) and Al(OPh)$_x$K100(300)(TEAL)is(*1.7*) as catalyst (1%, reuse from the reaction with a 60 to 100°C gradient temperature) carried out with a temperature gradient from 100°C to 60°C: reaction and reactor inner pressure profiles and isobutene consumption estimation.*(Original in colour)*

The catalyst is *ortho-* directing for the first alkylation, then largely *para-* directing for the second alkylation. As the maximum yield of OTBP was obtained using 100°C, and as the 2,6-DTBP would have been expected to be at a higher yield at low temperature, an experiment with a temperature gradient from 100 to 60°C was carried out (Figure 3.20). However the yield of 2,6-DTBP did not improve, the 2,4-DTBP being still largely the major di*tert*butylphenol.

The temperature has an important effect on the product distribution of the alkylation of phenol with isobutene. Increasing the temperature decreases the formation of ethers and favours the production of *para-* products. However, with catalysts prepared either from aluminium trichloride or TEAL and the silica gel pre-treated at 200°C as support, reducing the temperature does not improve the yield of 2,6-DTBP.

3.8 Effect of the amount of catalyst

Experiments with different amounts of catalyst, keeping all other parameters constant, were carried out. The reaction temperature was set at 100°C, and the catalyst was the Al(OPh)$_x$K100(200)(ATC)tp(*1.7*) material. Figures 3.21 to 3.24 show reactions results carried out with respectively 0.25, 1, 2 and 5% of catalyst (calculated on the amount of the theoretical aluminium species, hence the given percentages are in Almol%), based on the phenol amount.

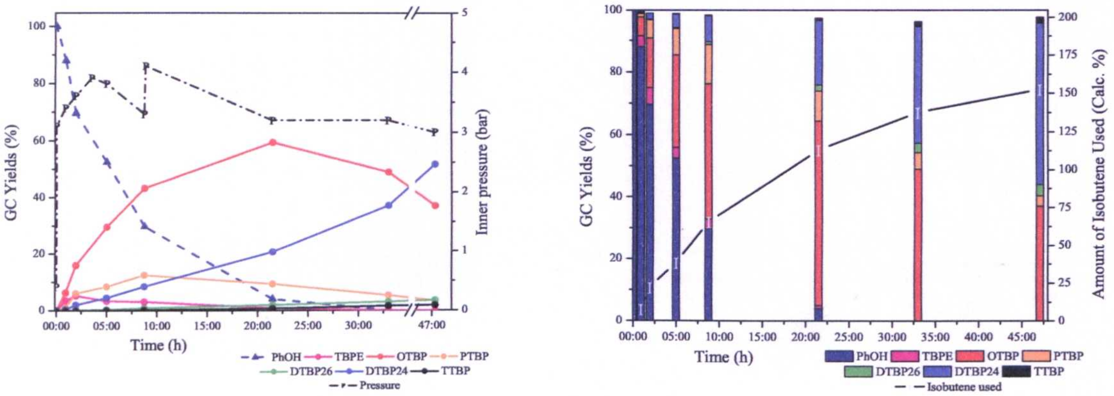


Figure 3.21: Alkylation of phenol with isobutene (1.67eq.) and Al(OPh)$_x$K100(200)(ATC)tp(*1.7*) as catalyst (0.25%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation.*(Original in colour)*

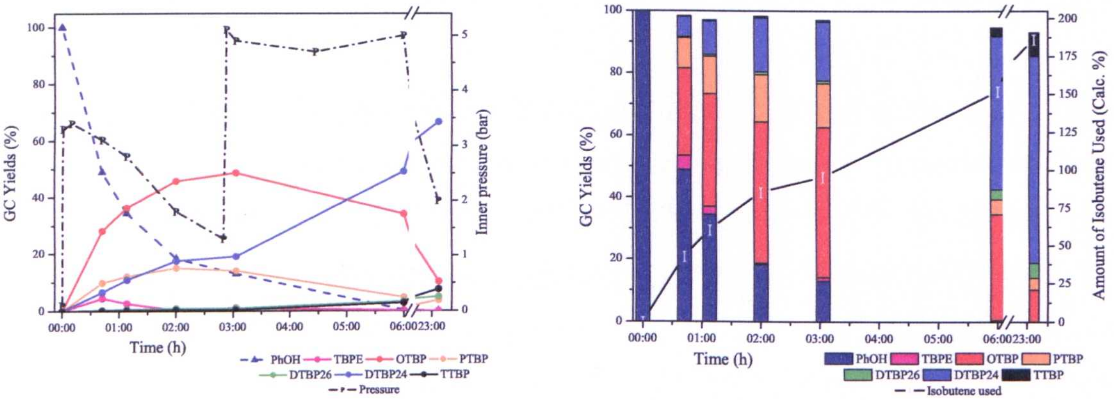


Figure 3.22: Alkylation of phenol with isobutene (1.96eq.) and Al(OPh)$_x$K100(200)(ATC)tp(*1.7*) as catalyst (1%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation.*(Original in colour)*

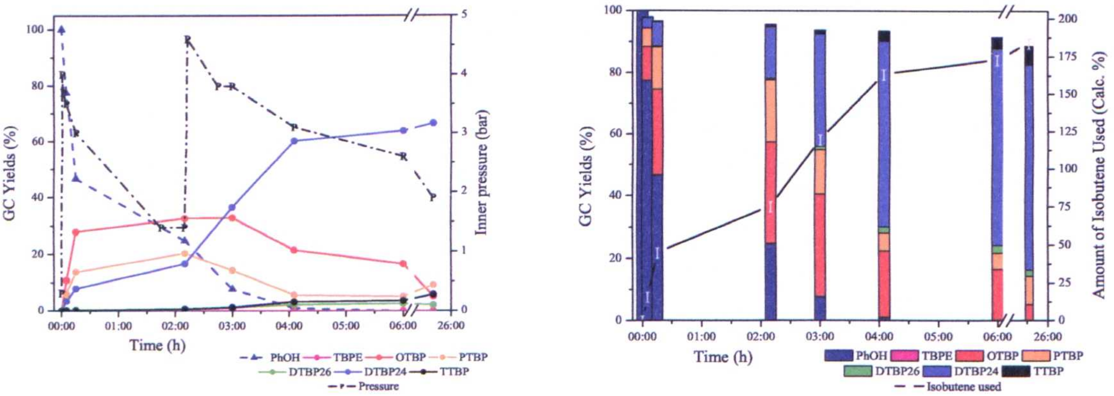


Figure 3.23: Alkylation of phenol with isobutene (1.94eq.) and Al(OPh)$_x$K100(200)(ATC)tp(*1.7*) as catalyst (2%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation.*(Original in colour)*

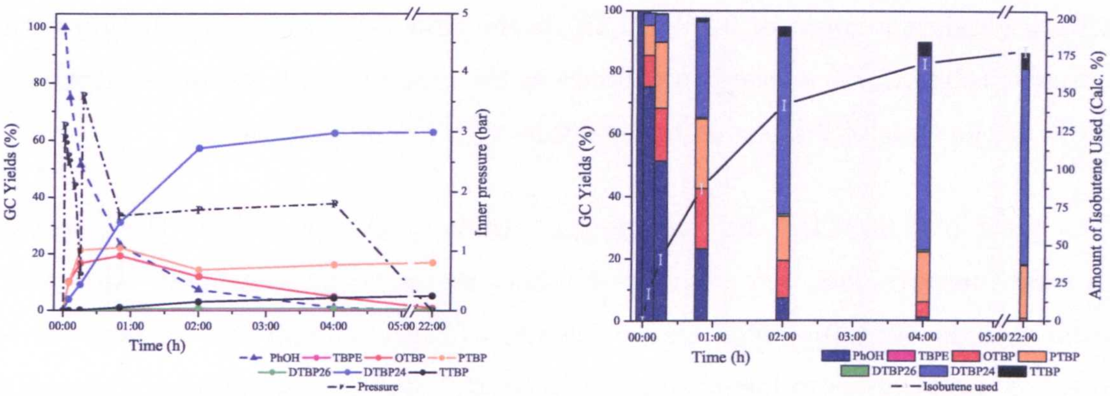


Figure 3.24: Alkylation of phenol with isobutene (1.95eq.) and Al(OPh)$_x$K100(200)(ATC)tp(*1.7*) as catalyst (5%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

In all reactions, phenol was fully converted and the major di*tert*butylphenol was the 2,4-DTBP. The reaction rate was, as expected, increasing with the catalyst amount. For example, at 47hours in the reaction carried out with a catalyst amount of 0.25%, the same product distribution was observed as at 6hours in the reaction carried out with a catalyst amount of 1%.

However, for larger catalyst amounts, selectivity between *ortho*- and *para*- products changed compared to all observed so far. If the 2,4-DTBP was still the main di*tert*butylphenol, the major mono-*tert*butylphenol, which was the OTBP in the reaction carried out with a catalyst amount of 1%, became the PTBP in the reaction carried out with a catalyst amount of 5%.

Increasing the catalyst amount led to more "dirtier" reaction product distribution, regarding by-products (non-plotted products). If the two ethers, TBOTBPE and TBPTBPE, were never observed at a level above 1.2%, 2,5-DTBP was detected at 0.2%, 1.3%, 1.8% and 2% when the catalyst amount was increased respectively from 0.25% to 1 to 2 and 5%. Heavy products levels increased in a more dramatic manner, they were recorded at 2.1%, then 5.6, 9.5 and 12.4% when the catalyst amount was increased respectively from 0.25%, to 1, 2 and 5%. These values correspond to samples at the reaction time of, respectively, 33 hours, 23h15, 25h30 and 22 hours.

The 2,6-DTBP level was in all cases lower than 3.6%. However, the trend was that the smallest catalyst amount yielded the highest 2,6-DTBP level, the highest catalyst amount yielded only traces. For each experiments, at the point where the yield of 2,4-DTBP reached a level between 50 and 60%, the yield of 2,6-DTBP was recorded at 3.6% at the time of 47h in the reaction carried out with a catalyst amount of 0.25%, 3.3% at the time 6 hours in the reaction with 1% of catalyst, 2.2% at the time 6hours in the reaction with 2% of catalyst and 0.7% at the time of 2 hours in the reaction with 5% of catalyst.

The yield of 2,6-DTBP did not improve dramatically by varying the catalyst amount, nevertheless, low catalyst amounts seems to be beneficial. However, other trends were observed. Increasing the catalyst amount led to more *para*-products and heavy products being produced. 2,6-DTBP yield followed a opposite trend, decreasing with the catalyst amount increase. OTBP maximum yield also decreased, when the catalyst amount was increased. Hence, low catalyst amount seem advantageous for the goal of this work.

3.9 Effect of the aluminium ligand

Coffield et al. described the preparation of 2,6-DTBP from OTBP[167]. High yields (above 94%) were obtained using very mild conditions (10°C) and aluminium tri-(*ortho-tert*butylphenolate) as catalyst. Küpper et al. also showed this effect in aliphatic solvents[168]. Knapp et al. studied the catalyst isolation in order to recover and reuse the homogeneous aluminium triphenolate[46]. If the catalyst was precipitated before the end of the first alkylation, the catalyst was reusable with the same activity and selectivity. However, around the end of the first alkylation or later in the reaction, precipitation of the catalyst became more and more difficult, the catalyst being more and more soluble in non-polar solvent. Hence the nature of the catalyst ligand evolved during the alkylation reaction, the ligand becoming more and more alkylated, and less and less phenolic. These two observations suggest that the ligand of the aluminium catalytic species evolves during the reaction, can become for example, $Al(OTBP)_3$.

So far, the new solid catalysts were prepared with phenol as ligand. One counterpart with OTBP as ligand was prepared and tested with phenol and OTBP as starting material. Figures 3.25 and 3.26 show the reaction profile, the reactor inner pressure and the isobutene consumption estimation of experiments carried out at 100°C with 1% of $Al(\underline{OPh})_x$K100(200)(ATC)tp(*1.7*) with, respectively PhOH as starting material and 2eq. of isobutene and OTBP as starting material and 1eq. of isobutene.

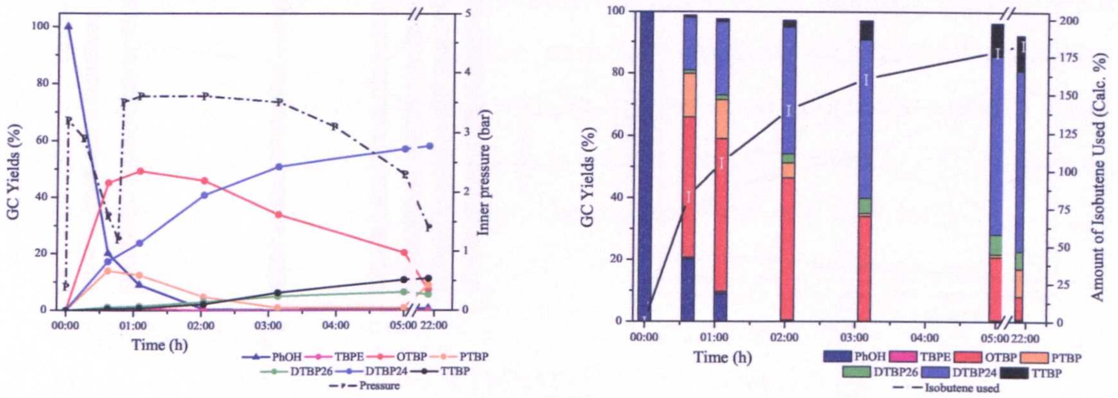


Figure 3.25: Alkylation of phenol with isobutene (1.94eq.) and Al(OPh)$_x$K100(200)(ATC)tp(*1.7*) as catalyst (1%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

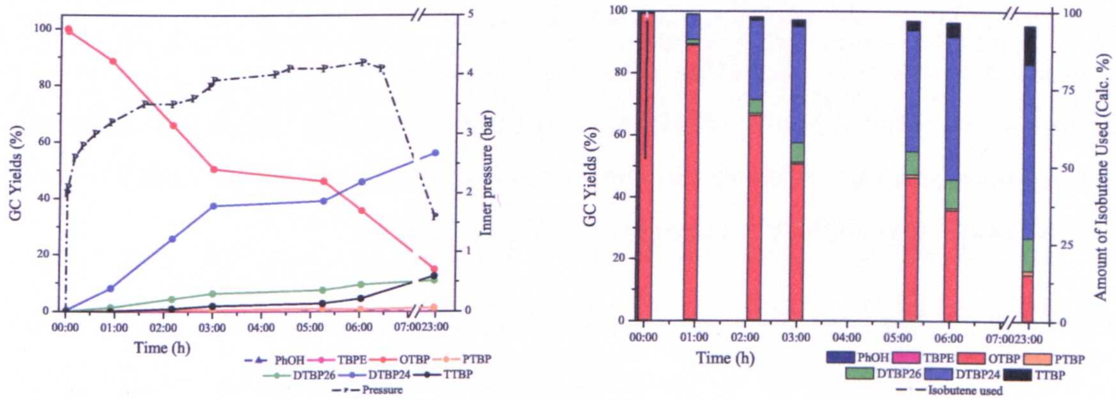


Figure 3.26: Alkylation of OTBP with isobutene (0.98eq.) and Al(OPh)$_x$K100(200)(ATC)tp(*1.7*) as catalyst (1%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

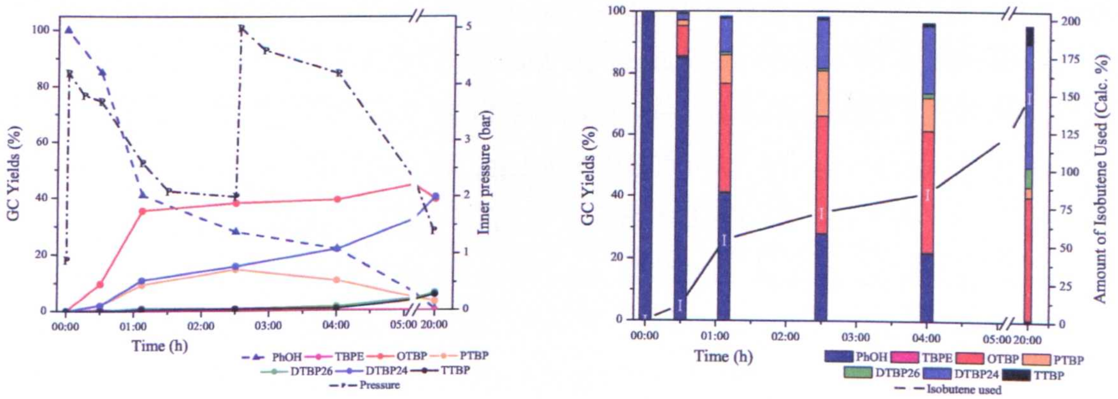


Figure 3.27: Alkylation of phenol with isobutene (1.94eq.) and Al(<u>OTBP</u>)$_x$K100(600)(ATC)tp(*1.7*) as catalyst (1%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

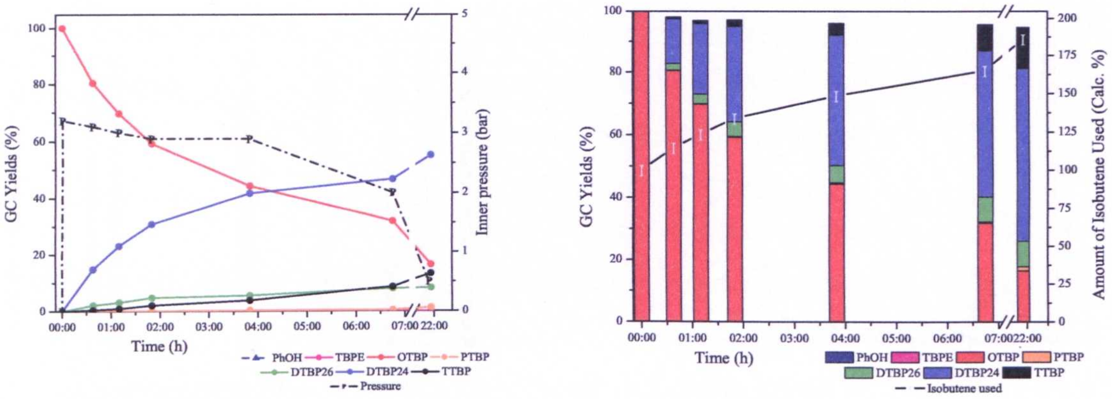


Figure 3.28: Alkylation of OTBP with isobutene (0.97eq.) and Al($\underline{\text{OTBP}}$)$_x$K100(600)(ATC)tp(*1.7*) as catalyst (1%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

In both cases, the main di*tert*butylphenol was the 2,4-DTBP. As expected, starting from OTBP, the reaction rate was slower as the second alkylation is slower compared to the first alkylation step, and the total phenol conversion was over 2hours when after 23hours, OTBP was still not completely converted. However, less by-products were observed in the reaction started with OTBP, and the yield of 2,6-DTBP was slightly higher (from 6.5% to 10.8%).

Figures 3.27 and 3.28 show the results of the reaction profile, the reactor inner pressure and the isobutene consumption estimation of experiments carried out at 100°C with 1% of Al($\underline{\text{OTBP}}$)$_x$K100(600)(ATC)tp(*1.7*) with, respectively PhOH as starting material and 2eq. of isobutene and OTBP as starting material and 1eq. of isobutene.

In the reaction starting with phenol, the phenol conversion rate was much slower compared to reactions carried out with catalyst based on phenol as ligand, 90% being converted in 5hours compared to less than 1hour for the reaction shown in Figure 3.25. Otherwise, the main mono-TBP was the OTBP and the main di*tert*butylphenol was the 2,4-DTBP. Starting from OTBP, the main di*tert*butylphenol was still the 2,4-DTBP, but a slightly higher yield of 2,6-DTBP was observed (8.3% compared to 6.3%) and also more TTBP(13.4% compared to 5.8%). Regarding the non-plotted products, both reactions exhibited the same amount of heavy products (respectively 3.9 and 3.6% at the reaction time above 20 hours).

Generally, it seems better to use the starting material as ligand. Starting with phenol, the reaction rate was higher with the catalyst with phenol as ligand than with the catalyst with OTBP as ligand. The same effect was noticed when starting with OTBP, however to a lesser extent. Starting with OTBP improved slightly the 2,6-DTBP yield, although the increase was not very large.

3.10 Effect of the theoretical loading

Two sets of experiments investigating the effect of the aluminium theoretical loading of the catalyst are presented using catalysts with the K100 silica gel pre-treated at 200°C, and catalysts with the silica support pre-treated at 600°C. All other parameters, such as aluminium precursor (aluminium trichloride), ligand (phenol), catalyst amount (1%) and reaction temperature (100°C) are kept constant.

Figures 3.29, 3.30 and 3.31 show the results of the reaction profile, the reactor inner pressure and the isobutene consumption estimation of experiments carried out at 100°C with 1% of $\mathrm{Al(OPh)}_x\mathrm{K100}(\underline{200})(\mathrm{ATC})\mathrm{tp}(xx)$ as catalyst with '*xx*' respectively 0.4, 0.8 and 1.7mmolg^{-1}.

The general selectivity remained similar to those observed so far, the major mono-TBP was the OTBP and the major di*tert*butylphenol was the 2,4-DTBP. No heavy products were observed in the reactions carried out with catalysts prepared with a theoretical loading of 0.4 and 0.8mmolg^{-1}, however 3.6% of heavy products were detected in the reaction using the catalyst prepared with an aluminium theoretical loading of 1.7mmolg^{-1}. 2,5-DTBP was also detected at a level below 2.5%.

Increasing the aluminium theoretical loading led to a 'cleaner' reaction mixture. At a reaction time longer than 20 hours, when all the phenol was converted, the final yield of 2,4-DTBP increased from 60.6% to 70.4% with the theoretical loading and the sum of OTBP, PTBP, TTBP and 2,6-DTBP decreased. However, the yield of 2,6-DTBP decreased from 8.7% - 9.4% to 3.9% when increasing the theoretical loading from 0.4 - 0.8 to 1.7mmolg^{-1}. The same trend was also observed for the TTBP product, decreasing (at the reaction time above 20 hours) from 15.5% to 12.5% to 8% when the theoretical loading was respectively increa-

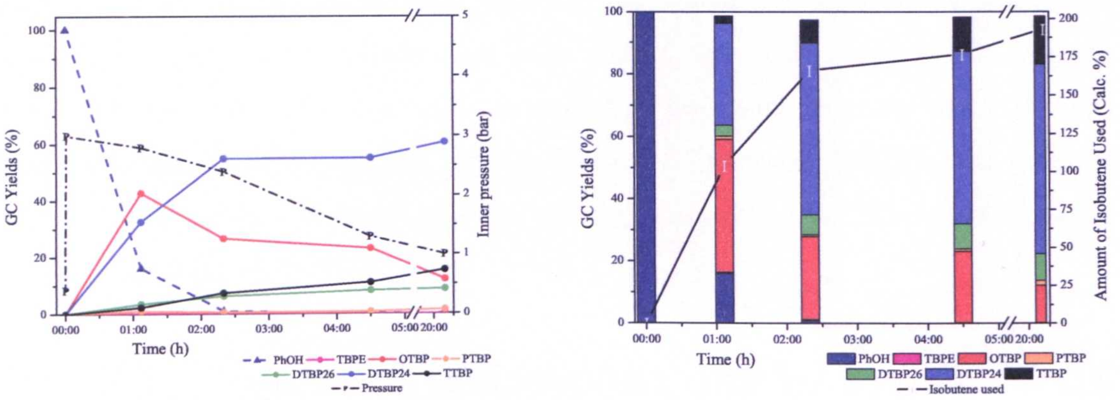


Figure 3.29: Alkylation of phenol with isobutene (1.97eq.) and Al(OPh)$_x$K100(<u>200</u>)(ATC)tp(*0.4*) as catalyst (1%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation.*(Original in colour)*

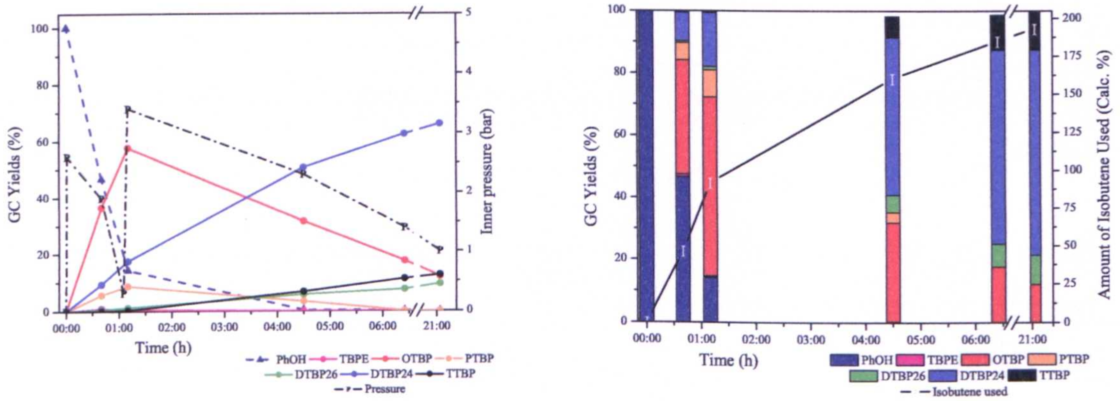


Figure 3.30: Alkylation of phenol with isobutene (1.94eq.) and Al(OPh)$_x$K100(<u>200</u>)(ATC)tp(*0.8*) as catalyst (1%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation.*(Original in colour)*

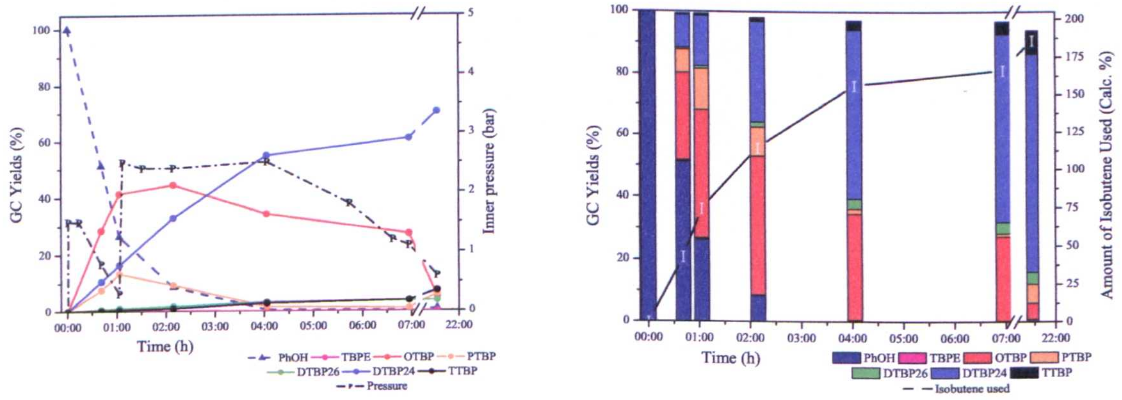


Figure 3.31: Alkylation of phenol with isobutene (1.95eq.) and Al(OPh)$_x$K100(<u>200</u>)(ATC)tp(*1.7*) as catalyst (1%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation.*(Original in colour)*

sed from 0.4 to 0.8 to 1.7mmolg^{-1}. From the OTBP point-of-view, its maximum yield was obtained in the reaction carried out with the catalyst prepared with a theoretical loading of 0.8mmolg^{-1}.

Figures 3.32, 3.33 and 3.34 show the reaction profile, the reactor inner pressure and the isobutene consumption estimation of experiments carried out at 100°C with 1% of Al(OPh)$_x$K100(<u>600</u>)(ATC)tp(*xx*) as catalyst with '*xx*' respectively 0.4, 0.8 and 1.7mmolg^{-1}.

The same general selectivity is observed in this set of reactions. The major mono-TBP was the OTBP and the major di*tert*butylphenol was the 2,4-DTBP. The conversion of phenol was complete in all cases, the rate of conversion increasing with the theoretical loading. Heavy products yields at the reaction time of around 22 hours also increased with the theoretical loading, from 1.8% in the reaction carried out with the catalyst prepared with a theoretical loading of 0.4mmolg^{-1}, to 2.9% in the reaction carried out with the catalyst prepared with a theoretical loading of 1.7mmolg^{-1}.

However, the trends for the 2,6-DTBP and TTBP yields, compared to the reactions carried out with catalyst, the surface of which was pre-treated at 200°C, are not the same: the observed maximum yield of 2,6-DTBP increased from 16% (21h45, 0.4mmolg^{-1}) to 19.7% (21h50, 0.8mmolg^{-1}) and 17% (4h15, 1.7mmolg^{-1}) respectively. The observed maximum yield of TTBP were from 18.9% to 28.9% and 24% respectively. The catalyst with a theoretical loading of 0.8mmolg^{-1} and a pre-treatment temperature of 600°C gave a higher yield of 2,6-DTBP observed at the reaction time of 21h50, however, a similar yield was obtained with the catalyst with the theoretical loading of 1.7mmolg^{-1} at a much shorter reaction time (4h15). The highest yield of OTBP from these three experiments was also obtained with the latter catalyst.

In the reaction carried out with the catalyst with the theoretical loading of 1.7mmolg^{-1}, the isobutene consumption estimation showed that the 2 equivalents of alkene were converted over the first four hours. The product distribution at that time being different compared to the product distribution at the reaction time of 22h10, shows that the products were undergoing trans-alkylations, rearrangements or other side-reactions. As already shown (Section 3.6.5), 2,6-DTBP is not stable in the presence of the catalyst and its yield decreased. However, the TTBP yield also decreased, showing that TTBP also underwent trans-alkylations

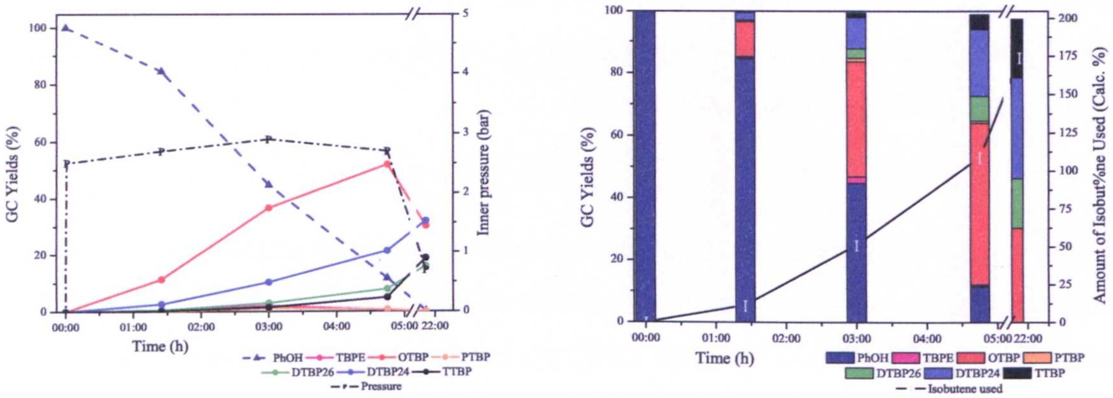


Figure 3.32: Alkylation of phenol with isobutene (1.94eq.) and Al(OPh)$_x$K100(600)(ATC)tp(*0.4*) as catalyst (1%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

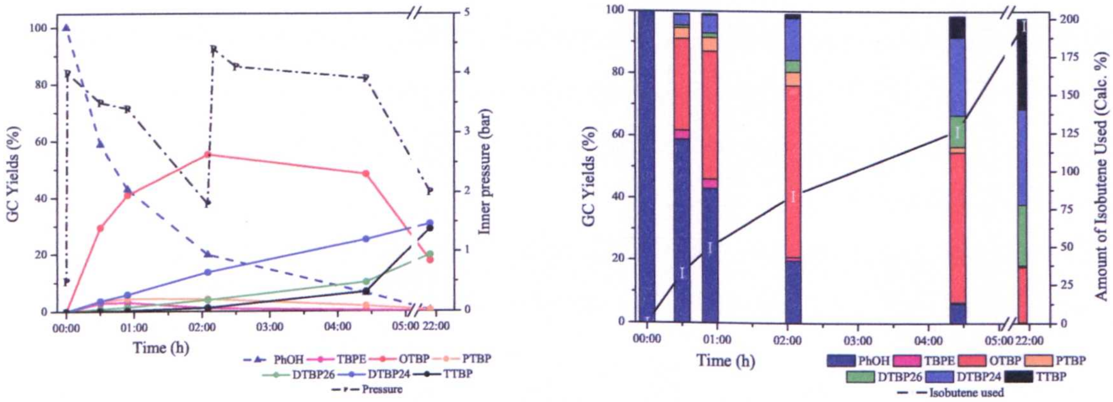


Figure 3.33: Alkylation of phenol with isobutene (1.94eq.) and Al(OPh)$_x$K100(600)(ATC)tp(*0.8*) as catalyst (1%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

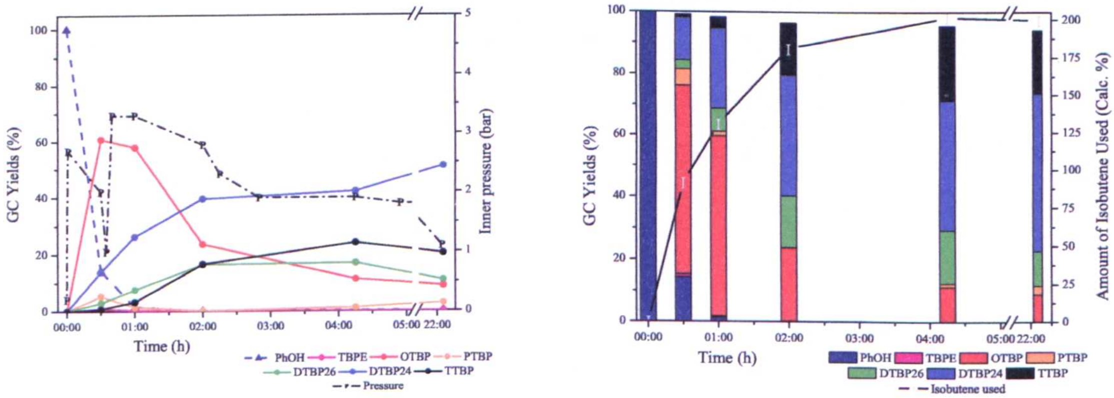


Figure 3.34: Alkylation of phenol with isobutene (1.94eq.) and Al(OPh)$_x$K100(600)(ATC)tp(*1.7*) as catalyst (1%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

or/and de-alkylations, and PTBP, which appeared then disappeared at the beginning of the reaction, reappeared at the end. The most stable product under these conditions was, as expected, 2,4-DTBP. Lack of alkene in the system does not 'freeze' the product distribution. These observations also suggest that a particular product may be produced at high level but is not observed as it undergoes rearrangements or side reactions.

From all these catalysts, prepared with support pre-treated at 200 or 600°C, a theoretical loading of 0.8mmolg^{-1} seems an interesting compromise regarding the reaction rate, and the yield of 2,6-DTBP.

The silica support surface pre-treatment temperature, as shown in this section, affects the product distribution all along the reaction. If we compare, for a certain aluminium theoretical loading, different catalyst support surface pre-treatment temperature, increasing temperatures increased the yield of 2,6-DTBP. For the samples taken at a reaction time above 20hours, at the theoretical loading of 0.4mmolg^{-1}, the 2,6-DTBP yield nearly doubled from 8.7% to 16%, at the theoretical loading of 0.8mmolg^{-1}, it more than doubled from 9.4% to 19.7% and at the theoretical loading of 1.7%, it increased from 3.9% to 8.9%.
The next section will investigate the effect of the catalyst silica gel support pre-treatment temperature.

3.11 Effect of the silica gel pre-treatment temperature

Several catalysts with an aluminium theoretical loading of 0.8mmolg^{-1} were prepared with aluminium trichloride as metal precursor, phenol as ligand and 'tp' as preparation method. The K100 silica gel was thermally pre-treated at four different temperatures under air, dried at 200°C in an oven, or calcined at 600°C in a muffle furnace, and at 750 or 900°C in a tubular furnace. The activity of these catalysts were investigated in the alkylation of phenol with isobutene at an amount of 0.5% or 1% by mole.

Figures 3.35 and 3.36 (same as Figures 3.30 on page 144 and 3.33 on page 146, reproduced for reading ease) and Figure 3.37 show the alkylation of phenol with

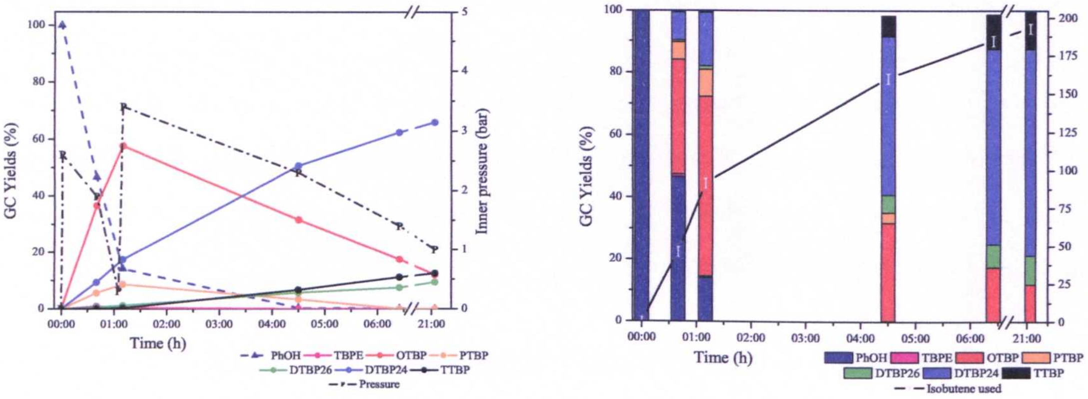


Figure 3.35: Alkylation of phenol with isobutene (1.94eq.) and Al(OPh)$_x$K100(<u>200</u>)(ATC)tp(*0.8*) as catalyst (1%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

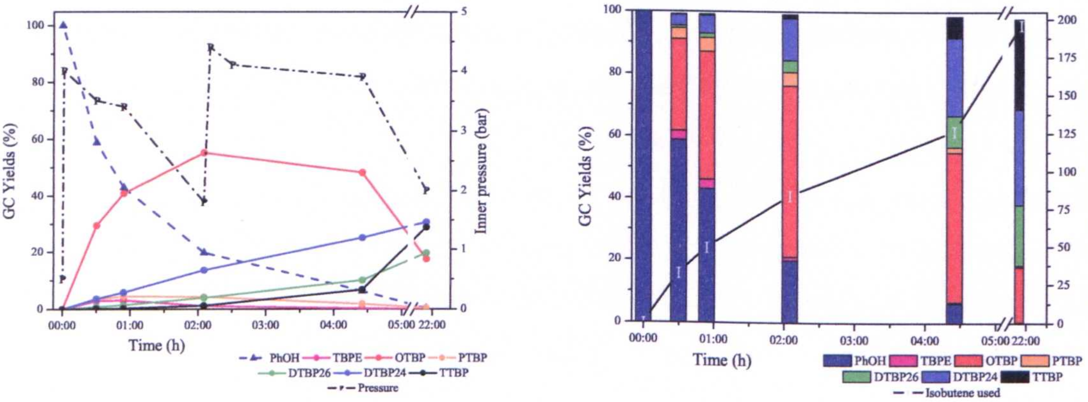


Figure 3.36: Alkylation of phenol with isobutene (1.94eq.) and Al(OPh)$_x$K100(<u>600</u>)(ATC)tp(*0.8*) as catalyst (1%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

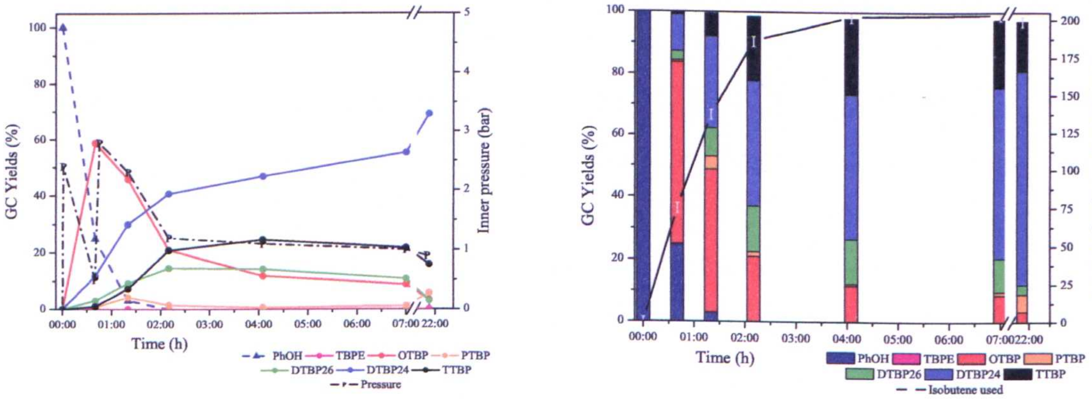


Figure 3.37: Alkylation of phenol with isobutene (1.95eq.) and Al(OPh)$_x$K100(<u>750</u>)(ATC)tp(*0.8*) as catalyst (1%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

isobutene carried out at 100°C with a catalyst amount of 1%, for which the support was pre-treated, respectively, at 200°C, 600°C and 750°C.
The results corresponding to the two first figures were both separately described earlier in this chapter. The reaction carried out with the catalyst, which support was pre-treated at 750°C, exhibited the same general selectivity, OTBP then 2,4-DTBP as major products. Only 0.5% of heavy products were detected and 2.5% of 2,5-DTBP, which shows that the reaction proceeded 'cleanly'. However, the reaction rate was fast; at the reaction time of 2h10, all the phenol was converted as well as nearly all the isobutene as shown by its consumption estimation. This point also corresponded to the maximum yield of 2,6-DTBP (14.6%). After 4 hours, all the isobutene being consumed, the same phenomenon described for the alkylation reaction carried out at 100°C with 1% of Al(OPh)$_x$K100(600)(ATC)tp(*1.7*) (Figure 3.34 on page 146) was observed: 2,6-DTBP and TTBP yields decreased, while PTBP reappeared and 2,4-DTBP yield increased.

Between the three catalyst support pre-treatment temperature, the highest yield of 2,6-DTBP was obtained with the catalyst, which support was pre-treated at 600°C, however, the catalyst, for which the support was pre-treated at 750°C, allowed a better compromise between the 2,6-DTBP yield and the reaction rate.

As discussed in the section 3.8, a low catalyst amount seems to be advantageous to improve the yield of *ortho-* products. To investigate the effects of both parameters together, experiments were carried out with an amount of 0.5% of catalyst, for which the supports were pre-treated at 200 and 750°C (respectively Figures 3.38 and 3.39). A new solid catalyst with a silica support pre-treated at 900°C, Al(OPh)$_x$K100(900)(ATC)tp(*0.8*), was also prepared and tested in the alkylation reaction of phenol with isobutene (Figure 3.40).
Phenol was totally converted in, respectively, 4hours, 1hour and 55min. The reaction profile of the reaction carried out with Al(OPh)$_x$K100(200)(ATC)tp(*0.8*) exhibited a similar general selectivity, the OTBP and the 2,4-DTBP being the major products. Compared to the alkylation reaction carried out with the same catalyst but with an amount of 1% (Figure 3.30 on page 144), the product distribution at a reaction time longer than 20 hours was very similar; however, at a reaction time of 6hours, the reaction using 0.5% of catalyst had not proceeded as far as the reaction using a catalyst amount of 1%.
With the Al(OPh)$_x$K100(750)(ATC)tp(*0.8*) catalyst, the general selectivity to-

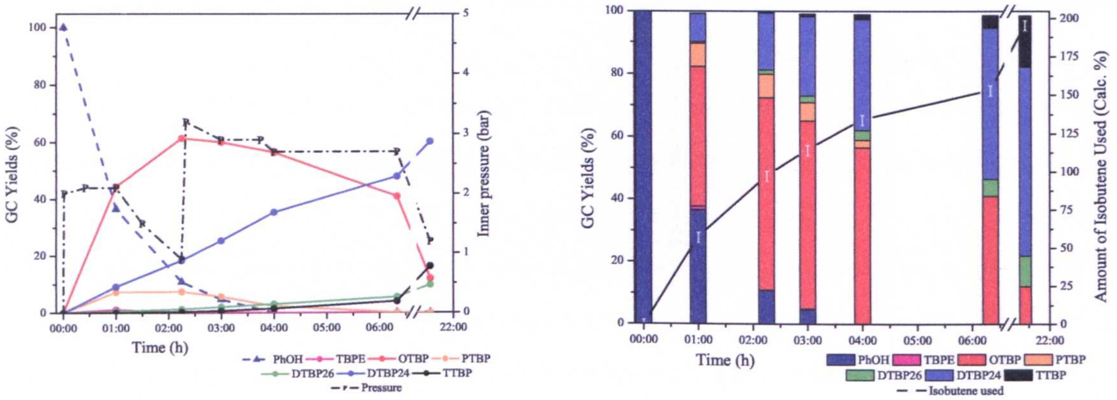


Figure 3.38: Alkylation of phenol with isobutene (1.95eq.) and Al(OPh)$_x$K100(<u>200</u>)(ATC)tp(*0.8*) as catalyst (0.5%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

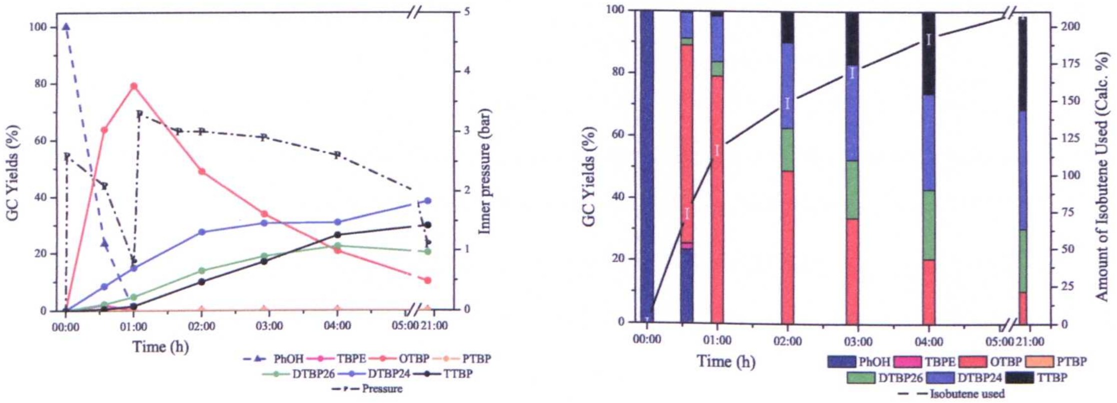


Figure 3.39: Alkylation of phenol with isobutene (1.95eq.) and Al(OPh)$_x$K100(<u>750</u>)(ATC)tp(*0.8*) as catalyst (0.5%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

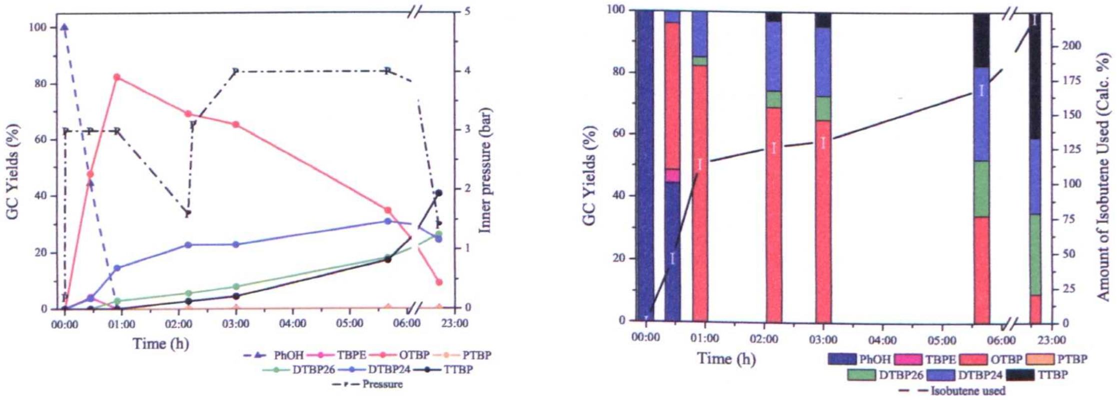


Figure 3.40: Alkylation of phenol with isobutene (1.93eq.) and Al(OPh)$_x$K100(<u>900</u>)(ATC)tp(*0.8*) as catalyst (0.5%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

ward *ortho-* products increased. The maximum yield of OTBP was 79.1%, the highest observed. At this reaction time (1hour), 2,6-DTBP and 2,4-DTBP were the main other products with no PTBP and only low levels of TTBP (1.5%). As the reaction proceeded, the yield of 2,6-DTBP increased up to 22% , and the yield of 2,4-DTBP leveled off to 30.5%. However, high levels of TTBP were recorded (26%).

With the $Al(OPh)_x$K100($\underline{900}$)(ATC)tp(*0.8*) catalyst, the first alkylation step was very fast as all the phenol was converted in less than a hour and the OTBP maximum yield reached its highest so far observed yield, 82%. The second alkylation step however was slower compared to the reaction carried out with the catalyst, for which the support was pre-treated at 750°C, as shown by the decrease in the isobutene consumption rate at the reaction time of 1hour. The maximum yield of 2,6-DTBP (26%, the highest so far) was obtained only at the reaction time of 22h35, but 40.5% of TTBP was also observed.

If reducing the $Al(OPh)_x$K100($\underline{200}$)(ATC)tp(*0.8*) catalyst amount from 1% to 0.5% did not improve the yields of *ortho-* products, the same decrease in the $Al(OPh)_x$K100($\underline{750}$)(ATC)tp(*0.8*) catalyst amount improved the maximum yield of OTBP by 34% (from 58.8% to 79.1%) and the maximum yield of 2,6-DTBP by 34.8% (from 14.6% to 22.4%). Using a pre-treatment temperature of 900°C was however not beneficial, as the yield of the undesired TTBP increased dramatically and the reaction rate was slower than the reaction carried out with the catalyst, for which the support was pre-treated at 750°C.

The fact that the two parameters, the support pre-treatment temperature and the catalyst amount for an aluminium theoretical loading of $0.8 mmolg^{-1}$, did not induce the same effect on the yield, show that they are not independent. 750°C seems the best pre-treatment temperature of the catalyst silica support for the aim of this work.

3.12 K60 silica gel as support

K60 silica gel from Merck was used as an alternative silica support, exhibiting a larger surface area and smaller pore volume than the K100 silica gel (see section 2.3.2.1), for the supported aluminium phenolate. From the studies involving

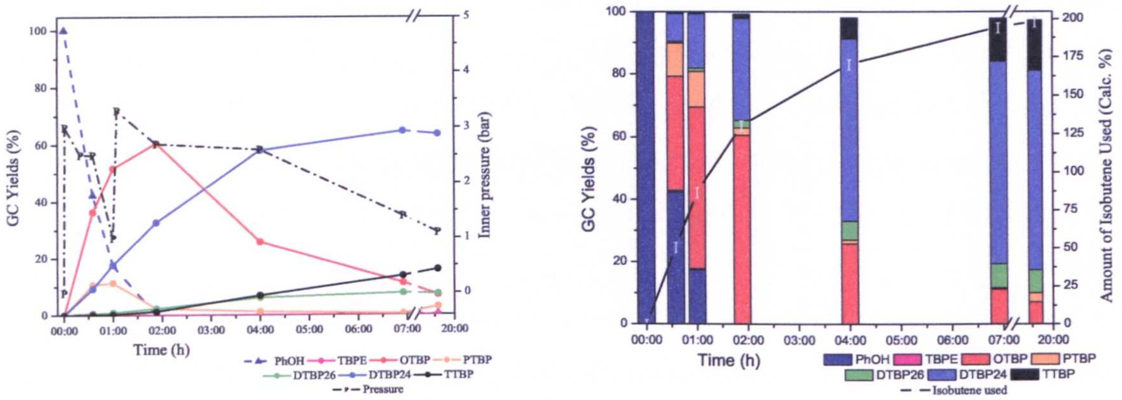


Figure 3.41: Alkylation of phenol with isobutene (1.94eq.) and Al(OPh)$_x$**K60**(200)(ATC)tp(*0.8*) as catalyst (1%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

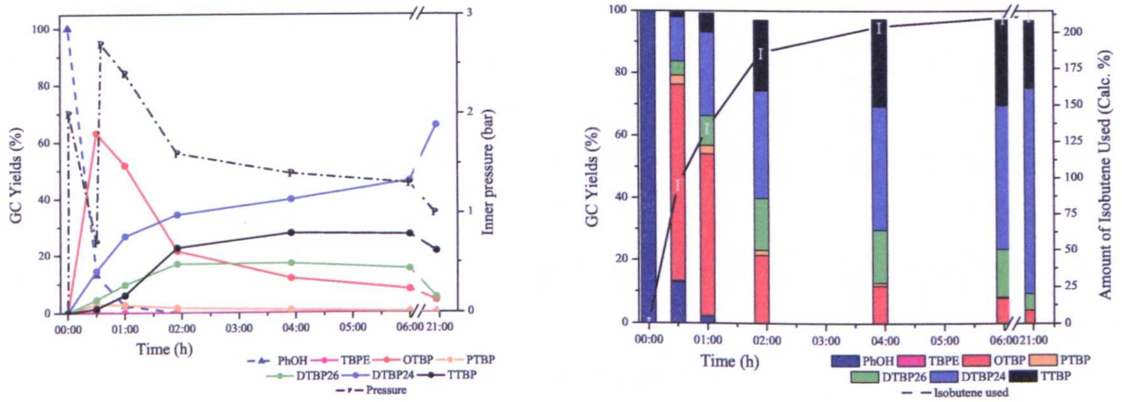


Figure 3.42: Alkylation of phenol with isobutene (1.95eq.) and Al(OPh)$_x$**K60**(750)(ATC)tp(*0.8*) as catalyst (1%) carried out at 100°C: reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

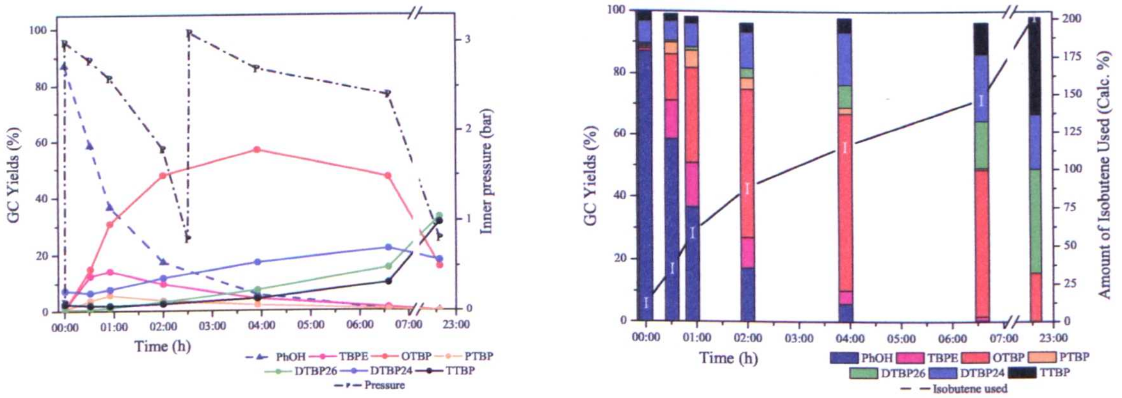


Figure 3.43: Alkylation of phenol with isobutene (1.95eq.) and Al(OPh)$_x$**K60**(750)(ATC)tp(*0.8*) as catalyst (1%) carried out at 70°C: reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

the silica gel K100, an aluminium theoretical loading of 0.8mmolg^{-1} led to the best yields of *ortho*- products. This loading was therefore chosen in the investigation of these catalysts activity. Two Al(OPh)$_x$K60(*xx*)(ATC)tp(*0.8*) materials were prepared, where '*xx*' is the pre-treatment temperature, 200 or 750°C. The reaction profile, the reactor inner pressure and the isobutene consumption estimation are shown, respectively, in Figures 3.41 and 3.42.

The product distribution of the reaction carried out with the catalyst, for which the support was pre-treated at 200°C, was similar to the reaction carried out with the corresponding catalyst on K100 (Figure 3.30 on page 144). All the phenol was converted in about 2hours. The maximum yield of OTBP was around 60% and the yield of 2,4-DTBP at a reaction time longer than 19hours was around 60-65%. The final yield of 2,6-DTBP was 7.4% compared to 9.4%. Heavy products were detected at a level of 1.3%.

The product distribution of the reaction carried out with the catalyst, for which the support was pre-treated at 750°C, was in general similar to the reaction carried out with the corresponding catalyst on K100 (Figure 3.37 on page 148). All the phenol was converted in about 2hours. The maximum yield of OTBP was 63% and the yield of 2,4-DTBP at a reaction time longer than 20hours was around 65.8%. The best yield of 2,6-DTBP was 17%, at the reaction time of 3h55, compared to 14.6%, at the reaction time of 2h10.

The use of the K60 silica gel as an alternative support for the new supported aluminium phenolate catalyst did not allow an improvement of the yields of the *ortho*- products, compared to the corresponding catalysts prepared with the K100 silica gel. As we showed in the reaction temperature study (Section 3.7), the yield of 2,6-DTBP increased when the reaction temperature was decreased from 100°C to 60°C. However, at this temperature, the ether was formed in a large amount.

Alkylation of phenol with isobutene using 1% of the Al(OPh)$_x$**K60**(750)(ATC)tp(*0.8*) material as catalyst was carried out at 70°C (Figure 3.43). Phenol was all converted at a slower rate than for the reaction carried out at 100°C (6hours instead of 2). TBPE was also observed, but at a lower level than for the reaction carried out at 60°C with the catalyst supported on the K100 silica gel (Figure 3.15 on page 134)(maximum yield at 14.1% compared to 34.9%). However, 2,6-DTBP after 23hours of reaction

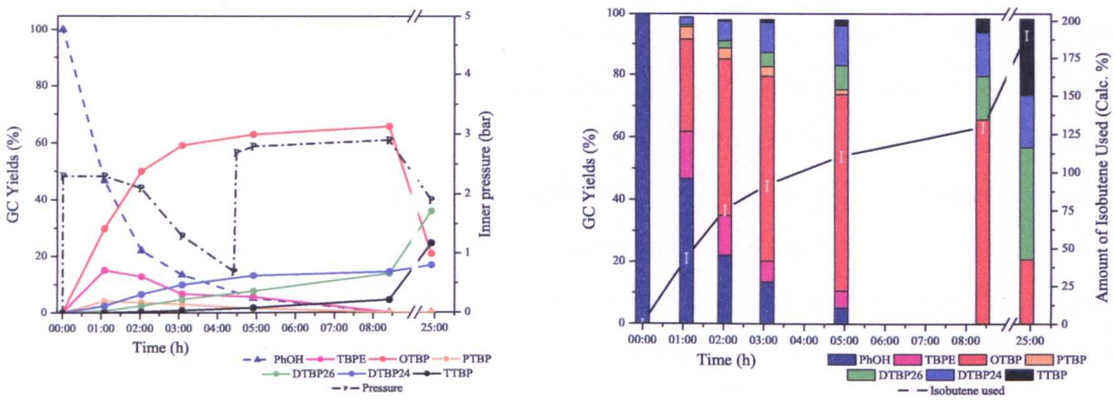


Figure 3.44: Alkylation of phenol with isobutene (1.95eq.) and Al(OPh)$_x$**K100(750)**(ATC)tp(*0.8*) as catalyst (1%) carried out at **70°C**: reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

became the major di*tert*butylphenol with a yield of 33%. The yield of 2,4-DTBP was at that time decreasing, probably contributing to the production of TTBP, which was recorded at high level. Few ethers of mono-*tert*butylphenol and less than 1.5% of heavy products were detected.

K60 silica gel as an alternative support did not improve the yield of 2,6-DTBP compared to the catalyst supported K100 silica gel used in the same reaction condition. However, by lowering the reaction temperature from 100°C to 70°C when using a catalyst based on K60 calcined at 750°C, a dramatic change in the product distribution was observed, as the desired 2,6-DTBP became the major di*tert*butylphenol, which represented a significant development.

3.13 Optimisation toward the synthesis of 2,6-DTBP

The increase of the 2,6-DTBP yield observed by lowering to 70°C the reaction temperature when using the catalyst supported on K60 silica gel, was promising. As this catalyst on K60 silica gel behaved in a similar manner as its K100 equivalent at 100°C, alkylation of phenol with isobutene was carried out at 70°C using Al(OPh)$_x$K100(750)(ATC)tp(*0.8*). The results are shown in the figure 3.44. The conversion of phenol was also slower compared to the reaction carried out at 100°C. TBPE was also recorded at a level of 15.1% at its maximum yield. If the 2,4-DTBP was at first the major di*tert*butylphenol, its yield did level off and the

2,6-DTBP yield ended up to 35.9%. Less TTBP (24.6%) was observed compared to the reaction carried out at 70°C with the catalyst supported on K60 silica gel. Less than 1% of ethers of mono-*tert*butylphenol and only traces (below 0.6%) of heavy products were detected.

The highest yield of 2,6-DTBP observed so far was obtained in this experiment carried out at 70°C with 1% of a catalyst, for which the support was thermally pre-treated at 750°C, and prepared at a theoretical loading of 0.8mmolg^{-1}.

3.14 Discussion on the effects of the parameters

The effects on the alkylation of phenol with isobutene of several parameters were investigated in this chapter. They were described in term of reaction profile, product yield and nature and amount of 'by-products' (called non-plotted products). In this section, for each parameter, selectivity *ortho-* / *para-* for the mono-alkyl and di-alkyl products will be tabulated at a reaction time corresponding to 80% phenol conversion (if a sample corresponding to a phenol conversion around the range 75% to 85% was available), at the maximum yield of OTBP (determined with the available samples), and at the time of the last sample, usually between 20 and 24hours. These results will be analysed and discussed in relation to the nature of the catalyst active species.

The reference catalyst is the $\mathrm{Al(OPh)}_x$K100(200)(ATC)tp(*1.7*). The parameter, which is studied, is indicated in the column entitled "Prmtrs. studied". Its level or value is listed in the next column. Any parameter, which is different from the reference catalyst, is indicated in the column entitled "Other prmtrs.". For each three reaction points, the time at which the sample was taken is given along with either the corresponding phenol conversion and / or the maximum yield of OTBP at that point. Then five other data are listed, the sum of all mono-*tert*butylphenols, with the ratio *ortho-* over *para-tert*butylphenol, the sum of all di*tert*butylphenols, with the ratio 2,6-DTBP over 2,4-DTBP, and the ratio total *ortho-* over total *para-*. This ratio was calculated with the following formula:

$$\frac{(Y_{OTBP} + 2Y_{2,6-DTBP} + Y_{2,4-DTBP} + Y_{2,5-DTBP} + 2Y_{TTBP})}{(Y_{PTBP} + Y_{2,4-DTBP} + Y_{TTBP})} \tag{3.1}$$

Y_{xxxx} standing for yield of the product xxxx.

This ratio illustrates the "power to *ortho-* alkylate" of the catalyst. Indeed, a high yield of 2,6-DTBP will increase this ratio significantly as the 2,6-DTBP contributes twice at the numerator of the ratio. A high yield of 2,4-DTBP will tend to level the ratio to the value 1, as it contributes once on top and on bottom of the ratio. A high yield of TTBP will also increase the ratio, but less significantly than 2,6-DTBP, as it contributes twice at the top of the ratio, but also once at the bottom. However, TTBP will not interfere in the ratio 2,6-DTBP over 2,4-DTBP. Therefore, analysis of these two ratios together will illustrate the "power to *ortho-* alkylate" only to the desired product 2,6-DTBP.

The two first rows of Table 3.3 show the data relating to the homogeneous alkylation of phenol with isobutene. These reactions were carried out to be able to compare the behaviour of the new solid catalyst with the actual commercial homogeneous catalyst. The reaction carried out at atmospheric pressure with the catalyst prepared *in-situ* gave an idea of the rate of the reaction and the selectivity of the catalyst. The second alkylation was much slower compared to the first, as the consumption rate of OTBP was lower than that of phenol. The selectivity of the catalyst was very high towards the *ortho-* products, 373:1 for OTBP:PTBP, and 8.3:1 for 2,6-DTBP:2,4-DTBP. The total *ortho*:*para* ratio leveled to 14:1, showing the goal, which should be at least reached. As known in the literature[38], the use of pressure improves the rate of the reaction and the selectivity. The commercial aluminium triphenolate behaved in a similar way to that prepared *in-situ*, ratio of 456:1 at the maximum OTBP yield, and 20.7:1 for the 2,6-DTBP, however, the total *ortho*:*para* ratio was lower (8.3:1), due to a higher level of TTBP, an unwanted by-product.

The preparation method of the solid catalyst led to different conclusions depending on which aspect is looked at. Regarding the rate of alkylation, the 'tp' method yielded the most active catalyst, the OTBP being consumed quickly and the high total yield of di*tert*butylphenols (77%) being reached after 21h27 while only 51.3% was reached after 31h40 with the catalyst prepared with the 'hf' method. However regarding the *ortho-* products, the 'is' preparation method led to the highest ratio towards *ortho*.

The addition method of the isobutene is also an important parameter (rows 6 to 8). A low concentration of alkene, induced by the gradual addition method, is disadvantageous for the *ortho-* selectivity, with ratio O.:P. of 5.4:1 and ratio 2,6:2,4 of 1:20.4, the lowest of the three alkene addition methods. One explanation could be that the aluminium species are more prone to induce trans-alkylation and isomerisation reactions with a low isobutene concentration. However, the final yield of di*tert*butylphenol products at the reaction time of 22hours is the highest observed in this work.

The 'kinetically controlled addition' led to better ratios. The isobutene was entering the reactor in order to replace the isobutene atmosphere inside the reactor as it was consumed. This was noticed because if the reservoir was disconnected from the reactor at various times of the equivalent addition, the weight of the reservoir was in proportion of the isobutene consumption until the reservoir disconnection. Addition of isobutene by the mean of the pressure pump at the fastest rate available led to a better selectivity towards *ortho-* products. This method led to the highest selectivity towards the *ortho-* products of the three experiments.

When TEAL was used as aluminium precursor for the catalyst preparation, the 'by pump addition' method also led to better *ortho-* selectivity, as at the OTBP maximum yield O.:P. of 7.6:1 compared to 3.5:1 and 2,6:2,4 of 1:14.5 compared to 1:22.5 (row 10 and 9).

So far the catalysts were prepared with the silica support dried at 200°C, and the aluminium species grafted on its surface using aluminium trichloride. The two main aluminium species identified on the surface of the silica supported aluminium chloride are the $ClAl(OSi)_2$ and $Cl_2Al(OSi)$, both either isolated or complexed with silanol groups *via* secondary bonds (Section 2.4.3). These two main species are believed to be converted into the corresponding phenolates during the ligand exchange step into the mono- and the di-phenolate aluminium species.

In order to check the role of any residual chlorine in the bulk of the catalyst, which could come from the aluminium trichloride, a different aluminium precursor, triethyl aluminium, was used. The reaction profile exhibited the same shape as for reaction carried out with catalyst from aluminium trichloride, however, a closer look at the ratios presented in rows 9 and 10, compared to rows 6 and 7, shows that the catalyst prepared with TEAL is in fact less *ortho-* selective at all three reaction times tabulated in the table. TEAL being more reactive than aluminium trichloride, the aluminium might be more strongly bonded to the

	Prmtrs. studied	Values	Other prmtrs.	Fig. (pg.)	At ~ 80% Phenol conversion						At OTBP maximum yield							After 19 hours reaction					
					Conv. (%)	Time	$\sum$ M. (%)	O.:P.	$\sum$ D. (%)	2,6:2,4	Time	Yld. (%)	$\sum$ M. (%)	O.:P.	$\sum$ D. (%)	2,6:2,4	tO.:tP.	Time	$\sum$ M. (%)	O.:P.	$\sum$ D. (%)	2,6:2,4	tO.:tP.
1	Homo. Cat.		atm. pres.	3.2,117	87.0	1h10	66.3	63.3:1	17.4	2.2:1	1h10	65.2		:		:	12.3:1	*7h20*	*48.7*	*373:1*	*44.7*	*8.3:1*	*14.0:1*
2			u. pres.	3.1,116	84.4	1h55	64.6	N:A	16.1	3.3:1	2h55	68.4	68.6	456:1	20.2	3.3:1	16.6:1	19h40	8	N:A	72.75	20.7:1	8.3:1
3	Prep.	*is*		3.3,118	76.6	1h55	60.8	5.4:1	12.2	1:7.3	3h40	60.3	66.3	10:1	26.3	1:6.9	3.1:1	N:A		:		:	:
4	meth.	*ishf*		3.5,120	73.0	3h00	64.7	8.8:1	7.5	1:9	4h00	65.4	68.8	19:1	21.4	1:7.7	4:1	31h40	43.1	6.1:1	51.3	1:6.2	1.9:1
5		*tp*		3.6,121	73.7	1h03	54.7	3.1:1	17.5	1:15.8	2h09	44.4	53.7	4.8:1	35.0	1:18.6	1.9:1	21h27	11.35	1:1.2	76.9	1:18.3	1.2:1
6	Alk.	pump		3.4,119	80.4	1h29	59.9	10.6:1	8.9	1:8.5	2h20	62.8	65.5	23.7:1	20.8	1:7.6	4.1:1	N:A		:		:	:
7	add.	k. c.		3.7,123	79.8	0h37	59.2	3.2:1	18.5	1:15.6	1h05	49.4	61.8	4.0:1	25.6	1:16.4	2.1:1	21h50	16.4	1:1.2	66.3	1:10.3	1.3:1
8	meth.	grd.		3.8,123	N:A			:		:	4h01	47.0	55.7	5.4:1	40.4	1:20.4	1.9:1	22h02	5.6	1.5:1	81.4	1:16.2	1.3:1
9	Al	TEAL	k. c.	3.9,127	84.2	0h30	64.7	3:1	16.3	1:22.2	0h55	51.7	66.4	3.5:1	22.7	1:22.5	2.1:1	21h20	10.6	1.3:1	76.9	1:9.2	1.4:1
10	Prcrsr.		pump	3.10,128	79.5	1h25	55.2	4.9:1	10	1:15.8	2h03	52.8	59.8	7.6:1	20.4	1:14.5	2.9:1	N:A		:		:	:
11		ClAlOPh		3.11,129	79.8	1h00	57.6	1.9:1	19.6	1:25.9	1h00	37.8		:		:	:	19h50	11.1	1.2:1	77.7	1:26.9	1.2:1
12		Al(OPh)$_3$	0.8mmolg^{-1}	3.12,130	N:A			:		:	0h32	57.0	72.6	3.7:1	26.3	1:37.0	2:1	19h45	13.9	1:1.2	76.9	1:18.7	1.2:1
13		(reuse)		3.13,131	86.2	0h40	54.1	2.4:1	27.1	1:23.3	2h10	54.6	68.33	4.0:1	28.1	1:21.2	2.1:1	24h10	10.6	10.7:1	73.1	1:9.7	1.5:1
14	Temp.	60°C	ishf	3.15,134	N:A			:		:	22h09	56.7	57.9	49.2:1	9.3	1:5.3	7.4:1	22h09		:		:	:
15		100°C		3.16,134	73.0	3h00	64.7	8.8:1	7.5	1:9	4h00	65.4	68.8	19:1	21.4	1:7.7	4:1	31h40	43.1	6.1:1	51.3	1:6.2	1.9:1
16		60°C	TEAL	3.17,136	83.8	1h28	34.5	5.8:1	6.9	1:47.1	6h00	43.6	46.4	15.7:1	29.0	1:24	2.4:1	N:A		:		:	:
17		100°C	pump	3.18,136	79.5	1h25	55.2	4.9:1	10	1:15.8	2h03	52.8	59.8	7.6:1	20.4	1:14.5	2.9:1	N:A		:		:	:
18		140°C		3.19,136	83.3	1h10	62.2	2.9:1	19.4	1:15.7	1h27	47.9	61.1	3.6:1	31.0	1:15.7	1.9:1	N:A		:		:	:
19		100→60°C		3.20,137	75.6	1h03	52.0	3:1	13.3	1:22.5	1h36	44.7	54.4	4.6:1	22.4	1:22.8	2.2:1	N:A		:		:	:

'N:A': non-applicable or non-available. 'Prmtrs.': Parameters. 'Yld.': Yield. 'O.:P.': ratio *ortho* over *para*. '2,6:2,4': ratio 2,6-DTBP over 2,4-DTBP. 'tO.:tP.': ratio total *ortho* over total *para*. 'Homo. cat.': Homogeneous catalysis. 'atm. pres.': atmospheric pressure. 'u. pres.': under pressure. 'Prep. meth.': Preparation method. 'Alk. add. meth.': Alkene addition method. 'Al Prcrsr.': Aluminium precursor. 'Temp.': Temperature.

Table 3.3: Alkylation of phenol with isobutene: effects of different parameters. Continue to table 3.4.

					At ~ 80% Phenol conversion						At OTBP maximum yield							After 19 hours reaction					
	Prmtrs. studied	Values	Other prmtrs.	Fig. (pg.)	Conv. (%)	Time	$\sum$ M. (%)	O.:P.	$\sum$ D. (%)	2,6:2,4	Time	Yld. (%)	$\sum$ M. (%)	O.:P.	$\sum$ D. (%)	2,6:2,4	tO.:tP.	Time	$\sum$ M. (%)	O.:P.	$\sum$ D. (%)	2,6:2,4	tO.:tP.
20	Cat.	0.25%		3.21,138	N:A			:		:	21h30	59.4	68.8	6.3:1	22.9	1:10.4	2.8:1	47h05	40.4	10.9:1	55.6	1:14.5	1.8:1
21	amount	1%		3.22,138	81.7	2h00	60.8	3.0:1	18.5	1:18.4	3h03	48.6	62.6	3.5:1	20.1	1:20.0	2.1:1	23h10	13.9	2.8:1	72.9	1:13.6	1.3:1
22		2%		3.23,138	75.3	2h10	53.0	1.6:1	17.3	1:31.5	3h00	32.8	47.3	2.3:1	38.0	1:32.0	1.4:1	25h33	14.4	1:1.8	70.3	1:32.2	1.1:1
23		5%		3.24,139	76.8	0h50	41.6	1:1.15	32.0	1:71.0	0h50	19.4		:		:	1:1	22h00	17.8	1:18.8	64.5	1:142	1:1.1
24	Al.	Al(OPh)$_x$		3.25,141	79.8	0h37	59.2	3.2:1	18.5	1:15.6	1h05	49.4	61.8	4.0:1	25.6	1:16.4	2.1:1	21h50	16.4	1:1.2	66.3	1:10.3	1.3:1
25	ligand			3.26,141	N:A			:		:	0h00	100		:		:	:	22h58	16.1	11.0:1	69.8	1:5.2	1.7:1
26		Al(OTBP)$_x$	600°Ccal.	3.27,141	78.1	4h00	50.1	3.6:1	23.4	1:13.7	9h30	44.5	49.3	9.3:1	36.8	1:7.7	2.3:1	20h00	42.6	12.2:1	47.0	1:6.3	2.1:1
27				3.28,142	N:A			:		:	0h00	100		:		:	:	21h55	17.8	12.7:1	65.1	1:6.7	1.7:1
28	Al.	0.4mmolg^{-1}		3.29,144	83.9	1h07	43.8	40.7:1	36.3	1:9.2	1h07	42.8		:		:	2.4:1	20h17	13.6	8.3:1	70.7	1:7.0	1.6:1
29	Th. ldg.	0.8mmolg^{-1}		3.30,144	85.9	1h10	66.3	6.7:1	18.7	1:14.9	1h10	57.6		:		:	3.0:1	21h05	12.0	1:0	75.4	1:7.0	1.6:1
30		1.7mmolg^{-1}		3.31,144	73.7	1h03	54.7	3.1:1	17.5	1:15.8	2h09	44.4	53.7	4.8:1	35.0	1:18.6	1.9:1	21h27	11.35	1:1.2	76.9	1:18.3	1.2:1
31		0.4mmolg^{-1}	600°Ccal.	3.32,146	N:A			:		:	4h45	52.0	52.6	75.6:1	29.5	1:2.7	3.7:1	21h45	30.3	N:A	48.8	1:2.0	2.6:1
32		0.8mmolg^{-1}		3.33,146	80.3	2h05	59.5	12.9:1	17.7	1:3.4	2h05	55.2		:		:	4.2:1	21h50	18.1	38:1	51.9	1:1.6	2.5:1
33		1.7mmolg^{-1}		3.34,146	85.6	0h30	66.2	11.3:1	17.1	1:4.7	0h30	60.8	66.2	11.3:1	17.1	1:4.7	4.1:1	22h10	11.8	3.1:1	64.9	1:4.7	1.7:1
34	K100				see row 29 and 32, for silica pre-treatment temperature 200 and 600°C																		
35	pre-t.	750°C	0.8mmolg^{-1}	3.37,148	75.2	0h40	59.4	87.7:1	14.8	1:3.9	0h40	58.8		:		:	5.9:1	21h50	9.1	1:1.7	74.5	1:22.7	1.2:1
36	temp.	200°C	0.5%	3.38,150	N:A			:		:	2h15	61.4	68.9	8.2:1	19.8	1:14.0	3.2:1	21h25	12.05	1:0	71.3	1:6.2	1.6:1
37		750°C	0.8mmolg^{-1}	3.39,150	76.6	0h34	63.8	1:0	10.5	1:3.9	1h00	79.1	79.1	1:0	19.4	1:3.2	6.5:1	20h50	10.11	1:0	59.6	1:1.9	2.2:1
38		900°C		3.40,150	N:A			:		:	0h55	82.4	82.4	1:0	17.6	1:4.9	7.0:1	22h36	9.2	1:0	50.3	1.1:1	2.6:1
39	Support	K60	0.8mmolg^{-1}	3.41,152	82.6	1h00	63.1	4.5:1	18.7	1:18.4	1h53	60.5	62.9	25.7:1	35.2	1:13.9	2.8:1	19h35	10.0	2.4:1	72.7	1:8.6	1.4:1
40			750°Ccal.	3.42,152	N:A			:		:	0h30	63.1	66.1	21.5:1	19.1	1:3.2	4.8:1	20h55	4.3	1:0	73.2	1:12.6	1.4:1
41		R. 70°C	(reuse)	3.43,152	82.7	2h00	51.6	12.7:1	15.2	1:3.7	3h55	56.7	58.8	27.1:1	24.8	1:2.3	4.1:1	22h35	15.7	1:0	51.9	1.8:1	3.3:1
42	0.8mmolg^{-1}, 750°Ccal., 70°C			3.44,154	77.9	2h02	53.7	13.7:1	9.0	1:2.7	8h25	65.6	65.6	1:0	28.2	1:1	6.2:1	24h55	20.8	1:0	53.1	2.1:1	3.8:1

'N:A': non-applicable or non-available. 'Prmtrs.': Parameters. 'Yld.': Yield. 'O.:P.': ratio *ortho* over *para*. '2,6:2,4': ratio 2,6-DTBP over 2,4-DTBP. 'tO.:tP.': ratio total *ortho* over total *para*. 'Cat. amount': Catalyst amount. 'Al.': Aluminium. 'Al. Th. ldg.': Aluminium theoretical loading. 'K100 pre-t. Temp.': K100 Pre-treatment Temperature.

Table 3.4: Alkylation of phenol with isobutene: effects of different parameters.Continued from table 3.3.

surface with TEAL than with aluminium trichloride, leading to more mono- phenolate aluminium species. The MAS-NMR showed that the coordination number of the aluminium on the surface of the catalyst prepared from TEAL was the same as for the catalyst prepared from aluminium trichloride, but with a higher relative abundance of the species with a coordination number of 4 compared to species with coordination number of 5. This suggests that using TEAL increased the mono- phenolate species concentration on the catalyst surface. Therefore, from the ratios tabulated, the mono- phenolate aluminium species seems less *ortho*-selective in the alkylation of phenol with isobutene. For example, at the OTBP maximum yield, the O.:P. ratio was lower than 8:1 for the catalyst prepared with TEAL compared to above 10:1 for catalyst prepared from aluminium trichloride. The same trend is observed for the 2,6:2,4 ratio. This observation encouraged us in the building of an aluminium species, which exhibits a geometry similar to the homogeneous catalyst.

The use of $ClAl(OPh)_2$ was to try to increase the number of aluminium sites on the silica surface, exhibiting a diphenolate environment, in order to reproduce as close as possible the geometry of the homogeneous catalyst. The same goal was targeted when grafting the commercial aluminium triphenolate on the surface. The latter exhibited aluminium coordination numbers of 5 and 6 only (MAS NMR study section 2.4.7.3), which shows that more phenolate ligands are present around the aluminium. However, the selectivity observed when using these materials was either worse or similar compared to catalysts prepared with aluminium trichloride.

From the mechanisms proposed for the homogeneous alkylation with aluminium triphenolate, the starting material or the corresponding ether has to complex the aluminium and then either react with the alkene or undergo a transfer of the alkyl group from the ether to another phenolate ligand. On the silica surface, if the aluminium is built from aluminium triphenolate, steric hindrance forbids the bulky *tert*butyl group to react in the *ortho-* position. The total *ortho*:*para* ratio for the solid catalyst prepared from aluminium triphenolate (row 12) is much lower than the ratio obtained in the reaction using homogeneously the aluminium triphenolate (8.3:1, row 2), hence the presence of the silica surface affects the catalytic centre, probably by steric hindrance and aluminium geometry modification.

The reaction temperature affects the product distribution of the alkylation using the new solid catalyst in the same way as for the homogeneous catalyst. At low temperature (60°C, row 14), a high level of ether is observed, and the alkylation rate is reduced. By doing so, the selectivity toward *ortho-* products improved dramatically, O.:P. at the OTBP maximum yield was up to 49.2:1, compared to 19:1 when the reaction was carried out at 100°C. The same trend is observed with the catalyst prepared from TEAL, even though the ratio value is lower as already discussed earlier. As shown in the stability studies (Section 3.6.5), 2,6-DTBP is less stable than 2,4-DTBP in presence of catalyst, therefore reducing the temperature decreased the reactivity of the products towards the catalyst leading to less trans-alkylation or isomerisation reactions.

Catalyst amount played an important role in the improvement of the selectivity towards *ortho-* products. With 5% of catalyst, the highest ratios towards *para-* products were observed, O.:P. of 1:18.8 and 2,6:2,4 of 1:142. Decreasing the catalyst amount down to 0.25% showed a reversal of the O.:P. ratio, 10.9:1 and a dramatic improvement of the 2,6:2,4 ratio, 1:10.4. This could also be explained by an 'activity' reduction when decreasing the amount of active sites by reducing the catalyst amount.

The aluminium theoretical loading illustrates another important parameter towards an efficient '*ortho*' catalyst. Two types of catalysts, with silica support thermally pre-heated at 200 and 600°C, were used for this study. For each catalyst type, the trend was the same, decreasing the aluminium theoretical loading improved both ratios towards the *ortho-* products. For example, with the catalyst dried at 200°C, the O.:P. ratio increased from 3.1:1 to 40.7:1 at 80% phenol conversion, and from 1:1.2 to 8.3:1 at the reaction time above 19hours, when the loading was decreased from 1.7 to 0.4mmolg^{-1}. The same trend was observed with the catalyst pre-treated at 600°C. The best 2,6:2,4 ratio value was obtained with the catalyst pre-treated at 600°C and with a theoretical loading of 0.8mmolg^{-1} (1:1.6). However, the same support pre-treatment temperature with a theoretical loading of 0.4mmolg^{-1} led to a ratio of 1:2.0, slightly lower indicating that in proportion more 2,4-DTBP was produced, but a ratio tO.:tP. of 2.6:1, slightly higher showing that less of the undesired TTBP was produced. From an industrial point-of-view, this product profile with less TTBP would be more interesting as TTBP is a waste (unless trans- or de-alkylation are attempted) while 2,4-DTBP is a marketable product.

The aluminium theoretical loading influences the saturation of the silica support surface by the aluminium species. Lowering the loading induced a dispersion of the aluminium over the support surface. Hence, the aluminium species are more isolated from each other, but also more silica sites is exposed to the reaction mixture. The dispersion of the aluminium species has a beneficial effect on the *ortho-* selectivity. One possible explanation for the observation of this effect is that once the product is formed it must desorb from catalytic species to the reaction mixture and "travel" back to another catalyst active species. However at low loading, more silica surface is exposed, hence the surface polarity is closer to the initial silica surface polarity, the two *tert*-butyl groups of the 2,6-DTBP being close to the hydroxyl group, they shield it and a more hydrocarbon behaviour is induced in the 2,6-DTBP than 2,4-DTBP. Therefore the 2,6-DTBP would be less prone to return to the silica surface and being subject to further reactions than the 2,4-DTBP.

The silica support thermal pre-treatment temperature also played an important role towards the selectivity, affecting the nature of the aluminium species on the catalyst surface. As described in section 2.3, at low pre-treatment temperature, the surface exhibits a high concentration of silanol groups. Increasing the pre-treatment temperature of the silica first dries the surface of the weakly physisorbed water, then the more strongly physisorbed water is eliminated and at the same time condensation of the silanol groups into siloxane groups occurs. The more the temperature is increased, the more the silanol groups become isolated. At the same time, the increase of the pre-treatment temperature induces a support structural change (as described in the chapter 2). Although the type of pores remains the same, the pore volume distribution is shifted towards lower diameters and the specific surface area is reduced when the pre-treatment temperature is increased.

From the ratios tabulated in rows 34 to 35, the increase of the pre-treatment temperature improved all ratios towards *ortho-* selectivity. The isolation of the aluminium species induced by this thermal pre-treatment is, as for the loading decrease, beneficial. When decreasing at the same time the amount of catalyst (rows 36 to 38), the ratios were further improved and 2,6-DTBP yield was slightly higher than the one of 2,4-DTBP (row 38, 2,6:2,4 of 1.1:1). With 0.5% of catalyst treated at 750 or 900°C, no PTBP was observed and the highest yield of

OTBP was recorded (82.4%). With more isolated active species at the surface of the catalyst support, 2,6-DTBP is less prone to return to the silica surface and being subject to further reactions than 2,4-DTBP. This could also explain why the yield of 2,4-DTBP leveled off and the yield of TTBP increased significantly at the end of the reaction (for example rows 37 and 38, Figures 3.39 and 3.40), as 2,4-DTBP returned to the catalyst surface and was re-alkylated in the second *ortho-* position.

Using silica gel K60 did not change the general behaviour of the catalyst compared to silica gel K100 (row 39 and 29, row 40 and 37). However, following the idea to reduce the 'activity' of the catalyst by either dispersing the aluminium on the surface (by lowering the loading or increasing the thermal pre-treatment temperature) or by reducing the reaction temperature and the catalyst amount, the reaction profile of the experiment tabulated in row 41 (K60(750), 0.8mmolg^{-1}, 1% of catalyst at 70°C) exhibited the highest ratios level towards the *ortho-* products, the 2,6-DTBP being the major di*tert*butylphenol. This was confirmed with the catalyst supported on silica gel K100 (row42). No PTBP was detected at the reaction time corresponding to the maximum OTBP yield, the 2,6:2,4 ratio up to 2.1:1 and the highest tO.:tP. at the reaction time longer than 19hours of 3.8:1, showing that the yield of TTBP was lower than the yield of 2,6-DTBP.

The different mechanisms proposed for the alkylation of phenol with alkene are discussed in chapter 1. Kozlikovskii et al. suggested the following mechanism for the first introduction of an alkyl group[66]: formation of the acidic species $HAl(OPh)_4$ by reaction between phenol and aluminium triphenolate, then complexation of an alkene molecule. Then, either the complex dissociates into an alkyl ion R^+ and $Al(OPh)_4^-$ leading to *ortho-*, *para-* and ether mono- alkyl derivatives, or the complex does not dissociate and leads to the reversible formation of ether or to the non-reversible formation of mono-*ortho-* derivative. The authors however did not propose a mechanism for the formation of the 2,6-dialkyl derivatives although they did detect it.

Knapp et al. also proposed the ether as a necessary intermediate for the first alkyl group introduction in the phenolic ring, when aluminium triphenolate was used as catalyst[46]. They, however, were never able to detect any ether of mono-alkyl-phenol.

In some of the alkylation reactions of phenol with isobutene using the new silica supported aluminium phenolate material as catalyst, *tert*butyl-(2-*tert*butylphenyl)ether and *tert*butyl-(4-*tert*butylphenyl)ether was identified by GC-MS. The relative yields of *tert*butyl-(2-*tert*butylphenyl)ether and *tert*butyl-(4-*tert*butylphenyl)ether were not always the same. This did not follow the trend of OTBP maximum yield improvement or 2,6-DTBP yield improvement, nor the relative yield of OTBP versus PTBP. They were however at higher levels when the reaction temperature was low, as for the *tert*butylphenylether. The mechanism involved in the alkylation of phenol with isobutene using the silica supported aluminium phenolate seems to be more complex than for the homogeneous reaction. The next chapter will report alkylation reactions of other systems and the chapter 5 will discuss aspects of the development of the catalyst towards industrial use, such as the reproducibility and the reusability. These alkylation reactions will bring more results, which will help us to discuss further the mechanism.

3.15 Conclusions

The silica gel supported aluminium phenolate was successfully applied to the phenol isobutene system. The catalyst was active in the di-alkylation reaction with a complete conversion of the starting material. The first *tert*butyl group was introduced in the *ortho-* position on the phenolic ring, when the second *tert*butyl group could be introduced mainly in *para-* or in the second *ortho-* position. Various mono- and di*tert*butylphenols are accessible during the reaction and reaction conditions as well as design parameters of the solid catalyst may allow us to tune the yield of one particular product.

Reaction temperature and catalyst amount were found to be critical parameters in the tuning of the selectivity of the reaction systems. High temperature and high catalyst amount induced more *para-* substitution of the phenolic ring allowing access to mono-*paratert*butylphenol (PTBP) and very high yield of 2,4-di*tert*-butylphenol (2,4-DTBP). Low temperature induced more *tert*butylphenyl ether (TBPE) formation at the beginning of the reaction, but this was then consumed; it also induced a better *ortho-* selectivity towards the 2,6-di*tert*butylphenol (2,6-DTBP), which is an important industrial *tert*butylphenol and precursor of many useful chemicals.

The tuning of various preparation parameters of the catalysts also led to improvement towards the preparation of this important industrial chemical. Aluminium loading of the support and thermal pre-treatment temperature of the silica gel support are important variables; high pre-treatment temperature of 750°C and an aluminium loading of 0.8mmolg^{-1} proved to be very efficient towards the di*ortho*-selectivity of the catalyst. We can expect further selectivity improvements when these are optimised.

Various other parameters were studied, such as aluminium precursor, aluminium ligand and preparation method as well as the isobutene addition method. Aluminium trichloride proved to be an efficient precursor for the grafting of the aluminium on the silica surface. The ligand was found to be better chosen as the starting material. The catalyst preparation method is also relevant to the tuning of the catalyst properties. When prepared *in-situ* (is or ishf), the selectivity was improved towards the di*ortho*- direction, however, preparation in a toluene-phenol solution (tp) led to improved rate of alkylation, but less di*ortho*-directing. Optimal alkene addition rate seemed to improve the selectivity towards *ortho*- product, with both aluminium trichloride or triethyl aluminium (TEAL), the 'by pump addition' method should be chosen.

Insight into the reaction mechanism was proposed, however it seems that the mechanism is more complex or the kinetics are different compared to the homogeneous equivalent. Ethers of mono-*tert*butylphenols were detected in most of the experiments when none were reported for the homogeneous catalysed reaction. The next chapters will discuss other alkylation systems and various parameters, such as reusability. A better mechanistic insight will then be reported.

Chapter 4

Other alkylation systems based on silica supported aluminium phenolate

4.1 Introduction

The new solid material, the Kieselguhr silica gel supported aluminium phenolate is active in the alkylation of phenol with isobutene. The preparation procedure was investigated (Chapter 3) to improve the yield of the desired di*ortho*- product, and 2,6-di*tert*butylphenol.

Applications to other phenols – alkene alkylation systems are reported in this chapter. Other alkenes, such as 1-octene, propene and cyclohexene were used to alkylate phenol. Cresols were alkylated with isobutene propene and cyclohexene.

4.2 Alkylation of phenol

4.2.1 With 1-octene

Alkylation of phenol with 1-octene was carried out with 1% of the catalyst $Al(OPh)_xK100(200)(ATC)tp(\mathit{1.7})$. At 100°C and 130°C, the reaction was very slow. When the reaction temperature was increased to 160°C, products were detected almost immediately. However, the reaction proceeded at a much slower rate than for the alkylation of phenol with isobutene.

Only 32.5% of phenol was converted into products over 8hours, and 50% over 18hours. Four sets of peaks and the peak corresponding to phenol were observed on the GC traces. The first was assigned to linear positional isomers of 1-octene. Their amounts were not estimated. However, their existence showed that the catalyst with the surface pre-treated at 200°C exhibits enough acidity to induce the double bond migration.

The second set of peaks was assigned to octyl-phenyl ether. The set was formed by three peaks, the integration value of the first one being 10% the integration of the second, itself being 10% the integration of the third peak. This peak was assigned by GC-MS to (2-octyl)-phenyl ether, the previous one to (3-octyl)-phenyl ether, and the smallest peak to (4-octyl)-phenyl ether.

The third set of peaks were assigned to mono-octylphenol. The biggest peak was assigned to (2-octyl)-phenol. The next biggest peak, with an integration of 8% the integration of the (2-octyl)-phenol peak, was assigned to (3-octyl)-phenol. The two other peak integrations were at least a further 50% lower. However, there mass spectra were similar to the mass spectra of the other two peaks. Hence, two of the peaks were corresponding to the *ortho*-(2-octyl) and the *ortho*-(3-octyl)-phenols, and the two other to there *para*- isomers. Darby studied the alkylation of phenol with 1-octene using Fuller's earth as catalyst and synthetised and analysed by MS all the isomers of octyl-phenol[169]. However, the mass spectra we obtained by GC-MS did not allow us an unambiguous identification of the isomers we detected. Nevertheless, the MS spectra gave the chain position where the octyl group was attached to the phenolic ring.

The fourth set of peaks were assigned by GC-MS to di-octyl products, either ether of mono-octyl-phenol or di-octyl-phenol. As positional isomers of 1-octene were detected, positional octyl-phenyl ethers and positional octyl-phenols mixture of various compounds, exhibiting phenolic ring positional isomers and octyl chains position isomers, are expected and no exact identifications of these products were attempted. The integration of their peaks contributed to only 0.5% of the total products.

In the GC sample taken at a reaction time of 4hours, three main products were detected, the starting material, phenol (51%), the (2-octyl)-phenyl ether (12%) and a (2-octyl)-phenol (31%). To identify in which position the alkyl group was attached to the phenolic ring, ^{1}H-^{1}H COSY NMR spectrum of the sample was recorded. Figure 4.1 reproduces the 1D ^{1}H NMR spectrum and Figure 4.2 reproduces the COSY spectrum. Both figures focus on the aromatic region of the ^{1}H NMR chemical shifts range. From the COSY experiment, three sets of peaks are identified, marked respectively '$*$', '$\sim$' and '@' corresponding to three compounds. The peak integrations measured on the 1D NMR experiment are given in an arbitrary unit.

The three main products present in the samples are phenol, for which we could expect three peaks (H_{ortho}, H_{para}, H_{meta}), octyl-phenyl ether, for which we could also expect three peaks, and the octyl-phenol. Regarding this product, three isomers exist, the *ortho*- octyl-phenol, for which four peaks are expected, the *meta*- octyl-phenol, for which four peaks are expected, and the *para*- octyl-phenol, for which two peaks are expected.

The three peaks associated with '$*$' are a doublet at 6.76ppm with a coupling constant of 7.7Hz and an integration of 23, a doublet of doublet at 7.18ppm with coupling constants of 7.5 and 8.4Hz with an integration of 23 and one unresolved

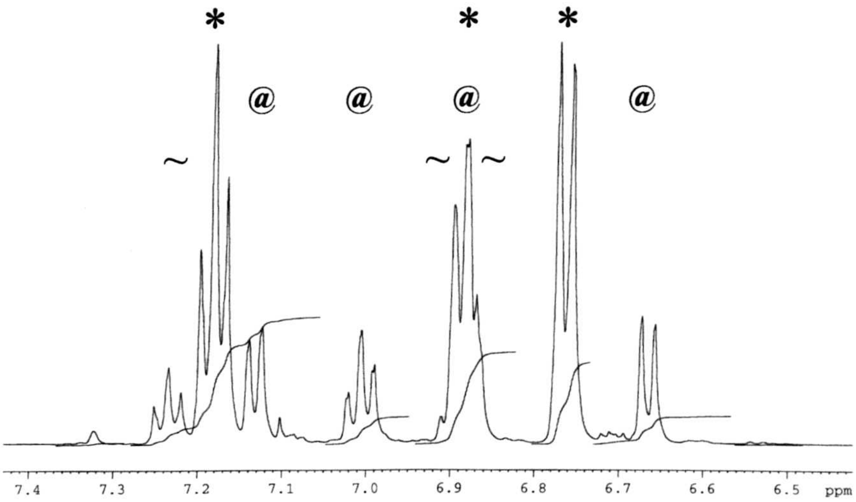


Figure 4.1: 1D ^{1}H NMR spectrum of the aromatic chemical shift region from the GC sample taken at a reaction time of 4hours.

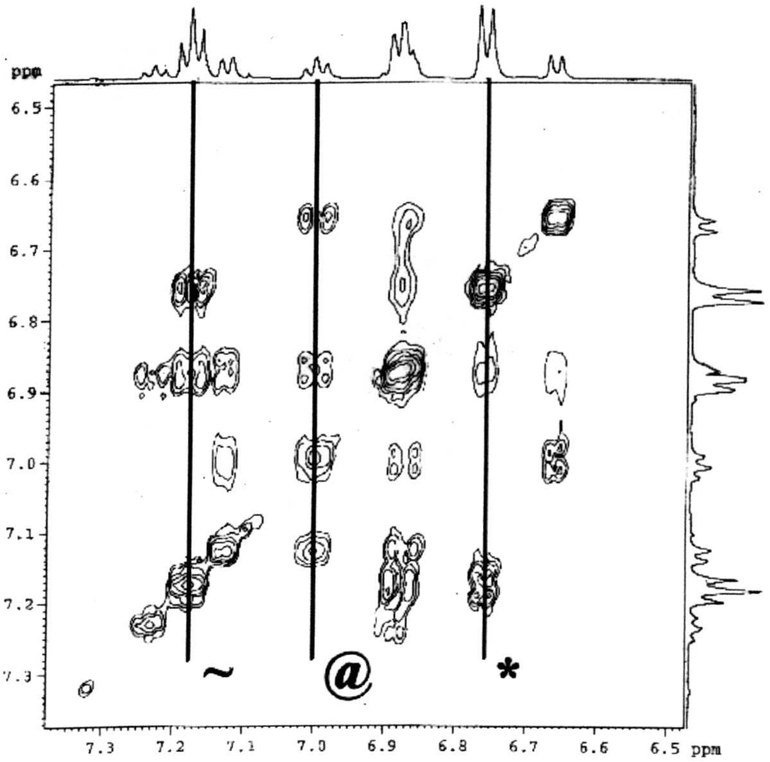


Figure 4.2: ^{1}H-^{1}H COSY spectrum of the aromatic chemical shift region from the GC sample taken at a reaction time of 4hours.

multiplet inside the undefined peak between 6.85 and 6.95ppm (called throughout the following discussion 'the multiplet'), the whole multiplet integrating at 26. The peaks associated with '$\sim$' are a doublet of doublet at 7.23ppm with coupling constants of 8.7 and 7.2Hz with an integration of 5, and one inside the undefined peak previously mentioned participating to the global integration of 26.

The peaks associated with '@' are a doublet of doublets at 6.66ppm with one measurable coupling constant of 7.9Hz and an integration of 7, a doublet of doublet of doublets at 7.00ppm with coupling constants of 7.4, 7.9 and 1.5Hz and an integration of 7, a doublet of doublet at 7.13ppm with one measurable coupling constant of 7.6Hz and an integration of 7, and one peak inside the undefined peak previously mentioned participating to the global integration of 26.

The multiplet between 6.85 and 6.95ppm is an overlap of at least three peaks, (as we do not know yet if two peaks of one of the three compounds are not overlapping with very close chemical shifts), one from each compound. The compound '$*$' has three distinct peaks, two peaks integrating at 23 and one inside the multiplet which integration is 26, hence this compound is not the *para*-octyl phenol. If the two peaks integrating at 23 belong to one hydrogen each, then the third peak contributing to the multiplet must be belonging to at least 2 hydrogens, as phenol, octyl-phenyl ether and the *ortho-* and the *meta*-octyl phenol exhibit at least four hydrogens. Hence, the integration of the peak belonging to the compound '$*$' contributing to the multiplet has to be 46 (2×23), which is impossible. Therefore, the peaks at 7.18 and 6.76ppm of the compound '$*$', both integrating at 23, must correspond to two hydrogens for each peak. Therefore the compound '$*$' corresponds to either the phenol or the ether, and the integration of the peak contributing to the multiplet is 11.5 (23/2).

The integration difference 14.5 ($26 - 11.5$) corresponds to contribution of peaks from compound '@' and '$\sim$'. Compound '@' exhibits three peaks integrating at 7 and one inside the multiplet. These three peaks must correspond to one hydrogen each, otherwise the phenolic ring would have at least six hydrogen atoms, which is impossible. The peak contributing to the multiplet therefore has an integration of 7 or 14, if it corresponds to two hydrogens. In the latter case, the contribution to the multiplet of the compound '$\sim$' would be of 0.5, which would imply that the peak at 7.23ppm belonging to the same compound would correspond to 10 aromatic hydrogens. This is also impossible.

The multiplet between 6.85ppm and 6.95ppm is therefore formed by the signal of one hydrogen of the compound '$*$' (integration of 11.5), one hydrogen of the compound '@' (integration of 7) and, hence peaks of the compound '$\sim$' with an integration of 7.5.
The compound '$\sim$' has a peak at 7.23ppm with an integration of 5 and peaks in the multiplet with an integration of 7.5. The only possible combination is that the peak at 7.23ppm corresponds to two hydrogens and the peaks in the multiplet to three hydrogens.

The three peaks above 7.05ppm are well separated and, from the COSY experiment, each peak belongs to a different compound. The integrations of each peak being now determined, 2H from the peak at 7.23ppm, 2H for the peak at 7.18ppm and 1H for the peak at 7.13, their relative ratios compared to the relative GC yields between these products (GC integration ratio octylphenol:ether 2.54 and PhOH:octylphenol 1.61, NMR integration ratio octylphenol:ether 2.8 and PhOH:octylphenol 1.64) allow the association of '$*$' with phenol, '@' with the octyl-phenol and '$\sim$' with the octyl-phenyl ether.
The compound '$\sim$' is the octyl-phenyl ether, and two coupling peaks are recorded by the COSY experiment. It can reasonably be assumed that two peaks are overlapping with very close chemical shifts. From the literature, the chemical shifts of the peaks corresponding to the hydrogen in *ortho-* and *para-* of the ether groups are of very similar values, a survey of various alkyl-phenyl ethers showed that two peaks, integrating 1H and 2H, are indeed overlapping. Estimation of the chemical shifts of each proton of the phenolic ring in the ether from NMR data tables[162] showed that the *ortho-* and the *para-* protons are overlapping at a chemical shift estimated at 6.8ppm, the *meta-* proton being estimated at 7.18ppm.
By comparison with the estimations of the chemical shifts of the protons in the phenol ('$*$', *ortho-* at 6.71, *meta-* at 7.15 and *para-* at 6.82ppm), the peak at 6.76ppm is assigned to hydrogens in *ortho-* of the hydroxyl group, the peak at 7.18ppm to hydrogens in *meta-* position, and the peak inside the multiplet to the hydrogen in *para-* position.

Octylphenol exhibits four distinct peaks, therefore it is not the *para-* isomer. As presented in chapter 1, the alkylation of phenol with alkene occurs in the *ortho-* and the *para-* position, the *meta-* position being obtained by secondary reactions with stronger conditions. It would be reasonable to believe therefore that the octylphenol obtained in the alkylation of phenol with 1-octene with the silica supported aluminium phenolate is the *ortho-* isomer, as from the NMR data, the *para-* isomer is not present. To the best of our knowledge, detailed NMR data for the *ortho-* and the *meta-* (2-octyl)phenol aromatic protons are not available. However, 1-octylphenol NMR data is available[170] and the aromatic protons NMR data are: 7.05–7.12, m, 2H, 6.81–6.89, m, 1H, 6.74–6.77, m, 1H. The chemical shifts of the compound '@' are consistent with these data. Estimations of the chemical shifts from NMR data tables[162] are as follows: 2-ethylphenol 7.01, 6.98, 6.76, 6.65 and 3-ethylphenol 7.09, 6.68, 6.57, 6.54. The *ortho-* compound would show two peaks above 6.95 and two below 6.8 when the *meta-* would show 1 above 6.95 and three below 6.8ppm. The compound '@' shows two peaks above 6.95 and two below 6.9, which could be consistent with an *ortho-* isomer. Finally, the compound '@' exhibits three coupling constants of 7.4, 7.6 and 7.9Hz. These coupling constants values correspond to $J(HH_{ortho})$[162]. In the *ortho-* isomer, these could correspond to $J(H_2H_3)$, $J(H_3H_4)$ and $J(H_4H_5)$, when in the *meta*-isomers, it is not possible to assign three different coupling constants corresponding to an *ortho-* pattern.

All the available data suggest that the main octylphenol is the 2-(2-octyl)phenol. The silica gel supported aluminium phenolate catalyst was active in the alkylation of phenol with 1-octene and, after 18hours of reaction, the two major products were the 2-octyl-phenyl ether and the 2-(2-octyl)phenol, obtained in a 29.4% yield. As the products were now identified, the reaction was carried out with 5% of the same catalyst, the main mono- alkylphenol was then obtained at a maximum yield of 54% after 23hours of reaction.

4.2.2 With propene

Alkylation of phenol with propene (Figure 4.3) was carried out with the catalyst $Al(OPh)_xK100(600)(ATC)tp(\mathit{0.8})$. The reaction was carried out in the laboratory of Schenectady at Pratteln, Switzerland. The temperature profile and the alkene amount (1.5eq.) were chosen in order to investigate briefly the behaviour of the catalyst. The propene addition, at a rate of 1 equivalent in an hour, was started at 220°C then increased gradually up to 270°C (full profile is given in

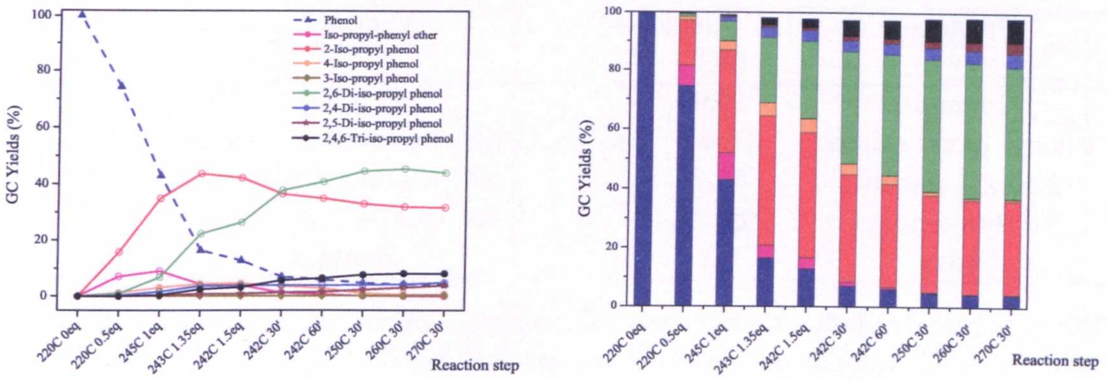


Figure 4.3: Alkylation of phenol with propene carried out with Al(OPh)$_x$K100(600)(ATC)tp(*0.8*) as catalyst.*(Original in colour)*

figure 4.3). 95% of phenol was converted into propyl products. The first alkylation was directed in the *ortho*-position as the main mono-propylphenol was the *ortho*-propylphenol. *Para*-propylphenol was observed, but disappeared as the second propene equivalent was added. Ether was also observed at a quite high level (9%). The profile at the beginning of the reaction was similar to those observed with the same catalyst in the alkylation of phenol with isobutene (Figure 3.33). However, the reaction profile changed dramatically for the second alkylation. The main dipropylphenol was the 2,6-dipropylphenol. Some 2,4- isomer and 2,4,6-tripropylphenol were also detected. As only 1.5eq. of alkene were added, an equilibrium between mono- and dialkyl products is reached.

With the same catalyst (Figure 3.33), the main di*tert*butylphenol was the 2,4-DTBP. A complete different selectivity is observed for the second alkylation. With homogeneous aluminium triphenolate, propene and isobutene do alkylate phenol in a similar manner, the di*ortho*-phenols are the main dialkyl products, with a yield above 75%[38]. However, it is known in the literature that propene and isobutene do not behave in a similar manner in the alkylation of phenol using solid catalysts. For example, with γ-alumina, to the best of our knowledge, the 2,6-DTBP is not accessible from phenol and isobutene only the OTBP, while the 2,6-diisopropylphenol may be produced from phenol and propene[64]. In the same patent however, Hahn also reported the synthesis of 2,6-di*sec*butylphenol from phenol and 1-butene or 2-butene, but isobutene was not listed as a possible alkene example. The behaviour of the new silica supported aluminium phenolate might also be influenced by the intrinsic reactivity of the alkene, and not only just preparation parameters.

Product	GC Yields (%)
Phenol	19.9
Phenyl hexyl ethers	9.4
2-Hexyl phenol	55.7
All mono-hexyl	63.3
Heavy	5.1

Product	GC Yields (%)
Phenol	2.1
Phenyl cylo-hexyl ethers	21.7
2-Cyclo-hexyl phenol	56.2
All mono-cyclo-hexyl	57.7
Heavy	16.6

Table 4.1: Product distribution of samples taken at a reaction time of 19hours from alkylation reaction of phenol with 1eq. of, respectively, 1-hexene (left) and cyclohexene (right) carried out batchwise at 100°C with $\mathrm{Al(OPh)}_x$K100(200)(ATC)tp(*1.7*) as catalyst.

4.2.3 With 1-hexene and cyclohexene

The new silica supported aluminium phenolate was applied to the alkylation of phenol with 1-hexene and cyclohexene. Table 4.1 shows the product distribution of the reaction mixture analysed at a reaction time of 19hours. All products were assigned from their MS spectra obtained by GC-MS.

In both cases, the main mono- alkyl phenol was the *ortho-* alkyl product, and in the case of 1-hexene, attached at the second carbon atom of the chain. Conversion of phenol was higher in the case of 1-hexene but higher level of ether was observed in the case of cyclohexene.

The catalyst was active in the alkylation of phenol with 1-hexene and cyclohexene. The catalyst was *ortho-* selective for the first alkylation. The nature of the second alkylation was not investigated in these alkylation systems.

4.3 Alkylation of cresols

As described in the chapter 1, cresols and their *tert*butyl derivatives are another important range of industrially important phenols derivatives. They are also produced using homogeneous catalysts such as aluminium triphenolate or sulfuric acids[38].

Alkylation of cresols with isobutene and propene were investigated with the new silica supported aluminium phenolate. The new solid catalyst was active in these

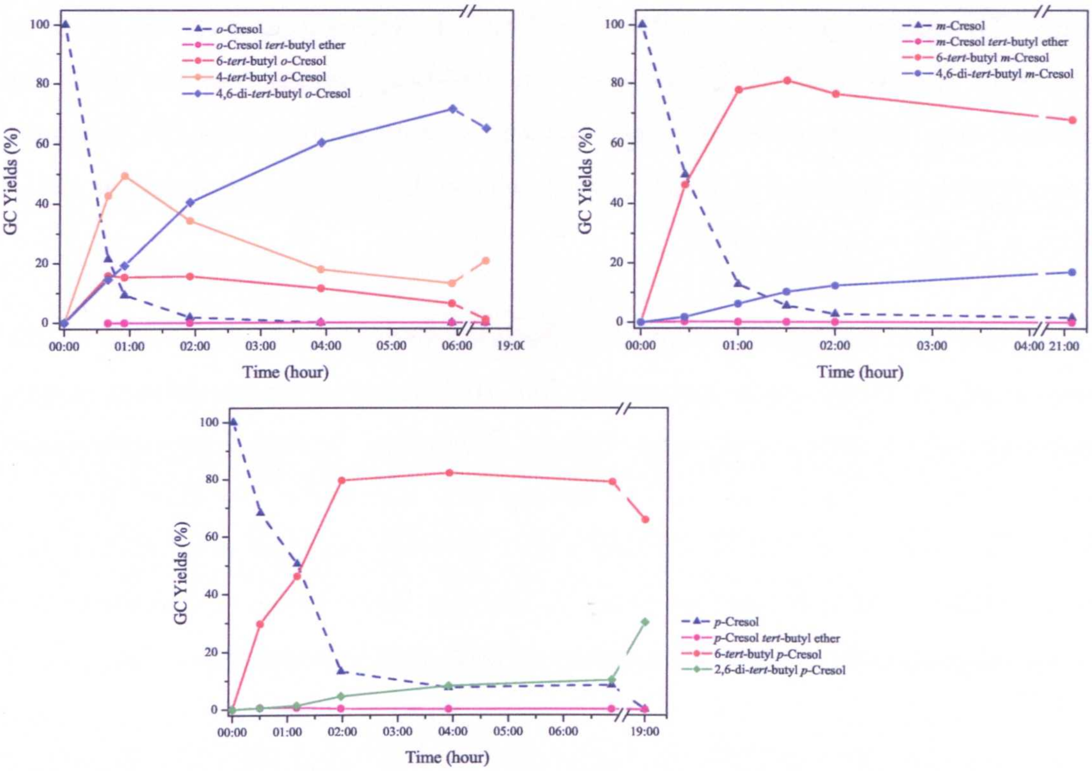


Figure 4.4: Alkylation of *ortho*-cresol (top left), *meta*-cresol (top right) and *para*-cresol (bottom) with isobutene carried out at 140°C with Al(OPh)$_x$K100(200)(ATC)tp(*1.7*) as catalyst (1%), reaction profile.*(Original in colour)*

alkylation systems and gives access to a range of cresol derivatives using an environmentally benign heterogeneous catalytic system.

4.3.1 With isobutene

Ortho-, *meta-* and *para-* cresols were alkylated with isobutene using the material Al(OPh)$_x$K100(200)(ATC)tp(*1.7*) as catalyst (Figure 4.4). All products were identified by GC-MS. All three cresols were successfully alkylated.

Ortho-cresol, having already one *ortho-* position occupied, was preferentially alkylated in the *para*-position with the first equivalent of isobutene then the only other available position, the *ortho-* position to the 4,6-di*tert*butylphenol. Also, as the reaction temperature was high, the level of ether was very low. And when all isobutene was consumed, the dialkyl product was dealkylated back into the mono-*para-* product.

Meta-cresol was alkylated preferably in the *ortho-* position opposite to the methyl group. The dialkyl product was produced only very slowly and at low yield. It is however known in the literature that the *tert*-butyl group does not enter the aromatic ring between the hydroxyl and the methyl groups, and the synthesis of 4*tert*butyl-*meta*-cresol is obtained only with difficulty (by debutylation of the 4,6-di*tert*butyl-*meta*-cresol)[38].

Para-cresol was alkylated in the only available *ortho*- position. If 90% of the *para*-cresol was converted in 2hours, the last 10% was only consumed very slowly, compared to the *ortho*- and *meta*- cresols. The mono *tert*butyl-*para*-cresol was produced in high yield (80%) as the second *tert*- butylation was slow. However this second *ortho*- alkylation did take place, showing that the di-alkylation was not forbidden. At the reaction time of 19hours, only 1.5eq. of isobutene was consumed, suggesting that higher yields of BHT may be obtained.

All three cresols were completely converted into butylated products, at various rates. If for the *meta*- and *para*- cresols, due to positional and steric hindrances rules, the selectivity for a mono-*ortho*-*tert*-butyl derivative was high, the selectivity for the *ortho*- derivative of the *ortho*- cresol was low. However, if the *ortho*- cresol is considered as already mono- *ortho*- alkylated, then the general selectivity is similar to the one observed with the phenol-isobutene system (Figure 3.28, page 142): it is similar to the alkylation of OTBP, being first alkylated in the *para*- position into 2,4-DTBP, then to the second *ortho*- position into TTBP.

4.3.2 With propene

Alkylation of *meta*-cresol was carried out with propene to investigate the production of thymol (6-isopropyl-3-methyl-phenol), an important industrial chemical, and precursor to I-menthol. In the Bayer industrial process (liquid phase), the *meta*- cresol:propene ratio is 1:0.7, the reaction temperature above 350°C, and catalyst is the γ-alumina, easily separated, but the main difficulty is the co-production of the 2-isopropyl-3-methyl-phenol positional isomer, which is separated from thymol with very great difficulties[38]. A gas phase process using zeolites as catalysts was also developed allowing lower reaction temperature to be used, between 230 and 270°C.

The reaction using the new silica supported aluminium phenolate was carried out

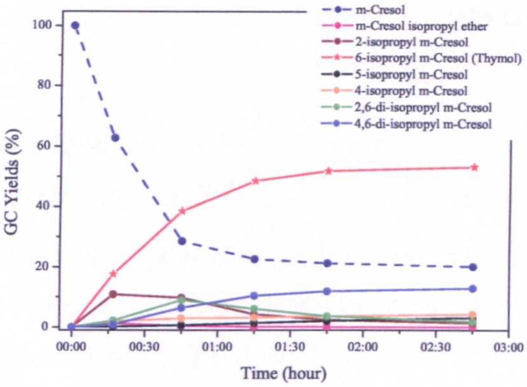


Figure 4.5: Alkylation of *meta*-cresol with propene (0.8eq.) carried out at 270°C with Al(OPh)$_x$K100(600)(ATC)tp(*0.8*) as catalyst (1%).*(Original in colour)*

in the Schenectady laboratory at Pratteln, Switzerland (Figure 4.5).

The cresol-propene ratio was chosen to be able to compare results with the literature. All the *meta*-cresol, which could be converted as only 0.8eq. of propene were used, was converted (79.9%). The production distribution shows 53.2% of thymol and 12.8% of the 4,6-diisopropyl *meta*-cresol (undesired products) were produced along with 10.8% of by-products. The level of the 2-isopropyl *meta*-cresol isomer was only of 1.4%, which represents 2.5% of the mono-*ortho*-isopropyl *meta*-cresols. Compared to the Bayer process, which gives 60% of thymol, 25% of *meta*-cresol and only 15% of by-products included the 4,6-diisopropyl derivative, the silica supported aluminium phenolate catalyst led to a somewhat less cleaner reaction.

The *meta*-cresol alkylation reaction with propene was also carried out using 0.5% of catalyst at 240°C. Here, a much higher level of 2-isopropyl *meta*-cresol, at the detriment of the thymol yield, was recorded. Raising the reaction temperature to 270°C induced isomerisation and yielded the same production distribution as reported for the reaction carried out completely at 270°C.

Further work would be needed to design an industrial viable heterogeneous system for the manufacture of thymol.

4.4 Conclusion

The new silica supported aluminium phenolate material was successfully applied to various alkylation with alkene systems. These involved cresols as phenol derivatives and 1-octene, 1-hexene and cyclohexene, and propene as alkene. These systems allow access to a range of various alkylphenols, some being important industrial chemicals, such as thymol or BHT. The general selectivity observed was similar to the one observed for the phenol – isobutene alkylation system, the first being directed in *ortho-* position, the second mainly in *para-*.

For all the alkylation systems, which involve aluminium triphenolate as homogeneous catalyst in the actual industrial process, if the new catalyst did not lead to higher yields of alkyl-phenols to be produced, the non-requirement of an washing step is an important improvement of the process, which could decrease the production cost as well as the cost of disposal of phenol contaminated aqueous washings, notwithstanding decreasing the environment concern.

However, the new catalyst material used under the reaction conditions described here did not improve the process, which already involves solid catalyst, such as the Bayer process for the thymol production. Nevertheless, the new solid catalyst for the alkylation with alkene of phenol derivatives is a promising one, as we have to remember that all results presented in this chapter were obtained before the final catalyst improvement reported in the chapter 3 (Section 3.13). These reactions should be further studied and improvements may therefore be expected for all systems reported here.

Chapter 5

Catalyst development towards industrial use

5.1 Introduction

In the previous chapters, the characterisation of the new silica supported aluminium phenolate was investigated. The application of this new catalyst in the alkylation of phenol with isobutene was reported as well as the studies of various reaction condition variables and catalyst preparation parameters. Then studies of the activity of the catalyst in other phenols alkylation systems with alkenes were presented.

Catalyst development towards industrial use involves every aspect of the catalyst life, from before its production until its disposal, including safety. One aspect of safety was investigated and is discussed here.
In all the alkylation reactions reported in this thesis, the activity and selectivity were tested and studied using freshly prepared catalyst. One advantage of the use of this new solid catalyst, hence the improvement of the greenness of the reaction, was for some alkylation systems the non-requirement of washing steps in the homogeneous process to quench and remove the homogeneous catalyst thus precluding its reuse. Another advantage of solid material used as catalyst is the ease to filter the solid material off the reaction mixture. Catalyst reusability studies were undertaken and are reported in this chapter.
The alkylation process does not required the use of a solvent. However solvent is required for the preparation of the catalyst. The amount of solvent required for the catalyst preparation was also investigated and its effect on the alkylation reaction of phenol with isobutene is discussed here.
Storage of the catalyst or exposure to air also have been studied as if the catalyst does decompose or retain its activity, as that will effect the method and cost of the catalyst storage.

5.2 Safety during the reaction

Reactions using heterogeneous catalyst are biphasic systems. As already presented, these systems have many advantages compared to their homogeneous counterparts. However, they also have some disadvantages, which have to be overcome. For example, if for any reasons the reaction has to be stopped during its course, which means turning off the stirrer, the solid material will settle on the bottom of the reactor. When restarting the reaction or emptying the reactor, stirring the mixture again is possible only if the solid catalyst does not behave as a rock, in other words, the solid catalyst should not block the stirrer in such a manner that the stirrer cannot be stirred again.

In the other hands, for production time and cost, the solid catalyst need to settle in a reasonable time, to allow a quick separation of the two phases.

Some alternating silica supports were investigated from this point of view. Bigger size of silica gel K100, named K100Big, mixture of the two K100 particle sizes, were used as support for the silica supported aluminium phenolate, and they exhibited the same general selectivity compared to the catalyst prepared with K100Small as support. However, once the stirrer was deliberately turned off, and the catalyst allowed to settle down, the reaction mixture was then only with great difficulty, often with external help, stirred again. It is true that the experiments were carried out with a magnetic stirrer, which is more sensitive to blockage than a mechanical stirrer.

The activity of the catalyst prepared with K100Big as support will be discussed later in the reusability study.

GASIL silica was also investigated as support. This silica material exhibits a slightly lower specific surface area and a slightly higher pore volume and average pore diameter compared to the K100 silica gel. If the K100 silica gel particles exhibit a bead shape, GASIL silica is more fluffy. This characteristic is an advantage regarding the problem discussed in the previous paragraph, as the catalyst material prepared with this support has a tendency to “fly” in the reaction solution. This support would solve the material settlement problem. However, there is a great disadvantage of this support, the tendency to “fly” in the solution is so great that the time required to settle completely down the material from a reaction mixture, where only 1% based on the amount of starting phenol was used, have in some cases taken more than one full day.

These few experiments give a small insight of some problems, which could come in the course of a catalyst development towards an industrial use. More works are required in this field and testing in a semi-industrial scale would have to be carried out before the final approval for industrial use.

5.3 Greening the catalyst preparation

As described in the chapter 2, the new silica supported aluminium phenolate is prepared in two steps, the first one being the grafting of an aluminium precursor on the silica surface, the second one being the exchange of the aluminium precursor ligand into phenolate ligand if necessary. The aluminium precursor mostly used for this work was the aluminium trichloride. The preparation of the supported aluminium trichloride reported by Clark et al. involved stirring aluminium trichloride with the silica support in benzene in a ratio of 10g of catalyst per mol of benzene(90mL)[155]. Shorrock improved the greenness preparation by replacing the benzene by the less toxic solvent, toluene, and prepared the supported aluminium trichloride with a lower silica – solvent ratio of 10g – 70mL[137]. The silica supported aluminium phenolate material used as catalyst in this work was prepared using this solvent ratio. The obtained catalyst was successful in the phenol alkylation reaction with alkenes as reported in the previous chapters.
In order to improve the greenness of the catalyst preparation by reducing the amount of volatile solvents, the amount of toluene used was decreased and the resulting catalyst tested.

The catalyst preparation methods were described in Table 2.15 on page 81. The preferred preparation method was the 'tp' as described in the section 2.4.4.1. This method was carried out in two ways. The first way was the 'two steps', where the supported aluminium trichloride was prepared in refluxing dried toluene, isolated, washed with dried toluene several times and dried under vacuum, before being mixed again in dried toluene with phenol at reflux in order to obtain the final material, which again was isolated, washed several times with dried toluene and dried under vacuum. The second way was the 'one-pot', where the supported aluminium trichloride was prepared in refluxing dried toluene, the mixture cooled down to 50°C, the phenol added and the mixture refluxed again to obtain the final material, which again was isolated, washed several times with dried toluene and dried under vacuum.
The 'one-pot' method was an improvement as the required amount of toluene was reduced by an half. Table 5.1 shows the product distribution of alkylation reaction carried out with catalysts prepared following the two types of 'tp' method at a reaction time above 20hours. The 'one-pot' method to prepare the catalyst

	Cat. 'tp' Prep. Mth.	
Product	'two steps'	'one-pot'
PhOH	1.9	0.3
TBPE	0.2	0.0
OTBP	39.3	17.6
PTBP	1.4	0.5
TBOTBPE	0.2	0.0
TBPTBPE	0.1	0.0
2,6-DTBP	11.1	19.7
2,4-DTBP	33.3	30.7
2,5-DTBP	0.8	1.5
TTBP	10.9	28.9
Heavy	0.8	0.8

Table 5.1: Product distribution (%) (at a time above 20hours) of the alkylation reactions of phenol with isobutene (1.94eq.) carried out at 100°C with (1%) of $Al(OPh)_xK100(600)(ATC)$**tp**(*0.8*) as catalyst, prepared following the 'two steps' tp method or the 'one-pot' method.

led to a more complete conversion of OTBP, a higher selectivity to the di*ortho*-product, but a higher yield of TTBP. Thus, the *ortho-* selectivity was improved by canceling a washing step between the aluminium grafting step and the ligand exchange step. Two reasons could explain this behaviour: either the washing was removing some unreacted aluminium trichloride, which were reacting with phenol and got grafted during the ligand exchange step increasing the aluminium loading and leading to aluminium species bearing higher number of phenolate ligand, or despite the care to remove the HCl formed during the aluminium grafting step, a low level remained dissolved and catalysed the ligand exchange step leading to aluminium species with a higher number of phenolate ligand. In both cases, the cancelation of this intermediate washing step helped us, to improve the *ortho*-selectivity and to improve the greenness of the preparation procedure.

A further reduction of the amount of toluene was attempted by canceling the final washing step after the ligand exchange step of a catalyst prepared with the 'one-pot' method. Hence, the aluminium was grafted in refluxing toluene on the silica gel support, the solution cooled down and the phenol added, the mixture refluxed again for a while and finally cooled down and the toluene removed straight away by vacuum. However, the resulting material when used as catalyst exhibited a different acidity, as the *ortho-* selectivity was slightly decreased but also, lot of diisobutene (DIB), until now not observed, was for the first time observed in high levels: 1.93eq. of isobutene was used but only 1.35eq. was found in the alkyl-

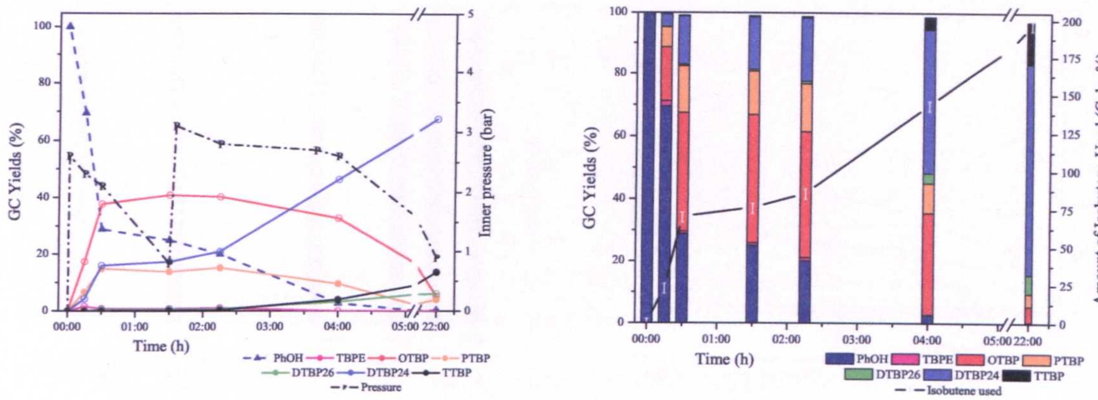


Figure 5.1: Alkylation of phenol with isobutene (1.95eq.) carried out at 100°C and Al(OPh)$_x$K100Big(200)(ATC)tp(*0.8*) as catalyst (1%): reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

phenol products (consumption estimation). The cancelation of the last washing probably left behind dissolved HCl from the grafting and the ligand exchange steps, which induced Brønsted acidity. This result showed that even by removing the HCl formed by bubbling nitrogen through the catalyst preparation mixture during the whole preparation time, some HCl remained dissolved and that was only removed by the final washing step, which is therefore necessary.

5.4 Reusability studies

One of the advantages of the solid catalyst is the ease with which it is separated from the reaction mixture, avoiding any quenching and washings steps, which, in the homogeneous steps, yield eventually to the destruction of the catalyst. Once the solid separated, the possibility of reuse is another advantage of these solid catalysts.

The silica supported aluminium phenolate is reusable in the alkylation reaction of phenol with isobutene, as some of the results in the chapter 3 were obtained when reusing the catalyst (see for examples section 3.7 with the catalyst prepared from TEAL).

The Al(OPh)$_x$K100Big(200)(ATC)tp(*0.8*) material was tested in the alkylation reaction of phenol with isobutene (Figure 5.1), and reused with the same reaction conditions (Figure 5.2).
Between the first use and the reuse, a decrease of activity of the catalyst can be

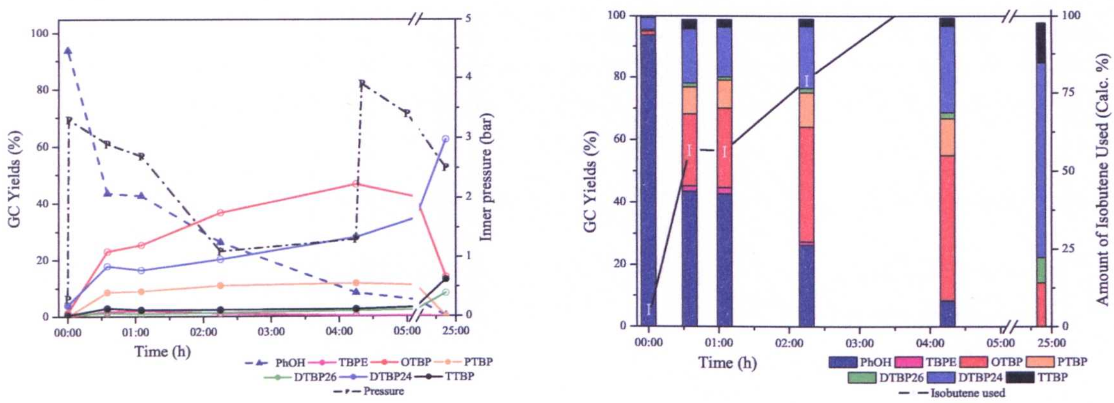


Figure 5.2: Alkylation of phenol with isobutene (1.94eq.) carried out at 100°C and Al(OPh)$_x$K100Big(200)(ATC)tp(*0.8*) as catalyst (1%, reuse): reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

Support pre-treatment temperature (°C)	Aluminium loading (mmol.g^{-1})	BET s.a. (m^2.g^{-1})	Tot. p. vol. (cm^3.g^{-1})	Av. p. diameter nm
200	0.8	340.8	0.507	5.6
		369.8	0.536	5.8
750	0.8	309.2	0.670	8.7
		315.9	0.712	9.0
900	0.8	228.6	0.472	8.3
		232.3	0.507	8.7
200	1.7	253.2	0.650	10.3
		281.6	0.653	9.3
600	1.7	315.6	0.727	9.2
		339.7	0.734	8.6

Table 5.2: BET surface area (BET s. a.), total pore volume (Tot. p. vol.) and average pore diameter (Av. p. diameter) of various silica supported aluminium phenolate before (first line) and after use (second line).

observed. At 24h30 reaction time, the reaction profile when using the catalyst for the first time was at a more advanced point than the reaction profile when reusing the catalyst: the yield of 2,4-DTBP was higher, the yield of OTBP lower and the yield of PTBP was increasing again, as observed previously when all isobutene was consumed. The activity of the reused catalyst being lower, the yield of 2,6-DTBP was however higher in the reuse experiment than for the first use. The conversion rate of phenol decreased between the first use and the reuse of the catalyst, 70% of the phenol was converted in about 30minutes in the first use, and in about 2hours in the reuse experiment. In both experiments, the isobutene was all converted into products as shown by the isobutene consumption estimation.

S. Pre-T. Temp. °C	Th. Ld. mmolg^{-1}	%O	%C	%Cl	%Si	%Al	Cl/Al	C/Al	Si/O	Si/C
200	0.8	50.12	28.98	0.16	18.71	2.03	0.08	14.29	0.37	0.64
		48.87	29.37	0.1	19.97	1.69	0.06	17.34	0.41	0.68
750	0.8	56.47	19.77	0.26	22.05	1.45	0.18	13.6	0.39	1.11
		52.04	25.79	0.06	20.67	1.44	0.04	17.9	0.4	0.8

S. Pre-T. Temp.: Surface pre-treatment temperature, Th. Ld.: Theoretical loading.

Table 5.3: Atomic concentrations of silica supported aluminium phenolate catalysts measured by XPES before (first line) and after use (second line).

To investigate this decrease in activity, catalysts were isolated at the end of their first use, washed in dried toluene to remove the reaction mixture and analysed by several techniques. Table 5.2 shows the the specific surface area and the total pore volume of several catalysts before and after their first use. The data show that the surface area and the pore volume of used catalysts did in fact increase slightly, and the isotherms and pore volume distributions (not plotted) exhibited an identical shape, showing that no dramatic structural change did occur. However for high theoretical aluminium loading, the average pore diameter decreased by more than half a unit, showing that either the biggest pores did collapse or that pores were filled with products, which were not removed by washings before the analysis. Another explanation can be proposed. XPES analysis showed that at the loading of 1.7mmolg^{-1}, the silica surface was covered with aluminium species. The decrease of the pore volume may be due to the exchange of the phenol ligand by a more bulkier *tert*butylphenol. However, it would not be understood why this effect was not observed also with the catalyst with a loading of 0.8mmolg^{-1}, as we actually observed an increase of volume and pore diameter.

Table 5.3 presents the XPES atomic concentrations of two sets of catalysts before and after use, along with atomic concentration ratios. The concentration of chlorine decreased slightly for the catalyst prepared with support pre-treated at 200°C, but decreased dramatically for the catalyst prepared with a support pre-treated at 750°C. In the same time, the concentration of carbon increased. This data shows that during reaction the chlorine was removed from the catalyst surface or catalyst aluminium species, which could explain the improvement in the *ortho-* selectivity observed in the reuse experiment. At the same time, the content of carbon increased, either showing that the part of the pores visible to

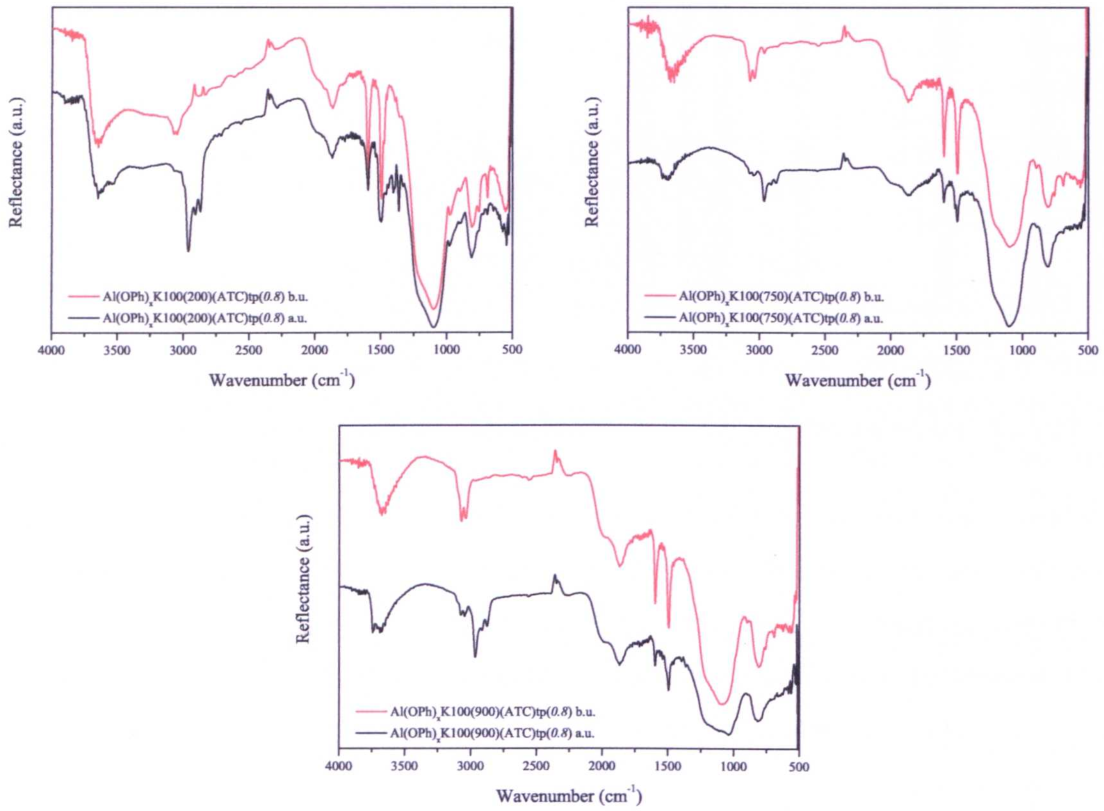


Figure 5.3: DRIFT spectra of silica supported aluminium phenolate prepared with support pre-treatment temperature of, respectively, 200 (top, left), 750 (top, right) and 900°C (bottom), before (b.u., red line) and after use (a.u., black line). *(Original in colour)*

the X-Ray beam were filled with products, or showing that the nature of the aluminium species changed and contained more carbon atoms than before the reaction, which would confirm that the nature of the aluminium ligand changed during the course of the reaction by becoming more alkylated.

Figures 5.3 show the DRIFT spectra of catalysts, prepared with support thermally pre-treated respectively at 200, 750 and 900°C, before and after use. Compared to the spectra before use, peaks in the area of aliphatic C – H bonds appeared ($3000 - 2800$ cm^{-1}), showing either that some isobutene oligomers did form at the surface, or that *tert*butylphenols are present on the catalyst surface. However, the isobutene consumption estimation of the use of these catalysts compared to the added amount(catalyst from 200°C pre-treated silica, Figure 3.30 on page 144; catalyst from 750°C pre-treated silica, Figure 3.39 on page 150; catalyst from 900°C pre-treated silica, Figure 3.40 on page 150) showed that all isobutene were converted into products. Also, the catalysts were well washed after use before recording their DRIFT spectra. Each *tert*butylphenol was reacted in toluene with the thermally treated at 200°C silica support, and their DRIFT spectra recorded. The peak patterns of the aliphatic C – H bond do correspond to the pattern observed in the used catalyst: one very weak peak at 3000cm^{-1}, one strong peak around 2965cm^{-1}, two medium peaks around 2915 and 2875cm^{-1}. These observations would therefore suggest that the ligand of the aluminium did effectively change during the reaction.

The reusability study of the catalyst show that the catalyst activity did decrease between the first use and the reuse. Characterisation by nitrogen adsorption show very little modifications of the surface area and the pore volume, and no fundamental structural changes were observed. X-Ray PhotonElectron Spectroscopy analyses show that the chlorine content decreased slightly and the carbon content increased. Solid Infra-Red analyses suggested that the aluminium ligand was exchanged during the reaction. In the homogeneous catalysis of the alkylation reaction of phenol with isobutene, Knapp et al. showed that the catalyst nature changed during the course of the reaction, becoming more and more soluble in aliphatic solvent as they were unable to precipitate the aluminium phenolate catalyst at the end of the reaction[46]. The change of ligand during the reaction would explain why the activity decreased in the reuse experiment, the aluminium environment being more sterically hindered. Knapp et al. also showed that the aluminium diphenolate hydroxide as catalyst was four times slower compared to the aluminium triphenolate. It also has to be kept in mind that, as the reactor was opened to allow a phenol recharge, even being done under a flow of argon, any trace of water might deactivate the solid catalyst.

5.5 Storage of the catalysts

The effect of storage of the catalyst following its preparation was studied. It is important that the catalyst can be stored for a relatively long time without being degraded, so as to allow transport and handling ease. Exposure to air and moisture and their effect on the catalyst activity and selectivity were also investigated. These are important parameters to know how much care is required for the catalyst storage and handling.

Two catalyst materials, the $\mathrm{Al(OPh)}_x$K100(600)(ATC)ishf(*1.7*) prepared from

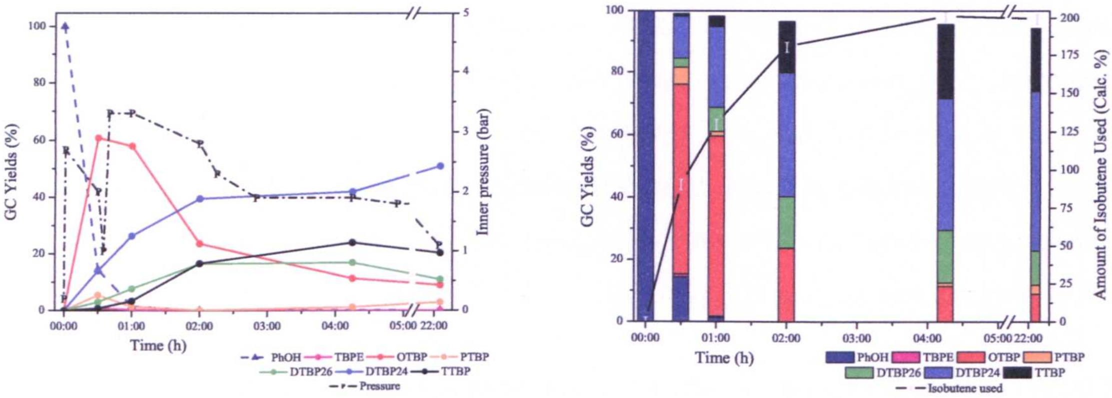


Figure 5.4: Alkylation of phenol with isobutene (1.94eq.) carried out at 100°C with Al(OPh)$_x$K100(600)(ATC)tp(*1.7*) as catalyst (1%), freshly prepared: reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

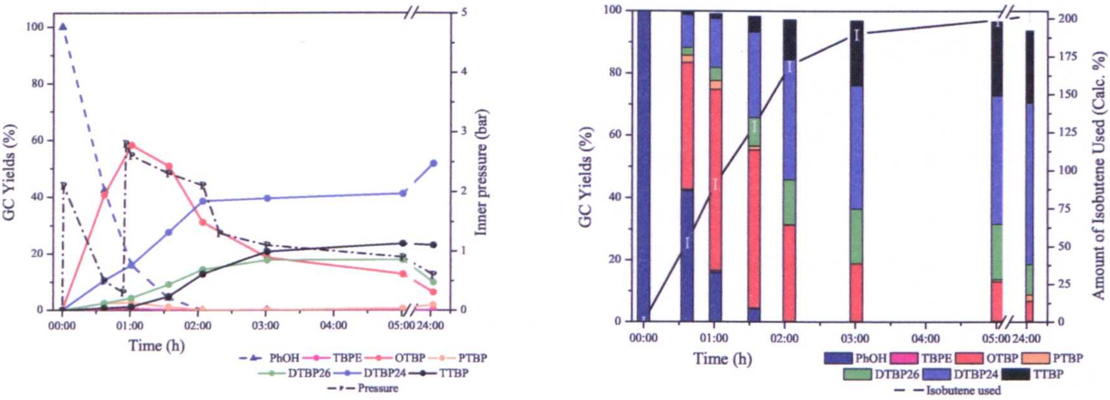


Figure 5.5: Alkylation of phenol with isobutene (1.95eq.) carried out at 100°C with Al(OPh)$_x$K100(600)(ATC)tp(*1.7*) as catalyst (1%), stored for six months in a well sealed flask under an inert atmosphere of argon inside a cupboard: reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

aluminium trichloride and Al(OPh)$_x$K100(200)(TEAL)ishf(*1.7*) prepared from TEAL, were kept in separated well sealed with grease flasks under an inert atmosphere of argon inside a cupboard for about six months and activity of these materials was investigated. Figures 5.4 and 5.6 show respectively the reaction and reactor inner pressure profiles and isobutene consumption estimation of the phenol alkylation reaction with isobutene and freshly prepared catalysts; Figures 5.5 and 5.7 show respectively the reaction and reactor inner pressure profiles and isobutene consumption estimation of the phenol alkylation reaction with isobutene carried out with the six months old catalysts. The colour of the Al(OPh)$_x$K100(600)(ATC)ishf(*1.7*) catalyst became whiter, changing from pink to a pale pink. The colour of the Al(OPh)$_x$K100(200)(TEAL)ishf(*1.7*) being creamy white when fresh, did also change colour to a grayish creamy white with

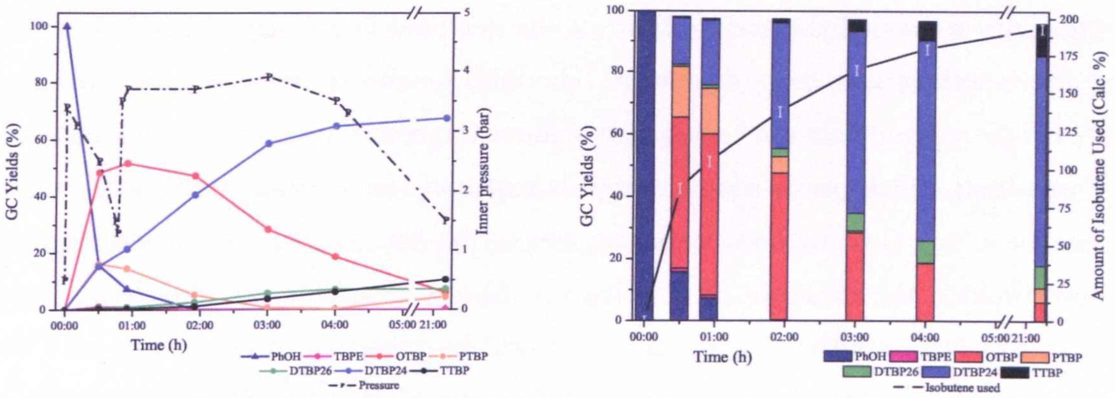


Figure 5.6: Alkylation of phenol with isobutene (1.95eq.) carried out at 100°C with Al(OPh)$_x$K100(200)(TEAL)tp(*1.7*) as catalyst (1%), freshly prepared: reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

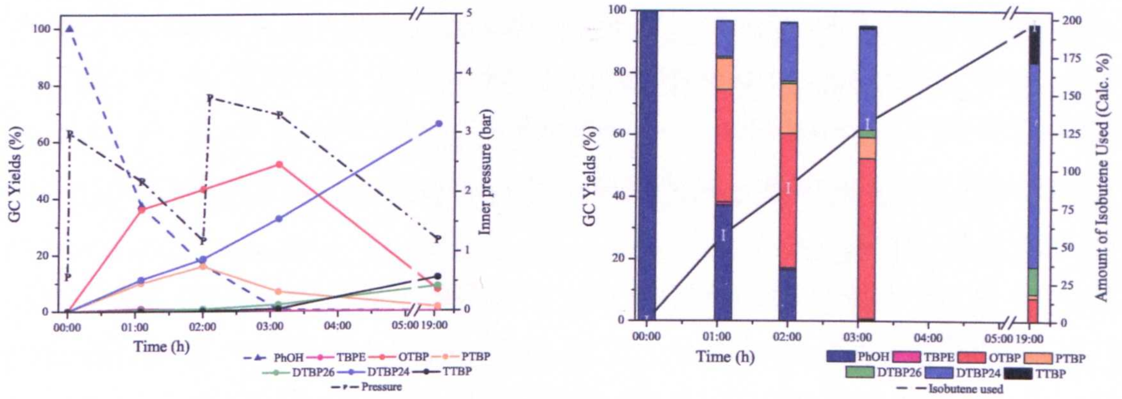


Figure 5.7: Alkylation of phenol with isobutene (1.94eq.) carried out at 100°C with Al(OPh)$_x$K100(200)(TEAL)tp(*1.7*) as catalyst (1%), stored for six months in a well sealed flask under an inert atmosphere of argon inside a cupboard: reaction and reactor inner pressure profiles and isobutene consumption estimation. *(Original in colour)*

some pink.

About the catalyst prepared from aluminium trichloride, the samples taken at around 4h30 and at above 22hours are ±1.5% the same for the fresh and for the 6 months old catalysts. All phenol was converted and the general selectivity remained the same. However, the activity of the catalyst decreased with time, the maximum yield of OTBP being slightly lower and reached after one hour with the old catalyst instead of 30 minutes. It is indeed twice the amount of time, but as the product distribution at about 5hours reaction time is the same, this shows that this material can be stored with some care for a long time losing some of its reactivity but without losing its selectivity.

For the catalyst prepared from TEAL, the sample taken at a reaction time above 19hours was also ±2% the same. All phenol was converted and the general selectivity remained the same. However the decrease in activity at the beginning of the reactions was more dramatic. The 90% phenol conversion point and the OTBP maximum yield were obtained at about the reaction time of 3hours, instead of one hour. This result shows that this material can also be stored with some care for a long time without losing its selectivity, but its activity will decrease. Nevertheless, the decrease in activity was observed after a six months storage time, this suggests that the catalyst can still be prepared in large scale and be transported and store for a short while before use without loss of selectivity. This is an important factor in an industrial context.

Exposure to air was not investigated in a systematic manner. For the supported aluminium trichloride, exposure to air leads very quickly to a change of colour, from dark yellow first to pink then gray. Both pink and gray are usually not active. Silica supported aluminium phenolate prepared from these two exposed silica supported aluminium trichloride led to unactive catalysts for the phenol alkylation reaction.

When a batch of catalyst was prepared, with experience, the author was usually able to predict if the catalyst would be good or not. Exposure to air modified the colour of the final material from dark pink to white pink then grey. If whitish pink coloured material retained some activity (as shown above), the grey material was inactive in the phenol alkylation reaction.

The thermal pre-treatment of the silica support was noticed to play an important role towards the stability of the catalyst to air (and air moisture) exposure. If a catalyst prepared from silica gel pre-treated at 200°C was exposed to air at 60°C for a short while, its general selectivity was unchanged with a small decrease of activity. However, with catalysts prepared with silica gel pre-treated at 750 or 900°C, air exposure turns the colour of the catalyst from light pink to gray in a matter of hours. These observations suggest that these materials, such as $\mathrm{Al(OPh)}_x\mathrm{K100(750)(ATC)ishf}(\mathit{0.8})$, which are the best so far for the production of 2,6-DTBP, require much more care in the storage and the handling if deactivation is to be avoided.

It has been shown by Knapp et al. that if aluminium triphenolate is active in the phenol alkylation reaction with various alkenes, the aluminium diphenolate hydroxide was four times slower[46]. This shows that a small moisture exposition could hydrolyse one phenolate ligand and induces an important decrease of activity of this particular aluminium species. As the solid is exposed, some aluminium sites are affected but the aluminium inside pores may be affected only with delays as the water need to migrate inside pores, which could be also filled with phenol from the ligand exchange step during the catalyst preparation. Hence the deactivation of the catalyst would be progressive.

5.6 Conclusion

Different aspects of the industrial development have been investigated. During the running of the reaction, the solid catalyst has to be well stirred. If the stirring is stopped, the catalyst settled on the bottom of the reactor. It was shown here that this could be a problem for the safety of the reaction industrial handling with the silica gel chosen for this work.
The preparation of the catalyst was also re-investigated from the point of view of the Green Chemistry, and the amount of solvent (toluene) required for the preparation was successfully reduced without any loss of selectivity or activity for the catalyst. The *ortho-* selectivity was in fact slightly enhanced by canceling a washing step between the two catalyst preparation steps.

Reusability of the catalyst was investigated. The new silica supported aluminium phenolate was reusable but a loss of activity was observed between the first use and the reuse. Nitrogen adsorption studies showed that the structure of the catalyst was not dramatically affected, however at high theoretical aluminium loading (1.7mmolg^{-1}), the average pore diameter decreased suggesting that the aluminium species nature changed during the reaction. This observation was also supported by the XPES and DRIFT data.

Catalysts have been carefully stored successfully for a long time. Catalysts prepared from aluminium trichloride showed only a small decrease of activity. Catalyst prepared from triethyl aluminium however lost significantly activity. Nevertheless, in both cases the catalysts retained their general selectivity in the alkylation reaction of phenol with isobutene, the major mono-*metatert*butylphenol being the OTBP and the major di*tert*butylphenol being the 2,4-di*tert*butylphenol.
In other hands, storage without care or deliberate exposure to moisture did deactivate progressively the catalysts.

Chapter 6

Experimental

6.1 Chemical reagents

Chemicals used during this work were supplied and used without further purification unless otherwise stated. In particular, phenol was purchased from Riedel & Hahn with a purity of 99.9+% and a maximum water content of 0.3% (measured by Karl-Fischer). Solvents, such as toluene and dichloromethane, were obtained from Fisher Chemicals, as used as obtained, except for toluene, which was dried and stored over sodium wire. Aluminium trichloride, aluminium triphenolate, solution of triethyl aluminium in toluene were purchased from Aldrich. Triethyl phosphine oxide was purchased from Sterm (98%) or Aldrich (97%). Kieselguhr silica gel K100 and K60 were purchased from Merck, and thermally pre-treated at the required temperature prior to use.

Samples of *tert*butylphenols, OTBP, MTBP, PTBP, 2,6-DTBP, 2,4-DTBP and TTBP were provided by Schenectady Pratteln GmbH. They also provided samples of *para*-cresol and cyclohexylphenols, such as 2-, 4-, 2,4-cyclohexylphenol.

In order to identify reaction products, MS and other data were obtained from databases available online from NIST[171] and Darebury[172, 173] or from literature obtained from Beilstein[174].

6.2 Instrumentation

6.2.1 Gas chromatography

Gas Chromatography analyses were carried out using a Varian 3800 Gas Chromatograph fitted with a Chrompack CP-SIL8CB capillary column and a FID detector, equipped with a 8200 Dual Autosampler. The apparatus was connected to a PC station.

6.2.2 Gas chromatography - mass spectroscopy

Gas Chromatography - Mass spectra (GC-MS) were recorded on a Hewlett-Packard 5890 Series II gas chromatograph interfaced to a VG Autospec Mk.I mass spectrometer interfaced to a PC station, by Dr. Trevor Dransfield or Ben Glennie of the analytical service of the Chemistry department of the University of York.

6.2.3 Infrared spectroscopy

Diffuse reflectance infra-red fourier transform spectra (DRIFT) of the solid materials and supports were obtained using a Bruker Equinox 55 FTIR spectrometer interfaced to a PC-OS/2 station, using a fast Mercury-Cadmium-Telluride (MCT) detector.

6.2.4 Nuclear magnetic resonance spectroscopy

^{1}H 1D and 2D COSY solution state NMR spectra of the sample from the phenol – 1-octene alkylation reaction (Section 4.2.1) were recorded on a Bruker Advance spectrometer (operating at 500MHz for ^{1}H) by Heather Fish from the NMR service of the chemistry department of the University of York.

^{27}Al MAS NMR spectra of the silica supported aluminium phenolate and ^{31}P MAS NMR of the silica supported aluminium phenolate loaded with tri-ethyl phosphine oxide were recorded by Dr. Stewart J. Tavener, from the Green Chemistry group, Clean Technology Centre, Chemistry department, University of York, on a Bruker Avance 400 spectrometer operating at 400MHz for ^{1}H. The samples were inclined at an angle of 54.44° to the magnetic field and the magic angle rotor spinning rate was typically 25kHz for ^{27}Al (2.5mm rotor) and 15kHz for ^{31}P (4mm rotor).

6.2.5 Nitrogen adsorption studies

Nitrogen adsorption isotherms, specific surface area and pore size distributions were obtained at 77K on a Coulter SA3100 surface area analyser.

6.2.6 Elemental analysis

All the elemental analyses were performed by Mr M Jennings at the Micro Analytical Laboratory, Department of Chemistry of the University of Manchester. Carbon elemental analyses were carried out by flash combustion using a Carlo Erba EA1108 Elemental Analyser, halogen determination were achieved by potentiometric titration with a Metrohm 686 Titroprocessor & 665 Dosimat, and metal contents were obtained by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) using a Fisons Instruments Horizon equipment.

6.2.7 X-Ray PhotoElectron Spectroscopy

X-Ray PhotoElectron Spectroscopy (XPES) analyses were carried out by Dr. Karen Wilson or Paul Elliott, from the Green Chemistry group, Clean Technology Centre, Chemistry department, University of York, on a Kratos AXIS His instrument with a Mg Kα X-ray source, at normal emission using an analyser pass energy of 20eV and a X-ray power of 225W. A charge neutraliser was used for the analysing insulating samples. Instrument sensitivity factors using reference chemical standards were taken as C(1s) = 0.318, O(1s) = 0.736, Si(2p) = 0.371, Cl(2s) = 0.964 and Al(2p) = 0.257.

6.3 The Premex Twister pressure reactor

All the alkylation reactions of phenol and cresols with isobutene or 1-octene performed at York were carried out in the Twister hpm380ed pressure reactor, showed in Figures 6.1 and 6.2. This pressure reactor was purchased from Premex Reactor AG, Switzerland[175].

This vessel is made out of alloy C-276 (Ni, Mo, Cr, Fe, W). This material allows reaction to be carried out in strong inorganic and organic acidic or basic medium, very oxidative conditions, in presence of salts, alkaline solutions and chlorine gas. The reactor is sealed with a pure silver ring and high-tensile bolt locks.

Reactions can very conveniently carry out at up to 350 °C and up to 325 bar. The heating fingers and the water-cooling coil allow the control of the reaction

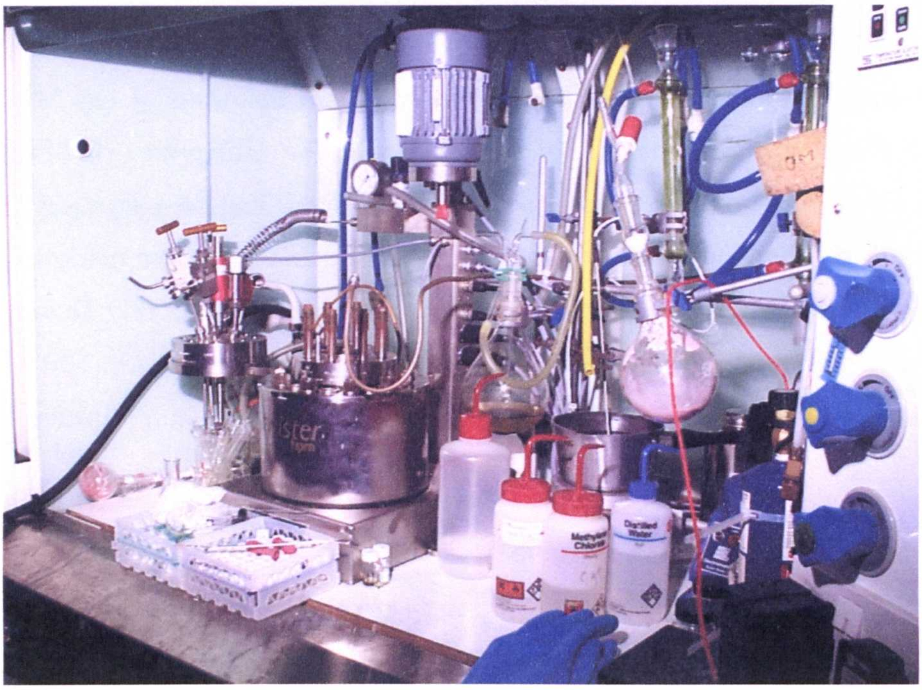


Figure 6.1: Premex Twister hpm380ed pressure reactor, large view of the fume cupboard (note the flask with a pink powder of supported aluminium phenolate).

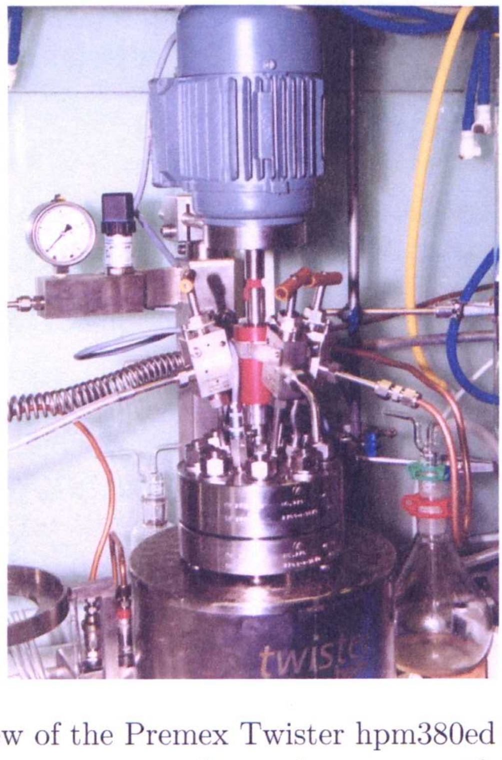


Figure 6.2: Closed view of the Premex Twister hpm380ed pressure reactor head. From left to right, pressure gauge and transducer, gas outlet valve, magnetic rotor (red), liquid sampling valve, gas inlet valve (connecting to a copper tubing), flask used to empty the reactor by suction.

temperature, measured either inside or outside in the jacket. Pressure is measured by a oil-gauge. The reaction mixture is stirred (up to 1500rpm) from a motor *via* a magnetic rotor by a gas stirrer, which enhances the mixing of the gas and liquid phases. Gas inlet and outlet valves allow gas reagent to be added during the experiment and gas samples to be withdrawn for analysis. Finally, liquid samples may be taken via a dip sampling tube with the help of the inside pressure. 50μm filter can be adapted at the end of the dip tube, allowing withdrawal of samples keeping any solid material, as for example solid catalyst, inside the reactor (also avoiding blockage of the ceramic needle valve by fine solid particles).

The reactor is interfaced to a control unit, displaying all the parameters in real time and allowing the control of the heating and / or cooling of the reactor and the stirring rate. Temperature programs can also be made for the inner or jacket.

6.4 Experimental work related to chapter 2

6.4.1 Preparation of thermally pre-treated silica gel support

Silica gel was thermally pre-treated before use. 200°C pre-treated silica gel was obtained by keeping a ceramic bowl filled with silica gel at all time in a oven set at 200°C. General practice was to have the silica gel in the oven for at least 18hours before use.

600°C pre-treated silica gel was obtained by placing a ceramic crucible in a muffle furnace for 18hours. The furnace was then turned off keeping the sample inside. Once the inside temperature reached a temperature between 120 and 150°C, the crucible was put in a glass desiccator equipped with a plate and drying silica gel. The sample was then allowed to cool down to room temperature.

750 and 900°C pre-treated silica gel was obtained by placing ceramic boats in a tubular oven for 18hours. The furnace was then turned off keeping the sample inside. Once the inside temperature reached a temperature between 120 and 150°C, the boats were emptied in a ceramic crucible, which was placed inside a glass desiccator equipped with a plate and drying silica gel. The sample was then allowed to cool down to room temperature.

6.4.2 Catalysts based on aluminium trichloride preparation procedures

6.4.2.1 General remarks regarding the chemical quantities required

In all the catalyst preparation procedures described below, the following amounts are used: for 10g of silica gel, 70mL of sodium-dried toluene and, for a loading of 1.7mmolg^{-1}, 2.27g of aluminium trichloride (133.34gmol^{-1}) was used. For other loadings, the amount of aluminium trichloride used was determined proportionally. 10eq. of phenol (94.11gmol^{-1}) based on the amount of aluminium trichloride was used.

6.4.2.2 Preparation method of $AlCl_x$K100 material, precursor of the $Al(OPh)_x$K100()(ATC)..() catalyst

All glassware were washed with acetone and dried overnight in a drying oven at 60°C. The required amount of aluminium trichloride was stirred with sodium dried toluene in a two-neck flask. Silica gel (prepared as described in section 6.4.1) was added and the flask was equipped with teflon neck liner and a condenser. The slurries were refluxed for three hours. Once the solution was cooled down to room temperature, the followed procedure was chosen depending on the desired supported silica aluminium phenolate preparation method. The next steps are described in the respective sections below.

If the $AlCl_x$K100 material was the desired material, the isolation procedure described in the section 6.4.4 was followed.

6.4.2.3 $Al(OPh)_x$K100()(ATC)is() preparation method (*in-situ*)

The desired amount of isolated $AlCl_x$K100 material was quickly weighted out under an atmosphere of argon and poured into the amount of molten phenol required for the alkylation reaction, stirred and refluxed (182°C) for one hour under an atmosphere of nitrogen. The catalyst – starting material solution was cooled down to the desired reaction temperature, ready to be used.

6.4.2.4 Al(OPh)$_x$K100()(ATC)ishf() preparation method (*in-situ hot-filtration*)

Isolated AlCl$_x$K100 material was poured into a stirred solution of molten phenol and the mixture refluxed (182°C) for one hour under an atmosphere of nitrogen. The slurry were cooled down to 50°C and portionwise transferred into a sintered funnel kept at 50°C. The catalyst was then filtered off, and washed with sodium-dried toluene until the washing solutions were clear.

6.4.2.5 Al(OPh)$_x$K100()(ATC)tp() 'two steps tp' preparation method

The AlCl$_x$K100 precursor material was prepared following the procedure described in the first paragraph of the section 6.4.2.2. The AlCl$_x$K100 material was isolated following the procedure described in the section 6.4.4. This isolated solid material was then stirred in sodium-dried toluene with the same solvent – solid ratio (70mL – 10g). 10eq. of phenol based on the used amount of aluminium trichloride was added to the stirred toluene solution of AlCl$_x$K100 and refluxed for 18hours. The solution was cooled down to room temperature and the isolation procedure described in the section 6.4.4 was followed.

6.4.2.6 Al(OPh)$_x$K100()(ATC)tp() 'one-pot tp' preparation method

The AlCl$_x$K100 precursor material was prepared following the procedure described in the first paragraph of the section 6.4.2.2. 10eq. of phenol based on the used amount of aluminium trichloride was directly added to the cooled stirred toluene solution of AlCl$_x$K100 and refluxed for 18hours. The solution was cooled down to room temperature and the isolation procedure described in the section 6.4.4 was followed.

6.4.3 Catalysts based on TEAL preparation procedures

6.4.3.1 General remarks regarding the chemical quantities required

In all the catalyst preparation procedures described below, the following amounts are used: for 10g of silica gel and for a loading of 1.7mmolg^{-1}, 7.45g (9.45mL) of the 1.8M solution of triethyl aluminium (TEAL) in toluene (Fluka) was used. For other loadings, the amount of TEAL used was determined proportionally. The volume of sodium-dried toluene to be added was determined in order to obtain a final volume of solvent of 70mL per 10g of silica gel. 10eq. of phenol (94.11gmol^{-1}) based on the amount of TEAL was used.

6.4.3.2 TEAL-K100 preparation procedure, precursor of the Al(OPh)$_x$K100()(TEAL)tp() solid catalyst

All glassware were washed with acetone and dried overnight in a drying oven at 60°C. The apparatus was built from a three necks round-bottom flask fitted with a condenser, a thermometer, and a pressure equalising dropping funnel closed with a suba-seal, through which was placed a needle as gas inlet. The top of the condenser was connected to a bubbler. The apparatus was flushed with nitrogen and dried with an hair-dryer. In the flask was strongly stirred the K100 silica gel prepared as described in the section 6.4.1 in the required amount of sodium dried toluene under an atmosphere of argon. TEAL was then transferred into the dropping funnel using normal Schlenk techniques. The TEAL solution was then dropped on the stirred silica - toluene solution, monitoring the temperature (kept below 35°C). Once the addition finished, the solution was allowed at reflux for three hours. If the TEAL-K100 solid was the desired material, the isolation procedure described in the section 6.4.4 was followed. Otherwise the conversion of TEAL-K100 into silica supported aluminium phenolate was carried out following the procedure described in the section 6.4.3.3.

6.4.3.3 $Al(OPh)_xK100()(TEAL)tp()$ preparation procedure

The TEAL-K100 precursor material was prepared following the procedure described in the first paragraph of the section 6.4.3.2. The TEAL-K100 material was isolated following the procedure described in the section 6.4.4. The solid material was then stirred in sodium-dried toluene in the same solvent – solid ratio than for the preparation of TEAL-K100, and 10eq. of phenol based on the used amount of aluminium trichloride was added to the stirred toluene solution of TEAL-K100 and refluxed for 18hours. The solution was cooled down to room temperature and the isolation procedure described in the section 6.4.4 was followed.

6.4.4 General solid material purification procedure

The toluene solution with the solid material was transferred into a one-neck flask. The solvent was decanted off in a such manner that the solid was at all time wet, fresh sodium-dried toluene was added, the mixture stirred for 10min, and then let to settle. This step was repeated until the washing solutions were clear. The final washing was decanted off (solids wet) and the flask was connected to a Schlenk line. The solid material was evacuated until the pressure reached a level lower than 1.10^{-1}mbar. The flask was then filled with argon and carefully sealed for storage (grease and 'parafilm'). Very moisture sensitive samples were stored in a vacuum desiccator dried with phosphorus pentoxide.

6.4.5 Nitrogen physisorption studies

Nitrogen adsorption – desorption isotherms, pore size distributions and surface area were carried out on the Coulter SA3100 using the recommended method described in the Coulter handbook[176]. The sample tube was cleaned with water and acetone and dried in a drying oven at 60°C overnight. Once cooled down to room temperature, the empty tube equipped with a glass rod was accurately (at ±0.0001g) weighted. About 100mg of sample was introduced into the sample tube and the glass rod replaced to occupy the majority of the empty space of the sample tube and to avoid sample suction on the machine. Prior to analysis, the sample was then outgassed for 180min at 120°C. The tube was disconnected from the outgas port and accurately re-weighted to determine the outgassed sample weight, which was considered as the sample weight subjected to analysis. The tube was then connected to the analysis port and the procedure dictated by the instrument followed. Analysis was carried out at the temperature of boiling liquid nitrogen. At the end of the analysis, the corrected weight was input as requested.

6.4.6 Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

Freshly finely ground anhydrous potassium bromide (KBr) was placed in the same conditions desired for the analysis of the catalysts, in order to tune the laser beam and mirrors. Then a background spectrum run at the same temperature as the sample was recorded and saved to be substracted from the samples spectra. DRIFT samples were mixed with a ten-fold excess of anhydrous KBr, and intimately ground together with a pestle and a mortar. The sample was placed in the cell instead of the KBr and the spectrum recorded.

If the sample was to be recorded under vacuum at different temperatures, an environmental chamber was used. The same procedure was followed with the background being also recorded at the different temperatures.

6.4.7 X-Ray PhotonElectron Spectroscopy (XPES)

Prior to submission for analysis, the samples were evacuated at 10^{-1}mbar on a Schlenk line for 3hours.

6.4.8 Magic Angle Spinning Nuclear Magnetic Resonance Spectroscopy (MAS-NMR)

Air and moisture sensitive solid samples were loaded in the rotor in a glove bag flushed with an inert atmosphere of nitrogen.

6.4.9 Acidity measurements

6.4.9.1 Pyridine titration by DRIFT

In a glass jar, open small tubes were placed upright. One small tube was filled with about 5mL with pyridine; the samples to be analysed were placed respectively in the other small tubes. The glass jar was closed after having flushed the atmosphere with nitrogen and the samples left exposed to the pyridine vapour for at least 48hours. DRIFT spectra were then recorded following the procedure described in the section 6.4.6.

6.4.9.2 TEPO titration by ^{31}P-MAS-NMR

A solution of 1molL^{-1} of tri-ethyl phosphine oxide (TEPO) in *n*-pentane was prepared a short time before the preparation of the samples and kept in a fridge. With a micro-pipette, the solution was homogenised and 200μL was taken and added to 100mg of the sample. Approximately 2mL of *n*-pentane was added to the sample to facilitate the mixing. The slurries were shaken regularly over a period of 30minutes. The samples were dried *in vacuo* at 50°C for 15min and the ^{31}P-MAS-NMR spectrum was recorded.

6.5 Experimental work related to chapter 3

6.5.1 General remarks about the amount of solid catalyst used

As described in the chapter 2, the theoretical aluminium loading and the real loading found by elemental analysis are not the same. The calculations showed that for a catalyst prepared at a theoretical aluminium loading of 1.7mmolg^{-1}, the average found loading was 1.35mmolg^{-1}. The amount of solid catalyst was therefore calculated based on this found value. Hence, for a catalyst prepared with a theoretical loading of 1.7mmolg^{-1}, 1% based on the starting amount of phenol for example 75g (0.797mol), corresponds to 7.97mmol, thus to $7.97/1.35 = 5.9$g. For experiments carried out with catalysts prepared at different loadings or with different amounts of catalysts, the weight amount required was determined proportionally.

6.5.2 General procedure for the alkylation of phenol with isobutene under pressure carried out in York with the Twister hpm380ed pressure reactor

The head of the reactor was placed on top of the reactor body without the bolts. The jacket temperature of the reactor was set to 100°C. Once the head of the reactor was warm, the head was set aside and 75g of phenol (0.797mol) was poured in the reactor. After all the phenol was melted, the catalyst (1% based on the phenol amount, 7.97mmol) was added. The reactor was then closed following the manufacturer recommended procedure. The gas inlet and outlet valves were open and the inner atmosphere flushed with nitrogen for 15seconds. The valves were closed and the inner temperature set to the desired reaction temperature and the temperature was allowed to equilibrate. During the course of the reaction, the inner temperature could be manually changed by input the desired new value on the control unit; temperature programs could also be set up. A reservoir of 75mL (1eq. based on the amount of phenol) was filled with liquid isobutene from a liquid isobutene tank equipped with a dip sampling tube. The reservoir was weighted out, then connected to the gas inlet valve, and the valves open at the time considered to be the reaction time zero. When all the first equivalent of isobutene was estimated to be consumed (monitored by the pressure profile), the reservoir valve and the gas inlet valve were closed, the reservoir disconnected and weighted out to determine the exact amount of isobutene added. If desired, a second and / or a third isobutene equivalent was added following the same procedure. During the reaction, the inner temperature, the jacket temperature, the inner pressure and the stirring rate were monitored by reading the parameter values on the reactor control unit. Samples for GC analysis were regularly taken by the mean of a tube dipping into the liquid phase (the liquid was pushed outside by the inner pressure through a 50μm filter leaving the solid catalyst inside the reactor; good practice was to discard the first 4-5mL as this corresponds to the reaction mixture being in the sampling tube without solid catalyst and isobutene since the last taken sample, before taking two drops which were diluted in toluene).

At the end of the reaction, the jacket temperature was set to 50°C, and the inner and jacket temperature allowed to equilibrate. The inner pressure was released by opening the gas outlet valve, the reactor open and the head put aside. The reactor body was then emptying by suction into a flask. If required, samples of used catalysts were taken at this time. The reactor was then cleaned with acetone and water, and every five experiments, the ball races of the magnetic stirrer were checked and replaced if necessary.

6.5.3 General procedure for the alkylation of phenol with isobutene under pressure carried out in the laboratory of Schenectady, Pratteln

The experiments were carried out under the author supervision by Mr. Moëller. The same general procedure as described in the section 6.5.2 was followed, but the isobutene was added against the reactor inner pressure by the mean of a pressure pump, and the reaction was carried out on a phenol scale of 4mol.

6.5.4 Homogeneous alkylation under pressure with commercial aluminium triphenolate as catalyst

The general alkylation procedure described in the section 6.5.2 was followed. GC samples were treated with a 10% aqueous solution of sodium hydrogen carbonate at 80°C, and two drops of the organic phase were taken and diluted in toluene for analysis.

6.5.5 Homogeneous alkylation at atmospheric pressure with *in-situ* prepared from phenol and aluminium metal aluminium triphenolate as catalyst

In a one-neck flask was stirred at 60°C 75g of phenol (0.797mol) and the required amount of phenol to form the aluminium triphenolate (23.9mmol, 2.25g). Aluminium metal (1%) was added and the flask was equipped with a condenser and a drying tube filled with a desiccant. The slurry was heated at the reflux temperature. When all the aluminium was dissolved, the solution was cooled down to 100°C and transferred into a three-neck flask equipped with a magnetic bar, a condenser fitted with a bobbler and a septum through which was set a metallic tube connected to a cylinder of isobutene gas fitted with a regulator. The apparatus atmosphere was flushed with nitrogen. The solution was heated at the desired temperature and the isobutene bobbled through in such a way that no gas was coming out or in the apparatus. Samples for GC analysis were regularly taken and treated following the same procedure described in the section 6.5.4.

6.5.6 Product stability studies

In a flask fitted with a magnetic bar and a condenser, 10g of phenol was stirred with 1% of solid catalyst at the desired temperature under an atmosphere of argon. Samples for GC analysis were regularly taken, diluted in toluene and filtered though cotton wool.

6.6 Experimental work related to chapter 4

6.6.1 General procedure for the alkylation of phenol with 1-octene under pressure carried out in York with the Twister hpm380ed pressure reactor

The head of the reactor was placed on top of the reactor body without the bolts. The jacket temperature of the reactor was set to 100°C. Once the head of the reactor was warm, the head was set aside and 75g of phenol (0.797mol) was poured in the reactor. After all the phenol was melted, the catalyst (1% based on the phenol amount, 7.97mmol) was added. 1 equivalent of 1-octene (59.65g, 83.4mL) was added. The reactor was then closed following the manufacturer recommended procedure. This point was considered to be the reaction time zero. The gas inlet and outlet valves were open and the inner atmosphere flushed with nitrogen for 15seconds. The gas outlet valve was closed to allow a pressure build-up, to allow withdrawal of samples. When the pressure reached 1bar above the atmospheric pressure, the gas inlet valve was closed and the inner temperature set to the desired reaction temperature and the temperature was allowed to equilibrate. During the reaction, the inner temperature, the jacket temperature, the inner pressure and the stirring rate were monitored by reading the parameter values on the reactor control unit. Samples for GC analysis were regularly taken by the mean of a tube dipping into the liquid phase (the liquid was pushed outside by the inner pressure through a 50μm filter leaving the solid catalyst inside the reactor; good practice was to discard the first 4-5mL as this corresponds to the reaction mixture being in the sampling tube without solid catalyst and isobutene since the last taken sample, before taking two drops which were diluted in toluene). At the end of the reaction, the jacket temperature was set to 50°C, and the inner and jacket temperature allowed to equilibrate. The inner pressure was released by opening the gas outlet valve, the reactor open and the head put aside. The reactor body was then emptying by suction into a flask. The reactor was then cleaned with acetone and water.

6.6.2 General procedure for the alkylation of phenol with propene under pressure carried out in the laboratory of Schenectady, Pratteln

The experiments were carried out under the author supervision by Mr. Moëller. The procedure for the alkylation of phenol with isobutene described in section 6.5.3 was followed with propene instead of isobutene.

6.6.3 General procedure for the alkylation of phenol with 1-hexene or cyclohexene at atmospheric pressure

In a flask fitted with a magnetic bar and a condenser, 10g of phenol (0.106mol) was stirred with 1% of solid catalyst at the desired temperature under an atmosphere of argon. 2 equivalents (0.212mol) of 1-hexene (17.9g, 26.6mL) or cyclohexene (17.5g, 21.5mL) were added. GC samples were regularly taken, diluted in toluene and filtered through cotton wool.

6.6.4 General procedure for the alkylation of cresols with isobutene or propene under pressure

Procedures for the alkylation of cresols with isobutene or propene were carried out in York or in the laboratory of Schenectady, Pratteln, following the same procedure as for the alkylation of phenol with isobutene (section 6.5.2) or propene (section 6.5.3). The starting amount of cresols using when carrying out the reaction with Twister pressure reactor was 0.797mol(86.2g), and 4mol(432.6g) when carrying the reaction in the laboratory of Schenectady, Pratteln.

6.7 Experimental work related to chapter 5

6.7.1 General procedure for the alkylation of phenol with isobutene under pressure carried out in York with the Twister hpm380ed pressure reactor

The alkylation of phenol with isobutene was carried out following the procedure described in the section 6.5.2.

6.7.2 "Greening" of the preparation method of the catalysts

The catalyst was prepared following the preparation method 'tp2' described in the section 6.4.2.6 but using a ratio silica – solvent of 10g – 40mL.

6.7.3 Reusability studies

The reaction corresponding to the nth catalyst use was carried out following the procedure described in the section 6.5.2. At the end of the reaction, the reservoir was disconnected from the gas inlet valve and pressurised nitrogen was applied instead. The reactor was then emptied through the dip sample tube. Once all the reaction mixture was taken out of the reactor, the pressure of nitrogen was removed and the gas outlet valve open to release the inner pressure. The reactor was open, the head set aside and a fresh load of phenol was poured inside under an atmosphere of argon (to protect the wet catalyst, which remained at the bottom of the reactor body). The head was replaced and the reactor closed. The reaction corresponding to the next catalyst use was then run following the general procedure.

Chapter 7

Concluding remarks

In the actual days, pressure from both governments and public builds up on the chemical industries to clean up their acts. Concerns grow also about our environment and its protection. The "Green Chemistry" illustrates these new variables and formalises the new goals that chemists and industrials in the chemistry field have to reach, such as decrease of energy consumption, reduction of the use of volatile organic compounds, diminishing of the amount of wastes, recycling and use of renewable resources.

The production of alkylphenols from phenol and alkene is already "green" from certain aspects. No solvent is generally required, the reaction is catalytic and no other reagents apart from the starting materials (phenol and alkene) are required. Depending on the alkylphenol to be produced, the use of solid catalyst is already implemented as an industrial process. One example is the synthesis of mono-*tert*butylphenols with γ-alumina. The use of solid catalyst presents various advantages compared to their homogeneous counterpart, they are easily separated and reused. They also allow milder conditions to be used. However the production of di*ortho*alkylphenols, one example being the important antioxidants or light-protection agents building block 2,6-di*tert*butylphenol (2,6-DTBP), is still generally produced with homogeneous aluminium triphenolate, as it is since the discovery of the reaction. The wastes generated by the quenching step of the catalyst becomes less and less acceptable from the environmental point of view and become more and more expensive to deal with, decreasing the cost-efficiency of the production. The need for a new solid catalyst for the production of 2,6-DTBP prompted for the work presented in this thesis.

7.1 New catalyst and characterisation

A new solid catalyst for the alkylation of phenol with isobutene was designed, the silica gel supported aluminium phenolate. The material was prepared by grafting an aluminium reagent, aluminium trichloride or triethyl aluminium or aluminium triphenolate itself, on the silica gel surface in toluene and, if required, exchange of the ligand with phenol to generate the aluminium phenolate species on the silica surface.

Various preparation methods were investigated. The general scheme was the preparation of supported aluminium on silica gel, then its transformation into the supported aluminium phenolate either in neat phenol or in a solution of toluene – phenol. Both methods led to active catalysts for the phenol alkylation with isobutene, however the former was isolated with great difficulty under a form, which could be easily analysed, while the latter was easily isolated and its characterisation was not prohibited by phenol crystalised on its surface or filling the pores.

Investigation of the nature of the aluminium species on the silica gel surface was undertaken by several techniques, such as nitrogen adsorption studies, elemental analyses, X-Ray PhotonElectron Spectroscopy, Diffuse Reflectance InfraRed Fourier Transform spectroscopy and Magic Angle Spinning Nuclear Magnetic Resonance.

Nitrogen adsorption studies confirmed that the grafting of the aluminium species occurred inside the pores and that this grafting step as well as the ligand exchange step did not alter the structure of the support. However silica gel pre-treatment temperature did have an important effect on the support structure: the pore nature remained the same however the pore volume and the surface area decreased dramatically with the pre-treatment temperature.

Elemental analyses showed that the found loading of aluminium was lower than the theoretical aluminium loading and that this was also depending on the pre-treatment temperature of the silica gel: for a same theoretical loading, the higher the pre-treatment temperature, the lower the found loading.

DRIFT spectra confirmed that the grafting did take place since the bands assigned to silanol groups decreased, and confirmed that the phenolate function was present on the surface of the catalyst. This exchange was also suggested by the MAS-NMR data.

However, not all aluminium ligand of the material, prepared by the grafting of the aluminium precursor reagent on the silica gel surface, were exchanged with phenol, as XPES showed that chlorine atom remained in the final catalyst when it was prepared from aluminium trichloride, and DRIFT showed that ethyl groups were still present on the surface of the catalyst prepared from triethyl aluminium.

Acidity measurements by pyridine titration and triethyl phosphine oxides experiments as well as ^{27}Al MAS-NMR analyses suggested that at least two types of aluminium species were present on the catalyst surface, a mono-phenolate and a diphenolate aluminium species. Depending on the silica pre-treatment temperature, these species are complexed with silanol groups of the silica surface. Two types of acidity, Lewis and Brønsted were identified, with Lewis acidity being the most important.

7.2 Alkylation of phenol with isobutene

The new solid material was successfully applied to the alkylation of phenol with isobutene. The new solid catalyst was active and the general selectivity for the first alkylation (introduction of the first alkyl group on the phenolic ring) was directed to the *ortho-* position. The second alkylation was however mainly directed to the *para-* position. Various reaction conditions and catalyst preparation parameters were investigated in order to tune the catalyst activity and to improve the *ortho-* selectivity for the second alkylation.

Stability of the the two major di*tert*butylphenols produced during the reaction in presence of the catalyst were investigated, and it was shown that the 2,4-di-*tert*butylphenol was more stable than the desired 2,6-DTBP. This stability order does correspond to the expected thermodynamic stability. Hence the stability of 2,6-di*tert*butylphenol would be increased if mild conditions are employed. It was indeed shown in this work that low reaction temperature and low catalyst amount were improving the final yield of 2,6-di*tert*butylphenol. It has however to be borne in mind that too low temperature reaction induced a high level of ether products to be produced.

Three methods of addition of the isobutene were investigated. An addition with a pressure pump has been found beneficial for the *ortho-* selectivity of the catalyst.

Catalyst preparation parameters were also investigated, as aluminium precursor, aluminium loading or support pre-treatment temperature. Aluminium precursor was investigated with the final geometry of the aluminium species on the surface in mind. Precursor like aluminium trichloride or triethyl aluminium led to chemisorbed species with at least one bridge Si-O-Al. The final species was further coordinated with surface silanol groups. These materials were the most active for the alkylation reaction. Catalysts prepared with aluminium triphenolate or aluminium diphenolate chloride, in order to generate a catalyst with more di- or triphenolate aluminium species were not as active.

Low aluminium loading was found beneficial for this alkylation system. Low loading should correspond to more isolated and dispersed aluminium species on the silica gel support, hence the product produced by one site would be less prone to react immediately with another closed aluminium species. The 2,6-di*tert*butylphenol product being less polar than 2,4-di*tert*butylphenol, and the silica gel surface being polar, it was suggested that low surface aluminium concentration would favor the production of 2,6-di*tert*butylphenol as the product would be produce by one aluminium site, diffuse away from the silica surface and have more difficulty to come back to an aluminium species to undergo rearrangements, dealkylations or transalkylations reactions.

Support pre-treatment temperature has been found to play an important role. High silica pre-treatment temperature (above 750°C) was found to be highly desirable. Calcination of the silica gel induces dehydratation of the surface by, first, removal of the physisorbed water, then, by condensation of the surface silanol groups leading to the formation of siloxane bridges. On the other hands, this silanol condensation induces their isolation. Once the aluminium precursor is grafted, the aluminium species is less prone to be complex with silanol groups, affecting the final aluminium coordination number.

Combination of all beneficial effects (aluminium precursor aluminium trichloride, reaction temperature of 70°C, theoretical aluminium loading of 0.8mmolg^{-1}, silica pre-treatment temperature of 750°C, catalyst preparation method ‘tp one-pot’) led to a (so far) optimised yield of 35% of 2,6-DTBP.

7.3 Other alkylation systems and catalyst development

The new catalyst was successfully applied to other alkylation systems. Alkylation of phenol with 1-octene, 1-hexene or cyclohexene led to the *ortho*-product for the mono-*tert*butylphenol. The dialkylated products were however not identified as positional isomers on the phenolic ring and on the alkyl chains led to complex mixtures.

Alkylation of cresols were also investigated. A wide range of cresols derivatives are accessible with the new catalyst.

Alkylation of phenol with propene was also investigated. Surprisingly the dialkylated product was the di*ortho*propylphenol.

Some aspects of the catalyst development towards an industrial use have been investigated. The nature of the chosen K100 silica gel support and its behaviour might prove to be a problem for the safe running of the reaction. The use of solvent during the catalyst preparation was successfully reduced by decreasing the required volume and canceling one washing step.
The new solid alkylation catalyst was reusable. Unfortunately, the reuse of the catalyst might also proved to be problematic in an industrial context as a noticeable decrease of activity was observed. More works would be required in this field to understand the nature of the deactivation. It was however suggest that one possible reason for the deactivation was the change of the aluminium species during the reaction, in particular the ligand nature becoming more and more alkylated, hence bulky.

7.4 General remarks

γ-Alumina is an *ortho*-selective catalyst. For small and linear alkenes, dialkylated products are accessible, but with bulky alkyl such as *tert*-butyl, only the mono--*tert*butylphenols are accessible. Other solid acids are used to produce alkylphenols but, to the best of our knowledge, they are *para*- directing first then the alkylation takes place on the only available *ortho*- position. When the desired product is the di*ortho*- alkylated phenol the catalyst used for its production is the homogeneous aluminium triphenolate.

The new silica gel supported aluminium phenolate described in this work seems to behave differently than all the other catalysts described here, the first alkylation takes place in the *ortho*- position, and the second can be tuned to take place mainly in the *para*- or the *ortho*- position. With small alkenes like propene, the catalyst leads to mainly 2,6-di*tert*butylphenol instead of the 2,4-di*tert*butylphenol observed with isobutene as reactant. This is a similar behaviour similar to

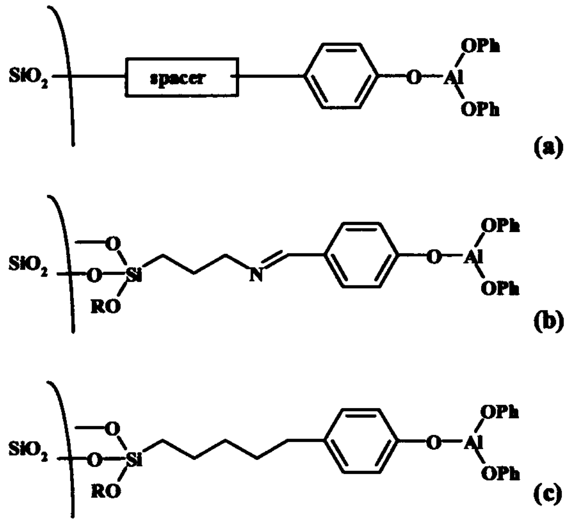


Figure 7.1: Further developments of the silica gel supported aluminium phenolate: (a) introduction of a spacer between the silica surface and the aluminium species; (b) spacer tried without success; (c) ideal spacer.

γ-alumina.

The results described in this thesis suggest that the aluminium species is probably too close from the surface and too close from each other inducing side reactions (these problems have been to a certain extent overtaken by tuning the preparation parameters). To prepare a solid catalyst where the aluminium species exhibits a geometry closer to the homogeneous one but attached to a surface, a spacer could be inserted between the aluminium and the surface (Figure 7.1, (a)). That way, the catalyst would be attached to the surface, hence easily separated, and probably reusable, and the aluminium species would be in a more free "three dimensional" geometry closer to the homogeneous species. Catalysts based on this idea were prepared (Figure 7.1, (b)) but unfortunately, no alkylation was obtained with such material. The material was prepared by grafting an aminopropyl silane on the silica surface. This organo-modified material was then reacted with an aluminium triphenoxy aldehyde. The generated spacer did contain a imine function, which we suggest, affects the acidity of the final catalyst material and may stop the alkylation reaction. A solution to this problem might be the design of spacer based only on alkyl chains (Figure 7.1, (c)).

In the alkylation phenol – isobutene, the preparation of the new silica supported aluminium phenolate can be tuned in order to maximise the yield of either mono-*ortho* *tert*butylphenol, 2,4-di*tert*butylphenol or 2,6-di*tert*butylphenol. However, the maximisation of the 2,6-di*tert*butylphenol yield induced a high yield of 2,4,6-tri*tert*butylphenol. More work is required in this area to further optimise the yield of the much desired di*ortho*- products and, and at the same time, decreasing the yield of the undesired trialkyl product.

All systems using the new silica supported aluminium phenolate required no quenching steps. This is an important improvement over the reaction using homogeneous aluminium triphenolate towards a greener industrial process.

Chapter 8

Notes and References

This thesis was produced using LaTeX[177–179] with the package XyMTeX for drawing the chemical formulas. The source files were edited with WinEdt[180, 181]. For those interesting in discovering of these softwares, numerous "Gentle Introduction" to "for advanced users" documentations can be found[179, 181–184].

To ease the bibliographical research of the reader, maximum details regarding each references are provided. ISBN numbers are given when known. Internet web addresses (URL) were checked and were valid at the time given.
Efforts were taken by the author to keep the same number for a particular reference through the whole thesis.

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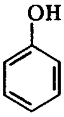
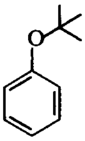
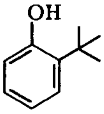
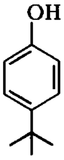
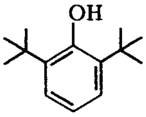
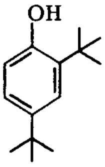
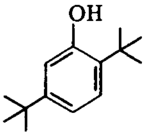
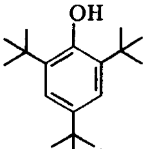
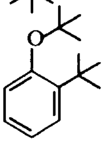
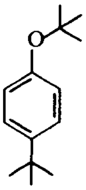
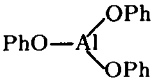
Appendix 1

Alkylation of phenol with isobutene

Molecule	Name	Abbrev.	Colour (plots)
	phenol	PhOH	Royal blue
	*tert*butylphenylether	TBPE	Magenta
	mono-*ortho tert*butylphenol	OTBP	Red
	mono-*para tert*butylphenol	PTBP	Orange
	2,6-di*tert*butylphenol	2,6-DTBP	Green
	2,4-di*tert*butylphenol	2,4-DTBP	Blue
	2,5-di*tert*butylphenol	2,5-DTBP	Not plotted
	2,4,6-tri*tert*butylphenol	TTBP	Black
	*tert*butyl-(2-*tert*butylphenyl)ether	TBOTBPE	Not plotted
	*tert*butyl-(4-*tert*butylphenyl)ether	TBPTBPE	Not plotted
	aluminium triphenolate	$Al(OPh)_3$	N. A.