



The
University
Of
Sheffield.

Sustainable Chemistry & Process Intensification of Bioinspired Silica Materials

Joseph Richard Henry Manning

A thesis submitted in partial fulfilment of the requirements for the degree of Doctor of
Philosophy.

The University of Sheffield
Faculty of Engineering
Department of Chemical and Biological Engineering

March 2019

Abstract

Silica is the world’s most abundant mineral, occurring naturally in both geological formations and biological minerals. Artificially, silica is used in wide ranging applications e.g. polymer fillers, creating a US\$6.9B/annum market. Current manufacturing methods require a silica salt and mineral acid for synthesis, achieving control over properties through careful modification of reaction conditions. Incorporation of non-reacting template molecules to the synthesis extends silica’s capability, imprinting complex and ordered porosity into the material, however this necessitates post-synthetic activation, stymieing commercialisation due to high environmental and processing costs.

Taking inspiration from natural silica materials deposited by complex biomolecular templates, bioinspired silica (BIS) materials made using organic ‘additives’ have been developed. These materials combine rapid, mild synthesis found in biological silicas with organic-imprinted porosity found in templated silicas, bridging the gap between material families. This work develops new BIS synthesis methods to further explore the relationship between biological, templated, and bioinspired silica materials, and to develop BIS as a technology suitable for commercialisation.

First, recent commercial feasibility calculations were validated by scaling up the synthesis and optimising it according to industrial feedback. Manipulation of BIS colloid chemistry was used to imprint mesopores of a uniform size into BIS’ structure for the first time. This is the first rapid (10 minute), room temperature, aqueous mesoporous silica synthesis (compared to several hours at high temperature in alcoholic solvents), greatly improving its behaviour and hence applications. Novel, room-temperature activation of BIS through acid extraction was also developed, the first such method for any templated silica. This enabled in-depth investigation of interfacial bonding, explaining BIS’s unusual surface chemistry and the mech-

anism of acid extraction, providing new insight into the relationship between additives and silica in BIS and other templated silicas. Finally, the ramifications of combining the above techniques is analysed along with the effect their development has on the large scale manufacturing techno-economics, establishing a clear route to commercialisation of the technology.

Acknowledgments

First of all, I would like to thank my supervisor, Professor Siddharth Patwardhan, for his constant encouragement and advice which have been instrumental in producing this work, spurring me onwards to take the initiative with my research and infer ever-deeper insights from the data I gathered. I would further like to thank my second supervisor, Dr. Sarah Staniland, for her support and guidance during the latter half of my PhD. Furthermore, I would like to thank the supervision of Professor Henrik Heinz of CU Boulder and his research group, who graciously hosted me for three months in 2018 to learn the technique of atomistic molecular dynamics. Although not reported there, the research I carried out at CU has been instrumental in helping guide my future career ambitions.

I would also like to thank my many academic collaborators who enabled me to use a more diverse range of techniques throughout this project. Dr Miguel Jorge and Dr Alessia Centi undertook several computational chemistry experiments to complement my experimental results. Dr Sandra van Meurs and Dr Brant Walkley both performed and provided copious amounts of advice regarding NMR spectroscopy (solution and solid-state). Dr Gemma-Louise Davies and her students provided valuable insight into the relaxometry behaviour of materials made herein for use in MRI. Carlos Brambila applied his extensive microscopy skills to produce some of the silica micrographs reported. My good friends Dr. Dorin Simionesie and Justin Driver provided guidance and discussion for dynamic light scattering at thermogravimetric analysis, respectively. Beyond this, the technical staff at Stratchylde, Sheffield, and Newcastle universities provided key help at several points of this project to aid in data gathering and equipment preparation. I would also like to thank my groupmates, both past and present, for their help with further techniques & discussions, and their patience with my never-ending presentations at group meetings.

Finally, I would like to thank my family, my partner Kasia Majerczak, and all of my friends for their love and support over the past 5 years, without whom this process would have been far less rewarding.

Research output

Several peer-reviewed publications have resulted from this project, which are listed below:

1. Manning, J.R.H., and Patwardhan, S.V., "A method for producing porous functional silica through acid treatment," *Patent WO2017037460*, (2015); based on the results described in chapter 5
2. Manning, J.R.H., Yip, T.W.S., Centi, A., Jorge, M., and Patwardhan, S.V., "An eco-friendly, tunable and scalable method for producing porous functional nanomaterials designed using molecular interactions," *ChemSusChem* **10**, 1683 (2017); based on the results described in chapter 5
3. Manning, J.R.H., Routoula, E. and Patwardhan, S.V., "Preparation of Functional Silica Using a Bioinspired Method," *J. Vis. Exp.* **138**, 1 (2018); based on the results described in chapter 3
4. Patwardhan, S.V., Manning, J.R.H, and Chiacchia, M., "Bioinspired synthesis as a potential green method for the preparation of nanomaterials: Opportunities and challenges," *Curr. Op. Green Sus. Chem.* **12**, 110 (2018); based on the results described in chapters 1 and 5
5. Centi, A., Manning, J.R.H., van Meurs, S., Patwardhan, S.V., and Jorge, M., "The role of charge-matching in nanoporous silica formation," *Materials Horizons*, accepted for publication (2019); based on work not reported herein
6. Manning, J.R.H., Walkley, B., Provis, J.L., and Patwardhan, S.V., "Catalysis -directed surface chemistry of inorganic surfaces by bioinspired sorbents," *JACS*, under review; based on findings reported in chapter 5
7. Manning, J.R.H., Brambila, C.M., Balashanmugam, A., and Patwardhan, S.V., "Colloidal seeding of mesoporous materials using bioinspired methods: a sustainable and scalable approach," *in preparation*; based on findings reported in chapter 4
8. Manning, J.R.H., Heinz, H., and Patwardhan, S.V., "Computationally-predicted purification of MCM-41 using environmentally-friendly methods," *in preparation*; based on work not reported herein

Contents

1	Introduction	1
1.1	Silica materials	2
1.1.1	Silica in the natural environment	2
1.1.2	Artificial silica materials	3
1.2	Sol-gel silica synthesis	4
1.2.1	Initial molecular polymerisation	4
1.2.2	Colloid-colloid interactions determining stability and aggregation . .	8
1.2.3	Practical ramifications of DLVO theory	12
1.2.4	Impact of the sol-gel pathway on silica manufacture	15
1.3	Flexibility of internal particle structure	17
1.3.1	Internal porosity in nanoparticles	17
1.3.2	Porous silica zeolites	19
1.3.3	Supramolecular templated silicas	24
1.4	Assessing the sustainability of templated silica materials synthesis	28
1.4.1	Green chemistry	28
1.4.2	Quantifying environmental friendliness	30
1.4.3	Green nanomaterials	31
1.5	The dichotomy between artificial and natural templated silicas	33
1.6	Bridging the gap: bioinspired silica	36
1.6.1	Bioinspired silica synthesis mechanisms	37
1.6.2	Application of bioinspired silicas	43
1.6.3	Technological development of bioinspired silica synthesis	44
1.7	Summary	45
1.8	Goals of this project	48
1.8.1	Aims and scope	48

1.8.2	Structure of this thesis	49
2	Materials and Methods	51
2.1	Synthetic techniques	51
2.1.1	Bioinspired silica synthesis	51
2.1.2	Silica nanosphere syntheses	54
2.2	Post-synthetic modification	56
2.2.1	Organics removal via calcination	56
2.2.2	Organics removal via acid elution	56
2.3	Analytical techniques	57
2.3.1	Reaction mixture analysis	58
2.3.2	Analysis of solid silica materials	70
2.3.3	Analyses performed by others	79
2.4	Chemical reagents	80
3	Scaleup and process intensification of BIS	83
4	BIS effluent recycling and synthesis using colloidal reagents	85
5	Post-synthetic silica modification through acid extraction	87
5.1	Introduction	87
5.1.1	Additives used within this chapter	89
5.2	BIS purification by acid washing	90
5.2.1	Structural investigation and chemical activation by partial extraction	96
5.3	Investigating additive-BIS bonding	98
5.3.1	Developing mechanistic understanding through atomistic molecular dy- namics	98
5.3.2	Spectroscopic investigation of the PEHA-BIS interaction	102
5.4	Impact of acid extraction on BIS technology	113
5.4.1	Impact upon proposed silica manufacturing processes	113
5.5	Conclusion	114
6	Conclusions and future work	117
6.1	Motivation	117

6.2 Main findings 117

6.3 Recommended future research 118

List of Figures

1.1	Schematic of sol-gel reaction pathway	6
1.2	Schematic of sol-gel reaction pathway	7
1.3	Visualisation of particle-size dependency of surface ionisation	9
1.4	Visualisation of overall interaction potential between two charged colloids . .	12
1.5	Visualisation of coagulation and gelation phase separation phenomena	14
1.6	Partial experimental phase diagram for the three component water-silica-organic base system	16
1.7	Scheme of possible pore types within a solid particle	18
1.8	Geometric representations of zeolite cages and their possible arrangements .	20
1.9	Proposed mechanism of template action using TPAOH to create zeolite type ZSM-5	22
1.10	Illustration of the action of a reversibly deconstructable template for the syn- thesis of zeolite ZSM-5	24
1.11	Scheme showing the various liquid-crystal topologies that can be templated into silica materials	25
1.12	Summary of a 4-stage iterative green emetrics analysis toolkit for development of new chemical processes	32
1.13	A range of diatom cell wall structures, showing their structural diversity . .	33
1.14	Structure of important diatom biomolecules for biomineralisation	34
1.15	Proposed heirarchical self-assembly mechanism for the formation of pore sys- tems in diatoms	35
1.16	Representative range of biological and bioinspired additives previously used for BIS synthesis	38
1.17	Repeat structure of ethylenediamine (MEDA) and its analogues used herein.	39

1.18 Scheme of silica condensation rate determining step with varying levels of assistance by amine templates	40
1.19 Comparison of particle coagulation in unbuffered and buffered BIS syntheses	43
1.20 Comparison of silica synthesis methods and the effect of (meso)structure-direction and activation on final properties	47
2.1 Schematic drawing of a pH probe.	60
2.2 Graph of changing photometric absorbance against Si concentration during the molybdenum blue test	65
2.3 Schematic of autocorrelation functions generated for two typical light scattered signals	69
2.4 Graph of scattering intensity versus particle size for a mixture of 10nm and 55nm silver nanoparticles	69
2.5 Graph of typical autocorrelation data generated in this study	71
2.6 Graph of 6 typical categories of BET adsorption isotherms as defined by the IUPAC	75
2.7 Four characteristic types of t-plot curves	76
2.8 Visualisation of the four key types of hysteresis as defined by IUPAC, and their associated typical pore structures	77
5.1 Structure of the bioinspired additives used within this chapter	90
5.2 Graph of additive concentration in silica versus washing pH determined by elemental analysis for materials A and V fitted to sigmoidal trend lines. . .	91
5.3 Effect of treatment method on BET surface area of material A after a range of post-synthetic modifications	92
5.4 Effect of treatment method on BJH pore size distribution for material A after a range of post-synthetic modifications	93
5.5 Total and microporous surface area of material A as measured by t-plot. . .	94
5.6 Scanning electron micrographs of material A as made and after extraction at pH 2	94
5.7 Calculated additive volume removed and measured micropore volume created from additive removal against treatment pH	95

5.8	Graph of CO ₂ uptake after 12 hour equilibration times at either 100 or 1000mbar.	97
5.9	CO ₂ uptake kinetic curves at 100 mbar of material A after acid washing to different pH	98
5.10	CO ₂ uptake kinetic curves at 1000 mbar of material A after acid washing to different pH	99
5.11	Visualisation additive molecule distribution within secondary particles of bioinspired silica, which are composed of primary particles	100
5.12	Representative snapshots from classical MD simulations of PEHA molecules on a silica surface under different pH conditions	101
5.13	Comparison of acid extraction effectiveness between poly(ethyleneimine) (PEI) and permethylated poly(ethyleneimine)	102
5.14	FTIR analyses of BIS silica A treated to pH 7, pH 5, pH 2, and untreated IPS. Raw data are in black, gaussian peak deconvolutions in green, sum of deconvoluted signals in red, and fitted curve error is in blue (offset for clarity).	103
5.15	Graph of relative Si–OH/Si–O–Si prevalence in BIS material A treated at difference pH values and IPS.	104
5.16	²⁹ Si single-pulse MAS NMR spectra for BIS and IPS after treatment at pH 7, 5, and 2	105
5.17	Relative abundance of Si species against extraction pH for IPS and BIS materials	106
5.18	¹ H- ²⁹ Si CP MAS NMR spectra for BIS and IPS washed at pH 7, 5, and 2 . .	107
5.19	Relative abundance of Si species against extraction pH for IPS and BIS materials	108
5.20	Proposed scheme for reactive adsorption of PEHA to bioinspired silica surfaces	112

List of Tables

1	A list of acronyms and abbreviations used in this project	xii
2.1	Absolute ammonia concentration, volume, and final particle size for Stöber silica synthesis	55
2.2	Reported ranges of thermal decomposition for different chemical species . . .	77
2.3	Chemicals used within this project	81
2.4	Synthesis, separation, and analytical equipment used within this project . . .	81
5.1	Silica surface charge density as a function of pH	100
5.2	Table of comparisons in relative peak area for silicon species within precipitated and bioinspired silica materials against pH for both single-pulse ^{29}Si MAS spectra and proton cross-polarised ^1H - ^{29}Si spectra for the same samples	116

List of abbreviations

Table 1: A list of acronyms and abbreviations used in this project

Term	Definition
SDV	Silica deposition vesicle
DLVO Theory	Derjaguin-Landau-Verwey-Overbeek theory of colloidal suspensions
TRL	Technology readiness level
CSTR	Continuously-stirred tank reactor
RPM	Revolutions per minute
HSP	Hard-sphere packing theory of colloidal assembly
CCC	Critical coagulation concentration
BIS	Bioinspired silica
IPS	Industrial precipitated silica
TEOS	Tetraethylorthosilicate - an alternative Si source
TPAOH	Tetrapropyl ammonium hydroxide - a zeolite template
ZSM-5	A zeolite templated by TPAOH
SDA	Structure-directing agent
PEO	Poly(ethyleneoxide) - part of a mesoporous silica template with PPO
PPO	Poly(propyleneoxide) - part of a mesoporous silica template
MCM	Mobil composition of matter - a mesoporous silica family
CTAB	Cetyl trimethyl ammonium bromide - template for the MCM family
HMS	MCM-equivalent material produced with dodecylene instead of CTAB
MSN	Mesoporous silica nanomaterials - discrete colloidal MCM silicas
DLS	Dynamic light scattering
SEM & TEM	Scanning and transmission electron microscopy
NMR	Nucleomagnetic Resonance Spectroscopy
FTIR	Fourier-transform Infrared Spectroscopy
UV-Vis	Ultraviolet and visual light Spectroscopy
BET	Brunauer-Emmet-Teller Theory of gas adsorption
BJH	Barrett-Joyner-Halenda Theory of pore-size distribution
MD	Molecular dynamics simulations
INTERFACE	An atom-atom interactions ‘force field’ used in MD

Table of materials

Redacted due to commercial sensitivity of contents.

Chapter 1

Introduction

1.1 Silica materials

1.1.1 Silica in the natural environment

Silica (SiO_2) is the world's most abundant material, comprising (in pure form or as silicate minerals) 85-90% of the Earth's crust by weight.¹ Geological silica and silicates are chiefly crystalline, however with a remarkable number of allotropes. This is largely based on the variety of ways in which the fundamental silica units (the tetrahedral, 4-valent SiO_4^{4-} ion) polymerise, as well as the effects of metal substitutions in the mineral framework. In the simplest example, where the tetrahedra are either unpolymerised or only bonded to one or two further tetrahedra, minerals such as olivine, pyroxene and bentonite act like conventional ionic salts. Further conjugation to three other silica tetrahedra creates flat sheets which stack together in parallel to form (industrially-useful) clay minerals such kaolinites or montmorillonites, with ionically-bonded counterions intercalated in between layers. Finally, fully conjugated tetrahedra form 3d structures wherein each corner of the silica tetrahedron is connected to another - creating closely-packed quartz for pure silica, or feldspar minerals in cases with transition metal substitutions.²

Silicate minerals' properties are heavily impacted by these structural features. Densely-packed quartz is very hard, scoring 7 on the Mohs hardness scale, leading to industrial applications in sandblasting, hydrofracking, and as an abrasive. Quartz also exhibits piezoelectricity, enabling applications as oscillators in watches, clocks in integrated circuits and quartz crystal microbalances.³ Kaolinites and other layered clays are also industrially useful, with a range of host-guest and intercalation chemistry between silicate sheets rendering them useful as cost-effective pollutant sorbents.⁴

Beyond the lithosphere, silica in its noncrystalline form is a key component in several biological and industrial systems, again because of its natural abundance and structural flexibility. Silica substitutes for cellulose in the cell walls of several common plants such as in grasses & sponges, as well as in diatoms - a water-dwelling plankton that is ubiquitous in both freshwater and saltwater systems - largely due to the lower energy requirements of silica cell wall formation compared to cellulose.⁵ Unlike geologically-formed crystalline silicas and silicates, these materials are formed through at ambient temperature and pressure in sparse

conditions (the ambient concentration of silica in the ocean is ca. 4 mM,⁶ barely above the reported solubility limit at ambient pH of ca. 2 mM).⁷ Despite these difficult conditions, biomineralised silica is incredibly abundant in nature - diatoms mineralise over 10 million tons of silica per annum.⁸

In order to achieve this, diatoms need to capture ambient dissolved silica, concentrate it within certain parts of the diatom cell, then provide the correct conditions for silica precipitation. Through evolution, biomolecules have specifically evolved to manipulate silicate ions. Specific silica transport proteins (SiTs) act to shepherd dissolved silicates into the diatom cell, ensuring that an ideal internal concentration is maintained regardless of external conditions.⁹ The mechanism of transport of these silica precursors within the diatom cell itself has yet to be fully understood, however eventually they end up in a specialised silica deposition vesicle (SDV).¹⁰ The SDV then simultaneously shapes silica and creates conditions for silica polymerisation - specialised proteins shape the silica as it forms and increase the local acidity to induce precipitation.¹¹

1.1.2 Artificial silica materials

Industrially, noncrystalline ‘precipitated’ silica (otherwise known as specialty silica) has been in use since the 1940s in a range of applications. Precipitated silica is a soft white powder comprised of solid silica spheres agglomerated into larger structures. Although the individual silica tetrahedra (the SiO_4^{4-} tetrahedra) are the same as in all natural silicas, the geometry by which those tetrahedra are connected is disordered in precipitated silicas, leading to its amorphous nature and controllable properties. At present, precipitated silica is largely used as a filler in polymer blends (notably rubber for tires and shoe soles),^{1,12} with lesser usages as a powder free flow or anti-caking agent, mild abrasive in toothpaste, and pharmaceutical excipient.¹² Indeed, current global manufacturing of silica exceeds 2.9 million tons per annum corresponding to a market worth US\$ 6.9 billion annually.¹²

The flexibility of precipitated silica (in terms of its physical characteristics) is the key factor that makes it so versatile and widely used. Properties such as surface area, particle size, and density can all be adjusted to the application with only minor modification to the

production method, leading to enhanced silica performance.¹³ Additionally, post-synthetic modification enables control over surface properties like hydrophobicity and -philicity, broadening the potential applications for silica.¹ To take the example of rubber blending for tires, silica has been adopted over the past 25 years to optimise tread characteristics such as wear, rolling resistance, and heat buildup, constituting up to 50% by mass to the final rubber blend.¹⁴ To achieve this, silica has to be tuned to improve its interactions with the (highly hydrophobic) rubber polymer. This is achieved by optimising the surface chemistry with sulphur-containing organic compounds e.g. TESPT (bis-(triethoxysilyl)propyl tetrasulphide - $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{S}_4(\text{CH}_2)_3\text{Si}(\text{EtO})_3$) to ensure the best crosslinking between rubber and silica.

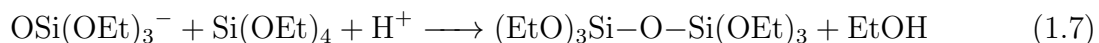
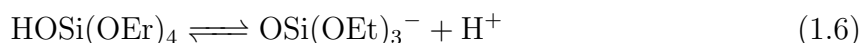
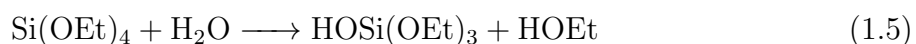
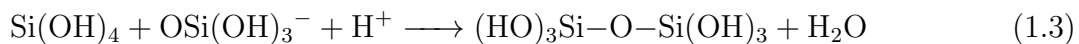
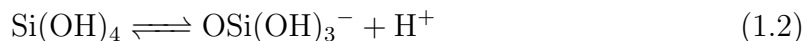
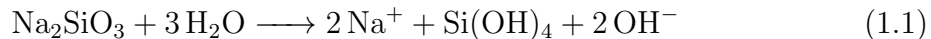
Besides these applications, silica has the advantage of being a highly safe material in general - it is registered as a food additive in the EU (E 551), and the US Food and Drug Administration has marked them as "generally regarded to be safe," indicating that they can be used in food and pharmaceutical agents with little to no regulatory hurdles.¹⁵ Combined with the environmental abundance and compatibility of silica in general (which simplifies widespread usage in consumer products and their later disposal), precipitated silica is a simple material for usage in a wide range of products to fine-tune their physical properties.

1.2 Sol-gel silica synthesis

1.2.1 Initial molecular polymerisation

Manufacturing of precipitated silica has varied little over the course of its industrial usage,^{1,16} following the sol-gel route developed in the early 20th century,¹⁷ which takes advantage of pH in an aqueous environment similarly to a diatom's SDV to induce silica polymerisation. Initially, a silica salt or alkoxide is (partially) hydrolysed to form silicic acid in solution (equations 1.1 and 1.5, respectively). After this, they undergo deprotonation in equilibrium with the water in solution, creating siloxide anions (equations 1.2 and 1.6) which are reactive to further silica monomers (equations 1.3 and 1.7). Finally, these undergo fur-

ther polymerisation to silicon dioxide, eliminating all water or alcohol from their structures (equations 1.4 and 1.8, respectively).¹⁸



Although reactions 1.1 to 1.8 appear equivalent despite their different precursors, there are several nuances to the sol-gel caused by the use of one over the other. Largely this is due to the equilibrium behaviour of the two precursors on solution: while TEOS polymerisation can only be possible after initial hydrolysis, sodium silicate naturally exists as an equilibrium between monomers and octamers in solution rather than a single, predictable species.^{19–21} Therefore, sol-gel syntheses using TEOS are advantageous for situations requiring greater control over the initial stages of polymerisation, both due to homogeneity of the starting material and control afforded by manipulating H_2O in equation 1.5. Conversely, the relative simplicity (and hence lower price) of sodium silicate molecules makes them more cost-effective in bulk situations such as industrial production on the ton scale.²²

Aside from hydrolysis behaviour, sol-gel polymerisation of silica is highly pH-dependent. Each step within the reaction procedure involves transfer of protons into and out of solution, therefore the ambient H^+ concentration changes the chemical equilibrium between neutral, anionic, and cationic silica species in solution (cationic species only being relevant at very acidic environments). As both neutral and charged species are required for the reactions in equations 1.3 and 1.7, this leads to regions of relative stability at extremes of the equilibrium

- at very high pH, for example, only anionic species are present and no silica will polymerise. In fact, above pH 12, silica will spontaneously dissolve into solution to form monomeric silicate anions. Similarly, at the point where the equilibrium is perfectly balanced between anionic and cationic (ca. pH 2), polymerisation rates will also be at a minimum (although it will not stop entirely due to the dynamic nature of the equilibrium enabling some short-lived charged species to exist. These phenomena are graphically summarised in figure 1.1.

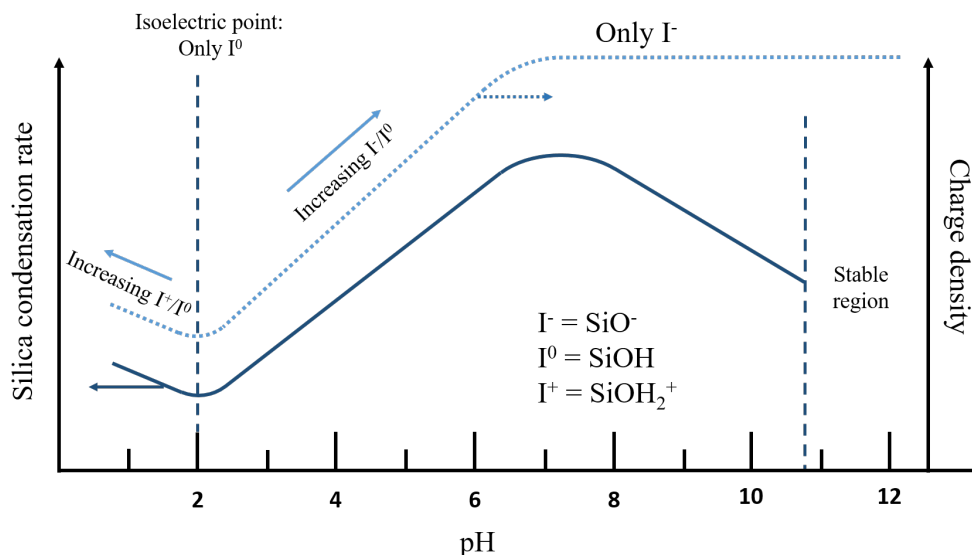


Figure 1.1: Graphical visualisation of relative silica condensation rates (solid line, left axis) and silica monomer charge density (dotted line, right axis) versus pH in aqueous solution. Adapted from reference 7.

As would be expected, polymerisation rates can also be controlled by changing water concentration within the reaction solution: incorporation of nonaqueous solvents with higher acid dissociation constants (pK_a) than water e.g. alcohols lowers the overall proton activity of the solution.^{23,24} This reduces the rates of proton transfer essential for every step of the silica condensation reactions, in essence stabilising the material regardless of its current polymerisation state.

Despite the similarities in polymerisation pathway, the initial chemical species has an important effect on the early stages of the sol-gel reaction pathway (shown in figure 1.2). Early stages of the sol-gel polymerisation are highly impacted by molecular polymerisation - forming small chains such as hexamers and octamers. These then polymerise further until they form a colloidal particle through a process similar to crystal nucleation.^{18,20} Although the exact mechanism of colloid nucleation and growth are an ongoing area of research,²⁵

herein the importance of TEOS comes to the fore - monodisperse silica colloids can only be formed using the alkoxide as a precursor rather than sodium silicate, because the partially-polymerised nature of sodium silicate solutions is incompatible with uniform nucleation.²⁶ Furthermore, the pK_a of silica lowers with greater polymerisation, so once colloids have been formed they immediately become the most highly deprotonated and hence the most reactive species. This leads to the phenomenon of Ostwald ripening, where smaller silica species are predisposed to dissolution and re-deposition onto larger particles, leading to particle growth (shown in the rightmost arrow of figure 1.2), creating a "sol" of colloidal particles.^{7,20} Regardless of the monodispersity of the colloidal sol, at this point the sol-gel mechanism is dominated by colloid-colloid interactions.

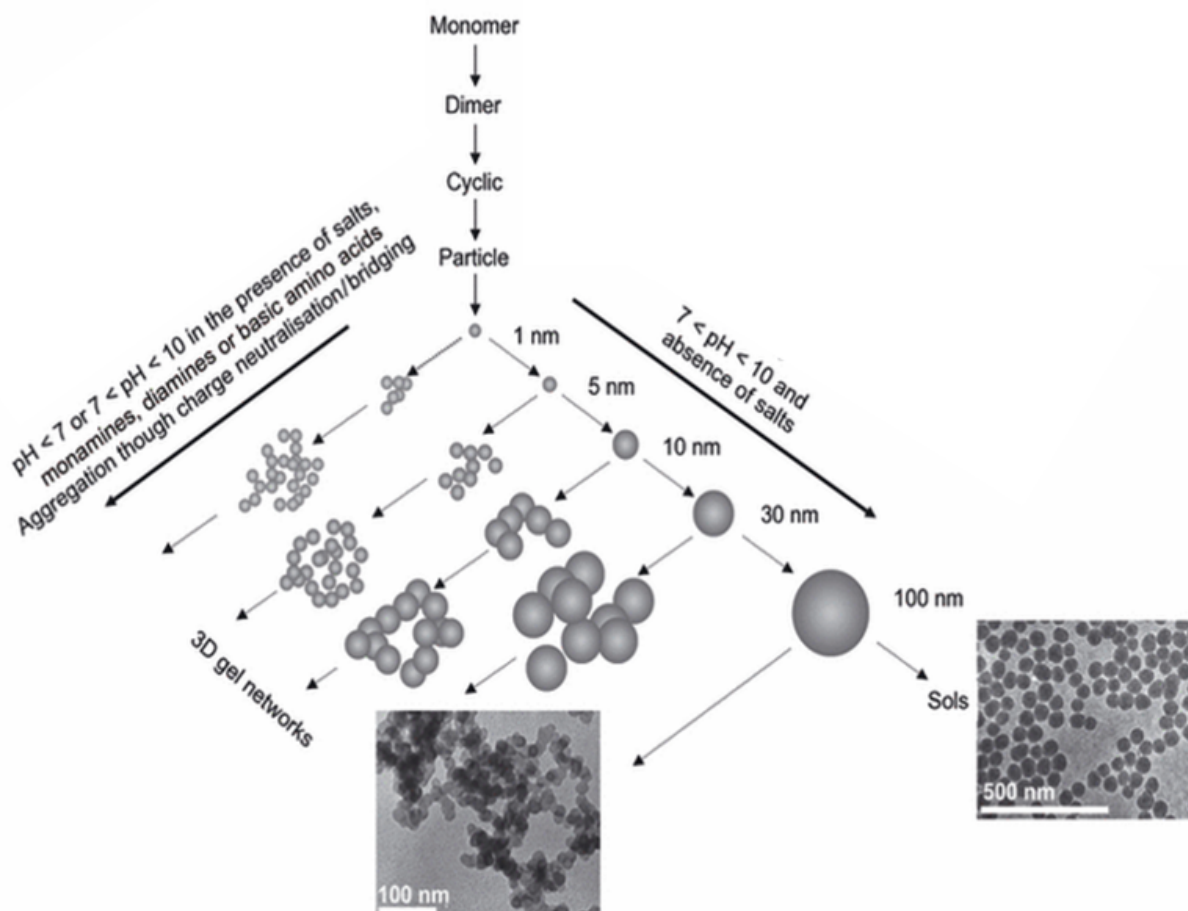


Figure 1.2: Schematic of sol-gel reaction pathway for silica originally proposed by Iler,⁷ showing initial particle formation, followed by reaction pathway divergence into (right) sol-style separated particle growth, and (left) particle coagulation or gelation. Adapted from reference 20.

1.2.2 Colloid-colloid interactions determining stability and aggregation

Surface charges of colloids

Once silica has polymerised to above a certain length scale (in the order of 1-10 nm),⁷ species stop acting like individual macromolecules but rather as solid particles dispersed within the reaction medium – a phase of matter known as colloids. Within these phases, the properties of individual molecules or monomeric constituents (here SiO_2) and their interactions with dissolved monomeric species become less significant, being superseded by properties of the bulk material. The transition from molecule-like to bulk material-like behaviour is highly size-dependent, however, creating the possibility of controlling colloidal behaviour e.g. fluorescence by changing particle radius alone.

For silica, this most highly impacts surface charge. Whereas charge in molecular SiO_4 is only a function of pH, mutual repulsion between neighbouring surface functionalities (i.e. $-\text{SiOH}$ moieties, hereafter surface hydroxyls) reduces the overall charge compared to an overall bulk material.²⁷ For smaller particles with very few surface hydroxyls this effect is highly pronounced due to the confinement of surface hydroxyls near one another. However, as particles grow so does the overall surface hydroxyl population, enabling the surface to act more like a bulk material (this is visualised in figure 1.3).²⁸

Surface charge on colloid particles has significant ramifications to their behaviour in solution, especially in terms of how they interact with dissolved electrolytes. As can be seen from figure 1.3, colloidal silica will have a net negative charge above pH 2 (similar to the monomer behaviour in figure 1.1). This will lead to association of dissolved cations towards the silica surface, creating an ‘electronic double layer’ of adsorbed and entrained ions around the particles, whose size depends on both surface charge and the solution ionic strength. Furthermore, as the particle grows its surface charge density changes, meaning the electronic double layer size is also a function of particle size.²⁹ Combined, this all leads to an overall potential difference between silica particle surfaces and the bulk solution - a zeta potential -

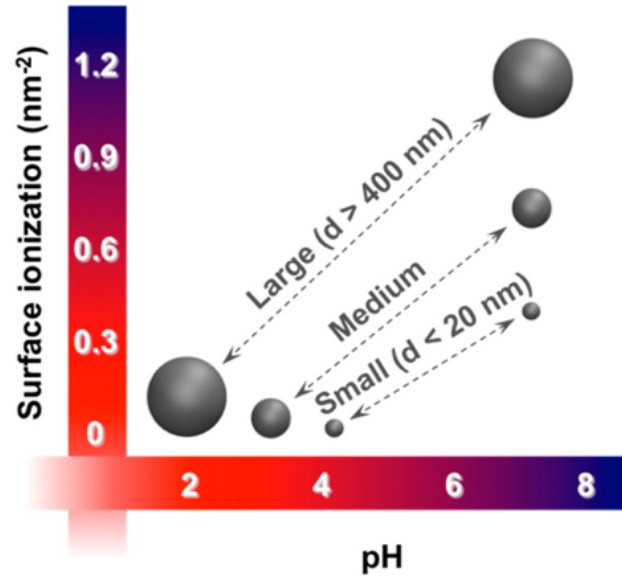


Figure 1.3: Visualisation of surface ionisation (hence charge) for silica particles of 3 different size categories with changing pH. Adapted from reference 28

which dominates interparticle interactions.

The DLVO theory of charged colloid interactions

So why is this important to the sol-gel mechanism? As shown in figure 1.2, after a certain amount of growth, a sol of colloidal particles forms. The behaviour of this sol, and the material that is eventually formed from them, is determined by the colloidal interactions occurring on them during this stage of the synthesis. Key to relating between electronic double layer behaviour and colloidal interactions is the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of forces acting between charged lyophobic surfaces in a liquid medium.³⁰ This theory states that the forces active between two charged colloids are a balance between their Van der Waals attractions and electrostatic repulsions.

The strength of Van der Waals interactions between individual molecules relates to the distance between those particles according to a 6th order decay (i.e. $U_{VdW}(r) \propto r^{-6}$ where U_{VdW} is the interaction strength and r the intermolecular separation). For macroscopic particles made of many molecules or atoms, the interaction is highly different, however.³¹ Due to the larger sizes of these particles, the interaction depends both on the size of each particle (R_i) and the distance between them (d), as shown in equation 1.9, where A is a constant

coefficient of interaction specific to the materials involved and $z = R_1 + R_2 + d$. Under the condition where the particle separation is significantly smaller than their radii (equation 1.10), i.e. all situations wherein the interaction is significant, the attractive potential simplifies to equation 1.12 which only decays according to r^{-1} rather than r^{-6} . Significantly, the interaction strength increases linearly with R , meaning that as individual colloids grow, so do their mutual attractions.

$$U_{VdW} = -\frac{A}{6} \left(\frac{2R_1R_2}{z^2 - (R_1 + R_2)^2} + \frac{2R_1R_2}{z^2 - (R_1 - R_2)^2} + \ln \left[\frac{z^2 - (R_1 + R_2)^2}{z^2 - (R_1 - R_2)^2} \right] \right) \quad (1.9)$$

$$\text{Let } d \approx 0 \text{ and } R = R_1 = R_2 \quad (1.10)$$

$$z \approx 2R \quad (1.11)$$

$$U_{VdW} \approx -\frac{A \cdot R}{12r} \quad (1.12)$$

As previously mentioned, Van der Waals attractions are balanced by repulsive electrostatic interactions, otherwise no stable colloids could exist. The electrostatic interaction potential energy $U_E(r)$ of two interacting colloids separated by distance r is defined according to equation 1.13.

$$U_E(r) = k_B T Z^2 \lambda_B \left(\frac{e^{\kappa R}}{1 + \kappa R} \right)^2 \frac{e^{-\kappa r}}{r} \quad (1.13)$$

Where k_B is the Boltzmann constant, T is the temperature, Z is the charge on each colloid, λ_B is the Bjerrum length (the value of r where electrostatic interactions become equal to $k_B T$, defined in question 1.14), and κ^{-1} is the Debye screening length (the characteristic persistence length of charged forces within the solution dielectric field, defined in equation 1.15).³²

$$\lambda_B = \frac{e^2}{4\pi\epsilon_0\epsilon_r k_B T} \quad (1.14)$$

$$\kappa^2 = \frac{\epsilon_0\epsilon_r k_B T}{4\pi e^2 c_{ion}} = \frac{1}{\lambda_B c_{ion}} \quad (1.15)$$

Where ϵ_0 is the vacuum permittivity, ϵ_r is the relative fluid permittivity, c_{ion} is the overall ionic strength of the solution. Equation 1.13 highlights a number of important parameters controlling the repulsion of colloids - higher surface charge Z (i.e. zeta potential) leads to stronger repulsion, whereas increasing c_{ion} significantly reduces it due to increased electrostatic screening. Although according to equation 1.13 increasing temperature would appear to strengthen the repulsion, in reality this may not occur as heightened temperature will also promote higher dissociation between dissolved electrolytes and hence greater screening. Finally, increasing colloidal particle size R also increases electrostatic interaction strength with a dependency of $(\exp(R)/(1+R))^2$. However, this is partly counteracted by increasing Van der Waals attractions, which varies linearly with R . This means that increasing R leads to overall increased repulsion, giving rise to stable colloids once they have grown above a certain size. Interestingly if the two interacting particles have difference sizes (i.e. the dispersion is polydisperse), aggregation of the smaller particles onto larger particles may occur, even in cases where the two particles are individually stable.¹⁸

With regards to particle separation, electrostatic interactions decay faster than Van der Waals interactions (with $r^{-1} \exp(-r)$, rather than just r^{-1}), leading to some potentially complex behaviour when the two are combined. This is visualised in figure 1.4, which shows the summation of U_{VdW} and U_E to form an overall interaction potential U . In this figure, high electrostatic repulsion leads to an energy barrier preventing colloids from directly interacting, however the faster decay allows for a weaker second minimum in the total interaction, enabling formation of a loose colloidal floc which is relatively simple to redisperse.

Although the DLVO theory is overly simplistic in its assumptions to accurately describe real-world situations outside of a very specific conditions, largely due to its key assumptions such as solvents and electrolytes behaving at uniform bulk conditions between particles,³⁰ it provides an invaluable starting point for understanding colloidal interactions. More complex

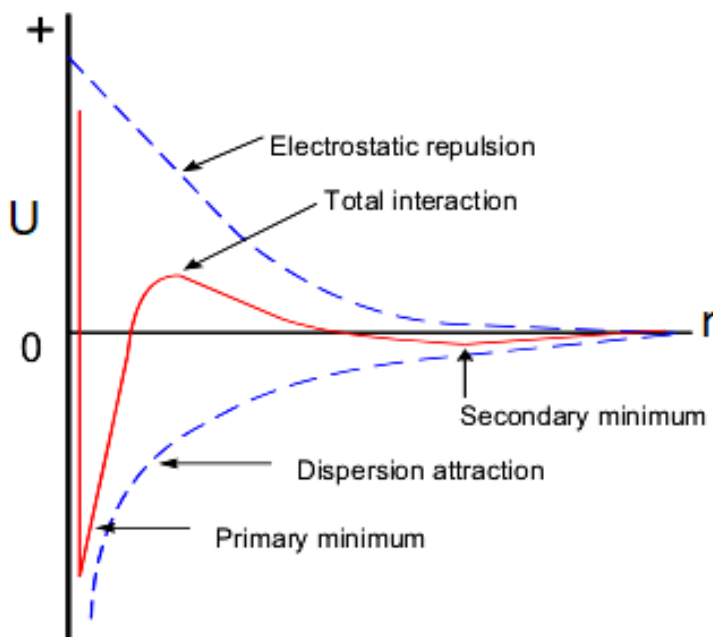


Figure 1.4: Visualisation of overall interaction potential (U) between two charged colloids separated by distance r .

situations such as the incorporation of charged polyelectrolytes (which will be discussed later in section 1.6) cause significant changes in colloidal behaviour, which can be leveraged to modify overall colloidal interaction strengths to the desired amount.³³

1.2.3 Practical ramifications of DLVO theory

On the basis of this theory, and the two component interaction shown in figure 1.4, three experimental conditions can arise from DLVO theory: a net repulsive interaction, balanced repulsive and attractive interactions, and net attractive interactions.

Net repulsion - stable colloids

So long as electrostatic repulsion remains high, silica sols are highly stable, allowing them to be stored practically indefinitely for later use and manipulated without fear of unwanted phase change. As a result, colloidal sols are often used as standard samples for techniques such as dynamic light scattering (a technique for measuring sizes of dispersed particles in liquids, further discussed in chapter 2). Furthermore, this allows colloidal sols to be used as reliable reagents for formation of complex materials. For example, sufficiently high repulsion

enables synthesis of artificial opals or "colloidal crystals" from monodisperse sols; by slow removal of the solvent, particles arrange themselves into close-packed, crystalline structures wherein the individual colloids take place of atoms.³⁴⁻³⁷

These crystals have useful optical properties which are highly dependent on the unit cell spacing (hence particle size), which can often be large enough to interact with visible light.³⁸ Therefore by tuning particle sizes, colloidal crystals cast onto surfaces can provide varying refractive indices, absorb light of prescribed wavelengths, or (through shifts in the wavelength of absorbed light) detect changes to their chemical environment. Accordingly, sol-gel silica colloidal crystals are highly useful as anti-reflective coatings,³⁹ pollutant or other chemical sensors,⁴⁰ and templates for the formation of macroporous materials.⁴¹

Net attractive interactions - aggregation

Should the inter-particle repulsion be overcome at any point, however, a different phase transition will occur. This can take two forms - either gelation or coagulation. In gelation, particles make loose bonds with neighbours to form long chains of multiple individual particle 'monomers'. These then propagate rapidly through the liquid to form networks, until a fully bicontinuous gel phase appears, with polymeric chains enclosing the entire solvent.⁴²

Conversely during coagulation particles aggregate by colliding with each other and bonding as a result. These aggregates go on to have further collisions, leading to growth until a large, dense particle forms which then settles out of solution. Collisions of this kind occur spontaneously through a number of mechanisms - for small particles brownian motion is the most important factor, causing collisions as particles move around; for slightly larger particles, shear forces caused by convection or other fluid flow lead to collisions between particles of different sizes; finally after growth to a large enough size, sedimentation through stokes settling causes particles of different sizes to collide as they fall out of suspension to form a 'coagulum'.⁴³

Although the difference between a gel and a coagulum are not very clearly defined,⁴⁴ one clear difference between the two are the system density.^{7,42} As-made, the loose interparticle connections in a gel lead to identical density to the parent sol thus making separation

significantly more difficult. Although gels tend to expel solvent from the framework over time (a process known as syneresis), this is impractically slow. On the other hand the density of coagulated aggregates is much closer to that of the bulk material (here silica), leading to spontaneous gravity-based settling. While the factors leading to one outcome over the other remain the subject of contemporary theoretical research,⁴⁵ colloid concentration has historically been identified as a key promoter for gelation over coagulation,⁷ primarily due to the enhanced likelihood of collisions at higher colloid concentration.⁴⁶ The three potential outcomes of the sol-gel process are visualised in figure 1.5, showing the differences in final solution composition after phase separation.

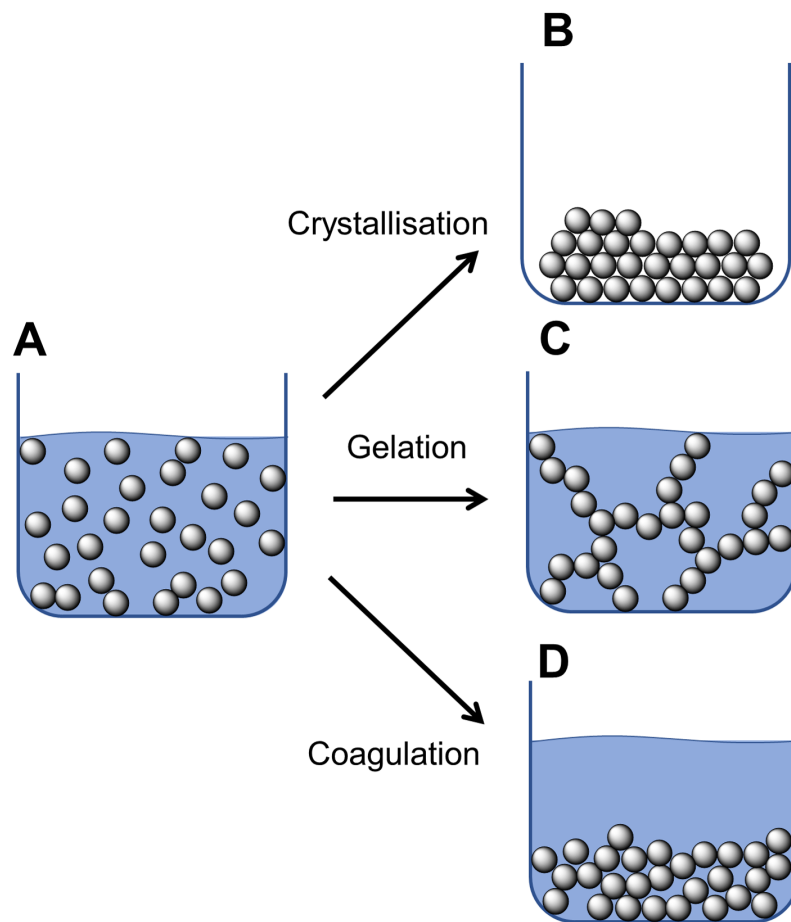


Figure 1.5: Visualisation of coagulation and gelation phase separation phenomena. (A) A sol of silica colloids grows in solution. (B) With overall interparticle repulsion the sol is stable, forming a crystal only upon solvent evaporation. Reduction of (or overcoming) the electrostatic barrier to interparticle collision leads to phase separation, either through (C) bicontinuous solvent-colloid gel network formation or (D) coagulation and gravity separation of colloidal aggregates and solvent.

1.2.4 Impact of the sol-gel pathway on silica manufacture

The distinction between gels and coagula leads to several important, industrially-relevant processing considerations.

First, gelation requires the colloids to make up a significant volume fraction of the sol, while the collision-based aggregation present in coagulation allow it to occur at lower concentration. Furthermore, as the gel network has the same density as its parent sol, separation is significantly more difficult compared to a coagulum, which can easily be separated by filtration. This causes issues with process design - while it is economically advantageous to operate a process at the highest concentration possible, this promotes gelation which makes separation much more complex.

While coagula can be separated by (relatively) simple filtration, a gel must instead have the sol phase removed through either evaporation leading to a xerogel - a far denser, collapsed network; or more complex methods such as supercritical extraction leading to a far less dense aerogel, maintaining the original 3-dimensional network structure.^{47,48} Xerogels are formed when the stress capillary forces place on the network during evaporation are strong enough to destroy the network, something which is not present when the fluid phase is supercritical (as supercritical fluids have no surface tension).

Finally, whereas gelation occurs spontaneously dependent on sol colloid concentration, coagulation must in most cases be induced by controlling the interparticle interactions (e.g. pH) after some amount of growth. This is advantageous as induction can occur after particles have grown to a predefined size, leading to a broad variety of possible morphologies and hence particle properties. However, the exact mechanism of colloid nucleation and growth are an ongoing area of research, with empirical phase behaviour only having been partially determined. This is shown in figure 1.6, showing the shift from nonreactive reagents to nanoparticles and finally a gel based only on relative base and silica concentration.⁴⁹ In phase (I) base concentration exceeds silica concentration, leading to a largely unreactive system as each individual SiO_4^{4-} anion is too deprotonated to react. Phase (II), where silica concentration exceeds base concentration, leads to colloid formation. Although small-angle X-ray-detectable particles appear, no particle interaction or agglomeration occurs sponta-

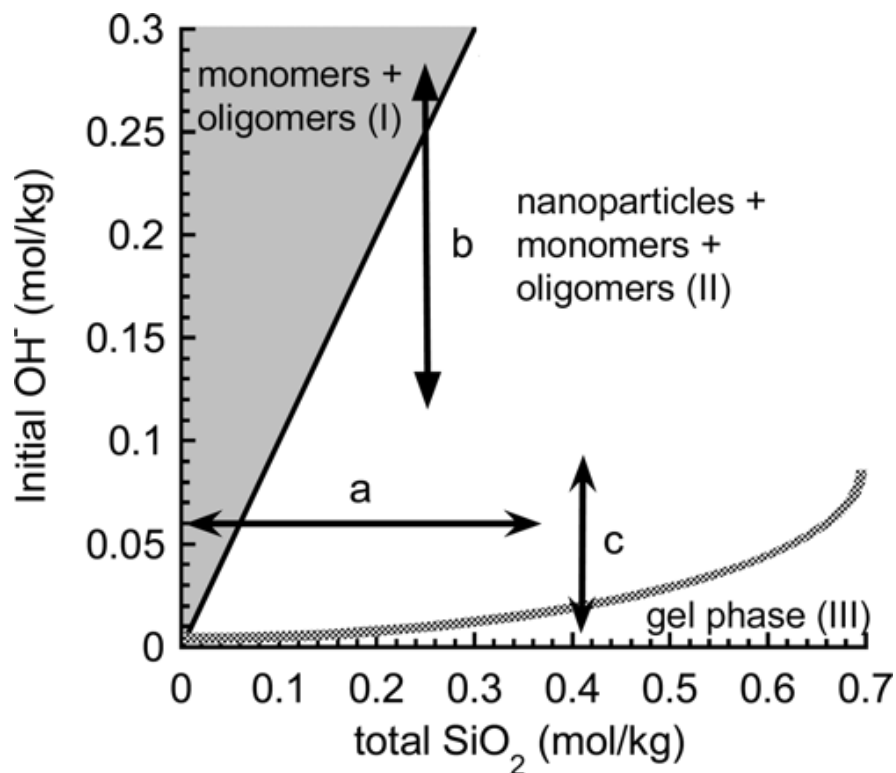


Figure 1.6: Partial experimental phase diagram for the three component water-silica-organic base system. Taken from reference 49, arrows represent reversibility of phase transitions.

neously. In this region, colloidal aggregation can be induced. Finally phase (III) occurs once silica concentration becomes sufficiently high to gel spontaneously. At low $[\text{SiO}_2]$ this is highly dependent on base concentration (hence electrostatic interparticle repulsion), however upon increasing silica concentration this becomes base-independent as colloids become more crowded in suspension, leading to inevitable spontaneous collision.

Despite the complexity of the sol-gel process and a lack of quantitative theoretical predictability of important process parameters such as particle size, empirical control over particle properties in both precipitated and colloidal silicas is easily achievable by strict adherence to a specific recipe. Industrially, precipitated silica is made in exactly this way - water glass (sodium silicate solution) and sulphuric acid are mixed together across the course of several hours and sequential batches at elevated temperature according to a well-defined procedure, leading to highly reproducible precipitated silica properties (some of these are summarised in reference 16).

1.3 Flexibility of internal particle structure

1.3.1 Internal porosity in nanoparticles

Aside from using sol-gel methods to control silica at a particulate level, the morphological flexibility of silica can be taken advantage of to imprint pores into the materials. Whereas the porosity of precipitated silicas or colloidal crystals arises from the space between coagulated or gelled particles, the individual particles themselves tend to be solid, hard spheres. Creating free space within these spheres broadens the possible applications of these materials, enabling nanoscale recreation of laboratory items such as bottles, filters, sponges, and reactors. Porous materials are well established, both academically and industrially, with uses in a myriad of applications dependent on the both the porous geometry and chemistry at the pore surface.⁵⁰

Pores can take several different shapes within a particle, impacting on their properties (visualised in figure 1.7).⁵¹ For instance closed, or inaccessible, pores (figure 1.7 A) do not meet the outside of the particle, therefore no transport into or out of the pore is possible. These pores impact only on bulk properties such as density and thermal conductivity. Open pores within a solid (figure 1.7 B-F) allow transport of fluids into or out of the pore system, performing operations on the fluid depending on their shape. Pore shape plays a significant part in this - differences in size between pore openings and their bulk lead to pores which act more like bottles (figure 1.7 B) or funnels (figure 1.7 D), i.e. relatively easier to fill than empty and vice versa. Further, pores which span the entire length of the particle (figure 1.7 C-E-C) enable fluids to pass through them, providing large fluid-surface contact times which are important for surface processes e.g. selective adsorption⁵² or reactions involving the surface.⁵³ Finally, broad pores which are wider than they are deep are generally classified as surface roughness, but still contribute to particle surface area.

In terms of size, pores are generally categorised into 3 groups, each predisposed to different applications: micropores, whose diameter is smaller than 2nm; macropores, which is anything above 50nm; and mesopores which lie between the two.⁵⁴ For reference, the kinetic diameters (essentially the minimum aperture through which a molecule can diffuse) of common test gases N₂ and CO₂ are ca. 0.36 and 0.33 nm, respectively.⁵⁵ This means that for microporous materials the pore width is similar to small molecules, leading to severely

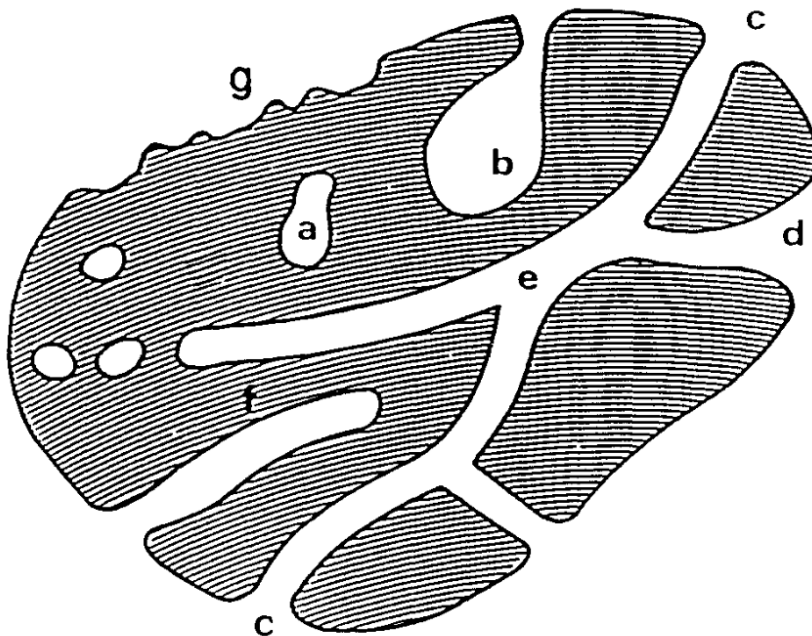


Figure 1.7: Scheme of possible pore types within a solid particle. (A) Closed pores, (B-F) open pores of various geometries, and (G) very shallow pores, generally classified as surface roughness. Reproduced from reference 51

restricted diffusion and a higher amount of sorbent-sorbate interaction.^{56,57} As a result, microporous materials are widely applied to perform separation of mixtures by shape and size (otherwise known as molecular filtration), wherein differences in diffusion rates or surface interactions are taken advantage of to separate gas mixtures rather than bulk physical properties such as boiling point (used for distillation) or solubility in a medium (used for solvent stripping). Therefore microporous materials are usually used for product purification of small molecule mixtures⁵⁸ or pollutant scrubbing.⁵⁹

Conversely, the large void spacing of macroporous materials provides far fewer sorbent-sorbate interactions, reducing their applicability to interact with gases directly. Instead, their high void spacing makes them highly useful for interacting with electromagnetic radiation or supporting materials with smaller pores, thereby enhancing mass transport into their structures.⁶⁰ Furthermore, the higher relative void fraction of macroporous materials predisposes them towards applications such as lightweight structural materials or thermal insulators, and again as filters for larger pollutants such as particulates in air or water.⁶¹

Finally, the intermediate size of mesoporous materials enables applications as molecular

reactors or stores. Unlike microporous materials whose internal geometry only permits single molecules, internal pore surfaces of mesoporous materials can be modified with reactive decorants, promoting selective adsorption of heavy metals e.g. Hg,⁶² or catalysing a range of chemical reactions.^{63,64} These decorants can further be used to induce or control chemical reactions,⁶⁴ enabling development of otherwise complex reaction conditions such as enantioselectivity⁶³ or cascade reactions.⁶⁵ Similarly, by covering the pore opening with a selective ‘gate’ (e.g. a biomolecule), the internal volume can be used as an efficient store for active ingredients such as pharmaceuticals.⁶⁶

Contemporary research into porous materials largely focuses on 5 materials families: metal organic frameworks, porous crystalline transition metal oxides, porous carbon materials, and two types of silica materials (zeolites and surfactant-templated mesoporous silica).⁶¹ The method of pore imprinting in the latter two instances will be discussed here.

1.3.2 Porous silica zeolites

By far the best-known example of silica-based porous materials are zeolites - crystalline silica materials with large internal surface areas and pore volumes. Unlike in other crystalline silicas i.e. quartz, where the silica tetrahedra are densely packed with no internal porosity, zeolite crystals form cages containing free space (visualised in figure 1.8).^{67,68} These materials remain co-ordinatively saturated (where each silicate tetrahedron is bonded to 4 more at its corners), however rather than a diamondoid-like structure seen in quartz, tetrahedra form into rings which connect together to form 3-dimensional shapes. This connectivity between rings gives rise to the materials’ final porosity.

Taking the example shown in figure 1.8, monomeric and dimeric SiO_4 can form into 24-membered cages (figure 1.8 A-B). These ‘sodalite’ cages have the approximate geometric shape of a truncated octahedron, where Si atoms form the vertices and Si–O–Si bridges create the edges (figure 1.8 C). This geometry is therefore made of both 6-membered and 4-membered silicate rings. The size of the pore depends both on the size of the constituent cages and how they arrange together - fusing of sodalite cages along the 4-membered rings leads to tightly packed sodalite (D in figure 1.8, with a pore window of 0.28 nm across each

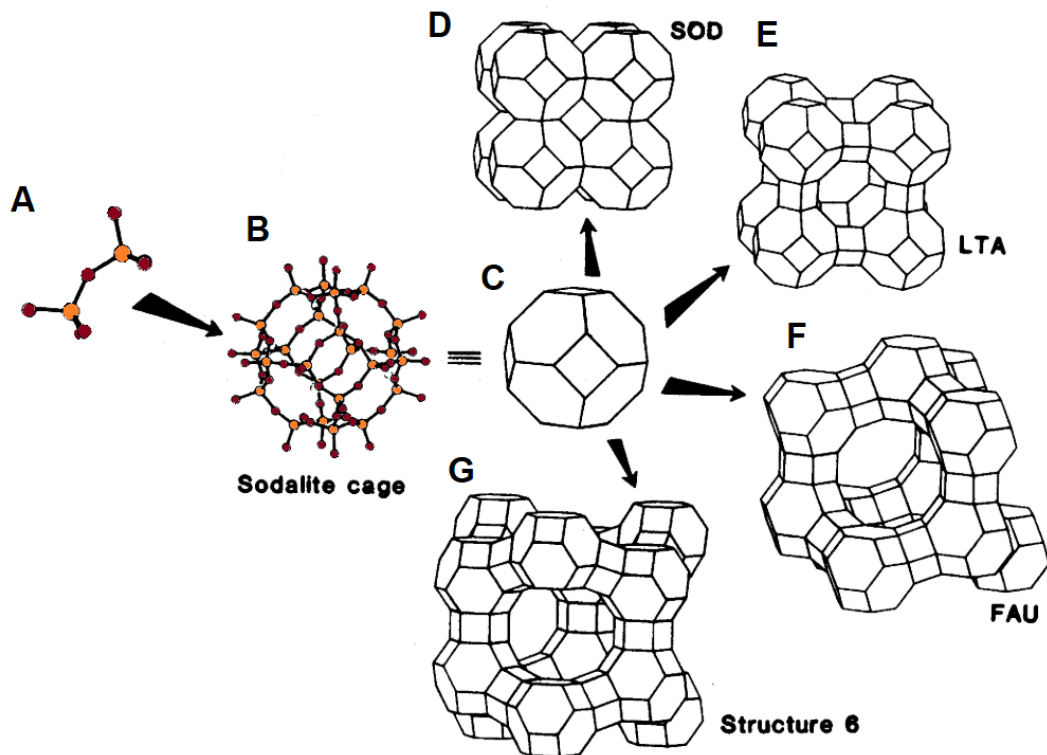


Figure 1.8: Geometric representations of zeolite cages and their possible arrangements. (A) A silicate dimer, forming part of (B) an $(\text{SiO}_4)_{24}$ sodalite cage, where orange balls represent Si and red represent O. (C) These have the approximate shape of a truncated octahedron, which can pack in a number of ways - (D) fusing of the 4-membered rings, (E) Bridging between 4-membered rings, and (F) bridging between 6 membered rings. The latter case can only happen in one direction, so phase (G) is experimentally inaccessible. Adapted from reference 67

hexagonal face).⁶⁹ Should the 4-membered rings be connected by a single Si–O–Si bond, zeolite alpha is formed (E in figure 1.8). These contain 8-membered rings formed between 4 sodalite cages, hence extending the pore window to 0.41 nm.⁶⁸ Connection at the hexagonal faces creates Faujasite-type zeolites with yet larger 12-membered rings (F in figure 1.8) with a pore window of 0.74 nm.⁶⁸

These structural details have a high impact on the zeolites' properties, enabling them to perform a range of host-guest chemistry specific to their pore size. Chief among these uses is handling gas mixtures, where the materials can take advantage of different adsorption strength, diffusion rates, or even physical molecular size to separate species from one another.⁷⁰ For example, separation of CO_2 such as from large point sources like power plants is highly dependent on adsorption strength.⁷¹ Selectivity based on diffusion rates allow zeolites to separate similar structural isomers, such as the xylene aromatic hydrocarbon family

(1,x-dimethylbenzene).⁷² This allows zeolites to perform shape-selective rearrangement of the organic compound xylene, allowing simultaneous purification as well as filtering of the compounds.⁷³ Finally, size-selectivity of zeolites can make them useful for sieving smaller molecules from larger ones e.g. removing hydrogen gas from isobutane dehydrogenation reactions to reduce side-products.⁷⁴

Zeolite synthesis methods

Unlike precipitated silica, zeolite aluminosilicate materials are produced under hydrothermal conditions both naturally and industrially. Natural zeolites are formed during the cooling of volcanic rocks when they come into contact with saline water, superheating the water and creating appropriately energetic conditions to trap the mineral into a higher-energy (zeolite) crystal polymorph. This is recreated artificially through the use of sealed pressure vessels - heating a solution of silica salts or amorphous silica gels above its boiling point to artificially increase the pressure, in a manner akin to using a domestic pressure cooker.⁷⁵ This obviously predisposes the synthesis to be batch in nature, however continuous processes for zeolite synthesis have recently been developed by mixing precursor solutions with supercritical water to recreate the high pressure and temperature conditions.^{76,77}

Inducing synthesis of different zeolite frameworks such as those shown in figure 1.8 requires assistance to ensure cages align in the desired pattern. This role is normally filled by small organic structural-directing agents (SDAs, hereafter templates) which fill space between cages as they grow and bond together.^{41,78} These most commonly comprise of quaternary ammonium salt molecule such as tetrapropyl ammonium hydroxide (TPAOH), which were originally introduced to provide better control over the zeolite structure, specifically to reduce the necessary amount of aluminate salt doping (which was the previous method of structure-induction in zeolites).⁷⁹ It was soon discovered that a range of organic materials can be used to template zeolites, regardless of size or chemical functionality (i.e. linear, branched, or cyclic aminoalkanes; ether, thioether, aza cyclic compounds), producing a range of cage types and shapes dependent only on the template size.^{75,80,81}

The mechanism of template action provides an explanation for its functionality-independence (shown in figure 1.9 for zeolites of type ZSM-5).^{82,83} Through weak attractive interactions

between the template TPAOH and silicate ions, the hydration shell around the former is slowly replaced leading to a template-precursor TPA^+ -silicate complexes due to their mutual hydrophobicity (figure 1.9 A-C). Under hydrothermal conditions, these complexes group together, creating crystalline zeolite nuclei (figure 1.9 D). These then grow to form the macroscopic crystals of organic-inorganic complexes, containing the zeolite cages arranged in an ordered pattern determined by the type of template used (figure 1.9 E).

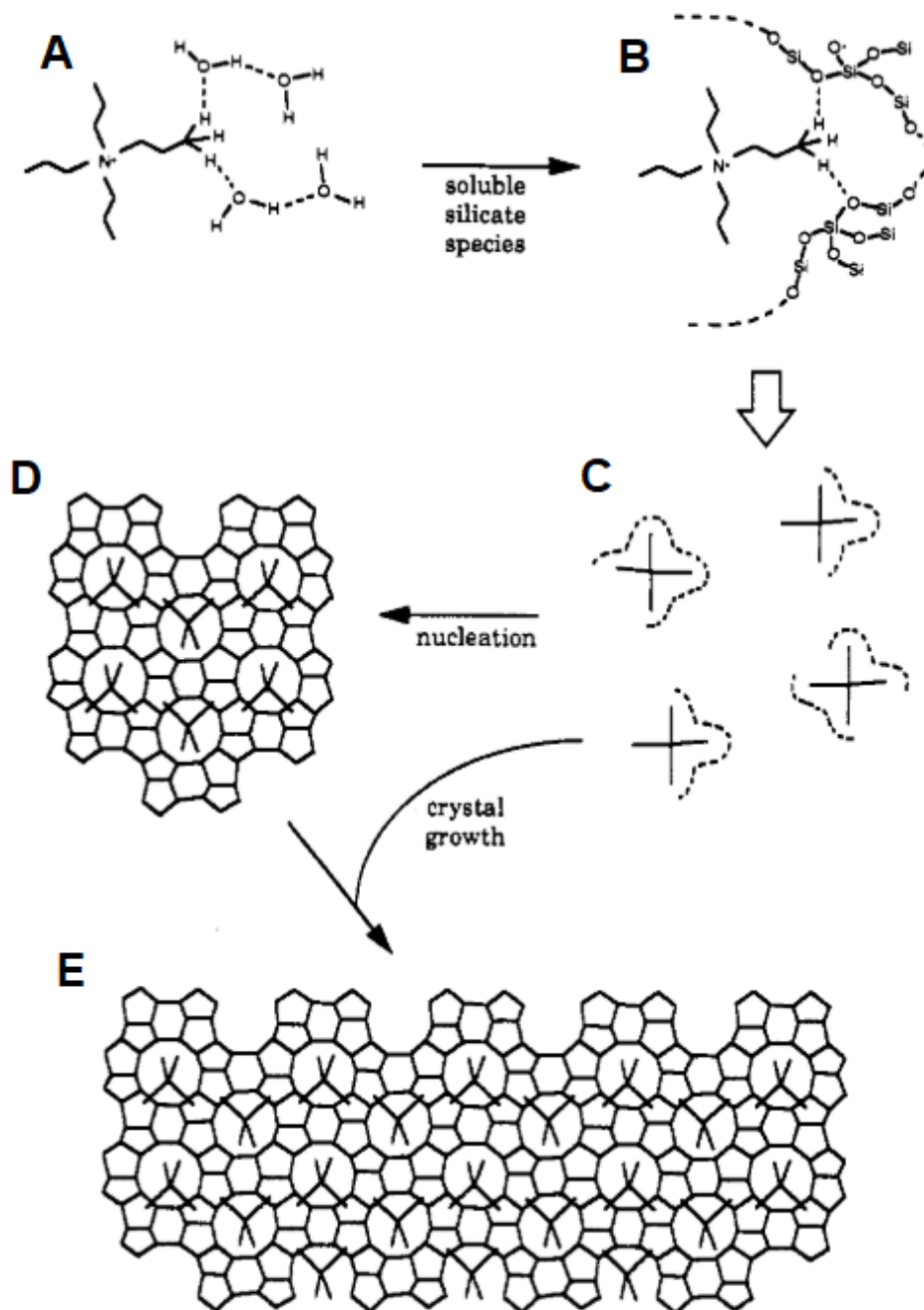


Figure 1.9: Proposed mechanism of template action using TPAOH to create zeolite type ZSM-5. Adapted from reference 82

Similarly to how amorphous silica gels require solvent extraction to activate their porosity, the incorporation of a template into a zeolite necessitates their removal to activate the pore structure. This is normally achieved through calcination - heat treatment of the as-made organic-inorganic hybrid material to fully decompose the organic template (e.g. to 500 °C for 12 hours). This has two obvious drawbacks, however - first that the heating itself is time consuming and energetically expensive, and second that degradation of the organic template destroys the most expensive component.^{84,85}

Alternatives to calcination avoiding both these drawbacks are therefore highly sought, however as yet no universal alternative has been found. For (microporous) zeolites, this may partially be due to the highly packed nature of the pore - bulky templates like TPA⁺ cannot easily diffuse out of the pore system. This has led to the development of reversibly-desconstructible templates containing ketal moieties to simplify extraction (illustrated in figure 1.10).^{78,80,86} Ketal functional groups are the condensation produce of a diol molecule and a ketone, creating a cyclic compound which has a larger and more rigid surface area than its two precursors (A in figure 1.10). After synthesis using the ketal form of the template (B in figure 1.10), treating with aqueous acid solutions hydrolyses the bonds to form a ketone and diol which can then be extracted from the structure directly and reused C-D. This removes the need for heat treating during activation of the zeolite and enables reuse of synthesis templates, removing or ameliorating both of the key issues with zeolite activation.

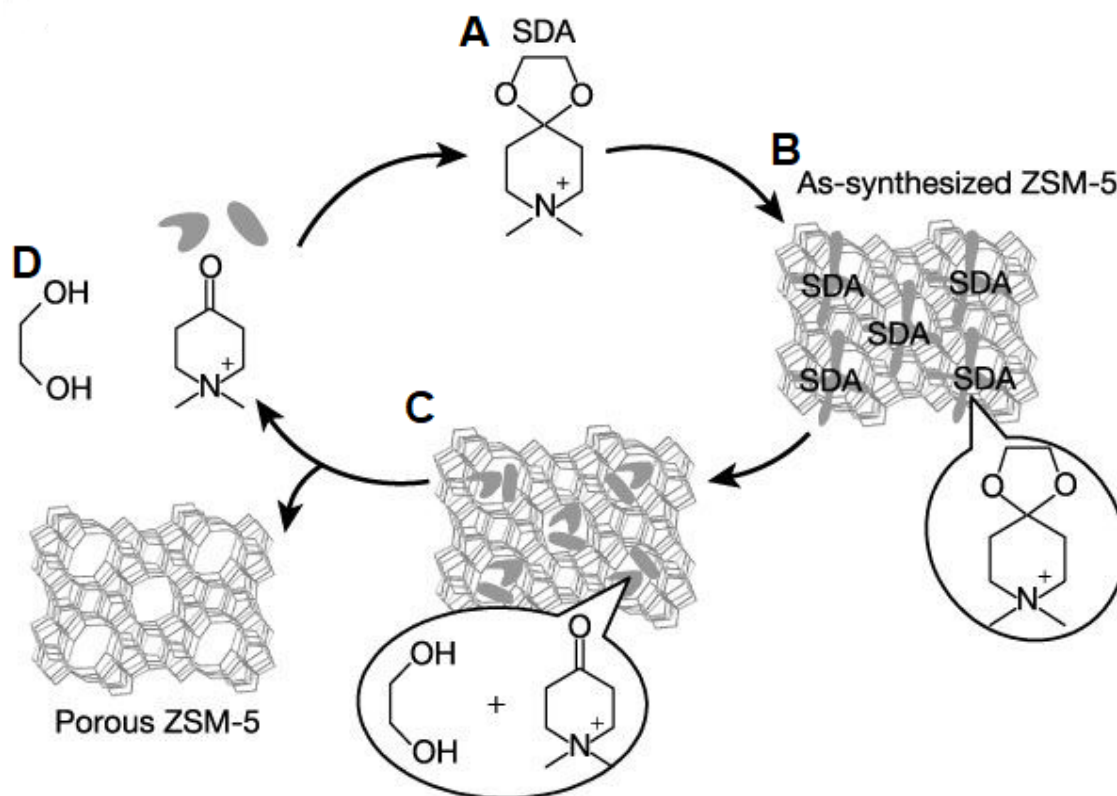


Figure 1.10: Illustration of the action of a reversibly deconstructable template for the synthesis of zeolite ZSM-5 as a catalytic template cycle. Adapted from reference 86.

1.3.3 Supramolecular templated silicas

Despite the seeming equivalence of the template materials' heteroatom moieties, the molecular geometry of the template clearly has a profound effect on the eventual material's porous structure. For zeolites, correlations between template molecule size and pore window are well established,⁸² however creation of larger pores through this method is complex, requiring substitution of Si in the framework with more metallic elements such as Be, Ga, or Ge.⁸⁷

An alternative method to using single molecular templates for mesopore imprinting is to supramolecular assemblies such as polymers or surfactants. Compared to the templates discussed previously, surfactant compounds consist of long, hydrophobic carbon "tails" (generally C₈-C₁₈)⁸⁸ with a single hydrophilic moiety e.g. trimethylammonium as the molecule's "headgroup." In the case of polymers, block co-polymerisation is used to create a hydrophobic centre (e.g. poly(ethyleneoxide), PEO) and hydrophilic ends (e.g. poly(propyleneoxide), PPO).⁸⁹

The amphiphilic nature of surfactant compounds leads them to spontaneously self-assemble in solution, creating mesophases analogous to nanoscopic soap bubbles around which silica can form (shown in figure 1.11, bottom left). These can take a variety of shapes ranging from spheres to hexagonally-packed channels, to bicontinuous or lamellar phases depending on the surfactant concentration.⁹⁰ This has enabled the development of silica materials with a variety of ordered mesoporous structures, chiefly the mobil compositions of matter or MCM family.⁹¹ A few key examples are shown in the right of figure 1.11 - at the bottom is MCM-41, containing a honeycomb-like structure of uniform cylindrical pores arranged into a hexagonal pattern. Above is MCM-48, a fully bicontinuous structure, and finally MCM-50 is a layered material where silica grows in sheets between lamellar phases of surfactant.

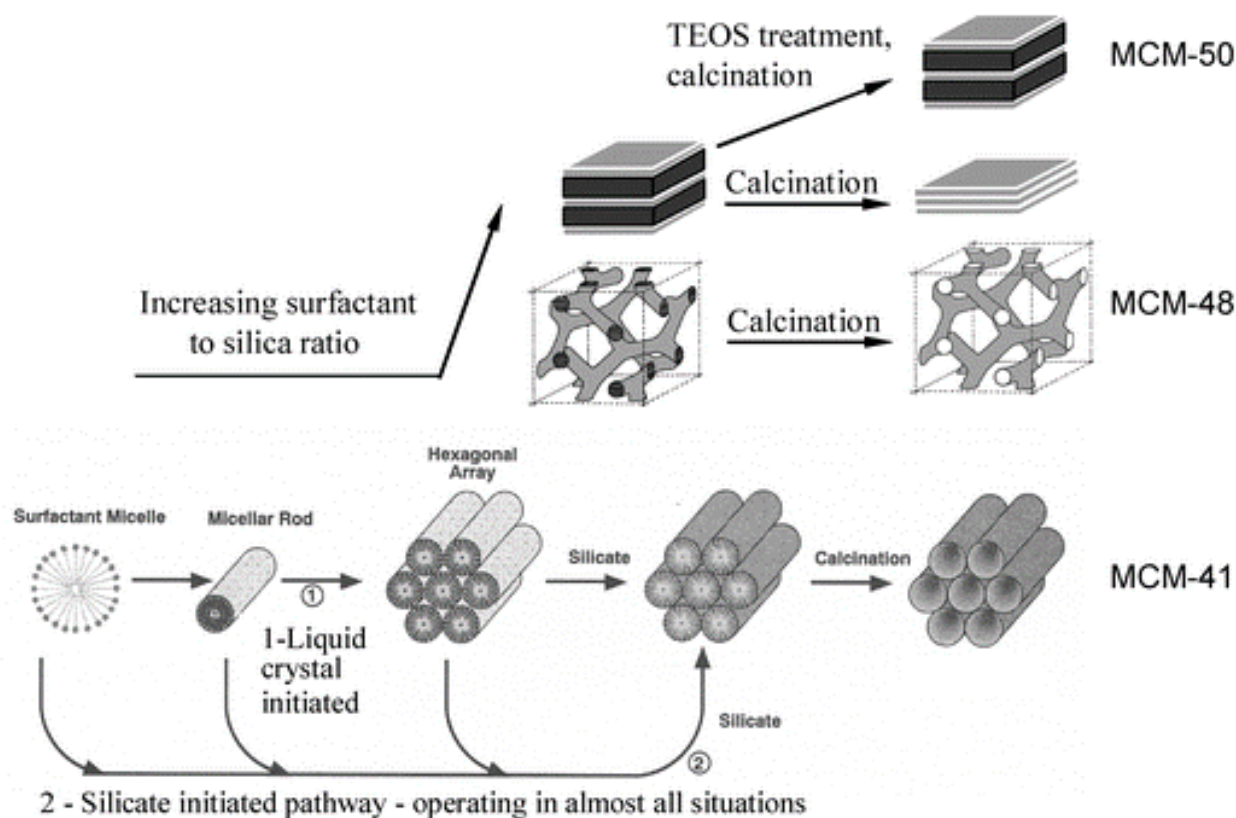


Figure 1.11: Scheme showing the various liquid-crystal topologies that can be templated into silica materials, and their eventual material structures. (Bottom row) Self-assembly mechanism for MCM-41. (Top row) Higher surfactant:silica ratios lead to bicontinuous or layered phases upon silicification (names MCM-48 and MCM-50, respectively). Adapted from reference 92.

All of these materials use CTAB (Cetyl Trimethyl Ammonium Bromide), a quaternary ammonium salt surfactant with similar headgroup functionality to the TPAOH used in zeolite synthesis, as a template. At low surfactant:silica ratios, spherical CTAB micelles co-assemble with silicate anions into tubular rods which then stack together forming silica at

the headgroups (figure 1.11 bottom row). CTAB is incorporated into silica synthesis wherein silica forms around the surfactant mesophases creating a non-porous hybrid surfactant-silica precipitate. After activation, which commonly involves calcination (in a further parallel to zeolites), ordered porosity in the shape of the surfactant mesophase is revealed. Since self-assembly can lead to a variety of different geometries, pores in MCM-type materials can either be channels, a bicontinuous cubic structure, or lamellae (summarised in figure 1.11).⁹²

Comparison of surfactant templating to zeolite templating

In contrast to zeolites, MCM-type materials are amorphous in framework structure due to the larger size of the pore, which would put unacceptably high strain on the structure if it were crystalline.⁴¹ This impacts on the synthesis methods significantly - while hydrothermal synthesis such as in zeolites is also possible in surfactant-templated mesoporous silicas, the majority of these materials are synthesised using a modified sol-gel method.⁹¹ Interestingly, this appears to be related to the chemical functionality of the template: although PEO-PPO block copolymers require hydrothermal conditions in the same vein as zeolite materials,⁸⁹ amine- or ammonium-headed surfactants can both be made by sol-gel methods.⁸⁸ However, in order to maintain the pore order, the sol-gel process proceeds at a significantly slower rate than in industrial precipitated silica, using much higher pH and alcoholic cosolvents to decelerate the synthesis.

While headgroup chemistry of the surfactant bears similarity to templates used in zeolite synthesis, and they both require equivalent post-synthesis activation, the mechanism of template action differs slightly amongst these materials. Unlike the hydrophobic-hydration mechanism proposed for zeolites wherein multiple silicate anions surround a single template molecule,⁸³ MCM-type materials rely on charge-charge interactions between individual CTAB headgroups and silicate anions to facilitate silica synthesis. This surfactant-silicate complexing leads to coassembly of surfactants and silica precursors during the self-assembly process, changing the micelle shape and hence leading to phenomena such as tight packing of cylindrical surfactant-silicate micelles and hexagonal shapes of the individual channels.⁹³ Furthermore, the phase-separation-based behaviour of the template allows changes to the micellisation behaviour (e.g. swelling with hydrophobic chemicals like trimethylbenzene)

without affecting the templating. From this, pore sizes of the materials can be tailored to imprint desired behaviour.⁹⁴

In the same vein that molecular templates can have a variety of functional moieties, a range of surfactant chemical functionality can produce mesoporous silica materials. Primary amine surfactants like dodecylamine are similarly capable of imprinting tubular mesopores into silica (named HMS or hexagonal mesoporous silica), albeit with more poorly-defined packing of pores compared to its charged analogue CTAB.⁹⁵ Tertiary amine intermediates between dodecylamine and CTAB can also be used (albeit with the headgroup requiring acid activation before self-assembly occurs), leading to similar structures, but different surface chemistry.⁹⁶

Furthermore, even more exotic surfactants such as bola-ampiphiles (tails with two head-groups) can be used, although no paradigm shift in pore geometry has been reported.⁹⁷ Even non-amine templates are effective, with block copolymers of poly(ethyleneoxide)-poly(propyleneoxide) (PEO-PPO) generating tubular pores in silica, with subtle differences in material structure in terms of spacing between pores and also secondary pore sizes.⁸⁹ This range of available chemistry allows surfactant choice to be made with other factors in mind than just efficacy in synthesis: surfactants either partially or fully derived from natural sources to make the synthesis more sustainable,⁹⁸ or synthesis involving weaker surfactant silicate bonds can promote simpler activation techniques (i.e. for neutral dodecylamine in HMS).⁹⁹

Applications of surfactant-templated silica materials

Development of large-scale synthesis methods has yet to be established for mesoporous materials, largely due issues with uneconomical activation processes (discussed in detail in chapter 5).¹⁰⁰ However, surfactant-templated silica materials have been widely studied for several applications.¹⁰¹

As previously discussed, the relatively large space within mesopores of MCM-41 enables surface binding of catalytic moieties within a pore without compromising on material transport, enabling the creation of shape-selective or cascade catalytic reactions.⁶⁵ Surface decoration can be used to create selective sorbents - by loading the surface with amine moieties

for example, carbon dioxide can be selectively adsorbed from flue gases into the channel-like pores.¹⁰² Similarly, porous silica-based materials are highly promising for electrochemical detection of a range of dissolved metallic or organic species, enabling the creation of sensors with wider ranges of applicability than are available with nonporous materials.¹⁰³

Furthermore, the ordered porosity and tunable pore size of mesoporous silica materials makes them promising agents for controlled delivery of pharmaceuticals¹⁰⁴ or MRI contrast carriers.¹⁰⁵ In order to be useful biologically, particle size and shape both need to be carefully controlled to avoid bioaccumulation or unwanted transmembrane diffusion.¹⁰⁶ Therefore MCM-41 synthesis has been combined with sol synthesis methods to imprint both controlled particle size and ordered porosity, hence enabling the development of mesoporous silica nanoparticles (MSNs) for biomedical applications.¹⁰⁷ With the addition of with surface decorations, MSNs can be functionalised to preferentially accumulate in specific parts of the body such as tumours deliver pharmaceuticals at a controlled rate to a controlled site.¹⁰⁸

1.4 Assessing the sustainability of templated silica materials synthesis

1.4.1 Green chemistry

One of the key issues with development of new nanomaterials is the sustainability and environmental friendliness of their production method. This is especially the case for templated nanomaterials, as the conditions of their templating introduce significant extra processing steps and materials requirements over traditional sol-gel precipitated silicas. Fortunately, the concept of process development for waste reduction and environmental sustainability is not novel - development of environmental sustainability in chemical processes is an important goal of several learned institutions such as the US' American Chemical Society and UK's Royal Society of Chemistry since the establishment of their Green Chemistry Institute and

Green Chemistry Network, respectively (both in the late 1990s).¹⁰⁹

Green chemistry as a concept was first defined in 1998 by Anastas and coworkers in their seminal book.^{110,111} In his work, they defined 12 principles for green and sustainable chemistry, adherence to which should ensure sustainability for new chemical methods. In order, these are:

1. Prevent waste - it is better to prevent waste than to remediate it once created
2. Atom Economy - green syntheses maximise the incorporation of reagents in the final product
3. Use less hazardous syntheses - wherever possible, syntheses should be designed to both use and produce non-hazardous chemical species
4. Design safer chemicals - chemical products should be designed to be functional while minimising their toxicity
5. Benign solvents and auxiliaries - when used, auxiliary chemicals (e.g. solvents, separating agents) should be non-hazardous
6. Design for energy efficiency - the environmental impact of synthesis energy requirements should be recognised and minimised
7. Use renewable feedstocks - raw materials should derive from non-depleting sources wherever possible
8. Reduce derivatives - unnecessary derivatives such as use of protecting groups in organic synthesis should be minimised wherever possible
9. Use catalytic methods - catalytic reagents are superior to stoichiometric ones
10. Design for degradation - chemical products should be designed so their disposal and degradation products are not environmentally harmful
11. Perform real-time analysis for pollution prevention - analytical methods should be developed for on-line process analysis to monitor and control hazardous material production
12. Use inherently safer conditions - reagents and processes should be designed to minimise the potential for industrial accidents

Several of these principles hinge on the *inherent* properties of a process, such as safety (first introduced by Kletz after the Flixborough disaster in 1974 - “what you don’t have

can't leak"),¹¹² and waste prevention rather than remediation. This means that, in order to adhere to the above principles, one must quantify the environmental friendliness of a particular method used.

1.4.2 Quantifying environmental friendliness

Full analysis of the environmental costs of a chemical synthesis is very complex. These so-called life-cycle analyses consider all costs within a system, from raw materials generation and transportation, to material and energy usage during a process, and all associated remediation. Naturally, a full life-cycle analysis is a complex and arduous undertaking, so a number of alternative methods for providing rough estimations of environmental friendliness have been developed. Chief among these are atom economy and E-factor.

Atom economy is an intrinsic aspect of a chemical reaction, comprising the percentage of mass of reagent atoms which end up in the desired product. This provides the theoretical maximum mass efficiency that can be achieved in a chemical process. To take the example of silica formation from sodium silicate and TEOS, atom economies are the percentage of reagents which eventually turn into SiO_2 . The stoichiometry of each overall process are shown in equations 1.16 and 1.17.



In equation 1.16, the atom economy is approximately 31% whereas in equation 1.17 it is ca. 26%.

Although on the face of it these two atom economies are similar, the second metric of E-factor provides a better reflection of the efficiencies involved. E-factor, standing for environmental factor, is a metric of the mass of waste generated per kilogram of product.¹¹³ E-factor was developed by Sheldon prior to the establishment of the 12 principles of green chemistry in response to excessive and cost-prohibitive waste in the fine chemicals industry.¹¹⁴ He found that industrial fine chemical processes generally created 25-100 kg waste/kg product, leading to significant advances in a number of industrial applications.

Although seemingly similar to atom economy, E-factor takes into account non-stoichiometric factors of a chemical process, such as excess reagents, solvents (during synthesis or washing), or non-recovered catalysts. Taking the above example, E-factors of 5-10 kg/kg are easily achievable for the sodium silicate example. However, the TEOS-based syntheses represented in equation 1.17 omits any proton transfer catalysts or templates incorporated. This can drive up the e-factor significantly by several hundreds or thousands of kg/kg.¹⁰⁰

Obviously metrics such as atom economy or e-factor can only paint a partial picture of the total environmental cost of a process, especially principle 6 (energy efficiency), and principles regarding hazards or environmental exposure. However, as first-principles estimates they remain useful tools for preliminary comparison, especially combined with energy balances and databases of environmentally-friendly industrial chemicals such as those within reference 115.

All-encompassing approaches to measuring process sustainability are clearly needed, but there is a risk of stifling progress by overburdening new discoveries with green metrics too early. This has recently been addressed with a European consortium of pharmaceutical companies and their regulators.¹¹⁶ Instead of performing all of the environmental analysis at once, this group proposes an iterative approach at different stages of technology development (shown in figure refiterativescreening). Using this paradigm, an initial 'zero-pass' screening can be performed at the lab scale to identify inherent critical issues with a new reaction or process, such as excess hazards or cost-prohibitive inefficiencies. For processes that appear initially promising and have no insurmountable inherent issues, a 'first pass' comprising more in-depth safety and mass efficiency investigations, as well as preliminary energy cost investigations. Second and Third pass investigations expand further on this, leading to full life-cycle analysis, waste remediation, and energy investigations have been considered.

1.4.3 Green nanomaterials

So how do contemporary nanomaterials adhere to the 12 green principles? In short, not well. Nanomaterials syntheses are characterised by high levels of dilution, stringent purity requirements for each constituent, and auxiliary chemicals in the form of templates

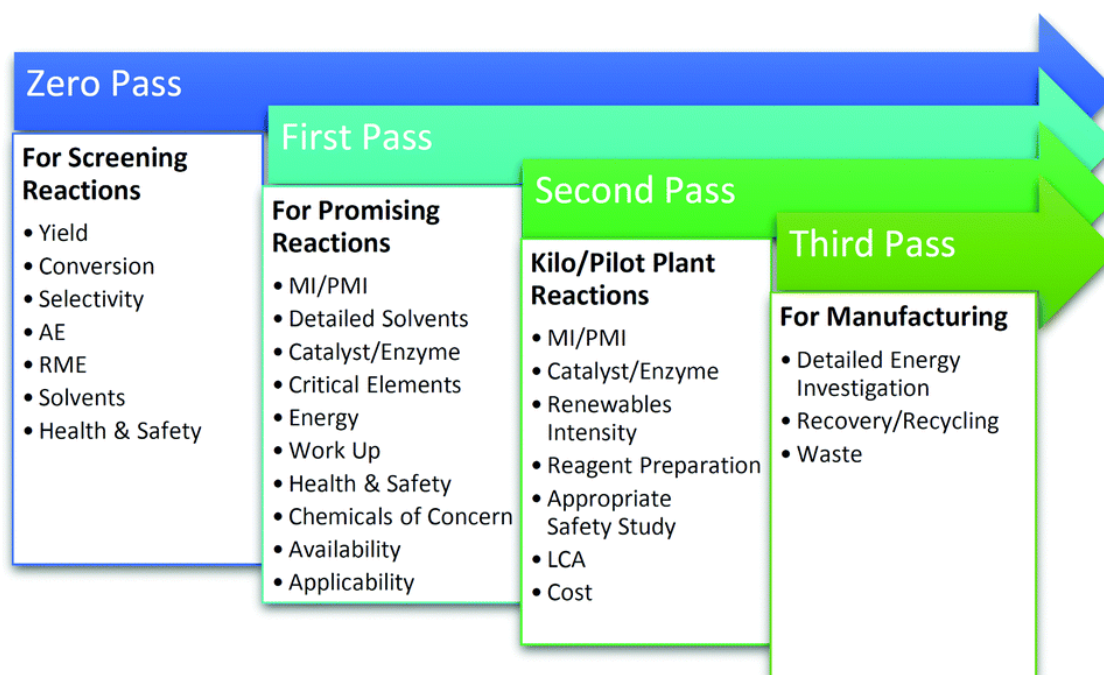


Figure 1.12: Summary of a 4-stage iterative green metrics analysis toolkit for development of new chemical processes. AE = Atom efficiency; RME = Reaction mass efficiency; (P)MI = (Process) mass intensity = $E\text{-factor} + 1$; LCA = Life-cycle analysis. Reproduced from reference 116.

or capping agents. Furthermore, finishing processes such as washing and activation create further significant increases in process wastefulness. In sum, these lead to E-factor values for nanomaterials generally produce 100-1000 times more waste than fine chemical processes.¹¹⁷

Developments in the field of green nanomaterials have historically been hard to come by due to the incompatibility of several green processing modifications (such as increasing concentration of reagents or incorporation of catalysts) with the nanoscale order often required. In general, some drastic changes such as the development of continuous mesoscale reactors for the synthesis of metal oxide nanoparticles (rather than batch hydrothermal bomb methods) have been effective,^{76,118} these do not address the issues with surfactant templated silica materials.

Instead, development of ‘eco-designed’ mesoporous silica materials has focused on the incorporation of more sustainable reagents or those conducive to more environmentally friendly activation processes.^{98,99} These methods tend to comprise of using bio-based surfactants or those with weaker surface interactions respectively. While effective to a degree, neither of these strategies can reproduce synthesis methods approaching the efficiency of biological templated silica synthesis, however.

1.5 The dichotomy between artificial and natural templated silicas

While artificial templating provides silica materials with a range of morphological features and porous properties, natural templates far supersede their complexity, leading to far more ornate structures than can be achieved in man-made materials. For example, diatom cell walls have incredible structural direction on length scales ranging from nanometers to microns unique to each species (figure 1.13).⁶

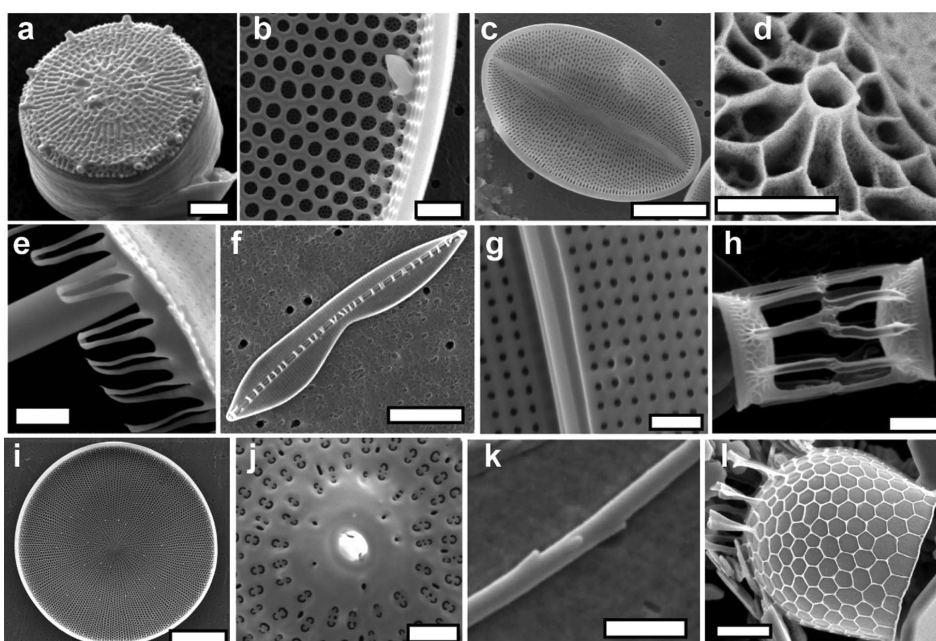


Figure 1.13: A range of diatom cell wall structures, showing their structural diversity. (A) *Thalassiosira pseudonana*, bar = $1\mu\text{m}$; (B) *Coscinodiscus wailesii*, bar = $5\mu\text{m}$; (C) *Cocconeis* sp., bar = $10\mu\text{m}$; (D) *Thalassiosira weissflogii*, bar = $0.5\mu\text{m}$; (E) *Ditylum brightwellii*, bar = $2\mu\text{m}$; (F) *Bacillaria paxillifer*, bar = $10\mu\text{m}$; (G) *Gyrosigma balticum*, bar = $2\mu\text{m}$; (H) *Skeletonema costatum*, bar = $2\mu\text{m}$; (I) *Coscinodiscus Wailesii*, bar = $50\mu\text{m}$; (J) *Ditylum brightwellii*, bar = $2\mu\text{m}$; (K) *Chaetoceros gracilis*, bar = $1\mu\text{m}$; and (L) *Stephanopyxis turris*, bar = $10\mu\text{m}$. Reproduced from reference 6.

As was previously discussed, diatomite silica is biomineralised in a special liposome within the single-celled organism: the silica deposition vesicle (SDV). This provides a confined space, appropriate pH, and an organic scaffold around which silica can form - entirely analogous to templated silicas. Naturally, the structure of the organic scaffold within the SDV and how that relates to its activity have been a matter of some study from a biological perspective, aiming to understand diatom cell wall growth both on a molecular level and its extension

to the micron scale. These studies are also useful from the perspective of organic-templated silica synthesis; diatomite silica represents an ideal templated silica material with highly controlled properties on a number of length scales, synthesised under ambient conditions.

One key discovery from this has been the structure of several biomolecules thought to be key in biosilicification, both full proteins (called silaffins) and smaller polyamine molecules.¹¹⁹ In a parallel with templates discussed earlier, each of these species is notable for its high relative composition of (amine-containing) lysine and arginine residues, as well as significant post-translation with (methylated) propylamines (see figure 1.14). A direct result of these discoveries was the identification of a silicifying 19-mer peptide, taken directly from a repeating unit of the above silaffins, named R5.¹²⁰

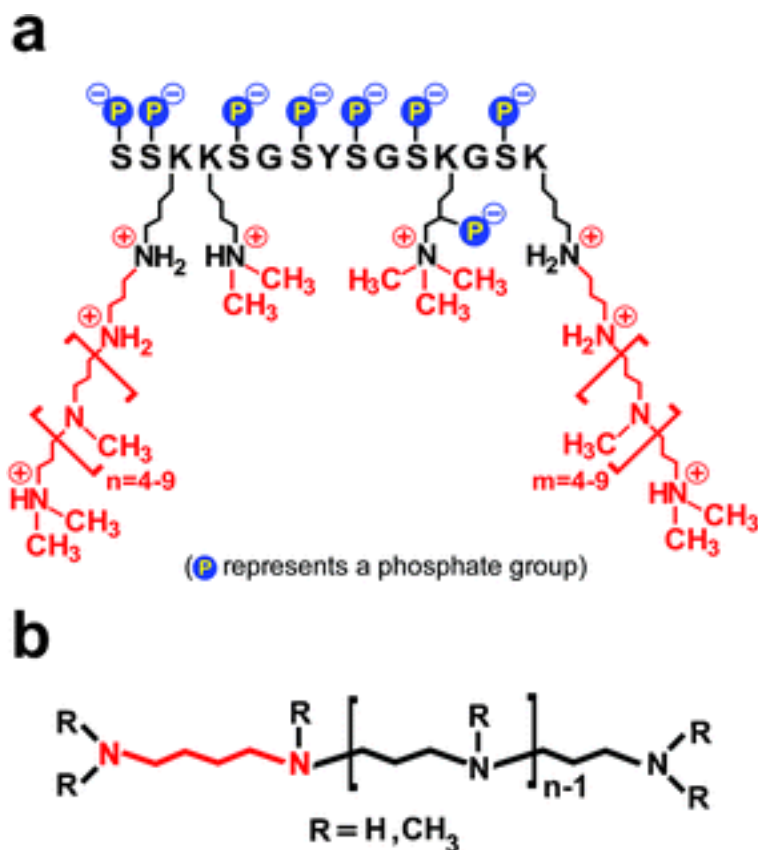


Figure 1.14: Structure of important diatom biomolecules for biomineralisation. (A) section of R5 repeating peptide sequence of a silaffin protein and post-translational modification with phosphate (P^-) and putrescine homologues (in red), and (B) generalised structure of a long-chain polyamine, showing putrescine homologues in red. Adapted from reference 119.

Although the amine moieties in figure 1.14 are individually similar to those found in zeolite templates or surfactants, the key structural difference is in the polyfunctionality of the biomolecules. Unlike the other template types, which are only usually singly or double

functional, the R5 peptide (and its analogous biomolecules) has several amine moieties with specific inter-moiety spacing. This polyfunctionality appears to be the key factor in both how biomineralisation can occur under such mild conditions, as R5-containing solutions are capable of silica precipitation in under 5 minutes compared to hours for commercial industrial precipitated silicas.¹¹⁹

Silica made in this way did not show any of the ornate features present in diatoms, however, only appearing as hard spheres similar to conventional sol-gel silica materials. This indicates that conditions within the SDV differ from those in a conventional reaction vessel, preventing self-assembly. This is presumably because the R5 peptide is only one segment of the total protein, also the shape of the SDV has been theorised to play a part.¹¹⁹ The SDV is shaped similarly to a flat disc, meaning silaffins self-assemble into circular monolayer with silicate-containing aqueous phases in the interstices, around which silica begins to mineralise (grey circles and white lines respectively, A in figure 1.15). An initial monolayer of templating polymaine solution forms within a silica deposition vesicle, around whose edges silica forms. The presence of silica at the edges of the silaffin monolayer changes its surface tension, causing separation into smaller mesophases in a similar fashion to the cooperative assembly of surfactant-templated silicas (B in figure 1.15). Further silica polymerisation induces repeated segmentation of the poylamine phase into smaller and smaller droplets (C-D in figure 1.15), forming a hierarchical honeycomb of pores.

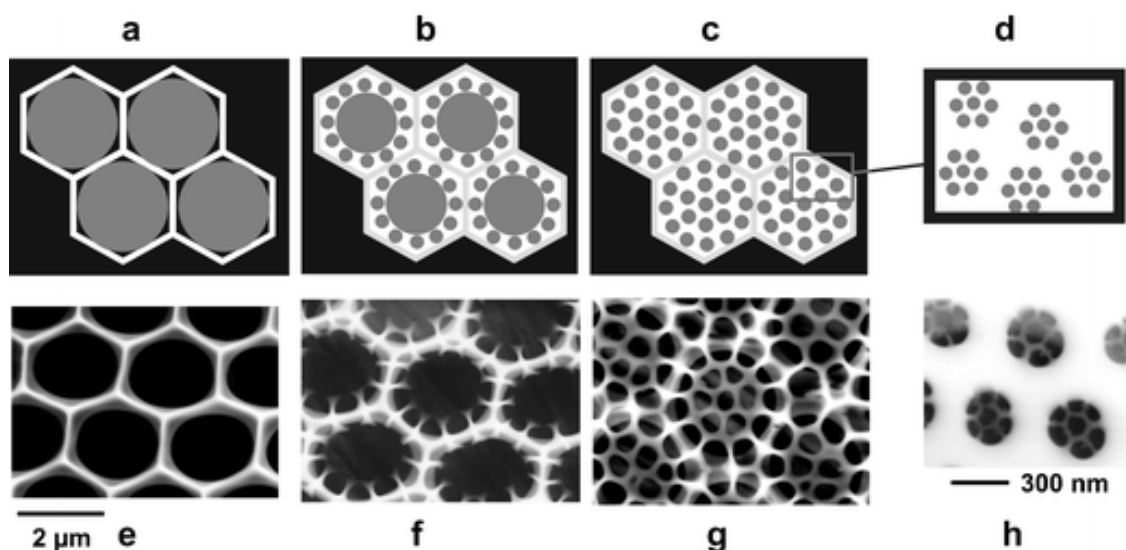


Figure 1.15: (A-D) Proposed heirarchical self-assembly mechanism for the formation of pore systems in the cell wall of diatom *C. Wailesii* juxtaposed (E-H) against electron micrographs of the same during growth. Reproduced from reference 119.

Application of biomolecules to template artificial materials

Beyond attempts to interpret the biomineralisation processes of diatoms, the R5 peptide and other biomolecules has been the subject of much study aimed at harnessing biomineralisation for synthesis of useful oxide materials.^{121,122} This can be used to template specific morphology within a material on a range of length scales. For example, by using large biomolecules such as viruses as a rigid template, intricate morphologies on much larger length scales can be achieved than with conventional templates.^{123,124}

Alternatively, biomolecules such as the R5 peptide are active towards silica formation. This enables milder silica syntheses than traditional sol-gels, permitting encapsulation of delicate species (e.g. enzymes) during precipitation.¹²⁵ R5 peptides can also be used as a functional component in biomimetic silica - by appending a drug or other cargo molecule to one of the cysteine residues in the R5-peptide, controlled release can be achieved by exposure to reductive conditions.¹²⁶

Although of significant scientific interest, especially from the perspective of designing ever more complex nanomaterials tailored towards specific applications, biomimetic synthesis methods have several drawbacks. Since biomolecules are naturally derived, researchers have little control over their structure or production rate within the natural system. As a result, scale up of biomimetic syntheses is stymied due to biomolecule availability issues. Despite this, the recreation of natural silaffin activity in vitro using the R5 peptide marks a clear path towards the goal of large-scale tailored nanomaterials - by using a reductionist approach to design of new template molecules based on the R5 structure, the perfect compromise between material properties, synthesis conditions, and process scalability can be achieved.

1.6 Bridging the gap: bioinspired silica

This is exactly what has been carried out for a range of biosimilar molecules, creating a family of ‘bioinspired’ silica materials. Made using organic ‘additives’ whose structure mimics the biological structures of the R5 peptide and silaffins, bioinspired silica (BIS) materials are synthesised at pH 7, ambient temperature, and within 5 minutes. This is both significantly

faster than industrial precipitated silica materials and uses significantly milder conditions than those used for templated silica materials.

1.6.1 Bioinspired silica synthesis mechanisms

Initial bioinspired materials were synthesised using polymers in an attempt to replicate the activity of the R5 peptide and silaffins directly. This was performed by poly(*L*-lysine) (PLL) and poly(allylamine) (PAH) to mimic the length and multifunctionality of biomolecular templates, silica particles in under 5 minutes reminiscent of R5-precipitated silica.^{127,128} For both of these additive molecules, BIS was formed as polydisperse spherical particles with no appreciable porosity, so while the benefits of biomineralisation conditions were maintained, the long-range order was lost. However, synthesis of these materials in controlled microfluidic mixing environments led to particle elongation (PAH)¹²⁹ or the creation of intricate particle structures (PLL) on the microscale.¹³⁰ Despite these developments, use of these polymeric amines such as these provided few benefits over peptides like R5: the system remained too complex to fully explore the templating effect, and the chirally pure polypeptides PLL has similar scalability issues to biological peptides due to difficulties associated with synthesis. Accordingly, bioinspired methods have expanded to use a range of amine-containing synthetic additives (shown in figure 1.16).¹³¹

Some recent research has focused on the "small molecules" category in figure 1.16 to reduce the system complexity and generate better additive structure-function relationships. In the first instance, simplification to oligopeptides containing 1-5 residues enabled investigation of additive catalysis during silica precipitation.¹³² Further experiments were largely carried out using ethylenediamine (MEDA, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$) and its homologues containing between 2 and 7 moieties (shown in figure 1.17 where MEDA has $n = 0$), revealing the effect these species have on sol-gel silica synthesis. These have demonstrated the importance of molecular length,^{133,134} functional moiety separation distance,¹³⁵ degree of amine methylation, and the presence of assisting chemicals such as pH buffers¹³⁶ on both the initial polymerisation and the interactions between colloidal silica particles.

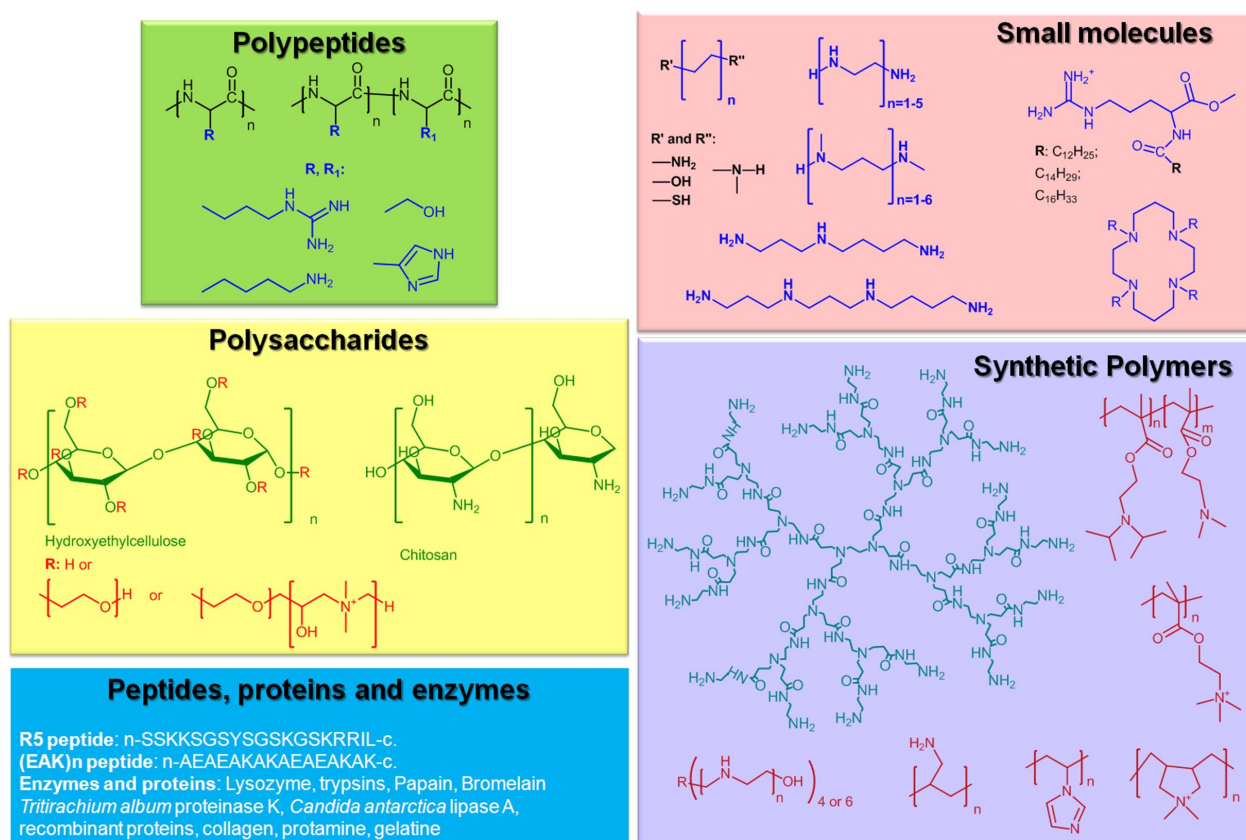


Figure 1.16: Representative range of biological and bioinspired additives previously used for BIS synthesis, categorised into 5 groups: biomolecules, polypeptides, polysaccharides, synthetic polymers, and small molecules. Reproduced from reference 131

Additive effect on molecular polymerisation

In accordance with prior studies of silica polymerisation,¹³⁷ initial silicate condensation occurs through third-order kinetics indicating a trimerisation reaction. These reactions are catalysed by the amine additives which aid in proton-transfer during condensation, becoming exponentially more active with polyfunctionality.¹³⁸

For the MEDA system, catalysis is promoted by methylating the molecule's amine moieties, creating permanently charged but highly more hydrophobic additives,^{136,139} contradicting the findings from reference 138 which correlated catalytic activity with conjugate base (i.e. uncharged amine) concentration. This may be a result of hydrophobicity - separation of the two amine moieties by increasing the bridging carbon chain also promotes catalysis with butylenediamine being ca. 2.5 times more active than MEDA in an otherwise equivalent system (although increase beyond this point had no further effect), presumably due to increased charge localisation at the edges of the additive's hydrophobic domains.¹³⁵

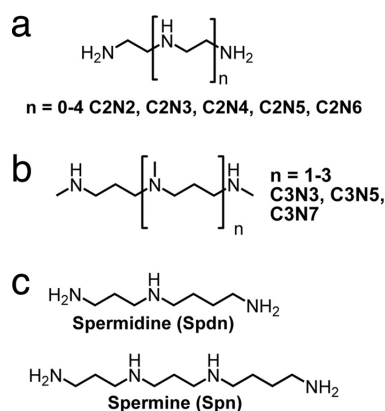


Figure 1.17: Repeat structure of ethylenediamine (MEDA) and its analogues. (A) ethylenediamine homologues, (B) partially *N*-protonated propylenediamine homologues, and (C) natural compounds spermine and spermidine with similar structure to the artificial additives in A and B. Adapted from reference 134

These factors of amine separation, homologation, and hydrophobicity appear to be somewhat additive. Penta- and hexa-functional MEDA homologues tetraethylenepentamine (TEPA, $n = 3$ in figure 1.17 A) and pentaethylenehexamine (PEHA, $n = 3$ in figure 1.17 A) are both significantly more active than their parent (3 and 8 times more active, respectively). This effect is compounded by increasing the separation between the amines (using propylenediamine or MPDA homologues), where homologation to tri-functional dipropylenetriamine (DPTA, $n = 1$ in figure 1.17 A) produced a fourfold increase in catalytic activity and further homologation increased this to as much as 14 times.¹³⁴

Interestingly, biomolecules with similar structures to DPTA (spermine and spermidine, both present within sidechains on silaffin proteins, shown in figure 1.17 C) showed little to no extra catalytic activity.¹³⁴ This indicates that indicating that some epitaxial effects occur in DPTA and its homologues, vastly accelerating the trimerisation reaction.

A general scheme for amine activity towards silica polymerisation, visualising the findings of these studies is shown in figure 1.18. In the absence of amine templates (figure 1.18 A), polymerisation is initiated through spontaneous collisions of three (partially) negatively charged monomers to form a trimer. This step is presumably rate-determining due to electrostatic repulsion between monomers. Complexing of the silica monomers with amine molecules (figure 1.18 B) in general do little to accelerate this stage, despite their proton-catalytic behaviour.¹³⁸ This can be explained as collisions between silica-amine adducts remaining infrequent despite charge neutralisation. Interaction between multiple silica monomers and

individual additives (figure 1.18 C), either as a result of greater additive length or ideal amine separation distances, leads to significantly accelerated trimerisation due to increased charge neutralisation and collision frequency though a similar mechanism to the principle of neighbour group participation in organic chemistry.

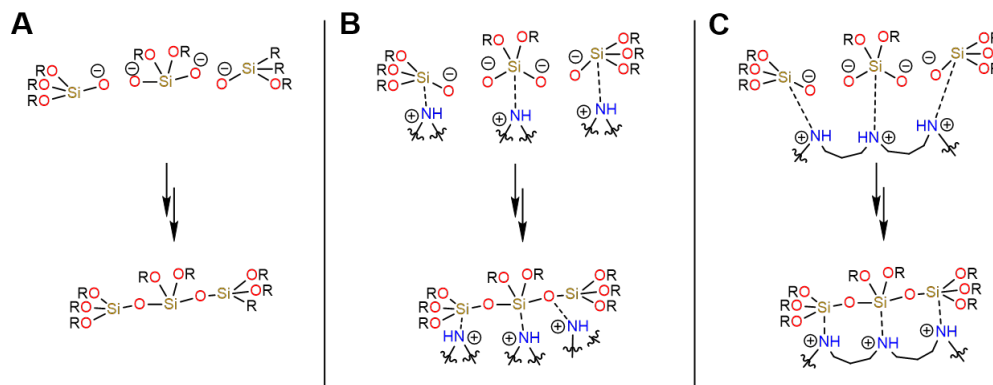


Figure 1.18: Scheme of silica condensation rate determining step with varying levels of assistance by amine templates. (A) No template, (B) mono-functional templates or short templates which cannot give rise to epitaxy. (C) Longer templates or those with 3 carbons between moieties lead to significant acceleration of polymerisation.

Investigations of coagulation

Beyond the molecular scale, additives impact coagulation of silica by interacting between colloidal particles. As was previously discussed, coagulation only occurs once interparticle repulsion forces have been overcome. This manifests in the form of an electronic double layer (EDL) between two particles - a layer of electrolyte ions in the solvent which screen electrostatic charge but are mutually repulsive between individual colloidal particles.

With regards to BIS, the EDL has been shown to be between 0.63 and 0.87 nm in width, corresponding to the length of additives butylenediamine and hexylenediamine. Between these (and the analogous MEDA and its homologue triethylenetetraamine (TETA), 0.39 and 1.1 nm in length), there is a step change in observed silica gel times and particle growth rates.^{133,135} Additives of this length are able to bridge across the EDL, significantly accelerating the onset of particle coagulation. This has been proposed as the cause behind the reduced reaction times in BIS (and R5-templated biomimetic silica) compared to industrial sol-gel silicas.¹³³

Contrasting with the largely hydrophilic MEDA homologues, amine moiety separation

of more than 6 carbon atoms introduces hydrophobic character into the molecule to induce phase separation behaviour similar to that seen in surfactant templated silicas. This leads to increased pore sizes in the BIS particles but comparatively reduced overall synthesis rates due to the lack of proximate polyfunctionality.¹³⁵ Increasing hydrophobicity of the templates, by either high homologation or methylation have also shown a tendency to form hollow silica particles. This is due to mesophase formation creating large microdroplets of the additive in solution around which silica shells form, in a parallel to both surfactant-templated and biomineralised silicas.¹³⁴

Although MEDA has been shown in reference 134 to be too short to bridge silica particles EDL, other studies using this additive have successfully achieved formation of silica.^{136,139} These found that increased electropositivity of amine moieties further promotes silica formation despite the inability to bridge the electric double layer,^{136,139} similar to findings for longer additive chemicals wherein hydrophobicity was correlated with increased activity.¹³⁴ The apparent contradiction between these studies can be explained by the use of buffered or unbuffered systems during synthesis.

Phosphate groups, ubiquitous in the original silaffin biomolecules, are often considered essential for BIS synthesis to be a success, spurred on by early studies of the R5 peptide.¹⁴⁰ This is theorised to be as a result of counterion condensation (coacervation) of the long, polycationic biomolecules or shorter bioinspired additives around phosphate anions, creating a large ‘liquid precipitate’ around which silica can very easily be precipitated. Beyond enabling short bioinspired additives to bridge the EDL, buffered BIS systems can create hollow silica nanoparticles by using a tri-functional citrate buffer along with the additive PAH; initially, the polymer condenses around the citrate to form a spherical structure (rather than fully elongated as it would be predisposed to be in solution), after which silica precursors can be added to create a shell.¹⁴¹ Interestingly, this is similar to hollow silica particles formed in the absence of counterions wherein highly hydrophobic additives phase separate into stable nanodroplets, creating a similar effect.¹³⁴

This, and the other key findings of bioinspired additive are summarised in the scheme in figure 1.19. In unbuffered systems (figure 1.19 A) use of small, positively charged additives such as ethylenediamine (MEDA) lead to stabilisation rather than coagulation of the

negatively charged silica colloids, as the additives cannot bridge the electric double layer. Incorporation of multivalent anionic buffers (figure 1.19 B) increases the effective length of the additive such that it can bridge the gap. This is equivalent to the activity seen with unbuffered PEHA in figure 1.19 C, where longer additives in unbuffered systems naturally bridge the electric double layer, leading to rapid coagulation of BIS. Hence, reports of additive derivatisation lead to similar conclusions for the buffered^{136,139} and unbuffered¹³⁴ studies. Similar effects are seen with longer additives that can self-assemble: unbuffered PAH (figure 1.19 D) does not self-assemble, producing materials similar to unbuffered PEHA. Incorporation of multivalent anionic buffers leads to coacervation with PAH ((figure 1.19 E), creating hollow silica spheres.¹⁴¹ Equivalent hollow silica is seen in the unbuffered system if the additive is sufficiently hydrophobic to spontaneously phase-separate ((figure 1.19 F) e.g. through greater amine-amine separation or high levels of derivatisation.

This scheme shows the importance of both additive structure and ionic conditions in determining the coagulation of BIS as well as its morphology. Furthermore, it demonstrates how bioinspired methods can produce similar morphological and mechanistic effects to other silica materials developed herein: short additives serve to stabilise BIS, forming pseudo-sols rather than induce precipitation;¹³³ longer additives serve to coagulate silica without forming a secondary structure; after phase separation through either hydrophobic effects (akin to surfactant templating) or through coacervation (similar to that seen in biological silica deposition vesicles), hollow silica spheres are formed.

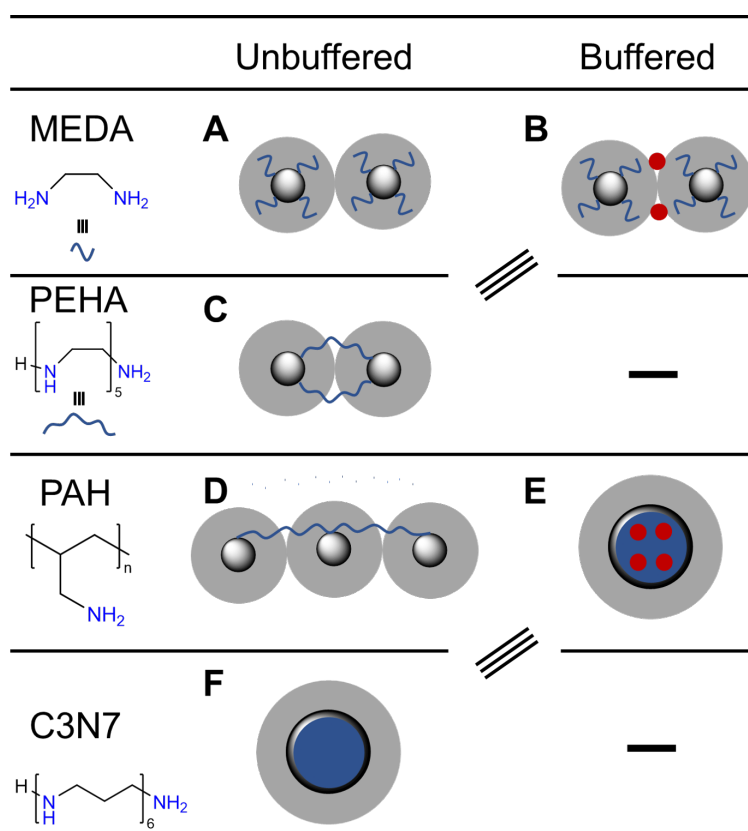


Figure 1.19: Comparison of particle coagulation in unbuffered and buffered BIS syntheses, as explained by the electric double layer model of Belton et al.¹³³ (A) Unbuffered and (B) buffered silica systems with short additives. (C) Unbuffered systems with longer additives. (D) Unbuffered and (E) buffered systems with polymeric additives, and (F) unbuffered systems with self-assembling polyfunctional additives. Key: Dark grey circles - silica colloids, light grey circles - charged electric double layer around colloid, blue lines - additive molecules, blue circles - additive aggregates, red dots - anionic buffer ions

1.6.2 Application of bioinspired silicas

Although no ordered porosity similar to those seen in zeolites or mesoporous silicas is imposed in these materials, the mild nature of their synthesis predisposes BIS to interact with other dissolved chemicals during synthesis, leading to rapid, efficient, and mild encapsulation. This has successfully been applied for a range of guest species to provide enhanced activity or to protect a delicate guest species.

Similarly to other porous silica materials, BIS materials can encapsulate active pharmaceutical ingredients to enable their controlled release within the body.¹⁴² Bioinspired silicas have two main advantages compared to conventional templated silica in this regard - bioinspired silicas are not cytotoxic unlike some other silica materials, and the guest species can be encapsulated during synthesis thus avoiding extra synthesis steps.

One example is in iron nanoparticles, which can selectively absorb arsenic from solution, but are prone to aggregation. Encapsulation in BIS provides enhanced reusability and kinetics to the iron species, enabling significantly more efficient pollutant removal, especially once cost/benefit analysis of the reduced synthesis costs are taken into account.¹⁴³

BIS further enables encapsulation of fragile chemical species like quantum dots to enhance their stability and reduce toxicity.¹⁴⁴ However, perhaps the most exciting such encapsulate are living biomolecules and whole cells. A range of enzymes such as lipase,¹⁴⁵ carbonic anhydrase,¹⁴⁶ and even full living yeast cells¹⁴⁷ have been successfully encapsulated in BIS during synthesis. Other encapsulation methods either rely on weak physisorption to entrap biomolecules (leaving the guest species prone to leaching) or covalent bonding to the substrate (leaving the guest species prone to deactivation),¹⁴⁸ however encapsulation during synthesis conveys key benefits of both methods - providing enhanced thermal and pH stability with little to no compromise in terms of activity.

1.6.3 Technological development of bioinspired silica synthesis

In light of both the deep understanding of BIS synthesis mechanism, and the overall benefits of bioinspired methods to reaction time, conditions, and material properties over current industrial silica materials, research focus has recently shifted to developing more industrially-relevant methods for BIS production. Continuous BIS synthesis has recently been demonstrated using a microfluidic plug-flow reaction system.¹⁴⁴ Continuous syntheses are rarely used during current silica manufacturing methods, but offer significant potential advantages in terms of lower capital expenditure (tubular plug-flow reactors being smaller in general than their batch or stirred-tank counterparts).

This, combined with the general benefits of bioinspired silica synthesis have been recently modelled on a full-scale perspective, by designing a range of potential manufacturing plants and comparing their economic potential against current methods in for several cost scenarios.¹⁶ Having been found economically favourable, further research is now required to establish the technical viability of manufacturing bioinspired silica at scale.

1.7 Summary

Through this introduction, several families of silica materials made with the assistance of organic molecules were described. These families use organic compounds to either ease the polymerisation of silica from silicates, or to impart structural order into the final material (or both). Although distinct in several aspects of their synthesis methods, properties and proposed usage, a key unifying factor are the organic templates, which the author has attempted to critically compare across families.

Organic-assisted silica synthesis is a powerful tool for producing materials with a range of intricate structural properties across several length scales. Ranging from ammonia-catalysed hydrolysis and colloid repulsion in sols to protein-imprinted porosity in natural diatom cell walls, silica synthesis this way is prevalent among several natural and artificial nanomaterial systems. These mostly fall within 4 distinct categories: silica sols, crystalline artificial zeolites, surfactant-templated mesoporous silica, and biomineralised & biomimetic silicas. Few relations between these categories are generally drawn due to the distinction between the final materials, despite the similarity in organic agent used during their synthesis.

Figure 1.20 demonstrates how, from the perspective of the organic precursors, all of these materials are formed on the same basis. Industrial precipitated silica is produced using no structural direction, only silica salts and acids to neutralise them (figure 1.20 A). This leads to silica with a range of possible pore sizes depending on how the sol-gel reactions progress (figure 1.2), requiring no activation of the pore structure to manipulate (figure 1.20 B). Incorporation of small additives like ammonia or mono-peptides leads to stable colloids where coagulation is impossible, especially under alcoholic conditions (figure 1.20 C). This leads to situations where silica sols of precisely-defined size can be prepared as seeds (figure 1.20 D), and upon addition of further precursors to induce regrowth, evaporation of the solvent creates a mesoporous interstitial pore network (figure 1.20 E-F).

Zeolite silicas are typically produced using hydrophobic tetra-alkyl ammonium templates along with similar precursors to precipitated silica (figure 1.20 G). Silica precursors replace water in the hydration shell of the hydrophobic template during initial gelation polymerisation (figure 1.20 H), building a mesostructure which (I) remains after hydrothermal gel

rearrangement and crystallisation. Calcination or other removal of the template activates the pore structure within the zeolite crystals, enabling their uses (figure 1.20 J). Use of self-assembling templates e.g. surfactants permits a higher range of templating to be incorporated (figure 1.20 K). In the case of surfactant molecules, supramolecular micelles co-condense with ethoxysilane precursors, leading to a similar environment to (H) but on a much larger length scale (figure 1.20 L). Sol-gel precipitation of these structures leads to a nonporous composite containing well-ordered organic domains, and again calcination of the organic template reveals an ordered pore network, but with much larger pore sizes than in zeolites (figure 1.20 M-N). The sizes of these pores can be easily manipulated by changing the self-assembling behaviour of the surfactant.

Finally, use of polyfunctional organic additives like PEHA (figure 1.20 O) unites some of the advantages of precipitated silicas (A-B) with zeolites and surfactant-templated silicas (G-N). In general, there is no pre-synthesis assembly observed in these materials, and a disordered silica-additive composite is rapidly formed (figure 1.20 P). Once again, calcination is required to activate porosity of these materials.

Bioinspired methods, using artificial organic analogues to silica-precipitating biomolecules, can provide a connection between these families and hence provide a deeper understanding of the general behaviours of this complex system. By synthesising BIS-mineralising additives whose behaviour mimics one of the different material categories, deeper insights into their formation mechanisms can be inferred, and new material properties can be explored. This study has attempted to use the basis of BIS to relate these materials to one another, showing how structural and mechanistic phenomena in BIS arise from similar phenomena. These are summarised graphically in figure 1.20, where the synthesis of each material family discussed is categorised into 4 stages - reagents, mesostructure generation, silica precipitation, and activation.

Therefore in order to fully relate these to one another, as well as to ameliorate their respective problems, BIS materials exhibiting synthesis features from multiple synthesis pathways should be developed. Further, whereas activation of silica materials has previously been studied singularly, combined approaches to solve the issue of organic removal are required. This would permit one of the larger technical problems facing these families of material to

be overcome simultaneously, greatly reducing the overall effort needed.

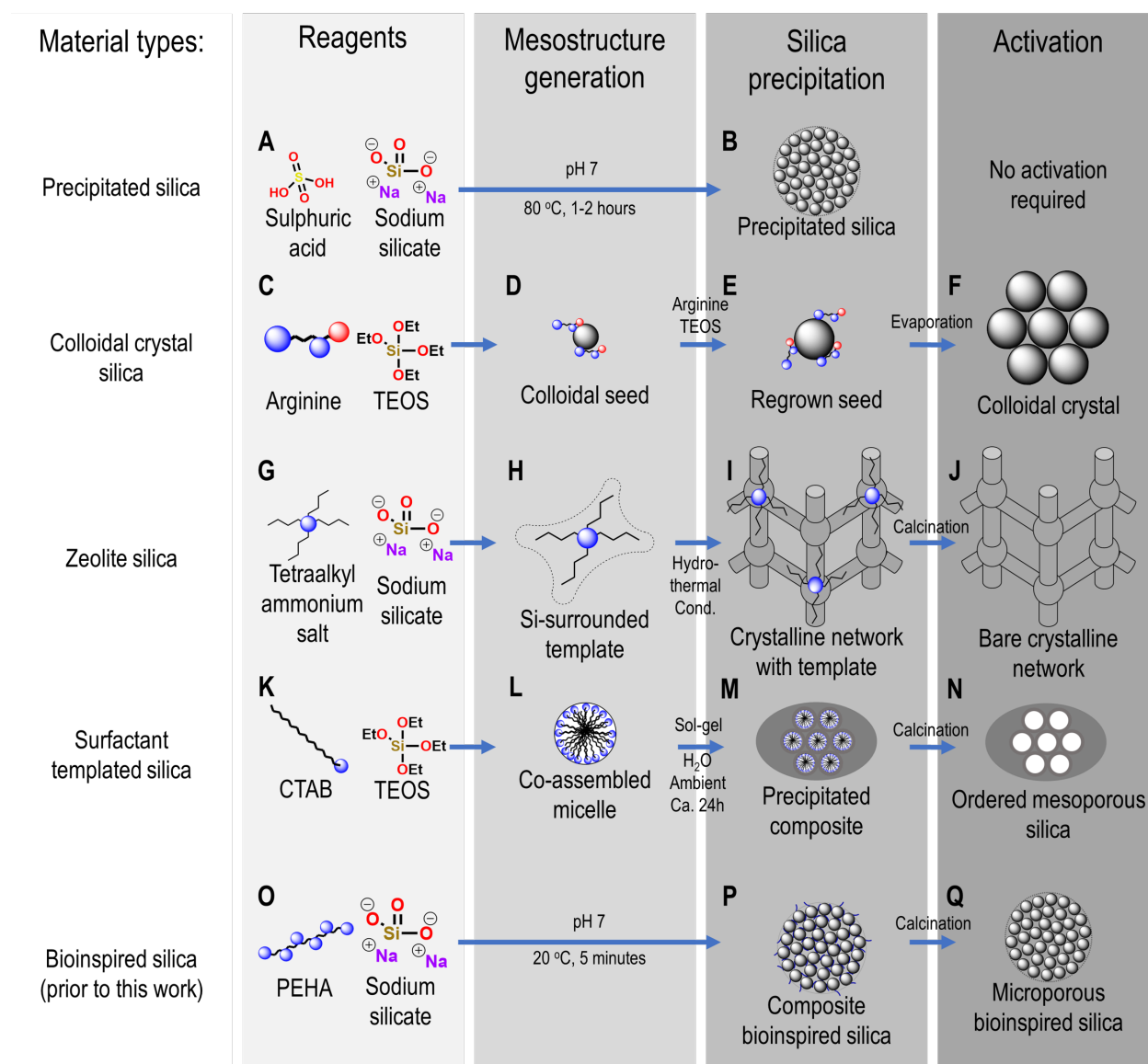


Figure 1.20: Comparison of silica synthesis methods and the effect of (meso)structure-direction and activation on final properties. (A-B) Industrial precipitated sol-gel silica, (C-F) Sol silica forming colloidal crystals, (G-J) hydrophobically-templated zeolite silica, (K-N) surfactant-templated mesoporous silica, and (O-Q) bioinspired silica.

1.8 Goals of this project

1.8.1 Aims and scope

This project focuses on developing new synthesis methods for BIS materials, both for the optimisation of preexisting production pathways and for discovery of novel material functionality. This is primarily with the focus of BIS scale-up from laboratory to commercial level, which will be required for the advantages of BIS to see widespread impact. Development of novel functionality, and concurrent investigations of synthesis mechanisms, will serve to both expand the possible uses for BIS and enable its better relation of to other silica types.

Further, ancillary processes required for BIS scaleup (i.e. BIS activation) will be considered in-depth for the first time. Prior studies of silica activation have highlighted the importance of mild purification for silica material scaleup; therefore before BIS production at scale can be achieved, this problem must be solved.

Despite the focus on new synthesis methods and material functionality, this project does not aim to establish new uses for BIS materials. Several potential applications for BIS have been reported elsewhere, however without sustainable process chemistry for BIS being developed (and from this information regarding process economics), further investigation would only be for academic interest.

Finally, as this project focuses on new synthesis methodologies, full analysis could not be performed by the author due to time constraints. As a result, the author collaborated with several other researchers who primarily study analytical techniques: Dr. TWS Yip & Ms. A Balashanmugam for CO₂ sorption experiments; Mr. CM Brambila for transmission electron microscopy; Mr. B Bowler for thermogravimetry-mass spectroscopy analysis; Dr. S van Meurs & Dr. B Walkeley for nucleomagnetic resonance spectroscopy; and Dr. M Jorge & Dr. A Centi for atomistic molecular dynamics simulations. Although these researchers manipulated the raw data prepared and aided in interpretation of results, all conclusions were drawn by the author.

1.8.2 Structure of this thesis

This thesis sets out to develop new methods for bioinspired silica synthesis, creating novel materials and synthesis approaches in order to help solve the above problems. First, chapter 2 describes the methodology of syntheses and analyses undertaken herein, describing the theory behind methods used wherever pertinent.

In chapter 3, bioinspired silica scaleup is addressed experimentally for the first time. Initially, current synthesis methods are scaled from 100 mL reaction volumes to 5 L, using continuous mesoscale methods to produce several hundred grams of bioinspired silica for the first time. Then, based on feedback from several process development experts based in industry, chemical intensification of the synthesis method is carried out to address their 6 shared concerns about bioinspired silica.

Chapter 4 describes the use of reaction effluent recycling for the synthesis of further bioinspired silica materials for the first time. Initial tests indicate that this can be done without any unwanted changes to the material properties, however novel silica morphologies can be easily obtained depending on which additive chemical is used. The development of this method to seed bioinspired silica with this specific mesoporosity is then reported, and its synthesis mechanism & methods for mesoporosity tailoring are then described.

Chapter 5 addresses finishing of bioinspired silica materials for the first time. Supported by molecular dynamics simulations of amorphous silica surfaces, a room temperature, pH-based method for extracting bioinspired additives from silica into water is developed and optimised. The use of partial extraction is further reported, enabling in-depth analysis of the silica surface chemistry and additive bonding mechanism through solid-state nucleomagnetic resonance spectroscopy. Direct chemical functionalisation of bioinspired silica through partial extraction is then shown, after which the ramification of this development upon prior methods developed herein are assessed, and technoeconomic comparisons with extraction methods developed for other silica materials families are made.

Finally, chapter 6 summarises the overall findings of this work, and suggests further research which can be done to extend the knowledge gained herein.

Chapter 2

Materials and Methods

2.1 Synthetic techniques

This project focuses on developing new methods for bioinspired silica synthesis to enable larger-scale production, new material properties, and hence new applications. Accordingly, bioinspired silica was synthesised with a range of different synthesis modifications. In addition Stöber silica nanospheres with a range of sizes were synthesised, primarily for use as feedstock for further bioinspired silica synthesis.

2.1.1 Bioinspired silica synthesis

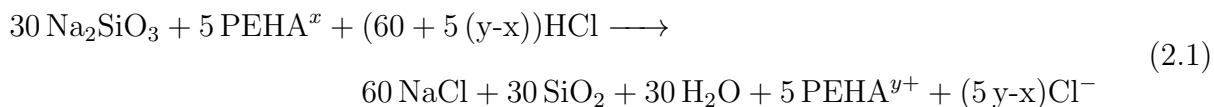
Background

Bioinspired silica (BIS) is a sol-gel silica modified by the inclusion of an organic additive to both accelerate particle growth and provide structural information. Accordingly, BIS synthesis has many potential variations both in terms of choice of additive molecule and also the concentration and ratios of both additive and silica source, with concurrent consequences to both reaction progression and silica properties.¹³¹ As discussed in chapter 1, investigations on the effect of additive structure to final silica material properties have been carried out focusing on amine-group electropositivity,^{134, 139} physical separation between amine moieties,¹³⁵ and additive molecule homologation.¹³³

Although no studies have previously collated the results from the above reports to provide generalised additive-microstructure relation rules (especially due to incompatibility between some of the units used within these studies), this project focussed on optimising the syntheses for the scale up to pilot or manufacture level, as well as mechanistic investigation to extend understanding of amine-templated silica sol-gels. The general procedure carried out is described below, with modifications described as they become pertinent later in this thesis.

Regardless of the additive structure, one thing that remains constant throughout BIS synthesis both in the literature and reported here are their pH progression. Initial reaction mixtures of amine and silicate are highly basic (pH ca. 12), which renders silica polymerisation essentially impossible due to negative charge on the silicate monomers. The reaction must then be initiated by reducing the pH to between ca. 9 and ca. 2. Obviously providing consistency between different experiment batches is of paramount importance, so reactions were initiating by titration to pH ca. 7.

While in theory the titre volume required to achieve the reaction endpoint of pH 7 is a fixed, stoichiometric quantity corresponding to neutralisation of the highly basic sodium silicate and weakly basic amine (shown in equation 2.1), There are several unknown factors that increase the complexity of determining the quantity of H^+ required. First, the charge state of the polyamine PEHA must be estimated. This can be theoretically determined, for example using the online group contribution tool SPARC,¹⁴⁹ which estimates that $x = 0.05$ at pH 11, and $y = 3.43$ at pH 7. This indicates that the overall amount of HCl required should be 76.9 mM.



However, equation 2.1 assumes complete conversion from sodium silicate to anhydrous, quartz-like silica, something which is demonstrably untrue for sol-gel materials. Although on the face of it, this should only change the quantity of water produced through condensation ($\text{SiO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{SiO}(\text{OH})_2$), silica pK_a changes as it shifts from monomeric units ($pK_a \approx 9.8$)⁷ to colloidal particles and bulk silica ($pK_a \approx 6.8$ for both colloids and bulk silica),⁷

creating a knock-on effect for the amount of acid required. Combined, these effects render the task of stoichiometrically determining the titre volume impossible. Instead, empirical determination of key titre volume was performed, leading to equation 2.2, where $[H^+]$ is the required final acid concentration in *mmol/l* (equivalent to titre volume in ml for 1M acid) and the Si:N ratio was maintained at 1.

$$[H^+] = 2.3[Si] + 0.12 \quad (2.2)$$

Equation 2.2 was determined empirically from a high number of experiments performed between $[Si]$ of 30 and 165 mM, remaining valid to within experimental accuracy constant throughout. From this, the total value of H^+ in equation 2.1 was determined to be 71.2 mM

Setup

Solutions of pentaethylenhexamine (PEHA) and sodium silicate in water were separately prepared such that the final concentrations at the end of the reaction would be 5 *mM* and 30 *mM*, respectively. This led to a Si:N ratio of 1, i.e. if DETA were used instead the concentration would be increased to 10 *mM* to maintain the ratio.

Once fully dissolved the solutions were combined and made up to 92% of the expected final volume with deionised water, then mixed either by magnetic stirrer or overhead stirring by a Radleys Reactor Ready system or IKA Eurostar Labortechnik overhead stirrer.

Reaction

Immediately prior to the reaction an aliquot of the mixture was removed for base digestion and silica quantification and the pH was measured by suspending a pH probe in the reaction mixture. Then sufficient acid was added in one aliquot to neutralise the solution according to equation 2.2.

The pH was monitored for 5 minutes, either manually or automatically, after which point the pH would have reached 7 ± 0.05 . The resultant slurry was decanted for workup and isolation.

Workup and isolation

Particles were isolated from their reaction mixture by centrifugation at ca. 4 300 *g* for 15 minutes in a Sorvall Legend ST16 centrifuge, after which further aliquots of the supernatant were taken for analysis using the silicomolybdic acid and digestion methods, as well as dynamic light scattering on occasion. The remainder of the supernatant was discarded, and the remaining silica cake was re-suspended in deionised water to be spun again. The supernatant was again discarded prior to further re-suspension and centrifugation for a final, third time.

After the final spin, the silica compacts were decanted from their centrifuge tubes to ceramic crucibles, then dried overnight in an oven set to 40 °C.

2.1.2 Silica nanosphere syntheses

Silica nanospheres were produced by the Stöber²⁶ method. The particles generated therein were either used for direct comparison to bioinspired silica colloids (e.g. by dynamic light scattering (DLS)) or for usage in further synthetic experiments described in chapter 4.

Stöber silica

Background

The synthesis of uniform silica nanospheres has been known in the literature since the landmark study of Fink, Bonn, and Stöber in 1968.²⁶ This material has been the subject of intense research since its discovery to improve both understanding of its formation mechanism (either as LaMer-style nucleation and growth, or a more complex nucleation-aggregation mechanism),²⁵ and how to improve control of particle size and uniformity during synthesis,^{150–152} although no consensus in terms of how best to control particle size and shape appears to have been reached.

Setup

For the Stöber silica, mixtures of aqueous ammonia in ethanol and TEOS in ethanol were separately heated in an oil bath at 50 °C for 80 minutes. Both ammonia and water have been previously found to catalyse TEOS hydrolysis,¹⁵² which is normally the rate-limiting step in Stöber synthesis and therefore correlates with final particle size. Accordingly, their concentration was varied, as shown in table 2.1.

Table 2.1: Absolute ammonia concentration, volume, and final particle size for Stöber silica synthesis

x	Volume $\text{NH}_3(\text{aq})$	Approx. size (nm)
0.311	0.216	8
0.467	0.324	12
0.622	0.432	40
$\vdots$	$\vdots$	$\vdots$
3.11	2.16	400

Reaction

After this incubation time, the TEOS solution was added dropwise to the ammonia solution leading to a final reaction composition of 1 TEOS: $x \text{ NH}_3$: 11.9 - 3.85 $x \text{ H}_2\text{O}$: 26.65 EtOH. The reaction mixture was then steeped under stirring in the same oil bath for a further 24 hours, before being decanted into bottles for storage at 4 °C to prevent further progression of the reaction.

Workup and isolation

Aliquots of the nanoparticle suspension were taken directly for analysis by DLS and silicomolybdate quantification methods. Purification of the materials prior to further manipulation was achieved by dialysis through 3.5 KDa tubing over the course of 24 hours, with solvent (typically H_2O) being changed 3 times over the duration. After this point, nanospheres of known concentration could be used to form bioinspired silica by heterogeneous seeding as described in chapter 4.

2.2 Post-synthetic modification

Materials synthesised in this project typically underwent post-synthetic modification, either to open up the porosity left by templating or to change the silica surface physical and chemical properties. To achieve this, templates were removed through classical calcination or ambient acid extraction.

2.2.1 Organics removal via calcination

Setup

A sample of silica prepared according to the procedures defined in section 2.1 was placed in a ceramic crucible.

Reaction

The crucible was then placed inside a muffle furnace at ambient temperature. This was then heated to 550 °C at a ramp rate of 2 °C/minute. Once at temperature, the sample was held for 12 hours before uncontrolled cooling to ambient.

Workup and isolation

Once cooled, the material was removed from the crucible and weighed into a sample bottle for further analysis.

2.2.2 Organics removal via acid elution

Setup

A sample of bioinspired silica was prepared as described in section 2.1.1, either as a dried powder after centrifugation or drying or used directly as a still-suspended coagulum. If the sample had been dried, it was re-suspended in water at a concentration of approximately

150mg/100ml. A pH probe was suspended into the resulting turbid liquid and the initial pH was recorded.

Reaction

To the above suspension, a mineral acid (typically HCl or H_2SO_4) was added until the pH dropped to the required level as described in chapter 5. pH was recorded after waiting for 1 minute for the pH reading to stabilise.

Workup and isolation

After the pH had stabilised and been recorded, centrifuge, the sample was washed and dried as described in section 2.1.1 before weighing into a sample bottle for further analysis and storage.

2.3 Analytical techniques

A number of analytical methods were used to characterise the synthesis methods developed within the synthesis and their resultant materials. pH was recorded throughout the synthesis of bioinspired silica to confirm inter-batch similarity; similarly, the silicomolybdate blue test was used to characterise extent of reaction both in terms of monomer consumption and concentration of stable colloidal silicas through the use of base digestion of colloidal silica species; finally, dynamic light scattering was also used to identify the size and dispersity of these colloidal silicas.

Solid silica precipitates were characterised with the following methods: electron microscopy (transmission and scanning) to determine the particle morphology and give a qualitative overview of particle size and dispersity; nitrogen surface area analysis was used to characterise the surface area and pore-size distribution of the materials; carbon dioxide adsorption was used to determine the surface chemical functionality and give a suggestion as to the rate-limiting step for sorption; thermogravimetric and elemental analyses were used to confirm the composition of the materials after various modification techniques; and fi-

nally solid-state nucleomagnetic resonance spectroscopy (SSNMR) was used to confirm the chemical composition and surface chemistry of the silica materials.

2.3.1 Reaction mixture analysis

Measurement of pH

Background

The concept of pH was originally brewed up in 1909 within the laboratories of the Carlsberg Research Centre in Copenhagen. Therein, Sørensen was attempting to measure the effect of certain ion concentrations on protein activity. After finding that hydrogen ion concentration was particularly important to activity, he devised a simple scale for quantifying $[H^+]$, the pH scale (shown in equation 2.3).

$$pH = 10^{-[H^+]} \quad (2.3)$$

In the intervening century, pH has become a cardinal property in a wide range of academic and industrial chemical laboratories, in the latter being chiefly for quality control to assess product reproducibility. Despite its ubiquity, there remains several issues with pH, largely stemming from the fact that it is impossible to measure $[H^+]$ directly. Instead, the electrochemical potential of a test solution is commonly used to infer pH through correlation with several standard solutions.

This is performed by using a pH probe, a specialised electrochemical cell designed to be immersed in an unknown test solution to determine its potential. Traditional electrochemical cells consist of an anode immersed in a first solution, a cathode immersed in a second solution,

and a junction (commonly known as a salt bridge) which connects the two. Both solutions contain salts which can perform a reduction or oxidation (redox) reaction with its anode or cathode, e.g. an anode made of metallic Ag would be in contact with a solution of Ag^+Cl^- , or a Cu electrode would be in contact with $\text{Cu}^{2+}\text{SO}_4^{2-}$.

The electrical circuit is completed by connecting the two electrodes together, and bridging the two solutions such that anions can diffuse towards the cathode, and cations towards the anode. Naturally, mixing of the dissolved electrochemical species can cause interference in each of the redox reactions (in the above example, solution mixing would enable $\text{Cu}^{2+}\text{Cl}_2^-$ to form for example), so the two solutions are connected by a porous membrane containing a saturated solution of inert ions (commonly KCl). The difference in electrochemical potential can then be measured as the potential difference (voltage) between the two electrodes, drawn schematically in equation 2.4, where a single vertical bar “|” indicates a phase boundary, and a double bar “||” indicates a salt bridge between two otherwise unconnected solutions.



A pH probe is constructed of a more complex electrochemical cell, as inducing a redox reaction in the test solution would interfere with the environment being tested. Instead, a pH probe is constructed of two electromechanical cells connected to the test solution on one side by a nonconductive glass bulb and on the other, a porous ionic salt bridge. In order to complete the circuit, the nonconductive glass bulb is coated by a porous gel on both sides; as ions diffuse from one side of the glass into its gel coating, an equivalent diffusion out of the gel on the other side occurs, leading to ion conductance. This is shown schematically in figure 2.1, where label 1 is the gel-coated glass bulb, 2 is a solid-solid electrode consisting of Ag and solid Ag^+Cl^- which is contact with a buffered K^+Cl^- solution and a constant dilute HCl solution to provide a reference (3), itself in contact with the bulb (1). Label 4 is a precipitate of AgCl that occurs after prolonged use of the probe, 5 & 6 are the second electrode-solution pair equivalent to label (2), but which are connected to the solution by the porous salt bridge (7), and finally 8 is the overall probe casing.

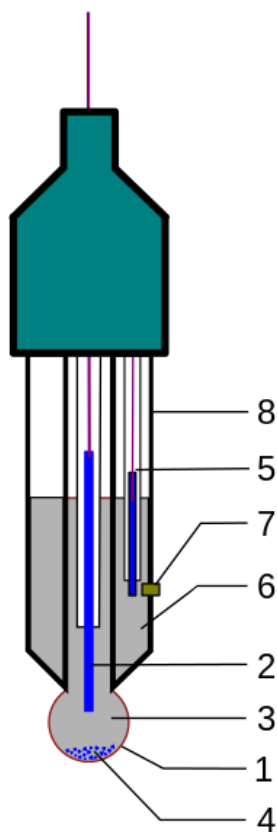
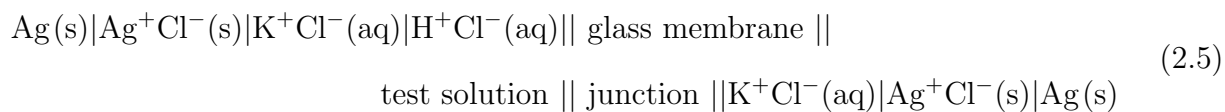


Figure 2.1: Schematic drawing of a pH probe. Originally drawn by Dr. Alexander Kaverin

Within the probe, the two cells are commonly the same, so theoretically the only source of potential difference is the test solution itself, as can be seen in the electrochemical cell drawing in equation 2.5, where the phases (s) for solid, and (aq) for dissolved aqueous species are shown for clarity.¹⁵³



From all of this, a test solution potential in millivolts can then be recorded. To transform this into pH, the Nernst equation is used to compare the test solution potential to the potential of a test solution of known pH (equation 2.8).

$$E = E_0 + \frac{RT}{F} \ln(Q) \quad (2.6)$$

$$E_{test} - E_{reference} = \Delta E = \frac{2.303RT}{F} \log \left(\frac{[H^+]_{test}}{[H^+]_{reference}} \right) \quad (2.7)$$

$$\Delta E = \frac{2.303RT}{F} (pH_{reference} - pH_{test}) \quad (2.8)$$

Where in equation 2.6 (the original Nernst equation), E is the overall electrochemical potential, E_0 is the reference cell potential, R is the ideal gas constant, T is Temperature, F is the Faraday constant, and Q is the quotient of a reaction being measured - the ratio of thermodynamic activity (equal to the under dilute conditions) of the redox products and reagents. For pH, the reactions being measured are acid-base dissociation culminating in a change in the activity (concentration) of H^+ . Therefore, the logarithmic term $\ln(Q)$ can be converted to $2.303 \log [H^+]$. In order to eliminate the unknown E_0 , pH is measured as the *difference* in potential between a reference solution and test solution.

This leads to a clear relation between electrochemical potential and pH, where an arbitrary pH (normally 7) is taken as $\Delta E = 0$ and $\partial E / \partial pH = 2.303RT/F \approx 60 \text{ mV}$.

However, in order to be valid, several stringent restrictions are placed on the composition of the test and reference solutions. In short the compositions and conditions of the test, reference, and internal solutions must be essentially identical in order for equation 2.8 to be valid, as any discrepancy in diffusion rates or ionic activities within the 3 solutions will lead to potential differences across the junctions within the electrochemical cell (hence differences in the E_0 values between the two solutions.¹⁵⁴ Fortunately these errors are generally systematic rather than proportional, meaning that, although the absolute value may be incorrect, measured pH differences between set reference and test solutions should be reproducible and therefore valid for quality assurance purposes.

Setup

To prevent depletion of ions within the probe's salt bridge, pH probes were held within 3M KCl storage solutions both for storage and between individual measurements. Probes were calibrated by removing them from their storage solutions, rinsing them in deionised water and drying carefully with a paper towel. They were then suspended into a reference solution of known pH (usually pH 7).

A calibration algorithm on the probe's connected pH meter was then used to record $E_{reference}$ for pH 7 in order to tare the recorded electrochemical potential and account for any systematic error in the probe cell. The probe was then rinsed and dried again, before being suspended in a reference solution of pH 10 in order to calibrate $\partial E/\partial pH$ and account for any proportional errors e.g. due to deviations in ambient temperature from 298 K.

Finally, the probe was rinsed and dried again, before returning to the storage solution.

Procedure

Measurement of test pH was performed similarly to pH calibration - the probe was removed from its storage solution, rinsed, dried, then suspended within the test solution (usually the BIS reaction mixture) under mild agitation by hand or by a stirrer bar. Initial pH was recorded for ca. 30 seconds until the reading stabilised, after which it was recorded. If measuring pH during a BIS synthesis, the reaction was then initiated as described previously. At this point, measured pH was recorded every 30 s (or 1-2 s during use of the Metrohm titrando equipment), in order to characterise the progression of the reaction. Once complete, the pH probe was rinsed, dried as described before, and returned to its solution for storage.

Analysis

pH measurements were primarily used in this study to measure similarity between synthesis batches of BIS silica. pH was measured before, during, and at the reaction endpoint in order to ensure uniformity at all stages of the sol-gel synthesis. Beyond this, pH measurement was used to measure acidic environment during post-synthetic modification of BIS materials produced (discussed in chapter 5, ensuring consistency in final composition of the modified BIS materials).

Silica speciation and extent of reaction

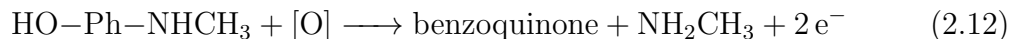
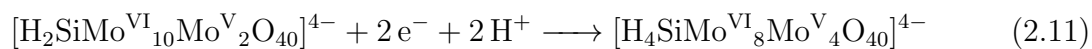
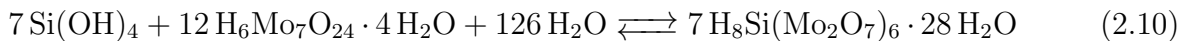
Background

Measurement of silica yield was generally achieved through measuring the mass yield, however in order to fully characterise the sol-gel synthesis, in-situ measurement of silicate monomer consumption is essential. This can be measured spectroscopically by reacting leftover silicate monomers to form light-interacting compounds. After this formation, absorbance of light can be related to concentration through the Beer-Lambert law (shown in equation 2.9, which measures the amount of light of a specific wavelength which is absorbed while passing through a solution.

$$A = \epsilon(\lambda) \cdot l_{path} \cdot C \quad (2.9)$$

In equation 2.9, A is the absorbance of a sample (equal to the logarithm of the relative amount of light transmitted through the sample), ϵ is the molar extinction coefficient - the rate by which light is absorbed while passing through the solution (in $M^{-1}cm^{-1}$, l is the transmission path length the solution must pass through, and C is the absorbing species concentration.

In order to determine the concentration of silicate ions in the reaction mixture, it was reacted with molybdic acid to form light-absorbing silicomolybdate poly(oxometalate) molecules in solution. In this, mono- and dimeric silicic acid species react with molybdic acid to form the yellow α -Keggin silicomolybdate complex (equation 2.10).^{155,156} This is then reduced to the blue β -Keggin ion (eq. 2.11) using a combined oxalic acid/metol sulphite reducing agent (Eq. 2.12¹⁵⁷).¹⁵⁸ This has two benefits, the first of which being that the reduction reaction prevents formation of further α -Keggin ions over time, therefore preventing dissolution of colloidal silica from contaminating the reading, and the second being that the β -Keggin complex has a higher molar extinction coefficient, enabling detection of silica down to ppb levels.¹⁵⁸



Once this solution had been prepared, standard spectrophotoscopic methods could be used to determine the concentration of silicic acid in the reaction mixture.

Setup

To prepare solutions for the silicomolybdic acid assay, 10g of ammonium molybdate (51 mmol) was dissolved in 500 mL deionised H_2O and 60 mL of 37 %wt HCl solution. The volume was then made up to 1 litre with H_2O . A reducing agent solution was prepared by dissolving 10g oxalic acid (111 mmol), 2g sodium sulphite (16 mmol), and 3.35g monomethyl-p-aminophenol hemisulfate (10 mmol) in 250ml H_2O , then adding 50 mL concentrated sulfuric acid solution while stirring. Once the solution had cooled, the volume was made up to 500 mL with water.

A stock solution of 4 mM sodium silicate was prepared by dissolving 0.8510 g of sodium silicate pentahydrate in H_2O and diluting to 1 L.

Procedure

For the analysis, a 300 μl aliquot of the molybdic acid solution was diluted with 3 *ml* of H_2O . 10 μl of the reaction mixture was then added to the solution, which was then mixed and slowly turned a pale yellow. After 15 minutes, 1.6 *ml* of the reducing agent solution was added and the solution changed colour to blue. This was then allowed to stand for 24 hours (or 72 hours in a refrigerator), before being analysed in a UV-Vis spectrometer.

To measure the absorbance, analysis solutions (as well as a blank containing only the above molybdic acid solution, reducing agent, and water) were loaded into polystyrene cuvettes with a 1cm path length. These were inspected to remove all bubbles and visible dust from the light path, and then placed into a GENYSYS UV-Vis spectrophotometer. UV light

at a wavelength of 810 nm was shined through, and the absorbance recorded.

This was then compared against a calibration curve generated using a volumetric solution of 4 mM. Aliquots ranging from 0 to 100 μl were then subjected to the molybdenum blue assay, with one data point being taken in triplicate to assess the variability in measurements. An empirical model was then made through linear interpolation (with an exemplar being shown in in figure 2.2), with a new calibration being performed each time a new analysis solution was made up.

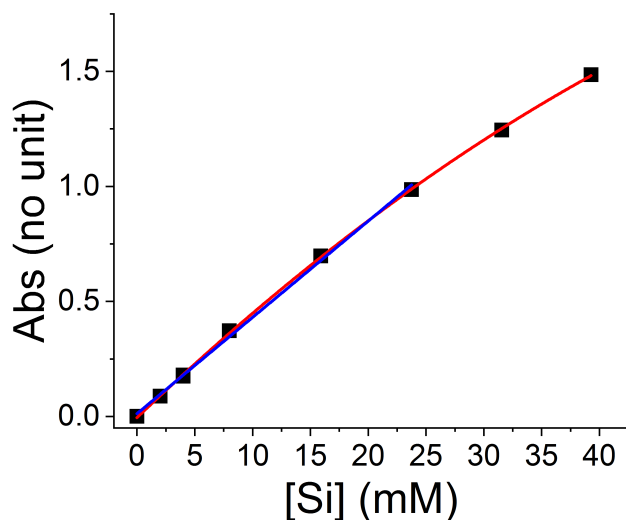


Figure 2.2: Graph of changing photometric absorbance against Si concentration during the molybdenum blue test. The data are fitted to a linear relationship (blue) below 27mM and a quadratic relationship for ranges above this, as the molybdenum will be stoichiometrically exhausted above this value according to equation 2.10.

For the analysis of suspended colloidal silica, the sample first had to be digested in sodium hydroxide prior to analysis to cause sufficient depolymerisation that all silica present could be detected. This was done by mixing equal volumes (typically 750 μl) of silica suspension and 2 M sodium hydroxide solution in a microcentrifuge vial, then sealing and heating the samples in a water bath 1 hour at 80 °C. After cooling, the digested silicas were usable directly for the molybdenum blue analysis.

Analysis

By combining conventional weighing of reaction products with molybdenum blue analysis both with and without colloid digestion, the extent of reaction both in terms of silica poly-

merisation and subsequent coagulation to form isolatable particles can readily be determined. This allows for investigation of how different reaction conditions impact upon both polymerisation and coagulation processes during sol-gel synthesis.

Infrared spectroscopy

Background

Similarly to ultraviolet spectroscopy, infrared (IR) spectroscopy uses electromagnetic radiation to investigate the presence of specific covalent bonds within a material. IR radiation matches the energy of the resonant frequencies of covalent bonds in chemicals, with different specific bond strengths corresponding to slightly different wavelengths. When a photon of this specific wavelength meets a covalent bond, it is absorbed by the bond in the form of vibrational energy, lowering the overall amount transmitted in the same vein as UV spectroscopy.

In contrast to UV spectroscopy, which is generally used to quantify concentration of a test species, IR spectroscopy is generally used to identify the presence of certain bonds within an unknown sample. This is largely because, while path length in the dilute solutions used in UV spectroscopy is an easily determined quantity, IR spectroscopy is performed on solid materials (either directly, using a technique known as attenuated total reflectance (ATR), or by transmission through a solid dispersion in the organic chemical nujol). Although absolute quantification through IR spectroscopy is nontrivial, *relative* quantification e.g. of Si–O–Si vs. Si–O–H functionality can be easily achieved.

In this study, ATR-IR was used to do exactly this - quantify the ratio of saturated to unsaturated silica at the surface of BIS, especially with varying organic additive content as shown in chapter 5. The characteristic wavelengths involved are 800 cm^{-1} , 950 cm^{-1} , 1050 cm^{-1} , and 1150 cm^{-1} . In order, these correspond to the symmetric Si–O–Si stretch region (in the transverse optical mode i.e. perpendicular to the incident light), Si–O stretching

associated with surface SiOH functionality, antisymmetric Si–O–Si stretching (also in the transverse optical mode), and antisymmetric Si–O–Si stretching in the longitudinal optical mode (coplanar with the incident light during analysis).¹⁵⁹

Setup

In this project, IR spectroscopy was performed using a Shimadzu IRAffinity 1S spectrophotometer with a SPECAC ATR attachment. The attachment was initially removed from the spectrophotometer prior to its startup sequence. The spectrophotometer was then switched on, and LabSolutions IR Spectrum software was opened to begin initialisation. After initialisation, the ATR attachment was replaced into the instrument.

The instrument was set to measure % transmittance of light between 400 and 4000 cm^{-1} in increments of 4 cm^{-1} , with 16 scans, using Happ-Genzel apodisation. Once these settings were made, the steel anvil was pressed onto the diamond ATR crystal without sample to gather a baseline signal.

Procedure

Once a baseline had been measured and stored, silica powder was crushed in an agar mortar and pestle and carefully loaded onto the diamond crystal to ensure complete coverage. The anvil was then pressed into place to ensure uniform contact, and a spectrum obtained. Once complete, silica was washed away from the ATR by suspending them in a 70% ethanol solution and wiping away with nonscratch tissues.

Given the region of interest in the silica samples was only between 650 and 1300 cm^{-1} , further high-resolution spectra were taken within this region. Unlike the procedure described above, this used 32 scans and a wavelength increment of 0.5 cm^{-1} to minimise the impact of noise. All other settings remained the same.

Analysis

Once extracted, further baseline correction was performed in the Fityk software,¹⁶⁰ and peak deconvolution using the Origin 2018 software, from which the relative peak areas for each of the four bending modes listed above could be identified. The ratio of the 950 cm^{-1}

silanol peak to either Si–O–Si bond stretch mode (800 cm^{-1} or 1050 cm^{-1}) could then be used for comparative analysis between samples.

Particle sizing

Background

Dynamic light scattering measures the intensity of light scattered by a suspension at a set angle. As typical solvents are composed of molecules which are too small to interact with light, any variations in the scattering signals will be due to light incident onto a particle. The rate at which this scattering changes is dependent on the diffusivity of the colloidal particles, from which particle diameter can be calculated using the Stokes-Einstein equation (equation 2.13).

$$D = \frac{k_B T}{6\pi\eta r_{hyd}} \quad (2.13)$$

Where D is the diffusivity of a particle, k_B is the Boltzmann constant, T is the temperature in Kelvin, η is the fluid's kinematic viscosity, and r_{hyd} is the particle hydrodynamic radius. Diffusivity itself can be calculated from the intensity signal using the process known as autocorrelation. In this, the scattered light signal at time t is compared to the signal after a short delay ($t + \tau$) to measure their similarity. Therefore, at $\tau = 0$, the autocorrelation value $G(\tau) = 1$, while at $\tau = \infty$, $G(\tau) = 0$. As can be seen in the illustrative scheme in figure 2.3, smaller particles move faster and hence have faster autocorrelation decay. From these autocorrelation functions, diffusivity can be calculated using equation 2.14

$$G(\tau) = A + B \cdot e^{-Dq^2} \quad (2.14)$$

$$q = \frac{4\pi n}{\lambda} \sin(\theta/2) \quad (2.15)$$

Where A and B are the function baseline and maximum (usually normalised to 0 and

1 respectively), q is the magnitude of the light scattering vector (equation 2.15), n is the fluid's refractive index, λ is the laser wavelength, and θ is the scattering angle in radians. While in theory the decay functions of a polydisperse colloidal suspension are simply additive (i.e. $G_{tot} = \sum_i G_i$), in practise the deconvolution of such mixtures is very difficult as scattering intensity is a function of incident surface area.^{161,162} Therefore even if a smaller particle is in large excess in terms of population, results will be skewed towards larger particles (demonstrated in figure 2.4). As a result, analysis of DLS spectra in isolation is often inconclusive.

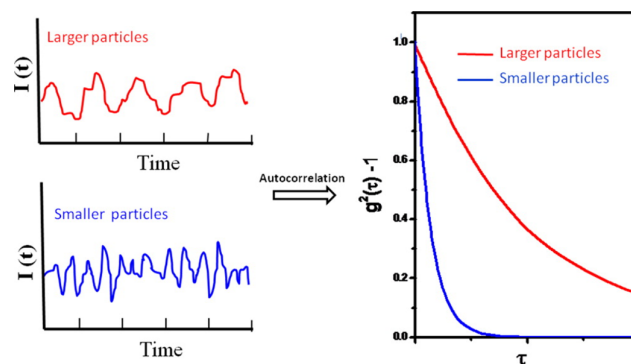


Figure 2.3: Schematic of autocorrelation functions generated for two typical light scattered signals. (left) raw scattering intensity for two different sizes of particle, and (right) their representative autocorrelation functions (here notated as $g^2(t)$). Reproduced from reference 163

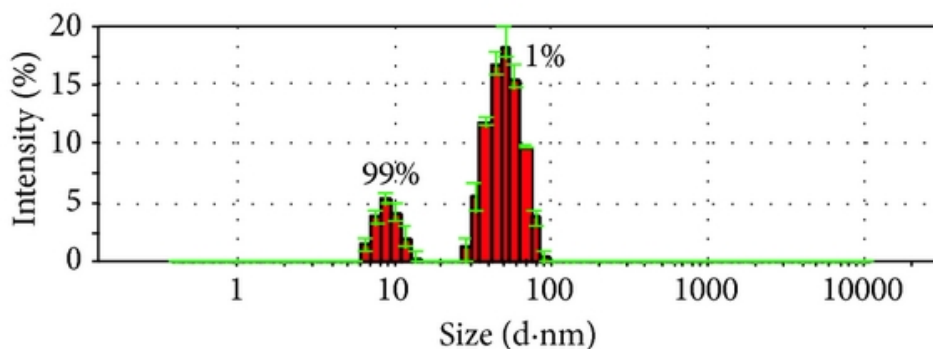


Figure 2.4: Graph of scattering intensity versus particle size for a mixture of 10nm and 55nm silver nanoparticles at true relative mass populations of 99% and 1%. Reproduced from reference 162

Setup

Dynamic light scattering experiments were performed at the University of Sheffield on a Brookhaven ZetaPALS instrument using a 660 nm red diode laser, scattering at 20 °C and

90° scattering angle. The viscosity of all samples was assumed to be negligibly different from pure water, due to the low concentration of nanomaterials present.

Analyses were performed either on as-made silica suspensions, silica suspensions which had been stored at 4 °C, or a suspension of 100 nm latex beads to confirm similarity between analyses on different days.

Procedure

A cuvette filled with undiluted reaction mixture or a dilute latex bead suspension was loaded into the ZetaPALS. Scattering intensity was measured for a 45 second duration, repeated 5 times, after which an average autocorrelation curve was determined. Particle sizes and their distribution were calculated internally using the non-negative least squares (NNLS) method developed by Morrison et al.¹⁶⁴ for mean square distribution of polydisperse samples.

Analysis

For the vast majority of data collected by DLS, manual calculation of hydrodynamic diameter could not improve upon the equipment's internal interpolation algorithms. To confirm this, raw autocorrelation data were manually compared against the theoretical curve corresponding to its fitted diameter (shown in figure 2.5), ensuring that the fit was appropriate to the data. Where this fit did not correspond to the raw data, manual fitting was performed.

2.3.2 Analysis of solid silica materials

Scanning electron microscopy

Background

Electron microscopy is the technique by which materials are imaged at length scales significantly lower than the frequency of light. By using electrons rather than photons as the detection medium (due to their correspondingly low De Broglie wavelength), images with features in the nanometer scale can be reliably taken.

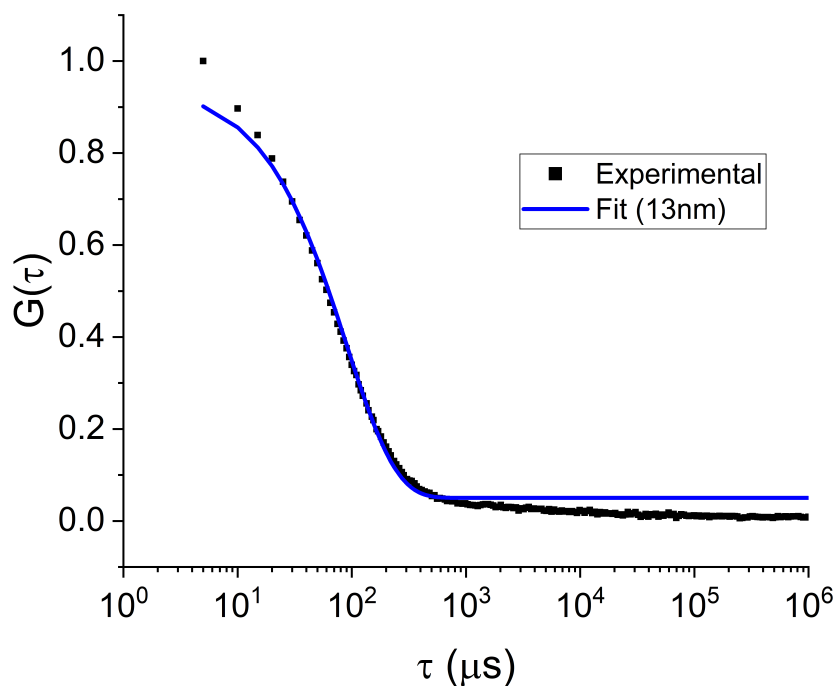


Figure 2.5: Graph of raw autocorrelation data (dots) superimposed onto a theoretical curve corresponding to equation 2.14 for $r_{\text{hyd}} = 13\text{nm}$.

Physically, an SEM works by firing a beam of electrons excited to a certain potential at a material sample. Those that strike the sample are scattered at a certain angle according to the specific topology of the material in that location. Moving the electron beam across the material surface in a known pattern (scanning) then allows for a picture to be generated.

Setup

Silica materials prepared elsewhere in this study were crushed into a fine powder and deposited directly onto a 10mm SEM stub which had been covered in carbon tape. Once a thin covering of the stage had been achieved, materials were coated in gold to prevent charging of the sample by electron absorption (absorbed electrons simply being conducted through the gold towards the stub).

Procedure

A loaded SEM stub was secured in the holder of a Hitachi SU-6600 instrument. The analysis chamber was then sealed and evacuated. Initial positioning of the stage was performed, after which the electron beam was introduced into the chamber and lens alignment & focus were corrected.

Analysis

Once focussed, image capture of the samples were made at a range of magnifications for at least 3 different sites on the sample. These were then compared qualitatively across samples at the same magnification to show morphological differences.

Surface area analysis

Background

One of the key features of nanomaterials is their specific surface area. As structures with complex and tortuous topologies shrink to the nanoscale, their surface area (measured in m^2/g) increases enormously, vastly changing the properties of the material. Surface area is typically measured through the adsorption of inert gases onto a surface. At a certain temperature and volume the amount of gas molecules which adhere to a chemical surface is a function of the environment pressure, mathematically described as an isotherm. This can then be manipulated in a number of ways to infer knowledge about the bulk properties of a material.

Several isotherm models for a purely physical interaction between adsorbent and adsorbate exist, most notably the Brunauer-Emmet-Teller (BET) and Langmuir theories.¹⁶⁵ BET theory is an extension of the earlier Langmuir isotherm, which considers the surface to be a uniform lattice of potential adsorption sites which can be singly occupied, depending on the interaction energy between surface and adsorbent and the system pressure. BET theory considers the adsorption of a second guest molecule on top of an initial monolayer, leading to a significant improvement in fitting for larger pore diameters.

Mathematically, the Langmuir isotherm appears as in equation 2.16, where θ is fractional adsorbent coverage of the monolayer, p is the adsorbent pressure and K is the interaction energy. Whereas Langmuir theory is expressed in terms of absolute pressure, BET theory assumes that further adsorption layers act equivalently to liquids hence above a certain pressure the number of layers will be infinite. Therefore, in the BET isotherm equation, equation 2.17, pressure is listed as relative ($\frac{p}{p_0}$). Likewise, the overall coverage extends from a fraction of the area θ to volume adsorbed above a monolayer (v and v_m , respectively). Finally, the interaction term c takes into account both the energy of initial layer adsorption (E_0) and later energy of liquefaction (E_L) as shown in equation 2.18.

$$\theta = \frac{Kp}{1 + Kp} \quad (2.16)$$

$$v = \frac{v_m c \frac{p}{p_0}}{(1 - \frac{p}{p_0})(1 + \frac{p}{p_0}(c - 1))} \quad (2.17)$$

$$c = e^{\frac{E_0 - E_L}{RT}} \quad (2.18)$$

Through measurement of v at several different pressures important key aspects of a material's surface can be understood.

Setup

Dry silica samples prepared as described earlier were weighed into a nitrogen adsorption analysis sample tube, taking care to record the weights of the empty tube explicitly. These were then outgassed in a Micromeritics SmartVacPrep instrument by heating the samples to 115°C under vacuum overnight. After evacuation samples were removed from the apparatus to cool, and the outgassed mass recorded. The samples were then sealed from the atmosphere to prevent contamination of water vapour.

Procedure

Samples were analysed at the University of Strathclyde on a Micromeritics ASAP 2420 instrument, and at the University of Sheffield on a Micromeritics 3flex instrument.

Analysis tubes were attached onto one of the above surface area analysis manifolds, creating an airtight seal from which nitrogen and helium were dosed. Analysis began by evacuating samples and immersing the samples in a liquid nitrogen bath to provide a constant temperature of 77K during the analysis. The total volume within the tube was measured using helium gas (N.B. this was performed at the end of the procedure to prevent contaminating the sample with a stronger sorbent than nitrogen). Specific volumes of nitrogen gas were then dosed onto the sample, and the pressure measured after after equilibrating. Given the tube volume was known, the volume of gas adsorbed could then be determined. This was performed both for increasing and decreasing pressure between points to provide information about the pore geometry.

Analysis

The basic output from nitrogen adsorption analysis is an adsorption isotherm. This can be analysed directly by comparing against the 6 IUPAC ideal adsorption isotherms (see figure 2.6). Type I are highly microporous, characterised by their high adsorption at low p/p_0 and relatively low further adsorption at higher pressures; type II isotherms are generally indicative of non-porous or macroporous materials, as there is little adsorption in the low-pressure regions, and no hysteresis in the high-pressure regions which would be indicative of mesoporosity; type III isotherms are highly unusual, as their shape indicates that adsorbate-adsorbate interactions are more important than adsorbate-adsorbent behaviour as with type I. Isotherm types IV and V are both similar to isotherms II and III, with both exhibiting hysteresis. This indicates the phenomenon of capillary condensation within the material, where a distinct liquid phase forms below p_0 within mesopores, therefore evaporation upon desorption is delayed. Finally, isotherm type VI represents the formation of sequential monolayers on an entirely flat surface such as graphite. Point B, the inflection between convex and concave behaviour, is considered to be the point of monolayer coverage.¹⁶⁶

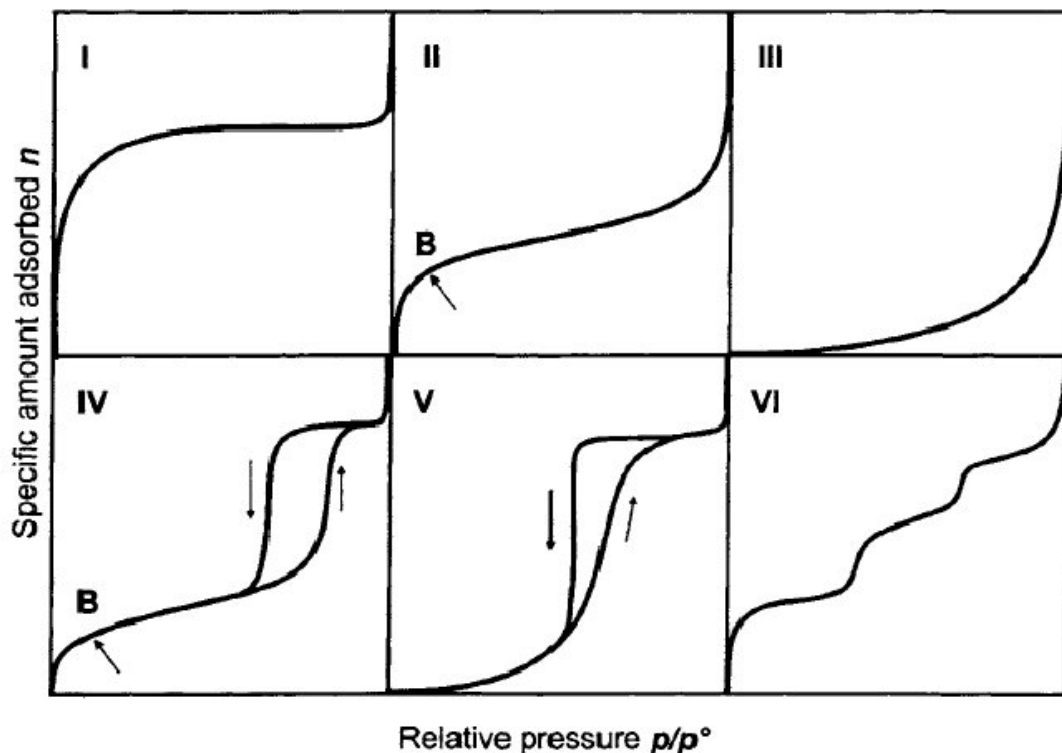


Figure 2.6: Graph of 6 typical categories of BET adsorption isotherms as defined by the IUPAC. Adapted from reference 166.

These data could then be manipulated to give quantitative information about the analysis material. Overall material surface area can be calculated by plotting $(1/v)[(p_0/p) - 1]$ against p_0/p , and fitting the points from $0.05 < p_0/p < 0.30$ to a straight line (approximately point B in figure 2.6), enabling the estimation of v_m .¹⁶⁵ To reduce subjectivity in this fitting, the Rouquerol protocol was used to ensure consistency: the adsorption energy (C) must be thermodynamically favourable and amount adsorbed ($n(1 - p/p_0)$) should be increasing with relative pressure.¹⁶⁷ Therefore only isotherm points complying with these conditions were fitted.

Pore geometry information could then be extracted from the isotherm through a variety of means. As indicated in figure 2.6, the partial pressure at which the majority of adsorption takes place can inform significantly on the pore size. This is based on the theory that saturation pressure within a pore is a function of its diameter, therefore differentiation of the isotherm can show the approximate size of pores within the material.¹⁶⁸ Furthermore, for analysis of micro- versus meso- and external porosity, the t-plot method can be used, where instead of pressure, volume adsorbed is plotted against estimated adsorption layer thickness.

Using this model, the relationship between adsorbed volume and layer thickness indicates pore size - a linear relationship with no inflection indicates that no pore-filling occurs (i.e. the material is nonporous). Inflection within this curve signifies a change in pore size. If the gradient reduces, this indicates that pores have become completely filled and further adsorption is on the outside of a particle; if the inflection is positive, this indicates that a condensation event within larger pores has occurred (illustrated in figure 2.7).¹⁶⁹

In figure 2.7, curve (A) represents nonporous materials, which show no inflection, as adsorption only occurs on their surface. only Microporous only materials (B) have a negative inflection point, signifying the point at which micropores are completely filled and further adsorption occurs on the future. Mesoporous materials (C) fill similarly to microporous material initially, until condensation within the pore occurs, leading to a positive inflection in the V-t curve. Finally, material structures composed of multiple pore types (D) have several inflections corresponding to type B or C depending on their geometry.

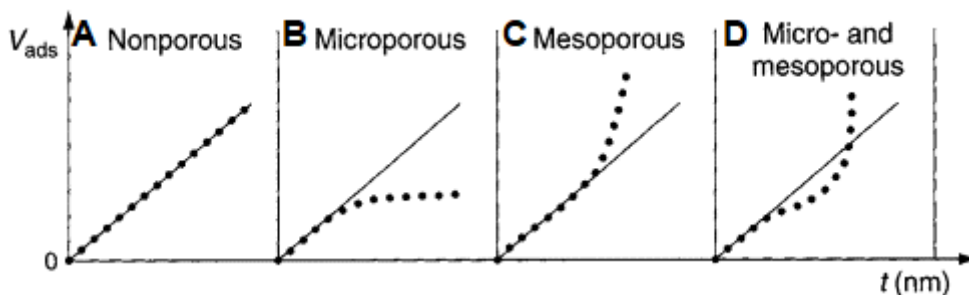


Figure 2.7: Four characteristic types of t -plot curves. Adapted from reference 169.

The final information that can be inferred from these isotherms lies in any hysteresis shown at higher pressures. As shown in figure 2.6 hysteresis occasionally occurs at high partial pressure, indicating a capillary condensation event within mesopores. The shape of the hysteresis desorption can then be used to infer geometric information about the mesopore system. In type I isotherms, the pressure-volume relationship is identical for both pore filling and emptying, indicating approximately cylindrical pore geometry. Type II isotherms display gradual adsorption but sudden desorption, indicating the pore has a smaller opening than its main body which presents no barrier to adsorption, but becomes plugged by condensed sorbate during desorption (hence only allowing the adsorbed fluid out once the fluid in the neck desorbs).

Types III and IV correspond to pores which have a very high aspect ratio i.e. are closer

to parallel plates rather than cylinders. Accordingly there is no well defined filling point of the pores during adsorption, nor any bottleneck effects upon desorption. Type IV differs from type III through the behaviour of the remainder of the isotherm - pore edges meet in a material with type IV hysteresis, leading to micropores which adsorb at low p/p_0 (an overall type I isotherm as shown in figure 2.6). Type III hysteresis has no such microporosity as the pores are akin to perfectly parallel plates, therefore the overall isotherm appears similar to type III from figure 2.6). There is a caveat at low pressure with hysteresis however, as below ca. $\frac{p}{p_0} = 0.4$ nitrogen will spontaneously cavitate and evaporate, forcing any hysteresis closed.⁵⁴

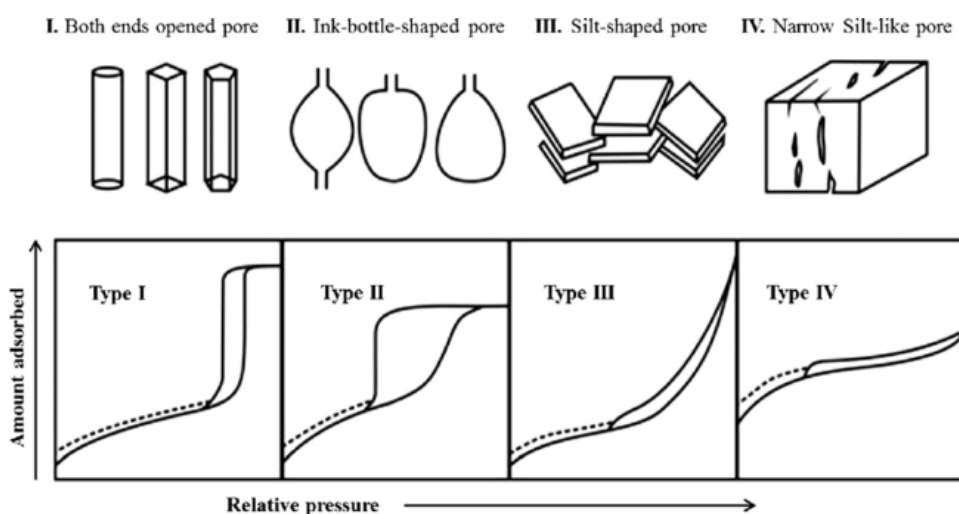


Figure 2.8: Visualisation of the four key types of hysteresis as defined by IUPAC (below), and their associated typical pore structures. Adapted from reference 170.

Thermogravimetric analysis

Background

Thermogravimetry studies the change in mass of a material as it is heated at a specific rate, therefore showing any decomposition or reactions of a material, and what temperature they occur at. Determination of organic's content within inorganic silica can easily be made by following the organics' thermal decomposition in this way. By comparing decomposition profiles and significant mass steps against literature values of thermal decomposition temperatures, changes in weight at characteristic temperatures can be ascribed to different chemical species. Some relevant temperature ranges for silica-organic composites are listed in table 2.2.

Table 2.2: Reported ranges of thermal decomposition for different chemical species. Taken from reference 88

Temperature (°C)	Chemical species
20-150	H ₂ O physisorbed
150-300	Organic material
300-520	H ₂ O from hydrated silica

Setup

Ordinary TGA experiments were carried out at the University of Sheffield on a Perkin Elmer TGA 4000. Some samples were run in the University of Newcastle by Mr. Bernard Bowler using a Netzsch STA449C TG-DSC-QMS to provide confirmation of the values in table 2.2.

Approximately 5-10mg of crushed silica was placed into a freshly cleaned crucible pan (cleaned by heating to 1000°C), which was then subsequently placed into a TGA instrument and the weight balanced. Flowing gas (air in Sheffield, 20%v/v O₂ balance He in Newcastle) was introduced into the system.

Procedure

Samples were heated at a constant rate of $10^{\circ}\text{C} \cdot \text{min}^{-1}$ from 25°C to 1000°C, after which they were held at 1000°C, before cooling back to ambient temperature.

Analysis

The raw experimental data were differentiated, and their component curves deconvoluted using Originpro 2018 to fit multiple Gaussian distributions to the data, whose area corresponds to the % weight loss attributable to each peak. Chemical species were assigned to peaks according to the data from Newcastle where it did not fit with those taken from table 2.2.

2.3.3 Analyses performed by others

NMR analyses

SS NMR experiments and raw data deconvolution were performed at the University of Sheffield by Dr. Brant Walkley. The following procedure was used:

Solid state single pulse ^{29}Si Magic Angle Spinning (MAS) NMR and ^1H - ^{29}Si Cross-Polarisation (CP) MAS NMR spectra were acquired on a Bruker Avance III HD 500 spectrometer at 11.7 T (B_0) using a 4.0 mm dual resonance CP/MAS probe, yielding a Larmor frequency of 99.35 MHz. ^{29}Si MAS NMR spectra were acquired using a 4.0 μs non-selective ($\pi/2$) excitation pulse, a measured 90 s relaxation delay, a total of 256 transients and spinning at 12.5 kHz.

^1H - ^{29}Si cross-polarisation (CP) MAS NMR experiments were performed using the same instrument with a spinning frequency of 12.5 kHz, a ^{29}Si non-selective ($\pi/2$) pulse width of 4.0 μs , an initial ^1H non-selective ($\pi/2$) pulse width of 2.5 μs , a recycle delay of 3 s and Hartmann-Hahn contact periods of 2 ms. A nominal ^1H decoupling field strength of 80 kHz was employed during acquisition and 1456 transients were collected per experiment. All ^{29}Si spectra were referenced to tetramethylsilane (TMS) at 0 ppm. Gaussian peak profiles were used to deconvolute the NMR spectra. The minimum possible number of peaks was fitted, and the chemical shift (δ_{iso}) and peak full width at half maximum (FWHM) of each resonance were required to be consistent in both the ^{29}Si MAS NMR and ^1H - ^{29}Si CP MAS NMR spectra. When fitting the data δ_{iso} and FWHM were held constant for each site within the same sample (i.e. only peak intensity was allowed to vary).

Carbon dioxide gravimetric absorption

Gravimetric gas sorption analysis was performed on a HIDEN analytical IGA by Dr. Thomas Yip at the University of Strathclyde and Ms. Abitha Balashanmugam at the University of Sheffield. A sample of silica was placed on a stage connected to a balance, and hermetically sealed into a chamber. This was subjected to a constant temperature (333 K), and a constant pressure of carbon dioxide gas was applied. The weight of the sample was measured at

constant time intervals until it equilibrated or 12 hours had passed or the pressure had equilibrated, at which point the pressure was changed to the next set point. From this, carbon dioxide adsorption rates could be determined and overall capacity could be measured in mmol/g.

Elemental analysis

Elemental analysis experiments were carried out at the University of Strathclyde by Mr. Alexander Clunie on a PerkinElmer CHNS2400 II analyser to determine the concentration of carbon- and nitrogen atoms within the silica sample. This was assumed to correspond directly with the the amount of amine additive within the sample, as no other source of nitrogen was present within the reaction mixture. A sample of silica was introduced into a high vacuum environment, after which any organic compounds were combusted fully. The gas evolved was trapped selectively by sequential hygroscopic and basic membranes with uptake detected by thermal conductivity detector to quantify evolution of CO₂, H₂O, and NO₂. From this, an original concentration of C, H, and N in the silica material can be determined.

Transmission electron microscopy

Transmission electron micrographs were captured by Mr. Carlos Brambila at the University of Sheffield Sorby Centre on a Jeol 420 microscope. A sample of silica was suspended in isopropanol and then cast onto a copper TEM grid. This was loaded into the microscope and evacuated, after which a bright-field image of the particles could be prepared at several magnification levels equivalently to the scanning electron microscopy similar to the approach taken during scanning electron microscopy.

2.4 Chemical reagents

A comprehensive list of the reagents used within this project is shown below in table 2.3, and a list of equipment used is shown below in table 2.4

Table 2.3: Chemicals used within this project

Chemical	Supplier	Grade/purity
Ammonia	Sigma-Aldrich	28-30% in water
L-Arginine	Sigma-Aldrich	98 %
Diethylenetriamine	Sigma-Aldrich	technical grade
Cyclam	Sigma-Aldrich	analytical grade
Peentaethylenehexamine	Sigma-Aldrich	analytical grade
poly(ethyleneimine)	Polysciences	1 200 g/mol
poly(ethyleneimine), permethylated	Polysciences	6 300 g/mol, 10 %wt in water
Hydrochloric acid 1M	Fisher Scientific	± 0.02 M, Stabilised
H ₂ SO ₄	Fisher scientific	1.0 N, Stabilised
H ₂ SO ₄	Fisher scientific	98-100 %
Sodium silicate pentahydrate	Fisher scientific	Technical grade
Crystal 79 water glass	PQ corporation	3.2:1 Si:Na, min 27.0 %wt SiO ₂
Tetraethylorthosilicate	Sigma-Aldrich	Reagent grade (98%)
Millipore deionised water	None	> 15 M Ω cm resistivity
Ethanol	Fisher Scientific	Absolute
Ammonium molybdate tetrahydrate	Fisher Scientific	98%
Oxalic acid	Acros organics	98%
Sodium sulphite	Fisher Scientific	98%
Monomethyl-p-aminophenol hemisulfate	Fisher Scientific	> 99%
4,4-dimethyl-4-silapentane-1-sulfonic acid	Sigma-Aldrich	1 %wt in D ₂ O

Table 2.4: Synthesis, separation, and analytical equipment used within this project

Equipment	Manufacturer	Model
pH probe	Hanna	Unknown
pH probe	Jenway	924 001
pH meter	Jenway	3510
pH probe	Metrohm	Aquatrode
Handheld conductivity probe	Fisherbrand	FB70411
Autotitrator	Metrohm	Titrand 902
Overhead stirrer	IKA	Eurostar Labortechnik
Reactor system	Radleys	Reactor ready process style
Peristaltic pump	Watson Marlow	323Du
Centrifuge	Sorvall	ST16
DLS	Brookhaven	ZetaPALS
Scanning Electron Microscope	HITACHI	SU-6600
UV-Vis spectrophotometer	Genesys	10S
FTIR	Shimadzu	IRAffinity 1S, SPECAC ATR attachment
BET surface area analyser	Micromeritics	ASAP 2420
BET surface area analyser	Micromeritics	3Flex

Chapter 3

Scaleup and process intensification of BIS

Redacted due to commercial sensitivity of contents.

Chapter 4

BIS effluent recycling and synthesis using colloidal reagents

Redacted due to commercial sensitivity of contents.

Chapter 5

Post-synthetic silica modification through acid extraction

5.1 Introduction

In this chapter, a further barrier towards industrial implementation of the BIS technology - that of material activation. As made, the material is a composite of entirely safe silica (regarded as entirely nontoxic by the US Food and Drug Administration)¹⁷¹ and the often-toxic amine additive (PEHA for instance is classified as toxic for humans and the environment).¹⁷² Accordingly, this often necessitates a finishing step for the material - the removal of organic material prior to its use. This step is vital for many reasons, chief among which is the activation of the silica material's organic-enabled porosity.¹⁷³ This is so vital to the synthesis that very few reports of surfactant-templated silica materials like MCM-41 report properties of the as-made composite.¹⁷⁴ Leaving aside the issue of porosity enhancement, removal of organics is also essential for certain applications such as drug delivery agents or biotechnology.^{175,176}

Conventionally, this purification step is performed using calcination – heat treatment of the material until the template decomposes leaving behind a pure, porous silica framework.⁹¹ Calcination is problematic for a number of reasons from the direct energy cost it incurs of the synthesis procedure, to the emissions created by destroying the template, to the prevention of any template recycling step (given that the template is the most expensive starting material

and is not chemically depleted during the synthesis). All of these reasons combined necessitate the replacement of calcination with a more environmentally- and process-friendly operation before materials scaleup can be achieved.

Accordingly, numerous studies have been carried out on surfactant-templated silica materials to remove the template in a non-destructive manner using solvent extraction.⁹⁸ However, to date, complete removal of templates from MCM-41 or SBA-15 via solvent extraction has not been possible due to the large energetic driving force required to break the organic-inorganic interfacial interaction.^{177,178} Therefore several studies have used promoters like microwave¹⁷⁹ or other irradiation,¹⁸⁰ supercritical¹⁸¹ or refluxing solvents,^{88,99} and saline or acidic environments¹⁸² to achieve complete extraction of templates and template recycling after extraction.¹⁸³

While there have been reports of complete template extraction without the need for such promoters, these require specific material design to enable extraction through the choice of template molecule, and therefore compromise materials properties compared to their parent materials.^{98,99} For example hexagonal-mesoporous silica (HMS), which uses dodecylamine templates rather than cetyltrimethylammonium salts (CTAB, used in MCM-41), but has lower ordered pore domains than MCM-41 as a result.^{88,95} Further, although greatly improved by their non-destructive nature, such extraction methods require refluxing (high temperature) in alcohol or acidified water for at least 1 hour. Hence these methods have high energy demands (more than calcination, see section 5.4.1) leading to prohibitive costs for industrial implementation (highlighted in technological concern 6 posed by industry). As such, significant advances are required to the solvent extraction methods in order to reduce the large environmental costs of purification.

This chapter focuses on the development of a solvent extraction rather than calcination method for purifying BIS. A novel, acid-based, room temperature additive extraction method to purify bioinspired silica in a single, rapid, post-synthetic step is described. Furthermore, by controlling the pH of suspended BIS, controllable partial extraction of PEHA (or other additives) is achieved thus directly functionalising the material's surface chemistry in a single step. This both reduces the synthesis complexity and obviates the need for hazardous organosilane reagents, which are commonly required for similar surface modifications.¹⁷³

Atomistic molecular dynamics simulations of the organic-inorganic interface were used for to model the noncovalent interactions between organic additive and silica surface for the first time. Using this, the experimental BIS purification is rationalised against previous literature examples of solvent extraction, and explain the differences in required purification driving forces against interaction strength and template hydrophobicity. A general strategy for developing mild solvent extraction using molecular dynamics to predict template extraction efficiency if then proposed. Further experimental investigations of this phenomenon using solid-state NMR were then carried out to experimentally investigate these findings, highlighting room for improvement in the molecular dynamics simulations.

This new modification technique is put into context. Recycling of additives as well as silica is established, fully answering technological question 5 posed earlier. Furthermore, combinations of this new extraction method with mesoporous BIS synthesis methods are performed to extend both methods' capabilities. Finally, preliminary techno-economic analysis of acid extraction to estimate and compare the environmental and economic savings of using acid extraction method over conventional calcination or solvent extraction techniques.

5.1.1 Additives used within this chapter

In this chapter a total of 7 different additives were used to produce BIS materials, shown in figure 5.1. Respectively these are:

- **i** (PEHA), used to make materials **A**, **J**, **N**, **T**, **X**, and **Z**
- **ii** (DETA), used to make materials **V** and **V'**
- **iii** (poly(ethyleneimine)), used to make material **W** and **W'**
- **v** (ammonia), used to make material **X**
- **vi** (arginine), used to make material **Z**
- **vii** (permethylated PEHA), used computationally only
- **viii** (permethylated poly(ethyleneimine)), used to make material **2**

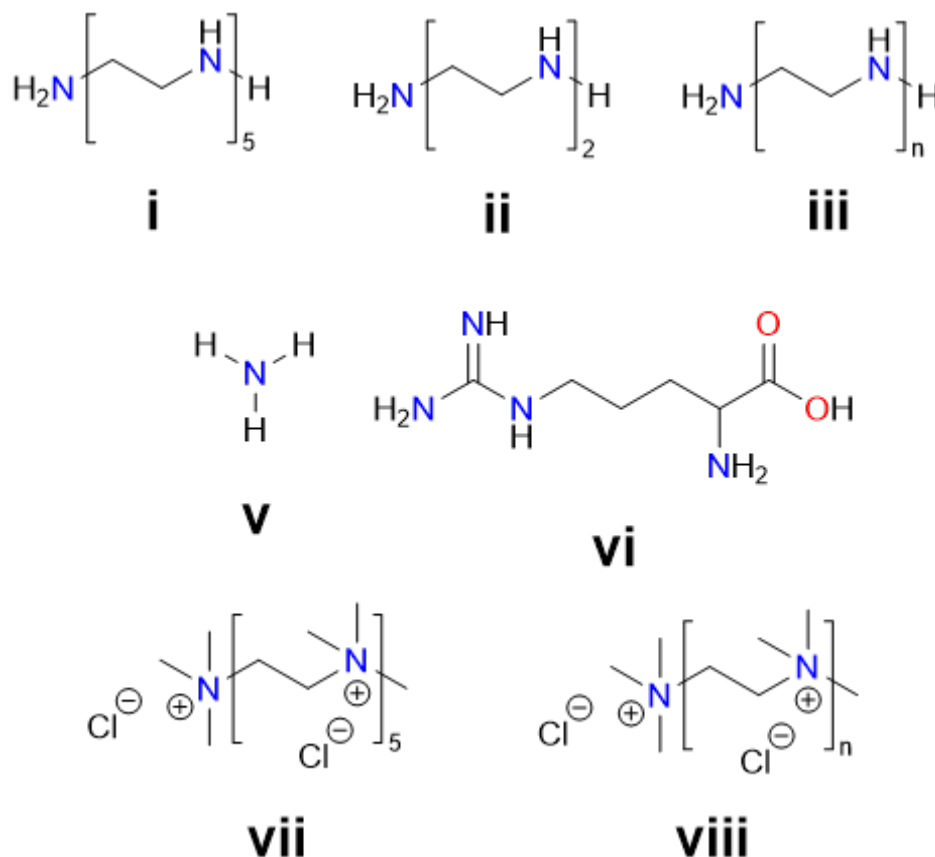


Figure 5.1: Structure of the bioinspired additives used within this chapter

5.2 BIS purification by acid washing

Initially, material **A** was synthesised as before, forming an opaque coagulum after 300s. Once synthesised at pH 7, the suspension was treated with acid for ca. 1 minute to reach a desired pH between 7 and 2 (the isoelectric point of silica).⁷ Upon such treatment the concentration of PEHA in **A** decreased, indicating PEHA had re-dissolved into solution (figure 5.2, squares). The removal did not have a linear relationship with pH - treatment to $pH \geq 5$ had a small effect on PEHA concentration (ca. 25% additive dissolution), however after further treatment to $pH 4$, the majority of additive (ca. 70%) had been eluted. Acidification to $pH \leq 3$ lowered the additive content to below the limit of detection with CHN elemental analysis, signifying complete purification of BIS through simple acid washing at room temperature. Recreation of these experiments with material **V** showed a similar relationship to **A**, although with a different trend (Figure 5.2, circles), indicating that acid treatment can be used across a range of BIS materials. Technologically, this is a significant advancement over previously reported solvent extraction methods of surfactant-templated silica which generally need both

high temperature (reflux) and longer duration (≥ 1 hr), and could not easily be abstracted between different material substrates.

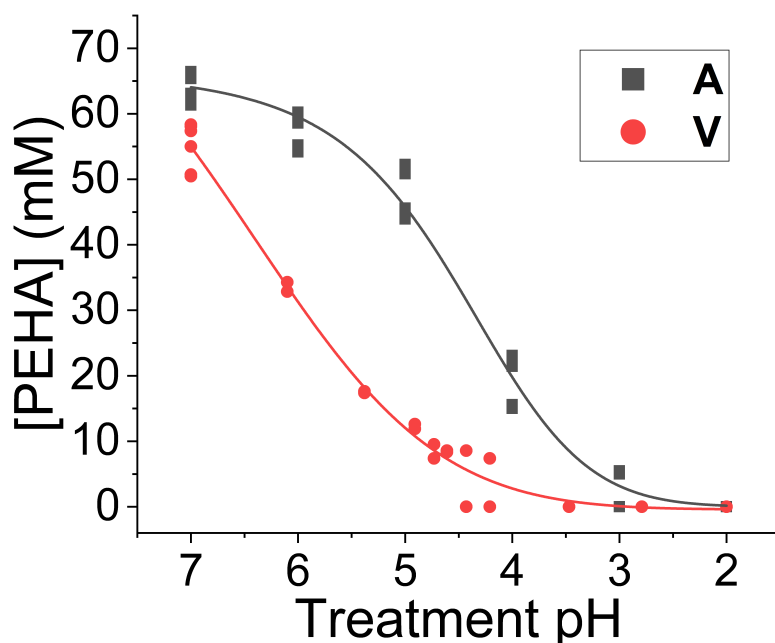


Figure 5.2: Graph of additive concentration in silica versus washing pH determined by elemental analysis for materials **A** and **V** fitted to sigmoidal trend lines.

Section redacted due to commercial sensitivity of contents.

Comparison against different purification methods

Material **A** was then treated under a range of conditions to compare acid extraction against traditional purification methods - solvent (water) reflux, calcination, acid washing, and acid washing-then-calcination. Given that calcination has been shown to increase the surface area of BIS,¹³⁴ these were analysed using surface area analysis to determine relative extraction efficiency (figure 5.3) and resultant pore-size distribution. In terms of overall surface area, acid washing had a similar effect on the surface properties of **A** compared to calcination (as seen in the relatively small changes between treatments C, A, and AC), confirming that acid treatment purified the BIS material. Pore size analysis of the materials (figure 5.4) showed that the final morphology was marginally different - larger pores were generated by calcination compared to acid washing or even acid washing-then-calcination. This degradation of the pore structure, which was only evident for calcined and not for A- or AC-treated BIS, indicates

that the thermal decomposition of PEHA during calcination damages BIS pore openings – an issue which has been reported for calcined silicas.¹⁸⁰ Therefore it can be concluded that room temperature acid treatment is as effective as calcination in purification, while also avoiding the degradation of delicate structures during purification due to the mild nature of this method compared to conventional techniques.

Interestingly, water reflux had no discernible effect on silica surface area, indicating no significant PEHA re-dissolution (figure 5.3). Comparing against studies of surfactant-templated HMS⁹⁹ and MCM-41,^{88,182} this is surprising; in each case neat solvent reflux (with neat water and ethanol, respectively) was partially effective. This indicates that the as-made BIS composite is more stable at pH 7 than HMS or MCM-41, but that the behaviour is also more switchable (as only low pH is needed to purify BIS, whereas both low pH and reflux was required for the others).

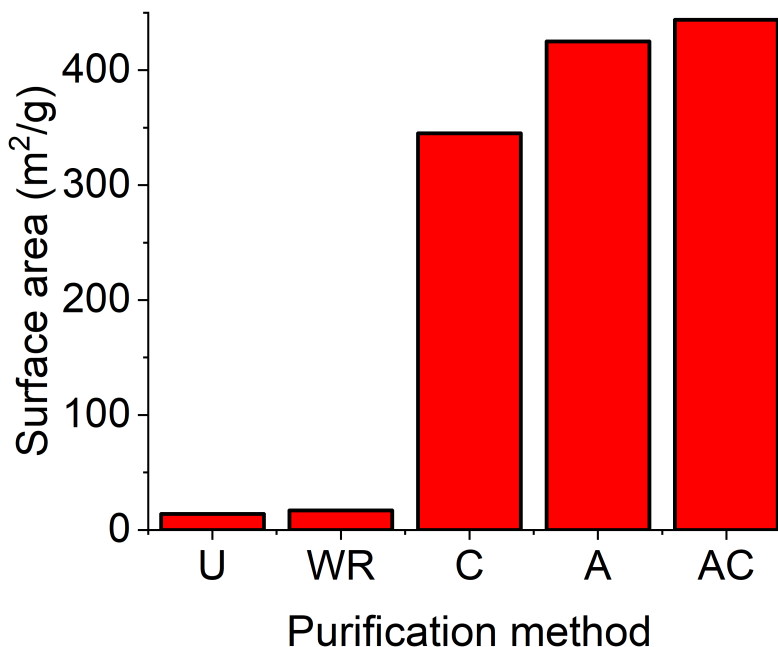


Figure 5.3: Effect of treatment method on BET surface area of material **A** after the following treatment: *U* – untreated; *WR* – Water Reflux; *C* – calcined; *A* – Acid washed; *AC* – acid washed then calcined.

Surface area analysis at different pH values was then employed to investigate this switching behaviour (figure 5.5). Similarly to purity (figure 5.2), the major change occurs between pH 5 and pH 4, although the rate of change is very different between the two. As seen in figure 5.4, the vast majority of the surface area increase was due to microporosity (with total

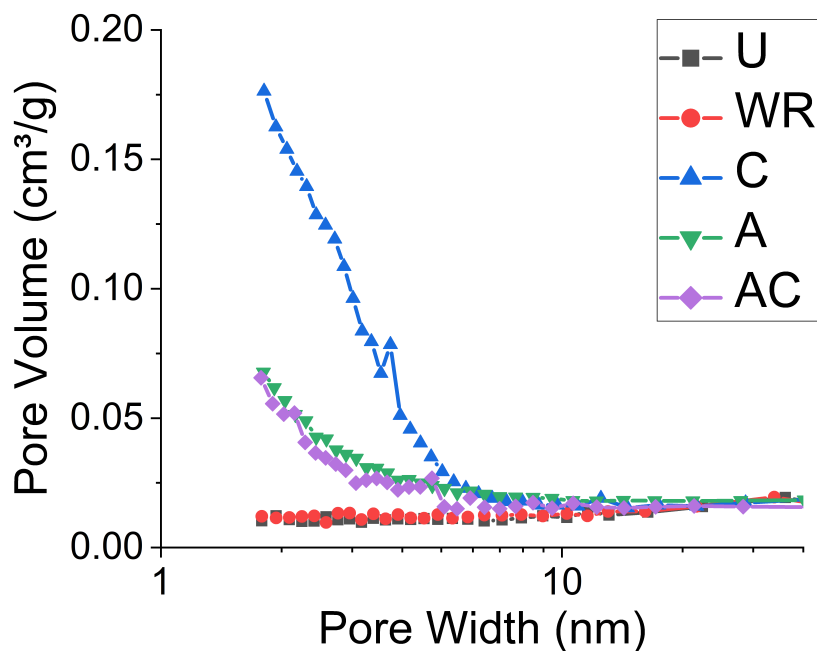


Figure 5.4: Effect of treatment method on BJH pore size distribution for material **A** after the following treatment: *U* – untreated; *WR* – Water Reflux; *C* – calcined; *A* – Acid washed; *AC* – acid washed then calcined.

non-microporous surface area $< 15\text{m}^2\text{g}^{-1}$ for all variants of **A**). Given previously observed changes to material surface properties as a result of accelerated coagulation (chapter 3) or seeding with colloidal spheres (chapter 4) led to mesoporosity within the material, acid extraction appears to be distinct in terms of how it affects BIS microstructure. To confirm this, scanning electron micrographs were made of unmodified and acid washed **A** showing no discernible change in morphology (figures 5.6b and 5.6a). Section redacted due to commercial sensitivity of contents.

Given the size of the PEHA molecules used (reported as 1.8nm^{133}), it is tempting to infer that the width of each pore created corresponds to the size of an individual PEHA molecule removed. To support this, the amount of PEHA removed (converted to volume) was compared against the volume of micropores created (figure 5.7). For the majority of pH treatments, the measured pore volume agrees well with the estimated volume of additive lost. The sole exception to this is at pH 5 where the measured pore volume is lower than the amount of amine removed, which may suggest that the initial additive removed was from the external surface of the material, in agreement with previous reports.¹⁸⁴

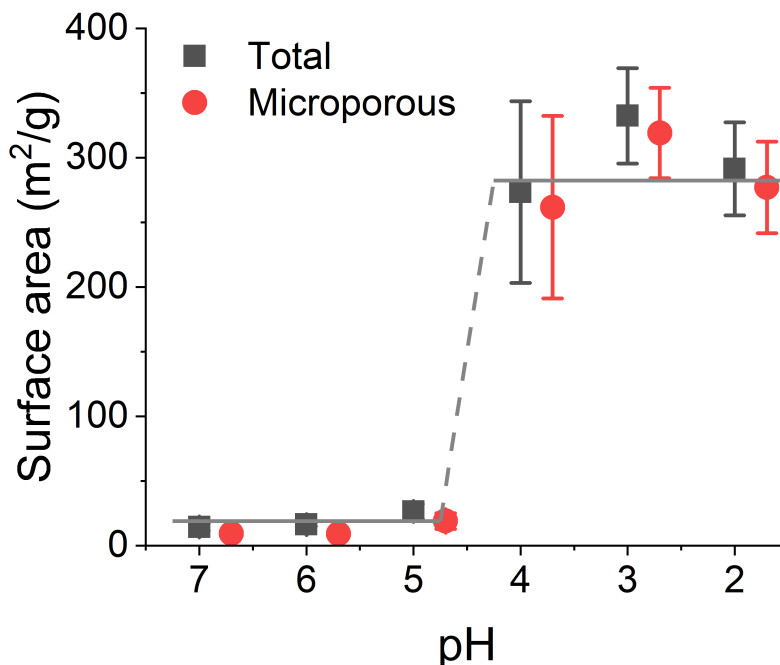


Figure 5.5: Total and microporous surface area of material **A** as measured by *t*-plot, with overlay lines at $30\text{m}^2\text{g}^{-1}$ and $300\text{m}^2\text{g}^{-1}$. Micropore values are offset by $x = 0.3$ for clarity.

Overall, acid extraction is a significant new development for the technology. Being able to fully purify BIS without the need for calcination or any other thermodynamic driving force is an exciting development, enabling many previously-inaccessible applications for the material caused by safety concerns of the PEHA. Beyond this, controllable partial extraction opens several new and interesting avenues of research into direct functionalisation of BIS, as well as extraction-enabled mechanistic investigations of BIS formation and interfacial chemistry.

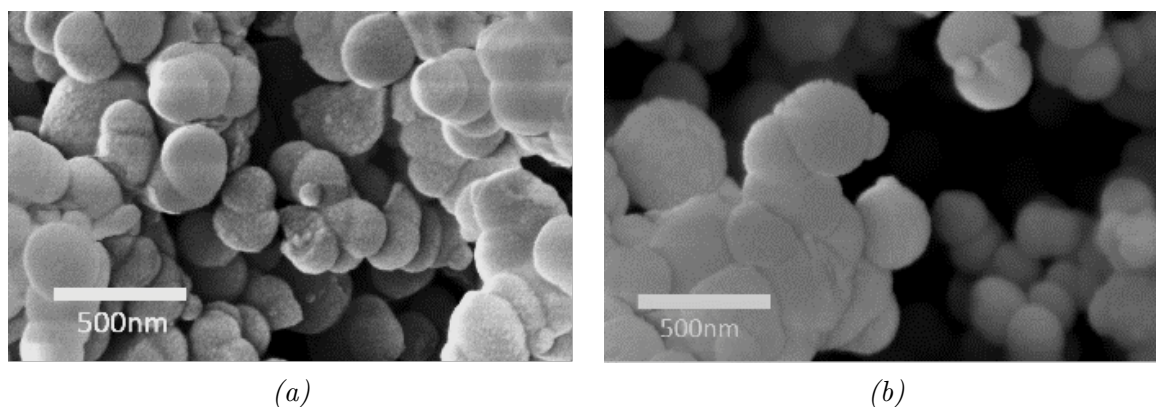


Figure 5.6: Scanning electron micrographs of material **A** as made (a) and (b) after extraction at pH 2, showing no observable change in morphology. Scale bars are 500nm.

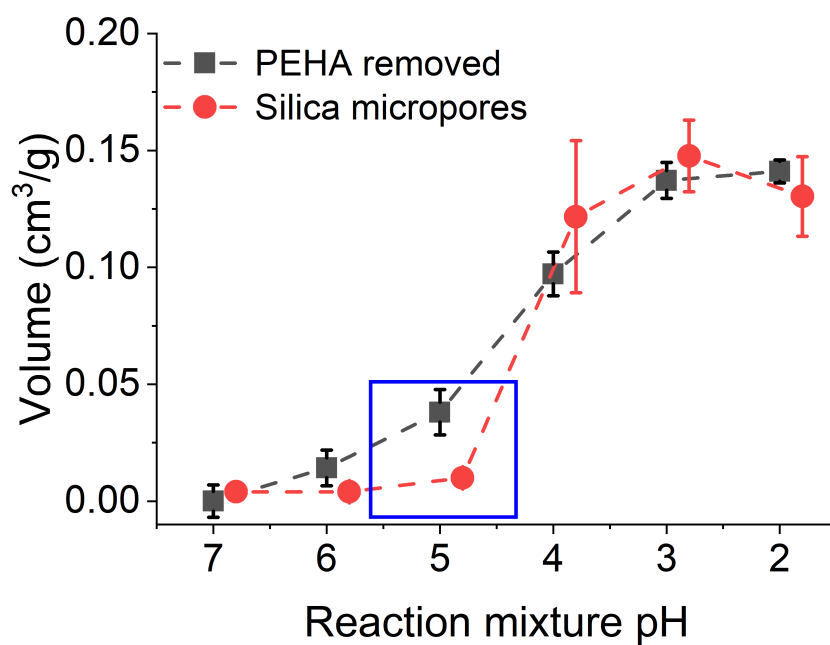


Figure 5.7: Calculated additive volume removed (squares) and measured micropore volume created from additive removal (circles) against treatment pH. Blue box indicates the point of discrepancy between the two metric

5.2.1 Structural investigation and chemical activation by partial extraction

To experimentally probe the additive localisation, the specific interaction between CO₂ and amines was exploited via CO₂ adsorption;¹⁸⁵ in particular, measured adsorption kinetics and capacity were measured against washing pH to assess additive accessibility and functionality, respectively. As this is a common method to investigate functional porous materials (e.g. as carbon capture agents),¹⁸⁶ CO₂ sorption will be a good test of whether acid treatment can be used as a single-step functionalisation tool in addition to purification. To do this, CO₂ was first dosed onto material **A** at pressures of 100 and 1000 mbar for 12 hours. CO₂ uptake was recorded during this process, allowing for kinetic data to be inferred by uptake rates and mechanistic data being inferred from equilibrium uptake (as physisorption is linearly proportional to pressure while chemisorption is largely pressure-independent).¹⁸⁷

For samples with high PEHA concentration (i.e. $pH7 - 5$) uptake was very slow, with the samples not equilibrating even after 3 days, regardless of pressure. Conversely, samples washed at low pH ($2 - 4$) equilibrated very quickly - in most cases before the full gas pressure could be reached. Regardless, by measuring at a constant time of 12 hours, qualitative comparisons could still be made between the different pressures (figure 5.8). These showed that, pressure had very little effect on CO₂ uptake in this first group of BIS composites but as the material became more and more pure (i.e. pH becomes lower), pressure became a defining factor. This is indicative of transfer from chemisorption-dominated adsorption to physisorption-dominated.¹⁸⁷

Within the high pH group of materials, figure 5.8 shows the extraction of PEHA initially leads to greater overall uptake after 12 hours. Inspecting the kinetics of adsorption found that, unlike the low-pH group, the kinetics of adsorption are not uniform for samples washed between pH 5 and 7 (figures 5.9 and 5.10 for 100 and 1000 mbar, respectively). Whereas samples treated to low pH had essentially adsorbed CO₂ to full capacity by the time the chamber pressure equilibrated, the as-made and pH 6-treated **A** had barely begun to adsorb. Interestingly, pH 5-treated **A** behaved somewhere between these two extremes: not fully equilibrating after 12 hours but having the vast majority of uptake occur on a similar time scale to pressure equilibration.

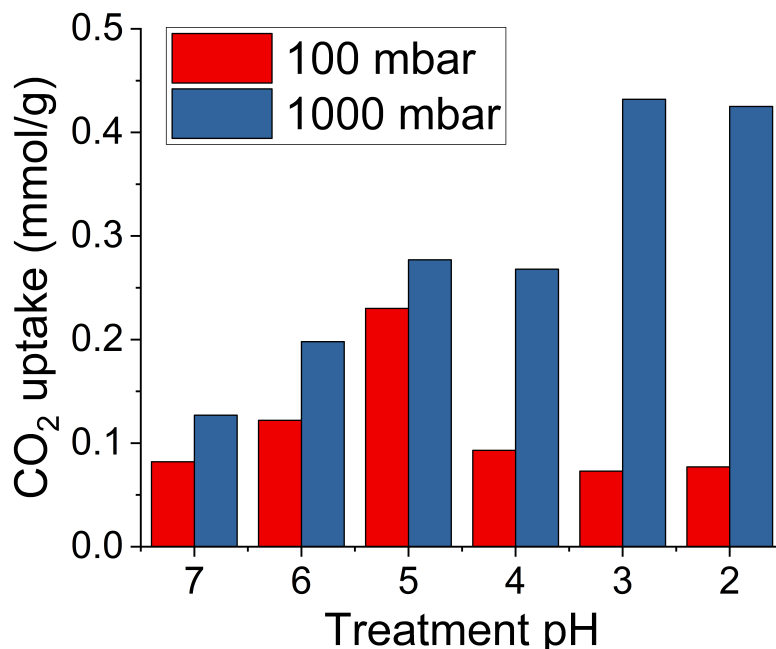


Figure 5.8: Graph of CO_2 uptake after 12 hour equilibration times at either 100 or 1000mbar.

Combined with the low surface area detected by N_2 adsorption (Figure 5.5), this indicates that PEHA-rich materials had pores blocked by the amine additive, giving high chemical activity but very low uptake rates (envisaged in figure 5.11a). Partial removal of the PEHA by washing at pH 5 removed approximately 25%mol of the PEHA, significantly improving both CO_2 uptake and capacity, but without significantly affecting surface area or porosity (figure 5.7). This agrees with the initial theory that PEHA was removed from particle exteriors first, leaving the internal pores full and with good access to chemisorb CO_2 but not N_2 (figure 5.11b). Further treatment stripped the remaining PEHA from the pore system, leaving a bare silica surface that could physisorb a relatively high amount of both CO_2 and N_2 , but with no appreciable chemisorption (figure 5.11b).

From the juxtaposition of the two gas sorbent behaviours, a scheme of proposed BIS particle compositions can be made describing as-made, partially extracted, and fully extracted material **A** (figure 5.11). The changing behaviour towards CO_2 demonstrates the ability of acid washing to optimize surface chemistry of bioinspired silica in a single post-synthetic step - a technology which is being widely investigated for use in post-combustion carbon capture technologies.¹⁸⁸ Although material **A** does not demonstrate competitive CO_2 capacity in any instance (with benchmarks being set at a working CO_2 capacity of 3.0 mmol/g),¹⁸⁹ this

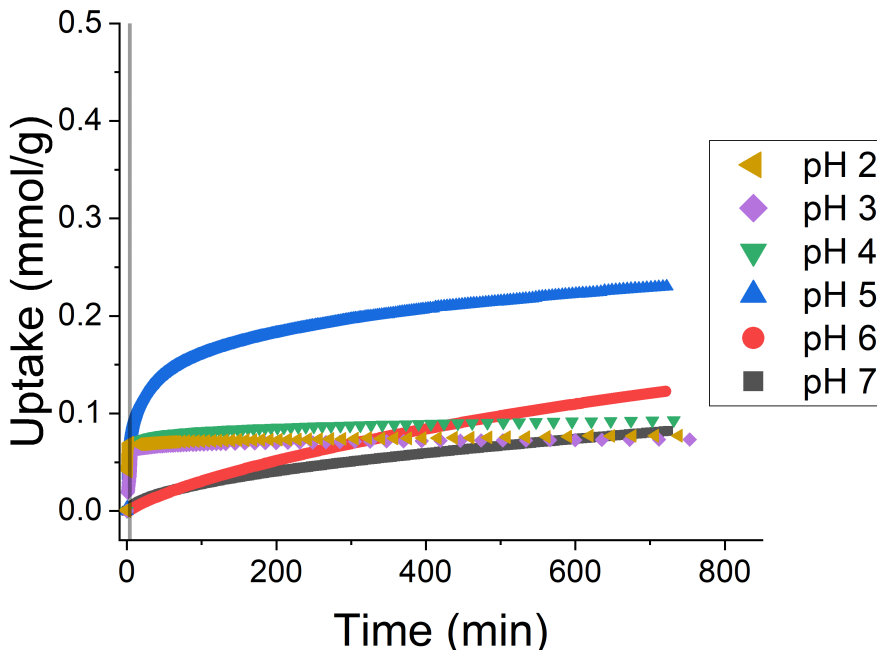


Figure 5.9: CO_2 uptake kinetic curves at 100 mbar of material **A** after acid washing to different pH. Grey overlay line represents average pressure equilibration time for each pressure. Data gathered by Dr. Thomap Yip.

surface tailorability represents an exciting new approach to functional surface preparation or purification in one step.

5.3 Investigating additive-BIS bonding

5.3.1 Developing mechanistic understanding through atomistic molecular dynamics

The next step after identifying the location of PEHA was to investigate how PEHA bonds to the BIS surface. The need for a pH driving force for the extraction of additive rather than just solvothermal conditions indicates a dynamic change in the additive-silica interactions. Understanding these interactions and how they depend on pH would enable generalisation of acid treatment to systems other than bioinspired silica, leading to milder purification for a variety of templated materials.

To do this, molecular dynamics simulations (MD) were applied of PEHA at the interface

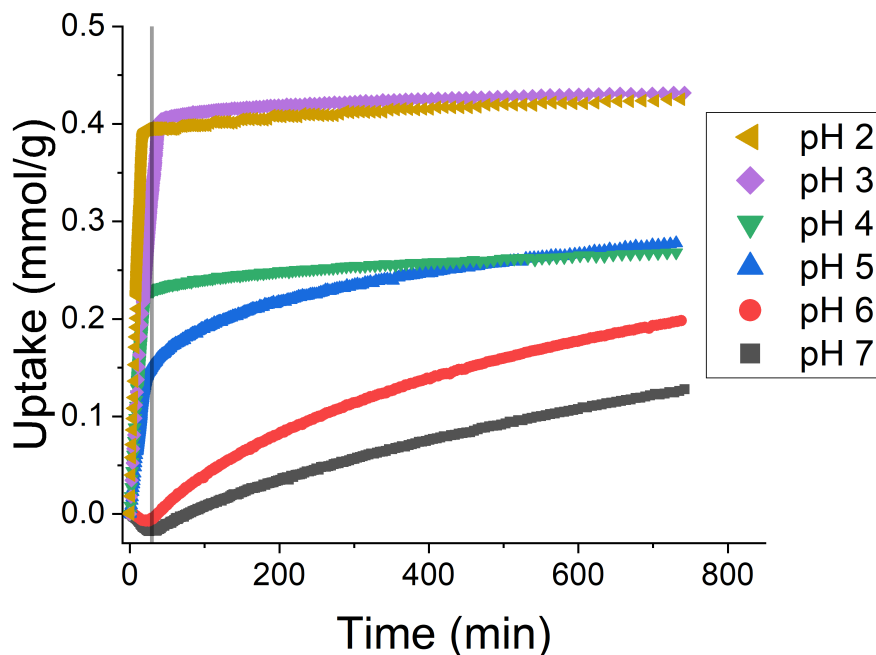


Figure 5.10: CO_2 uptake kinetic curves at 1000 mbar of material **A** after acid washing to different pH. Grey overlay line represents average pressure equilibration time for each pressure. Data gathered by Dr. Thomap Yip.

between water and a pre-generated flat silica surface using the recently-established INTERFACE forcefield parameters for an amorphous silica surface.^{190,191} pH-variations were simulated by removing H-atoms from certain surface hydroxyls to create siloxide anions and by adding protons to certain PEHA amine moieties to produce ammonium cations, balancing overall system charge with Na^+ and Cl^- , respectively. This created surface charges corresponding to experimentally measured silica surface charges from reference 192, and PEHA ionisation as predicted in reference 149.

Simulations suggested two key interactions controlling the removal of amine additives from silica: ionic attractions between charged PEHA and negatively charged silica, and solvation of PEHA in the bulk aqueous solution. The balance between these two types of interactions varies with pH, leading to the highly switchable behaviour witnessed in figure 5.2. For example at $\text{pH} \geq 5$, the silica surface is negatively charged and the amine additive positively charged, leading to strong charge-charge interactions between the PEHA and surface siloxide groups, consequently resulting in very little to no removal of the additive (Scheme 5.12a).

Despite the fact that at this pH both species were multiply charged, the simulations pre-

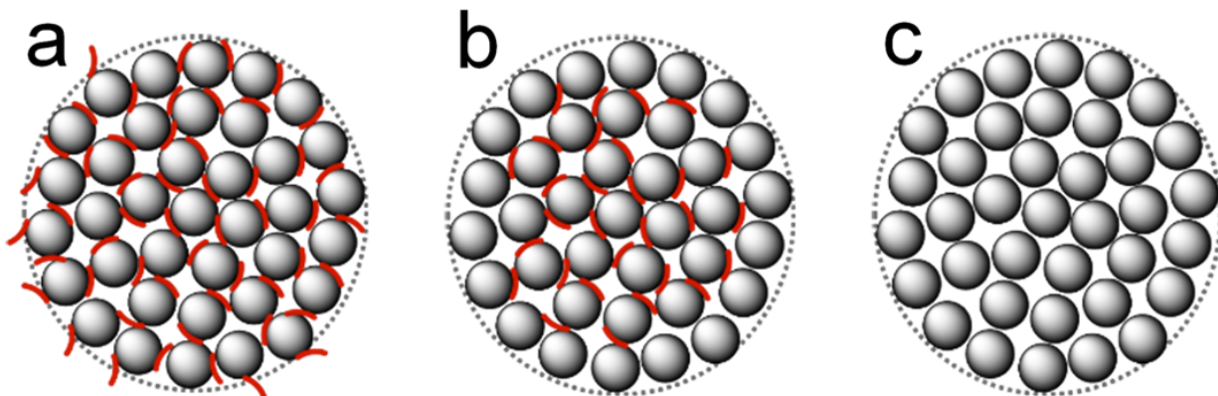


Figure 5.11: Visualisation additive molecule distribution (red lines) within secondary particles of bioinspired silica (dotted lines), which are composed of primary particles (grey circles). (a) Untreated silica composites contain additives adsorbed to both the particle surface and inside. (b) After partial treatment to pH 5, only the surface-adsorbed additive molecules are released. (c) After treatment at pH 2, all additive molecules are released

Table 5.1: Silica surface charge density as a function of pH (electrolyte concentration 0.1mol dm^{-3} NaCl ionic, σ in $\mu\text{C cm}^{-2}$).

(a) $10\text{ }\mu\text{C cm}^{-2} = 0.6\text{SiO}^{-}\text{nm}^{-2}$ (taken from reference 193), (b) interpolated values

pH	SiO ⁻ density (SiO ⁻ nm ⁻²) ^a	SiO ⁻ -SiO ⁻ separation (nm)
3	0	N/A
5 ^b	0.03	6
7	0.15	2.6

dicted that separation between surface siloxide ions was too high (ca. 2.6 nm) for PEHA to interact with more than one at a time given its length of ca. 1.8 nm (table 5.1). Therefore the individual PEHA-siloxide interaction strength did not change significantly with pH, remaining around -25 kJ mol^{-1} . While additive charge only increased upon acid treatment, below pH 4 the silica surface became predominantly uncharged (Table 5.1¹⁹³). In this case simulations predicted that PEHA would desorb from the surface, becoming fully solvated in the aqueous phase as the interaction strength becomes effectively zero (figure 5.12b).

To test the limits of this interaction, and attempt to understand why previous extraction studies using acidic conditions were only marginally successful,¹⁸² the simulations were repeated using a theoretical permethylated version of PEHA as an analogue of CTAB. Unlike with the original PEHA, when no charged interactions were found solvent extraction became ineffective at pH 2 (Scheme 5.12c) due to an increase in non-ionic interactions with the silica surface (calculated interaction strength of ca. -135 kJ mol^{-1} for the methylated PEHA compared to ca. 0 kJ mol^{-1} for PEHA). Although permethylated PEHA could not be

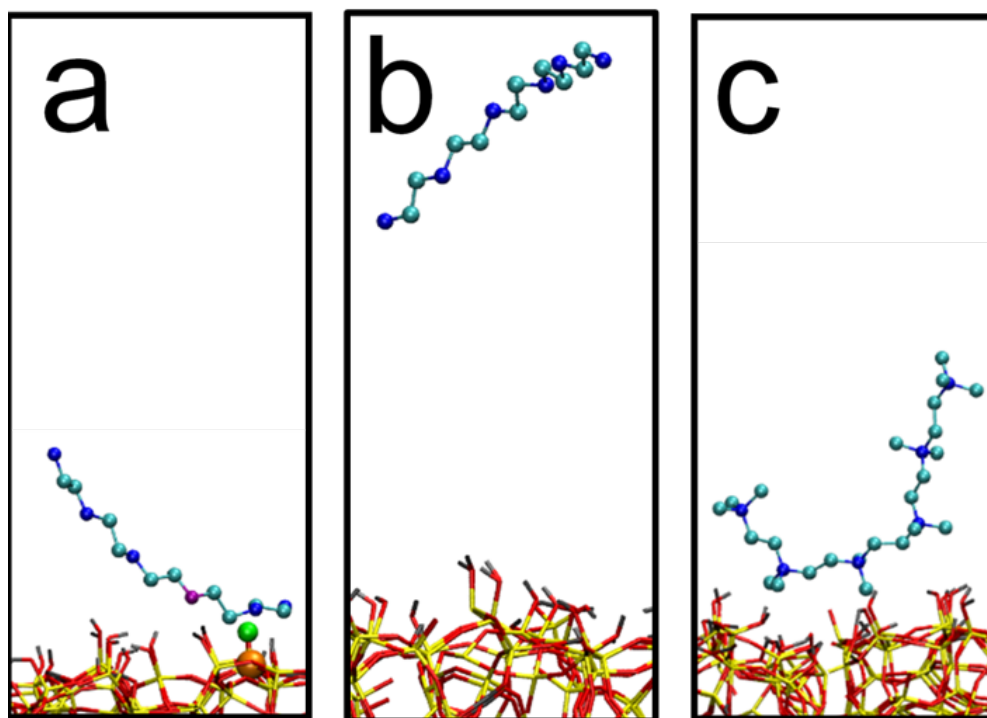


Figure 5.12: Representative snapshots from classical MD simulations of PEHA molecules on a silica surface (a) at ca. pH 7, (b) at ca. pH 2, and (c) using a permethylated PEHA analogue at pH 2. Atoms are coloured as follows: yellow - Si, red - O, cyan - C, blue - N^+ , purple - N, white - H. PEHA protons and solvent (water) molecules have been omitted for clarity, and key interacting Si-O groups in (a) are shown in orange and green for clarity. Simulations and representations were performed by Dr. A. Centi.

sourced for this study to compare experimentally, experiments on material **W** (made using poly(ethylenimine)) and BIS made using its permethylated counterpart (material **2**) showed a significant difference (with extraction being 25% less efficient in **2** than **W**, taking into account differences in initial concentration). This mirrors results in MCM-41 and HMS: in direct comparisons, solvent extraction of (N-permethylated) CTAB from the former was also 25% less effective than removal of (non-methylated) dodecylamine.^{88,99}

When taken together, these findings indicate two things: first, as MD predicted PEHA but not permethylated PEHA desorption upon removal of the charge-charge interactions, solvent extraction depends on a balance between energies of adsorption and solvation. Secondly, given the similarity of behaviour (both predicted and simulated) upon change in additive hydrophobicity between PEHA and permethylated-PEHA in materials **W** & **2**, and surfactant-templated silicas HMS & MCM-41 (templated using the primary amine dodecylamine and permethylated CTAB, respectively), MD appears promising as a general tool to

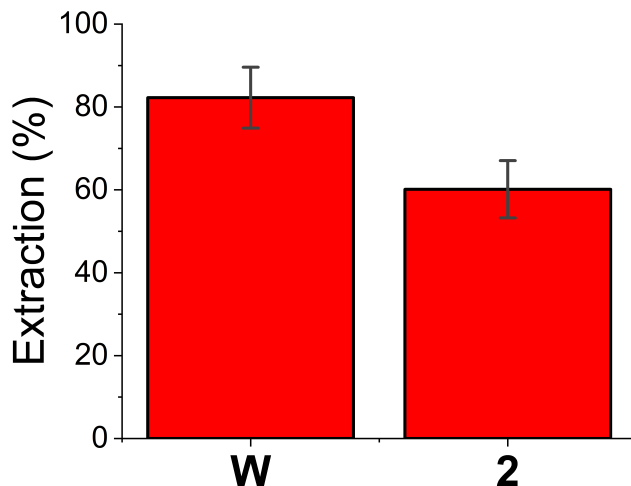


Figure 5.13: Comparison of acid extraction effectiveness between poly(ethyleneimine) (PEI) and methyl-substituted poly(ethyleneimine), showing 25% decrease in effectiveness of acid extraction in the latter.

predict surface modification phenomena. If true, this would enable conclusions to be drawn for a range of materials at once, contrasting with the substrate-specificity that hampers experimental-only investigations.

5.3.2 Spectroscopic investigation of the PEHA-BIS interaction

To confirm the effects seen in the molecular dynamics simulations, direct investigation of the bonding between PEHA and the silica surface was required.

Infrared spectroscopy

Initially this was performed using Fourier-transform infrared spectroscopy (FTIR), which can reveal the prevalence of unsaturated hydroxyls through the Si–O stretch band at 950 cm^{-1} . However, due to the nature of FTIR analyses, the absolute absorbance recorded is of little use as many factors including quantity of material exposed and incident light path length are uncontrolled. therefore in order for these signals to be comparable between samples, the measured data must be normalised internally i.e. by measuring the ratio of signals within each sample rather than the absolute absorbance.

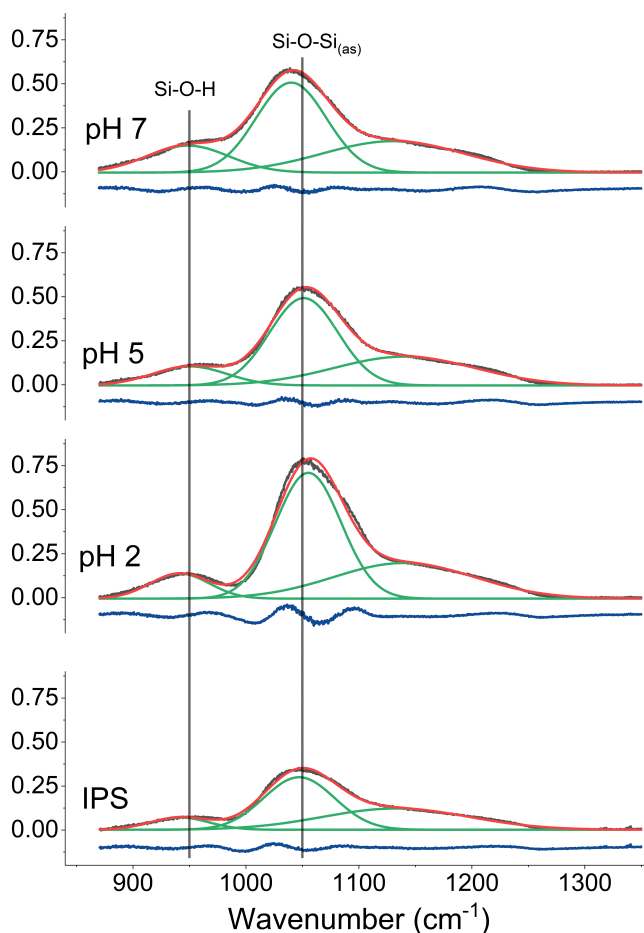


Figure 5.14: FTIR analyses of BIS silica **A** treated to pH 7, pH 5, pH 2, and untreated IPS. Raw data are in black, gaussian peak deconvolutions in green, sum of deconvoluted signals in red, and fitted curve error is in blue (offset for clarity).

Accordingly, samples of material **A** were extracted at various pH values (to pH 7, 5, and 2) and then analysed using FTIR. These were compared against a sample of industrially-precipitated ‘syloid’ silica (IPS) to assess the effect of bioinspired additives on the material’s surface chemistry. Spectra were recorded between 850 and 1350 cm^{-1} as shown in figure 5.14, encompassing both the Si–OH stretch and Si–O–Si transverse asymmetric bend.

From figure 5.14, the relative quantity of Si–OH to Si–O–Si could be determined. This is shown in figure 5.15. From this, it can be seen that there is a large difference in Si–OH/Si–O–Si ratio between as-made BIS and IPS. As-made material **A** had significantly more unsaturated moieties than IPS, which could be expected due to the presence of Si–O–HN adducts. Interestingly, as the PEHA was removed from the BIS, the relative ratio decreased slowly, approximately matching the IPS.

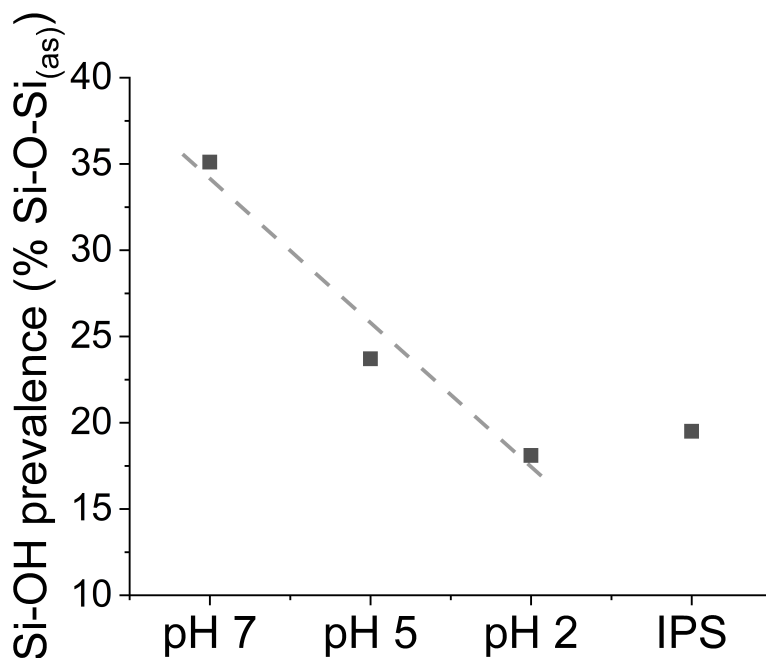


Figure 5.15: Graph of relative $\text{Si-OH}/\text{Si-O-Si}$ prevalence in BIS material **A** treated at difference pH values and IPS.

The change in BIS hydroxyl concentration with pH is unexpected, as it indicates that removal of the PEHA leads to a change in the surface chemistry overall, rather than a simple nonreactive desorption event as was predicted by the MD simulations. In order to better understand the exact PEHA-BIS bonding environment, the more specific technique of solid-state NMR was employed going forwards.

Solid-state NMR spectroscopy

Solid-state NMR is a well-established method for characterising bonding at silica interfaces,^{194–196} which has elucidated several important surface phenomena in surfactant-templated silicas e.g varied surface bonding in acid- or base-catalysed MCM-41 driven by changes in silica surface charge with pH,¹⁹⁷ or the importance of charge on dodecylamine in HMS silica both for formation and its subsequent solvent-based removal.⁸⁸

Herein, BIS surface chemistry was assessed to see how it was affected by the initial additive incorporation and the subsequent partial- or complete-extraction. To do this, material **A** and IPS were both treated to pH 7, 5, and 2 and analysed with ^{29}Si MAS NMR to assess

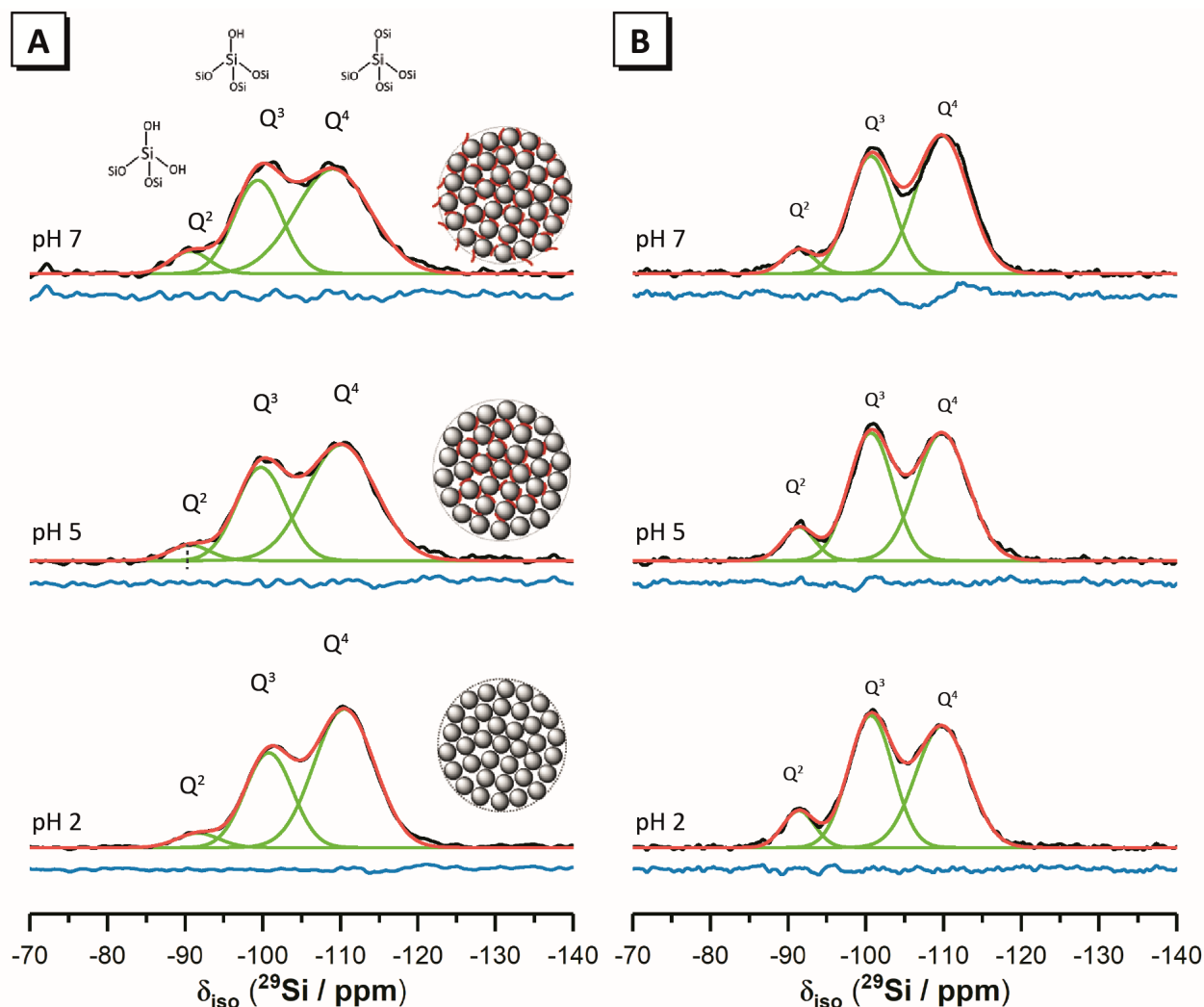


Figure 5.16: ^{29}Si single-pulse MAS NMR spectra for (A) BIS and (B) IPS after treatment at pH 7 (top), 5 (middle), and 2 (bottom) and their deconvolution to component Si species. Overlaid are BIS particle visualisations from figure 5.11 (silica primary particles (grey circles) containing PEHA molecules (red lines) at as-made concentration (top), partially extracted (middle) and fully extracted (bottom)). NMR spectra shown are the original data (black), individual resonance contributions (green), fitted sum of individual contributions (red), and residual (blue). NMR experiments and deconvolution were performed by Dr. B. Walkley

the relative concentrations of fully condensed (Q^4), singly hydroxylated (Q^3), and doubly hydroxylated (Q^2) Si centres (figure 5.16).

As-made, the degree of polymerisation in BIS was higher than in industrial silica (Table 5.2). This is unexpected, as polymerisation of silica from Q^3 to Q^4 is generally considered to occur through syneresis¹⁹⁸ – the slow condensation of silica to expel water from the framework – which should be more prevalent in the industrial silica material due to its significantly longer reaction times (2-3 hours vs 5 minutes),¹⁶ and similar micron-scale aggregate sizes (seen

in figure 5.6 and reference 199 for BIS and IPS, respectively).

Extraction only appeared to magnify this difference: while the IPS changed slightly to include fewer Q^4 sites (from 55% at pH 7 to 48% at pH 2), and correspondingly more Q^3 and Q^2 sites (Figure 5.17), for BIS no such pH-based changes were observed (Q^4 sites remained around 60% across all pH values). This is in good agreement with previous studies on the acid treatment of precipitated silicas, which found an increase in Q^3 abundance of up to 10% under similar conditions.²⁰⁰ The lack of change for BIS indicates higher overall hydrothermal stability, significantly even after full PEHA removal at pH 2.²⁰¹ These experiments (the first solid-state NMR investigation of BIS) represent the first evidence that bioinspired silica is chemically distinct from other silica materials, however does not provide any information about the bonding between PEHA and the silica surface.

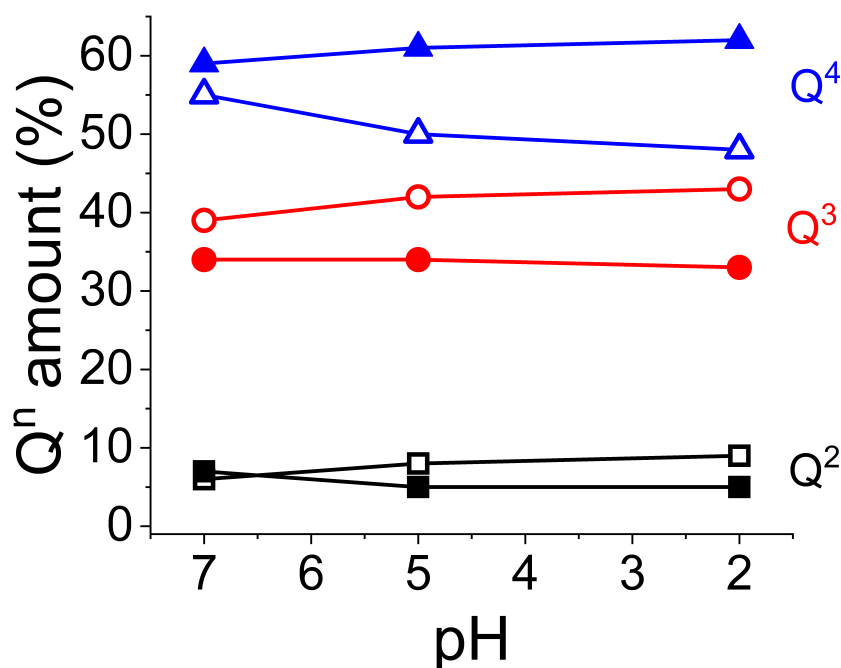


Figure 5.17: Relative abundance of Si species against extraction pH for IPS (open shapes) and BIS (closed) materials. Black squares represent Q^2 species, red circles represent Q^3 species, and blue triangles represent Q^4 species.

To analyse the interaction between silica and the adsorbed additive material, ^1H - ^{29}Si cross-polarisation (CP) MAS NMR was then used to probe the bonding environment of the silica with its proximate protons. These spectra show the same peaks as single pulse ^{29}Si NMR, but with peak amplitude modified by the proximity to protons. Accordingly, Q^2 and Q^3 silica (being covalently connected to hydroxyl groups) are always amplified, whereas Q^4

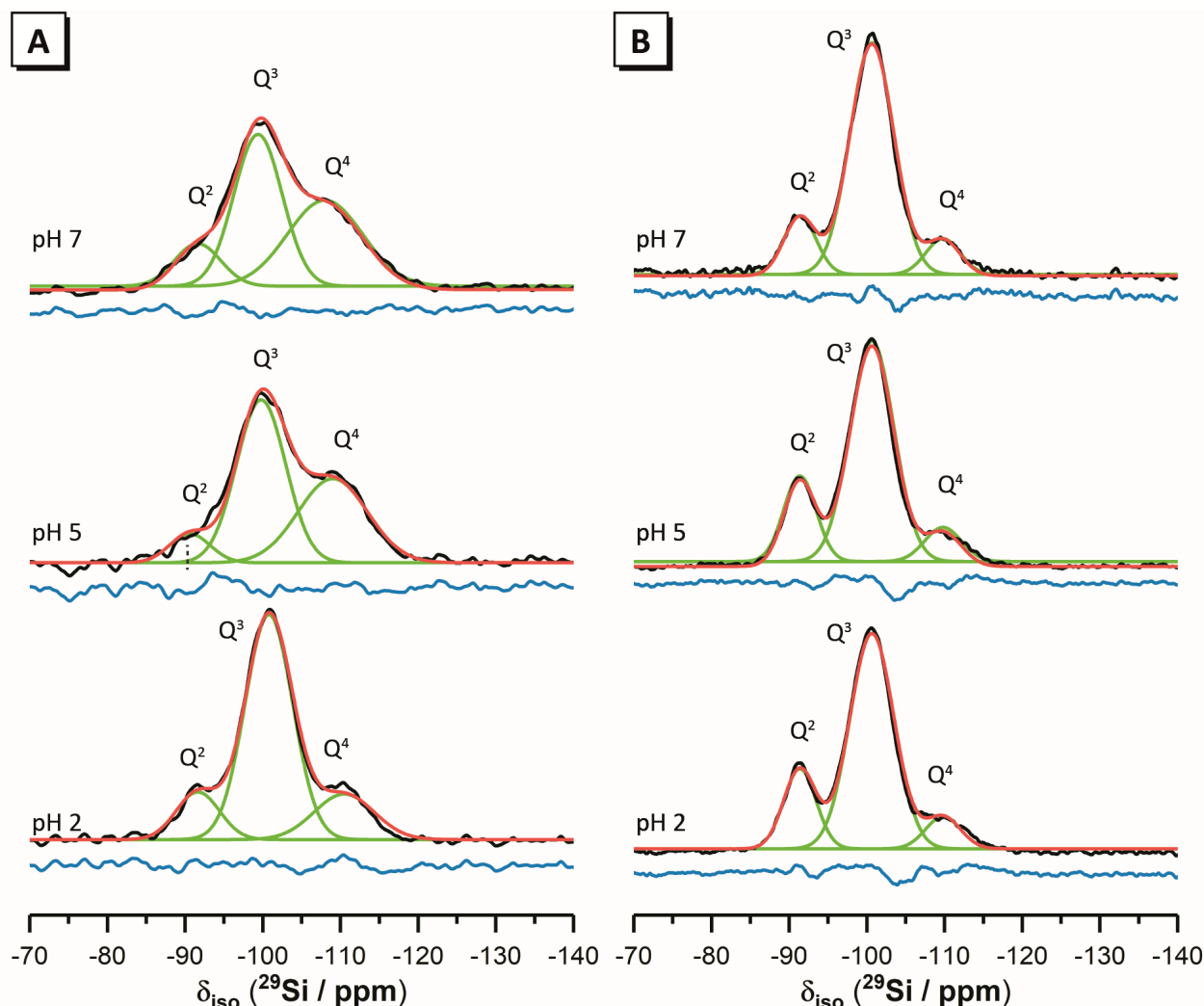


Figure 5.18: ^1H - ^{29}Si CP MAS NMR spectra for (A) BIS and (B) IPS washed at pH 7 (top), 5 (middle), and 2 (bottom) and associated deconvolutions. Shown are the original data (black), individual resonance contributions (green), fitted sum of individual contributions (red), and residual (blue). NMR experiments and deconvolution were prepared by Dr. B Walkely

silica peaks are dampened. For IPS, CP MAS acted as expected – Q^2 and Q^3 silica signals were amplified while Q^4 was suppressed (figure 5.18). Despite this, there was no change for IPS with pH as there had been in the single pulse ^{29}Si experiment, indicating that the bonding environment on the silica surface was unchanged.

For BIS, ^1H - ^{29}Si CP MAS NMR data showed significant differences for all pH treatments due to the presence (or absence) of PEHA (figure 5.19). Compared to IPS, BIS containing PEHA (pH 7 and pH 5) had relatively large Q^4 signals (40% vs 9%) and smaller Q^3 and Q^2 signals in the ^1H - ^{29}Si CP MAS NMR spectra. However, upon full removal of PEHA (pH 2) this effect diminished and the samples behaved identically to their IPS counterparts

(figure 5.19).

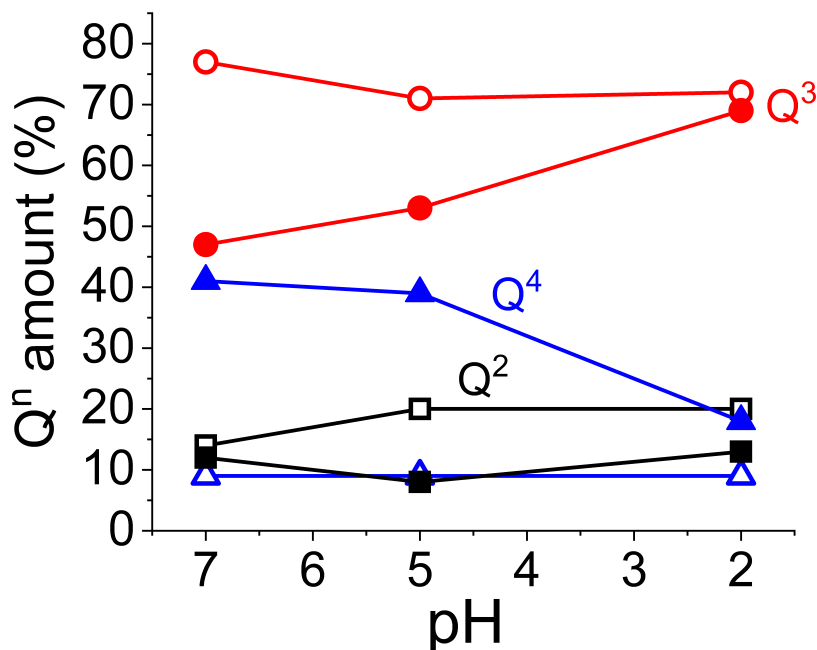


Figure 5.19: Relative abundance of Si species against extraction pH for IPS (open shapes) and BIS (closed) materials. Black squares represent Q^2 species, red circles represent Q^3 species, and blue triangles represent Q^4 species.

The ^1H - ^{29}Si CP MAS NMR data suggest that, in addition to creating more Q^4 species in BIS, PEHA forms an adduct with Q^4 Si sites in the final material. This is a new finding since it appears to contradict previous simulation and experimental results for silica, which show charge-charge or ion-pairing interactions between PEHA and silica.^{27,133} PEHA has been shown to act as a catalyst in the condensation of silicic acid monomers, presumably through proton transfer.²⁰² This leads to a new mechanism for silica surface bonding to a general proton transfer catalyst by considering the catalytic activity of PEHA towards silica condensation, which reconciles these two interpretations (figure 5.20). Previous theoretical and molecular models of PEHA-silica adsorption did not consider the surface reactivity of PEHA, only its electrostatics.¹³⁴ These findings indicate that electrostatic interactions initially draw PEHA towards the silica surface, forming silicate-N adducts, in agreement with previous studies.¹³⁶ After adsorption, PEHA causes condensation at the surface from Q^n ($n < 4$) to Q^4 species. This simultaneously leads to a higher overall proportion of Q^4 species observed in BIS compared to IPS, and an enhancement of the Q^4 signal seen in the ^1H - ^{29}Si CP MAS data (due to the proximity to PEHA protons in the dry state).

Per the proposed mechanism (figure 5.20), silica begins to condense around the proton transfer catalyst, restricting its mobility for the remainder of the synthesis. After a certain time, proximate partially-condensed silica species are in close contact with one another and with a proton transfer catalyst (figure 5.20 A). This enables unbound silanol moieties to nucleophilically attack neighbouring Si atoms, creating hypervalent Si centres which may be potentially stabilised through hydrogen bonding (figure 5.20 B).²⁰³ The catalyst species then mediates water elimination from the now-pentavalent Si centre (figure 5.20 B) as well as neutralisation of the oxonium ion in the newly formed bond (figure 5.20 C), leading to higher concentrations of fully condensed Q^4 Si species on the surface than is observed in IPS (figure 5.20 D). Notably, in cases where the organic species is not a proton transfer catalyst, steps B, C, and D cannot occur. This is the best explanation for all of the above data and, although the reaction site shown in figure 5.20 is overly simplistic, such conditions would be present during gel densification through aggregation or mixing-led fragmentation and restructuring.¹⁸

A potential alternative explanation would be that the polyfunctional nature of PEHA leads to a high Q^4 interaction due to the equilibrium separation of Q^3 sites being larger than the length of PEHA (table 5.1), i.e. interaction from 1 amine moiety to a Q^3 Si site and the remaining 5 moieties to Q^4 sites. However, this is inconsistent with the trend in Q^3 signal against pH during the ^1H - ^{29}Si CP MAS NMR experiments, which were amplified upon removal of PEHA from BIS rather than suppressed. This is therefore much less likely than the proposed catalytic mechanism.

The proposed post-adsorption condensation mechanism has significant implications for all organic-inorganic surface investigations. In systems where the amine moiety is catalytically active towards condensation of the metal oxide, condensation of unsaturated surface sites will modify surface interaction strength and potentially specific interaction moieties or conformations, which may heavily impact the conclusions of such studies. Examples include all investigations into the surface chemistry of biomineralization, and (poly)peptide adsorption onto inorganic surfaces including passivated layers of pure metal surfaces. One interesting case is in densification of sponge biosilica which has been found to undergo a ‘biosintering’ process after gel formation and syneresis, fusing parallel silica lamellae into a single hard cylinder.⁵² Significantly, no chemical mechanism for this phenomenon has been reported

to date.²⁰⁴ Given that the catalytic activity of PEHA is derived from its biomolecule-like polyfunctionality, it is possible that the mechanism proposed in figure 5.20 can be further extended to molecular interaction occurring during biosintering.

So why was this effect not observed before? In the case of molecular dynamics simulations, it is rare for a simulation to be able to consider covalent bond breakage and formation. Although such studies on silica-liquid interfaces exist,^{205,206} these are generally limited to “inorganic-only” systems and do not consider adsorption behaviour and its effect on the surface composition. Accordingly, molecular dynamics studies of sorption onto silica surfaces can only consider electrostatic effects on the surface^{28,207} and hence lead to the conclusion that surface adsorption occurs at Q^3 sites only.

In a similar vein, the majority of NMR studies on silica surface adsorption focus on aspects of adsorption other than the specific Si:N interactions present. For example, studies of polypeptide sorption often focus on conformational changes in the sorbate as it associates to the silica surface, but not on the effect on the chemistry of the silica itself.^{208,209} Similarly, studies into bonding of choline onto the surface of silica focus on the interaction site of the choline molecule and rely on molecular dynamics simulations to provide surface-side interaction sites, biasing the findings towards Q^3 site adsorption.¹⁹⁵ Despite this, there are some examples of studies that determine surface localisation on mesoporous silica, specifically of post-synthetically loaded glycine and the surfactant template CTAB.^{197,210} Both of these cases find exclusive bonding of the positively charged organic species to Q^3 silica sites through ^{29}Si - ^{15}N CP MAS and ^1H - ^{29}Si - ^1H CP MAS NMR, respectively. Significantly, neither organic compound is catalytically active towards silica condensation; neither has the polyfunctionality shown previously to accelerate silica condensation,¹³⁴ and further, the permanent charge on CTAB prevents proton transfer for catalysis. This indicates that the Q^4 binding effect observed herein only occurs when the organic is specifically catalysing the condensation reaction.

There is significant disagreement between MD and NMR about the exact interaction between PEHA and BIS surfaces, however each technique offers important information about BIS material chemistry and the mechanism of extraction. From MD it is clear that the balance between solvation and adsorption energy of the PEHA (or other organic on the BIS

surface) is a key determining factor in extraction efficiency. Although the simulations match PEHA acid extraction very well macroscopically, NMR casts doubt on the strictly charge-charge basis of surface bonding, showing significant PEHA interaction with Q^4 Si centres in contradiction of the MD. Clearly deeper investigation of these phenomena from both perspectives are warranted to fully reconcile the findings of the two techniques (either through reactive MD methods attempting to predict the adsorption-then-condensation mechanism, or through suspended-phase NMR to characterise the silica interface in solvated conditions).

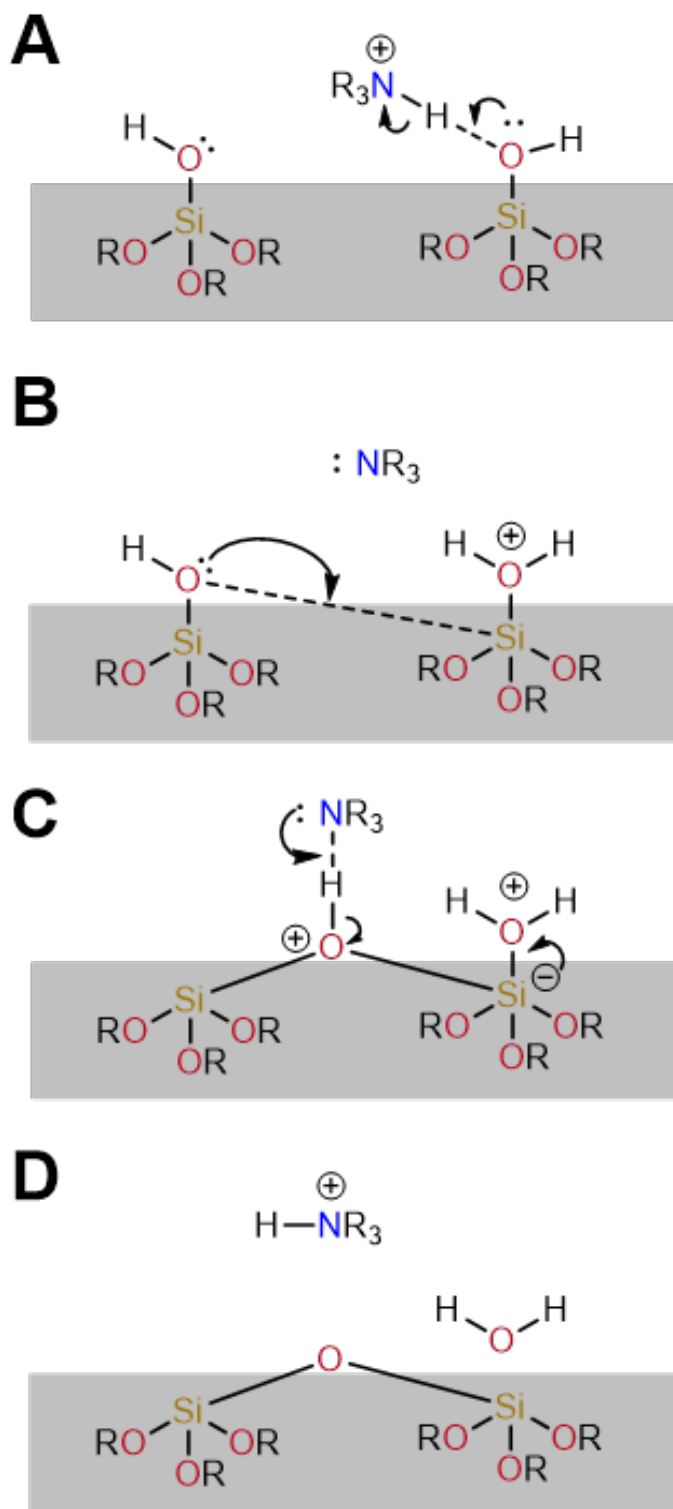


Figure 5.20: Proposed scheme for reactive adsorption of PEHA to bioinspired silica surfaces. (A) charged PEHA species are initially attracted to free hydroxyls on silica surfaces through electrostatic interactions; (B,C) Amine-catalysed proton transfer promotes condensation of adjacent Si species until they have reached the Q^4 condensation level; and (D) final PEHA- Q^4 adduct as observed by NMR.

5.4 Impact of acid extraction on BIS technology

Section redacted due to commercial sensitivity of contents.

5.4.1 Impact upon proposed silica manufacturing processes

As stated earlier, the drive for developing nondestructive template removal methods has stemmed from the uneconomical and environmentally unfriendly nature of calcination-based purification. Although this has led to the development of various methods discussed earlier and critically reviewed elsewhere,⁹⁸ this is not a significant enough improvement over calcination to render the production of templated silica materials industrially viable. To this end, in this section the industrial viability of bioinspired silica synthesis paired with acid treatment was demonstrated; furthermore the environmental and economical costs of acid treatment are estimated and compared against calcination and solvent extraction as described by Tanev and Pinnavaia.⁸⁸

When comparing the economic and environmental costs of different purification methods, it is obvious from the large variations in operating temperature for each method that matter efficiency alone (e.g. E-factor) cannot fully describe the relative costs of each purification method. Instead, the energetic costs of each purification method on an industrial scale are estimated and compared.

In the absence of existing examples of templated silica process plants, previous techno-economic analysis of the BIS synthesis process was used to provide an estimated annual production capacity of 40,000 tons.¹⁶ Given these, and a number of further assumptions detailed in the supplementary information, it was estimated that a calcination furnace for such a plant would have require 2.8 MW of power, or ca. 2000 MJ/ton silica produced. Through a similar method, it was further estimated that a stirred kettle boiler such as would be required for the ethanol reflux used in reference⁸⁸ would require 5.8 MW of power, or ca. 4320 MJ/ton silica. Finally, a stirred tank reactor as would be required for the room-temperature acid extraction described for this study would need only 461 kW, or 84 MJ/ton silica (only 4% and 2% of calcination and solvent reflux, respectively). Converting the energetic cost of silica purification for each method to their equivalent CO₂ emissions,²¹¹ acid extraction is found

to reduce the carbon footprint of purification by 95-97%.

Although the estimated duty values have significant uncertainty, it is clear that the energetic and environmental costs of acid treatment are orders of magnitude lower than the other methods considered here. Furthermore as the costs associated with conventional purification are largely thermochemistry-based (i.e. dependent on the latent heat or heat capacities of the materials involved), there is little room for improvement within these by process intensification. Conversely, such economisation is possible for acid treatment as this process is solely mixing- (and therefore equipment-) dependent.

5.5 Conclusion

In this chapter a mild, rapid, and scalable method of controlling organic additive content in bioinspired silica through post-synthetic acid treatment was demonstrated. By reducing the pH of an as-synthesised silica suspension, the concentration of organic additive within BIS was reduced for even eliminated entirely, concurrently increasing the particle porosity and modulating the silica surface chemistry.

Through a combination of experiments and simulations, a fundamental insight into the surface molecular interactions was gained, hence becoming able to predict additive extraction efficiency. Extraction was found to depend on two sets of pH-dependent interactions: ionic binding between additive and surface, and solvation energy of additive into solution. These simulations could therefore be extended to predict different additive chemistry: as additive hydrophobicity increased, so extraction efficiency decreased. This was found to be qualitatively similar to findings from previous extraction studies for different templated silica materials.

Analysis into the modelled reaction scheme using ^{29}Si SSNMR and ^1H - ^{29}Si CPMAS experiments then indicated clearly that the excess Q^4 sites were bonded to the bioinspired additive, contradicting the simulation results and proposed mechanisms from previous studies. The NMR study suggested that, as the PEHA was entrapped within the silica during synthesis, the prior studies discounted further condensation reactions happening at the adsorption site. Therefore, there is a need for future studies of organic-silica hybrid material to

account for proton transfer catalysis during surface adsorption in order to fully describe the silica chemistry present.

Finally, the economic and environmental viability of acid extraction was demonstrated by estimating both the energy requirements and carbon emissions associated with the acid extraction method and previous, heating-dependent purification methods. Acid extraction was found to produce orders of magnitude lower carbon emissions, notably being the only method considered which produced fewer emissions during purification than during synthesis. Furthermore, with the ability to directly modify silica surface chemistry rather than using separate purification and functionalisation steps, a synthesis step was entirely eliminated from the production of silica. Therefore, by applying green chemistry principles to the synthesis and purification of BIS, a cleaner, cheaper, and readily scalable method for silica production was developed, a significant technological advance.

Table 5.2: Table of comparisons in relative peak area for silicon species within precipitated and bioinspired silica materials against pH for both single-pulse ^{29}Si MAS spectra and proton cross-polarised ^1H - ^{29}Si spectra for the same samples. For single pulse spectra, condensation degree ($Q^4/(Q^2+Q^3+Q^4)$) is also shown.

Relative peak area (%)	pH 7 Blank		pH 7 Bioinspired		pH 5 Blank		pH 5 Bioinspired		pH 2 Blank		pH 2 Bioinspired	
	^{29}Si	^1H - ^{29}Si	^{29}Si	^1H - ^{29}Si	^{29}Si	^1H - ^{29}Si	^{29}Si	^1H - ^{29}Si	^{29}Si	^1H - ^{29}Si	^{29}Si	^1H - ^{29}Si
Q^2	6	14	7	12	8	20	5	8	9	20	5	13
Q^3	39	77	34	47	42	71	34	53	43	72	33	69
Q^4	55	9	59	41	50	9	61	39	48	9	62	18
Condensation degree	55		59		50		61		48		62	

Chapter 6

Conclusions and future work

6.1 Motivation

This project aimed to develop new, industrially-relevant methods for producing silica materials by bioinspired synthesis. In doing so it aimed to provide proof-of-concept for the industrial applicability of bioinspired silica materials enabling a transition from laboratory analysis to commercial development. More generally, this work aimed to draw parallels between BIS materials and similar organic-assisted sol-gel silicas materials (e.g. mesoporous silicas like MCM-41, colloidal silica sols like Stöber silica, and colloidal crystals made from the above), providing a synthesis-methods-based bridge between seemingly unconnected material types.

6.2 Main findings

Sections redacted due to commercial sensitivity of contents.

Development of mild BIS activation methods

Beyond the development of new synthesis techniques, novel activation techniques for BIS materials were also developed. A new, room-temperature acid extraction technique was de-

veloped to purify BIS materials without recourse to either calcination or reflux-based alternatives common in other materials like MCM-41 or zeolite materials. Unlike these methods, acid extraction could be tuned by modifying the pH of the treatment, creating hybrid organic-inorganic materials with tailored composition and porosity. Analysis using the reactive test gas CO₂ showed how partial extraction can tailor BIS chemical functionality in a single step, enabling direct synthesis of hybrid sorbent materials.

Through use of molecular dynamics simulation techniques, a thermodynamic basis for the attraction between PEHA and BIS was discovered, explaining why acid extraction was effective. This provided a potential mechanism for the partial extraction and properties seen in these BIS materials, and explaining why this had previously not been established in other organic-templated silica materials. Through use of solid-state NMR techniques, the exact bonding between PEHA and BIS was probed, indicating reactivity at the interface which could not be considered by the molecular dynamics simulations nor were detected in previous investigations of silica-organic interfaces. These findings were then compared against previous models for organic-mediated silica polymerisation, creating a proposed mechanism for reactivity at the interface, with potential ramifications to biomineralisation phenomena in nature.

Section redacted due to commercial sensitivity of contents.

6.3 Recommended future research

Sections redacted due to the commercial sensitivity of their contents.

Determining the applicability of mesoporous BIS to industrial applications

The establishment of a new family of mesoporous BIS materials in chapter 4 was very exciting technologically and scientifically, however no significant data on the usefulness of these materials has yet been gathered. The author therefore recommends further studies of these materials for the purposes of establishing their use as industrial sorbent, especially in the context of their industrially-friendly synthesis conditions and methods.

Predicting activation techniques of general organic-inorganic materials using molecular dynamics

The molecular dynamics simulations established in chapter 5 are highly interesting, as it indicates the possibility of molecular dynamics as a predictive tool for silica surface modification rather than simply a descriptive tool. Further investigation of these models would first enable relation of different techniques and studies in this field to one another, something which is currently hampered due to distinctions between the silica substrates, and afterwards enable simulations to become a true predictive tool for developing new surface modification on generalised silica materials. This would greatly accelerate the pace of progress in all silica material families discussed in this thesis.

Life-cycle analysis of the BIS process

Finally, although significant technoeconomic analysis of the bioinspired synthesis has been performed, chiefly in reference 16, there remain several unknown considerations with regards to the additional chemicals and processing steps involved in the BIS synthesis. In order to fully understand the environmental and safety ramifications of including bioinspired additives such as PEHA within the process, a full life-cycle analysis must be performed.

This analysis should encompass the cost of producing the bioinspired additive and other reagents, costs and additional environmental hazards associated with processing the amine-containing additives, as well as any considerations for their eventual disposal and accidental release prevention. Only by performing such a holistic analysis to understand the drawbacks of bioinspired additive usage can a complete picture of the overall advantages to using BIS over conventional precipitated silica syntheses be made.

Bibliography

- [1] Flörke, O. W., Graetsch, H. A., Brunk, F., Benda, L., Paschen, S., Bergna, H. E., Roberts, W. O., Welsh, W. A., Libanati, C., Ettlinger, M., Kerner, D., Maier, M., Meon, W., Schmoll, R., Gies, H., and Schiffmann, D. *Silica, in Ullmann's encyclopedia of industrial chemistry*. Wiley-VCH, Weinheim, Germany, (2008).
- [2] Deer, W., Howie, R., and Zussmann, J. *An Introduction to the Rock-Forming Minerals*. Prentice Hall, 2 edition, (1992).
- [3] O'Sullivan, C. K. and Guilbault, G. G. *Biosensors and Bioelectronics* **14**(8-9), 663–670 (1999).
- [4] Bhattacharyya, K. G. and Gupta, S. S. *Advances in Colloid and Interface Science* **140**(2), 114–131 (2008).
- [5] Raven, J. A. *Biological Reviews* **58**(2), 179–207 may (1983).
- [6] Hildebrand, M. *Chemical Reviews* **108**(11), 4855–4874 (2008).
- [7] Iler, R. K. *The chemistry of silica: solubility, polymerization, colloid and surface properties and biochemistry of silica*. A Wiley-Interscience publication. Wiley, (1979).
- [8] Treguer, P., Tréguer, P., Nelson, D. M., Van Bennekom, A. J., DeMaster, D. J., Leynaert, A., and Quéguiner, B. *Science* **268**, 375–379 (1995).
- [9] Shrestha, R. P. and Hildebrand, M. *Eukaryotic Cell* **14**(1), 29 (2015).
- [10] Poulsen, N., Scheffel, A., Sheppard, V. C., Chesley, P. M., and Krogöer, N. *Journal of Biological Chemistry* **288**(28), 20100–20109 (2013).

- [11] Vrieling, E. G., Gieskes, W. W. C., and Beelen, T. P. M. *Journal of Phycolgy* **35**(3), 548–559 (1999).
- [12] The Freedonia Group. Technical report, (2012).
- [13] Fu, S.-y., Feng, X.-q., Lauke, B., and Mai, Y.-w. *Journal of Composites B* **39**, 933–961 (2008).
- [14] Byers, J. T. *Rubber chemistry and technology* **75**(3), 527–548 (2002).
- [15] Food and Drug Administration. <https://www.accessdata.fda.gov/scripts/cdrh/cfdocs/cfcfr/CFRSearch.cfm?fr=172.480>, (2018). Accessed: 2019-1-09.
- [16] Drummond, C., McCann, R., and Patwardhan, S. V. *Chemical Engineering Journal* **244**, 483–492 (2014).
- [17] Dislich, H. and Hinz, P. *Journal of Non-Crystalline Solids* **48**(1), 11–16 (1982).
- [18] Brinker, C. and Sherer, G. *Sol-gel science: the physics and chemistry of sol-gel processing*. Elsevier, (1990).
- [19] Svensson, I. L., Sjöberg, S., and Öhman, L. O. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases* **82**(12), 3635–3646 (1986).
- [20] Belton, D. J., Deschaume, O., and Perry, C. C. *FEBS Journal* **279**(10), 1710–1720 (2012).
- [21] Provis, J. L., Duxson, P., Lukey, G. C., Separovic, F., Kriven, W. M., and Van Deventer, J. S. *Industrial and Engineering Chemistry Research* **44**(23), 8899–8908 (2005).
- [22] Berggren, A., Palmqvist, A. E. C., and Holmberg, K. *Soft Matter* **1**(3), 219–226 (2005).
- [23] Gelsema, W. J., de Ligny, C. L., Remijnse, A. G., and Blijleven, H. A. *Recueil des travaux chimiques des pays-bas* **85**(7), 647–660 (1966).
- [24] Castells, C. B., Ràfols, C., Rosés, M., and Bosch, E. *Journal of chromatography A* **1002**(1-2), 41–53 (2003).
- [25] Hyde, E. D., Seyfaee, A., Neville, F., and Moreno-Atanasio, R. *Industrial and Engineering Chemistry Research* **55**(33), 8891–8913 (2016).

- [26] Stöber, W., Fink, A., and Bohn, E. *Journal of Colloid and Interface Science* **26**(1), 62–69 (1968).
- [27] Patwardhan, S. V., Emami, F. S., Berry, R. J., Jones, S. E., Naik, R. R., Deschaume, O., Heinz, H., and Perry, C. C. *Journal of the American Chemical Society* **134**(14), 6244–6256 (2012).
- [28] Emami, F. S., Puddu, V., Berry, R. J., Varshney, V., Patwardhan, S. V., Perry, C. C., and Heinz, H. *Chemistry of Materials* **26**(19), 5725–5734 (2014).
- [29] Barisik, M., Atalay, S., Beskok, A., and Qian, S. *Journal of physical chemistry C* **118**(4), 1836–1842 (2014).
- [30] Ninham, B. *Advances in colloid and interface science* **83**(1-3), 1–17 dec (1999).
- [31] Hamaker, H. C. *Physica* **4**(10), 1058–1072 (1937).
- [32] Lee, Y. R., Soe, J. T., Zhang, S., Ahn, J. W., Park, M. B., and Ahn, W. S. *Chemical engineering journal* **317**, 821–843 (2017).
- [33] Hubbe, M. A. and Rojas, O. J. *BioResources* **3**(4), 1419–1491 (2008).
- [34] Yamamoto, E., Kitahara, M., Tsumura, T., and Kuroda, K. *Chemistry of Materials* **26**(9), 2927–2933 (2014).
- [35] Yokoi, T. *Journal of the Japan Petroleum Institute* **55**(1), 13–26 (2012).
- [36] Yokoi, T., Sakamoto, Y., Terasaki, O., Kubota, Y., Okubo, T., and Tatsumi, T. *Journal of the American Chemical Society* **128**(42), 13664–13665 (2006).
- [37] Watanabe, R., Yokoi, T., Kobayashi, E., Otsuka, Y., Shimojima, A., Okubo, T., and Tatsumi, T. *Journal of Colloid and Interface Science* **360**(1), 1–7 (2011).
- [38] Xia, Y., Gates, B., Yin, Y., and Lu, Y. *Advanced Materials* **12**(10), 693–713 may (2000).
- [39] Prevo, B. G., Hwang, Y., and Velev, O. D. *Chemistry of Materials* **17**(14), 3642–3651 (2005).

- [40] Zheng, H. and Ravaine, S. *Crystals* **6**(5), 54 (2016).
- [41] Schüth, F. *Angewandte Chemie (International ed. in English)* **42**(31), 3604–22 (2003).
- [42] Bergna, H. E. In *Advances in chemistry: the colloid chemistry of silica*, volume 80, 1–47. American Chemical Society (1994).
- [43] Mccave, I. *Deep sea research part A. oceanographic research papers* **31**, 329–352 (1984).
- [44] Schmidt, R. H. In *Protein functionality in foods*, 131–147. (1981).
- [45] Varga, Z., Wang, G., and Swan, J. *Soft matter* **11**(46), 9009–9019 (2015).
- [46] Coniglio, A., De Arcangelis, L., Del Gado, E., Fierro, A., and Sator, N. *Journal of physics condensed matter* **16**(42) (2004).
- [47] Goksu, E. I., Hoopes, M. I., Nellis, B. A., Xing, C., Faller, R., Frank, C. W., Risbud, S. H., Satcher, J. H., and Longo, M. L. *Biochimica et Biophysica Acta - Biomembranes* **1798**(4), 719–729 (2010).
- [48] Gauthier, B. M., Bakrania, S. D., Anderson, A. M., and Carroll, M. K. *Journal of Non-Crystalline Solids* **350**, 238–243 (2004).
- [49] Fedeyko, J. M., Vlachos, D. G., and Lobo, R. F. *Langmuir* **21**(11), 5197–5206 (2005).
- [50] Broach, R. W., Jan, D.-Y., Lesch, D. A., Kulprathipanja, S., Roland, E., and Kleinschmit, P. *Zeolites, in Ullmann’s encyclopedia of industrial chemistry*. Wiley-VCH, Weinheim, Germany, apr (2012).
- [51] Rouquerol, J., Avnir, D., Fairbridge, W., Everett, D. H., Haynes, J. H., Pernicone, N., Ramsay, J. D. F., Sing, K. S. W., and Unger, K. K. *Pure and Applied Chemistry* **66**(8), 1739–1758 (1994).
- [52] Wang, L. and Yang, R. T. *Journal of Physical Chemistry C* **115**(43), 21264–21272 (2011).
- [53] *New Journal of Chemistry* **32**(8), 1311 (2008).

- [54] Thommes, M., Kaneko, K., Neimark, A. V., Olivier, J. P., Rodriguez-Reinoso, F., Rouquerol, J., and Sing, K. S. W. *Pure and Applied Chemistry* **87**(9-10), 1051–1069 (2015).
- [55] Ismail, A. F., Khulbe, K. C., and Matsuura, T. *Gas separation membranes: polymeric and inorganic*. (2015).
- [56] Burggraaf, A. J. *Journal of Membrane Science* **155**(1), 45–65 (1999).
- [57] Yoshioka, T., Asaeda, M., and Tsuru, T. *Journal of Membrane Science* **293**(1), 81–93 (2007).
- [58] O’koye, I. P., Benham, M., and Thomas, K. M. *Langmuir* **13**(15), 4054–4059 (1997).
- [59] Presser, V., McDonough, J., Yeon, S.-H., and Gogotsi, Y. *Energy & Environmental Science* **4**(8), 3059 (2011).
- [60] Parlett, C. M., Wilson, K., and Lee, A. F. *Chemical Society Reviews* **42**(9), 3876–3893 (2013).
- [61] Studart, A. R., Gonzenbach, U. T., Tervoort, E., and Gauckler, L. J. *Journal of the American Ceramic Society* **89**(6), 1771–1789 (2006).
- [62] Mercier, L. and Pinnavaia, T. J. *Advanced Materials* **9**(6), 500–503 (1997).
- [63] Bae, S. J., Kim, S.-w., and Kim, B. M. *Chemical Communications* **20**(1), 31–32 (2000).
- [64] Stein, A., Melde, B. J., and Schroden, R. C. *Advanced Materials* **12**(19), 1403–1419 (2000).
- [65] Shang, F., Sun, J., Liu, H., Wang, C., Guan, J., and Kan, Q. *Materials Research Bulletin* **47**(3), 801–806 (2012).
- [66] Slowing, I. I., Vivero-Escoto, J. L., Trewyn, B. G., and Lin, V. S.-Y. *J. Mater. Chem.* **20**(37), 7924–7937 (2010).
- [67] Gillett, S. L. Technical report, The Foresight Institute, (1998).
- [68] Newsam, J. M. *Science* **231**(4742), 1093–1099 (1986).

- [69] Xu, X., Bao, Y., Song, C., Yang, W., Liu, J., and Lin, L. *Microporous and Mesoporous Materials* **75**(3), 173–181 (2004).
- [70] Kosinov, N., Gascon, J., Kapteijn, F., and Hensen, E. J. *Journal of Membrane Science* **499**, 65–79 (2016).
- [71] Bonenfant, D., Kharoune, M., Niquette, P., Mimeault, M., and Hausler, R. *Science and Technology of Advanced Materials* **9**(1) (2008).
- [72] Baertsch, C. D., Funke, H. H., Falconer, J. L., and Noble, R. D. *Journal of Physical Chemistry* **100**(18), 7676–7679 (1996).
- [73] Tukur, N. M. and Al-Khattaf, S. *Chemical Engineering Journal* **166**(1), 348–357 (2011).
- [74] van den Bergh, J., Gücüyener, C., Gascon, J., and Kapteijn, F. *Chemical Engineering Journal* **166**(1), 368–377 (2011).
- [75] Gies, H. and Marler, B. *Zeolites* **12**(1), 42–49 (1992).
- [76] Darr, J. A., Zhang, J., Makwana, N. M., and Weng, X. *Chemical Reviews* **117**(17), 11125–11238 (2017).
- [77] Liu, Z., Okabe, K., Anand, C., Yonezawa, Y., Zhu, J., Yamada, H., Endo, A., Yanaba, Y., Yoshikawa, T., Ohara, K., Okubo, T., and Wakihara, T. *Proceedings of the National Academy of Sciences* **113**(50), 14267–14271 (2016).
- [78] Davis, M. E. *Chemistry of Materials* **26**(1), 239–245 (2014).
- [79] Moliner, M., Rey, F., and Corma, A. *Angewandte Chemie (International ed. in English)* **52**(52), 13880–9 (2013).
- [80] Lee, H., Zones, S. I., and Davis, M. E. *Microporous and Mesoporous Materials* **88**(1-3), 266–274 (2006).
- [81] Shvets, O. V., Kasian, N., Zukal, A., Pinkas, J., and Cejka, J. *Chemistry of Materials* **22**(11), 3482–3495 (2010).
- [82] Burkett, S. L. and Davis, M. E. *The Journal of Physical Chemistry* **98**(17), 4647–4653 apr (1994).

- [83] Burkett, S. L. and Davis, M. E. *Chemistry of Materials* **7**(8), 1453–1463 (1995).
- [84] Patarin, J. *Angewandte Chemie (International ed. in English)* **43**(30), 3878–80 (2004).
- [85] Valtchev, V., Majano, G., Mintova, S., and Pérez-Ramírez, J. *Chemical Society reviews* **42**(1), 263–90 (2013).
- [86] Lee, H., Zones, S. I., and Davis, M. E. *Nature* **425**(6956), 385–388 (2003).
- [87] Jiang, J., Yu, J., and Corma, A. *Angewandte Chemie International Edition* **49**(18), 3120–3145 (2010).
- [88] Tanev, P. T. and Pinnavaia, T. J. *Chemistry of Materials* **8**(8), 2068–2079 (1996).
- [89] Zhao, D., Huo, Q., Feng, J., Chmelka, B. F., and Stucky, G. D. *Journal of the American Chemical Society* **120**(24), 6024–6036 (1998).
- [90] Lombardo, D., Kiselev, M. A., Magazù, S., and Calandra, P. **2015**, 1–22 (2015).
- [91] Beck, J. S., Vartuli, J. C., Roth, W. J., Leonowicz, M. E., Kresge, C. T., Schmitt, K. D., Chu, C. T. W., Olson, D. H., and Sheppard, E. W. *Journal of the American Chemical Society* **114**(27), 10834–10843 (1992).
- [92] Kresge, C. T. and Roth, W. J. *Chemical Society Reviews* **42**(9), 3663–3670 (2013).
- [93] Ying, J. Y., Mehnert, C. P., and Wong, M. S. *Angewandte Chemie International Edition* **38**(1-2), 56–77 jan (1999).
- [94] Sayari, A. and Yang, Y. *The Journal of Physical Chemistry B* **104**(20), 4835–4839 may (2000).
- [95] Tanev, P. T. and Pinnavaia, T. J. *Science (New York, N.Y.)* **267**(5199), 865–867 (1995).
- [96] Jiang, J., Yin, J., Dai, L., Liu, R., and Xiao, Z. *RSC Advances* **7**(40), 25066–25069 (2017).
- [97] Yuen, A. K., Heinroth, F., Ward, A. J., Masters, A. F., and Maschmeyer, T. *Physical Chemistry Chemical Physics* **15**(32), 13343–13353 jul (2013).

- [98] Gérardin, C., Reboul, J., Bonne, M., and Lebeau, B. *Chemical Society reviews* **42**(9), 4217–55 (2013).
- [99] Cassiers, K., Van Der Voort, P., and Vansant, E. F. *Chemical Communications* (24), 2489–2490 (2000).
- [100] Patwardhan, S. V., Manning, J. R., and Chiacchia, M. *Current Opinion in Green and Sustainable Chemistry* **12** aug (2018).
- [101] Albela, B. and Bonneviot, L. *New Journal of Chemistry* **40**(5), 4115–4131 (2016).
- [102] Hung, C.-T., Yang, C.-F., Lin, J.-S., Huang, S.-J., Chang, Y.-C., and Liu, S.-B. *Microporous and Mesoporous Materials* **238**, 2–13 (2017).
- [103] Walcarius, A. *Electroanalysis* **27**(6), 1303–1340 (2015).
- [104] Yang, P., Gai, S., and Lin, J. *Chemical Society Reviews* **41**(9), 3679 apr (2012).
- [105] Li, S., Liu, H., Li, L., Luo, N. Q., Cao, R. H., Chen, D. H., and Shao, Y. Z. *Applied Physics Letters* **98**(9), 2–5 (2011).
- [106] Rahikkala, A., Pereira, S. A. P., Figueiredo, P., Passos, M. L. C., Araújo, A. R. T. S., Saraiva, M. L. M. F. S., and Santos, H. A. *Advanced Biosystems* **2**(7), 1800020 (2018).
- [107] Narayan, R., Nayak, U. Y., Raichur, A. M., and Garg, S. *Pharmaceutics* **10**(3), 1–49 (2018).
- [108] Chen, Y., Chen, H., and Shi, J. *Expert Opinion on Drug Delivery* **11**(6), 917–930 (2014).
- [109] Linthorst, J. A. *Foundations of chemistry* **12**(1), 55–68 (2010).
- [110] Anastas, P. T. and Warner, J. C. *Green chemistry: theory and practice*. Oxford University Press, Oxford, 1 edition, (1998).
- [111] Sheldon, R. A. *Chemical communications* (29), 3352–3365 (2008).
- [112] Vaughen, B. K. and Klein, J. A. *Process safety and environmental protection* **90**(5), 411–418 (2012).

- [113] Sheldon, R. A. *ACS sustainable chemistry and engineering* **6**(1), 32–48 (2018).
- [114] Sheldon, R. A. *Green chemistry* **19**(1), 18–43 (2017).
- [115] Prat, D., Wells, A., Hayler, J., Sneddon, H., McElroy, C. R., Abou-Shehada, S., and Dunn, P. J. *Green chemistry* **18**(1), 288–296 (2016).
- [116] McElroy, C. R., Constantinou, A., Jones, L. C., Summerton, L., and Clark, J. H. *Green chemistry* **17**(5), 3111–3121 (2015).
- [117] Eckelman, M. J., Zimmerman, J. B., and Anastas, P. T. *Journal of Industrial Ecology* **12**(3), 316–328 (2008).
- [118] Ould-Ely, T., Luger, M., Kaplan-Reinig, L., Niesz, K., Doherty, M., and Morse, D. E. *Nature protocols* **6**(1), 97–104 (2011).
- [119] Sumper, M. and Kröger, N. *J. Mater. Chem.* **14**(14), 2059–2065 (2004).
- [120] Kroger, N., Deutzmann, R., and Sumper, M. *Science* **286**(5442), 1129–1132 (1999).
- [121] Janairo, J. I. B., Sakaguchi, T., Mine, K., Kamada, R., and Sakaguchi, K. *Protein & Peptide Letters* **25**(1), 4–14 (2018).
- [122] Xu, A.-W., Ma, Y., and Cölfen, H. *J. Mater. Chem.* **17**(5), 415–449 (2007).
- [123] Song, I. W., Park, H., Park, J. H., Kim, H., Kim, S. H., Yi, S., Jaworski, J., and Sang, B. I. *Scientific Reports* **7**(1), 1–7 (2017).
- [124] Albert, K., Huang, X.-C., and Hsu, H.-Y. *Advances in Colloid and Interface Science* **249**, 272–289 (2017).
- [125] He, P., Greenway, G., and Haswell, S. J. *Nanotechnology* **19**(31) (2008).
- [126] Lechner, C. C. and Becker, C. F. *Bioorganic and Medicinal Chemistry* **21**(12), 3533–3541 (2013).
- [127] Patwardhan, S. V., Mukherjee, N., and Clarson, S. J. *J. Inorg. Organomet. Polym.* **11**(3), 193–198 (2002).

- [128] Patwardhan, S. V., Mukherjee, N., and Clarson, S. J. *Silicon Chemistry* **1**(1), 47–54 (2002).
- [129] Patwardhan, S. V., Mukherjee, N., and Clarson, S. J. *Journal of Inorganic and Organometallic Polymers* **11**(2), 117–121 (2002).
- [130] Patwardhan, S. V., Mukherjee, N., Steinitz-Kannan, M., and Clarson, S. J. *Chemical communications* (10), 1122–1123 (2003).
- [131] Patwardhan, S. V. *Chemical Communications* **47**(27), 7567–82 (2011).
- [132] Belton, D., Paine, G., Patwardhan, S. V., and Perry, C. C. *Journal of Materials Chemistry* **14**(14), 2231 (2004).
- [133] Belton, D. J., Patwardhan, S. V., and Perry, C. C. *Journal of Materials Chemistry* **15**(43), 4629 (2005).
- [134] Belton, D. J., Patwardhan, S. V., Annenkov, V. V., Danilovtseva, E. N., and Perry, C. C. *Proceedings of the National Academy of Sciences of the United States of America* **105**(16), 5963–5968 (2008).
- [135] Belton, D. J., Patwardhan, S. V., and Perry, C. C. *Chemical Communications* **1**, 3475–3477 (2005).
- [136] Jantschke, A., Spinde, K., and Brunner, E. *Beilstein journal of nanotechnology* **5**, 2026–35 (2014).
- [137] Harrison, C. and Loton, N. *Journal of the Chemical Society, Faraday Transactions* **91**(23), 4287–4297 (1995).
- [138] Delak, K. M. and Sahai, N. *Chemistry of Materials* **17**(16), 4272–4272 aug (2005).
- [139] Robinson, D. B., Rognlien, J. L., Bauer, C. A., and Simmons, B. A. *Journal of Materials Chemistry* **17**(20), 2113 (2007).
- [140] Dickerson, M. B., Sandhage, K. H., and Naik, R. R. *Chemical Reviews* **108**(11), 4935–4978 (2008).

- [141] Kadali, S. B., Soultanidis, N., and Wong, M. S. *Topics in Catalysis* **49**(3-4), 251–258 (2008).
- [142] Davidson, S., Lamprou, D. A., Urquhart, A. J., Grant, M. H., and Patwardhan, S. V. *ACS Biomaterials Science and Engineering* **2**(9), 1493–1503 (2016).
- [143] Alotaibi, K. M., Shiels, L., Lacaze, L., Peshkur, T. A., Anderson, P., Machala, L., Critchley, K., Patwardhan, S. V., and Gibson, L. T. *Chemical Science* **8**(1), 567–576 (2017).
- [144] Patwardhan, S. V. and Perry, C. C. *Silicon* **2**(1), 33–39 (2010).
- [145] Forsyth, C. and Patwardhan, S. V. *Journal of Materials Chemistry B* **1**(8), 1164 (2013).
- [146] Forsyth, C., Yip, T. W. S., and Patwardhan, S. V. *Chemical communications* **49**(31), 3191–3 (2013).
- [147] Yang, S. H., Ko, E. H., Jung, Y. H., and Choi, I. S. *Angewandte Chemie* **50**(27), 6239–6242 (2011).
- [148] Magner, E. *Chemical Society reviews* **42**(15), 6213–22 (2013).
- [149] Hilal, S. H., Karickhoff, S. W., and Carreira, L. A. *Quantitative Structure-Activity Relationships* **14**(4), 348–355 (1995).
- [150] Nozawa, K., Gailhanou, H., Raison, L., Panizza, P., Ushiki, H., Sellier, E., Delville, J. P., and Delville, M. H. *Langmuir* **21**(4), 1516–1523 (2005).
- [151] Nozawa, K., Delville, M.-H., Ushiki, H., Panizza, P., and Delville, J.-P. *Physical Review E* **72**(1), 011404 (2005).
- [152] Chen, S.-L., Dong, P., Yang, G.-H., and Yang, J.-J. *Industrial & Engineering Chemistry Research* **35**(12), 4487–4493 (1996).
- [153] Kerridge, P. T. *Biochemical Journal* **19**(4), 611–617 (1925).
- [154] Bates, R. G. and Popovych, O. *CRC critical reviews in analytical chemistry* **10**(3), 247–278 jan (1981).

- [155] Rinder, T. and Oelkers, E. H. *Mineralogical Magazine* **78**(6), 1431–1436 (2014).
- [156] Coradin, T., Eglin, D., and Livage, J. *Spectroscopy* **18**(4), 567–576 (2004).
- [157] Andreozzi, R. *Water Research* **34**(18), 4419–4429 (2000).
- [158] Keller, K., Kampfer, H., Matejec, R., Lapp, O., Krafft, W., Frenken, H., Lührig, H., Scheerer, R., Heilmann, M., Meckl, H., Bergthaller, P., Hübner, D., Wolff, E., Morcher, B., Zahn, W., Buschmann, H., Blank, R., Tromnau, R., Plamper, J., Seiler, A., Nieswandt, K., Boie, I., Moisar, E., Winiker, R., Schellenberg, M., and Ketellapper, L. *Photography, in Ullmann’s encyclopedia of industrial chemistry*. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, (2000).
- [159] Warring, S. L., Beattie, D. A., and McQuillan, A. J. *Langmuir* **32**(6), 1568–1576 (2016).
- [160] Wojdyr, M. *Journal of applied crystallography* **43**(5), 1126–1128 (2010).
- [161] Patravale, V., Dandekar, P., and Jain, R. In *Nanoparticulate Drug Delivery*, 87–121. Elsevier (2012).
- [162] Tomaszewska, E., Soliwoda, K., Kadziola, K., Tkacz-Szczesna, B., Celichowski, G., Cichomski, M., Szmaja, W., and Grobelny, J. *Journal of Nanomaterials* **2013**, 1–10 (2013).
- [163] Hassan, P. A., Rana, S., and Verma, G. *Langmuir* **31**(1), 3–12 (2015).
- [164] Morrison, I. D., Grabowski, E. F., and Herb, C. A. *Langmuir* **1**, 496–501 (1985).
- [165] Brunauer, S., Emmett, P. H., and Teller, E. *Journal of the American Chemical Society* **60**(1), 309–319 (1938).
- [166] Sing, K. S. W. *Pure and Applied Chemistry* **57**(4), 603–619 (1985).
- [167] Rouquerol, J., Llewellyn, P., and Rouquerol, F. 49–56. (2007).
- [168] Barrett, E. P., Joyner, L. G., and Halenda, P. P. *Journal of the American Chemical Society* **73**(1), 373–380 (1951).

- [169] Mintova, S. and Čejka, J. *Studies in Surface Science and Catalysis* **168**, 301–326 (2007).
- [170] Xiong, F., Jiang, Z., Li, P., Wang, X., Bi, H., Li, Y., Wang, Z., Amooie, M. A., Soltanian, M. R., and Moortgat, J. *Fuel* **206**, 504–515 (2017).
- [171] an f Drug Administration, F.
- [172] Sigma-Aldrich. Technical report, Sigma Aldrich, (2015).
- [173] Ewlad-Ahmed, A. M., Morris, M. A., Patwardhan, S. V., and Gibson, L. T. *Environmental Science and Technology* **46**, 13354–13360 (2012).
- [174] Lin, W. G., Wei, F., Hou, Q., Zhang, T. Y., Wang, Y. K., and Zhu, J. H. *Microporous and Mesoporous Materials* **156**, 233–243 (2012).
- [175] Natarajan, S. K. and Selvaraj, S. *RSC Advances* **4**(28), 14328–14334 (2014).
- [176] Feng, Y., Panwar, N., Tng, D. J. H., Tjin, S. C., Wang, K., and Yong, K. T. *Coordination Chemistry Reviews* **319**, 86–109 (2016).
- [177] Baccile, N., Babonneau, F., Thomas, B., and Coradin, T. *Journal of Materials Chemistry* **19**(45), 8537 (2009).
- [178] de Ávila, S. G., Silva, L. C. C., and Matos, J. R. *Microporous and Mesoporous Materials* **234**, 277–286 (2016).
- [179] Gu, D., Zhang, F., Shi, Y., Zhang, F., Wu, Z., Deng, Y., Zhang, L., Tu, B., and Zhao, D. *Journal of colloid and interface science* **328**(2), 338–43 dec (2008).
- [180] Jabariyan, S. and Zanjanchi, M. A. *Ultrasonics sonochemistry* **19**(5), 1087–93 (2012).
- [181] Huang, Z., Miao, H., Li, J.-h., Wei, J.-l., Kawi, S., and Lai, M. *Separation and Purification Technology* **118**, 170–178 (2013).
- [182] Hitz, S. and Prins, R. *Journal of catalysis* **206**, 194–206 (1997).
- [183] Zanjanchi, M. and Jabariyan, S. *Journal of the Serbian Chemical Society* **79**(1), 25–38 (2014).

- [184] Steven, C. R., Busby, G. A., Mather, C., Tariq, B., Briuglia, M. L., Lamprou, D. A., Urquhart, A. J., Grant, M. H., and Patwardhan, S. V. *Journal of Materials Chemistry B* **2**(31), 5028 (2014).
- [185] Hahn, M. W., Jelic, J., Berger, E., Reuter, K., Jentys, A., and Lercher, J. A. *Journal of Physical Chemistry B* **120**(8), 1988–1995 (2016).
- [186] Zhang, W., Liu, H., Sun, C., Drage, T. C., and Snape, C. E. *Chemical Engineering Science* **116**, 306–316 (2014).
- [187] Kenarsari, S. D., Yang, D., Jiang, G., Zhang, S., Wang, J., Russell, A. G., Wei, Q., and Fan, M. *RSC Advances* **3**(45), 22739 (2013).
- [188] Drage, T. C., Snape, C. E., Stevens, L. A., Wood, J., Wang, J., Cooper, A. I., Dawson, R., Guo, X., Satterley, C., and Irons, R. *Journal of Materials Chemistry* **22**(7), 2815 (2012).
- [189] Pennline, H. W., Hoffman, J. S., Gray, M. L., Siriwardane, R. V., Fauth, D. J., and Richards, G. A. Technical report, National energy Technology Laboratory, (2009).
- [190] Heinz, H., Lin, T.-J., Kishore Mishra, R., and Emami, F. S. *Langmuir* **29**(6), 1754–1765 (2013).
- [191] Emami, F. S., Puddu, V., Berry, R. J., Varshney, V., Patwardhan, S. V., Perry, C. C., and Heinz, H. *Chemistry of Materials* **26**(8), 2647–2658 (2014).
- [192] Milonjic, K. *Colloids and Surfaces* **23**, 301–312 (1987).
- [193] Zerrouk, R., Foissy, A., and Mercier, R. *Journal of Colloid and Interface Science* **139**(1), 20–29 (1990).
- [194] Babonneau, F., Baccile, N., Laurent, G., Maquet, J., Azaïs, T., Gervais, C., and Bonhomme, C. *Comptes Rendus Chimie* **13**(1-2), 58–68 (2010).
- [195] Brückner, S. I., Donets, S., Dianat, A., Bobeth, M., Gutiérrez, R., Cuniberti, G., and Brunner, E. *Langmuir* **32**(44), 11698–11705 (2016).
- [196] Rimola, A., Costa, D., Sodupe, M., Lambert, J.-F. F., and Ugliengo, P. *Chemical Reviews* **113**(6), 4216–4313 (2013).

- [197] Baccile, N., Laurent, G., Bonhomme, C., Innocenzi, P., and Babonneau, F. *Chemistry of Materials* **19**(6), 1343–1354 (2007).
- [198] Muñoz-Aguado, M. J. and Gregorkiewitz, M. *Journal of Colloid and Interface Science* **185**(2), 459–465 (1997).
- [199] Grace Davison. Technical report, (2006).
- [200] Unger, K. K., Lork, K. D., Pfeiderer, B., Albert, K., and Bayer, E. *Journal of Chromatography A* **556**(1-2), 395–406 (1991).
- [201] Chen, C.-Y., Xiao, S.-Q., and Davis, M. E. *Microporous Materials* **4**(1), 1–20 (1995).
- [202] Delak, K. M. and Sahai, N. *Journal of Physical Chemistry B* **110**(36), 17819–17829 (2006).
- [203] Uhlmann, D. R. and Ulrich, D. R. In *Ultrastructure processing of advanced materials*, 47–55. John Wiley & Sons, New York (1992).
- [204] Schröder, H. C., Grebenjuk, V. A., Wang, X., and Müller, W. E. G. *Bioinspiration & Biomimetics* **11**(4), 041002 jul (2016).
- [205] Yu, Y., Wang, B., Wang, M., Sant, G., and Bauchy, M. *Journal of Non-Crystalline Solids* **443**, 148–154 (2016).
- [206] Fogarty, J. C., Aktulga, H. M., Grama, A. Y., van Duin, A. C. T., and Pandit, S. A. *The Journal of Chemical Physics* **132**(17), 174704 (2010).
- [207] Manning, J. R. H., Yip, T. W. S., Centi, A., Jorge, M., and Patwardhan, S. V. *ChemSusChem* **10**(8), 1683–1691 (2017).
- [208] Roehrich, A. and Drobny, G. *Accounts of Chemical Research* **46**(9), 2136–2144 sep (2013).
- [209] Buckle, E. L., Roehrich, A., Vandermoon, B., and Drobny, G. P. *Langmuir* **33**(40), 10517–10524 (2017).
- [210] Ben Shir, I., Kababya, S., and Schmidt, A. *The Journal of Physical Chemistry C* **116**(17), 9691–9702 (2012).

- [211] US EPA. <https://www.epa.gov/energy/greenhouse-gas-equivalencies-calculator>, (2016). Accessed: 2016-12-09.