Colloidal Zeolite-Preparation, Properties and Applications*

Brian J. Schoeman and Johan Sterte
Lulea University of Technology, Sweden*

Abstract

A method for the preparation of stable colloidal suspensions containing discrete molecular sieve crystals is presented. The hydrothermal synthesis of the all-silica tetrapropylammonium silicalite-1 molecular sieve illustrates the preparation. The discrete colloidal crystals (<150 nm) are aggregates of plate-like primary particles and they are stabilized in aqueous solution via steric forces that arise as a result of the strong adsorption of the tetrapropylammonium cation on the siliceous surface. The silicalite-1 surface charge is a function of pH as shown by electrophoretic measurements. These properties may be utilized for fabricating advanced materials. An example of the application of the colloidal materials is illustrated by the preparation of a thin silicalite-1 film on a non-charged gold substrate. Knowledge of the surface chemistry of the participating interfaces and the properties of the colloidal crystals allows for the preparation of microporous films with a thickness less than 300 nm.

1. Introduction

There are well over 150 known synthetic zeolites such as zeolite Na-Y, Na-A, ZSM-5 and zeolite Beta besides the approximately 34 naturally occurring counterparts, e.g. clinoptilolite, faujasite and mordenite. The synthesis procedures have been developed over the past 50 years, with much of the pioneering work performed by Barrer [1] and Milton [2,3]. The interest in these microporous aluminosilicates stems from their well-defined micropore channel geometries. The pore size range, approx. 3 to 8 Å, is similar to the sizes of numerous molecules of commercial interest. Hydrothermal treatment (normally ≥100°C) of hydrous alkaline amorphous aluminosilicate gels for extended periods of time (typically a few hours to several days) results in the crystallization of crystalline aluminosilicates or zeolites. The crystalline phase obtained is a function of the gel composition, the nature of the reagents, crystallization temperature and time [1]. Following completed crystallization, the precipitated solid phase is separated from the supernatant by conventional suction filtration and washed with water. Upon drying of the solid phase, a powder consisting of crystals with an average size >1 μm is obtained. The factors influencing crystal size are, among others, crystallization temperature, synthesis mixture composition and dilution and the source of the raw materials. While the majority of synthesis procedures describe the crystallization of zeolite from heterogeneous gels, there are (relatively few) reports dealing with the crystallization of zeolite from clear “homogeneous” solutions [4,5]. Irrespective, however, of whether the formation of zeolite takes place in the presence of a visible macroscopic solid phase or not, the final crystallization product is in most cases a material consisting of a large crystal size (termed conventional crystals) and with a broad crystal size distribution.

The conventional large-sized zeolite crystals have found applications in fields of commercial importance - notably as catalysts (cracking and reforming catalysts within the petrochemical industry) [6] and ion exchangers (zeolites A and P as a substituent for phosphates in laundry detergents) [7]. Several other promising application fields in which zeolites may be utilized are sensors, optical devices, supramolecular catalysis, photochemistry and electrochemistry.

It has been anticipated that certain applications require a zeolite with a smaller crystal size or a narrow crystal size distribution. An example is the molecular sieve TS-1 [8], a Ti-substituted silicalite-1, that has been shown to possess attractive properties as a mild oxidation catalyst in the presence of aqueous H\textsubscript{2}O\textsubscript{2}. The crystal size strongly influences the product distribution in reactions that are diffusion-limited - smaller crystallites resulting in
higher selectivities and activity [9]. A second example in which crystal size is anticipated as being of importance is within sensor technology. It is expected that in order to obtain shorter response times and higher selectivity and sensitivity in sensor composites, the active layer should be thin [10]. There is therefore a need to synthesize microporous materials with tailor-made properties. The property of interest in this respect is crystal size. Smaller crystals with a well-defined size and narrow size distribution are therefore interesting materials. In an effort to satisfy this demand, we have prepared several zeolite phases in the form of stable colloidal suspensions. These phases include silicalite-1, ZSM-5, N-Y, N-A, TS-1 and Beta [11-15]. In all cases, the average crystal sizes are less than 150 nm. Furthermore, the crystals exist as stable discrete entities in solution.

Our interest in this field of research is to utilize the colloidal properties of zeolites to prepare advanced materials, an example of which is the preparation of ultra-thin microporous films. In order to achieve this goal, however, it is necessary to understand the fundamental processes at work during the hydrothermal synthesis and the properties of the synthesized materials. The purpose of this report is to present the procedure used for the synthesis of discrete colloidal zeolite crystals, their properties and their application in thin-film fabrication. The all-silica tetrapropylammonium (TPA) silicalite-1 molecular sieve [11] has been chosen to illustrate the related nature of these three topics.

2. Experimental

Colloidal TPA-silicalite-1 synthesis

The silica source used in the syntheses of TPA-silicalite-1 was tetraethoxy silane, (TEOS, > 98%, < 5 ppm Al, Aldrich-Chemie) and the tetrapropylammonium hydroxide source was a 1M TPAOH in water (TPAOH, Na<5 ppm, K<5 ppm, Sigma). In those cases where aluminium and sodium were required, the aluminium was derived from aluminium isopropylate (Sigma) and the NaOH was NaOH pellets (Riedel-de-Haen, p.a.). Double-distilled water was used in all experiments.

Colloidal suspensions of TPA-silicalite-1 were prepared by hydrothermal treatment of synthesis solutions with the molar compositions

9TPAOH 25SiO₂ 480H₂O 100EtOH
(EtOH = ethanol)

(9TPAOH = TPAOH solution)

in polyethylene flasks submerged in a preheated silicone oil bath at 100°C with reflux under static conditions. A typical synthesis was performed as follows: TEOS was transferred to a polyethylene flask and an aqueous TPAOH solution was added. The mixture was placed on a gyratory shaker for at least 12 h until a single homogeneous phase was obtained, thus marking the completion of the hydrolysis reaction. The resulting clear synthesis mixture (denoted the precursor solution) was heated in the polyethylene flask for a period of up to 7 days. The reflux columns were capped to prevent the loss of ethanol (formed by the hydrolysis reaction).

Thin-film preparation

Gold-plated silver substrates were used for growing thin TPA-silicalite-1 films. Prior to use, the surface was cleaned at room temperature for 15 min. with acetone (p.a.) in an ultrasonic bath, rinsed with water and thereafter, the plates were treated with a solution having the molar composition:

9H₂O₂ : 15NH₃ : 280H₂O for 10 minutes. After this cleaning procedure, the plates were rinsed several times with distilled water. The gold surface was silanized by treating the substrate in a 10mM gamma-mercaptopropyltrimethoxysilane (MPT, OSI Specialties) solution in methanol. The silane was hydrolyzed in a 0.10M HCl solution for 15 h at room temperature.

Discrete negatively charged colloidal TPA-silicalite-1 crystals were synthesized according to the method presented above using a synthesis mixture molar composition

9TPAOH 25SiO₂ 480H₂O 100EtOH
(EtOH = ethanol)

The product sol was purified with high-speed centrifugation as described below. The purified colloidal suspension contains discrete negatively charged TPA-silicalite-1 crystals (90 nm). A 4.2 wt% TPA-silicalite-1 suspension was deionized to pH 3.4 to yield a suspension of positively charged discrete crystals which were subsequently adsorbed onto the negatively charged siliceous interface by contacting the substrate with this suspension. Excess colloidal material was rinsed off with excess water whereafter the composite was calcined at 300°C in air for 1 h as above. The composite was contacted with a precursor solution with the molar composition

3TPAOH 25SiO₂ 1500H₂O 100EtOH
(EtOH = ethanol)

and prepared as described above. The crystalliza-
3. Analysis

The as-synthesized aqueous TPA-silicalite-1 suspensions were purified by centrifugation in a Jouan High-Speed Centrifuge, model KR22i, with a relative centrifugal force of 50,000 g for 1 hour. The liquid phase was carefully decanted and the solid phase was redispersed in double-distilled water by ultrasonic treatment. This rinsing procedure was repeated 3-4 times. Purified and redispersed samples were freeze-dried and the organic template was removed by calcining samples at 550°C in air for approx. 3 hours.

Particle size analysis of dilute as-synthesized aqueous suspensions of silicalite-1 was performed using a Brookhaven Instruments ZetaPlus. The use of the light scattering technique for particle size analysis has been described in detail in a previous report [16]. The non-negative least squares (NNLS) data analysis method was used to determine the diffusion coefficients. Dust was removed from the precursor solution by filtration through a Gelman Sciences Supor Acrodisc membrane filter, 0.2 μm pore size, prior to the light scattering measurements.

SEM micrographs were taken with a Philips XL 30 scanning electron microscope (SEM). Dilute aqueous samples of purified suspensions were dried on a glass plate and thereafter coated with a thin carbon film. Crystal phases were identified by X-ray powder diffraction (XRD) with a Philips PW 1710 diffractometer using CuKa radiation. Powder samples for XRD analysis were prepared by freeze-drying purified sols followed by calcination of the powder at 550°C for three hours in air.

The DRIFT spectra of freeze-dried powder samples were obtained using the KBr wafer technique with a Perkin Elmer PE 2000 FT-IR spectrometer. Data were collected with 200 scans and a resolution of 4 cm⁻¹ in the frequency range 370-1300 cm⁻¹.

Specific surface areas of freeze-dried powder samples were measured by N₂-adsorption according to the BET method with a Micromeritics ASAP 2010 Surface Area Analyzer. The samples were outgassed at 200°C for 5 hours in vacuum before measurement. The N₂ adsorption isotherms were recorded at 77K.

Electrophoretic mobility [17] measurements were performed using a Laser Zee Meter instrument (PENKEM Model 501). Purified sol samples were diluted with a KCl solution to 10 mM KCl. The suspension pH was adjusted by the addition of NaOH or HCl. The samples were equilibrated for 2 h at room temperature by stirring. Before measurement, each solution was subjected to ultrasonic treatment for a few minutes, whereafter the pH was measured and a part of the solution injected into the sample cell to measure the electrophoretic mobility. The zeta potential was calculated from the electrophoretic mobility data with Smoluchowski's equation [17].

4. Results and Discussion

Synthesis of colloidal silicalite-1

The addition of TPAOH to TEOS results in two immiscible phases and hence the mixture requires a period of agitation during which the hydrolysis of the silane may take place. The resulting precursor sols with the molar compositions

9TPAOH 25SiO₂ xH₂O 100EtOH ; x = 480, 1500

following hydrolysis are water-clear suspensions with the apparent absence of particles. Dynamic light scattering (DLS) studies of the clear precursors show, however, that the greater part of the silica is in the form of polymeric species with an average diameter in the range 2.5-3.5 nm depending on the precursor composition [18]. It was observed that the average particle size increases with increasing dilution, from 2.6 nm in the concentrated precursor to 3.5 nm in the dilute precursor. Similar trends in the change in particle size of amorphous silica have been observed upon dilution with water [19]. Cryo-TEM analyses (not shown here [20,21]) confirm the DLS results. FT-IR, Figure 1a, and FT-Raman (not shown) data show the characteristic spectra of the MFI phase vide infra (MFI=structure code for the silicalite-1 and ZSM-5 phases) [22]. The results therefore indicate that the colloidal particles possess a structure similar to that of the MFI phase and hence they are believed to play an important role in the crystallization of silicalite-1. Although the exact role of these colloidal particles is not fully understood, certain colloidal particles are believed to serve as nuclei that, upon hydrothermal treatment, grow to larger crystal sizes.

Following hydrothermal treatment (approx. 30 h at 100°C), the precursor sol with the molar composition 9TPAOH 25SiO₂ 480H₂O 100EtOH yields a colloidal stable suspension containing
discrete TPA-silicalite-1 crystals as shown in the SEM micrograph in Figure 2. The average size is 95 nm and the particle size distribution is narrow. The crystal size is confirmed by light scattering analyses (DLS) as shown in Figure 3 where the DLS particle size distribution (PSD) was recorded at a scattering angle of 90°. The PSD is narrow and consists of a single particle population (i.e. no aggregates). Aggregation of the primary particles (95 nm) to larger entities would have been detected with ease using this technique since the scattering power of larger particles is considerably larger than that of smaller particles even if the former are present in small amounts. Despite the small size of the crystals, they are highly crystalline as shown by the XRD pattern in Figure 4. All peaks may be assigned as being due to silicalite-1. The IR data presented in Figure 1b show the characteristic bands of the MFI phase, approx. 550 cm⁻¹ (due to the presence of double-rings of tetrahedra in the MFI framework) and 1220 cm⁻¹ (due to external asymmetrical stretching). A weak band at approx. 970 cm⁻¹ is also evident and is thought to be due to external (dissociated) silanol groups. Considering the colloidal nature of the crystals (implying a high external surface area), the number of such silanol groups is expected to be large and hence their presence is expected to be detected with this technique. The FT-IR spectra of a truly amorphous colloidal silica is included in Figure 1 as a comparison. From this spectra it is evident that the non-crystalline silica does not exhibit the absorption bands at approx. 550 and 1220 cm⁻¹. Specific surface areas as calculated with the BET equation are typically in the range 450-550 m²/g - common for this class of microporous materials. It may be noted that the internal pore volume is only available to the N₂ molecules once the structure-directing agent (TPAOH) is removed.
Calcination, a fact that is of significance when preparing thin microporous zeolite films vide infra. The characterization methods used, the results from which are given above, show that the colloidal crystals are discrete crystalline silicalite-1 particles with a size less than 100 nm.

The second precursor mixture composition (9TPAOH 25SiO2 1500H2O 100EtOH) represents a dilution of the first mixture. It was shown above that the size of the sub-colloidal particles in the dilute precursor was slightly larger than those in the concentrated mixture. Hydrothermal treatment of the dilute precursor yields silicalite-1 crystals with an average size of 180 nm. Furthermore, the crystal number concentration is less by a factor 14 and the kinetics of crystallization are faster by a factor 2.5 [11].

If one assumes from the hypothesis above that only certain sub-colloidal crystals grow to a larger size, the fraction of which is the same in each precursor, then it is reasonable that the size of the product crystals in the dilute system is larger since fewer crystals grow while consuming the same amount of nutrient material (silica conversions in the concentrated and dilute precursors are 64 and 68%, respectively).

Although there are several parameters influencing the size of the product crystals and the crystallization kinetics, the water content is a suitable parameter with which these properties may be manipulated.

Colloidal properties

Of interest is the stability of the colloidal crystals - a property that allows one to maintain the discrete nature of the particles. The high electrolyte content in the synthesis mixture would suggest that the crystals should aggregate to form larger secondary particles. Evidence, however, points to the fact that the growing crystals do not increase in size via the aggregation of similarly sized crystals but rather via a surface reaction controlled process [23]. The question is therefore, what imparts stability to these colloidal crystals? Besides the van-der-Waals attractive forces and the electrostatic repulsive forces (which are far weaker than the former due to the high electrolyte content), forces due to steric hindrance are known to stabilize colloidal material.

The quaternary ammonium cations, e.g. TPA+ as is the case in this work, are also known to stabilize colloidal amorphous silica particles and serve as dispersants [19]. The TPA cations are thought to be strongly adsorbed onto the external surface of the crystals thus preventing aggregation upon collisions during growth. Taking into account the fact that the crystals are centrifuged down to form a solid mass at high speeds, corresponding to relative centrifugal forces of typically 50,000 g during the above-mentioned purification process and spontaneously redisperse upon standing, it would appear reasonable that the organic cations afford a barrier against aggregation. A purified suspension of silicalite-1 (i.e. free from excess TPAOH and unreacted silica) was characterized with respect to surface charge. The surface charge calculated from electrophoretic data and shown in Figure 5 shows clearly that the zeta potential is a strong function of pH, as may be expected. An unexpected result, however, is that the point of zero charge (p.z.c.) is at a pH of approx. 6, whereas the p.z.c. for amorphous silica is at approx. 2 [19]. The reason for this behaviour is possibly due to the fact that the surface charge is a function of the TPA surface coverage. This topic deserves further investigation. It is, however, clear that the TPA is associated with the crystal surface, imparting colloidal stability within a wide pH range except for pH values in the vicinity of the p.z.c. The fact that the crystals are negatively and positively charged in distinct pH ranges allows one to electrostatically adsorb the particles onto positively and negatively charged surfaces, as will be discussed below.

The surface charge behaviour of aluminium-containing zeolite materials has been investigated. As one may expect, the crystalline aluminosilicates are negatively charged throughout the measurable pH range, i.e. approx. 4.5-12. The crystal structure collapses in the pH interval below approx. 4.5 and hence the aluminosilicates do not exhibit a p.z.c., as seen in Figure 5.

A second aspect of interest is the morphology of the crystals thus preventing aggregation upon collisions during growth. Taking into account the fact that the crystals are centrifuged down to form a solid mass at high speeds, corresponding to relative centrifugal forces of typically 50,000 g during the above-mentioned purification process and spontaneously redisperse upon standing, it would appear reasonable that the organic cations afford a barrier against aggregation. A purified suspension of silicalite-1 (i.e. free from excess TPAOH and unreacted silica) was characterized with respect to surface charge. The surface charge calculated from electrophoretic data and shown in Figure 5 shows clearly that the zeta potential is a strong function of pH, as may be expected. An unexpected result, however, is that the point of zero charge (p.z.c.) is at a pH of approx. 6, whereas the p.z.c. for amorphous silica is at approx. 2 [19]. The reason for this behaviour is possibly due to the fact that the surface charge is a function of the TPA surface coverage. This topic deserves further investigation. It is, however, clear that the TPA is associated with the crystal surface, imparting colloidal stability within a wide pH range except for pH values in the vicinity of the p.z.c. The fact that the crystals are negatively and positively charged in distinct pH ranges allows one to electrostatically adsorb the particles onto positively and negatively charged surfaces, as will be discussed below.

The surface charge behaviour of aluminium-containing zeolite materials has been investigated. As one may expect, the crystalline aluminosilicates are negatively charged throughout the measurable pH range, i.e. approx. 4.5-12. The crystal structure collapses in the pH interval below approx. 4.5 and hence the aluminosilicates do not exhibit a p.z.c., as seen in Figure 5.
the colloidal crystals. Cryo-TEM micrographs (not shown here) clearly show that the colloidal particles are aggregates of plate-like primary particles. Figure 6 shows the idealized morphology of the MFI phase. The colloidal crystals may be envisaged as being built up of several such ideal lathe-like crystallites with the (010) planes as the common interface. The morphology is of interest with regard to the preparation of thin microporous films, as will be discussed below. The plate-like morphology is believed to influence the orientation of the adsorbed crystallites and the orientation of the deposited crystalline material in the following hydrothermal treatment which leads to the formation of the thin film.

Thin-film preparation

A schematic illustration of the principle of the seed-film method is shown in Figure 7. The basic steps constituting this method are (i) substrate surface modification, steps A and B in Figure 7, (ii) electrostatic adsorption of charged colloidal zeolite seed crystals, step C, and (iii) hydrothermal treatment of the substrate/seed composite in a fresh precursor solution to close the void spaces and form a continuous zeolite film, step D. The seed-film method is, in principle, applicable to all solid surfaces once the surface chemistry of the interfaces (substrate and seed crystal) are taken into account.

An area where thin microporous films may find an important application is that of electrochemistry (size and shape selective electrodes), wherein surface-modified gold electrode surfaces are encountered. The following example therefore illustrates the preparation of a thin silicalite-1 film on a modified gold surface. The surface of the noble metal substrate is modified by the adsorption and hydrolysis of a bi-functional silane to yield a negatively charged siliceous interface upon which charged colloidal crystals may be adsorbed. If the adsorption of the colloidal crystals is carried out in an acidic medium at a pH lower than the p.z.c. of the crystals (i.e. positively charged particles), adsorption occurs spontaneously and may therefore take place in a single step. If the adsorption is to take place at a pH higher than the p.z.c., the negatively charged interface must be charge-reversed by, for example, the adsorption of a cationic polymer to create a positively charged interface (see step B in Figure 7). It may be noted that no crystals are adsorbed onto the non-modified gold surface. In the following example, the gold surface was silanized in an acidic solution to yield a negatively charged interface. Silicalite-1 seed adsorption was achieved in an acidic solution in which the seed crystals are positively charged, approx. +55 mV. From Figure 8a, it is seen that the substrate is essentially fully covered by the adsorbed seed crystals. The composite (substrate and seed crystals) is then calcined at 250°C for 1h, whereafter it is exposed to a precursor solution at 100°C for varying periods of time. The precursor sol composition was chosen on the basis of previous results obtained from kinetic studies of the crystallization of TPA-silicalite-1 [11] and presented above, viz dilute solutions with relatively low TPA concentrations allow for rapid crystallization thus facilitating rapid closure of the voids between the adsorbed seed crystals. The adsorbed crystals serve as seeding agents in the crystallization process. The seed crystals are envisaged as growing in a lateral as well as a perpendicular direction. Growth in lateral direction ceases once
the crystal faces intergrow, whereafter growth is only in perpendicular direction. The uni-directional growth results in the orientation of the growing crystals - their orientation being determined by the orientation of the adsorbed seed crystals. The XRD pattern shown in Figure 9 after a 20 h crystallization period shows that only certain peaks are present, thus indicating a degree of orientation. The top-view image of the film, Figure 8b, shows the individual, apparently oriented crystallites constituting the film. In addition, there is no halo in the XRD pattern, indicating the absence of amorphous material. The SEM micrograph shown in Figure 8c shows a side-view image of the cracked composite. It is evident that the film is of uniform thickness and, more importantly, that it is continuous with a thickness of approx. 250 nm. Permeation data show that the films are gas-tight prior to calcination [24]. It is anticipated that the film thickness may be controlled by the suitable choice of (i) seed size and (ii) precursor sol composition (e.g. water and TPAOH content).

The seed-film method has important advantages when compared with conventional film preparation methods: thin-film preparation is relatively insensitive to the chemical and physical nature of the substrate, flexibility in determining film thickness and the possibility of influencing crystal orientation. Furthermore, the seed-film method is applicable to other zeolite phases [15] once knowledge of the crystal surface charge as a function of pH is known.

5. Summary

Stable colloidal suspensions of molecular sieves may be prepared in the presence of structure-directing agents such as illustrated by the synthesis of silicalite-1 in the presence of TPAOH. The pre-
cursor solutions contain sub-colloidal (<4 nm) siliceous particles with a structure resembling the product crystals, and hence it is believed that certain sub-colloidal particles serve as growth centres. The crystals grow as discrete entities via a mechanism whereby monomeric or very small oligomeric species attach to the growing crystal surface. A mechanism in which growth takes place by the aggregation of either similar-sized or dissimilar-sized particles may be ruled out on the basis of the inherent stability of the crystals. The colloidal stability of the crystals has also been observed experimentally. The colloidal stability is derived from the surface-active structure-directing agent that imparts steric stability to the growing crystals.

The colloidal crystals serve as growth centres in the preparation of thin microporous materials. Knowledge of the surface chemistry of the participating interfaces is necessary in order to facilitate the adsorption of the charged crystals onto substrates of varying chemical nature. A high surface coverage of the substrate with adsorbed seeds allows for the rapid closure of the growing film to yield a continuous gas-tight film suitable for membrane and sensor applications, to name only a few.

6. Acknowledgements

The authors would like to thank the Swedish Council for Engineering Sciences (TFR), the Preem Environmental Foundation and the Carl Trygger Foundation for their financial support of this work.

7. References

24) Unpublished results.
Author's short biography

Brian Schoeman

Brian Schoeman was born in South Africa, December 1961 and received his MScEng (chem) in 1989 from Chalmers University of Technology, Göteborg, Sweden in 1994. This work entailed the development of synthesis procedures for the preparation of stable colloidal zeolite suspensions. Post-doctoral studies were carried out at the Luleå University of Technology, Sweden. During the period 1994-1997, emphasis has been placed on the synthesis of colloidal microporous materials, nucleation and growth mechanisms and the application of such materials.

Johan Sterte

Johan Sterte graduated in chemical engineering from Chalmers University of Technology, Göteborg, Sweden in 1982 and gained a PhD in Chemical Technology at the same university in 1987. In 1994 he was appointed to his current position of professor of Chemical Technology at Luleå University of Technology. His research interests are concerned with the preparation, modification, characterization and applications of small particle systems and porous materials.