Ceramic Nanomaterials and Nanotechnology

Edited by
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Proceedings of the Nanostructured Materials and Nanotechnology Symposium held at the 104th Annual Meeting of The American Ceramic Society, April 28–May 1, 2002 in St. Louis, Missouri.

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Published by
The American Ceramic Society
735 Ceramic Place
Westerville, Ohio 43081
www.ceramics.org
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Nanotechnology — the creation and utilization of functional materials, devices and systems with dimensions on the order of 0.1 to 100 nanometers, and exhibiting novel properties and functions — has become a major national, and indeed international, research initiative. Much of the promise of nanotechnology will not be possible without continued advances in the synthesis of nanostructured materials, combined with progress in analytical and physical characterization techniques capable of probing phenomena at this length scale. Applications are foreseen in medicine, electronics, structural materials, catalysis, fluid separations, power generation, environmental management, and materials design.

Nanomaterials are the foundation for nanotechnology. Ceramics such as oxides, non-oxides (nitrides, carbides, etc.), and their composites represent a significant category of materials with great impact upon many applications. The synthesis, processing, and characterization of ceramic nanomaterials (or nanoceramics, for short) has thus become fundamentally important subjects for research and development. This is the first book focusing on nanoceramics and related nanomaterials, ranging from precursor nanoparticles and coatings to nanocomposites.

This volume of Ceramic Transactions is based on papers presented and submitted to the Symposium C2 on Nanostructured Materials and Nanotechnology, which was held during the 104th Annual Meeting of The American Ceramic Society (ACerS), April 28–May 1, 2002 in St. Louis, Missouri. The symposium consisted of 65 contributions (52 oral presentations and 13 posters) spanning the entire three days of the meeting. Reflecting the truly international character of the symposium and of nanoceramics research, this compilation contains papers with authors from nine countries and five continents.

While the coverage of this book is by no means exhaustive, the papers presented in this volume represent major current topics in nanoceramics-related research. The papers here are organized into three chapters reflecting these major topics: Synthesis and Processing of Nanomaterials (in the form of nanoparticles, coatings, nanowires, and fibers); Nanocomposites (processing, properties, and characterization); and Nanoscale Phenomena in Glasses, Glass-Ceramics, and Glass-Containing Composites.

It is hoped that this book will not only become a useful reference for scientists and engineers interested in nanostructured ceramics and ceramic-based nanomaterials, but also will serve as a stimulus for interdisciplinary collaboration that
is important for the advancement of nanotechnology.

The symposium on Nanostructured Materials and Nanotechnology was sponsored by ACerS and the Basic Science Division of ACerS, with cooperation from the Engineering Ceramics, Electronics, and Glass and Optical Materials Divisions of ACerS. The editors express special thanks to the co-organizers of this symposium, Professor Masahiro Yoshimura (Tokyo Institute of Technology, Japan) and Wolfram Hölland (IvoclarVivadent AG, Liechtenstein). Dr. Hölland was especially instrumental in initiating, organizing, and chairing the session on nanophase formation/structure in glasses and glass ceramics (most of these presentations appear as papers in the third section of this volume). Prof. Yoshimura’s influence was felt throughout the symposium, particularly in the areas of innovative synthesis and processing of nano-materials, where his group contributed several outstanding presentations.

Finally, the editors thank all of the authors who contributed manuscripts to, or who assisted with reviewing manuscripts for, this volume.

Michael Z. Hu
Mark R. De Guire
Synthesis and Processing of Nanomaterials
NUCLEATION AND GROWTH MECHANISM OF SILICALITE-1 NANOCRYSTAL DURING MOLECULARLY TEMPLATED HYDROTHERMAL SYNTHESIS

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ABSTRACT
Nano-/micro-sized zeolite particles with narrow size distribution are important building-block materials for nanofabrication and many applications. Template-directed self-assembly, nucleation and growth of zeolite crystal particles from solutions are not fully understood. This study is aimed at understanding the early-stage nucleation process of silicalite-1 nanocrystals, using both in-situ and ex-situ measurement techniques. In alkaline aqueous solutions of sodium silicate, tetrapropyl ammonium hydroxide (TPA) is used as organic templating molecule to assist silicalite crystallization. TPA-silicalite-1 particles have been synthesized under various hydrothermal conditions with incubation temperatures ranging from 100°C-180°C. The changes in the morphology, size and crystal structure of the particles formed during synthesis are carefully monitored. An X-ray diffraction (XRD) technique and a high-resolution transmission electron microscope (HRTEM) with a cryogenic holder were successfully used to study the gradual nucleation and growth of zeolite (i.e., TPA occluded silicalite-1) crystals in solutions. Amorphous gel particles (~ 50 nm), the first solid phase evolved in the solution, were for the first time imaged by HRTEM. Further hydrothermal
processing of the gel particles in solutions led to the formation of nanosized crystal nuclei, which were embedded in the amorphous gel. This observation supports the gel-to-crystal transformation mechanism for silicalite crystal evolution and growth. The Fast Fourier Transforms (FFT) of the TEM images provided complementary information to XRD on the crystallinity of transient forms from gel to fully-grown crystal. An in-situ high temperature X-Ray diffraction (HTXRD) was used for real-time monitoring of crystallization from gel precursors under progressive heating-up conditions (30-1200°C). The HTXRD spectral patterns proved that zeolite crystal nucleation from gel is more than a thermally induced crystallization phenomenon because the dried amorphous gel failed to crystallize into silicalite during high-temperature processing. However, further silicalite crystal growth was observed in dried gels containing coexisting nanocrystal seeds.

INTRODUCTION

Zeolites, which are generally microporous crystalline aluminosilicates with framework of corner-sharing TO₄ tetrahedra (in which the T-sites are occupied either by silicon or aluminum), have rather complex but precisely repetitive atomic network with submicroscopic channel or pores typically 3 to 10 Å in size. Their name was coined in 1756 by a Swedish chemist and mineralogist, Axel Fredrick Cronstedt (1722-1765), which was derived from the Greek words meaning, “boiling stones.”

Zeolites have outstanding characteristics that lead to diverse and widespread uses such as catalysts and molecular sieves in chemical and petrochemical industries, ion exchangers (for example in purification and treatment of wastewater), absorbents (for example in detergents), non-conductive supports in microelectronics, energy-storage material, membrane reactors where catalysis and separation is completed in one step, and most recently in micro-/nano-scale fabrications and devices.

Although the crystalline zeolite ZSM-5 (aluminosilicate with MFI-type structure) was discovered in 1972 and silicalite (the hydrophobic polymorph of silica with MFI-type structure) was synthesized in early 1978, little is known about the nucleation step or the early-stage crystal growth process in their hydrothermal synthesis solutions. Nucleation and growth mechanisms for different zeolite systems ranging from liquid-phase ion-transplantation to solid hydrogel reconstruction, have been proposed, but the complete conversion process from the synthesis solution to a fully-grown crystal is yet to be
understood. Additionally, there is a lack of crystallization kinetics data, which is required to develop a reliable predictive growth model.

The simplest way to crystallize a zeolite (discrete particle) is to produce a highly supersaturated aqueous solution of appropriate composition containing an alkali hydroxide at a relative low dissolution temperature. It is known that zeolite crystal formation in solutions typically go through a gel transient state, however, such gel material has not been observed by an electronic microscope imaging technique. Numerous studies have provided evidence that coprecipitated gels undergo an aging process at low temperature (~25 °C) in which the bulk physical nature (and consequently the intimate atomic linkages) changes, producing the appropriate structural units (or building blocks) that grow further at crystallization temperatures (~50-200 °C).

As silicalite-1 has not yet been obtained without a molecular template,\textsuperscript{16} the importance of the structure-directing species is evident. Many organic templating (structure-directing) ionic species have been used for the synthesis of purely siliceous MFI-type zeolite, but tetrapropylammonium cation (TPA\textsuperscript{+}) is the most suitable one for silicalite-1 crystallization,\textsuperscript{18} and is, therefore, used in the synthesis solution studied here. Silicalite-1 unit cell (uc) parameters for the studies were taken from the original reference listed in the International Zeolite Association (IZA) Tabulation\textsuperscript{19}.

During the synthesis, the organic structure-directing species are trapped (or occluded) in the framework through intermolecular van der Waals forces and can only be removed by thermal decomposition, but no covalent bonds occur.\textsuperscript{20} A study by small angle neutron scattering (SANS) suggested that the TPA\textsuperscript{+} ion is incorporated into the zeolite framework during aging and early nucleation\textsuperscript{21} as it is too large to enter the channels afterwards. Investigation of the mobility of occluded TPA\textsuperscript{+} inside a purely siliceous MFI framework using a combination of Magic Angle Spinning (MAS) and Cross Polarization (CP) NMR revealed an inter-cation dynamic equilibrium\textsuperscript{22} to satisfy the lowest energy state required for the crystallization process. Others have shown that hydrophobic TPA\textsuperscript{+} ions are occluded into the channel interactions of silicalite, with one cation per channel intersection, through NMR techniques.\textsuperscript{23}

Ultra-small-angle X-ray scattering (USAXS) studies have shown that amorphous colloidal aggregates (up to 9 nm in size) are formed during aging of the clear synthesis solution before crystallization begins.\textsuperscript{15} Combined \textit{in situ} small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering
(WAXS) suggest a solution-mediated growth mechanism where primary particles are less than 2.5 nm, but the complete process from amorphous particle to the fully grown crystals is still not fully understood. According to Watson et al., the nucleation process is represented by the formation of particles $R_g = 81 \text{ Å}$ which have nearly the same density as that of the fully crystalized silicalite particle containing the tetrapropylammonium template.24 SAXS/SWAXS data show that alkalinity of the synthesis solution affects the formation of different sized amorphous gel particles during silicalite-1 crystallization process.25 Further study suggested that the primary unit and aggregates, formed during early nucleation stage, are consumed later to form crystals.26

The purpose of this research is to obtain fundamental understanding of zeolite crystal nucleation and growth processes (in particular, at the early stage) during hydrothermal solution synthesis and thermal processing of gel precursor materials. Such understanding on zeolite crystallization has significant impact upon large-scale synthesis of high-quality zeolite particles, obtaining large single crystals of zeolite, growth of zeolite films, and fabrication of zeolite-top-layer inorganic membranes using gel precursors. As a better understanding of the early-stage nucleation mechanism helps to identify the role of the organic templating molecules in self-assembling synthesis of delicate microstructures/textures in single crystal materials, new methodologies in molecular-directed synthesis of exotic materials can be explored.

EXPERIMENTAL

Nanocrystals of TPA-silicalite-1 were hydrothermally synthesized using the composition mention in the Exxon patent,27 following the procedure outlined in Vroon et al.28 The silicalite synthesis solution was prepared in a capped teflon container by dissolving weighed amount of sodium hydroxide pellets (99.99%, Aldrich) in tetrapropylammonium hydroxide (TPAOH) solution (1M in water, Aldrich). The mixture was then heated and kept at 80°C while weighed amount of fumed silica (99.98%, Aldrich) was dissolved under vigorous stirring to obtain a clear solution. Filtered (0.2 μm filter), deionized water was then stirred in, so that the final molar ratio of the synthesis solution was 10 SiO$_2$ : 3 TPAOH : 1.05 NaOH : 140 H$_2$O (20 gm SiO$_2$ : 100 ml (1M solution in water) TPAOH : 1.4 gm NaOH : 3.2 gm H$_2$O).

The clear synthesis solution were cooled down and kept at room temperature for 3 hrs, which counts as the aging time. The aged clear solutions
were then transferred to a Teflon-lined autoclave vessel and heated in a convection oven to the specified synthesis temperature (180°C and 100°C; Error ±2 °C) and the exact synthesis times were recorded. The samples used for the in-situ high temperature X-ray diffraction (HTXRD) study were not washed. Also, unwashed samples were used for the early stage sample synthesized at 100°C for 2 hrs, to preserve the fragile amorphous gel particles. For the rest of the samples, the amorphous hydrogel and/or solid crystals were retrieved by centrifugation (20,000 rpm, 20 min) and washed by redispersion in filtered deionized water. The centrifugation-redispersion procedure was repeated until pH of the dispersion is around 8.

The size, morphology and microstructure of the synthesized zeolite particles were investigated using a scanning electron microscope (SEM) (Jeol JSM-T220A) and a high resolution transmission electron microscope (HRTEM) (Jeol 100CXII), depending on the particle size of the samples.

Silicalites have a 3D framework structure that can easily be decomposed/destroyed by electron beam during HRTEM analysis. As silicalites have a lower density (typically 1-2 gm/cm³) than silica SiO₂ (2.3-2.6 g/cm³), structure fragments resulting from broken bonds can quickly diffuse away, making bond reformation much more difficult than in SiO₂.²⁹ This creates the difficulty for high-resolution nanoscale imaging of a silicalite crystal by HRTEM. Therefore, a liquid nitrogen cooled cryogenic sample holder was used to enhance the stability of nanoscale crystal structure under electron beam. While focusing and stigmatism correction were performed on neighboring area away from the nanocrystal of interest, an image was captured by a Gatan 794 multiscan camera immediately after the beam is moved on the silicalite nanocrystal of interest.

The effective hydrodynamic diameter of zeolite particles was measured by a custom designed dynamic light scattering (DLS) spectrophotometer (details given in Hu et al.³⁰), which is accurate for measuring submicrometer-size particles, typically ranging from 5nm to 1 μm. The amorphous gel-type samples are air-dried overnight at near room temperature whereas the grown crystal samples are dried at 60°C for 1 h to get powder samples for room temperature X-ray diffraction (XRD) analysis. The crystallite size was estimated from the broadening of the diffraction peak [101] by using Sherrer equation from the diffraction peak breadths (full width at half maximum)³¹.
An *in situ* high temperature X-ray diffraction (HTXRD) instrument (details given in Hu et al.\textsuperscript{32}) at the ORNL HTML user facility was utilized for detailed study of the heating conversion process of gel or gel-containing precursor materials to crystals. Two samples were used for this study, the first is amorphous sample (S1) and the second is partially crystalline (S2) in nature. S1 is formed by hydrothermal treatment of synthesis solution at 100°C for 2hr, and the drying the resulting suspension, while S2 is incubated for 5.5hr at 100°C. The gel precursor material was placed on the platinum heating strip, and the temperature was then increased programmatically from room temperature (30°C) to 1200°C and then cooled down to room temperature. The heating and cooling rate was 10 degree/min. The spectra at various constant temperatures were scanned in the following order: 30°C, 50°C, increasing temperature every 50°C till 500°C, then increasing the temperature every 100°C till 1200°C, and then at 30°C. Each scan was taken from 6 to 50 degree of 2-theta at a rate of 1 minute/degree. Data acquisition was performed using DMS-NT software (Scintag Inc., Cupertino, CA) and data analysis was undertaken using Jade software (Materials Data Inc., Livermore, CA).

**RESULTS AND DISCUSSION**

Discrete zeolite (silicalite-1) crystal particles were first synthesized at 180°C. Particles appeared to be monodispersed and spherical (aspect ratio close to 1/1, Figure 1). At this temperature, particle growth kinetics are fast and submicron sized crystals were already well grown at reaction time as short as 1 hr. Particle size was found to increase with reaction time.

Therefore, lower hydrothermal processing temperature (i.e., 100°C) was chosen to be able to produce nanosized crystal particles and to monitor the transition processes from initial aged clear solution to a fully-grown crystal particle. At this lower temperature, reaction kinetics and nucleation and growth dynamics are slow enough for one to collect a solid sample with a transient state from solution to a fully-grown crystal.

1) Cryo-HRTEM study of transient solid phases during hydrothermal conversion of solution species to zeolite crystals

The complete zeolite growth process from clear solution, via amorphous gel particle formation, including several steps like early-stage zeolite nanocrystal nuclei formation and then the growth of these nuclei to fully-grown crystals were captured using HRTEM with the cryogenic sample holder. The field emission mode was used for our study as it gives a high amount of structural information with minimum interference with the zeolite sample. The HRTRM
Figure 1: SEM images of monodispersed silicalite crystalline particles synthesized at 180°C for various hydrothermal reaction times.

Images for samples incubated at 100°C for 2hr, 3hr, 4.5 hr and 6hr are shown in Figure 2, 3, 4, and 5, respectively. The corresponding electron diffraction pattern of these images, fast Fourier transform (FFT), are given as figure 2A, 3A, 4A and 5A. The FFT of the image for the zeolite sample incubated at 100°C for 2hr (figure 2A) confirms that the sample is amorphous, whereas the FFT of the image for the zeolite sample incubated at 100°C for 6hr (figure 5A) confirms that the sample is crystalline.

The first observed sample was obtained by incubating the aged, clear synthesis solution in the sealed Teflon lined stainless steel vessel for 2hrs. The
HRTEM image of the unwashed sample (Figure 2) shows spherical particles of approximately equal size of a diameter of 45 to 55 nm. The FFT of this image (Figure 2A) does not show any lattice reflections, therefore, suggesting that amorphous particles are present. Also, the XRD of the dried samples from this solution did not give any reflection peak (Figure 8). This confirms that the particles are indeed amorphous and no crystal structure is yet evolved.
As the incubation time is increased to 3 hrs, the sample changes from clear solution to slightly milkish in color. The HRTEM image of this sample (Figure 3) shows the presence of nanocrystals (average size ~15nm). FFT of this image (Figure 3A) indicates the presence of some crystalline materials. It is important to note that the early zeolite crystal nuclei co-existed with extensive amount of gels. The XRD spectra for the dried sample (Figure 8) confirmed that a small percentage of silicalite crystal structure is present in the sample.
Figure 4: HRTEM image of washed zeolite sample heated at $T_{\text{synth}}=100^\circ\text{C}$ and incubated for 4.5hrs

Figure 4A: Fast Fourier Transform (FFT) diffraction of the HRTEM image of washed zeolite sample heated at $T_{\text{synth}}=100^\circ\text{C}$ and incubated for 4.5hrs

The HRTEM image of the sample incubated for 4.5 hrs (Figure 4) shows a partially grown single crystal of around 60 nm. The crystal lattice structure corresponds to [101] plane of silicalite (Figure 4A). The gel is still present around this crystal structure, suggesting that there is considerable amount of amorphous silicalite species to help the crystal grow further. It appears that the silicalite crystal grows by direct consumption or reconstruction from the surrounding gels, supporting the gel-transformation mechanism for silicalite growth. Such mechanism of crystallization by direct gel transformation has also been recently reported for zeolite A nanocrystal growth$^{33}$ in solutions.
However, for silicalite crystallization, we observed neither the ideal core nanocrystallization phenomena inside a discrete gel particle nor the one-to-one correlation between a gel particle and a silicalite crystal.

The HRTEM image (Figure 5) for sample incubated for 6 hrs shows a completely grown crystal of about 80 nm and no transient gel materials were observed around the crystal particle. The crystal shows a reflection of the [100] plane of silicalite from analysis of the FFT of this image (Figure 5A). A closer view of the crystal shows the intricate crystal lattice structure on the surface of
Figure 6: Enlarged HRTEM image of a fully grown crystal showing the [100] plane

Figure 7: Computer simulated 3-D image of [100] plane for silicalite-1 showing the characteristic 10 ring channels (using Mac Tempas)

the crystal particle (Figure 6). This is also matched by a computer-simulated image of the [100] plane of silicalite (Figure 7).

Framework structure of silicalite-1 zeolite comprises of two different channel systems, each defined by 10-membered rings. Straight channels with an elliptical cross section of approximately 5.7-5.2 Å are parallel to the crystallographic axis b, and sinusoidal channels with nearly circular cross
section of 5.4 Å run along the crystallographic axis a. The resulting intersections are elongated cavities up to 9.0 Å in diameter. A single crystallographic cell, shown as a black box in the center of the computer-simulated image (Figure 7), contains 96 Silicon, 192 Oxygen.

2) XRD studies on hydrothermal gel-to-crystal transformation in solutions

In addition to the above HRTEM images, the evolution from early-stage gel to fully-grown crystals during hydrothermal treatment of the synthesis solution is also monitored by room temperature XRD study of washed, dried solid samples collected at different reaction times (Figure 8). Using the XRD spectrum for each sample, the size of the crystallite was calculated using the Sherrer’s approximation for the [101] peak (Table 1). When compared with the DLS effective hydrodynamic diameter measurements, the earlier gel samples are somewhat agglomerated because the particle size measured by DLS is larger than the crystallite size determined by XRD, which is agreeable to those determined by Cryo-TEM analysis. Note that the gel phase around the crystallite cannot be detected by the XRD size analysis method, but is clearly detected through imaging and DLS determination of particle diameter.

Figure 8: Room Temperature X-Ray Diffraction patterns of the silicalite nanocrystal evolution and its growth during hydrothermal synthesis
Table I. Comparison of zeolite particle size using various characterization tools

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<tr>
<th>Time</th>
<th>DLS</th>
<th>TEM</th>
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<tr>
<td>2hr</td>
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<td>-</td>
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</tr>
<tr>
<td>6hr</td>
<td>102</td>
<td>80</td>
<td>59</td>
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<tr>
<td>100hr</td>
<td>110</td>
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<td>64</td>
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3) HTXRD real-time studies of gel-to-crystal conversion process by heat treatment

Above results clearly show that silicalite will crystallize from some gel precursors in solutions under hydrothermal processing conditions. It is now necessary to verify the possibility of the crystallization of gel or early-stage gel-containing solid precursors materials crystallization by thermal treatment.

A HTXRD was used to allow the real-time monitoring of crystallization from the precursor materials. The first precursor material (SI) put on the Platinum-Molybdenum heating strip was an unwashed amorphous gel. The amorphous nature is clearly indicated by the characteristic hump of the initial HTXRD spectrum (Figure 9). TPA molecules, although being mixed and trapped inside the dried gel (proved by EDX elemental analysis), do not guide the nucleation/growth of desirable silicalite inorganic crystal phase. During the thermal treatment by increasing temperature, the hump spectra transform gradually into sharp peaks, which signifies the occurrence of crystallization. However, the crystals evolved from the dry gel are not silicalite but Crystoballite High. This result indicates that the silicalite crystallization process via TPA templates is not simply a heat induced crystallization event but requires some water and also possibly the availability of ionic species and their mobility in the gel.
Figure 9: HTXRD spectra during heat-induced crystallization from amorphous gels, showing no zeolite formation and final crystal is Crystoballite High.

Figure 10: HTXRD spectra during heat-induced crystallization from amorphous gel containing nanocrystals of silicalite, indicating that further silicalite growth can occur and at higher temperatures silicalite disappears and Crystoballite High appears.
The effect of increasing temperature on the second gel precursor material (S2) was then analyzed by HTXRD. The silicalite crystalline nature of this precursor material can be seen in the initial diffraction spectrum (Figure 10). As the precursor material is heated till 300 °C, X-ray diffraction peak height intensity increases, corresponding to the growth of silicalite crystals (Figure 10). This indicates the seeded growth occurs prior to the removal of templating TPA molecules from silicalite pore channels occurring around 400-500 °C. X-ray diffraction peaks are shifted at the onset of TPA removal temperature. With further increase of heating temperature to around 700 °C, the intricate zeolite cages rupture, as the signature peaks for silicalite-1 zeolite starts decreasing and disappearing. At 800°C and higher temperatures, the appearance of other peaks at 2theta ~ 21° signifies the formation of Crystoballite High crystal structure.

CONCLUSION

The early-stage nucleation and growth during silicalite-1 crystal particle synthesis have been studied by a high-resolution TEM and XRD techniques. The TEM images have captured the important transition phases in the formation of the silicalite crystal, starting from the early-stage amorphous gel particles, through the formation of nanosized zeolite crystallites, to fully-grown crystals. Our observations favor the gel-reconstruction mechanism for the formation of the zeolite nanocrystalline material. The gel particle are formed much earlier in the zeolite hydrothermal synthesis process, as evident through the TEM imaging. Afterwards these gel particles collapse and the zeolite nanocrystals appear, which then grows continuously at the expense of the hydrogel. The amorphous hydrogel is completely consumed during the zeolite synthesis process, as proven by the TEM and SEM images of the grown zeolite crystal samples.

In-situ high temperature XRD studies indicate that crystallization from amorphous gels is more than just a thermal event because heating of a dry gel material can not produce silicalite crystals but Crystallite High. Crystalline silicalite framework formation requires availability of ionic species, in addition to heating. However, further crystal growth was observed when nanocrystal-containing gel materials were heated. The silicalite nanocrystals in the starting gel materials may have functioned as seeds for further crystallization of silicalite from surrounding gels. At temperature above 700°C, nanostructure of silicalite crystals collapse and meanwhile a non-zeolitic crystal form (Crystoballite High) evolves above 800°C.
In summary, amorphous gel plays an important part in the formation of the initial zeolite (silicalite-1) crystal nuclei. In synthesis solution, nanosized silicalite crystal evolve by direct reconstruction or transformation from surrounding gels. Also, the presence of occluded water/solution in the gel is important for the TPA-templated growth of silicalite-1 nanoparticles.

REFERENCES


