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Multidiagnostic analysis of silicate speciation in clear solutions/sols for zeolite synthesis

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The formation of zeolites in presence of tetraalkylammonium cations from so-called clear solutions using silicon alkoxides is a highly complex process which challenges experimental chemistry. Most clear solutions are better described as clear sols as they contain nanosized silicate particles, which are formed during hydrolysis of the Si source before self-assembly into the zeolite framework. This process spans multiple time- and length-scales and only a combination of different analysis methods allows revelation of molecular level zeolite formation mechanisms. On the example of the early stages of the formation of zeolite beta from clear solutions/sols the different windows of observation of liquid-state ²⁹Si and ²⁷Al nuclear magnetic resonance (NMR) spectroscopy, small angle X-ray scattering (SAXS), dynamic light scattering (DLS) and mass spectrometry (MS) are demonstrated. Each diagnostic means by itself needs to be carefully assessed for its window of temporal and spatial resolution which can be achieved by exploiting the overlapping information available from their combination.

Keywords

zeolite beta, oligomers, nanoparticles, nuclear magnetic resonance, mass spectrometry, small angle X-ray scattering, dynamic light scattering, clear sols.

1. Introduction

Zeolites are key to a variety of industrial applications as catalysts, adsorbents or ion exchangers. Despite of their extensive use, the molecular mechanisms governing the early stages of zeolite formation remain elusive. For zeolites obtained from clear sols containing tetraalkylammonium cations, the early stages of formation have been investigated with combined experimental methods [1-6] and theoretical approaches [7, 8]. In presence of such cations, silicate nanoaggregates (NAs) form [9-11]. By progressive increase of the average silicon connectivity, NAs transform into larger nanoparticles (NPs). Zeolite crystallization proceeds, by aggregation of NPs into zeolite crystallites [5, 12-16].

This contribution shows how a multi-disciplinary approach combining DLS, NMR, ESI-MS and SAXS enables the observation of the evolution of silicate species in TEAOH synthesis mixtures while the initial oligo- and polymerization processes are in progress. As parameter to assess the potency of the various diagnostic means served the Si/OH ratio, which critically determines formation and size of nanoparticulates in the clear sols [12]. The information derived independently by the here employed methods is complementary and essential for obtaining a consistent view of the evolution in the samples which could allow the development of molecular scale models describing the zeolite synthesis precursors prior heating.

2. Experimental

2.1 Preparation of samples

For this proof of concept, a set of samples with a Si/Al ratio of 50 and Si/OH ratios of 0.7, 1.0 and 2 were prepared at room temperature. This series is expected to contain an evolving population of silicate species representative to the populations encountered in tetraalkyl ammonium zeolite synthesis mixtures. The molar composition of the precursor mixtures are x SiO_2 : 0.01 Al_2O_3 : 0.50 TEAOH : 16 H_2O : $4x$ EtOH, where x is 0.3, 0.5 and 1.0. The mixtures are prepared by dissolving the Al source [$\text{Al}(\text{s}^\text{O}\text{Bu})_3$, Sigma Aldrich] in TEAOH (Sigma Aldrich, 35% wt-%) diluted with distilled water for 1 h. Followed by the addition of TEOS (Sigma Aldrich, 98%) under vigorous stirring for 30 minutes.

2.2 Characterization

^{27}Al , ^{29}Si , and ^1H solution NMR measurements were carried out in 10 mm quartz tubes using a Bruker AVANCE-500 spectrometer. The ^{27}Al NMR spectra were recorded at a ^{27}Al frequency of 130.33 MHz with a $\pi/12$ rad pulse length of 2.1 μs , a recycle delay of 0.1 s, and acquisition of ca. 1000 pulse transients. The ^{29}Si NMR spectra were obtained at a ^{29}Si frequency of 99.35 MHz with a $\pi/4$ rad pulse length of 3.7 μs , a recycle delay of 7 s, and acquisition of ca. 1000 pulse transients. To account for longer relaxation times of Q^4 silicates [17, 18], correction factors were applied to the spectra. The ^1H NMR spectra were recorded at a ^1H frequency of 500.13 MHz with a $\pi/4$ rad pulse length of 10.6 μs , a recycle delay of 2 s, and acquisition of 8 pulse transients. The ^{27}Al chemical shifts are reported relative to $\text{Al}(\text{H}_2\text{O})_6^{3+}$, and the ^{29}Si and ^1H chemical shifts are referenced relative to tetramethylsilane (TMS). Decomposition and simulation of the NMR spectra were carried out using the *NMRnotebook* program [19].

All ESI-MS results were obtained by direct infusion (0.6 mLh^{-1}) into a Micromass ZMD quadrupole mass spectrometer with z-spray alignment of the ESI source (capillary voltage 3.5 kV, desolvation temperature 120°C).

Small angle X-ray scattering (SAXS) patterns were collected on an Anton Paar SAXSess instrument using line collimated Cu K α radiation (1.542 Å). The liquid samples were measured in a sealed quartz capillary (1 mm diameter and 10 μ m window thickness) that was mounted on a temperature controlled stage (TCS 120, Anton Paar) at room temperature. The sample to detector distance was 262 mm and the X-ray scattering patterns were recorded with a CCD detector.

DLS measurements were performed using an ALV/CGS-3 instrument (ALV, Langen, Germany). The samples were filtered by using 200 nm CHROMAFIL PTFE syringe filters. The DLS capillaries were cleaned with filtered acetone (450 nm CHROMAFIL PTFE filters) and dried in an oven at 110 °C prior to measurements. Samples were inserted 5 minutes before measurement to allow for temperature stabilization. DLS measurements of 60 s were performed at scattering angles of 30°, 90° and 150° with a wavelength of 632.8 nm.

3. Results and Discussion

Upon hydrolysis of TEOS in aqueous hydroxide solutions, pH provides an averaged measure of the proton release and consumption as result of the silicon alkoxide hydrolysis, condensation and surface complexation reactions. While pH is an easily accessible parameter, it cannot be interpreted correctly without significant additional input about the identity, nuclearity and charge of the silicate species and their interaction with other species in solution.

Liquid state ^{29}Si NMR is an excellent tool for investigating connectivity and relative amounts of silicate species present as monomers, oligomers and larger species designated as nanoparticles [3, 17, 20, 21]. Resonances of oligomers and NPs are distinguished by their line widths [17]. It was observed for the formation of silicalite-1 from clear sol that Si being part of aggregated species and NPs gave rise to significantly broadened signals which are clearly

distinguishable from the sharp signatures of small solution borne oligomers [1-3]. Further condensation of these species into large, fully condensed silicate particles, e.g., as crystalline zeolite, turns the involved Si atoms ‘silent’. The resulting decrease of the total signal intensity in a spectrum provides an estimate of the fraction of Si atoms contained in this solid fraction. The evolution of the silicate species in the precursor mixtures of zeolite beta were analyzed with ^{29}Si NMR spectroscopy (Figure 1). No NPs are detected at $\text{Si}/\text{OH} \leq 1.0$ which appears consistent with previous studies of related alkylammonium precursor mixtures [12, 20-22]. Within these ratios, silicate species are mostly present as monomeric and oligomeric hydrolyzed species, too small to cause detectable line broadening. The monomeric population containing partially deprotonated silicic acid is typically designated as Q^0 , while partially condensed oligomeric species are designated as Q^1 , Q^2 and Q^3 depending on their connectivity. However, above the threshold of the Si/OH ratio of 1.0 clearly the typical broadened signature of larger species assigned as NPs emerges.

Figure 1: Evolution of ^{29}Si NMR spectra of clear solutions/sols at different Si/OH ratios using TEAOH as template.

^{27}Al NMR spectra recorded for the same set of samples (Figure 2) are in agreement with the trend observed for other aluminosilicate systems [5, 21]. At $\text{Si}/\text{OH} \leq 1.0$, Al atoms are present in oligomeric species in various tetrahedral environments with increasing number of

connected silicon, i.e., q^1 (1Al1Si), q^2 (1Al2Si), q^3 (1Al3Si), and q^4 (1Al4Si). The lines are broadened due to two factors. First ^{27}Al is a 5/2 spin with quadrupolar interaction, broadening considerably resonances. In addition, some slow chemical exchange between aluminosilicate complexes occurs. ^{29}Si with a 1/2 spin does not exhibit the quadrupolar broadening and is in average not affected by the exchange phenomenon sensed on ^{27}Al , because of the very low amounts of aluminate species (ca. 1% Al of T atoms).

At $\text{Si}/\text{OH} > 1.0$, in contrast to Si atoms, Al atoms are occluded solely within the NPs as indicated in the spectra by the chemical shift and the broadening of the single q^4 line. These results are in agreement with previous investigations on silicalite-1 (MFI), silicalite-2 (MEL), SSZ-13 (CHA) and beta (BEA) using 4,4'-trimethylenebis(N-methyl, N-benzyl piperidinium) as templates [5, 21].

Figure 2: Evolution of ^{27}Al NMR spectra of clear solutions/sols at different Si/OH ratios using TEOAH as template. Once the NPs are formed at Si/OH ratio > 1.0 , only the q^4 line remains and it is shifted about 6 ppm to higher field.

At $\text{Si}/\text{OH} \leq 1.0$, the ^1H NMR spectra show the sharp signals typical for dissolved and freely moving TEA^+ template (Figure 3). With increasing the $\text{Si}/\text{OH} > 1.0$, the signals become broader due to template-silicate interaction [23]. Combining this result with the ^{29}Si and ^{27}Al NMR data, it can be deduced that the template interacts with the NPs formed at these ratios. Template mobility becomes restricted and consequently its signals broaden, particularly the *N*-methylene resonance at ca. 3 ppm where its linewidth increases from 3.1 to 8.4 Hz in the range of Si/OH ratio of zero up to 2.8 (Figure 1S in supporting information).

The intensity ratio between the sharp and broadened signals provides access to the fractions of free and adsorbed TEA⁺ cations. Indeed, considering the observed linewidth corresponds to weighted average of the two limit situations, i.e., free and immobilized TEA⁺ cations with 3.1 and ca. 50 Hz linewidths respectively, the fraction of the organic cation entrapped within and at the surface of the NPs is estimated to be 3% of total amount of TEA for the system with Si/OH = 2. This fraction rapidly increases with increasing the Si/OH ratio and reaches the value of ca. 11% with the Si/OH system of 2.8.

Figure 3: Evolution of ¹H NMR spectra of clear solutions/sols at different Si/OH ratios using TEAOH as template.

Mass spectrometry also has been shown to be a valuable tool for the investigation of pre-nucleating species in zeolite reaction gels [20, 24]. MS data, as shown in Figure 4, strongly correlate to NMR data. Increasing Si/OH ratios result in higher degree of condensation as indicated by the presence of silicate species with higher m/z. At Si/OH ≤ 1.0, at which only monomeric and oligomeric species are detected by NMR at room temperature, the main silicate species detected with MS were those with masses lower than ca. m/z 550 corresponding to oligomers with nuclearity equal to or below Si₈. In contrast, the

concentrations of silicate species with higher masses (m/z up to ca. 1300) are significantly increased at $\text{Si}/\text{OH} > 1.0$ where larger species are also present.

Figure 4: MS spectra of precursor solutions with different Si/OH ratios showing solution species detected by ESI-MS immediately after hydrolysis.

Small Angle X-ray scattering (SAXS) provides a unique view into the formation and organization of micelles and aggregates in zeolite synthesis mixtures [1, 3, 11, 25]. At $\text{Si}/\text{OH} \leq 1.0$, SAXS reveals the presence of a single species that can be described with a population of monodisperse charged spheres with a radius around 0.56 nm (Figure 5). The charged nature of this species is indicated by the characteristic depression at $q < 0.3 \text{ nm}^{-1}$ resulting from a strong inter-particle repulsion. Comparing the observation of a small highly charged species by SAXS with the NMR results leads to the tentative assignment this signal originates from oligomeric species too small to give rise to significant line broadening in NMR. Alternatively this signal may result from short-lived nanoaggregates or concentration fluctuations characteristic for this system. A correlation between increasing scattering intensity with increasing Si concentration shows that the concentration of these species is related to the total Si concentration, while its characteristic size is unaffected. At $\text{Si}/\text{OH} \geq 1.0$, a second

population of larger species appears next to the persisting smaller particle fraction. This new population can be described as polydisperse spheres of about 1 nm radius and it can be safely assumed this population directly relates to the nanoparticles detected by the other methods.

Figure 5: SAXS profiles for TEA synthesis mixtures at different Si/OH ratios. Experimental data shown in grey, the corresponding fits in black. Shown are also the two populations of particles which allowed satisfactory description of the data. The size of the particles in the two populations is also given.

This is also confirmed by DLS showing at Si/OH equal to 1.0 the presence of a population with radius of gyration of 1.2 nm for 1st order fits of the correlation function. Most important however is the detection of nanoparticles with a size of 1.0 nm radius even at lower Si/OH ratios, e.g., Si/OH = 0.7. Furthermore, DLS also indicates the presence of significantly larger species at Si/OH = 2.0. Particles with clearly increased size, corresponding to a radius of gyration of 17.7 nm, clearly could be observed. This indicates DLS already detects the presence of NPs earlier than any other method and also that DLS is the first diagnostic means which reveals evidence of nanoparticle aggregation at higher Si/OH ratios. The amounts of these populations should however be few in number since neither SAXS detected them nor NMR signal loss was observed.

Conclusion

The evolution of silicate speciation in the so-called clear solutions for zeolite synthesis can only be elucidated with a combination multidagnostic analysis and modeling. NMR, SAXS, DLS and MS provide a highly consistent and detailed view of the speciation changes occurring at the early stages of silicate oligo- and polymerization preceding zeolite formation. Combination of the input from these techniques with the evolution of macroscopic solution parameters (e.g. pH) obtained for a consistent spectroscopic data series should allow to formulate a refined molecular level mechanism describing the condensation of silicate species into polymeric units and their interaction with alkylammonium templates.

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Supplementary Information

Figure 1S: Evolution of ^1H NMR spectra of clear solutions/sols at different Si/OH ratios using TEAOH as template. The resonance of *N*-methylene of TEA at ca. 3 ppm undergoes progressive linebroadening: 3.1, 3.2, 3.5, 3.5, 4.6, and 8.4 Hz for Si/OH 0.0, 0.3, 0.7, 1.0, 2.0, and 2.8 respectively.

Combining NMR, MS, DLS, SAXS and Modeling

- We observe the presence of nanoparticles blind for NMR at $\text{Si}/\text{OH} = 0.7$.
- DLS detects the presence of nanoparticles earlier than any other method.
- Only combination of different analysis enables to assign properly the species involved.