

THE FORMATION OF ZEOLITES FROM SOLUTION - ANALYSIS BY MASS-SPECTROMETRY

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ABSTRACT

Silicate solutions have been analyzed by mass spectrometry in order to study silicate speciation in pre-nucleating and nucleating zeolite solutions. Structural elements of the zeolites to be formed were detected immediately before the nucleation point which was monitored by light scattering. Incorporation of heteroelements was analyzed as well. Pronounced differences are detected between different heteroelements.

Keywords: nucleation, silicate oligomers, mass spectrometry, structure.

INTRODUCTION

Zeolite nucleation is crucial in determining the properties of the final zeolite, with respect to structure, particle sizes and other properties. However, as important as it is, it is also one of the most elusive phenomena in zeolite science. NMR spectroscopy and light scattering have been the major experimental tools to study nucleation in the past, in recent years, theoretical methods have supplemented these experimental approaches, and they are nowadays highly valuable tools for the understanding of zeolite nucleation. However, detailed insight into zeolite nucleation is still lacking. Especially larger oligomers are difficult to analyze, and also heteroatom incorporation is not easily tracked, because especially quadrupolar nuclei hamper the understanding of NMR spectra. Over the last decade, we have developed electrospray ionization mass spectrometry (ESI-MS) to a powerful tool for the analysis of silicate solutions. This technique allows temporal analysis of the silicate species at a time resolution of minutes. While by conventional mass spectrometry essentially only the masses can be detected, MS/MS experiments can also yield information on the structure of oligomeric species.

EXPERIMENTAL

Primarily clear solutions are suitable for the analysis by mass spectrometry. Such solutions are prepared in the conventional manner as described in the literature for the respective systems developing slowly, i.e. in an open system or in specially designed autoclaves for reactions at temperatures exceeding 100 °C which allow sampling during synthesis. After mixing reagents, samples are taken via a syringe and injected into the mass spectrometer. For intermediate time scales on the order between 15 minutes and approximately one hour, reaction solutions can be placed directly in a syringe and injected continuously from the syringe into the mass spec. A tubular reactor with a split is used for the shortest reaction times in the minute range. Reagents are mixed in a T-mixer. The reaction time is determined by the length of the tube and the flow rate of the solution. After the desired tube length, a split is used to collect most of the solution, and a small fraction is fed into the mass spectrometer via a capillary for analysis. The different systems used can also be heated to be able to run reactions at different temperatures.

Different types of mass spectrometer and sprayer geometries have been evaluated for the analysis of pre-nucleating and nucleating zeolite solutions [1]. Off-axis sprayer geometries were found to be advantageous, since they prevent incrustations on the apertures and avoid memory effects. Thus, most experiments were carried out with a Micromass ZMD quadrupole mass spectrometer with z-spray alignment of the ESI source. For MS/MS experiments, a

Bruker Esquire 3000 system with ion trap was used. In selected cases, also high resolution spectra were recorded on different types of spectrometers.

RESULTS AND DISCUSSION

Initially, pre-nucleating systems have been studied with different goals. The hydrolysis of alkoxy silanes is important as the first step in the formation of zeolites from clear solution. MS analysis shows that depending on an organic additive (tetramethylammonium or tetraethylammonium) the system develops towards different oligomers, i.e. the cubic octamer or the trigonal prismatic hexamer, over a time period of several hours, if one starts with tetraethylorthosilicate (TEOS) as the silicate source [2]. While at the end of the reaction, either the octamer or the hexamer prevails, depending on the alkylammonium ion, both species are present at intermediate stages of the reaction. The temporal development of the system is highly dependent on the nature of the silicate source. The longer the alkyl chains of the alkoxy groups are, the slower is the hydrolysis and thus the development of the system. From methoxy over ethoxy to propoxy the time to reach the final species distribution increases by about one order of magnitude for each carbon atom in the alkyl chain (Fig. 1).

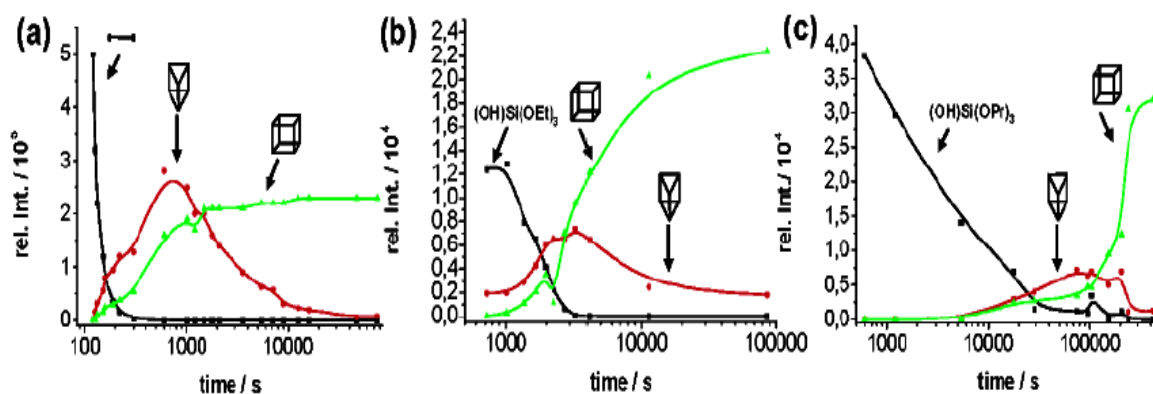


Figure 1. Temporal evolution of silicate oligomers in the presence of tetramethylammonium and different silicon sources: tetramethoxysilane (a), tetraethoxysilane (b) or tetrapropoxysilane (c).

The system is not static after reaching the final oligomer distribution, all oligomers interconvert into each other on time scales between seconds and hours, depending on temperature. Using isotope labelling with ²⁹Si, it could be shown that even highly stable species, such as the cubic octamer, exchange silicon atoms. This exchange proceeds in a concerted manner, i.e. it is not single silicon atoms which are exchanged, but complete faces of the oligomeric polyhedra [3].

Nucleating solutions are substantially more difficult to analyze, since the solutions can easily precipitate solids, especially after injection into the mass spec which is accompanied by the evaporation of the solid. Thus, often severe problems with incrustation or clogging occur. However, in spite of these problems, in most cases it was possible to run experiments over periods of several hours, before shutting down the system and cleaning was required.

All nucleating solutions, irrespective of their exact composition, were characterized by common general features. Initially, a population of small oligomers is formed from the monomers which are the primary product of the hydrolysis of alkoxide precursors. Gradually, more and more extended oligomers are formed. When solid material appears, as observed by light scattering, the heavier oligomers vanish again and a population of smaller units is observed. This is due to the reduced silicate concentration in solution which leads to depolymerization of the higher oligomers due to the mass action law.

The major differences between different zeolites occur immediately before the nucleation point: For four different zeolite systems, silicalite I, all-silica zeolite A, zeolite beta (polymorph C), and ITQ-21, it was observed that at this point structural elements of the structure, which is later observed, are already present in solution. These typical elements are five-ring species in the case of silicalite I, cubic octamers linked directly via corners for zeolite A, and cubic octamers linked via a silicate tetrahedron for polymorph C of zeolite beta [4]. For ITQ-21, also cubic octamers linked via a silicate tetrahedron and double-four ring linked via a tetrahedron to a single four ring are observed, again in agreement with the structure of the final zeolite (Fig. 2) [5]. Interestingly, in the solution no double four-rings containing a fluoride anion (in the fluoride based synthesis system) were observed, which implies that fluoride species are only later incorporated into the growing zeolite. The observation of structural elements in the solutions immediately before nucleation does not necessarily imply that the respective zeolite is formed by direct assembly of such oligomers, but does suggest, that the solution conditions favor the formation of specific structural elements, as they are also found in the later zeolite structure.

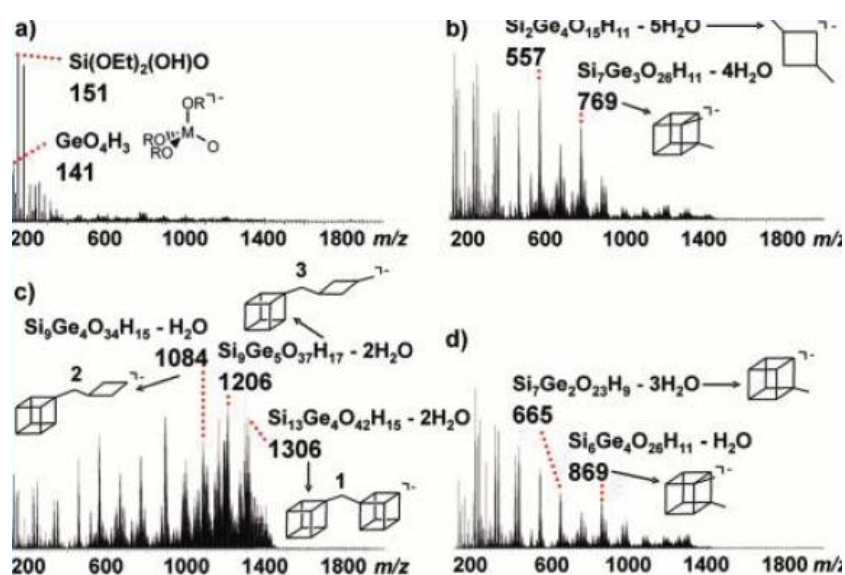


Figure 2. Temporal evolution of germanosilicate oligomers during ITQ-21 synthesis immediately after mixing (a), after 30 min (b), after 60 min (c) and after 70 min (d). Nucleation occurs after approximately 60 minutes. From ref. [5].

The evolution of specific oligomers was studied in more detail for the MFI system. MS-MS experiments were used to discriminate precisely between different oligomeric structures. Using this technique, it was possible to obtain insight into the processes occurring during the induction period for MFI-formation. Initially, different cubic octamer species are predominant, but over time, the fraction of double five-ring species increases on the expense of double four-rings. If the ratio of the signal intensity of double four-rings over double five rings reaches approximately ten, MFI starts to form. This takes approximately 6 h at 170°C, 13 h at 100°C and over 400 h at 40°C. Thus, the induction time is required for a sufficient concentration of species to form which seem to be required for nucleation [6].

Mass spectrometry is also highly suitable to analyze the incorporation of heteroelements into zeolites. Several different systems have been studied, including aluminum, germanium, gallium and titanium. ESI-MS confirms that germanium prefers sites in four-rings and double four-rings, while gallium was found to be located preferably in positions bridging closed ring species [7]. Aluminum incorporation is more difficult to study, since replacing silicon by

aluminum (which requires an additional proton for charge balancing) leads to species with almost identical mass. Nevertheless, high resolution MS experiments and experiments with ²⁹Si also allow the study of such systems. Interestingly, clear proof was found that in solution exist species which violate Loewenstein's rule, something rarely found in solid state structures.

CONCLUSION

ESI mass spectrometry has proven to be a highly suitable method to give complementary information on the silicate speciation in aqueous solution, before, during and after nucleation. The method does not allow pinpointing the exact nucleation mechanism, but does provide additional information which will bring us nearer to a more detailed understanding of one of the most crucial topics in zeolite science.

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