

Barriers in Decoding the Complexity of Zeolite Formation

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Short Communication

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Introduction

In the context of quantum chemical programs conductor-like screening models have become popular to describe long range electrostatic interactions between solutes and solvent which is also affecting the theory formation of synthesis of zeolites. But if synthesis parameters are taken into account, nucleation of zeolites gives rise to a restriction explaining the synthesis process in detail by modeling. This is supported by the fact that processes in front of crystallization are to a large extent depending on intermediates which are competing and mostly are directed by pH-values. It should provide clues as to whether the correlation between dependant and independent variables on the synthesis process is of monocausal order or superimposed by parameters. Seen from that point of view it is striking to handle the process of zeolitization of Na₂O and H₂O in the synthesis mixture.

Results and Discussion

Similar to phase transition from vapor to liquid, nucleation in zeolite systems is controlled by dynamic processes which are based on effects of supersaturation and typically understood using classical nucleation theory. The crystals formed in supersaturated solutions should therefore correspond to the energetics required for this purpose. However, modeling nucleation and crystal growth in zeolite systems still remain highly topical in microporous solids to understand the fundamental processes at atomic level and to bring reaction and molecular models closer together [1]. In this context reaction models are usually developed under consideration of experiments either based on kinetics or thermodynamic approaches. But in respect of each model one should be kept in mind that underlying assumptions and simplifications make it not seldom difficult to provide a comparison between the respective models and the corresponding data sets. Also from the computational point of view, theoretical prediction of dissociation constants are still an extremely challenging task with focus on solvation effects of neutral and ionic species which are involved in proton transfer reactions [2]. While standards of quantum chemistry techniques have no difficulty making accurate predictions for gasphase acidizes, the first principle computation of pKa represents a major challenge [3]. Moreover, when looking more deeply into details there is still disagreement if zeolitization is processed either by homogenous or heterogeneous nucleation. Much debate is in focus between these extremes that have not yet been properly researched in the progress of zeolitization. Most authors explained formation of nuclei based on liquid phase supersaturated with soluble silicates, aluminates and/or aluminosilicate species. From this point of view heterogeneous nucleation should either take place in the gel phase itself or at the liquid-solid phase boundary of the gel matrix and calculated with view of underlying assumptions of primary and secondary amorphous phases. Also the so-called autocatalytic

nucleation is faced by similar challenges and still understood as "a phase transition whereby a critical volume of a semi-ordered gel network is transformed into a structure which is sufficiently well ordered to form viable growth center from which the crystal lattice can propagate" [4]. But mathematical models of synthesis reactions still remain in place as represented by Thompson [5]. Although the composition of the reaction mixture - usually expressed as oxide ratio by Na₂O, Al₂O₃, SiO₂ - is of vital significance, the history of synthesis (influence of temperature, pH, hydration effects, ageing effects, reaction time, organic template molecules etc.) cannot hinder the labyrinth of parameters which are normally analyses in an experimental stepped hierarchical way. Altogether the field of research again and again shows a tessellation of building blocks which based kindly regarded on reliable acceptance. We recently studied the process of hydrothermal zeolite crystallization by in situ ultrasound using the nucleation-growth model developed by Avrami and Erofeyew [6]. In contrast to homogenous catalysis additional processes such as nucleation, diffusion, crystal growth and crystal morphology have to be taken into account. To avoid problems in interpretation, as mentioned by Sharp and Hancock [7]. The linearity of the plots were studied at low values of the fraction of crystalline product (proportional to the ultrasound attenuation) to develop access to the period of first crystal growth. Based on this procedure we were able to capture to as starting point of crystallization by extrapolation of data as exemplarily shown for zeolite X from the Avrami-Erofevew plots using the normalized attenuation of ultrasound and thereby ruling out the main disadvantage as mentioned by Miladinović et al. [8]. However, uncertainties still exist about the early stage of the synthesis assigned to the intermediates which are involved in the nucleation period. Evaluating the situation, much is expected to achieve a maximum of information by NMR spectroscopy, whereas magnetic-angle-spinning NMR (MAS-NMR) is widely used to characterize both wet gels and solids [9].

 29 Si NMR spectroscopy was used by Bell [10] for identifying structure and concentration of silicate and amino-silicate anions in gels and solutions for the zeolite synthesis. Distribution of these species which are depending on the pH and on the nature of the cations could be assigned to 19 specific silicate structures of about 85% of the peak areas. The distribution of silicon amongst the different structures was identified as a strong function of the ratio SiO₂/Na₂O. Studies have shown that the distribution of anionic structures in the solution is sensitive to the pH and the nature of cations. But a precise information about the environment of Al atoms is not known exactly because of quadrupolar broadening the 27 Al NMR signal. It should be noted that the pH of the synthesis mixture can be determined by the total alkali content, but tricky to be measured with focus to the buffering equilibrium of the corresponding species.

Shi et al. [11] who investigated time variation of ²⁷Al and ²⁹Si NMR spectra could not provide details about the early stages of the synthesis

of zeolite A. The broad resonance in the ²⁹Si MAS NMR spectrum demonstrates that it is nearly impossible to rule out selected aluminosilicate species [12]. Miladinović et al. [8] studied ²⁷Al NMR spectra from a silicate/aluminate synthesis mixture which was thermostated at 80°C, but unfortunately not at much lower temperatures. Miladinović et al. [13] studied the course of crystallization of zeolite A by in situ ²⁷Al NMR spectroscopy starting in the liquid phase. Two peaks could be clearly distinguished in all spectra which are assigned to Al(OH)₄ ions at 79 ppm and a broad nearby situated peak at 59 ppm which belongs to undissoved aluminosilcate species which are present in the hydrogel phase. The plots of normalized intensities of ²⁷Al NMR lines at 79 ppm showed typical sigmoid curves based on the synthesis mixtures of x Na₂O : y SiO₂: 1.0 Al₂O₃: zH₂O (x: 2.85 to 4.1; y: 2.0, 2.5; z: 77 to 130) and resulting in straight lines when the Avrami- Erofeyew equation was applied.

A short while ago the hydrothermal synthesis of zeolite A was monitored by in situ ultrasonic diagnostics to study the impact on nucleation and crystal growth by varying the amount of Na₂O in the synthesis mixture 0.4 Na₂O : 10 SiO₂ : 1.6 Al₂O₃ : 16 (TMA)₂O : 850 H₂O [14]. Among other factors the alkalinity of the synthesis mixture showed the most expressive effect on the crystallization process. With focus on increasing the alkalinity the amount of structure- forming Na ⁺ ions is multiplying the nuclei in the synthesis mixture [15]. Changes of the ion concentration in the liquid phase during the synthesis process illuminate the interdependence between nucleation and crystal growth [16]. Subsequent changes of the amount of Na, Si, and Al ions in the amorphous phase during the zeolite formation of zeolite A exemplarily demonstrate that Na in the liquid phase seems to be the limiting factor for the zeolite formation. Just after 7 hrs there are still 89% of Si, and 65% of Al remaining in the liquid phase whereas 95% of Na was exhausted. It could be clearly seen that the decrease of Na⁺ ions in the synthesis mixture is prolonging the incubation period and resulting in more bended angled lines [17].

The normalized US-attenuation based on the Avrami-Erofevev equation $\ln[-\ln(1-\alpha)]$ vs. $\ln(t-t_0)$ is shown in Figure 1 as an example for zeolite A, synthesized from the synthesis mixture 0.4 Na₂O : 10 SiO₂ : 1.6 Al₂O₃ : 16 (TMA)₂O : 850 H₂O at 95°C. Depletion of Na₂O and water in the synthesis mixture both shows reversal points in the Avrami exponents, which indicate a change in direction of a threedimensional crystal growth (n1=3) in a first step and an onedimensional crystal growth (n2=1) in a second step [18]. This phenomenon clearly demonstrates that crystal growth is not following an uniformed mechanism as verified for the synthesis from clear solution extracted from alkaline fused fly ash at a pH-values higher than 126. The reversal points in the Avrami exponents and the corresponding rate constants both are obviously an indicator to the sequencing deviation of concentrations in the synthesis mixtures. This is caused by the deviation of concentrations if we follow the underlying assumption of the thermodynamics-based equilibrium model between amorphous solid and solution species as proposed by Lowe. If we follow the proposed mechanistic scenario in the early stage of crystallization the results of AFM as published by Agger et al. [19] point out that each terrace comprises of an equivalent of one layer of sodalite cages and one layer of double-four rings (D4Rs) evolved in different rates. This obviously can be headed by selected parameters such as pH, water content etc.

It should be kept in mind that the influence of the pH on the crystallization process has been discussed in only a few papers.

Because many different clusters are present in solution it is an aggravating factor to study their properties individually. By variation of the amount of Na₂O in the synthesis mixture (depending on the concentration of Na⁺ and the corresponding pH value) the rate constants k1 and k2 as shown in Table 1 clearly demonstrate that a linear dependence for crystal growth is not visible. For this purpose either the amount of Na₂O or water of the standard synthesis mixture 0.4 Na₂O : 10 SiO₂ : 1.6 Al₂O₃ : 16 (TMA)₂O : 850 H₂O was modified in an experimental stepped hierarchical way. As already mentioned above, the pH is difficult to be controlled because of its change during the time curve of crystallization. It cannot be excluded that the system is affected by buffering in order to stabilize the pH during the synthesis which is considered as experimental measure. Silicate can be most probably found as [SiO₂(OH)₂]₂- or [SiO(OH)₃]-. Only comparatively low concentrations of higher condensed species have the chance of being present at pH-values above 12.0. At lower pH-values the amount of dimers and four-membered rings species is increasing. The aluminate is generally predominant in very low concentrations and often described to be present as [Al(OH)₃OSi(OH)₃]-.



Figure 1: US-attenuation based on the Avrami-Erofeyev equation $ln[-ln(1-\alpha)]$ vs. $ln(t-t_0)$ for the synthesis of zeolite A.

| x Na ₂ O | n ₁ [-] | n ₂ [-] | k ₁ [h ⁻¹] | k ₂ [h ⁻¹] | t ₀ [min] |
|---------------------|--------------------|--------------------|-----------------------------------|-----------------------------------|----------------------|
| 0.2 | 2.97 | 1.63 | 0.1 | 0.1 | 11.8 |
| 0.3 | 3.04 | 1.1 | 0.22 | 0,23 | 5.9 |
| 0.4 | 2.8 | 1.01 | 0.19 | 0.21 | 6 |
| 0.5 | 3 | 1.38 | 0.13 | 0.14 | 4.8 |
| 0.6 | 3 | 2.06 | 0.07 | 0.08 | 1 |
| y H ₂ O | | | | | |
| 650 | 2.54 | 0.68 | 0.36 | 0.49 | 2.2 |
| 750 | 2.77 | 1.11 | 0.24 | 0.31 | 3.6 |
| 850 | 2.8 | 1.01 | 0.19 | 0.21 | 6 |
| 950 | 2.82 | 1.47 | 0.11 | 0.12 | 6 |
| 1050 | 3.04 | 2.19 | 0.03 | 0.09 | 6 |

Table 1: Kinetic data obtained by variation of the amount of Na₂O and water in the synthesis mixture x Na₂O : 10 SiO₂ : 1.6 Al₂O₃ : 16 (TMA)₂O : y H₂O [13] for the synthesis of zeolite A at 95[°]C [20].

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By variation of the amount of water in the synthesis mixture also reversal points in the Avrami exponents can occur [14]. The plots of $\ln[-\ln (1-\alpha)]$ vs. $\ln(t-t_0)$ shown in Figure 2 demonstrate angled lines which are more unbent if additional water was added to the synthesis mixture. Also the rates of crystal growth k_1 and k_2 increase by reducing the amount of water. These changes become apparent as a result of the increasing alkalinity as discussed in [21]. The rate constants (k_1 and k_2) are an important indicator to study the influence of supersaturation by variation of the amount of water in the synthesis mixture.



Figure 2: Plots of normalized US-attenuation vs. synthesis time/h of zeolite A synthesized at 95°C by varying the amount of water of the synthesis mixture [14].

In conclusion Na₂O or H₂O are not acting independently at the same time because one parameter cannot be clearly kept constant in the experimental arrangement when the other is measured. It has been also observed that the Na2O content defines the period of incubation phase as well as the rate for crystal growth. Lechert reported that composition and ranges of the stability of zeolitic products depend on the pH as verified by the alkalinity and the Si/Al ratio. Based on our test runs it can be recognized when varying the amount of water or Na₂O as consequence also the pH will follow an adaptive ability. If ignored it subtracts itself the possibility to describe the physicalchemical state of the system in all it facets during the period of structural ordering because causal structures cannot be predefined with focus on the scope of competing reactants. As a consequence Lowe [22] preferred a more simplified thermodynamics- based approach using an equilibrium model in which the solution phase will be simulated by an idealized solution of silicate anions such as $(HO)_3$ SiO- and $(HO)_2$ SO₂²⁻. But Lowe at the same time was aware of these consequences of neglecting the aluminosilicate species in the solution phase as there was very little information available concerning structure and stability constants to calculate the pH. Irrespective of this the conceptual model of Lowe includes the series of pseudo-equilibria corresponding to amorphous solid, solution species, progress of zeolitisation. The phenomenon of structural ordering in front of the first crystal growth can often be seen when the synthesis mixture is monitored by in situ ultrasonic diagnostics but beyond control by kinetics [23].

Former AFM observations published by Sugiyama et al. [24] showed that fine pyramidal structures lie side-by-side on the surface and that the smallest step height corresponds well with the D4R structure. From there it cannot surprise that modeling the nucleation of zeolite A by

means of DMol3-code as standardised procedure for Density Functional calculations (DFT) together with COSMO (conductor-like screening model) favour the D4R four-ring key building unit as an intermediate as shown in Figure 3. But it seems that this approach of calculations is an



Figure 3: Nucleation mechanism based on D4R four-ring key building unit proposed by [25].

oversimplified model and neglecting other relevant synthesis parameters which are important to steer the synthesis and obviously acting simultaneous before the first crystal is formed. Although synthesis mixtures are adjustable and the process of crystallization can be followed by analytical techniques the internal interdependency of intermediates in front of the starting point t₀ of crystallization is still wrapped in mystery to be clearly understood at atomic level. Application of conductor-like screening models have been shown itself to be reliable and readily available method for calculations on liquid and solution phases, but it remains unanswered how to explain angled lines which are differently curved by varying the amount of water as plotted in Figure 2. With focus on forming prenucleation species Mora-Fonz et al. [26] briefly touched the role of pH and sovation. They discussed the important impact of water in stabilizing multiply charged anions and stated that the parameter of Gibbs free energy of the reaction is significantly less favourable for neutral then charged species. Calculated Gibbs free energies followed a deprotonation of Si(OH)₄ by the reaction of OH- to result in (OH)₃SiO- and H₂O. But interactions with charge-balancing ions such as H.

O⁺, Na⁺ or organic templates were not considered in this study. Interactions of solute molecules with the solvent can be theoretically handled by means of putting the solute in a cavity that is surrounded by a dielectric continuum which represents the solvent H₂O but neglecting data sets including the pH. Further theoretical approaches by Eckert et al. [3] did recognize the necessity to combine Gibbs free energy dissociation with pKa data by use of the Conductor-like Screening Model for Real Solvents (COSMO-RS). But COSMO-RS is still extremely problematic to study simultaneously the impact of Na₂O and H₂O in synthesis mixtures. The idea that events obey a monocausal order is a given issue to handle complex regimes. Based on this principle, it never is creating big problems if it is understood in terms of definite monocausal order in macroscopic view. Nevertheless, much controversy over the exact processes which occur and a number of theories have been finally proposed to form networks and eventually zeolite frameworks [27]. Also when looking at the period of the fundamental prenucleation, finally question should straightforwardly be asked if monocausal order is a necessary property of nature or rather a simplification to handle dynamic processes such as the crystallization of zeolites until nowadays [28].

Outlook and Conclusions

With reference to the paper published by Catlow et al. [23]. We think that the proposed nucleation mechanism which involves exclusively the formation of a double-four ring is well- created from the "end" to build up zeolite A. Because Ager et al. [17] stated that each layer comprises the equivalent of a sheet of sodalite cages and D4Rs the last word has therefore probably not been spoken yet. From our point of view the discussed reaction route in front is much simplified because kinetics showed that the processes in front are depending on competing intermediates and obviously directed by the pH which have to be taken into account.

Although a solvation model such as COSMO-RS has been shown to be reliable and readily available method for calculations on the basic understanding of liquid and solution phases the question remain unanswered how to explain angled lines which are differently curved by varying the amount of Na₂O and H₂O in the synthesis mixture. Therefore solution and solid-phase mediated reactions as part of the zeolite synthesis should be further on an active area of research in solvation models based on quantum-mechanical interactions with charge-balancing ions.

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