

Zeolite metastability as a function of the composition of the surrounding solution: The case of faujasite and zeolite omega

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ABSTRACT

The transient formation of faujasite has been observed during the synthesis of zeolite omega. The metastability between these zeolites has been studied by measuring their solubilities in alkaline solutions at temperature levels near to usual crystallization conditions. The use of silicate- and aluminate-enriched solutions has allowed to determine solubility curves at different alkalinity levels. The silicate concentration in solution controls the relative stability of the two structures. For Si/Al ratios in solution lower than 6–10 (80–115 °C), zeolite omega is more soluble than faujasite and can be dissolved to provide silicate and aluminate for the crystallization of aluminium-richer zeolite X. In the usual conditions for the synthesis of zeolite omega, with Si/Al in solution higher than 100, zeolite X is metastable and is dissolved to provide aluminate for the crystallization of silica-richer zeolite omega.

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1. Introduction

The variety of properties at the basis of the industrial applications of zeolites depends on the diverse topology of their aluminosilicate networks. Quite often, differences of topology do not rely on significant differences of network composition and zeolites with very different micropore openings can be formed in very similar synthesis conditions. This implies that selectivity of nucleation is a critical item in zeolite crystallization, as several phases can nucleate in parallel or in succession from the same synthesis batch. The transformation of a zeolite phase into another by dissolution–recrystallization is frequently observed during hydrothermal syntheses and can prove to be either a doom or an asset when the crystallization of a given phase is looked for. Many examples can be found in literature and industrial practice, like the dissolution of small-pore zeolite A to form large-pore zeolite X [1,2] or non-porous sodalite [3], the transformation of large-pore zeolite Y into small-pore zeolite P [4,5] or analcime [6], or the transient formation of zeolite Y in the early steps of crystallization of zeolite omega [7], the synthetic analog of mazzite.

The evolution from one phase to another is obviously driven by the higher stability of the second phase formed. The question why the most stable phase is not the first one to be formed or, in other terms, why a metastable phase is formed earlier has received several answers, based on kinetics or thermodynamics. The kinetic explanation of the phenomenon is based on the assumption that

the nucleation of a phase more related to the structure of the solvent requires a lower energy of activation and is faster than the nucleation of a less solvent-compliant phase [8]. Plain thermodynamics can also account for the early formation of a metastable intermediate phase, as the formation of the stable phase through several steps can significantly decrease the entropy of crystallization [9], in a chemical analog of a Hess cycle. Both kinds of explanation are based on a common point: the similarity, in structure or free energy, of the parent solution and the earliest phase formed. The structure-directing role of water molecules in the formation of the porosity of aluminosilicate zeolites adds credibility to this mechanism.

However, in most cases the nucleations of the metastable phase and of the stable phase do not occur in the same environment, as hydrothermal crystallization of zeolites is not a congruent solidification. Preferential incorporation of aluminate modifies the Si/Al ratio of the reactive system [10] and the condensation of silicate species modifies the buffer capacity of the silica present in the system [11]. As both the composition and the pH of the aluminosilicate solutions affect the selectivity of formation of zeolitic phases [12,13], the evolution of the synthesis system can bring to the nucleation of a series of different zeolites.

The metastability of faujasite towards zeolite P or zeolite omega is a textbook example of phase change during a zeolite synthesis. The phase composition during a synthesis of zeolite omega at 100 °C from a synthesis system 0.84 Na/0.05 TMA/0.13 Al/Si/32 H₂O, where TMA stands for tetramethylammonium cations, is reported in Fig. 1 [7], in which the experimental data are fitted by classical Avrami curves [14,15]. Zeolite Y is formed

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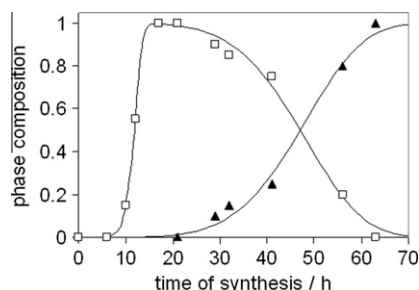


Fig. 1. Phase composition during a synthesis of zeolite omega [7]. Zeolite Y (void squares), zeolite omega (filled triangles). The lines are best fits by Avrami equations [14,15].

from aluminosilicate species after some hours of induction time. The crystallization of zeolite Y leave a significant amount of silicate species in solution. The silica-richer zeolite omega nucleates in this new environment and grows until zeolite Y, its aluminium source, is completely dissolved.

A quantitative evaluation of the relative stability of zeolitic phases requires the comparison of their solubilities. The purpose of this communication is to evaluate in which way the composition of the solutions in contact with the zeolite crystals affects the relative stability of faujasite and zeolite omega. Experimental studies of the composition of solutions at the equilibrium with phases involved in the synthesis of zeolites are not aplenty. The aluminosilicate gel formed at the beginning of the synthesis of zeolite A has been measured to be four times more soluble than the zeolite itself [16]. These data confirmed earlier reports which showed that the equilibrium concentrations increased with temperature and alkalinity of the solution [2,17,18]. It is interesting to observe that the same concentration levels were observed in dissolution experiments and by measurement of the concentrations in the synthesis media of the zeolite when only one phase (gel or crystals) was present [19]. Zeolite A has a Si/Al ratio near to 1 and the measured concentrations of aluminate and silicate at the equilibrium with a saturated alkaline solution have virtually the same values. For zeolites with higher Si/Al ratio, like zeolite Y, mordenite or ZSM-5, the saturation concentrations of silicates are much higher than the concentrations of aluminate [20–22].

2. Experimental

Zeolites X (Si/Al 1.15) and Y (Si/Al 2.3) (faujasite structure) in sodium form and zeolite omega (Si/Al 3.5) as such (Na, TMA form) and calcined at 550 °C in air (Na form) were used in the dissolution experiments. In a typical dissolution experiments, 200 mg of zeolite sample were introduced in 35 ml of 1.1 M solution of NaOH (Merck). The resulting suspension was stirred for 1 h at room temperature in a stainless steel vessel, which was sealed and heated at the required temperature (80 or 115 °C) for a given time. After cooling, the solid and liquid fractions were separated by filtration. The solid phase was washed with deionized water and characterized by X-ray diffraction (Bruker AXS D8, Cu K α radiation). The liquid phase was analyzed by atomic absorption spectroscopy at the Service Central d'Analyse of CNRS in Solaize. NaOH concentrations from 0.3 to 2 M were tested in reference experiments. In some dissolution experiments, given amounts of amorphous silica (Aerosil 200 V by Degussa) or sodium aluminate (Carlo Erba) were dissolved in the alkaline solution before introduction of the zeolite. Some dissolution experiments were carried out in the presence of dissolved TMAbr (Aldrich).

A reference synthesis of zeolite omega from zeolite X in alkaline silicate solution was carried out at 105 °C from a system of composition 0.83 Na/0.05 TMA/0.13 Al/Si/27 H₂O with a methodology already published [15].

3. Results and discussion

The evolution of silicon and aluminium concentrations in solution during the dissolution of faujasites X and Y and zeolite omega has been monitored at different temperatures (80 and 115 °C) in order to choose the duration of the dissolution experiments. The solid/liquid ratio was chosen in order to avoid complete dissolution. Constant concentrations are virtually reached after 8 h. As, in several cases, dissolution treatments of more than 24 h led to the nucleation of new phases (for instance, analcime from zeolite omega or phillipsite from zeolite Y), the concentrations at 24 h were assumed as reference values for equilibrium saturation.

Aluminium and silicon concentrations in solutions at different levels of alkalinity in the presence of zeolites omega and X are reported in Fig. 2. The Si/Al ratios in solution are very similar to the Si/Al ratios of the zeolites, indicating a congruent dissolution. The higher stability of silicate species at higher pH is the driving force for the increase of silicon concentration with alkalinity. As the dissolution is congruent, the concentration of aluminium increases in parallel with the concentration of silicon.

The easy polymerization of silicates and aluminosilicates generates a variety of species in solution and likely not all of them directly take part in the equilibrium with the zeolite [23]. However, equilibration between silicate species in highly alkaline solutions is much faster than the time scale of dissolution and crystallization [24,25] and the concentration of total dissolved silicates can be considered as an index of the concentration of the species involved in the equilibrium with the solid phase. In the dissolution experiments, a high

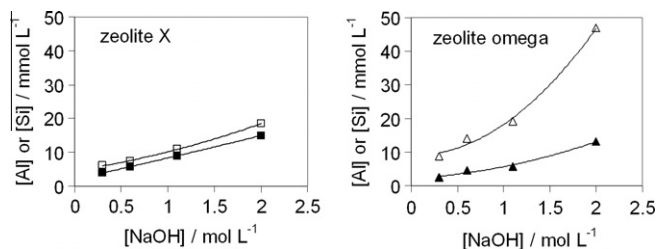


Fig. 2. Concentrations of silicon (void symbols) and aluminium (filled symbols) at the equilibrium with zeolites X and omega at 80 °C as a function of alkalinity.

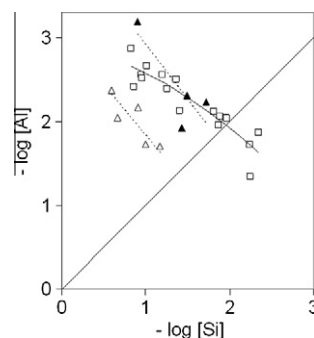


Fig. 3. Solubility of zeolites X and Y (void squares) and zeolite omega in Na (void triangles) and Na, TMA (filled triangles) forms in 1.1 M NaOH solutions at 80 °C. The lines (continuous for faujasite and dotted for zeolite omega) are guides for the eye. The diagonal represents the points at isoconcentration of silicon and aluminium.

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