

EMT Zeolite Synthesis: Na⁺ vs. OH⁻ Effect

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Addition of sodium chloride to hydrogels containing 18-crown-6 ether shows that EMT zeolite synthesis is controlled by the ratio OH⁻ : Al₂O₃ rather than by Na⁺ : Al₂O₃.

The crystallization of zeolites and related microporous materials usually occurs *via* the transformation of a hydrogel upon heating; such a reaction mixture contains at least one solid phase and one liquid phase. The evolution of the hydrogel towards the crystalline solid is a rather complex physico-chemical process. Before a full understanding of this process is possible, it is of great help to specify the role of each reagent. In the case of the synthesis of the hexagonal analogue of faujasite, EMT zeolite, as described by Delprato and coworkers,¹ the 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) molecule has a key templating effect. The structure-directing agent consists of the 18-crown-6-Na⁺ complex encaged in the large cavities of the microporous material during synthesis.² In other respects, the hydrated sodium cation is well known to direct the crystallization of the cubic FAU structure.³ However, the study of the potentially competitive templating effect between the hydrated Na⁺ cation and the 18-crown-6-Na⁺ complex is further complicated by the fact that Na⁺ and OH⁻ are provided by common sources (mainly soda and sodium aluminate). The hydroxide anions are used as mineralizers and obviously influence the gel chemistry and therefore the product. The effects of varying the Na⁺ and OH⁻ contents in the hydrogels prepared in the presence of 18-crown-6 are partially documented in the literature. Delprato⁴ and Weitkamp and Schumacher⁵ have shown that a gradual increase in the amount of soda leads to EMT/FAU mixed structures, and finally pure FAU zeolites. In these examples, it was not possible to discriminate the Na⁺ effect from that of the reaction mixture alkalinity. Other authors have tried to discriminate between

these two effects either by adding sodium nitrate to the chemical composition of the gel⁶ or by changing the aluminium source.⁷ Nevertheless, the Na⁺ : Al and OH⁻ : Al compositional ranges have not been fully investigated. Here we study the influence of both parameters in a selective way, by adding sodium chloride to hydrogels with fixed 18-crown-6 : Al and Si : Al molar ratios. The molar chemical composition of the gels used was as follows: 10 SiO₂ : 1 Al₂O₃ : x Na₂O : 0.7 18-crown-6 : y NaCl : 140 H₂O. The reaction mixture was prepared by dissolving pelleted sodium hydroxide (Prolabo) and, if required, sodium chloride (Fluka) in distilled water. 18-Crown-6 ether (Lancaster) was added and then sodium aluminate (Carlo Erba, 56% *m/m* Al₂O₃, 37% *m/m* Na₂O). Colloidal silica (Ceca, 40% *m/m* SiO₂) was then added to this solution. The resulting hydrogel was stirred gently for 24 h at room temperature. The crystallization was carried out in PTFE-lined stainless-steel autoclaves at 383 K, without agitation. After the heating time was completed, the solid was recovered by filtration, washed with distilled water until the pH of the filtrate was *ca.* 7 and dried at 333 K overnight. Fig. 1 shows the influence of the Na⁺ : Al₂O₃ (2x + y) and OH⁻ : Al₂O₃ (2x) ratios on the synthesis products. The highly crystalline phases were identi-

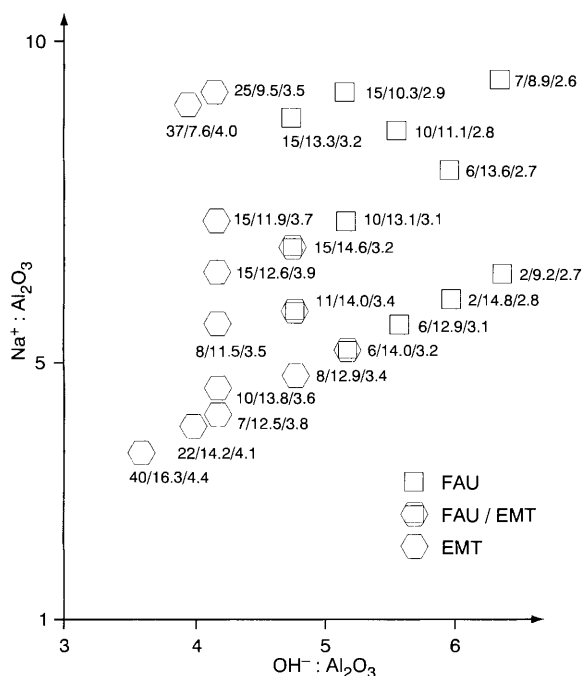


Fig. 1 Influence of the OH⁻ : Al₂O₃ and Na⁺ : Al₂O₃ ratios on the nature of the zeolitic phases. The significance of the three numbers close to each point is the following: heating time (days)/18-crown-6 (% *m/m*) occluded in the as-synthesized products (determined by TG)/Si : Al molar ratio (determined by ²⁹Si MAS NMR).

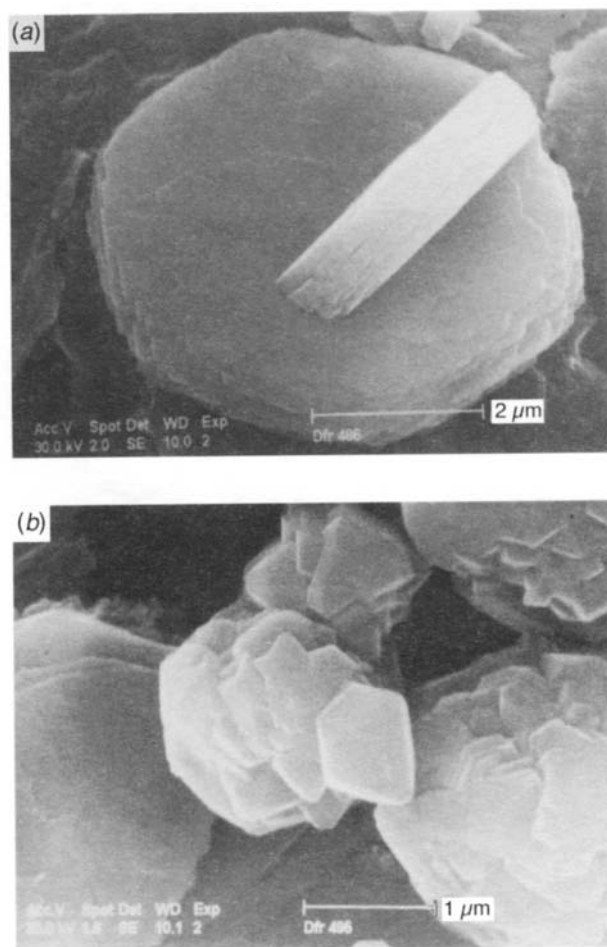


Fig. 2 Scanning electron micrographs of (a) EMT zeolite ($x = 2.1$, $y = 5.0$) and (b) FAU zeolite ($x = 2.4$, $y = 4.0$)

fied by X-ray powder diffraction and can be assigned to three structural types: cubic FAU-type, hexagonal EMT-type and mixed FAU-EMT polytype (intergrain phase). The third structural type was mainly deduced from the intensity of the lines in the $5-7^\circ$ 2θ region: the EMT materials exhibited three peaks indexed as 100, 002 and 101 reflections, and the second coincided with the 111 reflection of the FAU structure type.^{8,9} When $y = 0$, the transition from EMT to FAU with an increase of the NaOH content was confirmed. The crystallization of the gels with added NaCl generally required longer heating times, although they were not optimized. In that case, the diagram displays three zones: when the $\text{OH}^- : \text{Al}_2\text{O}_3$ ratio was $< ca. 4.5$, an EMT-type zeolite was obtained, whatever the amount of added sodium chloride. For a $\text{OH}^- : \text{Al}_2\text{O}_3$ ratio ranging from 4.5 to 5.5, a systematic evolution towards the cubic FAU structure was observed as the NaCl content increased. When the latter ratio was > 5.5 , only FAU-type materials crystallized. Thus, this set of experiments clearly demonstrates that EMT zeolite synthesis depends on the ratio of $\text{OH}^- : \text{Al}_2\text{O}_3$ rather than $\text{Na}^+ : \text{Al}_2\text{O}_3$, even if a narrow range of gel alkalinity, where the competing structure-directing effect of hydrated Na^+ cation and Na^+ -crown ether complex is visible, does exist. High sodium contents combined with low gel alkalinity lead to mordenite in an admixture with either EMT ($x = 1.8$, $y = 5$) or gmelinite and gismondine ($x = 2.1$, $y = 10$). In order to exemplify those results, SEM photographs reveal that EMT crystals prepared with 2.1 Na_2O and 5.0 NaCl have a hexagonal shape and a size of $ca. 2-3 \mu\text{m}$ [Fig. 2(a)]. The FAU material crystallized with a slightly higher soda content ($x = 2.4$) but lower sodium chloride amount ($y = 4.0$) shows aggregates ($1-2 \mu\text{m}$) of twinned octahedral crystallites [Fig. 2(b)]. Thermogravimetric measurements indicate that the average amount of entrapped 18-crown-6 is close to 12.4%

m/m. As can be seen (Fig. 1), the crystallization of FAU-type zeolites is not explained by a lower content of occluded organic molecules inside the supercages. The lattice Si : Al molar ratios of the samples (also reported in Fig. 1) decrease as the $\text{OH}^- : \text{Al}_2\text{O}_3$ ratio increases. The addition of sodium chloride induces only a very slight lowering of the Si content, which shows that, under a single but standard set of experimental conditions, the incorporation of silicon inside the framework essentially depends on the amount of soda used in the synthesis mixtures.

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