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Effectiveness of the tetramethylammonium size-modifier in the synthesis of faujasite nanocrystals

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ABSTRACT

This paper reports the effects of alkalinity, Si/Al ratio and amount of tetramethylammonium (TMA) on the formation of nanocrystals of faujasite. The presence of TMA allows to form faujasite crystals smaller than 0.1 μm. In a wide range of composition, there is no proportionality between the concentration of TMA in the synthesis system and the size of the zeolite crystals formed. TMA concentrations as low as 0.05 mmol L^{-1} are enough to induce the formation of crystals of 30 nm. The role of TMA in the formation of nanocrystals corresponds to a shift of the balance between nucleation and growth kinetics due to the adsorption of organics at the surface of the nuclei of zeolite. The field of composition of the faujasite crystals shifts from zeolite Y to zeolite X according to the alkalinity of the synthesis system. As expected, the effectiveness of silicon incorporation decreases with the alkalinity of the synthesis system. However, the effectiveness of silicon incorporation significantly increases with the content of TMA, suggesting that the large TMA cations contrast the depolymeryzing effect of alkalinity on the silicate species implied in the formation of the zeolite. This effect is modulated by the concentration of silicate in the synthesis system.

1. Introduction

The formation of nanocrystals of zeolites is a challenge with wide implications on the accessibility of active sites and on the diffusion paths in adsorption and catalysis. It was early realized that the decrease of crystal size can improve the efficiency of zeolite catalysts, be they used as single crystals [1] or embedded in a matrix [2]. The conditions of synthesis of nanocrystalline zeolites, with crystal sizes lower than 100 nm, have been extensively reviewed [3,4]. In the case of faujasite, the zeolite at the basis of most zeolite industrial catalysts and sorbents, Schoeman et al. [5] showed that the formation of nanocrystals was made possible by the use of large amounts of tetramethylammonium (TMA) cations in the synthesis system. After this seminal paper, the formation of nanocrystals of faujasite in the presence of TMA was successfully implemented by several research groups [6–12].

An additional advantage of the use of alkylammonium cations in the synthesis of zeolites is that, due to their size larger than alkali cations, they allow to form zeolites with a higher Si/Al ratio. This is potentially useful in the formation of faujasite for catalytic applications, as zeolite Y (faujasite with Si/Al 2.5) is more hydrothermally stable than zeolite X (Si/Al lower than 1.5) [13]. However, TMA, as other organic templates, is non-recyclable and relatively expensive, and its use in large amount as a dispersing agent is a significant drawback of the procedure. Some increase of the TMA yield in the synthesis of zeolite Y has been achieved by recycling the mother liquor in a series of successive syntheses [14]. The formation of nanocrystals of faujasite in the absence of organic agents has been attempted by introducing an ageing step in the preparation of the synthesis batch [15]. This approach has allowed to form crystals of faujasite with a size of 146 nm and a Si/Al ratio 1.86 or crystals with a size of 35 nm and Si/Al 1.48.

The aims of the present work are to investigate the role of TMA in the formation of nanocrystalline faujasite and to search for economically viable conditions of formation of nanocrystalline zeolites X and Y. To achieve this target, a study was carried out on the crystallization of faujasite from synthesis batches of different alkalinity, Si/Al ratio and TMA content.

2. Materials and methods

The reagents used for the synthesis of faujasite nanocrystals were Ludox HS-40 colloidal silica from Sigma-Aldrich (40 wt% suspension in water), sodium aluminate from Carlo Erba (36.6 wt% Na_2O, 50.3 wt% Al_2o_3), sodium hydroxide Prolabo, tetramethylammonium (TMA) bromide and hydroxide (25 wt% aqueous solution)

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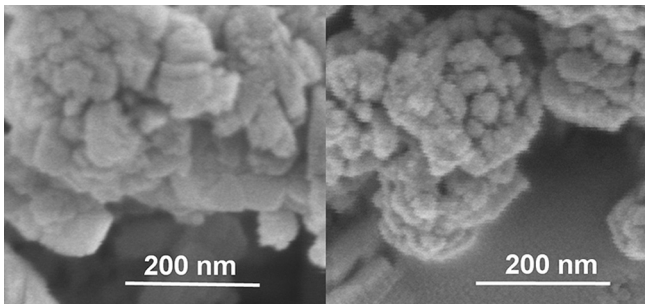

Fig. 1. Scanning electron micrograph of aggregates of crystals of zeolites Y (Si/Al 2.1, lefthand) and X (Si/Al 1.5, righthand) formed from synthesis batches with TMA/Si 0.15.

from Aldrich, and deionized water. Faujasite crystals were formed from synthesis gels in the field of molar composition Na/Al 2.26–10, TMA/SiO_2 0.09–1.37, Al/SiO_2 0.13–0.46, H_2O/SiO_2 9–36. The alkalinity of the synthesis system was defined as the molar ratio $OH^-/Si = (Na + TMA - Al - Br)/Si$. Sodium aluminate and silica were added to a stirred TMA-containing alkaline solution. The resulting gel was aged for 24 h at room temperature and then put in a steel vessel at 90–100 °C for 72 h. Different times and temperature were used in the case of individually specified literature syntheses. The material resulting after crystallisation was precipitated by centrifugation, washed with deionized water up to pH 9, and dried overnight at 80 °C.

The solids formed were characterized by powder X-ray diffraction ((Bruker AXS D-8 diffractometer with Cu *K*α radiation), scanning (Hitachi S-4800 microscope) and transmission (JEOL 1200 EX II) electron microscopy and EDX analysis (Hitachi S-4500). The effect of crystal size on XRD line broadening was determined by Williamson-Hall plots. The amount of organics in the zeolite was evaluated by thermal gravimetric analysis in air flow (Perkin Elmer STA 6000).

3. Results

In Table 1 the composition of synthesis batches and the composition and size of faujasite formed from literature syntheses in the absence of TMA or in the presence of large amounts of TMA are reported, together with the corresponding data for original syntheses of faujasites formed in the presence of small amounts of TMA. The data of Table 1 clearly indicate that the presence of TMA allows to obtain faujasite crystals smaller than about 0.1 μm. However, it seems also clear that it is possible to form crystals of this small size also in the presence of amounts of TMA much smaller than TMA/Si ratio higher than 1 reported in the literature.

Scanning electron micrographs of faujasites formed in the presence of small amounts of TMA are reported in Fig. 1. The nanocrystals of zeolite X or Y recovered from centrifugation are aggregated in irregular lumps. The size and composition of the crystals depend on the synthesis conditions and are especially affected by the alkalinity, the Si/Al ratio and the TMA content of the synthesis batches.

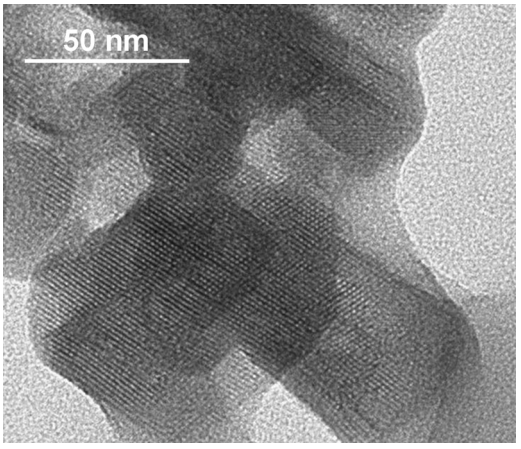

Fig. 2. Transmission electron micrograph of the cross-section of an aggregate of crystals of faujasite (Si/Al 1.8, formed from a synthesis batch with TMA/Si 0.10).

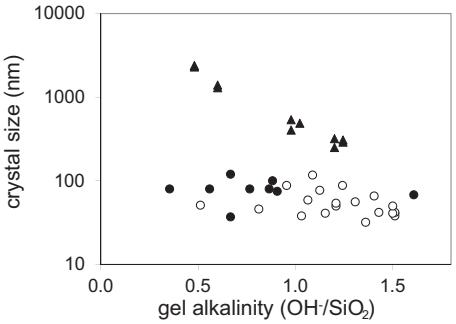

Fig. 3. Size of faujasite crystals as a function of the alkalinity of the synthesis system. Syntheses in the absence of organics (triangles) and in the presence of TMA with TMA/Si ratio higher than 1 (filled circles) or not higher than 0.18 (void circles).

The microstructure of the material was elucidated by transmission electron microscopy (TEM). TEM of the cross-section of a typical aggregate is shown in Fig. 2. Individual nanocrystals with size from 30 to 70 nm presents repeating modules in good agreement with the 111 spacing of faujasite.

In Fig. 3, the size of faujasite crystals formed in the presence of different amounts of TMA is presented as a function of the alkalinity of the synthesis system. In the case of zeolite Y formed in the absence of TMA [16,17], crystals in the micrometer size range are formed. Crystal size decreases at increasing alkalinity of the synthesis batch, as frequently observed in zeolite synthesis [18]. In the presence of TMA, smaller crystals are formed, in the size range 30–120 nm. It can be remarked that synthesis with TMA/Si ratio higher than 1 and lower than 0.18 produce crystals in the same

Table 1
Composition of synthesis batches and properties of zeolite formed.

Synthesis batch composition	Synthesis alkalinity	Zeolite dry composition	Crystal size (nm)
0.68 Na/0.20 Al/Si/16 H_2O [16]	0.48	$NaAl(SiO_2)_{2.6}$	2400
1.11 Na/0.09 Al/Si/20 H_2O [17]	1.02	$NaAl(SiO_2)_{2.2}$	500
0.01 Na/1.10 TMA/0.46 Al/Si/57 H_2O [9]	0.67	$Na_{0.46}TMA_{0.54}Al(SiO_2)_{2.35}$	120
0.01 Na/1.66 TMA/0.46 Al/Si/57 H_2O [9]	0.67	$Na_{0.40}TMA_{0.60}Al(SiO_2)_{2.37}$	37
0.90 Na/1.37 TMA/0.23 Al/Si/31 H_2O	1.61	$Na_{0.90}TMA_{0.10}AlO_2(SiO_2)_{1.54}$	70
0.92 Na/0.15 TMA/0.41 Al/Si/32 H_2O	0.51	$Na_{0.967}TMA_{0.033}AlO_2(SiO_2)_{2.1}$	50
1.23 Na/0.10 TMA/0.20 Al/Si/24 H_2O	1.03	$Na_{0.971}TMA_{0.029}AlO_2(SiO_2)_{1.8}$	40
1.76 Na/0.15 TMA/0.41 Al/Si/32 H_2O	1.36	$Na_{0.963}TMA_{0.037}AlO_2(SiO_2)_{1.57}$	32
1.96 Na/0.18 TMA/0.44 Al/Si/36 H_2O	1.51	$Na_{0.963}TMA_{0.037}AlO_2(SiO_2)_{1.50}$	38