Control of crystal size and morphology of mordenite

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The shape and size of the crystals of mordenite, as well as the Si/Al ratio, have implications as regards industrial applications in hydrocarbon conversion and separation. The ratio between the incorporation yields of silicon and aluminum is inversely proportional to the alkalinity level. The size of mordenite crystals can be modified by a factor of 10 by appropriate aging of the silica source. The alkalinity of the synthesis system is an important factor affecting the morphology of the mordenite crystals, with flatter crystals being formed at low alkalinity.

KEY WORDS: zeolite; mordenite; crystallization; silica hydrogel; diffusion pathway.

1. Introduction

The crystallization of mordenite, albeit reported by Barrer as early as 1948 [1], is still a rich field of research. Mordenite is one of the few zeolite structural types to find industrial application in catalysis. The main application is as an isomerization catalyst for C_5/C_6 naphtha and xylenes, with mordenite-based catalysts being also used for dewaxing, NO_x control and selective hydrogenation of olefins [2,3]. The shape and size of the crystals are critical parameters for catalytic reactions taking place inside microporous solids. Mordenite is an often-cited textbook example of the influence of diffusional limitations on the effectiveness of a catalyst [4,5]. 12-MR channels of mordenite are parallel to the *c* axis of the structure [6], and hence the length of the crystals in this direction is the proper size to be used in calculations of Thiele modulus and effectiveness factor. This characteristic size has implications for the industrial applications of mordenite in hydrocarbon conversion and separation.

The aluminum content of the zeolite is important from several points of view. It influences the number and strength of the Brønsted acid sites, as well as the volume and size of the mesoporosity opened in the dealumination treatment of the zeolite [7]. The zeolite composition is affected by the conditions of synthesis. Usually, a good correlation is observed between the alkalinity of the synthesis solution and the aluminum content of the product, more aluminum being incorporated at higher alkalinity [8,9].

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The most common morphology of crystals of natural mordenite is characterized by needles with *c*-elongation [10], sometimes thin in the [010] direction [11]. Synthetic mordenite presents several morphologies, as a function of the crystallization conditions [12]. From the synthesis of hydrogels with Si/Al = 4–6, aggregates of parallel acicular crystals have been obtained at alkalinity ratios Na^+/Al lower than 3, and large prismatic crystals at higher alkalinity. From more silicic hydrogels with Si/Al ~10 flat crystallites have been formed [12]. From silica-rich hydrogels, prismatic crystals were observed for Na^+/Al ratio >20 [13,14]. The formation of large prismatic crystals has been reported in the presence of sulfate anions or tetraethylammonium cations [14]. The morphology is also affected by the crystallization kinetics. Evolution of crystal habit from platelets to needles has been observed as a function of the synthesis time [15], and the dissolution rate of the source of silica affects both crystallization kinetics and crystal size [16].

2. Experimental

Syntheses were carried out in the absence of organic templates, in the composition range 0.12–0.30 Na_2O/0.012–0.076 Al_2O_3/SiO_2/13–36 H_2O. The source of silica was a precipitated silica (Rhône Poulenc Zeosil 175, BET surface area 175 $m^2 g^{-1}$, grain size 20–200 μm, H_2O 21%, Na 0.7%, Al 0.16%). The other reagents were $NaAlO_2$ (Carlo Erba), NaOH (Prolabo) and deionized water.

Several procedures for gel preparation were used. In method A, a gel I was prepared by adding the silica to a solution containing 75% of the total NaOH used and 80% of the total H_2O used. A solution II was prepared

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by dissolving the sodium aluminate in a solution containing the remaining NaOH (25%) and H_2O (80%). Solution II was added to gel I under stirring in about 5 minutes. In method B, a suspension I was prepared by stirring the silica in 85% of the total H_2O used for 30 min. A solution II was prepared by dissolving NaOH and $NaAlO_2$ in the remaining water (15%) and added to suspension I under stirring. Method C was similar to method A, except gel I was aged for 24 h under stirring before adding solution II.

In all cases, the hydrogels were aged under stirring for 30 min before sealing in an autoclave for the hydrothermal treatment. Static syntheses at 160 °C for 72–96 h are reported in this communication. The effect of stirring was tested, but no significant correlation was observed, probably due to sticking of the synthesis gel to the stirrer blades. After rapid cooling, the solid was filtered, washed to pH 9 and dried at 353 K. The mother liquor was collected and analyzed for elemental composition by atomic absorption spectroscopy. The solid formed was characterized by X-ray diffraction (XRD; CuKα radiation, CGR Thêta-60 diffractometer), atomic absorption spectroscopy and scanning electron microscopy (SEM; Cambridge Stereoscan 260 microscope). The particle size in the direction of each crystallographic axis was determined as an average of the measurements of nearly 100 appropriately oriented crystals on SEM images.

3. Results and discussion

The method of preparation of the gel did not modify the composition of the crystallized product. The composition of the mordenite crystals formed is shown in figure 1 versus the composition of the synthesis system. The results are quite scattered, but some regions of composition can be observed if the analyses are classified on the basis of the alkalinity of the synthesis system. The alkalinity of the synthesis gel is reported as OH^-/SiO_2, where OH corresponds to the $[Na^+–Al(OH)_4^-]$ balance. The results of figure 1 indicate that, at a given composition of the synthesis gel, aluminum-rich zeolites are formed at higher alkalinity. On the other hand, the same zeolite composition can be obtained from synthesis gels of different composition by varying their alkalinity. At low alkalinity ($OH^-/SiO_2 < 0.2$) the composition of the zeolite formed is nearly equal to the composition of the synthesis gel. At higher alkalinity the zeolites are much richer in aluminum than the synthesis gel.

The range of composition in which pure mordenite has been crystallized, as represented in figure 1, is limited by the formation of other phases [16]. Systems with low aluminum content were often affected by the formation of kenyaite, and no crystalline phase was formed under low aluminum–low alkalinity conditions. Analcime was formed at the highest alkalinity levels.

The increase of aluminum content in the zeolites formed at high alkalinity corresponds to a decrease of the yield of incorporation of silicon, $\eta(\mathrm{Si}) = n(\mathrm{Si})_{\mathrm{zeolite}}/n(\mathrm{Si})_{\mathrm{synthesis}}$, where $n(\mathrm{Si})_{\mathrm{zeolite}}$ and $n(\mathrm{Si})_{\mathrm{synthesis}}$ are the moles of silicon, respectively, in the crystallized zeolite and the initial synthesis gel. The composition of the final zeolite depends on the ratio between the incorporation yields of silicon and aluminum, $\eta(\mathrm{Si})/\eta(\mathrm{Al})$, which is equal to the ratio $(\mathrm{Si/Al})_{\mathrm{zeolite}}/(\mathrm{Si/Al})_{\mathrm{synthesis}}$ between the Si/Al ratios in the zeolite and the synthesis gel. This ratio is shown in figure 2 as a function of alkalinity, for synthesis systems containing Zeosil or Aerosil aged for 30 min before the hydrothermal treatment.

The results of figure 2 show that the ratio between the incorporation yields of silicon and aluminum is inversely proportional to the alkalinity level. Nearly quantitative incorporation of both aluminum and silicon is observed for syntheses at very low alkalinity ($OH^-/SiO_2 \sim 0.1$), whereas at higher alkalinity the incorporation of silicon is much less efficient than the incorporation of aluminum. The increased solubility of silica at higher pH accounts for the decrease of the incorporation yield of silicon, a greater amount of silicate species being left in solution at the end of the crystallization.

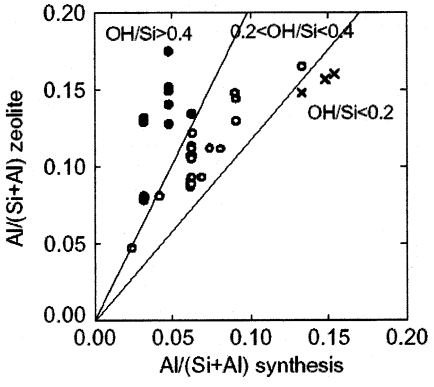

Figure 1. Aluminum content of mordenite as a function of the aluminum content of the synthesis gel. Alkalinity of the synthesis gel (OH^-/SiO_2): (×) <0.2, (○) 0.2–0.4, (●) >0.4.

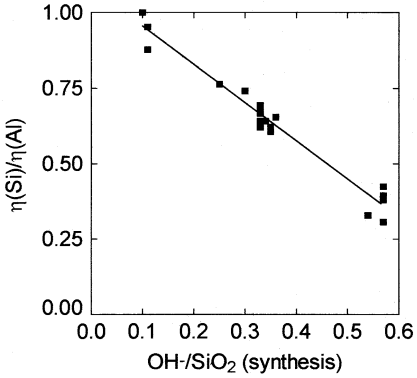

Figure 2. Ratio between incorporation yields of silicon and aluminum as a function of the alkalinity of the synthesis system.

Table 1
Size along the b and c axes of mordenite crystals prepared from a 0.20 Na_2O/0.033 Al_2O_3/SiO_2/13 H_2O gel according to three methods of gel preparation

Method	b (μm)	c (μm)	b/c
A	12	6	2
B	3.5	1.9	1.8
C	4.0	0.6	6.7

Differences of crystal size and crystallization rate for synthesis of mordenite from different silicic acids have been attributed to different dissolution rates of the silica sources [16]. The source of silica seems to play a double role in controlling crystallization kinetics, by controlling the feed of growth units through its dissolution kinetics and by providing sites of heterogeneous nucleation. Both effects are related in some complex way to the surface area of the gel [16]. It has been suggested that the aging time of the gel can modulate the effects of varying the silica source [17]. It is not surprising that the gel preparation procedure can significantly modify the size and morphology of the mordenite crystals.

The size of mordenite crystals prepared from a 0.20 Na_2O/0.033 Al_2O_3/SiO_2/13 H_2O gel according to the three different preparation methods are reported in table 1. The crystals have been measured along the b and c axes. The variations of the method of gel preparation induce large differences in crystal size and morphology. The morphology of the mordenite crystals can be described by the aspect ratio b/c between length (010) and thickness (001), the ratio being larger for thinner crystals. The aging of the source of silica in the preparation medium seems to be an important parameter influencing crystal size and morphology. Any kind of aging of the silica hydrogel before the addition of the aluminate solution (as in methods B and C) decreases the size of the final crystals. This effect corresponds to the availability of a larger number of nucleation sites during the crystallization. A long aging (24 h) of the silica hydrogel in alkaline solution (method C) brings about a significant change in the morphology of the crystals, corresponding to a change in the ratio of the growth rates of the different crystal faces. It is interesting to observe that a 24 h aging of the silica hydrogel brings about a decrease of the crystal thickness by a factor 10 in the direction of the 12-ring pores through which reagents and products diffuse inside the catalyst.

If the gel preparation procedure influences the morphology at a given composition, the composition of the synthesis system can modify the morphology obtained through a given synthesis method. The ratio b/c is shown in figure 3 as a function of the alkalinity of the synthesis system. At low alkalinity flat crystals with a high (010)/(001) ratio are formed. At higher alkalinity thicker crystals are formed, and the (001) thickness becomes larger than the (001) width. A best fit linear correlation is drawn among all experimental points and passes through the error bars at all alkalinity levels. The representation of the linear correlation is clearly non-linear in the logarithmic scale of figure 3.

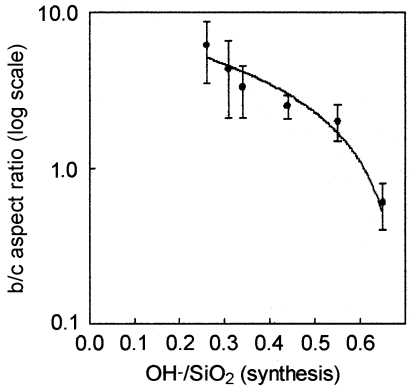

Figure 3. Ratio between width (010) and thickness (001) of mordenite crystals prepared by method A as a function of the alkalinity of the synthesis system. The connecting line is the best fit linear correlation.

Faces (001) present large 12-ring pores, and the crystal shape affects the diffusional constraints, flatter crystals with high b/c ratio allowing a higher efficiency of the catalytic particle. Two different mechanisms, possibly complementary, can be proposed to account for the influence of alkalinity on the morphology:

(a) It has been shown that crystals are flatter at the beginning of the crystallization, evolving towards higher b/c ratio when crystallized mordenite is kept longer in the synthesis solution [15]. It seems possible that, at high alkalinity, this morphological evolution is faster and bulkier crystals are directly observed at the end of the synthesis. In the case of less alkaline media, the morphological evolution would take a longer time, and the initial flat morphology would still be present at the end of the allotted synthesis time.

(b) The growth rates of the various faces can be formally described as a function of supersaturation. All crystallizations take place from gels that are metastable towards mordenite, and it can be assumed that supersaturation increases with alkalinity. In this case, the growth rate of the large-pore faces (001) would depend on alkalinity by a higher-order law than the rate of growth of the essentially non-porous faces (010) and (110). An equivalent description of the phenomenon would take into account that chains of interconnected five-rings run parallel to the c axis. This means that a higher alkalinity makes the growth of existing chains of interconnected five-rings easier than the formation of new chains, implied by the growth perpendicular to the c axis.

4. Conclusions

The composition of mordenite depends on both the aluminum content and the alkalinity of the synthesis

system. The alkalinity of the synthesis system is also an important factor affecting the morphology of the mordenite crystals, but kinetic effects can be used to control crystal size and morphology. The preparation of the hydrogel is a critical parameter to control heterogeneous nucleation in the synthesis system, and the conditions of aging of the silica source before addition of the aluminate solution are critical to obtain the small crystals of mordenite needed for catalytic applications. The problems related to the biphasicity of the synthesis systems are unlikely to be limited to mordenite, and its synthesis can be used as a useful test-bed for the crystallization mechanisms of other zeolites with medium-to-low aluminum content.

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