Journal of Applied Sciences

ISSN 1812-5654

science alert

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Journal of Applied Sciences 7 (5): 720-723, 2007
ISSN 1812-5654

Elaboration and Characterization of High Silica ZSM-5 and Mordenite Solid Microporous Materials

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Abstract: In this study, we were interested to use a hydrothermally method of elaboration of ZSM-5 and Mordenite solid microporous materials. This method is based on crystallization of amorphous gels composed of silicon and aluminium solutions. The elaborations were carried out in stainless steel Teflon lined autoclave over different operation conditions: heating temperature, contact time, pH and agitation of the reactional medium. After crystallization, samples were characterized by several techniques as X ray diffraction, scanning microscopy, infrared spectroscopy. The used method was allowed the obtaining of pure phases of solids belonging to ZSM-5 and mordenite structures respectively. The crystal growth environment during nucleation and crystallization was occurred at the liquid-gel interface in the dispersed gel-solution mixtures. The composition of these structures was found as high silica zeolites.

Key words: ZSM-5, mordenite, microporous materials, crystallization, silica, zeolite

INTRODUCTION

Zeolites are hydrated aluminosilicates having a structure formed by SiO_4 and AlO_4 tetrahedra linked between them by an oxygen atom. Thus, they form three dimensional frameworks of structural formula as follow: $Me_{x/n}(AlO_2)_x(SiO_2)_y)$ w H_2O, where n is the valence of exchanged cation Me, w is the number of water molecules and (x + y) is the total number of tetrahedra per unit cell (Smith, 1963; Baerlocher *et al*., 2001). Many of the interesting properties of zeolites are based on the fact that the framework is anionic and the balancing cations exchangeable. Pure silica ($Si O_2$) framework is neutral, but if some of the tetravalent Si is replaced by trivalent Al to produce an aluminosilicate, the ramework becomes negative and counter ions such as Na^+ are needed to balance its charge (Dyer, 1988; Barrer, 1978).

A very large number of high silica zeolites (Si/Al = 10-100) prepared by direct synthesis have now been reported, including beta, ZSM-5, -11, -12, -21, -34, NU-1 and FU-1 and ferrisilicate and borosilicate analogous of the aluminosilicate structures (Nibou, 1999; Breck, 1974). The intermediate zeolites (Si/Al of 2-5) consist of the natural zeolites erionite, chabazite, clinoptilolite and mordenite and the synthetic zeolites Y, omega and L.

But according to literature, few works were referring to the morphology and form of obtained ZSM-5 and mordenite crystals and the influence of the concentration of SiO_2. Initially, the aim of the present work will be to synthesis and characterization ZSM-5 and mordenite aluminosilcate structures according the hydrothermal crystallization method. In the second place, we will show that the crystal growth environment during nucleation and crystallization was occurred at the liquid-gel interface in the dispersed gel-solution mixtures.

MATERIALS AND METHODS

Elaboration process: Samples of zeolites were prepared by hydrothermal crystallisation (Table 1) at different temperatures, pH and heating times from starting gels of molar composition Al_2O_3. (x) SiO_2.(y) Na_2O. (z) R. (w) H_2O.

As shown in Table 1, zeolites products could only be obtained in the case of samples 2 and 4. As synthesis example, sample 2 was carried out following molar

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Table 1: Synthesis conditions and obtained phases

	Samples				
Molar composition	1	2	3	4	5
Al_2O_3	1	1	1	1	1
(x) SiO_2	100	100	13	13	13
(y) Na_2O	41	41	2.5	2.5	2
(z) R	4	15	-	-	-
(w) H_2O	1000	1834	90	110	110
pH	8	7,5	7,5	8,5	8,5
Time (h)	64	48	72	146	24
T (°C)	150	170	170	160	170
Phase	well not crystallized ZSM-5	ZSM-5	well not crystallized mordenite	Mordenite	Amorphous

reactants 1, x, y, z and w with the pH of the mixtures between 7.5 and 8. The reaction mixture was heated at 170°C and autoclaved for 48 h. After crystallization, the product was washed with distillate water and dried at 100°C. The used reactants are NaOH (Merck), SiO_2 (Degussa, 41%), Al_2O_3 (Catapal, 77%), tetrapropylammonium bromide (Merck, 98%).

Characterization: The obtained phases were characterized by powder X ray diffractometer (Philips PW 1800, using Cu Kα radiation), scanning microscope (Philips XL 30) and infrared spectroscope (Philips PU 9800). The differential thermal analysis was carried out using a M2 BDLSETARAM microanalyser.

RESULTS AND DISCUSSION

Table 1 shows the synthesis conditions of zeolite samples. For samples 2 and 4, pure ZSM-5 and Mordenite (structure code MOR) were obtained. The XRD patterns of as-elaborated samples are given in Fig. 1 and 2. They are in good agreement with that reported by Breck (1974) and the simulated pattern published in the collection of simulated powder patterns for zeolites (Treacy and Higgins, 2001).

Scanning electron micrographs of samples 4 are shown in Fig. 3. Individual hexagonal prismatic crystals (as needle) of about 10-16 μm in length are observed in Fig. 3. The morphology and/or form of zeolite crystals appear generally to be influenced by the concentration of SiO_2, guest molecule type cation and crystal growth inhibitors (Jansen, 2001). A frequently observed crystal form of mordenite is the needle form (with pore channel system parallel to needle direction). According to the synthesis conditions used (Table 1), the favour crystal form seems to be the needle.

Generally, the typical form and morphology of zeolite crystal reveals not only information on the type of the zeolite formed but also on the crystal growth history. There are four cases of crystal growth environment during

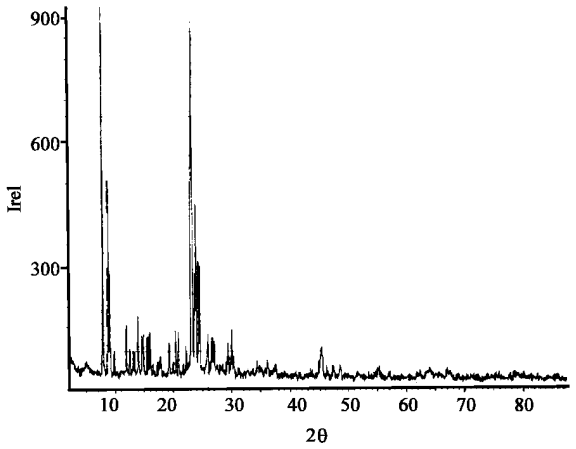


Fig. 1: XRD pattern of as-elaborated ZSM-8 (sample 2)

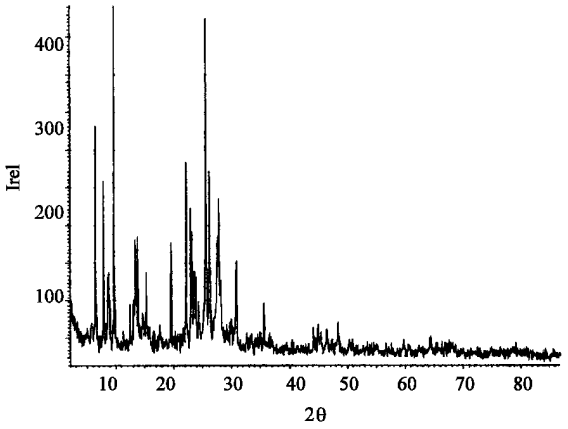
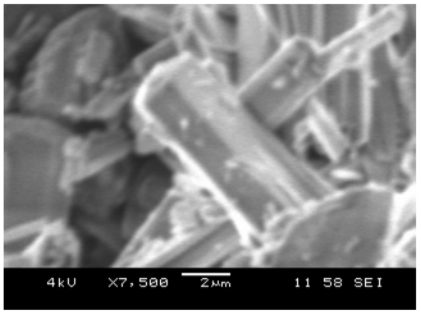


Fig. 2: XRD pattern of as-elaborated Mordenite (sample 4)

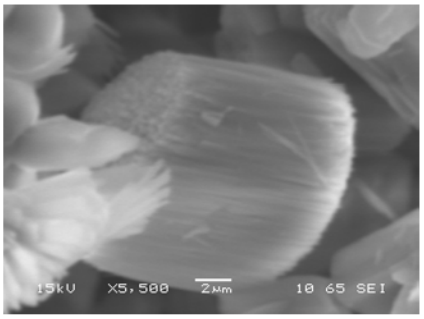
nucleation and crystallization: clear solution, dispersed low density gel, separated high density gel and solid phase (Jansen, 2001).

According to the obtained form of crystallization product shown in Fig. 4 (sample 2), it seems that the nucleation process is heterogeneous and occurs at the liquid-gel interface in the dispersed gel-solution mixtures. These results are in good agreement with those obtained by Kuperman *et al.* (1993).

The anhydrous framework composition found for samples 2 and 4 by chemical analysis is $Na_{0.0497}Si_{0.8962}Al_{0.054}O_2$ and $Na_{0.0964}Si_{0.7978}Al_{0.1057}O_2$, respectively. These results show that Al is essentially substituted for Si only according to the mechanism (sample 4): $2\ Al^{3+} + Na^{+} + (C3H7)3NH2^{+} = 2\ Si^{4+}$. Thus, each aluminium atom incorporated into the framework will generate a Brönsted acid site after removal of the template by calcinations. In the other hand, the cation Na^{+} of mordenite (sample 2) compensates the negative charge of the framework according to the following mechanism: $Al^{3+} + Na^{+} = Si^{4+}$.



(a)



(b)

Fig. 3: Scanning electron micrographs of samples 4 (a) Individual hexagonal prismatic crystals (as needle). (b) Typical needle aggregates of mordenite

Moreover, the investigation by infrared spectroscopy technique in the mid-infrared region of the zeolite spectrum is useful in this regard since it contains the fundamental vibrations of the framework Al, Si-O_4 or (TO_4) tetrahedral. A different vibration bands are observed in the spectra of samples 2 and 4. The first class of vibrations found at 1223-1230, 680-700 and 438-454 cm^{-1} are assigned to the internal tetrahedral. The second group of frequencies observed at 547-546, 446, 792-789 and 1084-1102 cm^{-1} are assigned to the linkages between tetrahedral and the topology of the units of structure of samples.

Figure 5 shows the DTA curve of ZSM-5 (sample 2). Four transformations during the heating are observed at

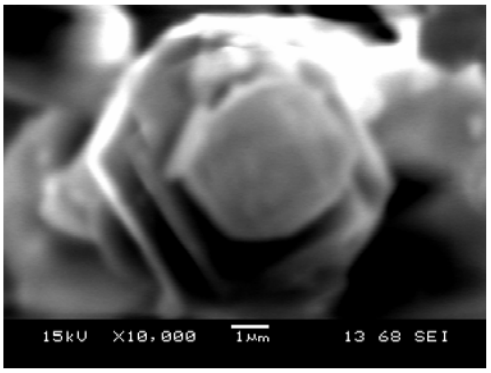


Fig. 4: Scanning electron micrograph of samples 2

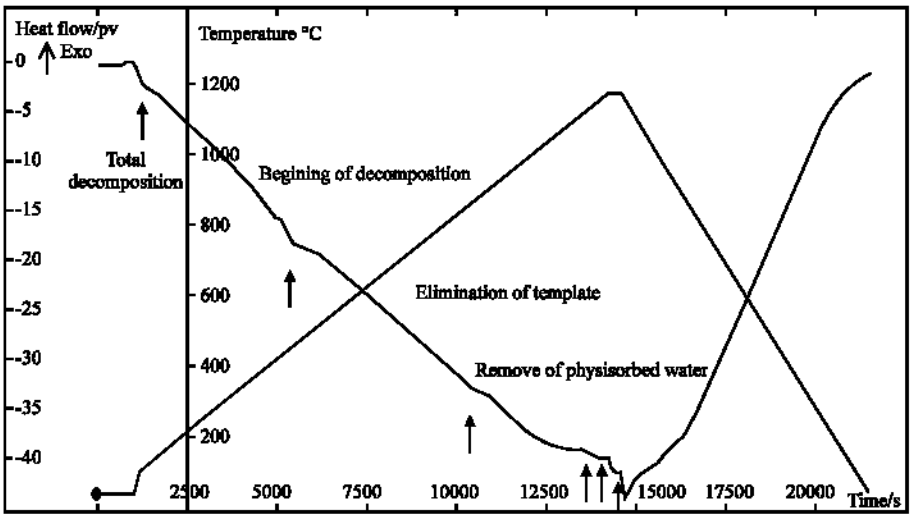


Fig. 5: Thermal decomposition curve (DTA) of sample 2

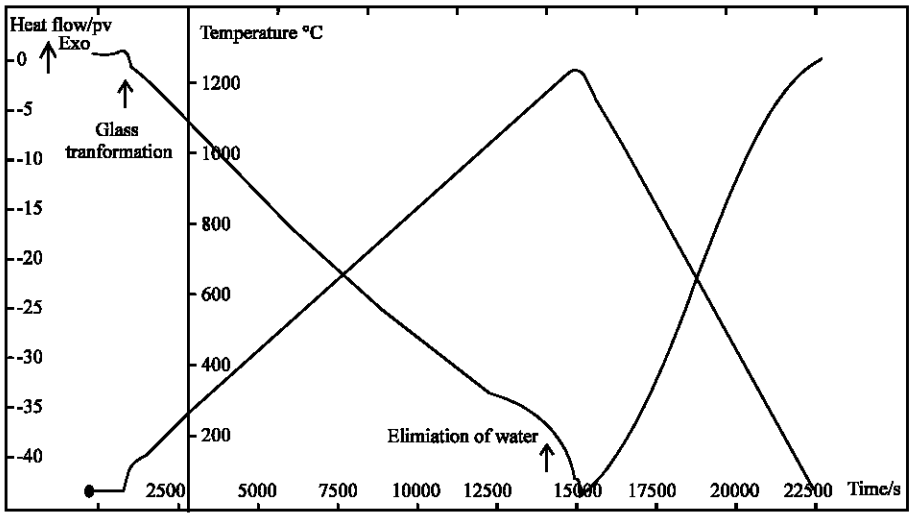


Fig. 6: Thermal decomposition curve (DTA) of sample 4

100-150, 350, 750 and 1200°C. They may be attributed to desorption of water, the oxidation of template, the beginning of framework decomposition and the total decomposition, respectively.

Thus, it seems that ZSM-5 is stable to calcinations to at least 800°C. In the other hand, the mordenite zeolite (sample 4) appears very stable as shown in Fig. 6.

Aside from the broad endotherm which is characteristic of the dehydration of sample 4 at lower temperatures, mordenite exhibits no thermal reactions up to a temperature of about 1150°C. However at 1200°C, a glass transformation was observed.

CONCLUSIONS

The hydrothermal elaboration route leads to well prismatic crystals as needle of mordenite which are very stable to calcinations to at least 1100°C. Scanning electron observations of ZSM-5 showed that heterogeneous nucleation is occurred at the liquid-gel interface in the dispersed gel-solution mixtures. The infrared spectroscopy technique in the mid-infrared region allowed characterizing the fundamental vibrations of the framework Al, Si-O_4 or (TO_4) tetrahedral.

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