

CHARACTERIZATION OF HIGH-SILICA MORDENITE OBTAINED BY DIRECT SYNTHESIS

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Abstract

Three high-silica mordenite zeolites differing in $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio were prepared by direct synthesis without using any template. The products $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is influenced by the starting gel composition. This ratio is increased upon ion-exchange with NH_4Cl and subsequent calcination to prepare protonic mordenite. The protonic mordenites with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of 14.6, 29.2 and 34.6 were characterized by X-ray diffraction, energy dispersive X-ray microprobe analysis, scanning electron microscopy and thermogravimetric analysis. Catalytic cracking of *n*-hexane was studied as a measure of catalytic activity of protonic mordenites. Catalytic activities are expressed as conversion percent of *n*-hexane. Catalysts with higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ were found to be more active.

Introduction

Mordenite is both a naturally occurring and a synthetic zeolite. Its synthetic form typically crystallizes with an $\text{SiO}_2/\text{Al}_2\text{O}_3$ range between 9 and 11 in an Al_2O_3 - SiO_2 - Na_2O - H_2O gel system [1].

Mordenite based catalysts are used as solid acids for various industrially important reactions like cracking, hydrocracking, alkylation and reforming [2-5]. Their dealuminated forms have shown high activity and selectivity for aromatic alkylation [6,7]. For its application as a potential catalyst, mordenite must be prepared in its

acidic form and preferably with a higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio.

Correlation between the silica-to-alumina ratio and catalytic activity in zeolite has been studied [8-12]. It was found that the acidity of zeolite depends primarily on the chemical composition (Si/Al ratio, number and type of cations) and secondly on crystal structure [13-17]. At present, it is generally accepted that an increase in the Si/Al ratio up to a limit increases the conversion of hydrocarbons in a cracking reaction [18]. Therefore, many investigators have tried to increase the Si/Al ratio of their mordenite catalysts (obtaining high-silica mordenite) by removal of framework aluminium. Extraction of aluminium can be readily performed by acid leaching [8, 19] or by combined cyclic thermal and acid treatments [20-23].

Recently authors reported the direct synthesis of high-silica mordenite. Chumbhale *et al.* synthesized high-silica mordenite with an Si/Al ratio of between 10-

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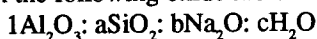
18.5 using tetraethylammonium bromide (TEABr) as a templating agent [24]. In their paper, they compared the properties of the *as*-synthesized high-silica mordenites with those of ones dealuminated by acid leaching. Later, Shiralkar *et al.* reported the direct synthesis of high-silica mordenite in the presence and absence of template [25]. They claimed synthesis of mordenites with an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of up to 25 in the absence of template.

The present work aims to study hydrothermal synthesis of mordenites with a higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the absence of template. We also investigate the catalytic activity of high-silica mordenites prepared by direct synthesis which, to our knowledge, has not been reported previously.

Experimental Section

Zeolite Synthesis

Sodium silicate solution (27% SiO_2 , 8% Na_2O , 65% H_2O , Merck) and aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$, Fluka) were used as sources for silica and alumina respectively. Sodium carbonate (Merck) was used to improve crystallization conditions. The starting gels were prepared with the following oxide mole composition:



Where a, b and c are listed in Table 1.

In a typical gel preparation, 8.0 g of sodium silicate solution was diluted by 20 ml deionized water. To it was added a solution prepared by dissolving 1.47 g aluminium sulphate and 1 g sodium carbonate in 30 ml deionized water. The gel formed was stirred vigorously for one hour. The homogenous gel was transferred to a Teflon-lined stainless-steel autoclave (100 ml capacity) elaborated in our laboratory [26]. The sealed autoclave was then placed in an oven at 170°C for 72 hours, after which it was removed and cooled at room temperature for 30 minutes then washed with cold tap water. The solid products were

filtered, washed with hot distilled water and dried in an oven at 110°C for 12 hours.

Preparation of Active Mordenite

The catalytically active, protonic form of mordenites was obtained by repeated ion-exchange (three times) with 0.5 molar solution of ammonium chloride. The ratio of solution volume/mordenite weight was 40. The final products were filtered, washed and dried at 120°C for 8 hours.

To transform the ammonium form of mordenite (NH_4MOR) into the protonic form (HMOR), samples were calcined at 550°C for 5 hours in a muffle furnace.

Characterization

The chemical composition of the samples was performed by energy dispersive X-ray micro-analysis system. A Philips XL-30 scanning electron microscope equipped with an EDX spectrometer and a computer-based multichannel analyzer were used. The crystalline phase identification was carried out using a Philips PW 1840 X-ray powder diffractometer with $\text{Cu K}\alpha$ radiation. XRD patterns were recorded with an automatic divergence slit adjustment. The *as*-synthesized mordenites were studied by scanning electron microscopy to assess the morphology of crystallites and also to evaluate the extent of amorphous materials in the samples. The *as*-synthesized and protonic forms of mordenites were further characterized by thermogravimetric method with a Polymer Laboratories TG1500 thermobalance. Thermograms were recorded in the range of 25-900°C with ramp of 10°C/min. The protonic form of mordenites was used for catalytic activity measurements. Catalytic experiments were performed in a conventional flow-type, fixed-bed microreactor, details of which are described elsewhere [27].

Cracking of *n*-hexane as a probe molecule was carried

Table 1. Composition of the starting gel, *as*-synthesized and protonic mordenites on the basis of Si and Al

Sample	a	b	c	Si	Al	Si/Al	$\text{SiO}_2/\text{Al}_2\text{O}_3$
MOR-15	15	8.5	1300	76.1	12.2	6.2	12.4
MOR-40	40	15.4	1200	85.8	7.1	12.0	24.0
MOR-60	60	21.0	1200	87.9	6.2	14.1	28.2
HMOR-15	---	---	---	80.6	11.0	7.3	14.6
HMOR-40	---	---	---	87.8	6.0	14.6	29.2
HMOR-60	---	---	---	90.3	5.2	17.3	34.6

a, b and c are molar proportions in the $1\text{Al}_2\text{O}_3; a\text{SiO}_2; b\text{Na}_2\text{O}; c\text{H}_2\text{O}$ systems

out. Samples were first activated *in situ* in a flow of oxygen with a flow rate of 85 ml/min at 500°C. A flow of helium with a flow rate of 18 ml/min saturated with *n*-hexane (water bath thermostated at 30°C) was passed over 30 mg catalyst in the microreactor at 600°C. A 100 microlitre sampling of gaseous products was injected into a GC packed column at 15 min intervals. The products, composed of light hydrocarbons and also non-converted *n*-hexane, were analyzed by a Unicam 4600 gas chromatograph equipped with an FID detector. Catalytic activity is expressed as a fraction of the *n*-hexane converted.

Results and Discussion

Based on our knowledge of the synthesis of mordenites, even though an alkaline medium is necessary to crystallize it, a strongly alkaline solution must be avoided. Therefore, in our procedure no sodium hydroxide other than that contained in the sodium silicate solution was added to the starting gel. Hydrothermal synthesis was proceeded in the presence of some sodium carbonate. Without this modification no product is obtained.

Extent of crystallization of the gel was studied by looking at the XRD pattern of the sample removed at

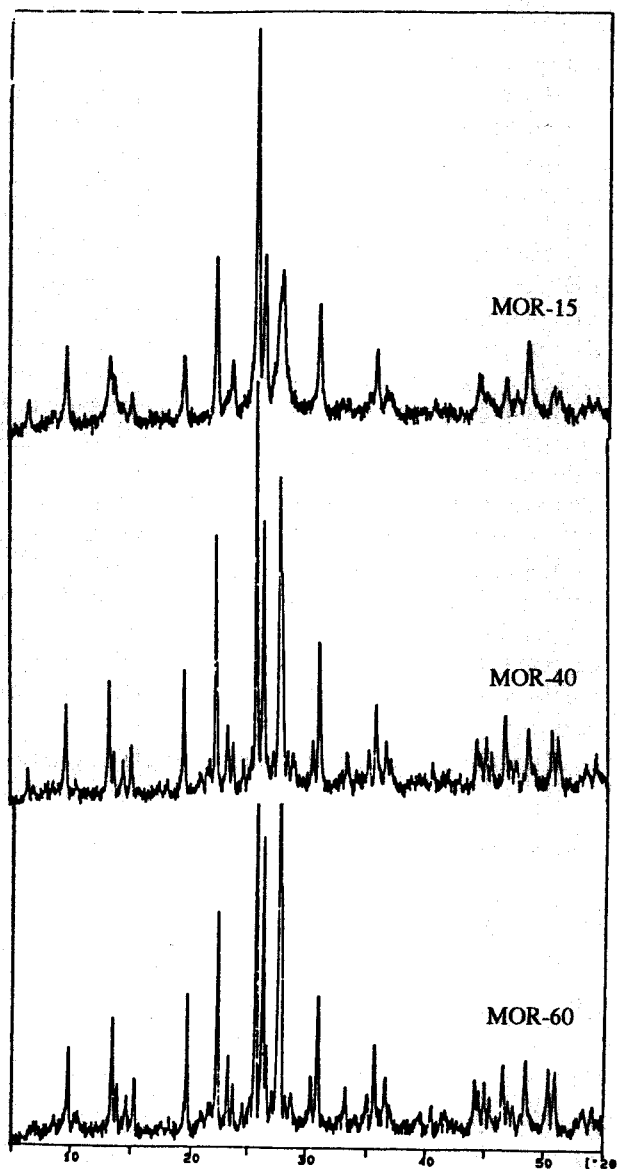


Figure 1. XRD patterns of the α -synthesized mordenites

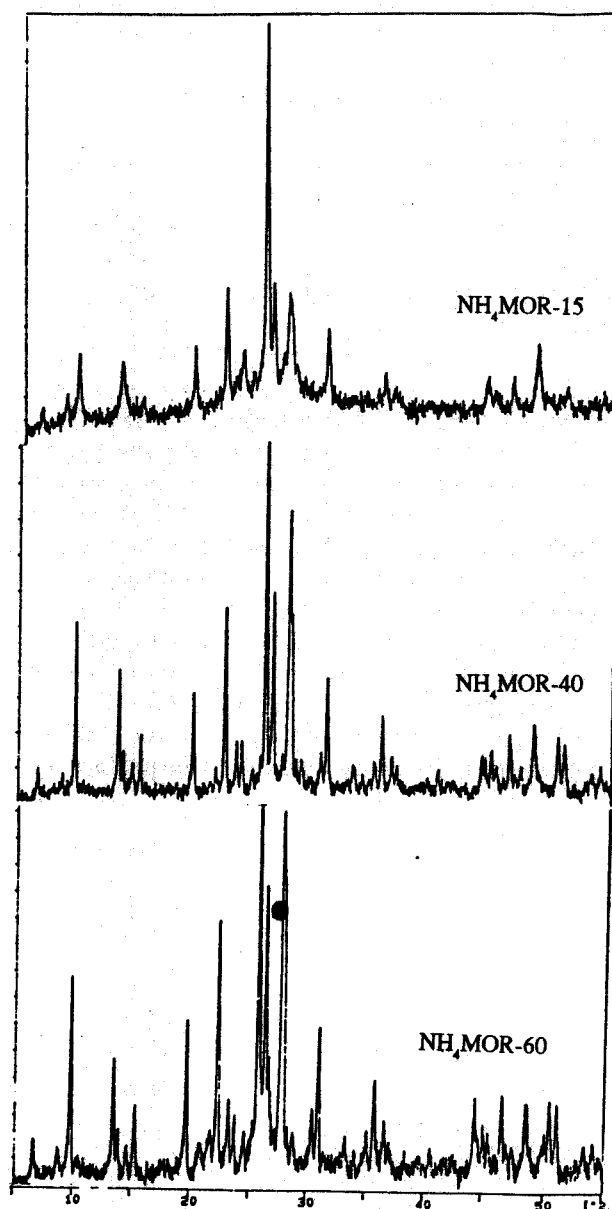


Figure 2. XRD patterns of the NH_4 -exchanged mordenites

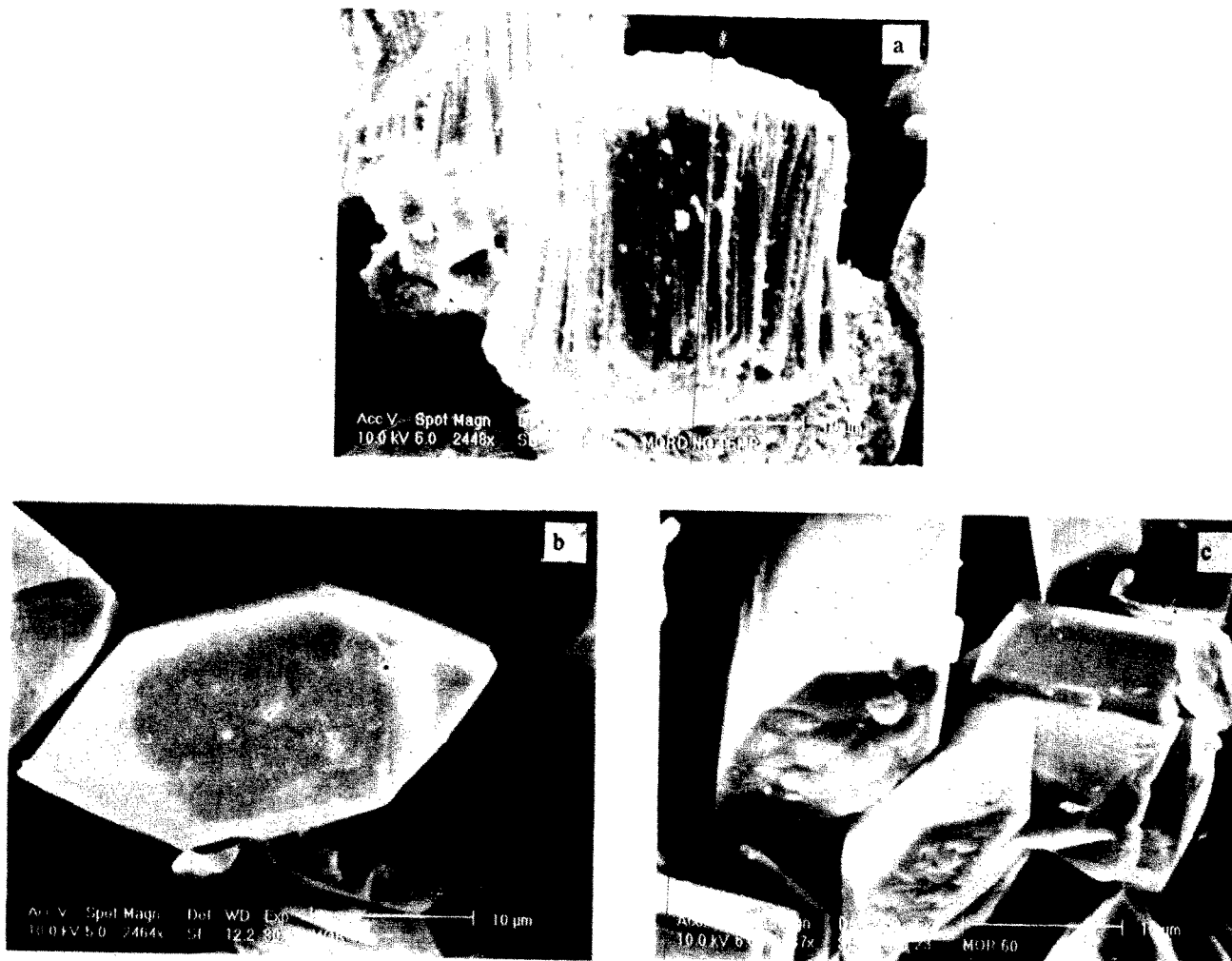


Figure 4. Scanning electron micrograph of the as-synthesized mordenites, a) MOR-15, b) MOR-40 and c) MOR-60

shown in Figure 6. To visualize the effect of Si/Al increasing and therefore stronger acidity, activity was stated as conversion per number of aluminium in the unit cell. Both initial activity ($t=15$ min) and activity after 120 min for the samples with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios have been depicted. Activity of HMOR catalysts is increased with increasing Si/Al ratio. Reduction of acidic site density in HMOR-40 and HMOR-60 (fewer aluminium atoms in the lattice) compared with HMOR-15 has not lowered their activity, on the contrary a considerable increase in activity was observed. This rise is greater for the catalyst with the lowest aluminium content (HMOR-60). Generally accepted justification given for this increase of activity is that in samples with a lower aluminium content, the concentration of acidic sites reduces but their strength increases [31]. This means samples with fewer sites in expense of their strength are more active.

Calculated conversion values for protonic mordenites

after being 120 minutes in contact with stream of feed are shown in Table 2. The results show all samples deactivate gradually. Deactivation in mordenites is attributed mainly to pore blocking by coke formation during reaction [32, 33]. According to the extent of deactivation (Table 2), the more active samples deactivate faster. Less activity reduction in HMOR-60 may be related to the consequence of opposing contribution of diffusion restraints and number of acid sites.

Conclusion

High-silica mordenite can be synthesized directly without the aid of template. Sodium silicate solution as the silica source and aluminium sulphate as the aluminium source were used. Sodium carbonate needs to be added to the starting gel. Upon ion-exchange with NH_4Cl and calcination to produce protonic mordenites, an increase in the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio was observed from EDX data. As-

different crystallization periods. The fully crystalline mordenites were obtained after 72 hours of crystallization time at 170°C.

Figure 1 shows X-ray diffraction patterns of the *as*-synthesized mordenites with different SiO₂/Al₂O₃ ratios in the prepared starting gel. They show characteristic peaks of mordenites having MOR crystal structure [28].

Figures 2 and 3 show XRD patterns of ammonium and protonic forms of the same mordenites respectively. They have been designated NH₄MOR and HMOR. As the patterns show, the crystallinity of the samples is highly preserved after ion-exchange and calcination treatments. The intensities of some reflections change upon ion-

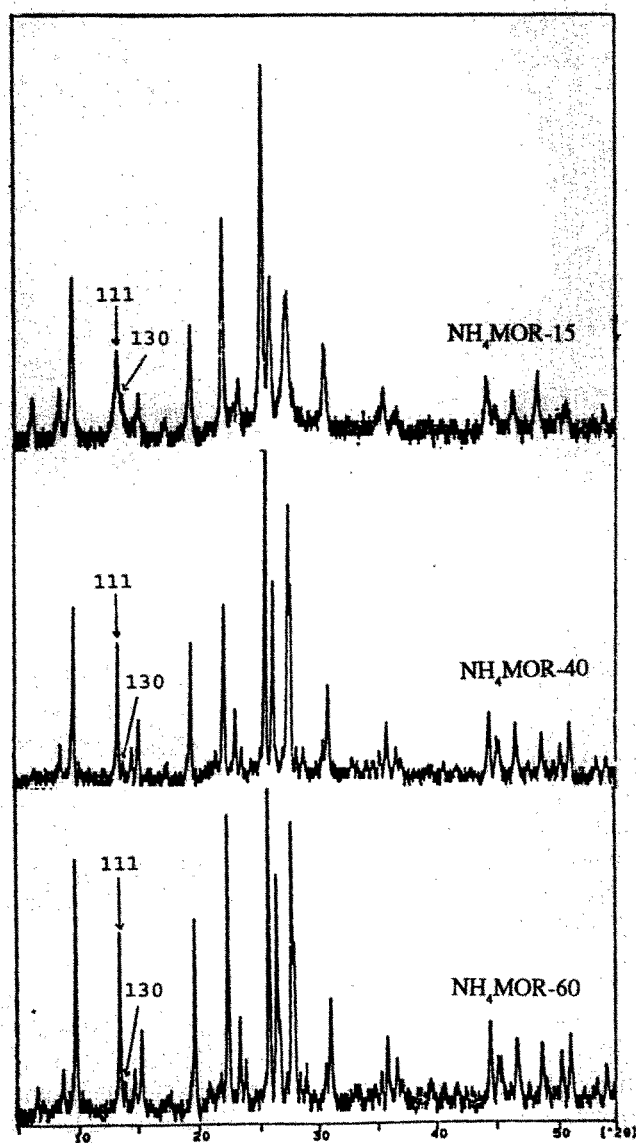


Figure 3. XRD patterns of the protonic mordenites

exchange and calcination and this can be related to the change of cation type and therefore different environments in the mordenite channels.

An interesting feature can be found among the XRD patterns of protonic mordenites. According to Itabashi *et al.*, the ratio between the peak intensities of planes 111 and 130 in acidic mordenite increases with increasing Si/Al ratio [29]. Therefore, the ratio between the intensities of these planes in our samples which correspond to the reflections at $2\theta = 13.42$ and 13.85 clearly shows increased Si/Al ratio in HMOR-40 and HMOR-60 lattices.

Values of the Si/Al ratio for the *as*-synthesized and protonic mordenites are shown in Table 1. It is observed that the nominal quantity of SiO₂/Al₂O₃ in the starting gel is not established in the mordenite lattice. The actual values of SiO₂/Al₂O₃ in MOR-15, MOR-40 and MOR-60 are 12.4, 24.0 and 28.2 respectively. EDX analysis of the protonic samples showed that these ratios increased to 14.6 for HMOR-15, 29.2 for HMOR-40 and 34.6 for HMOR-60. Our studies to inspect this show that a dealumination process took place during heat treatment reducing the surface aluminium concentration and leaving non-structural aluminium within the pores of the zeolites. Miller *et al.* have measured the aluminium contents of their mordenite samples by both elemental analysis and X-ray photoelectron spectroscopy methods. They observed a higher Si/Al ratio for samples calcinated and analyzed by XPS [20]. Obtaining a high-silica (SiO₂/Al₂O₃ higher than 25) acidic mordenite prepared by direct hydrothermal synthesis without the aid of template has not been reported previously.

Figure 4 shows SEM micrographs of the *as*-synthesized mordenites. The crystal morphology of the MOR-15 is different from the two other high-silica mordenites. MOR-40 and MOR-60 have large (10×15 micrometer) hexagonal prisms with flat surfaces whereas MOR-15 morphology is aggregates of long, narrow crystallites with about the same dimension. The crystal morphology is often influenced by different synthesis parameters [30]. Here it can be concluded that higher SiO₂/Al₂O₃ in the MOR-40 and MOR-60 starting gel gives a different crystal morphology from MOR-15.

The structural differences between the *as*-synthesized and also among protonic samples were highlighted by careful thermogravimetric studies of the samples. All *as*-synthesized samples released surface water and zeolitic water at about 370°C whereas protonic mordenites lose these waters much earlier (at about 250°C). Figure 5 shows thermograms of both *as*-synthesized and protonic mordenites. Based on framework charge density and number of crystallographic waters, the differences between water content of the materials are elucidated [27].

Results of *n*-hexane cracking over acidic catalysts are

Table 2. Conversion of *n*-hexane at 600°C over protonic mordenites activated in flow of oxygen at 500°C for 6 hours

Sample	Init. con. t=15 min	Con. after 120 min	Con. reduction after 120 min
HMOR-15	32.4	25.5	21.3
HMOR-40	35.4	26.3	25.7
HMOR-60	37.0	29.0	21.6

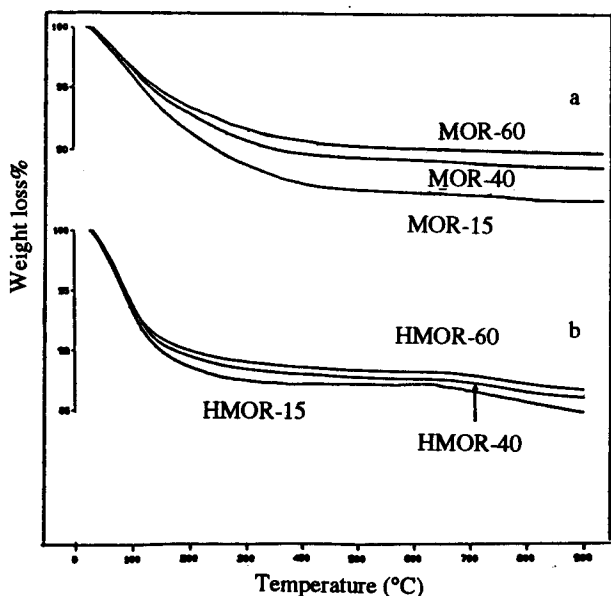


Figure 5. Thermograms of the a) *as*-synthesized and b) protonic mordenites

synthesized samples are highly crystalline and preserve their crystallinity after ion-exchange and calcination treatments. Acidic high-silica mordenites with SiO₂/Al₂O₃ ratios of 14.6, 29.2 and 34.6 prepared by our method show good catalytic activity for cracking of *n*-hexane. The activity is higher for the more siliceous mordenite.

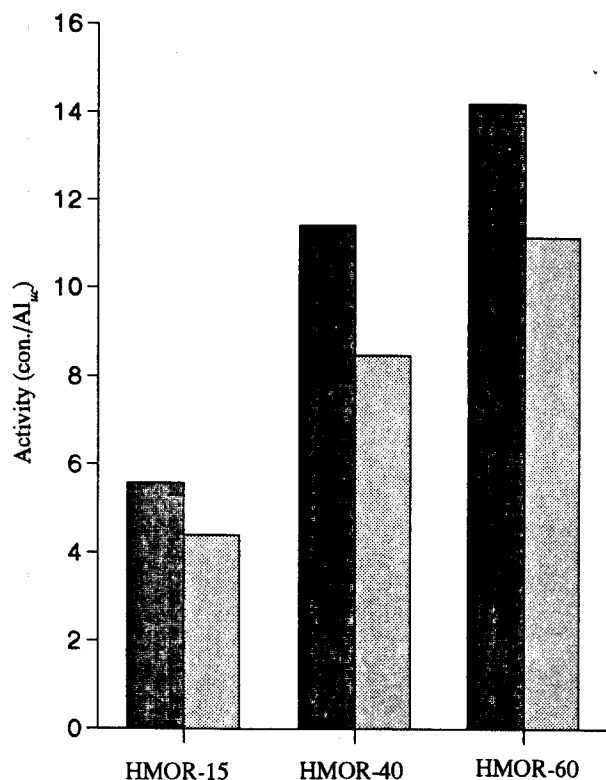
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■ initial conv. t=15 min □ conv. after 120 min



■ initial conv. t=15 min
□ conv. after 120 min

Figure 6. Comparison of conversion of *n*-hexane over protonic mordenites for the initial time (t=15) and after 120 min (for condition of catalytic test see the text)

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