

Direct synthesis and characterization of high-SiO₂-content mordenites

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A direct synthesis of high-SiO₂-content mordenite without addition of organic compounds was studied. The effects of starting raw materials, substrate composition, aging time, and reaction temperature on the crystallization rates were investigated. Morphology, N₂ sorption capacity, surface area, thermal stability of crystals, and hexane-cracking property of the silica-rich mordenite are also reported.

Keywords: Mordenite; synthesis; morphology; thermal stability; cracking

INTRODUCTION

Mordenite has parallel elliptical channels with free diameters of $6.95 \times 5.81 \text{ \AA}$, and its typical unit cell composition is $\text{Na}_8[(\text{AlO}_2)_8(\text{SiO}_2)_{40}] \cdot 24 \text{ H}_2\text{O}$.¹ Mordenite is used in adsorptive separation and in catalysis such as cracking or hydrocracking under severe environments. As a catalyst for the reactions at higher temperatures, and in particular where acidic components are involved, mordenite-type zeolites with high-silica contents are preferred.²

Synthesis of mordenite was recently reviewed extensively by Bajpai et al.³ Synthesis conditions for mordenite are, in general, confined within narrow limits of the SiO₂/Al₂O₃ ratios of the gel; most of the studies on mordenite synthesis were reported with SiO₂/Al₂O₃ ratios ranging from 9 to 12.

The SiO₂/Al₂O₃ ratio of mordenite can be increased by acid leaching of the structural alumina or by steaming treatment, but a direct preparation of mordenite with a SiO₂/Al₂O₃ ratio of 12–19.5 was also reported by Whittemore⁴ and by Ueda et al.⁵ Furthermore, a SiO₂/Al₂O₃ ratio of 25.8 was also claimed when organic bases were used as an additive.⁶

Itabashi et al.⁷ recently reported some interesting correlations among the SiO₂/Al₂O₃ ratio of the silica-rich mordenites, X-ray diffraction patterns and their adsorption properties. In this study, results of further investigations on the synthesis parameters and physicochemical properties of the high-SiO₂-content mordenite prepared directly are presented.

EXPERIMENTAL

Fine silica powder of Zeosil (KoFran Co., 91.8% SiO₂, 8.2% H₂O), sodium aluminate (Junsei Co., 32.6%

Na₂O, 35.7% Al₂O₃), and sodium hydroxide (Junsei Co., 95%) were used for the preparation of substrates, and crystallization was carried out in a stainless-steel tube of 100 ml capacity under autogeneous pressure at 150–170°C without agitation. The composition range expressed as oxide mole ratios was as follows:

$$\text{Na}_2\text{O}/\text{SiO}_2 = 0.1\text{--}1.6, \text{SiO}_2/\text{Al}_2\text{O}_3 = 7\text{--}150,$$

$$\text{H}_2\text{O}/\text{Na}_2\text{O} = 100\text{--}190$$

The crystalline phase of the products was identified using an X-ray diffractometer (Phillips, pw-1700, CuK α , Ni filter), and morphologies were examined using scanning electron microscopy (Hitachi, X-650). The compositions of reactants and mordenite crystals were analyzed using XRF, atomic absorption spectrometry, and wet chemical analysis. I.r. spectra were obtained with a Nicolet 10MX spectrometer, and the thermal stability and the structural change of mordenites were investigated by d.t.a. and XRD after calcination at 700–1200°C.

RESULTS AND DISCUSSION

Figure 1 shows the crystallization curves obtained at different reaction temperatures. An increase in reaction temperature was shown to cause a decrease in induction time and to shorten the overall crystallization time.

Crystals obtained at 170°C after 20 h reaction time exhibited X-ray diffraction characteristics identical to pure mordenite, as shown in Figure 2. Prolonged reaction time (> 96 h) has resulted in α -quartz formation. XRF analysis of the mordenite sample shows a SiO₂/Al₂O₃ ratio of 17.2, and this ratio was again confirmed (within $\pm 10\%$ accuracy) by wet chemical analysis.

The effect of aging time and crystal seeding on the crystallization rates of mordenite are shown in Figure 3. Aging treatment at room temperature had an adverse effect on crystallization rates, and, in addition, longer aging time led to larger mordenite crystals.

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Received 16 October 1990; revised 13 March 1991; accepted 3 April 1991

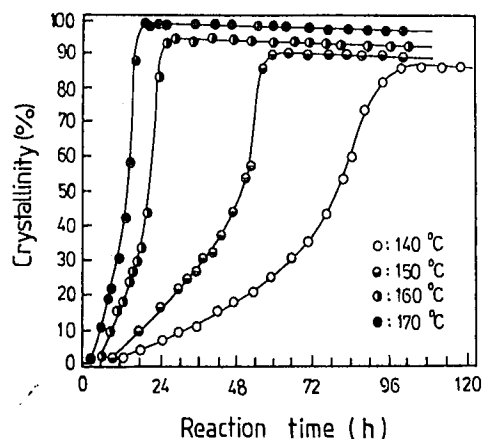


Figure 1 Effect of reaction temperature on the crystallization rates of Na-mordenite from the substrate composition of 6 Na₂O–Al₂O₃–30 SiO₂–780 H₂O (no aging)

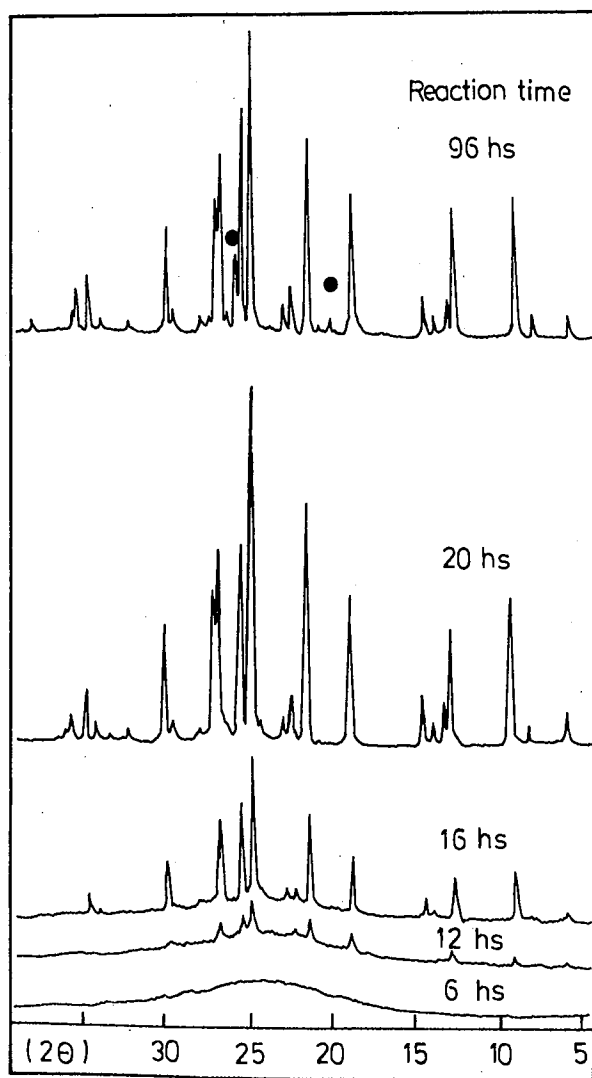


Figure 2 X-ray diffractograms of Na-mordenite at different reaction times. Substrate composition for Na-mordenite: 6 Na₂O–Al₂O₃–30 SiO₂–780 H₂O; no aging; reaction temp.: 170°C; (●) denotes the peaks for α-quartz

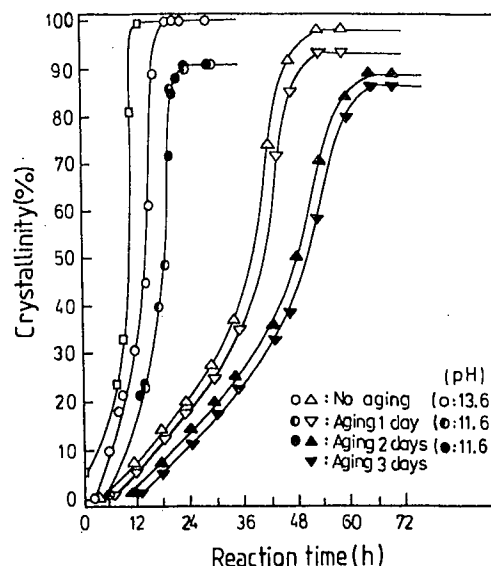


Figure 3 Effect of aging on crystallization rates for the Na-mordenite from the substrate composition of 6 Na₂O–Al₂O₃–30 SiO₂–780 H₂O, using Zeosil only (○, △, ●) and sodium silicate solution (34% of silica) in conjunction with Zeosil (66% of silica) (△, ▽, ▲, ▼) as silica source. Aging temp.: 25°C; reaction temp.: 170°C; (□) no aging and seeded with 5 wt% mordenite

tals. The pH of the substrate decreased significantly during the aging step, as a consequence of the reaction of OH[−] with silica particles producing silanol or soluble silicate ions. Seeding with 5 wt% of mordenite in the reaction batch substantially improved the crystallization rates. Most crystals were thin disk-shaped and the crystal sizes were typically 5–8 μm.

Figure 4 shows the effect of different silica sources on the mordenite crystallization. The degree of crystallization markedly increased with an increase in the contents of amorphous fine silica powder (Zeosil) of the starting substrate. The diameter of particles was about 20 nm. When the Zeosil was added to sodium

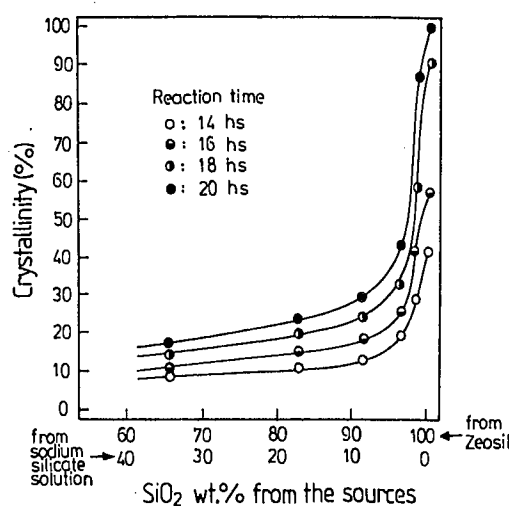


Figure 4 Effect of different silica source on Na-mordenite crystallization. Substrate composition: 6 Na₂O–Al₂O₃–30 SiO₂–780 H₂O; no aging; reaction temp.: 170°C

Table 1 Synthesis of mordenite at 170°C without addition of organic compounds

Run no.	Batch composition	Reaction time	Results
1	2 Na ₂ O-Al ₂ O ₃ -10 SiO ₂ -240 H ₂ O	60 h	100% mordenite
2	4 Na ₂ O-Al ₂ O ₃ -20 SiO ₂ -480 H ₂ O	18 h	100% mordenite
3	6 Na ₂ O-Al ₂ O ₃ -30 SiO ₂ -780 H ₂ O	20 h	100% mordenite
4	8 Na ₂ O-Al ₂ O ₃ -40 SiO ₂ -960 H ₂ O	18 h	45% mordenite
		48 h	100% mordenite
5	16 Na ₂ O-Al ₂ O ₃ -80 SiO ₂ -1600 H ₂ O	72 h	100% mordenite
6	6 Na ₂ O-Al ₂ O ₃ -20 SiO ₂ -600 H ₂ O	18 h	100% mordenite
7	12 Na ₂ O-Al ₂ O ₃ -40 SiO ₂ -1200 H ₂ O	18 h	100% mordenite
8	18 Na ₂ O-Al ₂ O ₃ -60 SiO ₂ -1800 H ₂ O	18 h	95% mordenite
9	24 Na ₂ O-Al ₂ O ₃ -80 SiO ₂ -2400 H ₂ O	48 h	85% mordenite
10	20 Na ₂ O-Al ₂ O ₃ -100 SiO ₂ -6000 H ₂ O	45 h	38% mordenite
11	20 Na ₂ O-Al ₂ O ₃ -100 SiO ₂ -4000 H ₂ O	22 h	20% mordenite + 80% α-quartz

silicate solution to make up the necessary silica contents of the substrate, the crystallization rates and crystallinity of mordenite were found enhanced with increasing weight percentage of Zeosil. This result indicates that the fine silica particles promote the

nucleation of mordenite better than do the dissolved silicate or aluminosilicate ions.

Table 1 lists the results of crystallization with different starting reactant compositions. Initial composition is apparently very important in deciding the zeolite types produced, and, especially, the SiO₂/Al₂O₃ ratio is a critical factor for the species obtained and its yields. In this experiment, mordenites were easily produced in high purity in SiO₂/Al₂O₃ ratios of 8–80. At the SiO₂/Al₂O₃ ratio of 80 (run no. 9), higher crystallinities than those shown in Table 1 could be achieved with extended reaction time.

Itabashi et al.⁷ found that a linear relationship does exist between the SiO₂/Al₂O₃ ratio of the mordenite crystals and the corresponding peak intensity ratios of diffractograms at particular crystalline planes. Figure 5 shows various diffractograms with different substrate compositions, and the peak intensity ratios of (111)/(130) planes are shown to develop progressively as the SiO₂/Al₂O₃ ratio of crystal increases. From our experimental data, we could obtain a linear plot between the peak intensity ratios of (111)/(130) planes and the SiO₂/Al₂O₃ ratio of the crystals, which were confirmed by XRF and the wet chemical method. As shown in Figure 6, this plot was very close to the one prepared earlier by Itabashi et al.⁷ The observed XRD peak intensity changes in the ratio of (111)/(130) plane were explained as a consequence of the atomic position shift and/or occupancies of extra-framework cation and water molecules with different Si/Al ratios of mordenite.⁸

Figure 7 shows the morphology of mordenite with various SiO₂/Al₂O₃ ratios at constant Na₂O/SiO₂ and H₂O/Na₂O ratios. Typical needle-shaped mordenite could not be obtained in this system, and most crystals formed as plates at SiO₂/Al₂O₃ ratio of 20 or 30 (A and B), whereas highly siliceous gels produced flat and prismatic crystals (C and D) with no aggregates of circular crystals being observed.

I.r. spectra of mordenites with different SiO₂/Al₂O₃ ratios are shown in Figure 8. As the Al contents increase, the absorption band near 600, 800, and 1100 cm⁻¹ shift toward the lower frequency region, indicative of increases in unit cell parameters and,

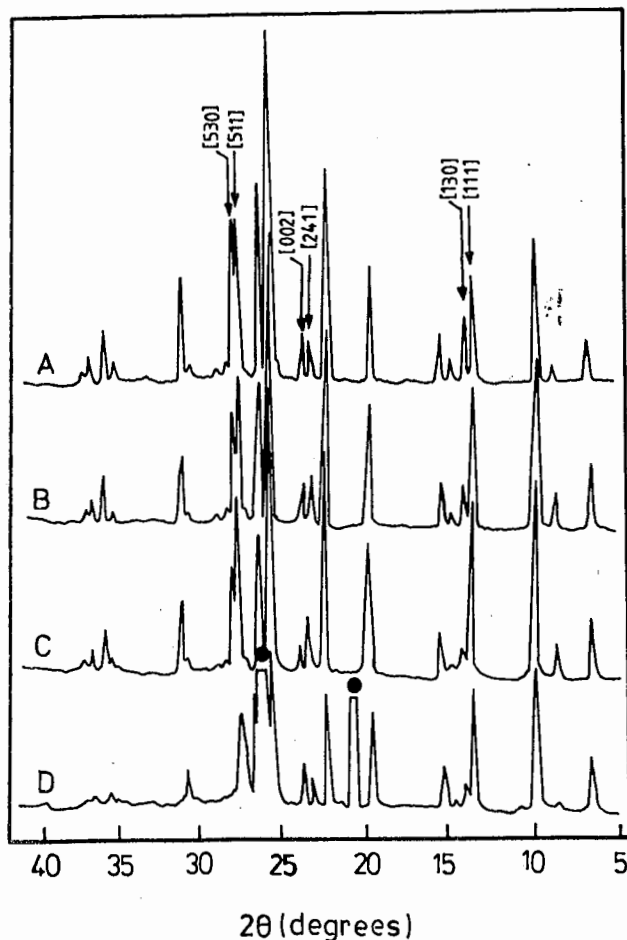


Figure 5 X-ray diffractograms of various products obtained from different substrate compositions: (A) 4 Na₂O-Al₂O₃-20 SiO₂-480 H₂O (SiO₂/Al₂O₃ of crystal = 12.6); (B) 8 Na₂O-Al₂O₃-40 SiO₂-960 H₂O (SiO₂/Al₂O₃ of crystal = 21.9); (C) 14 Na₂O-Al₂O₃-80 SiO₂-1680 H₂O (SiO₂/Al₂O₃ of crystal = 31.5); (D) 20 Na₂O-Al₂O₃-100 SiO₂-2400 H₂O; (●) α-quartz

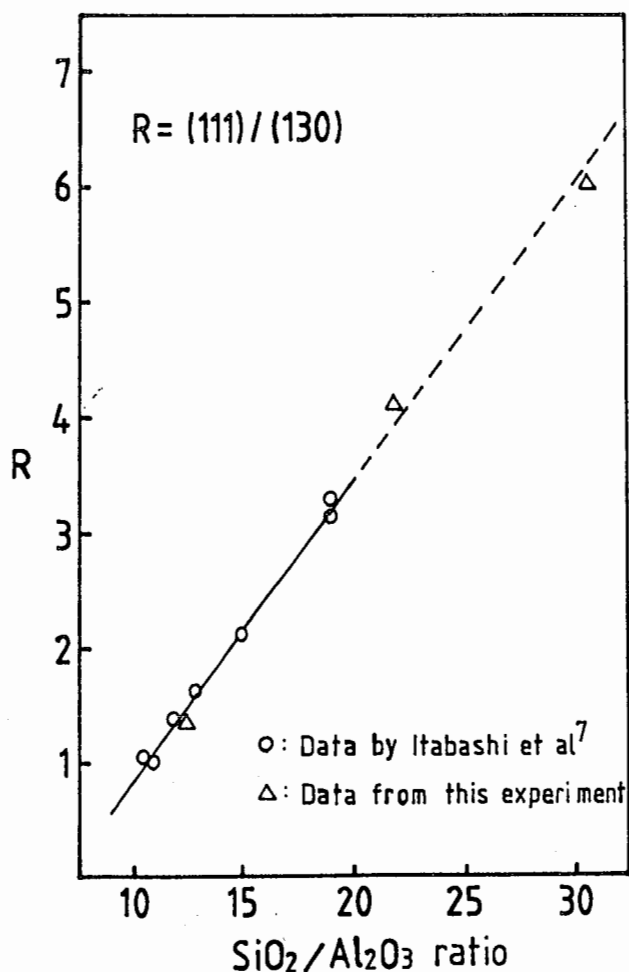


Figure 6 Ratio between peak intensities (R) of (111) and (130) as a function of mordenite SiO₂/Al₂O₃ ratio

consequently the pore structure. It has been well established that the substitution of Al or Fe for Si in the zeolite framework results in an absorption band shift to lower frequency region owing to a longer Al–O (Fe–O) bond distance as compared with the Si–O bond, whereas P substitution due to the shorter tetrahedral P–O distance leads to the absorption band shift to the higher frequency region.⁹ The absorbance of the internal tetrahedral symmetric stretch band near 730 cm⁻¹ clearly decreased with decreasing Al contents in crystals. Similar decreases in the 730 cm⁻¹ absorption band with an increasing SiO₂/Al₂O₃ ratio of mordenite by the acid-leaching process have been reported.¹⁰

Table 2 summarizes the chemical composition, adsorbed N₂ amount, and BET surface area of the mordenite obtained. As the SiO₂/Al₂O₃ ratio of mordenite crystals increased, the adsorbed amount of nitrogen and surface area increased accordingly, as a result of increases in the number of unit cell per gram zeolite as the SiO₂/Al₂O₃ ratio increases. High-silica contents of mordenites are also reflected by decreasing bulk density values, as the SiO₂/Al₂O₃ ratio increases.

Thermal stability of the high-silica mordenite

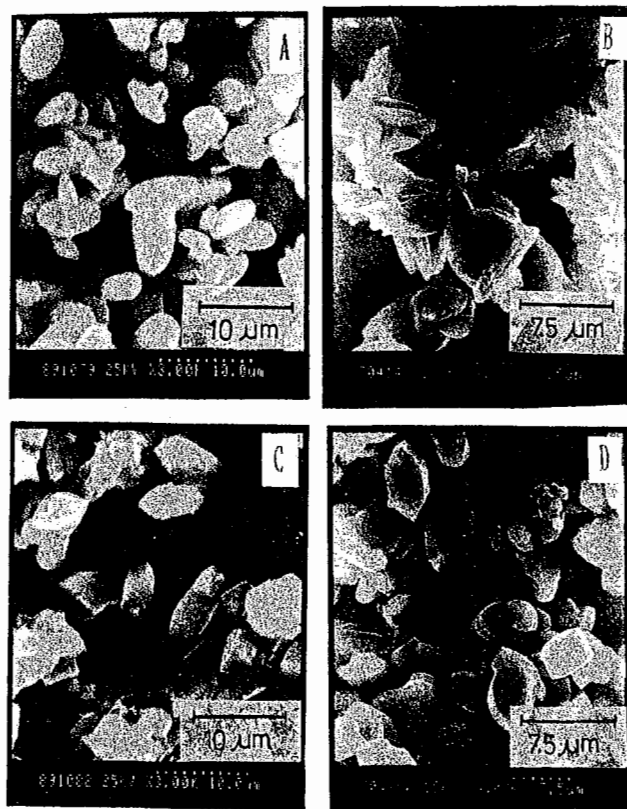


Figure 7 Scanning electron micrographs of Na-mordenite crystals obtained from the following substrate compositions: (A) Na₂O/SiO₂ = 0.3, H₂O/Na₂O = 120, SiO₂/Al₂O₃ = 20; (B) Na₂O/SiO₂ = 0.3, H₂O/Na₂O = 120, SiO₂/Al₂O₃ = 30; (C) Na₂O/SiO₂ = 0.3, H₂O/Na₂O = 120, SiO₂/Al₂O₃ = 40; (D) Na₂O/SiO₂ = 0.3, H₂O/Na₂O = 120, SiO₂/Al₂O₃ = 60. No aging; reaction temp.: 170°C; reaction time: 48 h

obtained was evaluated by differential thermal analysis and by comparing the structural changes of a sample after calcining for 1 h at 700–1200°C. Figure 9 illustrates the increases in thermal stability brought about by increases in SiO₂/Al₂O₃ ratio of the mordenite.

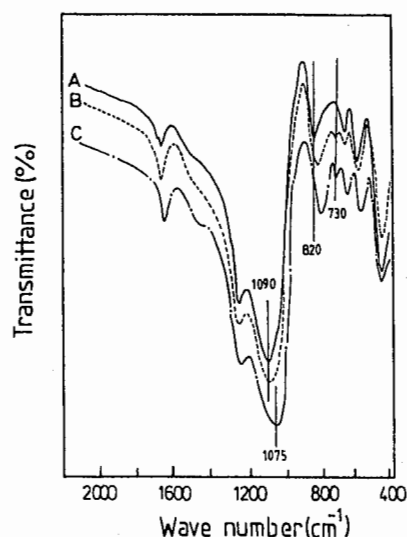
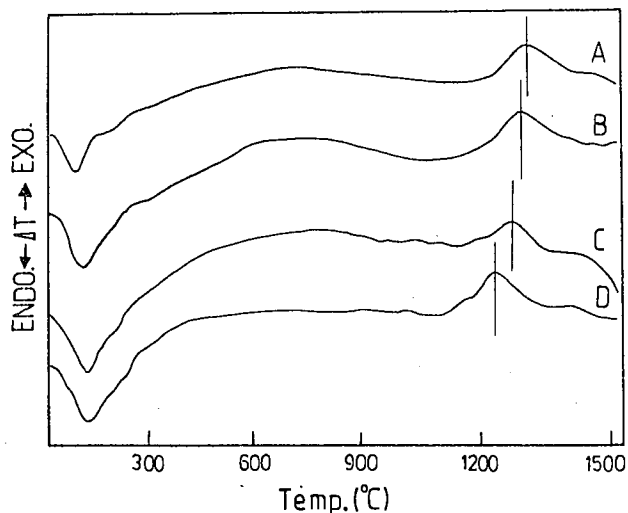


Figure 8 I.r. spectra of mordenite with different silica contents; SiO₂/Al₂O₃ of crystals: (A) 31.5; (B) 21.9; (C) 12.6

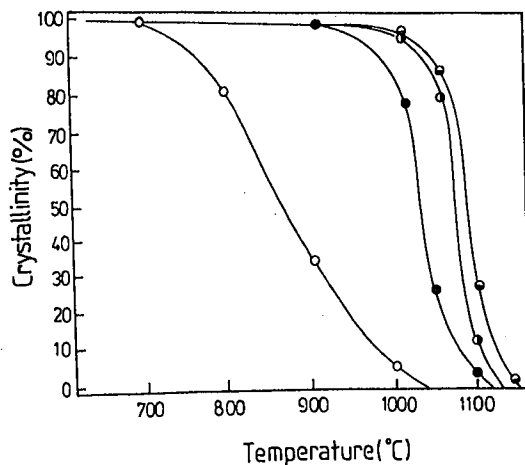
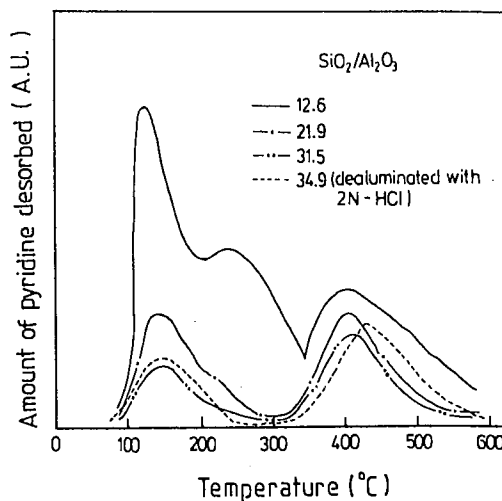
Table 2 Composition, lattice parameters, surface area, and sorption capacity of mordenite with different SiO₂/Al₂O₃ ratios

SiO ₂ /Al ₂ O ₃ ratio of mordenite crystal	Lattice parameters			BET surface area (M ² /g)	N ₂ sorbed (mg/g)	Bulk density (g/cm ³)
	<i>a</i>	<i>b</i>	<i>c</i>			
12.6	18.14	20.49	7.53	338	105	1.75
21.9	18.11	20.45	7.50	365	114	1.42
26.7	18.08	20.29	7.48	393	120	1.36
31.5	18.07	20.29	7.46	405	122	1.29

**Figure 9** Differential thermograms of various mordenites; SiO₂/Al₂O₃ = (A) 31.5; (B) 26.7; (C) 34.9, dealuminated with 2 N HCl; (D) 21.9

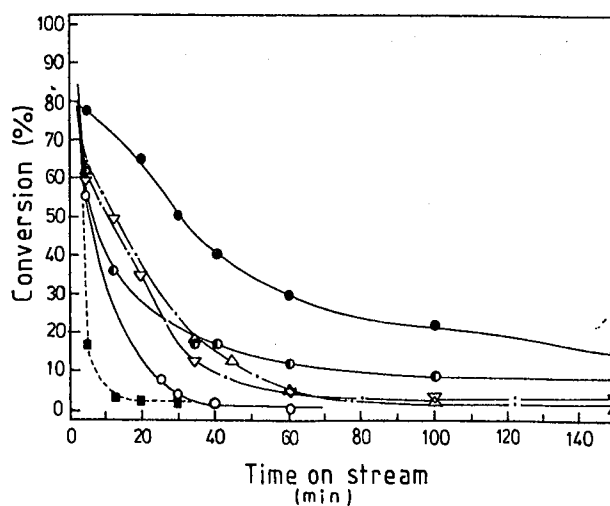
nite crystals. The exothermic peak resulting from the destruction of the mordenite structure has shifted to higher temperature as the SiO₂ contents increased.

In Figure 10, the crystallinity of mordenite (SiO₂/Al₂O₃ = 12.6) started to decrease at 700°C, but high-silica mordenite (SiO₂/Al₂O₃ = 31.5), at 1000°C. Dealuminated mordenite was not as thermally stable as was directly synthesized high-silica mordenite. H-type mordenite also showed a higher thermal stability

**Figure 10** Thermal stability of various mordenites; SiO₂/Al₂O₃ = (O) 12.6, (●) 26.7, (●) 31.5, (●) 34.9, dealuminated with 2 N HCl**Figure 11** Temperature-programmed desorption of pyridine from different mordenites with varying SiO₂/Al₂O₃ ratios; pyridine initially adsorbed at 100°C

compared to the Na type. Beyer et al.¹¹ have reported that dealumination of mordenite by acid leaching can result in a considerable decrease in thermal stability even with the high SiO₂/Al₂O₃ ratios of the crystal.

Typical temperature-programmed desorption (t.p.d.) spectra of pyridine on H-mordenite with

**Figure 12** *n*-Hexane cracking reaction over various H-mordenite catalysts; reaction temp.: 500°C; WHSV: 0.09 h⁻¹; SiO₂/Al₂O₃ ratio of catalyst = (■) Strem. Chem. Co., (O) 12.6, (●) 21.9, (●) 26.7, (▽) 21.3, dealuminated with 2 N HCl; (Δ) 34.9, dealuminated with 2 N HCl

varying SiO₂/Al₂O₃ ratios are shown in Figure 11. The shape of t.p.d. curves was in agreement with the observations made by Hidalgo et al.¹² in the acidity measurement of dealuminated mordenite (SiO₂/Al₂O₃ = 27–71). These spectra showed that the amount of desorbed pyridine increased with increasing Al contents (number of acid sites), and as the SiO₂/Al₂O₃ ratio increased, the peak area ratio of strong acid sites/weak acid sites was increased on the t.p.d. spectra.

The catalytic cracking activity of high-SiO₂-content mordenite and HCl-leached mordenite was measured in the *n*-hexane cracking reaction and the results are shown in Figure 12. With increasing the SiO₂/Al₂O₃ ratio of the mordenite catalyst, increased cracking activity was observed, but deactivation and coke deposition were suppressed significantly with the high-silica mordenites. These results seem to be attributable to the lower concentration of strong acid sites over the high-silica mordenite.

ACKNOWLEDGEMENT

This paper was supported by NON DIRECTED RESEARCH FUND, Korea Research Foundation, 1990.

REFERENCES

- 1 Breck, D.W. *Zeolite Molecular Sieves*, Wiley, New York, 1974
- 2 Benesi, H.A. *J. Catal.* 1967, **8**, 368
- 3 Bajpai, P.K., Rao, M.S. and Gokhale, K.V.G.K. *Ind. Eng. Chem. Prod. Res. Dev.* 1981, **20**, 721
- 4 Whittemore, O.J., Jr. *Am. Mineral.* 1972, **57**, 1146
- 5 Ueda, S., Murata, H. and Koizumi, M. *Am. Mineral.* 1980, **65**, 1012
- 6 Ueda, S., Fukushima, T. and Koizumi, M. *J. Clay Sci. Jpn.* 1982, **22**, 18
- 7 Itabashi, K., Fukushima, T. and Igawa, K. *Zeolites* 1986, **6**, 30
- 8 Shiokawa, K., Ito, M. and Itabashi, K. *Zeolites* 1989, **9**, 170
- 9 Borade, R.B. *Zeolites* 1987, **7**, 398
- 10 Lee, C.Y., Choi, K.Y. and Ha, B.H. *J. Korean Instit. Chem. Eng.* 1988, **26**, 404
- 11 Beyer, H.K., Belenykaja, I.M., Mishin, I.W. and Borbely, G., in *Structure and Reactivity of Modified Zeolites* (Eds. P.A. Jacobs, et al.) Elsevier, Amsterdam, 1984, p. 133
- 12 Hidalgo, C.V., Itoh, H., Hattori, T., Niwa, M. and Murakami, Y. *J. Catal.* 1984, **85**, 362