Synthesis and characterisation of silicious mordenite

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Mordenite, a zeolite, is widely used as adsorbent, catalyst, catalyst support and ion exchanger. The thermal stability and acid resistant characteristics of the zeolite are found to increase with increase of the silica alumina ratio (SAR). Direct synthesis of silicious mordenite using sodium polysilicate, aluminium sulphate and sodium hydroxide without involving templating agent and ageing and their characteristics are presented in this communication. Mordenite having SAR in the range of 11.65-16.07 crystallizes within 6-14 h in the temperature range of 165-185°C. The SAR of the mordenite increases with increase of this ratio and decrease of the Na₂O:SiO₂ ratio in the starting composition. Amorphous material and wairakite are formed when Na₂O:SiO₂ ratio is in the range of 1.96-1.45. Prolonging the reaction time beyond complete crystallization leads to mordenite degradation and formation of amorphous material. The mordenite formed have been characterized by chemical analysis, optical microscopy, particle size analysis, XRD, IR, NMR and thermal analysis.

Mordenite is a widely used naturally occurring zeolite having typical oxide composition, Na₂O·Al₂O₃·9-10SiO₂·6H₂O. It exhibits remarkable thermal stability and acid resistance characteristics. Because of these and other properties derived from the intracrystalline pores, mordenite finds industrial application as selective adsorbent, catalyst, catalyst support and in radioactive waste treatment. R.M. Barrer for the first time synthesised mordenite analogous of the natural one, in composition and adsorption characteristics, by crystallizing a sodium aluminosilicate gel prepared by using a mixture of sodium silicate, silica gel, aluminium hydroxide, water and alkali at 265-295°C temperature. Subsequently, large port mordenites having composition identical to the natural zeolite were synthesized by Sand by using sodium aluminate, sodium hydroxide, sources of silica and water as starting materials in a wide compositional and temperature range. The discovery of synthetic methods for preparing small port mordenite by Barrer and large port mordenite by Sand prompted many others to synthesise the zeolite using various starting materials.

The SAR (silica alumina ratio) of the mordenite can be raised by following various treatment procedures. Several methods have also been reported for direct synthesis of high silica (SAR more than 10) mordenite. Most of these methods employ quaternary organic bases, nitrogen containing organic dyes and transition metal complexes as crystal directing or templating agents. These are expensive, poisonous and require removal from the product mordenite prior to application. Synthesis of silicious mordenite using various combinations of silica sources and without involving any templating agent have also been reported. Most of these methods require ageing, separation and washing of the gel prior to putting for crystallization. Direct preparation of high silica mordenite in aqueous medium without involving templating agent, ageing, separation and washing of the gel using sodium silicate and aluminium sulphate as the silica and alumina source and their physico-chemical characteristics are reported in this communication.

Experimental Procedure

Synthesis—Sodium silicate (AR grade, Wilson Laboratory) obtained as white flakes and aluminium sulphate (GR, E. Merck) were
dissolved in hot distilled water to obtain clear solutions prior to using for the synthesis.

Sodium hydroxide and aluminium sulphate solutions were successively mixed with the sodium silicate solution in a polypropylene beaker under constant stirring at 27-30°C, temperature maintaining overall SiO₂/Al₂O₃, Na₂O/SiO₂ and H₂O:Na₂O mole ratios in the range of 16-51, 0.3801-0.689 and 137-204 respectively. The mixtures were transferred to a stainless steel autoclave and heated for 1-32 h in the temperature range of 150-185°C. The autoclaves were then cooled, contents filtered, washed with deionized water and dried at 100-110°C.

**Characterization**—The crystalline phase identification was carried out by XRD (Phillips model PW 1730) using Cu Kα Ni filter X-radiations. The morphology of the products was determined by scanning electron microscope (JXA B40, JEOL) and the particle size by laser diffraction particle size analyzer (Malvern 3600 E System). The IR patterns were recorded by the KBr pellet method using Perkin-Elmer spectrophotometer, model 580B. The thermal analyses (DTA, TG) were carried out using a Paulik-Paulik Erdey system MOM derivatograph. Around 200 mg of the sample was taken in a platinum crucible and heated at the heating rate of 8°C min⁻¹ up to 1200°C temperature at air atmosphere using calcined alpha alumina as the reference material. NMR spectra of the samples were recorded in a JEOL, GX270, NMR spectrometer equipped with a magic angle spinning attachment.

The mordenite contents in various samples were estimated from water adsorption data determined by using a Cahn electrobalance (sensitivity 0.1 μg). The samples, previously heated at 350°C temperature for 3 h to destroy the water adsorption ability of the amorphous materials were cooled and placed in a desiccator over saturated ammonium chloride solution till equilibrium is attained. Around 50 mg of the equilibrated sample was placed in the pan attached to the electrobalance and heated at the heating rate of 3-4°C per min up to 350°C temperature. The weight loss was simultaneously recorded in the strip chart recorder attached to the balance. Heating was continued till the weight loss became stationary.

The chemical analyses were performed by following standard wet chemical and atomic adsorption (Perkin-Elmer, model 2380) methods.

**Results and Discussion**

Mordenite with SAR 11-16 were obtained in the investigation. The crystallization field of mordenite at 165°C for various concentration of Na₂O, SiO₂ and Al₂O₃ (wt %) is represented in Fig. 1. The circled area in the figure designates the composition region for obtaining mordenite as the

<table>
<thead>
<tr>
<th>Starting composition</th>
<th>Nature of product</th>
<th>SAR of product</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂/Al₂O₃ 16.88</td>
<td>Amorphous material</td>
<td>3.448</td>
</tr>
<tr>
<td>SiO₂/Na₂O 16.88</td>
<td>Mordenite+trace</td>
<td>2.6308</td>
</tr>
<tr>
<td></td>
<td>amorphous material</td>
<td>13.2</td>
</tr>
<tr>
<td>SiO₂/Al₂O₃ 33.96</td>
<td>Mordenite</td>
<td>2.6308</td>
</tr>
<tr>
<td>SiO₂/Na₂O 50.95</td>
<td>Mordenite</td>
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<tr>
<td></td>
<td>Mordenite+very small</td>
<td>16.07</td>
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<td>amorphous material</td>
<td>13.09</td>
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<td>1.4512</td>
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<td></td>
<td>Mordenite+</td>
<td>7.98</td>
</tr>
<tr>
<td></td>
<td>Wairakite+trace</td>
<td>mordenite</td>
</tr>
</tbody>
</table>

Crystallization temperature 165°C, duration 20 h

**Table I—Influence of reactant composition on mordenite formation**

![Fig. 1—Reactant composition for preparing high silica mordenite at 165°C](image-url)
sole crystalline product. Reaction composition beyond the boundary leads to formation of amorphous material or wairakite. Table 1 shows the relationship of starting composition, nature and SAR of the product mordenite. The increase of SAR in the mordenite is not in proportion to the input ratios in the starting compositions. The SiO$_2$/Na$_2$O ratio in the reactant composition is critical for mordenite formation and their SAR. Mordenite does not crystallize even in 20 h when this ratio is 3.448 and at the ratio of 1.96 or below, amorphous material and wairakite are formed, possibly through degradation of mordenite.

The influence of temperature on crystallization of mordenite is presented in Fig. 2 for typical batch composition, 6.4115Na$_2$O·Al$_2$O$_3$·16.85SiO$_2$·1313H$_2$O. Mordenite does not crystallize within 24 h at 150°C but at 165°C, the crystallization is complete in 18 h. The crystallization time may be reduced to 10-6 h by raising the temperature to 175-185°C. Whitemore\(^5\) earlier reported requirement of 18 h at 184°C for crystallizing mordenite of SAR 12.0-19.5. Sodium silicate and aluminium chloride were used for preparation of the gel and it was washed free of the adhered salt before putting for crystallization. The less time required in the present investigation may be due to the starting materials and the presence of sulphate ions in the reaction mixture. Synthesis of siliceous mordenite in presence of various salts acting as mineralizer has been reported in patent literature\(^6\).

Prolonging the crystallization period at any temperature beyond complete crystallization causes mordenite degradation with the formation of amorphous material. Mordenite completely disappears on increasing the duration of crystallization to 24 h at 175°C temperature. The

![Fig. 2—Influence of temperature on mordenite crystallization](image)

![Fig. 3—Scanning electron micrographs of samples containing (a) only mordenite, (b) mordenite with amorphous materials](image)

![Fig. 4—Particle size distribution of some mordenite samples](image)
trend in mordenite crystallization from a starting composition can be depicted as:

Amorphous material → Mordenite → Amorphous material

Itabasi et al.\(^{17}\), earlier observed the same trend in preparation of silicious mordenite using reactive amorphous silica and sodium aluminate.

The sigmoid shape of the crystallization curves as presented in Fig. 2 indicates a long induction period (time taken to form stable nuclei), immediately followed by slow crystallization rate which becomes fast until most of the amorphous materials are converted to crystalline phase. The fast conversion rate of the amorphous material to crystalline product after the onset of the crystallization indicates that the rate limiting step of the overall process is nucleation. The activation energy \( E_n \) for nucleation is determined from the crystallization curves using the expression,

\[
d\ln \left( \frac{1}{\theta} \right) / d(1/T) = -E_n / R
\]

where \( \theta \) is the induction period, i.e., the point on the crystallization curves where the conversion to the crystallization phase is just starting, \( T \) is the temperature and \( R \) is the gas constant.

The calculated activation energy is 11.386 kcal/g mol against 11.0 kcal/g mol reported by Domine and Quobex\(^6\) for mordenite crystallization at 250-290°C from a gel of SAR 10-12 prepared using sodium silicate and aluminium sulphate. The slight difference may be due to difference in SAR of the starting compositions. Bajpai et al.\(^9\) reported 9.5 kcal/g mole for mordenite crystallization of aluminosilicate gel of SAR 10-12 prepared using sodium silicate (prepared using rice husk ash) and silica gel as the silica sources. The low activation energy was attributed to high reactivity of silica of rice husk ash\(^7\). Culfaz and Sand\(^8\) reported 16-24 kcal/g mol activation energy for mordenite crystallization from a batch composition, \(8.5\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 35\text{SiO}_2 \cdot 18\text{H}_2\text{O}\) prepared by using amorphous aluminosilicate of near mordenite composition and sodium silicate as the starting material. The crystallization was done in presence as well as in absence of sodium chloride.

Electron micrographs of (i) sample containing only mordenite and (ii) mordenite containing amorphous material (confirmed by XRD) are presented in Fig. 3. The morphology of the mordenite crystals are quite different from the
impurities and are obtained in the form of agglomerates of small crystals. The particle size distribution of mordenite in a batch varies in a wide range (Fig. 4); 25-45% of the particles are of below 10 micron size.

XRD patterns of mordenite of different SAR are presented in Fig. 5. The background of the peaks in the 2θ region 15-35Å is found to increase with increase of SAR indicating decrease in crystallinity of the product. The intensity of the peak at 13.5Å is also found to decrease with increase of SAR. Itabashi et al.17 also earlier reported changes in intensities of various peaks with SAR of mordenite. The IR spectra of mordenite (800-1400 cm⁻¹) presented in Fig. 6 shows that the bands at 1070 cm⁻¹ assigned to antisymmetric stretching vibrations of the Si(Al)-O bonds21 shift slightly to higher frequency with increase of SAR. The shift is attributed to higher bond strength of Si-O (bond strength 1) than Al-O (bond strength 0.7522).

²⁷Al and ²⁹Si NMR spectra of representative mordenite sample is presented in Fig. 7. The line at 53.75-53.41 of the ²⁷Al NMR spectra characterizes tetrahedrally coordinated Al atoms surrounded by four Si atoms in its second coordination shell23,24. Peaks around -105 and -122 ppm of ²⁹Si NMR are assigned to tetrahedrally bonded Si atoms via oxygen bridge to aluminium atom25,26.

The differential thermal analysis (DTA) and thermogravimetry (TG) curves of a mordenite sample (SAR 16.7) are presented in Fig. 8. The water content (calculated from TG curves) corresponds to 11.46% and is low compared to natural mordenite27 and some synthesised mordenite28. High SAR of the zeolite lowers the amount of charge balancing cation and consequently the water content. The DTA curve exhibits a small exothermic trend in the temperature range of 800-1000°C but does not exhibit sharp exotherm characteristics of distinct structural collapse.

![Fig. 6—IR Spectra of mordenite samples of different SAR](image)

![Fig. 7—(a) ²⁷Al NMR and (b) ²⁹Si NMR spectra of representative mordenite sample](image)
Conclusion

Mordenite having SAR 11.65-16.1 are obtained by reacting a mixture of sodium silicate and aluminium sulphate solution in alkaline medium in the temperature range of 165-185°C for a period of 6-20 h. The activation energy for crystallization is 11.386 kcal/g mol. The SAR of the mordenite is found to increase with increase of input SAR and decrease of Na₂O/SiO₂ ratio in the reactant composition. Mordenite is replaced by maitakite and amorphous material on prolonging the reaction period beyond complete crystallization as well as on maintaining the Na₂O:SiO₂ ratio of the starting composition at 1.45 or below.

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