Synthesis and characterization of mordenite-type zeolites via hydrothermal method using silica gel and sodium aluminate as Si and Al sources at varying temperature

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Abstract. Mordenite-type zeolites were prepared via hydrothermal method using silica gel and sodium aluminate as Si and Al sources respectively. The temperature was varied from 150 °C up to 190 °C to determine the minimum temperature to obtain crystalline mordenite using a 23 mL Teflon-lined stainless-steel autoclave. The samples were characterized using XRD, FTIR and SEM. With the given experimental conditions, mordenite-type zeolites with good crystallinity and excellent purity were produced at 190 °C. Amorphous materials with notable peaks that correspond to mordenite planes were produced at 170 °C. The sample produced at 150°C was completely amorphous. FTIR revealed that all the three samples contain bands associated to aluminosilicate vibrational groups. However, a significant decrease in the intensities of vibration bands associated to hydroxyl (HO) stretching and water bending were observed as the temperature is decreased. From the SEM, the sample treated at 190°C was composed of particles with strikingly linear edges having an average grain size of ~38.0 μm. Most particles are hexagonal in shape. Particle components of the samples synthesized at 170 °C and 150 °C have irregular sizes and shapes.

1. Introduction

Mordenite is a naturally occurring zeolite mineral that has vast range of applications in catalysis including hydrocracking, hydroisomerization, alkylation, reforming and dewaxing [1-3]. It is also used in the separation of gases and liquids [4] and in the adsorption of various pollutants like ammonium and heavy metals [5-6]. Moreover, it is considered as an effective support for semiconductors, chemical sensors and nonlinear optical materials [7]. Although the uses of natural mordenites are widespread, synthetic mordenites are favored in certain applications that need specific morphology and/or property and require minimal impurities that might interfere in its functions.

Mordenite has an orthorhombic structure with a unit cell dimensions of \( a = 18.121 \, \text{Å} \), \( b = 20.517 \, \text{Å} \), \( c = 7.544 \, \text{Å} \) belonging to Cmcm space group. [8] It has two channel systems, a 12-membered ring (MR) elliptical pore channel (6.7 × 7.0 Å) which runs parallel to the \( c \)-axis, and a smaller 8-MR channel which runs parallel to the \( b \)-axis (2.6 × 5.7 Å). The crystal structure consists of chains of 4-
and 5-MR of Si(O/2)₄ and Al(O/2)₄ wherein 5-MR predominate [9]. The high SiO₂/Al₂O₃ ratio, usually greater than or equal to 5, results to excellent thermal and chemical stability [10].

Mordenites are typically synthesized via hydrothermal method. The studies regarding the different aspects of the synthesis are so vast. There are extensive literatures that exploit various chemicals, natural materials and even waste products in the production of mordenites including but not limited to active alumina, silicic acid, sodium silicate, sodium aluminosilicate, amorphous silica, kaolin, rice husks and waste glasses [11-14]. Several reports focus on the control of the crystallite size [15-18] and on the modification of the morphology [15] of mordenite. There are articles that propose or suggest techniques that could reduce harmful effects brought by upscale production of the material to the environment [19]. There are also numerous studies that determine the optimum parameters (i.e. duration of crystallization time, water content, pH level, precursor ratio) that could lower the energy consumption [20-22]. These aspects were very necessary especially in industrial-scale applications to lower the production cost. Though there are many literatures regarding the synthesis of mordenites, the selection of the most cost-effective temperature is usually overlooked. In some studies, though this aspect is considered, the minimum temperature required for the formation of crystalline mordenite is different from other reports. This is because the precursors as well as the hydrothermal system used are not similar. With these, it is necessary to investigate the minimum temperature required for the formation of mordenite for each type of system and/or precursor.

In this study, the minimum temperature in the production of crystalline mordenite-type zeolites via hydrothermal method were determined for a hydrothermal system composed of a 23 mL Teflon-lined stainless-steel autoclave. The starting gel solutions were prepared using silica gel and sodium aluninate as precursors with molar composition of 6Na₂O:Al₂O₃:30SiO₂:780H₂O as provided by the International Zeolite Association (IZA) for the preparation of synthetic mordenites [23].

2. Experimental Methods
Mordenite-type zeolites were synthesized through hydrothermal method using a starting solution with molar composition of 6Na₂O:Al₂O₃:30SiO₂:780H₂O. In a typical preparation, 1.95 g of prepared 25 wt % sodium hydroxide (NaOH) solution [pellet, Macron Fine Chemicals] was diluted with 16.69 mL of deionized water. Half of the solution was used in dissolving 0.25 g of sodium aluninate [anhydrous, Sigma-Aldrich, Al (Al₂O₃): 50-56%, Na (as Na₂O): 40-45%] while the other half was used in dissolving 2.37 g of silica (SiO₂) gel [high purity grade, Sigma-Aldrich, 99%, pore size 60 Å, 60-100 mesh] by means of magnetic stirring (300 rpm) for 30 min. The two solutions were mixed at 600 rpm for 120 min and transferred to a PTFE-lined stainless-steel autoclave with a total capacity of 23 mL. The system was placed in a preheated oven at temperatures 150, 170 and 190°C for 24 h and then cooled rapidly by quenching with running water for few minutes.

The products were washed with deionized water until the pH was reduced to 9 or less. For samples which are in the form of pellet, these were air dried for at least 2 days and ground for 5 min using mortar and pestle. Finally, the products were dried in oven at 90°C overnight and sieved using a commercial silkscreen to filter large particles.

The synthesized products were analyzed with an X-ray diffractometer (SHIMADZU, XRD-7000 Maxima) using Cu Kα (1.5406 Å) radiation to check their composition and/or crystal structure. Continuous scan were conducted, typically from 3.00 up to 90.00° with a speed of 2.00°/min. FTIR analysis (SHIMADZU, IR-PRESTIGE-21) was done to determine the vibrational groups present in the samples and to further confirm if the desired product was obtained. The powder samples were mixed with KBr (HIMEDIA, Potassium Bromide, A.R., 99%) in a 1:10 ratio and ground for 5 min before undergoing IR analysis with an attenuated total reflectance (ATR) accessory. Finally, scanning electron microscopy (JEOL, JSM 6010LV) was used to observe the morphology.
3. Results and Discussion

3.1. Structure and crystallinity

The XRD patterns of the products synthesized at different temperatures are shown in figure 1. Hydrothermal synthesis for 24 h using the starting solution of molar composition 6Na₂O·Al₂O₃·30SiO₂·780H₂O produced amorphous products at 150°C which suggests insufficient energy for the crystallization of mordenite. At higher temperature equal to 170 °C, partially crystalline products were synthesized. Broad peaks at 2θ = 13.45, 19.61, 22.20, 25.63, 26.25 and 27.67° were observed. These peaks were attributed to the planes (1 1 1), (3 3 0), (1 5 0), (2 0 2), (3 5 0) and (5 1 1) of Na-type mordenite (amcsd 0003444) [24]. All peaks were associated to the same material as matched with the diffraction pattern of reference mordenite. At 190°C, the starting solution was completely transformed into mordenite structure without traces of other zeolitic impurities. It has also good crystallinity as implied by the significant reduction of the background noise in its diffractogram. Thus, the experiment confirms the result of previous study that states possible crystallization of mordenites at this temperature [20]. The results, however, show disagreement with other published articles that report the production of crystalline mordenite at 170°C using the same method with similar molar ratio of the starting gel [14,18]. Using Scherrer’s equation (see Appendix for the computations), the crystallite size of the sample treated at 190°C was found to be equal to 6.64 Å.

3.2. Vibrational groups

Figure 2 shows the transmittance spectra of the KBr and the products synthesized at the indicated temperature. For the sample treated at 190 °C, there are four major bands present; i) a broad band from 3671 cm⁻¹ to 3051 cm⁻¹ that centered around 3428 cm⁻¹ is attributed to the asymmetric stretching of hydroxyl bonds (OH), which is an indication of the moisture content, [17] ii) a narrow band with medium intensity which centered around 1629 cm⁻¹ is due to the usual bending vibration of water molecules attached to the zeolite framework, [17] iii) a band at 1224 cm⁻¹ which represents vibration of external asymmetric TO₄ (T=Al, Si). [22] This vibration determines how well Si and Al atoms are arranged in tetrahedra forming the mordenite framework and lastly, iv) an intense peak at around 1047 cm⁻¹ which is due to the internal anti-symmetric stretching vibration of the tetrahedral (T-O) bonds [25]. Additionally, a low intensity peak located at around 790.8 cm⁻¹ is a characteristic vibration of symmetric stretching of the (T-O) bonds [25]. The existence of these bands in the IR spectra of the synthesized sample at 190°C signifies the presence of zeolitic and/or aluminosilicate materials. The bands in the range 2679 cm⁻¹ to 1825 cm⁻¹ are characteristics of the KBr used and should not be confused with the vibration bands of the samples.

![Figure 1](image1.png)  
*Figure 1. XRD patterns of the synthesized products at varying temperatures.*

![Figure 2](image2.png)  
*Figure 2. FTIR spectra of the KBr and the synthesized products at varying temperatures.*
As the crystallization temperature is decreased, the intensities of the bands associated with the asymmetric (OH\(^-\)) stretching at 3428 cm\(^{-1}\) and water bending vibration at 1629 cm\(^{-1}\) weakened. This suggests that the holding capacity for water is decreased. Take note that zeolites including, mordenite-types, have high water storage capacity. The lower adsorbed moisture among the samples synthesized at lower temperatures suggests lesser amount of crystalline mordenite. The increase in the intensities of peaks associated to the internal anti-symmetric stretching vibration of the tetrahedral (T-O) bonds at 1047 cm\(^{-1}\) and symmetrical stretching of (T-O) bonds at 790.8 cm\(^{-1}\) for samples synthesized at lower temperatures indicates greater amount of amorphous phases (i.e. dehydrated amorphous aluminosilicates/ silicates).

3.3. Morphology

![SEM images of the synthesized products at temperatures (a) 190, (b) 170 and (c) 150 °C.](image-url)

**Figure 3.** SEM images of the synthesized products at temperatures (a) 190, (b) 170 and (c) 150 °C.
The SEM images of the powdered products synthesized at various temperatures are shown in figure 3. The sample synthesized at 190 °C is initially in the form of a pellet as recovered from the autoclave and was ground for 5 min prior to characterization. The sample is comprised of particles or grains with strikingly linear and well-defined edges. There are substantial number of particles that have hexagonal shapes, though most have irregular size and shapes. Some grains appear to be fragmented or damaged which probably brought by grinding. The grains crystals have width of ~20 µm and length of ~38 µm. The grains agglomerated together due to high pressure upon hydrothermal treatment that resulted to the formation of the pellet. Generally, the sample represents a typical prismatic morphology of mordenites [15].

At 170 °C, the micrographs showed varied sizes and irregularly-shaped particles. The bulk particles have rounded edges and contain few holes which are possibly amorphous mordenite and/or remnants of the dehydrated amorphous aluminosilicate hydrogel. Several particles have oblong or elongated shapes which are speculated to be mordenite grains that caused the peaks on the XRD pattern of the sample. The powder prepared at 150 °C is made up of particles with irregular size and shapes. Perhaps, these are amorphous aluminosilicate materials which were unable to transform into mordenite due to the inadequate energy.

4. Conclusions

Mordenite-type zeolite was prepared via hydrothermal synthesis using silica gel and sodium aluminate as Si and Al sources respectively. With the existing system for hydrothermal treatment, a Teflon-lined stainless-steel autoclave with 23 mL maximum capacity, the minimum temperature to produce mordenite with good crystallinity and excellent purity was 190 °C for a 24 h heating. The inadequate energy caused incomplete crystallization at 170 °C. Heating at 150 °C resulted to amorphous aluminosilicate materials. FTIR showed the presence of the usual vibrational groups of zeolites in the samples indicating the successful formation of zeolitic structures. It was also noted that the sample synthesized at 190 °C is the most crystalline. Scanning electron micrographs showed that the sample treated at 190 °C is composed of particles with strikingly linear edges which are mostly hexagonal in shape. The grains have width of ~20 µm and length of ~38.0 µm.

5. Appendix

The peaks at 22.20° and 25.63° representing planes (1 5 0) and (2 0 2) of mordenite respectively, were considered for the calculation of the crystallite size because these were the planes with the highest intensity. The crystal size \( L \) was computed using the Scherrer’s equation given as

\[
B(2\theta) = \frac{KL}{\lambda \cos \theta} B(2\theta) = K\lambda/L\cos \theta
\]

where \( B \) is the full width at half maximum (FWHM) of the peak located at \( 2\theta \), \( \lambda \) is the radiation wavelength used by the X-ray diffractometer (Cu \( K_\alpha \), 1.5406 Å) and \( K \) is the Scherrer’s constant which varies from 0.6 to 2.08 depending on the crystal morphology. For simplicity, its value is assigned to as 1. Table 1 shows the FWHM of the two peaks and their corresponding crystallite size ratio.

| Plane  | \( 2\theta \) (°) | FWHM | \( L \) (Å) |
|--------|------------------|------|-------------|
| (1 5 0) | 22.38            | 0.230| 6.41        |
| (2 0 2) | 25.80            | 0.217| 6.86        |
|        | **Average crystallite size** |      | **6.64**    |
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