



Original Research Paper

Synthesis of mordenite zeolite in absence of organic template

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ABSTRACT

Mordenite is a zeolite that has been used as a selective adsorbent and as a catalyst. Mordenite zeolite with crystal diameter 65 nm and crystal length 7 μm was successively synthesized in the absence of organic template by hydrothermal method at 180 °C for 5 days after stirring at high speed and aging in the synthesis mixture with the molar composition of $12\text{Na}_2\text{O}:100\text{SiO}_2:2\text{Al}_2\text{O}_3:500\text{H}_2\text{O}$. The produced samples were investigated using XRD, SEM, FT-IR, EDS, DTA/TG and BET surface area. The prepared sample, crystallized in needle shape crystals. Total (BET) surface area was 52.14 m^2/g whereas, total pore volume was 0.2 cm^3/g . Average pore diameter was 24.16 Å. Thermogravimetry analysis (DTA/TG) showed that, at room temperature to 800 °C, mordenite mass loss is 6%.

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1. Introduction

Mordenite is a zeolite with an ideal composition of $\text{Na}_8\text{Al}_8\text{Si}_{40}\text{O}_{96}\cdot n\text{H}_2\text{O}$. The unit cell of sodium mordenite has dimensions a : 18.121 Å, b : 20.517 Å, and c : 7.544 Å [1]. The most common morphology of mordenite is characterized by needles with c direction elongation [2]. The micropore system of mordenite consists of two pore channels; an elliptical pore channel (6.7 \times 7.0 Å) which runs parallel to the c -axis and, another pore channel which runs parallel to the b -axis (2.6 \times 5.7 Å) [3]. Due to its high thermal and acid stability, mordenite has been used as a catalyst for important reactions such as hydrocracking, hydroisomerization, alkylation, reforming, dewaxing, and the production of dimethylamines [4,5]. Mordenite has also been used in the adsorptive separation of gas or liquid mixtures [6]. In addition, mordenite has been considered for applications in semiconductors, chemical sensors, and nonlinear optics [7]. Nanosized zeolites are important in catalytic and adsorptive applications. Smaller crystals of zeolites will have larger surface areas and less diffusion limitations compared to zeolites with micrometer-sized crystals. Nanometer-sized zeolites also offer advantages in supramolecular catalysis, photochemistry, nanochemistry, electrochemistry, and optoelectronics [8]. Zeolite nanocrystals can also be used in the construction of other geometries such as thin films, fibers, and self-standing zeolite membranes [9]. Recently, a polycrystalline mordenite membrane with a small crystallite size was prepared using tetraethylammonium bromide as a template and by aging. The smallest crystals obtained were around 4–5 μm [10]. Although the templating effect of organic compounds such as TPA^+ cation is excellent, it can cause many

problems such as its producing poison and high production cost, the contamination of waste water by organic templates agent, air pollution arising from thermal decomposition of organic templates agent, and coke deposit due to incomplete decomposition, in some fields of the unsuitable handling in high temperature that needs to use nanosized zeolite as assembly component, nonreversible polymerization easily occur in the course of thermal decomposition of organic templates agent and thereby losing assembly performance. To the best of our knowledge there are no reports on the synthesis of mordenite with crystal diameter 65 nm and crystal length 7 μm in the absence of organic templates. In this study we have prepared mordenite crystals by adjusting gel compositions and crystallization conditions.

2. Experimental

2.1. Preparation of nanosized template-free mordenite zeolite

A template-free mordenite with an average size of 65 nm was synthesized from a synthesis solution by dissolving 7.98 g sodium hydroxide pellets (A.R.) and 12.485 g aluminum nitrate (Aldrich) in 69.5 g deionized water in a beaker. The mixtures in the beaker were thoroughly mixed and a 50 g Ludox AS30 colloidal silica (Aldrich) was slowly added to the above solution under stirring at high speed. The molar composition of the resulting synthesis gel was $12\text{Na}_2\text{O}:100\text{SiO}_2:2\text{Al}_2\text{O}_3:500\text{H}_2\text{O}$. Prior to being transferred to a Teflon-lined stainless steel autoclave, the above synthesis solution was aged for 20 h at room temperature and then hydrothermally treated for 5 days in an oven at a temperature of 180 °C. After the hydrothermal treatment, the products were recovered, thoroughly washed with deionized water, and then dried at 120 °C.

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2.2. General characterization

X-ray diffraction (XRD) patterns and average crystal size were collected with Bruker axis, D8 Advance. N_2 adsorption and desorption isotherms were obtained at 77 K using a volumetric adsorption apparatus (Nova2000 series, Chromatech). The pore structures were estimated according to the Brunauer–Emmett Teller (BET) method. The samples were degassed at 573 K for 24 h under vacuum prior to the analysis. The micropore area and volume were calculated by the t -plot method. The mesopore area was obtained by subtracting the micropore area from the BET surface area, and the mesopore volume was calculated by subtracting the micropore volume from the total pore volume at 0.985P/Po according to the method reported in the literature [11]. The micropore size distribution was obtained by applying the Horvath–Kawazoe method (H–K) [12]. FT-IR spectra were recorded using Jasco FT-IR-460 plus, Japan; the zeolite samples were also characterized by scanning electron microscopy using a Jeol scanning microscope model JSM5410. Elemental analysis was carried out using link, ISIS-300, Oxford EDS (energy dispersion spectroscopy) detector. Thermal analysis data (Shimadzu TGA-50/DT-50) were investigated to define the weight loss and thermal change at room temperature to 800 °C, where in atmosphere was nitrogen and the rate flow was 20.00 ml/min.

3. Results and discussion

3.1. X-ray diffraction and SEM studies

Fig. 1 shows the X-ray diffraction patterns of synthesized mordenite sample without organic template. As shown in Fig. 1 in the XRD pattern of the prepared mordenite powder, diffraction peaks corresponding to the typical structure of mordenite are observed [13,14]. This indicates that the synthesized samples are mordenite crystals. The average crystal sizes of the prepared materials were determined using the Scherrer equation [15]. The size of crystals obtained with X-ray method is the effective length, measured in the direction of the diffraction vector, along which diffraction is coherent. The term crystal size is preferred over particle size, since individual particles may contain several crystals or domains having different orientation [16]. The crystal size obtained by applying Scherrer's equation is interpreted as an average crystal dimension, perpendicular to the reflection plane [17]. The accuracy of crystal size determination is usually no better than 20–40%, because the sample analyzed do not have crystals of uniform size, but rather

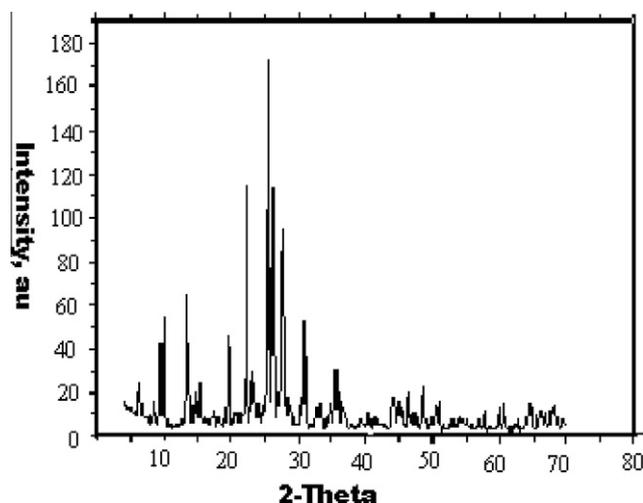


Fig. 1. XRD pattern of the prepared sample.

some type of distribution. Powder with needle shape crystals (like those of mordenite) tend to become aligned with the specimen axis in the preparation of the sample [18]. The crystal dimension measured by X-ray diffraction could be the crystal diameter (65 nm) instead of crystal length (7 μm) as shown in Fig. 2 (from SEM) which needle shape crystals of mordenite are formed with an average length of 7 μm and average diameter of 75 nm (50 particles). The crystal size of the prepared sample determined by XRD is 65 nm, this value is closer to the average diameter of the particles measured by SEM (75 nm) than to the average length (7 μm). Fig. 3 shows EDS of the prepared sample. The results showed the presence of Si, Al, Na and O in the synthesized sample. The weight % of elements (Si, Al, Na and O) of the prepared samples is summarized in Table 1. The Si/Al molar ratio equals 15.6 which are considered as relatively high compared with others in literature [14,19].

3.2. FT-IR studies

The FT-IR transmission spectra for nanosized mordenite without organic templates are shown in Fig. 4. Typical vibrations for mordenite are observed (asymmetric stretching: external 1225 cm^{-1} , internal 1050 cm^{-1} ; symmetric stretching: external 800 cm^{-1} , internal 720 cm^{-1} ; double ring: 580 and 560 cm^{-1} ; T–O bending; 450 cm^{-1}) [20,14].

3.3. Pore structure studies

The N_2 adsorption–desorption isotherm of the prepared sample are presented in Fig. 5. The large hysteresis loops in the isotherm appear with relative pressure P/Po ranging from 0.4 to 1.0 was due the mesopores structure. The pore structure parameters [micropore, mesopore area (volume) and average pore diameter] of the prepared sample are summarized in Table 2. The cumulative pore volume curve of the prepared sample are given in Fig. 6, the starting point of the cumulative pore volume of the prepared sample indicates the diameter of the smallest micropores (0–20 Å), and this is 17 Å. The micropore volume is increased from 0.001 cm^3/g to 0.080 cm^3/g as pore diameter increased from 17 Å to 20 Å. As the mesopore diameter (20–1000 Å) increased from 20 Å to 1000 Å the mesopore volume increased from 0.080 cm^3/g to 0.130 cm^3/g . There are many reasons for the formation of mesopores in zeolite crystals such as synthesis of zeolite nano particles, steaming, acid leaching, base leaching and by using soft and hard templates during synthesis [21,22]. In the prepared sample the mesopore formed may be due to both of relatively high Si/Al molar

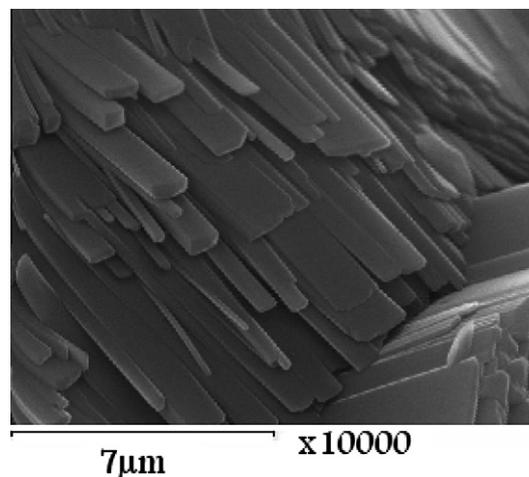


Fig. 2. SEM images of the prepared sample.

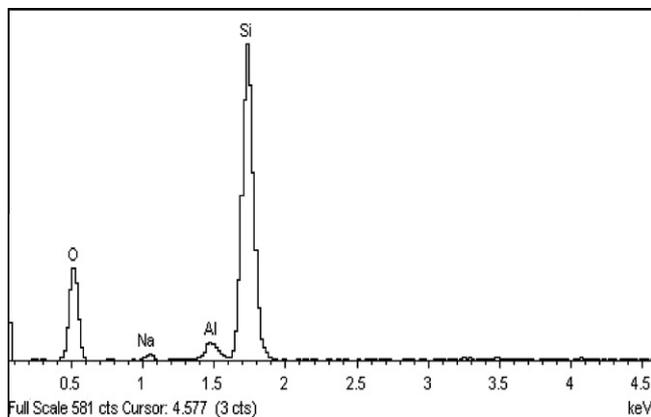


Fig. 3. EDS of the prepared sample.

Table 1
Weight % of elements (Si, Al, Na and O) of the prepared mordenite samples.

Weight % of elements			
Si	Al	Na	O
35.60	2.19	1.76	60.45

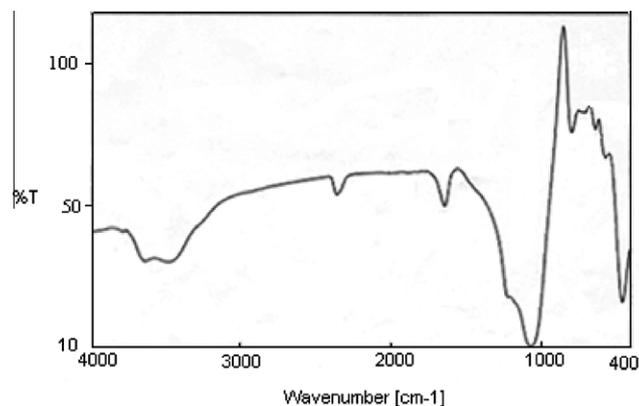


Fig. 4. IR spectra the prepared sample.

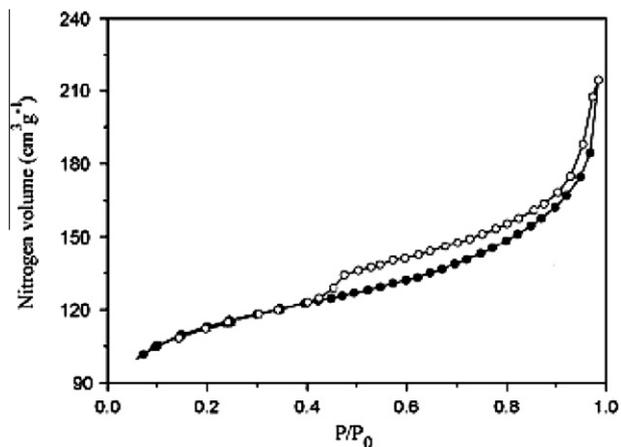


Fig. 5. N₂ adsorption–desorption isotherms of the prepared sample.

ratio and the presence of high percent of alkaline source (Na⁺) which generates shorter intracrystalline diffusion path lengths and relatively higher external (mesopore) surface area [14,23].

Table 2
Pore structure parameters of the prepared mordenite samples.

Surface area (m ² /g)			Pore volume (cm ³ /g)			Average pore diameter (Å)
Micropore	Mesopore	Total	Micropore	Mesopore	Total	
40.66	11.48	52.14	0.07	0.13	0.20	15.05

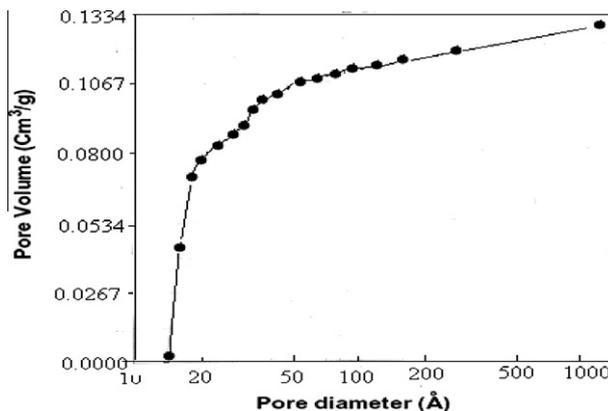


Fig. 6. H–K cumulative pore volume of the prepared sample.

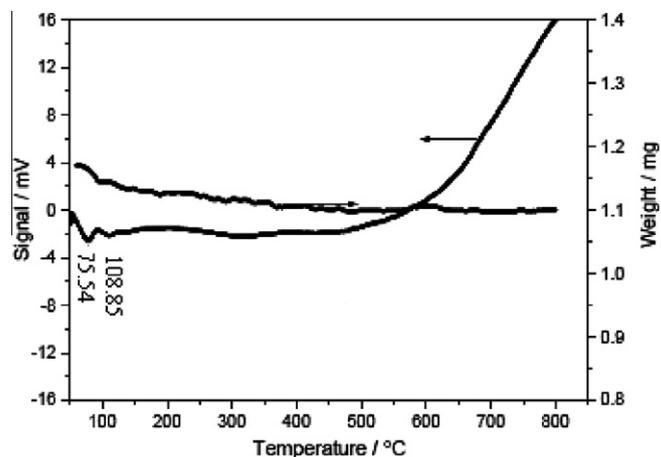


Fig. 7. TDA/TG curves of the prepared sample.

3.4. Thermal analysis data studies

The thermal analysis data and thermogravimetric analysis (DTA/TG) curves of the prepared sample are shown in Fig. 7. From Fig. 7, partial loss of adsorbed water at 75.54 °C and all adsorbed water is lost at 108.85 °C. The total weight loss is about 6% (very small) at room temperature to 800 °C due to there is no organic decomposition in the heating process.

3.5. Mechanism

In case of inorganic materials which characterized by positive tetrahedron with Na⁺ central body in his positive tetrahedral model, Na⁺ plays a role as positive templating agent instead of organic templates through enhancing nucleation process which leads to forming smaller crystals [24,25]. It was investigated that adding a certain amount of Na⁺ cation can stimulate the growth of crystals and the crystal size was decreased with the increase of Na₂O

content [26,27]. It was reported that the Al content in the framework of zeolite is normally observed to be less than that in the starting gel when template is used. Therefore, it was concluded that minimum Al (Si/Al = 100/1) should be required to form zeolite in the absence of organic template [28,29].

4. Conclusion

Mordenite with crystal diameter 65 nm and crystal length 7 μm was successively synthesized in the absence of organic template by hydrothermal method at 180 °C for 5 days after stirring at high speed and aging in the synthesis mixture with the molar composition of $12\text{Na}_2\text{O}:100\text{SiO}_2:2\text{Al}_2\text{O}_3:500\text{H}_2\text{O}$. Na^+ cation plays a structure directing role in place of an organic template, enhancing the nucleation and forming mordenite zeolite crystals.

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