

## Synthesis of large pores zeolite by soft templating strategy in the presence of novel organic template

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### Abstract

Zeolites have a great importance in catalytic process such as isomerization and alkylation. Large pores mordenite zeolite was hydrothermally prepared by soft templating strategy using N,N-dimethylaniline as a novel structure-directing agent. The synthesized mesoporous mordenite was characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), N<sub>2</sub> physical adsorption (BET), and Fourier transform infrared spectroscopy (FTIR). XRD and FTIR have been used to inform on the mordenite structure. SEM shows the crystals morphology and expanded pores opening, and N<sub>2</sub> physical adsorption confirms the presence of mesoporous channels. The results show that, in presence of N,N-dimethylaniline as organic template, mesoporous mordenite can be successfully synthesized.

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## 1. Introduction

Zeolites are crystalline aluminosilicates with a well-defined microporous structure [1]. Their frameworks are formed by  $\text{TO}_4$  tetrahedra, where T = Si and Al, generate three-dimensional structures defined by channels pores and cavities. In general, the aluminum content in the zeolite framework greatly influences the physical and chemical properties of zeolites such as thermal stability and catalytic abilities [2]. Mordenite is high-silica large pore zeolite. It has a channel system composed of a straight 12 member rings (0.65 x 0.7 nm), which are connected by small side-pockets with 8 member rings pores (0.26 x 0.57 nm) parallel to the *c*-axis, and an additional 8 member rings channel (0.34 nm x 0.48 nm) parallel to the *b*-axis [3]. The mordenite chemical composition is:  $\text{Na}_8\text{Al}_8\text{Si}_{40}\text{O}_{96}\text{nH}_2\text{O}$ . Unit cell parameters of sodium mordenite are:  $a = 18.121 \text{ \AA}$ ,  $b = 20.517 \text{ \AA}$ , and  $c = 7.544 \text{ \AA}$  [4]. Most of the studies on the synthesis of mordenite were performed to increase the Si/Al ratio and produce very large crystals [5]. Because the intracrystalline diffusion of guest molecules into the zeolite particle often results in severe limitations, the full application of a zeolite is rarely achieved. The slow diffusion inside a zeolite is responsible for diffusion limitations in many catalytic applications. Some catalytic reactions involving molecules larger than the zeolite pore apertures and in some cases the diffusion of reactants is sufficiently fast, but the zeolite catalyst produces by-products that are polymerized into bulky coke species that accumulate on the catalytic site and decrease the catalytic lifetime [6–8]. In these cases, different process have been done, such as zeolite demetallation or recrystallization around a surfactant, hard templating and downsizing the zeolite particle size which are helpful for improving intracrystalline diffusion and enhancing the zeolite lifetime [9,10]. On the other hand, N,N-dimethylaniline is a tertiary amine derivated from [aniline](#). According to the literature, N,N-dimethylaniline is one of amines which have not been used before in the synthesis of zeolites as organic template. Because of its interesting physical properties, with 0.622 Å of diameter and 76.7 Å<sup>3</sup> of volume [11], the N,N-dimethylaniline has been chosen as a voluminous molecule to have a zeolite, more or less, with large pores. In our previous work, large pores mordenite zeolite was prepared using soft templating strategy en the presence of N,N-dimethylaniline as novel organic template, through a one-step hydrothermal synthesis method. The sample was characterized by XRD, SEM, BET and FT-IR.

## 2. Materials and methods

### 2.1. Materials

The reagents used were: N,N-dimethylaniline (Sigma-Aldrich, 99%) as organic template, porous silica gel powder (Fluka) as silicon source, sodium hydroxide pellets (Sigma-Aldrich, 99.998%) as alkaline cation, aluminum chloride hexahydrate (Sigma-Aldrich, 99%) as aluminum source, and water was purified using Water Purification System Milli-Q (MERCK).

### 2.2. Mordenite synthesis

Different batches of reagents were used and the molar compositions of samples are listed in the Table 1. Initial hydrogel was prepared from the above reagents following the procedure: For known amounts of silica gel powder and sodium hydroxide solution, the N,N-dimethylaniline was added drop wise and the mixture was stirred for 1 hour. Calculated amounts of aluminum chloride and demineralized water were added. This new mixture was stirred for 2 to 24 hours till formation of homogenous hydrogel, than was let aging. One hour later, the homogeneous hydrogel was transferred to a Teflon lined autoclave with a volume full capacity of 50 ml and carried out in crystallization temperature of 423 K under autogeneous pressure, for 5 to 6 days without stirring. After crystallization had been completed the autoclave was rapidly cooled and the white solid was washed with deionized water, filtered off, and

then dried at 373 K overnight. The dried zeolite sample was calcined for 6 hours in atmospheric air at 773 K to eliminate the organic template.

**Table 1.** Molar compositions of prepared samples.

Sample Name	Si/Al	NaOH	R*	Crystallization time (days)	pH <sub>gel</sub>
BB-16	33.33	0.45	0.4	6	12.81
BB-15	33.33	0	0.4	5	12,23
BB-14	33.33	0.45	0.4	5	12.76
BB-12	33.33	0.45	0.5	5	12,83
BB-05	33.33	0.45	0.4	5	12,73
BB-02	33.33	0.45	0	5	12.07

R\*: Organic template.

### 2.3. Characterization

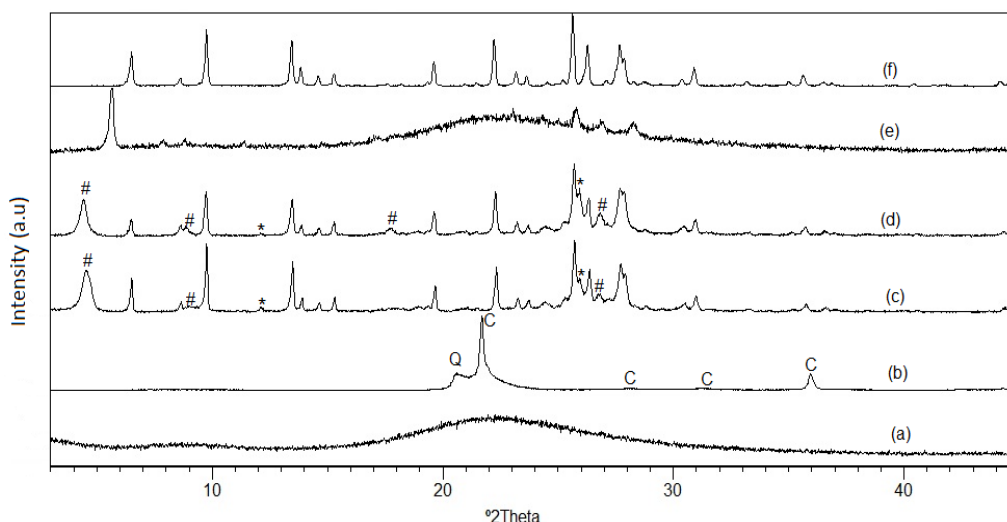
Characterizations of materials were performed by following instruments: The pH values of the homogenous hydrogel were measured by inoLab pH 730 (WTW). The crystalline structures were determined by X-ray diffraction (Bruker AXS D8 ADVANCE diffractometer with a CuK $\alpha$  radiation source). The porosity occupied by the organic template was released by a calciner (Nabertherm). The morphology of the product was analyzed by scanning electron microscopy (JEOL JSM-6340F). Examination of surface area and pore properties was performed by nitrogen physisorption (Micromeritics ASAP 2020); and the FTIR spectrum was taken in KBr pellets using Alpha-Bruker FTIR spectrophotometer.

## 3. Results and discussion

### 3.1. XRD

In this study the mixtures of starting materials were prepared, treated hydrothermally in same temperature (423 K), with different duration of crystallization. The Figure 1 shows the XRD patterns of the samples (a): BB-02, (b): BB-05, (c): BB-12, (d): BB-14, (e): BB-15, (f): BB-16. The reflection peaks are represented between the angles  $2\theta$  ( $^{\circ}$ ) = 3 to 45. As shown on Figure 1 (f), the important diffraction peaks of the powder sample BB-16 obtained after 6 days of crystallization are corresponding to typical mordenite structure [12] with high-resolution and without any additional phase. This pattern confirms higher purity of the sample BB-16. Both samples BB-12 and BB-14 represented on Figure 1 (d) and Figure 1 (e) respectively have the same appearance. The figure shows the presence of MOR structure peaks in both samples patterns and this is confirmed by characteristic peaks around  $2\theta$  ( $^{\circ}$ ) [hkl] = 6.51 [110], 9.77 [200], 13.45 [111], 13.83 [130], 22.2 [150], 25.63 [202], 26.25 [350] [12]. These patterns show also the presence of another transient phases assigned to kenyaite and magadiite [13] in addition to the mordenite. Those phases are mentioned in the patterns by (#) for kenyaite, and (\*) for magadiite. In fact, those two samples were prepared with same concentrations except a slight difference in the organic template. The presence of additional metastable structures is properly due to insufficient crystallization time. XRD pattern of the sample BB-15 obtained after 5 days of crystallization is showed on Figure 1 (e). This pattern shows a bump appearance with few peaks of unknown phase indicating a crystallization onset. This sample (BB-15) has the same conditions as BB-14 but without mineralizer which has a determinant role for the zeolites synthesis [14]. On the Figure 1 (b) is represented the XRD pattern of the

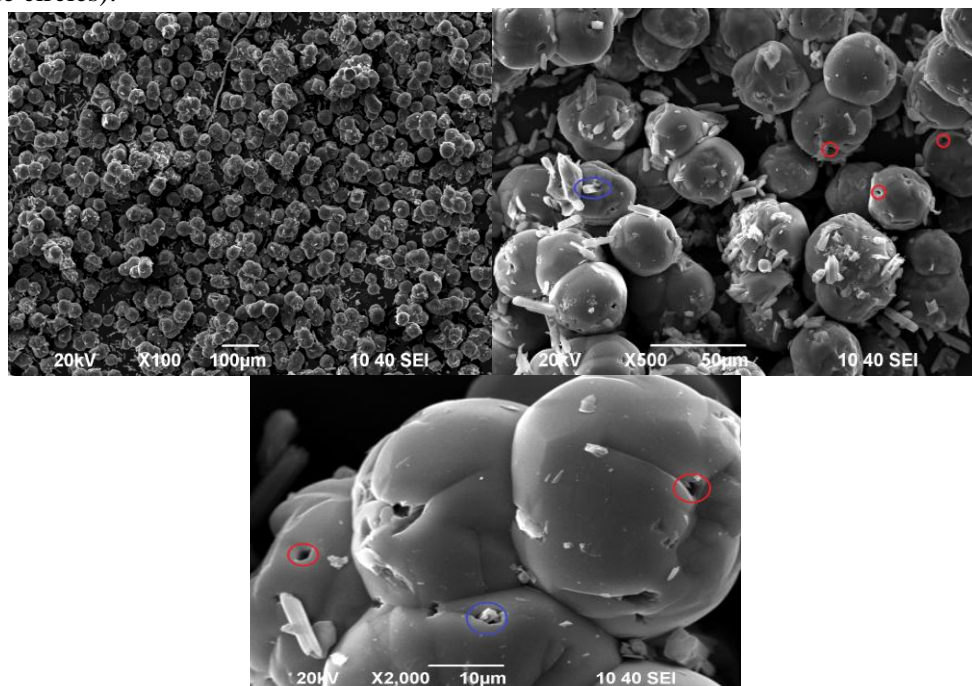
sample BB-05. This sample was prepared with same concentrations, it crystalized in same conditions as BB-14, but stirring time of 2 hours only. In this pattern, it can be seen the presence of two phases  $\alpha$ -Cristobalite and  $\alpha$ -Quartz which are mentioned by (C) and (Q) respectively. Those phases are confirmed by diffraction peaks at around of  $2\theta$  ( $^{\circ}$ )  $[hkl] = 21.8 [101]$ ,  $28.1 [111]$ ,  $31.2 [102]$ ,  $36 [200]$  for  $\alpha$ -Cristobalite and  $2\theta$  ( $^{\circ}$ )  $[hkl] = 20.6 [100]$ , for  $\alpha$ -Quartz [15].



**Figure 1.** XRD patterns of (a): BB-02, (b): BB-05, (c): BB-12, (d): BB-14, (e): BB-15, (f): BB-16.

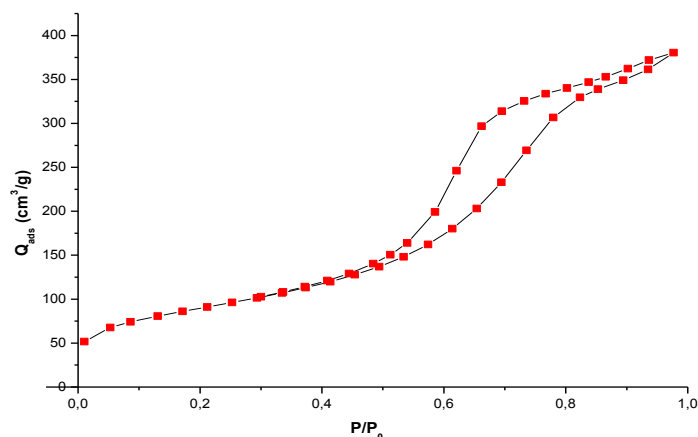
### 3.2. SEM

Figure 2 shows the SEM images of the sample BB-16. The images can show large and uniform crystals with a spherical shape and average diameter of  $40\ \mu\text{m}$ . From the pictures we can see that the crystals contain large pores shown by the red circles causing by the assembly of structural units around the condensed organic template in the synthesis gel (blue circles).

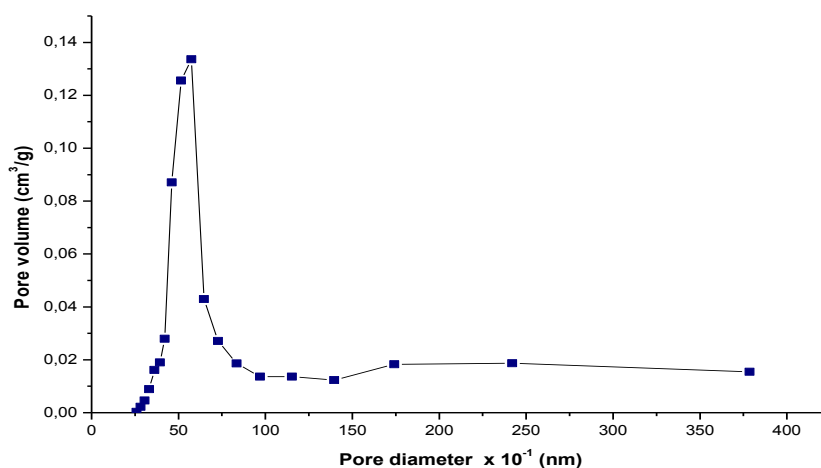


**Figure 2.** SEM images of non calcined sample BB-16.

### 3.3. BET



**Figure 3.** N<sub>2</sub> adsorption-desorption isotherm of synthesized mordenite.

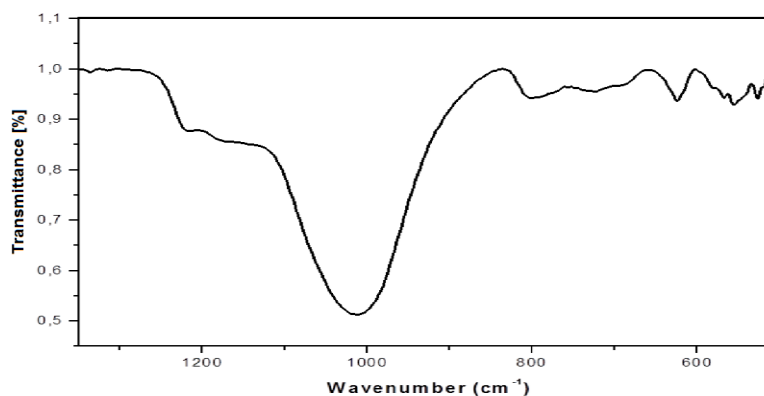


**Figure 4.** BJH pore size distribution of synthesized mordenite.

Nitrogen adsorption-desorption isotherm at 77 K of calcined BB-16 is presented on Figure 3. The sample exhibits type IV isotherm which is characterized by a level of saturation. This adsorption isotherm is obtained with mesoporous adsorbents in which occurs a capillary condensation. The saturation level indicates that, despite the increase in equilibrium pressure, there is no adsorption: this is interpreted by the fact that the mesopores, wherein occurred capillary condensation, are longer available for adsorption. The specific surface area is 319 m<sup>2</sup>/g. The hysteresis loop form is purely type H<sub>1</sub> that appears between relative pressure points 0.3 and 0.97. This type of hysteresis loop is often observed in the case of adsorbents having a very narrow pore distribution. The pore size distribution curve of the calcined sample BB-16 is obtained using the Barrett–Joyner–Halenda (BJH) model and is represented on the Figure 4. Correspondingly to this figure, the average pore size distribution for BB-16 shows mesopores at 51 and 57 Å.

### 3.4. FTIR spectrum

Infrared spectrum of calcined sample (BB-16) is shown on Figure 5. The typical framework vibrations of mordenite zeolite are observed. Asymmetric external and internal stretching are respectively observed at 1225 cm<sup>-1</sup> and 1020 cm<sup>-1</sup>. For the symmetric stretching, the external one is represented by vibrational band at 800 cm<sup>-1</sup> and the internal one is at 720 cm<sup>-1</sup>. Specific vibrations of mordenite double ring are at 560 and 580 cm<sup>-1</sup> [4,16].



**Figure 5.** FTIR spectrum of the calcined sample BB-16.

## 4. Conclusion

Expanded pores mordenite zeolite was successfully synthesized using N,N-dimethylaniline at 423 K, after 24 hours of gel stirring and 6 days of crystallization. The crystals morphology of the sample was uniforme with spherical shape. The surface area was higher containing interesting mesoporous channels. Experimental results showed that N,N-dimethylaniline has a good templating effect and played an important role to obtain large pores mordenite zeolite.

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