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# Preparation and Characterization of mordenite Zeolite from Iraqi Sand

H M Hussain<sup>1</sup> and A A K Mohammed<sup>2</sup>

<sup>1</sup>Department of Chemical Engineering, College of Engineering, University of Baghdad, Baghdad, Iraq

<sup>2</sup>Al-Farabi University College, Baghdad, Iraq

E-mail: hala\_muhammed@ymail.com (H M Hussain)

**Abstract.** Mordenite zeolite have been successfully synthesized from prepared nano-silica by hydrothermal method at 25 0C for 3 days. The produced sample was studied using XRD, XRF, SEM, FT-IR, AFM and BET surface area. SEM showed that the prepared sample crystallized in needle shape crystals. BET surface area and pore size of H-mordenite zeolite were 336.7 m<sup>2</sup>/g and 2.49 nm, respectively. AFM show that the average crystal diameter was 111 nm. Si/Al ratio and ion exchange percentage measured by XRF were 7.544 and 99.62 %, respectively.

**Keywords:** zeolite characterization, Na-MOR zeolite, H-MOR zeolite, hydrothermal method, nano-silica, Iraqi sand.

## 1. Introduction

Mordenite was a zeolite with a perfect 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 Na-mordenite has dimensions a: 18.121 Å, b: 20.517 Å, and c: 7.544 Å [1]. The greatest common morphology of mordenite has been characterized by needles with c direction elongation [2]. Mordenite has a high thermal and acid stability, and it has been used as a catalyst for vital reactions such as hydroisomerization, hydrocracking, reforming, alkylation, dewaxing, and the production of dimethyl amines [2]. Mordenite has been considered for applications in semiconductors, chemical sensors, and nonlinear optics [3]. In addition, mordenite has also been used in the adsorptive separation of gas or liquid mixtures [4]. Nano-sized zeolites are main in catalytic and adsorptive applications. Smaller crystals of zeolites can have greater surface areas and fewer diffusion limitations compared to zeolites with micrometer-sized crystals. Nanometer-sized zeolites additionally provides advantages in supramolecular catalysis, photochemistry, nanochemistry, electrochemistry, and optoelectronics [5]. Zeolite nano-crystals may be used in the construction of different geometries such as thin films, fibers, and self-standing zeolite membranes [6]. Recently, a crystalline mordenite membrane with a little crystal size was prepared using tetraethylammonium bromide as a seed and by aging. The smallest crystals obtained were around 4000-5000 nm [7]. Although the seed influence of organic compounds like TPA<sup>+</sup> cation is excellent, it can reason many problems such as producing poison and high production cost, the contamination of wastewater by seed, pollution arising from thermal decomposition of organic templates agent, and coke deposit owing to incomplete decomposition. In some fields of the unsuitable handling at high temperature that has to usage nano-sized zeolite as assembly component, nonreversible polymerization simply occurs in the course of thermal decomposition of organic templates agent and thereby losing assembly performance. To the simplest



of our information, there are no reports on the synthesis of mordenite in the absence organic template with a crystal diameter less than 4000 nm. In this study deals with the preparation of H-MOR with nanopore size and crystal diameter.

## 2. Experimental

### 2.1 Materials

Pure sodium aluminate ( $\text{NaAlO}_2$ ) supplied by Sigma Aldrich, sulfuric acid ( $\text{H}_2\text{SO}_4$ ) supplied by Sigma Aldrich, pure sodium hydroxide ( $\text{NaOH}$ ) supplied by Alpha Chemika were used as chemical in this work.

### 2.2 Raw material

Iraqi sand was supplied by Iraqi geological survey company, available in Al – Anbar city. It was used as a natural resource for the preparation of the catalyst. Table 1 shows the chemical composition of sand determined by XRF analysis.

**Table 1.** shows the chemical composition of Iraqi sand

Component	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{TiO}_2$	$\text{Na}_2\text{O}$	L.O.I	Others
Weight %	94.07	0.28	0.05	0.03	0.14	5.20	0.23

### 2.3 Nano silica preparation.

Sand and sodium hydroxide were crushed to a particle size  $\leq 45\mu\text{m}$ . 40 g of sodium hydroxide and 125 g of sand were mixed and calcined at  $500^\circ\text{C}$  for 30 min in a programmable electrical furnace. Water was added to the mixture until a homogeneous and clear solution was obtained and then sulfuric acid (98%) added slowly until pH reaches 3. The obtained gel was separated from the mother liquor by filtration (Whatman No. 41 filter paper) using a Buckner funnel with the aid of a vacuum pump. The gel is dried at  $110^\circ\text{C}$  overnight and then washed with hot deionized water at  $60^\circ\text{C}$  until pH reaches 7. To ensure the absence of  $\text{SO}_4^{2-}$ , a solution of 6 wt. %  $\text{BaCl}_2$  was added to the filtrate. The obtained crystalline mass was dried at  $110^\circ\text{C}$ . [8]

### 2.4 Synthesis of Na-mordenite (Na-MOR):

Na-MOR was synthesized from the prepared nano-silica. 38.90 g of  $\text{NaOH}$  was dissolved in 249.3 ml of water and then divided into two equal portions. In one portion, 5.56 g of nano-silica was completely dissolved. To the other portion, 10.19 g of  $\text{NaAlO}_2$  was added to prepare a clear aluminate solution. Then the silicate solution was slowly poured into the aluminate solution with vigorous stirring, and a homogenous gel was resulted. The resultant gel was stored in a water bath at room temperature ( $T = 25 \pm 2^\circ\text{C}$ ), in a sealed poly tetra fluoro ethylene (PTFE) bottle under stirrer at 250 rpm for 3 days at pH 14. The solid product was separated by filtration (Whatman No. 41 filter paper) using a Buckner funnel with the aid of a vacuum pump, then washed more times by distilled water until the pH value dropped to 8.69. The product was left at room temperature overnight, dried at  $110^\circ\text{C}$  for 2 hr and calcined at  $400^\circ\text{C}$  for 2 hr. [9].

### 2.5 Synthesis of H-mordenite (H-MOR):

The hydrogen form of zeolite H-MOR was obtained from Na-MOR exchange with a solution of 4 N  $\text{NH}_4\text{Cl}$ . Zeolite Na-MOR was slurred in an ammonium chloride solutions with mixing at  $70^\circ\text{C}$  for 2 hr and then left at room temperature overnight for ion exchange completion, after that the exchanged zeolite was filtered off, washed with distilled water. The product was left at room temperature overnight, dried at  $110^\circ\text{C}$  for 2 hr and calcined at  $400^\circ\text{C}$  for 2 hr. [10]

### 2.6 Characterizations:

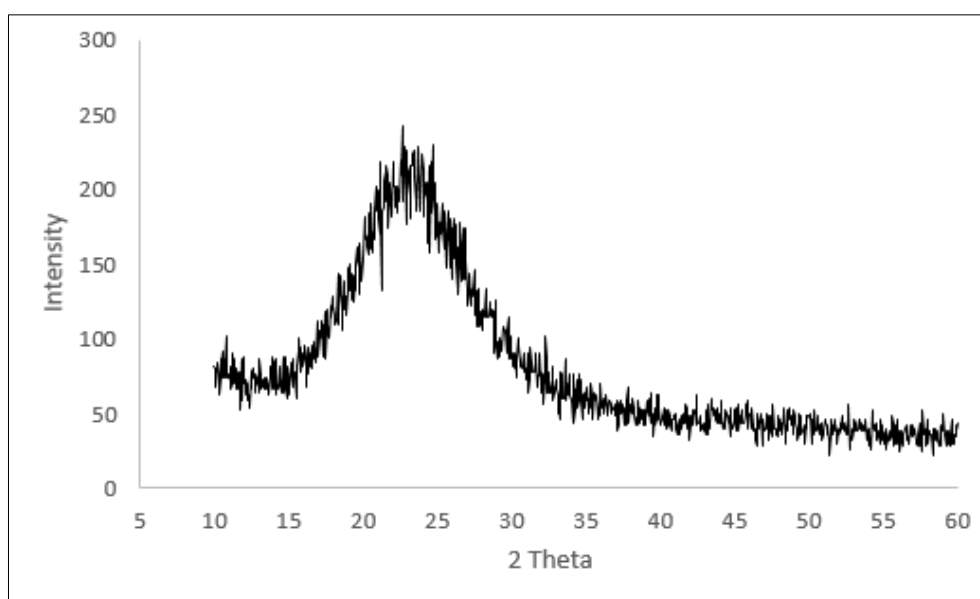
The prepared samples were characterized by different techniques. These techniques include X-Ray Diffraction XRD, Brunauer Emmett teller BET, X-ray fluorescence XRF, Fourier Transforms infrared

spectroscopy FTIR, Scanning electron microscope SEM, and atomic force microscopy AFM. XRD for the powder product was measured using Philips diffractometer with Cu target at  $2\theta$  value from  $5^\circ$  to  $60^\circ$ . BET (ASAP 2020) was determined for surface area and pore volume estimation. The IR spectrum was scanned using a Perkin-Elmer FTIR (Model 8400S) in the wavelength range of 400 to  $4000\text{ cm}^{-1}$  with KBr pellets method. XRF (Phillips PW 1480 Spectrometer) technique was used to determine the elements present in the zeolites quantitatively. The particle size and morphology of the microcrystalline and nano-crystalline zeolite were analyzed using SEM and AFM images. SEM (VEGA3 LM/SEM) that yields images of a taster by scanning it with a focused beam of electrons. The electrons interrelate with the electrons in the sample, producing signals that can be detected and that contain information about the sample's surface structure and composition. AFM (SPM-AT 3000) provides information parallel and perpendicular to the surface with resolution in the nm range.

### 3. Results and discussion

#### 3.1 Characterization of nano-silica

The XRD pattern diffractogram of nano silica is show in figure 1. This diffractogram detect that the synthesized nano-silica was perfectly amorphous as indicated by the featureless pattern and the forfeit of significant peaks and the appearance of diffuse maximum at  $2\theta = 23^\circ$  typical for amorphous nano-silica.[8]

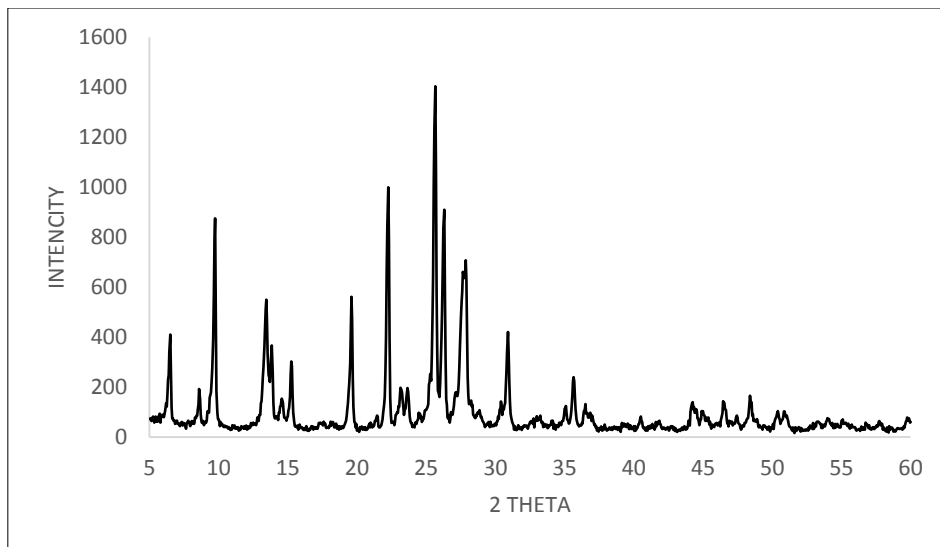


**Figure 1.** X-ray powder pattern of precipitated  $\text{SiO}_2$  with a characteristic amorphous peak

#### 3.2 Characterization of Na-MOR and H-MOR.

XRD Analysis:

Figure 2 shows that the X-ray diffraction patterns of synthesized Na-MOR corresponding to this types diffraction peaks Na-MOR [11][12]. This indicates that the synthesized sample is Na-MOR crystals.



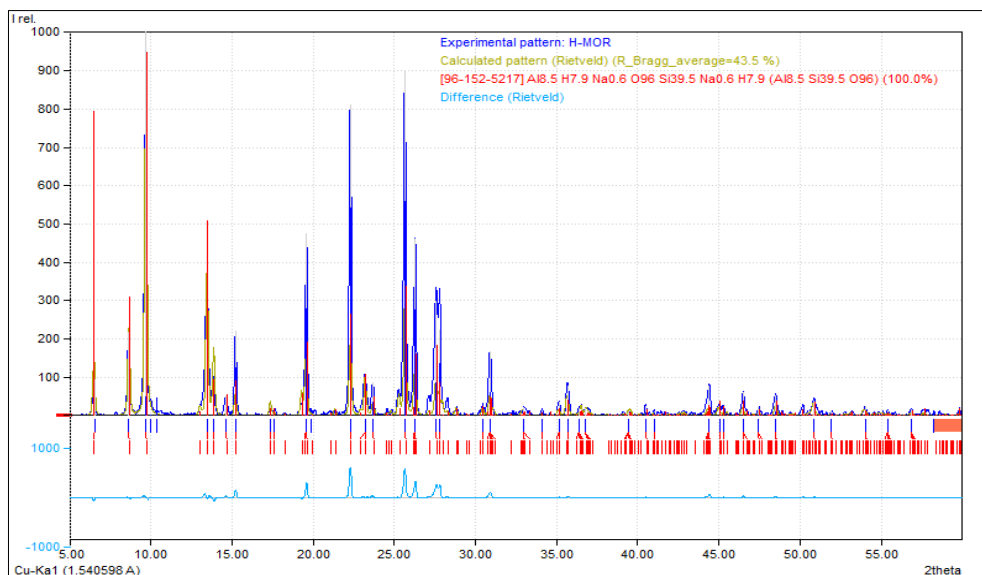
**Figure 2.** X-ray powder pattern of prepared Na-MOR zeolite

The exchange technique was used in this work is one step impregnation under a constant temperature to convert Na-MOR zeolite to H-MOR zeolite. Figure 3, illustrates the XRD patterns of the synthesized zeolite H-MOR. XRD phase is found to match with the show peaks at  $2\theta = 6.57, 9.77, 19.65, 22.36, 25.72$  and  $26.36$ . These peaks are characteristic for H-MOR zeolite. It can be seen from Figure 3, that the synthesized sample showed the formation of H-MOR phase[13]. The relative crystallinity of H-MOR was calculated from by using equation 1. This equation shows that the H-MOR has high relative crystallite 118 %.

$$\text{relative crystallinity of zeolite} = \frac{S_x}{S_r} * 100 \quad (1)$$

$S_x$  = sum of integral peak intensities for the prepared catalyst.

$S_y$  = sum of integral peak intensities for the standard catalyst.



**Figure 3.** X-ray powder pattern of prepared H-MOR zeolite.

Si/Al ratio calculated from these results of this analysis XRF was shown in table 2. This table shows that the sodium content of the H-MOR zeolite was 0.014 wt. % and this means that 99 % of sodium ions was exchanged by hydrogen.

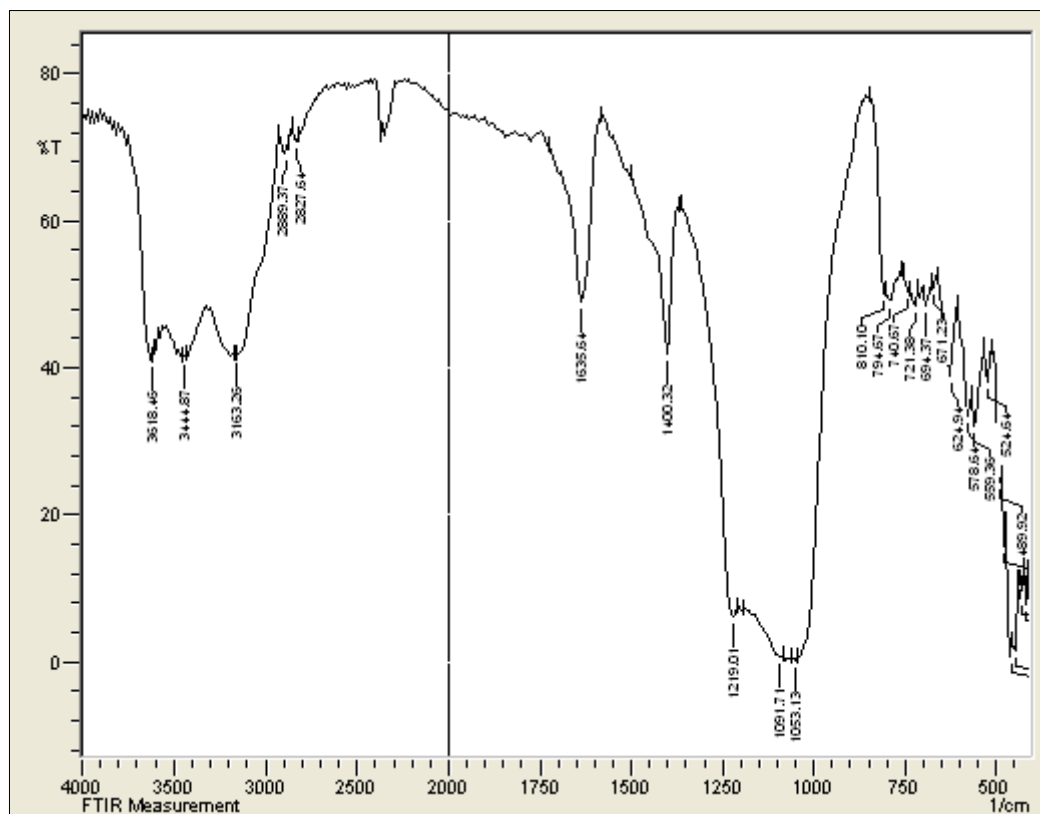
The sodium ion exchange equals 99% which are considered relatively high compared with others in the literature [14][10]

**Table 2.** XRF result for the prepared zeolite

Zeolite wt. %	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	Othe r	Si/Al
Na-MOR	3.723	<0.003	9.37	84.2	0.0175	<0.0005	0.03	0.1240	2.48	7.6
H-MOR	<0.014	<0.003	10.0	89.1	0.0216	0.00423	0.06	0.1395	0.52	7.5

FTIR spectrophotometer:

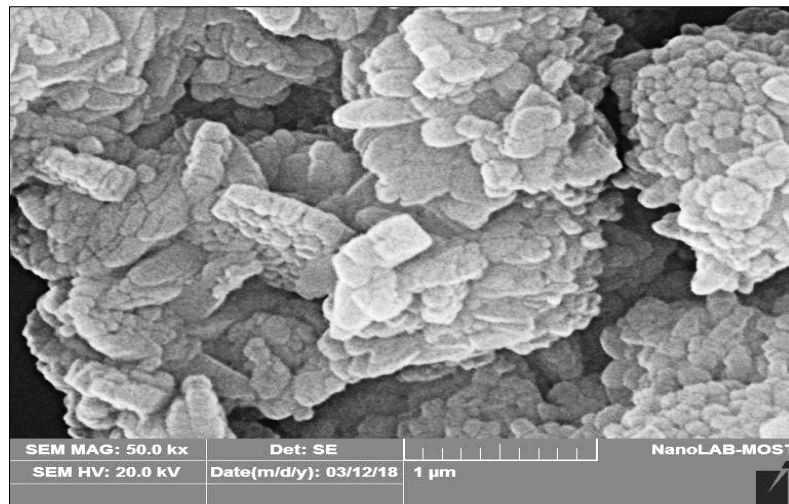
Typical vibrations for H-MOR are observed (asymmetric stretching: external 1219 cm<sup>-1</sup>, internal 1053 cm<sup>-1</sup>, symmetric stretching: external 810 cm<sup>-1</sup>, internal 721 cm<sup>-1</sup>; double ring: 578 and 559 cm<sup>-1</sup>, T–O bending; 451 cm<sup>-1</sup>) [15][12] from the FT-IR transmission spectrum shown in figure 4.



**Figure 4.** FTIR Spectrum for synthesized H-mordenite zeolite.

SEM Analysis:

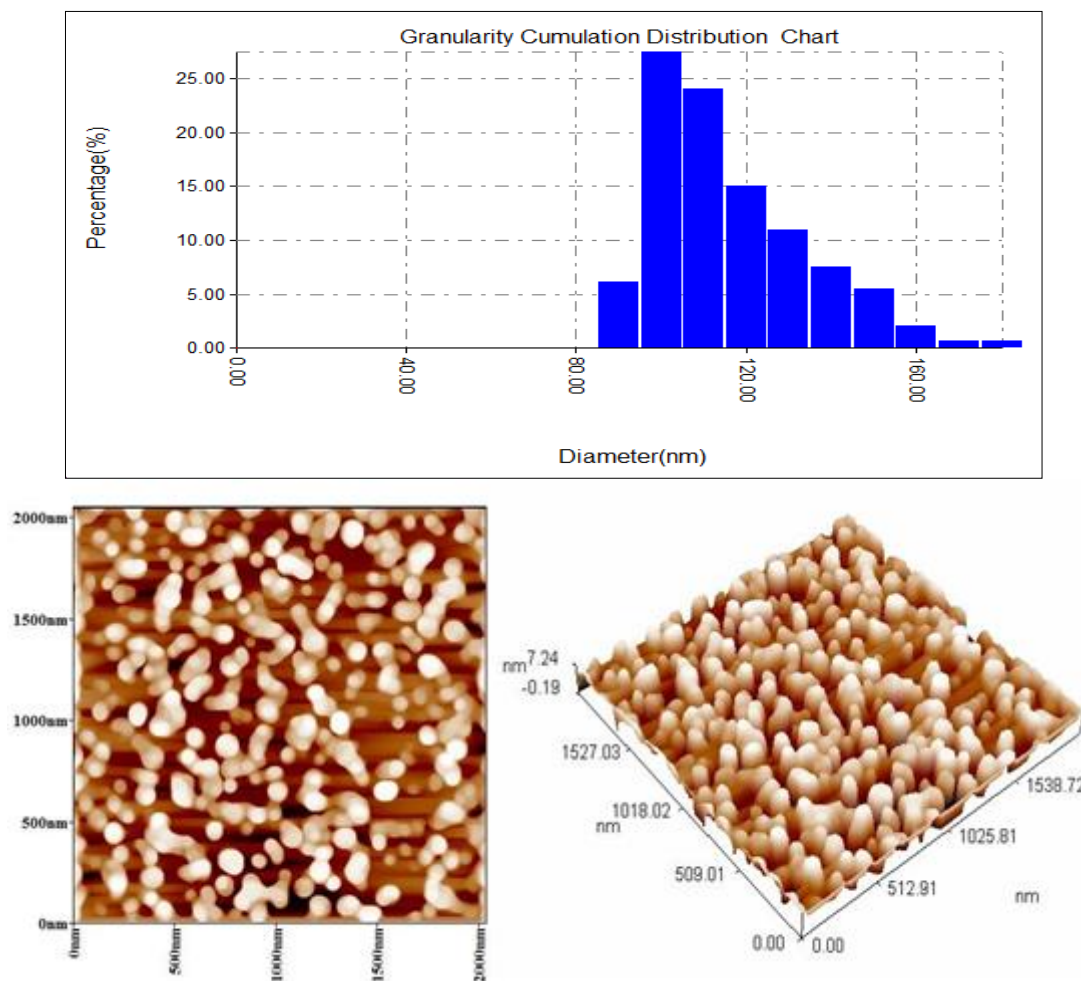
SEM micrograph of the studied H-MOR shows that the formation of twinned and intergrown lath-shape crystal. Furthermore, a small portion of the crystal cluster with a flaky habit is also depicted in the micrograph [16]. SEM images in figure 5, for synthesized H-MOR, shows that the most crystals formed are plates. Flat and prismatic crystals observed due to the high concentration of silica [17].



**Figure 5.** SEM image for synthesized H-mordenite zeolite.

#### AFM analysis

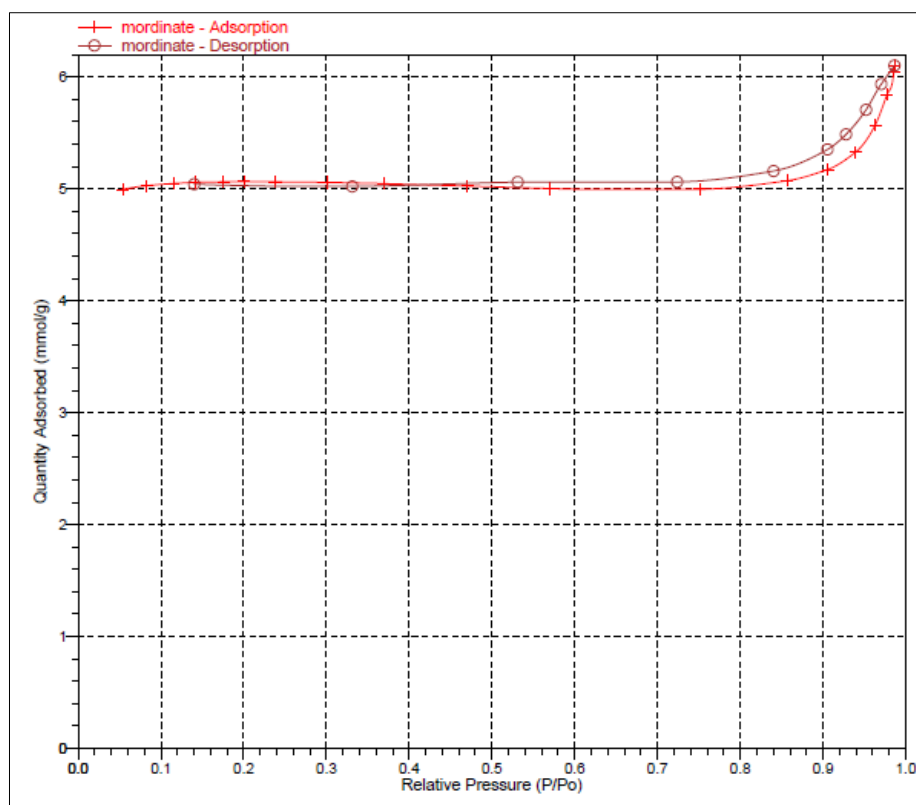
The obtained H-MOR zeolite in this work has an average particle size of 111 nm as shown by granularity cumulation distribution chart and particle size distribution, 2-D and 3-D dimensional image in figure 6.



**Figure 6.** Particle size distribution, 2-D and 3-D Dimensional image H-MOR zeolite.

#### Surface Area and Pore Distribution Analysis:

H-MOR was characterized using N<sub>2</sub> sorption to determine their surface area and pore volume. This characterized depending mainly on the structure of the solid, the adsorption of gasses and vapors gives rise to the isotherm. Figure 7 shows the N<sub>2</sub> sorption isotherm for synthesized H-MOR zeolite. It was found that the BET surface area and pore size of H-MOR were 336.7 m<sup>2</sup>/g and 2.49 nm, respectively. The pore size obtained in this work lower than those obtained by Heman et al, [18] and Beatriz et al, [19].



**Figure 7.** N<sub>2</sub> adsorption–desorption isotherms of H-MOR.

#### 4. Conclusion

H-MOR have crystal diameter 111 nm with high relative crystallite 118% and pore size 2.49 nm was successively synthesized from nano-silica prepared from Iraqi sand by hydrothermal method at 25 °C for 3 days. 99% of Na<sup>+</sup> ion-exchanged by using 4N NH<sub>4</sub>Cl to convert Na-MOR to H-MOR zeolite type.

#### References

- [1] Shiokawa K, Ito M and Itabashi K 1989 Crystal structure of synthetic mordenites *Zeolites*.
- [2] Bajpal P K, Rao M S and Gokhale K V G K 1978 Synthesis of Mordenite Type Zeolites *Ind. Eng. Chem. Prod. Res. Dev.*
- [3] Gilbert J E and Mosset A 1998 Large crystals of mordenite and MFI zeolites *Mater. Res. Bull.*
- [4] Shao C, Kim H-Y, Li X, Park S and Lee D-R 2002 Synthesis of high-silica-content mordenite with different SiO<sub>2</sub> / Al<sub>2</sub>O<sub>3</sub> ratios by using benzene-1,2-diol as additives *Mater. Lett.*
- [5] Mintova S and Valtchev V 1999 Synthesis of nanosized FAU-type zeolite *Studies in Surface Science and Catalysis*.
- [6] Zhu G, Qiu S, Yu J, Sakamoto Y, Xiao F, Xu R and Terasaki O 1998 Synthesis and Characterization of High-Quality Zeolite LTA and FAU Single Nanocrystals *Chem. Mater.*
- [7] Zhang Y, Xu Z and Chen Q 2002 Synthesis of small crystal polycrystalline mordenite membrane *J. Memb. Sci.*



- [8] Musić S, Filipović-Vinceković N and Sekovanić L 2011 Precipitation of amorphous SiO<sub>2</sub> particules and their properties *Brazilian J. Chem. Eng.* **28** 89–94.
- [9] Ghasemi Z and Younesi H 2012 Preparation Of Free-Template Nanometer-Sized Na-A And -X Zeolites From Rice Husk Ash *Waste and Biomass Valorization*.
- [10] Steen E Van, Callanan L H and Division C 2016 Synthesis and characterization of the nanocrystalline zeolite Y *Al-Khwarizmi Eng. J.* **12** 79–89.
- [11] Szostak R 1989 *Molecular Sieves Principles of Synthesis and Identification* New York
- [12] Mohamed M M, Nohman A K H and Zaki M I 2005 Development of Catalytic Properties of Mordenite Zeolite via Chemical Modification *Curr. Top. Catal.* **4** 80–99.
- [13] Treacy M M J and Higgins J B 2007 *Collection of Simulated XRD Powder Patterns for Zeolites* Fifth (5th) Revised Edition.
- [14] Thesis A 2015 *Catalytic Cracking of Furfural Extract Using Prepared Zeolite Catalyst*
- [15] Jansen J C, van der Gaag F J and van Bekkum H 1984 Identification of ZSM-type and other 5-ring containing zeolites by i.r. spectroscopy *Zeolites*.
- [16] Sang S, Chang F, Liu Z, He C, He Y and Xu L 2004 Difference of ZSM-5 zeolites synthesized with various templates *Catalysis Today*.
- [17] Kim G J and Ahn W S 1991 Direct synthesis and characterization of high-SiO<sub>2</sub>-content mordenites *Zeolites*.
- [18] Smail H, Shareef K and Ramli Z 2017 Synthesis of Mesoporous Mordenite Zeolite by Different Natural Raw Materials *Aust. J. Basic Appl. Sci.* **11** 27–34.
- [19] Hincapie B O, Garces L J, Zhang Q, Sacco A and Suib S L 2004 Synthesis of mordenite nanocrystals *Microporous Mesoporous Mater.* **67** 19–26.