



Synthesis and Characterization of Nano Y Zeolite Using MWCNT as Media for Crystal Growth

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Abstract

The present research was conducted to synthesis Y-Zeolite by sol-gel technique using MWCNT (multiwalled carbon nanotubes) as crystallization medium to get a narrow range of particle size distribution with small average size compared with ordinary methods. The phase pattern, chemical structure, particle size, and surface area were detected by XRD, FTIR, BET and AFM, respectively. Results shown that the average size of Zeolite with and without using MWCNT were (92.39) nm and (55.17) nm respectively. Particle size range reduced from (150-55) nm to (130-30) nm. The surface area enhanced to be (558) m²/g with slightly large pore volume (0.231) km³/g was obtained. Meanwhile, degree of crystallization decreased to 120%.

Keywords: Carbon nanotube, catalytic synthesis, Nano Y zeolite, MWCNT

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1- Introduction

Zeolite is considered one of the most common types of adsorbent which can remove the mercaptan action and other sulphide from gasoline [1]. Zeolite molecular sieves are crystalline microporous solids repleted with cavities and channels of molecular dimension between (3 to 10 Å diameter)[1].

A classical definition of zeolite is a crystalline aluminosilicate with a three dimensional framework structure that forms uniformly sized pores of molecular dimensions. Y-type zeolites are among the most widely used zeolites in catalysis, especially for the conversion of hydrocarbons, give a structure with large pores allowing the adsorption of a large variety of molecules, but also a thermal stability and remarkable opportunity to perform multiple structural modifications according to thereaction conditions [2].

Nano crystalline zeolite particles are becoming an important material in many technical applications (e.g. zeolite membranes). Synthetic methods that minimize the zeolite crystal diameter, while providing a narrow particle size distribution, are of primary importance in these technical applications [3]. Different methods have been proposed to synthesis a Nano crystal zeolite such as the microwave method that produce nanoparticles with relatively narrower particle size distribution, requiring much shorter heating times and which did not significantly change composition or crystallinity. The zeolite crystals were in the range of 100–300 nm, compared with the conventional heating method [4]. Another method is the Synthesis of Nano-zeolite from coal fly, the result was 400–500 nm in size [5].

A very reactive organic-template-free gel system is also used for the Nano zeolite preparation crystals averaging about 400–500 nm in size [6].

The carbon nanotube is one of the materials that currently gathering the best properties mechanical, thermal and electronic [7]. These additions make it possible to be used in zeolite synthesis. Multi-shell nanotubes have been used as media in Co/Y-zeolite catalysts support and the result was higher catalyst selectivity [8].

The aim of this research is to use the MWCNT as crystallization media in the synthesis of Nano Y zeolite catalyst with narrow range of particle size distribution, small average particle size and high texture properties. [SA .PV]. XRD, FTIR, BET and AFM will be measured to characterize the prepared catalyst.

2- Experimental Work

2.1. Feed stock and chemicals

Sodium Aluminate was provided by Kunshan Yalong Trading Co., Ltd China. Sodium Aluminate have molecular weight of 62 g/g mole, purity % =50-56(Al₂O₃), 40-45 (Na₂O). Sodium silicate used in the synthesis of zeolite was provided by SIGMA Aldrich. Chemical formula Na₂SiO₃, have a molecular weight of 122g/g mo', purity % =10.63 Na₂O, 26.5 SiO₂. Sodium hydroxide used in the Synthesis of zeolite was provided by SIGMA Aldrich. Chemical formula NaOH, have a molecular weight of 40 g/g mole, purity % =99.5.

Ammonium chloride used in the Synthesis of zeolite was provided by Merck.

The Multiwall Carbon Nanotubes (MWCNT) used in the experiment was made by ZHENGZHOU DONGYAO MATERIALS Company. The Purity was 97 % and the surface area $231.856 \text{ m}^2/\text{g}$.

2.2. Synthesis of Nano y Zeolite

The sol-gel and hydrothermal method was applied for synthesis of NaY zeolite. The aging solution was prepared from 4.07 g sodium hydroxide pellets dissolved in 19.95 g of demineralized water. 2.09 g of the sodium aluminate solution is stirred in 100ml plastic bottle until dissolution, then 33g of sodium silicate was added and aging for 24 h. the stock solution was 131 g of deionized water was added to 0.14 sodium hydroxide with 13.1 g sodium aluminate and 1 g MWCNT, the mixture was stirred then 206 g of sodium silicate was added and the mixture was mixed with 1600 rpm mixer for 20 min.

The solutions prepared in the previous steps were mixed in poly propylene bottle and subjected to a homogenization for 24h at room temperature; the products were centrifuged for 15 min for MWCNT separation and then the MWCNT was transferred to jacketed stainless steel autoclaves for crystallization. The autoclave was made from stainless steel, and lined with polytetrafluoroethylene (PTFE). As shown in Fig. 1. The mixture was heated at 100°C for 24 hours without agitation.

The product was then filtered, washed with distilled water until neutralization ($\text{pH} = 7$) and then dried in an oven at 110°C for 24 hours. Calcination was also carried at 550°C for 3 hours.

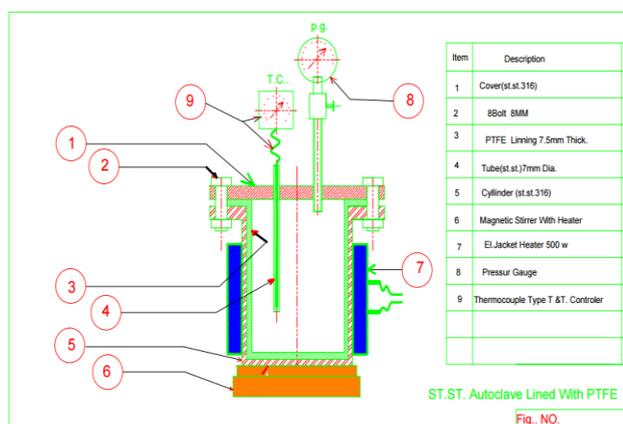


Fig. 1. Design of the Autoclave Lined with PTFE

2.3 Characterizations of Nano Y zeolite

a. X-ray diffraction (XRD)

The model of the X-ray diffractor meter (shimadzo xrd 6000) was located University of Baghdad College of education Ibn Al-Haytham.

The x-ray diffractometer was used to detect the phase of the Nano Y zeolite.

b. Scanning Electron Microscope (SEM)

The electron microscope uses a stream of electron rays to produce high magnification resolution. The instrument located in the minster of science and technology.

c. BET Surface Analyzer

Test Method according to ASTM D1993 for BET surface area and pore volume. Ministry of Oil, Research and development oil center.

d. Atomic Force Microscope

The instrument used was (AA3000-Scanning Probe Microscope, Angstrom Advance Inc.) located in College of Science, Department of Chemistry, University of Baghdad.

e. Measure sulfur concentration ASTM D7039

The sulfur concentration was measured using the ASTM D7039 method by the SINDIE OTG sulfur analyzer. The device located in Ministry of Oil, Research and development oil center, bob al sham.

f. Fourier-transform infrared spectroscopy (FTIR)

The instrument is used to obtain an infrared spectrum of emission of the prepared zeolite and its located in the minster of science and technology.

3- Results and Discussion

3.1. X ray diffraction

Fig. 2 shows the X-ray diffraction of the sample. This spectrum shows the characteristic diffraction peaks of a Na-Y zeolite, as are presented in the collection of simulated powder diagrams for zeolites. These peaks are intense, thin and no additional peaks are detected.

Table 1 shows the comparison of angle 2θ and d spacing between the sample and the standard zeolite. Both data listed in the table are close and represent the dominant peaks of the measurement. All the peaks of diffraction were indexed in the cubic system.

The mesh parameter determined at from the structural refinement is $a = 24.678 \text{ \AA}$. XRD analyses were carried out at room temperature using $\text{CuK}\alpha$ radiation nickel filter ($\lambda = 1.5418 \text{ \AA}$) and energy condition of (4 kv and 3 mA) Zeolite Y

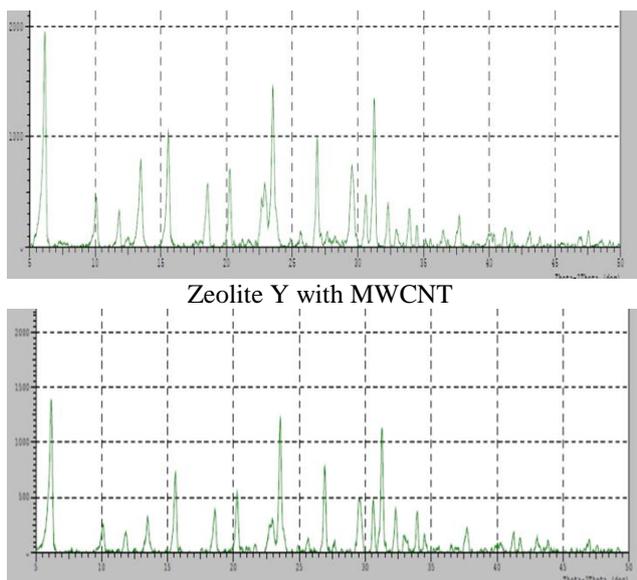


Fig. 2. XRD pattern for zeolite Y with and without the using of MWCNT

From the figure 2 it can be seen that the using of the MWCNT gives the same peaks but with different intensities. This means that no change has occurred on the crystal structure of the zeolite Y. The change occurs on the peak intensities which means that the degree of crystallization and the average crystal size has changed.

Table 1. Comparison of spacing and angle, between prepared catalyst with MWCNTs and standard

Prepared catalyst		Standard of catalyst	
Angle (2Theta)deg	d, spacing(Å)	Angle (2Theta) deg	d, spacing(Å)
7.202	12.402	7.18	12.41
10.105	9.205	10.172	9.210
16.120	5.501	16.103	5.503
21.862	3.881	21.901	3.890
23.380	3.721	23.532	3.701
27.201	3.284	27.251	3.279
32.014	2.824	32.120	2.830

The relative crystallinity was determined by dividing the sum of the peak intensities of the prepared zeolite at each stage according to equation 1 [10].

$$\text{Relative Crystallinity} = \frac{\text{Sum of peak intensities for sample}}{\text{Sum of peak intensities for Reference}} \times 100 \quad (1)$$

The degree of crystallinity without MWCNT was 144.84 % and has decreased to 120 % with MWCNT. The decrease of the degree of crystallinity was due to the effect of MWCNT as crystallization medium.

The diffraction peaks of Nano sized zeolites shows a decrease in crystallinity and crystal size, which can be described to the occurrence of extinction effects caused by the coexistence of particles with smaller sizes in the sample [11].

3.2. Scanning Electron Microscopy (SEM)

The SEM image provides information on the morphology of the crystals.

Fig. 3 shows that the crystalline image of the synthesized zeolite has small average size because of Nano sized particles as compared with that shown in literature revealing a uniform particle size with regular shape and uniform particle size distribution [12]

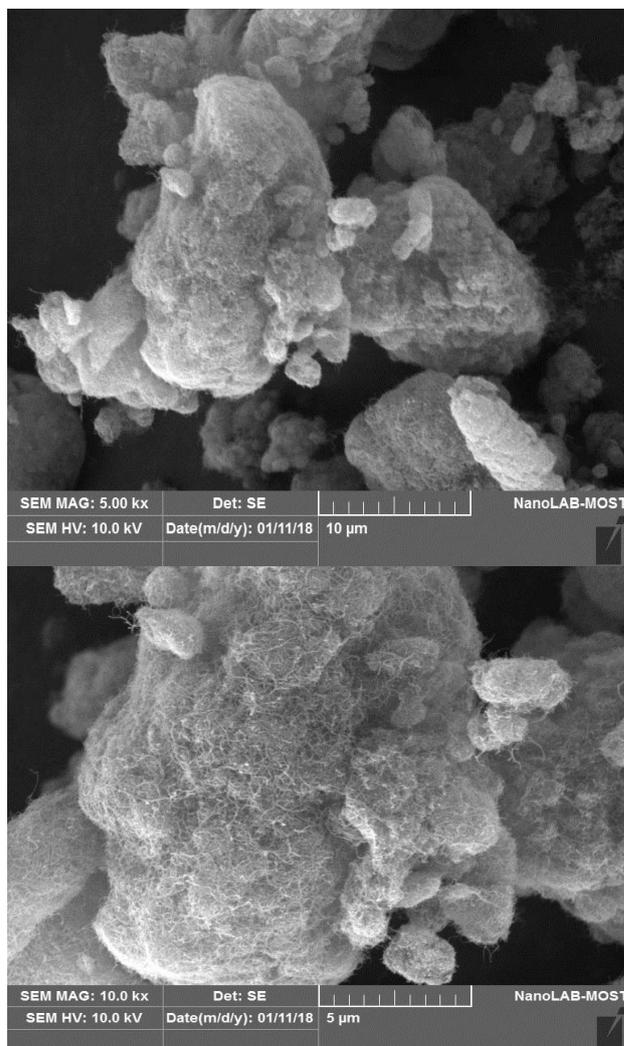


Fig. 3. SEM images of the prepared zeolite with different scales

3.3. Atomic Force Microscope (AFM)

The topography of the surface of the prepared zeolite was taken by the Atomic force microscope.

These images show details about particle size distribution.

AFM allowed a detailed observation of nanometer-size scale at crystal surfaces.

The effect of using the MWCNT on the average particle size of the prepared zeolite was shown in Fig. 4 and Fig. 5.

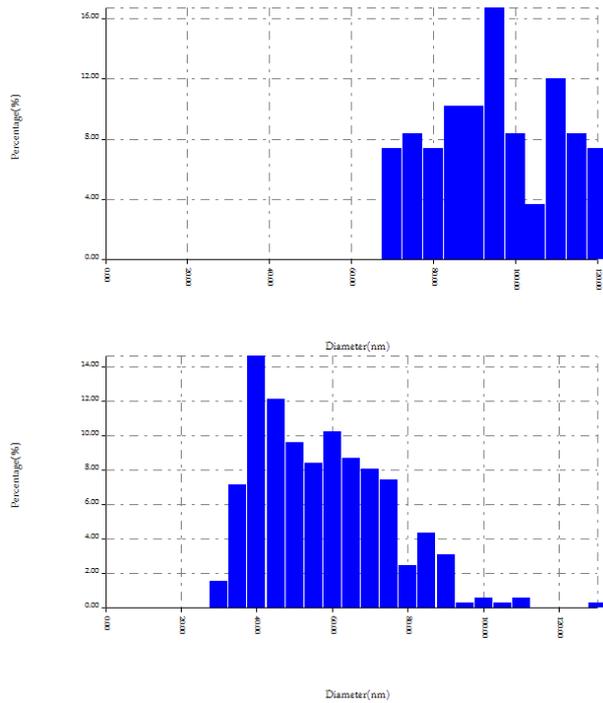


Fig. 4. AFM particle size distribution with average diameter with and without MWCNT

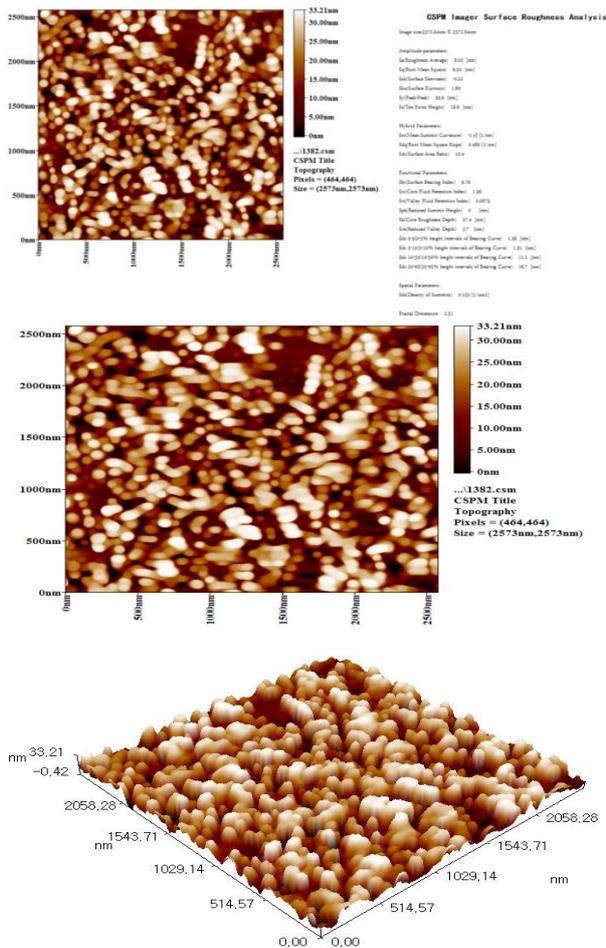


Fig. 5. AFM particle size distribution with average diameter with MWCNT

The average diameter of particle as shown by the AFM was reduced from 92.3 nm to 55.17 nm, also the particle size distribution has shifted toward a lower particle size range.

The differences in particle sizes with and without of the MWCNT was due to the small diameter of the MWCNT which acts as a nucleation point. Zeolite single crystal is grown around the carbon nanotubes.

It is essential that nucleation of the zeolite takes place exclusively between the carbon nanotubes [13].

3.4. Surface Area and Pore Volume

The surface area and pore volume have been measured for prepared Y-Zeolite with and without of MWCNT.

The surface area of the zeolite without MWCNT was 480 m²/g and the pore volume was 0.22 cm³/g while with MWCNT the surface area increase to 558 m²/g and the pore volume slightly increased to 0.231 cm³/g.

The increase of the surface area of the zeolite with MWCNT is due to the nucleation of the zeolite takes place on the carbon nanotubes which make the crystal size smaller [13].

3.5. Fourier Transform Infrared Spectroscopy Analysis

The study of zeolite after the addition of MWCNT by infrared spectroscopy FTIR aims to determine the different chemical functions present on the surface of these solids.

It is a complementary technique that focuses in general on the study of samples at the molecular level.

The FTIR image is shown in figure 6. The regions are found which characterized the faujasite structure are explained as the bands that appears in the region between 3365-3489 cm⁻¹ reveal to the OH stretching band also called low frequency band, SiO₄ molecules and Al-OH.

The bands in the range of 1010- 1019 cm⁻¹ indicate the presence of Si-O.

Absorption at about 443 -465 cm⁻¹ was assigned to Si – O – Al stretching where Al in the octahedral coordination and Fig. 6 show the vibration of Si-AL groups.

From above it was concluded that the FTIR spectra of the synthesis zeolite is matched with the typical absorption peaks of commercial one [12].

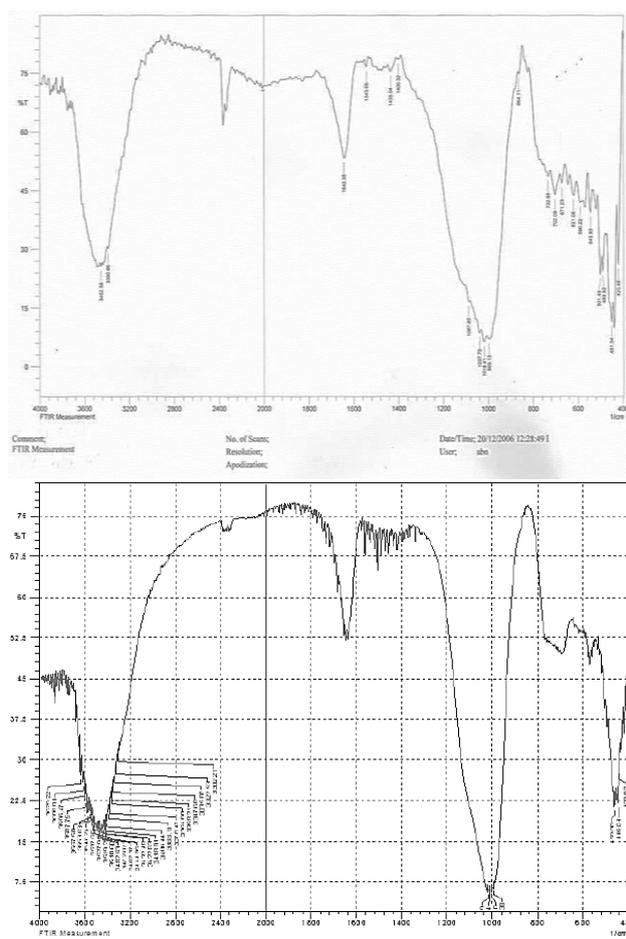


Fig. 6. FTIR analysis of(A) zeolite modified with MWCNT , (B) Y zeolite without MWCNT

4- Conclusions

The phases identification of the formed zeolite shows well-formed crystals having a cubo-octahedral form characteristic of a faujasite type zeolite. The surface area of the zeolite before addition was $480 \text{ m}^2/\text{g}$ and the pore volume was $0.22 \text{ cm}^3/\text{g}$.

After the addition of the MWCNT the surface area increases to $558 \text{ m}^2/\text{g}$ and the pore volume increase slightly with value of $0.231 \text{ cm}^3/\text{g}$. The addition of MWCNT while preparing the zeolite Y did not have an effect on the crystal structure of the zeolite and the resulting zeolite is still type Y but with different degree of crystallization and average particle size were the degree of crystallinity reduced from 144.84 to 120% .also the average particle size was reduced from 92.39 to 55.17nm.

Nomenclature

BET=Brunauer , Emmett, Teller
 SEM=Scanning Electron Microscopy
 MWCNT =Multi wall carbon Nano tube
 XRD=X-ray Diffraction

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توليف وتوصيف زيوليت نانو Y باستخدام MWCNT كوسائل للنمو البلوري

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الخلاصة

تم إجراء البحث الحالي للتوليف Y-Zeolite بتقنية sol-gel باستخدام MWCNT كوسيط تبلور للحصول على نطاق ضيق لتوزيع حجم الجسيمات مع متوسط حجم صغير مقارنة بالطرق العادية. تم الكشف عن نمط الطور والبنية الكيميائية وحجم الجسيمات ومساحة السطح بواسطة XRD و FTIR و AFM و BGT على التوالي. أظهرت النتائج أن متوسط حجم دقائق الزيوليت مع وبدون استخدام MWCNT كان (92.39) نانومتر و (55.17) نانومتر على التوالي وانخفض حجم الجسيمات من (92.39) نانومتر إلى (55.17) نانومتر. تم تحسين مساحة السطح لتصبح (558) م² / جم مع حجم مسامي كبير قليلاً (0.231) م³ / جم. وفي الوقت نفسه ، انخفضت درجة التبلور إلى 120 %.

الكلمات المفتاحية: الأنابيب النانوي الكربوني ، التوليف الحفزي ، زيوليت نانو Y ، MWCNT