



## Synthesis of Nanozeolite NaA from Pure Source Material Using Sol Gel

### Method

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### ABSTRACT

In this work, the nano particles of Na-A zeolite were synthesized by sol –gel method. The samples were characterized by X-ray diffraction (XRD), X-ray Fluorescence (XRF), Surface area and pore volume, Atomic Force Microscope (AFM) and Fourier Transform Infrared Spectroscopy (FTIR). Results show that the nano A zeolite is with average crystal size is 74.77 nm., Si/Al ratio 1.03, BET surface area was 581.211m<sup>2</sup>/g and the pore volume for NaA was found equal to 0.355cm<sup>3</sup>/g.

**Key words:** Nanocrystal, nanozeolite, zeolite type NaA, characterization.

### تحضير النانو زيولايت نوع (NaA) من مصدر المواد النقية بطريقة معاملة الجل حراريا

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### الخلاصة

في هذا العمل تم تحضير زيولايت نوع Na-A بجزيئات نانوية بطريقة معاملة الجل حراريا. تم اختبار خصائص العينات المحضرة بجهاز الاشعة السينية (XRD) وبجهاز المجهر ذو القوة الذرية (AFM) وحساب المساحة السطحية والحجم المسامي بالامتزاز بالنتروجين (BET) وتم حساب نسبة السيلكا الى الالومينا (XRF) والمطياف ذو الاشعة فوق الحمراء (FTIR). واثبتت النتائج فعالية عملية التحضير ونجاحها في الحصول على تركيب نانوي بقياس 74.77 نانومتر ونسبة سيلكا الى الومينا 1.03 ومساحة سطحية 581.211 متر<sup>2</sup>/غم وذو حجم فراغي 0.355 سم<sup>3</sup>/غم.

**الكلمات الرئيسية:** النانوية، النانوزيولايت، زيولايت نوع NaA، التوصيف.



## 1. INTRODUCTION

Nanoscience is considered as one of the key technological fields of the 21<sup>st</sup> century, **Olveira et al., 2014**. Nanozeolites are a type of zeolites which have narrow particle size distribution with sizes of less than 100 nm, **Song et al., 2004**. Compared to "ordinary" zeolites of which the particle diameters are of micrometer order, nanozeolites represent very small particle size, reducing the particle size from micrometer to nanometer scale leads to a significant change of material characteristics and their applications in catalysis and adsorption. The number of atoms in the unit cell increases when particle sizes decrease and nanozeolites have large external surface area. The diffusion path length in nanozeolites is shortened as compared to that in the conventional micrometer zeolites, **Song et al., 2004, Ngoc et al., 2013**. One of the advantages of nanozeolites is their higher external surface area. The external surface is of vital important in numerous processes, including adsorption and catalysis. Nano-crystalline zeolite is synthesized in many different synthetic methods mostly are: hydrothermal treatments, sol - gel method, and the emulsion method, **Radhi, 2015**.

The sol-gel method is a useful and attractive technique for the preparation of nanosized particles because of its advantages: good stoichiometric control and the production of ultrafine particles with a narrow size distribution in a relatively short processing time at lower temperatures, **Chen, and He, 2001**. One important factor in sol-gel technology is the ageing time allowing the gelation of the sol. It can vary from a few minutes to several weeks, depending on the concentrations in the sol, **Meille, 2006**.

**Azizi et al., 2006** prepared NaA nano-zeolite using microwave pretreatment and a hydrothermal method without organic additives. The result showed that the sizes of NaA nanoparticles are in the range of 40 to 90 nm with an average diameter of 60 nm. The specific surface area of the NaA nanozeolite is  $97.48 \text{ m}^2 \text{ g}^{-1}$  and the average pore diameter of 2.459 nm.

NaA Nanozeolite was synthesized by the hydrothermal method with different crystallization time (1, 2 and 3 days) at room temperature under stirring. Nanocrystals NaA with crystal sizes ranging from 50 to 120nm were synthesized at room temperature with 3 days aging, without adding any organic additives and external surface of the resulting NaA zeolite was  $62.520 \text{ m}^2 \text{ g}^{-1}$ , **Ghasemi and Younesi, 2011**.

**Jawad, 2009** Prepared nano sized particles zeolite Y by sol-gel method the results showed that the pore volume increased as the surface area increased of synthesized nano particles zeolite Y increased with increasing Si /Al ratio.

**Rahman et al., 2012** prepared zeolite Y using sol gel method and they obtained highly crystalline and surface area of about  $320 \text{ m}^2/\text{g}$  with pore volume  $0.15 \text{ cm}^3/\text{g}$ . In this study, a facile method for the preparation of nonocrystalline zeolite NaA is investigated using sol-gel method. Extensive characterization of the final product was done using (XRD), (BET), (XRF), (AFM), and (FTIR).

In this paper, prepared nanozeolite NaA from pure source materials was done using sol-gel method.

## 2. EXPERIMENTAL WORK

### 2.1 Synthesis of Nanozeolite NaA

#### 2.1.1 Materials

The chemical Materials used included NaOH (Sigma), sodium aluminate (Kunshan Yalong), sodium silicate (Himedia), and deionized water.

### 2.1.2 Methods

Nano\_Zeolite A was synthesized according to sol-gel method. The preparation involved three major steps, namely: seeding gel, feed stock gel and over all gel. Seeding gel is prepared by adding 4.1 g of sodium hydroxide, 20 g of deionized water and 2.1 g sodium aluminate, **Rahman et al., 2012, Al-Tabbakh, 2016**. The mixture was continuously stirred with magnetic stirrer in 50 ml plastic bottle until the mixture became an apparent solution then 20 g of sodium silicate solution was added and stirred moderately for at least 15 min, and then the bottle was capped and the solution is left to age at room temperature for 24hr. The feed stock gel was prepared by adding 131 g of deionized water to 0.14 g sodium hydroxide and 13 g sodium aluminate, stirred in 500 ml plastic beaker until dissolved then 140.5 g of sodium silicate solution was added with stirring vigorously with high shear 4 paddle mixers at 1600 rpm until the gel appears smooth. The overall gel was prepared by mixing the feed stock gel with 16.5g of the seed gel. The seed gel was added slowly under high shear mixing for 40 min at room temperature at 1600 rpm. After that the final gel was transferred to a poly propylene bottle and stored in a water bath at 87°C in a programmable electrical furnace for 24 hours.

The product obtained was filtered using Buckner funnel with the aid of a vacuum pump and repeatedly washed with deionized water until pH reached to 9. The product was dried in an electrical oven for 24 hours at 100°C and then was calcined by the programmable electrical furnace at 500°C for 3 hours. Experimental apparatus is shown in **Fig.1**.

### 2.1.3 Characterization

XRD analyses were carried out at room temperature using a Shimadzu 6000 (Japan) using CuK $\alpha$  radiation nickel filter ( $\lambda= 1.5418\text{\AA}$ ). Data were collected within the  $2\theta$  range of  $2^\circ$  and  $50^\circ$  with a  $2\theta$  step size of 0.02 and a step time of 0.24s per step (40kv and 30mA). The surface area of prepared catalyst was measured by nitrogen physical adsorption at liquid nitrogen temperature at -196 °C using the BET (Brunauer, Emmett, and Teller) method. Pore volume is a measure of the void space in the catalyst. It is measured by nitrogen adsorption BET and expressed in  $\text{cm}^3/\text{g}$ .

The chemical composition of the prepared zeolite was analyzed using XRF technique. The test was conducted by a device of the type SPECTRO XEROS (Germany) by weighing a sample of 3g in powder state and putting in plastic cup of 30mm diameter. Test conducted in inert atmosphere (Helium). Atomic Force Microscope (AFM) is a powerful technique for surface investigation by providing material topology in high resolution. The test was performed by Device (type Angstrom, Scanning Probe Microscope, Advanced Inc, AA 3000, USA), performed for samples by ethanol dispersion to conducted the surface morphology and the particles size.

And FT-IR spectroscopy analysis of zeolites was carried out to study the features their structure by the chemical bonds (functional group) between molecules. This test was done using a Shimadzu FTIR 8400S (Japan) with wave number range ( $400\text{-}4000\text{ cm}^{-1}$ ).

## 3. RESULTS AND DISCUSSION

### 3.1 X- Ray Diffraction (XRD)

X-ray diffraction was implemented to check the required pattern of NaA nanozeolite and its crystalline. From **Fig.2** X-ray diffraction pattern of the prepared NaA nanozeolite is approximately comparable with the standard. **Table 1** shows a comparison of lattice spacing and angle, between prepared NaA nano-zeolite and standard.

The highly crystalline zeolite is with no amorphous material and the relative intensities of the peaks which are related to the level of zeolite crystallization, **Alrubaye, 2013**.

The relative crystallinity of zeolite was determined by dividing the sum of the peak intensities of the prepared zeolite on the sum of the peak intensities of the standard zeolite and can be expressed mathematically, **Doneliene et al., 2010**. The relative crystallinity is calculated by Eq.(1) and it was found to be equal to 97.6%.

$$\text{Relative Crystallinity \%} = \frac{\sum \text{Intensities of peaks of sample}}{\sum \text{Intensities of peaks of reference sample}} * 100 \quad (1)$$

### 3.2 Surface Area and Pore Volume

The obtained value of surface area of prepared nanozeolite NaA was 581.211m<sup>2</sup>/g and the pore volume was found equal to 0.355cm<sup>3</sup>/g.

### 3.3 X- Ray Florescence (XRF)

The chemical composition of the prepared zeolites expressed in weight percent are listed in the **Table (2)**. The molar ratio of Si/Al for NaA nanozeolite was equal to 1.03. This result is in a good agreement with the result obtained by, **Ghasemi and Younesi, 2011** which is about 1.071.

### 3.4 Atomic Force Microscope (AFM)

The surface uniformity of the prepared nanozeolite was studied using Atomic Force Microscope with 408 pixel density. **Fig.3** shows AFM on two-dimensional surface profile while **Fig.4** shows AFM for three dimensional surface profiles.

The particle size distribution for prepared NaA nano\_zeolite was obtained as shown in **Fig.5**. This figure shows that the most volume percentage 11% of particle size distribution was at 95 nm and the lowest volume percentage 0.44 % was at 45 and 50 nm. It also shows the prepared zeolite consisted of particles with diameters ranged between 45 - 100 nm. This means that the particles of prepared zeolite are nanometer-sizes and the average particles diameter of NaA nano\_zeolite was 74.77nm. This result is in a good agreement with the result obtained by **Ghasemi and Younesi, 2011**.

### 3.5 Fourier Transform Infrared Spectroscopy (FTIR)

FT-IR spectroscopy analysis of zeolites was carried out to study the features of their structure by the chemical bonds (functional group) between molecules. This test was determined using a Shimadzu FTIR 8400S (Japan) with wave number range (400-4000 cm<sup>-1</sup>). Samples were prepared by mixing 1wt. % of zeolite and 99% KBr pressed as disk.

**Fig.6** illustrates the FTIR spectra of prepared NaA nanozeolite. From this figure it can be observed that, the bands in the region of 983-1030 asymmetric stretching vibrations Si-O in SiO<sub>4</sub> and Al-O in AlO<sub>4</sub>. The band in the region 711-767.62 was symmetric stretching vibrations Si-O-Si. Absorption at about 698 cm<sup>-1</sup> was assigned to Si – O – Al symmetric stretching where Al in the octahedral coordination. Peaks 1637.54cm<sup>-1</sup> and 3519.85 cm<sup>-1</sup> are assigned to the external linkage asymmetrical stretching and internal tetrahedral symmetrical stretching respectively. These results are comparable with the results obtained by many researchers such as **Omisanya et al., 2012, Mozgawa et al., 2011, Alkan et al 2005, and Aronne et al., 2002**.



## CONCLUSIONS

Nano crystalline NaA zeolite has been prepared successfully using sol-gel method. According to the results obtained from this study, it was found from X-ray that prepared NaA nanozeolite has crystallinity of 97.6% and nearly has the same crystal structure as the standard type A-zeolite with silica to alumina molar ratio 1.03, surface area  $581.211\text{m}^2/\text{g}$ , the pore volume  $0.355\text{cm}^3/\text{g}$  and the average particles diameter of NaA nanozeolite was 74.77nm.

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A

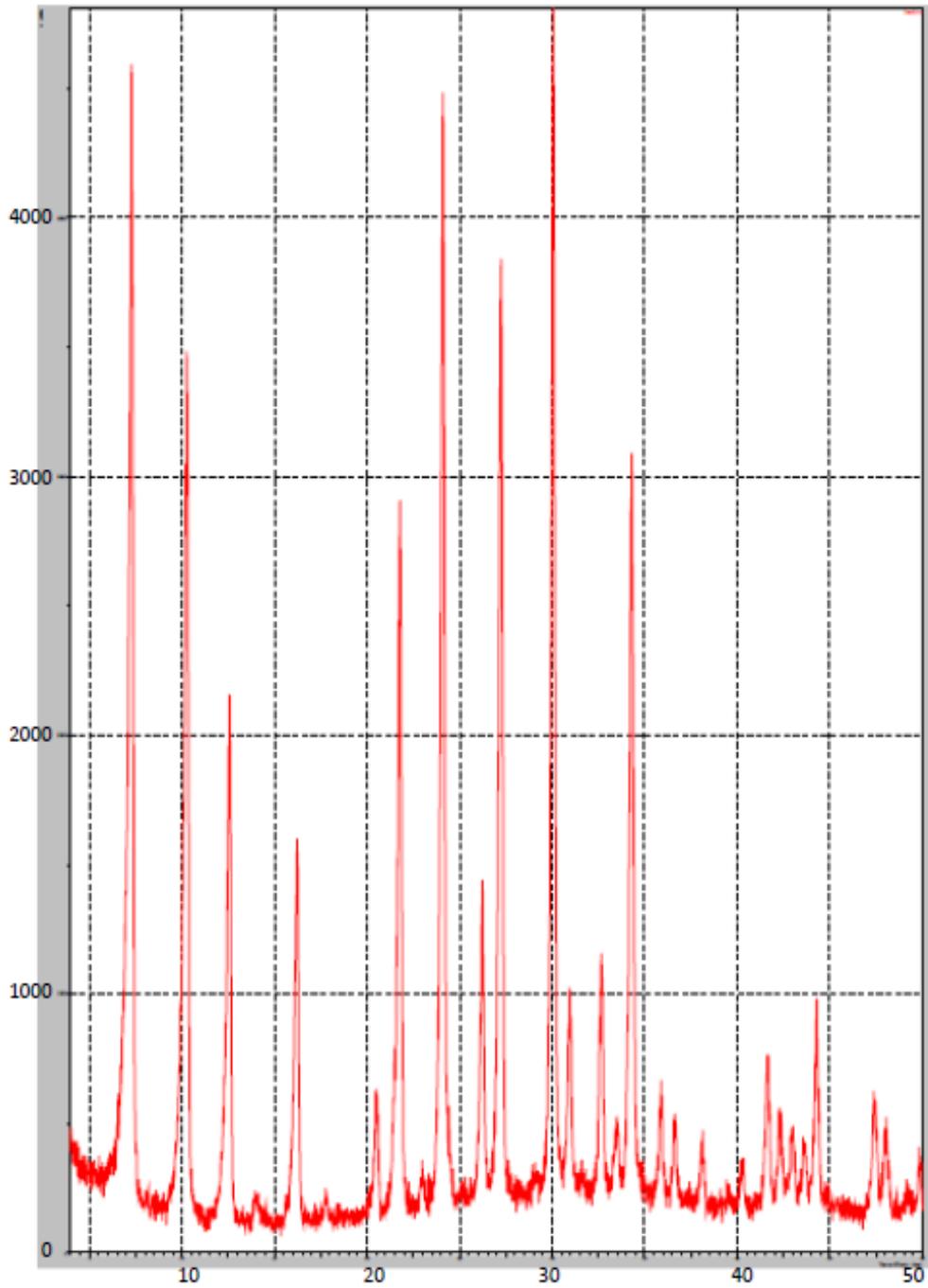


B



C

**Figure 1.** Preparation of NaA nano\_zeolite: A. mixing of overall gel B. Filtration and washing of final product C. final product.



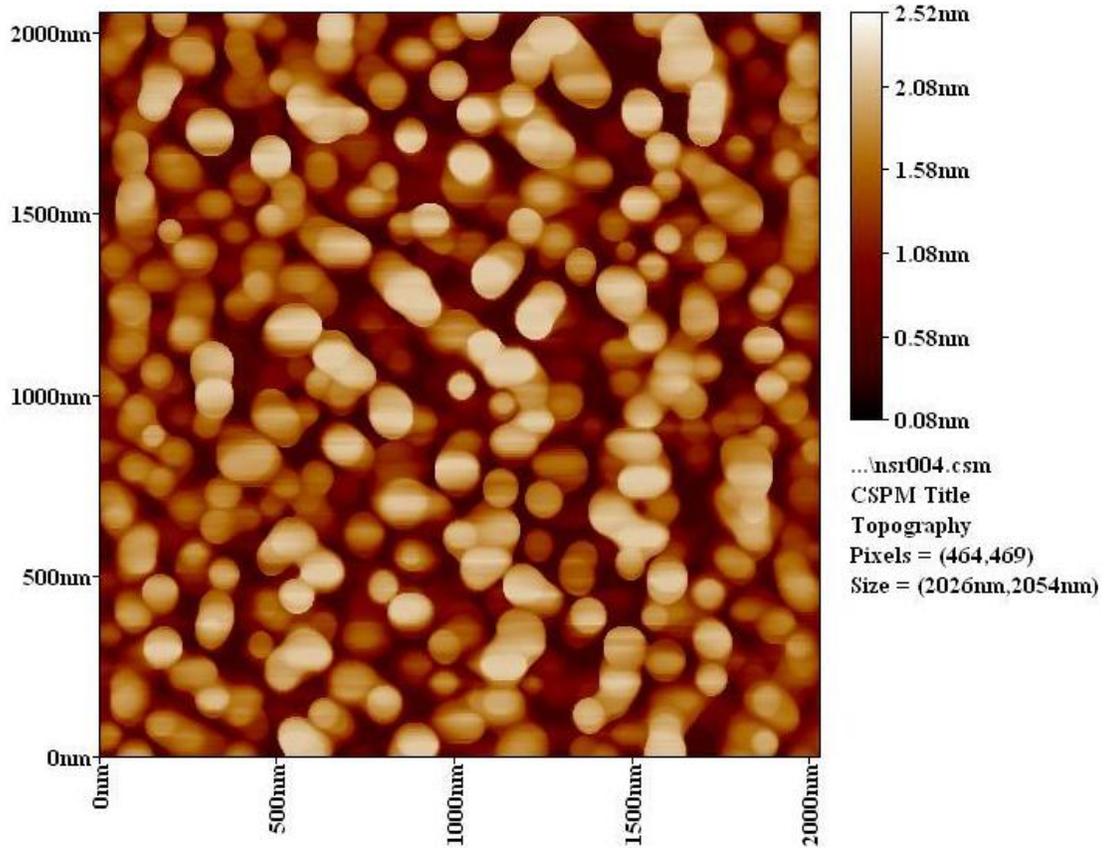
**Figure 2.** XRD pattern of prepared NaA nano\_zeolite.

**Table 1.** Comparison of lattice spacing and angle, between prepared NaA catalyst and standard A.

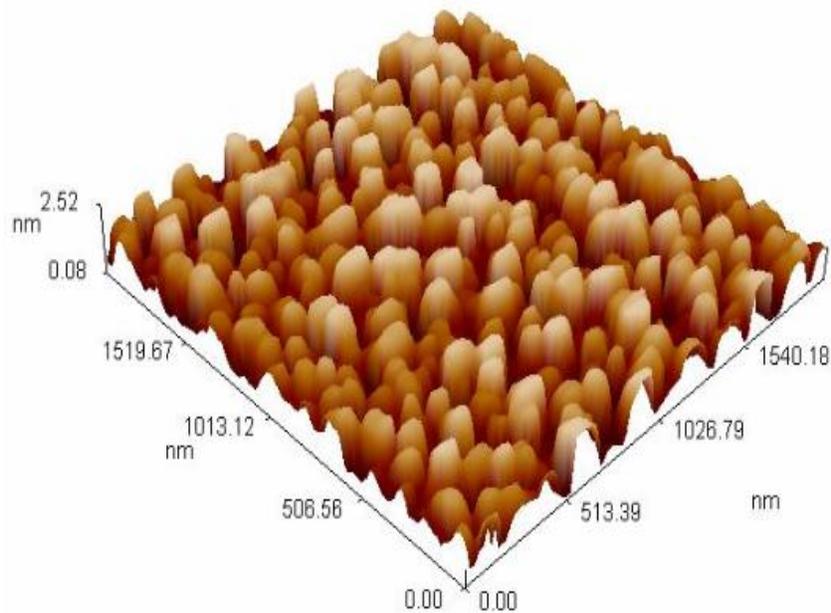
Prepared catalyst		Standard of catalyst	
Angle (2Theta)deg	d, spacing(Å)	Angle (2Theta)deg	d, spacing(Å)
7.2010	12.31045	7.18	12.305
10.2015	8.68842	10.17	8.701
12.4623	7.11194	12.46	7.104
16.1316	5.50085	16.11	5.503
22.8617	3.88825	22.85	3.891
23.9898	3.72044	23.99	3.710
25.0672	3.55128	25.07	3.552
27.0990	3.28787	27.11	3.289
30.8190	2.90025	30.83	2.900
31.7103	2.81953	31.70	2.823

**Table 2.** The chemical composition for the prepared zeolites.

Oxides, wt. %	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	MgO	CaO	ZnO
NaA	47.992	30.24	0.2314	0.2346	0.4913	1.8513	0.0063



**Figure 3.** AFM two-dimensional surface profiles for NaA.



**Figure 4.** AFM three-dimensional surface profiles for NaA.

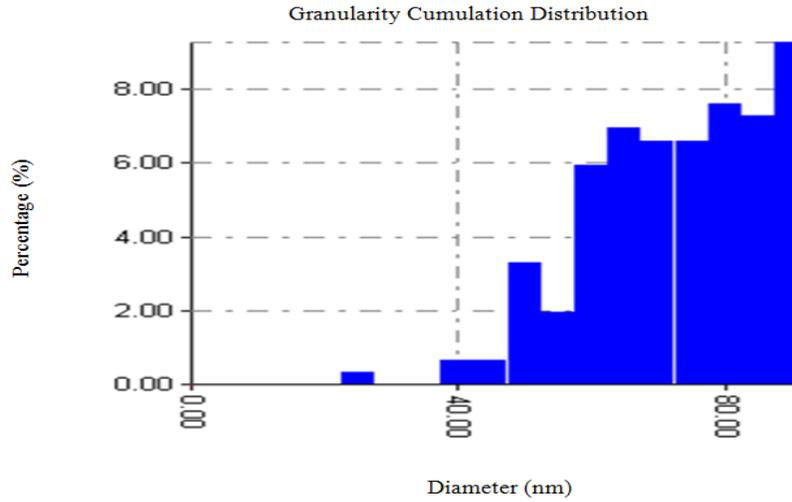


Figure 5. Granularity cumulation distribution for prepared NaA.



Figure 6. FTIR of synthesize nanozeolite NaA.