Int. J.Nano Dimens. 5(1): 91-95, Winter 2014
ISSN: 2008-8868

Contents list available at **IJND**

International Journal of Nano Dimension

Journal homepage: *www.IJND.ir*

Short Communication

Synthesis of nanocrystalline zeolite NaY by hydrothermal method and investigation of its structure and morphology

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Received: 24 September 2012
Accepted: 29 January 2013

ABSTRACT

Zeolite FAU type-Y is one of the most studied framework of all zeolites, and has been used as catalysts for number of reactions in the refinery and petrochemical industry. In this research, nanocrystalline zeolite Y was synthesized by hydrothermal method. The crystal size of zeolite Y is influenced by temperature, aging time, alkalinity, and water content. The synthesized zeolite NaY is identified and characterized by Brunauer-Emmett-Tell (BET), Fourier Transmission Infrared Spectroscopy (FTIR), X-ray diffraction (XRD), Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM). The mean crystallites size was measured by transmission electron microscopy (TEM) and it was determined also by Rietveld's method using Scherrer's equation; with similar results estimated was about 50 nm.

Keywords: *Zeolite NaY; Nanocrystals; Synthesis; Hydrothermal; AlP; Morphology.*

INTRODUCTION

Zeolites are crystalline aluminosilicates containing pores and channels of molecular dimensions that are widely used in industry as separations, ion exchange resins, molecular sieves, sorbents and catalysts [1-4]. One of the first successful applications of nanotechnology was the use of zeolites as catalysts for industrial processes, such as petroleum refining [5]. Recently, there has been a great deal of interest in another aspect of zeolites related to nanoscience, the primary crystal size, which can potentially be exploited for use in nanotechnology. Nanocrystalline zeolites are zeolites with discrete, uniform crystals with dimensions of less than 100 nm that have unique properties relative to conventional micrometer-sized zeolite crystals. Nanocrystalline zeolites have higher external surface areas and reduced diffusion path lengths relative to conventional micrometer-sized zeolites, which make them promising catalytic materials and adsorbents.

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A representative empirical formula of a zeolite is: $M_{2/n}.Al_2O_3.ySiO_2.wH_2O$, Where M represents the exchangeable cation of valence n. M is generally a Group I or II ion, although other metal, non-metal and organic cations may also balance the negative charge created by the presence of Al in the structure. Zeolite Y exhibits the FAU (faujasite) structure. It has a 3-dimensional pore structure with pores running perpendicular to each other in the x, y, and z planes similar to LTA, and is made of secondary building units 4, 6, and 6-6[7,8]. The framework of Zeolite Y consists of β-cage (sodalite) and α-cage (super cage). *β*-cage are linked together by double six membered rings (D6R). The pore diameter is large at 7.4 Å since the aperture is defined by a 12 member oxygen ring, and leads into a larger cavity of diameter 12Å. The cavity is surrounded by ten sodalite cages (truncated octahedral) connected on their hexagonal faces. The unit cell is cubic (a= 24.7Å) with Fd-3m symmetry. Zeolite Y has a void volume fraction of 0.48, with different framework Si/Al ratios between 1.5< Si/Al<3. It thermally decomposes a 793ºC (Figure 1).

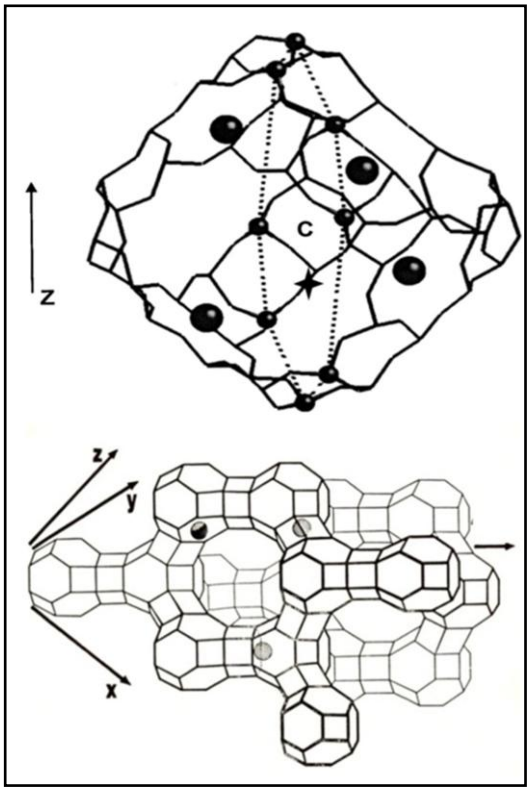

Fig. 1. Structure of zeolite type-Y, The framework solid line is formed from silicon, aluminum, and oxygen atoms.

The general formulation composition of a zeolite Y is Na_2O .Al_2O_3.4, 8 SiO_2.8, 9 H_2O [1, 2]. The primary application for Y zeolites has been in catalytic cracking of petroleum molecules into smaller gasoline range hydrocarbons [2]. Recently, the synthesis of nanocrystalline zeolite Y has been reported by several groups [3, 8-11]. The nanocrystalline zeolite materials have been used as photochemical hosts in optically transparent solutions and to study zeolite crystal growth mechanisms [3,4-8]. In this study, the synthesis, characterization, and of synthesized nanocrystallines zeolite Y are reported. The synthetic method used here is a modification of the method of Creaser and co-workers [8]. The physicochemical properties of the synthesized, nanocrystalline NaY samples; the functionalization of the external surface of nanocrystalline NaY; and the potential of these materials for applications in environmental remediation are discussed.

EXPERIMENTAL

Materials

Sodium hydroxide pellets, aluminium iso-propoxide (AlP), tetraethoxysilane (TEOS), tetramethylammonium hydroxide (TMAOH), 25% aq.), were purchased from Merck and were used without further purification.

Synthesis of nanocrystalline zeolite NaY

A solution of sodium hydroxide 0.05 N was diluted with deionized water. After that, tetramethylammonium hydroxide solution and aluminium isopropoxide, were added in that order, and stirred vigorously until the solution became clear. Tetraethylorthosilicate was added drop wise to the clear solution. This final mixture was aged for 3 days under vigorous stirring at room temperature. The final molar composition was: $0.72(TMA)_2O$: 0.0094 Na_20: 0.29 Al_20_3: 1 $Si0_2$: 108.82 H_20. The crystallization of zeolite was performed in a Teflon- lined stainless steel autoclave. After being filled with the prepared clear solution, the autoclave was completely sealed and heated at 100 °C and crystallization time was 6 days. The solid product was recovered by centrifugation at the speed of 14,000 rpm for 30 min, washed several times with distilled water,

dried over night at 80 °C, and calcined in air at 773 K for 16 h [12].

The synthesized nanocrystalline zeolite NaY was characterized by several different techniques, including Brunauer-Emmett-Tell (BET), Fourier transform infrared spectroscopy (FT-IR), X- ray diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM). Nitrogen Adsorption Isotherm was obtained on a quantachrome nova 1200 multipoint BET apparatus using approximately 0.1 g of sample for measurement. Immediately prior to the N_2 adsorption sample was vacuum degassed at 100 for 1 h. This method was collected to zeolite NaY sample before and after calcination removes the template. The IR spectrum was scanned using a Perkin-Elmer FTIR (Model 2000) in the wavelength range of 400 to 4000 cm^{-1} with KBr pellets method. The powder XRD patterns of catalyst were obtained using XRD measurement on a Philips diffractometer with Cu target Kα-ray. The analysis was conducted at 2 theta values of 10–50^o. The particle size and morphology of the microcrystalline and nanocrystalline zeolite were analyzed using SEM and TEM image. For SEM, the powder form samples were carefully put on a double-sided tape with the aluminum stub as the base. The observations were made at different magnifications using a Leica Cambridge S-360SEM and JEOL scanning electron microscope. For TEM, the powder sample was suspended in 100 % ethanol under ultrasonic treatment for 15 min. Several drops of ethanol containing the lightest powder sample were deposited on a copper grid. The TEM images were recorded using a Philip CM12 transmission electron microscope operated at 80 kV.

RESULTS AND DISCUSSION

Characterization of nanocrystalline zeolite NaY

- ***Nitrogen adsorption analysis of the nanocomposite***

The structure properties of nanocrystalline zeolite NaY was obtained from the nitrogen adsorption isotherm or Brunauer-Emmett-Tell (BET) and is listed in Table 1.

Table 1. Properties of synthesized nanocrystalline zeolite NaY

Size from BET area(nm)	50
BET surface area(m^2/g)	1123
External surface area(m^2/g)	580
Total pore volume	516
Si/Al	1.8
Median pore width(Å)	5.163

- ***Fourier Transmission Infrared Spectroscopy (FTIR)***

FTIR spectrum is shown in Figure 2 for nanocrystalline zeolite NaY. Peak position is nearly identical for the four samples. The peak at 466 cm^{-1} is assigned to the structure insensitive internal TO_4 (T=Si or Al) tetrahedral bending peak of zeolite Y. The peak at 566 cm^{-1} is attributed to the double ring external linkage peak assigned to zeolite Y. The peaks at 679 and 759 cm^{-1} are assigned to external linkage symmetrical stretching and internal tetrahedral symmetrical stretching respectively (D6R). Furthermore, the peaks at 1020 cm^{-1} and 1085 cm^{-1} are assigned to internal tetrahedral asymmetrical stretching and external linkage asymmetrical stretching respectively and peaks around 1634 and 3479 cm^{-1} are assigned to H-O-H bending and hydroxyl groups of zeolite, respectively.

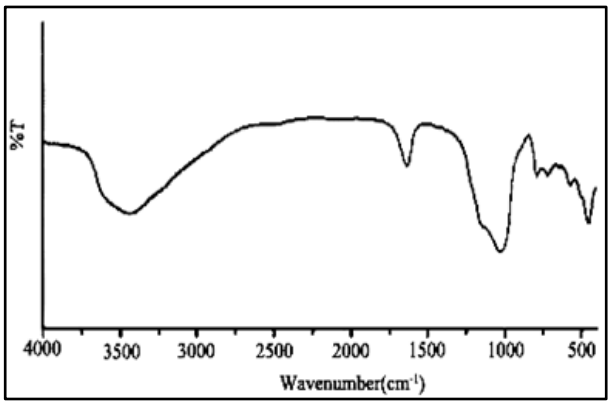

Fig. 2. FTIR spectrum of nanocrystalline zeolite NaY

- ***X-ray diffraction (XRD)***

The XRD pattern of the nanocrystalline zeolite Y synthesized is shown in Figure 3. The Scherrer equation (1) is used in x-ray diffraction and crystallography to correlate the size of sub-micrometer particles, or crystallites:

$$d= 0.94\lambda/\beta\cos\theta \qquad (1)$$

Where λ is the x-ray wavelength, β I s the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle ($6<2\theta<38$). The average diameter of synthesized nanoparticles calculated by XRD technique was estimated as 50 nm for prepared nanocatalysts zeolite NaY.

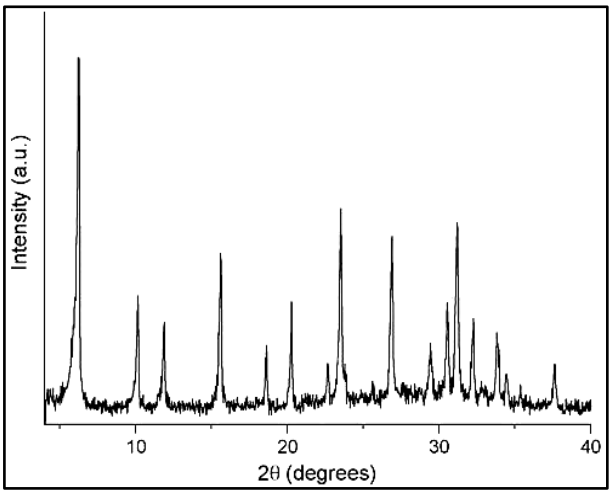

Fig. 3. XRD pattern of nanocrystalline zeolite NaY

- ***SEM and TEM analysis***

In order to establish the crystal size of the zeolite sample, the scanning electron micrograph (SEM) technique was used. Representative micrographs of the nanocrystalline zeolite Y is shown in Figure 4. A small average crystal size of about 50 nm was observed and it is also seen that the crystal size distribution appears to be uniform. This is expected since the precursors are protected from aggregation during the crystallization. In Figure 5 show TEM images of the nanocrystalline zeolite NaY.

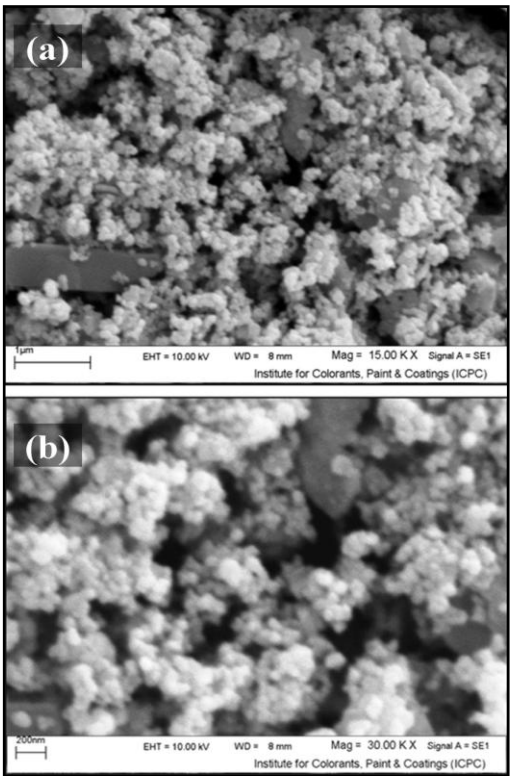

Fig. 4. SEM image of nanocrystalline zeolite NaY (a) 15000X and (b) 30000 X

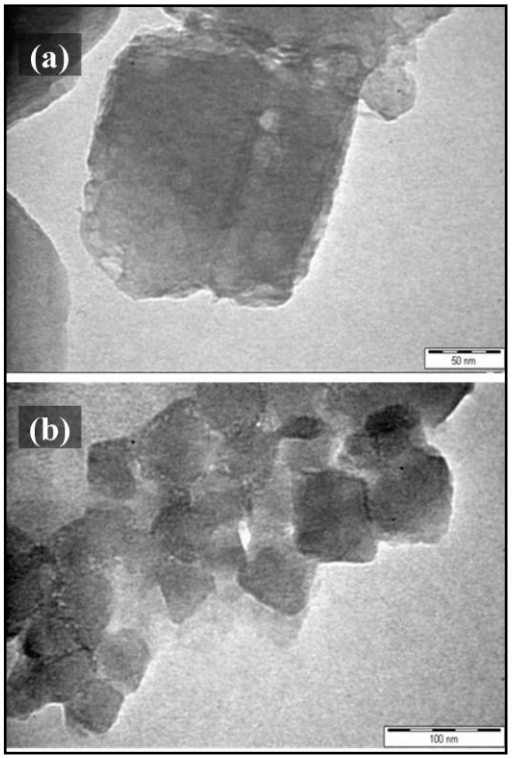

Fig. 5. TEM image of nanocrystalline Zeolite NaY (a) 50 nm and (b) 100 nm

CONCLUSIONS

Synthesis of nanocrystalline zeolite Y has been successful using hydrothermal synthesis from clear synthesis mixtures. The decrease in the crystal size to the nanoscale range produced changes in the physicochemical properties of the zeolite compare to microcrystalline zeolite.

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Cite this article as: M. Sadeghi *et al.*: Synthesis of nanocrystalline zeolite NaY by hydrothermal method and investigation of its structure and morphology.
Int. J.Nano Dimens. 5(1): 91-95, Winter 2014