Journal of Physical and Theoretical Chemistry
of Islamic Azad University of Iran, 8 (3) 245-249: Fall 2011
(J. Phys. Theor. Chem. IAU Iran)
ISSN 1735-2126

Synthesis of Nanozeolite NaX and Optimization of the Method

S. Jalilehvand[1], B. Amirpour[1], R. Fazaeli [2*], M. H. Givianrad[3] and A. Mashinchian moradi[1]

[1] Graduate School of Marine Science and Technology, Department of Marine Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran
[2] Modeling and Optimization Research Center in Science and Engineering, South Tehran Branch, Islamic Azad University, Tehran, Iran
[3] Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran

Received December 2011; Accepted December 2011

ABSTRACT

In this investigation we synthesized NaX-Nanozeolite by hydrothermal crystallization conditions. These nanoparticles were prepared at different conditions in a temperature controlled shaker. The synthesized zeolites were characterized by instrumental analysis methods, such as X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. The observed results showed particle size between 20 to100 nm. Then we examined the influence of different parameters on particle size such as reaction time, temperature and agitation. Crystallization with shaking at 60°C for 2 days was the best conditions for synthesis of NaX-Nanozeolite.

Keywords: NaX Nanozeolite; hydrothermal Crystallization; fumed silica; sodium aluminat

INTRODUCTION

Zeolite X is the large-pore zeolite with framework structural type (FAU). Zeolite X has a Si/Al~1.25 [$Al(SiO_4)$]. It is used primarily as an adsorbent and in gas drying. A synthesis protocol for zeolite X with a Si/Al~1 was reported in the 1980's [1]. The synthesis of nanometer-dimansion zeolite has received much attention in the past decade because nanometer-sized zeolitic crystals can have different properties than their micrometer-sized counterparts [2-10].The reduction of the particle size from the micrometer to the nanometer scale can change the mass- and heat transfer resistances in catalytic and sorption processes, thereby improving the catalytic selectivity and reducing coke formation in some petroleum reactions [11]. Various nanometer-sized zeolites can be synthesized via hydrothermal procedures using clear aluminosilicate solutions in the presence of organic templates [1-10]. For instance, nanocrystalline faujasite zeolites have been synthesized with the assistance of tetramethylammonium (TMA) as a template [1-6]. However, the organic template approach has several draw backs. These templates are expensive and nonrecyclable and the removal of the templates can lead to an irreversible aggregation of nanocrystals into larger solid particles [12]. We are interested in the synthesis of nanometer-

* Corresponding author: R. Fazaeli

Archive of SID

www.SID.ir

sized zeolites, in part because they are the most widely used catalysts in removal of organic and inorganic pollutants processes [13]. We reported our novel and organic-additive free method to synthesize nanocrystalline NaX zeolite (NaX-nano) [14]. In this study we have synthesized the NaX zeolite with nanometer size particles. Different Si and Al sources are reported for the synthesis of zeolite NaX such as SM-30, Fumed Silica and TEOS as Si sources and Aluminum Triisopropoxide, sodium alominate as Al source [13-15]. The use of different sources of Si and Al make result in deffrent structural parameters and elemental contents, surface area and average particle size of the synthesized zeolite [16]. In this experience we have been used fumed Silica as Si source and sodium Aluminate as Al source.

EXPERIMENTAL METHODS

Materials

The chemical reagents used included fumed silica (Sigma), tetraethyl orthosilicate (TEOS, Aldrich), NaOH (Merck), $NaAlO_2$ (Merck) and distillated water. All were used without further purification.

Preparation of Samples

The following molar composition was used for synthesis NaX-Nsnozeolite. 5.5 Na_2O:1.0 Al_2O_3:4.0 SiO_2:190 H_2O. As a result, an aluminosilicate gel containing 5.34 g of NaOH, 2.42 g of NaAlO2, 3.43 g of SiO_2, and 50.0 g of H_2O was prepared. The nanometer-sized faujasite-X zeolite was synthesized by hydrothermal crystallization in a temperature-cotrolled shaker. In this way the fumed Silica as a Si source and sodium aluminate as Al source was used for synthesis NaX-Nanozeolite. The Fumed Silica was directly mixed with freshly prepared aluminate solution at room temperature and then immediately moved to a shaker at the desired temperature for hydrothermal crystallization. This process was conducted at 60°C for 2-4 days in a shaker with a rotation rate of 250 rpm. The powdered products were recovered with centrifujation washed with DI water until PH<8 was reached and then dried at room temperature for 24h for further characterization. The synthesis product was characterized by XRD, XRF, SEM and TEM techniques. The morphology and the particle size of the synthesized samples were examined by XL30 Philips scaning electron microscope (SEM) and CM12 Philips transmission electron microscope (TEM).

RESULT AND DISCUSSIONS

Optimization of the synthesis method

We found that crystallite size of NaX zeolite can be modified by changing the synthetic conditions such as different temperatures, shaking conditions and crystallization time. The different conditions used in this research are shown in table 1. The SEM images for samples prepared using different synthetic conditions are shown in fig.1. SEM results show that crystallization at 60 °C for 2 days with shaking gave the smallest particle size (Fig.1a). crystallization at 90 °C for 2 days with no shaking or stirring gave NaX-µ particles (Fig.1c). Crystallization at 45 °C for 2 days and then at 90 °C for 16 h with stirring gave particles between NaX-nano and NaX-µ (Fig.1b). Based on our findings, production a wide variety of sizes of NaX zeolite, ranging from 35 nm to 1 µm, for various applications will be possible.

Table 1. Different conditions for synthesis

Synthesis conditions	Time	Temperature (°C)	sample
Shaking (250rpm)	2 days	60	a
Shaking	2 days	45	b
	16 hours	90	

Archive of SID

www.SID.ir

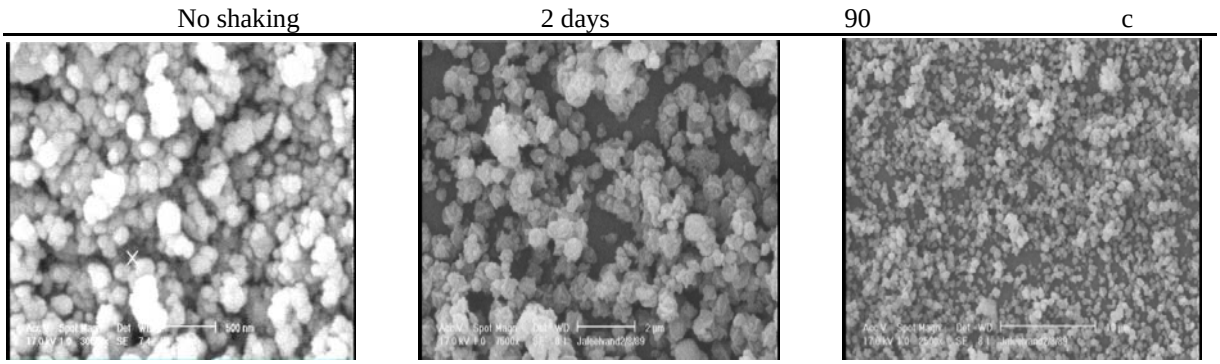

Fig. 1. SEM images of synthesized NaX- zeolite in different conditions.

Reaction temperature

Reaction temperature is one of the most important parameters that can directly affect the quality of the product. The synthesis procedure was performed at different temperatures from 45 to 90 ^{0}C. According to quality control tests, followed by X-ray diffraction of the prepared samples, 60 ^{0}C is the most suitable temperature for this reaction, which increases the purity of NaX nanozeolite while decreasing the particle size.

Reaction time

The effect of reaction time on synthesis process was investigated. The crystallization was improved by increasing the reaction time from 16 to 48 hours, however, after that no improvement was observed. Therefore, 2 days was selected as the optimum reaction time.

Si and Al Concentrations

The concentration of Si and Al are the most effective parameters on zeolite quality. Different solution concentrations were employed and optimum concentration of Si and Al solutions were achieved. Increasing the degree of crystallinity of zeolite is resulted by using solutions with suitable concentrations.

The crystallinity of the products can also be affected by temperature of Si and Al solutions at mixing process. Si and Al solutions at room temperature were mixed together. The zeolite quality showed that the primary solutions temperature at the mixing time should be in the room temperature.

The sources of Si and Al should be admixed at an appropriate time because of their effects on gel formation and crystallinity. Hence, 1 hour was selected as the best mixing time.

Mixing rate can also affect the crystallization process. Using mechanical mixer with 800 rpm led to high crystallinity of zeolite that demonstrated by XRD analysis. Under these conditions, according to SEM and TEM images, particle size of the product was 20-100 nm.

Drying process can affect physical properties of the products such as pore size and surface area.

Results of the analysis

Different analysis methods such as: XRD, XRF, SEM and TEM were used for quality control and the comparison of the synthesized samples. The XRD pattern of synthesized zeolite is shown in fig.2.

The patterns indicated that the synthesized samples have the structure of zeolite NaX. The average of particle size is about 35 nm.

TEM images of samples are shown in fig.3. According to the TEM images, particle size of the synthesized zeolite in common conditions has been estimated about 50 nm for the nanozeolite synthesized.

Elemental analysis of samples was performed with XRF and presented in table 2, the results were in good agreement with NaX general formula.

Archive of SID

www.SID.ir

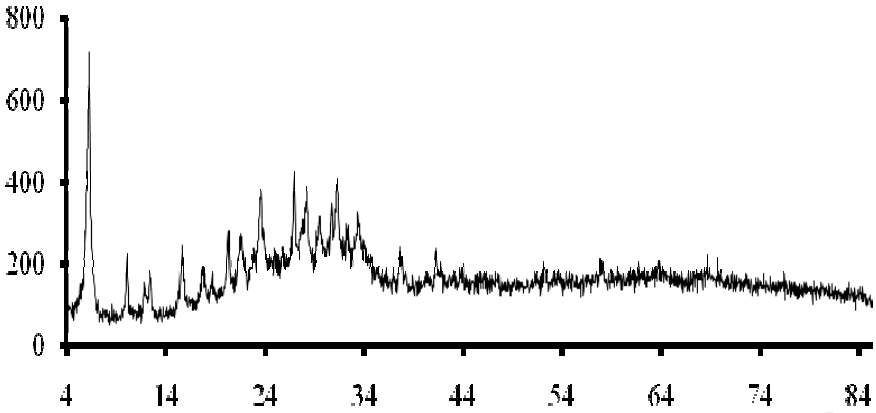

Fig. 2. X-ray powder diffraction patterns of NaX nanozeolite.

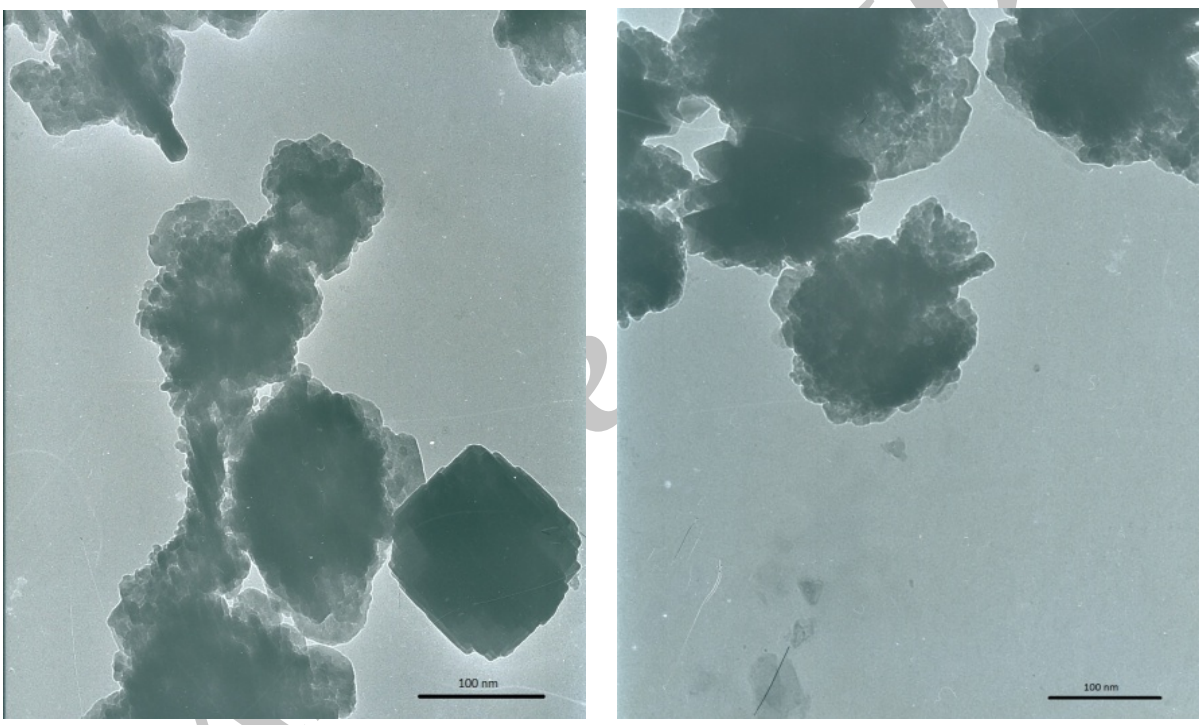

Fig. 3. TEM of NaX nano zeolite.

Table 2. XRF of NaX nanozeolite

Simple	SiO_2%	Al_2O_3%	Fe_2O_3%	CaO%	Na_2O%	K_2O%	MgO%	TiO_2%	MnO%	P_2O_5%
NaX	40.80	42.71	0.01	6.36	7.66	0.32	1.28	0.010	0.001	0.001

CONCLUSIONS

Various NaX zeolitic crystals with controlled sizes and surface properties hsve been synthesized with a newly developed organic-template-free approach using appropropriate silicate sources and control of hydrothermal crystallization conditions, such as temperature and agitation. Ultra-fine NaX zeolite (20-100 nm) was prepared by growth at 60 °C for 2 days several techniques, including SEM, TEM, XRD and XRF were employed characterize all of the synthesized materials.

www.SID.ir

REFERENCES

[1] B. J. Schoeman, J. Sterte and J. -E. Otterstedt, Zeolites. 14 (1994) 110.
[2] N. B. Castagnola and P. K. Dutta, J. Phys. Chem. B 102 (1998) 1696.
[3] G. Zhu, S. Qiu, J. Yu, Y. Sakamoto, F. Xiao and R. Xu, Terasaki, O. Chem. Mater.10 (1998) 1483.
[4] W. Bo, Hongzhu, M. Microporous Mesoporous Mater. 25 (1998) 131.
[5] Bi-Zeng Zhan, et al., Chem. Mater. 14 (2002) 3636-3642.
[6] S. Mintova, Valtchev, V. Stud. Surf. Sci. Catal. 125 (1999) 141.
[7] C. Madsen, Jacobsen, C. J. H. Chem. Commun. (1999) 673.
[8] S. Mintova, N. H. Olson and V. Valtchev, Bein, T. Science. 283 (1999) 958.
[9] M. Xu and M. Cheng, Bao, X. Chem. Commun. (2000) 1873.
[10] M. Lassinantti and J. Hedlund, Sterte, J. Microporous Mesoporous Mater. 38 (2000) 25.
[11] Method of Analysis for Fluid Cracking Catalysts, Grace and Co. Davison Chemicals: Baltimore, MD, (1980).
[12] L. Huang, Z. Wang, J. Sun, L. Miao, Q. Li and Y. Yan, Zhao, D. J. Am. Chem. Soc. 122 (2000) 3530.
[13] H. Wang and Z. Wang, Yan, Y. Chem. Commun. (2000) 2333.
[14] M. Estermann, L. B. McCusker, C. Baerlocher and A. Merrouche, Kessler, H. Nature. 352 (1991) 320.
[15] B. -Z. Zhan, M. A. White and K. N. Robertson, Cameron, T. S. Gharghouri, M. Chem. Commun. (2009) 1176.
[16] L. C. Boudreau and J.A. Kuck, Tsapatsis, M. J. Membr. Sci. 152 (2008) 41.

Archive of SID

www.SID.ir