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Optimization of Nanocrystals NaX Zeolite Synthesis with Different Silica Sources

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Abstract

The effects of varying the silica source on synthesis of NaX zeolite crystals via conventional hydrothermal method have been investigated. Five different silica sources were selected while other parameters like Al source, reaction and aging time, SiO_2/Al_2O_3 molar ratio and temperature were same. The prepared products were characterized by XRD technique. The results showed that different crystallites, different conversion rates and different amounts of impurity phase in the synthesized NaX zeolite. For more evidence the best obtained powder of NaX zeolite nanoparticles was checked by FTIR, SEM, TGA, and BET analysis. The corresponding sample had a good agreement with standard IR peaks, octahedral nanocrystals of zeolite X, thermal stability up to 800°C, surface area 751.88 m^2/g and total pore Volume 0.3599 cm^3/g respectively. Therefore, it can be concluded that the use of different silica sources significantly influence the synthesized products.

Keywords: *Zeolite NaX, Silica source, Nanocrystal, Hydrothermal method.*

Introduction

In categorization of porous materials zeolites are microporous (smaller than 2 nm) crystalline aluminosilicates with indefinitely extending three dimensional networks of aluminium and silicon tetrahedral linked by sharing of oxygen atoms [1-3]. Generally their structures include aluminosilicate framework, interconnected channels & cavities (typically 2.5–10Ǻ) with exchangeable cations, and H2O molecules [4]. Due to such unique structures with high specific surface area, zeolites have been

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widely used as ion exchangers, molecular sieves, adsorbents, and catalysts [2, 4].

Despite the need for exact monitoring of synthesis conditions and relatively high cost, synthetic zeolites have some advantages like uniformity in size and shape of channels, chemical composition, pre-defined in relation to the purposes intended and purity which persuade researchers to synthesis them in their efforts [1]. Among different kinds of zeolites the synthesis of NaX (FAU class) due to its unique properties which arise from open structure (internal cavity 13Ǻ) and large pore volume (8Ǻ), [5] has attracted much attention in the last two decades [6]. This group has vast and different applications in chemical, oil refining, gas, and petrochemical industries [7]. Adsorption of different gases and vapors such as H_2O [8], CO_2 [9, 10], N2 [11, 12], H_2, O_2, Ar, CH_4 ,SO_2, H_2S, hydrocarbons and benzene is due to its large pore diameter and polar properties [11]. Its catalytic character in hydrocarbons oxidation[13], hydrodechlorination of CCl_4 [14], synthesis of ammonia, etc. refers to ability of different cations exchange. Also this ion exchange property causes the zeolite NaX to be used for removal of heavy metal and radioactive ions [15].

Under stringent experimental conditions (hydrothermal crystallization) pure zeolites can be synthesized from supersaturated solutions of silicates and aluminates [16]. Hydrothermal crystallization is the most common liquid phase method in synthesis of zeolites. This reaction mechanism involves stages of dissolution, condensation or gelation and crystallization [17]. In this method, a freshly prepared aluminosilicate gel is formed by mixing various alumina and silica sources in presence of alkaline conditions [18]. Then in a closed hydrothermal system with autogenously pressure and defined temperature the gel changes to zeolite crystals [19]. Several factors have been identified as major contributing factors on the type and crystal size of the synthesized zeolite. Most of them involve reagent source, Si/Al ratio, initial & final pH, heating time, aging time, template, oven temperature, order of mixing, intensity of agitation and autoclave volume [20].

Selection of the raw material specifically the silica source is the main challenge in zeolite research. In addition to availability and cost, commercial silica which was supplied in different forms like fumed, sol-gel, and amorphous solid has variable reactivity and selectivity [20].

Freund studied the effect of different silica sources in presence of various amount of Al^{3+} ions on the crystallization of zeolite X and concluded that formation of some hydroxylated anions as impurities can act like cores in zeolite nucleation [5]. Hamilton et al. reported the relation between silica source and the number, size, and growth rates of crystals in zeolite [21]. The observation of particulates in silicate solutions and their role throughout the synthesis process was noted [22]. In year 2003 Krznaric et al. reported the analyses of the equilibrium distributions of Na_2O, Al_2O_3 and SiO_2 in two phases in the gels prepared from different silica sources[23].

In the present study on synthesis of NaX we have kept all the effective reaction parameters constant except silica source. Therefore, by using different typical silica sources we have tried to attain the optimum structure and properties of the nanocrystals of NaX zeolite. With this aim, we have chosen silicic anhydride, fumed silica, sodium silicate (water glass), silica gel, and colloidal silica, as our silica sources. Since the best technique for the identification of synthesized structures is X-ray diffraction (XRD); therefore, all the prepared powders were analyzed by this technique. Then the most acceptable result has been checked by Fourier transform infrared (FTIR), scanning electron microscope (SEM), thermo gravimetric analysis (TGA), and nitrogen adsorption-desoption isotherm [24].

Experimental

Materials

$NaAlO_2$ as aluminium source (Al2O3:50-56%, Na_2O:40-45% anhydrous) and NaOH (Laboratory Reagent Grade) were from Sigma-Aldrich. The selected silica sources were, silicic anhydride <100µ (Fluka), fumed silica 99.8% SiO2 11nm (Sigma-Aldrich), water-glass solution (sodium silicate) 10.54 wt.% Na_2O, 26.53 wt.%SiO_2, 62.93 wt.% H_2O (Sigma- Aldrich), silica gel 230 mesh 60 Å (Merck) and LUDOX AM-30 colloidal silica 30 wt.% suspension in water (Aldrich).

Synthesis

Syntheses of nanocrystals of NaX zeolite have been possible by hydrothermal synthesis at controlled temperature. Furthermore, the chemical composition of the reaction mixture and their correct ratios is exactly studied because these factors are effective on the quality characteristics of zeolite. Therefore the molar ratio for preparing the aluminosilicats gel was adjusted to 1.0 Al_2O_3:3.5 SiO_2:4.0 Na2O:160 H_2O.

As the formation of gel needs alkaline conditions, all of the reactions should be done in plastic ware. A clear solution of sodium aluminate was prepared by mixing the calculated amount of sodium aluminate, half of the require amount of NaOH and deionized water in a beaker with a stirring bar (300 rpm). Simultaneously, the rest of sodium hydroxide and H_2O were added to appropriate amount of silica source. All the mixtures were agitated carefully. Then the silicate sources were added to aluminate solutions at room temperature and immediately the gel was formed. After the aging time (40 min) the gel was transferred into a stainless steel-teflon autoclave and was heated under isothermal condition in an oven maintained at 90±5°C for 15 h. After this, crystallization of zeolite NaX was completed and the samples were cooled to room temperature, then filtered from mother liquor, washed with deionized water until pH 8-9 and dried in oven at 80°C for 6 h. Finally, the white powder of zeolite was cooled in a desicator over silica gel.

Physical characterization

In order to investigate the different silica sources effect on synthesis of NaX the five samples of synthesized zeolite were characterized by a number of techniques. At first X-ray Diffraction analysis has been used for identification of the phases formed during the reaction, position and types of atoms, and quality. This method has a high degree of accuracy and can readily be used to distinguish between zeolite and non-zeolite minerals in mixtures. The XRD patterns were recorded on a Bruker- D8 Advance powder diffraction system at 25°C. Data collection was carried out in the 2θ range 4-70° at the rate 0.02°/sec using Cu-Kα radiation. The information about the structural units was examined by FTIR (PerkinElmer Spectrum 65) and SEM (VEGAII TESCAN) was used for morphological features of the sample surface. Thermal behavior of the best product was checked by TGA (NETZSCH TG 209 F1 Iris). The measurement was carried out in N2 flow with a heating rate of 10°C/min.

Also nitrogen adsorption-desorption isotherms of the porous zeolite NaX samples were determined by an BELSORP mini II instrument at liquid nitrogen temperature (77 K) and 1 bar to calculate the specific surface areas, pore diameters, and pore size distributions.

Results and discussion

X-ray diffraction (XRD) study

Figure1 shows XRD diffraction patterns of synthesized NaX zeolites due to a) silicic anhydride, b) fumed silica, c) water-glass solution, d) silicagel, and e) colloidal silica. According to these diffractograms the main crystalline phases of the synthesized products by colloidal silica are in a good agreement with the standard NaX zeolite (JCPDS card No.38-0237). Appearance of the typical peak around 2θ = 6.2 in (a), (b), and (e) demonstrate the synthesis of NaX in these products but doesn’t observe in (c) and (d). Furthermore, sharpness and intensity of the diffraction peaks in (e) implicate the high crystallization of the synthesized NaX zeolite in hydrothermal reaction for 15 h at 90°C. In defined conditions other silica sources didn’t match completely with standard values. For example the crystallites in silicic anhydride and intensities in fumed silica are poor. Also the significant interference of the impurities is clearly visible.

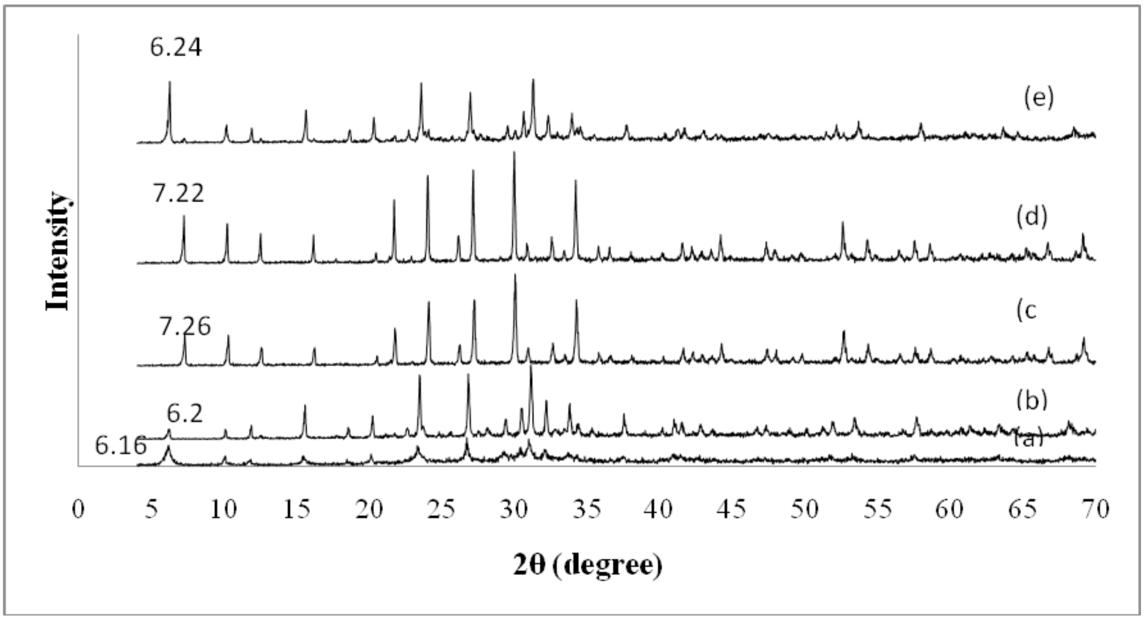

Figure 1. XRD patterns of product from a) silicic anhydride, b) fumed silica, c) water-glass solution, d) silicagel, and e) colloidal silica.

FTIR study

FTIR spectrum of the synthesized powder from colloidal is recorded in Figure 2. The major chemical groups and the typical bands presented in this product were identified by FTIR spectra. The appearance of the broad peak at 3476.23 cm^{-1} corresponds to H-O-H stretching belonging to the physically adsorbed water molecules or hydroxyl groups. Also O-H bending can be seen at 1638.62 cm^{-1}. The zeolite internal tetrahedron vibration (1250 – 950 cm^{-1}) that assigns an asymmetric stretch is observed clearly at 1002.88 cm^{-1}. Furthermore, the absorption band at 761.10 cm^{-1} is due to a symmetric stretching. Moreover, the weak peak located at 568.25 cm^{-1} is corresponds to external vibration of double six-member rings in faujasite type zeolites. The appearance of the peak at 463.82 cm^{-1} could be attributed to the Si (Al)-O bending vibration. Furthermore, no impurity phase was detected in this spectrum. Since zeolites P, A, and sodalite have characteristic bands at 600, 550, and 660 cm^{-1} respectively, the lack of these peaks demonstrate the purity of the product.

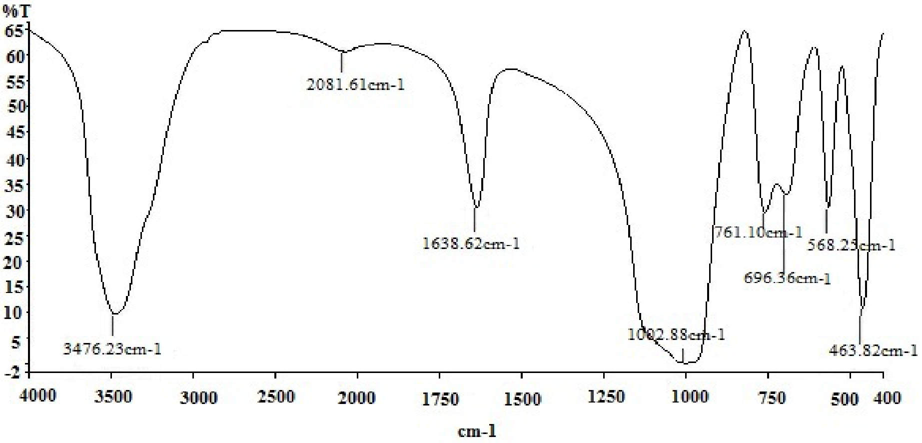

Figure 2. FTIR spectrum of the synthesized powder from colloidal silica.

SEM analysis

The SEM micrographs of the selected sample are depicted in Figure 3. The evaluation of the crystal appearance and its morphology indicate no remarkable amount of amorphous phases. The images show the zeolite particles in 2 and 10 micron magnifications. The typical octahedral crystals of zeolite X are clearly revealed and this is the sign of the proper reaction time for hydrothermal synthesis of nanocrystals NaX zeolite powder.

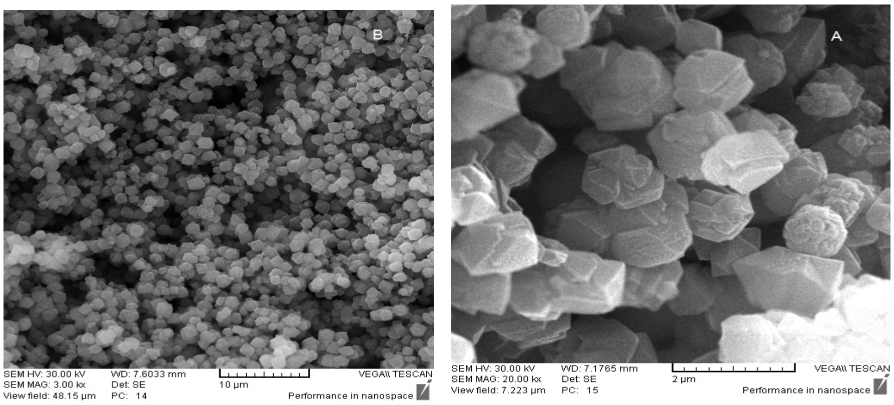

Figure 3. Scanning electron microscopy images of the synthesized powder from colloidal silica. Magnification A) 2 µm, B) 10 µm.

Thermal analysis

Crystalline zeolites because of their geometrical structure of framework are more resistive to heat than amorphous materials. Therefore, thermal curves that have been achieved by thermogravimetry analysis (TGA) are good guide to detect the very small structurally ordered units of a zeolite and its framework stability. The DTG/TGA profile of the studied sample is given in Figure 4. These curves show the total mass loss 24.12% in two steps. It can be seen that an obvious weight loss (22.75%) takes place under heating around 100-300 °C. This water desorbtion is due to held moisture on the surface and in the channels of the zeolite and dehydration of compensating Na+ ions. Also the endothermic peak about 130 °C in DTG profile confirms this. The heating was continued up to 800 °C and only 1.37% mass loss observed which indicates the stable structure of zeolite. Since the most important application of NaX zeolite is as catalyst and sorbent therefore, heat resistance will be a useful property.

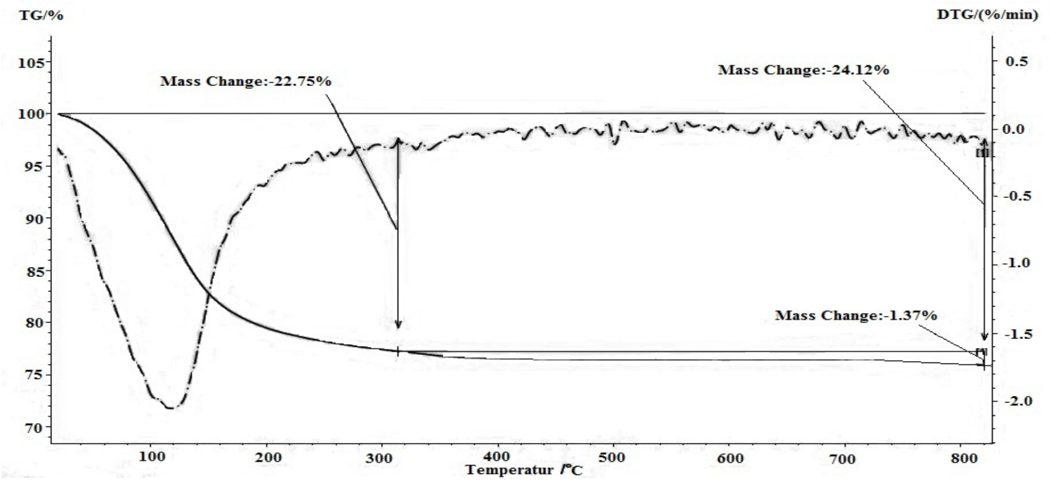

Figure 4. DTG/TGA profile of the synthesized sample from colloidal silica.

Nitrogen adsorption-desorption isotherm

Figure 5 shows the nitrogen adsorption-desorption isotherms measured at 77 K of the synthesized powder from colloidal silica. According to the classification of Brunauer et al. [25] the sample gives a typical type I isotherm curve that belongs to microporous (~2 nm), and the micropore system fills completely at very low partial pressure. The BET, t-plot and MP-plot are represented in Figures 6-8. Also in Table 1 the results of volume, surface area and pore size diameter measurements by different methods are recorded. As can be seen the specific surface area obtained 751.88, 888.75, 933.48 m^2g^{-1} by BET, t- plot and MP-plot methods respectively. Since a BET-plot with good linearity cannot be obtained from nitrogen isotherm for a sample with micropores, therefore, the results obtained by two other methods will be more reliable. Moreover the two different slopes in t-plot, in which one of them is sharp and passes from the original point and the other is more gradual which suggests that the adsorbent has homogeneous sized micropores. The curvature of plots suggests that there is distribution in pore size. In fact, MP method measures distribution from the curvature of t-plot. It can be seen from MP-plot that the synthesized NaX sample has micropores of 0.4

to 0.8 nm diameter (d_p), and has a distribution peak at 0.7 nm. High specific surface area and large pore diameter are good evidence for the synthesis of NaX zeolite successfully.

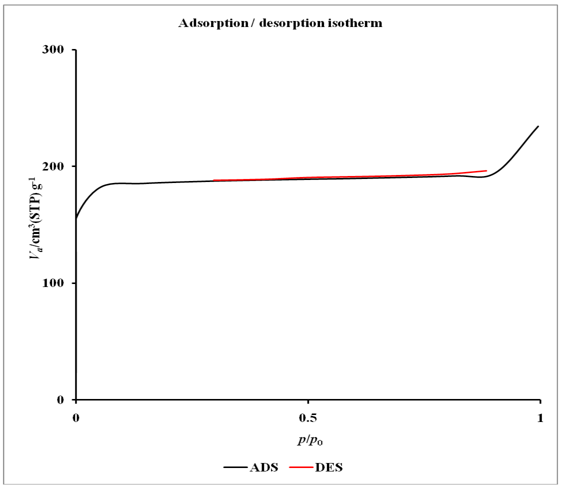

Figure 5. N_2 adsorption- desorption isotherm.

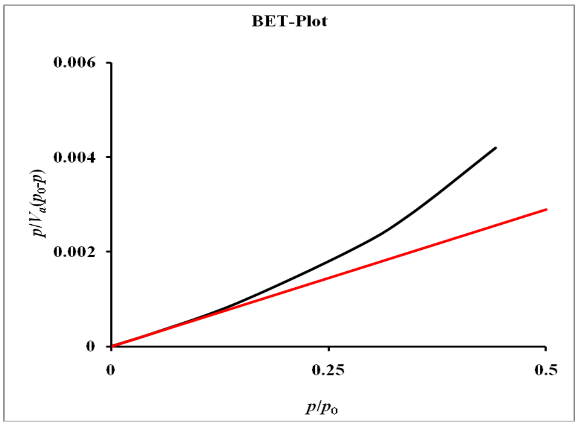

Figure 6. BET- Plot.

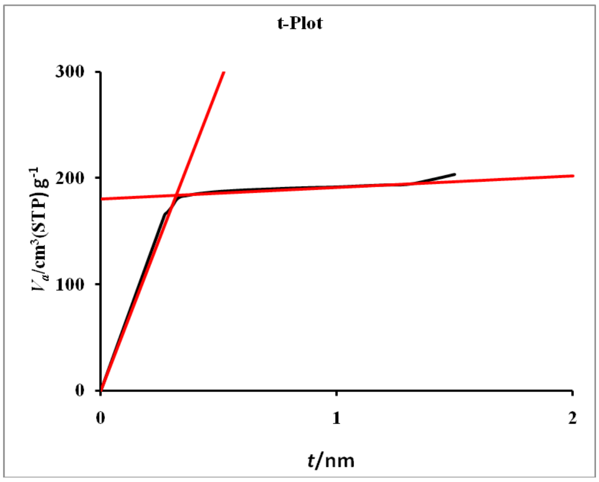

Figure 7. t - Plot.

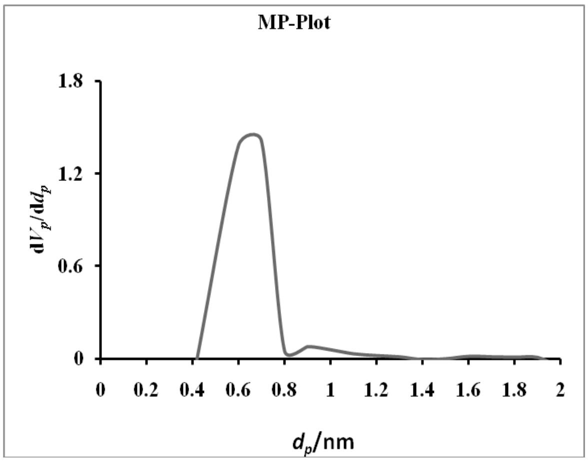

Figure 8. MP- Plot.

Table 1. Volume, surface area and pore diameter of synthesized NaX.

Volume cm^3/g		Surface area m^2/g					Pore diameter nm	
BET	t-plot	BET	t-plot		MP-plot		t-plot	MP-plot
V_p	V	a_s	a_1	a_2	a_1	a_2	2t	d_p
0.3599	0.2795	751.88	888.75	16.669	933.48	12.908	0.6372	0.7

V_p; total pore volume, V; micropore volume, a_s; specific surface area, a_1; total specific surface area, a_2; external surface area, 2t; pore diameter, d_p; micropore diameter.

Conclusion

The purpose of the current study was to attain the optimum structure and properties of the nanocrystals of NaX zeolite by using different silica sources. The hydrothermal synthesis of NaX from five different silica sources accomplished with a same gel formula (1.0 Al_2O_3:3.5 SiO_2:4.0 Na_2O:160 H_2O) and under the following conditions: aging the reaction mixture 40 min/room temperature, and hydrothermal treatment 15 h/90±5 °C. The XRD patterns of the synthesized products show that the process is only successful with colloidal silica. Further evidence like SEM images, FTIR spectrum, TGA/DTA, and nitrogen adsorption isotherm, all establish the presence of NaX nanocrystals with high specific surface area (933.48 m^2/g) and unique pore size (0.7 nm) in the synthesized product. Therefore, it can be concluded that the use of different silica sources significantly influence the synthesized product.

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