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Differences Between Sodium Metasilicate and Silicic Acid as Silica Source for Zeolite Y Nanoparticles Synthesis by Sol- Gel Method

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Abstract

Zeolite Y nanoparticles were synthesized by sol – gel method. Different samples using two silica sources were prepared. Sodium metasilicate (Na2SiO3) (48% silica) and silicic acid silica (H2SiO3) (75% silica) were employed as silica source and aluminum nitrate (Al(NO3)3.9H2O) was the aluminum source with tetrapropylammonium hydroxide (TPAOH) as templating agent.

The synthesized samples were characterized by X-ray diffraction, showed the requirement of different aging time for complete crystallization to be achieved. Transmission Electronic Microscope (TEM) images, showed the particles were in the same range of 30 – 75 nm. FT-IR spectroscopy, showed the synthesized samples having the zeolite Y crystal properties. The initial mixing silica to alumina ratio (SiO2/Al2O3) was 10, but, sodium metasilicate sample was of 2.55 final ratio, while silicic acid sample have 18.41 and the surface area as tested by BET was of 555.87 m2/g from sodium metasilicate sample and 276.3 m2/g from silicic acid sample.

Keywords: Zeolite Y, Nanoparticles, Sodium metasilicate, Silicic acid

Introduction

Nanoparticles zeolite Y gives high surface area, fast diffusion characteristics, adjustable porosity and enable to load inside the nanoporous materials such as silicate, aluminosilicate, and carbon hosts. This will possess pores of reduced diffusional path lengths, hence hydrocarbon substrates which diffuse in, are converted and the products quickly diffused out. This will prevent over-reaction to occure, blocking of the zeolite as well as the other properties of acid sites, and thermal stability of conventional zeolite [1]. Nanoparticles Zeolite Y is synthesized by using colloidal silica 30% [2], and using tetrethylorthosilicate (TEOS) as silica source [3], plus two of structure directing agents (SDA) of tetramethylammonium bromide (TMABr) as the second source of organic template with tetramethylammonium hydroxide (TMAOH), the effect of SDA is important to synthesis nanoparticles zeolites, which help to build the crystals and forming nanosize particles [4].

Zhang [5] synthesized mesoporous aluminosilicate material with different Si/Al ratios from tetraethylorthosilicate (TEOS) and aluminum nitrate nonahydrate (ANN) via sol-gel route. Cetyltrimethylammonium bromide (CTAB) was used as the structure-directing agent to create mesopore within the colloidal particles. It should be noted, here, that the normal zeolite Y is synthesized by using Kaolin as source of silica [6].

The aim of this work to study the effect of silica sources on the zeolite Y nanoparticles synthesized by sol gel method. Sodium metasilicate (Na_2SiO_3) (48% silica) and silicic acid (H_2SiO_3) of (75% silica) were used as silica source. Initial mixing silica to alumina ratio (SiO_2/Al_2O_3) was 10. Aluminum nitrate ($Al(NO_3)_3.9H_2O$) was used as alumina source and tetrapropyalammonium hydroxide

(TPAOH) $(CH_3CH_2CH_2)_4N(OH)$ 20% in H_2O) was the template agent.

Experimental Work

Two solutions of silica source and alumina source were prepared and the template was added to alumina solution. In alkali (basic) environment these two solutions were mixed producing white gel mixture.

Sample A

10 g of sodium metasilicate were dissolved in 25 ml of water and 3g NaOH was added. Another solution of 10.8 g aluminum nitrate dissolved in 25 ml water with 10g of TPAOH added. Then the two solutions were mixed forming white thick gel which turns to liquor gel by mixing for five minutes, (pH = 12). The resulting composition of this sample is:

10.7 Na2O : Al2O3 : 10 SiO2 : 6.3 TPAOH : 711.7 H2O

Sample B

10 g of silicic acid were dissolved in 25 ml of water during heating and 3 g of NaOH were added. Another solution of 17.2 g aluminum nitrate dissolved in 20 ml water with 10g of TPAOH added. Then the two solutions were mixed forming white thick gel which turns to liquor gel by mixing for five minutes, (pH = 12). The resulting composition of this sample is:

12.5 Na_2O: Al_2O_3: 10 SiO_2: 4 TPAOH: 454 H_2O

Aging and Filtration

Samples A and B were kept in a closed container in an oven at 100 °C for 72- 96 hr. This step allows the zeolite crystal to grow on the template molecules. The samples were, then, filtered and washed several times to remove the alkali and checking pH to be around 9.

Next, the samples were dried at 100 °C for 24 hr, to make sure all the water was removed.

Calcining

The prepared dry zeolite was subjected to calcining by raising temperature to 100 °C at a rate of 1°C/min to evaporate any possible water molecules (chemical water). Then it was heated by 10 °C/min to 500 °C and kept for 2 hr under this temperature. This step is to remove any TPAOH in the pores, to reach the thermal stability of the synthesis zeolite

Characterization

The x-ray diffraction in the angle Θ range of 5 – 30 to cover the peaks appears in small angle range. The test was done in Ministry of Science and Technology in Baghdad, the device used was Shimadzu SRD6000.

TEM test was done at the University of Nahrain / College of Medicine. The images of the samples show the particles sizes and give the ability to understand the nanoparticles distribution, the device used was Philips 10CM.

The Infrared Fourier Transform Spectroscopy (FT-IR) test was done to investigate the synthesized zeolite structure. This test was carried out at University of Baghdad/ College of Science/ Chemical Laboratory, the device used was Shimadzu FTIR 8400S.

BET nitrogen absorption was used to determine the surface area and pore size of synthesized zeolites. These tests were done to express the quality and activity of the zeolite. It was done at Oil Development and Research Center in Baghdad, the device used was Thrmo Finnigan.

In the final samples of nanopartical zeolite Y the molar ratio of silica (SiO2) and alumina (Al2O3) were analyzed chemically at the state establishment for Geological Survey and Mining.

Results and Discussion

White thick gel is the result of mixing aluminum solution and silica solution, after the aging this turns to clear liquid and white residue. Filtration step gives wet product, turns to powder after drying for 24 hrs. This powder is subjected to calcining and resulting a white fine powder, that are the nanoparticles of zeolite to be studied.

Fig.(1) shows sample A after aging for 48 hr. It represents zeolite Y still not complete crystallization. Aging for 72 hr results in a crystallized zeolite Y as shown in Fig.(3). For sample B prepared from silicic acid as silica source, Fig.(2) shows the x-ray test after 72 hr which shows non complete crystallization. In Fig.(4) the aging was 96 hr and it shows the complete crystallized zeolite Y. While Fig.(5) shows the standard zeolite Y, x-ray analysis [7]. From these figures, it can be seen that the prepared zeolite. is quite comparable with the zeolite Y nanoparticles prepared by Bretr [2].

On the other hand, X-ray results indicate that the silica source has an effect on aging time to achieve complete crystallization of zeolite. The aging temperature being 100°C for zeolite Y. Silicic acid with high silica contents 78% takes longer time to crystallize. But, sodium metasilicate of 48% silica contents takes shorter time for crystallization. This is also, due to the fact that the desolusion of sodium metasilicate easier than silicic acid.

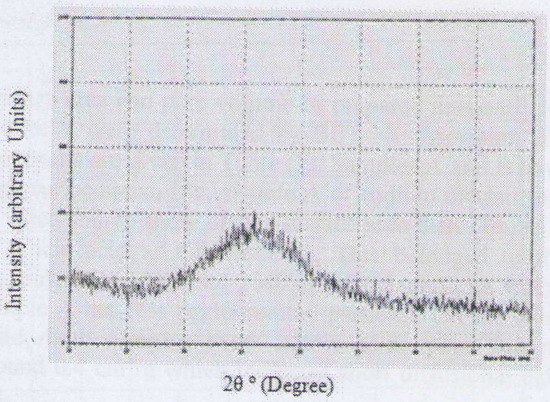

Fig.1 X-ray of zeolite Y from sodium metasilicate after 48 hr aging

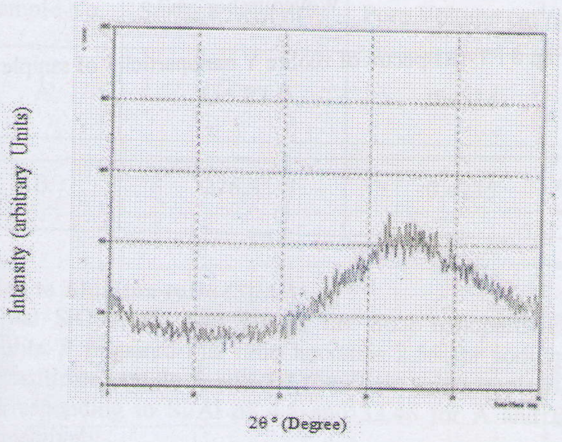

Fig. (2) X-ray of zeolite Y from silicic acid after 72 hr aging

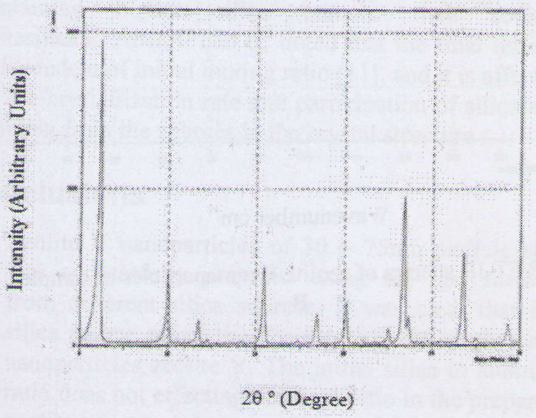

Fig. (3) X-ray of zeolite Y from sodium metasilicate after 72 hr aging

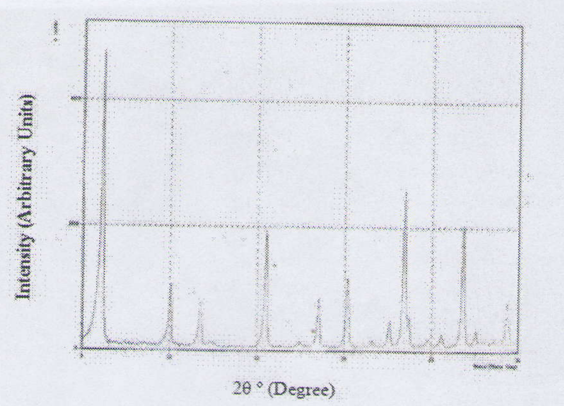

Fig. (4) x-ray of zeolite Y from silicic acid after 96 hr aging

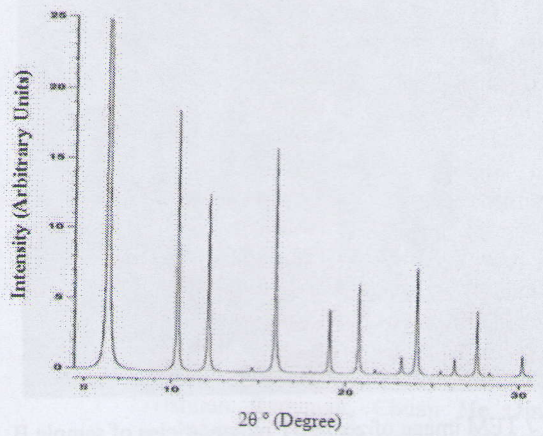

Fig.(5) Standard x-ray of zeolite Y aging

Fig.(6) and Fig.(7) show the TEM images of zeolite Y, where, sample A (after 72 hr crystallization) as shown in Fig.(6) and sample B (after 96 hr crystallization) as shown in Fig.(7). Both figures show that the morphology contain nanoparticles of 30 nm to 75 nm, this particles size difference is due to initial crystallization steps and effect of SDA [8]. These nanoparticles are in agglomerated form. The scanning with TEM gives the idea about particles size and their distribution also showing the way it agglomerated under the effect of Van Der Waal's forces, regarding the fact that on nanoscale the active forces are the Van Der Waals and the surface tension [9].

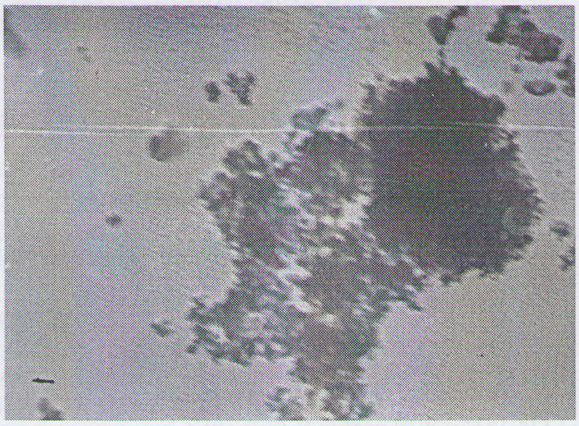

Fig. 6 TEM image of zeolite Y nanoparticles of sample A

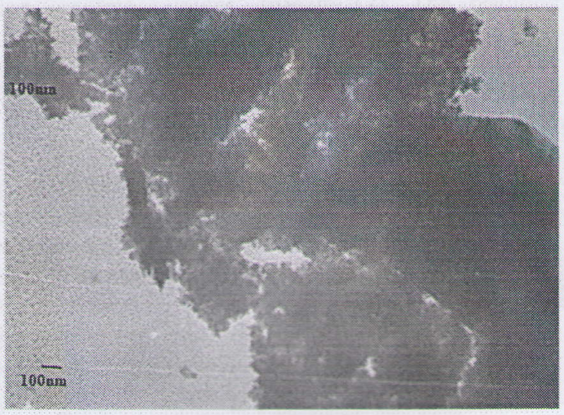

Fig. 7 TEM image of zeolite Y nanoparticles of sample B

FT-IR spectra of samples A and B are given in Fig. 8 and Fig. 9 respectively. The range of wavenumber is limited from 1500 cm^{-1} to 300 cm^{-1}, which includes the bands of zeolite Y categories [10].

For both samples the FT-IR spectra are compatible with categories of zeolites. The first category occur in the ranges from 1250 cm^{-1} to 950 cm^{-1}, from 790 cm^{-1} to 650 cm^{-1} and from 500 cm^{-1} to 420 cm^{-1}, which are tentatively assigned to the asymmetric stretching (-OT-O-) mode, the symmetric stretching (-OTO-) mode and the (T-O) bending mode of the $TO_{4/2}$ tetrahedra (T= Si or Al), respectively. Similarly, bands around 650 cm^{-1} to 500 cm-1 and 420 cm^{-1} to 300 cm^{-1} were ascribed to external linkage vibrations, vibration of double four-membered rings (D4R) or double six- membered rings (D6R), and pore opening vibrations, respectively [10].

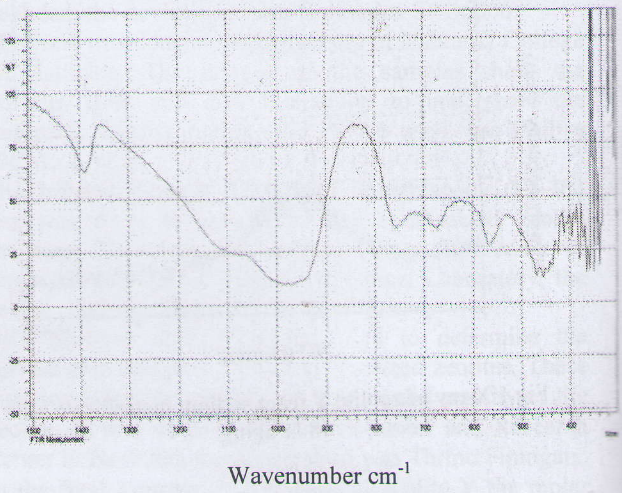

Fig. 8 FT-IR spectra of zeolite Y nanoparticles of sample A

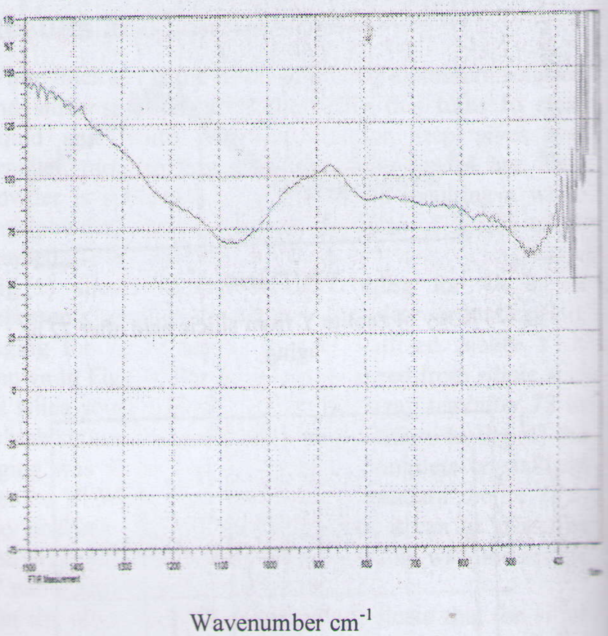

Fig.9 FT-IR spectra of zeolite Y nanoparticles of sample B

Surface area and pore volume of prepared nanoparticles zeolite Y were determined by BET N_2 absorption and the results are given in Table (1). Samples A and B have high surface area. But, sample A of sodium metasilicate as silica source show higher surface area than sample B of silicic acid as silica source. This belonged to the agglomeration state and packing of the particles where sample A has less agglomerated particles. On the other hand, both samples show nearly same pore volume around 0.4 cm^3/g which indicates short diffusional path [1].

Table (1) Surface area and Pore Volume of zeolite Y

Sample No.	Surface Area m^2/g	Pore Volume cm^3/g
A	555.87	0.4314
B	276.3	0.4235

Silica to Alumina ratio (Si/Al)

Initial SiO_2/Al_2O_3 was 10, in the final nanoparticles zeolite Y prepared this ratio becomes 2.55 for sodium metasilicate sample A and 7.7 for silicic acid sample B, corresponding to Si/Al of 4.5 and 32.46 for A and B respectively.

Both samples are with high Si/Al ratio as normal zeolite Y specification [1]. But, sample B shows more silica in the structure of the zeolite, since the silicic acid containing higher silica content than sodium metasilicate. Also, it can be noted that the final ratio is independent of initial mixing ratio [11], and it is affected by the crystallization rate and participation of silica and alumina from the sources in the crystal structure

Conclusions

Zeolite Y nanoparticles of 30 – 75nm particle size was successfully prepared using sol- gel method from different silica sources. It was clear that the silica source affect the characteristic of synthesized nanoparticles zeolite Y. The initial silica to alumina ratio does not effecting the final ratio in the prepared zeolite structure. Source of lower silica content, will result in zeolite with lower silica content and vice versa.

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