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Effect of Heating Period and Temperature on the Synthesis of Nano-Beta Zeolite Assisted by Microwaves

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Abstract

The nano-beta zeolite was synthesized by microwave method and characterized by X-ray powder Diffraction (XRD), X-ray Fluorescence (XRF), Brunauer–Emmett–Teller (BET), Scanning Electron Microscopy (SEM) and Dynamic Light Scattering (DLS) techniques. In all of the samples, the gel of nano-beta zeolite was prepared at room temperature (20°C) and the gel crystallization was performed in the microwave at different heating period and temperatures. The crystallization percentage of fabricated nano-beta zeolite was determined by XRD pattern. The particle size was calculated by SEM method then verified by DLS method. At the optimum synthesis condition, the Si/Al ratio and effective surface of nano-beta zeolite were determined by XRF and BET tests, respectively. The results showed that the zeolite crystals start to grow up after 180 minutes crystallization at the lowest temperature, 60°C, with the microwave method. Nano particles size of zeolite which are calculated by XRD then validated by DSL and SEM methods were between 100-200 nm. The specific surface area of the fabricated samples from BET adsorption was determined to be 632 m^2/gr.

Keywords: Crystallization; Microwave synthesis; Nano-beta zeolites; Synthesis condition; characterization

Abbreviations: XRD: X-ray powder Diffraction; XRF: X-ray Fluorescence; BET: Brunauer–Emmett–Teller; SEM: Scanning Electron Microscopy; DLS: Dynamic Light Scattering

Introduction

Now-a-days, zeolites have been used in many petroleum and petrochemical processes such as petroleum refinery, reactions, separation, hydrocracking and adsorption processes [1-3]. They have attracted more attention due to good thermal and chemical stability, strong acid sites, molecular sieve properties, and wide range of pore sizes. Moreover, the nano zeolites have a more specific surface area and more activation sites resulting in higher activity. One of the most useful zeolites is nano-beta zeolite which is known to be a versatile alternative adsorbent for Volatile Organic Compounds (VOCs), separation of aromatics from alkanes and mixtures of alkenes as well as isomerizing C6-C7 hydrocarbons to gasoline fractions, and many more [4-7].

Nano zeolites were usually synthesized by different methods such as hydrothermal, sol-gel, microwave, in situ processes, etc. [8]. Most of studies on nano-zeolite are performed with hydrothermal method [9]. Some researchers have focused on the effective parameters of the nano-beta zeolite synthesis, such as zeolite template, crystallization time and temperature, ageing time and gel compositions [10,11]. Recently, the microwave method has been used for nano-zeolite synthesis to fabricate nanoparticles of zeolite. This method was studied for synthesis of some zeolites such as NaY, NaX, NaA and ZSM5 [12-15]. However, there has been no research yet about the beta type of zeolite synthesis by microwave method.

In this study, the nanoparticles of nano-beta zeolite were successfully fabricated with the microwave method. Heating time and temperature of microwave crystallization were investigated and the synergetic effect was studied by XRD. SEM was used to characterize the particle size and shape of nano-beta zeolite. The particle size was validated by DLS as well. Finally, the chemical compositions and Si/Al ratios of synthesized nano-beta zeolite were determined by XRF analysis.

Experimental

The precursor gel of nano-beta zeolite was prepared at room temperature by mixing 59.4 gr deionized water, 89.6 gr tetraethylammonium hydroxide (TEAOH 40 wt%, Merck Co.), 0.53 gr sodium chloride (Merck Co.) and 1.44 gr potassium chloride (Merck Co.) and stirring the mixture until it is dissolved. Solution A was prepared by adding 29.54 gr silica into gel solution while stirring until SiO_2 completely dissolved. Solution B containing 20.0 gr deionized water, 0.33 gr sodium hydroxide and 1.79 gr sodium aluminate (Sigma Alderich) was slowly added to solution A and was stirred for 1 hr.

The prepared gel moved to a 60 mL Teflon autoclave. Crystallization was done in the microwave setup which was equipped with a temperature controller (Figure 1). The temperature was controlled by varying the input microwave power via a PID controller within the microwave oven. The thermocouple was fixed at the middle of Teflon autoclave. This type of experiment enabled us to control temperature variations within different crystallization reactions. A series of experiments were designed to evaluate the effect of time on crystallization at 60, 90 and 120°C as shown in Table 1.

X-ray diffraction measurements were performed on a Philips (model PC-APD) diffractometer using C u-Kα radiation (k= 1.5406 A)° operated at 40 kV and 30 mA using Bragg–Brentano geometry. Scans were made in the 5°-40° 2θ range, with a scan rate of 2.0° 2θ/min, Pt diffractions were fit using Gaussian to achieve FWHM values and particle size were calculated by Scherrer equation with a

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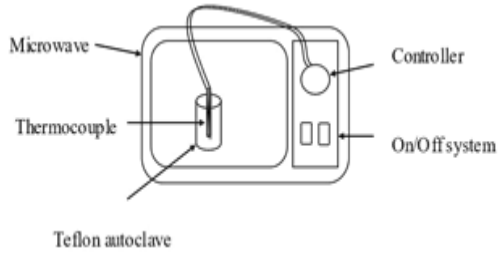

Figure 1: The schematic of microwave set up and instrument.

Samples	Crystallisation time (h)	Crystallisation Temperature (°C)
Beta11	1	60
Beta12	2	60
Beta13	3	60
Beta21	1	90
Beta22	2	90
Beta23	3	90
Beta31	1	120
Beta32	2	120
Beta33	3	120

Table 1: The condition of beta zeolite synthesis.

shape factor of 0.94. The percentage of crystallization and the type of fabricated zeolite were determined by evaluating the XRD pattern.

Si/Al ratio and elemental compositions of nanoparticles were determined by XRF (Phillips PW 2404). Samples were also characterized with BET. BET was performed with an SORPTOMATIC 1990 Series apparatus. The specific surface areas (SBET) were calculated with the BET equation. The morphologies and particles size were examined with a Hitachi S-2500 SEM which was confirmed by DLS Mastersizer 2000 (Malvern instrument). The crystallization yield of nano-beta zeolite was calculated by the equation below:

$$\text{Crystallization yield (\%)} = M_o\text{-}M_z/M_o \times 100 \quad (1)$$

Where, M_o= initial weight of solid in the gel; M_z=nano zeolite crystal weight

Results and Discussion

There were no crystals of nano-beta zeolite formed at the minimum temperature of 60°C and minimum time of 1 hr for crystallization with the microwave method. At the constant temperature of 60°C, increasing the crystallization time caused nano particles of nano-beta zeolite to appear which was investigated by analyzing the XRD patterns.

We speculate that the reaction enhancement due to microwave heating compared to the conventional method is due to specific interactions between microwaves and the precursor species as well as reduction in heat transfer resistance during the nucleation and growth processes. The precursor species, reaction intermediates and reaction mechanisms differ depending on the specific zeolite synthesis and therefore, microwaves will affect the reaction rates depending on the interaction between mentioned parameter. In our nano-beta zeolite synthesis method, the precursor contains a complex mixture of water solvent which strongly interacts with microwaves and low dielectric inorganic compounds silica and alumina.

The mechanism of the microwave enhancement is not completely understood [16]. Conflicting explanations and experimental results for zeolite synthesis reactions have been reported by various researches. This is primarily due to differences in experimental procedures such as ageing, temperature ramp rate, reaction vessel geometry, power delivery and volume of precursor gel reacted. Often, these parameters are not reported.

XRD results

Figure 2 compares XRD patterns of fabricated nano-beta zeolite at different times and temperatures. The pure zeolite beta phase was synthesized successfully. The XRD pattern of sample beta13 (60°C and 3 hrs) showed the lowest crystallization percentage. The XRD patterns of fabricated nano-beta zeolite show characteristic diffraction peaks at 2θ=7.6°, 21.66°, 22.42°, 26.32°, 28.40°, 29.40°, and 33.84°, which corresponds to beta zeolite [16]. At 900°C, the crystallization percentage increased to about 98% which did not have significant change from 2-3 hrs. Also, the percentage of crystallization was same in the sample beta31, beta22 and beta23 which showed time and temperature have the same effect on the nano-beta zeolite synthesis. Also, the weight of fabricated nano-beta zeolite product and the formed gel were measured to determine the percent yield of the synthesis. As shown in Table 2, the yield of crystallization rises as the synthesis time increases at 900°C, and the value reaches maximum about 44.32% at 3 hrs crystallization time. It can be seen that yield declined by increasing the time while crystallization temperature was 120°C. Thus, the best temperature for nano-beta zeolite synthesis is 90°C using the microwave synthesis method.

The Scherrer equation, in X-ray diffraction and crystallography, is a formula that relates the size of crystal, in a solid to the broadening of a peak in a diffraction pattern. The Scherrer equation can be written as:

$$r = k\lambda/\beta\cos\theta \quad (2)$$

Where, k=shape factor; λ=x-ray wavelength typically 1.54 Å; β=line broadening at half the maximum intensity (FWHM) in radians; θ=Bragg angle.

Beta zeolite is an important catalyst due to its stability, acidic

Researcher	Synthesis condition	Particles size	Crystallization percentage and yield
G. Talebi [18]	48 hr at 140 °C (at 60 rpm)	400- 700 nm	80 % and 30 %
L. Liu [19]	60 hr at 140 °C	300-350 nm	NR*
Sh. H. Chien [20]	20 days at 140 °C	400- 600 nm	90 % and NR*
F. Cao [21]	10 days at 140 °C	Around 500 nm	93% and NR*
This work	1 to 3 hr at 90 °C	100-200 nm	99% and 44%

* NR: not reported

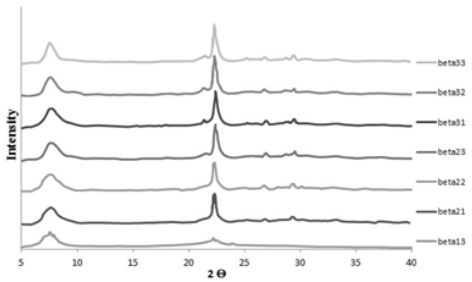

Figure 2: The XRD Pattern of Nano-beta Zeolite.

sites, hydrophicity and large pore dimensions [17,18]. In Table 3, the fabricated nano-beta zeolite is compared with other reported synthesis. Our synthesized beta zeolites are produced faster with more crystallization percentage and smaller particle size. Beta zeolite samples were synthesized with hydrothermal heating using tetraethylammonium hydroxide as a structure directing agent. Tetraethylammonium fluoride was used as a fluoride source which enhanced the rate of product formation. This hydrothermal synthesis method was previously the quickest method used to produce beta zeolite in 48 hrs [10]. However, using microwave synthesis method we were able to decrease the synthesis time to less than 2 hrs without using template.

Particles size and distribution

The average particle size of fabricated nano-beta zeolite calculated by XRD was 120 nm. This particle size was confirmed by DLS and SEM results. In Figure 3 the DLS results of sample beta23 show that there is a narrow particles size distribution between 80-250 nm of nano-beta zeolite. Also, a peak can be seen at 750 nm which relates to nano particle agglomerations [11].

The morphology and the size of the synthesized nano zeolite beta crystals were observed using scanning electron microscope. Figure 4 shows the sample micrographs of beta23 which had highest crystallite and yield percentage. The nano-beta zeolite crystals formed in a spheroid land shape and had a particles size between 100-200 nm. The similar morphology was found in zeolite beta sample synthesized in the previous study of Fathizdeh [15].

N2 adsorption/desorption and XRF

The N2 adsorption/desorption isotherm for zeolite beta, sample beta23, was shown in Figure 5. The variation type of adsorption with pressure showed the fabricated nano-beta zeolite as hydrophobic materials. The total surface area of nano-beta zeolite particles was 632 m^2/g and was calculated by using BET theory. Also, the XRF results of sample beta23 showed that the elemental composition of the synthesized zeolite is Na 0.9 K 0.62 (TEA) 7.6 [Al4.43Si59.58O128]. Therefore, the ratio of Si/Al was calculated to be 13.

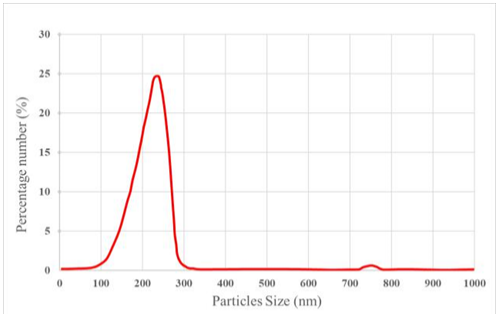

Figure 3: Particles size distribution of sample beta 23.

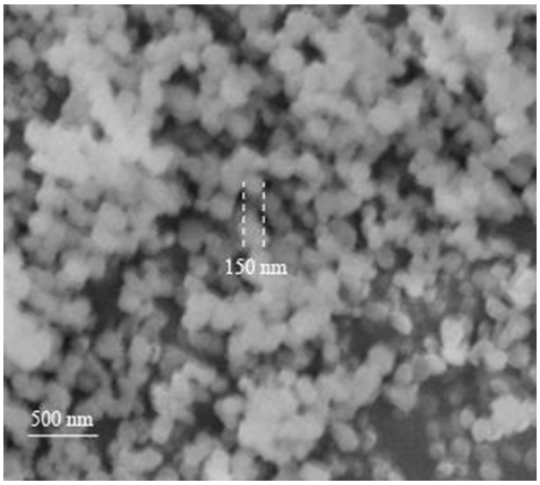

Figure 4: SEM picture of nano-beta zeolite (sample beta 23).

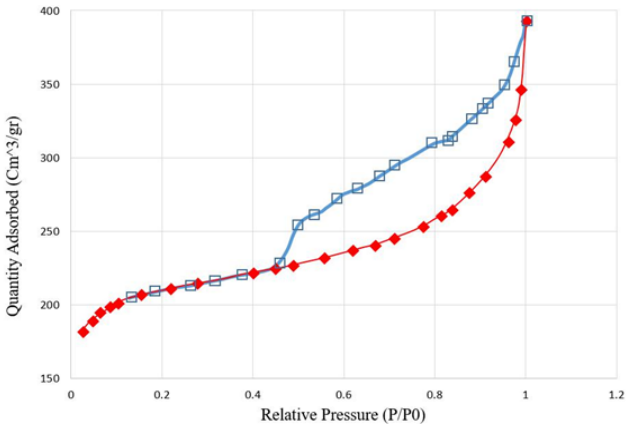

Figure 5: BET adsorption of synthesized nano-beta zeolite.

Samples	Beta11	Beta12	Beta13	Beta21	Beta22	Beta23	Beta31	Beta32	Beta33
Yield %	-	-	-	34.67	43.53	44.32	43.21	41.27	38.67
Crystallisation %	8.1	21.4	43.2	90.2	98.1	98.3	98.8	99.1	99.1

Table 2: The percentage yield of the synthesized nano-beta zeolite.

Researcher	Synthesis condition	Particle size	Crystallisation % and yield
G. Talebi [18]	48 hr at 140°C (at 60 rpm)	400-700 nm	80% and 30%
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This work	1 to 3 hr at 90°C	100-200 nm	99% and 44%

Table 3: Comparing the fabricated nano-beta zeolite with previous researches.

Conclusion

The nano-beta zeolite was synthesized by microwave method at the different times and temperatures. The results showed that time and temperature had the same effect on nano-beta synthesis process. At the lowest temperature, 60°C, the percentage of amorphous phase was more than the percentage of crystal particles. The best time and temperature of crystallization was determined to be 90°C and 3 hrs, which had high crystallization and percentage yield. This sample had a nano particles size distribution between 100-200 nm, BET surface about 632 m^2/gr, and Si/Al ratio around 13. Noticeable impact on application of nano-beta-zeolite in enhancing shale oil and gas recovery and CO_2 sequestration could be observed by this improvement [19-21].

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