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EFFECTS OF HYDROTHERMAL PARAMETERS ON THE SYNTHESIS OF NANOCRYSTALLINE ZEOLITE NaY

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Abstract—Synthesized zeolites are extremely important as industrial minerals and are most commonly prepared using organic templates. Because these organic templates present undesirable environmental hazards, a synthesis method which avoids their use is desirable. The objective of the current study was to develop such a synthesis method. Zeolite NaY was synthesized hydrothermally starting from a mixture of 1.0 Al_2O_3:10 SiO_2:4.6 Na_2O:180 H_2O molar gel composition, without adding any organic additives. Experiments were carried out to investigate the effects of molar compositions including water content (H_2O/SiO_2), crystallization conditions including temperature, and time on the crystal size and yield of NaY-type zeolite. The results showed that increasing the crystallization time from 5 to 12 h increased the crystal size, while increasing the crystallization temperature from 80 to 100ºC also increased crystallinity. The crystal species of zeolite NaY were characterized by X-ray diffraction, X-ray fluorescence, and scanning electron microscopy analysis. Zeolite NaY crystals in the size range 25−150 nm were synthesized successfully over a period of 8 h at 100ºC.

Key Words—Crystallinity, Hydrothermal, Nanocrystal, Zeolite NaY.

INTRODUCTION

Zeolites are important industrial minerals. In the most popular synthesis method for preparation of zeolites, organic templates which cause undesirable environmental hazards are used. Synthesis of zeolites without the use of organic templates is, therefore, very desirable. The main objective of the present work was to develop such a synthesis method to prepare NaY zeolite.

Zeolites as microporous inorganic materials have different applications, such as membranes, catalysts, adsorbents, and ion-exchangers, in many chemical and petrochemical processes due to their superior properties including strength, acidity, size or shape selectivity, thermal stability, and large ion-exchange capacity (Huang *et al.*, 2010; Yuan *et al.*, 2011). More than 50 different types of zeolites exist (*e.g.* faujasite (FAU), chabazite, phillipsite, mordenite, *etc*.) and these have different pore sizes and properties (Algieri *et al.*, 2009). The FAU-type zeolite has cavities with diameters of 1.3 nm interconnected by pores of 0.74 nm. Depending on the Si/Al ratio, this zeolite can be subdivided into X-type zeolite (Si/Al = 1.0−1.5) and Y-type zeolite (Si/Al > 1.5) (Algieri *et al.*, 2009). Applications of zeolite Y are largely in the fields of fluid catalytic cracking (FCC) of vacuum gas oil and adsorption of volatile organics from wet off-gas streams (Karami and Rohani, 2009). The size of the zeolite crystals plays a significant role in the catalytic performance. Zeolite Y with small crystal size is one of the best candidates for improving catalytic cracking selectivity, and it also enhances diesel production and gasoline quality with reduced coking (Sang *et al.*, 2006).

Reduction of the particle size increases the ratio of the number of external to internal atoms and causes the zeolite nanoparticles to have large external surface areas and high surface activity. The role of external surface acidity is significant when zeolite is used as a catalyst. A large, accessible external surface area and a large surface activity, achieved using nanosized zeolites, lead to better performance (Vuong *et al.*, 2010). In catalytic cracking of gas oil, for example, most hydrocarbon molecules are imprisoned in zeolite pores, and so only the zeolite's external surface contributes to the reaction. Most of the cracking of the hydrocarbon molecules is realized at the interface between the zeolite and the matrix component of the FCC catalyst. Reduction of the zeolite crystallite size increases both the gas oil conversion and selectivity. Nanozeolite is a good solution as an FCC catalyst. A larger accessible external surface area of nanozeolites leads to more cracking of large hydrocarbon molecules (Vuong *et al.*, 2010). Therefore, interest in the development of nanozeolite-based FCC catalysts is growing.

Preparations of zeolite nanocrystals, *e.g.* zeolite A (Zhu *et al.*, 1998; Mintova *et al.*, 1999b; Wang *et al.*, 2003; Kuanchertchoo *et al.*, 2006), sodalite (Yao *et al.*, 2006, 2008), silicate-1 (Corkery and Ninham, 1997; Wang *et al.*, 2000; Valtchev *et al.*, 2004; Song *et al.*, 2005a), FAU (X or Y) (Mintova *et al.*, 1999a; Holmberg *et al.*, 2003; Song *et al.*, 2005b), and SAPO-34 (Dargahi

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et al., 2011) are often carried out in aluminosilicate solutions in the presence of organic templates.

Synthesis of zeolite NaY nanocrystals has been investigated with the aid of different kinds of organic materials as templating agents to prepare nanoparticles effectively (Kim *et al.*, 2009). Tetramethylammonium hydroxide (TMAOH) is the most typical organic template and has excellent properties for controlling the zeolite size. However, using templates in the synthesis procedure has many unwanted effects, such as high production cost and water and air pollution arising from thermal decomposition. New synthesis procedures without templates are, therefore, required (Kim *et al.*, 2009). A series of nanosized NaY synthesis procedures without organic templates and under various conditions was provided by Bo and Hongzhu (1998).

NaY crystals, with a molar ratio in the gel of 10 Na_2O:1.0 Al_2O_3:15 SiO_2:300 H_2O and a crystallization time of 48 h, were synthesized by Sang *et al.* (2006) using a two-stage variable-temperature program without an organic template. The results showed that temperature is a crucial factor in the control of crystal size. Valtchev and Bozhilov (2004) synthesized 100–300 nm zeolite NaY aggregates after a three-week period of hydrothermal treatment. The results showed that, at high alkaline concentrations, the aggregation dominates during the period of NaY crystal growth.

In another, similar work, Huang *et al.* (2010) synthesized zeolite NaY with small variations in the composition of the gel (9.6 Na_2O:1.0 Al_2O_3: 14.4 SiO_2:αH_2O [α = 175.3, 198, 220.7, 243.4, 288.8, and 334.2]) but with a longer crystallization time (120 h) using a three-stage crystallization process. The results showed that the zeolite gel with a smaller water content favored the formation of the smaller FAU zeolite nanocrystals. The template synthesis approach for making zeolite Y is the method found most widely in the literature. In the present study, uniform nanocrystals of zeolite NaY were synthesized in an organic-template-free environment and without the use of directing agents, seeding crystals, or other additives. The required hydrothermal parameters were optimized.

EXPERIMENTAL

Materials and methods

The materials used to form the aluminosilicate gel were sodium aluminate ($NaAlO_2$, powder, Riedel-dehaen, Germany [Na as (Na_2O) 43% + Al as (Al_2O_3) 55%]), sodium silicate (SiO_2, Merck, Germany [27% SiO_2 + 8% Na_2O + 65% H_2O]), sodium hydroxide (NaOH, 98% wt., Merck, Germany), and deionized (DI) water (resistivity of 13.2 MΩ·cm).

The hydrothermal method was used to prepare zeolite NaY crystals. The molar composition of the gel was 4.6 Na_2O: 1.0 Al_2O_3: 10 SiO_2:x H_2O. The values of x were adjusted to 180, 300, and 420. The silicate solution was prepared by mixing sodium silicate with sodium hydroxide and DI water. The sodium aluminate solution was also prepared by mixing sodium aluminate, sodium hydroxide, and DI water. The synthesis procedure was performed in two stages: first, the initial gel was prepared by mixing the required amounts of sodium aluminate and sodium silicate solutions together and stirring moderately for at least 10 min. The mixed solution, referred to as 'seed gel' was left at ambient temperature for 24 h. The molar composition of the seed gel was 10.7 Na_2O:Al_2O_3:10 SiO_2:180 H_2O. Feedstock gel (4.30 Na_2O:Al_2O_3:10 SiO_2:180 H_2O) was prepared by mixing the required amounts of sodium aluminate solution and sodium silicate solution. This solution was mixed until homogenous. The overall gel was prepared by adding the seed gel to the feedstock gel slowly and stirring vigorously for up to 15 min. After aging unstirred at room temperature for 1 h, the gel was transferred to an autoclave for crystallization. The crystallization was completed after 5–12 h at 80–110ºC.

The synthesis powder was then filtered and washed with DI water until the pH of the filtrate dropped below 9. The powder collected was finally dried for 24 h at 90ºC. The procedure is presented schematically in Figure 1. To optimize the synthesis conditions, many sets of operating conditions were investigated (Table 1).

Characterization

The samples synthesized were characterized using X-ray diffraction (XRD) (SIEMENS D5000 X-ray diffractometer, Germany, 1500W, 35 kV, 20 mA) with Cu radiation. The morphology of the crystals was examined by scanning electron microscopy (SEM) (JEM-1200 or JEM-5600LV equipped with an Oxford ISIS-300 energy dispersive spectroscope (EDS), manufactured by Rontec, Germany). X-ray fluorescence (XRF) analyses were used to determine the chemical formula of the NaY zeolite. The Si/Al ratio in the bulk of

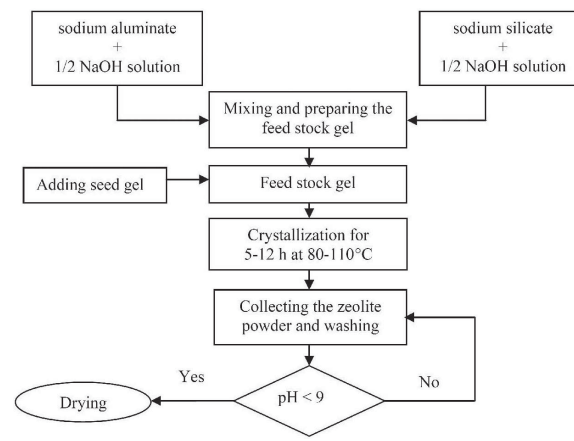

Figure 1. Work-flow chart for gel preparation.

Table 1. Experimental parameters of the zeolite synthesis.

Gel	Reaction time (h)	Crystallization temperature (ºC)	H_2O/SiO_2
Z1	8	100	18
Z2	8	100	30
Z3	8	100	42
Z4	5	100	18
Z5	12	100	18
Z6	8	80	18
Z7	8	90	18
Z8	8	110	18

Table 2. XRD pattern º2θ values for characteristic peaks of NaY zeolite crystalline structures (Treacy and Higgins, 2007).

º2θ	Relative intensities (RI) (%)
6.19	100
15.61	45
23.58	56
11.86	20
18.64	27
20.30	25
26.97	24
31.31	20

the synthesized zeolite was identified by XRF (PW 1480 instrument from Philips, The Netherlands). The standard Debye-Scherrer equation was employed to estimate the primary size of NaY crystals as follows (Maghsoodloorad *et al.*, 2011):

$$D = 0.89\lambda/\varphi\cos\theta \quad (1)$$

where D is the average crystal size; λ, the X-ray wavelength (CuKα); φ, the line broadening (FWHM) of the peak; and θ, the diffraction angle. As the coherent effect is ignored by this formula, the nanoparticle size measured must be used as an approximation only.

A quantitative measure of the NaY zeolite crystallinity was made using the sum of XRD-peak areas at º2θ values (Table 2) (Treacy and Higgins, 2007).

Experimental

The most important parameters for preparing NaY-type zeolite are as given below:

Aluminosilicate module $\gamma = SiO_2/Al_2O_3$

Water content, $\alpha = H_2O/SiO_2$

Crystallization temperature, T (ºC)

Crystallization time, t (h)

In the present study, the effects of three parameters (α, T, and t) on the formation of zeolite NaY crystals (in particular on the crystal size and crystallinity) were investigated. Other synthesis conditions such as silicon module and stirring time were kept unchanged during all the experiments.

RESULTS AND DISCUSSION

Si/Al ratio in bulk

The Si/Al ratio in the bulk of zeolite NaY was characterized by XRF analysis (Table 3). By converting wt.% to mol.%, the molar ratios of SiO_2/Al_2O_3 and Si/Al were calculated to be 5.15 and 2.575, respectively.

Effect of gel composition (water content)

In zeolite crystallization, the role of water content is known to be very important as a mineralizing agent. The XRD patterns of samples produced using three different H_2O/SiO_2 molar ratios (18, 30, and 42) under the same synthetic conditions revealed that pure zeolite NaY crystals were obtained at molar ratios of 18 and 30 at 100ºC (Figure 2). The XRD patterns of these samples are very similar but their degree of crystallinity is different. Furthermore, the XRD peaks of zeolite NaY synthesized with a molar ratio of 18 are more intense than those with a molar ratio of 30. These two patterns have no other peaks beyond those of standard NaY-type zeolite crystals (Table 2). Increasing the molar ratio to 42 weakened the intensity of the zeolite NaY peaks. This important observation confirmed that the zeolite gel with a smaller H_2O/SiO_2 molar ratio favors the formation of zeolite NaY. Meanwhile, increasing the water content leads to longer reaction (crystallization) times (Kim *et al.*, 2009). For a shorter reaction time (8 h), increasing the H_2O/SiO_2 molar ratio led to less crystallinity. Scherrer's equation and SEM images were used to estimate the primary crystal size of each NaY sample (Table 4, Figure 3), which revealed that the crystal size decreases to 120 nm at a H_2O/SiO_2 molar ratio of 30.

Effect of crystallization time

Crystallization time is an important parameter in the hydrothermal synthesis of zeolites. It influences the growth of the crystals. Crystallization time depends heavily on the crystallization temperature: the time required at high temperature was 5 h while for low

Table 3. XRF analysis (wt.%) of zeolite NaY (Z1).

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	K_2O	MgO	TiO_2	MnO
NaY (Z1)	63.29	20.86	0.10	0.19	15.50	0.05	0.01	0.00	0.00

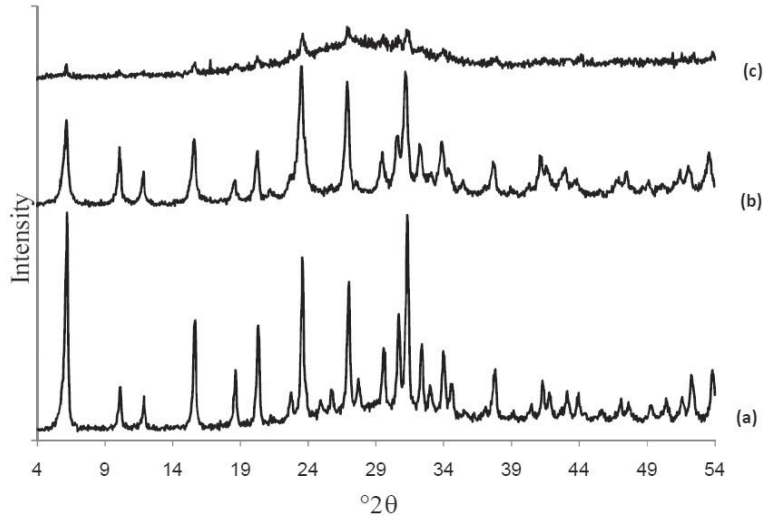

Figure 2. XRD patterns of the samples (a) $H_2O/SiO_2 = 18$, (b) $H_2O/SiO_2 = 30$, and (c) $H_2O/SiO_2 = 42$ (t = 8 h and T = 100ºC).

temperature 120 h was required (Sang *et al.*, 2006; Huang *et al.*, 2010). The XRD patterns of zeolite NaY samples crystallized at 100ºC for different crystallization times are shown in Figure 4. An amorphous phase was observed in the sample synthesized for 5 h (Figure 4a). Therefore, 5 h was insufficient for synthesis of zeolite NaY. This amorphous phase may be related to unreacted materials. A rapid crystallization occurred between 5 and 8 h of treatment. A longer crystallization time of 8 h led to sharper zeolite NaY peaks in the XRD pattern. Pure zeolite NaY crystals were obtained when the synthesis time was 8 h (Figure 4b). Further increase of the crystallization time to 12 h had no effect on the degree of crystallinity but the crystal size increased considerably. Finally, well crystallized FAU-type zeolite with a small crystal size can be prepared within a crystallization time of 8 h *via* a hydrothermal method. Scherrer's equation and SEM images were used to estimate the primary crystal size of each NaY sample (Table 4).

Table 4. Primary nanocrystal size and particle size of porous aggregated zeolite NaY particles.

Gel	Crystallite size from XRD (nm)	Particle size from SEM (nm)
Z1	23	25–150
Z2	19	25–120
Z3	13	–
Z4	11	–
Z5	40	–
Z6	–	–
Z7	9	–
Z8	43	200–500

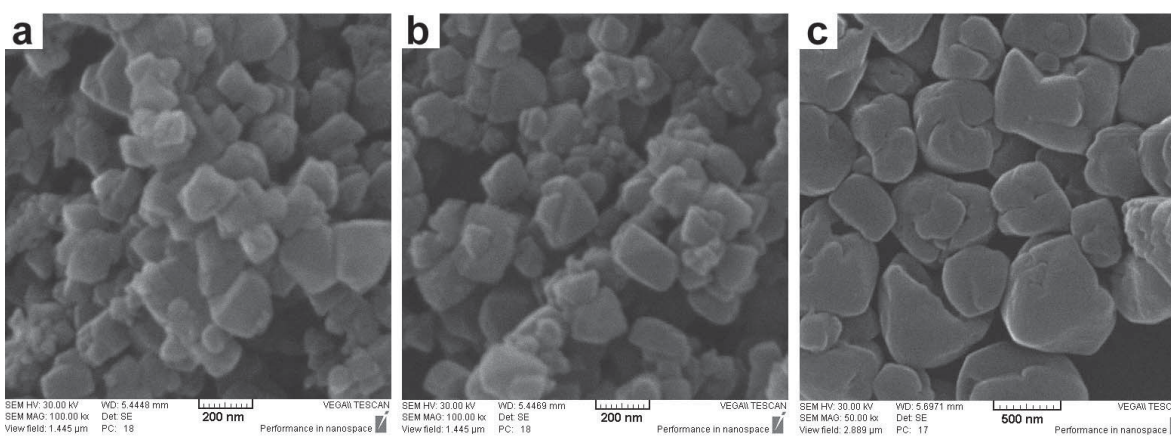

Figure 3. SEM images of the samples (a) $H_2O/SiO_2 = 18$, (b) $H_2O/SiO_2 = 30$ (t = 8 h and T = 100ºC), and (c) $H_2O/SiO_2 = 18$ (t = 8 h and T = 100ºC)

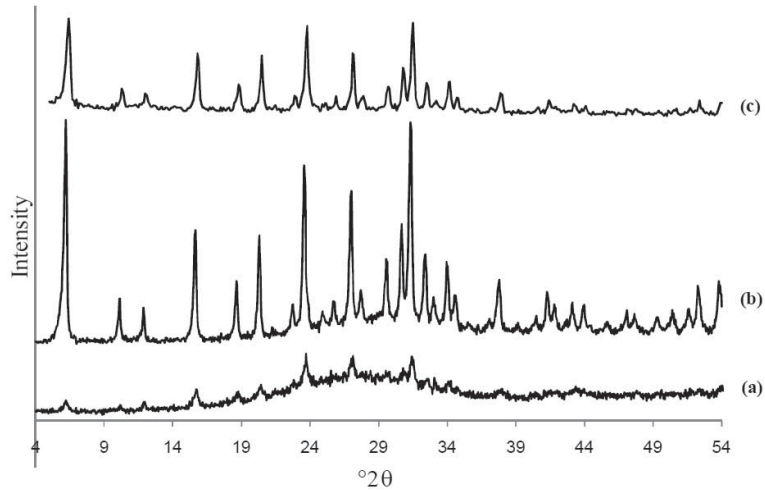

Figure 4. XRD patterns of samples (a) 5 h, (b) 8 h, and (c) 12 h (100ºC and H_2O/SiO_2 = 18).

Effect of crystallization temprature

Crystallization temperature also influenced the growth of the crystals and interface reactions of active crystal particles. The XRD patterns of zeolite NaY crystals synthesized at different temperatures for 8 h (Figure 5) revealed that the zeolite NaY crystals grew more at higher crystallization temperatures. At 80ºC, no crystalline phase was formed (Figure 5a), indicating that this temperature was insufficient for the formation of zeolite NaY (Faghihian and Godazandeha, 2009). A mixture of zeolite Y and an amorphous phase was obtained when the synthesis was performed at 90ºC (Figure 5b) and weak peaks of zeolite NaY were observed. Increasing the crystallization temperature to 100ºC made the peaks sharper, and pure zeolite NaY was obtained when the synthesis was performed for 8 h at 100ºC (Figure 5c). A mixture of the zeolite Y and P phases was obtained when the synthesis was performed at 110ºC (Figure 5d). The primary crystal size of each NaY sample was estimated using Scherrer's equation and the SEM images (Table 4). Decreasing the temperature favored the synthesis of nanozeolite crystals (Sang *et al.*, 2006). The crystal size was increased to 500 nm at 110ºC.

CONCLUSIONS

Zeolite NaY-type crystals were prepared *via* a hydrothermal synthesis method. The effect of gel composition and water content were investigated first to find the optimum H_2O/SiO_2 molar ratio and then the effects of crystallization conditions on zeolite NaY

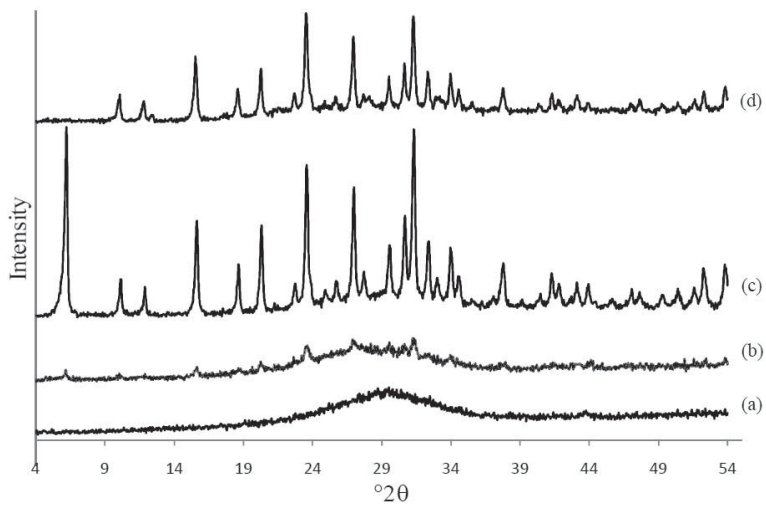

Figure 5. XRD patterns of zeolite heated to (a) 80ºC, (b) 90ºC, (c) 100ºC, and (d) 110ºC prepared under the same synthesis conditions (8 h and H_2O/SiO_2 = 18).

formation. The XRD patterns revealed that the smallest and purest zeolite NaY-type crystals were obtained when using a gel composition of 1.0 Al_2O_3:10 SiO_2:4.6 Na_2O:180 H_2O at 100ºC for 8 h. Increasing both the crystallization temperature and the time increased the crystallinity and the crystal size. Using the optimized parameters, zeolite NaY crystals in the size range 25−150 nm were obtained.

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