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EFFECTS OF GEL PARAMETERS ON THE SYNTHESIS AND CHARACTERISTICS OF W-TYPE ZEOLITE NANOPARTICLES

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Abstract—The objectives of this study were to investigate the effects of chemical parameters on the characterization of W-type zeolite crystals and their intergrowths with other types of zeolites. The crystal size and purity of W-type zeolites are affected significantly by the gel composition with respect to the molar ratios of SiO_2/Al_2O_3 (aluminosilicate module, α), H_2O/K_2O (alkainity, β), and water content (H_2O/SiO_2, γ). The effects of these gel parameters on the synthesis and characterization of W-type zeolite were investigated.

Crystalline W-type zeolite of high purity was synthesized using a gel with a molar ratio of Al_2O_3:6.4SiO_2:5.6K_2O:164.6H_2O at T = 165ºC for a period of 72 h. The effect of excess K_2O/SiO_2 ratio in a mono-cation (K)-SiO_2-Al_2O_3 gel-composition system on the nanoparticle size and purity of the product was also investigated. Experiments were carried out using the following levels of alkalinity: 21.4, 29.4, and 51.9; aluminosilicate module: 5.0, 6.4, and 10.0; water content: 16.5, 25.7, and 32.9; and excess K_2O/SiO_2 ratio : from 0.65 to 3.33. The results showed that by increasing the aluminosilicate module at high K_2O/SiO_2 ratio, the crystallinity and crystal size of the zeolite synthesized increased, while at low alkalinity, the crystallinity and crystal size decreased. Decreasing alkalinity at low aluminosilicate module increased the crystallinity and decreased the crystal size, while at high aluminosilicate module, both decreased. Finally, by increasing the water content at all aluminosilicate module and alkalinity values, the crystallinity and crystal size of the W-type zeolite increased. Excess K_2O/SiO_2 ratio was the key factor that should be adjusted in the range 0.7−1.0 for synthesis of pure crystals of W-type zeolite.

Key Words—Crystallinity, Gel Parameters, Nanoparticle Size, Optimum Gel Compositions, W-type Zeolite.

INTRODUCTION

Zeolites are microporous crystalline materials with a uniform pore-size distribution on a molecular scale and with high thermal, mechanical, and chemical stability. Zeolites have been developed for many industrial-separation processes such as adsorption and membrane technologies due to their molecular sieve properties (Tarlan-Yel and Önen, 2010; Gutiérrez *et al.*, 2010; Hasegawa *et al.*, 2010; Seo *et al.*, 2010; Nagase *et al.*, 2009; Lee *et al.*, 2011). Zeolites can be used in many separation processes, *e.g.* gas separation, pervaporation, and membrane reactors (Cejka *et al.*, 2007).

More than 50 different types of zeolites exist (clinoptilolite, chabazite, phillipsite, mordenite, merlinoite, *etc.*) with different physical and chemical properties. W-type zeolite is a synthetic zeolite that has the same framework topology as the mineral merlinoite (MER) (Baerlocher *et al.*, 2001). It was first synthesized in 1953 by Breck, 24 years before the natural counterpart was discovered in cracks of a kalsilite-melilitite lava in Cupaello, Rieti, Italy (Bieniok *et al.*, 1996 and references therein). W-type zeolite has an eight-membered ring (8MR); the channel dimensions are 0.31 nm × 0.35 nm, 0.27 nm × 0.36 nm, and 0.51 nm × 0.34 nm (Baerlocher *et al.*, 2001; Passaglia *et al.*, 1977; Galli *et al.*, 1979).

W-type zeolite was applied to the catalytic dehydration of methanol to dimethyl ether (DME) with 100% selectivity as well as high stability due to the mild acidity of W-type zeolite (Seo *et al.*, 2010). Membranes consisting of W-type zeolite have a unique nanopore structure which is stable at low pH (Hasegawa *et al.*, 2010).

W-type zeolite has been synthesized *via* different gel compositions under different synthesis conditions (time and temperature) (Nagase *et al.*, 2009; Skofteland *et al.*, 2001; Barrett *et al.*, 1998). W-type zeolite can be synthesized with and without an organic template. The effect of organic templates has been reported widely in the literature (*e.g.* Hasegawa *et al.*, 2010; Kim *et al.*, 2001). Seo *et al.* (2010) synthesized W-type zeolite with ethylene glycol as an organic template using microwave and conventional hydrothermal methods (Robson, 2001) and used KOH as the only basic solute.

Quirin *et al.* (1997) studied the effects of temperature and gel pH on the synthesis of W-type zeolite by varying the synthesis temperature from 150 to 200ºC and the gel pH from 9 to 14. Gels containing NaOH and KOH were

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used to produce several zeolites by changing the temperature and pH. Synthesis of pure W-type zeolite was achieved by keeping the Na/K molar ratio in the gel <1. Increasing the Na^+ content required a greater time for crystallization. Further studies of the effect of Na^+ content on the gel were undertaken by Milton (1961), Sand (1978); and Donahoe and Ltou (1984).

A large K^+ content is a key factor in facilitating the formation of pure W-type zeolite. Skofteland *et al.* (2001) studied the effect of K^+ cation sources (KOH and KNO_3) and their concentrations in the gel. The optimum gel compositions for these sources were Al_2O_3:$5SiO_2$:$7.5K_2O$:$600H_2O$ with KOH as the K source, and Al_2O_3:$5SiO_2$:$2.5K_2O$:$11KNO_3$:$600H_2O$ with KNO_3.

In mono-cation (K)-SiO_2-Al_2O_3 gels, the relationship between synthesis gel parameters (water content, aluminosilicate module (molar ratio of SiO_2 to Al_2O_3), and alkalinity) is still not well understood. In the present research, successful synthesis of W-type zeolite with KOH only was performed using a conventional hydrothermal method and optimum synthesis conditions to obtain zeolite crystals of uniform morphology. The effects of these parameters on the crystallinity and nanoparticle size of the zeolite synthesis were studied.

EXPERIMENTAL

The hydrothermal method (*i.e.* a method of crystallizing substances from high-temperature aqueous solutions at high vapor pressure) was used to synthesize W-type zeolite nanoparticles. Crystal growth was performed in a steel autoclave in which nutrient is supplied along with water. The materials used to form the aluminosilicate gel were aluminum hydroxide ($Al(OH)_3$, Merck), silicic acid (SiO_2, Merck), potassium hydroxide (KOH, Merck, 98%), and deionized water.

The molar ratio of the gel was Al_2O_3:$aSiO_2$:bK_2O:cH_2O. In the experimental design, the coefficients *a, b*, and *c* were fixed within the ranges $a = 5.0-10.0$, $b = 3.0-7.7$, and $c = 164.6$.

The W-type zeolite gel with a molar ratio of Al_2O_3:$6.4SiO_2$:$5.6Ka_2O$:$164.6H_2O$ was prepared by dissolving and mixing 18.80 g of KOH in 30 mL of deionized water and then dissolving 3.92 g of aluminum hydroxide in this KOH solution tp produce an aluminate solution. The mixture was weighed and heated gently with stirring to boiling until a clear solution was produced. The solution was then cooled to room temperature and deionized water was added until the original weight was restored. A silicate solution was prepared by adding 9.66 g of silicic acid to 70.63 mL of deionized water. The aluminate solution was poured into the silicate solution and mixed until a thick, homogeneous gel was formed.

After aging (for 5 h), the aqueous gel was poured carefully into a Teflon-lined bomb. The bomb was sealed and kept in an oven at 165ºC for 72 h to synthesize the W-type zeolite nanoparticles. The bomb was then removed from the oven to halt the crystallization process. The crystals synthesized were filtered and washed several times with distilled water and then dried in the oven at 80ºC for 12 h. This process yielded ~100 g of the zeolite powder.

In the present study, the effects of the chemical parameters on the formation of W-type zeolite nanoparticles were investigated, including the molar ratio of the source materials, *i.e.* $\alpha = SiO_2/Al_2O_3$ (aluminosilicate module), $\beta = H_2O/K_2O$ (alkalinity), $\gamma = H_2O/SiO_2$ (water content) (Table 1). Other synthesis conditions were kept constant in all the experiments as follows: stirring time = 5 h; stirring temperature = 25ºC; and drying temperature = 80ºC.

Finally, complementary experiments were carried out in order to investigate the interactions among the above parameters. These various combinations of chemical parameters (Table 1) yielded nine different gels for the synthesis of the W-type zeolite crystals.

CHARACTERIZATION OF THE SYNTHESIZED W-TYPE ZEOLITE SAMPLES

The zeolite crystals were characterized by X-ray diffraction (XRD) (SIEMENS, D5000, 1500 W, 35 kV, 20 mA, $\lambda = 1.54056$ A), from which the average crystal size was estimated using the standard Debye-Scherrer equation (Kril and Birringer, 1998):

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

where D is the average crystal size, λ is the X-ray wavelength (CuKα); φ is the line broadening (FWHM) of the peak, and θ is the diffraction angle. As the coherent effect is ignored by this formula, the nanoparticle size measured must be used as an approximation only. The crystallinity of the powder synthesized was measured based on the XRD data (intensity of the three highest peaks) compared with reference patterns (Treacy and Higgins, 2007).

The morphology of the crystals synthesized was examined by scanning electron microscopy (SEM) using a JEM-1200 or JEM-5600LV scanning electron microscope equipped with an Oxford ISIS-300 energy dispersive spectroscope (EDS).

RESULTS AND DISCUSSION

The XRD patterns of the W-type zeolite crystals synthesized using different compositions (Table 1, Figure 1) indicated that the zeolite crystals were formed with various compositions under different conditions and with different degrees of crystallinity. As mentioned, the crystallinity of the zeolites was measured using the intensity of the three most intense peaks of the XRD patterns and comparing the results with the reference patterns (Treacy and Higgins, 2007).

Table 1. Values of chemical parameters and gel compositions in the synthesis of zeolite crystals.

Sample	SiO_2/Al_2O_3	H_2O/K_2O	H_2O/SiO_2	Gel composition
S1	5.0	54.9	32.9	Al_2O_3:5.0SiO_2:3.0K_2O:164.6H_2O
S2	5.0	29.4	32.9	Al_2O_3:5.0SiO_2:5.6K_2O:164.6H_2O
S3	5.0	21.4	32.9	Al_2O_3:5.0SiO_2:7.7K_2O:164.6H_2O
S4	6.4	54.9	25.7	Al_2O_3:6.4SiO_2:3.0K_2O:164.6H_2O
S5	6.4	29.4	25.7	Al_2O_3:6.4SiO_2:5.6K_2O:164.6H_2O
S6	6.4	21.4	25.7	Al_2O_3:6.4SiO_2:7.7K_2O:164.6H_2O
S7	10.0	54.9	16.5	Al_2O_3:10.0SiO_2:3.0K_2O:164.6H_2O
S8	10.0	29.4	16.5	Al_2O_3:10.0SiO_2:5.6K_2O:164.6H_2O
S9	10.0	21.4	16.5	Al_2O_3:10.0SiO_2:7.7K_2O:164.6H_2O

The SEM images (Figure 2a,b) show crystals for sample S5 at two different magnifications. The crystals were clearly synthetic and the size of particles could be estimated.

EFFECT OF ALUMINOSILICATE MODULE (SiO_2/Al_2O_3)

The effects of the aluminosilicate module (SiO_2/Al_2O_3) at constant water content (H_2O/SiO_2) and high alkalinity ($H_2O/K_2O = 21.8$) on the crystallinity and crystal size of the zeolite (Figure 3) indicated that, for low aluminosilicate module ($SiO_2/Al_2O_3 = 5$), two types of zeolites (W-type zeolite and chabazite (CHA)) were synthesized. Increasing the aluminosilicate module decreased the amount of byproduct produced and increased the amount of amorphous phase produced. The amorphous phase was related to the amount of unreacted raw materials in the gel. Further increases in the aluminosilicate module decreased the amount of amorphous phase and increased the crystallinity.

At moderate alkalinity and low aluminosilicate module, more of the amorphous phase was produced. Increasing the aluminosilicate module increased the degree of polymerization of the polysilicate and aluminate anions, and, as a result, less of the amorphous phase was produced. Further increase of the aluminosilicate module led to overlap between zeolites, and, as a result, CHA and K-H zeolites were synthesized (Figure 4). (K-H is a synthetic zeolite type with orthorhombic symmetry and the same framework topology as the mineral phillipsite (Mimura *et al*., 2001).)

The crystallinity decreased with increasing aluminosilicate module at low alkalinity ($H_2O/K_2O = 54.9$) (Figure 5). Reduction in the crystallinity may be related, firstly, to the greater amount of amorphous phase and, secondly, to the overlap between the W-type and erionite zeolites. The transformation from W-type zeolite to erionite decreased the crystallinity.

The aluminosilicate module had a significant effect on the degree of polymerization of the polysilicate and aluminate anions and led to various zeolite structures

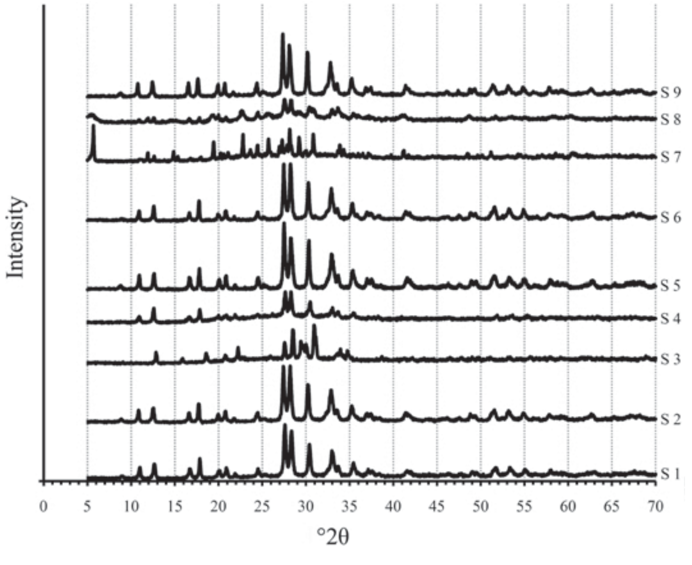

Figure 1. XRD patterns of W-type zeolite crystals synthesized according to the conditions listed in Table 2.

Table 2. Crystallinities and crystal sizes for the zeolites synthesized.

Sample	Crystallinity (%)	*D* (nm)	Phase	Group
S1	93.5	23	MER[*]	2
S2	96.3	29	MER	2
S3	48.8	29	MER+CHA[**]	1
S4	59.4	13	MER	1
S5	100.0	33	MER	3
S6	97.6	34	MER	2
S7	31.5	9.0	MER + Erionite+ ECR-2[***]	1
S8	20.0	9.0	MER+ CHA+ Zeolite K-H	1
S9	98.4	35	MER	3

*: Merlinoite (Linde W)
**: Chabazite
***: Potassium aluminum silicate

(Robson, 2001). Although the aluminosilicate module for the synthesis gel of any zeolite is in a certain range, changing the crystallization conditions such as time, temperature, molar ratio of the gel, alkalinity, or water content may lead to the formation of other zeolites.

The effects of the aluminosilicate module on the crystallinity and crystal size of the zeolites synthesized at different water contents were investigated. The variation in the crystallinity with the aluminosilicate module can be explained as follows: (1) the effect of the aluminosilicate module on the crystallization products; and (2) the interactions between alkalinity and the aluminosilicate module.

Effect of alkalinity (H_2O/K_2O)

Alkalinity is one of the most important parameters controlling the crystallization of zeolites, which are usually synthesized from initially amorphous gel phases. A high level of alkalinity ensures supersaturation for nucleation and growth processes. Crystallization generally proceeds from an amorphous phase, so the species of silicate, aluminate, and aluminosilicate in the solution are important for the crystallization mechanism (Robson, 2001).

The alkalinity determines the composition and is responsible to a great extent for the type of crystallizing product (Robson, 2001). Greater alkalinity increases the solubility of the silica and aluminum sources, decreases the degree of polymerization of the silicate anions, and accelerates polymerization of the polysilicate and aluminate anions. Consequently, increasing the alkalinity reduces the induction and nucleation periods and accelerates the crystallization of zeolites (Cejka *et al.*, 2007). Kawano and Tomita (1997) studied the formation of zeolites from obsidian by interaction with NaOH and KOH solutions at 150 and 200ºC and showed that several zeolites could be obtained by changing these parameters. The main zeolite phases obtained from KOH-type aluminum-silicate gels can be controlled by alkalinity (K^+ concentration). High alkalinity is the key factor in facilitating the formation of pure W-type zeolite (Skofteland *et al.*, 2001). The effects of alkalinity (H_2O/K_2O) at constant water content (H_2O/SiO_2) for different aluminosilicate modules on crystallinity and on

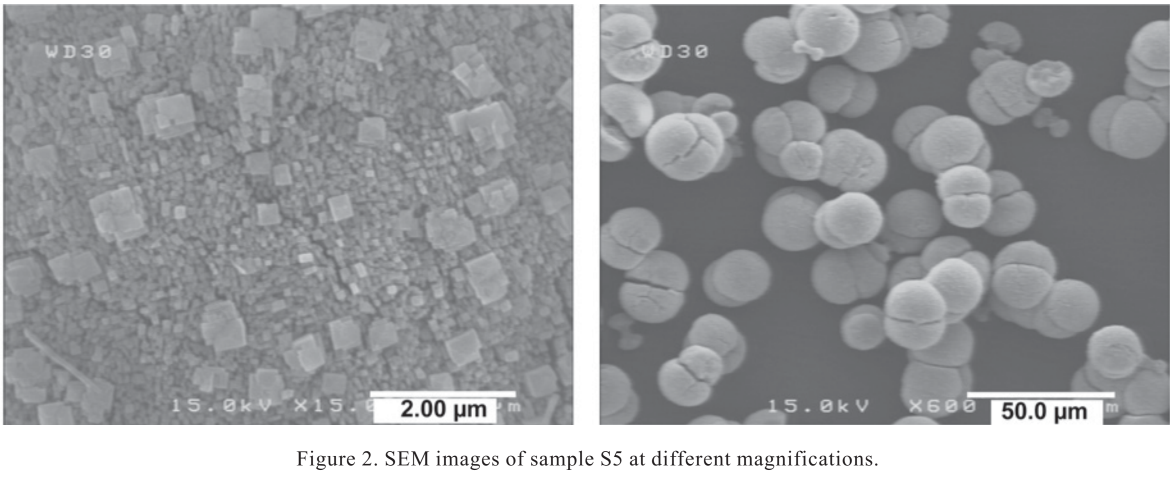

Figure 2. SEM images of sample S5 at different magnifications.

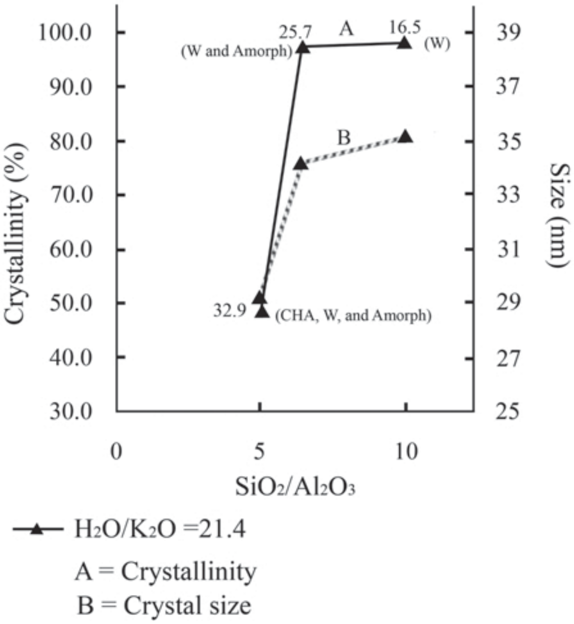

Figure 3. Effect of aluminosilicate module on the crystallinity and crystal size at high alkalinity (W = W-type zeolite; Amorph = amorphous material; CHA = chabazite).

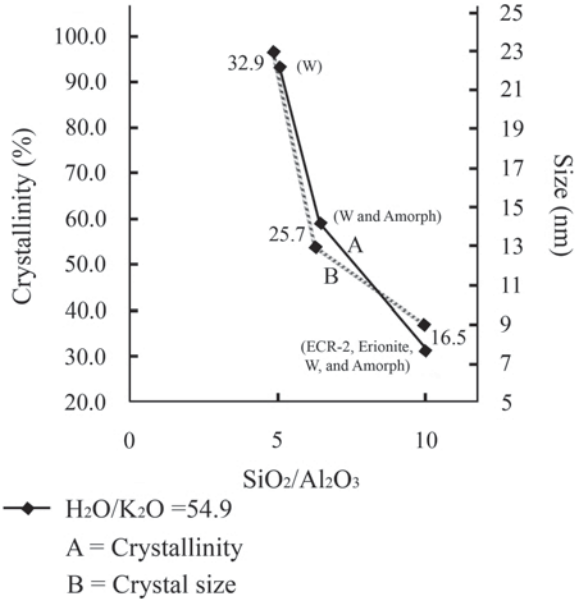

Figure 5. Effect of aluminosilicate module on crystallinity and crystal size at low alkalinity (abbreviations as in Figure 3; ECR = potassium aluminum silicate).

the crystal size of the zeolite (Figures 6–7) indicated that, in gel compositions with low aluminosilicate module, decreasing the alkalinity increased the crystallinity. Increasing the alkalinity increased the solubility of silica in the gel, which in turn caused the gel to become less supersaturated. Supersaturation of the gel was important for nucleation and growth processes, so at low aluminosilicate module, the crystallinity decreased. For low alkalinity at low aluminosilicate module, the gel was supersaturated and, therefore, the crystallinity was not affected.

For high aluminosilicate-module values with decreasing alkalinity, the crystallinity decreased (Figure 7). Reduction in crystallinity may be related to lesser supersaturation of the gel, which means that more of the amorphous phase remained in the synthesis gel and an overlap between zeolites occurred, producing byproducts such as CHA-type zeolite, erionite, or K-H-type zeolite.

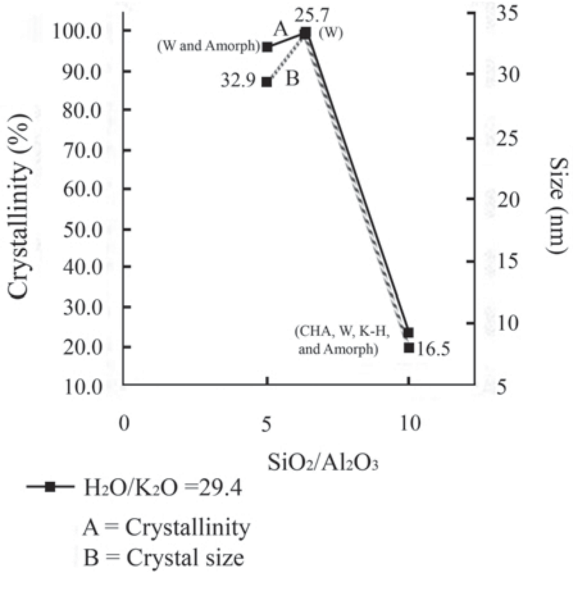

Figure 4. Effect of aluminosilicate module on crystallinity and crystal size at moderate alkalinity (abbreviations as in Figure 3; K-H = K-H-type zeolite).

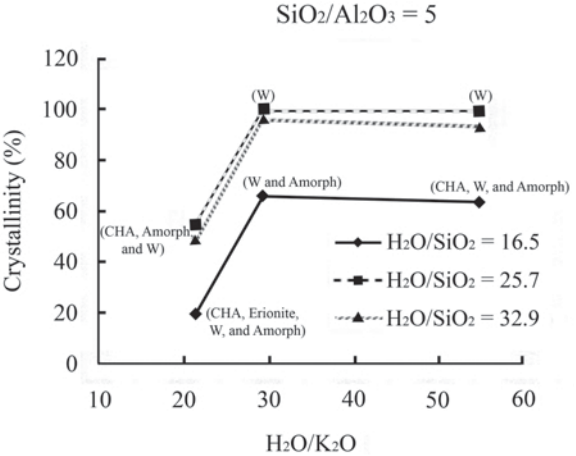

Figure 6. Effect of alkalinity on crystallinity at low aluminosilicate module (abbreviations as in Figure 3).

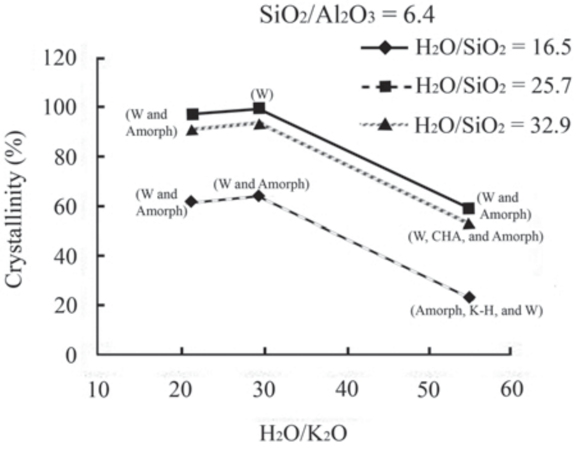

Figure 7. Effect of alkalinity on crystallinity at moderate aluminosilicate module (abbreviations as in Figures 3 and 4).

The effect of excess alkalinity (K_2O/SiO_2)

The zeolite was synthesized from reaction of amorphous raw materials in the gel. The raw materials in the gel first make an active complex which produce the zeolite. If the molar ratio of raw materials in the gel is selected correctly, pure zeolite is produced.

Silicic acid is relatively water insoluble but it is soluble in alkaline solutions, so the solubility of silicic acid in the reaction mixture is related to the alkalinity. On the other hand, according to Skofteland *et al.* (2001), the structure formed by a hydrogen-bonded K-H_2O network acts as an inorganic template in the crystallization of W-type zeolite. This K-H_2O structure also stabilizes the structure of as-synthesized crystals. Removal of the water results in a major structural deformation of W-type zeolite (Skofteland *et al.*, 2001). The excess K_2O/SiO_2 ratio is the total alkalinity (KOH) per mole of SiO_2 (Robson, 2001). The excess K_2O/SiO_2 ratio may indicate the effect of the inorganic template over the concentration of silicate in the synthesis mixture.

In order to investigate the effects of excess K_2O/SiO_2 ratio on W-type zeolite crystallization, the results were classified into three groups of crystallinities (Table 2). Group 1 included products with crystallinity of <60% with byproducts; group 2 included products with crystallinity of 60−98% without byproducts; and group 3 included products with crystallinity >98%. The effect of the K_2O/SiO_2 molar ratio on the synthesis of W-type zeolite (Figure 8) can be divided into three zones. In zone C ($0.70 < K_2O/SiO_2 < 1.00$), the reactants were adjusted for production of pure and high-crystallinity W-type zeolite; in zone B ($0.58 < K_2O/SiO_2 < 0.70$ and $1.00 < K_2O/SiO_2 < 1.40$), the reactants in the gel led to production of relatively pure W-type zeolites; in zone A the K_2O/SiO_2 molar ratio was <0.58 and >1.37 and overlap of zeolites occurred, meaning that amorphous phases and other crystal phases were produced. An increase in unreacted materials led to an increase in the formation of amorphous phases. In zeolite syntheses with different excess K_2O/SiO_2 ratio under the same crystallization conditions, minor zeolite phases such as CHA and K-H type zeolite were produced.

Pure W-type zeolite crystals were obtained only with excess K_2O/SiO_2 ratio in the range 0.70−1.00. Variation of the excess K_2O/SiO_2 ratio decreased the crystallinity of zeolite and led to the production of other zeolites such as erionite, with CHA and K-H zeolite types as minor phases.

Effect of water content (H_2O/SiO_2)

H_2O acts as a solvent in the hydrothermal synthesis of zeolites. Typically, the amount of water is varied within a certain range for synthesis of a particular zeolite. The concentration of the reactants is altered with variation of the H_2O content, thus affecting crystallization of zeolites. In general, an overall dilution of the synthetic gel mixture reduces supersaturation, and, thus, crystal growth is favored at the expense of nucleation, and consequently, large crystals are obtained (Cejka *et al.*, 2007).

Variations in the crystallinity of the zeolites synthesized with different amounts of water (H_2O/SiO_2) at constant alkalinity and aluminosilicate module (Figures 9−10) indicated that the crystallinity of the synthesized

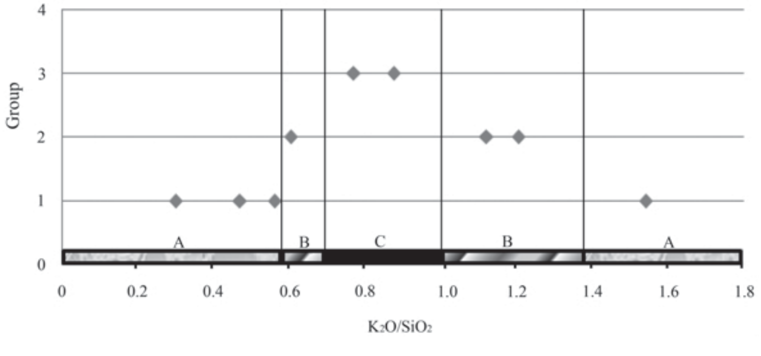

Figure 8. Effect of the K_2O/SiO_2 molar ratio on the synthesis of W-type zeolite.

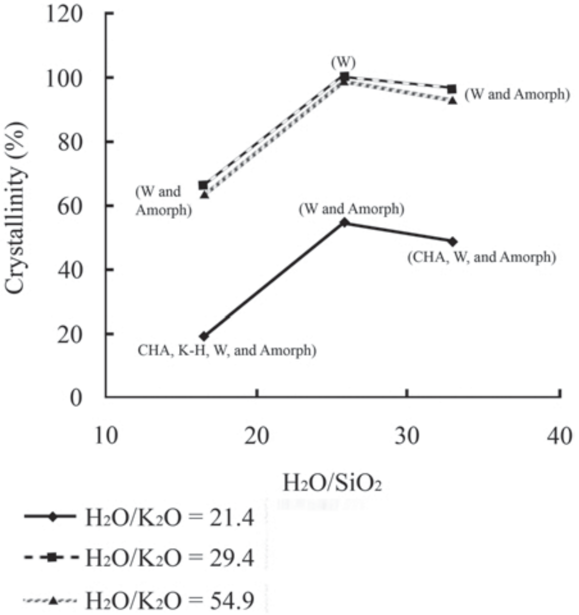

Figure 9. Effect of water content on crystallinity at different alkalinities (abbreviations as in Figures 3 and 4).

zeolites increased strongly with increasing water content between 16.5 and 25.7 and then decreased slightly with increasing water content, from 25.7 to 32.9. Decrease in the degree of crystallinity of the zeolite is due to dilution of the synthetic gel mixture, with water, *i.e.* reducing gel supersaturation.

CONCLUSIONS

Results from this study revealed that many parameters affect the synthesis of zeolites and that their interactions control the product formed. For example, pure W-type zeolite can be synthesized using Al_2O_3:6.4SiO_2:5.6K_2O:164.6H_2O and Al_2O_3:10SiO_2:7.7K_2O:164.6 H_2O gel compositions at 165ºC and for 72 h. The crystallinity increases: (1) by increasing the aluminosilicate module at high alkalinity; (2) by increasing the alkalinity at low aluminosilicate module; (3) by increasing the water content at any aluminosilicate module and alkalinity; and (4) with excess K_2O/SiO_2 ratio between 0.7−1.0. The results also showed that the crystal size of W-type zeolite varies directly with crystallinity.

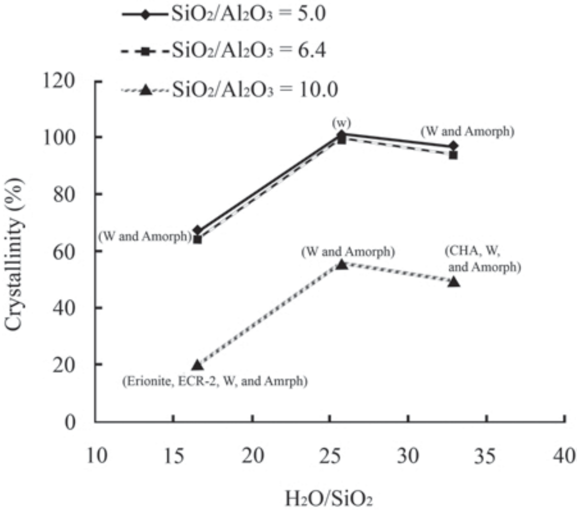

Figure 10. Effect of water content on crystallinity at different aluminosilicate modules (abbreviations as in Figures 3−5).

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