

TRANSFORMATION OF ZEOLITE NaY SYNTHESIZED FROM RICE HUSK SILICA TO NaP DURING HYDROTHERMAL SYNTHESIS

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Abstract

Rice husk silica powder with approximately 98% purity was used as a silica source for zeolite syntheses. This study investigated the transformation of zeolite NaY to zeolite NaP during hydrothermal synthesis at 100°C by fixing the ratio of SiO₂, Al₂O₃, and Na₂O at 10:1:4.6, the optimum ratio for NaY synthesis. The studied parameters included aging time (1, 2, and 3 days) and crystallization time (1, 2, 3, 4, and 5 days). The transformation was observed by powder X-ray diffraction. The aging time did not have much effect on the transformation because when the crystallization time was fixed at 1 day, the synthesis with 1-day aging produced pure phase NaY and that with 2 and 3 days produced only a small amount of NaP. In contrast, changes of the crystallization time, with a fixed aging time at 1 day, caused a significant transformation. The transformation of NaY to NaP was observed in the synthesis with crystallization of 2 days and the amount of NaP increased with the crystallization time. The NaY phase was not observed after a crystallization time of 4 days and NaP with a cleaner phase was obtained after crystallization of 5 days. Consequently, the synthesis condition with an aging time of 1 day and crystallization time of 5 days was the optimum condition for the transformation. Scanning electron micrographs at this optimum condition showed a narrow size distribution in the range of 7 - 14 μm.

Keywords: Zeolite synthesis, NaP, NaY, rice husk silica, crystallization time, aging time, hydrothermal

Introduction

Zeolite P class includes a series of synthetic zeolite phases such as cubic configuration (also termed B or P_C) or tetragonal configuration (also termed P₁). Its conformation depends on the extra-framework ion, the state of dehydration and the chemical composition (Nery *et al.*, 2003). The zeolite P class has the typical oxide

formula: M_{2/n}O·Al₂O₃·1.80-5.00SiO₂·5H₂O, where M is an n-valent cation, normally an alkali metal. Crystallines of zeolite P with a Si/Al ratio from 0.90 to 1.33 are useful as molecular sieves and detergent builders (Huang *et al.*, 2001). Zeolite P can be synthesized from various silica sources and methods, for example,

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from a natural clay, Kaolinite, and crystallization at 75–85°C (Sathupunya *et al.*, 2002); from coal fly ash by agitation at 120°C (Murayama *et al.*, 2002); or from sodium aluminate and sodium silicate solution by hydrothermal treatment in a microwave oven (Zubowa *et al.*, 2007).

Sang *et al.* (2006) synthesized small crystals of zeolite NaY by hydrothermal method and found that crystallization at 120°C caused the formation of zeolite NaP instead of zeolite NaY. Moreover, in the synthesis of zeolite NaY with rice husk silica (RHS), zeolite NaP was observed when the crystallization at 100°C was longer than 48 h (Wittayakun *et al.*, 2008). Thus, we investigated further to determine the synthesis conditions such as aging and crystallization time that facilitated the transformation of NaY to NaP.

Here we report the transformation of zeolite NaY, synthesized with the RHS as reported previously, to NaP under different aging times (1, 2, and 3 days) and crystallization times (1, 2, 3, 4, and 5 days). The product from each condition was characterized by X-Ray Diffraction (XRD). The sample with the highest degree of transformation was characterized further by Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Laser Diffraction Particle Size Analyzer (DPSA) and Simultaneous Differential Thermal Analysis (TGA-DTA).

Experimental

Materials

Chemicals for the preparation of the RHS and zeolite synthesis were hydrochloric acid (37% HCl, Carlo-Erba, Rodano, Italy), sodium aluminate (~55–56% of NaAlO₂, Riedel-de Haën, New Jersey, United States), sodium hydroxide (97% NaOH, Carlo-Erba, Rodano, Italy), and rice husk (local rice mill in Lampang, Thailand). The standard zeolites were NaY with a Si/Al molar ratio 5.7 (JRC with Tosoh Corp, Tokyo, Japan) and NaP (Fluka, New South Wales, Australia).

The RHS was prepared by the acid-leaching method reported previously (Khemthong *et al.*,

2007). Briefly, the rice husk was washed and dried at 100°C overnight; refluxed with 3 M HCl for 6 h; filtered and washed again with water until the filtrate was neutral and dried at 100°C overnight before the pyrolysis in a furnace (Carbolite, CWF1200, Hope valley, United Kingdom) at 550°C for 6 h to remove the hydrocarbon and volatile organic compounds. The obtained RHS contain amorphous silica with approximately 98%wt purity. This RHS was dissolved in 3.5 M NaOH solution to produce Na₂SiO₃ for further zeolite synthesis.

Transformation of Zeolite NaY to NaP

The transformation was investigated with the synthesis gel of zeolite NaY prepared similarly to that in a previous work by Khemthong *et al.* (2007) by mixing a seed gel and feedstock gel. The seed gel was prepared by dissolving NaOH and NaAlO₂ in deionized water followed by the addition of Na₂SiO₃ solution and kept at room temperature for 1 day. The feedstock gel was prepared in a similar method to that of the seed gel except that it was used immediately without aging. In the synthesis, both gels were mixed to form overall gel, aged (kept undisturbed) at room temperature, and crystallized at 100°C. After the crystallization step, the resulting white powder was separated by filtration, washed, and dried at 100°C.

The transformation of zeolite NaY to NaP was investigated by changing the aging time or crystallization time. In the first set, the overall gel was aged at various times (1, 2, and 3 days) and crystallized for 1 day. These conditions were chosen because the aging time of 1 day and the crystallization of 1 day was the optimum condition for the synthesis of NaY. Another set of the experiment, the effect of crystallization time, was investigated by fixing the aging time at 1 day and varying the crystallization time to 1, 2, 3, 4, and 5 days.

The product from each condition was characterized by XRD (Bruker AXS GmbH, Karlsruhe, Germany) with nickel filter Cu K_α radiation scanning from 4° to 50°. The XRD pattern was compared with that of standard NaY and NaP. A product with the highest degree of transformation was characterized further by FTIR (Spectrum GX, Perkin-Elmer,

Massachusetts, United States) using KBr as a medium. IR spectra were scanned in the range of $4,000\text{ cm}^{-1}$ to 400 cm^{-1} with a resolution of 4 cm^{-1} . Crystallite size and morphology were studied by Scanning Electron Microscopy (SEM) with a JEOL JSM-6400 (Tokyo, Japan) with applied potential 10 - 20 kV. Particle size distribution of zeolites was determined by DPSA (Malvern Instruments, Mastersizer 2000, Worcestershire, United Kingdom) with the sample dispersed in distilled water and analyzed by He-Ne laser. The standard volume percentiles at 10, 50, and 90, or denoted as $d(0.1)$, $d(0.5)$, and $d(0.9)$, respectively, were recorded from the analysis and used to calculate the width of the distribution. The width was calculated from the equation below:

$$\frac{d(0.9) - d(0.1)}{d(0.9)}$$

Thermal stabilities were investigated by TGA-DTA (TA Instrument/SDT 2960, Delaware, United States) by heating from 0°C to $1,000^{\circ}\text{C}$ with a heating rate of $10^{\circ}\text{C}/\text{min}$ in

nitrogen flow ($100\text{ ml}/\text{min}$).

Results and Discussion

Effect of Aging Time on Transformation of NaY to NaP

The XRD patterns of the sample prepared at aging time of 1, 2, and 3 days were compared with that of NaY and NaP standards in Figure 1. The spectrum of the 1-day aging sample was similar to that of standard zeolite Y without any other peaks indicating that the pure phase of NaY was obtained. With increased aging time, the peaks at 12.5 , 21.6 , and 28.1 degrees with low intensity emerged in the products from 2- and 3-day aging times. The positions of those extra peaks were the characteristic peaks of NaP, indicating that a longer aging time than 1 day causes the transformation of NaY to NaP. The transformation was not significant at these conditions. It was found in the next section that the transformation occurred faster at a higher temperature. Thus, this transformation is endothermic.

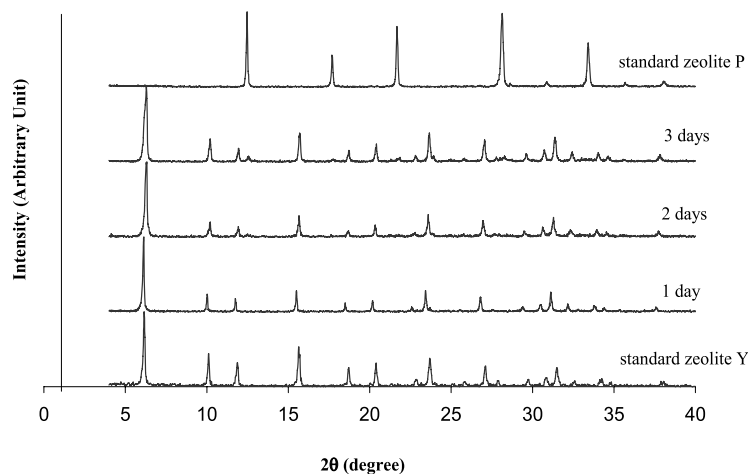


Figure 1. Normalized XRD patterns of zeolite synthesized with different aging times compared with the patterns of standard zeolite Y and zeolite P

Effect of Crystallization Time on the Transformation of NaY to NaP

The effect of crystallization time on the transformation of NaY to NaP was investigated with the aging time of 1 day because it showed no effect on the transformation. The XRD patterns of the products with a crystallization time from 1 to 5 days are displayed in Figure 2 along with that of standard zeolites. Only the sample with the 1-day crystallization time showed the pure phase of NaY with the 3 – strongest peaks at 6.5, 15.6, and 23.7 degrees. These 3 peaks had the same positions as those of zeolite Y reported in JCPDS files (International Centre for Diffraction Data, 1979). Characteristic peaks of NaP started to emerge in the sample with the 2-day crystallization time and the intensities of those peaks increased with a longer crystallization time. The main peak of NaY was not observed after crystallization for 4 days and NaP became a major component. Because there was another phase along with NaP, this condition was not suitable for the synthesis of zeolite P.

The first peak of NaP ($2\theta = 12.5$) from this study split into 2 peaks but the position was similar to that of the standard NaP and the peaks of zeolite P from JCPDS database (International Centre for Diffraction Data, 1979). It was possible that there were two types of NaP in this sample and this was confirmed by SEM in

the next section. From the literature, the position of this peak of NaP with different morphology was slightly different (within 0.5 degree) (Sathupunya *et al.* 2002; Zubowa *et al.* 2007).

Characterization of Product with 5-day Crystallization

The product obtained after the 5-day crystallization time contained NaP as a major component. It was further characterized by FTIR, SEM, DPSA, and TGA-DTA. The FTIR spectrum in transmittance mode in Figure 3 shows peaks at 3,487, 1,638, 1,002, 773, 690, 571, and 465 cm^{-1} . These peaks were similar to those of zeolite P reported by Flanigen *et al.* (1971). The peaks at 571 - 460 cm^{-1} and 1,002 cm^{-1} were assigned to T-O (T = Si, Al) bending and Si-O, Al-O tetrahedral vibration, respectively. The appearance of the peaks at 690, 1,638, and 3,487 cm^{-1} was attributed to the double ring external linkage, vibration of water molecule, and OH stretching, respectively (Albert *et al.*, 1998).

The SEM micrograph in Figure 4 illustrates the morphology of the product from the crystallization of 5 days. There were two types of particles: spherical and multifaceted. The spherical shape was similar to that of NaP reported by Sathupunya *et al.* (2002) and the

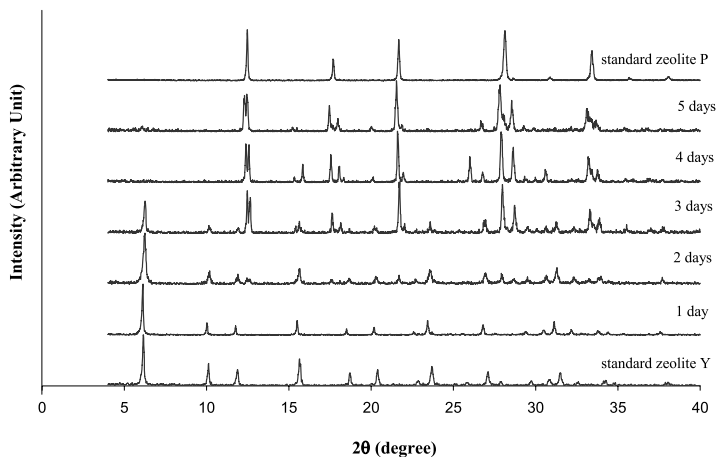


Figure 2. Normalized XRD patterns of zeolite synthesized with different crystallization times compared with the patterns of standard zeolite Y and zeolite P

multifaceted shape was similar to that of NaP reported by Zubowa *et al.* (2007). The mixed morphology might be the reason that the XRD peak at 12.5 degrees (Figure 2) split into 2 peaks.

Particle size distribution of the product with the 5-day crystallization time obtained from the DPSA is shown in Figure 5. The major population had a particle size in the range of 4 - 25 μm with a small population with a size in the range of 0.7 - 3.0 μm . Note that the particle sizes from the DPSA were the size and distribu-

tion of bulk particles which might be composed of several small particles aggregated together, and thus were different from the results from the SEM which displayed images of isolate crystals.

The thermal stability of the product with the 5-day crystallization time obtained from the TGA-DTA experiment is shown in Figure 6. The weight loss during heating was approximately 17% up to 400°C, accompanied by 3 endothermic peaks at about 60, 100, and 150°C which was

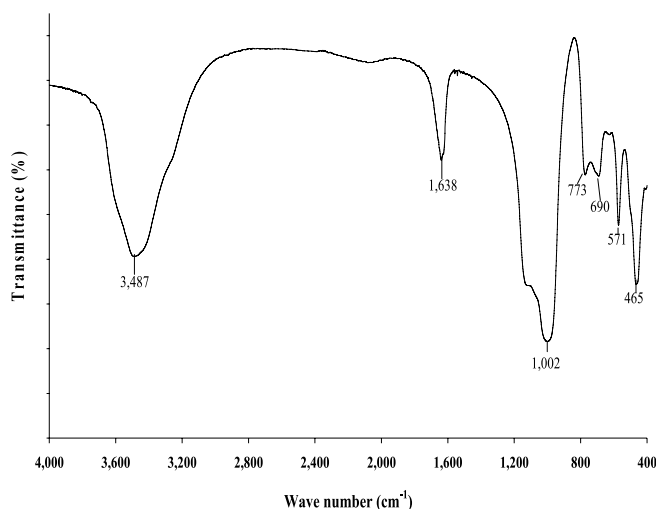


Figure 3. FTIR spectrum of product obtained from 1-day aging and 5-day crystallization time

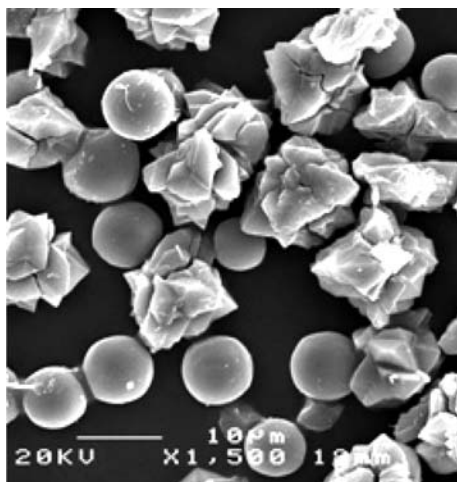


Figure 4. SEM image of products obtained from 1-day aging and 5-day crystallization time

attributed to the loss of water (Zubowa *et al.*, 2007). Further weak endothermic peaks were observed at about 200, 300, and 600°C. These 3 peaks resulted from a 3 step endothermic water loss and, at 900°C at which the zeolite P was irreversibly converted into nepheline, a dense NaAlSiO_4 phase (Albert *et al.*, 1998).

Conclusions

Two parameters that affected the transformation of zeolite NaY to zeolite NaP were the aging

time and crystallization time. When the crystallization time was fixed at 1 day, the aging time of 1 day was suitable to produce the pure phase of zeolite NaY whereas 2 and 3 days aging times produced a small amount of NaP. The crystallization time showed a more significant effect on the transformation. The phase of NaY was not observed after crystallization for 4 days and, after a crystallization time of 5 days, NaP was a major product.

With the 5-day crystallization time, NaP was a major product with a trace amount of NaY.

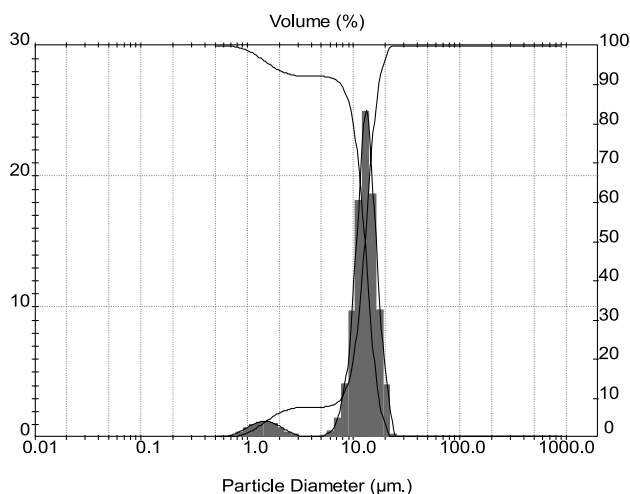


Figure 5. Particle size distribution of product obtained from 1-day aging and 5-day crystallization time

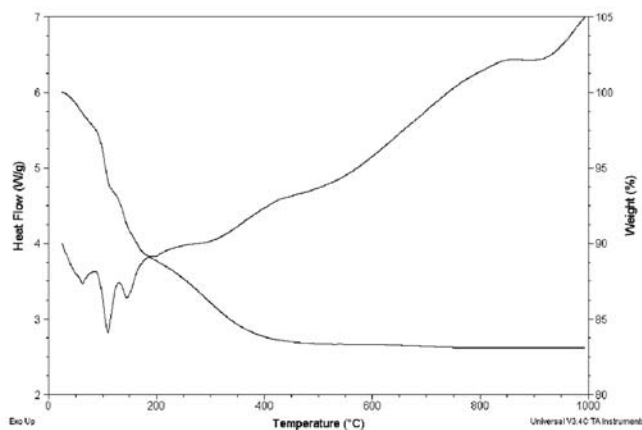


Figure 6. TGA-DTA thermogram of product obtained from 1-day aging and 5-day crystallization time

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