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Synthesis of Zeolite Y Nanocrystals from Clear Solutions

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ABSTRACT

Synthesis of zeolite nano-sized crystals has attracted much attention because of their properties, some of which maybe different from the normal sized crystals. A synthesis adopted by Voltchev and Mintova was used as the starting point: 0.078 Na_2O: 4.35 SiO_2: 1.0 Al_2O_3: 2.35 $(TMA)_2O$: 248 H_2O. Both the silicate and aluminum starting solutions were clear. Zeolite Y nanocrystals with zeolite A nanocrystals as an impurity were obtained with a size range of 20-100 nm through this synthesis technique.

INTRODUCTION

There has been considerable research over the years in synthesis of large zeolite crystals with sizes approaching the sub-millimeter range. This interest was driven by specific technological applications favoring larger crystals or because crystal structure – property relations could be better determined using larger crystals. Zeolite Y, in particular, plays an important role today in the field of cracking process catalysis - hence, this work focused on this zeolite.

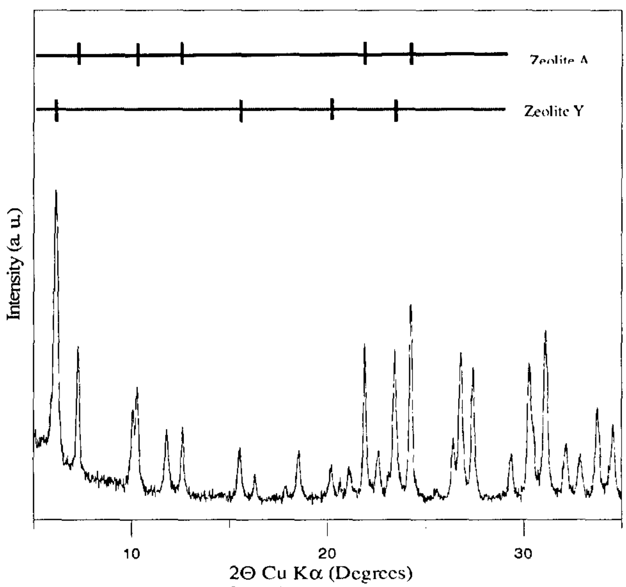
There have been several reports recently on the synthesis of small zeolite crystallites, such as zeolites A, X, L, Beta, ZSM-5 and Silicalite [1-7]. However, there are only few articles about synthesis of nano-sized zeolite Y [1,2]. Those articles explored the possibility of the synthesis of nano-sized particles [1] and the effect of Na_2O/Al_2O_3 on the particle size [2]. The influence of the Si/Al ratio, aging time, the sodium content and TMA content in starting solution on the purity, crystal size, Si/Al ratio in crystals and yield of nano-sized zeolite Y was investigated.

EXPERIMENTAL

In this synthesis, zeolite Y nanocrystals were grown from clear aluminosilicate solutions with different composition. The following reagents were used: Ludox SM-30 colloidal silica (30 wt% SiO_2, 0.56 wt% Na_2O, 0.01 wt% NaCl, 0.03 wt% Na_2SO_4, 69.4 wt% H_2O, Aldrich), aluminum isopropoxide ($Al(OiPr)_3$, 98+%, Aldrich), tetramethylammonium hydroxide (TMAOH, 25 wt% aqueous solution, Aldrich), and deionized water. From the literature in which nanocrystals were obtained Ludox SM-30 has always been used as the silica source. Deionized water was filtered twice through 0.2 and 0.1 μm membrane filters to reduce the particulate sources of undesired ions. All other reagents were used as received. The synthesis mixtures were prepared from two clear precursor solutions. Solution I was prepared in a 60 ml HDPE bottle by adding $Al(OiPr)_3$ into the double-filtered deionized water and TMAOH mixed solution. A white precipitate appeared in solution I upon addition of $Al(OiPr)_3$, and therefore the mixture was stirred at room temperature using a magnetic stirrer until a clear solution formed. Solution II was formed by combining Ludox SM-30 with double-filtered deionized water in 30 ml HDPE bottle. The precursor solutions were mixed together in a 125 ml HDPE bottle, hand shaken, and put into a 95°C oven. After predetermined times the solids from the synthesis were recovered by centrifugation at 3300 rpm. Between centrifugation cycles supernatants were decanted and solids re-dispersed in deionized water. These processes were repeated about four times until the pH of the decanted solution was between 7 and 8.

RESULTS AND DISCUSSION

The effect of Si/Al ratio in the synthesis mixture on the zeolite Y nanocrystals. Samples, with the reactant solution composition of 0.078 Na_2O: 4.35 SiO_2: 1.0 Al_2O_3: 2.35 $(TMA)_2O$: 248 H_2O, were synthesized by crystallizing in a 95 °C oven for 3 days. By comparing the product X-ray pattern shown in figure 1 with a standard X-ray pattern of zeolite A and that of zeolite Y, it can be concluded that the sample is a mixture of mostly zeolite Y and some zeolite A. In the scanning electron microscope, cubic and octahedral crystal shapes were found as shown in figure 2. Most of the crystals are octahedral zeolite Y nanocrystals with a small amount of zeolite A as impurity.



Sample trial # 2-1

Figure 1. XRD pattern of sample

The results of experiments aimed at finding the relation between the Si/Al ratio in the starting solution and the Si/Al ratio in the final crystals are shown in Table 1. From Table 1, we can see that the higher the Si/Al ratio in the starting solution, the higher this ratio in the final products. It was also found that the higher this ratio, the less zeolite Y and the more zeolite A in the final product. When the SiO_2/Al_2O_3 ratio is 5.44, about 90% of the final crystals are Zeolite Y. However, when SiO_2/Al_2O_3 ratio is 7.6, 90 percent of products are zeolite A. Figure 3 shows the Si/Al ratio in the zeolite Y crystals increased as the Si/Al ratio in the starting solution increased.

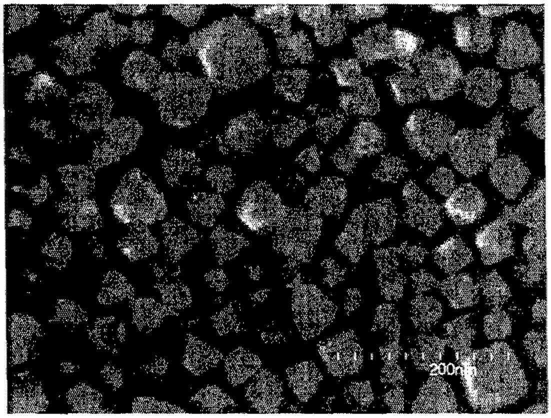


Figure 2. SEM of sample

Table 1: Results for the experiment Trial # 2

Sample No.	SiO_2/Al_2O_3 ratio in the starting solution	SiO_2/Al_2O_3 ratio of zeolite Y in the crystal products [b]	Yield (%)[a]	Size (nm)		Products purity (wt %)	
				Zeolite Y	Zeolite A	Zeolite Y	Zeolite A
# 2-1	4.35	3.3	1.20	50$\pm$30	80	60	40
# 2-2	5.44	4.16	1.40	50$\pm$ 25	150$\pm$50	90	10
# 2-3	6.53	4.5	2.47	50$\pm$ 25	150$\pm$50	40	60
# 2-4	7.62	5.56	2.79	50$\pm$ 25	120$\pm$20	10	90

[a]: the calculation is based on the mass of the chemicals without water.

[b]: SiO_2/Al_2O_3 ratio of zeolite A is 1.48

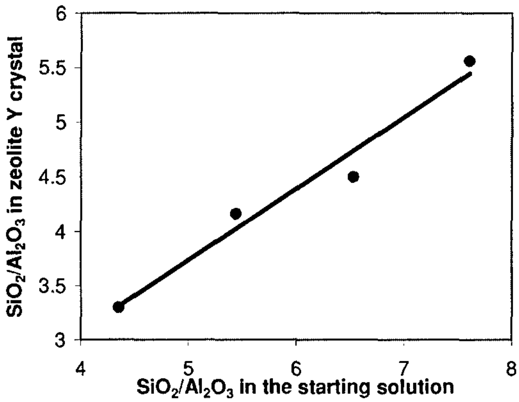


Figure 3. The effect of SiO_2/Al_2O_3 in the starting solution

The effect of Na_2O/Al_2O_3 ratio on the crystalline phase of nanocrystals. Since Ludox SM-30 contains 30 wt % SiO_2, 0.56 wt % Na_2O, and 69.4 wt % water, the amount of Na_2O content increases as the amount of SiO_2 increases. In order to find out whether SiO_2/Al_2O_3 ratio or the Na_2O/Al_2O_3 ratio affects the product purity, a series of experiments, trial # 3 were performed. This was done to investigate the effect of the sodium content in the synthesis mixture on the crystalline phase obtained and on the ultimate particle size of colloidal zeolite particles. Three different chemicals were used as the silica source: Ludox SM-30, Ludox LS-30 and Cab-O-Sil. The results are shown in Table 2. Experiment 3-1 was performed with Cab-O-Sil to have no sodium in the starting solution, but with otherwise unchanged composition compared to samples 3-2, 3-3 and 3-4. Except for sample 3-1, lower sodium contents in the synthesis

Table 2. Effect of Na_2O/Al_2O_3 on the product purity.

Sample number	Na_2O/Al_2O_3 ratio in the starting solution	SiO_2/Al_2O_3 ratio in the starting solution	Yield (%)	Size (nm)		Products purity (wt %)	
				Zeolite Y	Zeolite A	Zeolite Y	Zeolite A
# 3-1	0	4.35	12.45	N [a]	N [a]	Unconfirmed crystals	
# 3-2	0.014	4.35	0.38	50± 25	80	90	10
# 3-3	0.04	4.35	1.07	50± 25	100±30	70	30
# 3-4	0.078	4.35	1.10	50± 25	80	60	40

mixture results in a lower yield as shown in Table 2. Lower sodium content produces more zeolite Y than zeolite A nanocrystals. Zeolite Y is the main product from samples 3-2, 3-3 and 3-4 with zeolite A as the impurity. The result from sample 3-1 is not as expected. An unknown product material was formed other than zeolite A or zeolite Y.

The effect of aging time on the crystalline phase of nanocrystals. Samples 7-A, 7-B, and 7- C were aged at room temperature for 4, 6 and 9 days separately with crystallization at 95 °C for 3 days. Sample 14 and 17 were aged for 15 days and 25 days separately and crystallized at 95 °C for 4 days. Sample 11, 15 and 18 aged for 0 day, 15 days and 25 days with crystallization for 9 days. From Table 3, it can be concluded that longer aging time results in lower yields. But the particle size does not change a lot with the variation of aging time.

Table 3. Results on investigation of aging time

Trial Number	Aging (days)	Crystallization (days)	Yield [a]	Size of Crystals (nm) (From SEM)	
				Zeolite Y	Zeolite A
# 7- A	4	3	2.89	50 ± 30	100 ± 10
# 7- B	6	3	2.98	50	60 ± 10
# 7- C	9	3	2.33	60 ± 20	100 ± 40
# 14	15	4	2.15	40	N/A
# 17	25	4	2.00	50 ± 20	90
# 11	0	9	2.97	60 ± 20	80
# 15	15	9	2.45	50	100 ± 25
# 18	25	9	1.86	55	100 ± 20

[a]: Mass of product/Mass of chemicals used in the starting solution except water

The effect of crystallization time on the crystalline phase of nanocrystals. Experimental results are presented in Table 4 and Figure 4. Samples # 2-2, # 11, # 12 and # 13 were crystallized for 5, 9, 12 and 16 days at 95 °C oven separately without aging. Sample # 14, # 15 and # 16 were aged at room temperature for 15 days and crystallized at 95 °C for 4, 9, 16 days. # 17 and # 18 aged for 25 days and crystallized for 15 days. From the results it can be seen that the longer the sample stayed in the oven for crystallization, the larger of the yield.

In conclusion, the higher the SiO_2/Al_2O_3 ratio is in the starting solution, the higher this ratio in the final products. It was also found that the higher this ratio, the less zeolite Y and the more zeolite A in the final products and yield. When the SiO_2/Al_2O_3 ratio is 5.44, about 90% of the final crystal is zeolite Y. However, when SiO_2/Al_2O_3 ratio is 7.6, 90 percent of products are zeolite A. Since aging time enhanced the nucleation, crystals obtained after longer aging time are more uniform and the size is smaller. Yield of the crystals increased with longer crystallization time. In these experiments, no relationship was observed between the amount of zeolite Y product and the crystallization time.

Table 4. Effect of crystallization time on crystalline phase

Sample Number	Crystallization (days)	Aging (days)	Yield of crystals *(%)	Production (%) #		Size of crystals (nm)	
				Zeolite Y	Zeolite A	Zeolite Y	Zeolite A
# 2-2	5	0	1.40	90	10	50± 25	150±50
# 11	9	0	2.97	60	40	60 ± 20	80
# 12	12	0	2.30	75	25	50± 30	120
# 13	16	0	5.63	80	20	50	80-200
# 14	4	15	2.15	60	40	40 ± 10	120± 20
# 15	9	15	2.45	55	45	45 ± 10	100± 25
# 16	16	15	6.46	95	5	50	N/A
# 17	4	25	2.00	65	35	40	90
# 18	9	25	1.86	25	75	55	100± 20

*: The yield is based on the mass of feeding chemicals except H_2O.

#: Estimated from X-ray diffraction pattern.

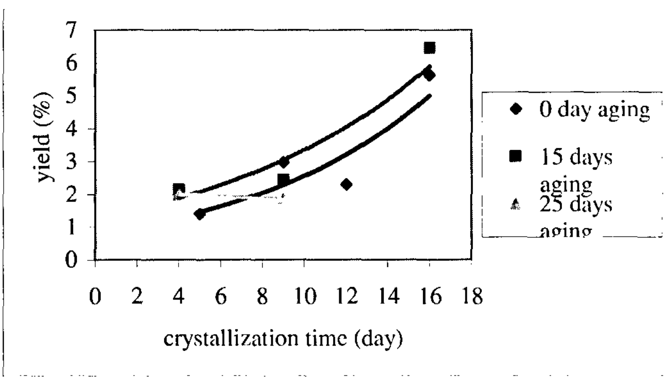


Figure 4. Effect of crystallization time on crystalline phase

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