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An Investigation of the Nucleation/Crystallization Kinetics of Nanosized Colloidal Faujasite Zeolites

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A two-stage varying-temperature technique was utilized to study the nucleation/crystallization kinetics of nanosized faujasite zeolites from clear solutions. At 100 °C, the nucleation period of zeolite Y was determined to be about 6.5 days, which extended over almost the whole period of crystal growth. The crystallization kinetics of colloidal zeolite Y differed from those for another clear solution, colloidal zeolite system, namely, TPA−silicalite-1, where the nucleation and crystal growth were found to occur as separate processes. Despite the occurrence of simultaneous nucleation and crystal growth, the colloidal zeolite Y product had a crystal size distribution similar to that for TPA−silicalite-1. In addition, the influence of the growth-limiting nutrient (Na^+) on the crystallization of zeolite Y was investigated. The sodium concentration in the synthesis solution could be controlled below a critical level to avoid the nucleation of zeolite A.

Introduction

Commonly, the synthesis of molecular-sieve zeolites is carried out in concentrated aluminosilicate solutions that contain amorphous gel phases. During the growth process, an amorphous gel can serve as a reservoir for the components that are eventually deposited at the surface of the growing crystals. A great deal of work has sought a better understanding of the mechanisms for nucleation and crystal growth of zeolites from gels.[1−6] However, it is also possible to synthesize several zeolites from clear solutions in which the amorphous phase is not visible to the naked eye.[7−10] In the clear solutions, the synthesis products can be directly observed through microscopy and/or dynamic light scattering spectroscopy with little interruption of the complex processes. Recently, an experimentally direct two-stage varying-temperature method was developed to investigate the nucleation profile of nanosized TPA−silicalite-1 crystals from clear solutions.[11−14] It was found that, for the synthesis of TPA−silicalite-1 crystals, independent of the silica source and aging time, the nucleation process occurred over a substantial period but was mostly completed before crystal growth was detected. Thus, the stages of nucleation and crystal growth for TPA−silicalite-1 crystallization were distinct.

For TPA−silicalite-1 synthesis, only silicate species and organic template are likely to be involved in the crystallization. For the synthesis of zeolite Y, however, an aluminosilicate species is formed when the reaction components are mixed even at room temperature, in addition to the alumina and silicate species in the solution. Thus, the nucleation and crystallization of zeolite Y is more complex than that of TPA−silicalite-1 even in clear solutions. In addition, it is known that clear solutions are favorable for the synthesis of nanosized zeolites that have a potential for applications such as the preparation of zeolite films/membranes by using nanosized crystals as seeds or the synthesis of various zeolite macrostructures.[15,16] To optimize the characteristics of a zeolite product for such applications (e.g., crystal size, size distribution, and purity), it is essential to have a good understanding of the nucleation and growth processes and their interactions.

The purpose of this work is to examine whether a two-stage varying-temperature technique can also be used to resolve the nucleation kinetics of zeolite Y. The kinetics of the nucleation/crystallization of nanosized zeolite Y and TPA−silicalite-1 crystals were compared,

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(1) Golemme, G.; Nastro, A.; Nagy, J. B.; Subotic, B.; Crea, F.; Aiello, R. *Zeolites* **1993**, *11*, 776.

(2) Burkett, S. L.; Davis, M. E. *Chem. Mater.* **1995**, *7*, 920.

(3) Liu, C.; Gao, X.; Ma, Y.; Pan, Z.; Tang, R. *Microporous Mesoporous Mater.* **1995**, *7*, 920.

(4) Lechert, H.; Kacirek, H. *Zeolites* **1993**, *13*, 192.

(5) Ginter, D. M.; Went, G. T.; Bell A. T.; Radke, C. J. *Zeolites* **1992**, *12*, 733.

(6) Zhdanov, S. P.; Samulevich, N. N. In *Proceedings of the 5th International Zeolite Conference*; Rees, L. V. C., Ed.; Heyden: Chichester, U.K., 1980; p 75.

(7) Schoeman, B. J.; Sterte, J.; Otterstedt, J.-E. *Zeolites* **1994**, *14*, 208.

(8) Persson, A. E.; Schoeman, B. J.; Sterte J.; Otterstedt, J.-E. *Zeolites* **1995**, *15*, 611.

(9) Wiersema, G. S.; Thompson, R. W. *J. Mater. Chem.* **1996**, *6* (10), 1693.

(10) Gora, L.; Streletzky, K.; Thompson R. W.; Phillies, G. D. J. *Zeolites* **1997**, *18*, 119.

(11) Li, Q.; Creaser, D.; Sterte, J. *Microporous Mesoporous Mater.* **1999**, *31*, 141.

(12) Li, Q.; Mihailova, B.; Creaser, D.; Sterte, J. *Microporous Mesoporous Mater.* **2000**, *40*, 53.

(13) Li, Q.; Mihailova, B.; Creaser, D.; Sterte, J. *Microporous Mesoporous Mater.* **2001**, *43*, 51.

(14) Li, Q.; Creaser, D.; Sterte, J. Presented at the 13th International Zeolite Conference (13IZC), Montpellier, France, July 8−13, 2001; Paper 02-O-03.

(15) Lassinantti, M.; Hedlund, J.; Sterte, J. *Microporous Mesoporous Mater.* **2000**, *38*, 25.

(16) Valtchev, V.; Schoeman, B. J.; Hedlund, J.; Mintova, S.; Sterte, J. *Zeolites* **1996**, *17*, 408.

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and the influence of the growth-limiting nutrient (Na^+) on the crystallization of zeolite Y was investigated. Clear solution syntheses were used in this study.

Experimental Section

Zeolite Y synthesis was accomplished using clear solutions with the molar composition of 2.46 $(TMA)_2O$:0.032 Na_2O:1.0 Al_2O_3:3.40 SiO_2:370 H_2O:13.6 EtOH. Two solutions (A and B) were prepared for the formation of the precursors. Solution A was obtained by dissolving sodium hydroxide and one-half of the tetramethylammonium hydroxide (TMAOH) in distilled water and then adding aluminum isopropylate (alumina source) to the alkali solution. Solution B was prepared by adding tetraethyl orthosilicate (TEOS, silica source) to the remainder of the TMAOH solution. Solutions A and B were mixed after they were filtered through a 0.2-μm disposable filter membrane. The mixture was agitated on a gyratory shaker for 24 h to ensure that the clear homogeneous solution was free of gel particles, and then the solution was sealed in PTFE-lined stainless steel autoclaves and maintained at a fixed temperature (100 or 130 °C) without agitation. This process is referred to as one-stage synthesis. During the crystallization, the autoclaves were removed from the oven at various times and cooled to room temperature so that the progress of the synthesis of zeolite Y could be investigated. In some cases, the autoclave was rapidly transferred from an oven at 100 °C to another preheated to 130 °C during the crystallization. This process is referred to as two-stage varying-temperature synthesis.[11]

In the experiments concerning the effect of the growth-limiting nutrient (Na^+) on the crystallization of zeolite Y with the above molar composition, an appropriate amount of 1.0 M NaOH solution was added at varying times during the crystallization to obtain a final Na_2O/Al_2O_3 ratio of 0.43. When the ratio of 0.43 was used at the beginning of a synthesis, it favored the crystallization of zeolite A.[17] This process is referred to as midsynthesis addition of sodium.[14]

The particle size distribution (PSD) was measured by dynamic light scattering (DLS) and confirmed by scanning electron microscopy (SEM) (Philips XL 30). X-ray diffraction (XRD) analysis was performed on extracted powder samples before and after calcination to determine the crystal phase and crystallinity. Detailed information on the equipment and the measurement procedures was reported earlier.[11,12] The silicon and aluminum contents in zeolite Y were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

The zeolite Y yield was determined gravimetrically from the sum of the SiO_2 and Al_2O_3 contents in the final products. The crystallization time was the duration from the initial to the completed crystal growth in the solution (the average crystal size became constant when the crystal growth was completed). The crystal number concentration was estimated on the basis of the yield, average crystal size, and density of zeolite Y by assuming the particles to be spherical.[11] The PSD of the product was represented by a coefficient of variation (CV), the standard deviation (s) relative to the mean particle diameter ($\bar{x}$), given by CV = $s/\bar{x} \times 100\%$.

Results and Discussion

Determination of the Nucleation Period of Zeolite Y. For comparison with the results of two-stage syntheses, one-stage syntheses of zeolite Y at a constant temperature were performed. Figure 1 shows the particle size monitored by DLS during the course of a one-stage synthesis at 100 °C. Only particles in the size range of 30−40 nm were observed before hydrothermal treatment and during the first 3 days of hydrothermal treatment. Two possibilities were considered about the nature of these particles. One is that these particles were formed rapidly after solutions A and B were mixed, and the other is that they had already been present in one of the components. To test these possibilities, both solutions A and B were analyzed with DLS. The silicate solution (solution A) contained small particles with a size of 5 nm, which was consistent with previous observations from the early stages of TPA−silicalite-1 synthesis,[11] and no particles were detected in solution B. Therefore, the 30−40 nm particles were likely amorphous aluminosilicate particles formed after the two solutions were mixed. Similar observations were reported by Mintova et al.[18] These particles were present in the solution before and during the first 4 days of hydrothermal treatment and appeared to slowly decrease to 20 nm before the detection of a second larger particle population after 4 days. This particle population increased in size almost linearly during the crystallization until reaching a size of 75 nm after 7 days. Thus, these particles were regarded as the growing crystals of zeolite Y. A SEM image of the final product confirmed the final crystal size from the DLS measurements, as shown in Figure 2a. XRD analysis showed that the final product is pure zeolite Y with a high crystallinity. The chemical analysis indicated that the ratio of Si/Al in the product was 1.89. The same general features were observed for experiments at 130 °C, as shown in Figure 2b. Table 1 lists the final crystal size, zeolite yield, crystallization time, and crystal concentration for one-stage syntheses at two temperatures. As expected, a higher temperature produced larger crystals with a higher yield after a shorter reaction time and with a lower crystal concentration. Thus, at 130 °C, the size of the final crystals was increased to 137 nm with a yield of 11%. Meanwhile, the duration for the crystallization was reduced to 3 days and about one-quarter of the crystal concentration was obtained at 130 °C, compared to the amount obtained at 100 °C.

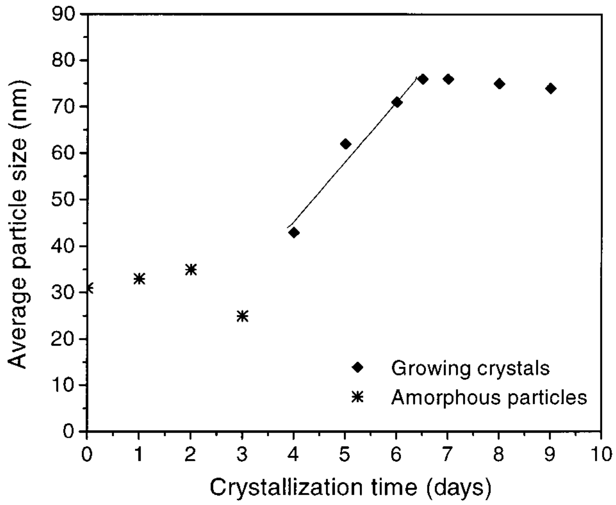

Figure 1. Crystal size as a function of crystallization time for zeolite Y at 100 °C with the molar composition of 2.46 $(TMA)_2O$:0.032 Na_2O:1.0 Al_2O_3:3.40 SiO_2:370 H_2O:13.6 EtOH.

Two-stage varying-temperature syntheses, which involved starting a crystallization at 100 °C and rapidly

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(17) Schoeman, B. J.; Sterte, J.; Otterstedt, J.-E. *Zeolites* **1994**, *14*, 110.

(18) Mintova, S.; Olson, N. H.; Valtchev, V.; Bein, T. *Science* **1999**, *283*, 958.

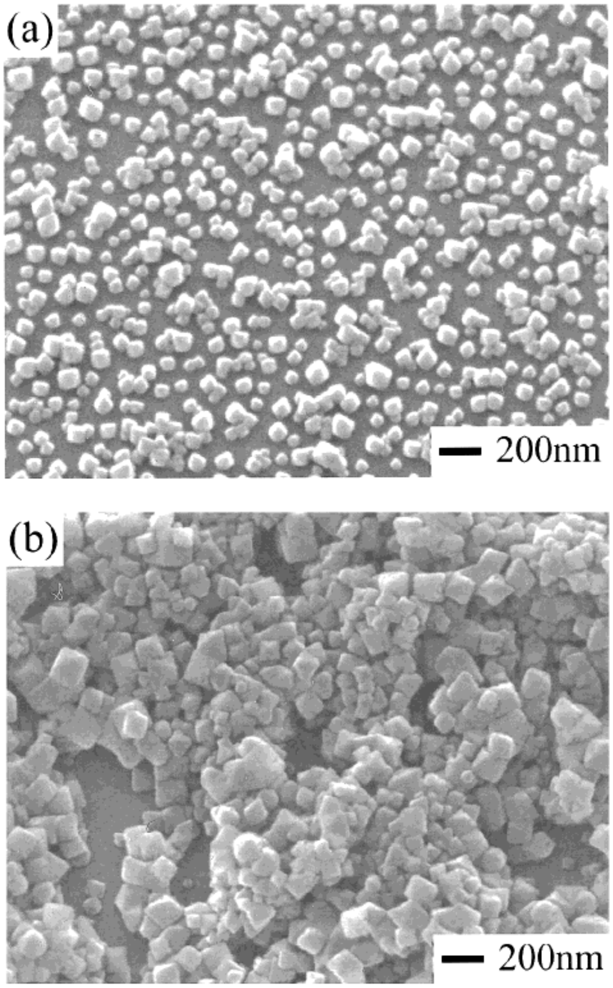

Figure 2. SEM images of final product of zeolite Y at different treatment temperatures: (a) 100 °C, (b) 130 °C.

Table 1. Final Crystal Size, Yield, Crystallization Time, and Crystal Concentration of Zeolite Y for One-Stage Syntheses at Two Temperatures

synthesis temp (°C)	crystal size (nm)	zeolite yield (%)	cryst time (days)	cryst conc [number (g of sol)$^{-1}$ × 10^{13}]
100	75	8.1	7	0.47
130	137	11.0	3	0.11

increasing the temperature to 130 °C to halt further nucleation, were used to determine the nucleation period for zeolite Y at 100 °C. Figure 3 shows the final crystal size versus the duration of the first stage at 100 °C. When the duration of the first stage was 2 days or less, the final crystal size was about the same as that for a one-stage crystallization at 130 °C. As the duration of the first stage was increased, the final crystal size decreased until it was approximately equal to that for a one-stage synthesis at 100 °C.

Table 2 lists the final yield and crystallization time for two-stage syntheses. In all cases, for two-stage syntheses, the zeolite yield obtained was almost constant, ranging from 9.4 to 10.3%, which was closer to the value obtained for a one-stage synthesis at 130 °C. Thus, the zeolite yield was likely controlled by the thermodynamic equilibrium at the final synthesis temperature.

Because the reaction temperature strongly affects the nucleation process, the number of crystals nucleated in the final products, which is influenced by the temperature variation, can be used as a means to determine when the nucleation is completed.[11,12] Figure 4 shows the crystal concentration, calculated from the yield and the final crystal size for two-stage syntheses, as a function of the duration of the first stage. The nucleation process was considered to continue until the crystal concentration was constant and independent of when

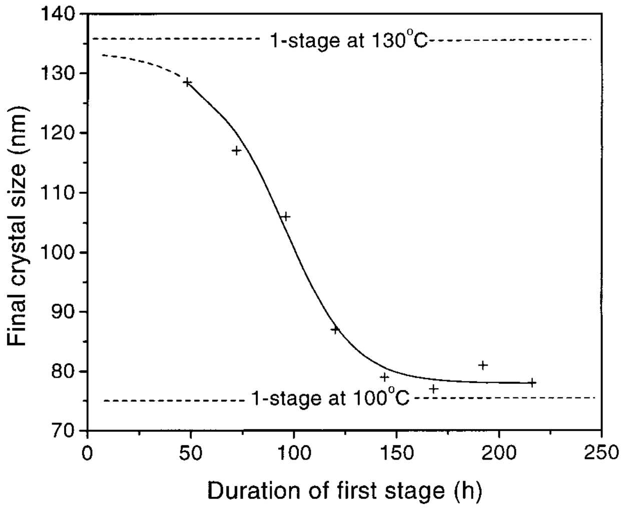

Figure 3. Final crystal size of zeolite Y after two-stage synthesis with the first stage at 100 °C and the second at 130 °C. (Note that the horizontal lines represent the final crystal sizes for one-stage syntheses at 100 and 130 °C, where the durations of first stage are infinity and zero, respectively.)

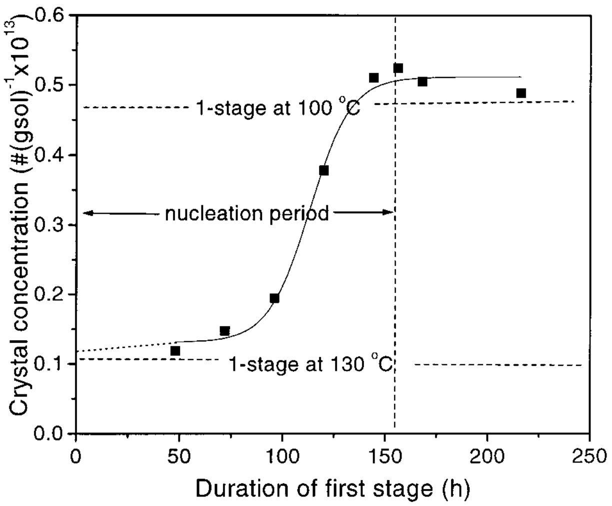

Figure 4. Crystal concentration of zeolite Y after two-stage syntheses.

Table 2. Yield of Zeolite Y and Crystallization Time for Two-Stage Syntheses with the First Stage at 100 °C and the Second Stage at 130 °C

duration of first stage (days)	yield (%)	total synthesis time (days)
0[a]	11.0	3
2	9.4	4.5
3	9.6	5
4	9.4	5.5
5	10.1	6
6	10.2	7
7	9.7	7.5
8	10.3	8.5
9	9.6	9.5

[a] One-stage synthesis at 130 °C.

variations in the treatment temperature were made. It was found that the crystal concentration gradually increased with increasing duration of the first-stage treatment until it was approximately equal to that obtained for a complete synthesis at the initial temperature of 100 °C, i.e., 0.5×10^{13} (g of sol)$^{-1}$. When the duration of the first stage was extended to about 6.5 days, the second treatment at 130 °C did not reduce the crystal concentration, i.e., it hindered further nucleation. Therefore, this time span (6.5 days) represented the nucleation period for zeolite Y at 100 °C. It was shown that the total crystallization time at 100 °C was 7 days, which indicated that the nucleation period extended over almost the whole period of crystal growth (by comparison of Figure 1 and Table 1).

Comparison of the Nucleation and Crystallization of Zeolite Y and TPA−Silicalite-1. The curve in Figure 5a calculated from the derivative of the curve in Figure 4 gives the nucleation profile of zeolite Y during the course of crystallization at 100 °C. The scatter plot and linear curve show the rate of crystal growth. The nucleation profile shows that the rate of nucleation during the first 2 days of crystallization was rather low, suggesting that few crystals were nucleated during this period. In Figure 4, however, the number of the crystals nucleated during the first 2 days was the same as that for a one-stage synthesis at 130 °C, i.e., 0.11×10^{13} (g of sol)$^{-1}$. This indicates that the temperature increase early in the nucleation period did not halt nucleation but allowed the continuation of nucleation at 130 °C until the number of crystals nucleated approached that for the crystallization entirely at 130 °C.[12] This most likely occurred because, after the temperature increase, a higher aluminosilicate concentration in the solution was formed by the dissolution of amorphous particles, which was above a supersaturation value for the nucleation even at a higher temperature. However, after 2 days of crystallization, a rapid increase in the nucleation rate occurred. As a result, much of the amorphous phase was probably consumed, which might have been reflected by the decrease in size of the amorphous particles observed after 2 days.

The induction time, which was estimated by extrapolating the linear part of the crystal growth curve to the crystallization time axis, was found to be less than 1 day for the synthesis of zeolite Y. This time period was significantly shorter than the nucleation period of 6.5 days, and thus, most of the nucleation occurred just after this period.

Figure 5b and c compares the nucleation profiles and crystal growth curves for TPA−silicalite-1 at 60 °C with different silica sources. A molar composition of 9 TPAOH: 25 SiO_2:0.13 Na_2O:595 H_2O:100 EtOH was used for the synthesis solutions. These nucleation profiles were also determined for two-stage varying-temperature experiments.[12] The nucleation with the TEOS silica source in Figure 5b occurred as a burst early in the crystallization and declined throughout the induction period. This almost "instantaneous" nucleation event was followed by a separate growth phase during which the particles grew linearly by consuming active solute from solution. With the Ludox TM silica source (an amorphous silica with a particle size of 30 nm), the nucleation profile consisted initially of a self-accelerating nucleation rate, which was similar to that for zeolite Y. However, the majority of the nucleation again occurred during an induction period when no measurable growth of crystals occurred.

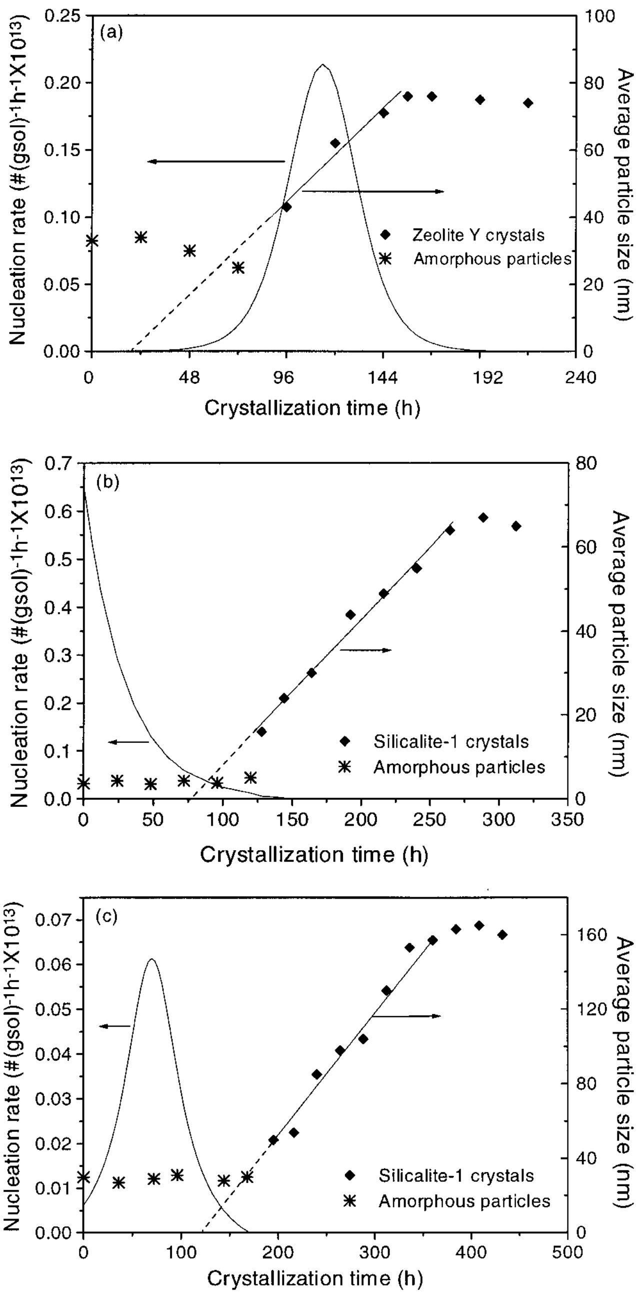

Figure 5. Crystal growth curves and nucleation profiles of various zeolites from two-stage varying-temperature experiments: (a) zeolite Y crystallized at 100 °C, (b) TPA−silicalite-1 crystallized at 60 °C with a TEOS silica source, (c) TPA−silicalite-1 crystallized at 60 °C with a Ludox TM silica source.

The most significant difference between the crystallization kinetics of colloidal TPA−silicalite-1 and zeolite Y was whether the nucleation and crystal growth occurred simultaneously. For the synthesis of TPA−silicalite-1, it has been widely observed that small subcolloidal particles are present throughout the crystallization.[11] However, according to classical crystallization theory, the nucleation must lead to a lower soluble silicate concentration that is below the supersaturation level for nucleation but high enough for crystal growth. On the other hand, for the synthesis of

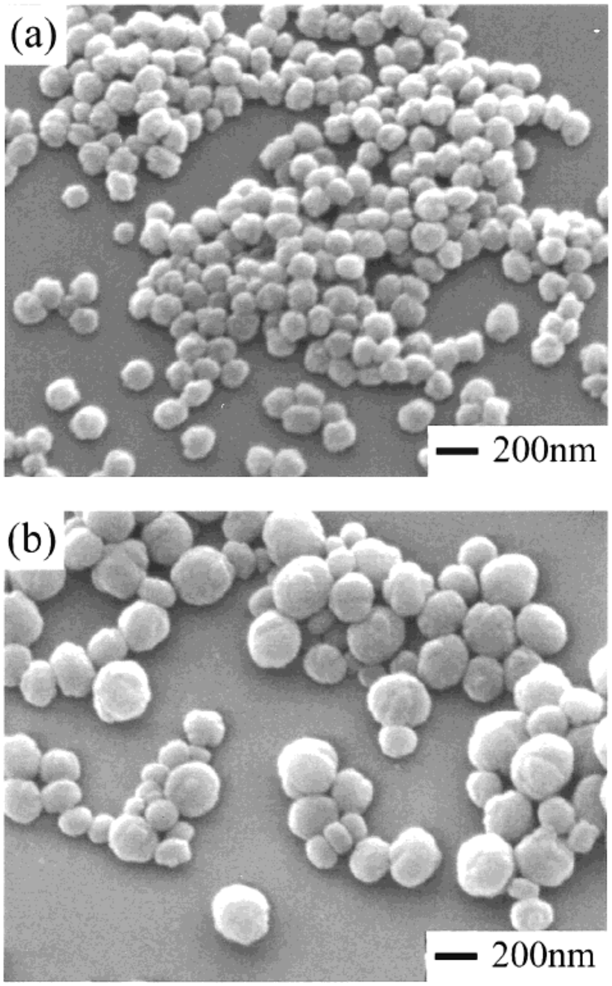

Figure 6. SEM images of the final products of TPA−silicalite-1 synthesized at 100 °C with (a) TEOS and (b) Ludox TM as the silica source.

Table 3. Average Crystal Size and Coefficient of Variation (CV) for Zeolite Y and TPA−Silicalite-1 Obtained from Two Silica Sources at 100 °C

zeolite type	silica source	final crystal size (nm)	CV (%)
TPA−silicalite-1	TEOS	101	9.97
TPA−silicalite-1	Ludox TM	290	11.71
zeolite Y	TEOS	75	10.89

colloidal zeolite Y, the dissolution of the larger aluminosilicate aggregates might be sufficiently fast to maintain an aluminosilicate concentration that is above the supersaturation level throughout much of the crystallization.

Table 3 shows the average crystal size and the coefficient of variation (CV) obtained for TPA−silicalite-1 and zeolite Y. As previously reported,[12] for the synthesis of TPA−silicalite-1, the use of amorphous silica gives rise to larger crystals with a broader PSD. SEM images of final products of TPA−silicalite-1 with various silica sources at 100 °C confirmed the results from Table 3, as shown in Figure 6a and b. Despite the fact that nucleation and crystal growth occurred simultaneously for zeolite Y, the PSD was still rather narrow with a CV of 10.89%, which is comparable to that for the TPA−silicalite-1 products. This is probably due to a low rate of crystal growth compared to the nucleation rate during the crystallization of colloidal zeolite Y.

Table 4. Effect of the Amount and Rate of Midsynthesis Addition of 1.0 M NaOH after the Nucleation Period of Zeolite Y (6.5 days) on the Product Distribution and Zeolite Yield[a]

number of equal portions of NaOH added	frequency of NaOH addition (h)	product distribution (%)		yield (%)
		Y	A	
1	–	9	91	53.0
4	4	48	52	55.1
6	8	72	28	55.0
8	4	80	20	53.9
8	6	87	13	54.2
8	8	100	0	54.4

[a] In all cases, the Na_2O/Al_2O_3 ratio of the synthesis solution was increased from 0.03 to 0.43 after all of the NaOH solution was added.

It is well accepted that, for the crystallization of zeolites from gel systems that typically result in products with large PSDs, the nucleation and crystal growth processes occur simultaneously.[6,19,20] An important finding here is that, even for syntheses from clear solutions yielding colloidal zeolites with relatively narrow PSDs, crystal growth and nucleation can occur simultanesouly. Thus, our earlier findings for the colloidal TPA−silicate-1 system with separate nucleation and crystal growth events might be the exception and not the rule for colloidal zeolites.

Effect of Sodium on the Formation of Zeolite Y. It is known that the crystallizations of faujasite zeolites and related zeolite A and zeolite P are very sensitive to factors such as the alkali concentration, Si/Al ratio, aging time, and hydrothermal treatment.[21,22] In some cases, a small variation in one of these factors results in the formation of a different crystal phase. It has been found[17] that, for the synthesis of zeolites with the molar composition of 2.46 $(TMA)_2O$:x Na_2O:1.0 Al_2O_3:3.40 SiO_2:370 H_2O:13.6 EtOH ($0.03 < x < 0.43$) from clear solution, the sodium concentration of the batch is crucial for controlling which zeolite phase crystallizes. A larger Na_2O/Al_2O_3 ratio (0.43) in the batch favors the formation of zeolite A with a higher yield of 56.5% after a shorter crystallization time. A lower Na_2O/Al_2O_3 ratio (0.03) in the batch produces smaller zeolite Y crystals with a lower yield of 8.1% after a longer crystallization time. It was also found that sodium was the growth-limiting nutrient in the formation of zeolite Y. Midsynthesis addition of sodium allowed for a considerable increase in zeolite yield, with zeolites Y and A as the final product.

We have previously reported that, if sodium is added before the completion of the nucleation of zeolite Y, no single-crystalline phase can be obtained even if the amount and rate of midsynthesis addition of sodium are rather low.[14] If the NaOH solution is added after the nucleation is completed, then the zeolite phase crystallized is strongly dependent on the sodium concentration in the synthesis mixture. Table 4 lists the effect of the amount and rate of midsynthesis addition of 1.0 M NaOH after the nucleation period of 6.5 days on the

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(19) Cundy, C. S.; Lowe, B. M.; Sinclair, D. M. *J. Cryst. Growth* **1990**, *100*, 189−202.
(20) Myatt, G. J.; Budd, P. M.; Price, C.; Hollway, F.; Carr, S. W. *Zeolites* **1994**, *14*, 190.
(21) Den Ouden, C. J. J.; Thompson, R. W. *J. Colloid Interface Sci.* **1991**, *143*, 77.
(22) Lechert, H.; Kacirek, H. *Zeolites* **1991**, *11*, 720.

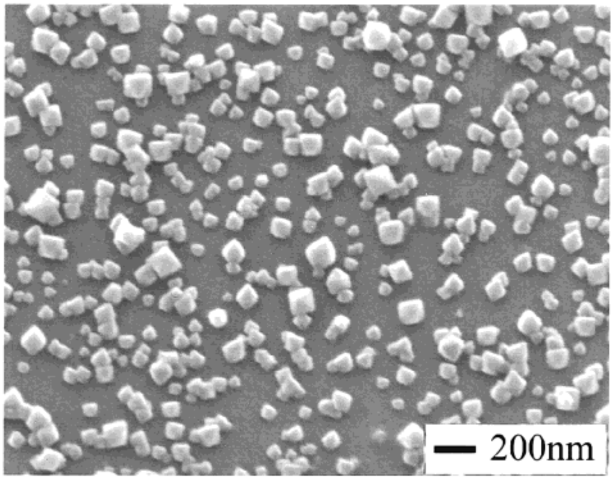

Figure 7. SEM image of final product of zeolite Y obtained with the midsynthesis addition of sodium.

crystalline phase of the final product and on the yield. When the sodium was added as a single portion, a mixture of zeolite Y and A was obtained. Thus, it is apparent that an excessive sodium concentration promotes the nucleation of zeolite A. To control the sodium concentration, the total amount of 1.0 M NaOH solution to be added was divided into several equal portions and added into the synthesis mixture at varying regular intervals (frequency of addition). When the total amount of NaOH was separated into six portions, the final crystalline phase was still a mixture of zeolite Y and A irrespective of the frequency of addition, but the proportion of Y in the mixture increased. When the number of portions of added NaOH were increased to eight, the crystalline phase in the final product was strongly dependent on the addition frequency. For instance, when the addition frequency was 4 or 6 h, a mixture of zeolite Y and A was obtained. XRD analysis showed that the zeolite Y fraction in the mixture increased as the addition frequency was prolonged. When the total amount of NaOH solution was added as eight equal portions with an 8-h period, a pure zeolite Y crystalline phase was detected by XRD. Figure 7 shows the SEM image of this product. Pure zeolite Y crystals with their typical octahedral shape were the sole crystalline phase in the final product. Therefore, there was a threshold sodium concentration in the synthesis solution, which, if exceeded, allowed for the nucleation of zeolite A. Figure 7 shows that the largest crystal size was about 135 nm and that numerous smaller crystals of 30−70 nm were formed. The PSD of zeolite Y obtained by the midsynthesis addition of sodium was broader than that obtained without sodium addition (see Figure 2).

In all cases, the midsynthesis addition of NaOH produced a constant yield of product, approximately 55%, which was almost the same as that of zeolite A obtained from a larger Na_2O/Al_2O_3 ratio (0.43), as shown in Table 4. This indicates that, for the midsynthesis addition of sodium, the yield of final product is determined by the total amount of limiting reagent added, namely, sodium. A significant finding for the midsynthesis addition of sodium was that, by controlling the amount and rate of the midsynthesis addition of sodium, pure zeolite Y with a slightly increased crystal size and a more than 6-fold increase in yield could be obtained. The number of zeolite Y crystals obtained from the midsynthesis addition of sodium was calculated on the basis of the yield and final crystal size. The crystal concentration was more than twice that obtained without sodium addition. The increased crystal concentration with the corresponding larger average crystal size indicates that the addition of sodium after the nucleation of zeolite Y can both promote the growth of the existing zeolite Y crystals and cause the secondary nucleation of new zeolite Y crystals.[14]

Conclusions

A two-stage varying-temperature synthesis procedure was performed to determine the nucleation profile of colloidal zeolite Y from clear solutions. At 100 °C, nucleation was completed within 6.5 days and occurred throughout the process of crystal growth. Because the crystal concentration during the first 2 days of crystallization determined from two-stage syntheses was the same as that for a one-stage synthesis at an elevated temperature of 130 °C, the nucleation rate was underestimated during the early part of the nucleation period.

The two-stage varying-temperature method was also used to compare the kinetics of the nucleation/crystallization kinetics for different colloidal zeolite systems. For the synthesis of TPA−silicalite-1, regardless of the silica source, the nucleation event occurred during the early stages of crystallization and was followed by a separate growth phase during which the crystals grew linearly. However, for the synthesis of colloidal zeolite Y, the nucleation and crystallization occurred simultaneously. The PSD of colloidal zeolite Y was still rather narrow and comparable to that for colloidal TPA−silicalite-1 despite the simultaneous growth and nucleation, probably because of a slow rate of crystal growth. It can be concluded that a separation of the nucleation and growth processes for the synthesis of colloidal zeolites from clear solutions is not true in all cases.

An appropriate amount of 1.0 M NaOH solution was added at varying times during the process of crystallization to obtain a final Na_2O/Al_2O_3 ratio of 0.43, which normally favored the formation of zeolite A in high yield. The midsynthesis addition of sodium caused the formation of a mixture of zeolites Y and A before the nucleation period of 6.5 days, independent of the amount and rate of addition of sodium. However, after the nucleation period, pure zeolite Y as the sole crystalline phase could be obtained with a sufficiently low rate of sodium addition. The sodium concentration in the synthesis solution could be maintained below a critical level to avoid zeolite A nucleation during the crystallization of zeolite Y.

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