High yield method for nanocrystalline zeolite synthesis

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Nanocrystalline zeolites, such as silicalite-1 and zeolite Y, were synthesized in high yield by periodically removing nanocrystals from the synthesis solution and recycling the unused reagents, including the template and T-atom sources.

Zeolites have well-defined, crystalline structures with pores that are in the molecular size range.[1] Zeolites also have ion exchangeable sites and high hydrothermal stability. These properties enable zeolites to be widely used as catalysts in petrochemical processing. Nanocrystalline zeolites (with crystal sizes of 100 nm or less) may have advantages over conventional micron sized zeolites in that they have larger external surface areas, shorter diffusion path-lengths and lower tendencies to form coke.[2,3] The improved properties of nanocrystalline zeolites may lead to new applications for these materials in catalysis,[2] environmental protection[4] and chemical sensing.[5] Pure silica nanocrystalline zeolites are promising low-dielectric constant materials for electronics applications.[6] Composite polymer zeolite nanocomposite membranes may be useful in air separation.[7]

Several methods have been reported in the literature for the synthesis of nanocrystalline zeolites.[4,8–14] The core concept of all these methods is to terminate the synthesis process while the zeolite crystals are still in the nanometer size range, thus prohibiting further crystal growth. Using these methods, nanocrystalline zeolites are synthesized at low temperature and ambient pressure which leads to low product yields and long synthesis times. Low synthesis temperature results in slow nucleation and crystal growth, and thus prolonged synthesis time. Typical product yields for nanocrystalline zeolites reported in the literature are less than 10% based on the synthesis gel composition, as compared to nearly 100% yields for conventional micron-sized zeolites. After the synthesis is complete, nanocrystalline zeolites are present in colloidal suspensions and powder products are recovered by centrifugation. The remaining synthesis solution is usually discarded after the nanocrystalline zeolites are recovered resulting in the disposal of valuable chemical materials and adverse environmental effects. Recycling unused chemicals after zeolite synthesis has been reported for micron-sized zeolite synthesis.[15–18]

In this communication, we report the synthesis of nanocrystalline zeolites in high yield by periodically removing nanocrystals from the synthesis solution and reusing the synthesis solution. The rationale to reuse the clear solution is two-fold. First, since the yield of nanocrystalline zeolite product is very low, only a small portion of nutrients in the synthesis solution is consumed and the clear solution composition is very close to the original synthesis solution composition. In addition, since only zeolite crystals that are heavy enough are recovered by centrifugation, it is fair to assume that very small zeolite crystals (10 nm or less) are still present in the clear solution. These small crystals can serve as nucleation sites and can directly grow into larger crystals, eliminating the long nucleation and growth time originally required.

Silicalite-1 and zeolite Y were chosen for this study because the synthesis methods have been well developed in our laboratory.[4,10] The original synthesis gel composition for silicalite-1 is: 9 TPAOH : 0.16 NaOH : 25 Si : 495 H_2O : 100 EtOH where TPAOH is tetrapropylammonium hydroxide, tetraethylorthosilicate (TEOS) is the silicon source and ethanol (EtOH) is the hydrolysis product of TEOS. The synthesis gel was heated to 60 °C in a glass flask for 240 h for the first round of synthesis, and 72 h for subsequent batches. The original synthesis gel composition for zeolite Y was: 0.07 Na : 2.4 TMAOH : 1.0 Al : 2.0 Si : 132 H_2O : 3.0 *i*-PrOH : 8.0 EtOH where TMAOH is tetramethylammonium hydroxide, and aluminium isopropoxide and TEOS were used as aluminium and silicon sources, respectively, with *i*-PrOH and EtOH as their respective hydrolysis products. The synthesis solution for zeolite Y was heated to 90 °C in a glass flask containing a magnetic stirrer for 144 h for the first batch, and 48 h for later batches. After each batch, the zeolite crystals were recovered by centrifugation at 14 000 rpm for 30 min. After washing and drying, X-ray powder patterns and BET surface areas of the powders were measured to determine crystal structures and crystal sizes.

After centrifugation, the remaining clear solutions were returned to the glass flask for the next synthesis batch. For silicalite-1, only clear solution was returned to the flask; while for zeolite Y, the same amount of NaOH as in the original synthesis gel was added to the clear solution before it was returned to the flask for the next synthesis batch. The synthesis processes for silicalite-1 and zeolite Y can be monitored visually. The clear synthesis solution gradually becomes cloudier and cloudier during the synthesis process. With fresh synthesis solution, it takes approximately 10 days to produce enough nanocrystalline silicalite-1 to produce the desired cloudiness of the solution, while with recycled synthesis solution, the time was considerably shorter ($\sim$48 h).

Figs. 1 and 2 depict the XRD powder patterns of silicalite-1 and zeolite Y, respectively, obtained from multiple rounds of zeolite synthesis in which the clear solution recovered after removal of zeolite nanocrystals was reused. Each XRD pattern is consistent with the silicalite-1 or Y zeolite structure, respectively. The intensities and line widths of the XRD peaks are similar to each other for each zeolite, suggesting that the different batches of the same zeolite have similar crystal sizes.

The BET surface areas (of as-synthesized samples) and the Si/Al ratios (for Y zeolites) were measured and are listed in Table 1 along with the cumulative nanocrystalline zeolite yields for each

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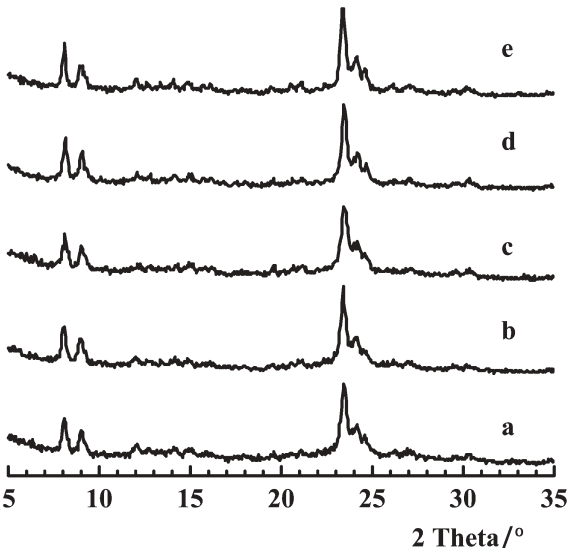

Fig. 1 XRD patterns of five consecutive batches of silicalite-1 crystals synthesized from the same synthesis solution. (a) First batch; (b) second batch; (c) third batch; (d) fourth batch; and (e) fifth batch.

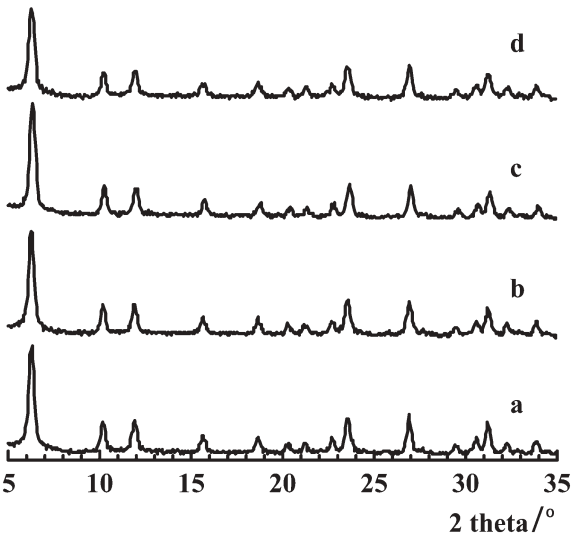

Fig. 2 Selected XRD patterns of four batches of Y zeolite nanocrystals synthesized from the same synthesis solution. (a) First batch; (b) fourth batch; (c) seventh batch; and (d) tenth batch.

Table 1 BET surface areas, Si/Al, crystal sizes, and product yields of as-synthesized nanocrystalline silicalite-1 and Y zeolites

Sample	Batch	Si/Al	Surface area/m^2 g^{-1a}	Crystal size[b]/nm	Product yield[c] (%)
Silicalite-1	1	NA[d]	165	20	6.8
Silicalite-1	2	NA	158	20	13.6
Silicalite-1	3	NA	160	20	22.4
Silicalite-1	4	NA	148	22	32.5
Silicalite-1	5	NA	126	26	41.8
NaY	1	1.87	168	26	4.0
NaY	4	1.74	141	31	15.8
NaY	7	1.80	217	20	28.8
NaY	10	1.83	178	25	43.3

[a] External surface area of as-synthesized sample. [b] Crystal size calculated from external surface area as described in reference 10. [c] Cumulative product yield. [d] Not applicable.

batch. The zeolite yield was calculated from the initial synthesis solution composition and the mass of the zeolite nanocrystals recovered for each batch. The BET surface area for the as-synthesized zeolite samples which have template still present in the pores represents the external surface area of the nanocrystalline zeolites. The zeolite crystal size can be estimated from the external surface area as described previously[10] and the results are listed in Table 1. Scanning electron microscope (SEM) images were also used to confirm the crystal size and representative images are shown in Fig. 3.

For silicalite-1, all five batches of synthesis produced roughly the same amount of silicalite-1 crystals with crystal sizes ranging from 20 to 26 nm. A representative SEM image of the fifth batch of silicalite nanocrystals is shown in Fig. 3a. The crystal size of approximately 20 nm is close to the crystal size of 26 nm estimated from the external surface area. After five batches, the total product yield was 42% and the total time elapsed was 22 days. The attempt for the sixth round failed to produce a colloidal suspension of nanocrystals.

For NaY, the total product yield was 43% after 10 batches and the time elapsed was 24 days. The Si/Al ratio remained approximately constant at 1.8 for each batch and the crystal size ranged from 20 to 31 nm for the 10 batches. A representative SEM image of the seventh batch of zeolite Y is shown in Fig. 3b and the crystal size of $\sim$20 nm observed in the SEM image is also consistent with the crystal size of 20 nm estimated from the external surface area. The yield from each round was less than 6%, which appears to be limited by the sodium content in the synthesis gel (7% relative to Al content).

In summary, by repeatedly reusing the clear synthesis solutions after periodically removing zeolite nanocrystals, significantly higher product yields (6 and 10 fold increases) were achieved for nanocrystalline silicalite-1 and Y zeolites, respectively. The crystal sizes of zeolites synthesized using recycled synthesis materials are uniform and the Si/Al ratios of the different batches of Y zeolites are constant. Using this method, high quality, monodisperse, nanocrystalline zeolites such as silicalite-1 and zeolite Y can be synthesized more rapidly and more efficiently. From an environmental perspective, this process is extremely beneficial because the amount of waste produced is minimized by the reuse of starting products.

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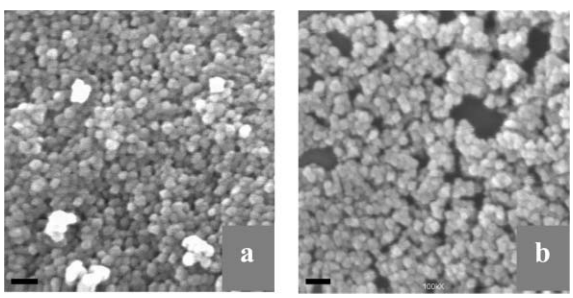

Fig. 3 Two representative SEM images of Silicalite-1 and zeolite Y nanocrystals. (a) Fifth batch silicalite-1; (b) seventh batch zeolite Y. The crystal sizes in each image are approximately 20 nm, consistent with the size estimated from the BET external surface area. Scale bars are 100 nm.

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