Synthesis of TBA–Silicalite-2 Zeolite Nanocrystals

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Siliceous MEL-type (silicalite-2) zeolite nanocrystals with average particle size of less than 100 nm were hydrothermally synthesized in a reactant system of TBAOH–TEOS–H_2O. Investigation by using XRD, SEM, ^{13}C and ^{29}Si MAS NMR, FT-IR and N_2 adsorption shows that the nanocrystals are aggregates of primary particles free of intergrowth with MFI (silicalite-1) zeolite, and possess ~ 34% silanol groups in the framework as well as ~0.9 $mL·g^{-1}$ of mesopore volume. Silicalite-2 nanocrystals exhibit the particular structural characteristics: vibration at 550 cm^{-1} in IR spectrum splits; the signal of methyl group of TBAOH in ^{13}C MAS CP NMR spectrum appears as singlet, which is different from that of silicalite-2 single crystals.

Zeolites are crystalline aluminosilicalites with uniform pore dimension and high thermal stability and internal surface area. Many researches have been focused on the preparation of large single crystals of zeolite suitable for X-ray diffraction determination of structure over the past years. In recent years, there are growing interests in the synthesis of nano-sized zeolite[1–5] due to the potential application in catalysis, membrane science,[6–8] in which zeolite silicalite-1 received considerable attention. Zeolite silicalite-2 with MEL topology is structurally related to zeolite silicalite-1 (MFI type).[9] Both zeolites belong to the members of pentasil family, which are useful catalysts in petrochemical industry. Metal containing MEL zeolites such as Zn-ZSM-11, Mo-ZSM-11, Ti-ZSM-11, V-ZSM-11 and H-ZSM-11 reveal the valuable catalytic properties. On the other hand, MEL zeolite possesses medium pore size like MFI zeolite fit for the separation of hydrocarbons. Here, we presented the synthesis and characteristics of nano-sized silicalite-2 zeolite. At first this work laid a foundation for the further synthesis of nano-sized MEL zeolite catalysts and more importantly, we hope that some information can be obtained by comparing silicalite-2 with silicalite-1 in nanoscale range, which were often done in micro-sized crystals.[10] Finally from the viewpoint of application, MEL zeolite film, another hydrophobic inorganic film, can be easily prepared by using silicalite-2 nanosols, which have got preliminary results in our laboratory at present.

This paper explored a well-controlled way for preparation of the nano-sized silicalite-2 zeolite in the reactant system of TBAOH–TEOS–H_2O. The syntheses were carried out in the temperature range of 100–170 °C in the reactant with a molar composition of (0.15–0.50)TBAOH : 1TEOS : (10–25)H_2O. TBA–silicalite-2 zeolite crystals of 60 to 90 nm were prepared in the reactant with an optimum molar composition of TBAOH/TEOS = 0.35 and H_2O/TEOS = 12. The typical procedure of the synthesis is as follows: 8.22 g tetraethylorthosilicalite (TEOS, > 98%, Shanghai Baihe Chemical Factory) was added to 8.93 g tetrabutylammonium hydroxide (TBAOH, 40% solution, Aldrich Chemical Company) under vigorous stirring, then 2.91 g distilled water was added. The mixture was stirred for 24 h at room temperature until a clear solution was formed. The solution was then heated in an autoclave lined with PTFE at 114 °C for 6 days. The as-synthesized products were separated from the mother liquor by centrifugation at 15000 rpm, and washed with distilled water until the pH of the filtrate became less than 8. The samples were then freeze-dried. All samples prepared in various synthetic conditions are pure TBA–silicalite-2 zeolite identified by XRD.

The XRD patterns of the as-synthesized samples show that only a sharp single diffraction pattern is present at $2\theta \approx 45.2°$, while the peaks at $2\theta = 9.05°$ and 24.4° (the characteristic diffraction of MFI structure) are absent. This fact indicates that the as-synthesized samples are pure MEL phase free of intergrowth with MFI zeolite, in agreement with the previous report on the characteristics of silicalite-2 structure.[11] The diffraction patterns of the samples broaden as a result of the decrease in crystalline size (see Figure 1). The average size of TBA–silicalite-2 zeolite nanocrystals is 11 nm calculated from the peak broadening by Scherrer's equation using Win-Crysize software package (Bruker Analytical X-ray System, a member of the WIN-POWDER team of software packages). However, SEM photograph (see Figure 2) shows that the particle size of the nanocrystals is 60 to 90 nm, implying that the zeolite nanocrystals are agglomerates composed of primary particles of 11 nm.

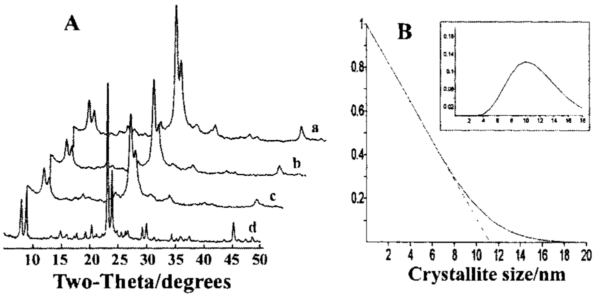

Figure 1. (A) XRD patterns of samples synthesized in the reactant with the molar composition of xTBAOH–TEOS–12H_2O:a, x=0.45; b, x=0.25; c, x=0.35; d, reference sample with size of ~50 µm single crystals. (B) Particle size distribution of TBA–silicalite-2 nanocrystals.

The ^{29}Si MAS NMR of the as-synthesized sample is performed (not shown). Two broad resonance signals are at –113 ppm and –102 ppm, which belong to Q^4[Si(4Si)] and Q^3[Si(3Si,1OH)], respectively. The intensity of the resonance at –102 ppm is about 34% of the total ^{29}Si NMR signals. To the best of our knowledge, the content of silanol groups in this sample is the highest among the so far-reported samples, indicating that the defects of silanol groups greatly increase with reduction of particle size.

The ^{13}C CP MAS NMR spectrum of TBA ion trapped in silicalite-2 zeolite nanocrystals (shown in Figure 3A) exhibits

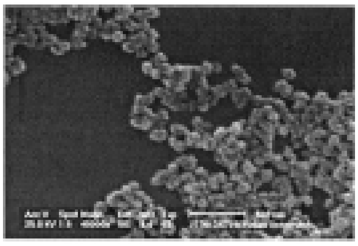

Figure 2. SEM photograph of TBA–silicalite-2 zeolite nanocrystals.

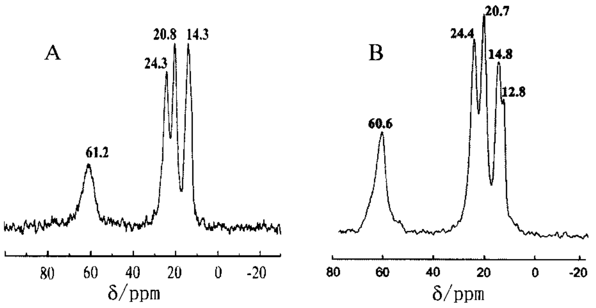

Figure 3. ^{13}C CP MAS NMR spectra of TBA–silicalite-2 nanocrystals(A) and single crystals(B).

four peaks at 61.2 ppm, 24.3 ppm, 20.8 ppm, and 14.3 ppm corresponding to C(1), C(2), C(3), and C(4) in $N^+[C(1)H_2-C(2)H_2-C(3)H_2-C(4)H_3]_4$, respectively. Obviously, the line of methyl group (C4) does not split, while the doublet of C4 signals was observed in micro-sized TBA–silicalite-2 zeolite[12] (shown in Figure 3B), which indicates that C4 groups locate in positions with various chemical environments in the same 10-ring straight channels of silicalite-2 zeolite. The difference in C4 signals suggests a possibility of less ordered arrangement of TBA in nano-sized silicalite-2 zeolite. According to the work of Ravishankar et al.,[13] however, the splitting signals of CH_3 group of TPA in ^{13}C CP MAS NMR spectrum are very similar to each other for both nano-sized and micro-sized crystals of silicalite-1. Thus it is assumed that the splitting of methyl group is related not only to the framework structure but also to the location of the template and decreased crystal size.

The FT-IR spectra (see Figure 4) of as-synthesized nanocrystals and the ~5 μm single crystal TBA–silicalite-2 samples show the typical framework vibration of MEL type zeolite.[14,15] Compared with single crystals (sample c), a peak at 978 cm^{-1} for nanocrystals (sample b) is assigned to silanol groups bonded to Q^3 silicon species, in agreement with the observation by ^{29}Si MAS NMR. It is obvious that the strong vibration of double-ring at 550 cm^{-1} for single crystals shifts to high wavenumbers (ca. 555 cm^{-1}) and splits with the reducing of crystal size, whereas its splitting is not as distinct as nano-sized silicalite-1's (see sample a). As we know, double-ring is a basic building block of pentasil zeolites such as silicalite-1 and silicalite-2. It seems that double-ring vibration is more sensitive to the change of particle size (or to the amount of surface defects) than the other vibration forms. However, it is worth to note that the splitting of the vibration at 550 cm^{-1} is not observed in micro-sized crystals of TBA–silicalite-2 as well as TPA–silicalite-1.

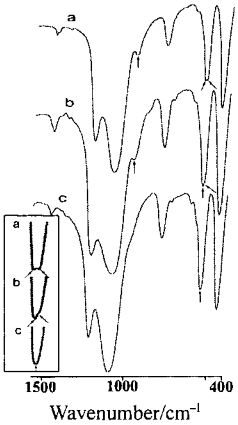

Figure 4. FTIR spectra of: a, TPA–silicalite-1 zeolite nanocrystals; b,TBA–silicalite-2 zeolite nanocrystals; c, silicalite-2 single crystals with size of ~5 μm. The insert is enlargement of sample a, b and c at 550 cm^{-1}.

After calcination at 550 °C for 10 h, the nanocrystals sample of TBA–silicalite-2 zeolite exhibits 376 $m^2\ g^{-1}$ of BET surface area and 0.9 mL g^{-1} of mesopore volume with the major pore size of 25 nm measured by nitrogen adsorption at 77 K with a Micromeritric ASAP 2000 instrument.

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References and Notes

1 A. E. Persson, B.J. Schoeman, J. Sterte, and J. -E. Otterstedt, *Zeolites*, **14**, 557 (1994).

2 G. Zhang, J. Sterte, and B. J. Schoeman, *J. Chem. Soc., Chem. Commun.*, **1995**, 2259.

3 M. A. Camblor, A. Corma, and S. Valencia, *Micropores Mesopores Mater.*, **25**, 59 (1998).

4 G. Zhu, S. Qiu, J. Yu, Y. Sakamoto, F. Xiao, R. Xu, and O. Terasaki, *Chem. Mater.*,**10**, 1483 (1998)

5 M. Tsapatsis, M. Lovallo, T. Okubo, M. E. David, and M. Sadakata, *Chem. Mater.*, **7**, 1734 (1995).

6 S. Mintova, S. Mo, and T. Bein, *Chem. Mater.*, **10**,4030 (1998).

7 J. Hedlund, B. J. Schoeman, and J. Sterte, *Chem. Commun.*, **1997**, 1193.

8 J. Hedlund, B. J. Schoeman, and J. Sterte, *Stud. Surf. Sci. Catal.*, **105**, 2203 (1997).

9 C. A. Fyfe, H. Gies, G. T. Kokotailo, C. Pasztor, H. Strobl, and D. E. Cox, *J. Am. Chem. Soc.*, **111**, 2470 (1989).

10 C. E. A. Kirschhock, R. Ravishankar, L. Van Looveren, P. Jacobs, and J. A. Martens, *J. Phys. Chem. B*, **103**, 4972 (1999).

11 D. M. Bibby, N. B. Milestone, and L. P. Aldridge, *Nature*, **280**, 664 (1979).

12 J. B. Naggy, Z. Gabelica, and E. G. Derouane, *Zeolites*, **3**, 43 (1983).

13 R. Ravishankar, C. Kirschhock, B. J. Schoeman, P. Vanoppen, P. J. Grobet, S. Storch, W. F. Maier, J. A. Martens, F. C. De Schryver, and P. A. Jacobs, *J. Phys. Chem. B* , **102**, 2633 (1998).

14 G. Coudurier, C. Naccache, and J. C. Vedrine, *J. Chem. Soc., Chem. Commun.*, **1982**, 1413.

15 J. C. Jansen, F. J. van der Gaag, and H. van Bekkum, *Zeolites*, **4**, 369 (1984).