Chinese Chemical Letters Vol. 14, No. 12, pp 1299 – 1302, 2003
http://www.imm.ac.cn/journal/ccl.html

Hollow Cancrinite Zeolite Spheres *in situ* Transformed from Fly Ash Cenosphere

De Ju WANG, Yi TANG,* An Gang DONG, Ya Hong ZHANG, Ya Jun WANG

Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University, Shanghai 200433

Abstract: A novel hollow microsphere structure with cancrinite zeolite grown from the shell of fly ash cenosphere has been successfully prepared through *in situ* transformation in vapor phase; the orientation and morphology of cancrinite can be greatly improved by adding tetrapropylammonium hydrate into the synthetic system.

Keywords: Cancrinite, fly ash cenosphere, zeolite, hollow microsphere.

Zeolites are microporous crystalline solids with well-defined structures containing molecular-sized void space[1]. Such structures can be employed as hosts for atoms, molecules or clusters to prepare host-guest materials, which may have applications in advanced materials[2, 3]. Recently, many researchers have paid great attention to prepare zeolites with desired macroscopic shapes to satisfy their effective uses. Hollow zeolite spheres represent a special group of these unique structured materials for their zeolitic shells and have been prepared by several groups[4-8].

Fly ash is a waste of large amount in thermal power plants and poses many environmental problems. Great effort has been made toward finding applications for this kind of waste. As one of the effective utilities, the active silica and alumina constituents in the fly ash could be converted into zeolitic materials[9-11]. Fly ash cenosphere (FAC) with hollow core-shell structure might be a kind of more attractive raw material for the morphology-controlled zeolite synthesis. Here, using the specific hollow structure and the convertible constituents in the shell of FAC, we prepared the hollow microspheres of cancrinite zeolite (CAN) by an *in situ* crystallization process in vapor phase. More interesting, hollow spheres with oriented needle-like CAN crystals perpendicular to the shells were obtained when TPAOH was added to the synthetic system. The oriented CAN crystals with parallel microchannels epitaxial grown from the surfaces of the hollow spheres would be attractive in advanced materials[12, 13].

---

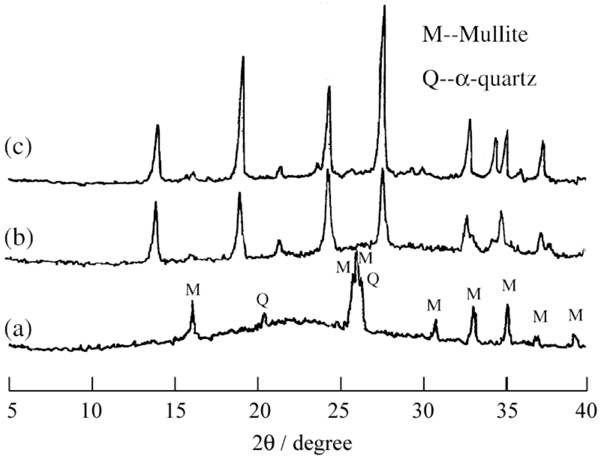
* E-mail: ytang@fudan.ac.cn

Experimental

The FAC used in this work, which was provided by the Research Centre for the Application of Fly Ash in Henan Province of China, has the listed chemical composition of SiO_2, 56.21; Al_2O_3, 29.45; Fe_2O_3, 3.60; CaO, 1.66; MgO, 0.85; K_2O, 0.78; Na_2O, 0.47; TiO_2, 0.52 and ignition loss, 3.51 in weight percentage. The sample was sieved by a 200-mesh sieve and treated by floatation in boiling water to remove the fragments, and then dried.

The preparation of hollow cancrinite zeolite spheres was fulfilled *in situ* through the vapor-phase transport[14] (VPT) treatment of NaOH mixed FAC with or without TPAOH. Typically, 0.2 g of FAC was added into 0.7 g of 14 wt % NaOH aqueous solution, and then dried with stirring to form a solid precursor. The precursor was then placed on a porous stainless steel board that was placed horizontally in the middle of PTFE-lined stainless steel autoclave, and a liquid mixture of 1 mL ethylenediamine, 2 mL triethylamine and 1 mL distilled water was poured into the bottom of the autoclave in advance. Then the sample was crystallized at 190°C for 5 days in the vapor of amine and water. To further improve the morphology and the orientation of CAN, a proper amount of TPAOH was added in the NaOH solution during the precursor formation process.

Figure 1 The XRD patterns

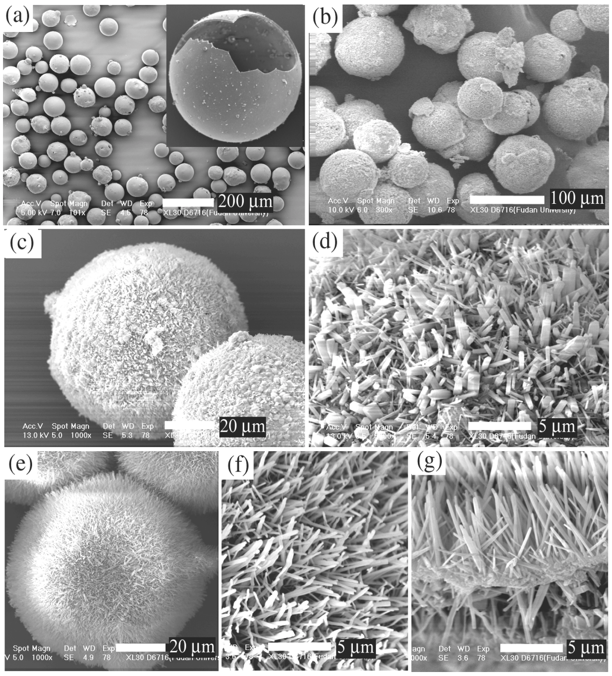


(a) The original FAC, (b) the products prepared without TPAOH and (c) the products prepared with TPAOH.

Results and Discussion

FAC was firstly crystallized without TPAOH addition. The X-ray diffraction (XRD) patterns of the FAC and the products are shown in **Figure 1**. Mullite and α-quartz are the main crystalline phase components in the original FAC besides an amorphous glassy phase [**Figure 1(a)**]. However, after crystallization, only the sharp diffraction peaks of CAN were observed in the XRD patterns of the products **[Figure 1(b)]**, demonstrating that most of the components in fly ashes including the amorphous phase and the crystalline mullite and α-quartz have been effectively converted to CAN after the crystallization. The scanning electron microscopy (SEM) images of the samples before and after crystallization process are shown in **Figure 2**. The original FAC has the spherical morphology with the diameters of 50-80 μm [**Figure 2(a)**], and some broken spheres show their hollow structure [**Figure 2(a)**, inset]. The thickness of the shells is estimated as 2-4 μm from the SEM images at high magnification. After crystallization process, most of the products retained the initial spherical morphology of the FAC [**Figure 2(b)**], but the sphere surface became much rougher [**Figure 2(c)**]. From the high magnification SEM images [**Figure 2(d)**], needle-like crystals with different size can be clearly observed on the shell surface. Combined with the XRD result, they should be attributed to the CAN crystals converted from the nutrient components in the FAC shells. Such characteristic hollow structure with zeolitic shell would find some new possibility in the practical applications$^{4-8}$.

Figure 2 SEM micrographs



(a) The original FAC, (b, c and d) the hollow CAN spheres prepared without TPAOH (e, f and g) the hollow CAN spheres prepared with TPAOH.

Many potential applications of zeolite need the precise control of crystal orientation and morphology. Here, by adding a proper amount of TPAOH in the NaOH solution during the precursor formation, the hollow spheres with oriented CAN crystals were obtained from FAC after the crystallization process in vapor. **Figure 1(c)** is the XRD pattern of the sample transformed from the precursor containing TPAOH at the molar ratio 0.15 of $(TPA)_2O/SiO_2$. Compared with the counterpart without TPAOH, the products prepared with TPAOH show more intensive diffraction peaks of CAN in the XRD pattern [**Figure1(c)**], and the SEM images [**Figure 2(e)-(g)**] show the CAN crystals on the shell possess more uniform morphology and orientation. The needle-like CAN crystals with width of 100-200 nm and length of 3-5 μm grew in the direction almost perpendicular to the shell [**Figure 2(f)** and **(g)**]. These facts indicate that TPAOH has great contribution to the morphology and orientation of CAN on the shell. The remnant shell thickness of cenosphere after treatment is estimated about 500 nm from the SEM image of the cross section of the shell [**Figure 2(g)**], much thinner than that of the original FAC, further confirming that CAN crystals were generated from the "nutrition" in the FAC shell. It is also found from **Figure 2(g)** that CAN crystals grew on both sides of the shell, probably because the alkali species penetrate the shell during the precursor formation or/and crystallization process, which induce the crystallization on the inner side, or the species observed in the **Figure 2(g)** was converted from the original existent fragments of broken FAC particles.

In conclusion, the hollow zeolite microspheres with needle-like CAN crystals have been successfully prepared by treating FAC, a waste of the power plants, through ***in situ*** transformation in vapor phase. The hollow spherical morphology of the FAC is retained and most of the nutrient components in the shell, including α-quartz, mullite and amorphous phase, are effectively converted into CAN. The addition of TPAOH in the precursor can conduce to the formation of characteristic hollow sphere with the shell of oriented needle-like CAN.

Acknowledgments

This work is supported by the NNSFC (Grant No. 20233030，20273016) and the Doctoral fund of Education Ministry.

References

1. D. W. Breck, *Zeolite Molecular Sieves*, Wiley, New York, **1974**.
2. J. Lautanen, V. Kettunen, P. Laakkonen J. Turunen, *J. Am. Chem. Soc.*, **2000**,*122*, 8583.
3. D. Bruhwiler, R. Seifiert, G. Calzaferri, *J. Phys. Chem. B*, **1999**, *103*, 6397.
4. K. H. Rhodes, S. A. Davis, F. Caruso, B. J. Zhang, S. Mann, *Chem. Mater.*, **2000**, *12*, 2832.
5. X. D. Wang, W. L. Yang, Y. Tang, Y. J. Wang, S. K. Fu, Z. Gao, *Chem. Commun.*, **2000**, 2161.
6. V. Valtchev and S. Mintova, *Micropor. Mesopor. Mater.*, **2001**, *43*, 41.
7. V. Valtchev, *Chem. Mater.*, **2002**, *14*, 4371.
8. A. G. Dong, Y. J. Wang, Y. Tang, N. Ren, Y. H. Zhang, Z. Gao, *Chem. Mater.*, **2002**, *14*, 3217.
9. X. Querol, A. Alastuey, A. LopezSoler, F. Plana, J. M. Andres, R. Juan, P. Ferrer, C. R. Ruiz, *Environ. Sci. Technol.*, **1997**, *31*, 2527.
10. G.G. Hollman, G. Steenbruggen, M. Janssen-Jurkovicova, *Fuel*, **1999**, *78*, 1225.
11. C. L. Choi, M. Park, D. H. Lee, J. E. Kim, B. Y. Park, J. Choi, *Environ. Sci. Technol.*, **2001**, *35*, 2812.
12. V. V. Poborchii, G. G. Lindner, M. Sato, *J. Chem. Phys.*, **2002**, *116*, 2609.
13. T. Okubo, T. Wakihara, J. Plevert, S. Nair, M. Tsapatisis, Y. Ogawa, H. Komiyama, M. Yoshimura, M. Davis, *Angew. Chem. Int. Edit.*, **2001**, 1069.
14. W. Y. Xu, J. X. Dong, J. P. Li, J. Q. Li, F. Wu, *J. Chem. Soc., Chem. Commun.*, **1990**, 755.

Received 13 December, 2002