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Preparation of mesoporous aluminophosphate using poly(amido amine) as template

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Abstract Mesoporous aluminophosphate was prepared by using G4.0 poly(amido amine)dendrimer as a template and characterized by Fourier transform infrared spectrometer (FTIR), X-ray diffraction (XRD), transmission electron microscopy (TEM) and N₂ adsorption/desorption methods. Results show that the title compound exhibits a typical mesoporous structure with the average pore size from 5 to 8 nm. The formation mechanism of the nanoporous structure using dendrimer as a template was also discussed.

Keywords poly(amido amine)dendrimer, mesoporous, aluminophosphate

The synthesis and characterization of the mesoporous materials have been attracted growing interests due to their great potential applications as absorbents, catalysts and ion exchangers in chemical industries [1,2]. The preparation of mesoporous metal phosphate and metal oxides by supramolecular assembly pathway has been reported [3–5]. Most of mesoporous materials were prepared with the supramolecular assembly of surfactants, which template the inorganic components during synthesis. However, it is difficult to prepare mesoporous aluminophosphate by a simple surfactant template method. Therefore, the study on developing new templates for the mesoporous materials will enrich the field of preparation of this kind of materials.

It has been known that high generation poly(amido amine) (PAMAM) dendrimers are oligomeric molecules with quasispherical morphology (Fig. 1). The special structure of dendrimers should make them suitable to be used as unimolecular templates for the preparation of the mesoporous materials. Larsen et al. [6] and Mitra and Imae [7] reported on the preparation of dendrimer-templated cavities in amorphous

silica. Recently, Huang et al. [8] presented an approach to produce nanopores in titania ultrathin film using generation 4.0 OH-terminated PAMAM dendrimer monolayer as the template. In this paper, a method is reported to form meso-structural pores in aluminophosphate using generation 4.0 NH₂-terminated PAMAM dendrimer (G4.0-NH₂) as a single molecular template.

The typical sample preparation route is depicted as follows: 0.2 g of G4.0-NH₂ and 0.6 g of NaH₂PO₄·2H₂O were dissolved in 15 mL of distilled water and stirred for 15 min. In the mixed solution (pH = 6.5), 0.47 g of AlCl₃ dissolved in 10 mL of distilled water was added under vigorously stirring. The mixture was stirred at room temperature for 4 h. The resulting white precipitate was collected by filtration, washed with distilled water and dried in vacuum at 120°C for 12 h. The PAMAM dendrimer was removed from the as-synthesized solid by calcinations at 600°C for 3 h. The methods of Fourier transform infrared (FTIR) spectrometer, X-ray diffraction (XRD), transmission electron microscope (TEM) and N₂ adsorption/desorption were used to characterize the obtained solid.

Figure 2 shows (infrared) IR spectra of the as-synthesized and calcined samples. The curve 1 of Fig. 2 shows that the strong and broad band in the range of 3,400–3,200 cm⁻¹ is assigned to the N–H vibration of PAMAM and the O–H vibration of crystalline water that exists in the as-synthesized sample. The peaks appearing in 1,640 and 1,383 cm⁻¹ are the characteristics of the PAMAM macromolecule [9]. The strong band at 1,130 cm⁻¹ is ascribed to the symmetric stretching mode P–O of PO₄³⁻. These results prove that the obtained solid is a hybrid material of AlPO₄ and dendrimer. After calcination, the strong band at the range of 3,400–3,200 cm⁻¹ becomes weak and the signals of 1,640 and 1,383 cm⁻¹ vanished (curve 2 of Fig. 2), indicating that no residual dendrimer species are remained in the calcined sample. This result shows that the dendrimer templates in AlPO₄ solid can be removed completely by calcination.

The characteristic peaks for AlPO₄ were observed clearly in curve 2 of Fig. 3, but curve 1 shows that the as-synthesized solid was amorphous. This may result from the dispersion of PAMAM in the hybrid.

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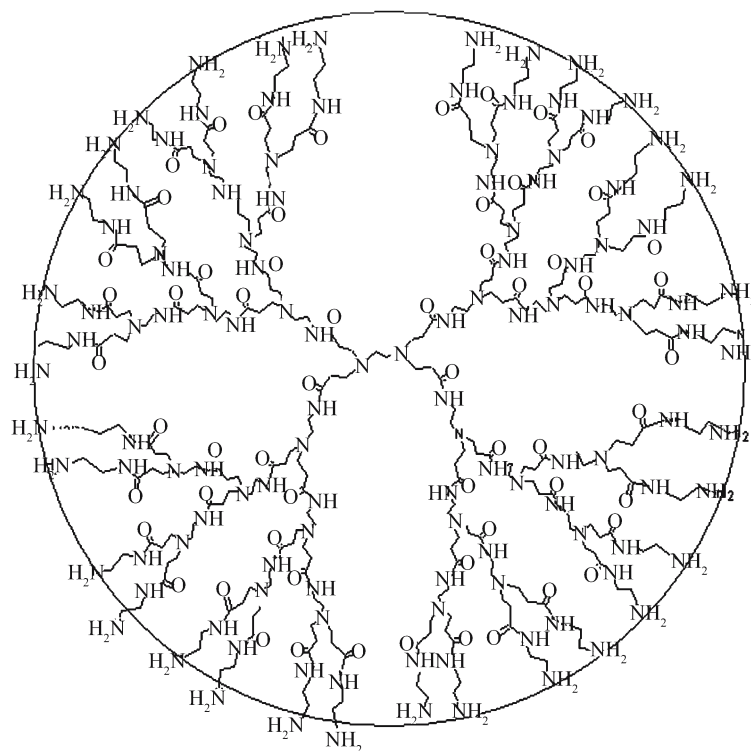


Fig. 1 Structure of G4.0-PAMAM

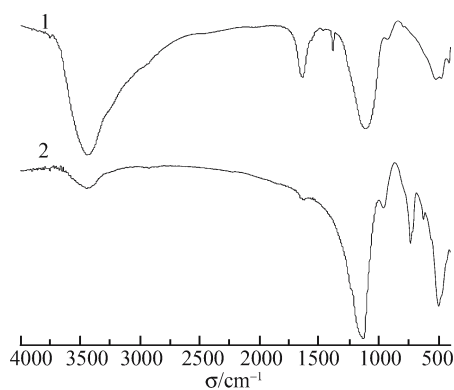


Fig. 2 IR spectra of the samples
(a) As-synthesized; (b) calcined

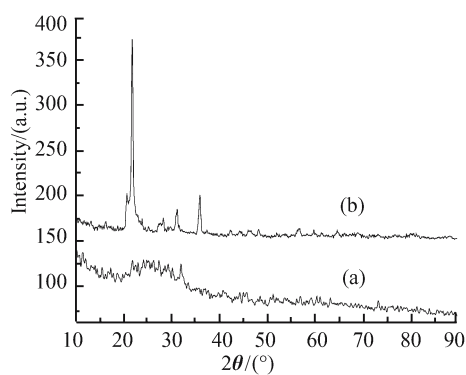


Fig. 3 XRD patterns of the samples
(a) As-synthesized; (b) calcined

As shown in Fig. 4, the title compound has narrow pore size distribution. The pore diameters were determined to be 5 to 8 nm, which is the characteristic of the mesoporous structure.

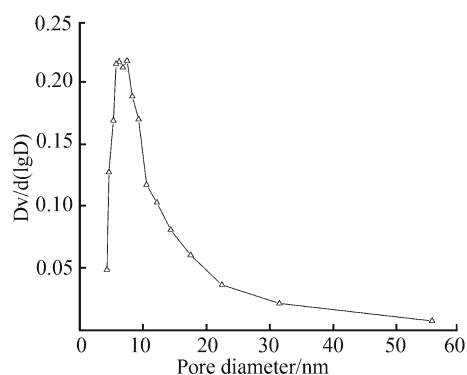


Fig. 4 Pore size distribution of the title compound

This was also confirmed by TEM (Fig. 5) in which the spherical spots were shown clearly. The average diameter of these spots is around 5 nm, which is bigger than the size of free generation 4.0 PAMAM dendrimer in solution (*ca.* 4.5 nm) [10]. The difference between the diameter of the spots observed on TEM and the size of free dendrimer may be due to the deposition of AlPO₄ on the surface of dendrimers.

The proposed mechanism of the nanopore replication in aluminophosphate from PAMAM dendrimer molecules is shown in Fig. 6. In the NaH₂PO₄ solution, negative charged

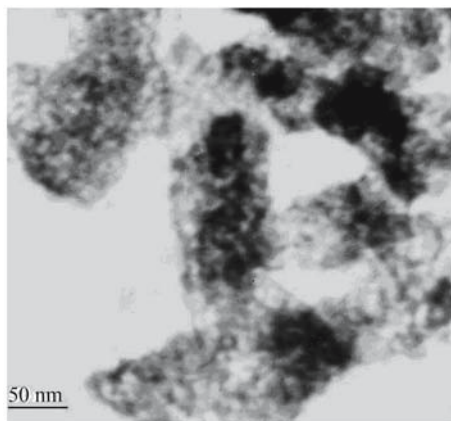


Fig. 5 TEM image of the title compound

phosphate groups surrounding the protonated primary amine terminal groups of G4.0 PAMAM dendrimer by electrostatic interaction. After adding aqueous AlCl_3 solution, AlPO_4 precipitate including PAMAM dendrimer was formed as an organic-inorganic hybrid. Removing the PAMAM dendrimer in the hybrid by calcination, the replication of PAMAM dendrimer molecules as nanopores in aluminophosphate was achieved.

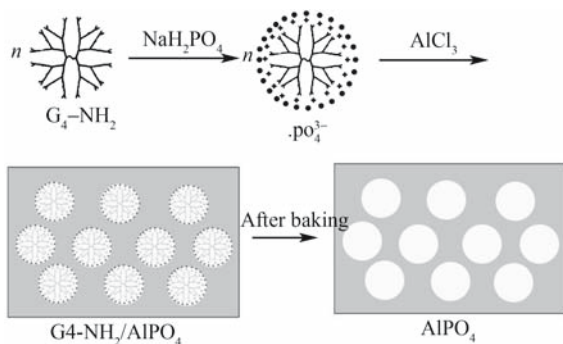


Fig. 6 Schematic representation of the formation process of mesoporous AlPO_4

In conclusion, a mesoporous aluminophosphate has been synthesized using PAMAM dendrimer as a template. A single PAMAM dendrimer produced a nano-sized pore. It is expected that the pore size of mesoporous aluminophosphate can be controlled by using different generation of PAMAM dendrimer as the template.

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References

1. Bake J S, Vartuli J C, Roth W J. A new family of mesoporous sieves prepared with liquid crystal templates. *J Am Chem Soc*, 1992, 114(27): 10,834–10,843
2. Corma A. From microporous to mesoporous molecular sieve materials and their use in catalysis. *Chem Rev*, 1997, 97(6): 2,373–2,420
3. Bhaumik A, Inagaki S. Mesoporous titanium phosphate molecular sieves with ion-exchange capacity. *J Am Chem Soc*, 2001, 123(4): 691–696
4. José J J, Pedro M T, Pascual O P, Enrique R C, Antonio J L, Deborah J J, Jacques R. Surfactant-assisted synthesis of a mesoporous form of zirconium phosphate with acidic properties. *Adv Mater*, 1998, 10(10): 812–815
5. Feng P Y, Xia Y, Feng J L, Bu X H, Stucky G D. Synthesis and characterization of mesostructured aluminophosphates using the fluoride route. *Chem Commun*, 1997, 949–950
6. Larsen G, Lotero E, Marquez M. Use of polypropyleneimine tetrahexacontaamine (DAB-Am-64) dendrimer as a single-molecule template to produce mesoporous silicas. *Chem Mater*, 2000, 12(6): 1,513–1,515
7. Mitra A, Imae T. A novel approach for the preparation of silver-silica nanocomposite. *Chem Lett*, 2004, 33(7): 930–931
8. Huang J, Ichinose I, Kunitake T. Preparation of nanoporous titania films by surface sol-gel process accompanied by low-temperature oxygen plasma treatment. *Langmuir*, 2002, 18(23): 9,048–9,053
9. Manna A, Imae T, Aoi K, Okada M, Yogo T. Synthesis of dendrimer-passivated noble metal nanoparticles in a polar medium: Comparison of size between silver and gold particles. *Chem Mater*, 2001, 13(5): 1,674–1,681
10. Tomalia D A, Naylor A M, Goddard W A. Starburst dendrimers: Molecular-level control of size, shape, surface chemistry, topology, and flexibility from atoms to macroscopic matter. *Angew Chem Int Ed Engl*, 1990, 29(2): 138–175