

A Stable Hexagonal Mesoporous Aluminophosphate Assembled from Preformed Aluminophosphate Precursors

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A hexagonal mesoporous aluminophosphate with high thermal stability (JLU-50) is successfully synthesized from the assembly of preformed aluminophosphate precursors with a cationic surfactant cetyltrimethylammonium bromide (CTAB) by a two-step procedure.

Since the discovery of mesoporous aluminosilicates and silicates such as MCM-41 materials by Mobil scientists,¹ a large number of mesoporous aluminophosphates have been successfully prepared.² Notably, compared with mesoporous silicates,^{3,4} most of mesoporous aluminophosphates prepared through surfactant synthetic strategies exhibit relatively low thermal stability, which limits their wide applications in catalysis and adsorption. To overcome this disadvantage, various approaches based on surfactant-assisted ordering have been used to improve the thermal stability by Kuroda, Kevan, Amorós, and Zhao et al.^{5–8}

It has been reported that thermal and hydrothermal stabilities of ordered mesoporous aluminosilicates could be improved significantly by assembly of the preformed aluminosilicate precursors,^{9,10} which are mainly attributed to the zeolite-like connectivity of TO₄ in the mesoporous walls. Notably, the syntheses of ordered mesoporous materials assembled from preformed precursors (zeolite nanoclusters) are only limited in silica-based mesoporous materials. We show here that the assembly of preformed aluminophosphate precursors with the surfactant of CTAB can synthesize an ordered hexagonal mesoporous aluminophosphate that is thermally stable.

The stable mesoporous aluminophosphate (JLU-50) was synthesized by a two-step procedure. A typical synthesis is as follows: (1) the preformed aluminophosphate precursors were prepared by mixing 7.5 mL of tetraethylammonium hydroxide (TEAOH) aqueous solution (20%) with 5 mL of H₂O, followed by adding 0.6 g of aluminum triisopropoxide. Then, 0.7 mL of phosphoric acid (85%) was slowly added into the mixture. After stirring at room temperature for 4 h and aging at 140 °C for 3 h, the mixture was formed into the clear solutions, which are considered as the preformed aluminophosphate precursors containing primary and secondary aluminophosphate zeolite building units. (2) 0.6 g of CTAB was dissolved in 18 mL of ammonia aqueous solution (4.2%), followed by adding 5 mL of preformed aluminophosphate precursors. The mixture was stirred at room temperature for 20 h, then transferred into an autoclave at 100 °C for 48 h. The product (JLU-50) was collected by filtration, washed, and calcined at 550 °C. Additionally, the compared mesoporous aluminophosphate was synthesized by similar procedures of JLU-50, except for no using preformed aluminophosphate precursors.

Small-angle X-ray (XRD) diffraction patterns of as-synthe-

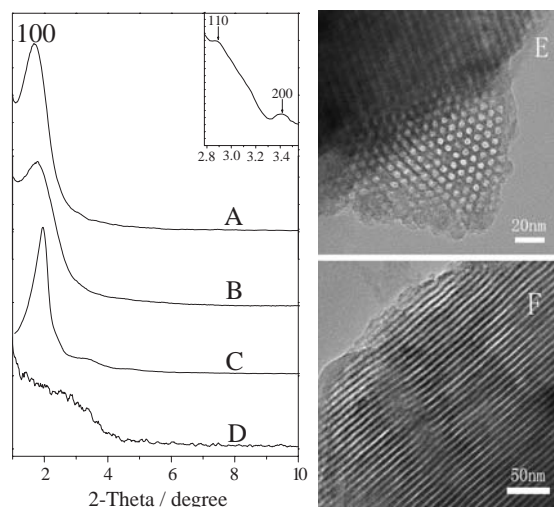


Figure 1. Powder X-ray diffraction patterns of (A) as-synthesized, (B) calcined JLU-50, (C) as-synthesized, and (D) calcined compared mesoporous aluminophosphate and TEM images recorded along E [100] and F [110] directions of JLU-50. Inset: The XRD patterns of Sample A were collected between 2θ 2.8–3.5°.

sized JLU-50 exhibits three peaks at 1.68, 2.92, and 3.38°, which are assigned to (100), (110), and (200) reflections associated with hexagonal symmetry (Figure 1a and inset). After calcination at 550 °C, JLU-50 (P/Al = 1.1) still exhibits a strong peak at 1.75°, indicating that the *meso*-structure is basically retained in the mesoporous aluminophosphate (Figure 1b). Furthermore, it is worthy to note that the thermal shrinkage of *d* (100) spacing in JLU-50 is only 0.2 nm after calcination at 550 °C, which is much less than that in other stable mesoporous aluminophosphates synthesized from C₁₆-surfactants reported previously (0.4–1.3 nm).^{5–7} In contrast, the same calcination for the compared mesoporous aluminophosphate results in complete disappearance of XRD peaks in the small angle region (Figure 1d), indicating full destruction of mesostructure in the sample. TEM images recorded along [100] and [110] directions of JLU-50 (Figures 1e and 1f) show well-ordered hexagonal arrays of mesopores with uniform pore size and further confirm that JLU-50 has a 2-D hexagonal mesostructure.

N₂ adsorption-desorption isotherms of calcined JLU-50 (Figure 2) show a large surface area and uniform pore size, giving at 534 m²/g and 2.1 nm (BJH), respectively. In contrast, calcined compared mesoporous aluminophosphate shows relatively low surface area (40 m²/g), confirming the complete destruction of mesostructure. Interestingly, the wall thickness of

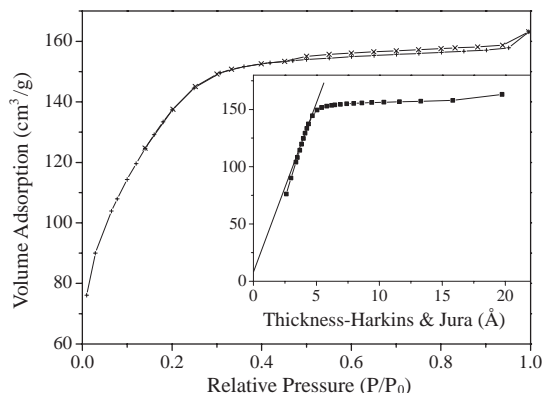


Figure 2. N₂ adsorption-desorption isotherms and *t*-plot curve (inset) of calcined JLU-50.

JLU-50 is near 3.7 nm, which is much thicker than that of other mesoporous aluminophosphates by assembly from C₁₆-surfactants reported previously.⁵⁻⁷ Possibly, the thicker walls of JLU-50 may be assigned to preformed aluminophosphate precursors used in the synthesis. Similar phenomena have been observed in previous reports.⁹⁻¹¹ Very importantly, *t*-plot curve of JLU-50 (Figure 2 inset) does not pass zero of axis, giving a micropore volume at 0.01 cm³/g although it is a little, which is reasonably related to the presence of preformed aluminophosphate precursors, in good agreement with syntheses of mesoporous aluminosilicates assembled from preformed aluminosilicate precursors (zeolite nanoclusters).¹¹

Figure 3a shows IR spectra of various samples. Obviously, JLU-50 exhibits a band at 554 cm⁻¹, which is very similar to that of AlPO₄-18 zeolite. The band at 554 cm⁻¹ may be related to the vibration of double 6-rings of AlPO₄-18 zeolite, similar to that of microporous aluminosilicates. In contrast, the compared mesoporous aluminophosphate does not exhibit this IR band. These results suggest that mesoporous walls of JLU-50 contain AlO₄ and PO₄ units with zeolite-like connectivity in microporous crystals of aluminophosphates.

Figure 3b shows ²⁷Al MAS NMR spectra of various samples. The compared mesoporous aluminophosphate gives a small peak at 45 ppm and a strong peak at 0 ppm, assigned to aluminum species in tetrahedral and octahedral environment, respectively. In contrast, as-synthesized JLU-50 shows a very strong peak at 45 ppm, indicating that JLU-50 has a large amount of tetrahedral aluminum species, which is similar to that of AlPO₄-18. This also suggests that the mesoporous walls of JLU-50 are partially zeolite-like connectivity.

TEAOH is known to be a very good structure directing agent in the synthesis of AlPO₄-18.¹² When a small amount of preformed aluminophosphate precursors used in this study (7 wt %) are added into aluminophosphate gel at 180 °C for 4 days, AlPO₄-18 zeolite with high crystallinity is formed in the absence of organic templates. The preformed aluminophosphate precursors appear to serve as seeds for the formation of AlPO₄-18 zeolite. IR characterization of our preformed aluminophosphate precursors shows a clear band at near 555 cm⁻¹, which is characteristic of double 6-rings in AlPO₄-18 zeolite. ²⁷Al NMR spectrum of preformed aluminophosphate precursor solution gives a strong peak at 44 ppm, which is very similar to the strong peak at 45 ppm in AlPO₄-18. These results indicate

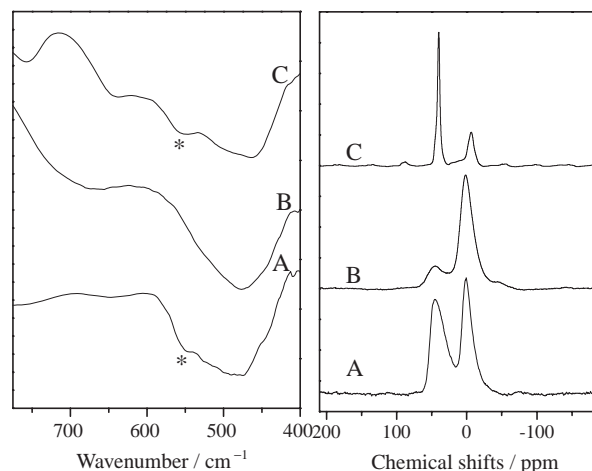


Figure 3. (a) IR spectra of calcined (A) JLU-50, (B) compared mesoporous aluminophosphate, and (C) AlPO₄-18 zeolite; (b) ²⁷Al MAS NMR spectra of as-synthesized (A) JLU-50, (B) compared mesoporous aluminophosphate, and (C) AlPO₄-18 zeolite.

that the preformed aluminophosphate precursors contain zeolite primary and secondary structure units.

The high thermal stability might be associated with our unique approach for the synthesis of JLU-50. The preformed aluminophosphate precursors containing AlPO₄-18 zeolite structure building units are successfully introduced into the mesoporous walls of JLU-50 and the partial zeolite-like connectivity would play an important role for increasing thermal stability.

Currently, we are carrying out further experiments to explore the applications of this concept in the synthesis of JLU-50 containing heteroatoms such as Si⁴⁺, Ti⁴⁺, Co²⁺, Cu²⁺ as catalytically active sites, and characterization of these samples is under investigation.

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