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$[Al_{12}P_{13}O_{52}]^{3-}[(CH_2)_6N_4H_3]^{3+}$: An Anionic Aluminophosphate Molecular Sieve with Brönsted Acidity

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Crystalline aluminophosphates ($AlPO_4$-*n*), which are promoted by hydrothermal synthesis in the presence of organic amines as the structure-directing agents, are a family of microporous solids with great structural diversity.[1−3] These materials, like aluminosilicate zeolites, have considerable potential applications to adsorption, catalysis, and host−guest assembly chemistry. In contrast to the negatively charged aluminosilicate zeolites, the structures of $AlPO_4$-*n* are built up from strict alternation of AlO_4 and PO_4 tetrahedra through corner sharing to form neutral frameworks with the Al:P ratios of unity. Thus, $AlPO_4$-*n* do not have ion-exchange capacity and Brönsted acidity, both of which are important for various catalytic reactions. It is clear that for generating a Brönsted acid site in aluminophosphate molecular sieves, it is necessary to endow the framework with negative charges that can be balanced by extraframework protons.

Typically, isomorphous substitution of P by Si^{4+} (SAPO) or Al^{3+} by divalent Me^{2+} cations (MeAPO; Me = Mg, Mn, Zn, Co, etc.) produces remarkable catalytic activity due to the negative charges on the framework introduced and thus, the Brönsted acid sites.[4−7]

Another preparative strategy is to form the Brönsted acid centers on aluminophosphates by creating the anionic open framework, which is charge compensated by protons. In recent years, our group and others have successfully synthesized a variety of aluminophosphates with anionic frameworks. These materials are formed with 1D chain and 2D layer extended networks, and 3D open frameworks, and with an Al/P ratio less than unity due to the existence of terminal P−OH and/or P═O groups.[8] Their empirical formula are generally expressed as $Al_nP_{n+1}O_{4(n+1)}^{3-}$ (n = 1, 2, 3, 4, 5), with notable examples, JDF-20 ($Al_5P_6O_{24}^{3-}$)[9] and AlPO−HDA ($Al_4P_5O_{20}^{3-}$).[10] The negative charges of the frameworks are balanced by protonated amine molecules. However, the fact that these compounds are not thermally stable upon removing the templates, limits their further applications to catalysis.

In this work, we report the first anionic aluminophosphate molecular sieve $[Al_{12}P_{13}O_{52}]^{3-}[(CH_2)_6N_4H_3]^{3+}$, denoted AlPO-CJB1, (CJB1: China, Jilin, Brönsted, Number 1), which possesses Brönsted acidity upon removing the templates.

AlPO-CJB1 was synthesized in a solvothermal system with the gel molar composition of $Al(^{i}PrO)_3$:2.4H_3PO_4:3.0$(CH_2)_6N_4$:30EG, in which ethylene glycol (EG) was used as the solvent and hexamethylenetetramine ($(CH_2)_6N_4$) as the template. Typically, 1.0 g of aluminum triisopropoxide was first dispersed in 8.2 mL of EG, followed by the addition of 2.0 g of hexaethylenetetraamine. Finally 0.8 mL of phosphoric acid (85 wt % in water) was added dropwise to the above mixture with stirring. The reaction mixture was stirred until it was homogeneous, and then was sealed in a Teflon-lined stainless autoclave, and heated under autogenous pressure at 195 °C for 5 days. The product containing large single crystals was separated using sonication, washed with deionized water, and dried at 70 °C. One suitable single crystal was selected for single-crystal X-ray diffraction analysis.[11] Comparison of the X-ray powder diffraction pattern of the product with a calculated X-ray diffraction pattern shows that the as-synthesized product is a single phase. Inductively coupled plasma (ICP) analysis gives the Al and P contents in the product as 18.2 and 21.5 wt %, respectively, which are in agreement the theoretical Al and P contents of 19.0 and 23.7 wt %, respectively. The elemental analysis gives that the contents of C, H, and N elements are 4.5, 1.24, and 3.7 wt %, respectively, which accord with the calculated values of 4.3, 0.9, and 3.3 wt %, respectively.

AlPO-CJB1 crystallizes in the tetragonal space group $P\bar{4}2_1c$ (no. 114) with a = 13.610 (1) Å and c = 15.547 (2) Å. The structure of AlPO-CJB1 is composed of anionic framework with stoichiometry $Al_{12}P_{13}O_{52}^{3-}$. The charge neutrality is achieved by protonated hexamethylene tetraamine template molecules. The framework is constructed from strict alternation of Al-centered polyhedra (AlO_4 and AlO_5) and P-centered PO_4 tetrahedra by

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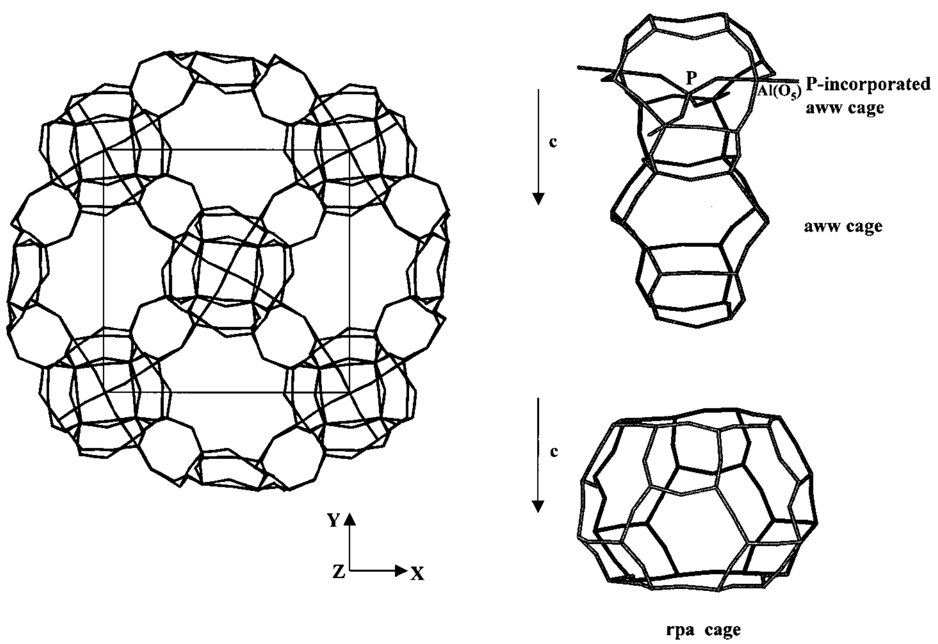

Figure 1. The framework structure of AlPO-CJB1, viewed along the [001] direction.

sharing oxygen atoms at vertexes. This structure is strikingly different from that of $AlPO_4$-*n* where there are PO_4 and AlO_4 tetrahedra.

The open-framework of AlPO−CJB1, viewed along the [001] direction, is shown in Figure 1. Three kinds of cages exist, i.e., an aww cage, a P-incorporated aww cage,[12,13] and an rpa cage featured in cloverite.[14] The aww cages and P-incorporated aww cages alternate along the [001] direction to form a column. Four of such columns are connected with each other through four-membered ring (MR) and 6-MR to form the rpa cages sharing 8-MRs (4.3 × 2.6 Å) along the [001] direction. The maximum cavity diameter measured between the oxygen atoms of the rpa cage is ∼10.7 Å. The oxygen atoms of each PO_4 group in the P-incorporated aww cage form four covalent bonds with adjacent crystallographically equivalent Al atoms that become five-coordinated.

There are four crystallographically distinct P atoms in AlPO−CJB1, the P(1) atoms incorporated in the aww-cage centers locate at −4 site symmetry and form −4 axis along the *c* axis. The P−O bond distances vary between 1.490(5) and 1.536(4) Å. Although the distances of 1.490(5) Å for P(2)−O(1) and 1.497(4) Å for P(3)−O(6) are shorter than normal bridging P−O distances, this is easy to understand by considering the bond valence calculation through the contributions of Al(3)−O(1) and Al(3)−O(6) of the $Al(3)O_5$ polyhedron. There are three crystallographically distinct Al sites, two of which are four-coordinated, Al(1) and A(2), and the third is five-coordinated Al(3). The Al−O distances in AlO_4 tetrahedra exhibit common distances between 1.698(5) and 1.760(4) Å and those in the $Al(3)O_5$ polyhedron again fall in a normal five-coordinated distances between 1.782(5) and 1.887(4) Å. Such two kinds of coordination states around Al are supported by a measurement of ^{27}Al MAS NMR spectrum with two distinct signals at 40.3 and 11.7 ppm, corresponding to AlO_4 and AlO_5, respectively.[15] In contrast to neutral framework $AlPO_4$-*n*, the existence of AlO_5 species confers the negative charge center onto the framework of AlPO-CJB1.

Thermogravimetric (TG) analysis performed on a Perkin-Elmer TGA 7 thermogravimetric analyzer in the air with a heating rate of 10 °C/min suggests that the template molecules are occluded in AlPO-CJB1. Two mass losses at approximately 100−200 °C (1.26 wt %) and 380−550 °C (8.2 wt %) are observed, and these are attributed to the release of adsorbed water and the

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(11) Crystal structure data for $[Al_{12}P_{13}O_{52}]^{3-}[(CH_2)_6N_4H_3]^{3+}$, F_W = 1701.6, tetragonal, space group $P42_1c$ (no. 114), a = 13.610(1) Å, c = 15.547(2) Å, V = 2879.8(5) Å^3, T = 293(2) K, Z = 2, D_{calcd} = 1.962 mg m^{-3}, $F(000)$ = 1692, λ(Mo Kα) = 0.689 mm^{-1}. D_{max} = 30.01. Goodness-of-fit on F^2 was 1.104, R_1[for $I > 2\sigma(I)$] = 0.0641, wR_2 = 0.1802. Data/restraints/parameters 4204/0/174. A colorless tetragonal prism single crystal (0.04 × 0.04 × 0.12 mm) was selected for the structural analysis. The intensity data were measured by using Mo Kα radiation (λ = 0.71069 Å) on a four-circle diffractometer (Rigaku AFC7R) equipped with a rotating anode X-ray tube and incident beam monochromator. Intensity data of 8909 reflections, which corresponds to one-eighth of the full reciprocal space, were collected in the $\omega - 2\theta$ scan mode up to $(\sin \theta/\lambda)_{max}$ = 0.704. The independent data set of 4204 averaged reflections was used for the present analysis. Measured data were corrected for Lorentz and polarization effects together with the absorption correction by an ordinary Ψ-scan algorithm. Intensity distribution suggests the possible space group of $P42_1c$ (no. 114) and this leads an initial structural model of the aluminophosphate framework by using the program package SIR92. The framework structure was refined by the least-squares program SHELXL97 coupled with difference Fourier synthesis. Nevertheless, the charge balancing $[(CH_2)_6N_4H_3]^{3+}$ cations, which are suggested to be included in the product by C, H, N, and TG analyses, could not be located properly in the extraframework region. Therefore, the present results indicates only the parameters for framework atoms of $[Al_{12}P_{13}O_{52}]^{3-}$. The largest difference Fourier peak of 2.85eÅ^{-3} was found at (0.564, 0.069, 0.168) inside the rpa cage and this corresponds to the part of charge-balancing amine molecules. It should be noted that no residual electron was detected at (0.5, 0.5, 0.5). The lattice constants are determined by the 25 well-centered reflections with their 2θ values between 22° and 30°, and obtained values (a = 13.612(2) Å, b = 13.608(2) Å, c = 15.547(2) Å, α = 90.01(1)°, β = 89.99(1)°, γ = 89.98(1)°) indicate no obvious deviation from the tetragonal lattice.

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decomposition of template molecules (calcd 8.23%), respectively. The template molecules can be completely removed at 550 °C. X-ray powder diffraction analysis shows that AlPO-CJB1 is stable up to 600 °C. The reason AlPO-CJB1 shows higher thermal stability than previous anionic aluminophosphates is that there are no terminal P—OH or P=O groups in the structure which interact strongly with the template molecules through H-bonds. It is noted that upon calcination the negative charge of the framework must be balanced by protons. These protons act as Brönsted acid centers.

The N_2 adsorption isotherm of AlPO-CJB1 measured at 77 K is a typical Langmuir adsorption isotherm, characteristic of microporous materials. The surface area is 288 m^2/g for BET and 290 m^2/g for Langmuir.

Temperature-programmed desorption (TPD) of ammonia for AlPO-CJB1 calcined at 550 °C for 24 h is performed and compared with neutral framework $AlPO_4$-5. The NH_3 TPD curve of AlPO-CJB1 shows a strong peak at about 200 °C in contrast to the very weak peak at about 150 °C for $AlPO_4$-5 which is attributed to weakly acidic groups, i.e., framework P—OH groups, and weak Lewis sites. The peak at 200 °C for AlPO-CJB1 is to be attributed to the Brönsted acid sites.

The infrared spectra ranging from 4000 to 3500 cm^{-1} for AlPO-CJB1 samples, (a) calcined at 550 °C (denoted H-AlPO-CJB1), (b) ion-exchanged with ammonia (NH_4-AlPO-CJB), and (c) NH_4-AlPO-CJB calcined at 300 °C (H′-AlPO-CJB1), are shown in Figure 2 together with that of $AlPO_4$-5 (d) for comparison. One main band of hydroxyl groups is observed at 3729 cm^{-1} for AlPO-CJB1. It is noted that no obvious bands are observed under the same experimental condition for $AlPO_4$-5, which mainly possesses Lewis acidity. After ion exchanged with 0.1 N NH_4Cl aqueous solution at 90 °C for 2 h, the band at 3729 cm^{-1} for H-AlPO-CJB1 disappears, indicating the substitution of the protons by NH_4^+. Further calcination of the NH_4-AlPO-CJB1 sample at 300 °C results in the reappearance of the band of 3729 cm^{-1}. As inferred from the structure analysis, the Brönstedacid sites must be associated with O_4Al-OH-PO_3 species, where the protons balance the negative charge generated at the five-coordinated Al sites.

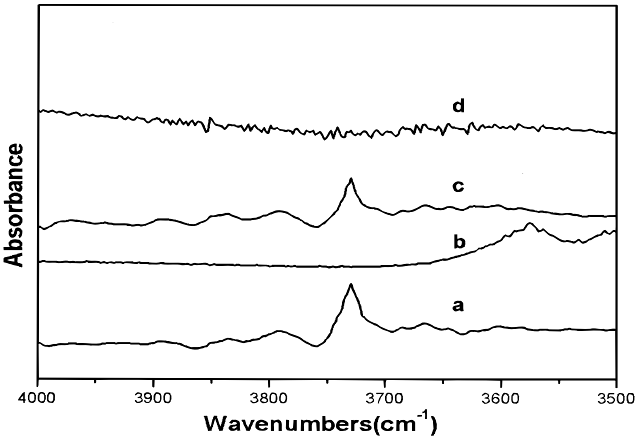

Figure 2. The infrared spectra ranging from 4000 to 3500 cm^{-1} for H-AlPO-CJB1 (a), NH_4-AlPO-CJB1 (b), H′-AlPO-CJB1 (c), and $AlPO_4$-5 (d).

In conclusion, the first anionic aluminophosphate molecular sieve with Brönsted acididy is found for $[Al_{12}P_{13}O_{52}]^{3-}[(CH_2)_6N_4H_3]^{3+}$, which contains three kinds of cages, i.e., aww cage, P-incorporated aww cage, and rpa cage with 8-MR openings. The discovery of AlPO-CJB1 suggests that a variety of anionic aluminophosphate molecular sieves with Brönsted acidity could be synthesized. These materials will be useful for further catalytic applications.

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Supporting Information Available: X-ray crystallographic data, including crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, and anisotropic displacement parameters, for AlPO-CJB1. This material is available free of charge via the Internet at http://pubs.acs.org.

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