Origin of Microporosity of Ammonium Dodecatungstophosphate Unveiled by Single Crystal Structure Analysis

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The single crystals of ammonium dodecatungstophosphate were successfully synthesized and the structure was analyzed. The intrinsic crystal structure (cubic, $Pn\overline{3}m$) had no cavity. It follows that the microporosity observed for the powdery sample originated from narrow spaces surrounded by the fine nanocrystallites.

Ammonium dodecatungstophosphate (denoted as ADTP hereafter) has been well-known as an insoluble fine powder with microporosity and high surface area.[1,2] The high surface area renders it effective as ion exchange media[3] and heterogeneous acid catalysts.[4] As for ADTP[5,6] as well as cesium hydrogendodecatungstophosphate,[7] the uniform microporosity like zeolites has been realized. The microporosity is of great interest on the standpoint of shape-selective catalysis.

Recently, microporous ADTP has been found to be the self-organized aggregates of fine nanocrystallites.[6] Fundamental query about the microporosity of ADTP is whether its intrinsic crystal structure has pores[1,2,5] or not.[8–10] Therefore, the clarification of the crystal structure of ADTP can make the decision, but has not been reported yet.[11] It has also been reported that the crystal structure of ammonium dodecamolybdophosphate changed with the stoichiometry.[12] In this report, we successfully synthesized single crystals of ADTP and the crystal structure was determined to clarify the origin of the micropores.

Single crystals of $(NH_4)_3PW_{12}O_{40}$ were synthesized by hydrothermal method followed by the slow cooling as follows. Dodecatungstophosphoric acid hexahydrate ($H_3PW_{12}O_{40}\cdot 6H_2O$) was prepared by the evacuation of $H_3PW_{12}O_{40}\cdot nH_2O$. $H_3PW_{12}O_{40}\cdot 6H_2O$ (1.5 g, 0.5 mmol) and urea (45 mg, 0.75 mmol) were dissolved in water (25 mL). To the 3 mL of the resulting solution were added a small amount of acetone and seed crystals. The solution was heated in 30-mL Teflon-lined stainless containers at 473 K for 4 h, and then cooled to 433 K for 24 h followed by the cooling to 313 K for 3 h. Colorless prismatic crystals of 0.03–0.15 mm in size were isolated by the decantation (30% yield based on W). The SEM image is shown in Figure 1. The crystal was subjected to the X-ray structure analysis. Elemental analysis (Mikroanalytisches Labor Pascher, Remagen, Germany) of air-dried materials (%). Found: N, 1.39; H, 0.45; P, 0.99; W, 73.7%. Calcd for $H_{12}N_3O_{40}PW_{12}$: N, 1.43; H, 0.41; P, 1.06; W, 75.3%. The ^{31}P NMR spectra were recorded at room temperature in a special glass cell after dehydration under vacuum.[13] Single pulse excitations were used with MAS rate = 3 kHz.

Elemental analysis of the crystals almost agreed with that calculated for $(NH_4)_3PW_{12}O_{40}$. The ^{31}P NMR spectrum is shown in Figure 2. One sharp signal was observed at –14.7 ppm, assignable to $PW_{12}O_{40}^{3-}$ anion without proton.[13,14] These results show that the single crystals consist of stoichiometric ammonium salts of $H_3PW_{12}O_{40}$ (with an $NH_4^+/PW_{12}O_{40}^{3-}$ ratio of 3:1) and are highly pure.

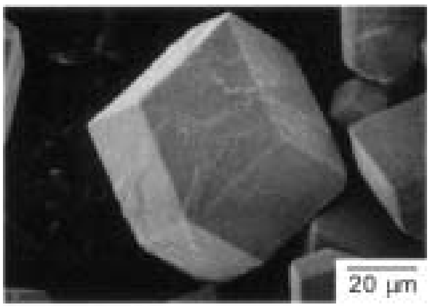

Figure 1. SEM image of single crystals of $(NH_4)_3PW_{12}O_{40}$.

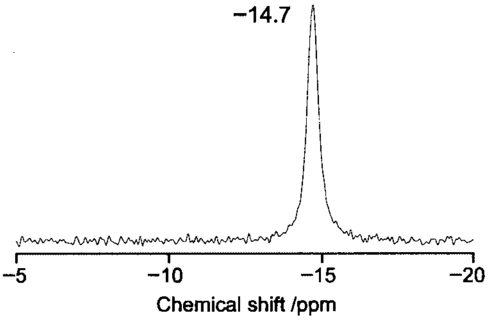

Figure 2. ^{31}P NMR spectrum of $(NH_4)_3PW_{12}O_{40}$ single crystals.

The crystal structure is demonstrated in Figure 3.[15] The heteropolyanion had an α-Keggin structure as shown in Figure 3a. The crystal structure of $(NH_4)_3PW_{12}O_{40}$ was cubic ($Pn\overline{3}m$), basically the same as that of $H_3PW_{12}O_{40}\cdot 6H_2O$:[16] The ammonium ion occupied the position of $H_5O_2^+$ in $H_3PW_{12}O_{40}\cdot 6H_2O$ as discussed on $Cs_3PW_{12}O_{40}$ in the literature.[16] Figures 3b and 3c show the polyhedral and space-filling representation of the crystal structure, respectively. No space for N_2 or Ar adsorption remained in the crystal lattice of stoichiometric ADTP, $(NH_4)_3PW_{12}O_{40}$.

The powder XRD pattern and the chemical formula of powdery ADTP were the same as those of the single crystals. Therefore, the agreements show that the micropores of powdery ADTP do not originate from the crystal lattice.

It was reported that the defect of polyoxometalates may lead to the microporosity.[17] On the assumption that the micropores originate from defects of $PW_{12}O_{40}^{3-}$ (0.8 nm in diameter), powdery ADTP with the surface areas of 49–65 $m^2\ g^{-1}$ [6b,10] is estimated to have the anion defects of 3%. The defects can be

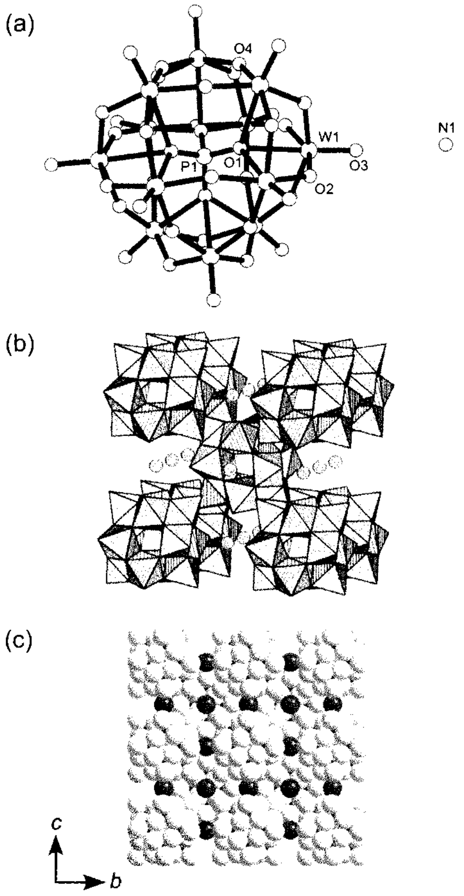

Figure 3. Crystal structure of $(NH_4)_3PW_{12}O_{40}$. (a) Local structure. (b) Crystal structure in polyhedral representation. (c) Space-filling representation. (Gray: oxygen (1.52 Å), black: ammonium ion (1.43 Å); phosphorus and tungsten atoms can hardly be seen.).

analyzed by ^{31}P NMR or elemental analysis and could not be detected. Therefore, the microporosity would not originate from such defects.

All these results lead to the conclusion that the micropores of powdery ADTP are the narrow spaces surrounded by the fine nanocrystallites.

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15 Crystal data: Crystal dimensions $0.13 \times 0.13 \times 0.10$ mm, formula $(NH_4)_3PW_{12}O_{40}$, cubic, $Pn\bar{3}m$, $a = 11.684(4)$ Å, $V = 1595.3(7)$ Å^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 6.102$ g cm^{-3}, $2\theta_{\mathrm{max}} = 60.0°$, 530 reflections collected, 270 observed $[I > 2\sigma(I)]$, $\mu = 433.01$ cm^{-1}, $T_{\mathrm{max/min}} = 1.0000/0.6311$, $R = 0.060$, $R_{\mathrm{w}} = 0.039$. The intensity data were collected on a Rigaku AFC-5R automated four-circle diffractometer with graphite-monochromated Mo Kα radiation. Lorentz polarization and empirical absorption correction based on psi-scans were applied. All calculations were carried out with teXsan program package. The W atoms were located by the direct method and other non-H atoms were found out by successive Fourier syntheses. Tungsten and phosphorus atoms were refined anisotropically, and oxygen and nitrogen atoms isotropically.

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