# Porous Aggregates of Unidirectionally Oriented $(NH_4)_3PW_{12}O_{40}$ Microcrystallites: Epitaxial Self-Assembly

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Microcrystallites of $(NH_4)_3PW_{12}O_{40}$ self-assembled to form symmetric dodecahedral aggregates (ca. 0.5 - 6 μm in size) in which the microcrystallites joined together with the same crystal orientation, by controlled deposition of $NH_4$ salts from a heated aqueous solution of $H_3PW_{12}O_{40}$. These aggregates were highly porous, where microcrystallites were connected each other by epitaxial interfaces.

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Recently, self-assembly of molecules[1,2] and particles[3] has attracted much attention as a strategy to design new materials with dimensions of the order of 100 nm or above. In the molecular self-assembly, noncovalent bonds such as hydrogen bonds join molecules to form structurally well-defined aggregates.[1,2] These materials are interesting because of their potential application as electronic devices[1,4] and as models of biological energy transfer system.[5] As for self-assembly of particles, three-dimensional periodicity in liquid phase has been known as "colloidal crystals", in which electrostatic repulsive force plays an essential role.[6] For example, particles of latex and silica are known to form such ordered structures.[7] Fixation of the colloidal crystal array in a polymer and application as optical devices were also reported.[3] In these self-assembled particles, although the location of primary particles is ordered, the orientation of the particles is usually random. Recently, it was reported that α-$Fe_2O_3$ formed polycrystalline particles in which rod like crystallites had the same crystal orientation.[8] Cs salts of a heteropolyacid, $H_3PW_{12}O_{40}$, which is known as solid "superacid" catalysts,[9] form random aggregates of ultrafine crystallites (ca. 10 nm in diameter) having controlled porosity in the spaces between the crystallites.[10] It was possible to develop a shape-selective solid "superacid" taking advantage of the controlled microporosity of $Cs_{2.2}H_{0.8}PW_{12}O_{40}$.[11] In order to design pore structure, it is important to control aggregation of microcrystallites.

We here report the formation of a novel type of porous aggregate (ca. 0.5 - 6 μm in size) of an ammonium salt of heteropolyacid, $(NH_4)_3PW_{12}O_{40}$, in which microcrystallites were connected each other by epitaxial interfaces. These large aggregates have symmetrical shape and high porosity. This phenomenon is expected to be a new strategy for design of porous catalysts.

$(NH_4)_3PW_{12}O_{40}$ was prepared by two methods; a conventional titration method and a homogeneous precipitation (HP) method using $(NH_2)_2CO$ as an ammonium source. In the titration method, aqueous solution of $NH_4HCO_3$ or $NH_4OH$ (0.13 mol dm$^{-3}$) was added dropwise to aqueous solution of $H_3PW_{12}O_{40}$ (0.025 mol dm$^{-3}$) with vigorous stirring. In some cases, $H_3PW_{12}O_{40}$ solution was heated to 368 K during the addition of an ammonium source. In the case of the HP method, aqueous solution of $(NH_2)_2CO$ and $H_3PW_{12}O_{40}$ was sealed in a glass-made microautoclave and heated to 383 K for 48 h. $NH_3$ was produced in the solution by the hydrolysis of $(NH_2)_2CO$ at the elevated temperature. In both methods, white colloidal solutions formed were dried up at 328 K with a vacuum rotary evaporator to obtain white powder of $(NH_4)_3PW_{12}O_{40}$. Powder X-ray diffraction gave identical patterns regardless of the preparation method except for the line widths.

The diffraction patterns showed a cubic structure with 11.7 Å of cell parameter, in which Keggin anions, $[PW_{12}O_{40}]^{3-}$, are densely packed to form a bcc structure similar to $H_3PW_{12}O_{40} \cdot 6H_2O$.[12]

Figure 1a shows a SEM image of $(NH_4)_3PW_{12}O_{40}$ prepared by the titration method at 383 K using $NH_4HCO_3$. Large symmetrical aggregates were observed. The SEM observation revealed all aggregates had identical dodecahedral shape, while the sizes are different (0.5 - 2 μm). Roughness of the surface was also observed, suggesting that the dodecahedra were aggregates of small particles (10-20 nm in size). The BET surface area was 78 m$^2$ g$^{-1}$, which is much greater than the outer-surface of the dodecahedra. The latter was estimated from the SEM image in Figure 1 to be less than 3 m$^2$ g$^{-1}$. Even if the roughness of the surface is considered, this surface area would be about 6 m$^2$ g$^{-1}$. Hence, it is evident that dodecahedra as shown in Figure 1 are porous inside. Essentially the same results were obtained when $NH_4OH$ was used in stead of $NH_4HCO_3$. The HP method

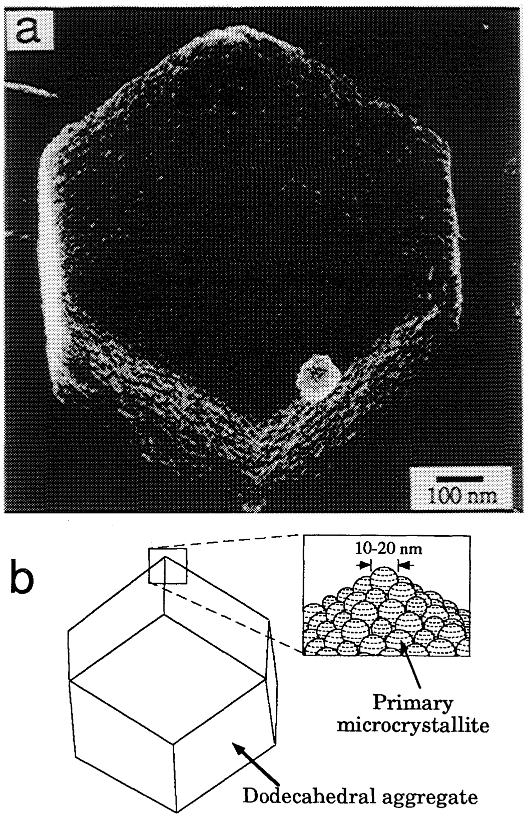

**Figure 1.** (a) SEM images of $(NH_4)_3PW_{12}O_{40}$ prepared at 368 K using $NH_4HCO_3$. (b) Schematic illustration of dodecahedron shown in the SEM image.

using $(NH_2)_2CO$ also gave similar dodecahedral aggregates, of which the size distributed from 0.5 to 6 μm. In contrast, the aggregates were spheric (0.2 - 1 μm in diameter, BET surface area; 115 $m^2$ $g^{-1}$) when they were formed by titration at room temperature.

Figure 2 compares the sizes of microcrystallites calculated from the BET surface area assuming spherical shape and the lengths of ordered crystal structure estimated by Scherrer's method from the calibrated (222) linewidth of powder X-ray diffraction (XRD). The former and the latter values are denoted here by d(BET) and L(XRD), respectively. The roughness of the surface observed in SEM images is consistent with the size of microcrystallites estimated from the BET surface area, d(BET). In the case of $Cs_3PW_{12}O_{40}$, d(BET) and L(XRD) are comparable as shown in Figure 2 and its porosity is reasonably explained by the spaces between the microcrystallites of which the size was estimated by XRD.[10] In contrast, $(NH_4)_3PW_{12}O_{40}$ prepared at 368 K or above exhibited L(XRD) 11 - 13 times greater than d(BET). This fact demonstrates that the ordering of Keggin anion of the ammonium salt continues to a much longer distance beyond the particle size of each microcrystallite. That is, the microcrystallites assembled together by epitaxial interfaces.

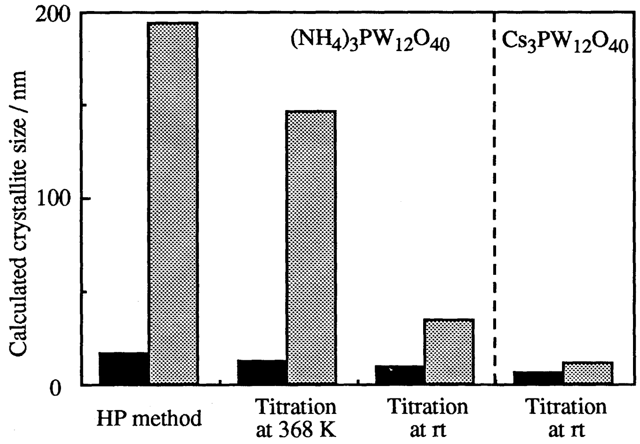

**Figure 2.** Comparison of the particle size calculated from BET surface area (solid box) with the length of the ordered structure estimated from XRD (shaded box). $NH_4OH$ was used in the titration method (Titration using $NH_4HCO_3$ gave the same results).

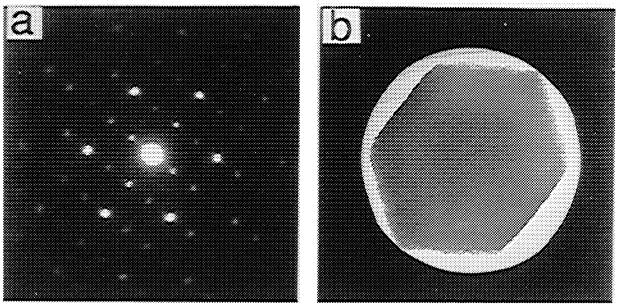

**Figure 3.** (a) Electron diffraction pattern of $(NH_4)_3PW_{12}O_{40}$ prepared at 368 K using $NH_4HCO_3$. (b) The area in which the diffraction pattern of (a) was taken.

These structure was confirmed by an electron diffraction experiment as shown in Figure 3. Even when the diffraction of the entire dodecahedral aggregate was taken (Figure 3b), regular discrete spots were observed (Figure 3a). Intense spots due to (222) and (004) diffractions as well as the other weaker spots are all interpreted assuming electron incident in [110] direction. This fact clearly demonstrates that the microcrystallites in an aggregate had the same crystal orientation. Also in this case, the residual spaces between the microcrystallites in each aggregate are the origin of the porosity as described above. The model inferred by these observations is schematically illustrated in Figure 1b.

Direct precipitation from solution was proposed for the formation of polycrystallites of α-$Fe_2O_3$.[8] However, in the case of heteropolyacid, self-assembly of *preformed* crystallites seems plausible, since the aggregates were porous and precipitation of insoluble ammonium or Cs salts occurred right after the cation source was added. Moreover, there are not $Cl^-$ or $SO_4^{2-}$ ions as in the case of α-$Fe_2O_3$. A possible explanation for the formation of the epitaxial interfaces is: During the growth of the dodecahedra, *preformed* microcrystallites precipitate on the outer-surface of the aggregates, and then slight dissolution and precipitation which occur at the interface of the microcrystallites in the aggregates form epitaxial interfaces accompanied by slight reorientation. If so, the appropriate solubility must be the requisite controlling the orientation. As expected, the titration method at 368 K gave the dodecahedral aggregates while the same method at room temperature did not.

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## Refernces and Notes

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