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Pore Structure and Surface Area of $Cs_xH_{3-x}PM_{12}O_{40}$ (x = 0 - 3, M = W, Mo)

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The pore-size and particle-size distributions as well as the surface areas of $Cs_3PW_{12}O_{40}$ and $Cs_3PMo_{12}O_{40}$ have been determined by N_2 adsorption and electron micrograph. It was first demonstrated by the quantitative comparison of these data that their micro-and/or mesopores which gave these compounds very high surface areas were due to the space between the very fine primary particles and that there were no intrinsic micropores in their crystal structure.

The salt formation often greatly changes the surface area, the thermal stability, and the catalytic activity of heteropoly acids.1-5) For example, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ shows high catalytic activity for the dehydration of alcohols presumably due to its very high surface area.3,4) Some investigators indicated that the high surface areas are due to intrinsic pore structure of Cs salts, which originates from the crystal structure and could be shape-selective as in the case of zeolites.7,8) It is also suggested that the physical properties such as pore structure and surface area are important in the selective oxidation of methacrolein,6) and that the shape-selectivity is present for the reduction of $K_3PMo_{12}O_{40}$.2) We assumed that the pores of $H_3PMo_{12}O_{40}$ were the space between primary particles and that there were no structural microporosity.9) In order to elucidate these fundamental properties of heteropoly compounds as catalysts, we examined in detail the pore structures of $Cs_xH_{3-x}PM_{12}O_{40}$ (x = 0 - 3, M = W, Mo) by quantitative comparison of particle-size distribution, pore-size distribution, and BET surface area.

12-Molybdophosphoric acid ($H_3PMo_{12}O_{40}$, abbreviated as PMo_{12}) and 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$, abbreviated as PW_{12}) were commercially obtained and usually used after purification. The cesium salts ($Cs_xH_{3-x}PM_{12}O_{40}$ (x = 1 - 3, M = Mo, W), abbreviated as Cs_xPM_{12}) were prepared as described previously.3,10) The powder patterns of X-ray diffraction were recorded on an X-ray diffractometer (Rigaku Denki, Rotaflex). The pore-size distribution was measured by means of N_2-adsorption using Sorptmatic 1800 (Carlo Erba) and calculated based on the Dollimore's equation. The transmission electron micrographs (TEM) were obtained with a JEOL JEM 1250 electron microscope (1000 keV, final magnification: x 150 000). Particle size distributions were estimated from 200-400 particles for each sample.

Figure 1 shows the particle-size distributions of Cs_3PMo_{12} and Cs_3PW_{12}

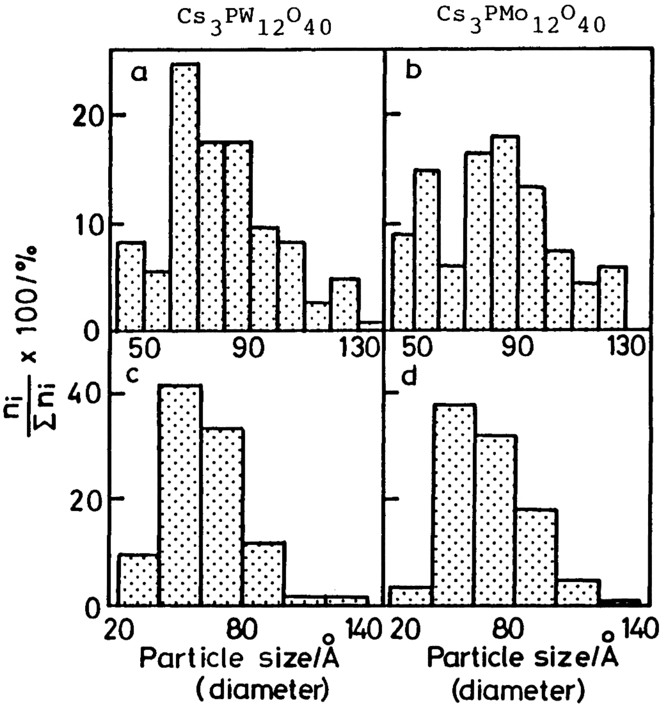

Fig. 1. Particle-size distributions of Cs_3PW_{12} (a, c) and Cs_3PMo_{12} (b, d).
a, b; fine particles.
c, d; spongy particles (aggregates of fine particles).

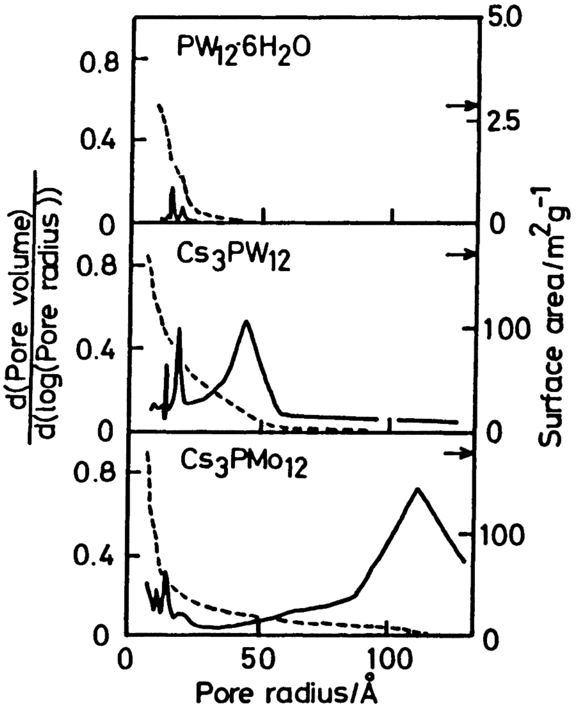

Fig. 2. Pore-size distributions (solid line) and integrated surface areas (broken line) estimated from pore-size distributions of $PW_{12}\cdot 6H_2O$, Cs_3PW_{12}, and Cs_3PMo_{12}. Arrows on the right ordinate indicate the BET surface areas.

measured by TEM, where particle sizes are expressed by diameter. Samples evacuated at 200 °C were dispersed on microgrids. Both fine particles (40 -140 Å) and spongy particles (1 000 - 5 000 Å), as reported by Gregg et al.,[11] were present for Cs_3PMo_{12} and Cs_3PW_{12}. The average sizes of the fine particle were estimated to be 79 Å and 77 Å for Cs_3PW_{12} and Cs_3PMo_{12}, respectively. Spongy particles are aggregates of fine particles, and the average sizes of these fine particles are 62 Å and 67 Å for Cs_3PW_{12} and Cs_3PMo_{12}, respectively. SEM indicated that the the size of secondary particle of $PW_{12}\cdot 6H_2O$ was ca. 2 000 - 10 000 Å.

Pore-size distributions of Cs_3PMo_{12}, Cs_3PW_{12}, and PW_{12} are shown in Fig. 2. Prior to the measurements, the samples were evacuated at 200 °C (Cs_3PMo_{12} and Cs_3PW_{12}) or at room temperature (PW_{12}). The presence of micropores from 10 to 20 Å in radius was indicated for Cs_3PMo_{12} and Cs_3PW_{12}. Mesopores from 90 to 120 Å for Cs_3PMo_{12} and from 30 to 60 Å for Cs_3PW_{12} were also present. These results are in general agreement with our previous data,[1,9] and the data of McMonagle and Moffat.[8] On the other hand, only micropores were present for PW_{12}.

The surface areas have been estimated by three different methods; from the particle-size distribution assuming spherical particles, from the pore-size distributions by assuming cylindrical pores, and from the BET equation. The densities calculated from the crystal data (6.59 and 4.57 g/cm^3 for Cs_3PW_{12} and Cs_3PMo_{12}, respectively) were used for the first method. These surface areas are compared in Table 1. Particle-size for PW_{12} was measured by SEM. The three values are in good agreement with one another for each substance. This agreement demonstrates that the BET surface is the surface of the walls of pores shown in Fig. 2 and is at the same time the surface of the primary particles shown in Fig. 1. Therefore, these substances are composed of fine primary particles observed by TEM, and inside these particles there are no pores detectable by N_2 adsorption. Thus, it is concluded that the micro- and/or mesopores of these substances are the space between the fine primary particles, and there are essentially no pores in the crystal structure.

Table 1. Surface Areas of Cs_3PW_{12} and Cs_3PMo_{12}

	Surface area/m^{2}g^{-1}		
Catalyst	Particle-size distributon	Pore-size distribution	BET
Cs_3PW_{12}	150	169	157
Cs_3PMo_{12}	188	185	175
PW_{12}	1.8	2.9	2.8

Brown et al.[12)] reported that the structure of $PW_{12}\cdot6H_2O$ was made up of two interpenetrating substructures constituting of anions and disordered $H_5O_2{}^+$, the anions being packed in bcc. Cs_3PW_{12} has the same structure as $PW_{12}\cdot6H_2O$ except that $H_5O_2{}^+$ is replaced by Cs^+. The similarity of the XRD patterns (see Fig. 3)

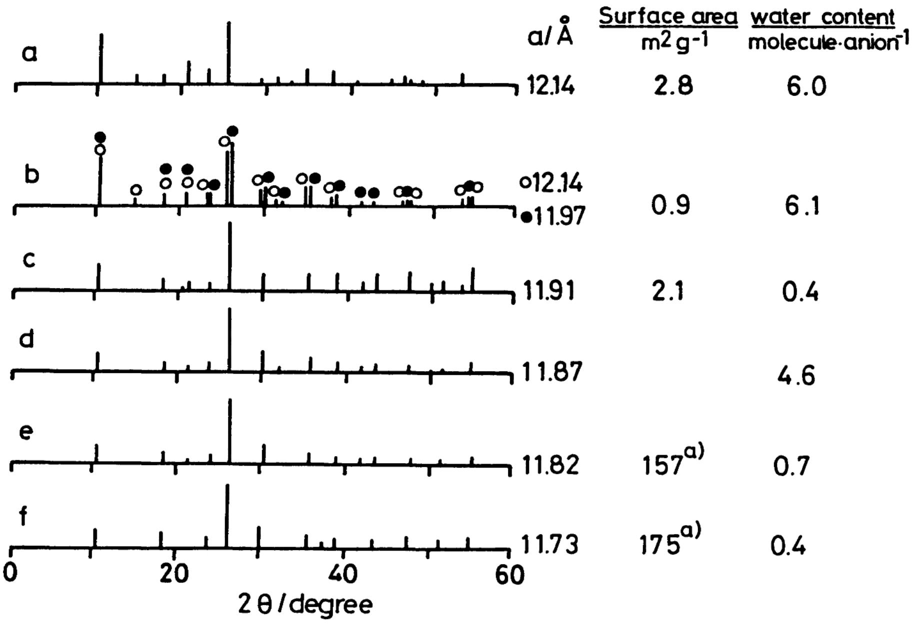

Fig. 3. X-Ray diffraction patterns, water contents, and surface areas of heteropoly compounds.

a: PW_{12}, b, c: Cs_1PW_{12}, d: Cs_2PW_{12}, e: Cs_3PW_{12}, f: Cs_3PMo_{12}.

a) Surface area after heat treatment at 200 °C.

The XRD pattern "c" was measured after evacuation at 300 °C. The other XRD patterns were measured after evacuation at room temperature for 3 h.

indicates that Cs_3PMo_{12} has the same structure as Cs_3PW_{12}. If one considers the size and shape of the Keggin anion, the space between the anions in the above structure is estimated to be less than about 2 Å. Therefore, nitrogen molecule (4.5 Å in diameter) cannot pass through the space between the anions in the crystal. These consideration is consistent with the above conclusion.

In Fig. 3 the XRD patterns of the other Cs salts are also shown. All salts were single cubic systems except for Cs_1PW_{12}. The lattice constants of PW_{12} and PMo_{12} were in good agreement with those reported by Keggin13) (12.14 Å) and Santos14) (11.83 Å), respectively. It was noted that although the XRD patterns of Cs_2PW_{12}, Cs_3PW_{12}, and Cs_3PMo_{12} did not change by the evacuation at 300 °C, the XRD pattern of Cs_1PW_{12} which consisted of two cubic systems (a = 12.14 and 11.97 Å) changed to one cubic system after evacuation at 300 °C (from b to c in Fig. 3). This result shows that as we have reported previously3) Cs_1PW_{12} which precipitated after evaporation to dryness was a mixture of Cs_2PW_{12} and PW_{12}, and transformed to a nearly homogeneous acidic salt (Cs_1PW_{12}) after 300 °C-evacuation by the diffusion of Cs^+ and H^+. The low surface areas of $Cs_xH_{3-x}PW(Mo)_{12}O_{40}$ $(0<x\leq 2)$ indicate the absence of intrinsic micro- or mesopores for these salts as in the case of PW_{12}.

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