

## Hydrothermal Synthesis of Cubic Mesostructured Vanadium–Phosphorus Oxide

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Previously unknown cubic mesostructured vanadium–phosphorus oxide was synthesized by using V metal not only as a V source but also as a reducing agent for  $V_2O_5$ .

Surfactant templating methods for syntheses of mesoporous silicates have first been reported by researchers of Mobil Oil Co.<sup>1,2</sup> and Inagaki et al.<sup>3,4</sup> The extension of MCM-41 and MCM-48 structures into the realm of transition-metal oxides is important from catalytic, electronic, and magnetic standpoints, and the synthesis of siliceous mesoporous materials was applied. To date, the hexagonal and lamellar phases have been reported for various transition metal oxides.<sup>5–7</sup> On the other hand, cubic mesostructured phases have been reported only for oxides of Nb,<sup>8</sup> Sb,<sup>9</sup> and Zr,<sup>10</sup> and nothing is known of cubic mesostructured vanadium-based oxides. Therefore, the synthesis of cubic mesostructured vanadium–phosphorus oxide is also interesting from the standpoint of inorganic chemistry, even though the templates can not be removed. Here we wish to report the one-pot synthesis of cubic mesostructured vanadium–phosphorus oxide (CVPO).

The reagents used were commercially obtained and used without further purification. The synthesis of CVPO was carried out in a Teflon vessel as follows; 2.31 g of 85%  $H_3PO_4$  (Nacalai Tesque) was added to an aqueous solution of cetyltrimethylammonium ( $C_{16}$ TMA) hydroxide/chloride (30  $cm^3$ , 0.66  $mol \cdot dm^{-3}$ ,  $C_{16}$ TMAOH/Cl=2.77), followed by the addition of V metal (0.204 g, Mitsuwa chemical) and  $V_2O_5$  (1.46 g, Nacalai Tesque) at room temperature. A typical molar composition of reaction mixture was 1.0 V : 2.0  $V_2O_5$  : 5.0  $H_3PO_4$  : 5.0  $C_{16}$ TMAOH/Cl : 420  $H_2O$ . The solution was stirred for 1 h and the pH of the solution was adjusted to 3.36 with dilute HCl. The resulting suspension was purged with Ar and then the Teflon vessel was moved to a stainless autoclave. The autoclave was kept at 473 K for 48 h. Finally, the solution was filtered and the resulting moss green powder was washed with ca. 700  $cm^3$  of water followed by evacuation at room temperature for 5 h. The yield was ca. 4 wt% on V-basis.

The powder X-ray diffraction (XRD) pattern was recorded on a powder X-ray diffractometer (MXP<sup>3</sup>, MAC Science Co.) by using  $CuK\alpha$  radiation.

Cubic mesostructured compounds show characteristic XRD patterns and therefore, the structures and homogeneity have often been characterized by XRD method.<sup>8–12</sup> Figure 1 shows the XRD pattern of CVPO. Ten lines were observed at  $2\theta = 2.53, 2.92, 3.88, 4.11, 4.63, 4.85, 5.06, 5.24, 6.50,$  and  $7.12^\circ$  corresponding to  $d$  spacings of 3.49, 3.02, 2.28, 2.15, 1.91, 1.82, 1.74, 1.68, 1.36, and 1.24 nm, respectively. All lines can be assigned to (211), (220), (321), (400), (420), (332), (422), (431), (620), and (444) reflections of cubic mesostructured phase, respectively. The unit cell constant ( $a$ ) was 8.54 nm. No signals other than those of CVPO were observed, sug-

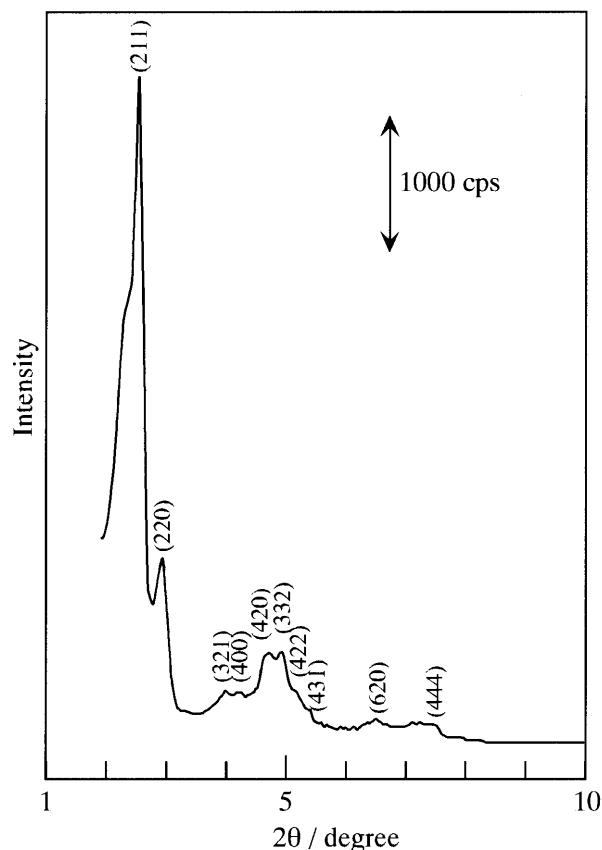


Figure 1. XRD pattern of CVPO.

gesting the high purity of CVPO. This is the first report of the formation of cubic mesostructured vanadium–phosphorus oxide. The signals were well resolved in comparison with the other mesostructured cubic materials of non-silica oxides, suggesting the high crystallinity of CVPO.<sup>8–10</sup> No signals due to the wall structure were observed, but a broad halo pattern was observed around  $2\theta = 20^\circ$ .

The amounts of V, P, C, H, N, and O in CVPO were 14.5, 6.7, 40.1, 7.7, 2.7, and 28.3 wt%, respectively, as shown in Table 1. On the basis of these data, the chemical formula of CVPO was estimated to be  $VP_{0.76}O_{4.42}\{C_{16}H_{33}N(CH_3)_3\}_{0.62} \cdot 1.74 H_2O$ , of which the content of V was taken as unity. The P/V and  $C_{16}$ TMA/V ratios of CVPO were 0.76 and 0.62, respectively, and different from those (P/V ratio, 0.5<sup>13,14</sup> and 1.0<sup>15,16</sup>;  $C_{16}$ TMA/V ratio, 0.2 – 0.6<sup>15</sup> and 0.9<sup>16</sup>) reported for hexagonal and lamellar mesostructured vanadium–phosphorus oxides.

CVPO was formed at pH 3.36, while pure lamellar ( $2\theta = 2.74, 5.53,$  and  $8.33^\circ$  corresponding to (001), (002), and (003) reflections of lamellar phase, respectively) and hexagonal ( $2\theta = 2.02, 3.58, 4.11,$  and  $5.47^\circ$ , corresponding to (100), (110),

**Table 1.** Elemental analysis and valence of vanadium of CVPO

Found	Elemental analysis <sup>a</sup> / wt%						Atomic ratio of P/V	Valence of Vanadium <sup>c</sup>
	V	P	C	H	N	O <sup>b</sup>		
	14.5	6.7	40.1	7.7	2.7	28.3	0.76	4.42
	(14.4)	(6.7)	(40.1)	(8.4)	(2.5)	(27.9)		

<sup>a</sup>Numbers in parentheses were the theoretical values for  $\text{VP}_{0.76}\text{O}_{4.42}[\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3]_{0.62} \cdot 1.74 \text{H}_2\text{O}$ . <sup>b</sup>100 - sum of contents of V, P, C, H, and N. <sup>c</sup>Average valence of vanadium obtained by titration with  $\text{KMnO}_4$ .

(200), and (210) reflections of hexagonal phase, respectively) mesostructured vanadium–phosphorus oxides were formed at pH 3.45 and 2.74, respectively. Not only cubic but also lamellar and hexagonal mesostructured vanadium–phosphorus oxides were tunably synthesized by changing pH and reaction compositions, which has not been reported.<sup>13–16</sup> The increase and decrease in  $\text{C}_{16}\text{TMA}/\text{V}$  ratios in synthetic solution resulted in the formation of lamellar and hexagonal phase, respectively. The same phenomenon was reported for MCM-41.<sup>17</sup>

In conclusion, the present results demonstrate the synthesis of previously unknown cubic mesostructured vanadium–phosphorus oxide. Unfortunately, attempts to observe the TEM photograph by decreasing the accelerating voltages and to remove templates were unsuccessful. This may be due to the complicated cubic pore system as has been pointed out,<sup>18,19</sup> and mesoporous cubic structure has been reported only for silicates. The applications of mesostructured oxides of Zr and Si to adsorbents and host materials even in the presence of templates have been reported.<sup>20–22</sup> Further detailed studies on not only CVPO but also lamellar and hexagonal mesostructured vanadium–phosphorus oxides are in progress.

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