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One-Pot Synthesis of $VOHPO_4\cdot0.5H_2O$ with High Growth of the (001) Plane: An Important Catalyst Precursor of $(VO)_2P_2O_7$

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$VOHPO_4\cdot0.5H_2O$ is a good catalyst precursor of $(VO)_2P_2O_7$, which is an active phase or active component for the industrialized oxidation of *n*-butane into maleic anhydride.[1−20] In addition, the (100) plane of $(VO)_2P_2O_7$, which is an active plane for the selective oxidation,[2,3,7,8,11,13] originates from the (001) plane of $VOHPO_4\cdot0.5H_2O$.[8,21,22] Therefore, the easy synthesis of $VOHPO_4\cdot0.5H_2O$ with a high growth of the (001) plane is interesting from the standpoint of catalyst preparation. $VOHPO_4\cdot0.5H_2O$ is also a catalyst precursor of $(NH_4)_2[(VO)_3(P_2O_7)_2]$ active for ammoxidation.[23−25]

To date, four methods have been reported for the preparation of $VOHPO_4\cdot0.5H_2O$: (1) the reduction of V_2O_5 with alcohols followed by reaction with H_3PO_4,[1−4,8,12,14−16,21,22,26−28] (2) the reaction of a mixture of V_2O_5 and H_3PO_4 with $NH_2OH\cdot HCl$ or oxalic acid followed by heat treatment at 403 K,[1,3,5,10,12,25,26,29] (3) the preparation of $VOPO_4\cdot2H_2O$ followed by reduction with alcohols,[3,8,12,13,21,22,30] and (4) hydrothermal synthesis with V_2O_4 and H_3PO_4 at 773 K.[31] Methods 1−3 consist of two steps and method 4 requires a high temperature of 773 K.

Here, we report the one-pot synthesis of highly crystalline $VOHPO_4\cdot0.5H_2O$ at 473 K and its successive transformation to $(VO)_2P_2O_7$ by using V metal not only as a V source but also as a reducing agent for V_2O_5.

The reagents used were commercially obtained and used without further purification. The synthesis of $VOHPO_4\cdot0.5H_2O$ was carried out in a Teflon vessel as follows: 2.31 g of H_3PO_4 (85%) was added to an aqueous solution of cetyltrimethylammonium chloride (30 cm^3, 0.66 $mol\cdot dm^{-3}$), followed by the addition of V metal (0.204 g, 4.00×10^{-3} mol) and V_2O_5 (1.46 g, 8.00×10^{-3} mol) or $NaVO_3$ (1.95 g, 1.60×10^{-2} mol), or only $VOSO_4$ (4.35 g, 2.00×10^{-2} mol) at room temperature. 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 powder was washed with ca. 700 cm^3 of water followed by evacuation at room temperature for 5 h. The yield was ca. 50% on a V basis. The BET surface area was 4 $m^2\cdot g^{-1}$. Samples a−c of $VOHPO_4\cdot0.5H_2O$ were prepared according to methods 1−3, respectively, which were described in refs 5 and 12.

The powder X-ray diffraction (XRD) patterns were recorded on a powder X-ray diffractometer (Materials Analysis and Characterization, MXP^3) by using Cu $K\alpha$ radiation. The infrared spectra of KBr pellets were recorded on a Perkin Elmer Paragon 1000PC spectrometer. Thermogravimetric and differential themal analysis (TG/DTA) was carried out in a N_2 flow (10 $cm^3\cdot min^{-1}$) with Seiko Instruments TG/DTA 220. Transmission electron micrograph (TEM) and scanning electron micrograph (SEM) analyses were carried out with JEOL JEM-4000 FXII and JEOL TSM-T840, respectively. The elemental analysis and XRD, SEM, TG/DTA, and IR spectra of the prepared sample were consistent with the formation of pure $VOHPO_4\cdot0.5H_2O$. Elemental analysis: calculated (found): V, 29.6 (29.5); P, 18.0 (18.0).

Figure 1a shows the XRD pattern of the sample prepared. All lines can be assigned to $VOHPO_4\cdot0.5H_2O$ with an orthorhombic structure ($a = 7.434$ Å, $b = 9.620$ Å, $c = 5.699$ Å) and agreed well with those reported.[3,12,21,31,32] Thus, a one-pot hydrothermal synthesis of $VOHPO\cdot0.5H_2O$ was achieved at a temperature as low as 473 K. The half-width of the signal at 15.5°, which corresponds to the (001) plane, was about $0.08 \pm 0.02°$ (2θ). The thickness calculated by the XRD data is 0.07−0.15 μm in the [001] direction.

The XRD pattern of the sample prepared from $VOSO_4$ instead of V_2O_5 showed the formation of single phase of $VOHPO_4\cdot0.5H_2O$, but the intensity of the (001) reflection was one-twentieth of that from V_2O_5. No

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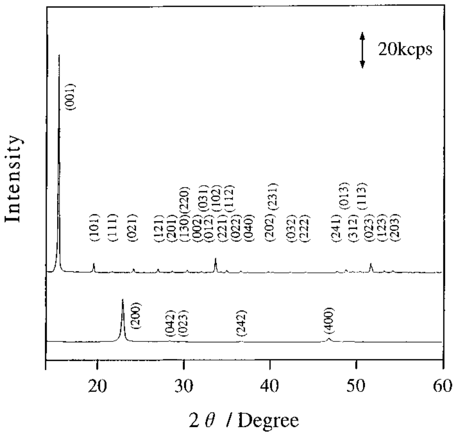

Figure 1. XRD patterns of as-prepared $VOHPO_4{\cdot}0.5H_2O$ and $(VO)_2P_2O_7$: (a, upper) $VOHPO_4{\cdot}0.5H_2O$, (b, lower) $(VO)_2P_2O_7$.

diffraction peaks due to $VOHPO_4{\cdot}0.5H_2O$ were observed when $NaVO_3$ was used instead of V_2O_5. In addition, the intensity of (001) reflection in Figure 1 was a factor of 3−12 higher than those of samples a−c. The strongest XRD peak intensities were obtained at 473 K, for the range of the synthesis temperatures of 413−523 K and by using cetyltrimethylammonium chloride among cetyltrimethylammonium chloride, octyltrimethylammonium bromide, and tetrabutylammonium chloride.

Figure 2a shows the SEM micrograph. $VOHPO_4{\cdot}0.5H_2O$ mainly consisted of platelet crystals with the size of 15−30 μm and a thickness of 0.1−0.3 μm. The values of the size and thickness were 10−30 and 1−2 times larger than those of samples a−c, respectively. Accordingly, the area ratio of the (001) plane to the (220), (020), $(\bar{3}10)$, (220), (020), and $(3\bar{1}0)$ side planes of as-prepared $VOHPO_4{\cdot}0.5H_2O$ was 5−30 times larger than those of samples a−c. When the electron beam was incident to $VOHPO_4{\cdot}0.5H_2O$ along [001], which is the vertical to the basal plane, spots were obtained as shown in Figure 3. The transmission electron diffraction pattern was the same as those reported,[8,22] and the orthorhombic cell parameters (a = 7.43 Å, b = 9.62 Å) agreed well with those obtained from Figure 1.

The IR spectrum showed the 1198 cm^{-1} ($\nu_{as}(PO_3)$), 1134 cm^{-1} (δ_{ip}(P-OH)), 1104 cm^{-1} ($\nu_{as}(PO_3)$), 1052 cm^{-1} ($\nu_{as}(PO_3)$), 978 cm^{-1} (ν(V=O)), 931 cm^{-1} (ν(P-OH)), 684 cm^{-1} (ω(coordinated H_2O)), 643 cm^{-1} (δ_{oop}(P-OH)), 548 cm^{-1} (δ(OPO)), 532 cm^{-1} (δ(OPO)), 482 cm^{-1} (δ(OPO), and 417 cm^{-1} (δ(OPO)) bands, which are characteristic of the $VOHPO_4{\cdot}0.5H_2O$ structure.[7,28]

A sharp weight loss was observed with an endothermic peak at around 740 K for the TG/DTA analysis. The total weight loss was 10.5 wt %, which agreed well with the calculated value of 10.5 wt % for the transformation shown by eq 1. The IR spectrum of the sample used for

$$2VOHPO_4{\cdot}0.5H_2O \rightarrow (VO)_2P_2O_7 + 2H_2O \qquad (1)$$

the TG/DTA measurement agreed well with that of $(VO)_2P_2O_7$. The formation of pure $(VO)_2O_2O_7$ was confirmed by the XRD pattern shown in Figure 1b as well, supporting the occurrence of the transformation. The BET surface area of $(VO)_2P_2O_7$ was 12 $m^2{\cdot}g^{-1}$ and the $(VO)_2P_2O_7$ mainly consisted of platelet crystals as shown in Figure 2b. It has been reported that the catalytic performance is influenced by the morphology of $(VO)_2P_2O_7$.[7,8,12]

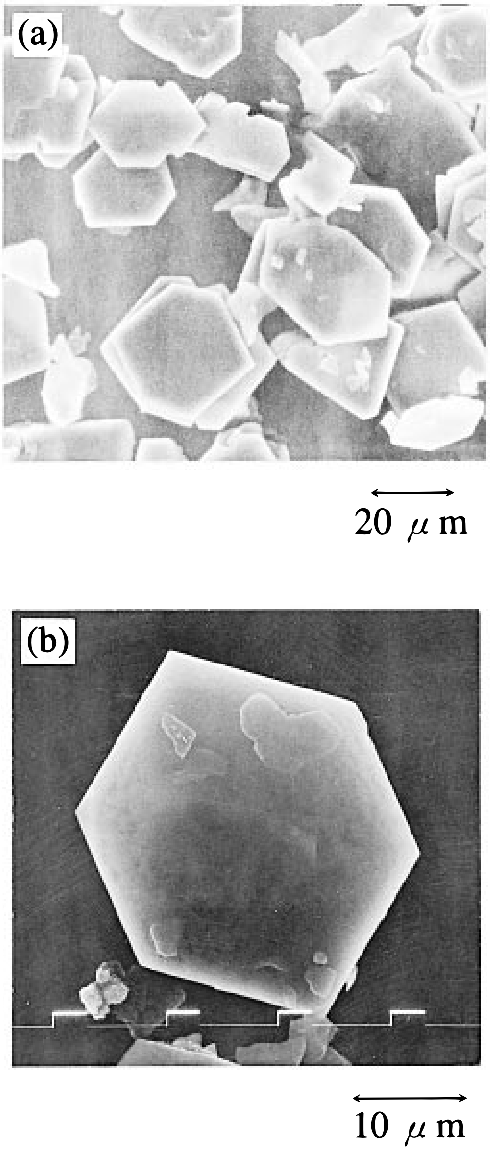

Figure 2. Scanning electron micrographs of as-prepared $VOHPO_4{\cdot}0.5H_2O$ and $(VO)_2P_2O_7$: (a) $VOHPO_4{\cdot}0.5H_2O$, (b) $(VO)_2P_2O_7$.

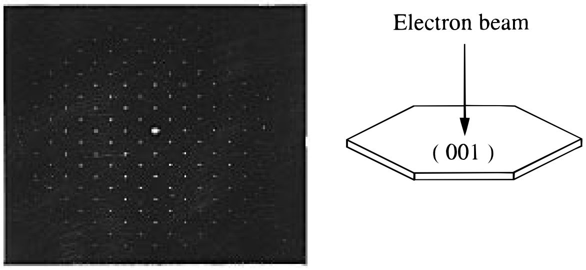

Figure 3. Transmission electron diffraction pattern of as-prepared $VOHPO_4{\cdot}0.5H_2O$.

In summary, the present results demonstrated the one-pot synthesis of $VOHPO_4{\cdot}0.5H_2O$ with a high growth of the (001) plane.

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