Synthesis of a novel mesoporous VPO compound

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A novel mesoporous VPO compound is synthesized from $VOHPO_4{\cdot}0.5H_2O$ by intercalation of surfactant and subsequent hydrothermal treatment.

Vanadium–phosphorus oxides, so-called VPO catalysts, are useful for selective oxygenation reactions such as maleic anhydride production. Recently VPOs having novel structures have been reported.[1–9] For example, Matsubayashi *et al.*[1] studied the synthesis of lamellar VPO compounds by intercalation of organic molecules and Jacobson *et al.*[3] investigated redox intercalation reactions of $VOPO_4{\cdot}2H_2O$ with inorganic cations. VPOs containing micropores have also been reported and Soghomonian *et al.*[5] prepared a vanadium phosphate framework solid with a cavity diameter of 1.84 nm. These novel compounds are expected to afford possibilities as novel catalysts based on their specific structures.

With this background, we have concentrated on the synthesis of novel VPO compounds and report here a three-dimensional, mesoporous crystalline example.

Lamellar $VOHPO_4{\cdot}0.5H_2O$ was synthesized by reduction of $VOPO_4{\cdot}2H_2O$ in benzyl alcohol,[10] and shown to be pure by XRD; the P : V molar ratio as measured by ICP was 1.0. The valency of V as measured by a double titration method[11] was 4.0.

A 8.49 g portion of *n*-tetradecyltrimethyl ammonium chloride (surfactant) was dissolved in 290 ml of water. A 5.0 g portion of $VOHPO_4{\cdot}0.5H_2O$ was added followed by conc. aq. NH_3 (4 ml) dropwise up to pH 7.5 under stirring at room temperature. At this stage the solid changed from light blue to dark green. The temperature was then raised to 349 K and after 48 h the pH of the reaction mixture was 2.7. The reaction mixture was then decanted and the solid obtained was washed with water (300 ml, 5 times).

After drying under vacuum at 313 K for 15 h, the structure was analysed by XRD (Mac Science M18XHF; 40 kV, 100 mA) and TEM (Nippon Denshi JEM2000FX; 200 kV), and the results are shown in Figs. 1 and 2. The XRD pattern indicated a layered structure with a layer separation of *ca.* 3.0 nm. This was also confirmed by TEM (Fig. 2), which showed the layer structure very clearly. The amount of the surfactant occluded was measured by TG–DTA (Seiko Denshi TG–DTA 220) and the molar ratio of surfactant to V was 0.40. The molar ratio P : V was < 1.0 (P/V = 0.85) indicating that some phosphorus had dissolved into solution. The valency of V was 4.2, caused by gradual oxidation during the synthesis [when performed under nitrogen, no oxidation occurred (valency = 4.03)].

A 3.0 g portion of the layered material containing surfactant was suspended in 100 ml of water and the temperature raised to 443 K and maintained for 48 h under stirring. During this time, the material changed from dark blue to dark green. After decanting and washing as before, the solid material was dried as before.

From the XRD pattern (Fig. 3), it is clear that the material has a hexagonal structure with a pore diameter of *ca.* 3.0 nm, as also confirmed by TEM (Fig. 4). The valency of V was the same as before the hydrothermal treatment. The amount of the surfactant remaining in the pore was also the same indicating that the bond between the surfactant and the phosphoric acid (P–O–N) did not dissociate. The occurrence of a hexagonal structure upon hydrothermal treatment can be understood in terms of the surfactant remaining in the layer forming a micelle in water and forcing the layer to bend.[12–14] The P : V molar ratio was *ca.* 0.5, indicating that further phosphorus dissolved into the reaction mixture during the hydrothermal treatment.

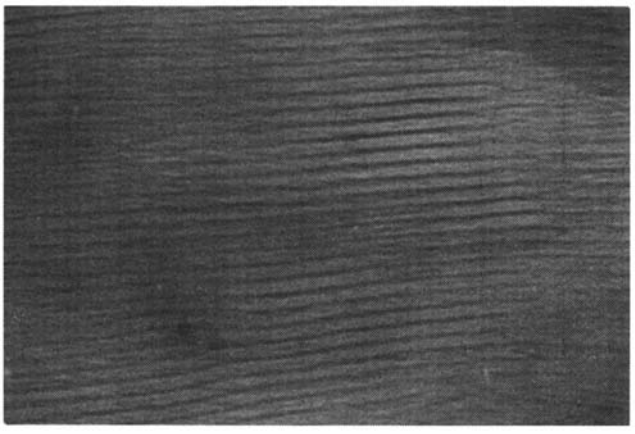

Fig. 2 TEM photograph of the lamellar VPO compound containing intercalated surfactant

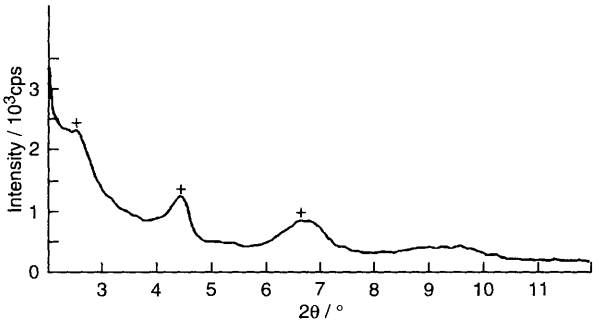

Fig. 1 XRD pattern of the lamellar VPO compound containing intercalated surfactant

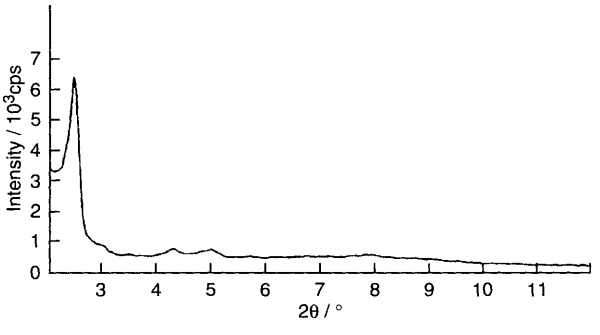

Fig. 3 XRD pattern of the mesoporous VPO compound obtained by hydrothermal treatment

As far as we are aware, this is the first report showing the formation of a mesoporous and crystalline VPO compound. This material may be useful as a catalyst precursor, catalyst support, adsorbent, *etc.*

The synthesis and characterization will be reported in detail in a full paper.

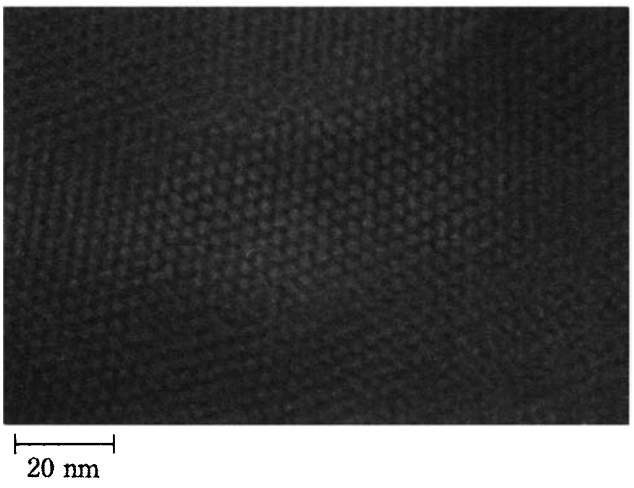

Fig. 4 TEM photograph of the mesoporous VPO compound obtained by hydrothermal treatment

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Received, 9th April 1996; Com. 6/02431I