

Exfoliation of Layered Oxovanadium Phosphate $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ in Tetrahydrofuran through Intercalation of 4-Butylaniline

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VOPO_4 intercalated with 4-butylaniline was exfoliated in THF to form a homogeneous solution, thereby yielding delaminated sheets. The exfoliated oxide layers were reassembled into a thin film morphologically much differed from the intercalation compound.

Intercalation is a technique useful for nanostructural modification of layered materials. Recently, "exfoliation" technique has been developed from intercalation for some layered materials which are metal chalcogenides,¹ clay minerals,^{2,3} zirconium phosphate,⁴ niobates,^{4,5} and titanate.⁶ This is a method of delaminating stacked inorganic sheets in a solvent by infinite swelling of their interlayer spaces where appropriate guest species are intercalated. Novel microstructures such as multilayered heterostructures^{3,4} and porous aggregates^{5,6} have been constructed by reassembling the exfoliated sheets under controlled conditions. These nanofabricated materials may exhibit various advanced functions of, for example, electronics, photochemistry, sensing, and catalysis, by the use of their unusual microstructures.

In the present study, we attempted exfoliation and reconstruction of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$, which is a layered material being capable of intercalating organic molecules exemplified by aromatic amines such as pyridine and aniline.⁷⁻¹¹ $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ is reduced to layered oxide $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ and then topotactically pyrolyzed to $(\text{VO})_2\text{P}_2\text{O}_7$,¹² which is a catalyst used in industries for selective oxidation of *n*-butane to maleic anhydride.^{13,14} Since the catalytic activity and selectivity of $(\text{VO})_2\text{P}_2\text{O}_7$ have been claimed to largely depend on its crystal plane,^{15,16} morphological control of the layered precursors is a promising way to improving the catalytic function of the V-P oxide. Intercalation chemistry of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ should be useful for such microstructural designing, and exfoliation of the oxide is regarded as the first step of preparing novel flaky V-P oxide catalysts consisting of molecular scale thin layers.

$\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ was prepared according to the literature¹⁷ by refluxing a mixture of V_2O_5 (25 g), 85% H_3PO_4 (223 g) and H_2O (577 cm³) at 403 K, followed by washing with acetone. IR spectrum and XRD pattern of the material yielded (Figures 1A-a and 1B-a) agreed with those in the literature.¹⁸ The obtained $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ (0.5 g) was added to liquid 4-butylaniline (20 cm³), and the mixture was stirred at room temperature for 15 min. The product was washed with acetone after filtration, and dried under ambient conditions.

The reaction of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ with 4-butylaniline yielded an intercalation compound as evidenced by the following results. Organic content of the resulting solid was determined by the elemental analysis as C: 37.8%, H: 5.5%, N: 4.4%, showing the composition of the sample as $(\text{C}_4\text{H}_9\text{C}_6\text{H}_4\text{NH}_2)_{1.2}\text{VOPO}_4 \cdot n\text{H}_2\text{O}$ (calcd. for $(\text{C}_4\text{H}_9\text{C}_6\text{H}_4\text{NH}_2)_{1.2}\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$: C: 38.2%, H: 5.9%, N: 4.5%). IR spectrum of the sample exhibited many absorption bands characteristic to 4-butylaniline: e.g. $\nu_{\text{C-H}}$ (2960—2850

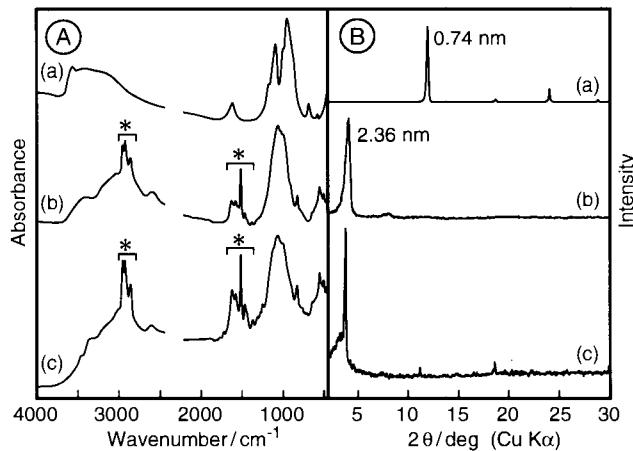


Figure 1. IR spectra (A, left) and XRD patterns (B, right) of (a) $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$, (b) VOPO_4 -4-butylaniline intercalation compound, and (c) the intercalation compound evaporated after the dispersion in THF. Samples (a) and (b) were subjected to the measurements with a conventional KBr disc (IR) or powder (XRD) technique. For sample (c), the THF dispersion was dip-coated on a piece of Si wafer (IR) or glass plate (XRD). Asterisks indicate the absorption bands due to the intercalated 4-butylaniline.

cm⁻¹), $\delta_{\text{N-H}}$ (1515 and 1460 cm⁻¹), and $\nu_{\text{C-N}}$ (1280 and 1265 cm⁻¹) (Figure 1A-b). A broad band due to lattice vibration of VOPO_4 layers was observed at around 900—1100 cm⁻¹, and the profile of this band was quite similar to those previously reported for intercalation compounds of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ with aniline⁹ and 4-anilinoaniline.¹¹ The XRD patterns showed that the basal spacing of the sample (2.36 nm, Figure 1B-b) was larger than that of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ (d_{001} , 0.74 nm, Figure 1B-a), indicating the intercalation of 4-butylaniline. The basal spacing was larger than those of VOPO_4 -aniline (≤ 1.5 nm)⁹ and VOPO_4 -4-anilinoaniline (≤ 1.8 nm)¹¹ intercalation compounds, being rationalized by bulkiness of 4-butylaniline. The gallery height of the intercalation compound was estimated to be 1.95 nm by subtracting the basal spacing of anhydrous VOPO_4 (0.41 nm)¹⁹ from that of the intercalated sample.

SEM images demonstrated that both $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ and the intercalation compound consisted of square platelets with the lateral dimension of around 10 μm and the thickness of less than 1 μm (Figures 2-a and 2-b). Namely, plate-like morphology of initial $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ was retained after intercalation, reflecting the layered nature of the samples, although the warped shape of the intercalated platelets would be based on mechanical stress by the interlayer expansion.

The powder of the intercalation compound (0.3 g) was then added to THF (40 cm³) followed by stirring at room temperature

for 24 h, thereby a nearly homogeneous suspension was obtained. A brown transparent solution was yielded after removal of a small amount of remaining solid by decantation, and it did not change at least for 2 weeks. In contrast, when $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ was added to THF, the oxide powder was only sedimented, indicating that VOPO_4 layers themselves are stable without dissolution or swelling in THF. Hence, we deduce that VOPO_4 -4-butylaniline intercalation compound was exfoliated in THF. The transparency of the solution suggests that the VOPO_4 layers were

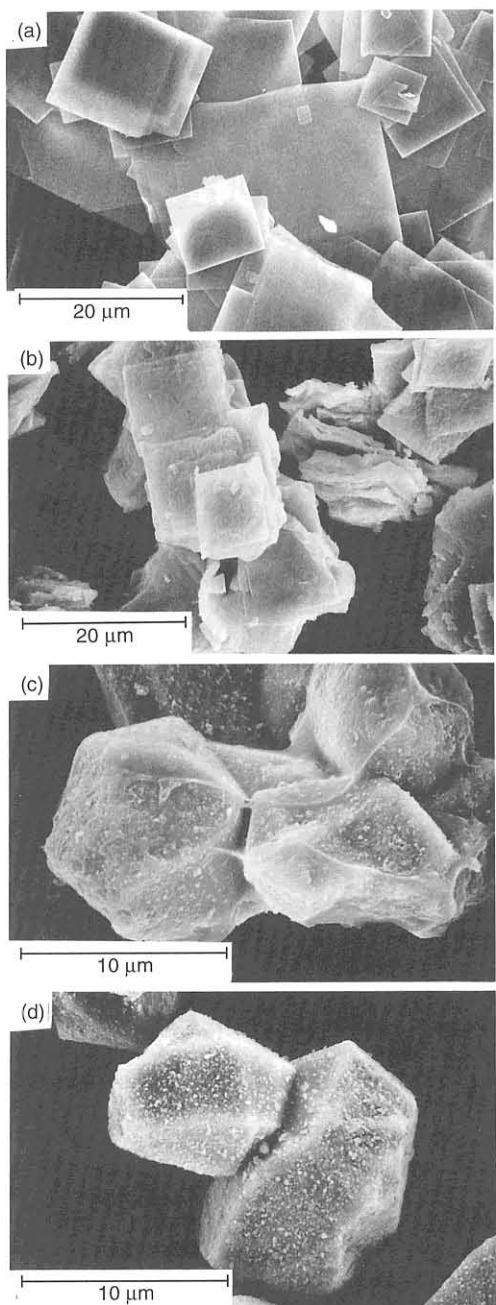


Figure 2. SEM images of (a) $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$, (b) VOPO_4 -4-butylaniline intercalation compound, (c) the sample obtained from the suspension of the intercalation compound dropped onto α -alumina, and (d) bare α -alumina.

highly delaminated although their thickness was not determined.

When THF was removed from the solution by dip-coating onto a flat substrate at room temperature, the VOPO_4 -4-butylaniline intercalation compound was reconstructed into a thin film; XRD pattern of the sample coated on a glass slide showed peaks assignable to the intercalation compound (Figure 1B-c) and IR spectrum of the sample on Si wafer was the same as that of the intercalation compound (Figure 1A-c). The sharp XRD peaks of the sample would not indicate its high crystallinity because preferred orientation could occur during the coating process.

To confirm the exfoliation, we attempted to directly observe the delaminated oxide sheets. When a small amount of the suspension was dropped and dried on fine particles of α -alumina (Sumitomo Chemical, AA-10), SEM showed twisted sheets like thin silks dressed by the α -alumina particles (Figure 2-c). The sheets were much thinner than the platelets of the intercalation compound before the treatment with THF. This is evidence for the exfoliation of the VOPO_4 layers; the exfoliated V-P oxide layers were assembled into a very thin film whose morphology was largely different from those of VOPO_4 and the intercalation compound. This novel morphological control developed for the first time by using the intercalation-exfoliation strategy will open a way to constructing various nanoassemblies of V-P oxides which can be applied to catalysts, sensors, etc.

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