

Reaction of layered vanadium phosphorus oxides, $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$, with amines and formation of exfoliative intercalation compounds

Teruyuki Nakato,*† Yoko Furumi, Naoshi Terao and Toshio Okuhara*

Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060-0810, Japan. E-mail: tnakat@cc.tuat.ac.jp

Received 11th October 1999, Accepted 11th January 2000

Reactions of layered vanadium phosphorus oxides, $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$, with aliphatic and aromatic amines were investigated with regard to the formation of intercalation compounds. $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ was intercalated with 4-butylaniline, and the obtained intercalation compound was exfoliated by stirring in THF. The layered structure of the intercalation compound was reconstructed by removal of the solvent from the suspension of exfoliated solid, while ordering of the restacked layers was sensitive to the experimental conditions. The reactions with 4-butylaniline for prolonged periods caused partial collapse of the layered structure, indicating metastability of the intercalated structure. $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ formed intercalation compounds with aniline and 4-anilinoaniline as well as 4-butylaniline. On the other hand, reactions with *n*-alkylamines, which are more basic than aromatic amines, brought about collapse of the layered structure of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$. In addition, $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ did not react with aromatic amines such as aniline and pyridine, while reactions with *n*-alkylamines did not give intercalation compounds but led to the formation of salts, where the structure of the host lattice was not retained.

Introduction

Oxovanadium phosphate $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ is a layered compound possessing high intercalating capability.¹ The layered structure consists of VOPO_4 layers and interlayer water molecules; VO_6 octahedra and PO_4 tetrahedra are linked together through corner-sharing to form the layers.² $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ has been reported to accommodate various molecules and ions through a variety of routes. Organic molecules, such as alkylamines,^{3,4} amides,^{5,6} alcohols,⁷ carboxylic acids,⁸ aromatic amines,^{9–14} and glycine,¹⁵ are intercalated by polar adsorption. Pyridine is coordinatively immobilized within the interlayer space.¹⁶ Some cationic species are taken up *via* a redox mechanism in the presence of reductive reagents such as iodide anions.^{17–20} Among these guest species, organic basic molecules, exemplified by amines, have most widely been investigated; nevertheless the reactivity of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ is not well understood systematically.

These intercalation compounds are of interest not only as fundamental samples of 2D nanocomposites organized on $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ but also as intermediates for constructing novel V–P–O nanostructures. In fact, $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ can be utilized as a catalyst precursor; it is reduced to the layered material $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ and then pyrolyzed to $(\text{VO})_2\text{P}_2\text{O}_7$,²¹ which is an industrial catalyst for selective oxidation of *n*-butane to maleic anhydride.²² Intercalation of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ should be important as a method of preparing novel nanostructurally modified catalyst precursors. We have recently found that VOPO_4 intercalated with 4-butylaniline was exfoliated in THF to form thin flexible oxide layers which may be applied for preparing various novel nanoassemblies of V–P oxides.²³ Such nanostructural fabrication of layered V–P oxides is achieved by utilizing inorganic–organic interactions in the interlayer region. Investigation of reactions between the layered oxovanadium

phosphates and organic basic molecules with different basicity should be helpful for understanding the interactions of the V–P oxide layers with organic molecules.

In the present study, we examined reactions of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ with some amines. The layered structure was not retained by reactions with strongly basic molecules such as alkylamines. In contrast, weak bases such as aniline and its derivatives were intercalated into $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$. The intercalation compound with 4-butylaniline was characterized by an exfoliative property; it was delaminated in polar organic solvents, exemplified by THF. Since Gulians *et al.* claimed that $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ is intercalated, as well as $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$, with alkylamines,²⁴ we also examined the reactions of $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ with these amines.

Experimental

Materials

$\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ was prepared according to the literature by refluxing a mixture of V_2O_5 (25 g, Wako), 85% H_3PO_4 (223 g, Wako) and H_2O (577 cm³) at 403 K for 16 h.¹ The yellow product was filtered off, washed with acetone, and then kept under ambient conditions. Powder X-ray diffraction (XRD) and IR spectroscopy identified the product as $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$.^{1,25}

$\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ was synthesized by refluxing a mixture of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ (15 g) and butan-2-ol (150 cm³) at 378 K for 18 h.²⁶ The light-blue product was filtered off, washed with acetone, and dried under ambient conditions. Formation of $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ was confirmed by XRD and IR. The $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ sample exhibited plate-like morphology according to scanning electron microscopy (SEM) images.

Reactions of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ with amines

Commercially available amine reagents (*n*-butylamine, *n*-hexylamine, di-*n*-butylamine, pyridine, aniline, and 4-anilinoaniline (purchased from Wako or Aldrich)) were used without

†Present address: Department of Environmental and Natural Resource Science, Faculty of Agriculture, Tokyo University of Agriculture and Technology, 3-5-8 Saiwaicho, Fuchu 183-8509, Japan.

further purification. $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ (0.5 g) was added to neat amines (20 cm^3), and the mixtures were stirred at room or an elevated temperature for 15 min to 24 h. 4-Anilinoaniline (obtained as a solid from Wako) was allowed to react as an ethanolic solution (0.3 mol dm^{-3}).¹¹ The products were washed with acetone after filtration, and dried under ambient conditions.

Reactions of $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ with the amines were carried out by stirring the oxide (0.5 g) in the neat amine (10 cm^3) at room temperature for 2 days. The products were characterized after washing with acetone.

Exfoliation of VOPO_4 intercalated with 4-butylaniline

The powder of the VOPO_4 -4-butylaniline intercalation compound (0.3 g) was added to THF (60 cm^3) followed by stirring at room temperature for 72 h. The obtained suspension was allowed to stand for more than 1 week, after which the residual solid had settled out and the liquid phase had become transparent. The solution was then removed by decantation, and dried to solid in a vacuum desiccator at room temperature. The settled solid was dried under ambient conditions.

Analytical instruments

Powder XRD patterns were recorded on a Rigaku Geigerflex 2027 diffractometer (monochromated $\text{Cu-K}\alpha$ radiation). IR spectra of the solid samples were measured by using a Bio-rad FTS-7 spectrometer using the KBr disk technique. SEM images were taken by using a Hitachi S-2100A scanning electron microscope.

Results and discussion

Reactions of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ with 4-butylaniline

As we preliminarily reported, $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ was intercalated with 4-butylaniline by reaction at room temperature for 15 min.²³ Fig. 1 shows XRD patterns of the products obtained from the reaction of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ with neat 4-butylaniline. The product obtained by the reaction for 15 min exhibited a strong peak of $d = 2.36 \text{ nm}$ ($2\theta = 3.74^\circ$), the basal spacing, with a small second-order diffraction peak (Fig. 1b). Other definite peaks were not observed in the 2θ range of $2\text{--}60^\circ$. The results of Fig. 1 imply that the layered structure of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ was basically retained but the crystallinity of the oxide decreased after the reaction. The basal spacing of the product ($d = 2.36 \text{ nm}$) was larger than those of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ (0.74 nm) and anhydrous VOPO_4 (0.41 nm).²⁷ This value is enough to accommodate 4-butylaniline with a bilayer arrangement in the interlayer space of VOPO_4 since the distance between a hydrogen atom of $-\text{NH}_2$ and that of $-\text{CH}_3$ is roughly estimated as 0.92 nm.

Fig. 2 shows IR spectra of the samples obtained by the reaction with 4-butylaniline. The product obtained at room temperature for 15 min exhibited many absorption bands due to 4-butylaniline:²⁸ 2956, 2927, and 2860 cm^{-1} , C-H stretching; 1621 cm^{-1} , NH_2 bending; 1514 cm^{-1} , ring; 1460 cm^{-1} , CH_2 bending. The band at 1574 cm^{-1} is assignable to NH_2 bending of the 4-butylanilinium cation.²⁹ Thus, 4-butylaniline is probably present partly as the protonated form. Nakajima and Matsubayashi reported intercalative protonation of aniline within $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$; V^{5+} ions are partly reduced in parallel with the protonation.¹¹ On the other hand, the product gave only a broad band at around 1060 cm^{-1} in the VOPO_4 lattice vibration region while the spectrum of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ displayed the following bands: 1087 cm^{-1} , P-O stretching; 944 cm^{-1} , V-OH stretching; 992 cm^{-1} (shoulder), V=O stretching.²⁵ This difference may be explained by a change of the interlayer microenvironment caused by displacement of interlayer water molecules during the reaction. The spectrum with the single

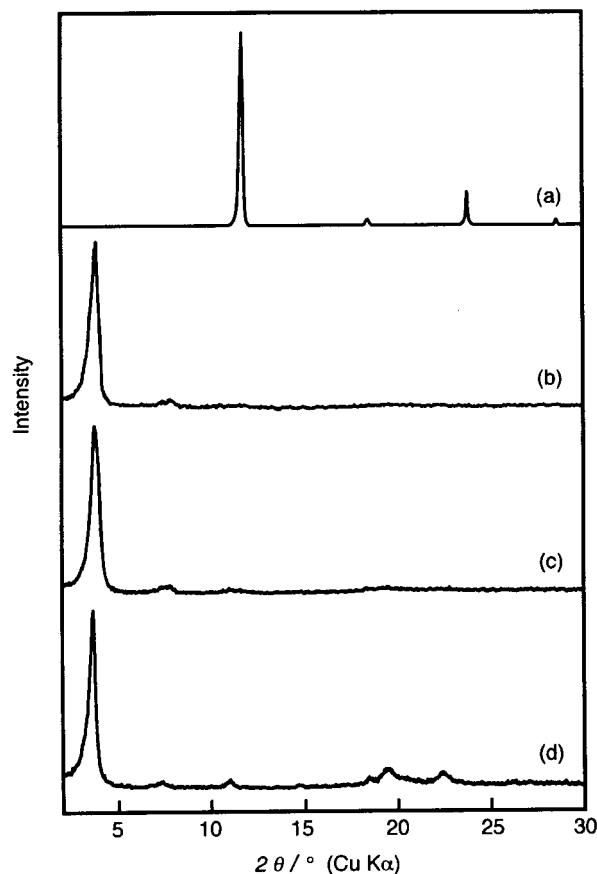


Fig. 1 XRD patterns of (a) $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ and the products obtained by reaction with 4-butylaniline at room temperature for (b) 15 min, (c) 1 h, and (d) 16 h.

broad band at 1060 cm^{-1} resembled that observed for anhydrous $\alpha\text{-VOPO}_4$,³⁰ reflecting the absence of interactions of VOPO_4 layers with interlayer water molecules. Similar band profiles were observed in the IR spectra of the VOPO_4 -aniline⁹ and VOPO_4 -4-anilinoaniline¹¹ intercalation compounds. The results of XRD and IR analyses indicate that the VOPO_4 -4-butylaniline intercalation compound was formed from the reaction of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ and 4-butylaniline for 15 min at room temperature. The CHN analysis (C: 37.8%, H: 5.5%, N: 4.4%, C/N atomic ratio = 10) determined the composition of the intercalation compound to be $(\text{C}_4\text{H}_9\text{C}_6\text{H}_4\text{NH}_2)_{1.1}\text{VOPO}_4 \cdot n\text{H}_2\text{O}$ ($n \approx 1.3$).

The products obtained by reaction for more than 1 h were, however, different from the intercalation compound prepared by reaction for 15 min. XRD patterns of the samples showed some peaks in addition to those indicating the basal spacing, which was 2.44 nm, being somewhat larger than that of the intercalation compound (Fig. 1c and d). They appeared at around $2\theta = 11^\circ$ and $19\text{--}23^\circ$, and their intensities increased for products obtained from longer reaction periods. IR spectra of these samples were also different from that of the intercalation compound; the samples gave several sharp absorption bands in the VOPO_4 lattice vibration region while the intercalation compound exhibited a single broad band (Fig. 2c and d). These bands were stronger for the samples obtained from longer reaction periods. These observations indicate that by-products were formed upon prolonging the reaction time.

On the other hand, the IR spectra of the products from the long-period reactions exhibit definite adsorption bands due to 4-butylaniline. The organic contents of these samples were determined by CHN analysis as follows: for the product obtained by reaction for 1 h, C: 41.3%, H: 5.9%, N: 4.8%, and for the sample after reaction for 16 h, C: 52.2%, H: 7.13%, N:

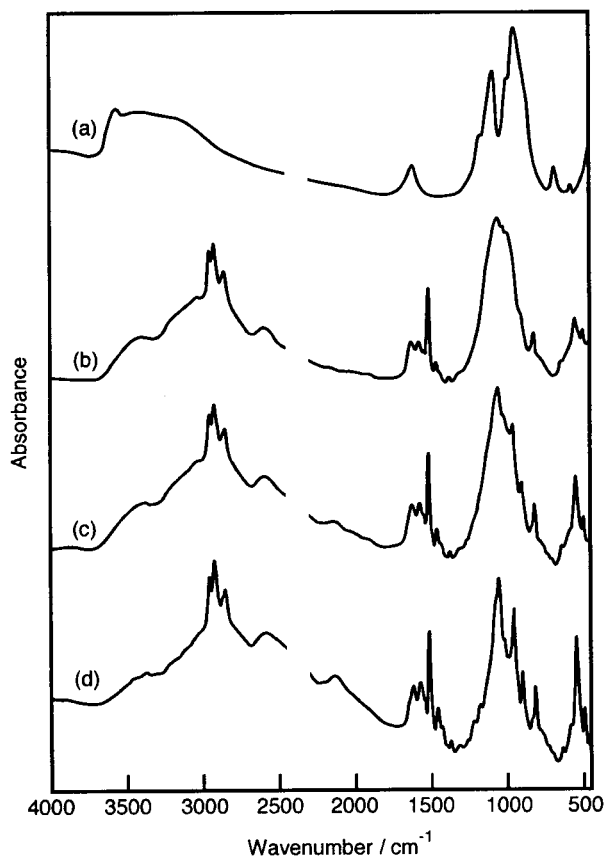


Fig. 2 IR spectra of (a) $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ and the products obtained by reaction with 4-butylaniline at room temperature for (b) 15 min, (c) 1 h, and (d) 16 h.

6.2%. The C/N atomic ratio of the organic species in both the samples was estimated as 10, corresponding to that of 4-butylaniline. Thus, we suggest that organic species were mostly present as 4-butylaniline. The compositions of the samples after 1 h and 16 h of reaction were estimated as $(\text{C}_4\text{H}_9\text{C}_6\text{H}_4\text{NH}_2)_{1.3}\text{VOPO}_4 \cdot n\text{H}_2\text{O}$ ($n \approx 1.3$) and $(\text{C}_4\text{H}_9\text{C}_6\text{H}_4\text{NH}_2)_{2.3}\text{VOPO}_4 \cdot n\text{H}_2\text{O}$ ($n \approx 1.5$), respectively.

SEM images of the samples shown in Fig. 3 indicate retention of the platy morphology characteristic of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ after the intercalation process. The intercalation compound prepared by reaction for 15 min consisted of square platelets whose shape and size were similar to those of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$; namely, the plate-like morphology of the initial layered oxide was retained. The warped shape of the intercalated platelets would be caused by mechanical stress due to the interlayer expansion. On the other hand, the products obtained from the longer reaction times did not have the initial morphology although they still retained platy character. This observation supports the results of XRD and IR which indicate the formation of by-products through a chemical reaction accompanied by degradation of the VOPO_4 layers.

Exfoliation of the VOPO_4 -4-butylaniline intercalation compound

We obtained a nearly homogeneous suspension by stirring the powder of the VOPO_4 -4-butylaniline intercalation compound in THF. A stable transparent solution was decanted off from the undissolved powder, whereas $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ was found to be completely insoluble in THF. The transparent solution was stable for at least 6 months. In our earlier communication, we presumed that VOPO_4 layers were exfoliated in this solution from XRD and IR analyses of a film sample obtained by dip-

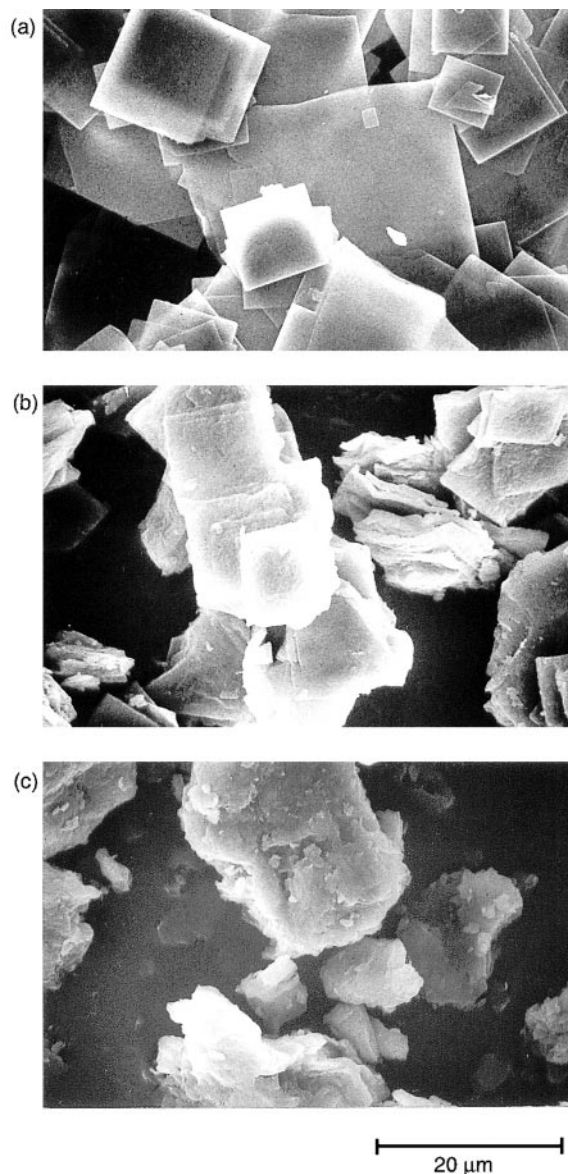


Fig. 3 SEM images of (a) $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ and the products obtained by reaction with 4-butylaniline at room temperature for (b) 15 min and (c) 16 h.

coating the solution.²³ We characterized in the present study the powder obtained by evaporating the solvent and subsequent grinding of the resulting solid.

The powder XRD pattern of the powder sample, shown in Fig. 4a, exhibits a diffraction peak at $d = 2.84$ nm, which was somewhat larger than the basal spacing of the initial intercalation compound. The broadness of this peak and the halo around $2\theta = 20^\circ$ indicate poor crystallinity, contrasting with a sharp diffraction peak observed for the film sample (Fig. 4c).²³ The IR spectrum of the powder (KBr disk) was similar to that of the initial intercalation compound, as shown in Fig. 5, while the relative intensity of the absorption bands due to 4-butylaniline increased. This phenomenon is common to both the recovered powder and film samples. The CHN analysis of the recovered powder gave the following results: C: 55.3%, H: 7.0%, N: 5.9% (although the C/N atomic ratio was 11, slightly larger than the theoretical value ($C/N = 10$) for 4-butylaniline; this may be due to an experimental error or incomplete removal of the solvent). These values determine the composition of the sample as $(\text{C}_4\text{H}_9\text{C}_6\text{H}_4\text{NH}_2)_{2.1}\text{VOPO}_4 \cdot n\text{H}_2\text{O}$ ($n \approx 1.5$); the recovered sample contained a large amount of 4-butylaniline. These results indicate that the layered structure of the VOPO_4 -4-butylaniline intercalation compound was

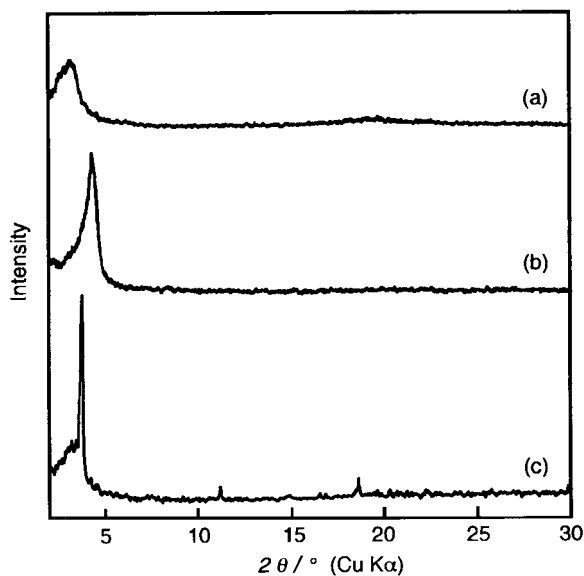


Fig. 4 XRD patterns of the samples obtained after the exfoliation of the VOPO₄-4-butylaniline intercalation compound in THF: (a) powder recovered from the liquid phase by evaporating THF from the liquid phase, (b) residual powder deposited in the suspension, and (c) film obtained from the solution by dip-coating at room temperature onto a glass substrate.

mostly reconstructed by evaporating the solvent from the exfoliated solution, and that the organic guest species was enriched in the solution through the exfoliation process.

In contrast with the exfoliated sample, the sedimentary (not exfoliated) deposit separated from the THF suspension was found to have reduced organic content. The composition of the sample was estimated as (C₄H₉C₆H₄NH₂)_{0.7}VOPO₄·*n*H₂O (*n* ≈ 1.5) by CHN analysis (C: 28.5%, H: 4.6%, N: 3.3%, C/N atomic ratio = 10); the amount of 4-butylaniline was smaller than in the initial VOPO₄-4-butylaniline intercalation compound ((C₄H₉C₆H₄NH₂)_{1.1}VOPO₄·*n*H₂O (*n* ≈ 1.3)). The IR spectrum (Fig. 5b) was similar to that of the initial intercalation compound, while the intensity of the adsorption bands due to the guest was somewhat small. The XRD pattern (Fig. 4b) exhibited a definite peak at *d* = 2.03 nm, which was smaller than the basal spacing of the initial intercalation compound. The small basal spacing would be in agreement with the small organic content, and tailing of the XRD peak to lower 2θ angle suggests that the sample was a mixture of intercalated VOPO₄ crystallites in which the organic content, and thus the basal spacing, varied.

We therefore suppose that 4-butylaniline is not tightly immobilized within the interlayer space of VOPO₄ but partly liberated into the exfoliated solution. This behavior would affect the basal spacing and crystallinity (ordering of stacked sheets) of the reconstructed samples. The basal spacing of the reconstructed sample should increase if liberated 4-butylaniline is entirely confined in the interlayers of the exfoliated sheets through reconstruction. In such a sample, the stacking regularity of the VOPO₄ layers would be altered because the arrangement of the organic species in the interlayer spaces is not the same as that in the initial intercalation compound. It is also possible that VOPO₄ layers themselves are partially degraded to form an amorphous precipitate with 4-butylaniline during exfoliation and subsequent drying. The XRD patterns indicate that the crystallinity of the reconstructed samples is sensitive to the experimental conditions; the dip-coating technique is favorable for obtaining samples with well-ordered stacking.

We also note that the reduced crystallinity of the powder sample after the exfoliation–reconstruction process was accompanied by morphological alteration (photographs are

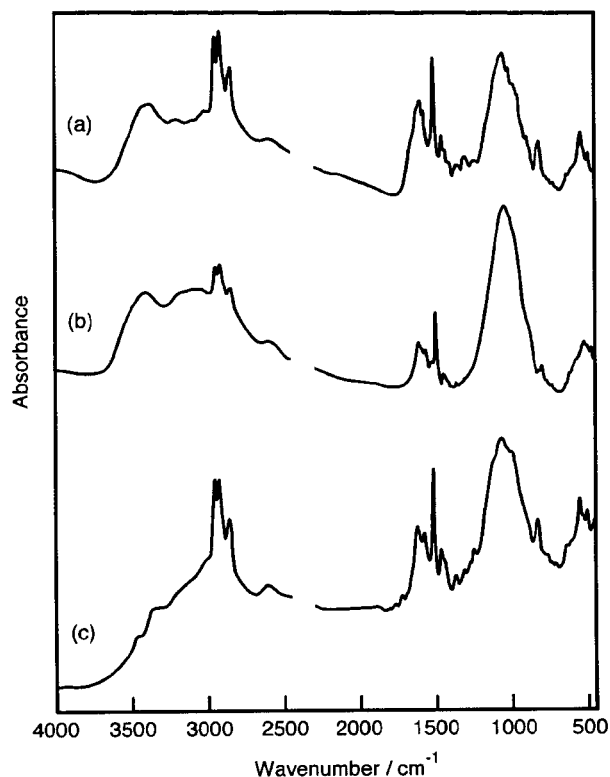


Fig. 5 IR spectra of the samples obtained after the exfoliation of the VOPO₄-4-butylaniline intercalation compound in THF: (a) powder recovered from the liquid phase by evaporating THF from the liquid phase, (b) residual powder deposited in the suspension, and (c) film obtained from the solution by dip-coating at room temperature onto an Si wafer.

not shown); the particle size of the reconstructed powder is small and the square shape is unclear although the platy character is retained. This morphology of the reconstructed powder differed greatly from the thin film-like shape of the sample obtained by careful dip-coating of the exfoliated solution onto α-Al₂O₃ particles.²³ This fact indicates that the morphology of the reconstructed solids is largely sensitive to, in other words controllable by, the conditions of the solvent removal.

Such modifications of the VOPO₄-4-butylaniline intercalation compound in its stacking regularity and morphology through the exfoliation–reconstruction treatment will be related to the structural features of VOPO₄·2H₂O. The oxide layers of this material consist of nearly coplanar single-layered sheets constructed by corner-sharing of VO₆ octahedra and PO₄ tetrahedra. Two of the oxygen atoms on each VO₆ octahedron do not contribute to the intralayer network but point to the interlayer space. This structure should be characterized by less thick and rigid inorganic sheets than those of other layered materials which have been reported to be exfoliated, *e.g.*, zirconium phosphate³¹ and montmorillonite.³² For example, the layers of zirconium phosphate consist of ZrO₆ octahedra whose six oxygen atoms are shared by PO₄ tetrahedra, and the tetrahedra are situated above and below the coplanar ZrO₆ plane to construct relatively thick and rigid layers.³³ Therefore, the VOPO₄ layers will be mechanically less rigid and more easily deformed.

Reactions with aniline and 4-anilinoaniline

Fig. 6(a) shows the XRD pattern and IR spectrum of the product obtained from the reaction of VOPO₄·2H₂O with aniline at 373 K for 24 h. The product gave a strong diffraction peak of *d* = 1.67 nm, indicating an increase in the basal spacing

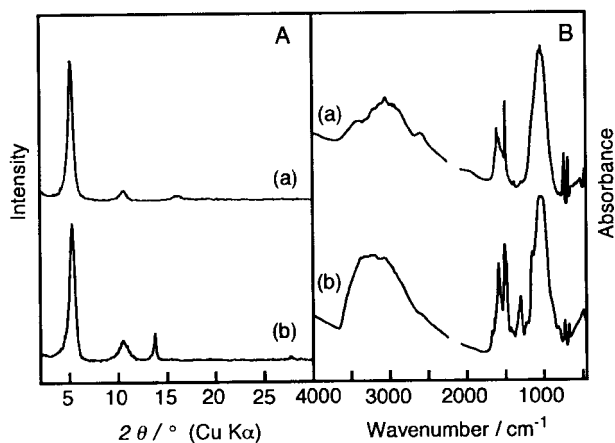


Fig. 6 XRD patterns (A, left) and IR spectra (B, right) of the products of the reaction of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ with (a) aniline at 373 K for 24 h and (b) 4-anilinoaniline at room temperature for 24 h.

of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$. When the reaction was conducted at room temperature for 24 h, diffraction peaks due to residual $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ were observed (not shown); an elevated reaction temperature (373 K) was necessary to obtain a single-phase product. The IR spectrum of the sample exhibited several absorption bands due to aniline: 1604 cm^{-1} , NH_2 bending; 1497 and 687 cm^{-1} , ring; 739 cm^{-1} , C–H bending. Platy particles similar to those of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ were observed in an SEM image (not shown) of the product.

The reaction of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ with 4-anilinoaniline gave similar results. The XRD pattern and IR spectrum of the product obtained by the reaction at room temperature for 24 h in an ethanolic solution are also given in Fig. 6. The XRD pattern shows an expansion of the basal spacing to 1.71 nm while peaks due to residual $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ can also be observed, and the IR spectrum exhibits absorption bands due to 4-anilinoaniline. The morphology of the sample (observed by SEM, not shown) was similar to that of the VOPO_4 -aniline intercalation compound.

These results are in accordance with the previous studies of the intercalation compounds of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ with aniline^{9,12} and 4-anilinoaniline.¹¹ In addition, the crystallographic, spectroscopic, and morphological characteristics of these intercalation compounds are common to the VOPO_4 -4-butylaniline intercalation compound. The single broad IR band around 1000 cm^{-1} was similarly observed in all the intercalation compounds.^{9,12}

The present study indicated that both aniline and 4-anilinoaniline were less reactive than 4-butylaniline. Intercalation of these aromatic amines proceeded slowly at room temperature for more than 24 h. In contrast, 4-butylaniline was intercalated within 15 min, and the layered structure of VOPO_4 was partly collapsed when the reaction was longer than 1 h at room temperature. This difference is related to the difference in basicity of the used amines. Aniline and 4-anilinoaniline have been reported to have $\text{p}K_a$ values of 4.6 and 2.2, respectively.³⁴ 4-Butylaniline should be more basic than these molecules owing to the electron-donating *n*-butyl group. Cas an *et al.* reported that interlayer water molecules coordinated to vanadium atom within $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ act as Br nsted acid sites.³⁵ Thus, basic molecules react with the interlayer acid sites to be accommodated within the host matrix. However, as mentioned above, the layered structure of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ will not be as mechanically rigid as typical layered metal phosphates, exemplified by $\text{Zr}(\text{HPO}_4)_2$, and the VO_6 octahedra in the layers should be reactive due to the presence of the unshared oxygen atoms. We presume that the $-\text{NH}_2$ group of aromatic amines can react with the interlayer acid sites, but

that the basicity of 4-butylaniline is stronger than the other amines, thus it can cleave the V–O–P bonding of the VOPO_4 framework during long reactions. Results of the reactions between $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ and *n*-alkylamines support this assumption (*vide post*).

Reactions of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ with *n*-alkylamines

Reactions of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ with *n*-alkylamines gave more complicated results than those with the aromatic amines. Fig. 7A shows XRD patterns of the products with *n*-hexylamine obtained by the reaction at room temperature. After reaction for 10 min, the diffraction peaks due to $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ disappeared, and an intense peak at $d = 1.81 \text{ nm}$, accompanied by higher-order peaks, and a shoulder at a slightly higher 2θ angle was observed. This d -value was smaller than the basal spacing of the VOPO_4 -*n*-hexylamine intercalation compounds investigated previously ($2\text{--}2.4 \text{ nm}$).^{3,4} When the reaction time was prolonged to 24 h, the shoulder became a definite diffraction peak at $d = 1.61 \text{ nm}$ with higher-order peaks (Fig. 7A(b)). These results imply the successive formation of two different compounds, which perhaps have lamellar structures.

The IR spectra of the samples shown in Fig. 7B, however, did not give evidence for the formation of intercalation compounds. The profile of the absorption bands due to the VOPO_4 lattice vibration around 1000 cm^{-1} drastically changed after the reaction. Many sharp absorption bands were observed, in contrast with the spectra of the intercalation compounds of VOPO_4 with aniline and its derivatives. This strongly suggests that the VOPO_4 layers were destroyed and that the connecting manner of the V–P–O unit was quite altered. On the other hand, the region around 1500 cm^{-1} indicates the presence of ammonium groups ($-\text{NH}_3^+$) in the products because of their characteristic adsorption bands, *e.g.*, 1580 and 1540 cm^{-1} , NH_3^+ bending; 1465 cm^{-1} , C–H bending. SEM observations (not shown) indicated that the morphology of the products was quite different from that of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$; flaky round fine particles much smaller than the $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ platelets were observed.

These facts imply that the reaction of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ with *n*-hexylamine produced a salt of V–P–O species with *n*-hexylammonium ion through dissolution–recrystallization by which the layered structure of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ was collapsed. We also note that reactions with *n*-butylamine and *n*-octylamine caused similar structural and spectroscopic changes of the host oxide. In these products, the connecting manner of the VOPO_4 unit was not retained, and such behavior was different from that of the reactions with aromatic amines.

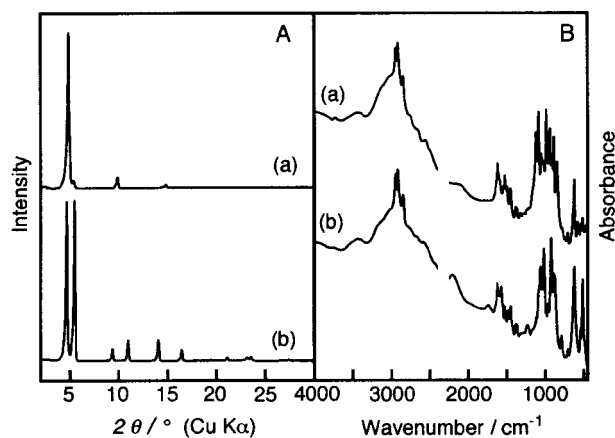


Fig. 7 XRD patterns (A, left) and IR spectra (B, right) of the products of the reaction of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ with *n*-hexylamine for (a) 10 min and (b) 24 h.

A major difference between *n*-alkylamines and aromatic amines, the latter which form intercalation compounds without collapsing of the VOPO₄ layers, is their basicity. Alkylamines are much more basic than aromatic amines, as characterized by their large p*K*_a value, around 10.³⁴ It is to be expected that such strong bases collapse the VOPO₄ layers, because less basic 4-butylaniline even led to partial collapse of the layered structure as described above. This phenomenon is in contrast with typical layered metal phosphates exemplified by Zr(HPO₄)₂, which form intercalation compounds with *n*-alkylamines.³⁶

Reactions of VOHPO₄·0.5H₂O with amines

In contrast with VOPO₄·2H₂O, VOHPO₄·0.5H₂O did not react with aromatic amines; in this study we examined pyridine, aniline, 4-anilinoaniline, and 4-butylaniline. In addition, reactions did not occur with *tert*-butylamine and di-*n*-butylamine. The low reactivity of VOHPO₄·0.5H₂O can be rationalized by its strong interlayer hydrogen bonding. The interlayer water molecule of VOHPO₄·0.5H₂O is located at a corner of the face-sharing VO₆ octahedra in a VOHPO₄ layer, and its hydrogen atom is held by a PO₄ tetrahedron in the adjacent layer through hydrogen bonding.³⁷ The VOHPO₄ layers are thus rather tightly linked together in contrast with the layers of VOPO₄·2H₂O.

Only *n*-alkylamines reacted with VOHPO₄·0.5H₂O. Fig. 8A shows XRD patterns of typical products obtained by the reactions with *n*-hexylamine and *n*-octylamine at room temperature for 2 days. Both the products gave diffraction peaks at 2θ angles lower than that corresponding to the basal spacing of VOHPO₄·0.5H₂O. The peaks due to VOHPO₄·0.5H₂O were also observed clearly for both the products, reflecting the low reactivity of VOHPO₄·0.5H₂O. The reaction product with *n*-hexylamine gave three anomalous diffraction peaks in the low 2θ region, while the diffraction pattern of the product with *n*-octylamine suggests a single-phase layered compound. However, the IR spectra, shown in Fig. 8B, showed that formation of the usual intercalation compounds did not occur for either *n*-alkylamine. The profile of the IR absorption bands due to the VOHPO₄ lattice (1200–500 cm⁻¹) was largely modified in the reaction products. We found that SEM images (not shown) of the products show that the particles of the products were considerably different in morphology from those of VOHPO₄·0.5H₂O.

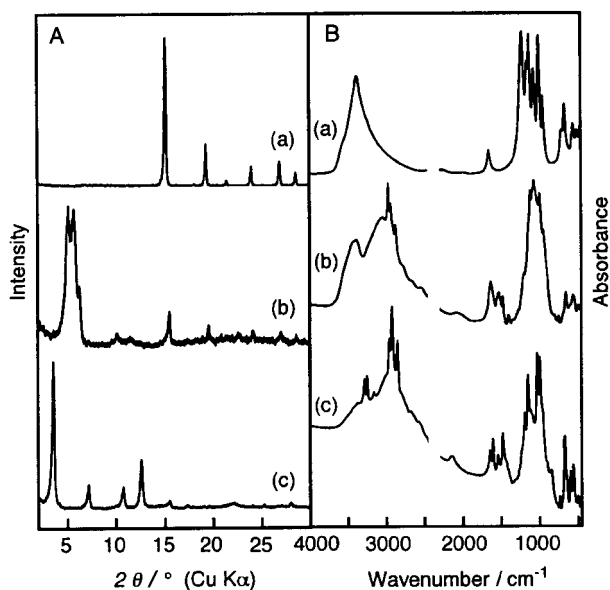


Fig. 8 XRD patterns (A, left) and IR spectra (B, right) of (a) VOHPO₄·0.5H₂O and the products of its reaction with (b) *n*-butylaniline and (c) *n*-octylamine at room temperature for 2 days.

Hence, we conclude that the reaction of VOHPO₄·0.5H₂O with *n*-alkylamines did not give intercalation compounds but products structurally very different from VOHPO₄·0.5H₂O, through dissolution–recrystallization. The strong basicity of *n*-alkylamines would collapse the VOHPO₄ lattice frameworks, as in the case of the reaction of VOPO₄·2H₂O with *n*-alkylamines.

Conclusions

The present study clarifies that the layered structures of VOPO₄·2H₂O and VOHPO₄·0.5H₂O are collapsed by reaction with strong basic compounds such as *n*-alkylamines. This is due to the relatively low stability of the layered frameworks of the V–P oxides to reactions with organic bases, in comparison with layered structures of tetravalent metal phosphates, exemplified by zirconium phosphates and tin phosphates.³⁶ The reactions of VOPO₄·2H₂O with 4-butylaniline indicate that the layered host can be collapsed by reaction even with aromatic amines under severe reaction conditions. The results also show the metastable nature of the intercalation compounds.

The THF treatment of the VOPO₄–4-butylaniline intercalation compound evidenced that oxovanadium phosphates can be exfoliated similarly to zirconium phosphate,^{31,38} although the tendency of the VOPO₄ sheets to degrade during the exfoliation–reconstruction process would reflect the relatively low stability of the lattice structure. Various molecular assemblies based on vanadium phosphorus oxides may be constructed by careful intercalation–exfoliation experiments, which are necessary to avoid severe structural alteration of the host lattice.

Acknowledgments

T. N. thanks the financial support of the Sumitomo Foundation, the Mitsubishi Chemical Corporation Fund, and a Grant-in-Aid for Encouragement of Young Scientists (No. 11750722) from the Ministry of Education, Science, Sports, and Culture of Japan. Mr. Naoki Yamamoto (Graduate School of Environmental Earth Science, Hokkaido University) is acknowledged for his help in preparation of the manuscript.

References

- 1 G. Ladwig, *Z. Anorg. Allg. Chem.*, 1965, **338**, 266.
- 2 H. R. Tietze, *Aust. J. Chem.*, 1981, **34**, 2035.
- 3 K. Beneke and G. Lagaly, *Inorg. Chem.*, 1983, **22**, 1503.
- 4 L. Beneš, R. Hyklová, J. Kalousová and J. Votinský, *Inorg. Chim. Acta*, 1990, **177**, 71.
- 5 M. M. Lara, L. M. Real, A. J. Lopez, S. B. Gamez and A. R. Garcia, *Mater. Res. Bull.*, 1986, **21**, 13.
- 6 L. Beneš, J. Votinský, J. Kalousová and J. Klikorka, *Inorg. Chim. Acta*, 1986, **114**, 47.
- 7 L. Beneš, K. Melánová, V. Zima, J. Kalousová and J. Votinský, *Inorg. Chem.*, 1997, **36**, 2850.
- 8 L. Beneš, J. Votinský, J. Kalousová and K. Handlř, *Inorg. Chim. Acta*, 1990, **176**, 255.
- 9 H. Nakajima and G. Matsubayashi, *Chem. Lett.*, 1993, 423.
- 10 A. De Stefanis and A. A. G. Tomlinson, *J. Mater. Chem.*, 1994, **5**, 319.
- 11 H. Nakajima and G. Matsubayashi, *J. Mater. Chem.*, 1995, **5**, 105.
- 12 A. De Stefanis, S. Foglia and A. A. G. Tomlinson, *J. Mater. Chem.*, 1995, **5**, 475.
- 13 T. Yatabe and G. Matsubayashi, *J. Mater. Chem.*, 1996, **6**, 1849.
- 14 T. Yatabe, M. Nakano and G. Matsubayashi, *J. Mater. Chem.*, 1998, **8**, 699.
- 15 V. Zima, L. Beneš and K. Melánová, *Solid State Ionics*, 1998, **106**, 285.
- 16 J. W. Johnson, A. J. Jacobson, J. F. Brody and S. M. Rich, *Inorg. Chem.*, 1982, **21**, 3820.
- 17 A. J. Jacobson, J. W. Johnson, J. F. Brody, J. C. Scanlon and J. T. Lewandowski, *Inorg. Chem.*, 1985, **24**, 1782.
- 18 M. M. Lara, A. J. Lopez, L. M. Rael, S. Bruque, B. Casal and E. Ruiz-Hitzky, *Mater. Res. Bull.*, 1985, **20**, 549.

- 19 G. Matsubayashi, S. Ohta and S. Okuno, *Inorg. Chim. Acta*, 1991, **184**, 47.
- 20 V. Zima, L. Beneš, J. Votinský and J. Kalousová, *Solid State Ionics*, 1995, **82**, 33.
- 21 J. W. Johnson, D. C. Johnston, A. J. Jacobson and J. F. Brody, *J. Am. Chem. Soc.*, 1984, **106**, 8123.
- 22 G. Centi, F. Trifirò, J. R. Ebner and V. M. Franchetti, *Chem. Rev.*, 1988, **88**, 55.
- 23 T. Nakato, Y. Furumi and T. Okuhara, *Chem. Lett.*, 1998, 611.
- 24 V. V. Gulians, J. B. Benziger and S. Sundaresan, *Chem. Mater.*, 1994, **6**, 353.
- 25 C. R'Kha, M. T. Vandenborre, J. Livage, R. Prost and E. Huard, *J. Solid State Chem.*, 1986, **63**, 202.
- 26 H. Igarashi, K. Tsuji, T. Okuhara and M. Misono, *J. Phys. Chem.*, 1993, **97**, 7065.
- 27 E. Bordes, P. Courtine and G. Pannetier, *Ann. Chim.*, 1973, **8**, 105.
- 28 *The Aldrich Library of FT-IR Spectra*, ed. C. J. Pouchert, Aldrich Chemical, Milwaukee, 1st edn., 1985, vol. 1.
- 29 4-Butylanilinium hydrochloride was prepared by the following method: HCl was added to 4-butylaniline to form a precipitate, which was then washed with diethyl ether and recrystallized from butanol. It exhibited characteristic IR bands at 2928, 2860, 2607, 1618, 1578, and 1510 cm^{-1} .
- 30 G. Centi, I. Manenti, A. Riva and F. Trofirò, *Appl. Catal.*, 1984, **9**, 177.
- 31 G. Alberti, M. Casciola and U. Costantino, *J. Colloid Interface Sci.*, 1985, **107**, 256.
- 32 E. R. Kleinfeld and G. S. Furgason, *Science*, 1994, **265**, 370.
- 33 A. Clearfield and G. D. Smith, *Inorg. Chem.*, 1969, **8**, 431.
- 34 *Dissociation Constants of Organic Bases in Aqueous Solution*, ed. P. D. Perrin, Butterworth, London, 1965.
- 35 N. Casãn, P. Amorós, R. Ibañez, E. Martínez-Tamayo, A. Beltrán-Porter and D. Beltrán-Porter, *J. Incl. Phenom.*, 1988, **6**, 193.
- 36 A. Clearfield, in *Progress in Intercalation Chemistry*, ed. W. Müller-Warmuth and R. Schöllhorn, Kluwer Academic Publishers, Dordrecht, 1994, p. 223.
- 37 E. Bordes, P. Courtine and J. W. Johnson, *J. Solid State Chem.*, 1984, **55**, 270.
- 38 S. W. Keller, H.-N. Kim and T. E. Mallouk, *J. Am. Chem. Soc.*, 1994, **116**, 8817.

Paper a908139i