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Intercalation compound of $VOPO_4 \cdot 2H_2O$ with acrylamide: preparation and exfoliation

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Reaction of acrylamide with vanadium phosphorus oxide $VOPO_4 \cdot 2H_2O$ at room temperature yielded the intercalation compound without degradation of the $VOPO_4$ layers. Two types of intercalation compounds were formed: the intercalation compound washed with *n*-heptane accommodated acrylamide with a bilayer arrangement, and the sample washed with acetone occluded the guest species with a monolayer. Both the $VOPO_4$–acrylamide intercalation compounds were exfoliated in 1- or 2-butanol. The exfoliated oxide layers were reconstructed to layered $VOPO_4$ materials by removal of the solvents, while acrylamide was partly deintercalated during the exfoliation–reconstruction process. The layered materials reconstructed from the exfoliated $VOPO_4$ layers were characterized by their morphology: the reconstructed samples consisted of aggregated small flakes which were morphologically very different from relatively large square platelets observed for both the starting vanadium phosphorus oxide and the initial intercalation compound.

Introduction

Oxovanadium phosphate $VOPO_4 \cdot 2H_2O$ is a layered compound characterized by its 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 V–P–O sheets.[2] $VOPO_4 \cdot 2H_2O$ intercalates various molecules and ions through different routes.[3] Organic molecules, such as amines,[4–11] amides,[12] alcohols,[13,14] carboxylic acids,[15] amino acids,[16] and poly(oxyethylene) compounds[17] are accommodated by polar adsorption. Pyridine is coordinatively incorporated into the interlayer space.[18] Some cationic species are taken up *via* a redox mechanism in the presence of reductive reagents.[19–21] $VOPO_4 \cdot 2H_2O$ is also known as a catalyst precursor; it is reduced to the layered material $VOHPO_4 \cdot 0.5H_2O$ and then pyrolyzed to $(VO)_2P_2O_7$,[22] which is an industrial catalyst for the selective oxidation of *n*-butane to maleic anhydride.[23] Intercalation of $VOPO_4 \cdot 2H_2O$ may be utilized as a method of preparing nanostructurally modified catalyst precursors.[24]

We have recently reported the intercalation of $VOPO_4 \cdot 2H_2O$ with 4-butylaniline.[24–26] The $VOPO_4$–4-butylaniline intercalation compound is characterized by its exfoliation properties: it is delaminated in THF and reconstructed by removal of the solvent while ordering of the restacked layers is sensitive to the experimental conditions. However, we found that $VOPO_4 \cdot 2H_2O$ partially collapsed upon reaction with 4-butylaniline for prolonged periods. In addition, the $VOPO_4$–4-butylaniline intercalation compound tends to degrade during the exfoliation–reconstruction process. Exfoliation of $VOPO_4$ sheets without such structural damage should be preferable for utilizing the exfoliated layers to prepare nanostructurally modified catalyst precursors.

In the present study, we attempted the exfoliation of $VOPO_4 \cdot 2H_2O$ through intercalation of amides which are expected not to degrade the oxide layers because of their relatively low basicity. Acrylamide was incorporated into $VOPO_4 \cdot 2H_2O$, and the obtained intercalation compound was successfully exfoliated in butanols, which have been utilized for reducing $VOPO_4 \cdot 2H_2O$ to the catalyst precursor $VOHPO_4 \cdot 0.5H_2O$.[22,27] The intercalated structure was reconstructed from the exfoliated sheets, but the morphology of the reconstructed sample, characterized by aggregated small flakes, was different from that of the initial intercalation compound which consisted of large plate-like particles.

Experimental

Materials

$VOPO_4 \cdot 2H_2O$ was prepared according to the literature by refluxing a mixture of V_2O_5 (24 g, Wako), 85% H_3PO_4 (133 cm^3, Wako) and H_2O (577 cm^3) at 388 K for 16 h.[1] The product was filtered, washed with acetone, and then kept under ambient conditions. Powder X-ray diffraction (XRD) and IR spectroscopy identified the product as $VOPO_4 \cdot 2H_2O$.[1,28] Organic reagents used were purchased from Wako, and used without further purification.

Synthesis of intercalation compounds

We prepared intercalation compounds of $VOPO_4 \cdot 2H_2O$ with acrylamide and *N*,*N*-dimethylformamide (DMF). For the reaction of $VOPO_4 \cdot 2H_2O$ with acrylamide, powder $VOPO_4 \cdot 2H_2O$ (1 g) was added to acrylamide (10 g) dissolved in ethanol (40 g), and the mixture was stirred at 303 K for 72 h. The product was washed with *n*-heptane or acetone, and then dried under ambient conditions. The reaction with DMF was carried out at a relatively high temperature according to the literature:[12] $VOPO_4 \cdot 2H_2O$ (0.8 g) was added to neat DMF (10 cm^3), and the mixture was stirred at 383 K for 6 h. The product was washed with acetone and dried under ambient conditions.

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Exfoliation of the intercalation compounds

The $VOPO_4$–acrylamide intercalation compound, in powder form (0.5 g), was added to 1- or 2-butanol followed by stirring at room temperature for 24 h. The obtained suspensions were allowed to stand for more than 7 days, after which the residual unexfoliated powder had settled out and the liquid phase had become transparent. The supernatant was then separated by decantation, and dried to solid under ambient conditions. The residual solid was dried under ambient conditions.

Analytical instruments

Powder XRD patterns were recorded on a Rigaku MiniFlex diffractometer (Ni-filtered CuKα radiation). IR spectra of the solid samples were measured by a Bio-rad FTS-7 spectrometer using the KBr disk technique. SEM images were taken by using a Hitachi S-2100A scanning electron microscope. The organic content of the sample was measured by CHN analysis at Center for Instrumental Analysis, Hokkaido University.

Results and discussion

Formation of $VOPO_4$–acrylamide intercalation compound

The reaction of $VOPO_4{\cdot}2H_2O$ with acrylamide in ethanolic solution expanded the basal spacing of the layered oxide to form an intercalation compound. Fig. 1 shows the XRD patterns of the samples. The product washed with *n*-heptane (Fig. 1b) has a basal spacing (d_{001} spacing) of 1.40 nm ($2\theta = 6.30°$), which is larger than those of $VOPO_4{\cdot}2H_2O$ (0.74 nm) and anhydrous $VOPO_4$ (0.41 nm).[29] The gallery height of the reaction product is estimated as 0.99 nm by subtracting the basal spacing of anhydrous $VOPO_4$ from that of the product. This value is the same as the gallery height of the montmorillonite–acryalmide intercalation compound where acrylamide molecules are accommodated with a bilayer arrangement.[30]

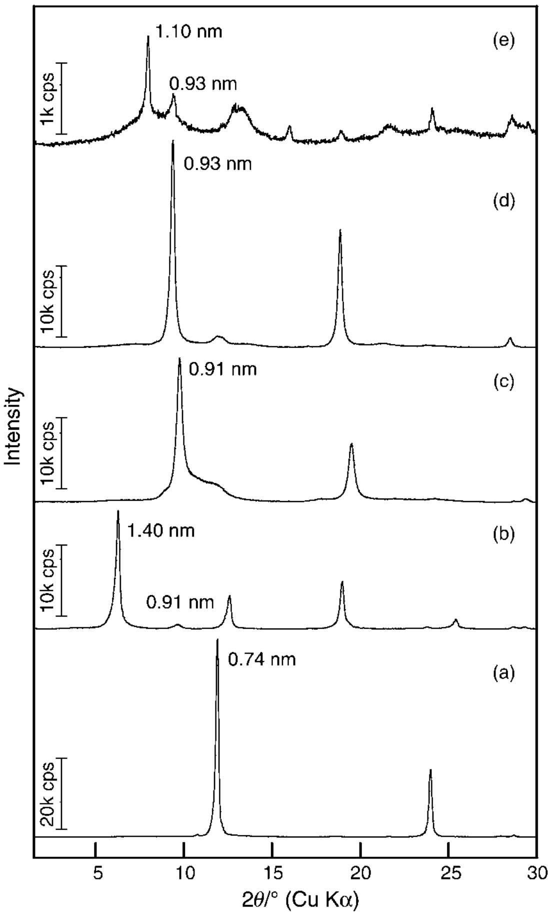

Fig. 1 XRD patterns of (a) $VOPO_4{\cdot}2H_2O$, the $VOPO_4$–acrylamide intercalation compounds washed with (b) *n*-heptane and (c) acetone, and the products obtained by reaction with DMF for (d) 6 h and (e) 24 h.

Fig. 1b also exhibits a small diffraction peak at $d = 0.91$ nm ($2\theta = 9.68°$), in addition to the peak at $d = 1.40$ nm. If we regard this peak as another phase of the acrylamide-intercalated $VOPO_4$ compound, the increment in the basal spacing is estimated as 0.50 nm. It has been reported that acrylamide molecules are intercalated into montmorillonite with both bilayer and monolayer arrangements; the monolayer orientation expands the basal spacing by 0.54 nm.[30] In addition, the kaolinite–acrylamide and α-$Zr(HPO_4)_2$–acrylamide intercalation compounds, in which acrylamide is arranged in monolayers, have been reported to have gallery heights of 0.41 nm[31] and 0.35 nm,[32] respectively. Hence, we assign the minor diffraction peak at $d = 0.91$ nm observed in the present study to another phase of the $VOPO_4$–acrylamide intercalation compound which is characterized by a monolayer orientation of the intercalated acrylamide.

The IR spectrum of the product obtained by the reaction of $VOPO_4{\cdot}2H_2O$ with acrylamide exhibits many absorption bands due to acrylamide, as shown in Fig. 2b: *e.g.*, 3490–3170 cm^{-1}, ν(N–H); 1683 (shoulder) and 1660 cm^{-1}, ν(C=O); 1615 cm^{-1}, ν(C=C); 1588 and 1560 cm^{-1}, δ(NH_2); 1431 cm^{-1}, δ(CH_2).[33,34] As for the absorption bands assignable to $VOPO_4$ lattice vibrations (1100–400 cm^{-1}), the band due to ν(P–O), which appears in the spectrum of $VOPO_4{\cdot}2H_2O$ at 1090 cm^{-1},[28] is weak in the product, whereas the other bands are essentially the same as those observed for $VOPO_4{\cdot}2H_2O$. This absorption profile indicates retention of the layered structure of $VOPO_4$ and suggests a certain interaction between the acrylamide and the P–O groups of the $VOPO_4$ layers. These results support the formation of the $VOPO_4$–acrylamide intercalation compound. The CHN analysis (C: 21.4%, H: 3.4%, N: 8.6%, C/N atomic ratio = 3.0) determined the composition of the product to be $(CH_2{=}CHCONH_2)_{1.8}VOPO_4{\cdot}nH_2O$. SEM observations, shown

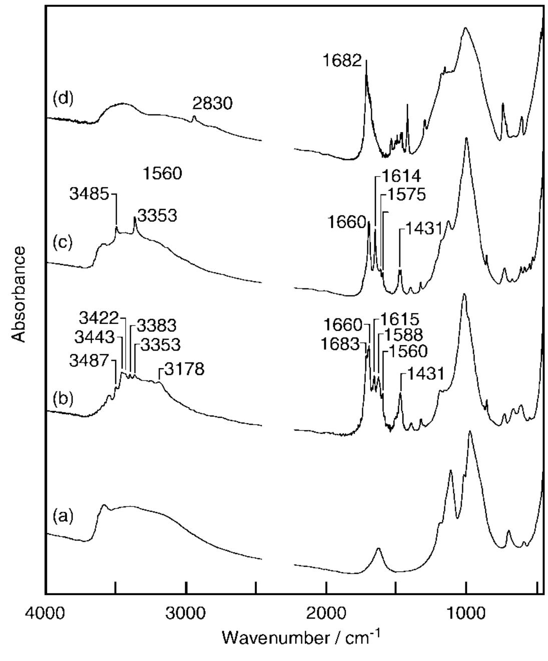

Fig. 2 IR spectra of (a) $VOPO_4{\cdot}2H_2O$, the $VOPO_4$–acrylamide intercalation compounds washed with (b) *n*-heptane and (c) acetone, and (d) the product obtained by reaction with DMF for 6 h.

in Fig. 3, proved that the $VOPO_4$–acrylamide intercalation compound consisted of plate-like particles morphologically similar to those of $VOPO_4 \cdot 2H_2O$. This result supports that the layered structure of the starting material is retained in the product, while the corners of the square $VOPO_4 \cdot 2H_2O$ particles become round after the intercalation.

Intercalation compound obtained after washing with acetone

When the reaction product was washed with acetone instead of *n*-heptane, only the 0.91 nm phase of the intercalation compound was observed in the XRD pattern, as shown in Fig. 1c. While a shoulder at around $2\theta = 12°$ indicates the presence of $VOPO_4 \cdot 2H_2O$, which may form through complete deintercalation of acrylamide, the major diffraction peak of $d = 0.91$ nm is assigned to the $VOPO_4$–acrylamide intercalation compound with a monolayer interlayer arrangement of acrylamide, as described above. SEM images of this sample (not shown) were essentially the same as those of the $VOPO_4$–acrylamide intercalation compound washed with *n*-heptane, indicating that morphological alterations, which often reflect severe structural modifications such as partial degradation of the $VOPO_4$ layers, did not occur during the acetone treatment. The IR spectrum of the sample, shown in Fig. 2c, exhibits several absorption bands due to acrylamide: *e.g.*, 3485 and 3353 cm^{-1}, ν(N–H); 1660 cm^{-1}, ν(C=O); 1615 cm^{-1}, ν(C=C); 1575 and 1560 cm^{-1}, $\delta(NH_2)$; 1431 cm^{-1}, $\delta(CH_2)$.[33,34] The composition of the sample was estimated from the CHN analysis as $(CH_2{=}CHCONH_2)_{1.1}VOPO_4 \cdot nH_2O$ (C: 15.9%, H: 2.9%, N: 6.2%), indicating that the amount of intercalated acrylamide is smaller than that in the above-described intercalation compound where acrylamide is accommodated with the bilayer arrangement. We distinguish hereafter the two intercalation compounds as the monolayer-type and bilayer-type intercalation compounds.

The IR spectra of the intercalation compounds give information about the interlayer microenvironments of acrylamide. For both types of intercalation compound, the absorption bands due to ν(C=O), ν(C=C), and $\delta(NH_2)$ all appear at wavenumbers lower than those of free acrylamide.[33] A similar shift to lower wavenumbers has been observed in the spectra of acrylamide–metal comlexes,[34] where the $-NH_2$ group of acrylamide has been presumed to interact with metal ions. Thus, we infer the presence of interactions between the $-NH_2$ group of the intercalated acrylamide and the $VOPO_4$ layers in the $VOPO_4$–acrylamide intercalation compounds. On the other hand, the spectra indicate a difference in the microenvironments of acrylamide between the bilayer- and monolayer-type intercalation compounds. The spectrum of the bilayer-type intercalation compound is characterized by the appearance of several absorption bands due to ν(N–H), which overlap each other, at 3490–3170 cm^{-1}. The band due to ν(C=O) at 1660 cm^{-1} is not a singlet but is accompanied by a shoulder at 1683 cm^{-1}. In contrast, the monolayer-type compound exhibits two distinct bands due to ν(N–H) at 3485 and 3353 cm^{-1}, and a single band of ν(C=O) at 1660 cm^{-1}. These differences suggest that acrylamide molecules in the bilayer-type compound are in a heterogeneous state while the guest species in the monolayer-type compound are in a rather homogeneous state.

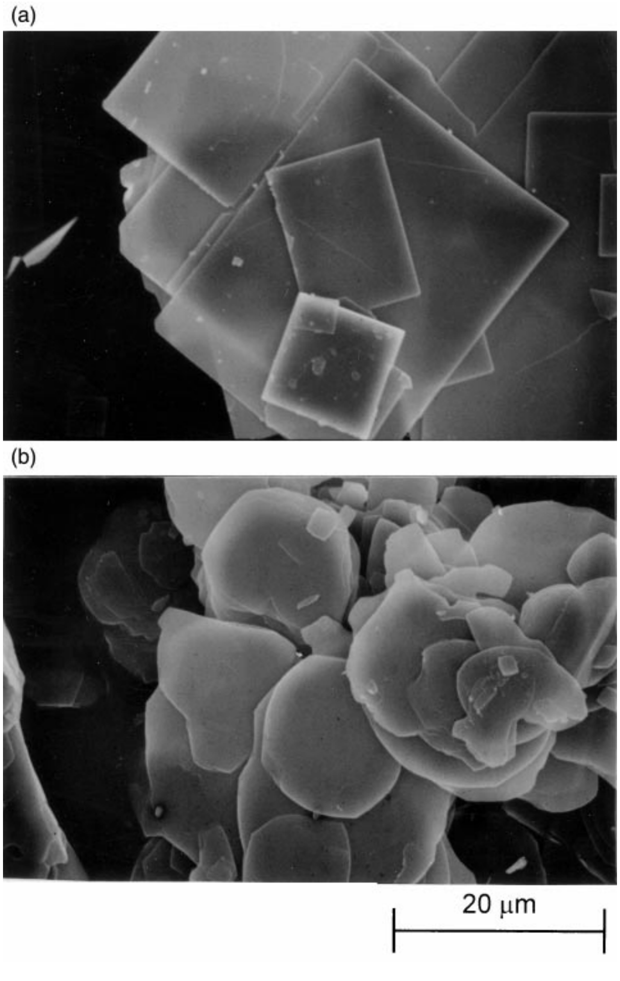

Fig. 3 SEM images of (a) $VOPO_4 \cdot 2H_2O$ and (b) the $VOPO_4$–acrylamide intercalation compound washed with *n*-heptane.

Formation of $VOPO_4$–DMF intercalation compound

The reaction of $VOPO_4 \cdot 2H_2O$ with neat DMF at 383 K for 6 h yielded a product whose XRD pattern (Fig. 1d) showed expansion of the basal spacing by 0.93 nm. This value is similar to the basal spacing of the $VOPO_4$–DMF intercalation compound (0.949 nm) synthesized by Lara *et al.*[12] The IR spectrum of the product (Fig. 2d) exhibits characteristic absorption bands due to DMF (*e.g.*, 1680 cm^{-1}, ν(C=O); 1650 cm^{-1}, $\delta(NH_2)$), again similarly to the spectrum previously reported.[12] The absorption profile of the $VOPO_4$ lattice vibrations suggests interactions of DMF with the P–O group on the layers, as observed for the $VOPO_4$–acrylamide intercalation compounds. SEM observations confirmed the presence of plate-like particles (images not shown) which were morphologically very similar to those observed for the $VOPO_4$–acrylamide intercalation compounds. These data indicate the formation of the $VOPO_4$–DMF intercalation compound.

However, we found that reactions with DMF almost collapsed the layered structure of $VOPO_4 \cdot 2H_2O$ by prolonging the reaction period to 24 h. The XRD pattern of the sample after the reaction with DMF for 24 h (Fig. 1e) is characterized by poor crystallinity with several small peaks, although the layered nature of $VOPO_4 \cdot 2H_2O$ appears to be retained as evidenced by small peaks around $d = 1.1$ nm and $d = 0.93$ nm. Thus, the $VOPO_4$ layers should not be stable but should degrade under the present reaction conditions with DMF. We have already reported a comparable phenomenon: the layered structure of $VOPO_4 \cdot 2H_2O$ tends to collapse during lengthy reactions with 4-butylaniline although intercalation compounds can form without severe structural alteration of the $VOPO_4$ lattices through shorter reaction times.[26] The present results exemplify again the relatively low structural stability of $VOPO_4 \cdot 2H_2O$ against reactions with organic basic compounds. We did not examine the exfoliative properties of the $VOPO_4$–DMF intercalation compound because of this tendency to degrade.

Exfoliation of the bilayer-type $VOPO_4$–acrylamide intercalation compound in butanol

When a powder of the bilayer-type $VOPO_4$–acrylamide intercalation compound was stirred in 1-butanol, the solvent became green. After the stirring was stopped, most of the powders were settled out, while the colored liquid phase was found to be stable without any obvious change for at least a week; such behavior was similar to that observed for exfoliation of the $VOPO_4$–4-butylaniline intercalation compound.[26] About 24 mass% of the sample treated was transferred into the liquid phase. Preliminary XRD measurement of the colored supernatant dried by dip-coating onto a glass slide showed retention of the layered structure, suggesting exfoliation and reconstruction of the intercalation compound. We then prepared and characterized powder samples from the liquid phase by evaporating the solvent under ambient conditions.

The intercalated structure of $VOPO_4$ with acrylamide was reconstructed from the colored solution obtained by the treatment of the intercalation compound with 1-butanol, indicating the presence of the exfoliated $VOPO_4$ layers in the suspension. The XRD pattern of the powder sample prepared by evaporating 1-butanol from the supernatant, shown in Fig. 4a, reveals the presence of the bilayer-type $VOPO_4$–acrylamide intercalation compound and crystalline acrylamide. The diffraction peaks due to acrylamide disappeared after washing the sample with *n*-heptane to give a single-phase diffraction pattern of the bilayer-type intercalation compound (Fig. 4b). The composition of the washed product was determined from the CHN analysis (C: 15.5%, H: 3.1%, N: 6.0%) to be $(CH_2{=}CHCONH_2)_{1.1}VOPO_4{\cdot}nH_2O$, while that of the initial intercalation compound was $(CH_2{=}CHCONH_2)_{1.8}$-$VOPO_4{\cdot}nH_2O$ as mentioned above. The IR spectrum of this sample (Fig. 5a) exhibits a partially recovered P–O stretching absorption which is weak in the spectrum of the initial intercalation compound (Fig. 2b). These results indicate that the amount of acrylamide intercalated in the reconstructed sample is smaller than that in the initial intercalation compound; acrylamide is deintercalated to some extent during the dispersion–evaporation process.

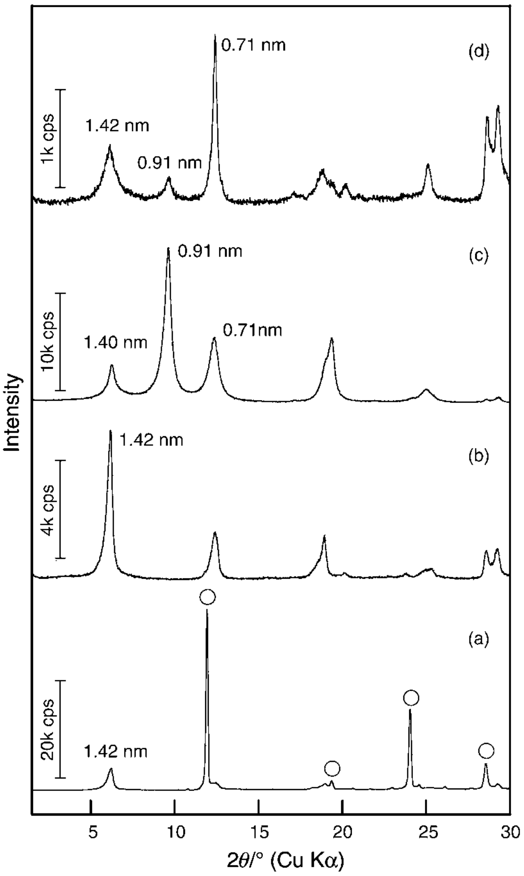

Fig. 4 XRD patterns of the samples obtained after the exfoliation of the bilayer-type and monolayer-type $VOPO_4$–acrylamide intercalation compounds in 1-butanol: (a) unwashed powder recovered from the bilayer-type intercalation compound exfoliated in 1-butanol by evaporating the solvent, (b) sample (a) after washing with *n*-heptane, (c) residual solid deposited in the suspension, and (d) powder recovered from the monolayer-type intercalation compound exfoliated in 1-butanol. Circles indicate diffraction peaks due to acrylamide.

We also note that the amount of acrylamide intercalated in the reconstructed intercalation compound is similar to that in the monolayer-type sample, although the acrylamide molecules are arranged in a bilayer. However, the IR bands due to acrylamide in the reconstructed sample resemble those in the initial bilayer-type intercalation compound. These data reveal that the interactions between acrylamide and the $VOPO_4$ layers in the initial bilayer-type intercalation compound are maintained to a large extent during exfoliation–reconstruction in 1-butanol. This result is in contrast with that of the acetone treatment which alters the host–guest interactions to yield the monolayer-type intercalation compound.

On the other hand, the residual sedimentary solid separated from the suspension did not completely retain the structure of the original bilayer-type intercalation compound. This sample was a mixture of three phases, as shown by its XRD pattern (Fig. 4c). The bilayer-type intercalation compound having a basal spacing of 1.40 nm ($2\theta = 6.30°$) was present only as a minor phase. The major phase characterized by the diffraction peak of $d = 0.91$ nm ($2\theta = 9.68°$) is assigned to the monolayer-type intercalation compound. In addition, the intense diffraction peak at $d = 0.71$ nm ($2\theta = 12.40°$), which is close to the basal spacing of $VOPO_4{\cdot}2H_2O$ (0.74 nm) and is overlapped by the second-order peak of the 1.40 nm-phase (bilayer-type intercalation compound), suggests the presence of deintercalated $VOPO_4{\cdot}nH_2O$. The IR spectrum of this sample (Fig. 5b) shows that the absorption bands due to acrylamide are weak

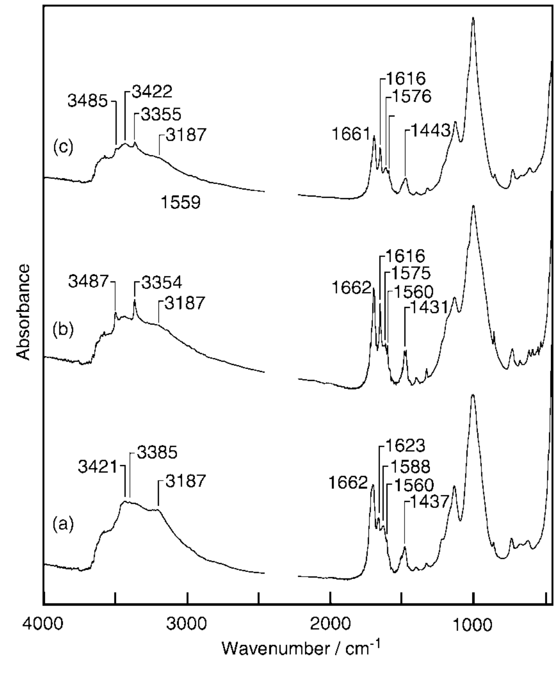

Fig. 5 IR spectra of the samples obtained after the exfoliation of the bilayer-type and monolayer-type $VOPO_4$–acrylamide intercalation compounds in 1-butanol: (a) powder recovered from the bilayer-type intercalation compound exfoliated in 1-butanol by evaporating the solvent and subsequent washing with *n*-heptane, (b) residual solid deposited in the suspension, and (c) powder recovered from the monolayer-type intercalation compound exfoliated in 1-butanol.

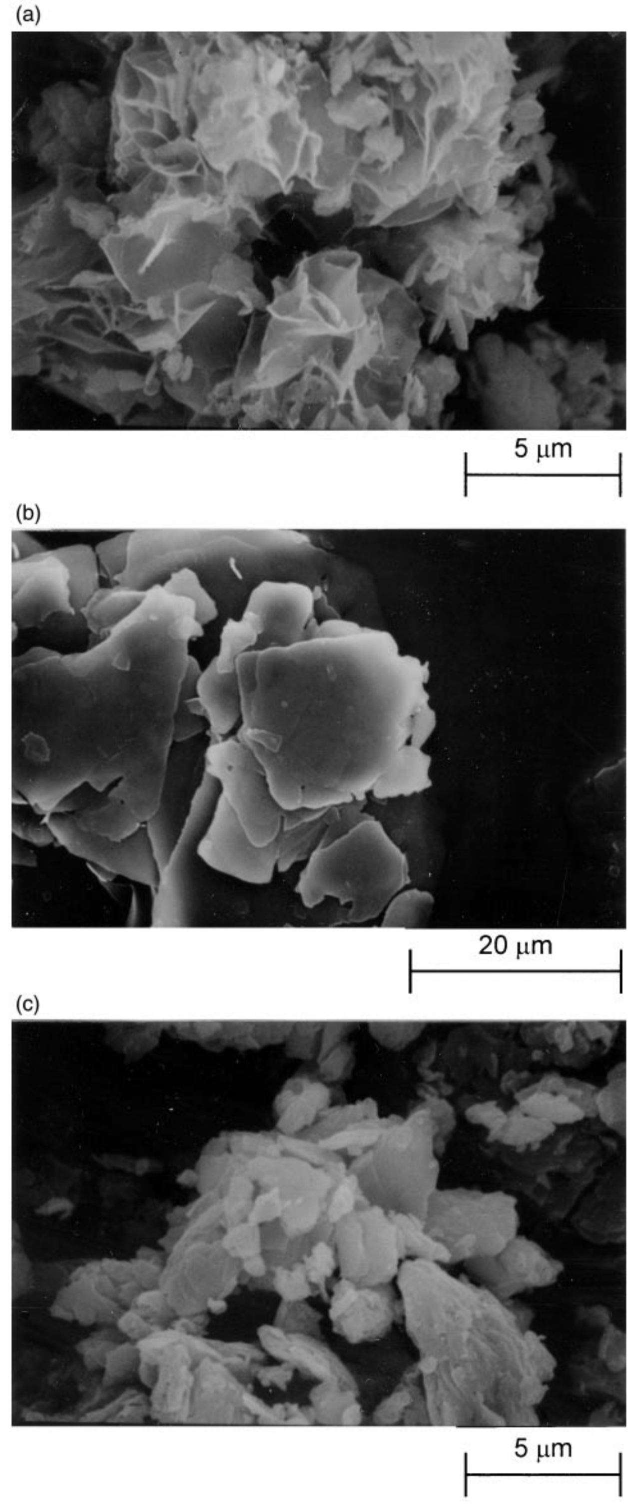

Fig. 6 SEM images of the samples obtained after the exfoliation of the bilayer-type and monolayer-type $VOPO_4$–acrylamide intercalation compounds in 1-butanol: (a) powder recovered from the bilayer-type intercalation compound exfoliated in 1-butanol by evaporating the solvent and washing with *n*-heptane, (b) residual solid deposited in the suspension, and (c) powder recovered from the monolayer-type intercalation compound exfoliated in 1-butanol.

relative to those of the initial bilayer-type $VOPO_4$–acrylamide intercalation compound. The composition of the sample was estimated from CHN analysis as $(CH_2{=}CHCONH_2)_{0.8}$-$VOPO_4 \cdot nH_2O$ (C: 12.1%, H: 2.4%, N: 4.8%). These results indicate again that a certain amount of acrylamide is deintercalated from the initial intercalation compound which was dissolved in 1-butanol during the alcohol treatment.

Treatment of the bilayer-type $VOPO_4$–acrylamide intercalation compound with 2-butanol gave results essentially the same as those observed for the 1-butanol treatment. The intercalation compound was partially and stably dispersed in 2-butanol, and the bilayer-type intercalated structure was reconstructed. Partial deintercalation of acrylamide was also observed as in the case of the treatment with 1-butanol.

We observed a remarkable difference between the initial and reconstructed intercalation compounds in their morphology. This morphological change occurred in both 1- and 2-butanols. The SEM image of the intercalation compound reconstructed from the exfoliated layers, shown in Fig. 6a, exhibits aggregates of small flakes which are much smaller than the plate-like particles of the initial intercalation compound (see Fig. 3b). However, this morphological change was observed only for the samples reconstructed from the supernatant; the powders which settled out after the butanol treatments almost retained the size and plate-like shape of the initial intercalation compound (Fig. 6b).

Therefore, we conclude that the bilayer-type $VOPO_4$–acrylamide intercalation compound is (partially) exfoliated in butanols. The platelets of the initial intercalation compound are cracked and cleaved during the butanol treatments into small flakes, which are stably dispersed into the solvents; the intercalation compound exfoliated in butanols should be present as small and thin (probably nm thickness) layers. The small flakes are reconstructed into the intercalation compound by evaporating the solvent, but form aggregated particles which are morphologically different from the initial intercalation compound. In contrast, the residual large plate-like particles of the intercalation compound which avoided the cleavage process cannot be exfoliated in the solvents, and thus the unexfoliated solid retains the morphology of the initial intercalation compound. This exfoliation–reconstruction process is schematically represented in Fig. 7.

Exfoliation of the monolayer-type $VOPO_4$–acrylamide intercalation compound

The monolayer-type $VOPO_4$–acrylamide intercalation compound was exfoliated in 1- and 2-butanols, similarly to the bilayer-type intercalation compound. Stable green supernatants were obtained when the monolayer-type $VOPO_4$–acrylamide intercalation compound was treated with butanols, suggesting exfoliation of the monolayer-type intercalation compound. However, this behavior was not absolutely the same as the exfoliating behavior of the bilayer intercalation compound; the difference was evidenced by XRD measurements of the solution phase dried by evaporating the solvent and washed subsequently with *n*-heptane.

The XRD pattern of the powder sample recovered from the suspension of the monolayer-type intercalation compound in 1-butanol, shown in Fig. 4d, resembles that of the unexfoliated solid of the 1-butanol-treated bilayer-type intercalation compound, rather than that of the reconstructed material obtained from the exfoliated part. The diffractogram indicates the presence of the bilayer-type intercalation compound by a peak

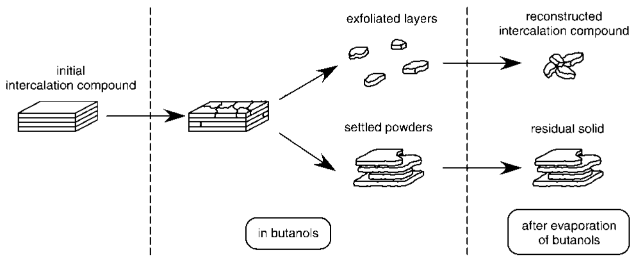

Fig. 7 Schematic representation of the exfoliation–reconstruction process of the $VOPO_4$–acrylamide intercalation compounds.

at $d = 1.42$ nm ($2\theta = 6.22°$) as well as the monolayer-type intercalation compound ($d = 0.91$ nm) and deintercalated $VOPO_4 \cdot nH_2O$ ($d = 0.71$ nm). This fact indicates that both deintercalation and re-intercalation dynamically occur in the suspension containing the exfoliated intercalated layers. As a result, the exfoliated monolayer-type $VOPO_4$–acrylamide intercalation compound would disproportionately form the three types of product after the exfoliation–reconstruction process. This structural alteration was not observed for the solid unexfoliated during the 1-butanol treatment; its XRD pattern indicated the presence of both the monolayer-type intercalation compound and $VOPO_4 \cdot 2H_2O$.

Powder samples reconstructed from the suspensions of exfoliated layers of the monolayer-type $VOPO_4$–acrylamide intercalation compound were morphologically different from the intercalation compound before exfoliation, as in the case of the exfoliated bilayer-type intercalation compound. The SEM image of the reconstructed sample, shown in Fig. 6c, exhibited aggregated flakes which are observed for the sample after reconstruction of the exfoliated monolayer-type intercalation compound. In contrast, the unexfoliated samples retained the plate-like morphology of the initial monolayer-type intercalation compound (photographs not shown). Such morphological alteration was essentially the same as that observed for the bilayer-type intercalation compound, suggesting that exfoliation–reconstruction of the $VOPO_4$–acrylamide intercalation compound proceeds independently of the interlayer orientation of acrylamide molecules through the process represented in Fig. 7.

We additionally note that the morphological alteration during the exfoliation–reconstruction of the $VOPO_4$–acrylamide intercalation compounds in butanols is somewhat similar to that observed in the preparation of $VOHPO_4 \cdot 0.5H_2O$ from $VOPO_4 \cdot 2H_2O$ by reduction using alcohols.[22,35] It has been reported that $VOPO_4 \cdot 2H_2O$ can be reduced by several alcohols to $VOHPO_4 \cdot 0.5H_2O$ which is morphologically characterized by "rose-like" aggregates. The rose-like particles consist of small flaky platelets, which are comparable with the flaky aggregated particles observed in this study. The alcohols have been presumed to be incorporated into the structure of $VOPO_4 \cdot 2H_2O$; they work as templates during the reduction process to determine the morphology of $VOHPO_4 \cdot 0.5H_2O$.[22] Our results strongly suggest that interlayer reactions of $VOPO_4 \cdot 2H_2O$ with alcohol play an important role in the morphological change during the reduction.

Conclusions

The present study demonstrates that the reaction of $VOPO_4 \cdot 2H_2O$ with acrylamide expands the interlayer space of the oxide to form two types of $VOPO_4$–acrylamide intercalation compound with different orientations of the intercalated guest species, and that both the intercalation compounds are exfoliative in alcohols. The exfoliation of $VOPO_4$ layers occurs together with partial deintercalation while the exfoliated layers can be reconstructed to the intercalation compound or $VOPO_4 \cdot 2H_2O$ by removal of the solvents. The morphology of the reconstructed samples, characterized by aggregated particles of small flakes, is very different from that of the sample before exfoliation. Such morphological alteration is a characteristic of the exfoliation process of layered compounds, as has been observed for other materials.[36] This property should be useful for preparing novel microstructurally modified V–P oxide materials. In addition, the morphological similarity between the reconstructed samples obtained in the present study and the previously reported rose-like particles of $VOHPO_4 \cdot 0.5H_2O$ should give a new insight to the formation of the important catalyst precursor $VOHPO_4 \cdot 0.5H_2O$.

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References

1 G. Ladwig, *Z. Anorg. Allg. Chem.*, 1965, **338**, 266.
2 H. R. Tietze, *Aust. J. Chem.*, 1981, **34**, 2035.
3 J. Kalousová, J. Votinský, L. Beneš, K. Melánová and V. Zima, *Collect. Czech. Chem. Commun.*, 1998, **63**, 1.
4 K. Beneke and G. Lagaly, *Inorg. Chem.*, 1983, **22**, 1503.
5 L. Beneš, R. Hyklová, J. Kalousová and J. Votinský, *Inorg. Chim. Acta*, 1990, **177**, 71.
6 H. Nakajima and G. Matsubayashi, *Chem. Lett.*, 1993, 423.
7 A. De Stefanis and A. A. G. Tomlinson, *J. Mater. Chem.*, 1995, **5**, 319.
8 H. Nakajima and G. Matsubayashi, *J. Mater. Chem.*, 1995, **5**, 105.
9 A. De Stefanis, S. Foglia and A. A. G. Tomlinson, *J. Mater. Chem.*, 1995, **5**, 475.
10 N. Kinomura, T. Toyama and N. Kumada, *Solid State Ionics*, 1995, **78**, 281.
11 T. Yatabe, M. Nakano and G. Matsubayashi, *J. Mater. Chem.*, 1998, **8**, 699.
12 M. M. Lara, L. M. Real, A. J. Lopez, S. B. Gamez and A. R. Garcia, *Mater. Res. Bull.*, 1986, **21**, 13.
13 L. Beneš, J. Votinský, J. Kalousová and J. Klikorka, *Inorg. Chim. Acta*, 1986, **114**, 47.
14 L. Beneš, K. Melánová, V. Zima, J. Kalousová and J. Votinský, *Inorg. Chem.*, 1997, **36**, 2850.
15 L. Beneš, J. Votinský, J. Kalousová and K. Handlíř, *Inorg. Chim. Acta*, 1990, **176**, 255.
16 V. Zima, L. Beneš and K. Melánová, *Solid State Ionics*, 1998, **106**, 285.
17 K. Melánová, L. Beneš, V. Zima and R. Vahalová, *Chem. Mater.*, 1999, **11**, 2173.
18 J. W. Johnson, A. J. Jacobson, J. F. Brody and S. M. Rich, *Inorg. Chem.*, 1982, **21**, 3820.
19 A. J. Jacobson, J. W. Johnson, J. F. Brody, J. C. Scanlon and J. T. Lewandowski, *Inorg. Chem.*, 1985, **24**, 1782.
20 M. M. Lara, A. J. Lopez, L. M. Real, S. Bruque, B. Casal and E. Ruiz-Hitzky, *Mater. Res. Bull.*, 1985, **20**, 549.
21 G. Matsubayashi, S. Ohta and S. Okuno, *Inorg. Chim. Acta*, 1991, **184**, 47.
22 J. W. Johnson, D. C. Johnston, A. J. Jacobson and J. F. Brody, *J. Am. Chem. Soc.*, 1984, **106**, 8123.
23 G. Centi, F. Trifirò, J. R. Ebner and V. M. Franchetti, *Chem. Rev.*, 1988, **88**, 55.
24 N. Hiyoshi, N. Yamamoto, N. Terao, T. Nakato and T. Okuhara, *Stud. Surf. Sci. Catal.*, 2000, **130**, 1715.
25 T. Nakato, Y. Furumi and T. Okuhara, *Chem. Lett.*, 1998, 611.
26 T. Nakato, Y. Furumi, N. Terao and T. Okuhara, *J. Mater. Chem.*, 2000, **10**, 737.
27 I. J. Ellison, G. J. Hutchings, M. T. Sananes and J.-C. Volta, *J. Chem. Soc., Chem. Commun.*, 1994, 1093.
28 C. R'Kha, M. T. Vandenborre, J. Livage, R. Prost and E. Huard, *J. Solid State Chem.*, 1986, **63**, 202.
29 E. Bordes, P. Courtine and G. Pannetier, *Ann. Chim.*, 1973, **8**, 105.
30 M. Ogawa, K. Kuroda and C. Kato, *Clay Sci.*, 1989, **7**, 243.
31 Y. Sugahara, S. Satokawa, K. Kuroda and C. Kato, *Clays Clay Miner.*, 1990, **38**, 137.
32 Y. Ding, D. J. Jones, P. Maireles-Torres and J. Rozière, *Chem. Mater.*, 1995, **7**, 562.
33 N. Jonathan, *J. Mol. Spectrosc.*, 1961, **6**, 205.
34 M. F. Farona, W. T. Ayers, B. G. Ramsey and J. G. Grasselli, *Inorg. Chim. Acta*, 1969, **3**, 503.
35 M. T. Sananes, I. J. Ellison, S. Sajip, A. Burrows, C. J. Kiely, J. C. Volta and G. J. Hutchings, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 137.
36 G. B. Saupe, C. C. Waraksa, H.-Y. Kim, Y. J. Han, D. M. Kaschak, D. M. Skinner and T. E. Mallouk, *Chem. Mater.*, 2000, **12**, 1556.