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The First $VOPO_4 \cdot 2H_2O$ Intercalation Compound Synthesized through a Solid-State Reaction at Room Temperature

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This communication reports the first intercalation into $VOPO_4 \cdot 2H_2O$ performed through a solid-state reaction at room temperature. Ethyleneurea, EU (2-imidazolidone) was intercalated into the oxovanadium phosphate by grinding in a mortar stoichiometric amounts of both reagents at room temperature for 30 min. C, H and N elemental analyses of the obtained intercalation compound gave the formula $VOPO_4 \cdot (EU) \cdot H_2O$. The profile of the absorption bands due to the $VOPO_4$ lattice vibration around 1000 cm^{-1} was retained after reaction, providing evidence that an intercalation compound and not merely a salt of V–P–O species was produced. For α-$VOPO_4 \cdot 2H_2O$, the interlayer distance is 0.75 nm, whereas for the EU intercalation compound it is 0.95 nm. The obtained SEM micrographs show that the microstructure of $VOPO_4 \cdot 2H_2O$ is changed after reaction, with a total exfoliation of the oxovanadium matrix. © 2002 Elsevier Science (USA)

INTRODUCTION

Oxovanadium phosphate $VOPO_4 \cdot 2H_2O$ is a layered compound exhibiting a high intercalating capability. Due to its uses as catalyst, or catalyst precursor, this compound has been extensively investigated (1–4). However, the intercalation reactions are always performed in solution, or employed as the guest species in the liquid state, at room temperature or under heating (5–7). Intercalation reactions in the vapor phase are also described (8). However, discrepancies between the neat liquid, solution and vapor-phase reactions are observed.

The aim of this communication is to report the first intercalation reaction involving oxovanadium phosphate, performed through a solid-state synthesis at room temperature.

EXPERIMENTAL

$VOPO_4 \cdot 2H_2O$ was synthesized as previously described (7). Ethyleneurea EU (2-imidazolidone) was of analytical grade from Aldrich, and was used without further purification. Ethyleneurea, whose structural formulae is shown in Fig. 1, was intercalated into the oxovanadium phosphate by grinding in a mortar stoichiometric amounts of both reagents at room temperature for 30 min.

Carbon, hydrogen and nitrogen elemental analyses were performed in a Perkin-Elmer apparatus. Infrared spectra were obtained in a Bomem apparatus in the range 4000–400 cm^{-1} with a resolution of 4 cm^{-1} by dispersing the samples in KBr disks. The X-ray diffraction patterns were obtained in a Shimadzu XD-3A equipment, using Cu$K\alpha$ radiation (35 kV, 25 mA). SEM micrographs were taken with a Jeol model JSM T-300 equipment with an accelerating voltage of 15 kV.

RESULTS AND DISCUSSION

The obtained elemental analysis results gave the values C = 13.40%, H = 2.21% and N = 10.38%, in good agreement with the calculated values of 13.54, 2.26 and 10.53%, respectively, for a compound of formula $VOPO_4 \cdot (EU) \cdot H_2O$.

Two types of molecules are present in $VOPO_4 \cdot 2H_2O$: one water molecule is coordinated to vanadium in a *trans* position to the V=O group (9). The other is situated between the layers, and both water molecules hold the layers together by hydrogen bonding to the oxide framework.

In the infrared spectrum of ethyleneurea, the amide I (C=O) band is located at 1685 cm^{-1}. On the other hand, for the intercalation compound, the same band is shifted to 1675 cm^{-1}. Such a decrease in the C=O vibration mode for EU is characteristic of a coordination through oxygen (10). Hence, an EU–V bond was formed, with EU replacing the water molecule coordinated to vanadium. The profile of the absorption bands due to the $VOPO_4$ lattice vibration around 1000 cm^{-1} was retained after reaction, providing evidence that an intercalation compound and not merely a salt of V–P–O species was produced (7).

The X-ray diffraction for α-$VOPO_4 \cdot 2H_2O$ (001, 101 and 002 diffraction peaks (9), with *d* values of 0.75, 0.48 and

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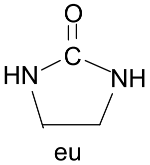

FIG. 1. Structural formulae for ethyleneurea.

0.37 nm, respectively) and the obtained intercalation compound (001 and 002 diffraction peaks with *d* values of 0.95 and 0.48 nm, respectively) are shown in Fig. 2. The diffraction pattern obtained for $VOPO_4 \cdot 2H_2O$ are in agreement with the previously reported results (9, 11). Based on the 001 diffraction peak shift, a Δd value of 0.20 nm can be calculated. The results shown in Fig. 1 imply that the layered structure of $VOPO_4 \cdot 2H_2O$ was retained after reaction, that is, the nanostructure remained unchanged.

The obtained SEM micrographs are shown in Fig. 3. $VOPO_4 \cdot 2H_2O$ exhibits a typical plate-like morphology. The SEM micrograph for $VOPO_4 \cdot (EU) \cdot H_2O$ shows that the microstructure of $VOPO_4 \cdot 2H_2O$ changes after reaction, with a total exfoliation of the oxovanadium matrix.

CONCLUSION

Based on the obtained experimental results, it can be concluded that the intercalation of organic species into lamellar $VOPO_4 \cdot 2H_2O$ can be performed through a solid-state reaction (with both, host and guest species in the solid state) by grinding in a mortar stoichiometric amounts of the inorganic matrix and the organic guest species. Preliminary results obtained for the solid-state intercalation of other organic species (ethylenethiourea, propyleneurea, hexamethylenetetramine, urea, glycine and nicotinamide, among others) (12) prove that the solid-state route employed for the intercalation of EU can be successfully employed as a routine intercalation procedure.

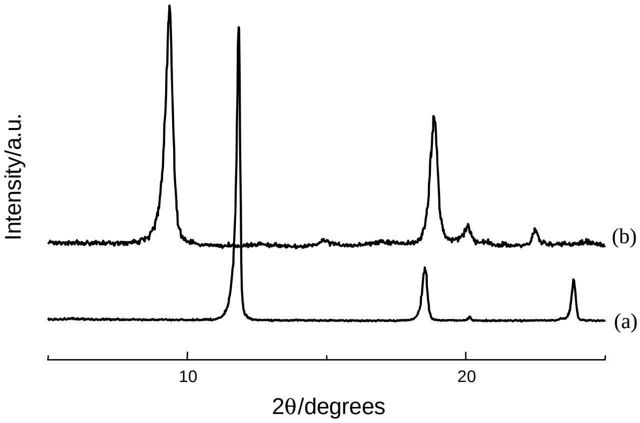

FIG. 2. X-ray diffraction patterns for $VOPO_4 \cdot 2H_2O$ (a) and $VOPO_4 \cdot (EU) \cdot H_2O$ (b).

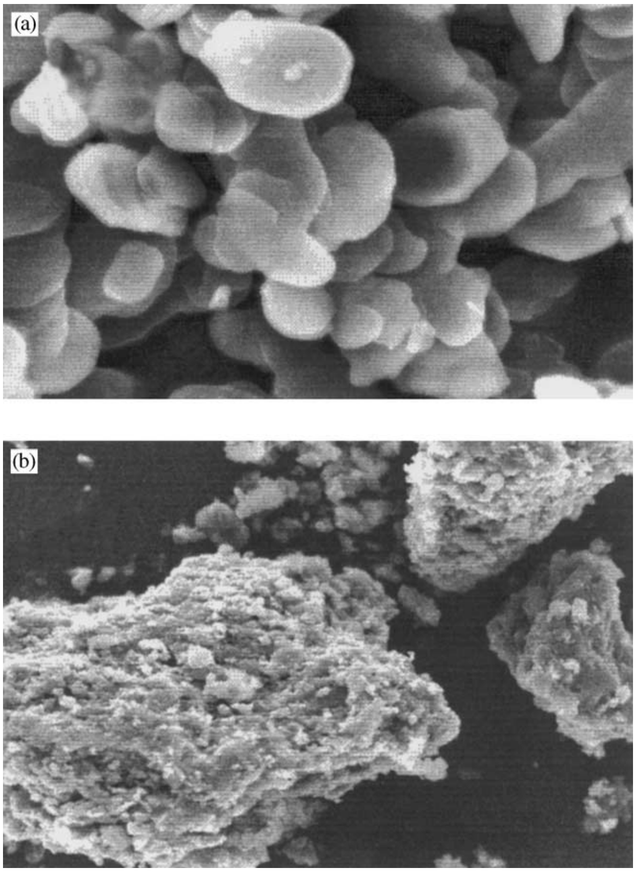

FIG. 3. SEM micrographs for $VOPO_4 \cdot 2H_2O$, 750X (a) and $VOPO_4 \cdot (EU) \cdot H_2O$, 1000X (b).

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