JOURNAL OF SOLID STATE CHEMISTRY **106**, 517–520 (1993)

LETTERS TO THE EDITOR

Intercalation of Alcohols into Layered Vanadyl Phosphonates

P. GENDRAUD,* M. E. DE ROY, AND J. P. BESSE

Laboratoire de Physico-Chimie des Matériaux, U.R.A. 444 Université Blaise Pascal, 63177 Aubiere Cedex, France.

Communicated by J. B. Goodenough, June 21, 1993

Layered vanadyl organophosphonates of general formula $VO(RPO_3) \cdot nH_2O$, where $R = CH_3, C_2H_5, C_6H_5$, were synthesized in alcoholic solution. Intercalation of alkanols, $C_nH_{2n+1}OH$ ($n = 1 - 4$), and benzyl alcohol with each phosphonate previously prepared is reported and discussed. Samples and intercalation compounds were characterized for their X-ray powder diffraction patterns, IR spectra, and TGA analyses. © 1993 Academic Press, Inc.

INTRODUCTION

Among layered-structure compounds acting as hosts in intercalation reactions, metal organophosphonates form a particular group of hybrid organic/inorganic materials. The structure is directed by the choice of metal and reaction conditions; the nature of the interlayer region depends on the organic moiety. Recent reports (*1–4*) have shown the interest of such lamellar solids having general formula $M(RPO_3)x \cdot nH_2O$, where R is an organic radical and M a metallic or an oxometallic cation. Since pillared and intercalated structures can be easily generated, they have been extensively investigated as catalysts, sorbents, ion exchangers, or for highly specific functions (*5*).

The layered vanadyl phenylphosphonate $VOC_6H_5PO_3 \cdot H_2O$ has already been prepared by hydrothermal synthesis and characterized by single-crystal X-ray diffraction (*1*). The structure consists of layers of corner-sharing VO_6 octahedra and PO_3C tetrahedra. Phenyl groups are attached to the layer by a P–C covalent bond and extend out from both sides of the oxide sheet to form a bilayer, resulting in a layer repeat distance of 14.14 Å. Several hydrates exist for these compounds and it seems that the layer connectivity and the water content act upon the interlamellar organic packing.

In this paper we describe the intercalation reactions of alcohols into vanadyl phosphonates, $VO(RPO_3) \cdot nH_2O$, where $R = CH_3$, C_2H_5 and C_6H_5.

EXPERIMENTAL SECTION

Materials and Methods

Reagents and solvents used were obtained from commercial sources. Powder X-ray diffraction patterns were performed on a Siemens D501 diffractometer. Thermogravimetric analyses (TGA) were carried out with a Setaram TGA-DTA/DSC 92 analysis unit at a rate of 5°C/min under air atmosphere. Infrared spectra were recorded on

---

To whom correspondence should be addressed.

0022-4596/93 $5.00

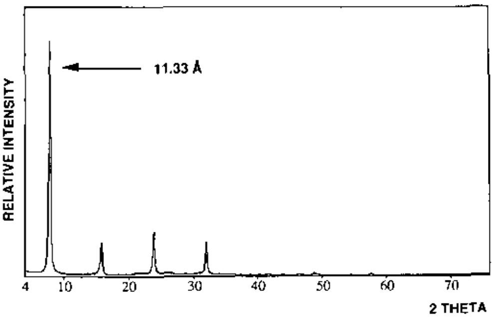

FIG. 1. PXRD of $VOC_2H_5PO_3 \cdot H_2O$.

a Perkin–Elmer PC16 FTIR spectrophotometer by the KBr disk method.

Compound Syntheses

The alcohol intercalation compounds of each phosphonate were first prepared by combining a suitable phosphonic acid RPO_3H_2 with V_2O_5 in refluxing alcohol $R'OH$ which is incorporated during the reaction and causes the reduction of the vanadium atom from the V to the IV oxidation state (*6, 7*). In a subsequent step this alcohol is removed by vacuum drying to form the host compound. The comparison between intercalated phases and the respective host compounds gives information about the alcohol intercalation behavior of the phosphonates.

Another possible synthesis consists in preparing the phosphonates directly by refluxing an aqueous solution of phosphonic acid combined with an aqueous solution of $VOSO_4 \cdot 5H_2O$ as vanadium source. The same vanadyl phenylphosphonate phase is obtained by both syntheses; in contrast, when $R = CH_3$ or C_2H_5, this method leads to well crystallized compounds, but with hydration states different from those observed in alcoholic solution. The products synthesized by this way give X-ray powder patterns exhibiting a prominent series of reflections indicative of a layered compound as shown in Fig. 1.

In the following, we comment only on the results obtained in alcoholic solution.

RESULTS AND DISCUSSION

Table I summarizes the interlamellar distances of vanadyl phosphonates and their alcohol intercalation compounds.

The X-ray diffractograms of vanadyl methylphosphonate (Fig. 2), synthesized in methanol, ethanol, and propanol, indicate only a single phase whose characteristic ray, representing the interlayer distance, evolves with the length of the alcohol chain R'. In contrast, the insertion of butanol results in the appearance of a second phase: one phase containing this alcohol (d = 10.60 Å) and the other being alcohol-free (d = 8.46 Å). This presence of two phases demonstrates the difficulty with which butanol intercalates. Benzylalcohol, which possesses an even more important R' group, does not intercalate. Thus, the insertion of alcohols of too large a size is not possible. In fact, the $R = CH_3$ groups of the matrix vanadyl methylphosphonate determine an interlayer space of limited size and it is, thus, the obstruction of the alcohol which limits the intercalation process.

Powder X-ray diffraction data from the microcrystalline vanadyl phenylphosphonate $VOC_6H_5PO_3 \cdot 2H_2O$ (orthorhombic symmetry, space group *Pbca*) (*6, 7*) show that the b lattice constant corresponds to double the interlayer distance, certainly due

TABLE I

INTERLAYER DISTANCES OF VANADYL PHOSPHONATES AND ALCOHOL INTERCALATION COMPOUNDS

	Layer spacings		
	$R = CH_3$ d (Å)	$R = C_2H_5$ d (Å)	$R = C_6H_5$ d (Å)
No intercolation	8.46	9.71	9.72
Intercalated alcohol:			
CH_3OH	8.76	9.71	10.79
C_2H_5OH	9.18	9.99	12.25
C_3H_7OH	9.65	11.39	13.25
C_4H_9OH	10.60	11.45	13.75
$C_6H_5CH_2OH$	[a]	13.06	15.21

[a] No intercalation occurs.

to some minor differences between adjacent layers. This material presents unexpected intercalation reactions with alcohols. It is not possible, in the case of this compound, to obtain a complete insertion of alcohol. In fact, the X-ray diffractograms (Fig. 2) are always characteristic of a two-phase mix, one phase with alcohol inserted and the other containing no alcohol. It is worthy of note that the amount of alcohol that can be inserted is much greater when the alcohol is bulky. This is perhaps due to lipophilic interactions between the carbon chain of the alcohol and the organic groups $R = C_6H_5$; such interactions must be stronger when the length of R' increases. The fact that intercalation of methanol increases the vanadyl phosphonate interlayer distance leads us to think that phenyl groups tightly interpenetrate into the interlamellar space.

The TGA data for $VOC_6H_5PO_3 \cdot 2H_2O$ show a first weight loss occurring between 40 and 120°C which corresponds to release of one water molecule. Then we observe the loss of one H_2O per formula unit, which begins at 180°C, accompanied by loss/reaction of the organic component from about 260°C until complete combustion. The first weight loss for the benzyl alcohol intercalation compound does not start until $T \geq 125°C$. We propose that the less thermally stable water molecule may be replaced totally or partially by an alcohol molecule according to the amount of alcohol inserted. Infrared spectra confirm this assumption (Fig. 3). In fact the ν_{OH} stretching vibrations at 3653 and 3622 cm^{-1}, attributed to a weakly bonded water molecule, gradually diminish as the alcohol intercalates in greater quantity.

CONCLUSION

This work evidences that *n*-alkanols, $C_nH_{2n+1}OH$ ($n = 1 - 4$), and benzyl alcohol can be intercalated into vanadyl phosphonates when $R = C_2H_5$ and C_6H_5, whereas only alkanols are intercalated into the methyl phosphonate. The failure of benzyl alcohol to intercalate into this compound indicates that increases of the interlayer distance of the vanadyl methylphosphonate are limited; as expected, the bulkiness of the alcohol chain R' does not permit intercalation. In contrast, the vanadyl phenylphosphonate shows unusual alcohol intercalation behavior. Results show that the

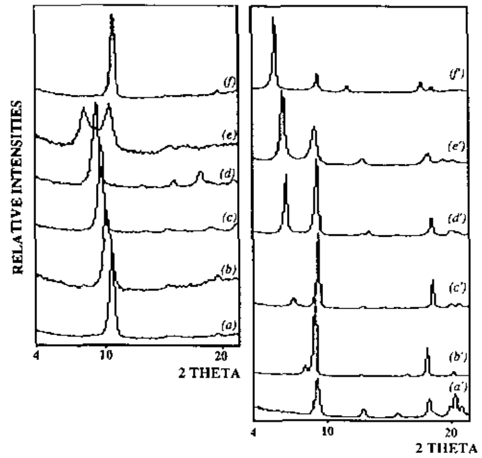

FIG. 2. X-ray diffraction patterns of (*a*) vanadyl methylphosphonate, (*a'*) vanadyl phenylphosphonate, and their alcohols intercalation compounds with (*b*) methanol, (*c*) ethanol, (*d*) propanol, (*3*) butanol, and (*f*) benzyl alcohol.

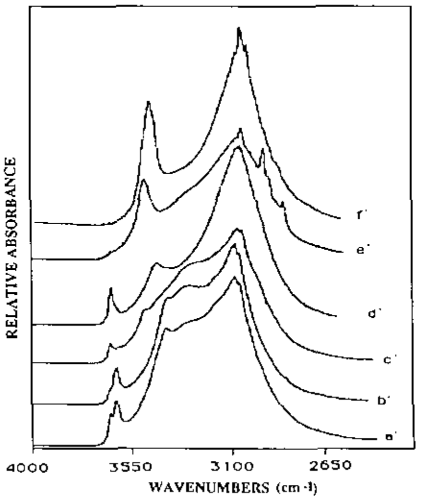

FIG. 3. Infrared spectra of vanadyl phenylphosphonate (*a'*) and alcohol intercalation compounds.

intercalation reaction of this sample with liquid alcohols occurs more rapidly and efficiently when the length of R' is larger. In this case, intercalation compounds exhibit a regular increase in the interlayer spacing as a function of the number of carbon atoms in the alkyl chain. We are currently trying to intercalate other organic species which introduce functional groups into the interlayer space.

References

1. G. Huan, A. J. Jacobson, J. W. Johnson, and E. W. Corcoran, Jr., *Chem. Mater.* **2,** 91 (1990).
2. G. Cao, L. K. Rabenberg, C. N. Nunn, and T. E. Mallouk, *Chem. Mater.* **3,** 149 (1991).
3. R. C. Wang, Y. Zhang, H. Hu, R. R. Frausto, and A. Clearfield, *Chem. Mater.* **4,** 864 (1992).
4. Y. Zhang and A. Clearfield, *Inorg. Chem.* **31,** 2821 (1992).
5. G. Cao, M. E. Garcia, M. Alcala, L. F. Burgess, and T. E. Mallouk, *J. Am. Chem. Soc.* **114,** 7574 (1992).
6. J. W. Johnson, A. J. Jacobson, J. F. Brody, and J. T. Lewandowski, *Inorg. Chem.* **23,** 3842 (1984).
7. J. W. Johnson, A. J. Jacobson, W. M. Butler, S. E. Rosenthal, J. F. Brody, and J. T. Lewandowski, *J. Am. Chem. Soc.* **111,** 381 (1989).