

Intercalation of Dimethyl Carbonate, Diethyl Carbonate and Ethylene Carbonate into Vanadyl Phosphate

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Abstract

Intercalation compounds of vanadyl phosphate with dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethylene carbonate (EC) were prepared from $\text{VOPO}_4 \cdot 2\text{C}_2\text{H}_5\text{OH}$ intercalate by a molecular exchange. The intercalates prepared were characterized using powder X-ray diffraction and thermogravimetric analysis. The EC intercalate is stable at ambient conditions, whereas the DMC and DEC intercalates transform to vanadyl phosphate dihydrate. Infrared spectra indicate that carbonyl oxygens of the guest molecules are coordinated to the vanadium atoms of the host layers. The arrangement of the guest molecules in the interlayer space was proposed.

Introduction

Vanadyl phosphate dihydrate $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ and other isostructural layered compounds are able to accommodate some types of organic molecules in the interlayer space [1]. Aliphatic alcohols and diols [2–4], amines [5], carboxylic acids [6], carboxamides [7], and aliphatic nitriles [8], belong to the compounds which can be intercalated in such a way. Much attention has been devoted to the intercalation of heterocyclic N- and S-donors [9–13]. In some of these compounds, a turbostratic disorder, that is a random rotation or translation between adjacent host layers, was observed. Recently, intercalations of ketones [14, 15], aldehydes [16], poly(ethylene glycol)s [17, 18], and heterocycles with O-donor [18–20] into vanadyl phosphate have been described. These guests are anchored to the host layers by donor–acceptor bonds of their carbonyl or etheric oxygen to the vanadium atoms. Therefore, it was of interest to determine which kind of donor atoms (carbonyl or etheric oxygen) is preferred when both of them are present in the guest molecule. Recently, intercalates of some lactones have been prepared and characterized [21, 22]. Infrared and Raman spectra indicate a coordination of the carbonyl oxygen of the lactone molecule to the vanadium atom of the host structure. Quantum mechanical calculations at the ab initio level support the proposed structure in which the γ -butyrolactone guest molecules are arranged with the plane of the ring

perpendicular to the host layers and are anchored to the layers through the carbonyl oxygen coordinated to the transition-metal atom of the host [21]. Successful intercalation of lactones into VOPO_4 indicates that other esters could also be intercalated. To confirm that the preferred coordination of the carbonyl oxygen is retained also in the case when carbonyl group is attached to two oxygen atoms we used as guests compounds containing a carbonate group.

The present paper reports the results of the intercalation of dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethylene carbonate (EC) into vanadyl phosphate.

Experimental

The ethanol intercalate was prepared by suspending microcrystalline $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ in dry ethanol and subsequent short exposure to a microwave field. The intercalation compounds were obtained by replacing ethanol in $\text{VOPO}_4 \cdot 2\text{EtOH}$ with the corresponding guest. The DMC and DEC intercalates were prepared by refluxing the ethanol intercalate (0.5 g) with the corresponding guest (20 ml) for 30 min. The intercalates prepared were dried by evaporation of the guest at 25 °C in an evacuated ampoule. The EC intercalate was prepared by refluxing the ethanol intercalate in an acetonitrile solution of the guest for 30 min. The intercalate was filtered off, washed with acetonitrile and dried in nitrogen.

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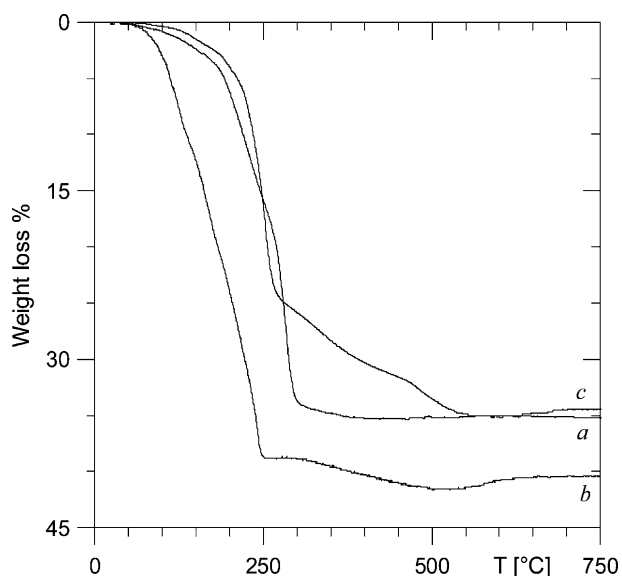


Figure 1. TG curves of the DMC (a), DEC (b), and EC (c) intercalates.

Powder data were obtained with a D8-Advance diffractometer (Bruker AXE, Germany) using $\text{CuK}\alpha$ radiation with secondary graphite monochromator. Diffraction angles were measured from 5 to 37° (2θ). The samples were covered with protection foil during the measurement.

TG analyses were performed using a Netzsch STA 449C. The measurements were carried out in air between 30 and 750°C at a heating rate of 5°C min^{-1} .

Infrared spectra of the solids were recorded on FT-IR spectrometer NEXUS (Nicolet, USA) in the range from 400 to 4000 cm^{-1} using dry KBr powder containing 10% of the sample. The resulting reflectance spectra were converted to the Kubelka-Munk format. The spectra of the liquid guests were measured in a KBr cell.

Results and discussions

None of the carbonates used can be intercalated directly in anhydrous vanadyl phosphate or $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$. All the intercalates can be prepared by replacing ethanol in the $\text{VOPO}_4 \cdot 2\text{EtOH}$ intercalate with the desired guest. The intercalates prepared were yellow crystalline solids. This indicates that vanadium(V) was not significantly reduced during the intercalation. The composition of the intercalates was determined by thermogravimetric and elemental analyses. The TG curves of the intercalates prepared are given in Figure 1. During heating, DMC and DEC are released in one step. In the case of the EC intercalate, a steep weight loss observed at about 250°C is followed with a slow weight decrease which could be caused by burning of organic residuals. A small weight increase above 550°C is probably caused by oxidation of vanadium(IV) which was formed during the decomposition of the organic part. The product of the thermal decomposition of all the intercalates is anhydrous vanadyl phosphate. Total weight losses correspond to the stoichiometric ratio x given in Table 1 together with the

Table 1. Tetragonal lattice parameters of the intercalates prepared, the guest content x , and the results of elemental analysis

guest	a [Å]	c [Å]	x^a	C % found/cal. ^b	H % found/cal. ^b
DMC	6.20	22.32	0.98	14.31/14.30	2.22/2.40
DEC	6.21	12.17	0.93	21.22/21.45	3.44/3.60
EC	6.19	9.82	0.97	14.01/14.42	1.67/1.61

^a determined from total weight loss.

^b calculated for $\text{VOPO}_4 \cdot 1.0(\text{guest})$.

results of elemental analysis. All the intercalates prepared contain one molecule of the guest per formula unit.

The diffractograms (see Figure 2) of the intercalates show a series of sharp $(00l)$ reflections. Only weak (200) and (110) reflections can be seen in the diffractogram of the EC intercalate. The absence of (hkl) lines in the intercalates is characteristic of a turbostratic structure where the original tetragonal layers of the host are retained but mutually shifted in the directions of the x and/or y axes. The diffractograms of the DEC and DMC intercalates contain a number of the (hkl) diffraction lines (see Figure 2a, b) giving evidence of a regular structure. In the case of the DMC intercalate, diffraction lines can be indexed using the c parameter as a double of the basal spacing. This is most likely caused by a relative shift of the neighboring host layers by $a/2$. The lattice parameters of all the intercalates prepared are given in Table 1.

The DMC and DEC intercalates are not stable in air (at relative humidity (RH) higher than 50%). When the intercalates are exposed to an air with ambient humidity, the guest molecules are gradually replaced by water molecules. At 30% RH, the DMC intercalate is stable for several hours whereas the DEC intercalate slowly transform to $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$. The EC intercalate is more stable, the formation of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ was not observed after 24 h exposure to an air with 43% RH.

The character of the bonding between the guests and the host layers in the intercalates was studied by infrared spectroscopy. The IR spectra of DMC, $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$, and DMC intercalated vanadyl phosphate are given in Figure 3. The positions of the main spectral bands of the host structure only slightly differ from those of anhydrous vanadyl phosphate or its hydrated forms [23]. It confirms that the structure of the original VOPO_4 layers remains unchanged after the intercalation reaction. The broad intense band in the spectrum of the DMC intercalate at 940 cm^{-1} corresponds to the symmetric $\nu(\text{PO}_4)$ stretching vibration. The position of the $\text{V}=\text{O}$ stretching vibration appears to be sensitive to atoms coordinated to the vanadium atom. For instance, when the water molecules are intercalated into VOPO_4 , the position of this band at 1035 cm^{-1} in the anhydrous form of vanadyl phosphate changes to 995 cm^{-1} typical of mono- and dihydrates [23]. In the spectrum of vanadyl phosphate dihydrate we can observe the $\text{V}=\text{O}$ stretching vibration at 997 cm^{-1} corresponding to the hydrate

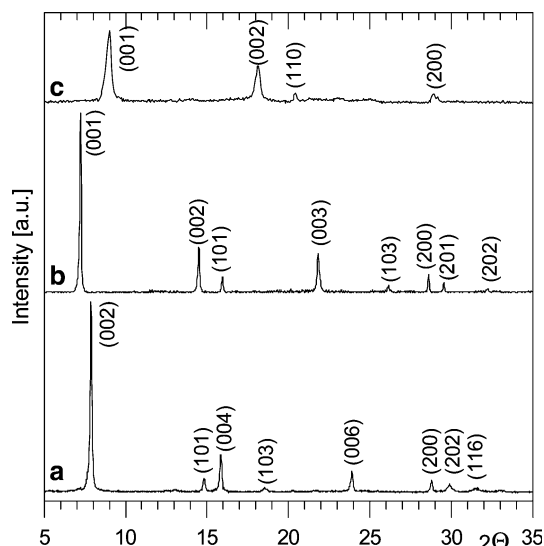


Figure 2. X-ray diffractograms of the DMC (a), DEC (b), and EC (c) intercalates.

form. In the spectrum of the DMC intercalate, the peak at 1008 cm^{-1} corresponds most probably to the $\text{V}=\text{O}$ stretching vibration.

When the carbonyl oxygen atom of an ester is the donor, a weakening of the $\text{C}=\text{O}$ bond can be expected together with a strengthening of the adjacent $\text{C}-\text{O}$ bonds as a secondary effect. In complexes, where metal ions are hexacoordinated by ester molecules, the ester show a negative shift in their carbonyl stretching vibrations and a positive shift in their $\text{C}-\text{O}$ stretching frequency [24]. A complete assignment of the infrared vibrations of DMC has been reported [25]. Bands of DMC are shifted in the spectrum of the DMC intercalate. The $\text{C}=\text{O}$ stretching vibration observed at 1755 cm^{-1} in the spectrum of pure DMC is shifted to 1724 cm^{-1} in the spectrum of the DMC intercalate. The band of CO_2 antisymmetric

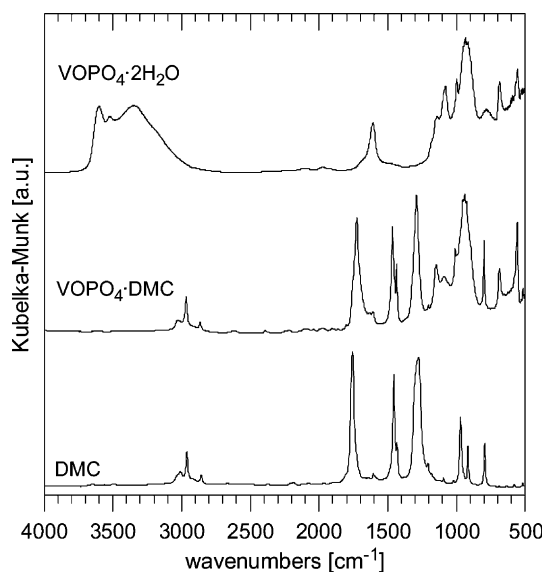


Figure 3. IR spectra of pure DMC, DMC intercalated VOPO_4 and vanadyl phosphate dihydrate.

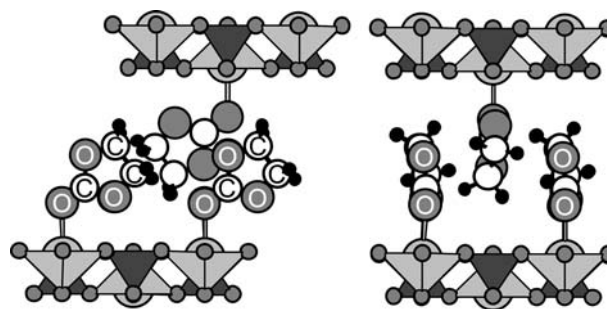


Figure 4. Proposed arrangement of EC molecules in the interlayer space viewed along the x and y directions.

stretching vibration is shifted from 1275 cm^{-1} in the spectrum of pure DMC to 1292 cm^{-1} in the spectrum of the intercalate. The band of the CO_3 out-of-plane deformation vibration is shifted to slightly higher wavenumbers (794 cm^{-1} for pure DMC, 800 cm^{-1} for the intercalate). Positions of the bands corresponding to CH_3 vibration did not change after the intercalation.

In the case of DEC, similar shifts of the bands corresponding to the $\text{C}=\text{O}$ stretching vibration (1747 cm^{-1} for pure DEC, 1736 cm^{-1} for the intercalate) and the CO_2 antisymmetric stretching vibration (1302 cm^{-1} for pure DEC, 1310 cm^{-1} for the intercalate) were observed. The band of the CO_3 out-of-plane deformation vibration is not shifted. The positions of the bands corresponding to the CH_3 and CH_2 vibrations did not significantly change after the intercalation.

The changes of the infrared spectra caused by the coordination of Li^+ to the EC molecule were studied theoretically using quantum chemical calculations [26]. The lithium coordination induces shifts mainly in the peaks corresponding to the ring motions and in the carbonyl stretching bands. Most of the vibrations is shifted to higher wavenumbers except that for the carbonyl stretching mode, which exhibits a red shift typically found in the bond containing an oxygen atom directly coordinating to a metal cation. Assignments of the infrared vibrations of EC has been reported [27, 28]. The doubling of the $\text{C}=\text{O}$ stretching vibration observed at 1801 and 1774 cm^{-1} in the spectrum of pure EC can be explained as a Fermi resonance effect [27, 28]. In the spectrum of the EC intercalate, these bands are shifted to the lower wavenumbers of 1793 and 1759 cm^{-1} . The band of the ring stretching vibration observed at 1163 cm^{-1} in the spectrum of pure EC is shifted to 1194 cm^{-1} in the spectrum of the EC intercalate. The band of the ring stretching vibration at 1072 cm^{-1} in the spectrum of EC is probably overlapped with the band of $\nu_3(\text{PO}_4)$ in the spectrum of the EC intercalate. The band of the ring breathing vibration (892 cm^{-1} in spectrum of pure EC) is shifted to higher wavenumbers and is observed as a shoulder at about 900 cm^{-1} in the spectrum of the EC intercalate.

Analogously to the arrangement of γ -butyrolactone and cyclopentanone which were calculated using quantum chemical methods [15, 21], also the arrangement of the carbonates in the interlayer space of the host layers

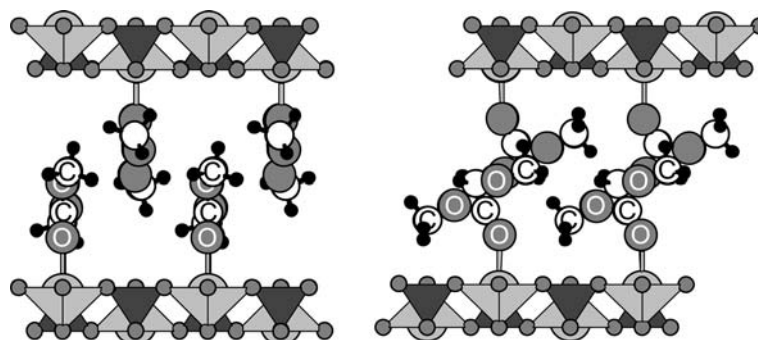


Figure 5. Proposed arrangement of DMC molecules in the interlayer space viewed along the x and y directions.

can be deduced. Taking into account the interlayer distance and assuming that the distance between the ketonic oxygen and the vanadium atom is the same as in the γ -butyrolactone or cyclopentanone case, we proposed the structure of the intercalates.

The arrangement of the EC molecules is nearly the same as in the case of γ -butyrolactone molecules, the guests form a monomolecular layer where the EC rings are oriented in the x or y direction and the molecules anchored to the lower and upper host layer are interdigitated (see Figure 4). Two successive VOPO₄ layers are mutually shifted with respect to the original host structure along the $x(y)$ axis. As the orientation of the EC molecules can be different in every interlayer space, the directions of the shifts are random which leads to a turbostratic arrangement of the layers. This is in agreement with the absence of the hkl lines in the diffractogram of the EC intercalate. As a result of the interdigitation, the basal spacings of the EC and γ -butyrolactone intercalates are very similar and significantly lower in comparison with that of the cyclopentanone intercalate where the cyclopentanone molecules are only slightly interdigitated. The arrangement of the EC molecules is more compact than the arrangement of the cyclopentanone molecules which leads to a higher stability of the EC intercalate in humid air in comparison with the cyclopentanone intercalate.

The proposed arrangement of the DMC molecules in the interlayer space is shown in Figure 5. The DMC molecules are oriented in x or y direction of the tetragonal host layer and are partially interdigitated. The interdigitation leads to the shift of the two adjacent layers by $a/2$ in the x or y direction, which means that every other layer is shifted by $a/2$ and the c parameter is doubled. The arrangement of the DMC molecules is less compact than the arrangement of the EC molecules which leads to a lower stability of the DMC intercalate in humid air in comparison with the EC intercalate.

Acknowledgements

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