Vanadyl Phosphate Intercalated with Diethyl Ether

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Vanadyl phosphate intercalated with diethyl ether has been prepared by replacing 2-propanol molecules in the corresponding $VOPO_4$ intercalate with diethyl ether. The intercalate contains one diethyl ether molecule per formula unit. The guest molecules are anchored to the host layers by an O–V donor–acceptor bond. The local structure and interactions in the intercalate have been suggested on the basis of quantum chemical calculations. The intercalate is thermally stable. Its diffractogram does not change up to 100 °C. A new phase with lower basal spacing appears at 130 °C. The intercalate is very moisture-sensitive; the diethyl ether molecules are easily replaced by water molecules. The replacement of diethyl ether in the vanadyl phosphate intercalate by the water molecules has been monitored by infrared spectroscopy.

Introduction

The ability of vanadyl phosphate dihydrate $VOPO_4{\cdot}2H_2O$ and other isostructural layered compounds to accommodate organic molecules having the character of Lewis bases in the interlayer space has been reviewed.[1] Compounds with functional groups containing oxygen atoms, i.e. alcohols, ketones, carboxylic acids and ethers, form a large group of such compounds. Intercalations of etheric oxygen-containing glycols[2] and cyclic ethers[3,4] have been described recently.

With glycols, diethylene glycol (DEG), triethylene glycol, and poly(ethylene glycol)s (PEG 200, 400, and 1000) have been intercalated into vanadyl phosphate. Depending on the reaction temperature, two phases are formed: a low-temperature phase, with guest chains arranged parallel to the host layer in a bimolecular way, and a high-temperature phase, where the chains are arranged monomolecularly. All these intercalates are stable in a dry environment but decompose slowly in humid air.[2] The structure of the DEG intercalated vanadyl phosphate, $VOPO_4{\cdot}HO(CH_2)_2O(CH_2)_2OH$, has been determined using a combination of synchrotron powder diffraction and molecular modeling.[5] The crystal system was determined to be tetragonal, space group *P*4/*n*, with the DEG molecules anchored to the vanadium atoms of the host layers through their etheric oxygen atoms.

The cyclic ethers tetrahydrofuran, tetrahydropyran,[3] dioxane, trioxane, and 18-crown-6[4] have been intercalated into vanadyl phosphate. All these guest molecules are anchored to the host layers by a donor−acceptor bond between an oxygen atom of the guest and a vanadium atom. These intercalates are stable at ambient conditions, and some are surprisingly thermally stable (the tetrahydrofuran intercalate is stable up to 160 °C). The structure of tetrahydrofuran intercalate has been determined using a combination of synchrotron powder diffraction and molecular modeling.[5] We report here on a diethyl ether intercalated vanadyl phosphate.

Results and Discussion

Diethyl ether cannot be intercalated directly in anhydrous vanadyl phosphate, and the replacement of water in $VOPO_4{\cdot}2H_2O$ does not lead to an intercalation. Consequently, the intercalate was prepared by replacing 2-propanol in the corresponding $VOPO_4$ intercalate with diethyl ether, to give a yellow crystalline solid, indicating that the vanadium(v) atom had not been significantly reduced. We did not succeed in intercalating dipropyl ether, dibutyl ether, or diisopropyl ether.

The diffractogram of the diethyl ether intercalate indicates that the tetragonal structure of the $VOPO_4$ host layer is retained. Three sharp (00*l*) and one weak (200) reflections appear in the pattern (Figure 1, a). The tetragonal lattice parameters a = 6.208 Å, c = 11.664 Å were determined from these lines. The absence of (*hkl*) lines is characteristic of a turbostratic structure in which the original tetragonal

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layers of the host are retained but shifted in the directions of the *x* and/or *y* axes. The intercalate is very moisture-sensitive − the diethyl ether molecules are easily replaced by water. At a relative humidity (r.h.) of 25% the intercalate is stable, and only a small broad (001) reflection of vanadyl phosphate dihydrate is observed in the diffractogram after 1 h of exposure (Figure 1, b). At ambient conditions (r.h. = 55%), however, the intercalate rapidly decomposes, and only a small (001) reflection of the intercalate is present, together with a strong (001) line of the dihydrate, in the diffractogram measured immediately after exposure to ambient air (Figure 1, c). After 16 min, the sample is completely converted into vanadyl phosphate dihydrate (Figure 1, d).

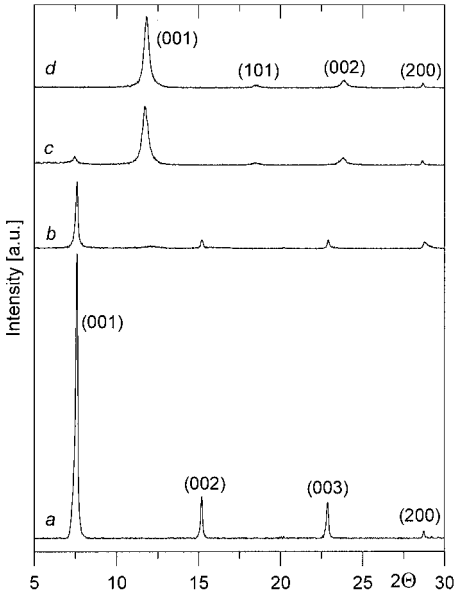

Figure 1. Diffractograms of samples of vanadyl phosphate intercalated with diethyl ether: (a) with excess diethyl ether; (b) after 1 h at r.h. =25%; (c) immediately after exposure to r.h. = 55%; (d) after 16 min exposure to r.h. = 55%

The thermal behavior of the intercalate was monitored by TG-DTA and X-ray diffraction. TG-DTA curves are given in Figure 2. The total weight loss (31%) corresponds to the formula $VOPO_4 \cdot C_2H_5OC_2H_5$ (theoretical weight loss 31.4%). As with intercalates of cyclic ethers, the diethyl ether intercalate is thermally stable. About half of diethyl ether is liberated in the first endothermic step up to 115 °C. The rest is released in two steps: the first up to 212 °C (the exothermic peak of the DTA curve is caused by the burning of diethyl ether) and the second, very slow, up to 550 °C. A small increase in weight between 550 and 750 °C is probably caused by oxidation of vanadium(IV). The basal spacing of the diethyl ether intercalate has been monitored as a function of temperature (Figure 3); it increases slightly up to 120 °C. The intensity of the (001) diffraction line does not change up to 100 °C and then decreases. A new phase with a basal spacing of about 8.2 Å appears at 130 °C and is present up to 170 °C. Above this temperature, the sample becomes green and amorphous. The new phase is probably caused by the loss of half of the guest molecules and by a change in arrangement of the guest molecules from bimolecular to monomolecular. Diethylene glycol intercalated $VOPO_4$ shows similar behavior during heating.[2]

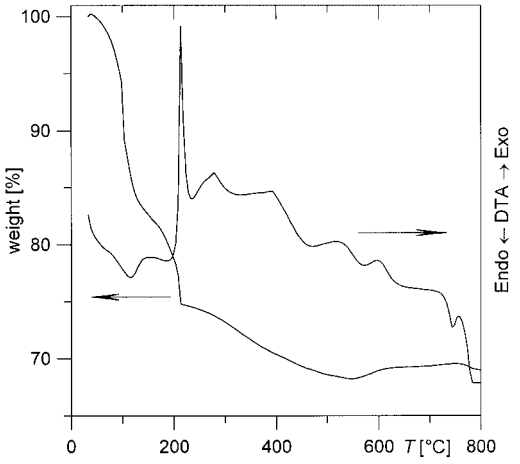

Figure 2. TG-DTA curves of vanadyl phosphate intercalated with diethyl ether

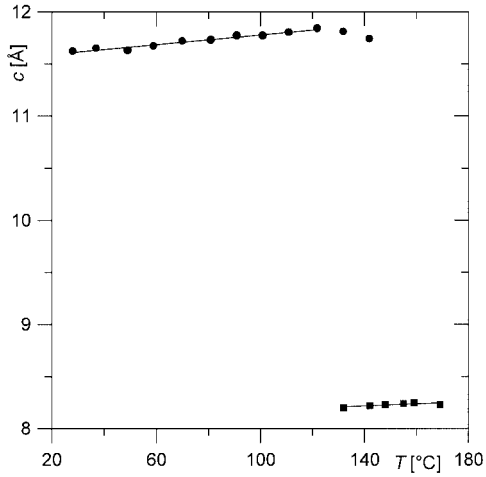

Figure 3. Basal spacing as a function of temperature during thermal decomposition of vanadyl phosphate intercalated with diethyl ether; circles represent basal spacings of the low-temperature phase, squares correspond to the high-temperature phase; errors of the basal spacings are within the dimensions of the data symbols

For infrared measurements, a sample of vanadyl phosphate intercalated with diethyl ether was placed in a purged sample compartment of the spectrometer (r.h. = 5%) for 5 min and for 7 and 22 h without removing the sample from the crystal between subsequent spectral measurements. Another sample was exposed to ambient conditions (r.h. = 60%) for 22 h and for 6, 10, 14 and 17 d. Such conditions allow a progressive replacement of the diethyl ether molecules in the vanadyl phosphate intercalate by atmospheric water. The infrared spectra of the intercalate at various stages of the deintercalation process under ambient conditions were compared with that of vanadyl phosphate dihydrate and with the spectrum of pure diethyl ether [Fig-

ure 4 (2000 to 600 cm^{-1}) and Figure 5 (4000 to 2500 cm^{-1})].

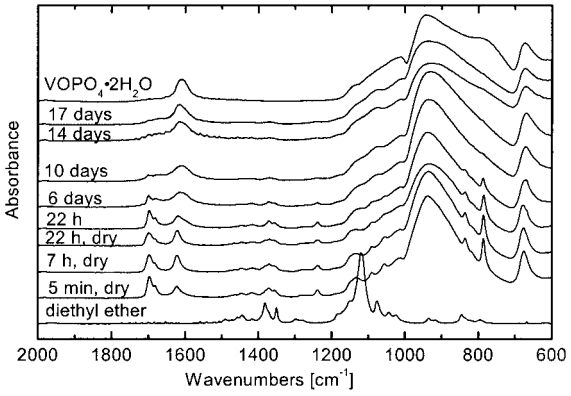

Figure 4. FTIR spectra (2000 to 600 cm^{-1}) of vanadyl phosphate dihydrate, of pure diethyl ether and of vanadyl phosphate intercalated with diethyl ether after 5 min, 7 h and 22 h in a purged spectrometer (r.h. = 5%), and after 22 h and 6, 10, 14 and 17 d under ambient conditions (r.h. = 60%)

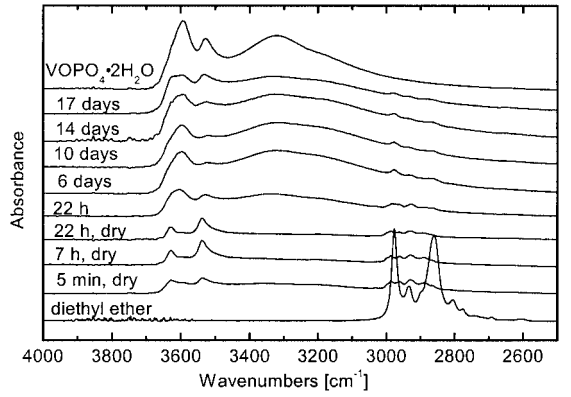

Figure 5. FTIR spectra (4000 to 2500 cm^{-1}) of vanadyl phosphate dihydrate, of pure diethyl ether and of vanadyl phosphate intercalated with diethyl ether after 5 min, 7 h and 22 h in a purged spectrometer (r.h. = 5%), and after 22 h and 6, 10, 14 and 17 d under ambient conditions (r.h. 60%)

The Raman spectra (3500−600 cm^{-1}) of vanadyl phosphate dihydrate, vanadyl phosphate intercalated with diethyl ether and pure diethyl ether are shown in Figure 6. Unfortunately, it was not possible to measure the kinetics of the replacement process of diethyl ether by Raman spectroscopy because of a partial escape of the diethyl ether molecules due to the laser beam during measurements.

Vibrational bands of the PO_4 tetrahedron, the vanadyl group V=O, and the P−O−V group can be identified in all spectra. The intense band at 945 cm^{-1} in the spectrum of vanadyl phosphate dihydrate (Figure 6) corresponds to the symmetric $\nu(PO_4)$ stretching vibration of the phosphate tetrahedron in $(VOPO_4)_\infty$. This band is shifted to 940 cm^{-1} in vanadyl phosphate intercalated with diethyl ether. The sharp band at 995 cm^{-1} in the vanadyl phosphate dihydrate spectrum is due to a vanadyl V=O stretching vibration. Its

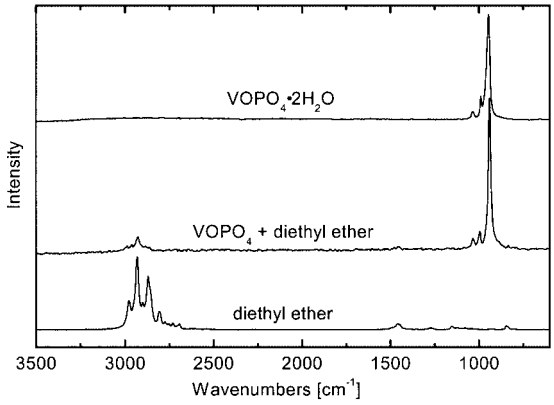

Figure 6. Raman spectra (3500−600 cm^{-1}) of vanadyl phosphate dihydrate, of vanadyl phosphate dihydrate intercalated with diethyl ether and of pure diethyl ether

position corresponds to the coordination of the oxygen atom of the water molecules in the VO_6 octahedron. The vanadyl stretching band appears to be especially sensitive to atoms coordinated to the vanadium atom within an octahedral arrangement in the host lattice structure. During the intercalation of water molecules into $VOPO_4$ its position at 1035 cm^{-1} in the anhydrous form changes to that typical for mono- and dihydrate (995 cm^{-1}).[6] In the Raman spectrum of the intercalate with diethyl ether the band at 994 cm^{-1} corresponds most probably to the coordination of the oxygen atom of diethyl ether to the vanadium atom, and the band at 1033 cm^{-1} to the anhydrous form of the host compounds. With the help of the Raman spectrum, we can assign the band with the maximum at 945 cm^{-1} in the IR spectrum (Figure 4) of vanadyl phosphate dihydrate to the symmetric $\nu(PO_4)$ stretching vibration, which is infrared-active due to distortion of the phosphate tetrahedron in the intercalate. The shoulder at 1011 cm^{-1} in the IR spectrum is most probably the V=O stretching band of the vanadyl group, while the band at 1135 cm^{-1} in the IR spectrum of the host is the asymmetric $\nu(PO_4)$ stretching vibration of the phosphate tetrahedron. The positions of the main spectral bands of the host structure differ only slightly from those of anhydrous vanadyl phosphate or its hydrated form.[6] This confirms that the structure of the original $VOPO_4$ layers remains unchanged after the intercalation reaction.

Conversely, bands due to pure diethyl ether are shifted in the spectrum of the intercalate; some bands disappear and some new bands appear (Figures 4 and 5). The C−H stretching vibration at 2978 cm^{-1} splits into 2985 and 2964 cm^{-1}, the bands at 2934, 2891 and 2862 cm^{-1} retain their positions but change in relative intensity. The C−H deformation vibration bands at 1490, 1448, 1383, 1351 and 1295 cm^{-1} shift to lower wavenumbers and a new band appears at 1238 cm^{-1} in the spectrum of the intercalate. The asymmetric COC stretching mode at 1120 cm^{-1} in the spectrum of pure diethyl ether is at about 1134 cm^{-1} in the spectrum of the intercalate. The bands at 1076 and 1025 cm^{-1} are overlapped by the symmetric $\nu(PO_4)$ stretching vibrational

band and are observed as shoulders at 1089 and 1057 cm^{-1}. The symmetric COC mode at 935 cm^{-1} is completely overlapped and the bands at 846 and 796 cm^{-1} are shifted to 838 and 787 cm^{-1}. The diethyl ether bands reduce in intensity during exposure to the external conditions.

Most surprising are two sharp bands with maximum at about 3627 and 3530 cm^{-1} and a broad band with two maxima at 3354 and 3182 cm^{-1} seen during the first 5 min after removing the sample from the ampoule and placing it in the purged sample compartment of the spectrometer (r.h. = 5%). At the same time we observed a band at 1699 cm^{-1} with a shoulder at 1682 cm^{-1} and a band at 1624 cm^{-1}. When the sample is not removed from the purged sample spectrometer compartment, these bands remain unchanged and the broad band with two maxima at 3354 and 3182 cm^{-1} disappears in the spectrum measured after 22 h. In the spectra of the sample measured at ambient conditions (r.h. = 60%) the two sharp bands are shifted to 3594 and 3530 cm^{-1}, and the band at 1624 cm^{-1} is shifted to 1612 cm^{-1}. These new positions correspond to the spectrum of vanadyl phosphate dihydrate. The shoulder at 3627 cm^{-1} and the band at 1699 cm^{-1} disappear when the sample is kept under ambient conditions. The last spectrum of the intercalate, measured after 17 d, is very similar to that of $VOPO_4 \cdot 2H_2O$.[6]

We suppose that the new bands in the spectrum of the very fresh sample taken in the purged sample compartment of the spectrometer (r.h. = 5%) correspond to adsorbed water on the surface of the sample. As attenuated total reflection (ATR) is a very surface-sensitive method, we observed relatively strong bands of water in the spectra. In the spectra of samples taken under ambient conditions (r.h. = 60%), the positions of the bands of water correspond to bulk water molecules, and the spectra correspond to those of vanadyl phosphate dihydrate.

The character of the bonding between the guest molecules and the host layer in the diethyl ether intercalate was investigated by quantum mechanical calculations and modeling. Figure 7 shows the DFT-optimized structure of the molecular segment representing local interactions of vanadyl phosphate with diethyl ether, using the B3LYP functional and 6-31G(d) basis set. Calculations with the LanL2DZ basis set give an analogous geometry with slight differences in bond lengths (Figure 7). To keep the overall planar structure of the segment during full geometry optimizations, and to make the electronic structure in the segment close to the conditions appearing in the intercalates, an oxygen atom was inserted between two neighboring PO_4 groups and terminal oxygen atoms were substituted by OH groups.[7] The total charge of the model compound was set to +3. All geometry optimizations with various starting orientations of diethyl ether with respect to the vanadyl group lead to the structure displayed in Figure 7, indicating the formation of the C−O(−C)→V bond in the intercalates. The diethyl ether molecule exhibits central symmetry with respect to the oxygen atom and a gauche conformation around both C−O bonds (calculated dihedral angle C−C−O−C 71.4°).

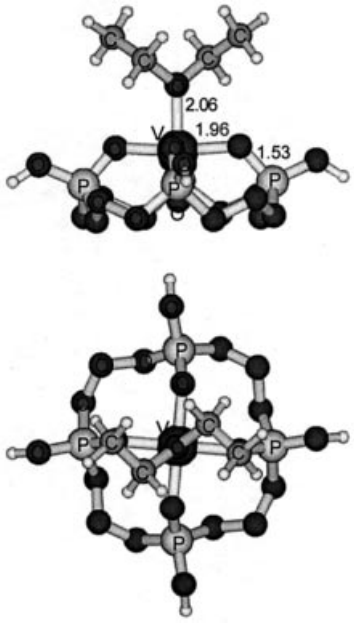

Figure 7. Optimized B3LYP/6-31G(d) structure of the molecular segment modeling the vanadyl phosphate−diethyl ether interaction, with indicated bond lengths [Å]

Simulations of larger local intercalate structures including two $VOPO_4$ layers were performed using the semiempirical quantum-chemical methods PM3 and AM1. The adequacy of the semiempirical methods for vanadyl phosphate intercalates has been illustrated in a previous study of intercalates with benzonitrile and tolunitrile, in which the results of modeling are in a very good agreement with experimental data obtained by X-ray, IR and Raman spectroscopy.[8] When the model structure shown in Figure 7 was reoptimized with the PM3 and AM1 methods, only slight changes in parameters were found in comparison with the DFT method. Optimized geometries of the molecular segment representing two layers of $VOPO_4$ and five molecules of diethyl ether intercalated between the two layers are shown in Figure 8. Terminal oxygen atoms were replaced by OH groups and the total charge of the model compounds set to −2. Coordinations of the vanadium atoms to the diethyl ether molecules in adjacent host interlayer spaces were simulated by coordinations with dimethyl ether molecules (not shown in Figure 8). The initial bond lengths and angles for the $VOPO_4$ layers were taken from the previous study of vanadyl phosphate intercalates with benzonitrile,[8] the initial basal spacing was set to the above given value of the lattice parameter c = 11.664 Å, determined by the X-ray diffraction, and the structure and bonding of diethyl ether were taken from the DFT calculations (Figure 7). In a series of geometry optimizations with various symmetry constraints and the parameter c fixed, the initial molecular and lattice parameters were refined to values suitable for the final overall energy minimization. All the variables defining the positions of the atoms both in the host and guest layers were fully optimized with the excep-

tion of the constraints exposed by the symmetry conditions defining polyhedra in the $VOPO_4$ layers and relative orientations of the guest molecules in the interlayer with respect to the $VOPO_4$ layer. The basal spacings calculated with the PM3 and AM1 methods are 11.28 and 11.07 Å, respectively. In agreement with X-ray results, the mutual positions of the successive layers exhibit a shift characterized by a vector with calculated components of 0.02 and 0.53 Å by the PM3 method and of 0.99 and 1.29 Å with the AM1 method.

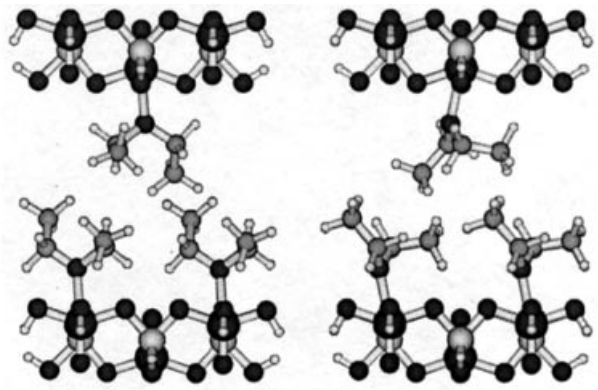

Figure 8. Side views of the PM3-optimized geometry of the molecular segment modeling the arrangement of diethyl ether molecules between the $VOPO_4$ layers

Experimental Section

Preparation: The 2-propanol intercalate was prepared by suspending microcrystalline $VOPO_4{\cdot}2H_2O$ in dry 2-propanol with subsequent short exposure to a microwave field. The intercalation compound was obtained by replacing 2-propanol in $VOPO_4{\cdot}2C_3H_7OH$ with diethyl ether. The 2-propanol intercalate (0.5 g) was dispersed in diethyl ether (15 mL) and exposed to a microwave field for 5 min. Samples used for XRD measurements contained small amounts of free diethyl ether. Dry samples for the TG and spectroscopic measurements were prepared by evaporation of diethyl ether at 25 °C in an evacuated ampoule.

X-ray: Powder data were obtained with a D8-Advance diffractometer (Bruker AXE, Germany) using Cu-K_α radiation with a secondary graphite monochromator. Diffraction angles were measured from 7 to 80° (2θ). The temperature measurements (22−200 °C) were carried out on the heated corundum plate with a thermocouple.[9] Each diffractogram was measured at constant temperature and a cycle of heating and measuring lasted about 30 min. The sample was covered with a foil for protection.

TG: TG analyses, using a Netzsch STA 449C instrument, were carried out in air between 30 and 800 °C at a heating rate of 5 °C·min^{-1}.

IR: Infrared measurements (400−4000 cm^{-1}) were carried out with a fully computerized Bruker IFS 55 EQUINOX FTIR spectrometer with a DLATGS detector (256 scans per spectrum at 4 cm^{-1} resolution). Spectra of the intercalates were recorded ex situ by an ATR technique using the Golden Gate™ Heated Diamond ATR Top-Plate (Specac Ltd.) at ambient temperature. The spectrum of the corresponding liquid diethyl ether was measured by an ATR technique with a ZnSe crystal. Spectra were corrected for the H_2O and CO_2 content of the optical path.

Raman: FT Raman spectra were collected using a Bruker IFS 55 EQUINOX FTIR spectrometer equipped with an FT Raman module FRA 106/S with a diode-pumped, temperature-stabilized Nd YAG laser, and an InGaAs detector [128 interferograms were coadded per one spectrum in the range 4000−(−1000) cm^{-1} at 4 cm^{-1} resolution].

Calculations: Quantum chemical calculations were carried out at the ab initio and semiempirical levels of theory employing GAUSSIAN 98[10] and MOPAC 2002[11] program packages, respectively. Local interactions and structures in the intercalates of vanadyl phosphate with diethyl ether were studied at the DFT level using a functional B3LYP with the basis sets 6-31G(d) and LanL2DZ. Geometrical optimizations of larger structures including two vanadyl phosphate layers were performed at a semiempirical level using PM3 and AM1 methods.

Acknowledgments

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