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# From Plates to Spheres: Tuning the Vanadyl Phosphate Morphology by Intercalation of Nitrosyl Oxide

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## From Plates to Spheres: Tuning the Vanadyl Phosphate Morphology by Intercalation of Nitrosyl Oxide

José C. V. de Miranda,<sup>1</sup> Deyse de S. Dantas,<sup>2</sup> João E. T. S. Dantas,<sup>3</sup> Francisco C. Pereira,<sup>3</sup> and Robson F. de Farias<sup>3</sup>

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The lamellar matrix VOPO<sub>4</sub>.2H<sub>2</sub>O was used to the intercalation of nitrosyl (NO) ligand. The vanadyl phosphate matrix, as well as the prepared intercalated compound (VOPO<sub>4</sub>.NO.H<sub>2</sub>O), were characterized by infrared spectroscopy, thermogravimetry, X-ray difractometry, and SEM microscopy. The X-ray diffraction patterns shown that the VOPO<sub>4</sub>.NO.H<sub>2</sub>O synthesis occurs with a decrease in the lamellar distance in comparison with VOPO<sub>4</sub>.2H<sub>2</sub>O. The SEM micrographs obtained for VOPO<sub>4</sub>.2H<sub>2</sub>O and VOPO<sub>4</sub>.NO.H<sub>2</sub>O shown that microstructure of vanadyl phosphate is flat square whereas the compound VOPO4.NO.H2O exhibits spheroid grains.

Keywords nitrosyl oxide, morphology, spheres, vanadyl phosphate

#### INTRODUCTION

Vanadium pentoxide,  $V_2O_5$ , has been used as precursor material in the synthesis of vanadyl phosphate, VOPO<sub>4</sub>.2H<sub>2</sub>O.<sup>[1–12]</sup> This compound is one of the catalysts used in the oxidation of organic molecules.<sup>[3]</sup> In VOPO<sub>4</sub>.2H<sub>2</sub>O, a central vanadium atom is connected to six oxygen atoms, giving a regular octahedral structure.<sup>[4–12]</sup> The organization of the structures form an open lattice which can accommodate positive ions and/or organic molecules.<sup>[1–12]</sup> Because of the oxidative properties of VOPO<sub>4</sub>.2H<sub>2</sub>O, when neutral molecules enter the lamellar structure, they undergo oxidation by transferring one or more electrons to the host species. The chemical species, V<sup>5+</sup>, is the promoter of such oxidative processes, especially for organic molecules.<sup>[4–12]</sup>

The vanadyl phosphate is a lamellar compound and therefore able to accommodate> in their nanostructure molecules of small dimensions. In the literature<sup>[4–12]</sup> is reported that changes in the

structure and chemical composition of this new molecule enhance chemical, physical and morphological vanadyl phosphate properties. Furthermore, it was shown that the intercalation of metal ions such as Mn<sup>2+</sup>, Li<sup>+</sup>, K<sup>+</sup>, Al<sup>3+</sup>, Cr<sup>3+</sup>, Fe<sup>3+</sup>, Ga<sup>3+</sup>, and organic molecules such as aniline, can cause changes in its nanostructure and form various compounds with several catalytic applications.<sup>[1–13]</sup> On the other hand, studies aimed at the trapping of inorganic gases are still very incipient and not illuminating.

Due to its uses as catalyst, the morphology of oxovanadium phosphate grains it an important characteristic to be controlled. In this connection, in the present work it is shown that the "regular" shape of VOPO<sub>4</sub>.2H<sub>2</sub>O crystals, that is, flat plates, can be turned into spheres by reaction (intercalation) with nitrosyl oxide (NO).

#### **EXPERIMENTAL**

The compound VOPO<sub>4</sub>.2H<sub>2</sub>O was prepared according to the methodology described elsewhere<sup>[6-12]</sup>: 12.5 g of vanadium pentoxide, V<sub>2</sub>O<sub>5</sub> (Aldrich), 111 g of H<sub>3</sub>PO<sub>4</sub> 85% (Vetec), 288 mL of distilled water, and 1.5 mL of HNO<sub>3</sub> 65% (Vetec) were mixed under reflux for 16 h. After this period, a yellow solid was obtained and filtered off, washed with acetone, and dried under vacuum at room temperature.

In order to obtain the complex VOPO<sub>4</sub>.NO.xH<sub>2</sub>O, a NO flux was created by reacting metallic copper with HNO<sub>3</sub> 6.0 mol/L. Then, a constant flow of NO gas was bubbled in an aqueous solution of vanadyl phosphate for 6 h. After this period, the greenish compound VOPO<sub>4</sub>.NO.xH<sub>2</sub>O was precipitated by adding anhydrous ethyl alcohol, and then filtered off and dried in a desiccator at low pressures.

TG analyses were performed using a Shimadzu TG-50 apparatus. Curves were recorded over a range of temperatures up to 900°C at a heating rate of 5°C min<sup>-1</sup> on N<sub>2</sub> atmosphere.

The FT-IR spectra were obtained in a PerkinElmer apparatus, model Spectrum 65 in KBr discs ( $4000-400 \text{ cm}^{-1}$ ).

The X-ray diffraction patterns were obtained in a Rigaku diffractometer model Miniflex II, with a scan rate of  $5^{\circ}$ /min,

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FIG. 1. X-ray diffraction patterns for  $VOPO_4.2H_2O$  (a) and  $VOPO_4.NO.H_2O$  (b).

angle equal to 0.05 with the step, the applied voltage of 15 kV, and current of 15 mA, using Cu detector.

The SEM images were obtained using a microscope Phillips model XL30-ESEM.

#### **RESULTS AND DISCUSSION**

The X-ray diffraction pattern for VOPO<sub>4</sub>.2H<sub>2</sub>O is shown in Figure 1. The main peaks observed in the XRD pattern are in agreement with those previously reported in the literature,<sup>[1–12]</sup> with characteristic peaks at 11.7°, 18.6°, and 23.8°, associated with the (001), (101), and (002) diffraction planes, respectively. From the 001 plane, an interlayer distance of 0.75 nm can be calculated.

Powder X-ray diffraction pattern for  $VOPO_4$ .NO.H<sub>2</sub>O is shown in Figure 1. The 001 plane diffraction peak is dislocated to 12.19. So, the intercalation of NO implies in a decrease of the interlayer distance.



FIG. 2. Infrared spectra for VOPO<sub>4</sub>.2H<sub>2</sub>O (a) and VOPO<sub>4</sub>.NO.H<sub>2</sub>O (b).

The infrared spectrum, shown in Figure 2, presented the principal bands for VOPO<sub>4</sub>.2H<sub>2</sub>O located at 3580, 1626, 1093, 946, and 685 cm<sup>-1</sup>, due to the v(OH),  $\delta$ (OH),  $v_{as}$ (P-O), v(V-O), and  $\delta$ (V-OH) or (P-OH) vibration modes, respectively, as has been previously assigned.<sup>[6–12]</sup> For the compound VOPO<sub>4</sub>.NO.H<sub>2</sub>O the main characteristic peak is of that at 1383 cm<sup>-1</sup> (asymmetric stretching) as shown in Figure 2, indicating the presence of NO species in the chemical structure of the compound.

The profile of the absorption bands due to the VOPO<sub>4</sub> lattice vibration around  $1100 \text{ cm}^{-1}$  was retained after reaction, providing evidence that an intercalation compound and not merely a salt of V-P-O species was produced.<sup>[6–12]</sup> This infrared data, on the other hand, supports the X-ray diffraction ones.

The SEM images obtained for VOPO<sub>4</sub>.2H<sub>2</sub>O and VOPO<sub>4</sub>.NO.H<sub>2</sub>O are presented in Figure 3. The compounds exhibit distinct morphologies. The compound VOPO<sub>4</sub>.2H<sub>2</sub>O, comes in the form of square plates with slightly varying sizes, while the compound VOPO<sub>4</sub>.NO.H<sub>2</sub>O displays morphological structure similar to regular-sized spheres. The proposal for the arrangement of the nitrosyl ligand in the structure of vanadyl phosphate is schematically shown in Figure 4.

The thermogravimetric curves and their derivatives, obtained for VOPO<sub>4</sub>.2H<sub>2</sub>O and VOPO<sub>4</sub>.NO.H<sub>2</sub>O are presented in

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FIG. 3. SEM micrographs for VOPO<sub>4</sub>.2H<sub>2</sub>O (a) and VOPO<sub>4</sub>.NO.H<sub>2</sub>O (b).

Figure 5. As can be seen in Figure 5 vanadyl phosphate exhibits shows two mass loss steps in the 77–124°C range. The first one is associated with dehydration, forming the monohydrate (VOPO<sub>4</sub>.2H<sub>2</sub>O  $\rightarrow$  VOPO<sub>4</sub>.H<sub>2</sub>O + H<sub>2</sub>O), and the second one is associated with the formation of the anhydrous compound: VOPO<sub>4</sub>.H<sub>2</sub>O  $\rightarrow$  VOPO<sub>4</sub> + H<sub>2</sub>O).<sup>[6–12]</sup> Two types of molecules are present in VOPO<sub>4</sub>.2H<sub>2</sub>O: one water molecule is coordinated to vanadium, in a trans position to the V=O group.<sup>[6–12]</sup> The other one is situated between the layers, and both water molecules hold the layers together by hydrogen bonding to the oxide framework. Based on these considerations, the first mass



FIG. 4. Arrangement proposed for the intercalation of the NO molecule in the structure of vanadyl phosphate.



FIG. 5. TG curves for VOPO<sub>4</sub>.2H<sub>2</sub>O (a) and VOPO<sub>4</sub>.NO.H<sub>2</sub>O (b).

loss can be attributed to the release of interlayer water molecules, and the second mass loss to the coordinated ones.<sup>[6–12]</sup>

The thermogravimetric curve for VOPO<sub>4</sub>.NO.H<sub>2</sub>O is shown in Figure 5. The main mass loss in this curve is that in the 372–400°C range, associated with the release of NO molecules coordinated to vanadium. So, in comparing Figure 5 it can be concluded that the coordinative covalent bond NO-V is stronger than the H<sub>2</sub>O-V bond.

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