Preparation of High Surface Area VOHPO$_4$·0.5H$_2$O with the Alkoxide Method

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Abstract

Vanadium phosphorous oxides (VPO) catalyze the partial oxidation of butane to maleic anhydride. These VPO are commercially manufactured from solid vanadium oxides by treating them with a sequence of two processes. The first is the reflux of V$_2$O$_5$ with organic compounds, e.g. alcohols, to reduce the metal to the +4 oxidation state and also phosphoric acid as a phosphorous source to obtain the precursor (VOHPO$_4$·0.5H$_2$O). The second is the dehydration and calcination of the precursor at a high temperature to produce the active phase comprising vanadyl pyrophosphate ((VO)$_2$P$_2$O$_7$).

The purpose of the present work is to study the implementation of an alternative method, namely the alkoxide method, to synthesize the precursor (VOHPO$_4$·0.5H$_2$O) with an increased surface area, thus enhancing its characteristics as the raw material for the synthesis of (VO)$_2$P$_2$O$_7$. The alkoxide method has been frequently adopted as a suitable route to obtain metal oxides with high surface areas. The method resorts to wet preparation, proceeding through hydrolysis and condensation reactions of the liquid metal alkoxides with water, or other acidic hydrolyzing agent, to yield metal oxides.

Alternative approaches are available to synthesize VPO via the alkoxide method. For such approaches the starting materials are vanadium (V) alkoxides that are reacted with the orthophosphoric acid in different solvents; the reaction products are dried under atmospheric conditions. A procedure that uses aprotic solvents is modified by drying the product into an autoclave with controlled excess of solvent.

Two important facts occur during the modified autoclave drying. The first is that high surface area material is obtained due to a sustainable gel structure allowed by low values of surface tension at the critical point. The right amount of solvent determines wether the liquid passes to the gas phase at or before the critical point influencing the surface area of the material. The second fact is the reduction process that is carried out inside the autoclave; the high temperature and the alcohol produced during the alkoxide hydrolysis reduce the vanadium form. Two simultaneous steps, reduction and drying are now yielding an improved precursor for the vanadyl pyrophosphate.

The resultant oxides are characterized by diffuse reflectance infrared Fourier transform spectrometry (DRIFTS), and X-ray diffraction (XRD). Moreover, their surface areas are measured with BET analysis.

1. Introduction

The preparation of VPO catalysts for the partial oxidation of butane to maleic anhydride has been demonstrated to strongly influence their catalytic activity [1, 2]. The first step for this preparation is the synthesis of the precursor. Many aspects as the type of reagents, the ratio of phosphorous to vanadium, the nature of the solvent and the conditions of the reduction step can control the morphology of this precursor and thus the catalytic characteristics of the final active phase [2]. Increasing the surface area of the precursor has been also considered as viable way to improve the catalytic performance [3]. Therefore, synthetic routes that can be oriented to the manipulation of these factors are candidates to yield an improved catalyst.

The objective of the sol-gel process is to control the composition and nanostructure of the final material during the earlier stages of synthesis [4]. The alkoxide method is one of the most traditional sol-gel process procedures. Metal alkoxides undergo controlled reactions of hydrolysis and condensation to obtain colloidal gels whose structural characteristics can be controlled and yield high surface area metal oxides with an appropriate drying process [4]. Thus, the alkoxide method might be a good synthesis route to improve VPO precursor.

The application of the alkoxide method to the vanadium phosphorous oxides has shown that reactions in aprotic solvents and the absence of water benefit the formation of small and compact particles [5]; however, the catalytic activity of the materials is decreased due to this particle morphology [11]. Other studies have shown that through sol-gel process the active phase can be synthesized and explored the application of colloidal and polymeric gelation to form membrane reactors [6]. Other methods that involve the use of proton exchange resin are also reported in the synthesis of $VOPO_4 \bullet 2H_2O$ [7].

After the sol-gel reactions are completed the solvent needs to be removed. This drying process can be by evaporation or by the well known supercritical drying [15]. During the evaporation process the gel structure is affected by the high surface tension present in the liquid-gas interface. The very small pores of the gel are filled with liquid. As the liquid is vaporized, the walls of the pores can not resist the applied force and collapse, significantly reducing the surface area and damaging the gel structure [8]. This problem can be avoided if the evaporation process is carried out close to the critical point of the solvent where there is not any surface tension [8,15]. The process is carried out in an autoclave an appropriate excess of solvent is added to reach the critical point before gel loses the solvent [15].

The purpose of this work is to apply the alkoxide method as one of the sol-gel synthesis techniques, followed by an autoclave drying in order to increase the surface area of the vanadium phosphorous oxide. During the autoclave drying not only is the solvent removed, but also the V^{5+} is reduced yielding $VOHPO_4 \bullet 0.5H_2O$, the VPO catalyst precursor.

2. Experimental

2.1 Sol-Gel Synthesis in THF

The procedure was based on the reported one [11]. Two 1M solutions were prepared: (i) vanadium (V) isopropoxide oxide (Alfa-Aesar) in tetrahydrofuran (THF), (Fisher); and (ii) orthophosphoric acid, anhydrous solid (Fluka), in THF (Fisher). Then, equal volumes (10 ml) of each solution were mixed; the phosphoric acid solution was added to the alkoxide solution while vigorous stirring was applied to the mixture. An immediate gelation process was seen whose

result was an orange gel. After three hours of reaction the mixture turned into bright yellow slurry.

2.2 Drying Process.

As a control procedure, the yellow slurry was dried at atmospheric pressure under a nitrogen stream. The gel was put into a flask and a stream of nitrogen was allowed to flow through while stirring during four hours, the product was collected and put into a vial to be characterized.

To dry the materials under high pressure a reported procedure was followed [9]. The slurry was transferred into a glass-lined 600-ml capacity Parr reactor. This autoclave reactor was equipped with a temperature control system that permitted a well controlled heating process stirring and a pressure gauge. After flushing the reactor with a flow of nitrogen gas, it was pressurized with nitrogen gas to 100 psig. Then, the reactor was heated from 25 C to 265 C at a rate of 1 C/min. After the maximum temperature was reached and equilibrated for about 10 min, the reactor was slowly vented. The product was evacuated in a quartz cell to about 5mTorr while heating at 200 C to remove any remaining solvent.

In order to reach the critical point and avoid the collapse of the fragile gel, some solvent is necessary to be added before the slurry is dried in the autoclave reactor [15]. To determine the influence of the amount of added solvent in the final product a completely randomized design was carried out with three levels or treatments: adding 20 ml, 50 ml or 100 ml (low, medium and high level, respectively) of THF. Three replications at each level were carried out.

2.3 Characterization

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) was carried out in a Thermo Nicolet Nexus™ 670 FT-IR spectrophotometer equipped with a Smart Collector™. The samples were diluted to 1-10 weight % in KBr infrared grade (Acros). The X-ray diffraction was carried out with a Bruker axs D8 advance diffractometer that was set at 40 kV and 40 mA, scans were from 5^0 to 70^0 (2θ) with step size of 0.05^0 and 1.5 s/step. The diffractometer ratiation is copper Kα (λ=1.54Å). The sample was put on the sample holder and exposed to the atmosphere at room temperature during the analysis.

The surface areas of the samples were determined by a Quantachrome Nova 1200 instrument version 6.11. The oxidation state of the Vanadium in the samples was determined with the volumetric method reported in the literature [10].

3. *Results and Discussion*

3.1 Sol-Gel Synthesis in THF

The procedure reported by Ennaciri et al [11] yields a bright yellow slurry. The DRIFTS spectrum and X-ray diffraction pattern of the product after drying it in a nitrogen stream are shown in Figure 1 and Figure 2 respectively. The DRIFTS bands are 978 cm^{-1} typical of V=O; 3500 cm^{-1} and 3611 cm^{-1} typical of O-H; 1085 cm^{-1} typical of P-O; 684 cm^{-1} typical of V-OH and 1636 cm^{-1} typical of H-O-H; all of the vibrations in $VOPO_4 \bullet 2H_2O$ [17]. However, some of the bands assigned to this compound are missing, and some other weak ones (2993 cm^{-1}, 2893 cm^{-1}, 1445 cm^{-1}, 1332 cm^{-1}, 1124 cm^{-1}, 1076 cm^{-1} and 894 cm^{-1}) are not related to any of the vanadium phosphates.
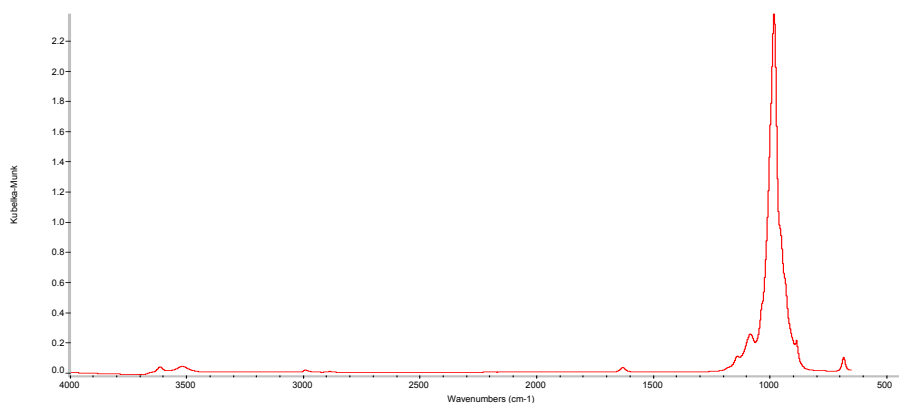
Figure 1. DRIFTS of VPO slurry in THF after drying it in a stream of N$_2$

The X-ray diffraction pattern, Figure 2, shows the presence of many of typical reflections of α-VOPO$_4$, 4.41Å, 3.59Å, 3.07Å, 3.09Å, 1.95Å, 1.87Å, 1.55Å, 1.52Å and 1.45Å as well as some of the reflections of $VOPO_4 \bullet 2H_2O$ 7.32 Å, 3.07 Å and 2.18 Å [19]. The other very important reflections at 8.71Å, 5.03Å and 2.91Å, might be respectively attributed to the displacement of 7.45Å, 4.76Å and 2.86Å of $VOPO_4 \bullet 2H_2O$ due to the intercalation of either solvent or isopropyl alcohol that could be possible as reported in the literature [12,13]. This possibility is also supported by the presence of the weak bands in the DRIFTS spectrum since 2993 cm^{-1} and 2893 cm^{-1} correspond to significant THF bands.   The surface area of the dried slurry is about 50 m^2/g that is slightly higher than the observed for the atmospheric drying in air (40 m^2/s), reported in the literature [11].
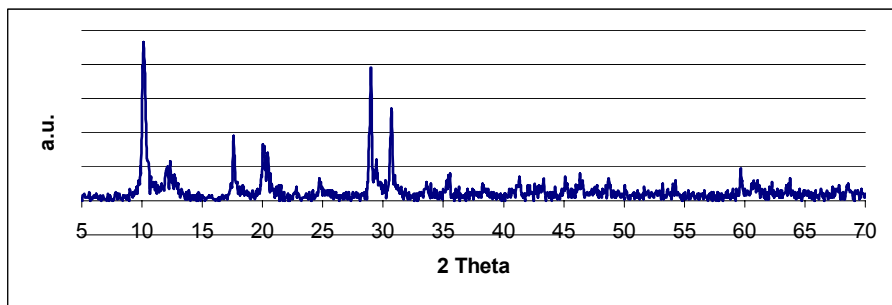
Figure 2. XRD of VPO slurry in THF after drying it in a stream of N_2.

3.2 Autoclave Drying

The autoclave drying is analyzed in terms of the pressure-temperature diagrams. The pressure in the autoclave was measured for three levels of solvent (100 ml, 50 ml and 20 ml) as a function of temperature and is shown in Figure 3. As a comparison tool in Figure 3 a theoretical curve of the liquid-vapor equilibrium of THF is plotted [14]. When high and medium amount of solvent are added to the slurry before the drying step, the system develops a behavior similar to the vapor-liquid equilibrium of pure solvent and the liquid vaporizes very close to the critical point. In contrast, when a low amount of solvent is added, the liquid completely vaporizes and never reaches the critical point.
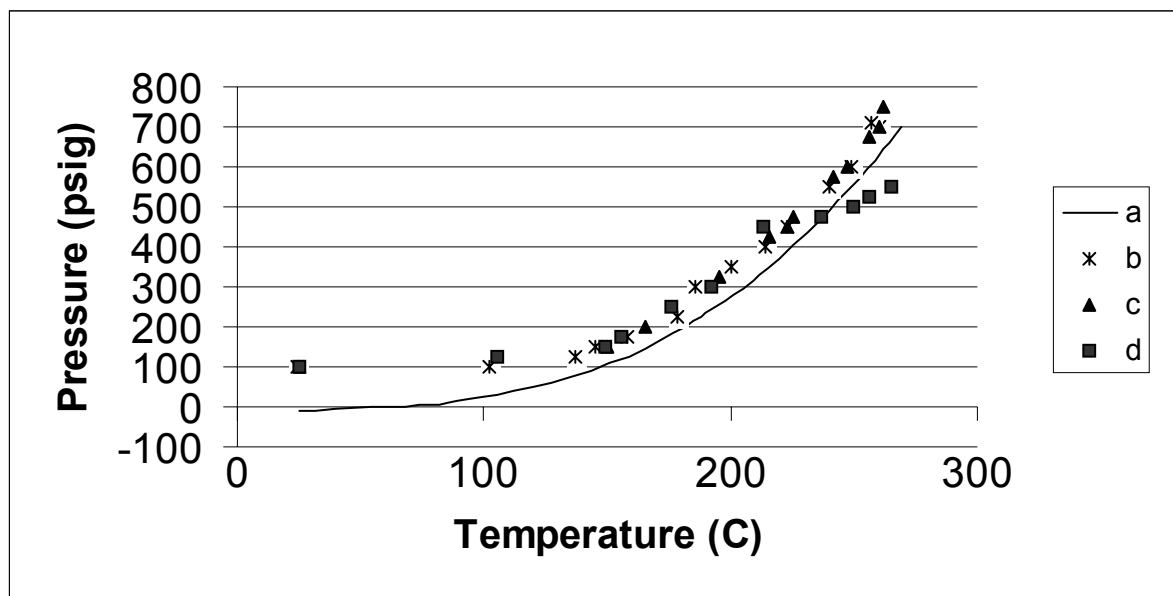
Figure 3. Pressure-Temperature diagram for the autoclave compared with the vapor pressure of THF. (a) Vapor Pressure of Pure THF (b) High amount of Solvent (100 ml) (c) Medium Amount of Solvent (50 ml) (d) Low amount of Solvent (20 ml).

Thus, in the autoclave drying of the slurry the amount of added solvent influences the conditions where it is completely vaporized which agrees with the literature [15].

3.3 Surface Area Measurements

The surface areas of all autoclave-prepared vanadium phosphates are shown in Table 1 and the influence of the amount of added solvent in this parameter is evident. The values are also higher than the above-mentioned results of 40 m^2/g reported for atmospheric pressure drying in air [11]. The analysis of variance for the experiment with the three levels of solvent results in the conclusion that there is no statistical difference between high and medium levels of solvent but the low-level mean is statistically different to the average of the two former. The Bonfferoni t test was used to compared the means [16].

These results indicate that vaporization of the solvent during drying before the critical point leads to dramatic loss of surface area.

Table 1

BET Surface areas for the products dried after adding the three amounts of solvent

| Amount of solvent	Average (m^2/g)	Standard Error
Low	65	9.6
Medium	102	9.6
High	121	9.6

3.4 DRIFTS and XRD analysis

Besides the influence of the amount of added solvent on the surface area of the materials, the infrared spectra and the X-ray diffraction patterns are also affected by the conditions of the drying step. Thus, not only physical but also chemical transformations occur at during autoclave drying.

As said in the previous section, in terms of surface area there is not a significant difference between the materials that were treated with high and medium amount of solvent. However, the results of the infrared analysis report changes in the composition of the products as they are dried with high, medium or low level of additional solvent. These results are shown in Figure 4.

Figure 4 a) and e) are fingerprints of combination of $VOPO_4$ compounds shown in Figure 1 and $VOHPO_4 \bullet 0.5H_2O$ respectively [17,18]. Figure 4 b) to d) show the evolution of spectra towards $VOHPO_4 \bullet 0.5H_2O$ bands as the amount of added solvent is decreased. Bands at 1054 cm^{-1}, 977 cm^{-1} and 1196 cm^{-1} appear in Figure 4 b), then 1104 cm^{-1} and 932 cm^{-1} are added in Figure 4 c) and finally 1133 cm^{-1} band shows up in Figure 4 d) to complete the six characteristic bands in the fingerprint spectra of $VOHPO_4 \bullet 0.5H_2O$. The amount of added solvent in the three studies influences the chemical composition of the final materials.
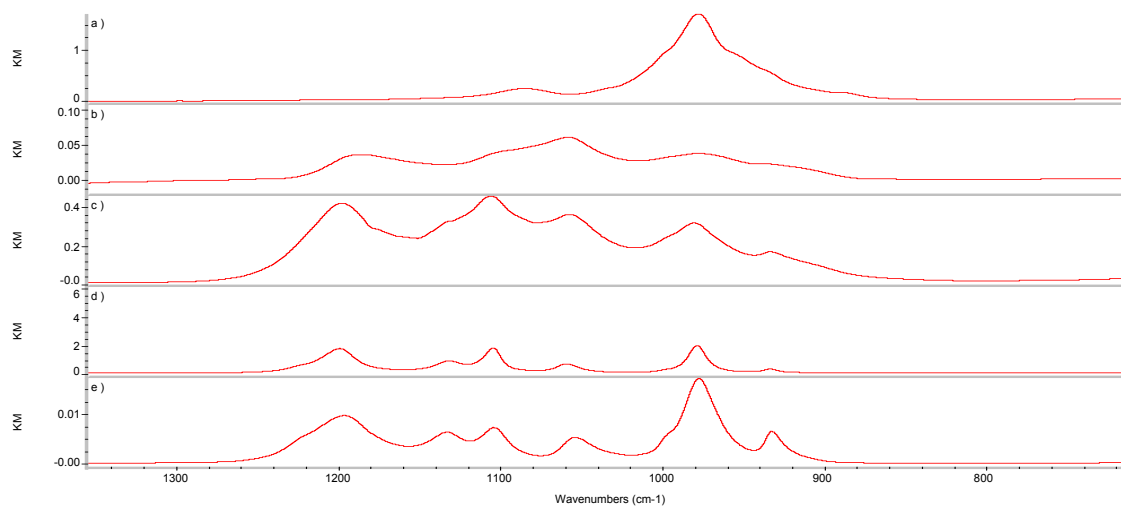
Figure 4. DRIFTS of different VPO materials, fingerprints a) Slurry dried on N₂ b) High amount of solvent c) Medium amount of solvent d) Low amount of solvent e) VOHPO₄•0.5H₂O.
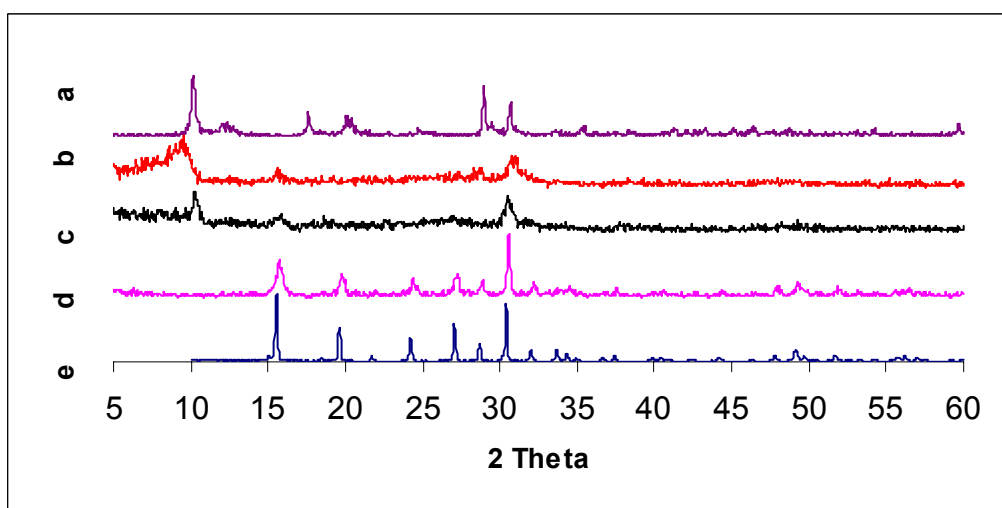
Figure 5. XRD of different VPO materials a) Slurry dried on N₂ b) High amount of solvent c) Medium amount of solvent d) Low amount of solvent e) VOHPO₄•0.5H₂O.

Similarly, Figure 5 a) and e) are X-ray diffraction patterns of combination of VOPO₄ compounds shown in Figure 2 and VOHPO₄•0.5H₂O respectively [19]. In Figure 5 b) the reflections at 5.67Å and 2.91Å appear as the first sign of the presence of the hemihydrate. Figure 5 c) is mostly equal to the a), however the peak at 4.5Å can be also observed and associated to other main reflection of the hemihydrate (4.53 Å). Figure 5 d) is the closest pattern to the e) since its analysis results in additional reflections at 3.64 Å, 3.08Å, 2.77Å, 2.59Å, 2.39Å, 1.89Å and 1.84Å. Thus the crystallography of the resultant materials evidences the transformation of the yellow slurry into a compound that can be identified as the catalyst precursor, VOHPO₄•0.5H₂O.

3.4 Reduction process inside the autoclave

As it was said in the previous sections, when the material is dried inside the autoclave, chemical transformations occur which yield products that contain reduced-vanadium phases. The reduction process can be attributed to the alcohol generated as a byproduct during the hydrolysis of the vanadium alkoxides. It is known that alcohols are good reducing agents for vanadium towards the precursor [20]. As more solvent is added to the slurry the concentration of alcohol decreases and less reduced products are obtained. In contrast, low amount of added solvent results in more reduced phases. As measured through titration, the average oxidation state of the samples decreases with the amount of solvent.

4. Conclusions

Gelation process leads to production of α-VOPO$_4$, and some intercalation compounds, i.e. compounds that have molecules of solvent or alcohol entrapped in the layers of the oxide. The possibility of interlayer-entrapped molecules for the vanadium phosphorous oxides has been reported in the literature [12,13]. THF, as a donor reagent, might intercalate in the solid layers. Intercalated molecules generate faults in the active phase crystal structure and those faults are responsible for the higher activity in the selective partial oxidation of butane to maleic anhydride [21]. This indicates that the product from the gelation process might be a candidate to yield enhanced catalyst in terms of the possible faults generated by the intercalated molecules.

Autoclave drying is a suitable procedure to increase the surface area of the vanadium phosphorous oxides that are prepared with the alkoxide method. Aprotic solvents, such as THF, benefit the sol gel-gel synthesis of VPO because of the rapid gelation process during the hydrolysis and condensation reactions and the ability to be removed from the gel at the critical point. The surface areas are dramatically affected by the amount of solvent that is retired from the solid, since it influences the final pressure of the autoclave. When the amount of solvent is duplicated the surface area is also increased in a 100%.

The changes suffered by the solid during autoclave drying are not only physical but also chemical. One of the byproducts of the hydrolysis reactions, i.e. iso-propanol might behave as a reducing agent for the V^{5+} compounds present in the slurry. The appearance of the catalyst precursor VOHPO$_4 \bullet 0.5$ H$_2$O is evidenced in its characteristic IR bands and the development of the 001 and 220 planes that are observed after the drying step. The reduction of vanadium is also evidenced through the average oxidation state of the materials that lower than 5+ after the drying process. Therefore, autoclave drying also modifies the chemical composition of the vanadium phosphorous oxides towards a high surface area and prospectively enhanced catalyst precursor (VOHPO$_4 \bullet 0.5$ H$_2$O).

5. *References*

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