Effect of calcination temperature on the structure of vanadium phosphorus oxide materials and their catalytic activity in the decomposition of 2-propanol

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Abstract The synthesis of vanadyl phosphate by reaction of an alcoholic solution of V₂O₅ and o-H₃PO₄ has been studied. The solids obtained were investigated by various physico-chemical techniques as in situ X-ray diffraction (XRD), thermogravimetric analysis (TGA), and differential thermal analysis (DTA) under inert atmosphere. The compounds have been further characterized by infrared and UV–Visible spectroscopies. The isopropanol conversion is carried out to evaluate the catalytic activity of the samples. The isopropanol conversion increases with the reaction temperature from 433 to 503 K for vanadyl phosphorus oxides calcined at a different temperature. However, the conversion attains 100% at 503 K, and the solid calcined at 973 K exhibits high selectivity towards propene (100% at 503 K).

1. Introduction
Vanadium phosphates (VPO) have many important applications. They have attracted much attention among catalysis researchers and electrochemists. The most active phase of VPO catalysts for synthesis of maleic anhydride (MA) is made up of a well-crystallized (VO)₂P₂O₇ which is considered to possess unique structural and surface features to allow the activation of alkane (Centi, 1993; Ballarini et al., 2006). Vanadium phosphorus oxide catalysts have also been widely investigated for the partial oxidation and oxidative dehydrogenation of other lower hydrocarbons (Centi, 1993; Pillai and Sahle-Demessie, 2003; Pillai and Sahle-Demessie, 2002; Kandi et al., 2003; Savary et al., 1996; Michalakos et al., 1993). Catalysts based on vanadyl phosphate (VOPO₄·2H₂O) were used...
in some reactions involving Bronsted and Lewis acid sites, such as dehydration (Carlini et al., 2004) and isomerization (Benes et al., 1997). Taufig-Yap and Saw (2008) have studied the effect of different calcination environments on the vanadium phosphate catalysts for selective oxidation of propane and n-butane. In lithium battery research, δ- and especially ε-VOPO₄, the most recently discovered polymorph (Lim et al., 1996) show promising electrochemical properties (Kerr et al., 2000; Azmi et al., 2002; Azmi et al., 2003; Song et al., 2005). In both fields of research, knowledge of the crystal structure of the respective phases is desirable, since it is a prerequisite to uncover structure--(re)activity relationships.

Decomposition of 2-propanol is frequently used as a test reaction to determine acid–base properties of different catalysts by many groups (Aramendia et al., 1996; Chen et al., 2001; Gervassini et al., 1997; Ortiz-Islasa et al., 2005; El-Molla et al., 2004; El-Shobaky et al., 2006; Oukerroum et al., 2001). It has been reported that the decomposition of 2-propanol occurs by two parallel reactions: (i) the dehydration carried out in acid sites giving the propene and the isopropyl ether (DIPE) (Ortiz-Islasa et al., 2005; Satoh et al., 2000) and (ii) the dehydration to acetone occurring on basic sites or both types of site (acid and basic) via a concerted mechanism (López et al., 2000).

The aim of this paper is to study one of the methods of preparation leading to (VO)₂P₂O₇ solid, and to examine the treatment temperature effect on the transformation of precursor to active phase in the inert atmosphere and catalytic dehydration of isopropyl alcohol at temperatures within 433–503 K.

2. Experimental

2.1. Solid synthesis

An organic protocol of the VPO precursor preparation consists of refluxing V₂O₅ (6 g) in a 100 ml of tert-butanol for 6 h at a reflux temperature of 373 K under agitation. An 85% ortho-phosphoric acid solution was then added to the resulting vanadium suspension and was refluxed for a further 16 h at 393 K. The reactant P:V mole ratio was 1:1. The resulting solid was recovered by filtration, washed by ethanol and dried at 383 K.

2.2. Characterization techniques

Powder X-ray diffraction (XRD) measurements were recorded on a Siemens D5000 diffractometer using CuKα radiation. The patterns were recorded with a step of 0.015° using a counting time of 0.2 s per step over the 2θ range from 10° to 80°, under an N₂ flow (2L/h).

TGA–DTA analysis has been recorded with a TA Instruments balance, model SDT 2966 (TGA–DTA). It allows to obtain simultaneous DTA and TGA diagrams under similar experimental conditions. Experiments were performed under an N₂ flow, from 298 K to 1073 K using a heating rate of 5 K min⁻¹.

Diffuse reflectance infrared spectra for the synthesized solids were recorded from 4000 to 400 cm⁻¹ on a Nicolet 460 spectrophotometer. Samples were prepared by mixing 1 mg of powdered solid with 150 mg of KBr.

UV–Visible spectra in diffuse reflectance mode were recorded by a Varian Cary 100 Scan spectrometer, from 200 to 800 nm.

2.3. Catalytic test

Decomposition of isopropanol was carried out in a fixed-bed type reactor with a continuous flow system at atmospheric pressure. The catalyst (100 mg, 200–500 μm particle size) was packed in a glass reactor (Pyrex tube, 10 mm I.D) placed in a furnace. Before carrying out such catalytic activity measurements, each catalyst sample was activated by heating in a stream of nitrogen for 2 h at 673 K then cooled to the catalytic reaction temperature. The reactant, 2-propanol (3.7 kPa), was diluted in nitrogen by bubbling the gas through the liquid reactant in saturator maintained at 291 K. The isopropanol decomposition was performed at a temperature between 433 and 503 K. The products were analysed by on line gas chromatography (Varian-3700 GC with a flame ionization detector FID) using a 10% 0 V–101 on Chromosorb-WHP (80/100 mesh) packed column (4 m) maintained at 353 K. A blank test showed that insignificant thermal reaction developed in the absence of the catalyst.

3. Results and discussion

3.1. XRD Results

Fig. 1 shows the evolution of the XRD patterns of the dried precipitated VPO solid calcined at different temperatures. The most intense diffraction lines at 14° present in the diffraction pattern of the dried VPO solid is attributed to the crystalline phase VOPO₄H₂O (JCPDS 47-0949) which disappeared completely at 473 K. The XRD pattern of the sample calcined at 473 K shows the formation of two anhydrous VOPO₄ allotropic phases characterised by low intense diffraction lines at 2θ = 21.6° for δ-VOPO₄ and at 28.6° for γ₂-VOPO₄ phase. The crystallinity of these phases increases with the temperature up to 773 K. These results are in agreement with those reported by Gulians et al. (1996) and Cavani et al. (2010). The diffraction lines at 2θ = 23° and 30°, observed at 673 K, have been assigned to (VO)₂(P₂O₇) (JCPDS 83-2388) which progressively crystallised with increasing of the temperature of calcination. Beyond 1073 K, a crystalline material could be clearly identified as vanadium phosphate, VPO₄ (JCPDS 76-2023) which remained stable after return to an ambient temperature.

3.2. DTA and TG analyses

Fig. 2 shows the thermogravimetric and differential thermal analysis diagrams of samples VPO. Below 773 K, the TG curve for VPO exhibits two successive mass losses. The first one occurs between the ambient temperature and 364 K. It corresponds to the loss of water potentially adsorbed on its surface. The second loss of mass takes place between 364 K and 720 K. It is due to the crystallization water from the VOPO₄H₂O phase. In this temperature range (364–720 K), the experimental mass loss amounts to 9.5% of the initial vanadium phosphate mass, which is very close to the theoretical mass loss (10%) calculated from the content of water in the
VOPO₄₋H₂O structure. The DTA curve for this solid presents two endothermic peaks at 333 K corresponding to the loss of physisorbed water, and at 412 K corresponding to the conversion of VOPO₄₋H₂O into VOPO₄ structure. An endothermic peak observed around 840 K and without loss mass can be attributed to transition phase from δ-VOPO₄ to α-I-VOPO₄ phase. This result is in agreement with XRD analysis (see Fig. 1). The endothermic peak at about 1005 K is attributed to the conversion of VOPO₄ phase into crystalline (VO)₂(P₂O₇) previously deduced from the XRD patterns. It gives place in TGA to a loss of weight of 2.8% corresponding to the reaction:

\[ 2\text{VOPO}_4 \rightarrow \langle\text{VO}\rangle_2\langle\text{P}_2\text{O}_7\rangle + \frac{1}{2}\text{O}_2 \]

3.3. IR spectroscopy

Infrared spectra of vanadium–phosphorus oxide VPO calcined at different temperatures are given in Fig. 3. Table 1 summarizes the normal modes of different phases and their attribution according to Imai et al. (2007), Kamiya et al. (2003) and Sadiq (2007). From the absorption bands, we observe that the structure of VPO evolves during the heat treatment which confirms the results XRD and TGA–DTA.

3.4. UV–Vis diffusive reflectance spectroscopic

The UV–Vis spectra of the VPO samples dried and calcined are compared in Fig. 4. The shape of the bands observed indicates the presence of different vanadium species on the surface of vanadium–phosphate solids. All spectra of VPO samples exhibit one major CTLM (charge transfer ligand–metal) band centred at about 286 nm broadened by two shoulders at 242 and 310 nm, that is, normally attributed to vanadium V⁵⁺ in...
tetrahedral coordination (VO$_4$) (Eon et al., 1994; Busca et al., 2000; Lindbald et al., 1994; Concepcion et al., 1995); in addition, the VPO samples dried and calcined at 723 K exhibit a broader band with a maximum at about 420 nm that has been attributed to V$^{5+}$ species in square-pyramidal coordination (Busca et al., 2000; Sadiq et al., 2007). But then, after calcinations at 973 K, the presence of absorption band at 650 nm corresponding to d–d transitions of vanadyl VO$_2^+$ ions in the (VO)$_2$(P$_2$O$_7$) phase indicates the reduction of V$^{5+}$ species to VO$_2^+$ (Cavani et al., 2010).

3.5. Catalytic activity

Table 2 shows the activity and selectivity in the isopropanol decomposition in the gas phase using the studied solids (VPO calcined at 723 and 973 K). The main reactions promoted by these catalysts are dehydration of the 2-propanol to the corresponding alkenes (propene) and dehydrogenation to the carbonyl derivative (acetone).

As it can be seen from Table 2 and Fig. 5 the activity of solids increases with the increasing reaction temperature in all instances. The calcined solid at 723 K (VOPO$_4$) exhibits catalytic activity higher than that calcined at 973 K ((VO)$_2$(P$_2$O$_7$)) at a reaction temperature of 433 K, and similar results obtained at a reaction temperature ≥ 473 K. The latter catalyst ((VO)$_2$(P$_2$O$_7$)) exhibits high selectivity to propene in all reaction temperatures. This higher selectivity is attributed to the increase of active site numbers on the surface of catalysts. It can be also correlated to the acidity of the catalyst (Zhu et al., 2006; Elassal et al., 2010). This selectivity attains 100% at 503 K (Table 2). In other words, the solid contains (VO)$_2$P$_2$O$_7$ phase favored dehydration over dehydrogenation, so the solid can be assumed to be essentially acid. All values shown were obtained at $t = 175$ min, beyond which conversion remained constant.

4. Conclusion

The results obtained in this work show that the synthesis of vanadium phosphate depends on the procedure of preparation. The thermal treatment at high temperature under inert atmosphere leads to vanadyl pyrophosphate (VO)$_2$(P$_2$O$_7$) whereas the treatment below 973 K leads to VOPO$_4$, as shown by XRD analysis and confirmed by DTA–TGA results. The results obtained from FT-IR and UV–Vis spectroscopy are in agreement with the previous data, showing that this technique is efficient for the analysis of vanadium–phosphate materials. The synthetic catalysts showed high activity and selectivity towards propene for the isopropanol decomposition at low reaction temperature in comparison with the others catalysts. It was found that the VOPO$_4$ samples exhibited high catalytic activity in the 2-propanol decomposition than (VO)$_2$P$_2$O$_7$ samples. The 2-propanol dehydration to propene is the predominant reaction and proceeds via an elimination E$_1$-like mechanism catalysed by acid sites.

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| Table 2 | Isopropanol conversion (%) and selectivity towards propene, acetone and diisopropyl ether (DIPE) at various temperatures over VPO catalyst calcined at 725 and 973 K. |
| --- | --- | --- | --- | --- | --- | --- |
| Temperature (K) | Catalysts | VPO calcined at 723 K | VPO calcined at 973 K |
| | Conversion (%) | Selectivity (%) | Conversion (%) | Selectivity (%) |
| | Propene | Acetone | DIPE | Propene | Acetone | DIPE |
| 433 | 30 | 49 | 49 | 2 | 18 | 69 | 31 | 0 |
| 473 | 97 | 99 | 1 | 0 | 97 | 99.5 | 0.5 | 0 |
| 503 | 100 | 99.5 | 0.5 | 0 | 100 | 100 | 0 | 0 |
References