# Effect of the temperature of calcination in the VPO

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## Introduction

The vanadium-phosphorus-oxygen (VPO) catalysts mainly the crystalline phase $(VO)_2P_2O_7$, characteristic of $V^{4+}$, are being proposed for the oxidative deshydrogenation (DHO) of $C_2$-$C_4$ hydrocarbons, showing good selectivity but low activity [1]. The chemical properties of major relevance for this type of processes is the acidity, and the characteristics redox, which has been reported are closely bound with the activity and selectivity in the formation of olefins, as well as in the carbon monoxide production [2].

## Experimental

The vanadates of phosphorus were synthesized dissolving $V_2O_5$ in isobutyl-benzyl alcohol mixture, volumetric ratio 2:1. The stage of reduction was carried out by 4 h to 110 ºC. The obtained mixture was let cool to room temperature and $H_3PO_4$ in the amount necessary was added to obtain molar ratio P/V = 0.9, 1.0 and 1.1. The synthesis system stayed at 110 ºC with constant stirring during 2 h. The resulting paste filtered to emptiness and it was washed with isobutyl alcohol; then it was dried to 125 ºC h by 16 h and calcined to 400, 500 and 600 ºC in nitrogen atmosphere.

## Results and discussion

The diffraction signals to 14.2, 18.4, 22.8, 28.4, 29.9 33.7, 36.8, 43.2, 49.4 and 58.5º (JCPDS: 50-380), confirm the presence of crystalline phase $(VO)_2P_2O_7$ (*figure 1*), when the calcination temperature is increased the intensity of the peak increases suggesting a major crystallinity of the VPO.

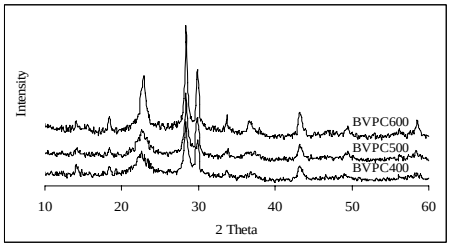


Fig. 1. Diffractions of VPO with P/V = 1.0 calcined to 400 ºC (BVPO400), 500 ºC (BVPO500) and 600 ºC (BVPO600), respectively.

Table 1. Specific area and total acidity of the synthesized VPO.

| Catalyst | Crystal size (nm) | S ($m^2/g$) | Acidity (μmol $NH_3/g$) |
|---|---|---|---|
| AVPO | 181.93 | 31.9 | 110.77 |
| BVPO | 179.61 | 36.4 | 111.15 |
| CVPO | 135.53 | 38.3 | 75.36 |
| BVPO400 | 161.45 | 38.7 | 207.55 |
| BVPO500 | 179.61 | 36.4 | 111.15 |
| BVPO600 | 231.72 | 33.4 | 118.07 |

P/V = 0.9 (AVPO), P/V = 1.0 (BVPO) y P/V = 1.1 (CVPO)

The crystal size in the VPO increased with the calcination temperature, but phosphorus content major causes a diminution in the particle size of such (*table 1*). On other hand, the phosphorus content increased the specific area of the VPO, nevertheless this is little significant with relation to P/V = 0.9, 1.0 and 1.1, being diminished with the increase of the calcination temperature (31-39 $m^2/g$), although these are three times higher than reported in the literature for prepared materials under identical conditions but with a P/V=1.15 ratio and calcined to 500 °C [3]. Nevertheless, has been reported vanadates of phosphorus with specific area of 43 $m^2/g$ prepared from a $VCl_3$ and $V_2O_5$ mixture in medium organic [4].

The high adsorption of ammonia that presents the VPO is related to the enrichment of phosphorus in the surface of the catalysts (*table 1*), which is responsible of the increase in the acid sites [3], nevertheless, that adsorption diminishes by effect of calcination temperature, due to loss of functional groups of the pyrophosphate of vanadium [1].

IR spectra, show bands between 900-1300 $cm^{-1}$ assigned to V=O and $PO_3$. In addition, strong signals of absorption around 500-800 $cm^{-1}$ corresponding to P-O-P and O-P-O vibrational modes, which confirm the presence of the $(VO)_2P_2O_7$ in the catalysts [3]. The intensity of the peaks slightly diminishes due to the modification that undergoes vanadium pyrophosphate structure by the increase of calcination temperature. Nevertheless, by the increase in the phosphorus content the peaks were a little more defined, probably the phosphorus helps to a good crystallization of the phase of the vanadium pyrophosphate.

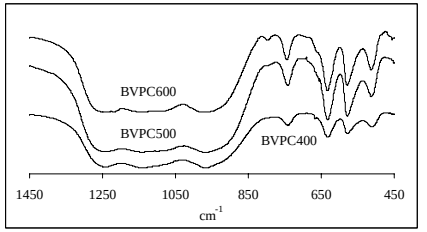


Fig. 2. IR spectra of the VPO with relation molar P/V = 1.0 calcined to 400, 500 and 600 ºC.

## Conclusions

The vanadium pyrophosphate is present in the VPO with a P/V=1.0 molar ratio and calcined to 400, 500 and 600 ºC, respectively, obtaining a higher crystallinity with the heat treatment to 600 ºC, taking to a development in the crystal size, confirmed by X-rays diffraction. The calcination temperature has a little significant effect on the specific area of the VPO, since they presented specific areas from 31 to 39 $m^2/g$ in all the cases, with P/V=0.9, 1.0 and 1.1 ratio, although improves the specific area of the vanadates of phosphorus, reaching areas of around 39 $m^2/g$. The acidity is favored by the increase in the phosphorus content, orienting in a major proportion towards the generation of very strong acid sites, nevertheless, the increase in the calcination temperature undergo to a gradual reduction of the acidity.

**Gratefulness**: To the Conacyt by the scholarship granted with number 181667.

## Reference

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