Electron Microscopy Studies Of VPO and New NbPO-VPO Catalyst

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Abstract

A new family of vanadium phosphorus oxides (VPO) catalysts has been identified. Its consists in a preparation of the phase $VOHP0_4.0,5H_20$ where a well crystallized $NbP0_4$ is introduced. Electron microscopy, in conjunction with other techniques (XFR, XDR, and BET) has been used to understand the link between catalytic performance and micro-structural interactions of vanadium phosphate and niobium phosphate phases in NbP0-VPO catalyst.

Keywords: VPO catalysts; Niobium Phosphate, Vanadium phosphate

Introduction

Vanadium phosphorus oxides (VPO) are used for the mild oxidation of n-butane to maleic anhydride [1-3].Industrially, the activation of VPO catalysts needs more than 1000h in a classical bed reactor. In previous work [4], we showed, in agreement with Mattsuura et alli [5-6], that niobium phosphate is a good material to improve the catalytic performance for n-butane oxidation to maleic anhydride. In this communication, we show, by SEM, TEM and HREM aspects of micro-structural interactions of vanadium phosphate and niobium phases, in NbPO-VPO catalysts.

Materials and Methods

a) Preparation of the $NbPO_4$ phase.

The niobium phosphate has been prepared from niobium oxide (Nb_20_5 PA – 99,9985 % - ALFA). The Nb_20_5 was dissolved in presence of HF at 70° C during 12 hours and the H_3PO_4 (85%) was added. After 8 hours at 70° C, a white precipitate was obtained and washed with HNO_3 (5M) and distillated water.

The white powder was dried at 80°C during 70 hours.

b) Preparation of the$VOHPO_4$,0.5 H_2O and VPO-NbPO precursors.

The $VOHPO_4$,0.5 H_2O precursor were prepared following the classical Exxon method by refluxing V_2O_5 (3,2g) with isobutanol and H_3PO_4 85%(4,5g) [7]. The VPO-NbPO precursor were prepared by introducing the $NbPO_4$ (0,5g) just before the nucleation of the $VOHPO_4$,0.5 H_2O in organic medium [7]. The mixture was refluxed for 24 hours. A blue precipitate was formed, centrifuged at room temperature, washed with isobutanol and dried at 100°C for 16 hours.

c) Physicochemical characterization

The chemical analysis of the solids was obtained by XRF using a Philips model PW 2400. The x-ray analysis was obtained using a Siemens diffractometer and CuKα radiation. A Scanning Electron Microscope Hitachi S 800 was used to study the morphology of the materials. Textural measurements were performed on a ASAP 2000 apparatus.

Results

The XRF chemical analysis of the solids NbPO-VPO and $VOHPO_4$ $0.5H_2O$ are showed in the Table 1 .

Table I – XRF Chemical Analysis (%w)

	Nb	V	P	P/V (mol)
$VOHPO_4,0,5H_2O$	-	26.99	23.94	1.46
NbPO-VPO	3.21	25.41	21.85	1.41

The BET area of the VPO-NbPO precursors is given in Table II.

Table II – BET area

Solids	S_{BET} (m^2/g)
$VOHPO_4,0,5H_2O$	**7.26**
NbPO-VPO	**10.63**
$NbOPO_4$	**17.14**

The x-ray diffraction pattern of the VPO-NbPO and $VOHPO_4,0,5H_2O$ oxides are presented in Figures 1 .

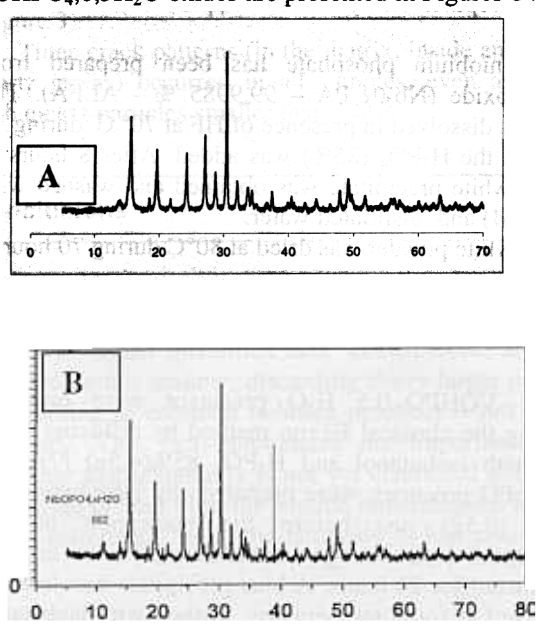


Figure 1. Powder X-ray diffraction of

A =$VOHPO_4.0,5H_2O$ and B =NbPO-VPO catalysts

Electrons microscopy was used to study the microstructural interactions between the phases. The Figure 2 shows the Scanning Electron Microscopy (SEM).

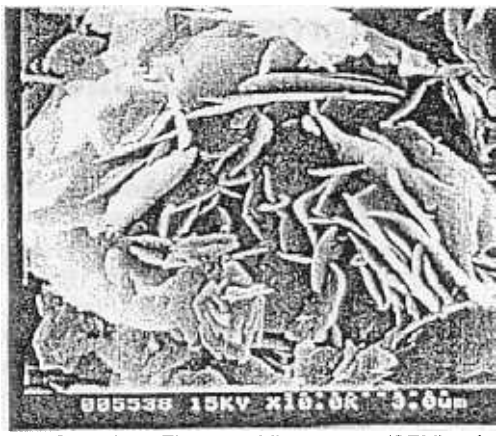


Figure.2. Scanning Electron Microscopy (SEM) of $VOHPO_4$ $0.5H_2O$

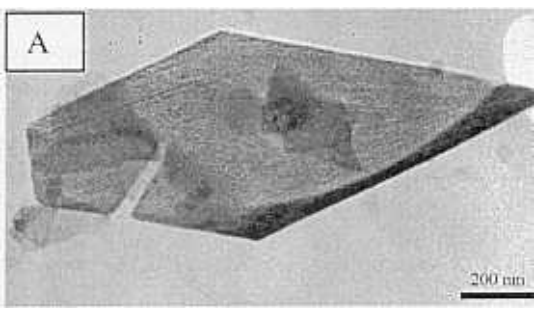
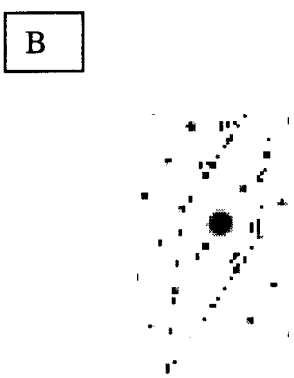


Figure. 3.Transmission Electron Microscopy (TEM) and select area diffraction pattern (SADP) of $VOHPO_4,0,5H_2O$ phase (B)



The high Resolution electron micrograph of $VOHPO_4.0,5H_2O$ and NbPO - VPO. Phases are presented in Figures 4 and 5 respectively.

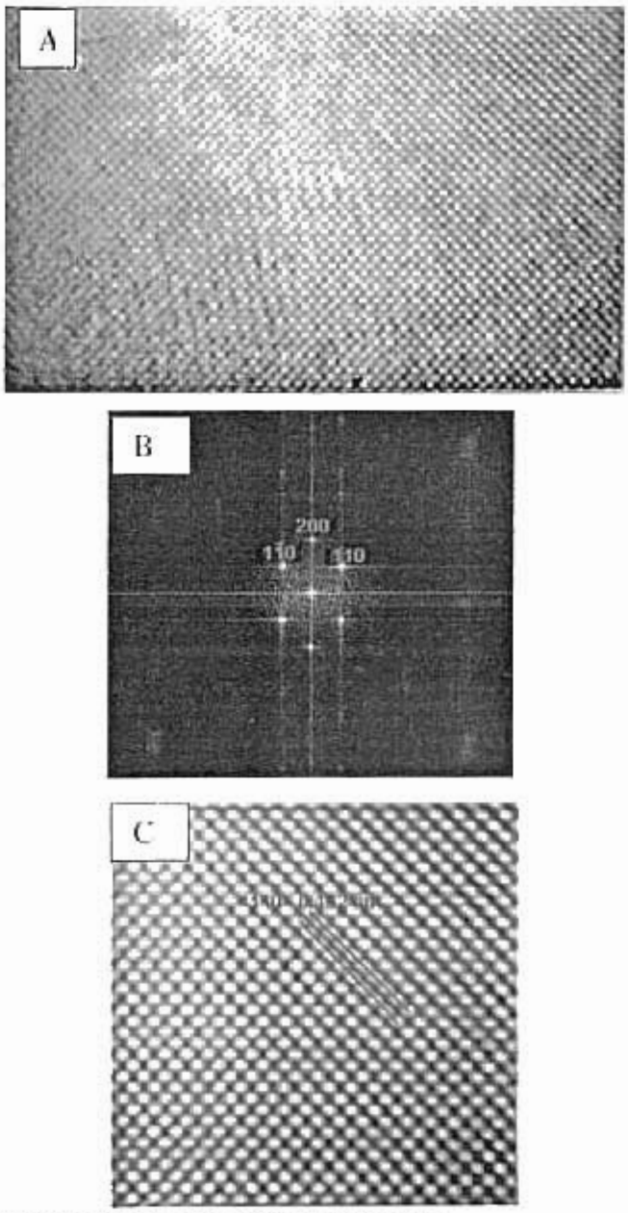


Figure.4. High resolution electron micrograph of $VOPO_4.0.5H_2O$.projection (A), (B) filtered FFT of 4A, (C) FFT of 4B

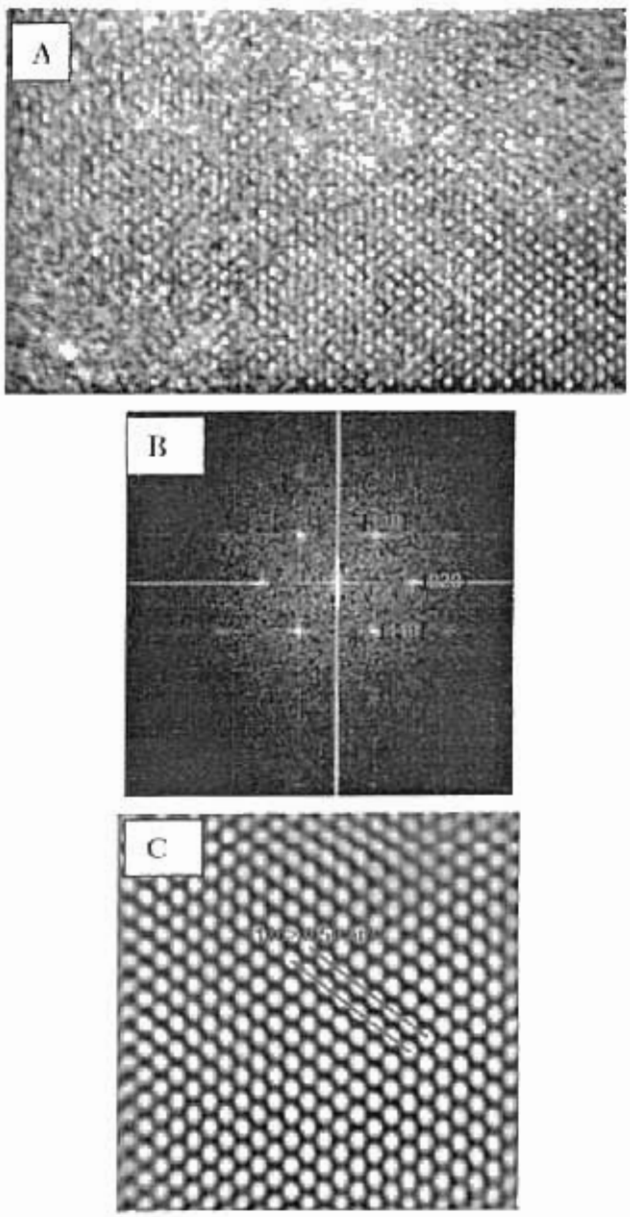


Figure.5. High resolution electron micrograph of NbPO - VPO.projection , (B) filtered FFT of 5A, (C) FFT of 5B

Discussion

The BET area of the VPO-NbPO precursors is given in table 1. It increases with the NbPO contribuition.

The XRD spectra of VPO and NbPO-VPO are presented in fig.2 They are characteristic of the $VOPO_4.0.5\ H_2O$ phase. However the (002) line observed in the spectra of the figure 1B is characteristic of the $NbOPO_4.xH_2O$.

Scanning Electron Microscopy (SEM) shows that the material is composed of platelets sometimes agglomerated

forming structures resembling flattened flowers. The use of isobuthanol alcohol in VPO and NbPO-VPO synthesis leads to the formation of a high surface " rosette" form of $VOPO_4$, $0,5H_2O$. TEM of the hemihydrate precursor material revealed that the material was composed of rhomboidal-type plates (as shown in figure 3A). The platelets were very crystalline and the selected area diffraction pattern (SADP) is characteristic of the commonly reported [001] projection of $VOPO_4$, $0,5H_2O$ (figure 3B). The major and minor axes of plated correspond to [-1-10] and [130] directions of the hemihydrate structure respectively. The angles have of 151^0 as mesured on the TEM negative.

Typical high resolution image of the compound as well as analysis of fringe spacings and intersection angles confirmed that this corresponds to the [001] projections of $VOPO_4$, $0,5H_2O$. Figure 4 shows an indexed filtered FFT of the image and the diffraction pattern is a close match to the figure 4. In this study using TEM coupled with EDX analysis, did not find any segregation of Nb in doped VPO-type catalysts. Since XRD profiles of all the materials showed relatively broad peaks corresponding to only the $VOPO_4$, $0,5H_2O$ phase.

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References

1. Hodnett, B.K., Catal Rev.Sci.Eng. 27 (1986) 373. [
2. Hodnett, B.K., Catal Today 1 (1987) 477.
3. Centi, G, Trifiro, F., Edner, J.R., Francheti, J.M., Chem. Rev. 88 (1988) 55.
4. Pries, P.G. de Oliveira,. Eon, J.G., Chavant, M,. Riché, A. S., Martin, V., Caldarelli, S., and Volta, J.C., Catal Today 57 (2000) 177-186
5. Matsuura,I., Ishimura, T., Hayakawa, S., Kimura, N., in Abstract, Second International Symposium on Niobium Compouds, Tokyo, 1995,p.39
6. Matsuura, I., Ishimura, T., Hayakawa, S., Kimura, N Catal. Today 28 (1996) 133.
7. Sananés- Schulz, M.T., Bem Abdelouahab, F., Hultchings, G.J., Volta, J.C., J. Catal. 163 (1996)346.