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NOTE

Characterization of Different Precursors and Activated Vanadium Phosphate Catalysts by ^{31}P NMR Spin Echo Mapping

In a previous publication (1), we emphasized the use of the spin echo mapping technique applied to ^{31}P NMR to obtain information on the valence state of vanadium in different environments of phosphorus for several VPO reference structures. In this paper we describe the use of this technique, combined with knowledge of reference phases (1), to study VPO catalysts prepared from different precursors and used for the oxidation of *n*-butane into maleic anhydride.

It is generally considered that the vanadyl pyrophosphate $(VO)_2P_2O_7$ is the catalytically active phase in the reaction (2). However, an equilibrium V^{4+}/V^{5+} can be postulated on the surface of vanadyl pyrophosphate. Some authors have stressed the importance of a surface layer of V^{5+} sites or of $VOPO_4$ islands on the $(VO)_2P_2O_7$ matrix (2–4). Moreover, we have observed by *in situ* Raman spectroscopy a restructuring of the VPO catalysts in the course of the activation of a $VOHPO_4$, 0.5 H_2O precursor which shows, first, a growing of $VOPO_4$ domains on a disorganized $(VO)_2P_2O_7$ matrix, followed by a redispersion of the $VOPO_4$ structures as V^{5+} sites on the basal (100) face of $(VO)_2P_2O_7$ when the activation proceeds (5).

From these considerations, it appears important to detect the different valence state of vanadium for the VPO catalysts and their corresponding precursors, and to avoid ambiguities of the bulk determination of the valence states by titration methods which require a chemical dissolution in sulfuric acid with possible modification of the vanadium oxidation state using one such method (6). The spin echo mapping technique offers a nondestructive determination of the valence state of the vanadium.

Here we report the characterization by ^{31}P spin echo mapping of different VPO precursors which differ in their conditions of preparation and in the corresponding VPO catalysts after activation under the *n*-butane/air catalytic atmosphere. The information obtained is discussed in relation to other physicochemical characteristics of the materials and their catalytic performances. The preparation of three $VOHPO_4$. 0.5 H_2O precursors denoted P1, P2, and P3 has been previously described (7). Catalyst precursor P1 was prepared by dissolving V_2O_5 (6.06 g) in aqueous HCl (35%, 79 ml) at reflux for 2 h. H_3PO_4 (8.91 g, 85%) was added and the solution was refluxed for a further 2 h. The solution was then evaporated to dryness and the resulting solid was refluxed in water (20 ml H_2O/g solid) for 1 h, filtered hot, washed with warm water, and dried in air (110°C, 16 h). Catalyst precursor P2 was prepared by adding V_2O_5 (11.8 g) to isobutanol (250 ml). H_3PO_4 (16.49 g, 85%) was then introduced to the mixture which was then refluxed for 16 h. The light blue suspension was then separated from the organic solution by filtration and washed with isobutanol (200 ml) and ethanol (150 ml, 100%). The resulting solid was refluxed in water (9 ml H_2O/g solid), filtered hot, and dried in air (110°C, 16 h). Catalyst precursor P3 was prepared via $VOPO_4 \cdot 2H_2O$. V_2O_5 (12.0 g) and H_3PO_4 (115.5 g, 85%) were refluxed in water (24 ml H_2O/g solid) for 8 h. The resulting $VOPO_4$, $2H_2O$ was recovered by filtration and washed with a little water. $VOPO_4$, $2H_2O$ (4 g) was refluxed with isobutanol (80 ml) for 21 h, and the resulting solid was recovered by filtration and dried in air (110°C, 16 h).

Three VPO catalysts denoted C1, C2, and C3 were obtained from the corresponding precursors P1, P2, and P3 after 75 h of activation under identical conditions. 1.5 ml of the precursors were treated at 385°C under a *n*-butane/air mixture (1.5%) GSHV 1000 h^{-1}. Reactor products were analyzed on-line by gas chromatography.

^{31}P NMR experiments were performed on a BRUKER MSL 300 NMR spectrometer. Conventional spectra were obtained at 121.5 MHz using a $90°x$-(acquire) sequence. The 90° pulse was 4.2 μs and the delay time between two consecutive scans was 10 s. Samples were typically spun at 4 kHz in zirconia rotors using a double bearing probehead.

The ^{31}P spin echo spectra were recorded under static conditions, using a $90°x$-τ-$180°y$-τ- (acquire sequence). The 90° pulse was 4.2 μs and τ was 20 μs. For each sample, the irradiation frequency was varied in increments of 100 kHz above and below the ^{31}P resonance of

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H_3PO_4. The number of spectra thus recorded was dictated by the frequency limits beyond which no spectral intensity was visible. The ^{31}P NMR spin echo mapping information was then obtained by superposition of all spectra.

Figure 1A gives the ^{31}P spin echo mapping spectra of the three precursors. In all cases, we observe a characteristic spectrum with an intense line at 1625 ppm. This line corresponds to PO_4 groups bonded to the V^{4+} cations of the hemihydrate structure, in agreement with our previous observation of the reference phase (1). The higher intensity of this line for P1 and P2 can be explained by the higher crystallinity of these materials. It is also noteworthy that the weak shoulder observed between 200 and 1200 ppm is higher for P3, which appears less crystallized as compared to P1 and P2. This shoulder has been previously interpreted as being associated to V^{4+} cations in a disorganized environment (1). It is obvious that the ^{31}P spin echo mapping spectra are not sensitive to the difference of morphology observed between P1–P2 and P3 by XRD (7) and by electronic microscopy (8). The small peak observed at 0 ppm was attributed to residual H_3PO_4. This was confirmed by ^{31}P MAS-NMR with a signal at the same position.

Figure 2 gives the XRD spectra of the three activated catalysts. C1 shows principally the $VOPO_4$ phases with a higher content of α_{II} as compared to γ and δ $VOPO_4$. Some $(VO)_2P_2O_7$ can be present but it is difficult to index. C2 is poorly crystallized and cannot be indexed by XRD or by laser raman spectroscopy (7). On the contrary, C3 is mainly $(VO)_2P_2O_7$ (all lines can be indexed with this phase) without any $VOPO_4$ phases. An enlargement of the (200) line is typical of this catalyst, which is significant of crystals of $(VO)_2P_2O_7$ with thin platelets in the ⟨100⟩ direction with a high development of the basal (100) face. The peculiar morphology of catalyst C3 is consistent with the special morphology of the corresponding precursor P3 and the well known (001) $VOHPO_4$, 0.5 H_2O/(100) $(VO)_2P_2O_7$ epitaxial transformation (8).

Figure 1B gives the ^{31}P NMR spin echo mapping spectra of the three catalysts. By reference with the reference phases as previously published (1), the presence of the only $VOPO_4$ phases with a line at 0 ppm is confirmed for

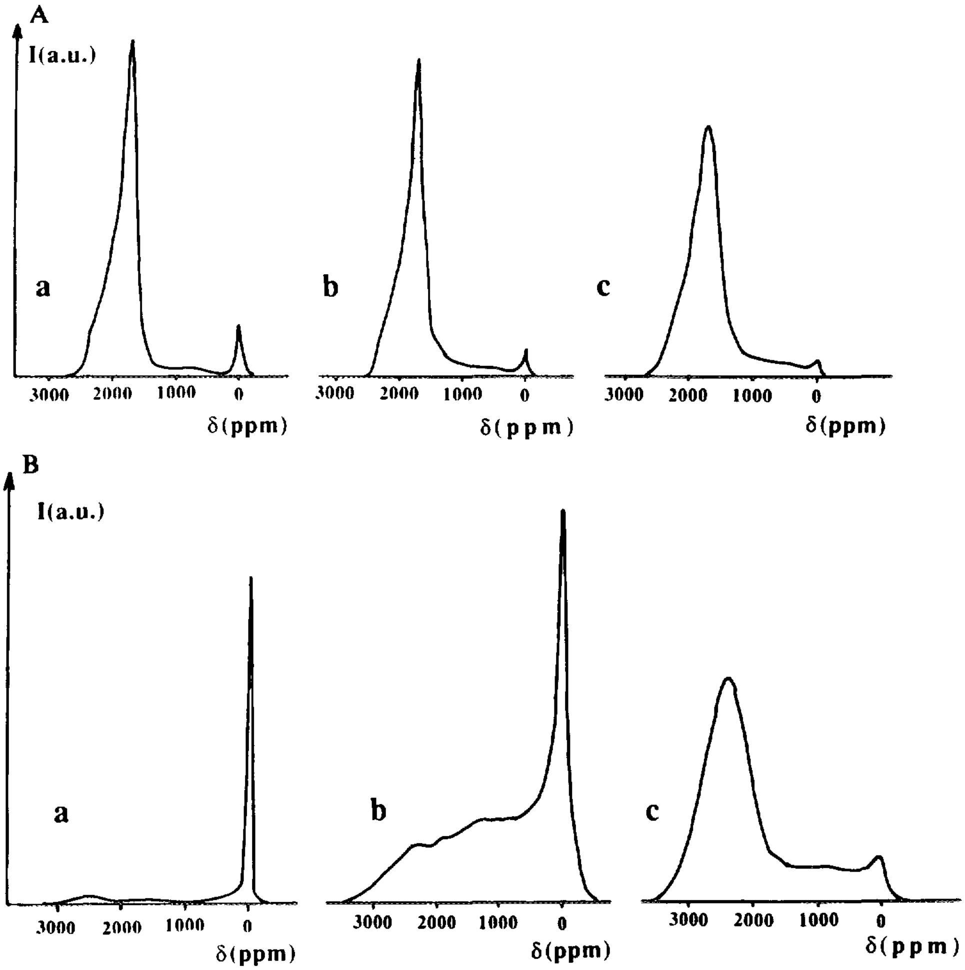

FIG. 1. (A) ^{31}P NMR by spin echo mapping of the three VPO precursors. (a) Precursor P1, (b) precursor P2, (c) precursor P3. (B) ^{31}P NMR by spin echo mapping of the three activated VPO catalysts. (a) Catalyst C1, (b) catalyst C2, (c) catalyst C3.

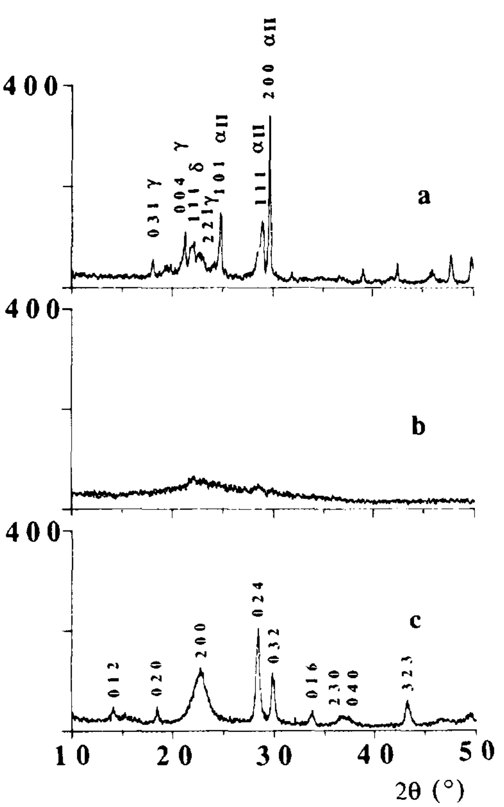

FIG. 2. XRD spectra of the three activated VPO catalysts. (a) Catalyst C1, (b) catalyst C2, (c) catalyst C3.

C1 with traces of $(VO)_2P_2O_7$ (small signal at 2600 ppm). This is consistent with the XRD examination (Fig. 2). The different $VOPO_4$ phases cannot be distinguished by ^{31}P NMR spin echo mapping (1) and it is necessary to use other techniques, e.g., *in situ* laser raman spectroscopy (5). For C2, the presence of the $VOPO_4$ phases (signal at 0 ppm) is also detected by ^{31}P MAS-NMR. The specificity of the ^{31}P NMR spin echo mapping technique as compared to that of XRD and laser raman spectroscopy stems from the consideration of the spectrum of catalyst C2 and C3. Indeed, the broad signal observed between 400 and 3000 ppm has been interpreted as disorganized $(VO)_2P_2O_7$ (Fig. 2b). The weak intensity of the signal at 2600 ppm indicative of crystallized $(VO)_2P_2O_7$ (1) confirms the high disorder of the V^{4+} structure of vanadyl pyrophosphate on this catalyst. The spectrum of C3 is characteristic of crystallized $(VO)_2P_2O_7$ (signal at 2600 ppm) with no $VOPO_4$ phase (almost no signal at 0 ppm) (1). The shoulder at 200–1800 ppm as for the spectrum of C2 is indicative of the presence of a disorganized V^{4+} structure observed also on some spectra of $VOHPO_4$, 0.5 H_2O (1).

From the XRD, ^{31}P MAS-NMR (7) and ^{31}P NMR by spin echo mapping studies, C1 can be considered as a mixture of α_{II}, γ, and δ $VOPO_4$, while C2 can be considered as a disorganized $(VO)_2P_2O_7$ structure supporting α_{II}, γ, and δ $VOPO_4$ phases but with less α_{II} as compared to C1. Catalyst C3 can be considered as crystallized and disorganized $(VO)_2P_2O_7$.

The catalytic performance of the catalysts after a period of 75 h (conditions of Ref. (9)) under the 1.5% *n*C4/air mixture at 385°C and GSHV 1000 h^{-1} is presented in Table 1.

It clearly appears that catalyst C3 is much more active and selective as compared to catalysts C1 and C2. The higher activity of C3 is in agreement with its higher BET area: 43 $m^2\,g^{-1}$ for C3, and 4 and 14 $m^2\,g^{-1}$ for C1 and C2, respectively (7). However, a comparison of the specific activities of C1, C2 and C3 shows comparable values (1.24, 1.35, and 1.19 $\times$ 10^{-5} mole MA $\cdot$ $m^{-2}\,h^{-1}$, respectively), which shows that even with complete different physicochemical characteristics of the catalysts, as observed by XRD, ^{31}P MAS-NMR, and ^{31}P spin echo mapping, the distribution of the catalytic sites on the equilibrated catalysts is the same on the three catalysts with respect to activity. However, it is clear that the catalyst consisting of mainly $(VO)_2P_2O_7$ is the most selective.

In conclusion, ^{31}P NMR by spin echo mapping is a very powerful technique to distinguish the different valence state of vanadium surrounding the phosphorus atoms in different matrix environment of the V, P, O catalysts for *n*-butane oxidation into maleic anhydride.

The difference of morphologies of the $VOHPO_4$, 0.5 H_2O precursors cannot be distinguished by ^{31}P NMR spin echo mapping.

The main interest of the ^{31}P NMR spin echo mapping technique stems from the possibility to detect low amounts of the $(VO)_2P_2O_7$ phase, particularly on poorly crystallized materials, and to be able to discriminate between crystallized $(VO)_2P_2O_7$ (signal at 2600 ppm) and a disorganized V^{4+} vanadyl pyrophosphate matrix (postulated with a broad signal at 200–1800 ppm). This has to be confirmed by TEM examination. This appears highly important since the catalytic role of the amorphous phase has sometimes been considered by some authors to explain the catalytic activity of the VPO catalysts. The different $VOPO_4$ phases cannot be distinguished by ^{31}P NMR spin echo mapping (1).

^{31}P NMR by spin echo mapping appears to be a complementary technique to ^{31}P MAS-NMR, XRD, and *in situ*

TABLE 1

Performance of the Catalysts (75 h Activation, 385°C, 1.5% *n*-butane/air, GSHV 1000 h^{-1}) (According to Ref. (9))

		Products selectivity (%)		
Catalysts	*n*-Butane conv (%)	MA	CO	CO_2
C1	11	51	41	7
C2	27	52	34	14
C3	62	64	21	14

Raman spectroscopy for the study of the equilibrated VPO catalysts and to follow the different steps of its activation from the precursor since the position of V^{4+} appears at different positions in $VOHPO_4$, 0.5 H_2O and in $(VO)_2P_2O_7$.

Another interesting conclusion from this study is the fact that the best catalytic results are associated with a structure for which phosphorus atoms are connected both to V^{4+} ions corresponding to crystallized $(VO)_2P_2O_7$ and to V^{4+} ions in a disorganized matrix. Our opinion is that such a disordered structure could favour improved reoxidation of V^{4+} to V^{5+} and thereby enhance the involvement of the V^{4+}/V^{5+} redox cycle which is known to be required for the mild oxidation of *n*-butane.

The same specific activity to maleic anhydride has been observed independently of the very different VPO structure of the catalysts considered. It can be thus concluded that the VPO catalyst changes its superficial structure under the *n*-butane/air mixture under catalytic conditions to arrive to the same favourable final surface V^{4+}/V^{5+} distribution independently of the bulk composition. This distribution appears to be influenced also by the reaction products and particularly by maleic anhydride as we have recently evidenced by *in situ* laser raman spectroscopy (5).

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