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Dynamic processes on vanadium phosphorous oxides for selective alkane oxidation

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Abstract

The use of complementary physicochemical tools (XRD, Raman spectroscopy, XPS, ^{31}P NMR, and electron microscopy techniques), sometimes used in in situ conditions has allowed to evidence the dynamic processes occurring during the oxidation of light alkanes on the vanadium phosphorus oxide (VPO) system. The transformations of the VPO system in the course of the oxidation of *n*-butane to maleic anhydride and of the oxidation of propane to acrylic acid are contrasted in connection with the evolution of the catalytic performances.

Keywords: Dynamic processes; Vanadium phosphorous oxides; Selective alkane oxidation

1. Introduction

Oxides can be used as acid–base and redox catalysts to prepare valuable chemicals from hydrocarbons [1].

For redox catalysts, the chemical reaction implies usually the interaction of the organic reagent and dioxygen at the surface of the oxide matrix. The well-known Mars and Van Krevelen mechanism is often considered to explain the different steps which allow the hydrocarbon to be transformed to the desired chemicals. According to this scheme, the hydrocarbon is activated on a site S_1 while O_2 can interact on a different site S_2. The facility for the hydrocarbon to be activated strongly depends on its nature. While it is relatively easy for olefins due to the reactivity induced by C = C double bond, it is much more difficult for less reactive alkanes. In this second case, the reactivity will depend on different properties of the oxide surface where acid–base and redox sites have to be simultaneously considered, with a molecular description of the active sites [2]. Electron and oxygen species are carried between sites S_1 and S_2 which makes of the bulk of the oxide a living material as it is also for the surface. Products of the reaction likes oxygenates, water and CO_x can interact with the catalytic material which should have for consequence to change the surface and the bulk composition and thus change the distribution of the generated products all along the period of activation. Sometimes, the catalyst is generated from a precursor, directly in the industrial reactor, which implies a continuous transformation of the chemistry of the material during the catalytic process.

Dynamic processes have been considered for the case of the oxidation of olefins [3], and the role of interfacial effects have been proposed to influence the catalytic properties in this case [4]. Synergy effects observed for multicomponent

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molybdates in the case of propene oxidation can be also explained by the dynamic processes which occur in the course of the industrial procedure [5].

However this aspect has not been considered so far in the case of the oxidation of alkanes. It is the aim of this communication to highlight the dynamic processes which occur in the case of the oxidation of *n*-butane to maleic anhydride and of the oxidation of propane to acrylic acid for the vanadium phosphorus oxide catalyst.

2. The vanadium phosphorus oxide system for *n*-butane oxidation to maleic anhydride. Dynamic processes occurring during the activation of the precursor and the role of promotors

The study of this system has been the subject of extended research, due principally to its wide use as catalyst for the oxidation of *n*-butane to maleic anhydride [6]. Many phases have been identified with different oxidation state of vanadium [7].

The VPO catalyst is usually obtained from the $VOHPO_4 \cdot 0.5H_2O$ precursor, the vanadyl hemihydrate (V^{4+}) often prepared according an organic route as in this work [6]. Then it is calcined under nitrogen to obtain the vanadyl pyrophosphate $(VO)_2P_2O_7$ (V^{4+}) or, directly, under the *n*-butane/air atmosphere (1–3%). The γ- and δ-$VOPO_4$ phases (V^{5+}) can also be obtained from the same $VOHPO_4 \cdot 0.5H_2O$ precursor by direct oxidation under oxygen at 680 and 450°C, respectively [8]. The vanadyl pyrophosphate has been considered as the main phase for the oxidation of *n*-butane to maleic anhydride but the participation of some V^{5+} species has also been postulated by some authors [6,9] which appeared quite plausible since the δ-$VOPO_4$ phase is obtained in the same temperature range as the temperature of catalysis. A study of the superficial structure of the VPO catalyst during the pretreatment and the activation was done by X-ray diffraction which demonstrated a considerable difference between ex situ and in situ catalysts and the presence of some $VOPO_4$ phases(V^{5+}) at the moment of the transformation of the precursor [10].

The dynamic processes that occurred during the activation of the $VOHPO_4 \cdot 0.5H_2O$ precursor under the *n*-butane/air atmosphere appeared to us as a key to identify the active sites for the oxidation of *n*-butane to maleic anhydride. This is the reason why we decided to follow this activation using the information given by laser Raman spectroscopy (LRS) [8,11]. An in situ Raman cell was built at the Institut de Recherches sur la Catalyse, CNRS. It was connected to a FID detector in order to obtain simultaneously catalytic and spectroscopic information during the activation process. Fig. 1a shows three spectra in the temperature range (350–370°C) where the vanadyl hemihydrate is decomposed. From this spectra, it is obvious that maleic anhydride is produced once the $VOPO_4$ (α_{II}-, γ- and δ-) (bands at 1080 cm^{-1}) and the $(VO)_2P_2O_7$ structures (bands at 1120 and 1176 cm^{-1}) are simultaneously detected by LRS. This experimental result evidenced the necessity of the presence of V^{4+} and V^{5+} sites to oxidize *n*-butane to maleic anhydride. By increasing the temperature from 370 up to 410°C, catalytic performances were improved with time but the LRS spectra changed after 17 h as is evidenced from Fig. 1b. The new spectra were characteristic of the $(VO)_2P_2O_7$ phase (bands at 928 and 1172 cm^{-1}) and of disorganized $VOPO_4$ structures evidenced by a very large signal around 1108 cm^{-1} envelop of the characteristic bands of the $VOPO_4$ phases [8]. We observed separately by in situ Raman and ^{31}P MAS-NMR that δ-$VOPO_4$ was progressively transformed to α_{II}-$VOPO_4$ under the catalytic conditions [8]. These observations confirmed the fact that dynamic processes were occurring in the course of the activation of the VPO catalyst and that these phenomena changed the physicochemical characteristics and the performances of the catalyst.

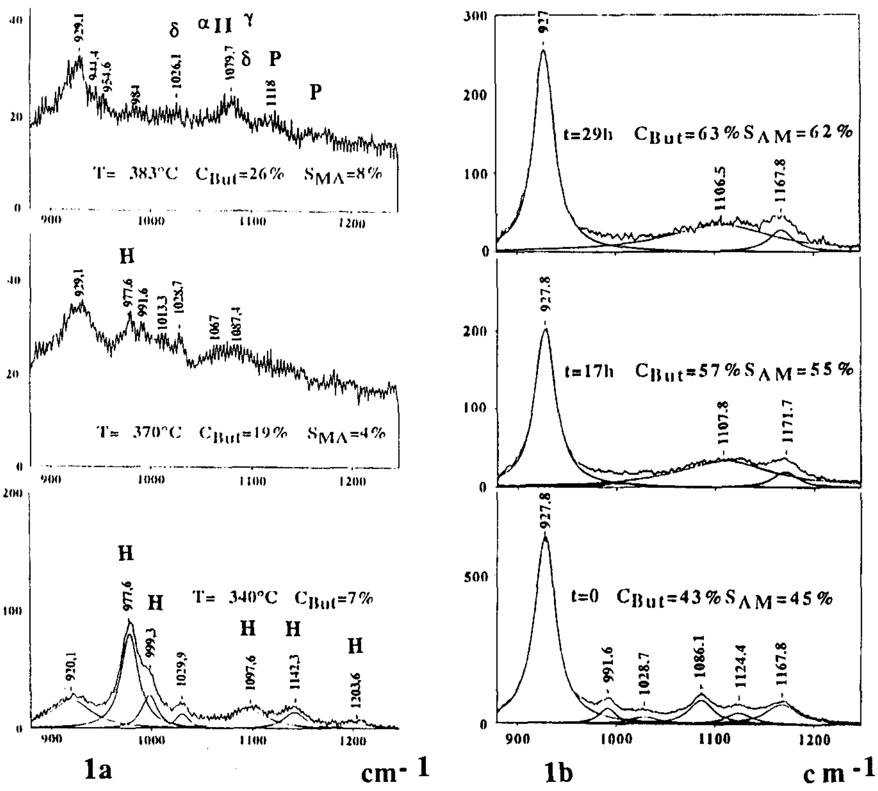


Fig. 1. Raman spectra of the VPO catalyst during the activation of the $VOHPO_4 \cdot 0.5H_2O$ precursor under *n*-butane/air (1.5%): (a) between 340 and 383°C; (b) at 410°C with time increase.

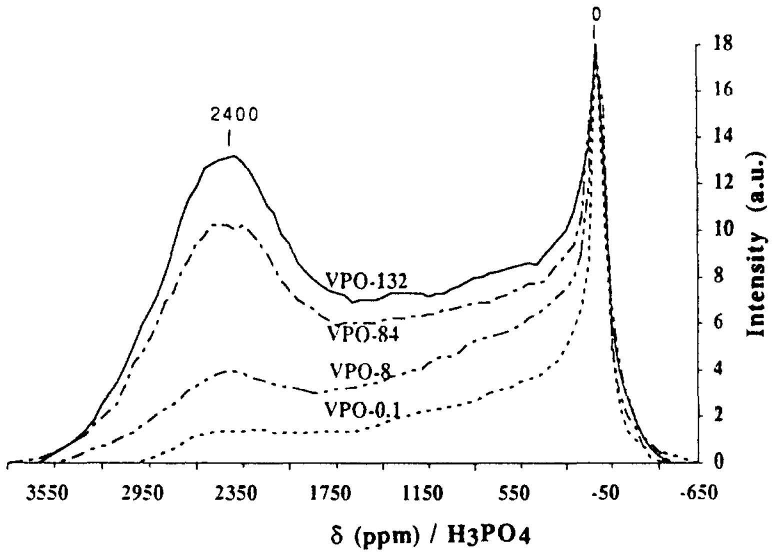


Fig. 2. ^{31}P NMR by spin echo mapping of the VPO catalysts as function of the time of activation (from [12]): VPO0.1, 0.1 h; VPO8, 8 h; VPO84, 84 h; VPO132, 132 h.

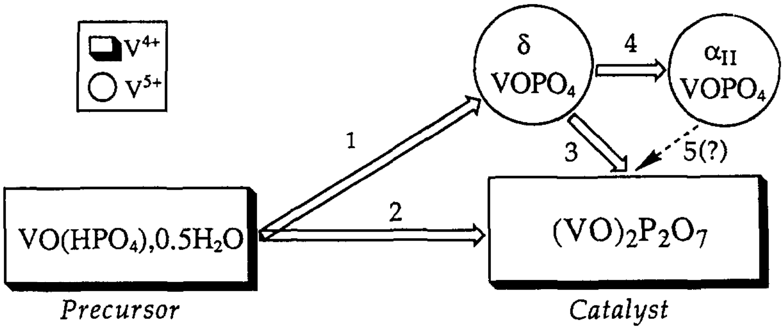


Fig. 3. Scheme of the proposed evolution of the VPO catalyst with activation time (from [12])

Further studies at the Institut de Recherches sur la Catalyse confirmed the evolution of the VPO catalyst during the activation time and that both the surface and the bulk of the materials were thus modified [12]. VPO catalysts were examined at different periods of the activation by XRD, ^{31}P MAS-NMR, ^{31}P NMR by spin echo mapping and by XPS [12]. While XRD revealed the presence of a disorganized $(VO)_2P_2O_7$ material the crystallinity of which was improving with time, the ^{31}P NMR by spin echo mapping technique (Fig. 2) showed three

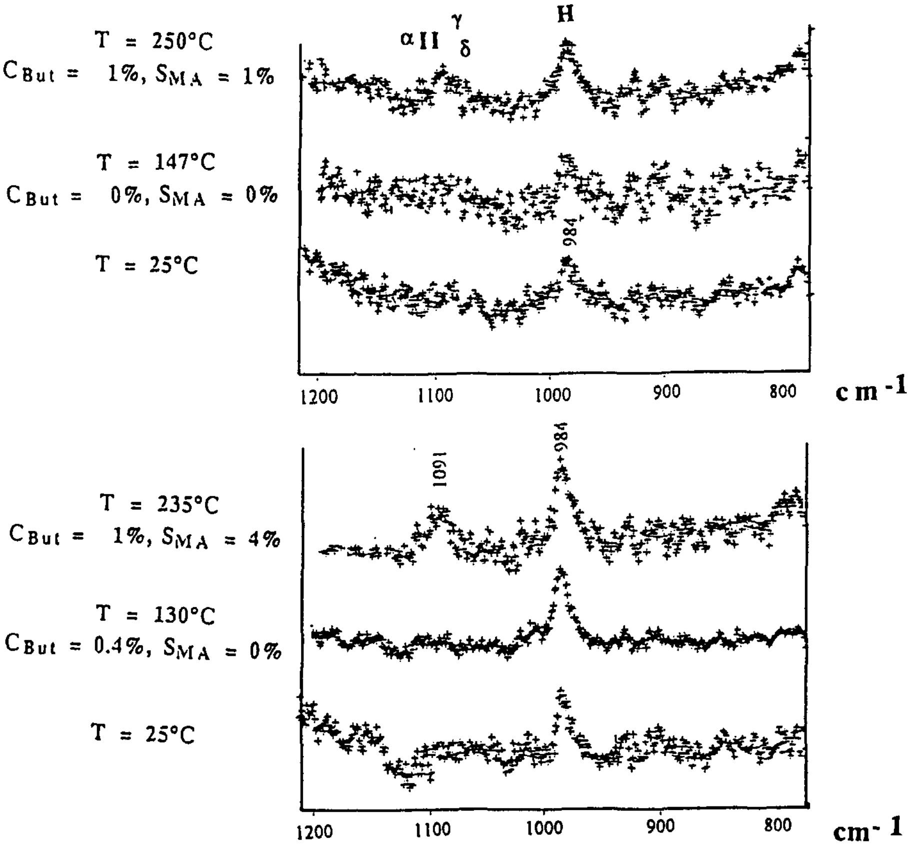


Fig. 4. Raman spectra of the doped VPO catalysts when activated from the $VOHPO_4 \cdot 0.5H_2O$ precursor (from [14]): (a) 5% Co/V; (b) 5% Fe/V.

signals characteristic of the $VOPO_4$ phases (0 ppm), crystallized $(VO)_2P_2O_7$ (2400 ppm) and a disorganized $(VO)_2P_2O_7$ (200–1200 ppm). The relative distribution of these three signals changed with time with a progressive increase of the contribution of crystallized pyrophosphate at the expense of $VOPO_4$ and poorly crystallized $(VO)_2P_2O_7$. ^{31}P MAS-NMR allowed one to confirm that among the $VOPO_4$ phases, δ-$VOPO_4$ was progressively transformed to α_{II}-$VOPO_4$. A decomposition of the V2p3/2 XPS peak showed that the distribution of the two signals characteristic of V^{4+} (516.9 eV) and V^{5+} (518 eV) was changing with the time of activation. V^{4+} signal was progressively increasing at the expense of V^{5+} showing that the surface of the VPO catalyst was slowly reduced with the time of activation. Taking into account of the information obtained by all these techniques and also by the previous in situ Raman study [11], a model was proposed to explain the dynamic processes which were occurring during the activation of the $VOHPO_4$, 0.5 H_2O precursor under the *n*-butane/air atmosphere. This model is presented in Fig. 3. Two parallel routes are considered for the evolution of the precursor:

1. the oxydehydration of $VOHPO_4 \cdot 0.5H_2O$ to $VOPO_4$ phases;
2. the dehydration of $VOHPO_4 \cdot 0.5H_2O$ to $(VO)_2P_2O_7$.

which are associated with a progressive transformation of the $VOPO_4$ structures (δ- to α_{II}-) which parallels their progressive reduction.

We questioned ourselves about the eventual effects which should be induced by promotors on these dynamic processes.

Indeed it is well known that the addition of promotors can strongly improve the catalytic performances affecting both the *n*-butane conversion and the MA selectivity [13].

The LRS in situ examination of the evolution of two VPO catalysts doped with Co and Fe (Co or Fe/V = 5%), during the period of activation of their corresponding precursors, showed that, at variance with the undoped VPO, the $VOPO_4$ signals (band at 1091 cm^{-1}) appeared at much lower temperature (230–250°C) (Fig. 4) and that this observation was associated with the simultaneous detection of MA in the flow [14].

These results show that, for redox considerations, the promotor facilitates the oxidation route of the VPO material and thus changes the sequence of the dynamic processes which occur during the activation of the $VOHPO_4 \cdot 0.5H_2O$ precursor under the *n*-butane/air atmosphere. This may explain the favourable role of doping since the $VOPO_4/(VO)_2P_2O_7$ dispersion should be strongly affected by this effect and the local V^{5+}/V^{4+} distribution should be modified, thus changing the time to reach a stationary state for the physicochemical composition at the surface of the VPO catalyst. This information is highly important for industrial considerations: 'equilibrated VPO catalysts' should be reached more rapidly by doping, saving time in unit plants, and thus money.

3. The vanadium phosphorus oxide system for propane oxidation to acrylic acid. Dynamic processes occurring during the activation of the precursor

Few studies have been devoted to the synthesis of acrylic acid from propane by direct oxidation. Such a process should become industrially competitive, even at low conversion, with the condition that selectivity of the transformation is preserved. Vanadium Phosphorus oxides still appear to be the most interesting catalytic system for this reaction [15–17]. The experimental conditions which give the best yields to acrylic acid appeared to be very important, and the conditions of adding water vapour crucial to control the performances of the VPO catalyst. As a consequence, a study was conducted on the dynamic processes occurring during the activation of the $VOHPO_4 \cdot 0.5H_2O$ precursor under the propane/oxygen/water vapour reacting atmosphere [18].

The catalytic oxidation of propane was studied by changing the feed composition and the temperature of reaction. Best yield for acrylic acid was obtained in the case of high oxidising conditions corresponding to the composition $C_3H_8/O_2/H_2O/N_2$:1.6/17.8/0–40/80.6–40.6. GHSV was 1050 h^{-1} ($W/F = 0.4$ g h dm^{-3}). $VOHPO_4 \cdot 0.5H_2O$ was first activated at 430°C for 18 h without water in the feed ($C_3H_8/O_2/H_2O/N_2$: 1.6/17.8/0/80.6). Fig. 5 summarizes the evolution of the catalytic performances with time. Propane conversion first increases up to 54% while acrylic acid is not detected. Temperature is then decreased to 400°C for 8 h which causes a decrease of propane conversion (28%). At this temperature, up to 40%, water is added in the feed. Acrylic acid is detected when 10% water is added in the flow and its selectivity increases up to 30% with an evolution similar to that of acetic acid (12% maximum). Propane conversion decreases to 10%.

The dynamic processes which occurred during the activation of the precursor, before and after the addition of water, were followed by XRD, ^{31}P MAS-NMR, ^{31}P NMR by spin echo mapping, by measurements of the acidic properties by NH_3 thermodesorption and by a control of the modification of the microstructure using the complementarity of the electron microscopy techniques [19]. Results are summarized in Table 1. Before the addition of water, the VPO catalyst shows two distinct morphologies: chains of $(VO)_2P_2O_7$ crystallites and lozenge shaped platelets of poorly crystallized δ-$VOPO_4$ showing edges of $(VO)_2P_2O_7$ crystallites which appeared to be the precursors of the previous chains. The addition of water which has been observed to be responsible for the production of acrylic acid has four major consequences:

1. to improve the crystallinity of $(VO)_2P_2O_7$;
2. to strongly decrease the δ-$VOPO_4/(VO)_2P_2O_7$ ratio;
3. to considerably increase the δ-

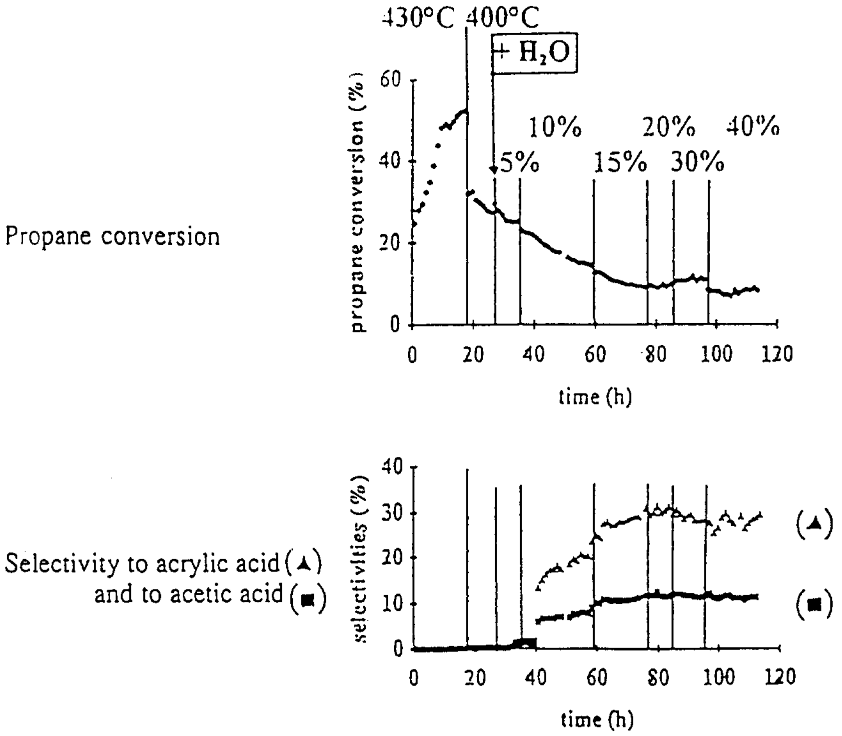
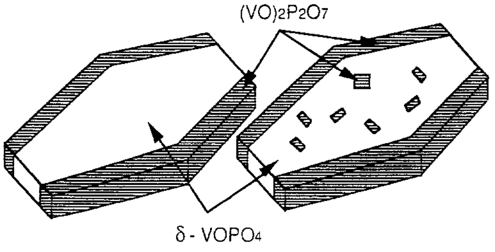


Fig. 5. Evolution of the catalytic performances with time (from [18]).

Table 1
Modifications induced by adding water

	bef. H_2O addition	after adding H_2O
Color	green	grey-yellow
S_{BET} (m^2/g)	15	21
Phases identified	$(VO)_2P_2O_7$ δ-$VOPO_4$	$(VO)_2P_2O_7$ δ- and α_{II}-$VOPO_4$
Cristallinity	poor	improved
V^{5+}/V^{4+}	1.7	0.1
Brönsted acidity		
strength	+++	++++
number	++	+++
Lewis acidity		
strength	++	+++
number	++	+++
Microstructure		

$VOPO_4/(VO)_2P_2O_7$ interface by developing numerous $(VO)_2P_2O_7$ crystallites in the (100) face of δ-$VOPO_4$;

4. to increase both the number and the strength of the Lewis and Brönsted acidic sites.

4. Conclusions

The two previous examples concerning the oxidation of *n*-butane and propane performed on vanadium phosphorus oxides show that strong dynamic processes affect the materials in the period of activation of the VPO precursor.

The activation of the $VOHPO_4 \cdot 0.5H_2O$ precursor under the *n*-butane/air reacting atmosphere goes through two parallel routes which allow in a first step a simultaneous oxidation to $VOPO_4$ phases (α_{II}-, γ- and δ-) and a dehydration to $(VO)_2P_2O_7$ and a progressive reduction of the $VOPO_4$ phases to $(VO)_2P_2O_7$. Catalytic performances to maleic anhydride improve with the increase of the crystallinity of $(VO)_2P_2O_7$ while both the superficial and bulk V^{5+}/V^{4+} ratio decreases.

The addition of doping elements (Fe and Co) strongly increases the dynamic processes which occur on the VPO system.

The activation of propane to acrylic acid needs a much higher initial $VOPO_4/(VO)_2P_2O_7$ ratio and a high percentage of water in the flow. The addition of water to the propane–air mixture results in the formation of acrylic acid which parallels, the reduction of the catalyst, an improvement of the crystallinity of $(VO)_2P_2O_7$ and a strong increase of the δ-$VOPO_4/(VO)_2P_2O_7$ interface.

By crossing different physicochemical techniques which approach both the surface and the bulk structure of the catalysts with the electron microscopy techniques, it was possible to approach the microstructure of the catalysts. We stressed the importance of three interdependent parameters: the oxidation state which can be controlled by promotors, the crystallinity and the acidity which can be controlled by hydration of the VPO material.

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