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Nature of active oxygen in the *n*-butane selective oxidation over well-defined V–P–O catalysts: an oxygen isotopic labelling study

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Abstract

Using gaseous $^{18}O_2$, we have investigated the respective role of lattice and adsorbed oxygen in the *n*-butane oxidation to maleic anhydride (MA) and CO_x on well-crystallized $(VO)_2P_2O_7$ and on a long term activated VPO catalyst. The reaction was performed at 350°C in a glass reactor, with a dry-ice cold trap and a recirculation pump. The reactor was connected to a mass spectrometer for on-line gas analysis. It has been checked that oxygen isotopic heteroexchange did not occur at a significant rate. The changes with reaction time of the ^{18}O isotopic labelling shows that only lattice oxygen is active for the formation of MA and the other products. For MA, this conclusion has been further confirmed by comparing the experimental evolution of the isotopic distribution (amu 98, 100, 102 and 104) with calculated mass spectra assuming a progressive replacement of lattice ^{16}O by ^{18}O in agreement with a redox mechanism. When the steady-state ^{18}O labelling of products is achieved, the oxygen balance indicates the presence of ^{18}O within a few surface layers of the catalyst. This result has been further confirmed by post-reaction analysis using low energy ion spectroscopy, providing a direct evidence of both ^{18}O and ^{16}O on the surface.

Keywords: Active oxygen; *n*-Butane selective oxidation; VPO catalysts; Oxygen isotopic labelling study

1. Introduction

Maleic anhydride (MA) is an important chemical intermediate produced at an industrial scale by selective oxidation of *n*-butane over VPO catalysts [1–5]. The respective role of lattice and gas-phase oxygen in the formation of partial and complete oxidation products is indeed a most important question relevant to the mechanism of this reaction. In early works, Trifirò et al. [6] proposed that adsorbed oxygen was involved in the oxygen insertion steps from 1,3 butadiene to MA. This question has been also addressed using gaseous $^{18}O_2$ by Kruchinin et al. [7], Pepera et al. [8] and Misono et al. [9]. These works concluded that lattice oxygen ions located in a few surface layers would be responsible of the formation of MA and CO_x at least under steady state conditions. It may be observed that in these studies the catalyst was first treated with $^{16}O_2$ at high temperature just before performing the *n*-butane oxidation with $^{18}O_2$. Such a treatment could lead to surface oxidation of the catalyst or to the adsorption of some form of oxygen. It may be added that the catalyst was not always clearly characterized. Kruchinin et al. [7] only stated that they used 'a

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model VPO catalyst with an addition of cobalt oxide'.

Using a pulse flow reactor, Zazhigalov et al. [10] conversely concluded that MA formation over $(VO)_2P_2O_7$ is mainly due to gas phase oxygen. More recently, Gleaves et al. [1,11,12] using the TAP reactor system concluded that the VPO catalyst functioned with two types of oxygens: surface lattice oxygen responsible of the ring closure (furan formation) and activated chemisorbed oxygen O^* involved in the further step of MA formation. Furthermore, chemisorbed oxygen could also react directly with *n*-butane to form CO_2 directly by a fast process. This would be the main non selective route of *n*-butane conversion.

This literature survey shows that the role of lattice and chemisorbed oxygen is still far from clear and this prompted us to reexamine this question on a well-defined vanadyl pyrophosphate phase. We have used gaseous $^{18}O_2$ in a recirculation reactor connected to a mass spectrometer for the on-line analysis of the labelling of product. Using a similar experimental device, we have previously shown that lattice oxygen is responsible of the formation of acrolein over MoO_3 catalysts [13].

2. Experimental

The *n*-butane oxidation using $^{18}O_2$ (isotopic purity 98 at%) has been performed in a closed-circulation system (volume: 160 cm^3). As shown in the schematic diagram (Fig. 1), the system was connected to a mass spectrometer to monitor the gas phase composition and indeed the percentage of ^{18}O (F) in the products. A metering leak valve allowed to direct a constant gas flow from the system to the mass spectrometer under a low pressure (2×10^{-6} Torr usually). The whole line could be baked at 80–100°C to prevent the condensation of MA. Prior to the reaction, the reaction mixture was allowed to circulate for 30 minutes to ensure a good gas mixing, the reactor being by-passed. A cold trap (cooled with dry-ice in acetone) located just after the reactor was used to separate the condensable product, mainly MA and water. The catalyst (mass = 200 mg) was put in a glass reactor and the reaction was performed at 350°C. The mass spectrometer signal has been first calibrated for the different gases involved in the reaction, using mixtures with nitrogen of known composition. The introduction of gases in the reactor line, previously outgassed and evacu-

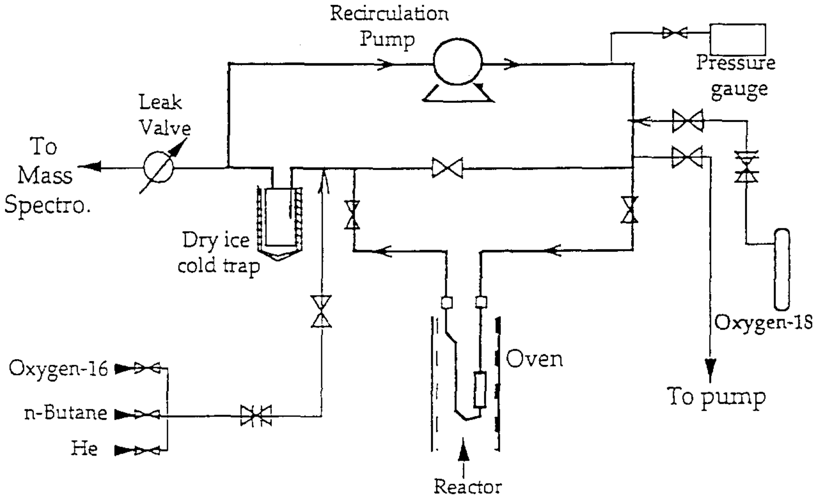

Fig. 1. Schematic diagram of the closed circulation reactor.

ated, was monitored using an absolute pressure gauge and precision metering valves.

The evolution of the reaction with time was followed by choosing six selected masses recorded with a computer. For the condensable product, the analysis was done after evacuation of the line and by-passing the reactor. The reaction was always performed with a large excess of $^{18}O_2$ (with an initial ratio $^{18}O_2/n$-butane = 12) as in the industrial process. Helium was added to reach the atmospheric pressure in the circulation line.

Low energy ion spectroscopy (LEIS) has been used to analyse the surface of the catalyst after completion of the reaction with $^{18}O_2$. This technique, also know as ion scattering spectroscopy (ISS), is most sensitive to the very first surface layer of a solid. He^+ ions with a primary energy of 1 keV have been used with a low current (20 nA under a spot of about 1 mm^2). For a given scattering angle (142°C), the energy of the elastically scattered ions is directly related to the mass of surface atoms. The catalyst, put on a metallic sample holder was transferred in the ultra high-vacuum chamber. The energy analysis of scattered ions was performed at room temperature using a hemispherical electrostatic analyser.

3. Preparation, characterization and catalytic performance of the catalyst

It is well known that the nature and the catalytic performances of VPO catalysts strongly depend on their preparation. $VO(HPO_4)$, $0.5H_2O$ has been prepared by refluxing V_2O_5 in isobutanol [14] with H_3PO_4 85% ($P/V = 1.1$). This precursor was first dried at 110°C and then dehydrated under a nitrogen flow at 750°C for 72 h. The X-ray diffraction pattern of the obtained solid (Fig. 2) is in agreement [15] with a pure and well crystallized pyrophosphate of vanadyl phase. This catalyst has been also characterized using the ^{31}P NMR Spin Echo Mapping technique. Schrader et al. [16] and later Sananes et al. [17] have shown that this technique is very sensitive to the precise nature of the VPO phase. As shown in Fig. 3, the spectrum displays a chemical shift centered at 2600 ppm, typical of V^{4+} in the $(VO)_2P_2O_7$ phase [16,17]. XPS analysis showed that the binding energy of vanadium (BE ≈ 517 eV) corresponded to the V^{4+} oxidation state [5] as expected for $(VO)_2P_2O_7$ with the presence of about 15% of V^{5+} according to a decomposition procedure of the $V_{2p3/2}$ peak as shown in Fig. 4, already described in a recent paper [5]. XPS analysis on the used catalyst gave exactly the same results, showing that the oxidation state of surface vanadium did not change.

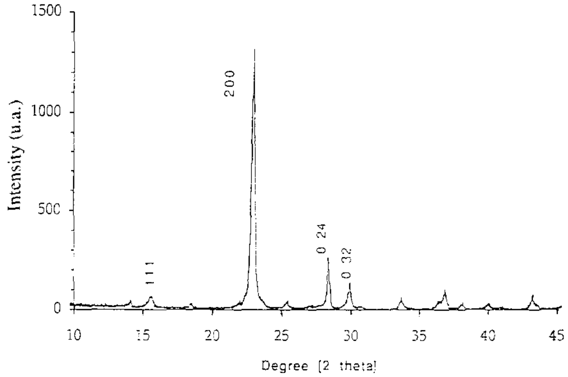

Fig. 2. X-ray diffraction pattern of the $(VO)_2P_2O_7$ catalyst.

The catalytic performance of this solid (with a BET surface area of 5 m^2 g^{-1}) was checked in a conventional flow microreactor (fixed bed) with GC analysis. At 350°C, with a GSHV =

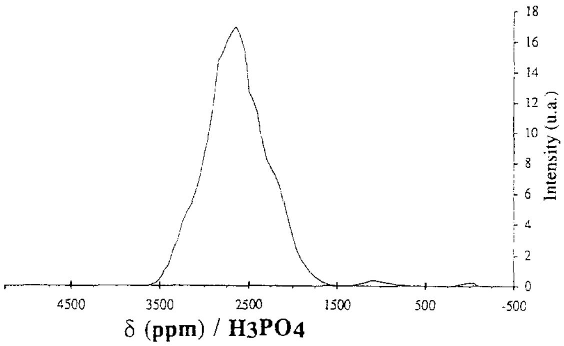

Fig. 3. ^{31}P NMR spin echo mapping spectrum of the $(VO)_2P_2O_7$ catalyst.

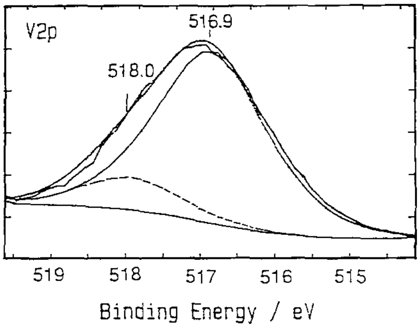

Fig. 4. XPS analysis of the $(VO)_2P_2O_7$ catalyst: $V_2p3/2$ level decomposed into V^{4+} (516.9 eV) and V^{5+} (518 eV).

1500 h^{-1} and a reaction mixture n-$C_4H_{10}/O_2/He$: 1.5/18/80.5, the selectivity for MA formation was 80% for a n-butane conversion of 6%.

4. Study of the isotopic exchange of oxygen with $(VO)_2P_2O_7$

The interpretation of the ^{18}O-labelling of products using gaseous $^{18}O_2$ relies on the fact that unlabelled molecules are formed with the ^{16}O of the oxide catalyst (at least at the beginning of the reaction). This conclusion may not be clear if a significant oxygen exchange occurs between the solid and ^{18}O labelled molecules.

Recall that water and MA were trapped just after their formation in the reactor (see Fig. 1). Therefore these molecules could not participate to the oxygen exchange. This is important because the rate of exchange of oxygen between water and metal oxides can be extremely rapid [18,19].

The exchange between $^{18}O_2$ and $^{16}O_2$ has been studied at 350°C on $(VO)_2P_2O_7$ (mass = 0.15 g) in the recirculation reactor, using a mixture $^{18}O_2/^{16}O_2/He$: 2.5/2.5/95, at 350°C. The initial ratio of ^{18}O (in gaseous $^{18}O_2$) over ^{16}O (in the mass of the catalyst) was less than 0.1. This value is low enough in order to be able to follow the experimental evolution with time of the labelling of the products before achieving the isotopic equilibrium. No detectable exchange was observed. After 2 h, the mass 34 signal did not increase at all and the equilibrium constant was $K = 7 \times 10^{-3}$ (compared to $K = 6 \times 10^{-3}$ at the beginning). The heterophase exchange has been also investigated using a mixture $^{18}O_2/He$: 2.5/97.5, at 350°C. Again we did not notice any significant exchange. After 150 min, the ^{18}O labelling of oxygen decreases only from $F = 92.7\%$ to $F = 91.3\%$.

Recall that K and F are defined as usual by:

$$K = \frac{I^2(34)}{I(32) \cdot I(36)} \tag{1}$$

$$F = \frac{2I(36) + I(34)}{2[I(32) + I(34) + I(36)]} \tag{2}$$

In Eqs. (1) and (2), $I(32)$, $I(34)$ and $I(36)$ correspond to the intensity of the O_2 isotopes $^{16}O_2$, $^{16}O^{18}O$ and $^{18}O_2$, respectively.

The rate of exchange between CO_2 and metal oxides may be fairly rapid in some cases. We have therefore also investigated the heterophase exchange between $(VO)_2P_2O_7$ (mass = 0.224 g) and $C^{18}O_2$ (nominal isotopic purity 97 at%), using a mixture $C^{18}O_2/He$: 1.5/98.5. The ratio ^{18}O (in $C^{18}O_2$)/^{16}O (in the solid) was 0.03. The evolution of K and F with time at 350°C is shown in Table 1.

Table 1 shows that there is indeed some exchange now, but with quite a slow rate. Even after a long time, 300 min, the statistical equilibrium ($K = 4$) was not reached with only a 10% decrease of the ^{18}O labelling of gaseous CO_2.

We have also performed the reaction at 350°C on $(VO)_2P_2O_7$ in the presence of a large amount

Table 1
Heteroexchange of $C^{18}O_2$ with $(VO)_2P_2O_7$ at 350°C

t (min)	K	F (%)
0	1.05	85.1
90	1.50	83.6
150	1.57	81.7
210	1.64	79.5
300	1.86	76.6

of $C^{18}O_2$ using a mixture n-$C_4H_{10}/{}^{16}O_2/C^{18}O_2$/He: 1.5/18/20/60.5. The initial rate of conversion of n-butane was exactly the same than in the usual conditions, that is in the absence of $C^{18}O_2$: 2.5×10^{-8} mol min^{-1} m^{-2}. The presence of CO_2 in the close circulation reactor has then no effect on the reaction rate. After the complete consumption of n-butane (200 min), the ^{18}O-labelling of the MA formed was 9%, showing that the exchange between $C^{18}O_2$ and the catalyst was limited but not negligible. However, in the usual conditions, the reaction was never performed with such a large amount of $C^{18}O_2$. We will see later on that the formation of ^{18}O-labelled CO_2 does not occur to a large extent, especially at the beginning of the reaction (n-C_4H_{10} + $^{18}O_2$). To sum up, it may be concluded that the isotopic scrambling of oxygen was actually quite limited on $(VO)_2P_2O_7$ in our experimental conditions.

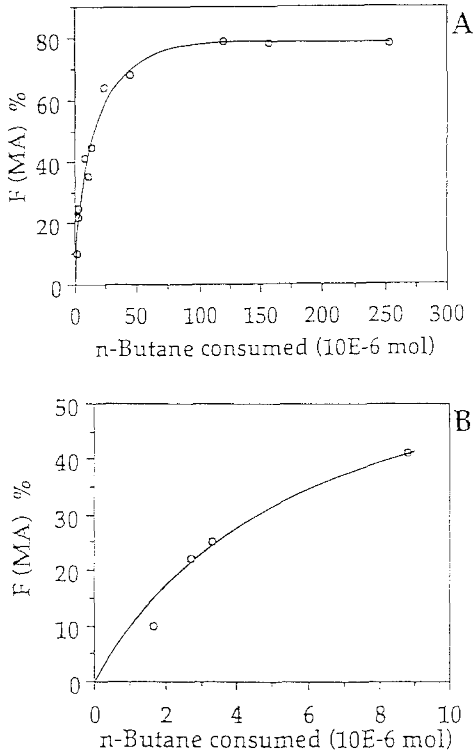

Fig. 5. Evolution of F_{MA} on $(VO)_2P_2O_7$ at 350°C with reaction time (A) (initial part of Fig. 5A shown in Fig. 5B).

5. Evolution of the ^{18}O-labelling of MA and of the other products with the course of the reaction

This evolution was followed by measuring the relative amount of ^{18}O in MA (F_{MA} in %) with reaction time. Recall that F_{MA} is given by:

$$F_{MA} = \frac{I(100) + 2I(102) + 3I(104)}{3[I(98) + I(100) + I(102) + I(104)]} \tag{3}$$

where $I(98)$, $I(100)$, $I(102)$ and $I(104)$ are the intensities of the four possible isotopes of MA. Several successive runs were performed on the same $(VO)_2P_2O_7$ catalyst at 350°C, always starting with the same ratio $^{18}O_2/n$-$C_4H_{10} = 12$. Fig. 5(A) shows the evolution of F_{MA} as a function of the cumulative amount of n-C_4H_{10} consumed. F_{MA} first steeply increases and then goes to a plateau where $F_{MA} \approx 80\%$. The ^{18}O-labelling clearly starts from zero, this important point can be seen more clearly in Fig. 5(B) which is a magnification of the initial part of Fig. 5(A). This result shows that only surface lattice oxygens (^{16}O oxide ions) are involved in the formation of MA. If lattice oxygen was used only in the cycle formation step, as proposed by Gleaves et al. [1,11,12], we should observe, even at the very beginning of the reaction, the isotope at $m = 102$ with two ^{18}O in the lateral positions, and F_{MA} would start at 66% instead of 0%.

As the reaction proceeds, consumed lattice ^{16}O are replaced by ^{18}O from $^{18}O_2$ in the gas phase, thus explaining the steep increase of the ^{18}O labelling of MA. However, F_{MA} should reach the gaseous $^{18}O_2$ labelling (i.e. 97 at%) if only lattice oxygens of the first layer were able to participate to the MA formation. The ^{18}O-labelling at the steady state was actually less than 97%, about 80% as shown in Fig. 5(A). It may then be concluded that surface oxygen vacancies created by the reaction are also reoxidized by the diffusion of oxide ions from the sublayers. However, the kinetics of the supply of oxygen from the bulk is about four times slower than the kinetics of direct reoxidation from the gaseous $^{18}O_2$.

If only surface lattice oxygens are involved in the formation of MA, then the surface labelling F_S of active oxygens (capable of the redox reaction of oxygen insertion) will dictate the MA labelling (F_{MA}) and also the isotopic distribution of the MA molecules. This distribution, that is the relative intensity of the four MA isotopes, can be calculated according to a simple statistical analysis:

$$I(104) \propto F_S^3$$

$$I(102) \propto 3F_S^2(1 - F_S)$$

$$I(100) \propto 3F_S(1 - F_S)^2$$

$$I(98) \propto (1 - F_S)^3$$

Fig. 6 shows that quite a good fit is obtained between the evolution of the experimental and computed mass intensities as a function of F_S, giving then an additional support to the conclusion that only lattice surface oxygens are active in the formation of MA.

The present observations were gained on a pure and well crystallized $(VO)_2P_2O_7$ catalyst. We have checked that similar results can be reproduced over a 'VPO' catalyst prepared by a long-term (132 h) activation of $VO(HPO_4)$, $0.5H_2O$ at 400°C under the reaction mixture, as previously described [5]. As shown in Fig. 7, the evolution of the MA labelling on this solid (more close to the real industrial catalyst than a pure $(VO)_2P_2O_7$ phase) is quite similar with $F_{MA} \approx 80\%$ at the equilibrium (see Fig. 5(A) for comparison). It may then be concluded that the present conclusions on the role of lattice oxygen are very likely general and not restricted to a given preparation or to a given active phase of VPO catalysts.

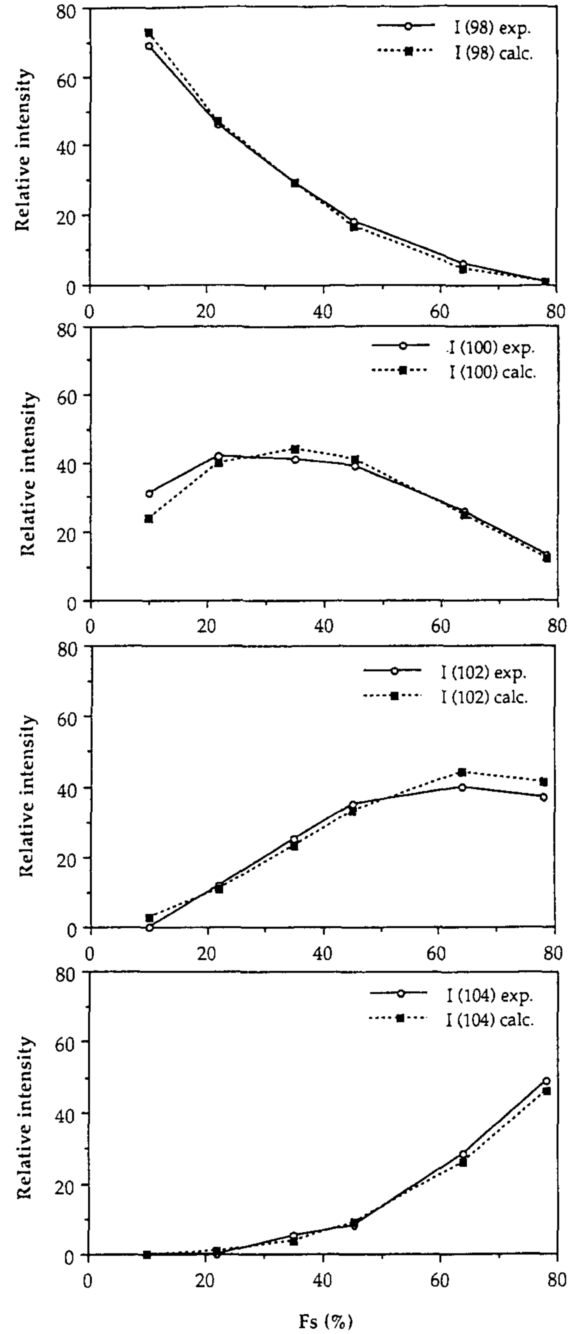

Fig. 6. Comparison of the experimental and calculated isotopic distribution of MA with the course of the reaction.

The ^{18}O-labelling of CO, CO_2 and H_2O has been also determined in the meantime as the MA labelling on $VO_2P_2O_7$. Fig. 8 shows that the evolution of the labelling follows the same general trend already observed for MA. For the three gases the curves start from zero at the very beginning of the reaction. As for MA, lattice oxygen would be then also involved in the

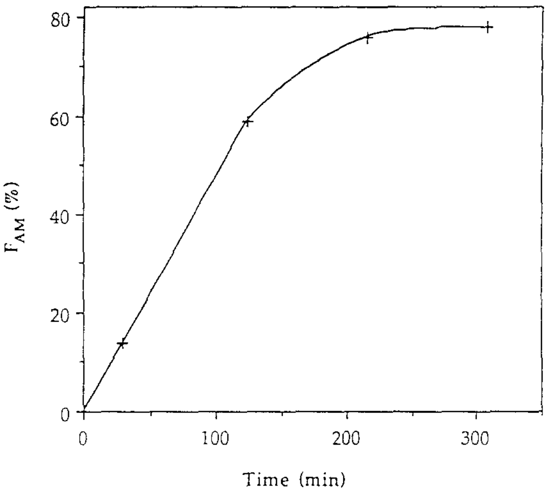

Fig. 7. Evolution of F_{MA} on a 'VPO' catalyst (see the text).

initial oxydehydrogenation of n-butane and in the combustion products. It appears that the steady-state labelling of these products is even lower than for MA (below 80%). It can be tentatively proposed that this lower labelling could be related to the preferential formation of CO_x on different crystal faces, as this reaction is believed to be structure sensitive [1,20–22]. MA would be formed on the basal (100) face whereas side faces such as (001) and (021) would be more active for CO_x formation. Owing to the lamellar structure of $(VO)_2P_2O_7$, the rate of diffusion of $^{16}O^{2-}$ oxide ions toward (001) or (021) faces could be more rapid, explaining the lower steady state ^{18}O-labelling of CO_x and H_2O.

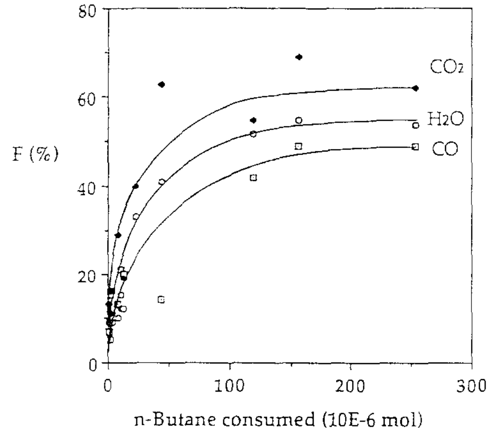

Fig. 8. Evolution of the ^{18}O-labelling F of H_2O, CO and CO_2 with reaction time on $(VO)_2P_2O_7$ at 350°C.

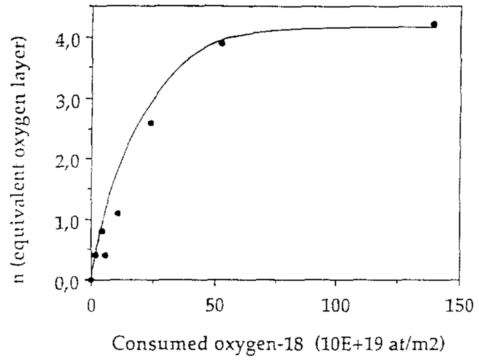

Fig. 9. Number of equivalent oxygen layers of the catalyst which participate to the reaction.

The number of equivalent lattice oxygen layers which participate to the reaction can be calculated from the ^{18}O-oxygen balance (^{18}O in the products and total amount of ^{18}O consumed). If we take $n_1 = 3 \times 10^{19}$ O at/m^2 [23] in a layer of 0.55 nm depth on the (100) face of $(VO)_2P_2O_7$, the number n of oxygen layers is calculated in Fig. 9 as a function of the amount of $^{18}O_2$ consumed. n increases up to a steady state corresponding to about 4 equivalent layers when the ^{18}O labelling of product reaches an equilibrium. This result indeed supports the participation of a few sublayers to replenish the surface oxygen vacancies created by the reaction, thanks to a diffusion process. These observations also suggest a gradient of ^{18}O concentration from the surface to the bulk within a few layers.

6. Post-reaction analysis of the catalyst by LEIS

After completion of the previously described experiments (a series of reaction with n-C_4H_{10} + $^{18}O_2$), the catalyst was analyzed by low energy ion spectroscopy (LEIS) using $^4He^+$ ions (1 keV, 5 nA). LEIS is known to be the most

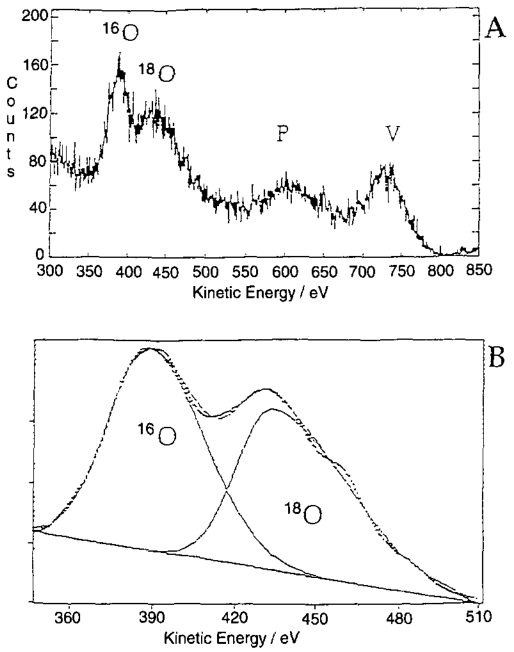

Fig. 10. Post-reaction analysis of the used $(VO)_2P_2O_7$ catalyst by LEIS. (A) Complete spectrum. (B) Oxygen region with decomposition in to two peaks corresponding to ^{16}O and ^{18}O.

sensitive technique to the outermost surface layer of a solid. As shown in Fig. 10(A) the LEIS spectrum shows the presence of V, P and O. In our experimental conditions, with a scattering angle of $\theta = 142°$, ^{16}O was expected near 400 eV and ^{18}O near 450 eV. The two isotopes can be actually resolved with some shift caused by the electric charge effect. According to the decomposition shown in Fig. 10(B), there is nearly 50% of ^{18}O on the $(VO)_2P_2O_7$ surface. This figure is in agreement with the average ^{18}O labelling of the reaction products at the end of the reaction (55%). The LEIS analysis then provides a direct evidence of the participation of lattice oxygens to the reaction, in good agreement with the study of the labelling of the product. Furthermore this analysis also shows that quite a large fraction (at least 50%) of the surface lattice oxygens are active in the different steps of the reaction.

We observed only a slow evolution with time of the LEIS spectrum. After 1 h under the ion beam, the amount of ^{18}O was reduced only from 50 to about 40%. As the experimental conditions were very mild (He^+ ions with a very low current), the sputtering rate was expected to be slow. However, at least a large fraction of the first surface layer was certainly removed after 1 h. It may then be concluded that ^{18}O atoms are not strictly located in the very first layer. There is instead a gradient of concentration of ^{18}O towards the bulk, in agreement with the conclusions based on of the labelling of the product and the number of equivalent oxygen layers which participate to the reaction.

7. Conclusions

The nature of active oxygens in the *n*-butane selective oxidation over VPO catalysts is still debated. In the present work this question has been addressed using gaseous $^{18}O_2$ (97 at%) in a close-circulation reactor. It has been first checked that no significant exchange of oxygen occurred between the catalyst and ^{18}O containing molecules, at least under our experimental conditions at 350°C and with a dry-ice cold trap in the line. Most experiments have been performed on a pure and well-crystallized $(VO)_2P_2O_7$ phase, as characterized by XRD, ^{31}P NMR and XPS.

The evolution of the ^{18}O-labelling of products has been followed using on-line mass spectrometry. The catalyst was first outgassed at 350°C and the reaction was performed with a large excess of $^{18}O_2$. The results have shown that only lattice surface oxygens were active for the formation of maleic anhydride (MA) and also of CO, CO_2 and H_2O. The fact that the products are not labelled at the very beginning of the reaction precludes the participation of any form of chemisorbed oxygen. For MA, this conclusion has been further supported by the good fit observed between the experimental evolution of the isotopic distribution and calculated mass spectra. These observations showed that the MA labelling and its isotopic distribution is only dictated by the labelling of surface lattice oxygens active in the reaction. According to the oxygen balance, only about four equivalent oxygen layers of the catalyst participate to the reaction. Post-reaction analysis of the catalyst by LEIS provided a direct confirmation of the presence of ^{18}O on the surface in agreement with a Mars and Van Krevelen redox mechanism. At least 50% of surface oxygens would be active in the reaction. Indeed, it is already well-known that a VPO catalyst can work at least for a short time in the absence of gaseous oxygen. However, in that case it is not clear whether lattice or adsorbed oxygens remaining on the surface are working. It could also be claimed that some abnormal mechanism is operating when the catalyst is forced to work in the absence of gaseous oxygen. The same questions arise when one considers the processes developed by Contractor et al. [23] or Emig et al. [24] where the step of reaction (reduction by *n*-butane) is separated from the step of regeneration (reoxidation by oxygen). According to the present results, the reaction in the absence of gaseous oxygen can be readily explained in so far as surface lattice oxygens are the active species. Indeed the rate will progressively decrease and the reaction will stop after the consumption of the active lattice oxygens located within a few surface layers because the diffusion of oxide ions toward the surface will be too slow for the supply of oxygens The same species are also involved in the CO_x formation and it may then be inferred that the surface concentration of adsorbed oxygen such as O^- or O_2^- must be very low, as these electrophilic moieties are believed to be very active in the complete oxidation of hydrocarbons [25].

Acknowledgements

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