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Study by XPS and TPD of the interaction of *n*-pentane and *n*-butane with the surface of 'non-equilibrated' and 'equilibrated' V–P–O catalysts

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Abstract

Surface characterization of V–P–O catalysts used in the oxidation of *n*-butane and *n*-pentane to maleic and phthalic anhydrides is reported. Two different states for the same catalyst are selected: after a short time under reaction conditions (100 h), the 'non-equilibrated' system, and after a much longer time-on-stream (1000 h), the 'equilibrated' catalyst. Characterization has been carried out by following the desorption of molecules with a mass spectrometer after catalysts had been in contact with the hydrocarbons and/or O_2 mixtures at 613 K. Valence state of vanadium under environmental conditions similar to those used in the desorption studies was obtained by XPS. It was concluded that both V^{V} and V^{IV} are capable of interacting with the hydrocarbon and that not all the V^{IV} present at the $(VO)_2P_2O_7$ surface can interact. On the other hand, desorption of molecules resulting from such interaction occurs at lower temperatures from V^{IV}-rich surfaces ('equilibrated' catalyst), than from the V^{V} richer surface ('non-equilibrated' catalyst). © 1998 Elsevier Science B.V.

1. Introduction

The selective oxidation of *n*-butane to maleic anhydride is commercially carried out with a heterogeneous process by means of a V/P mixed-oxide-based catalyst. A peculiar compound, well crystallized vanadyl pyrophosphate $(VO)_2P_2O_7$, possesses unique structural and surface features which allow the paraffin to be activated at relatively mild conditions and with the highest conversion and selectivity to maleic anhydride (MA) [1–3]. Also, *n*-pentane oxidation is carried out on V–P–O catalysts rendering MA and phthalic anhydride (PA). Besides its practical interest, this reaction constitutes a more sensitive test to study the surface properties of V–P–O catalysts than *n*-butane oxidation because additional cyclization and aromatization centres are needed in the transformation of C_5 paraffin to the C_8 oxygenated aromatic compound [4–10].

Much research has been devoted to studying the effect of the bulk and surface properties of V–P–O phases on their catalytic performances [3,11–15] but the reason why $(VO)_2P_2O_7$ phase is much more active and selective than other V–P–O phases such as the $VOPO_4$ phases or ill-crystallized $(VO)_2P_2O_7$ is still unknown. The most active and selective phase, well-crystallized $(VO)_2P_2O_7$, is developed under the reac-

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tion environment after 1000 h on-stream [10,16]. Any study should, therefore, preferentially be carried out on the phase obtained in this way. In a previous work [10], the catalytic properties and bulk and surface characterization of a 'non-equilibrated' catalyst (after 100 h under reaction environment) and of an 'equilibrated' catalyst (after 1000 h under reaction conditions) were presented. The ill-crystallized $(VO)_2P_2O_7$ and γ-$VOPO_4$ phases were detected by XRD in the 'non-equilibrated' system and both V^{V} and V^{IV} were detected by XPS at its surface, whereas well-crystallized $(VO)_2P_2O_7$ and V^{IV} alone were detected in the 'equilibrated' system.

A study of the 'non-equilibrated' and 'equilibrated' catalysts of a previous work [10] has the advantage that it characterizes 'real' systems which had been working as catalysts in addition to the fact that their catalytic properties, phases present and V valence state at the surface are well known. The research was carried out by following with a mass spectrometer the desorption of products from surface under evacuation after the 'non-equilibrated and 'equilibrated' catalysts had been in contact with a hydrocarbon and O_2 mixture intending to mimic the reaction environment. It is expected that while the sample is in contact with O_2 and hydrocarbon at reaction temperatures many oxidation products can be formed and released to the gas phase (CO, CO_2, selective oxidation products and H_2O) but a deposit of partially dehydrogenated and oxidized hydrocarbons are left on the surface (hereinafter, they will be referred as to HCOs). Actually, partially oxidized hydrocarbons have been detected by IR on the surface of V–P–O catalysts, under similar experimental conditions to those used in this work [9,17,18]. When TPD is carried out, the sample is heated under vacuum and processes, closely related with the reaction mechanism, can occur and molecules such as those left on the surface can be transformed and/or released. This study of the TPD can help to elucidate some aspects of the interaction of the hydrocarbon with the catalysts surface. For example, it can give a relative estimation of the surface coverage of C-containing species and, as a result, a relative quantification of the extent of interaction of surface with hydrocarbon. Besides, the temperature at which desorption process takes place can also be determined, thus providing information on the strength of the interaction of products left over with surface. The absence of O_2 from the environment while heating (TPD was carried out under vacuum) does not necessarily separate the oxidation processes from the real reaction mechanism to a great extent, because surface and subsurface lattice oxygen have been demonstrated to be involved in the oxidation of the *n*-pentane at the surface: gaseous O_2 reactant is used to heal the O defects at the surface [19,20]. The changes in V valence state at the surface in the samples exposed to the hydrocarbon and/or O_2 atmospheres were monitored by XPS. Some conclusions about the role of V^{V} and V^{IV} sites in the activation and transformation of *n*-butane and *n*-pentane were obtained. The temperature at which adsorbed products are released during the TPD study is discussed in regard to the catalytic properties.

2. Experimental

2.1. Preparation of samples

Precursors of catalysts were prepared in organic medium: 15 g of V_2O_5 (Merck, reagent grade) were suspended in 90 ml of isobutyl alcohol and 60 ml of isobenzyl alcohol (Merck, reagent grade). The suspension was stirred continuously under reflux for 3 h, cooled to room temperature, and then 16.2 g of 99% *o*-H_3PO_4 were added (Scharlau, analytical grade). The slurry was heated under reflux with constant stirring for 2 h, cooled, filtered, washed with isobutyl alcohol and the filtrate was dried at 423 K for 24 h. The catalyst precursor powder so prepared, $VOHPO_4 \cdot 0.5H_2O$, was tabletted, pelletized, sieved (0.3-0.5 mm) and calcined at 653 K for 5 h. Catalytic behaviour in the oxidation of *n*-pentane or *n*-butane were tested. Experimental conditions and results are published elsewhere [10]. Catalytic properties of the system changed with time-on-stream under reaction conditions but, after 1000 h, a steady state was reached. After 1000 h on-stream (1% *n*-pentane in air, W/F=3.0 g s ml^{-1}) at 613 K, the catalyst was cooled down to room temperature under reaction conditions, withdrawn from the reactor and stored in room atmosphere. It is referred to as 'equilibrated' ('e') catalyst. A representative 'non-equilibrated' ('ne') catalyst was selected after 100 h on-stream. Catalytic results [10] can be summarized as follows: 'e' catalyst is more active than 'ne' sample. However, the 'e' sample is not able to convert hydrocarbon above a certain concentration, which means that the surface is saturable at high hydrocarbon concentration while the 'ne' catalyst surface cannot become saturated and has a greater ability to process a higher concentration of hydrocarbons. Moreover, the 'e' catalyst converts hydrocarbons to anhydrides more selectively than the 'ne' catalyst.

2.2. TPD measurements

A sample of 100 mg, after *n*-pentane oxidation, was loaded in a glass reactor (volume ca. 25 cc) connected to a vacuum line and outgassed at 393 K for 1 h ($P<10^{-4}$ torr). The sample was then heated (5 K/min) at 773 K under vacuum and the desorbed products analyzed by a quadrupole mass filter (Balzers QMG 125) connected to the reactor outlet. The principal molecules, such as CO, CO_2, H_2O and O_2, were followed by recording the signals, respectively, at $m/z=18$, 28, 32, and 44. Other m/z signals were also recorded in order to follow partially oxidized or dehydrogenated hydrocarbons such as alkenes, 2,5 dihydrofurane, maleic anhydride, and furan. Many products were desorbed as expected, considering that samples had been on-stream for a long time, and that reactants, products, by-products and intermediates could be attached to the surface. The sample was kept at 773 K overnight under evacuation. This procedure (heating from 393 to 773 K at 5 K/min and at 773 K overnight) was repeated until no product was desorbed as detected by mass spectrometry. The sample was then cooled to 613 K (a typical reaction temperature) and 100 torr of hydrocarbon and 200 torr of O_2 were dosed simultaneously in the glass reactor. The catalyst was kept at 613 K for 1 h and, subsequently, cooled under this atmosphere to 393 K and then outgassed for 1 h ($P<7.5\times10^{-5}$ torr). The temperature was then increased at 5 K/min up to 773 K following the products desorbed from the surface by mass spectrometry. The results were reproducible in respect of the intensity and desorption pattern of signals as the experiments were carried out under the same experimental conditions.

2.3. XPS measurements

Photoelectron spectra were recorded using a Fisons Escalab 200R spectrometer equipped with a hemispherical electron analyzer employing MgK_α radiation (photon energy 1253.6 eV) and an electron take-off angle of 45°. The base pressure of the spectrometer was typically 10^{-9} torr. The X-ray gun was operated at 12 kV and 10 mA, corresponding to a power of 120 W. A PDP 11/53 computer from Digital Equipment was used for collecting and analyzing the spectra. The powder samples were pressed into small aluminium cylinders and then mounted on a sample rod placed in a pretreatment chamber, where samples were subjected to several O_2 and hydrocarbon atmosphere and evacuation treatments. The 1*s* O, 2*p* P, 2*p* V and 1*s* C energy regions were recorded for each sample and each pretreatment. The spectra were collected in 20–90 min, depending on the peak intensities, at a pass energy of 10 eV ($1\ \mathrm{eV}=1.602\times10^{-19}$ J) which is typical of high resolution conditions. The intensities were estimated by calculating the integral of each peak after smoothing and subtraction of the 'S-shaped' background and fitting the experimental curve to a combination of Lorentzian and Gaussian lines of variable proportion. The methodology employed for peak fitting and peak deconvolution for V $2p_{3/2}$ was the following: typically, 1.8–2.7 eV line widths and a Gaussian/Lorentzian combination with a Lorentzian contribution of 30% were employed. Spectra were corrected for sample charging by referencing photoelectron peaks to the C 1*s* peak at 284.9 eV. This reference gave BE values within an accuracy of ±0.2 eV.

3. Results

3.1. TPD characterization

Figs. 1 and 2 show the main signals detected by the mass spectrometer after the co-adsorption of O_2 and *n*-butane on the 'ne' and 'e' samples, respectively. None of the fragments detected and represented in these (and later) figures were present in the TPD pattern of the last cleaning performed before the co-adsorption of *n*-butane (or *n*-pentane) and O_2. Therefore, these signals must arise from the interaction of hydrocarbon

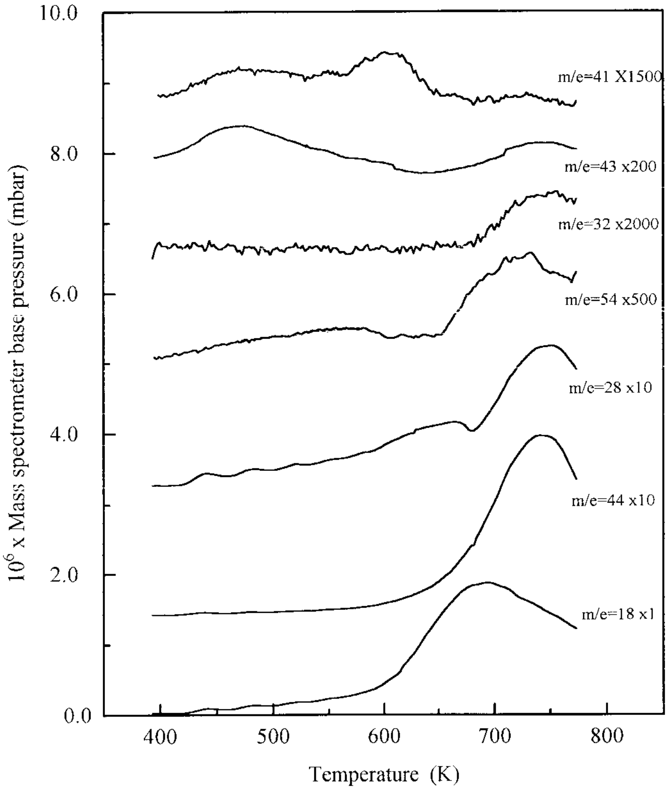

Fig. 1. TPD pattern of 'non-equilibrated' catalyst after cleaning the surface and dosing 100 torr of *n*-butane and 200 torr of O_2 at 613 K for 1 h.

with the surface. In both cases, H_2O, CO and CO_2 were the major molecules detected and H_2O was the most important product desorbed from the surface. In the 'ne' sample (Fig. 1), CO and CO_2 were mainly desorbed at high temperatures (desorption peaks centred at 750 K). The H_2O desorption peak is ca. 700 K, but a weak shoulder is detected simultaneously to the release of CO and CO_2. Other weak m/z signals (assigned to the desorption of HCOs) were detected at the same temperatures as the carbon oxides peaks (the unequivocal assignation of this m/z fragment is difficult and could not be done, probably because most of the products of the oxidation reaction have many common m/z fragments). These results can be explained considering that butane interacts with sites at the surface in the presence of O_2, thus resulting in the formation of HCOs and H_2O which can be released to the gas phase or kept attached to the surface. H_2O desorption itself is a probe of interaction between hydrocarbon and surface. H_2O is strongly adsorbed to surface sites (temperatures >600 K are needed to start dehydration of such sites). HCOs are strongly adsorbed to the surface sites and they are released mainly at high temperatures. During this desorption process, some of these molecules undergo further oxidation, probably due to the high temperatures, yielding simultaneously CO, CO_2 and H_2O, with only a small fraction being released as HCOs. It may also be possible that, due to the very long time that the hydrocarbon–O_2 mixture is in contact with catalyst, the HCOs can be deeply oxidized to CO_x, which represent a very important fraction of the products desorbed as CO_x under evacuation. Catalyst 'e' (Fig. 2) presents, along with a smaller number of sites capable of interaction with butane, as deduced from the weaker intensities of the signals (see multiplication factors), a completely different desorption pattern. The most noticeable feature is that CO, CO_2 and HCOs displayed several desorption peaks at temperatures <600 K (there are other desorption processes at

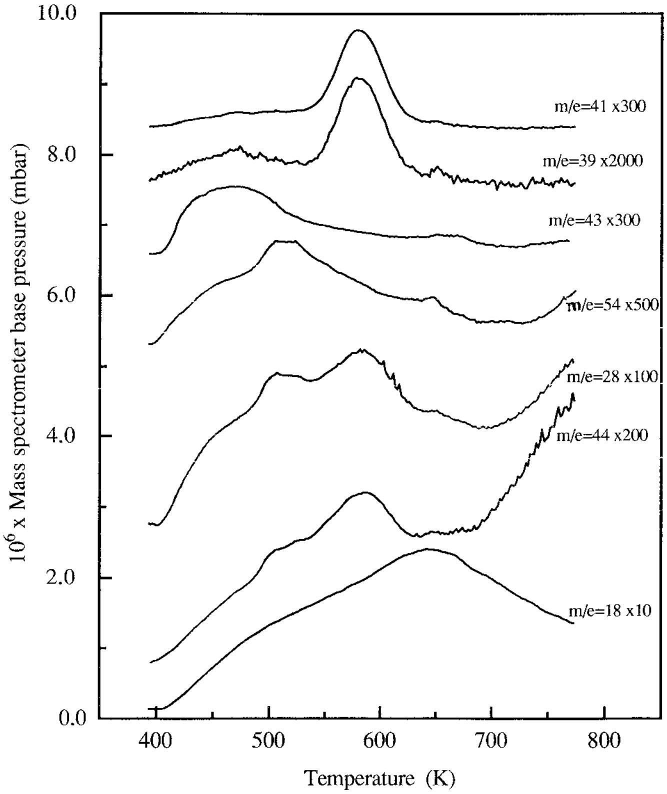

Fig. 2. TPD pattern of 'equilibrated' catalyst after cleaning the surface and dosing 100 torr of *n*-butane and 200 torr of O_2 at 613 K for 1 h.

temperatures >773 K). H_2O desorption presents a maximum at around 650 K. It may be proposed that CO_x can be adsorbed on the surface, whereas the sample is in contact with the hydrocarbon–O_2 mixture for 1 h, since CO and CO_2 can be present as an oxidation product in the gas phase environment. But such a possibility can be discarded, since 25 torr of CO and 25 torr of CO_2 were co-dosed on a previously cleaned 'e' catalyst at 613 K (results are not shown in this work) and no CO and CO_2 were desorbed in the subsequent TPD experiment.

Figs. 3 and 4 represent the *m*/*z* fragments detected after dosing *n*-pentane and O_2 on the 'ne' and 'e' samples, respectively. The TPD pattern of the 'ne' catalyst (Fig. 3) is quite similar to the results obtained after butane–O_2 co-dosing: part of H_2O desorption occurs at lower temperatures than CO_x which were desorbed at high temperatures with evolution of water (shoulder at 750 K). Moreover, weaker signals (probably arising from HCOs) are also released at high temperatures far from the temperatures at which catalytic activity was carried out: it seems that pentane interacts with the 'ne' surface and the products resulting from this interaction are strongly attached: these are removed at high temperatures. During desorption they are probably oxidized mainly to CO and CO_2 and again only a small fraction is transformed and desorbed as HCOs. The 'e' sample (Fig. 4) presents desorption of CO and CO_2 at temperatures lower than the 'ne' catalyst. Less intense *m*/*z* signals, which can be assigned to HCOs, are detected at even lower temperatures, thus indicating that the products of the pentane interaction with the 'e' surface are transformed and/or released at temperatures lower than those in the case of 'ne' sample. Another interesting point is that the multiplication factor of the signals in the 'e' sample are smaller than in 'ne' sample, which clearly indicates that the 'e' surface interacts, to a lesser extent, with pentane (and butane) in the presence of O_2 than the 'ne' surface.

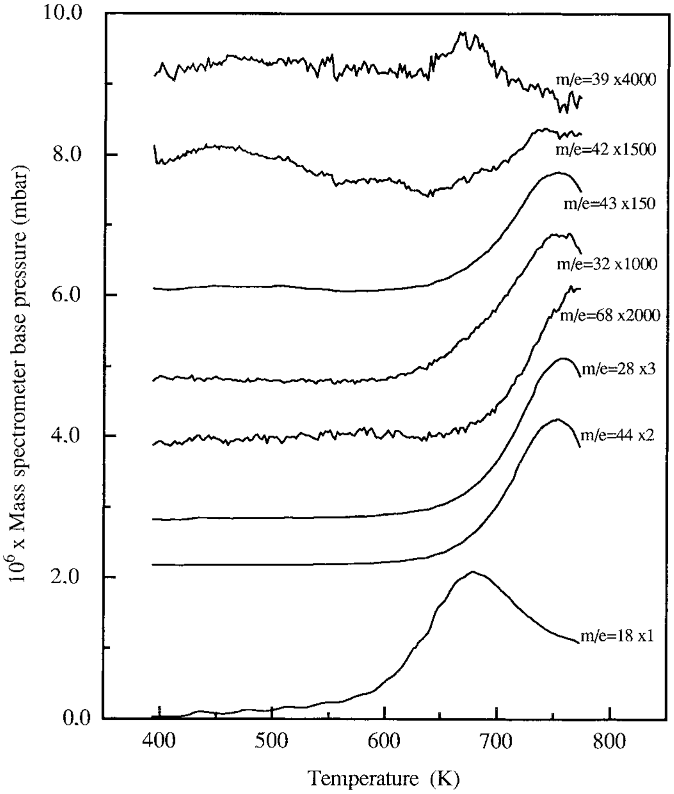

Fig. 3. TPD pattern of 'non-equilibrated' catalyst after cleaning the surface and dosing 100 torr of *n*-pentane and 200 torr of O_2 at 613 K for 1 h.

Fig. 5 presents the molecules desorbed from a previously cleaned 'e' surface when only 100 torr of *n*-pentane is dosed (no O_2 was co-dosed) while the sample was at 613 K. H_2O was the most important product desorbed from the surface (peak at 700 K). CO and CO_2 are also evolved but in a different way than when pentane and O_2 were co-dosed. Most carbon oxides desorption seems to occur at temperatures >773 K. Weaker *m*/*z* signals (ascribed to HCOs) are also released at lower (close to reaction) temperatures. H_2O desorption may arise from the processes occurring while pentane is adsorbed and transformed to HCOs at the surface sites.

3.2. XPS results

The valence of vanadium sites generated at catalyst surfaces when exposed to a typical O_2+C_4H_{10} atmosphere under conditions which approach reaction operation has been elucidated by XPS. Fig. 6 shows the deconvolution of the V 2*p* core level energy region for 'ne' and 'e' samples after evacuation at room temperature, evacuation at 773 K and after co-dosing of butane and O_2 at 613 K. Deconvolution of V $2p_{3/2}$ peak is more appropriate, since the V $2p_{1/2}$ peak overlaps the O 1*s* peak satellites, originating because of non-monochromaticity of the X-ray source. Only V^{IV} (BE=516.8 eV) was detected after evacuation at RT at the 'e' surface as expected, since only $(VO)_2P_2O_7$ was detected by FTIR and XRD in this sample [10]. V^{IV} and V^{V} (BE=518.3 eV) were seen by XPS at rather similar concentrations at the 'ne' surface. $(VO)_2P_2O_7$ and γ-$VOPO_4$ structures, respectively, were detected in this sample by XRD [10] but, since V^{V} can be accommodated in an ill-crystallized $(VO)_2P_2O_7$ framework [21], V^{V} at the surface cannot unequivocally be assigned as located in the γ-$VOPO_4$ structure. Evacuation does not seem to significantly affect the vanadium valence state at the surface of both catalysts. However, when butane

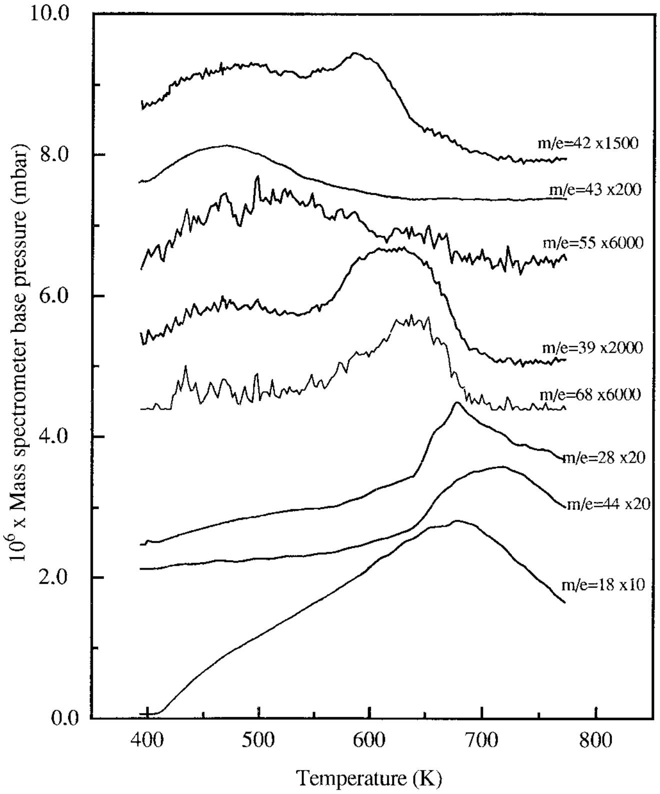

Fig. 4. TPD pattern of 'equilibrated' catalyst after cleaning the surface and dosing 100 torr of *n*-pentane and 200 torr of O_2 at 613 K for 1 h.

and O_2 were co-dosed at 613 K, a small but detectable V^V contribution was developed at the surface of the 'e' sample (statistical parameters of the peak simulation for the V $2p_{3/2}$ XPS signal, by assuming that only V^{IV} was at the surface, were significantly worse than when a mixture of V^{IV} and V^V were proposed). Therefore, it seems that butane+O_2 atmosphere slightly oxidizes the surface even at this high butane concentration. It must be mentioned that surface vanadium recovered their initial oxidation state when evacuated at 773 K. Co-dosing of butane+O_2 at 613 K on the 'ne' sample does not significantly increase the high amount of V^V already present at its surface.

In order to verify that V^V is produced at 613 K under O_2 atmosphere on the 'e' surface, 100 torr of O_2 were dosed at temperatures in the 513–663 K range, and then XPS spectra were recorded. Fig. 7 shows the $V2p_{3/2}$ XPS peak at different oxidation temperatures. Contributions of deconvolution of the V $2p_{3/2}$ peak into V^V and V^{IV} were assumed for all spectra. It can be seen that the V^V contribution, which is not present at low temperatures, becomes more important as the temperature is increased. The V^V contribution at 613 K is significantly more important than at lower temperatures, a fact which reinforces the hypothesis that some V^V can be developed at the 'e' surface at 613 K under oxidizing conditions. However, it must also be stressed that V^{IV} at the 'e' surface is very stable under oxidizing conditions and is not extensively transformed to V^V.

4. Discussion

As explained above, when dosing the hydrocarbon and O_2 mixture at 613 K on catalysts of this work, the surface must be left covered with different kinds of HCOs, including products of the reaction. When the sample is heated, molecules can be desorbed as they are, or they can also undergo oxidation at the surface

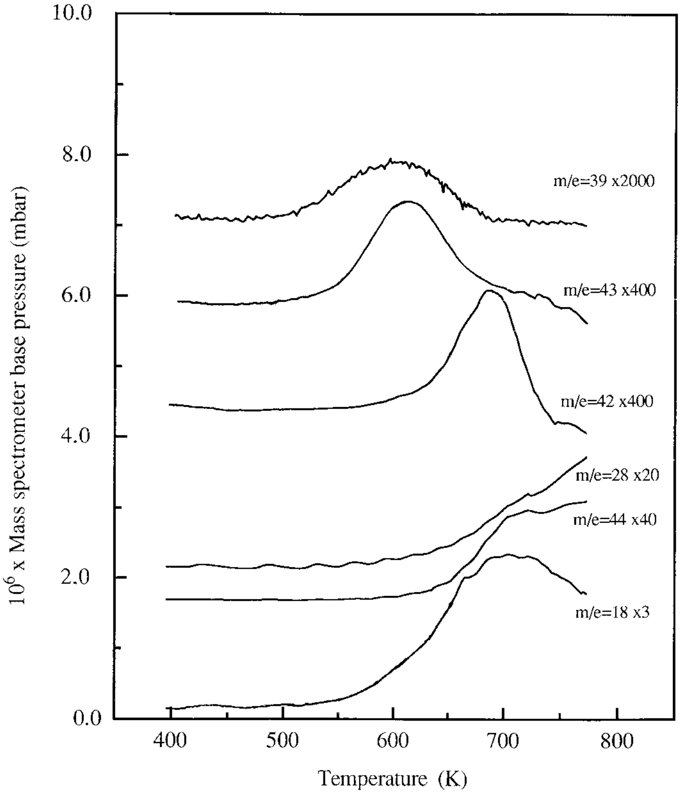

Fig. 5. TPD pattern of 'equilibrated' catalyst after cleaning the surface and dosing 100 torr of *n*-pentane (no O_2 was co-dosed) at 613 K for 1 h.

resulting in the formation of other species which can either react or be released. The temperature at which these molecules are released obviously depends on the transformation that the molecules can undergo at the surface (CO and CO_2 are the main C-containing products released, because the surface is in contact with the hydrocarbon for 1 h and these TPD experiments can be considered as long contact-time experiments) and on the strength of interactions with surface sites. Therefore, TPD studies under evacuation of samples after contact with reaction mixture is a valuable tool for understanding several aspects of the interaction of surface centres with hydrocarbon.

Obviously, the first step in the process of interaction of hydrocarbon with the surface is to anchor the hydrocarbon, then the intermediate formed is transformed on the surface. The activation process has been claimed to consist of the dehydrogenation of butane or pentane in a V centre [19,22,23] resulting in the formation of an alkene. Later, surface and subsurface O transform this intermediate to other HCOs molecules (MA, PA and CO_x, among others) [19,20]. Grasselli et al. [24] have proposed that V^V is required to carry out this step. The signals arising from C-containing molecules evolved from the 'ne' surface after careful cleaning and hydrocarbon–O_2 treatments of the 'ne' catalysts (Figs. 1 and 3) clearly indicate that butane and pentane interact in the presence of O_2 with this surface at 613 K. These signals are more intense than those from the 'e' surface and it is reasonable to think that there are more sites capable of interacting with hydrocarbons at the 'ne' surface. Considering that the 'ne' surface exhibits a higher fraction of V^V (50% of the V atoms, see Fig. 6(A)) than the 'e' surface (ca. 10%, see Fig. 6(B)), it can be assumed that V^V sites are principally responsible for the more extended anchoring of hydrocarbon at the 'ne' surface.

The desorption of C-containing molecules shown in Figs. 2 and 4 also indicates that there has been hydro-

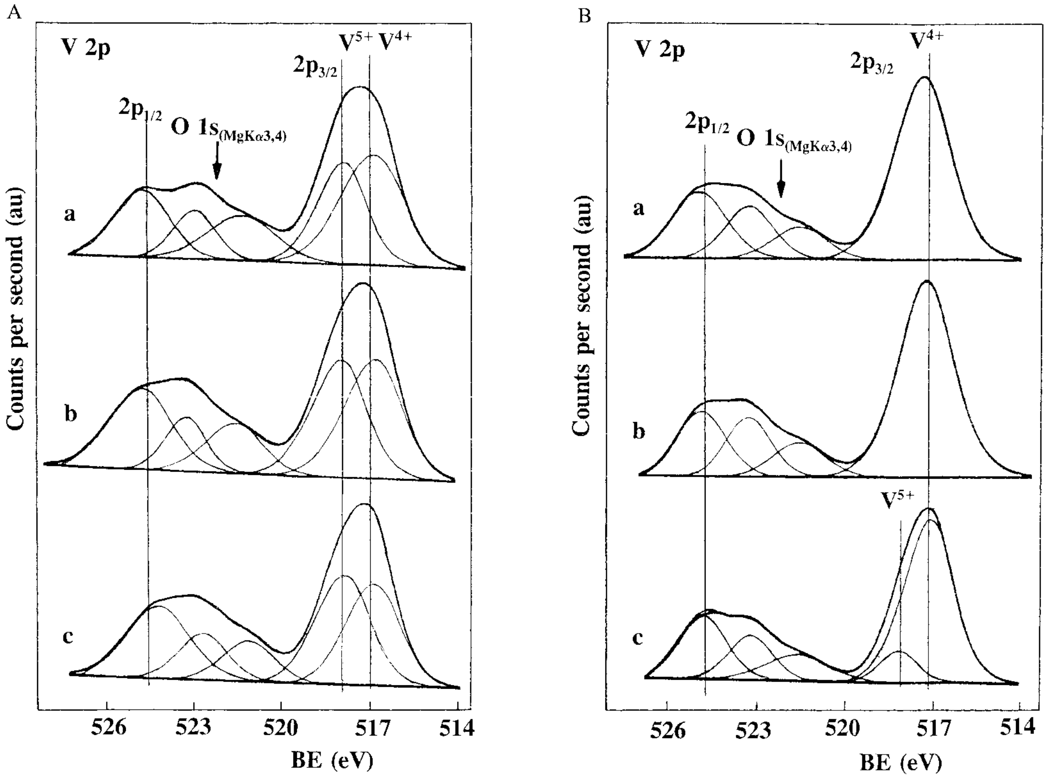

Fig. 6. XPS V 2*p* peak and its deconvolution for (A) 'non-equilibrated' catalyst and (B) 'equilibrated' catalyts: (a), after evacuation at room temperature; (b), after evacuation at 773 K; and (c), after dosing of 100 torr of *n*-butane and 200 torr of O_2 at 613 K for 1 h.

carbon interaction with the 'e' surface. XPS results have shown that this surface also displays observable amounts of V^{V} under hydrocarbon–O_2 mixtures which, according to the literature, would activate the hydrocarbon. On the contrary, only V^{IV} is present at the 'e' surface (as seen by XPS) after dosing only pentane (see Fig. 6(b), O_2 was not dosed), and desorption of C-containing molecules and H_2O occurred. It could be inferred that there has been an interaction of the surface with pentane and that V^{V} is not indispensable in assuring that the hydrocarbon interacts with the surface. Not all V^{IV} can anchor and react with the hydrocarbon, otherwise the amount of molecules desorbed from the 'e' surface would be higher and comparable to the 'ne' case. Thompson et al. [25,26] have shown that the crystallography of $(VO)_2P_2O_7$ is very complex and many polytypes with variations in the bulk and surface framework can exist. Recently, the activity and MA selectivity in $(VO)_2P_2O_7$, prepared by decomposing the precursor in an inert atmosphere at different temperatures, has been related with changes in the short-range order in the framework around the V^{IV} centres [27]. We, therefore, propose that only V^{IV} centres with an appropriate short-range framework are capable of anchoring the hydrocarbon at the 'e' surface.

It may be also possible that amounts of V^{V} at the 'e' surface, undetected by XPS, may account for the ability of this surface to interact with hydrocarbons. However, the presence of V^{V} does not notably increase the adsorption of *n*-pentane at the 'e' surface. Thus, the desorption pattern after pentane–O_2 co-dosing (see Fig. 4) is different to that obtained when only pentane is dosed (see Fig. 5) although the signals are not much more intense: the presence of measurable amounts of V^{V} (seen by XPS) and the availability of O_2 make new ways of transformation of the molecules interacting with the surface possible. Therefore, the possibility that only undetected V^{V} justifies the hydrocarbon activation on the 'e' surface when no O_2 is dosed

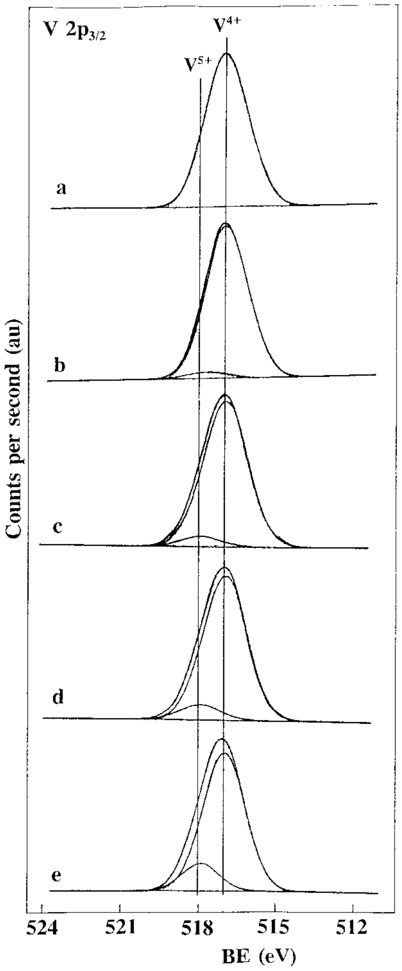

Fig. 7. XPS V $2p_{3/2}$ peak and its deconvolution for the 'equilibrated' catalyt after evacuation at 773 K for 1 h and after dosing of 200 torr of O_2 for 1 h: (a), at room temperature; (b), 530 K; (c), 565 K; (d), 610 K; and (e), 660 K.

can be discarded. Moreover, it can also be concluded that the interaction of hydrocarbons on the 'e' surface when O_2 is present must be dominated by the higher concentration of V^{IV} sites.

An important point worth considering is that HCOs left on the 'ne' surface after O_2–hydrocarbon pretreatment are transformed and released at higher temperatures than from the 'e' surface. This suggests that the V^V sites interact and hold the HCOs more strongly than V^{IV} of the 'e' surface. And it can also explain some of the catalytic properties of 'ne' and 'e' systems. The lower ability of the 'e' catalyst to anchor pentane (and butane) as seen by TPD accounts for the saturation of the 'e' surface when converting hydrocarbon rich mixtures. The 'ne' surface adsorbs a larger amount of hydrocarbon and is, consequently, capable of processing richer hydrocarbon feeds. On the other hand, the V^{IV} at the 'e' surface releases HCOs by an oxidation process at a lower temperature than V^V at the 'ne' counterparts. Assuming that oxidation processes involved in the TPD experiments are closely related with those of the oxidation mechanism, the activity of the 'e' sample is probably higher because products are easily released from its surface at temperatures at which they are not released from the 'ne' surface. Another consequence of the lower temperature desorption processes occurring at the 'e' surface is that these intermediates could be released and/or transformed under milder oxidation conditions which can account for the higher anhydride yield of the 'e' catalyst. However, intermediates desorbing at higher temperatures are attached more strongly at the 'ne' surface sites, which favours deeper oxidation to carbon oxides.

It could be suggested that the stability against oxidation (as confirmed by XPS) of V^{IV} in well-crystallized $(VO)_2P_2O_7$, the sole phase present in the 'e' catalyst [10], could explain the better catalytic properties of this phase: V^{IV} sites prevail on the V^V centres. The results here suggest that V^{IV} is capable of anchoring and activating the hydrocarbons and that V^{IV} transforms and releases the HCOs formed after activation of hydrocarbons at lower temperatures than V^V, favouring more selective transformations. On the contrary, the V^V-rich surface would transform hydrocarbons with a poorer conversion and/or selectivity.

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