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Catalysis Today 61 (2000) 203–210

CATALYSIS TODAY

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Relationship between structural/surface characteristics and reactivity in *n*-butane oxidation to maleic anhydride
The role of V^{3+} species

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Abstract

V/P/O-based catalysts were prepared by thermal treatments of $VOHPO_4 0{\cdot}5H_2O$ precursors prepared with the organic procedure. Different methods for precursor dehydration led to compounds which were characterized by the prevailing presence of crystalline $(VO)_2P_2O_7$, but which also contained either V^{5+} species or V^{3+} species. The catalytic performance of these compounds in *n*-butane oxidation under almost-equilibrated conditions was compared. It was found that the presence of either V^{3+} or V^{5+} enhances the specific activity in *n*-butane oxidation, while the selectivity to maleic anhydride at low *n*-butane conversion (30%) remains substantially unaffected. A fully equilibrated, well-crystallized $(VO)_2P_2O_7$ was reduced with H_2. The reduced compound was more active than the fully equilibrated vanadyl pyrophosphate, while exhibiting comparable selectivity to maleic anhydride. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: *n*-Butane; Maleic anhydride; V^{3+} species; Vanadyl pyrophosphate

1. Introduction

V/P/O-based catalysts are industrially employed for the selective oxidation of *n*-butane to maleic anhydride, and are also known to be efficient in the oxidation of *n*-pentane to maleic and phthalic anhydrides [1]. The active component of V/P mixed oxides is $(VO)_2P_2O_7$, the presence of which is necessary to have active and selective catalysts. Many papers have been published which deal with the analysis of relationships between chemical–physical features and catalytic performance [2]. An important aspect concerns the role of the different crystallographic planes of vanadyl pyrophosphate in the transformation of the paraffin to the anhydride. In particular, it is widely accepted that a plate-like morphology, with preferential development of the $\{1\,0\,0\}$ crystal face, gives rise to a catalyst characterized by better performance, while side crystal faces are non-selective ones [3]. Another important aspect concerns the possibility for the vanadyl pyrophosphate to retain a certain number of oxidized V^{5+} sites (generated during the synthesis of the compound). The presence of patches of crystalline or amorphous $VOPO_4$ grown on particular faces of the vanadyl pyrophosphate crystallites, or of dispersed V^{5+} sites, leads to a catalyst with better selectivity to maleic anhydride than a non-oxidized $(VO)_2P_2O_7$ [4,5]. On the other hand, it is known that in fully equilibrated catalysts the number of oxidized vanadium sites is very low (with an average oxidation state for vanadium between 4.005+ and 4.01+) [6].

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PII: S0920-5861(00)00383-7

Therefore, the performance of catalysts containing relatively large amounts of V^{5+} is fated to change during prolonged time-on-stream, getting closer to that typical of the aged catalyst, in corresponding with the progressive equilibration of the surface with the gas phase. The term equilibrated should however be viewed in respect to the reaction conditions, i.e., reaction temperature and gas-phase composition. In other words, it is possible that for reactions which are carried out under hydrocarbon-lean conditions the surface distribution of vanadium sites in equilibrated catalysts is different from that of systems which operate at hydrocarbon-richer conditions.

A second aspect concerns the presence of vanadium species with a valence state other than 4+, not only V^{5+}, but also V^{3+}. The presence of V^{3+} species was demonstrated several years ago [7], and recently discussed by Gai and Kourtakis [8], but the role of this species in affecting the catalytic performance in both non-equilibrated and equilibrated catalysts has not yet been fully examined. Indeed, the nature of the V/P mixed oxide obtained after the thermal treatment of the precursor, $VOHPO_4 \cdot 0.5H_2O$, is a function of the characteristics of the precursor itself, and of the procedure employed for the transformation of the latter to the final catalyst (i.e., temperature and atmosphere of treatment).

The aim of the present work was to study the following effects relative to the reactivity of non-equilibrated V/P/O-based catalysts:

1. Catalytic performance of V/P/O-based systems, prepared with a thermal treatment to obtain catalysts characterized by the presence of either V^{3+} or V^{5+}.
2. Role of V^{3+} in an equilibrated catalyst which has undergone a reductive treatment.

2. Experimental

The catalyst precursor, $VOHPO_4 \cdot 0.5H_2O$, was prepared by the "organic procedure", using isobutanol as the reducing agent for V_2O_5 in the presence of H_3PO_4. The precipitate was filtered, washed with isobutanol and dried at 125°C overnight. Proper control of the preparation procedure made it possible to obtain precursors characterized by different degrees of crystallinity. The compounds obtained were thermally treated with different procedures, either "oxidizing" (i.e., calcination in air at 450°C), or "mildly oxidizing" (i.e., treatment in nitrogen-diluted air, so to obtain an oxygen content of 5 vol.%, at 450°C; alternatively, pretreatment in nitrogen-diluted air at 300°C, followed by treatment in N_2 at $T>450°C$), or "mildly reducing" (pretreatment in air at 300°C followed by treatment in nitrogen at $T>450°C$). Catalysts obtained after these treatments were characterized by means of X-ray diffraction (Phillips diffractometer PW 3710, with Cu Kα radiation), FT-IR spectroscopy (Perkin-Elmer 1700, KBr disk technique), Raman spectroscopy (Renishaw 1000, Ar laser, 25 mW), UV–Vis–NIR Diffuse Reflectance Spectroscopy (Perkin-Elmer Lambda 19), and chemical analysis. Chemical analysis consisted of a volumetric titration for the determination of the different valence states of vanadium according to the procedure originally developed by Niwa and Murakami [9]. Specifically, 1 g of sample was first dissolved in hot concentrated H_2SO_4; V^{5+} was directly determined by titration with Fe^{2+}, ($V^{3+}+V^{4+}$) were titrated with a MnO_4^- solution, and the solution exclusively containing V^{5+} was again titrated to V^{4+} with Fe^{2+} solution. It was thus possible to determine the relative amounts of the three vanadium species. This analysis also suffers from the following limitations: V^{3+} and V^{5+} can disproportionate yielding V^{4+}: $V^{3+}+V^{5+} \leftrightarrow 2V^{4+}$, and therefore the quantitative determination of V^{5+} and of V^{3+} would be correct only when there is not the contemporaneous presence of the two cations. A second problem is the oxidation of V^{3+} by air during the dissolution of the sample. However, blank tests were carried out, which demonstrate that the disproportion is a very slow process; in addition, no variation of vanadium valence state occurred when both V^{4+} and V^{5+} were present. In addition, since measurements of samples which clearly contained all types of V cation species (as demonstrated by UV–Vis–DR spectroscopy) effectively led to the titration of both V^{3+} and V^{5+}, this confirms that disproportionation is either reversible (i.e., not complete), or quite slow. A further source of error is the carbon content, present as residual C from the organic compounds trapped during the synthesis procedure, or in small amounts in catalysts after reaction. Carbon can be oxidized by MnO_4^- during titration, thus leading to an overestimation of V^{3+}. In order to overcome all these problems, the following procedure was adopted:

1. The dissolution of the sample was carefully carried out, avoiding those conditions which might lead to modification of the valence state of vanadium.
2. The C content was determined in all samples, and when present the amount of MnO_4^- consumed in C oxidation was subtracted from the final value.
3. A balance on vanadium was done (comparison between expected and titrated vanadium), and only results obtained corresponding to a V balance in the range 99–101% were taken as reliable.

Catalytic tests were carried out in a stainless-steel laboratory flow reactor operating at atmospheric pressure, loading 3 g of catalyst shaped in particles 0.3–0.5 mm in diameter, diluted with inert material. The following reaction conditions were used, unless otherwise specified: feedstock composition 1.7 vol.% *n*-butane, 17% oxygen, remainder helium. The W/F ratio was equal to $1.3\,g\,s\,ml^{-1}$. The products were collected and analyzed by means of gas chromatography.

3. Results and discussion

3.1. The performance of pseudo-equilibrated catalysts having different chemical–physical characteristics

As described in Section 2, the nature of the precursor and the procedure employed for thermal treatment finally led to compounds having different bulk and surface features. Thereafter, these samples were loaded in the reactor, and were put on stream under reaction conditions at 400°C for approximately 30–50 h. During this period of time, changes in catalytic performance were remarkable for all catalysts, and after this ageing the catalysts exhibited a catalytic behavior which was almost constant with time. However, these catalysts are not to be considered as fully equilibrated ones, and are subjected to further minor changes in catalytic performance with further ageing. Full equilibration to a definitely constant behavior can take a few hundreds of hours, depending on reaction conditions and on the characteristics of the fresh catalyst. We shall refer to samples after the first 30–50 h on stream as pseudo-equilibrated ones.

During this period some modifications occur in the characteristics of the samples; an example is shown in Fig. 1, which compares the UV–Vis–DR spectra for the several catalysts after thermal treatment (calcined fresh samples) and after reaction (pseudo-equilibrated samples). Reported in Table 1 are the main characteristics of the pseudo-equilibrated catalysts, i.e., the specific surface area and the average oxidation state of vanadium, as determined by chemical analysis (see Section 2 for a detailed description of the titration procedure).

It is shown that sample 1 is the most reduced one, both before and after reaction (the catalyst contained 9% V^{3+}). The presence of V^{3+} is clearly evident from the absorption band at around 500 nm, which is much more intense in the sample before reaction. This means that during ageing a considerable fraction of the V^{3+} species which has developed during the thermal treatment is transformed to V^{4+} species. The presence of V^{5+} in this sample can be excluded, on the basis of the results of chemical analysis, which is very sensitive to even traces of V^{5+}. Another two absorption bands at lower energy are relative to d–d transitions of V^{4+}. Samples 2–4 possess comparable features after calcination (Fig. 1 left), with absorption bands relative to V^{5+} (CT band at around 400–450 nm relative to octahedral V^{5+}), and to V^{4+}; a weak absorption band at 500 nm cannot be excluded. After reaction they have clearly developed a band at 500 nm, and in all cases the

Table 1
Main characteristics of the pseudo-equilibrated catalysts

Sample No.	Surface area (m^2/g)	V^{3+}/V_{tot} (at.%)	V^{5+}/V_{tot} (at.%)	Specific activity, mole $C_4/(m^2\,h)\times10^5$	Selectivity MA (%)[a]
1	20	9	0	3.4	60
2	23	≤1	0	1.1	58
3	19	≤1	0	1.9	58
4	32	≤1	0	1.5	61
5	24	≤1	3	0.7	57
6	6	0	30	3.0	55

[a] MA: maleic anhydride; selectivity at 30% *n*-butane conversion.

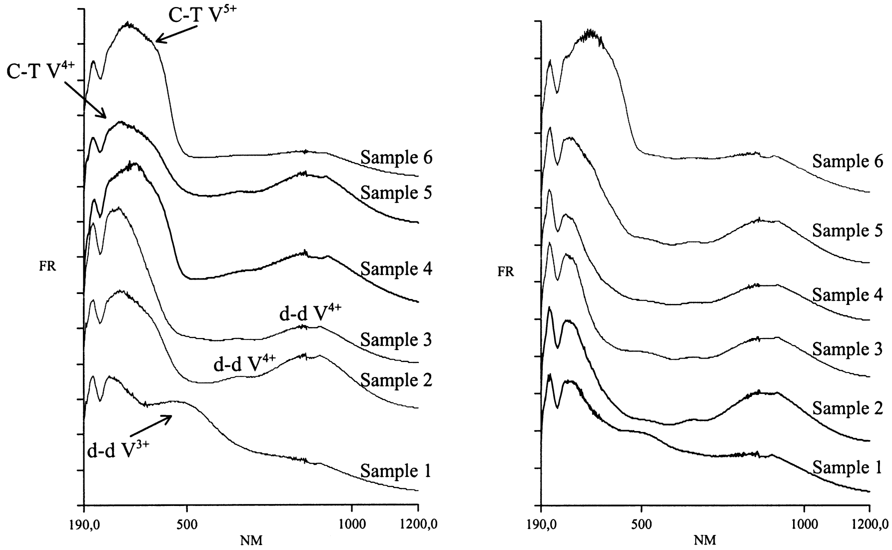

Fig. 1. UV–Vis–DRS spectra of calcined catalysts (left) and of pseudo-equilibrated catalysts (right). The characteristics of the samples are listed in Table 1.

absorption relative to V^{5+} has considerably decreased in intensity. Chemical analysis confirms the absence of V^{5+} in samples after reaction, and indicates the presence of less than 1% V^{3+}. Also sample 5 after calcination has features similar to those of samples 2–4, but after reaction shows some differences with respect to these, since it does contain both V^{3+} and V^{5+} (as also evident by UV–Vis–DR spectroscopy, with a shoulder at around 400 nm and a band at 500 nm), with an average oxidation state which however is higher than 4.00+. This situation can be due to the fact that the reduction of V^{5+} species, with development of V^{4+} and V^{3+} species, did not reach completion during ageing. Finally, sample 6 was strongly oxidized before reaction, and is still oxidized after reaction. In this case the catalyst contained 30% V^{5+}. This catalyst is also characterized by the lowest value of specific surface area. A further aspect is that in general a good correspondence exists between the results of chemical analysis (a bulk characterization), and those obtained by means of UV–Vis–DR spectroscopy, a more surface-sensitive technique. This indicates that qualitative relationships between catalytic activity and chemical analysis can be done, with an acceptable degree of reliability.

Fig. 2 (left) compares the XRD patterns of the pseudo-equilibrated catalysts. Samples 2–5 exhibit the typical pattern of vanadyl pyrophosphate; sample 6 shows additional reflections at d=7.01 Å (2θ=12.6°), 3.05–3.03 Å (29.2–29.5°) and 3.51 Å (25.4°) which can be attributed to an hydrated $VOPO_4$ phase [10]. Sample 1 is the one containing the largest fraction of amorphous component, as shown by the high noise to signal ratio.

Raman spectra of the pseudo-equilibrated samples are shown in Fig. 2 (right). Once again, the main differences involve samples 1 and 6, while samples 2–5 only show the bands which are typical of vanadyl pyrophosphate, at ∼922, ∼1133 and ∼1184 cm^{-1}. Absorption bands relative to V^{5+} phosphate at 1027, 687 and 535 cm^{-1} are clearly observed in sample 6, and are also present in sample 5, which contains traces of V^{5+} (as determined by chemical analysis). In the case of sample 1, the main difference with respect to the spectra of samples 2–5 concerns the presence of a broad absorption band around 990 cm^{-1}. This band can be related, on the basis of the results of the other characterization techniques, to the presence of V^{3+} sites, either as defects in the vanadyl pyrophosphate or as a separate, amorphous or microcrystalline phase. An alternative explanation might be the presence of dispersed $VOPO_4$, which also exhibits absorptions in this range; however, the catalyst does not contain

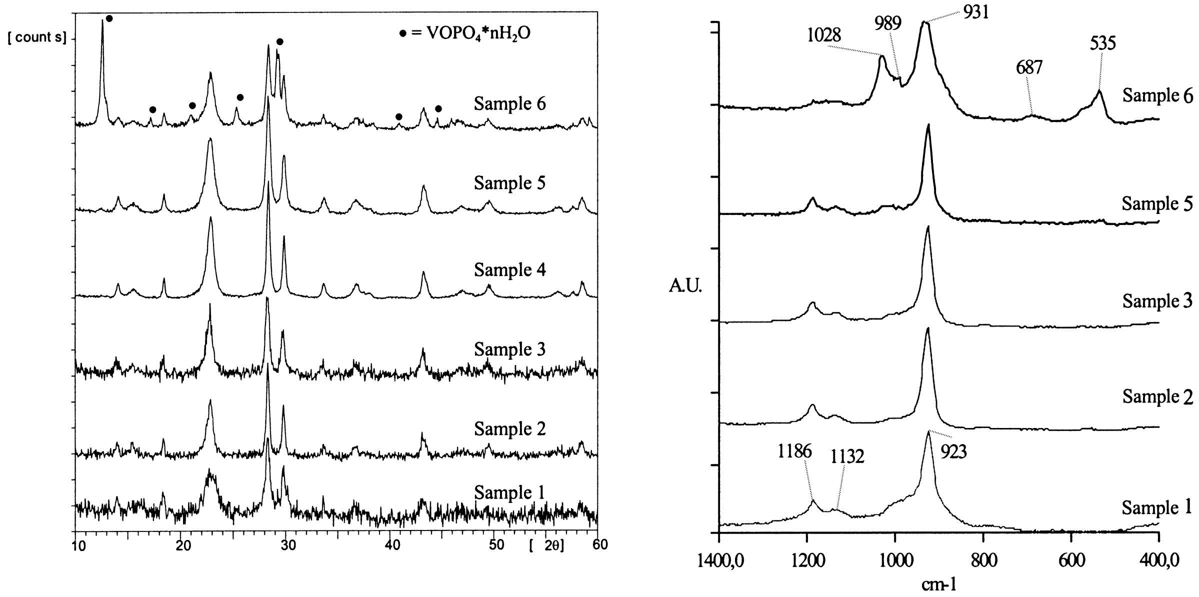

Fig. 2. XRD spectra (left) and Raman spectra (right) of pseudo-equilibrated samples 1–6.

V^{5+} at all, as demonstrated by chemical analysis. Moreover, other bands relative to any form of $VOPO_4$ compound are absent. The main differences in the IR spectra (not reported here) of sample 1 concern the absorption band at 1090 cm^{-1} (relative to the ν_s of PO_3 groups), which is much less intense than in spectra of vanadyl pyrophosphate (samples 2–5).

The characterization of these compounds indicates that 30–50 h ageing in the reactor leads to the transformation of most V^{5+} or V^{3+} ions developed during the thermal treatment. The catalysts after reaction exhibit very similar characteristics, except when the starting catalyst (obtained after the thermal treatment) was either considerably reduced or considerably oxidized.

Comparison of the reactivity of these catalysts can yield information concerning the role of the different vanadium species identified in the catalysts. The catalytic performances of samples 1–6 under pseudo-stationary conditions are summarized in Table 1, which reports the specific overall activity, expressed as moles of *n*-butane converted per unit time per unit surface area at 350°C, and the selectivity to maleic anhydride at 30% *n*-butane conversion. The latter represents the ratio between the rates for the parallel reactions of maleic anhydride formation and *n*-butane combustion, in the absence of consecutive reactions of combustion over the anhydride, due to the low *n*-butane conversion. The same comparison was not possible for higher levels of *n*-butane conversion, since the less active catalysts could not reach high paraffin conversion. The results show that the specific activity of samples 2–5 was similar, as well as the selectivity to maleic anhydride at low *n*-butane conversion. Higher specific activities were instead obtained for the most strongly oxidized and reduced catalysts, samples 6 and 1, respectively. In the former case, however, the catalyst had a very poor activity, due to the low surface area, while the reduced catalyst was considerably more active. These results agree with that reported in the literature concerning the role of V species with valence states other than 4+. Indeed many papers report that catalysts containing discrete amounts of V^{5+} sites have in general a better catalytic performance than catalysts which exclusively contain V^{4+} sites [4,5]. In our case, the only catalyst with such characteristics is sample 5. It seems from our data that also in the presence of extensively oxidized surfaces (sample 6) the specific activity of surface active sites is higher than for non-oxidized vanadyl pyrophosphate.

Much less information is available for catalysts containing V^{3+} species. In a recent paper Rodemerck et al. [4] report that catalysts possessing an average oxidation state for vanadium located between 3.96+ and 4.02+ all behave similarly, and all of them are less active than a catalyst possessing an average valence state of 4.10+. Gai and Kourtakis [8] also point out the fact that anionic vacancies created by O^{2-} removal from the lattice can develop at the surface of the vanadyl pyrophosphate and extend throughout the bulk via a shear-plane type mechanism. The extent of defects is a function of the reduction conditions employed, and it can be as high as leading to a valence state for vanadium of 3.7+. It is claimed that notwithstanding this the main structure of the vanadyl pyrophosphate is retained, and that partly reduced catalysts are more active than non-reduced ones, due to the fact that these anionic vacancies are associated with strong acid Lewis-type sites [8]. Alternatively, it is possible to postulate that these anionic vacancies can be sites for O_2 adsorption and activation, with development of O^- species particularly active in *n*-butane activation [11], or that V^{5+} species develop under reaction conditions by oxidation of V^{4+} or V^{3+}.

The selectivity at 30% *n*-butane conversion was in the range 57–61% for samples 1–5, while it was lower (55%) for sample 6. This indicates that excessively oxidized catalysts exhibit lower selectivity, due to the higher contribution of parallel *n*-butane combustion; this is in agreement with indications from the literature [5]. On the other hand, sample 1 (considerably reduced) also is characterized by good selectivity to maleic anhydride, thus indicating that the presence of high amounts of V^{3+} does not negatively affect the O-insertion capacity of the vanadyl pyrophosphate, at least at low *n*-butane conversion. Volta et al. [5] reported that on increasing surface concentrations of V^{5+} ions, a maximum in selectivity to maleic anhydride is observed; in our case, information is missing for average oxidation states of vanadium beween 4.02 and 4.30+.

The absence of V^{5+} in pseudo-equilibrated catalysts after reaction contrasts with data reported in the literature, which indicate the presence of a small amount of V^{5+} for equilibrated catalysts, with an average oxidation state for vanadium between 4.005+ and 4.010+. This difference can be due to the reaction conditions employed. It is likely that the presence of vanadium with a valence state other than 4.0+ in equilibrated catalysts is a function of the reaction temperature, and of the *n*-butane to oxygen ratio (i.e., the reducing power of the gas phase). Our conditions were chosen to operate in proximity of the hydrocarbon-lean side of the flammability bell (the lower limit is 1.8% *n*-butane in air), but in many cases conditions are described in the literature which make use of more “oxidizing” conditions, i.e., a lower partial pressure of *n*-butane. Nevertheless, these data clearly indicate that even though the presence of V^{5+} can have a positive effect on the catalytic performance, as claimed by many authors, under defined reaction conditions and under stationary conditions this species may not be present; nevertheless the catalyst performs well.

3.2. Confirmation of the role of V^{3+}: chemical–physical characteristics and reactivity of an equilibrated catalyst reduced in hydrogen flow

In order to confirm the role of the V^{3+} species on the catalytic performance, a fully equilibrated catalyst (sample 7, after more than 300 h time-on-stream), was treated at increasing temperatures and for increasing times to a reducing treatment in diluted hydrogen flow. The chemical analysis indicates a progressive increase in the amount of V^{3+}. The catalyst contained 1% V^{3+} for the sample which underwent a treatment of 1 h at 500°C in diluted H_2 (sample 8), and 5% V^{3+} for sample 9, which underwent the treatment for 1 h at 550°C. No V^{5+} was found, as expected for samples which have been treated in H_2 flow. The X-ray diffraction patterns and FT-IR spectra did not change after the treatment, thus indicating that the structure of the vanadyl pyrophosphate was retained, while changes were observed in Raman and UV–Vis spectra (Fig. 3). In particular, Raman spectra show for sample 7 the features typical of vanadyl pyrophosphate with a further broad absorption band at around 990–970 cm^{-1}, which by comparison with the spectrum for sample 1 can be considered as indicative of the presence of low amounts of V^{3+}. With increasing reduction this broad absorption band clearly increases in intensity, and new bands become evident which cannot be clearly attributed to $V(PO_3)_3$ [12] or to any other V^{3+}/P/O phase. Since XRD spectra indicate that the structure of the vanadyl pyrophosphate is substantially retained in sample 9, modifications in Raman spectra either refer

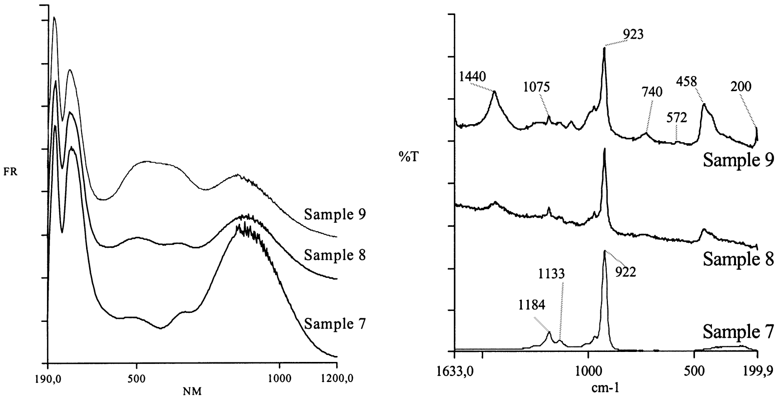

Fig. 3. UV–Vis–DRS spectra (left) and Raman spectra (right) of an equilibrated vanadyl pyrophosphate subjected to a reducing treatment (see text for explanation).

to defects in the structure of vanadyl pyrophosphate, or are relative to a minor fraction of the compound.

The electronic spectra of samples 7–9 show a progressive increase in the absorption band at 500 nm, thus confirming the attribution of this band to a V^{3+} species. Some differences between samples 1 (9% V^{3+}) and 9 (5% V^{3+}) are found in the FT-IR spectra (in the former case the spectrum is different from that of vanadyl pyrophosphate, while in the latter case it is the same as that of vanadyl pyrophosphate), as well as in UV–Vis and in Raman spectra (see Figs. 2 and 3). These differences may be attributed to different factors: (i) the presence of residual C in sample 1 (which is instead absent in sample 9), possibly responsible for the higher overall background of the electronic spectrum, (ii) the different amounts and distributions of defect species or amorphous reduced compounds, since in sample 1, V^{3+} originates by interaction of the bulk with the trapped organic compounds during thermal treatment in nitrogen, and thus is probably distributed in a more homogeneous fashion over the entire bulk of the catalyst, while in sample 9, V^{3+} originates from a surface interaction between the solid and hydrogen in the gas phase. Moreover, in sample 1 the V^{3+} phosphate likely accounts for the amorphous phase, evidence for the presence of which is clearly seen in the X-ray diffraction pattern, while in sample 9 the defects are developed on a well crystallized vanadyl pyrophosphate. This might account for the differences observed in the FT-IR and Raman spectra.

Sample 9 was loaded in the reactor and left under reaction at 400°C, with 1.7% *n*-butane and 17% oxygen. Plotted in Fig. 4 are the conversion of *n*-butane and the selectivity to maleic anhydride as a function of time-on-stream. With increasing time-on-stream, during which a pseudo-equilibrated state developed, the conversion decreased, while the selectivity increased progressively. After a few days the conversion reached an almost constant value. Further time-on-stream led to a very slow additional increase in conversion, only a few 2–3% points in several days. Thus it can be considered that a pseudo-equilibrated state was reached after approximately 100 h reaction. This behavior confirms the role of the V^{3+} species, which

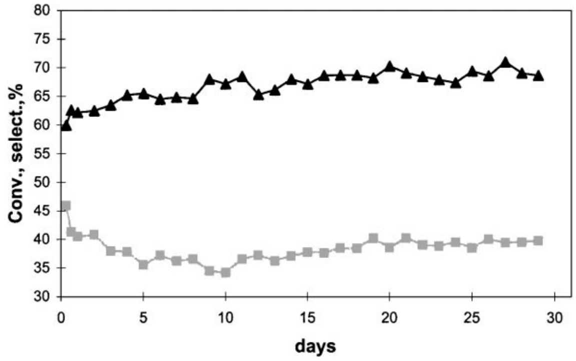

Fig. 4. Conversion of *n*-butane (■) and selectivity to maleic anhydride (▲) as a function of time-on-stream for sample 9 (equilibrated vanadyl pyrophosphate reduced under H_2 flow).

is particularly active in the conversion of *n*-butane. The increase in selectivity can simply be attributed to the decreasing conversion, which lowers the contribution of the consecutive reaction of maleic anhydride combustion. A similar effect due to two overlapping phenomena, namely the progressive oxidation of V^{3+} and the progressive increase in crystallinity of the vanadyl pyrophosphate, has been recently reported for a catalyst obtained by thermal treatment in nitrogen, and starting from a reduced state [13]. This corresponded to an initial decrease in activity (analogous to that obtained in the present case), followed by a considerable increase in activity. The selectivity at low conversion was found to be unaffected by these modifications. In the present case we have isolated the effect of V^{3+} oxidation under reaction conditions, responsible for the decline in activity, since the starting compound was highly crystalline.

After reaction, all features of the catalyst were the same as before reduction (sample 7), thus suggesting that (i) the reducing treatment is completely reversible, and (ii) the reaction environment is oxidizing with respect to the average oxidation state for vanadium developed by reduction.

4. Conclusions

The results obtained indicate that V^{3+} ions which develop during the thermal treatment of the catalyst precursor to vanadyl pyrophosphate may have an effect on the enhancement of the activity of the latter compound in the oxidation of *n*-butane to maleic anhydride. This V^{3+} species can be identified by several techniques. Under reaction conditions (1.7% *n*-butane) this species is in part oxidized, but a small fraction is also found in equilibrated catalysts. A considerable enhancement in activity of the vanadyl pyrophosphate can be obtained by applying a reductive treatment of the catalyst with hydrogen.

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