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The effect of cobalt and iron dopants on the catalytic behavior of V/P/O catalysts in the selective oxidation of *n*-pentane to maleic and phthalic anhydrides

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V/P/O catalysts were prepared using isobutanol as solvent, which contained either cobalt or iron as the dopant (Me/V 0.01). The catalysts were characterized with several techniques, both after thermal treatment and after reaction in *n*-pentane/air. The catalytic performance was compared for the selective oxidation to maleic and phthalic anhydrides under conditions at which results were stable (i.e., after at least 200 h time-on-stream). It was found that iron had a dramatic effect on the structural evolution of the catalyst both during calcination and during aging; in contrast, the effect of cobalt was much less marked. Doping with 1% cobalt remarkably improved the selectivity to the phthalic anhydride at the expense of the maleic anhydride with respect to the undoped catalyst, while doping with iron led to a catalyst less selective to phthalic anhydride and more selective to carbon oxides.

Keywords: heterogeneous oxidation, selective oxidation of *n*-pentane, synthesis of maleic anhydride, synthesis of phthalic anhydride, vanadyl pyrophosphate, cobalt and iron dopants

1. Introduction

Vanadyl pyrophosphate is the industrial catalyst for the selective oxidation of *n*-butane to maleic anhydride [1–3]. In recent years, many papers have been published which take into consideration how the structural features of the catalyst affect the catalyst performance [4–9]. This is of particular importance during the period of catalyst aging in the reactor, since with increasing time-on-stream a modification of the surface and bulk properties of the V/P mixed oxide are observed.

One of the factors which can greatly affect the catalytic performance is the presence of metal dopants [10–19]. The effect of dopants on the catalytic performance of V/P/O catalysts in the oxidation of *n*-butane to maleic anhydride can be summarized as follows:

(1) Addition of ions that interact with free phosphoric acid (all the V/P/O catalysts contain a slight excess of phosphorus with respect to the stoichiometric amount for the $(VO)_2P_2O_7$) as a means of fine tuning of the optimal surface P/V ratio and acidity. These ions are the basic ions such as Zn, and they can also act in avoiding the migration and loss of phosphorus.

(2) Addition of ions that can substitute for phosphorus in the precursor, such as Si and S. The partial or total elimination of these ions by calcination from the vanadyl pyrophosphate structure influences the morphology and defects of the $(VO)_2P_2O_7$. These ions have been proposed to play the same role that has been proposed for benzyl alcohol, which remains trapped inside the structure of the precursor, $VOHPO_4 \cdot 0.5H_2O$, during the preparation in alcoholic medium.

(3) Addition of transition elements that substitute for vanadium that can act as modifiers of the reactivity, forming a stable solid solution and possibly being directly involved in the catalysed reaction. This type of promotion was not well studied to date. The effect observed by the addition of Ti, Zr, Ce and Mo can fall into this category.

More specifically, the effect of cobalt has been studied by Zazhigalov et al. [14]. The authors detected the formation of $Co_2P_2O_7$ when the cobalt was coprecipitated together with vanadium and with phosphorus. Increasing amounts of cobalt led to a decrease in the cat-

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alytic activity, with a corresponding increase in the selectivity to maleic anhydride. This was attributed to an increase in surface acidity. Abdelouahab et al. [17] have found that both Co and Fe remarkably improve the selectivity to maleic anhydride; in addition, iron favourably affects the activity, while cobalt deactivates the catalyst. The observed effects were attributed to a different dispersion of $VOPO_4$ phases on the $(VO)_2P_2O_7$ matrix.

The aim of the present work is to compare the catalytic performance of the V/P/O catalysts in the oxidation of *n*-pentane to maleic and phthalic anhydrides when the compounds are doped with iron and with cobalt. This reaction is more suitable for checking the effect of structural or morphological features on the catalytic performance, due to the larger number of products formed and to the nature of surface functions which are needed in the formation of these products [5,20–25].

2. Experimental

The catalysts were prepared according to the procedure in alcoholic medium. V_2O_5 (11.8 g) was added to isobutanol (250 ml) in which Co or Fe acetylacetonate had been previously dissolved; H_3PO_4 (16.49 g 85%) was then introduced to the mixture which was refluxed for 16 h. The blue suspension was then separated from the organic solution by filtration and washed with isobutanol. The resulting solid was refluxed in water (9 ml of water per gram of solid), filtered hot and dried in air at 110°C [17]. The calcination treatment was effected by heating the precursors in air at 380°C for 6 h. The amount of the dopant, determined by atomic absorption, was 0.31 wt% (for both dopants), corresponding to a Co/V atomic ratio of 0.0102, and an Fe/V ratio of 0.0106.

Specific surface areas of the precursors and catalysts were measured by N_2 adsorption at the liquid nitrogen temperature.

X-ray diffraction spectra were recorded with a Siemens diffractometer using Cu Kα radiation. ^{31}P MAS NMR experiments were performed using a Bruker MSL 300 NMR spectrometer. Conventional spectra were obtained at 121.5 MHz using a 90°x-(acquire) sequence. The 90° pulse was 4.2 μs and the delay time between two consecutive scans was 10 s. Samples were typically spun at 4 kHz in zirconia rotors using a double bearing probehead.

X-ray photoelectron spectroscopy (XPS) was performed with a Hewlett-Packard 5950 interfaced to a data system which allowed the accumulation of spectra. The spectrometer was equipped with an aluminium anode (Al Kα = 1486.6 eV). All binding energies were referred to the C_{1s} line at 284.6 eV.

The catalytic tests were carried out at atmospheric pressure and were performed in a tubular stainless steel flow reactor at atmospheric pressure. The reaction products were collected by bubbling the outlet stream into pure acetone-containing condensers and analyzed on a 1 h reaction time basis. Permanent gases were collected with a gas-tight syringe. All products were analyzed using a Hewlett-Packard 5890II gas chromatograph, equipped with TCD and FID. Carbon oxides and oxygen were separated and analyzed by means of a packed Carbosieve S column, with oven temperature programmed from 40 to 240°C. Condensable products and unreacted hydrocarbons were separated and analyzed in a 0.53 mm OV-17 column, with oven temperature programmed from 80 to 200°C. Catalyst (1 g) was used for catalytic tests, sieved into particles with size ranging from 0.3 to 0.5 mm. The usual experimental conditions for catalytic tests were the following: *n*-pentane 1 mol% in air, 340°C; W/F (weight of catalyst/volumetric flow ratio measured at normal conditions) was varied.

3. Results and discussion

The surface areas of the catalysts precursors were 11 m^2/g (undoped), 9 m^2/g (Co-doped) and 7 m^2/g (Fe-doped). The XRD spectra of the catalyst precursors (undoped, Co- and Fe-doped) are shown in fig. 1. In the

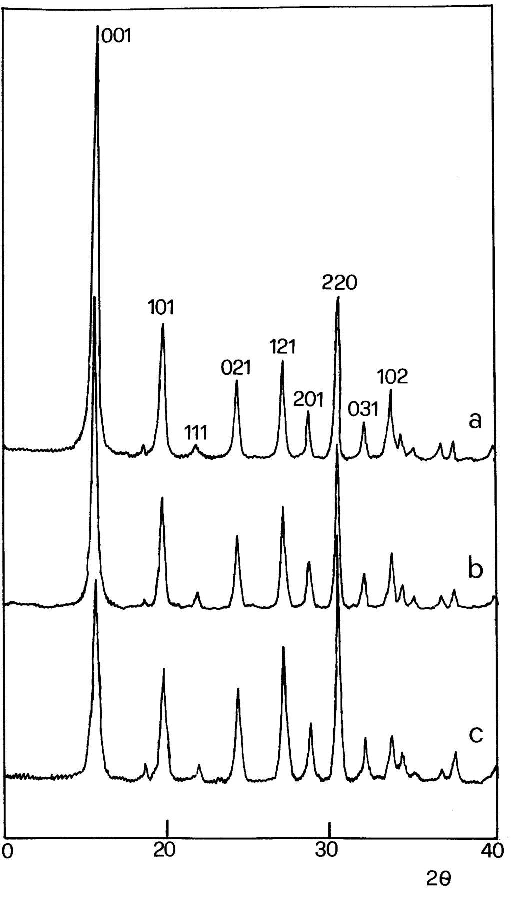

Fig. 1. XRD spectra of precursors: (a) undoped, (b) Co-doped, (c) Fe-doped.

case of the Co-doped sample, the addition of the metal leads to a slight variation in the relative intensity ratio of the (001) and (220) reflections, from 3.4 to 2.7. This effect is much more marked for the Fe-doped catalyst, where the value is decreased to approximately 1.8. It seems therefore that the addition of the dopants leads to different morphologies for the $VOHPO_4{\cdot}0.5H_2O$, in agreement with the different surface areas. This effect was also observed in previous work, but for higher dopant levels (metal/V atomic ratio 0.05) [17].

Fig. 2 compares the XRD patterns of the three samples after calcination in air at 380°C, for 6 h. After this treatment, the surface areas were the following: undoped 12 m^2/g, Co-doped 15 m^2/g, Fe-doped 23 m^2/g. The comparison of the XRD patterns indicates for the undoped and Co-doped catalysts (the spectra are very similar) the presence of $(VO)_2P_2O_7$ and of three diffraction lines ($d = 7.12$, 3.55 and 3.04 Å) that have been attributed by some authors to a hydrated phase possessing an average valence state for vanadium close to 5+, with stoichiometry $VOH_{0.16}PO_4{\cdot}1.9H_2O$ [5,26–28]. Alternatively, it is possible to attribute the reflection at the highest d value to the $VOPO_4{\cdot}2H_2O$ phase (but the other main reflections of this phase are absent), and the other two less intense reflections to the (101) and (111) planes of α_{II}-$VOPO_4$ (but the very intense reflection typical of this compound, at $d = 4.42$ Å, is absent) [4]. The Fe-doped sample appears more amorphous (the intensities of the reflections are weaker), and the reflections relative to the vanadyl pyrophosphate are very weak with respect to those of the oxidized phases; other lines are also present that can be attributed to the δ-$VOPO_4$ (4.02, 3.68 and 3.12 Å). In addition, in this sample all the bands that are reported in literature as belonging to the $VOPO_4{\cdot}2H_2O$, at $d = 7.45$, 4.75, 3.71 and 3.10 Å, are observed.

Information concerning the $VOPO_4$ phases can be gained from the examination of the ^{31}P MAS NMR spectra of the catalysts (fig. 3). A comparison with literature data [4,6,26] indicates that in the undoped sample (fig. 3a) the main signal can be assigned to

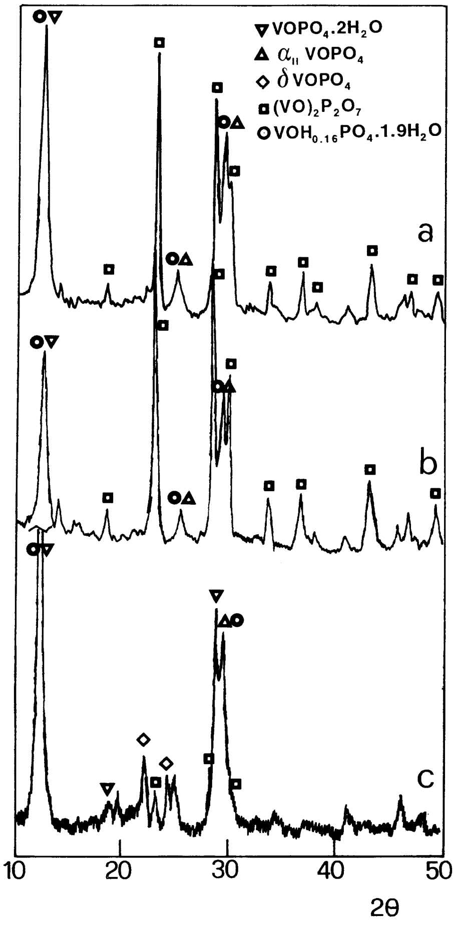

Fig. 2. XRD spectra of the compounds obtained by calcination of precursors in air for 6 h: (a) undoped, (b) Co-doped, (c) Fe-doped.

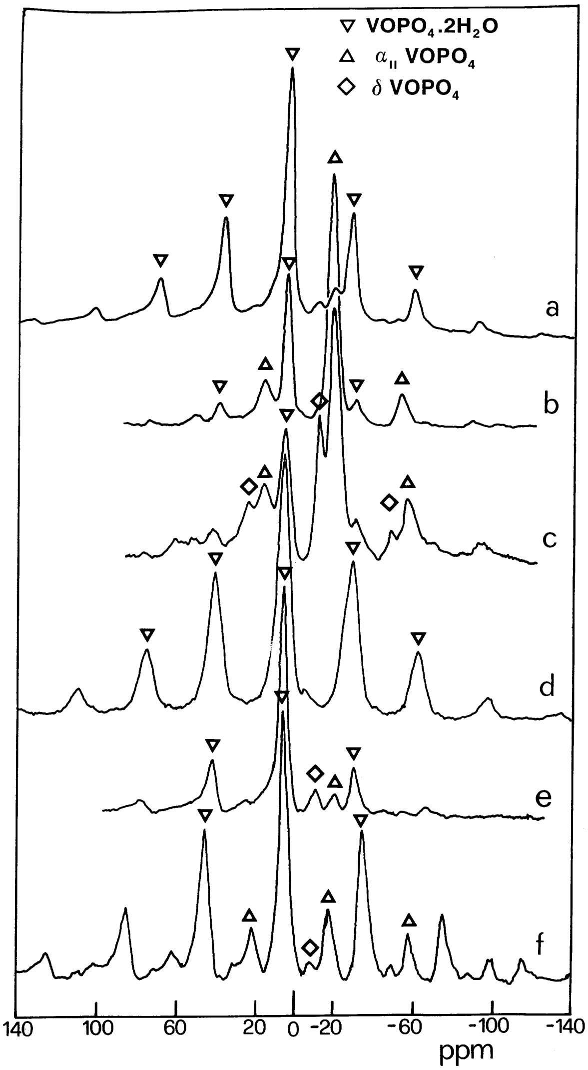

Fig. 3. ^{31}P MAS NMR spectra of calcined samples: (a) undoped, (c) Co-doped, (e) Fe-doped, and of used catalysts: (b) undoped, (d) Co-doped, (f) Fe-doped.

$VOPO_4 \cdot 2H_2O$, with some α_{II}-$VOPO_4$. The height of the spinning side bands of $VOPO_4 \cdot 2H_2O$ as referred to the central band is in favour of a high dispersion of this phase. The same type of spectrum is observed for the Fe-doped catalyst (fig. 3e), with a lower dispersion. By contrast, despite indications given by XRD, the Co-doped catalyst (fig. 3c) clearly shows the presence of three phases, $VOPO_4 \cdot 2H_2O$, δ-$VOPO_4$ and α_{II}-$VOPO_4$. The discrepancy with XRD patterns can be explained by taking into account that all anhydrous oxidized $VOPO_4$ phases (with the exception of β-$VOPO_4$) are in a hydration/dehydration equilibrium with $VOPO_4 \cdot 2H_2O$ [31]. Therefore, the spectra obtained are affected by the conditions used for sample storage, as well as the conditions used for data collection.

In conclusion, it seems that iron has an important effect in determining the structural evolution of the precursor when it is dehydrated in air, whereas cobalt does not have a significant effect. It can be assumed that the presence of iron favours the oxidation of V^{4+} during the treatment of precursor dehydration in air, leading to the formation of amorphous and crystalline $VOPO_4$ phases. This has been observed previously for V/P/O catalysts prepared using the aqueous HCl procedure [32].

Catalysts have then been characterized after reaction (200 h time-on-stream under reaction conditions); the surface areas of spent catalysts are the following: undoped 9.4 m^2/g, Co-doped 12 m^2/g, Fe-doped 9 m^2/g. After reaction, the XRD (fig. 4) exhibit only the reflections of crystalline $(VO)_2P_2O_7$; the undoped and Co-doped samples are quite similar, while the Fe-doped catalyst appears largely amorphous. The line observed at around $2\theta = 21^\circ$ could be indicative of some residual γ-$VOPO_4$ [4]. This indicates that under reaction conditions the crystalline oxidized phases, originally present in samples after calcination, are either reduced to a V^{4+}-containing phase (mainly the vanadyl pyrophosphate), or have become amorphous. The Fe-doped sample remains amorphous.

More significant indications are obtained from the analysis of the ^{31}P MAS NMR spectra of spent samples (fig. 3). The undoped catalyst shows signals which can be attributed [4,6,26] to a mixture of $VOPO_4 \cdot 2H_2O$ and α_{II}-$VOPO_4$ phases. Since crystalline V^{5+} phases are not detected in the corresponding XRD patterns, it can be inferred that this oxidized phase is present as microcrystalline, nearly amorphous compounds. The same is true for the Co-doped catalyst with dispersed $VOPO_4 \cdot 2H_2O$ phase. In the case of the used Fe-doped sample, signals corresponding to $VOPO_4 \cdot 2H_2O$, α_{II}-$VOPO_4$ and, to a minor extent, to δ-$VOPO_4$ can be observed. ^{31}P NMR spin echo mapping confirmed the presence in spent catalysts of V^{5+} phases (signal at 0 ppm), as well as of amorphous V^{4+} and V^{5+} phases (signal in the 500–1500 ppm range [29,30]).

The results of XPS characterization of the used catalysts are summarized in table 1. In all catalysts the presence of V^{4+} (signal at 516.8–516.9 eV BE) and V^{5+} (signal at 517.9–518.0 eV BE) are observed. These results confirm the presence of oxidized vanadium in used samples; the relative amount of V^{4+} and V^{5+} on the surface does not seem to have any relationship with the bulk structure; in fact, the samples demonstrating the highest degree of surface reduction are the doped ones, while bulk characterization clearly indicates a higher extent of reduction for the undoped one. It therefore seems that the degree of surface reduction is more a function of the reaction conditions (i.e., time-on-stream, temperature and hydrocarbon-to-oxygen ratio). The V^{4+}/V^{5+} ratio in used catalysts is generally higher than in fresh calcined catalysts; for instance, in the case of the Fe-doped sample the relative amount of the two species is V^{4+} 41%, V^{5+} 59%. It is thus confirmed that the reaction environment reduces the V^{5+} formed during the calcination treatment.

In conclusion, the characterization of the used cat-

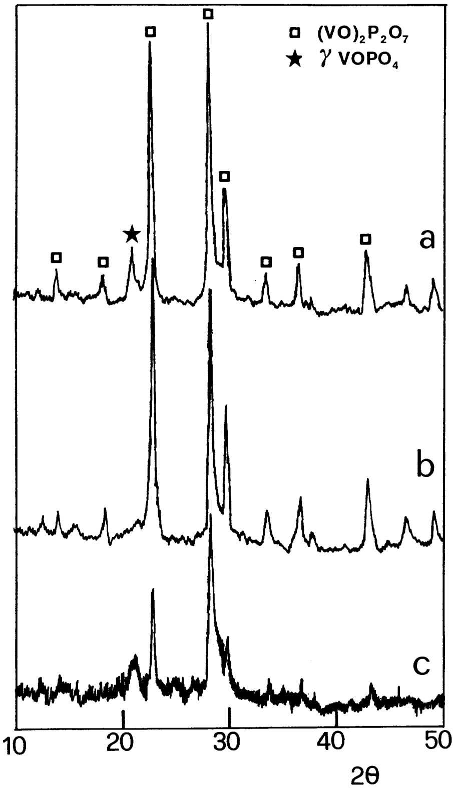

Fig. 4. XRD spectra of the quasi-equilibrated catalysts: (a) undoped, (b) Co-doped, (c) Fe-doped.

Table 1
Results of XPS characterization of used samples

Sample	V^{4+} (%)	V^{5+} (%)	P/V at. ratio
undoped	40	60	2.2
Co-doped	64	36	2.2
Fe-doped	56	44	1.7

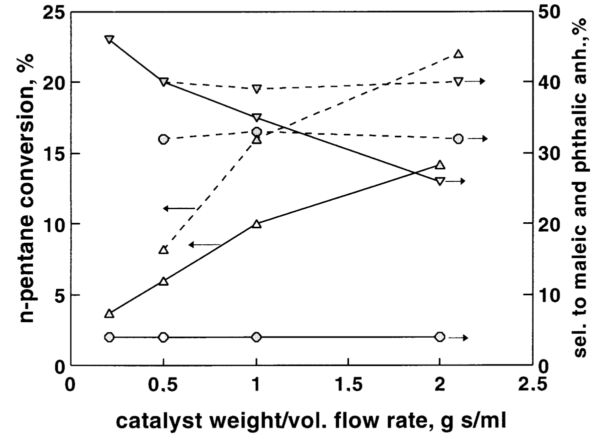

Fig. 5. *n*-pentane conversion (△), selectivity to maleic anhydride (▽), selectivity to phthalic anhydride (○) as a function of *W/F* ratio for the undoped catalyst (data collected after 20 h time-on-stream, full lines), and for the undoped catalyst (data collected after 200 h time-on-stream, dotted lines).

alysts indicates that all catalysts possess, both on the surface and in the bulk, a relatively large fraction of V^{5+} phases, besides the crystalline $(VO)_2P_2O_7$ phase. These oxidized phases are largely microcrystalline. However, the relative amount of the different phases, as well as the nature of the oxidized $VOPO_4$ phases, are affected by the presence of the dopant; while the presence of cobalt does not remarkably affect the structural composition, the presence of iron has a marked effect: it hinders the dehydration of the precursor during thermal treatment, and favours the oxidation of vanadium with formation of amorphous $VOPO_4$ phases.

Catalytic results were collected after 200 h time-on-stream; for shorter periods of reaction it was not possible to get reliable results, since catalytic performance continuously changed. After 200 h, the performance was stable and reproducible results were obtained. The only products which were obtained under these conditions were maleic anhydride, phthalic anhydride and carbon oxides.

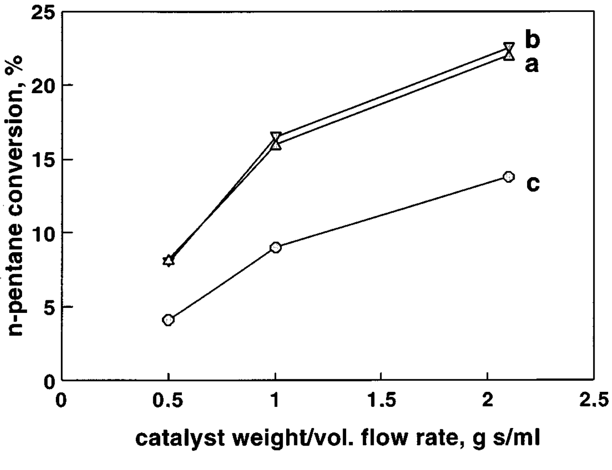

Fig. 6. *n*-pentane conversion as functions of the *W/F* ratio for catalysts (data collected after 200 h time-on-stream): (a) undoped, (b) Co-doped, (c) Fe-doped.

A comparison of the catalytic performance for the undoped catalyst after 20 h time-on-stream and after 200 h (fig. 5 , which reports the catalytic performances as a function of residence time) shows that during aging all catalysts exhibited (i) an increase in the activity, as demonstrated by the increase in the *n*-pentane conversion; (ii) an increase in the selectivity to phthalic anhydride, at the expense mainly of carbon oxides; (iii) a change in the reaction pathway. For the fresh catalyst a consecutive combustion reaction upon maleic anhydride is responsible for the remarkable decrease of selectivity when the conversion is increased. In the quasi-equilibrated catalyst, in contrast, the selectivity to maleic anhydride is constant. The phthalic anhydride does not undergo consecutive oxidative degradation either in fresh and in aged catalysts. A quite comparable evolution with time-on-stream was also observed for the Co-doped catalyst.

The conversion of *n*-pentane as a function of residence time after 200 h time-on-stream (quasi-equilibrated catalyst) is plotted in fig. 6, for the three catalysts examined. It appears that the catalytic activity of the undoped and Co-doped catalysts is the same, while the Fe-doped catalyst is significantly less active. Since surface areas of samples are comparable, the observed difference must be related to a structural effect.

Figs. 7 and 8 show the trend of the selectivity to the products of partial oxidation, maleic and phthalic anhydrides, as function of the *n*-pentane conversion. The selectivity to CO_x is the balance to 100%. The data clearly indicate that the formation of the products occurs through parallel oxidation reactions of *n*-pentane. Therefore, it is possible to interpret these results to the different ability of the catalysts in transforming the intermediate obtained by paraffin activation to either maleic anhydride, or phthalic anhydride or carbon oxides, depending on the microstructure of the V/P/O catalyst.

It is shown that the product distribution is different for the three catalyst samples. In particular, doping with cobalt leads to a catalyst that gives higher specificity to the formation of phthalic anhydride (the most desired product in the selective oxidation of *n*-pentane); this mainly occurs at the expense of maleic anhydride. The Fe-doped compound yields an amount of maleic anhydride which is comparable to that obtained with the undoped catalyst, but the selectivity to phthalic anhydride is far lower; therefore the overall selectivity to carbon oxides is highest for this catalyst.

It is known that the bulk composition of the V/P/O based catalyst, i.e. the relative amounts of vanadyl pyrophosphate, and of other crystalline V^{4+} or V^{5+} phosphate phases, affect the *n*-butane oxidation. In particular, the importance of a well crystallized

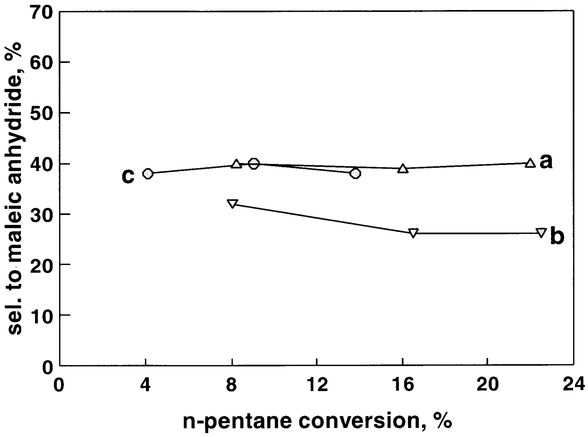

Fig. 7. Selectivity to maleic anhydride as a function of the W/F ratio for catalysts (data collected after 200 h time-on-stream): (a) undoped, (b) Co-doped, (c) Fe-doped.

$(VO)_2P_2O_7$ is known to be fundamental in achieving a good catalytic performance [1–3], but also the presence of surface V^{5+} domains contribute in giving good selectivities [17,32,33]. It is possible that the role played by V^{5+} phases in the transformation of *n*-pentane could be analogous to that occurring in the oxidation of *n*-butane, but further work is required to investigate this aspect.

In previous papers, we described how the products distribution in *n*-pentane oxidation is affected by structural features [5,20]. The presence of well crystallized $(VO)_2P_2O_7$ guarantees the geometrical constraints that are necessary in order to facilitate the bimolecular reactions included in the pathway leading to the phthalic anhydride formation. Indeed, one main difference between the spent samples concerns the presence of crystalline $(VO)_2P_2O_7$ (together with V^{5+} phases), which is clearly observed in XRD patterns for the undoped and Co-doped samples (those yielding the highest relative amount of phthalic anhydride), while it is present only in minor amount in the Fe-doped spent catalyst.

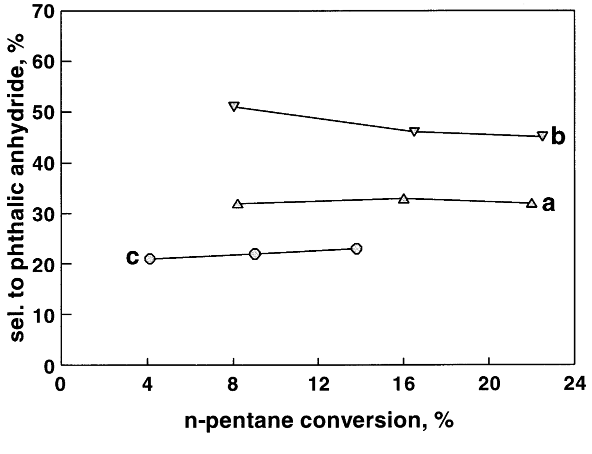

Fig. 8. Selectivity to phthalic anhydride as a function of the W/F ratio for catalysts (data collected after 200 h time-on-stream): (a) undoped, (b) Co-doped, (c) Fe-doped.

This is also confirmed by comparing the performance of fresh and aged catalyst (fig. 5). The progressive crystallization of the vanadyl pyrophosphate, occurring as a consequence of the reduction of V^{5+} in amorphous and crystalline phases, leads to a corresponding increase in the selectivity to the phthalic anhydride.

4. Conclusions

The most pronounced effect observed in the study is the promotion of the formation of phthalic anhydride with the Co-promoted catalyst, a feature not observed in previous catalysts for this reaction.

The main effect of the Co and Fe dopants on the catalytic performance in *n*-pentane oxidation is likely to be attributed to a modification of the microstructure all along the evolution of the V/P/O catalyst from the precursor to the fresh catalyst, and from the latter to the used (quasi-equilibrated) catalyst. This affects both the bulk and surface composition, and correspondingly changes the catalytic performance during aging. The presence of iron hinders the crystallization of the $(VO)_2P_2O_7$, while this is not the case for the Co dopant. The effect of the two dopants is also different when we consider the $VOPO_4$ phases which are generated; Co promotes the nucleation of the only $VOPO_4{\cdot}2H_2O$ phase, highly dispersed on the crystallized $(VO)_2P_2O_7$ matrix, while Fe favours the nucleation of α_{II}-$VOPO_4$ and δ-$VOPO_4$ with less dispersed $VOPO_4{\cdot}2H_2O$.

At present it is not possible to give a complete explanation of the specific effect of cobalt as compared to iron in *n*-pentane oxidation. Previously published data indicate that both cobalt and iron had a positive effect in the selectivity to maleic anhydride in *n*-butane oxidation [17], but this reaction is clearly less surface-demanding than the oxidation of *n*-pentane, in which the formation of the phthalic anhydride clearly requires additional surface properties associated to the condensation of intermediates. In the present case, it is possible to hypothesize that the better selectivity to phthalic anhydride exhibited by the Co-doped catalyst is related to the higher crystallinity of the vanadyl pyrophosphate, even though a possible role played by the oxidized $VOPO_4$ phases (which are different in the three samples examined) cannot be excluded.

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