# $n$-butane oxidation to maleic anhydride: effect of Co and Fe addition by the method of incipient wetness on vanadium phosphate catalysts prepared by the aqueous HCl method

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Received 21 December 1995; accepted 6 January 1996

The effect of the addition of $Co^{2+}$ and $Fe^{3+}$ on the catalytic performance and structure of vanadium phosphate catalysts is described and discussed. The catalyst precursor $VOHPO_4 \cdot 0.5H_2O$ was prepared using the aqueous HCl route and $Co^{2+}$ and $Fe^{3+}$ were incorporated using the incipient wetness method. Addition of $Co^{2+}$ improves the selectivity to maleic anhydride, but is found to decrease the specific activity for the formation of maleic anhydride, whereas the addition of $Fe^{3+}$ increases the specific activity up to a maximum level at ca. 2 mol% Fe. The effects are not due to changes in the specific surface area of the final catalyst, which remains $6.5 \pm 0.5\ m^2\ g^{-1}$ for all the catalysts studied. Part of the effect is due to the formation of $VOPO_4$ phases in the catalyst precursor due to the method of addition of the $Co^{2+}$ or $Fe^{3+}$ and this is both related to the effect of the oxidation potential of the additive cation and to the pH of the impregnating solution. It is apparent that the use of the incipient wetness method for the addition of promoter compounds should be used with care for the VPO system at variance with the direct incorporation of the promoter during the preparation of the $VOHPO_4 \cdot 0.5H_2O$ precursor.

**Keywords:** vanadium phosphorus oxides; $VOHPO_4 \cdot 0.5H_2O$; catalyst promotion

## 1. Introduction

Vanadium phosphorus catalysts continue to attract considerable research attention as they represent one of the few catalysts capable of selective alkane activation [1]. Numerous academic studies have been carried out and these almost exclusively consider only pure vanadium phosphate phases in the absence of promoter compounds [2–4]. As noted previously [5] vanadium phosphorus catalysts used in the industrial production of maleic anhydride are not used as pure phases, but incorporate a broad range of promoter compounds. The identification and nature of the effects of promoter compounds has only been considered to any appreciable extent in the patent literature and this has been reviewed recently [6]. A very wide range of cations has been used and beneficial effects have been claimed with Co, Cd, Ni [7], Zn, Bi, Cu, Li [8–10], Zr [11], Mo, Nb [12] and Fe, Cr [13]. To date there have been few definitive studies of the promotion of vanadium phosphate catalysts and in particular the effect of additive concentration on the catalytic performance and catalyst structure has received scant attention. The aim of this paper is to study the effects of the addition of $Co^{2+}$ and $Fe^{3+}$, both of which have been previously considered as promoters [6] for vanadium phosphate catalysts.

## 2. Experimental

### 2.1. Catalyst preparation

$V_2O_5$ was prepared from thermal decomposition of $NH_4VO_3$ at 500°C for 3 h. $V_2O_5$ and aqueous HCl (35%, 13 ml/g $V_2O_5$) were refluxed for 3 h to give a dark blue solution. $H_3PO_4$ (88%, V : P mole ratio = 1 : 1.05) was added and refluxed for a further 2 h. The solution was evaporated to dryness and the resulting solid dried (110°C, 16 h). The dried material was ground and boiled in water (20 ml $H_2O$/g solid) for 1 h, filtered hot, washed with warm water and dried in air (110°C, 16 h). The precursor was characterised by X-ray powder diffraction and laser Raman spectroscopy, and found to be $VOHPO_4 \cdot 0.5H_2O$.

### 2.2. Addition of $Co^{2+}$ and $Fe^{3+}$

$Co^{2+}$ and $Fe^{3+}$ were added to $VOHPO_4 \cdot 0.5H_2O$ using the method of incipient wetness to give catalysts comprising 1, 2 and 5 mol% Co or Fe. The porosity of $VOHPO_4 \cdot 0.5H_2O$ was determined by measuring the amount of water required to just moisten a known mass of $VOHPO_4 \cdot 0.5H_2O$. Aqueous solutions of $Co(NO_3)_2 \cdot 6H_2O$ or $Fe(NO_3) \cdot 9H_2O$ were prepared and $VOHPO_4 \cdot 0.5H_2O$ was then impregnated using these solutions. The resulting solids were then dried at 110°C for 16 h in air.

### 2.3. Catalyst testing

Catalyst precursors were used in powder form and evaluated for the oxidation of *n*-butane in a fixed bed microreactor. Catalyst precursors were transformed to the final catalyst in situ in the reactor under standard reaction conditions (385°C, gas hourly space velocity GHSV $= 1000\ h^{-1}$, 1.5 *n*-butane in air) and the catalytic performance was allowed to stabilise for about 70 h. Reactants and products were determined using on-line gas chromatography and satisfactory carbon mass balances were obtained for all data reported.

### 2.4. Catalyst characterisation

Catalysts were characterised using powder X-ray diffraction, laser Raman spectroscopy, and differential scanning calorimetry. Surfaces areas were measured according to the BET method with $N_2$ adsorption. In addition, the transformation of the catalyst unpromoted precursor to the final catalyst was studied using two in situ techniques: (a) Raman spectroscopy as described previously [14,15] and (b) X-ray powder diffraction. In situ X-ray powder diffraction studies were carried out using a Siemens D500 diffractometer with STOE rotating anode Cu X-ray source at the Davy Faraday Laboratory, The Royal Institution of Great Britain. In a typical experiment, catalyst powder (0.14 g) was loaded to the in situ cell, which was designed to allow the butane/air reactant mixture to flow through the catalyst bed. The flow rate of the reactants (1.5% *n*-butane in air) was controlled using a mass flow controller. A thermocouple positioned in the catalyst bed permitted monitoring of the catalyst temperature. Products were analysed by on-line gas chromatography. The catalyst was heated from ambient temperature to 360°C in flowing *n*-butane/air (GHSV $= 3900\ h^{-1}$) in 1 h and the X-ray powder diffraction patterns were recorded over a reaction period of 82 h. Under these reaction conditions, no thermal non-catalysed gas phase decomposition of *n*-butane was observed in the in situ cell.

## 3. Results

### 3.1. Characterisation of catalyst precursors

The $Co^{2+}$ and $Fe^{3+}$ containing precursors were analysed using powder X-ray diffraction. The results are shown in table 1. The X-ray powder diffraction pattern of the catalyst precursor corresponds to a well crystalline sample of $VOHPO_4{\cdot}0.5H_2O$ with the (001) reflection being dominant. Treatment of this sample with water (pH = 6.2) followed by drying at 110°C does not lead to any significant changes in the diffraction pattern. When $Co^{2+}$ and $Fe^{3+}$ are present it is apparent that new reflections, that can be assiged to $VOPO_4{\cdot}2H_2O$, are present and the relative intensity of these new reflections increases relative to the intensity of the (001) reflection of $VOHPO_4{\cdot}0.5H_2O$ as the concentration of $Co^{2+}$ or $Fe^{3+}$ increases. It is also apparent that the relative intensity of the (001) reflection of $VOHPO_4{\cdot}0.5H_2O$ decreases relative to the other major reflections for this compound as the concentration of $Co^{2+}$ or $Fe^{3+}$ increases. Hence the addition of $Co^{2+}$ and $Fe^{3+}$ by the method of incipient wetness leads to some oxidation and hydration of the $VOHPO_4{\cdot}0.5H_2O$ to $VOPO_4{\cdot}2H_2O$ with higher levels of $VOPO_4{\cdot}2H_2O$ being observed with the $Fe^{3+}$ samples. In addition, the degree of oxidation was related to the concentration of the additive. The pH of the impregnation solutions of cobalt nitrate was ca. 6.2 ± 0.1. Treatment

Table 1
Powder X-ray diffraction data for unpromoted and Co, Fe promoted catalyst precursors

| *d* (Å) | Assignment [a] | Sample $I/I_{max}$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | VPA [b] | $VPA_{(H_2O)}$ [c] | 1% Co | 1% Fe | 2% Co | 2% Fe | 5% Co | 5% Fe |
| 7.43 | D (001) | – | – | 1.4 | 2.3 | 8.0 | 9.6 | 18.3 | 17.3 |
| 5.69 | H (001) | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| 4.79 | H (020) | 0.4 | 0.5 | 0.6 | 0.8 | 1.2 | 2.6 | 2.6 | 3.8 |
| 4.52 | H (101) | 6.0 | 10.2 | 10.0 | 11.9 | 23.7 | 22.4 | 34.8 | 35.6 |
| 4.09 | H (111) | 0.8 | 1.2 | 1.6 | 1.5 | 3.3 | 3.3 | 5.6 | 6.7 |
| 3.66 | H (200) | 3.8 | 5.3 | 6.9 | 7.6 | 16.9 | 15.2 | 26.5 | 25.0 |
| 3.29 | H (121) | 4.5 | 7.2 | 8.4 | 8.9 | 20.6 | 20.2 | 33.1 | 31.0 |
| 3.10 | H (201) | 2.4 | 3.6 | 4.4 | 4.9 | 11.5 | 10.7 | 20.9 | 26.2 |
| 3.02 | D (200) | – | – | – | – | – | 2.2 | – | 8.0 |
| 2.93 | H (211) | 5.8 | 9.3 | 11.5 | 13.2 | 27.4 | 27.8 | 52.3 | 42.7 |
| 2.79 | H (031) | 1.5 | 2.8 | 2.8 | 3.2 | 7.2 | 7.6 | 14.0 | 11.8 |
| 2.66 | H (102) | 3.3 | 6.0 | 5.5 | 6.0 | 11.3 | 11.9 | 14.0 | 14.7 |
| 2.54 | D (003) | – | – | – | – | – | 1.9 | – | 2.9 |

[a] D = $VOPO_4{\cdot}2H_2O$, H = $VOHPO_4{\cdot}0.5H_2O$.

[b] VPA = untreated unpromoted $VOHPO_4{\cdot}0.5H_2O$.

[c] $VPA_{(H_2O)}$ = unpromoted $VOHPO_4{\cdot}0.5H_2O$ treated with water (pH = 6.2) by the incipient wetness technique and dried (110°C, 16 h).

with water alone (pH = 6.2) using the incipient wetness technique previously described did not lead to the formation of $VOPO_4{\cdot}2H_2O$, hence the oxidation observed was considered to be due to the presence of $Co^{2+}$. The pH of the impregnation solutions of iron nitrate were 1.7, 1.4 and 0.85 respectively for the solutions used to prepare the 1, 2 and 5 mol% Fe samples. The effect of acidity of the impregnation solution was studied and the effect characterised by laser Raman spectroscopy, as shown in fig. 1. It is clear that treatment of the precursor with water at $pH \geqslant 3$ using the incipient wetness technique does not affect the structure of the precursor and the bands can all be assigned to $VOHPO_4{\cdot}0.5H_2O$ [14]. However, treatment with water at pH = 1 leads to the formation of $VOPO_4{\cdot}2H_2O$ as a new characteristic band at 1040 $cm^{-1}$ is observed in the laser Raman spectrum [14]. In the case of $Fe^{3+}$ containing precursors, it is therefore apparent that the formation of the $VOPO_4{\cdot}2H_2O$ is related to both the presence of $Fe^{3+}$ and the increased acidity of the iron nitrate solutions, although the acidity of the impregnation solution is probably the dominant parameter.

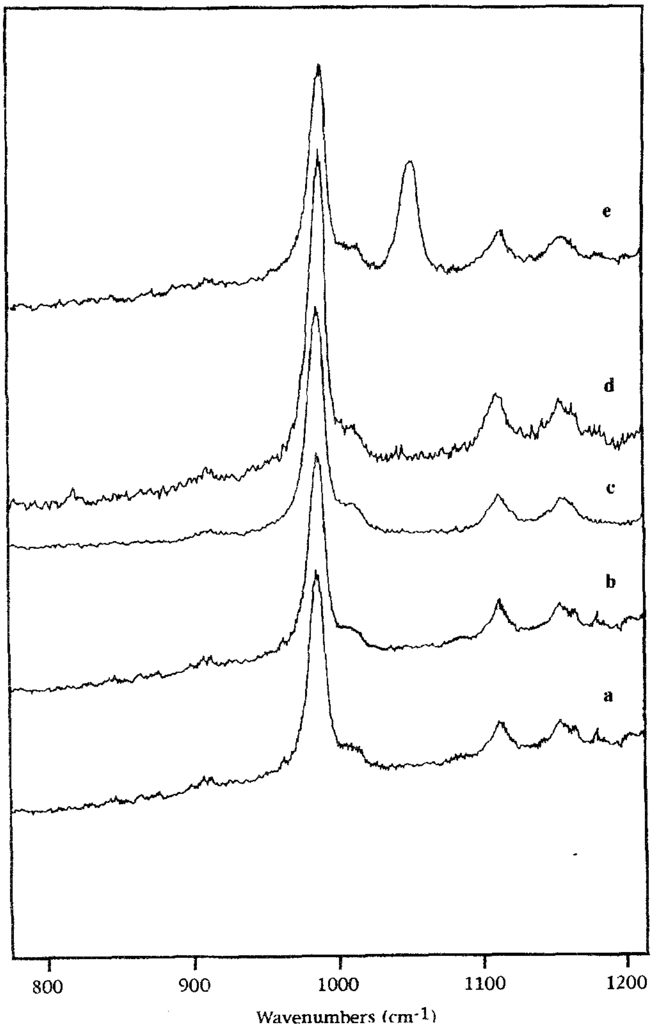

Fig. 1. Laser Raman spectra of catalyst precursors. (a) Unpromoted $VOHPO_4{\cdot}0.5H_2O$, (b) sample (a) treated with water pH = 6.2 by the incipient wetness method, dried (110°C, 16 h), (c) sample (a) treated with water pH = 5.0 by the incipient wetness method, dried (110°C, 16 h), (d) sample (a) treated with water pH=3.0 by the incipient wetness method, dried (110°C, 16 h), (e) sample (a) treated with water pH = 1.0 by the incipient wetness method, dried (110°C, 16 h), pH adjusted using aqueous $HNO_3$.

The catalyst precursors were further characterised using differential scanning calorimetry. The data are shown in fig. 2 and, as expected, the major feature in these data is a large endotherm associated with the transformation of $VOHPO_4{\cdot}0.5H_2O$ to $(VO)_2P_2O_7$ at ca. 470–480°C. However, in the 5% Fe promoted catalyst small endotherms in the region 100–300°C are evident, which on comparison with a reference spectrum for $VOPO_4{\cdot}2H_2O$ (fig. 2a) indicates that these low temperature endotherms can be assigned to the formation of this phase in this precusor.

### 3.2. Catalyst testing

The catalysts were evaluated for the oxidation of *n*-butane after being stabilised under the reaction conditions (385°C, 1.5 *n*-butane in air, GHSV = 1000 $h^{-1}$) for 75 h. Since the catalyst precursor structure was affected by the acidity of the impregnation solution, the performance of Fe containing catalysts was referenced to a catalyst prepared from $VOHPO_4{\cdot}0.5H_2O$ that had been treated with $HNO_3$ (1 mol $\ell^{-1}$) by the incipient wetness technique and dried at 110°C for 16 h. Similarly the performance of the Co containing catalysts was referenced against $VOHPO_4{\cdot}0.5H_2O$ that had been treated with water (pH = 6.2) under equivalent conditions. During the stabilisation period the catalyst performance gradually improved and in particular both the conversion and selectivity to maleic anhydride increased and the selectivity to carbon dioxide decreased. The catalytic performance (table 2) shows that the addition of $Co^{2+}$ leads to a decrease in the yield of maleic anhydride, whereas the addition of $Fe^{3+}$ does improve the catalytic performance. Both additives do, however, lead to an increase in the selectivity in the formation of maleic anhydride. Following catalyst testing the samples were analysed by powder X-ray diffraction and were not found to be highly crystalline, but the major reflections could be assigned to $(VO)_2P_2O_7$ with lesser amounts of $\gamma$-$VOPO_4$ and $VOPO_4{\cdot}2H_2O$ being present. The diffraction patterns of the Co promoted samples were all virtually identical. Fe promoted catalysts showed increased amounts of $VOPO_4{\cdot}2H_2O$ being present when compared with the Co promoted samples.

### 3.3. In situ characterisation of the transformation of the precursor to final catalyst

The transformation of non-promoted $VOHPO_4{\cdot}0.5H_2O$ to the final catalyst was studied using two in situ techniques. First the transformation was studied using

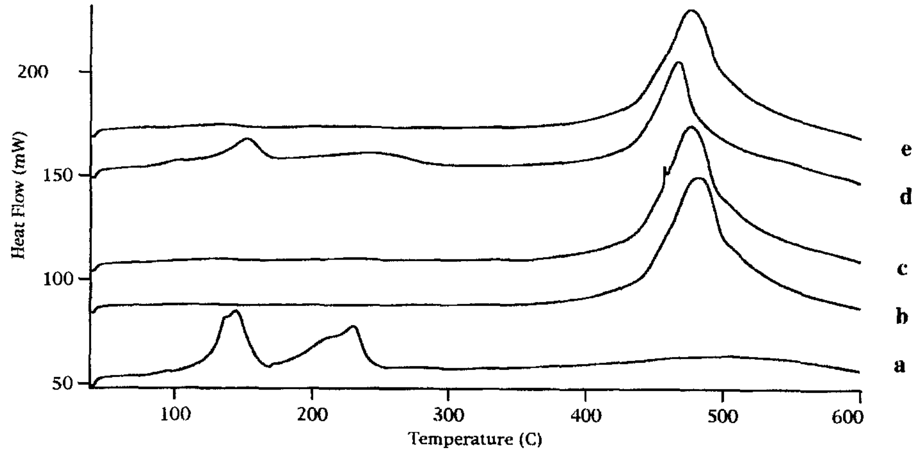

Fig. 2. Differential scanning calorimetry of catalyst precursors in an air atmosphere. (a) $VOPO_4 \cdot 2H_2O$ reference sample, (b) unpromoted $VOHPO_4 \cdot 0.5H_2O$ treated with water pH = 6.2 by the incipient wetness method, dried (110°C, 16 h), (c) $VOHPO_4 \cdot 0.5H_2O$ promoted with 1% Co, (d) $VOHPO_4 \cdot 0.5H_2O$ promoted with 5% Fe, (e) $VOHPO_4 \cdot 0.5H_2O$ promoted with 5% Co.

in situ laser Raman spectroscopy. $VOHPO_4 \cdot 0.5H_2O$, in powder, was loaded into the in situ cell and heated to reaction temperature with *n*-butane/air flowing through the catalyst bed. The results are shown in fig. 3. In addition, the crystallisation process was studied using in situ powder X-ray diffraction. In this case the maximum temperature that could be used was 360°C, since higher temperatures resulted in some gas phase *n*-butane oxidation due to the design of the in situ cell. In this case the reaction gases were passed through the catalyst and the temperature was raised to 360°C and then the X-ray diffraction patterns and the catalytic performance were recorded. The results are shown in fig. 4. It is clear that the transformation of the precursor to the final catalyst is gradual and occurs over many hours. During this time both the selectivity to maleic anhydride and *n*-butane conversion were observed to gradually increase by on-line gc analysis. Concomitant with this improvement in catalytic performance, the structure of the catalyst was transformed from the $VOHPO_4 \cdot 0.5H_2O$ precursor to form mainly $(VO)_2P_2O_7$, together with some amounts of $\gamma$- and $\delta$-$VOPO_4$. The appearance of the $VOPO_4$ structures stems from the intense reflection observed at 21–23° $2\theta$ while the presence of $(VO)_2P_2O_7$ is indicated by the characteristic (200), (024) and (032) diffraction lines at 23, 28.4 and 29.9° $2\theta$, respectively. Hence, after ca. 25 h reaction time the catalyst comprised a mixture of V(IV) and V(V) phases.

## 4. Discussion

The addition of $Co^{2+}$ and $Fe^{3+}$ has a significant effect on the catalytic performance of the catalyst derived from $VOHPO_4 \cdot 0.5H_2O$. The effects observed are not, however, due to variation in surface area, since from all these final catalysts, the surface area was $6.5 \pm 0.5$ $m^2$ $g^{-1}$. This is important since the effects observed by the addition of additives to vanadium phosphorus catalysts can often be ascribed to variation in surface area of the final catalyst [5]. In particular, it has been shown that there exists a linear relationship

Table 2
Catalytic performance of Co and Fe promoted vanadium phosphate catalysts [a]

| Promoter (mol%) | Conversion (%) | Selectivity (%) | | | MA yield (%) | Final surface area ($m^2$ $g^{-1}$) |
|---|---|---|---|---|---|---|
| | | MA | CO | $CO_2$ | | |
| none[b] (0) | 8 | 47 | 42 | 9 | 3.8 | 6.9 |
| Fe (1) | 19 | 54 | 33 | 12 | 10.3 | 6.4 |
| Fe (2) | 20 | 55 | 29 | 16 | 11.0 | 6.4 |
| Fe (5) | 29 | 34 | 45 | 21 | 9.9 | 8.2 |
| none[c] (0) | 33 | 56 | 25 | 18 | 18.5 | 6.5 |
| Co (1) | 22 | 62 | 26 | 10 | 13.6 | 6.4 |
| Co (2) | 18 | 55 | 33 | 10 | 9.9 | 6.4 |
| Co (5) | 20 | 55 | 33 | 11 | 11.0 | 6.5 |

[a] Experimental conditions: 382°C, GHSV = 1000 $h^{-1}$, 1.5% butane in air, data collected after stabilisation for 72 h.
[b] Reference unpromoted sample treated with dilute aqueous $HNO_3$ (0.1 mol $\ell^{-1}$) by the incipient wetness method and dried (110°C, 16 h).
[c] Reference unpromoted sample treated with water (pH = 6.2) by the incipient wetness method and dried (110°C, 16 h).

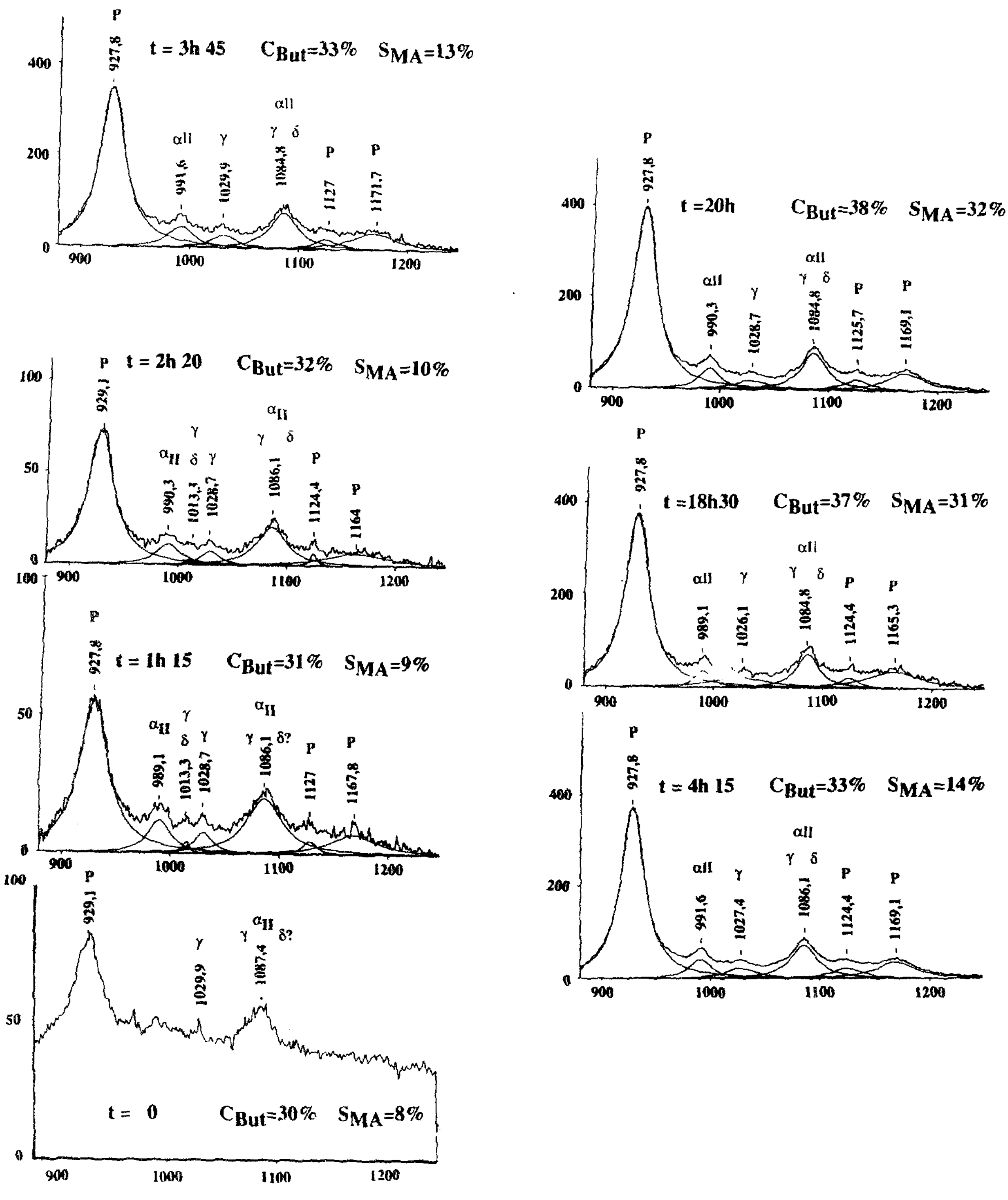

Fig. 3. In situ laser Raman spectra of the transformation of unpromoted $VOHPO_4{\cdot}0.5H_2O$ to the final catalyst in 1.5% butane in air. The precursor was heated in 1.5% butane in air from ambient temperature to 394°C at 3°C $min^{-1}$, $t = 0$ taken when the temperature first reached 394°C. $P = (VO)_2P_2O_7$, $\alpha_{II} = \alpha_{II}$-$VOPO_4$, $\gamma = \gamma$-$VOPO_4$, $\delta = \delta$-$VOPO_4$.

between catalyst activity and surface, and so an increase in catalyst activity can easily result merely from an increase in catalyst surface area. The effects of $Co^{2+}$ and $Fe^{3+}$ on the catalytic performance are different, $Fe^{3+}$ addition leads to an increase in the yield of maleic anhydride, whereas $Co^{2+}$ addition causes a decrease in the yield of maleic anhydride. The variation of specific activity with additive concentration relative to a reference non-promoted catalyst is shown in fig. 5. For $Fe^{3+}$ a distinct maximum in specific activity is observed at ca. 2 mol% Fe. $Fe^{3+}$ therefore acts as a promoter for this vanadium phosphorus catalyst prepared from the aque-

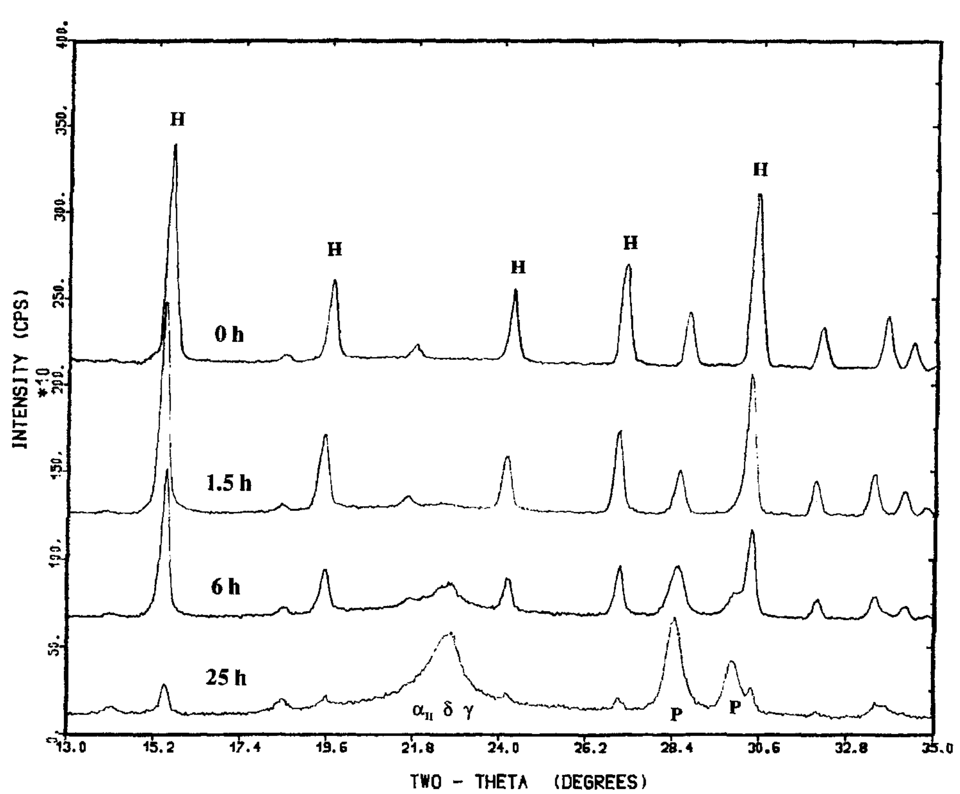

Fig. 4. In situ X-ray powder diffraction analysis of the transformation of unpromoted $VOHPO_4{\cdot}0.5H_2O$ to the final catalyst in 1.5% butane in air, GHSV = 3900 $h^{-1}$, taken at increasing time-on-line, $t = 0$ taken when the temperature first reached 360°C. (Radiation Cu $K\alpha$.) $H = VOHPO_4{\cdot}0.5H_2O$, $P = (VO)_2P_2O_7$, $\alpha_{II} = \alpha_{II}\text{-}VOPO_4$, $\gamma = \gamma\text{-}VOPO_4$, $\delta = \delta\text{-}VOPO_4$.

ous HCl method. These results confirm the studies that the addition of Fe can be beneficial [6,13]. The origin of the effect is considered to be related to the control of the oxidation state of V in the catalyst. The in situ characterisation studies indicate that the active catalyst contains V(IV) and V(V) phases, and it is possible that $Fe^{3+}$ plays a role in controlling the optimum oxidation state under reaction conditions.

Addition of $Co^{2+}$, in this system, leads to a decrease in specific activity (fig. 5). This is unexpected, since previous studies have indicated that $Co^{2+}$ addition can have a beneficial effect [6,7]. However, as discussed below, the addition of $Co^{2+}$ also leads to the formation of $VOPO_4{\cdot}2H_2O$ in the precursor by oxidation and hydration during the impregnation process. In this case, the level of $Co^{2+}$ may be non-optimal for this precursor

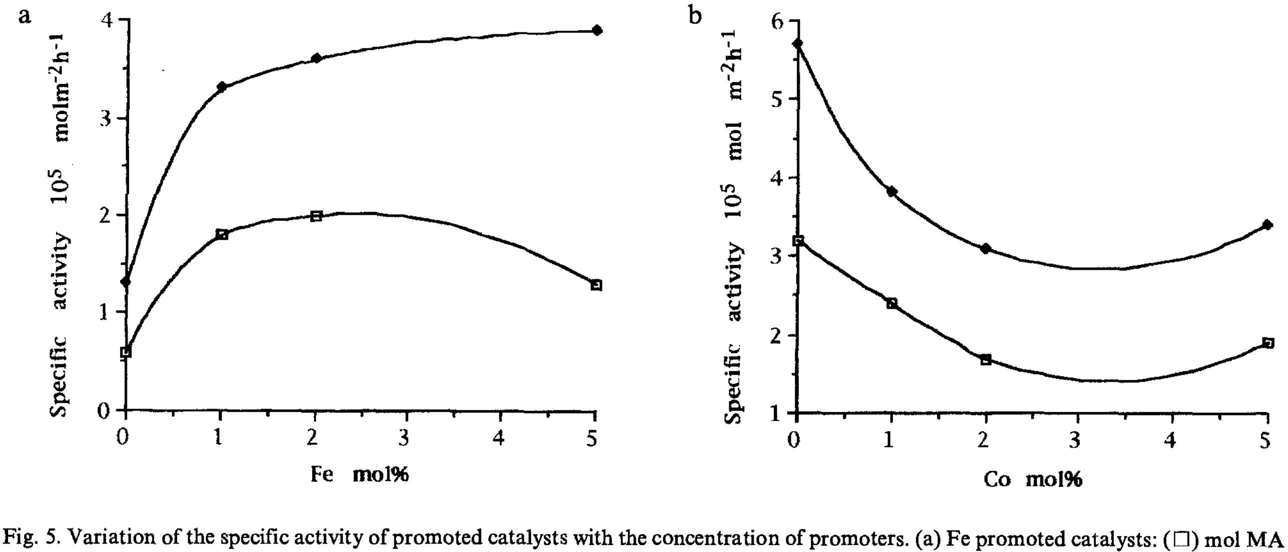

Fig. 5. Variation of the specific activity of promoted catalysts with the concentration of promoters. (a) Fe promoted catalysts: (□) mol MA $m^2$ $h^{-1}$, (◆) mol[butane conv] $m^2$ $h^{-1}$, (b) Co promoted catalysts: (□) mol MA $m^2$ $h^{-1}$, (◆) mol[butane conv] $m^2$ $h^{-1}$.

structure prepared in this way, although it does significantly enhance the selectivity to maleic anhydride at low concentrations.

It is apparent that the method used to add the $Fe^{3+}$ and $Co^{2+}$ to the catalyst leads to formation of $VOPO_4 \cdot 2H_2O$ from $VOHPO_4 \cdot 0.5H_2O$. In the case of $Co^{2+}$ this is solely related to the presence of the $Co^{2+}$ cation, whereas with $Fe^{3+}$ there is an additional effect due to the acidity of the solution. The effect of $Co^{2+}$, $Fe^{3+}$ and pH on the formation of $VOPO_4 \cdot 2H_2O$ are shown in table 1 and fig. 2. It should be noted that in many studies [6] impregnation by incipient wetness is a standard method of addition of catalyst additives. It is therefore recommended that the method must be utilised with care and in particular the acidity of the impregnation solution should be carefully monitored. This is important, since the effects of additives may be due in part to the effect of treatment of the catalyst with an acidic solution and hence these findings are of more general applicability in the synthesis of promoted catalysts. In the case of vanadium phosphate catalysts it is considered that the addition of the promoters during the synthesis of the $VOHPO_4 \cdot 0.5H_2O$ precursor may provide a route to avoid the difficulties encountered with the addition of promoters at a later stage in the synthesis using the incipient wetness technique.

## Acknowledgement

We thank the EC for financial support under the Human Capital Mobility Programme (Contract CHRX-CT92-0065). We also thank Professor Sir John Meurig Thomas and Dr. P.A. Wright for their invaluable assistance with the in situ X-ray diffraction studies.

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