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Effect of Promoters on the Selective Oxidation of *n*-Butane with Vanadium-Phosphorus Oxide Catalysts

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The effect of additives on the catalytic performance of vanadium phosphate catalysts is described and discussed in detail for materials prepared using HCl as the reducing agent for V_2O_5 in water or isobutanol solvents. Performance data are compared on the basis of a simplified kinetic model for *n*-butane oxidation involving a series-consecutive reaction scheme of pseudo first-order reactions (where $C_4H_2O_3$ signifies maleic anhydride):

$$\begin{tikzcd} C_4H_{10} \arrow[rr, "k_1"] \arrow[dr, "k_2"'] & & C_4H_2O_3 \arrow[dl, "k_3"] \\ & \mathbf{CO + CO_2} & \end{tikzcd}$$

Using this simplified kinetic scheme it is possible to calculate three factors: (a) the rate constant for butane conversion corrected for surface area $(k_1 + k_2)$/sa which is a measure of the specific activity; (b) the primary selectivity S_0 (selectivity extrapolated to zero conversion); and (c) the relative rates of oxidation of *n*-butane and maleic anhydride $k_3/(k_1 + k_2)$, the latter two factors being a measure of the selectivity of the catalyst. It is proposed that these can be used to determine the relative catalytic performance of promoted catalysts. Hence an improved catalyst would require high specific activity (i.e., a high value of $(k_1 + k_2)$/sa) together with high maleic anhydride selectivity (i.e., a high value of S_0 and a low value of $k_3/[k_1 + k_2]$). For catalysts prepared by the isobutanol/HCl method the addition of Co is found to promote the specific activity while Mo is found to promote both the specific activity and the selectivity to maleic anhydride at high conversion (>90%). However, for most additives no effect on the specific activity is observed although certain additives are found to act as poisons (Ag, Cs) while others promote the oxidation of maleic anhydride (Cs, Pd, Ru, Zn). The specific activity of catalysts prepared using water/HCl with an additional water-washing step was found to be promoted by the addition of a range of transition metal additives and the effect is described in detail with Co promoted catalysts. The mechanism of the promotion is discussed in terms of structural and electronic effects.

INTRODUCTION

The partial oxidation of *n*-butane to maleic anhydride has continued to receive much research attention (1–8) since vanadium-phosphorus oxide catalysts were found to catalyze this reaction (9). In recent years considerable progress has been made in understanding the solid state chemistry of this catalyst system, both of the precursor (10), the final catalyst (11) and *in situ* characterization of the transformation step (12, 13). To some extent this progress has been due to the improvements in techniques available for characterization, e.g., nmr techniques (14), *in situ* Raman spectroscopy (15), *in situ* powder X-ray diffraction (13), and HREM (16). To date there is general consensus that the major component of the active catalyst is $(VO)_2P_2O_7$ which is formed via a topotactic transformation of the precursor $VOHPO_4 \cdot 0.5H_2O$ (7, 10, 11). Detailed spectroscopic and diffraction studies have shown that a number of other compounds are present in the final catalyst, namely: α_{II}-, δ-, and γ-$VOPO_4$ (12, 13, 16) and current academic research in this area mainly concerns the respective roles of the components of the final catalyst.

Vanadium-phosphorus oxide catalysts remain the only example of a catalyst employed industrially for the partial oxidation of an alkane. In view of this it is unsurprising that several hundred patents have been published concerning the preparation and operation of improved catalysts. There are a number of themes that are apparent from the patent literature that reflect the current research interest of industrial research laboratories which contrast significantly with the research of many academic research groups. One major observation is that industrially operated catalysts include promoters [6]. A very wide range of cations have been added to vanadium phosphorus catalysts and beneficial effects have been claimed with Co, Cd, Ni (17), Zn, Bi, Cu, Li (18–20), V (21), Zr (22), Mg (23), Ti, Ti and Li (24), La (25), Mo, Nb (26), B (27) and Fe, Cr (28). Up to now there have been few definitive studies concerning the role of promoters in vanadium phosphorus catalysts, although the effect of simultaneous addition of Mo and Ce has been studied in detail (29). One reason for the limited progress achieved concerning the role of promoters with these catalysts is that the addition of promoters can readily induce both structural as well as electronic changes to the bulk and surface of the catalysts and it is necessary to unravel the

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complex interplay of these two effects. In this paper we introduce a new approach, involving a simple kinetic analysis, that is shown to be of value in gaining an improved understanding of the role of promoters in oxidation catalysts.

EXPERIMENTAL

Preparation of Catalyst Precursors

Standard aqueous HCl preparation method. V_2O_5 (60.6 g) and aqueous HCl (35%, 790 ml) were refluxed with stirring for 1.5 h at which time the solution was dark blue in color. H_3PO_4 (88%, 89.1 g) was added and the solution was refluxed for a further 1.5 h. The solution was then evaporated to near dryness by sidearm distillation (rate of solvent removal 100 ml h^{-1}) to a blue green paste which was dried in air (110°C, 16 h) to give a blue-green solid. The $P:V$ atomic ratio of this precursor was 1.20 ± 0.01.

Standard aqueous HCl preparation method with additional water washing. The precursor prepared by the standard aqueous HCl method (50 g) was refluxed for 2 h with distilled water (1 liter) and the suspension was filtered hot to give a blue solid that was dried in air (110°C, 16 h) to give a blue solid. The $P:V$ atomic ratio of this precursor was 1.05 ± 0.01.

Standard nonaqueous HCl preparation method. V_2O_5 (182 g) and isobutanol (100 ml) were stirred together and dry HCl gas was passed through the mixture at *ca* 30°C until the V_2O_5 dissolved to give a dark brown solution. H_3PO_4 (100%, 236 g) dissolved in isobutanol (240 ml) was added and the resulting solution was refluxed for 2 h at which time the solution was dark blue in color. This solution was then treated in either of two ways. In some cases the solvent was removed completely by evaporation to give a blue solid that was dried in air (110°C, 16 h). The $P:V$ atomic ratio of this precursor was 1.20 ± 0.01. Alternatively in some cases the solvent was partially removed by sidearm distillation (*ca* 1 liter solvent removed) to give a pale blue precipitate which was washed with isobutanol and dried in air (110°C, 16 h). The $P:V$ atomic ratio of this precursor was 1.20 ± 0.01.

Preparation of $VO(H_2PO_4)_2 \cdot H_3PO_4$. This compound was prepared according to the method of Ladwig (30). $VOCl_2$ (58 ml, 50% w/v in H_2O) was refluxed with H_3PO_4 (100%, 65.5 g, $P:V = 4.0$ in ethanol) for 2 h and the solvent was removed by evaporation. The resulting green solid ($P:V$ ratio $= 3.0$) was dried in air (110°C, 16 h) and stored in a desiccator.

Catalyst precursors prepared by the above methods were too soft to be used directly in the oxidation microreactor. The precursors were therefore mixed with a pelleting agent (3% by weight Sterotex), pelleted, ground and sieved to give particles of the required size range (500–710 μ).

Preparation of promoted catalyst precursors. Promoted catalysts were prepared by a variety of techniques which are described as follows. For the standard nonaqueous preparation method, promoted catalysts were prepared by adding an appropriate compound of the additive at the beginning of the preparation. For example, the preparation of the Co promoted catalyst precursor was as follows.

V_2O_5 (182 g) and $CoCl_2 \cdot 6H_2O$ (90.4 g) were suspended in isobutanol (1 liter) and dry HCl gas was passed through the mixture at *ca* 30°C until all the V_2O_5 had dissolved to give a dark brown solution. H_3PO_4 (100%, 233 g) dissolved in isobutanol (250 ml) was added and the resulting solution was refluxed for 2 h, then it was evaporated to dryness to give a green solid which was dried in air (110°C, 16 h). The $V:P:Co$ atomic ratio of this precursor was $1:1:20 \pm 0.01:0.19 \pm 0.01$.

Promoted catalysts were also prepared by impregnation using the incipient wetness technique. The catalyst precursor (10 g, 500–710 μ particles) was dried for 16 h at 150°C in air, cooled in a desiccator, and then impregnated with a solution of a suitable metal salt (typically the nitrate or the chloride) in a solvent (water or isobutanol) using the incipient wetness method. The impregnated particles were dried in air (16 h, 100°C) and then sieved to remove any dust. The precursor was then analyzed by atomic absorption spectroscopy or X-ray fluorescence spectroscopy to determine the elemental composition of the precursor.

Catalyst Characterization

Catalysts were characterized using powder X-ray diffraction, IR spectroscopy, and X-ray photoelectron spectroscopy. Surface areas were determined according to the BET method using N_2 adsorption or in the case of low surface areas by Kr adsorption.

Powder X-ray diffraction was used to determine the composition of the crystalline components and the final catalysts. For final catalysts prepared by the water-washed method the amount of α_{II}-$VOPO_4$ was estimated using the intensities of the most intense diffraction lines for the phases present according to the following relationship:

$$\frac{\alpha_{II}\text{-VOPO}_4}{(\text{VO})_2\text{P}_2\text{O}_7 + \delta\text{-VOPO}_4} = \frac{\text{area of } d = 3.00\ \text{Å}\ [\alpha_{II}\text{-VOPO}_4]}{\text{area of } d = 3.87\ \text{Å}\ [(\text{VO})_2\text{P}_2\text{O}_7] + \text{area of } d = 4.02\ \text{Å}\ [\delta\text{-VOPO}_4]}.$$

Catalyst Testing

Butane oxidation was carried out using fixed-bed laboratory microreactors. Butane and air, in appropriate ratios, were fed to a reactor containing 5 ml catalyst (0.6-cm i.d., 18-cm bed length). Exit lines from the reactor were heated to prevent deposition of maleic anhydride prior to analysis. Both feed and product compositions were monitored by on-line gas chromatography. Test experiments showed that

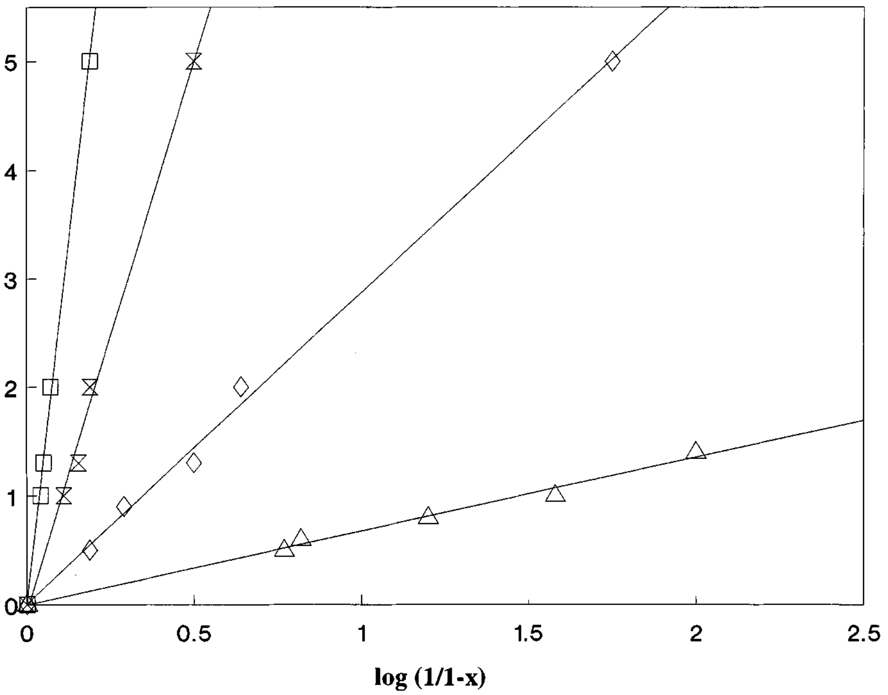

FIG. 1. Plots showing first-order oxidation of *n*-butane for a cobolt promoted catalyst: △, 450°C; ◇, 385°C; ⧖, 340°C; □, 300°C.

in the absence of a catalyst, blank thermal reactions were negligible below 500°C and in all experimental work mass balances typically between 97 and 103% were obtained. Experiments using standard techniques (31) showed that no diffusion limitations were present under these conditions. As a further check on the analysis of maleic anhydride the effluent gas from the microreactor was scrubbed with acetone for a known time and the resulting solution was analyzed specifically for maleic anhydride by polarography. Excellent agreement was obtained between the gc and polarographic methods.

For all catalysts tested in this study the transformation of the precursor to the final catalyst was carried out *in situ* in the reactor by heating in 1.5% *n*-butane in air at 385°C for 100 h. The data presented in this paper were collected typically between 100–300 h time on line. Representative data obtained from the testing of over 200 catalysts are reported.

Performance Characterization Using a Simplified Kinetic Approach

The data obtained from the microreactor tests enable the *n*-butane conversion and product selectivity to be determined for the different experimental conditions investigated. However, it is necessary to compare different catalyst formulations using a measure of specific activity and selectivity and in this paper the following method is used. When using inlet butane concentrations of 1–2 mol%, it is found that CO and CO_2 are the only significant by-products (acetic and acrylic acids are only formed at <1% selectivity). Under these experimental conditions for the catalyst used in this study butane loss is found to be first order and representative data are shown in Fig. 1. On this basis it is proposed that the reaction data can be satisfactorily modelled by a simplified kinetic scheme involving a series-consecutive reaction scheme of pseudo first-order reactions, where $C_4H_2O_3$ signifies maleic anhydride:

$$\begin{tikzcd}
C_4H_{10} \arrow[rr, "k_1"] \arrow[dr, "k_2"'] & & C_4H_2O_3 \arrow[dl, "k_3"] \\
& CO + CO_2 &
\end{tikzcd}$$

Using this simplified model and assuming plug flow conditions, Eqs. [1] and [2] can be derived at constant temperature;

$$k_1 + k_2 = \mathrm{GHSV} \ln\left[\frac{1}{1-x}\right] \qquad [1]$$

$$k_3 = \frac{k_1x - (k_1 + k_2)Sx}{[k_1/\mathrm{GHSV} - Sx]} \quad \text{when } \frac{k_3}{\mathrm{GHSV}} \ll 1, \qquad [2]$$

where x is the fractional conversion of butane, S is the fractional selectivity to maleic anhydride, and GHSV is gas hourly space velocity measured at STP. From the plot of $\ln(1/1-x)$ versus 1/GHSV the value of $k_1 + k_2$ can be obtained from the slope. The rate constant k_1 can be obtained from Eq. [3],

$$k_1 = S_0(k_1 + k_2), \qquad [3]$$

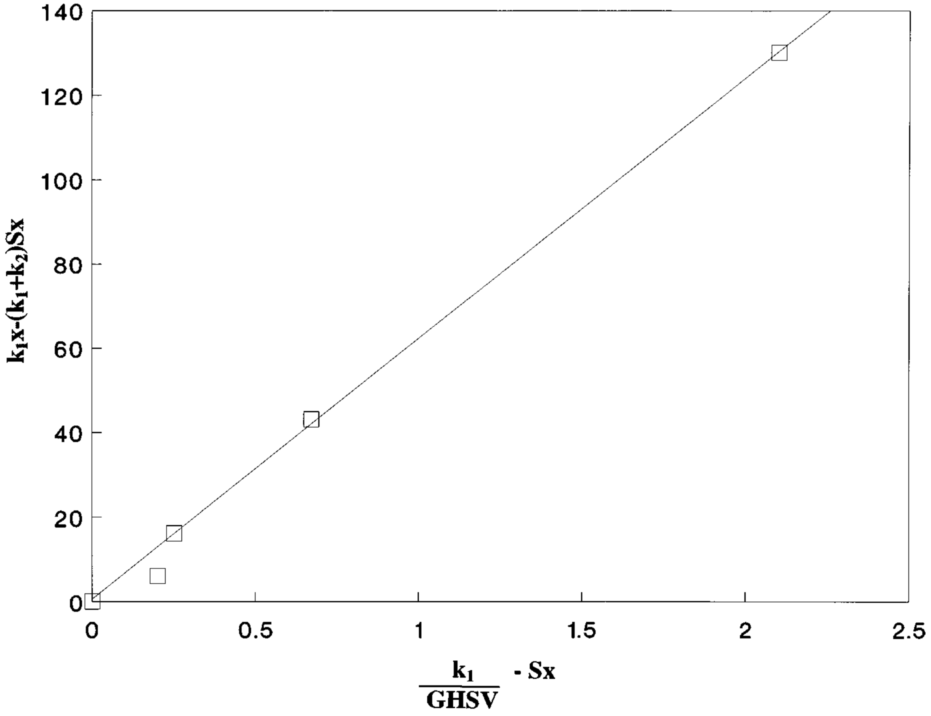

FIG. 2. Plot for determination of k_3 at 385°C for catalyst as in Fig. 1.

where S_0 is the primary selectivity, which is defined as the selectivity to maleic anhydride at zero conversion of *n*-butane. S_0 is determined by measuring the variation in selectivity with conversion as the space velocity is varied at constant temperature and extrapolating the plot of selectivity versus conversion to zero conversion.

The rate constant k_3 can be obtained from the slope of the plot of $[k_1x + (k_1 + k_2)Sx]$ versus $[k_1/\text{GHSV} - Sx]$ and a representative plot is shown in Fig. 2.

Using this simplified kinetic scheme it is possible to calculate three factors: (a) the rate constant for butane conversion corrected for surface area $(k_1 + k_2)/\text{sa}$ which is a measure of the specific activity, (b) the primary selectivity S_0, and (c) the relative rates of oxidation of *n*-butane and maleic anhydride $k_3/(k_1 + k_2)$, the latter two factors being a measure of the selectivity of the catalyst. It is proposed that these can be used to determine the relative catalytic performance of promoted catalysts. Hence an improved catalyst would require high specific activity (i.e., a high value of $(k_1 + k_2)/\text{sa}$), together with high maleic anhydride selectivity (i.e., a high value of S_0 and a low value of $k_3/[k_1 + k_2]$).

RESULTS

Catalytic Performance of Unpromoted Catalysts

Catalysts were prepared using the standard procedures with HCl as the reducing agent with water or isobutanol as solvent and the results for the oxidation of *n*-butane, after *in situ* pretreatment for 100 h, are shown in Table 1. The P : V ratio of the two precursors are the same (P : V = 1.20 ± 0.01) and analysis of the catalyst precursors and the final catalysts by X-ray diffraction showed that they comprised mainly $VOHPO_4 \cdot 0.5H_2O$ and $(VO)_2P_2O_7$, respectively. The principal difference between catalysts prepared using water and isobutanol was that the surface area of the isobutanol prepared material was significantly higher. This has been observed in previous studies of these catalysts (32–34). As a result, the activity of the catalyst prepared using HCl as the reducing agent with isobutanol as solvent is significantly better than that prepared using water as solvent. In particular, the catalyst prepared using isobutanol can be used at lower temperatures, and as maleic anhydride selectivity is a function of temperature, improved pass yields are obtained. For example, the optimum pass yield of maleic anhydride for the isobutanol catalyst is 60% at 385°C, 1000 h^{-1}, whereas the optimum pass yield for the aqueous catalysts is 50% at 500°C, 1000 h^{-1}. However, when the activity is corrected for this surface area effect, then the specific activities are very similar, with the values of $(k_1 + k_2)/\text{sa}$ being 35 ± 2 and 40 ± 3 g $m^2 h^{-1}$ for the precursors prepared using water and isobutanol, respectively. Hence, it is apparent that the difference in the overall performance of these two catalysts is solely related to the final surface area and the use of isobutanol as solvent readily enables the attainment of a high surface area catalyst.

The surface P : V ratio of the catalyst precursors prepared using water and isobutanol, determined using X-ray

TABLE 1

Catalytic Performance of Unpromoted Catalysts

Preparation method	V : P[a]	Final surface area ($m^2\,g^{-1}$)	Temp °C	Pseudo first-order rate constants (h^{-1})			S_0 %	$k_1 + k_2$/sa ($gm^{-2}\,h^{-1}$)
				k_1	k_2	k_3		
$V_2O_5 + H_3PO_4 +$ HClaq[b]	1 : 1.2	1.5	385	38	14	—	73	35
evaporated to dryness			450	246	151	24	62	265
$V_2O_5 + H_3PO_4 +$ HCl[c]	1 : 1.2	14	340	134	28	—	83	12
isobutanol solvent			385	403	157	31	72	40
evaporated to dryness			410	1267	596	92	68	133
$V_2O_5 + H_3PO_4 +$ HCl[d]	1 : 1.05	14	340	180	37	—	83	16
isobutanol solvent			385	653	242	48	73	64
precipitate removed			410	1496	704	90	68	157
$V_2O_5 + H_3PO_4 +$ HClaq[e]	1 : 1.05	9	385	472	83	—	85	62
evaporated to dryness			420	650	160	80	80	90
followed by water extraction			430	777	259	92	75	115

[a] V : P atomic ratio of catalyst precursor following drying step.

[b] Standard aqueous HCl method.

[c] Standard nonaqueous HCl method.

[d] Standard nonaqueous HCl method with partial solvent removal, blue precipitate collected, and washed with cold solvent.

[e] Standard aqueous HCl method with additional water extraction of precursor (100°C, 2 h, 10 ml H_2O/g precursor) and filtered hot.

photoelectron spectroscopy, were found to be very similar (Table 2). As has been observed previously (7, 8), there is considerable enrichment of the surface with phosphorus and argon ion etching was found to decrease the surface P : V ratio towards that of the bulk. To simulate the activation step, the precursors were heated in a butane/air mixture in a side chamber of the spectrometer and for both samples the surface P : V ratio increased with increasing temperature to P : V = 2.2 (Table 2). This is comparable to the values observed for the respective final catalysts discharged from the reactor (P : V = 2.3). It is clear that during pretreatment significant surface enrichment with phosphorus occurs.

DTA of the catalyst precursors indicates that the material prepared with isobutanol in general exhibits a single endotherm in the temperature range 470–500°C which results from the topotactic transformation of $VOHPO_4 \cdot 0.5H_2O$ to $(VO)_2P_2O_7$, whereas the material prepared using water exhibits an additional endotherm between 365 and 420°C. This difference has also been observed in previous patent literature (35, 36) and it has been attributed to differences in

TABLE 2

Surface P : V Atomic Ratios

Catalyst	Sample treatment			Surface P : V
Standard aqueous HCl method	Initial sample			1.86
	Heated butane/air	5 min	50°C	2.09
	Heated butane/air	5 min	150°C	2.21
	Heated butane/air	5 min	250°C	2.26
	Heated butane/air	5 min	350°C	2.26
	Heated butane/air	5 min	400°C	2.24
	Discharged[a]			2.38
Standard nonaqueous HCl method partial solvent removal precipitate collected	Initial sample			1.76
	Heated butane/air	5 min	50°C	1.89
	Heated butane/air	5 min	150°C	1.87
	Heated butane/air	5 min	300°C	1.92
	Heated butane/air	5 min	400°C	2.15
	Heated butane/air	5 min	500°C	2.22

[a] Sample discharged after cooling in N_2. Catalyst tested at 385°C, GHSV = 1000 h^{-1}, 100 h time on stream.

the level of hydration of the two precursors. Detailed analysis of the powder X-ray diffraction pattern for the two precursors indicated that the precursor prepared using water as solvent contained the additional compound $VO(H_2PO_4)_2$ (30, 37) in amounts of up to *ca* 10%. However, the amount of $VO(H_2PO_4)_2$ present in precursors was found to vary quite markedly. In addition, $VO(H_2PO_4)_2$ was also found to be present in catalyst precursors prepared using isobutanol although the amounts were generally lower than when water was used as solvent. When catalyst precursors prepared using isobutanol as solvent contained $VO(H_2PO_4)_2$ at levels >1% it was observed that the surface area of the final catalysts was significantly lower (typically 3–8 $m^2\,g^{-1}$) than when $VO(H_2PO_4)_2$ was absent. $VO(H_2PO_4)_2$ was prepared according to a literature method (30) and by DTA was found to have an endotherm in the temperature range 365–420°C associated with the decomposition at this temperature to $VO(PO_3)_2$ (38) which is considered to be less active for the selective oxidation of butane (39). Hence it is apparent that the presence of $VO(H_2PO_4)_2$ in the catalyst precursor appears to impede the formation of a high surface area catalyst but does not affect the specific activity of the catalyst. The solvent used in the precursor preparation is important in this respect since the use of water as solvent results in the formation of $VO(H_2PO_4)_2$ in significant quantities (*ca* 10%).

In the two standard preparation methods, an excess of phosphorus was utilized as it has been shown previously to be necessary for the formation of high activity catalysts when HCl is used as reducing agent (6, 7). However, it is apparent that the stoichiometric ratio of vanadium to phosphorus is unity if the precursor contained only $VOHPO_4 \cdot 0.5H_2O$ as a pure phase. The method of preparation involving total solvent removal necessitates that the overall P : V ratio is considerably higher than the stoichiometric value. It was therefore decided to investigate the effect of partial solvent removal. This was done using the isobutanol method as it was observed that during the solvent removal stage of the preparation a pale blue precipitate formed after about two-thirds of the solvent had been removed. This obsevation represents a further difference between the isobutanol and the water solvent methods since when water is used as a solvent no precipitate is observed during solvent removal even when 90–95% of the solvent has been removed. This observation is of interest since $VOHPO_4 \cdot 0.5H_2O$ is insoluble in water and so it can be concluded that there can be no appreciable formation of $VOHPO_4 \cdot 0.5H_2O$ in solution when water is used as solvent. The precipitate formed during the isobutanol method was collected and investigated further. Analysis by atomic absorption showed that the P : V atomic ratio of this precursor was 1.05 ± 0.01. By powder X-ray diffraction it was found to contain $VOHPO_4 \cdot 0.5H_2O$ as the only crystalline phase and microscopy indicated that very little (<1%) amorphous material was present. This therefore represents a preparative route to a precursor containing only $VOHPO_4 \cdot 0.5H_2O$. The catalytic performance of the final catalyst derived from this precursor was investigated and the results are given in Table 1. It is apparent that, although the primary selectivity of this material is identical to the other HCl preparations, the specific activity of this material is significantly higher. Powder X-ray diffraction analysis of the final catalyst showed that it comprised highly crystalline $(VO)_2P_2O_7$.

As noted previously, catalyst precursors prepared using water as a solvent contain up to 10% $VO(H_2PO_4)_2$ in addition to the precursor phase $VOHPO_4 \cdot 0.5H_2O$. $VO(H_2PO_4)_2$ is known to be water soluble (30), whereas $VOHPO_4 \cdot 0.5H_2O$ is insoluble and it is possible to exploit this differential solubility to remove $VO(H_2PO_4)_2$ from the catalyst precursor. This was achieved by refluxing the precursor in water (100°C, 2 h , 20 ml water/g catalyst). The extracted precursor was recovered by hot filtration and analysis by powder X-ray diffraction showed the material to be crystalline $VOHPO_4 \cdot 0.5H_2O$ and by microscopy no amorphous material was observed. DTA of the extracted precursor revealed that the endotherm at 365–420°C was absent in the water washed material confirming the removal of $VO(H_2PO_4)_2$ (Fig. 3). The aqueous extractate was then evaporated to dryness and was confirmed by powder X-ray diffraction and DTA (Fig. 3) to be $VO(H_2PO_4)_2$.

The water-washed precursor was pretreated *in situ* in the reactor and the catalytic performance determined (Table 1). The surface area of the final catalyst is significantly higher when compared with the non-water-washed precursor confirming that removal of $VO(H_2PO_4)_2$ from the precursor enables the attainment of a high final surface area. In addition the specific activity was also higher (e.g., at 385°C, $k_1 + k_2/\text{sa} = 62 \pm 6$ and 35 ± 2 $m^2\,g^{-1}$ for the water-washed and non-water-washed catalysts, respectively). At 385°C the activity of the water-washed catalyst is similar to the sample prepared by the isobutanol/HCl route with partial solvent removal; however, at higher temperatures this is not observed. Powder X-ray diffraction of the final catalyst showed that the catalyst now contained α_{II}-$VOPO_4$ and δ-$VOPO_4$ as crystalline phases in addition to $(VO)_2P_2O_7$.

The effect of the preparation conditions on the formation of these additional phases was examined. Variation of the conditions tended to alter significantly the concentration of α_{II}-$VOPO_4$ but in most cases had relatively little effect on δ-$VOPO_4$ which under most conditions was estimated to constitute *ca* 5% of the final catalyst. The only exception to this was observed when the precursor was pretreated in nitrogen initially prior to reaction with 1.5% *n*-butane in air at 385°C. With this method of pretreatment the specific activity of the final catalyst was identical to that pretreated only in *n*-butane/air. X-ray diffraction analysis indicated that the concentration of α_{II}-$VOPO_4$ in the two

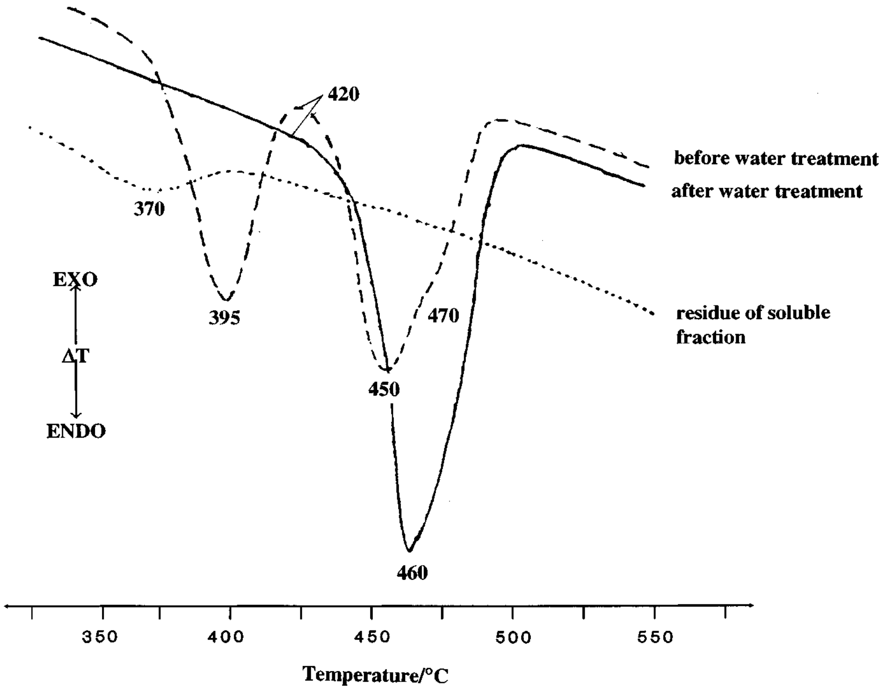

FIG. 3. DTA for standard aqueous HCl precursor.

final catalysts was similar *ca* 30%) but the nitrogen pretreated catalyst comprised significantly more δ-$VOPO_4$ than $(VO)_2P_2O_7$. On the basis of these results it can be concluded that the specific activity of these catalysts was controlled mainly by the α_{II}-$VOPO_4$ content.

The percentage of α_{II}-$VOPO_4$ in the final catalyst was found to vary with the preparation method. In particular, for the water extraction step the use of temperatures <100°C and times >2.5 h significantly decreased the amount of α_{II}-$VOPO_4$ in the final catalyst. The drying step was also found to be important and in general the use of temperatures <100°C and short times significantly decreased the amount of α_{II}-$VOPO_4$ in the final catalyst. The acidity of the precursor preparation solution during solvent removal is also important. It was found that the amount of α_{II}-$VOPO_4$ could be significantly enhanced to >50% when following partial solvent removal and prior to the formation of the $VOHPO_4 \cdot 0.5H_2O$, the addition of aqueous HCl was followed by further refluxing. In this case the amount of α_{II}-$VOPO_4$ formed was correlated with the duration of the additional reflux. Using this procedure a range of final catalysts were prepared using the standard *in situ* pretreatment and the specific activity was correlated with the proportion of α_{II}-$VOPO_4$ (Fig. 4).

A sample of $VO(H_2PO_4)_2$ was prepared according to the method of Ladwig (30). This method of preparation was selected as it is analogous to the aqueous HCl method for the preparation of the catalyst precursor. Powder X-ray diffraction, IR spectroscopy, and DTA confirmed the sample to be $VO(H_2PO_4)_2$ with H_3PO_4 occluded in the structure, as had been noted by Ladwig (30), with P : V ratio = 3.0. The final catalyst prepared from this precursor exhibited a low surface area (1 $m^2\,g^{-1}$) and low primary selectivity ($S_0 = 45\%$ at 420°C) although the specific activity was comparable to the standard catalyst ($k_1 + k_2/\text{sa} = 150$ at 420°C).

Catalytic Performance of Promoted Catalysts Prepared by the Standard Nonaqueous HCl Method

Catalysts containing a range of additives were prepared by the addition of a suitable compound, typically the oxide or the nitrate, together with the V_2O_5 at the start of the standard nonaqueous HCl precursor preparation and the results are given in Table 3. Additives and the concentrations used were chosen as representative examples of additives investigated in the previous literature. In addition Sb and Th were selected as they are known components of selective oxidation catalysts; Cs was selected as an example of a basic additive and Pd and Ru were chosen as representative Group 8 additives. Cr, Nb, Pd, Sb, Ru, Th, Zn, and Zr were found to have very little effect on the specific activity, although with Cr, Zn, and Zr a significant increase in surface area was observed. A plot of the rate constant for butane conversion ($k_1 + k_2$) versus the final surface area is shown in Fig. 5 and it is apparent that the catalysts with these additives correlate well with the activities of the unpromoted catalysts. This indicates that the specific activity for these catalysts is comparable and the principal role of

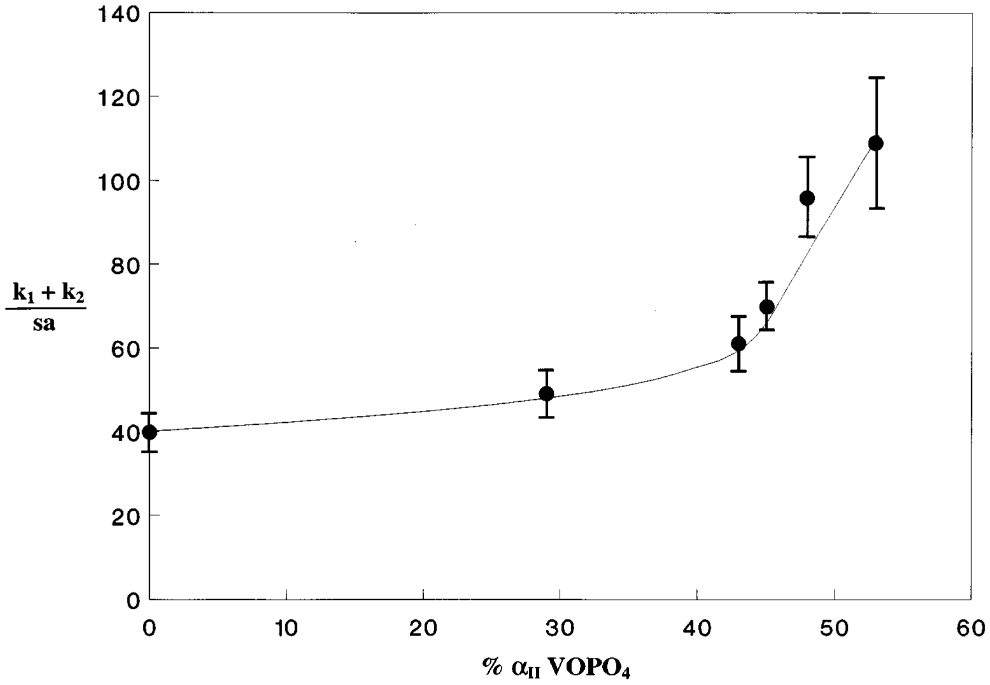

FIG. 4. Relationship between specific activity of water-washed standard aqueous HCl catalysts and the content of α_{II}-VOPO$_4$ in the final catalyst at 385°C.

TABLE 3

Catalytic Performance of Promoted Catalysts at 385°C Prepared by Standard Nonaqueous HCl Method[a]

Additive	Atomic ratio V : additive	Final surface area (m^2 g^{-1})	Pseudo first-order rate constants (h^{-1}) k_1	k_2	k_3	S_0 (%)	$k_1 + k_2$/sa (gm^{-2} h^{-1})	$k_3/k_1 + k_2$
None	—	14	405	151	31	72	40	0.055
Ag	1 : 0.08	13	240	60	32	80	23	0.017
Co	1 : 0.19	17	1246	246	109	82	88	0.073
Cr	1 : 0.03	21	1276	280	130	82	74	0.092
Cs	1 : 0.08	11	159	106	98	60	24	0.370
Fe	1 : 0.03	17	551	225	33	71	46	0.043
Mo	1 : 0.037	24	1856	722	58	72	107	0.022
Nb	1 : 0.07	14	609	203	60	75	58	0.074
Pd	1 : 0.01	7	126	189	70	40	46	0.222
Ru	1 : 0.03	9	142	286	150	33	50	0.350
Sb	1 : 0.15	14	479	120	51	80	43	0.085
Th	1 : 0.14	13	549	200	41	73	59	0.055
Zn	1 : 0.14	19	421	983	300	30	94	0.214
Zr	1 : 0.13	25	884	886	366	50	71	0.207
None[b]	—	14	655	242	48	73	64	0.054

[a] Precursor prepared by standard non aqueous HCl method. V : P ratio of precursor = 1 : 1.2. Promoted catalysts were prepared by adding an appropriate compound together with V_2O_5 at the beginning of the preparation. Co, Cr, Cs, Fe, Pd, Ru, Th, Zn, and Zr were added as chlorides; Mo, Nb, and Sb were added as oxides and Ag as the nitrate.

[b] Precursor prepared by standard nonaqueous HCl method with partial solvent removal. The precipitate formed was collected by filtration, washed, and dried.

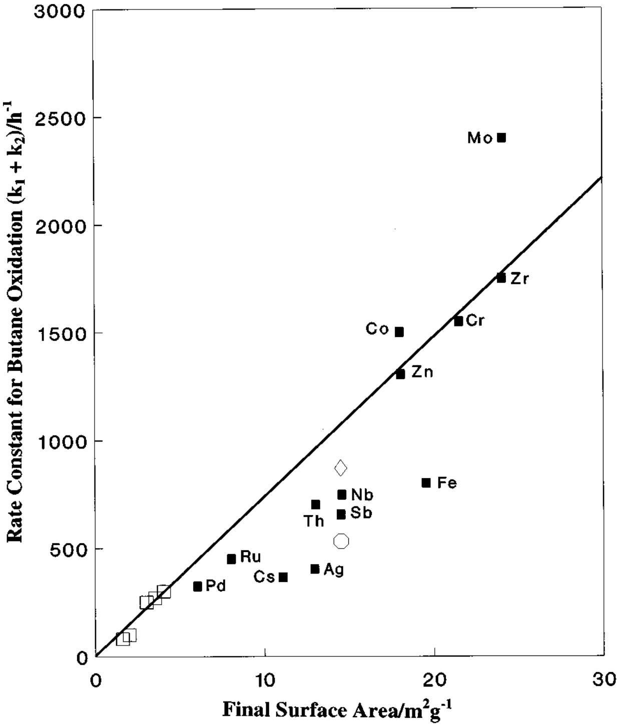

FIG. 5. Dependence of rate constant for butane oxidation on final catalyst surface area: □, unpromoted aqueous HCl; ○, unpromoted nonaqueous HCl evaporated to dryness; ◇, unpromoted nonaqueous HCl precipitate collected by filtration; ■, promoted catalysts, promoter added as described in Table 3.

these promoters is to enable the formation of high surface area final catalysts. Fe, Cs, and Ag were found to decrease significantly the specific activity. Only Co and Mo gave an increase in specific activity. With respect to selectivity, significant decreases in the primary selectivity were observed with Cs, Pd, Ru, Zn, and Zr. The magnitude of k_3 is indicative of the extent to which consecutive oxidation of maleic anhydride is occurring and, in general, k_3 increases with increasing surface area (Fig. 6); however, it is apparent that k_3 for Cs, Pd, Ru, Zn, and Zr is markedly higher than suggested by the general trend. With Fe and Mo the value of k_3 is lower than suggested by the trend. The relative rates of maleic anhydride and butane oxidation can be determined by the ratio $k_3/(k_1 + k_2)$ and on this basis Ag, Cs, Pd, Ru, Zn, and Zr all promote the over-oxidation of maleic anhydride but significantly Mo acts as a poison for the overoxidation.

Analysis of the final catalysts by powder X-ray diffraction and electron microscopy showed that the promoters were present in separate phases. In particular, Co and Zn were present as phosphates and Zr was present as the pyrophosphate. In all the catalysts investigated $(VO)_2P_2O_7$ was the main crystalline phase present and no other VPO phases were observed.

Using the specific activity $(k_1 + k_2)$/sa and the relative oxidation rate $k_3/(k_1 + k_2)$ as performance indicators for the effectiveness of the additives it is apparent (Table 3) that only Co and Mo can be considered to act as promoters and the effect of these two additives is now considered in more detail. A range of Co promoted catalysts was prepared and the Co was added either during the precursor preparation or by impregnation of the precursor (Table 4). Comparison of catalysts with the same Co : V ratio (0.19) but with different P : V ratios (1.05 and 1.2) shows that when P : V ratio is decreased the promotional effect of Co decreases and in this case a lower Co : V ratio (0.08) is more effective. Impregnation of the final catalyst with Co also gives an enhancement in specific activity but a significant loss in primary selectivity is observed and additionally the relative rate of oxidation of maleic anhydride is increased. Hence, Co must be added at the precursor stage for the promotional effect to be observed and this indicates that plays a role in the formation of the final active surface. It was observed that the impregnated precursors required a much shorter pretreatment time when compared to catalysts prepared by addition of Co during the preparation of the precursor. Analysis of Co catalysts by XPS indicated that both the Co and P surface concentrations increase on heating and the addition of Co by impregnation can be expected to aid this process.

Mo-promoted catalysts were prepared by addition of MoO_3, together with V_2O_5 in the standard nonaqueous HCl method with total solvent removal. The results for the catalytic performance of the final catalysts are shown in Table 5

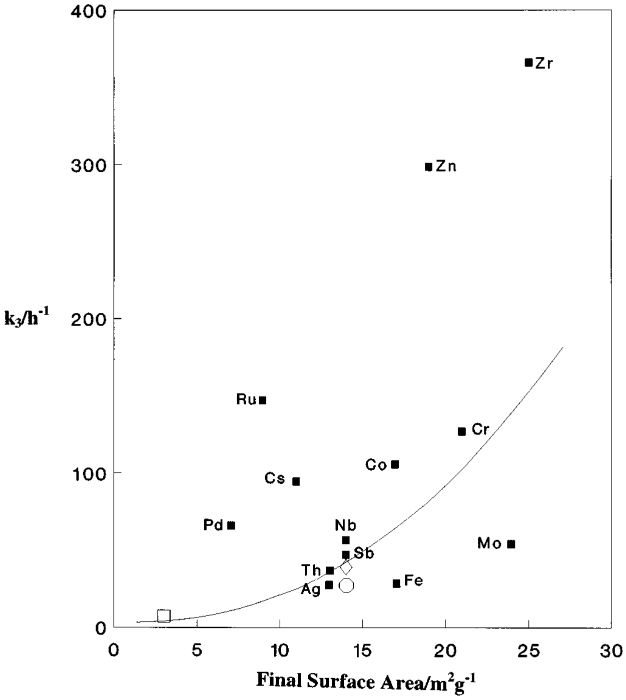

FIG. 6. Dependence of rate constant for butane oxidation on final catalyst surface area. Symbols as in Fig. 5.

TABLE 4

Catalytic Performance of Co Promoted Catalysts at 385°C

Preparation method	Precursor V : P : Co	Final surface area ($m^2\,g^{-1}$)	Pseudo-first-order rate constants (h^{-1})			S_0 (%)	$k_1 + k_2$/sa ($gm^{-2}\,h^{-1}$)	$k_3/k_1 + k_2$
			k_1	k_2	k_3			
$V_2O_5 + H_3PO_4 + HCl(g)$ isobutanol solvent evaporated to dryness	1 : 1.2 : 0	14	403	157	31	72	40	0.055
$V_2O_5 + H_3PO_4 + CoCl_2 + HCl(g)$ isobutanol solvent evaporated to dryness	1 : 1.2 : 0.19	17	1246	246	109	82	88	0.073
$V_2O_5 + H_3PO_4 + HCl(g)$ isobutanol solvent partial solvent removal precipitate removed (Precursor A)	1 : 1.05	14	653	242	48	73	64	0.054
Precursor A impregnated with $CoCl_2 \cdot 6H_2O$ in water	1 : 1.05 : 0.19	19	936	264	113	78	63	0.094
Precursor A impregnated with $CoCl_2 \cdot 6H_2O$ in isobutanol	1 : 1.05 : 0.08	20	1410	400	110	78	91	0.061
Final catalyst derived from Precursor A impregnated with $CoCl_2 \cdot 6H_2O$ in isobutanol	1 : 1.05 : 0.08	16	894	825	207	52	107	0.120

and it is apparent that there is an optimum level for Mo at a Mo : V ratio of *ca* 0.04; moreover, for this formulation both the specific activity is enhanced and the relative rate of oxidation of maleic anhydride relative to *n*-butane is decreased. This latter point is demonstrated by the data in Fig. 7 and is the most significant promotional effect for Mo and one which has not been observed with the other additives evaluated. Of particular importance is that, as the magnitude of $k_3/(k_1 + k_2)$ is decreased, it is possible to observe pass yields of maleic anhydride ≥70% with Mo promoted catalysts.

Catalytic Performance of Promoted Catalysts Prepared by the Standard Water-Washed Aqueous HCl Method

A series of promoted catalysts was prepared by the impregnation of a catalyst precursor prepared by the aqueous HCl route with additional water extraction of $VO(H_2PO_4)_2$. The results for the catalytic performance of the final catalyst are given in Table 6. It is apparent that, in contrast to the non-water-washed catalysts, virtually all the additives investigated gave a promotional effect on the specific activity $(k_1 + k_2)$/sa. Interestingly, addition of Zn did not lead

TABLE 5

Catalytic Performance of Mo Promoted Catalysts at 385°C

Precursor[a] V : P : Mo	Final surface area ($m^2\,g^{-1}$)	Pseudo first-order rate constants (h^{-1})			S_0 (%)	$k_1 + k_2$/sa ($gm^{-2}\,h^{-1}$)	$k_3/k_1 + k_2$
		k_1	k_2	k_3			
1 : 1.2 : 0	14	403	157	38	72	40	0.055
1 : 1.2 : 0.026	22	1203	468	67	72	76	0.040
1 : 1.2 : 0.037	24	1856	722	58	72	107	0.022
1 : 1.2 : 0.076	16	899	349	116	72	78	0.093

[a] Catalysts prepared by standard nonaqueous HCl method with evaporation to dryness. MoO_3 added together with V_2O_5 at start of the preparation.

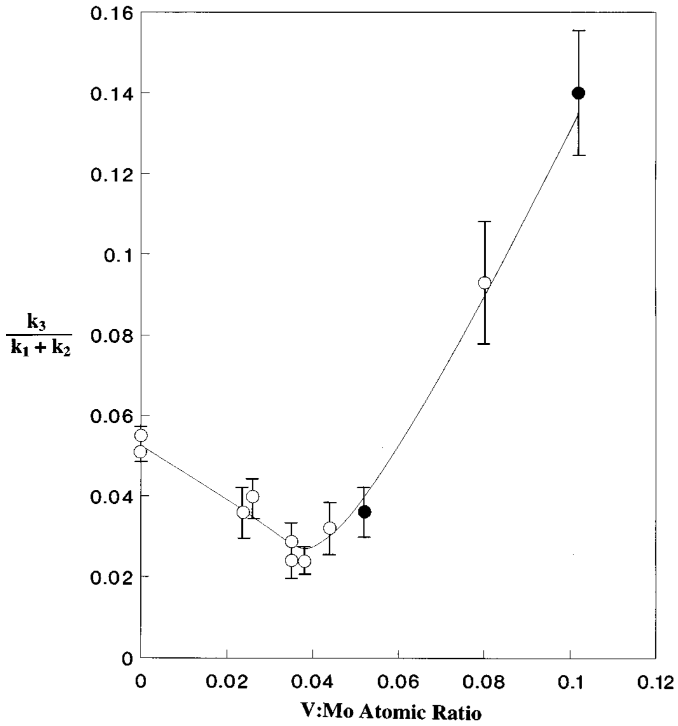

FIG. 7. Effect of Mo on oxidation of maleic anhydride relative to butane, 385°C, isobutanol solvent. ○, Mo added as MoO_3; ●, Mo added separately prior to activation by grinding MoO_3 with $VOHPO_4 \cdot 0.5H_2O$.

to any increase in specific activity or surface area but it did increase the rate of overoxidation of maleic anhydride as determined by $k_3/(k_1 + k_2)$. Significant promotional effects are observed for $(k_1 + k_2)$/sa with Ce, Co, Cr, La, and Mo without any significant loss in selectivity as determined by S_0 and $k_3/(k_1 + k_2)$. However, the origin of the enhanced activity is complicated by the observation that for any one additive it can significantly affect both the final surface area of the catalyst and the proportion of α_{II}-$VOPO_4$ present in the activated catalyst. To try to resolve these different effects a series of Co promoted catalysts was prepared by impregnation of the water-washed precursor using either water or isobutanol solutions of $CoCl_2 \cdot 6H_2O$. It is apparent that, although the proportion of α_{II}-$VOPO_4$ present in the activated catalyst varies slightly, there is a distinct optimum [Co] for this catalyst at Co : V = *ca* 0.07 (Fig. 8). It is also apparent that up to quite high [Co] there is no significant loss of primary selectivity or the selectivity to maleic anhydride at 90% *n*-butane conversion (Fig. 9). Plots of the specific activity $(k_1 + k_2)$/sa versus the proportion of α_{II}-$VOPO_4$ present in the activated catalyst at constant Co : V ratio and reaction temperature confirm that there is a significant promotional effect for Co which is independent of the proportion of α_{II}-$VOPO_4$ (Fig. 10).

DISCUSSION

Comments on the Structure of Nonpromoted Catalysts

Most preparative methods for the $VOHPO_4 \cdot 0.5H_2O$ catalyst precursor for the active VPO catalyst utilize V_2O_5 as the starting material. Hence, a reducing agent must be employed to facilitate the formation of the V(*IV*) phase. In the present study HCl has been employed as the reducing agent, while other studies utilize a range of organic reducing agents, e.g., isobutanol which reacts to form isobutanal (10). In all such cases when V_2O_5 is used as the starting material, then 1 mol of H_2O per mol of V_2O_5 will be pro-

TABLE 6

Effect of Additives on the Performance of Water-Washed Catalyst Precursor Prepared by Standard Aqueous HCl Method at 420°C

Additive	Atomic ratio V : P additive	Final surface area ($m^2 g^{-1}$)	α_{II}-$VOPO_4$ (%)	Pseudo first-order rate constants (h^{-1}) k_1	k_2	k_3	S_0 (%)	$k_1 + k_2$/sa ($g \cdot m^{-2} \cdot h^{-1}$)	$k_3/k_1 + k_2$
None	1 : 1.05	9	43	650	160	80	80	90	0.099
Ce[a]	1 : 2.05 : 0.0125	11	57	1600	400	—	80	182	—
Co[b]	1 : 1.05 : 0.053	16	35	3070	765	380	80	240	0.099
Cr[a]	1 : 1.05 : 0.004	10	58	1920	640	200	75	256	0.077
Cu[a]	1 : 1.05 : 0.01	12	43	1775	445	—	80	185	—
La[a]	1 : 1.05 : 0.027	18	32	4150	730	560	85	271	0.114
Mo[c]	1 : 1.05 : 0.02	6	48	1100	340	120	76	241	0.083
Ni[a]	1 : 1.05 : 0.008	12	12	1310	540	200	71	154	0.108
Zn[b]	1 : 1.05 : 0.03	9	32	714	136	127	84	99	0.149

[a] Promoted catalysts were prepared by impregnation of the unpromoted water-washed precursor by the method of incipient wetness using an aqueous solution of the nitrate.

[b] Promoted catalysts were prepared by impregnation of the unpromoted water-washed precursor by the method of incipient wetness using an aqueous solution of the chloride.

[c] Mo added as MoO_3, together with V_2O_5 at start of preparation and prior to water-washing step.

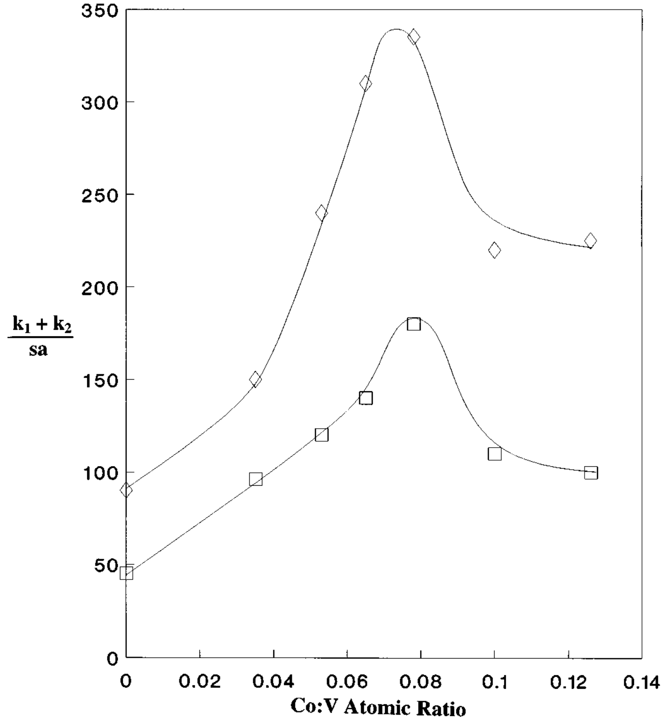

FIG. 8. Relationship between specific activity of cobalt promoted water-washed standard aqueous HCl catalysts and the Co : V atomic ratio: □, 385°C; ◇, 420°C.

duced as a by-product of the reduction step. In the HCl method it is possible that the halogen also plays a significant role; however, analysis of the catalysts did not indicate the incorporation of halogen to any significant extent and, hence, the results of this study can be considered to have general significance. When isobutanol is used either as solvent, as in the low temperature HCl digestion method, or as solvent and reductant in the higher temperature reflux method, at the end of the reduction there will be the stoichiometric quantity of H_2O present for the formation of the precursor $VOHPO_4 \cdot 0.5H_2O$. When aqueous HCl is used as solvent and reductant, there is a significant excess of H_2O present. It should be noted that the final product $VOHPO_4 \cdot 0.5H_2O$ is not soluble in water and so it is clearly not present in any preparation method prior to the start of solvent removal. It is observed that when H_2O is limited to the stoichiometric amount, the $VOHPO_4 \cdot 0.5H_2O$ readily precipitates from the solution once sufficient solvent has been removed. This is not the case when a significant excess of H_2O is present, and hence the presence of H_2O may be critical during the formation of the precursor crystallites. In the aqueous HCl method the material has to be evaporated almost to dryness to obtain the precursor crystallites. Since most preparation methods employ an excess of phosphorus, this route necessarily produces a more impure product containing phosphorus-rich VPO compounds, and in this case it is found to be $VO(H_2PO_4)_2$. It is known that $VOHPO_4 \cdot 0.5H_2O$ is transformed topotactically to $(VO)_2P_2O_7$ during the subsequent calcination step (10). The presence of significant impurity phases, particularly $VO(H_2PO_4)_2$, which transforms at a lower temperature than $VOHPO_4 \cdot 0.5H_2O$, clearly interferes with the establishment of the final surface microstructure. This is evident from the observation that the final surface area of catalysts containing $VO(H_2PO_4)_2$ is low compared to catalysts which are prepared from precursors in which it is either absent or has been removed by solvent extraction. It is possible that the presence of $VO(H_2PO_4)_2$ interferes with the topotactic transformation particularly if it contains occluded H_3PO_4, but it is also possible that the $VO(PO_3)_2$ formed on calcination of $VO(H_2PO_4)_2$ merely phase-separates during the slow calcination procedure. Previous studies have shown that the calcination procedure is very important in controlling the final surface area and, hence, catalyst activity. In addition, previous studies have shown that there are differences in the morphology of $VOHPO_4 \cdot 0.5H_2O$ prepared in aqueous and nonaqueous media [34], but the present study shows that this is not the only difference that is significant concerning the formation of the final active catalyst.

However, it is important to note that the extraction of $VO(H_2PO_4)_2$ from catalyst precursors using a water extraction procedure does not merely involve removal of the unwanted VPO compound, since catalysts treated in this way give rise to higher activity final catalysts containing α_{II}-$VOPO_4$ in addition to $(VO)_2P_2O_7$. Many studies have considered that $(VO)_2P_2O_7$ alone is the active bulk phase for VPO catalysts and a number of studies have involved the specific crystal faces of this compound as models for the active surface (40–42). Indeed Ebner and Thompson (40) have recently noted that studies in which V(*V*) phases have been found to be present are not representative, since the V(*V*) had not been given sufficient time to reduce under the reaction conditions. This is not the case in the present study, since only activated catalysts obtained after at least 100 h treatment in 1.5% *n*-butane/air have been utilized, together with a subsequent reaction under these conditions for up to a further 400 h. The present study indicates that catalysts containing both α_{II}-$VOPO_4$, together with $(VO)_2P_2O_7$, have considerably higher catalytic activity than those containing solely $(VO)_2P_2O_7$. Bordes and Courtine (39) considered that α_{II}-$VOPO_4$ and $(VO)_2P_2O_7$ were related by the following redox reaction:

$$2\alpha_{II}\text{-}VOPO_4 \rightleftharpoons (VO)_2P_2O_7 + O$$

and this type of redox couple may be important for the high activity and selectivity observed with these catalysts. However, in catalysts containing solely $(VO)_2P_2O_7$, α_{II}-$VOPO_4$ is not formed in any significant quantity and, hence, it is more probable that the origin of the α_{II}-$VOPO_4$ effect may be more morphological than redox in its origin.

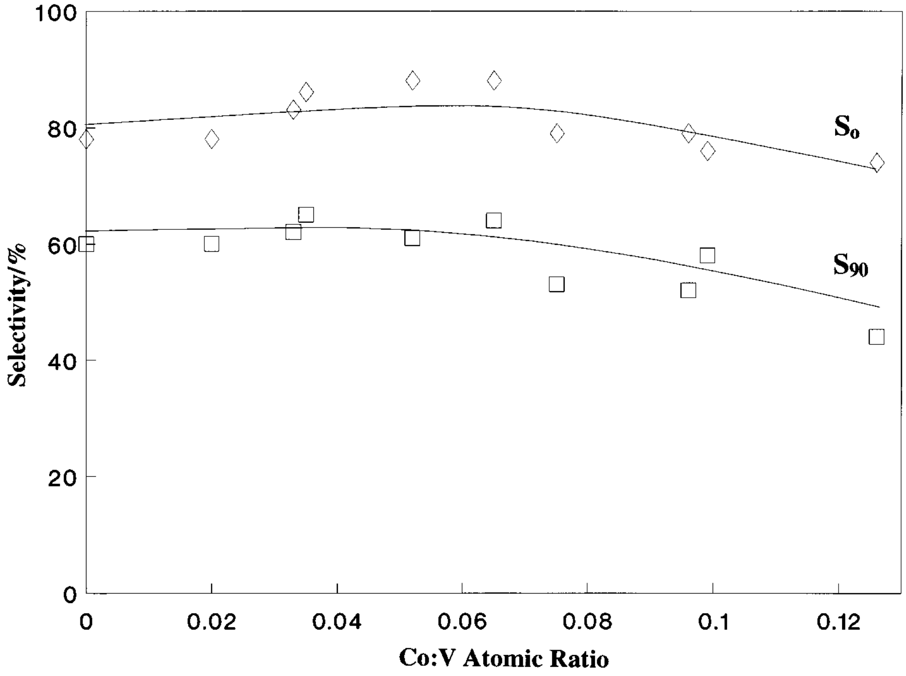

FIG. 9. Relationship between maleic anhydride selectivity at 0% (S_0) and 90% (S_{90}) butane conversion and the Co : V atomic ratio at 385°C.

Recent ^{31}P nmr studies have also suggested that a combination of VPO phases will be more active than a single phase (43, 44) and, also, that the amorphous material may play a significant role (45). In addition *in situ* laser Raman spectroscopy studies of the activation of the catalyst precursor prepared using the aqueous HCl method, together with water extraction used in this study have confirmed the existence of $(VO)_2P_2O_7$, α_{II}-VOPO$_4$ and δ-VOPO$_4$ in

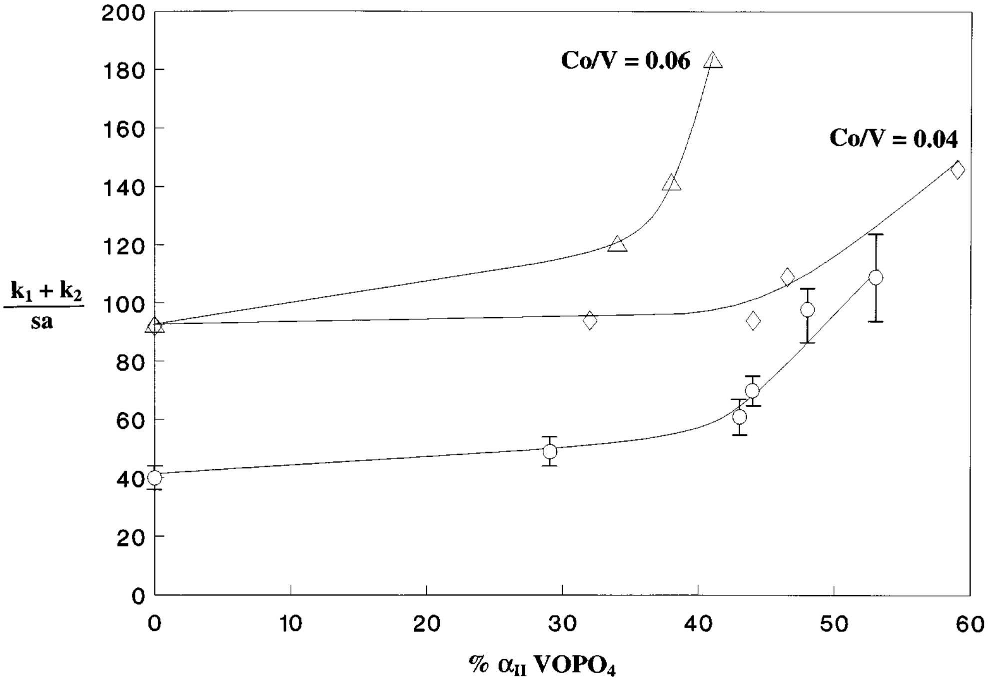

FIG. 10. Relationship between specific activity of water-washed cobalt-promoted standard aqueous HCl catalysts and the content of α_{II}-VOPO$_4$ in the final catalyst at 385°C and the dependence on the Co : V atomic ratio.

the activated catalyst (12). High resolution electron microscopy studies (43) have indicated that these compounds are present mainly as separate phases that are in intimate contact. Further evidence that it is a combination of phases which is important is provided by the studies of Moser and Schrader [46], since when pure $(VO)_2P_2O_7$ ($V:P = 1.0$) was used as a catalyst, the activity and selectivity were very poor when compared to VPO catalysts prepared by standard procedures ($V:P = 1.05$). Detailed studies using ^{31}P MAS nmr and *in situ* Raman spectroscopy (12, 47) have given further support to the model in which domains of V(*V*) are present on the surface of the $(VO)_2P_2O_7$ for catalysts in which this is the main phase by X-ray diffraction. Recent detailed experiments using a TAP reactor (48) have also provided evidence in support of a mixed $VOPO_4/(VO)_2P_2O_7$ system as the active catalyst. It is clear that from this study that when significant quantities of α_{II}-$VOPO_4$ are present the catalyst activity is enhanced and in this case it is possible that active sites are formed at the boundary of the V(*V*) and V(*IV*) phases.

It is interesting to note that the final catalysts prepared from $VO(H_2PO_4)_2 \cdot H_3PO_4$ prepared by the method of Ladwig (30) demonstrates low selectivity for maleic anhydride. This is in contrast to the recent observation (49) that pure $VO(H_2PO_4)_2$ prepared from $VOPO_4 \cdot 2H_2O$ by reduction with 3-octanol is ultra-selective for the oxidation of *n*-butane to maleic anhydride when used in a pure form. This difference probably results, either from the testing conditions used in this study which with a 5-ml catalyst bed and reasonably high conversion are somewhat different from the differential conditions used with pure $VO(H_2PO_4)_2$, or from the presence of H_3PO_4 occluded in the $VO(H_2PO_4)_2$ structure.

Role of Catalyst Promoters

A number of promotional effects have been observed for vanadium-phosphorus oxide catalysts in this study, i.e., the effect of Mo on the specific activity and maleic anhydride selectivity of $(VO)_2P_2O_7$ and the promotion of the specific activity by Co and other transition and rare earth cations on catalysts containing α_{II}-$VOPO_4$, in addition to $(VO)_2P_2O_7$. However, one important result of this study is that the role of many promoter compounds cited in the literature is mainly to control the final catalyst surface area of $(VO)_2P_2O_7$, as shown in Fig. 5. In these cases the metal cation is observed to be present in a phase other than $(VO)_2P_2O_7$ and often as a phosphate or pyrophosphate. Since most vanadium-phosphorus oxide catalyst preparations use excess phosphorus over the stoichiometric amount required for the formation of the precursor $VOHPO_4 \cdot 0.5H_2O$, it is possible that the role of the metal cation is to act as a P scavenger, since in the absence of the metal cation $VO(H_2PO_4)_2 \cdot xH_3PO_4$ would be formed, which when present would lead to the formation of a low surface area catalyst, as has been demonstrated in this study. Nevertheless, with these catalysts there is a small effect on the specific activity and the main effect is due solely to an increase in surface area. However, in many cases the selectivity to maleic anhydride is significantly decreased, as is observed with Ag, Cs, Pd, Ru, Zn, and Zr. The loss of selectivity to maleic anhydride with Cs addition is probably a result of the product remaining adsorbed on the catalyst surface on the basic sites introduced by Cs. Naumann and Behan (50) have demonstrated that additives such as Ag, Pd, and Ru increase the ease of reduction of V_2O_5 and, therefore, such additives may decrease the vanadium oxidation state and this then adversely affects the selectivity. Zn and Zr are present in the final catalysts as phosphate and pyrophosphate, respectively, and it is possible that the reaction of maleic anhydride on these phosphates may be responsible for the loss in selectivity.

An important promotional effect observed in this study relates more to selectivity than to catalyst activity and this is obtained by the addition of low levels of Mo to $(VO)_2P_2O_7$. In particular, the rate constant for maleic anhydride oxidation is decreased relative to the rate constant of butane oxidation. This could be caused by selective poisoning of active sites on the catalyst surface and, hence, improving site isolation. However, if that were the sole mechanism in operation, then the overall catalyst activity would be decreased. This is not observed and, indeed, a small but significant enhancement in specific activity is observed. It is therefore most likely that the promotional effect of Mo is electronic in origin, in which the desorption of maleic anhydride from the surface and/or the insertion of oxygen into the hydrocarbon intermediate is enhanced. For such an effect it is essential that the Mo should be intimately involved with the $(VO)_2P_2O_7$ active phase. It is interesting to note that $VOPO_4$ and $MoOPO_4$ are isostructural and it is possible that during the long stabilization period used in this study, a small amount of solid solution formation of a mixed V and Mo phase could have occurred, although for the formation of $MoOPO_4$ reduction of Mo would have to occur.

For catalysts which have been extracted with water, very pronounced promotional effects have been observed with very low levels of cations. The significant enhancement in activity, particularly observed with Co and other cations, is not considered to be due to the formation of separate phosphates, and no evidence for the formation of separate phosphates was observed by powder X-ray diffraction. Other studies [6] have shown that low levels of Ce, Cr, Cu, Fe, and Hf are also effective promoters and, although the catalysts have not been extracted by water, the precursors in general had $P:V$ ratios close to or slightly higher than unity. It has been shown (51, 52) that these cations are capable of forming solid solutions with $(VO)_2P_2O_7$ to form compounds of the type $((VO)_xM_{1-x})_2P_2O_7$, where M is the promoter cation. Otake (53) has shown that solid solutions of this type, e.g., $((VO)_{0.95}Fe_{0.05})_2P_2O_7$ are particularly active and selective in butane oxidation. Promoter compounds present in the solid solution could therefore play a role in maintaining the overall oxidation state of the catalyst surface. It must be noted that in the present study no evidence was observed in the powder X-ray diffraction pattern for the formation of solid solution; however, the levels of promoters used in this study are very low and so the effects are probably below the limit of detection. Further evidence in support of the proposal that the promoters influence the redox chemistry of the surface is suggested by the results obtained when fuel-rich conditions are used, i.e., when the partial pressure of butane is significantly increased. At higher *n*-butane partial pressures no significant promotional effect is observed on the addition of transition metal cations [6]. Matsuura *et al.* (54) have shown that $(VO)_2P_2O_7$ can be oxidized to $(VO)^{2+}_{2-x}(VO)^{3+}_{x}(P_2O_7)^{4-}_{1-x/2}(PO_4)^{3-}_{x}$ and this process may be involved in the formation of solid solutions incorporating the metal cation into the lattice during the slow stabilization period. The cation present in such a solid solution may act electronically to enhance the activation of butane or conversely the addition of cations in low levels may induce the formation of lattice defects which could provide active sites for butane oxidation. Such defect sites are considered crucial in oxidation catalysts for alkene oxidation and ammoxidation (55) and may also be important in alkane activation. Very recently Gai and Kourtakis (56) have shown that defects can be induced in $(VO)_2P_2O_7$ and so it is possible that at low *n*-butane partial pressures the presence of Co and Mo may act to maintain the optimal defect concentration and control the surface oxidation state of the vanadium.

Comments on the Use of the Simple Kinetic Model

In the present study the catalytic performance of promoted and unpromoted catalysts are compared on the basis of a set of quantities [S_0, $(k_1 + k_2)$/sa, $k_3(k_1 + k_2)$] that are derived from a simple kinetic model based on the oxidation of *n*-butane being described by three pseudo first-order reactions. This represents a major simplification of a deep oxidation in which eight hydrogen atoms are removed and three oxygen atoms are inserted. The reaction is considered to proceed (11) via the sequential formation of a number of surface intermediate, i.e., butene, butadiene, furan. However, under fuel-lean conditions these intermediates are not observed and it is considered that the reaction occurs sequentially on a single active surface site. TAP reactor experiments confirm that for a fully oxidized sample $(VO)_2P_2O_7$ only maleic anhydride is initially observed and the intermediates are only observed on a reduced catalyst (57). Hence the assumption that the conversion of *n*-butane to maleic anhydride can be represented by a single reaction is not unreasonable. Under the experimental conditions used in this study the conversion of *n*-butane $(k_1 + k_2)$ was found to be first order (representative plots are shown in Fig. 1). In addition, for the majority of catalysts the selectivity to maleic anhydride was independent of conversion, at constant temperature, for conversions up to *ca* 70–80%. This indicates that the ratio of the rate constants k_1/k_2 remains reasonably constant throughout this conversion range and, consequently, k_1 and k_2 are both considered to describe first-order reactions. Hence, there is some experimental basis for the simplifications utilized in the kinetic model.

This study demonstrates that the above simple approach can be used to gain an improved understanding of the promotion effects of catalyst additives. Traditionally, comparison of catalyst performance is made on the basis of selectivity versus conversion plots at constant temperature. Comparison of a large number of catalysts can be difficult by this method and, in addition, no account can be taken of surface area effects; in the present study these are demonstrated to be a dominant feature for vanadium-phosphorus oxide catalysts. The present study shows that these data can be compared readily on the basis of performance indicators determined at constant temperature, namely: S_0, $(k_1 + k_2)$/sa, $k_3/(k_1 + k_2)$. However, it must be stressed that this approach is only an initial step in the design approach for improved catalysts and, in particular, it is useful in the identification of catalysts that require more detailed appraisal. It is possible that the approach demonstrated will be of value for other oxidation reactions, e.g., propane/propene oxidation, particularly for the comparison of the performance of promoted catalysts.

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