

INFLUENCE OF PHOSPHORUS AND POTASSIUM IMPURITIES ON THE PROPERTIES OF VANADIUM OXIDE SUPPORTED ON TiO₂

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ABSTRACT

The catalytic properties of vanadium oxide catalysts supported on TiO₂ from Tioxide were strongly affected by phosphorus and potassium, present as impurities in the TiO₂ support. The effects observed were strongly dependent on the type of hydrocarbon oxidised. In the oxidation of toluene to benzoic acid the impurities had a large negative influence on the activity and maximum yield. For the oxidation of *o*-xylene to phthalic anhydride this negative effect was only observed at relatively low vanadium contents. At higher contents (above monolayer coverage) improved catalytic properties were obtained for catalysts supported on the contaminated TiO₂ support. When the phosphorus and potassium impurities were both largely removed by extraction with water optimum catalytic behaviour was achieved at much lower vanadium contents in both oxidation reactions.

The effect of each of the two impurities separately was also investigated using vanadium oxide catalysts deliberately contaminated with various amounts of either phosphorus or potassium. From the results of the catalytic oxidation experiments it was concluded that the addition of phosphorus resulted in an increase of the surface acidity of vanadium oxide/TiO₂ catalysts. The effect of potassium was much larger and was attributed to an alternation of the nature of the reactive sites, possibly because of the formation of amorphous bronzes.

INTRODUCTION

In a previous paper [1] it was shown that a combination of vanadium oxide with TiO₂ from Degussa was most effective in the oxidation of toluene to benzoic acid. When the TiO₂ support was completely covered with a monomolecular layer of the active phase, optimum catalytic results were obtained. When, on the other hand, TiO₂ from Tioxide was used as support, both the activity and the maximum yield of benzoic acid were significantly lower and they increased continuously with increasing vanadium content (up to 4x monolayer coverage). This different catalytic behaviour was attributed to the presence of phosphorus and potassium impurities in the Tioxide material. The impurities had a major influence on both the reducibility and the catalytic behaviour of the vanadium oxide phase [2]. The exact role of phosphorus and potassium, both often used as promoters in industrial oxidation catalysts, could however not be established.

According to Ai et al. [3], phosphorus reduces the surface acidity of a vanadium oxide catalyst. On the other hand, when phosphorus was added to a relatively basic

V-Ti mixed oxide catalyst, the acidity increased sharply [4]. They interpreted the activity and selectivity in mild oxidation reactions in terms of the acid-base properties of both the catalyst and the reactants. Nakamura et al. [5] and Fricke et al. [6] studied the structure and activity of α -Al₂O₃- and SiO₂-supported V₂O₅-P₂O₅ catalysts. They concluded that lower valence states of vanadium are stabilised when phosphorus is present. When the average charge of the vanadium ions was 4.0 under reaction conditions, maximum activity and selectivity were obtained in the oxidation of butene-1 to maleic anhydride.

The influence of alkali metals on the oxidation of o-xylene over V/TiO₂ catalysts has been studied by Boreskov et al. [7] and by Ilyinich et al. [8]. They observed that the initial selectivity increased and that the activity decreased with increasing alkalinity of the metal. The promoting effect of these alkali metals was attributed to a reduction of the surface acidity of the catalyst. Alkali metals can also form bronzes with the active phase, even at relatively low temperatures (400°C), as was observed by Fotiev et al. [9]. Bond et al. [10] suggested that part of the active phase might be deactivated because of the formation of these bronzes.

It is obvious that the effect of promoters strongly depends on the properties of both the catalyst used and the hydrocarbon oxidised. The combined effect of phosphorus and potassium was studied only briefly in our previous papers [1,2]. In the work reported here, this effect was studied more extensively as well as the effect of each of the two impurities separately.

EXPERIMENTAL

Materials

The TiO₂ used as support in this study was obtained from Tioxide (anatase; 10 m² g⁻¹). In order to remove the phosphorus and potassium impurities, the material supplied (TiO₂(Tiox.)) was extracted with water at 363 K in a Soxhlet apparatus to give the sample which we designate as TiO₂ (extr.). The amounts of phosphorus and potassium present in (or on) TiO₂(Tiox.) and TiO₂(extr.) are given in Table 1. Phosphorus or potassium were applied to the TiO₂(extr.) support by wet impregnation using aqueous solutions of H₃PO₄ (Fluka AG) or KOH (Baker). The vanadium oxide phase was applied by successive impregnation of vanadyl acetylacetonate (Merck)

TABLE 1

Amounts of phosphorus and potassium present in (or on) the TiO₂ supports

Support	P ₂ O ₅ /wt%	K ₂ O /wt%	Remarks
TiO ₂ (Tiox)	0.38	0.24	before extraction
TiO ₂ (extr.)	0.14	0.07	after extraction

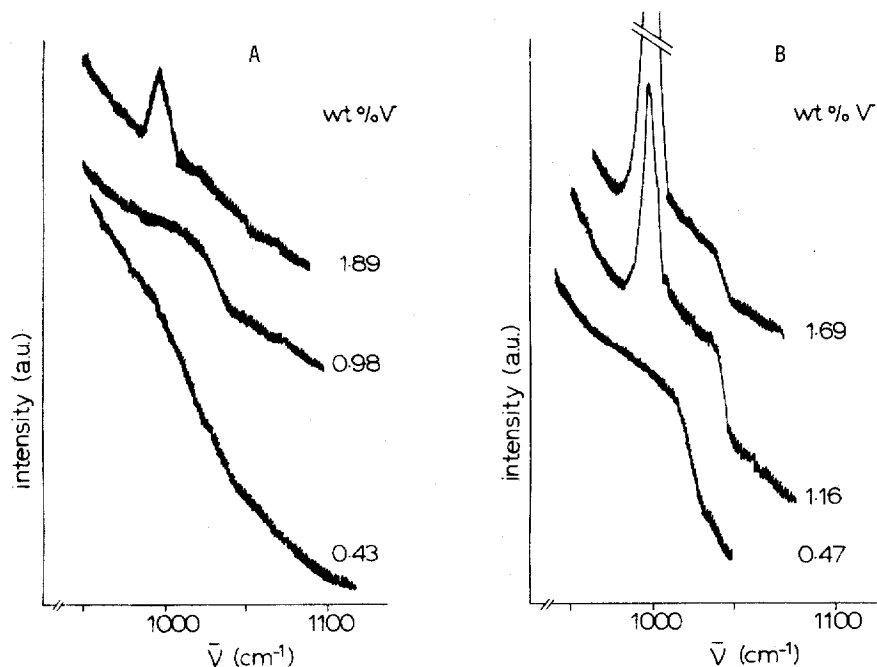


FIGURE 1 Laser Raman spectra of vanadium oxide catalysts supported on TiO_2 (TiOx.) (= A) and TiO_2 (extr.) (= B).

from ethanol (Merck) or by adsorption from toluene (Merck) [11,12]. The other materials used have been described previously [1,2].

Analysis

The content of vanadium as well as that of impurities was determined by X-ray fluorescence using a Philips 1410 X-ray spectrometer [13]. The surface areas were determined as described previously [14]. The surface area of the catalysts discussed in this paper was found to be equal to that of the support. Laser Raman spectroscopy was used to detect crystalline vanadium oxide. The output power of the laser was reduced to 15 mW, the spectral slit width was 11 cm^{-1} and the scanning speed $10 \text{ cm}^{-1} \text{ min}^{-1}$. The apparatus used to record the spectra has been described in a previous paper [11]. The reducibility of the catalysts was determined using temperature programmed reduction (T.P.R.) [2]. The oxidation reactions of toluene and o-xylene were performed in a conventional flow apparatus operated at atmospheric pressure, as described previously [1,2].

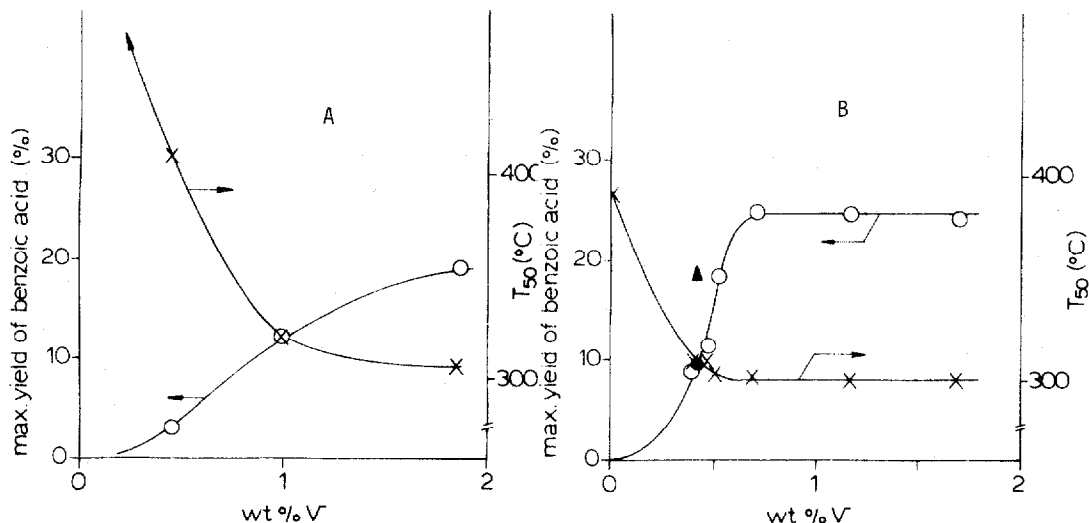


FIGURE 2 Effect of the vanadium content on the activity (x) and the maximum yield of benzoic acid (o) for TiO_2 (Tiox.) (= A) and TiO_2 (extr.) (= B) supported catalysts in the oxidation of toluene; ● and ▲: activity and maximum yield of benzoic acid for V/TiO_2 (0.41 wt% V, 0.08 wt% P_2O_5 , 0.03 wt% K_2O) [1].

RESULTS

Experimental results are first given here for vanadium oxide catalysts supported TiO_2 (Tiox.) and on TiO_2 (extr.). The observed differences between the catalysts supported on these two types of TiO_2 must be the result of the combined influences of phosphorus and potassium. Results of experiments in which the effect of each of these two impurities is examined separately are given subsequently.

Combined effect of phosphorus and potassium impurities

Analysis. A range of samples with various vanadium contents has been prepared using TiO_2 (Tiox.) and TiO_2 (extr.) as support. Laser Raman spectroscopy was used to detect crystalline vanadium oxide on the surface of the catalyst (sharp line at 996 cm^{-1} [11,15,16]). Some typical results are given in Figure 1. In the spectrum of the 1.16 wt% V catalyst supported on TiO_2 (extr.) a sharp line at 996 cm^{-1} can be seen, this indicating the presence of crystalline vanadium oxide. At higher vanadium contents, the intensity of this band increases enormously. When, on the other hand, TiO_2 (Tiox.) is used to support no line at 996 cm^{-1} could be detected for 0.98 wt% V, while for 1.89 wt% V only a relatively weak band was observed. These results are in reasonable agreement with the results published by Bond et al. [17]; they reported that the line at 996 cm^{-1} was absent from catalyst samples made by impregnation using a similar type of TiO_2 (from Tioxide), also contaminated with

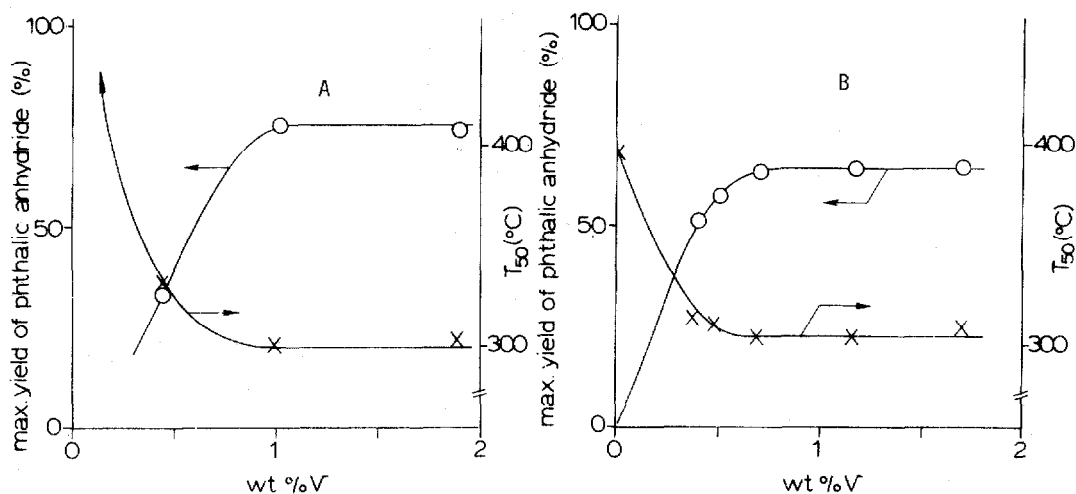


FIGURE 3 Effect of the vanadium content on the activity (x) and the maximum yield of phthalic anhydride (o) for TiO₂ (Tiox.) (= A) and TiO₂ (extr.) (= B) supported catalysts in the oxidation of o-xylene.

phosphorus and potassium, up to a vanadium content of 2.8 wt%. It is thus clear that the impurities present in (or on) the support strongly influence the structure of the supported vanadium oxide phase. Above monolayer coverage, the vanadium oxide applied to the contaminated TiO₂ (Tiox.) sample does not form crystalline V₂O₅, as is usually observed for supported vanadium oxide catalysts [11,15,16], but gives some kind amorphous structure not detectable with laser Raman spectroscopy. The broad band at a frequency of around 1020-1030 cm⁻¹, which is not only observed for most of the catalysts studied here, but also for vanadium oxide catalysts supported on TiO₂ from Degussa [18], may be due to a crystallographically ill defined vanadium oxide species present in the monolayer structure, but more research has to be done on this subject.

The reducibility of the vanadium oxide phase is strongly affected by the presence of phosphorus and potassium impurities. It was shown in a previous paper [2] that a catalyst containing phosphorus and potassium was reduced at much higher temperatures than one without impurities.

Catalytic measurements. Important parameters in the oxidation of toluene and o-xylene are the activity and selectivity. The activities of the catalysts tested are expressed as the temperature at which 50% of the toluene or o-xylene has been converted (= T₅₀). The important product formed by the selective oxidation of the side-chain of toluene under the experimental conditions used here was benzoic acid. Benzaldehyde was formed only in relatively small amounts (<3%). Phthalic anhydride

TABLE 2

Composition of P-containing catalysts supported on TiO_2 (extr.)

Sample number	P_2O_5 /wt%	V /wt%
P_0	0.14	0.47
P_1	0.30	0.53
P_2	0.43	0.45
P_3	0.82	0.32

was the product of partial oxidation of o-xylene; o-tolualdehyde, o-toluic acid and other oxidation products were formed in only relatively small amounts (together <5%). The selective properties of a catalyst in the oxidation of toluene and o-xylene are expressed in this paper as the maximum yield of or the selectivity to benzoic acid and phthalic anhydride respectively. The selectivity is defined as: (moles of product formed/moles of reactant converted) \times 100%, the maximum yield as: (maximum number of moles of product formed/moles of reactant fed) \times 100%.

Both series of catalysts were studied in the selective gas phase oxidation of toluene. The effect of the vanadium content on the activity and maximum yield of benzoic acid is given in Figure 2 for catalysts supported on TiO_2 (Tiox.) and TiO_2 (extr.). The experimental results of the catalysts supported on TiO_2 (Tiox.) have already been published [1], but are given again in this paper for comparison. The values of the yield presented for these catalysts had to be modified slightly in the light of additional measurements. This modification does not have any influence on the interpretation given previously.

It is clear from these figures that the support with phosphorus and potassium is much less active than the extracted material. (The temperature of 50% conversion for the TiO_2 (Tiox.) support exceeded the maximum temperature that could be obtained with the apparatus used (>500°C)). It is furthermore clear that when TiO_2 (extr.) with only minor amounts of impurities is used as support, the activity and maximum yield of benzoic acid do not increase continuously with increasing vanadium content, as is observed for the TiO_2 (Tiox.) supported catalysts, but become constant at higher loadings. A previous paper [1] reported briefly the effect of washing of the contaminated support on the properties of a single vanadium oxide catalyst. The TiO_2 sample used in that case contained slightly less impurity than the sample TiO_2 (extr.) used in the present work. Figure 2 also shows the experimental result for this single sample (●,▲). It can be seen that the remaining amounts of impurities in (or on) the TiO_2 (extr.) material still have a distinct influence on the catalytic properties of the vanadium oxide phase. This explains the fact that the amount of vanadium necessary to obtain constant catalytic properties for these catalysts (~ 7 atoms V per nm^2) is somewhat larger than the

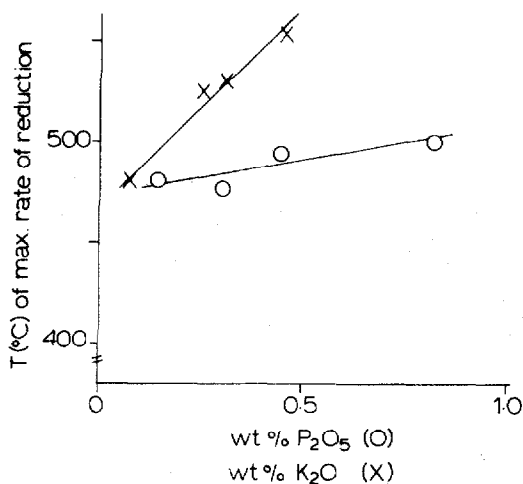


FIGURE 4 Temperature of maximum reduction rate in T.P.R. experiments, as function of the phosphorus (o) and potassium (x) content of vanadium oxide/TiO₂ catalysts.

amount found previously to be necessary for complete monolayer coverage of the support (5.2 atoms V per nm²). It is thus again clearly demonstrated that phosphorus and potassium impurities present in (or on) the Ti oxide material have a large negative effect in the selective oxidation of toluene.

Bond et al. [17] have studied supported vanadium oxide catalysts in the oxidation of *o*-xylene to phthalic anhydride, using a similar type of TiO₂ (from Ti oxide) contaminated with phosphorus and potassium. They found that the catalytic properties of these catalysts did not improve continuously with increasing vanadium content, but were constant above 0.8 wt% V, in contrast to the results observed here for the oxidation of toluene. We have therefore also tested our catalysts in the oxidation of *o*-xylene. The experimental results are given in Figure 3. From these results it is clear that the contaminated support is also less active for this oxidation reaction. Furthermore, it can be seen that for the catalysts both without and with phosphorus and potassium, the activity and the maximum yield of phthalic anhydride are both constant above a certain vanadium content. The values of yield and activities found for our catalysts supported on TiO₂ (Ti ox.) are in good agreement with the catalytic results reported by Bond et al. [17]. From the results presented in Figure 3, the minimum amount of vanadium necessary to obtain optimum catalytic properties cannot be determined accurately. However, when the results published by Bond et al. [17] are compared to those presented in Figure 2 it is clear that constant activity and maximum yield of phthalic anhydride are obtained at a much lower vanadium content for catalysts supported on TiO₂ (extr.). This is obviously due to the effect of the phosphorus and potassium impurities

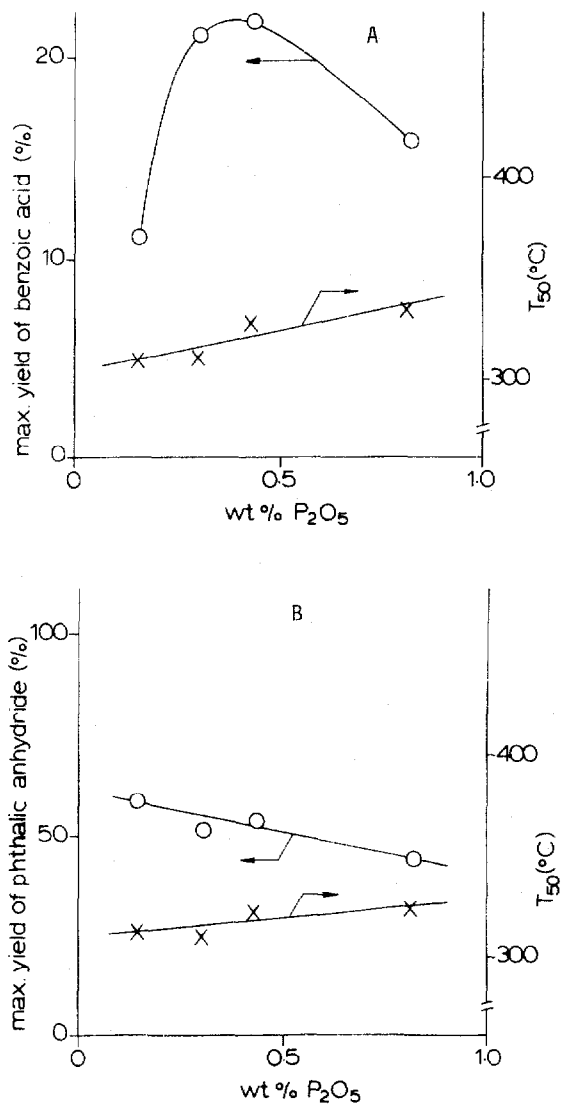


FIGURE 5 Effect of phosphorus on the catalytic properties of vanadium oxide/TiO₂ catalysts in the oxidation of toluene (A) and o-xylene (B).

present in (or on) the TiO₂ (Tiox.) support. At low vanadium contents, there is a distinct negative effect of these impurities on the catalytic behaviour of the vanadium oxide. At high vanadium contents, however, catalysts containing phosphorus and potassium are more active and give higher yields of phthalic anhydride than catalysts without these impurities, which is totally different from the results obtained for the oxidation of toluene. It can thus be concluded that the influence

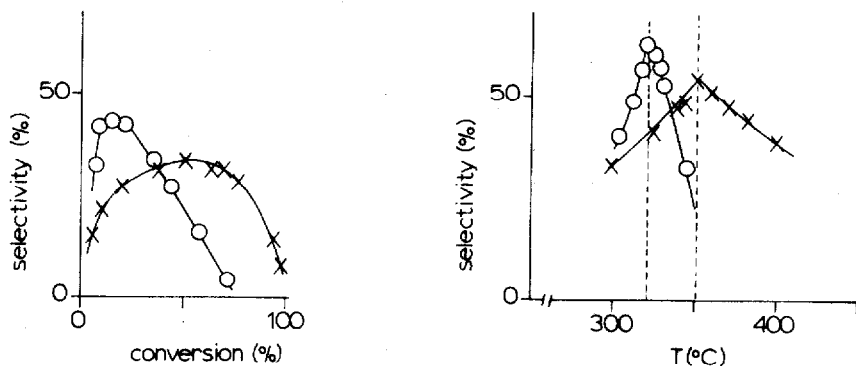


FIGURE 6 Selectivity to benzoic acid as a function of the total conversion for vanadium oxide/TiO₂ catalysts with (P₂ : (x)) and without phosphorus (P₀ : (o)) in the oxidation of toluene.

FIGURE 7 Selectivity to phthalic anhydride as a function of the reaction temperature for vanadium oxide/TiO₂ catalysts with (P₂ : (x)) and without phosphorus (P₀ : (o)) in the oxidation of o-xylene; -----: temperature of 100% conversion.

of phosphorus and potassium impurities on the catalytic properties of the vanadium oxide phase also depends strongly on the characteristics of the hydrocarbon oxidised.

Effect of phosphorus

Three catalysts with different amounts of phosphorus were prepared. At higher phosphorus content, however, it appeared that a lower amount of vanadium oxide could be applied under a given set of conditions, as can be seen in Table 2. The catalytic experiments were performed in such a way that the total number of vanadium atoms in the reactor was identical to that of the catalyst without added phosphorus (P₀). For none of the catalysts could crystalline vanadium oxide be detected with laser Raman spectroscopy. The reducibility of the vanadium oxide phase, given as the temperature of maximum reduction rate in T.P.R. experiments, is only slightly affected by the presence of phosphorus as shown in Figure 4. The results of the catalytic experiments are summarised in Figure 5. The effect of phosphorus on the activity is comparable for both oxidation reactions and seems to run parallel with the reducibility of the catalysts given in Figure 4. The effect on the maximum yield is quite different. The addition of phosphorus leads to an increase of the maximum yield of benzoic acid in the oxidation of toluene but to a slight decrease of the maximum yield of phthalic anhydride in the oxidat-

TABLE 3

Composition of K-containing catalysts supported on TiO_2 (extr.)

Sample number	K_2O /wt%	V /wt%
K_0	0.07	0.47
K_1	0.25	0.43
K_2	0.31	0.40
K_3	0.45	0.39

ion of o-xylene. The influence of phosphorus can be illustrated more clearly for the oxidation of toluene when the selectivity to benzoic acid is given as a function of the total conversion. It is obvious that the selectivity to benzoic acid at low conversions is higher for the catalyst with only minor amounts of phosphorus than for that with phosphorus, while the reverse is observed at higher conversions. For the oxidation of o-xylene the influence of phosphorus is most pronounced in the temperature region in which all the o-xylene has been converted to products. It is shown in Figure 7 that the presence of phosphorus discourages the further oxidation of phthalic anhydride under these circumstances.

Effect of potassium

Three catalysts with different amounts of potassium have been prepared. In contrast to the phosphorus containing catalysts, the amount of vanadium oxide that could be applied was practically unaffected by the presence of potassium. No crystalline vanadium oxide could be detected with laser Raman spectroscopy for these catalysts. When potassium is added to a vanadium oxide/ TiO_2 catalyst, the reducibility is decreased as shown in Figure 4.

The results of the catalytic experiments are summarised in Figure 8. It can be seen, that potassium has a negative influence on the maximum yield in both oxidation reactions. At low potassium content, the effect on the activity is relatively small. At higher contents, the activity is strongly reduced, especially in the oxidation of toluene. The parallelism between activity and reducibility is not as clear in this case as was observed for the phosphorus containing catalysts. The effect of potassium can be illustrated more clearly by giving the conversion of the aromatic hydrocarbon as a function of the reaction temperature, as shown in Figure 9 for the oxidation of toluene. Comparable results were obtained for the oxidation of o-xylene.

In the absence of full kinetic data, it is not possible to analyse these results quantitatively. If it is assumed that the reaction is first order in the concentration of the hydrocarbon, as is often proposed in the literature [19] we find that the activation energies drop from 110 kJ mol^{-1} for catalyst K_0 to 50 kJ mol^{-1}

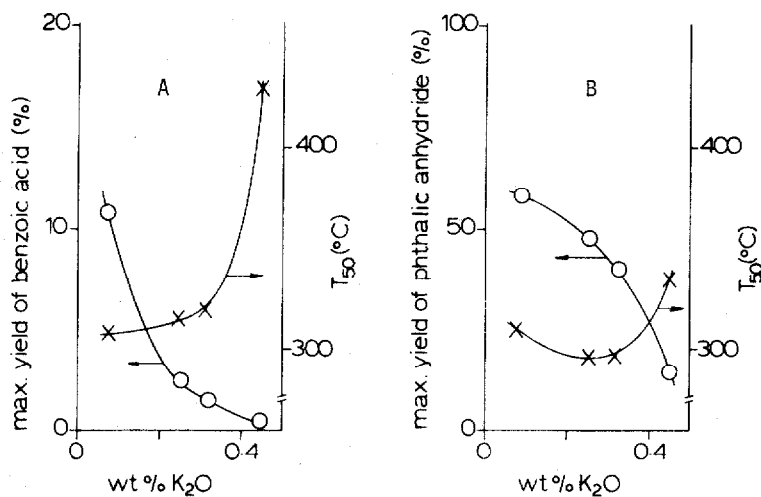


FIGURE 8 Effect of potassium on the catalytic properties of vanadium oxide/TiO₂ catalysts in the oxidation of toluene (A) and o-xylene (B).

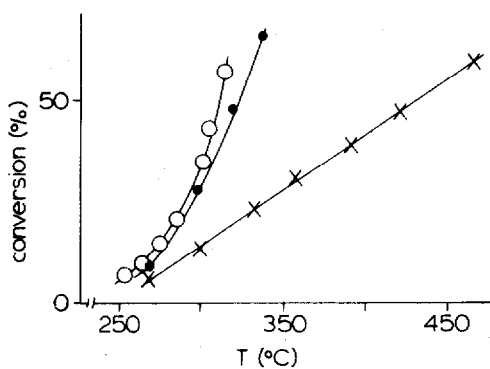


FIGURE 9 Conversion of toluene as a function of the reaction temperature; (o): K₀ (0.07 wt% K₂O), (●): K₂ (0.31 wt% K₂O), (x): K₃ (0.45 wt% K₂O).

for K₃. Hence, it is concluded that potassium is having a major effect on the nature of the reactive site, possibly because of the formation of amorphous bronzes.

DISCUSSION

From the results presented in this paper, it can be concluded that phosphorus and potassium impurities in (or on) the TiO₂ support have a large influence on the

properties of the vanadium oxide phase. It is clearly demonstrated that by removal of these impurities optimum catalytic behaviour can be obtained in the oxidation of toluene (Figure 2) and o-xylene (Figure 3) at a much lower vanadium content. The minimum amount of vanadium oxide necessary for this optimum behaviour is somewhat higher than the amount necessary for complete monolayer coverage of the support, as described in a previous paper [1], because of the influence of the remaining amounts of phosphorus and potassium in the extracted material. It can furthermore be concluded that the effect of these impurities is different for the oxidation of two quite similar aromatic hydrocarbons indicating that not only the oxidation of toluene and o-xylene is affected but also the oxidation of the products formed. From the results of experiments in which the influences of phosphorus and potassium have been studied separately, it is clear that potassium has a larger effect than does phosphorus (Figures 5 and 8). Potassium is often used as promoter in commercial oxidation catalysts [20]. According to Boreskov et al. [7], the surface acidity of the catalyst is reduced by adding potassium or other alkali metals and this will result in a reduction of the extent of the destructive oxidation of the basic benzene ring. Other authors [21] assign the effect of potassium to a weakening of the M=O bonds, which are considered to play an important part in selective oxidation. The promoting effect of potassium is however only observed at a relatively low ratio of potassium to the active component. At higher potassium contents, bronzes are formed, as was observed by Balandin et al. [22]. According to Fotiev et al. [9], who studied the phase equilibria of the $K_2O-TiO_2-V_2O_5$ system, a type ψ vanadium oxide bronze, $K_2V_8O_{20.8}$, is formed at low K_2O concentrations. This bronze, which is nonselective in the oxidation of o-xylene, decomposes under reaction conditions to give other bronzes ($K_xV_2O_5$) and VO_2 . Callahan et al. [23] studied several K-V catalysts in the oxidation of propylene and found that the oxidation capacity decreased with increasing K-content (potassium metavanadate (KVO_3) being inactive) while the selectivity to acrolein increased. The K : V ratio is relatively high for most of the catalysts studied in this paper (Table 3). It is therefore to be expected that at least part of the vanadium oxide phase applied will have reacted with the potassium present to form amorphous bronzes. This is supported not only by the low reducibility of these catalysts (Figure 4) compared to catalysts without potassium but also by the observed changes in the activation energies of the oxidation reactions (calculated from the results present in Figure 9). When the vanadium content is increased, the extra amount of vanadium (above monolayer coverage) will not form crystalline V_2O_5 , as is observed for catalysts without potassium, but will react with the first layer (a K-V-bronze) forming another type of amorphous compound not detectable with laser Raman spectroscopy (Figure 1). It is thus clear that for most of the catalysts studied, the promoting effect of potassium, often mentioned in the literature is obscured by the formation of bronzes which have a negative effect on the catalytic oxidation of toluene and o-xylene.

As was mentioned above, the effect observed for phosphorus was not as large as that observed for potassium. According to Ai et al. [3,4] and Bondareva et al. [24], phosphorus affects the surface acidity of a catalyst. A change in surface acidity will definitely influence the adsorption/desorption of reactants and products. The results for the P-containing catalysts in the oxidation of o-xylene show that the complete oxidation of the acidic product phthalic anhydride is suppressed (Figure 7), suggesting that the surface acidity has been increased by the addition of P. An increase of the acidity also leads to a stronger adsorption of the basic benzene ring of the aromatic reactant and hence to an increase of the destructive oxidation [7]. This is in agreement with the lower selectivity observed for these catalysts. For the oxidation of toluene, a lower selectivity to benzoic acid is only observed at low conversions (Figure 6). At higher conversions, the desorption of the product benzoic acid will be enhanced when the surface acidity of the catalyst is increased, resulting in a higher selectivity.

CONCLUDING REMARKS

The work presented in this paper shows that relatively small amounts of phosphorus and potassium, often present as impurities in commercial TiO_2 samples, have a large influence on the catalytic properties of the vanadium oxide phase. These "secondary" effects might lead to a wrong interpretation of experimental results. It is also clear that the effect is strongly dependent on the type of hydrocarbon oxidised, the oxidation of toluene being more sensitive than the oxidation of o-xylene. The effect of phosphorus can be explained in terms of acid-base properties of the catalyst, reactants and products. The effect of potassium is more complicated because of the formation of bronzes with the active phase and this obscures the often observed promoting effect of this element.

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