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Oxidation of o-Xylene to Phthalic Anhydride over V_2O_5/TiO_2 Catalysts

I. Influence of Catalyst Composition, Preparation Method and Operating Conditions on Conversion and Product Selectivities

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The oxidation of *o*-xylene and of *o*-tolualdehyde over V_2O_5/TiO_2 (anatase) catalysts has been studied at 533–633 K under steady state conditions; catalysts were prepared either by wet impregnation employing NH_4VO_3 solution or by a grafting technique with $VO(O\text{–}i\text{-}C_4H_9)_3$. At lower temperatures and lower contact times, for both *o*-xylene and *o*-tolualdehyde, part of the reactant feed disappeared due to the formation of an involatile polymeric residue, the formation of which was enhanced at lower temperatures, lower contact times, and higher organic reactant concentrations. At lower contact times, the part of the residue deposited on the catalyst surface constituted an important CO_2 source. The catalyst prepared by grafting showed higher phthalic anhydride selectivity and less of the residue. The formation of nonselective oxidation products seems to be favoured by uncoated TiO_2 since 0.6% V_2O_5/TiO_2 showed higher CO_2 selectivity than other catalysts. Crystalline V_2O_5 caused greater residue formation. © 1995 Academic Press, Inc.

INTRODUCTION

The oxidation of *o*-xylene over V_2O_5 catalysts is the most important industrial process for phthalic anhydride production (1, 2); among the various systems studied, those containing V_2O_5 supported on TiO_2 (anatase) show superior behaviour (3–5).

For *o*-xylene oxidation, products besides phthalic anhydride include *o*-tolualdehyde, *o*-toluic acid, phthalide, maleic anhydride, and carbon oxides (1–8). Published studies (6–8) show that phthalic anhydride is formed through a complex consecutive-parallel scheme including *o*-tolualdehyde and phthalide as intermediates. Some authors (6, 9) reported that, at low temperatures (below 590–610 K), part of the reactant fed to the system was not recoverable as a product detected by chromatography; this has been attributed to the formation of tar and low-volatility polymers.

Several studies have aimed to establish the optimal V_2O_5 loading on V_2O_5/TiO_2 catalysts (6, 9–16). There is still, however, some discrepancy between the results of these studies. Bond and Brückman (12) prepared catalysts by chemically fixing the V_2O_5 phase to hydroxylated anatase by means of $VOCl_3$ in benzene; the best performance was obtained with V_2O_5 loadings in the range 0.9–1.4 wt.%. Activity and phthalic anhydride selectivity improved with increasing V_2O_5 content up to the limit of 1.4 wt.% V_2O_5. Catalysts prepared by reaction between the hydroxyl groups on the surface of anatase and vapour of $VOCl_3$, containing 1.7 wt.% V_2O_5, also performed well in *o*-xylene oxidation (9).

Gąsior *et al.* (13) prepared V_2O_5/TiO_2 catalysts by deposition on titania of different amounts of V_2O_5, using $(NH_4)_2V_6O_{16}$ as precursor. They concluded that for low reaction temperatures (583 K) the selectivity to C_8 products decreased in the concentration range 0.8–2.5 mol% V_2O_5, remaining practically constant for V_2O_5 loadings above this range. At 623 K, for a V_2O_5 content of 1.2 mol%, after an initial increase, a high constant value of conversion was attained. The selectivity to partial oxidation products did not change significantly for V_2O_5 contents in the range 1.2–20 mol%, but decreased for contents above this value.

According to Wachs *et al.* (6, 14, 15) two different vanadia species are present in active V_2O_5/TiO_2 (anatase) catalysts; these are a surface species VO_x coordinated to the TiO_2 support and crystallites of V_2O_5. The VO_x is the active site for the oxidation of *o*-xylene to phthalic anhydride and shows higher activity and selectivity than crystalline V_2O_5. However, moderate amounts of crystalline V_2O_5, showing low effective surface area and poor catalytic activity, do not significantly affect the catalytic performance of V_2O_5/TiO_2 (anatase) catalysts.

Nobbenhuis *et al.* (16) prepared V_2O_5/TiO_2 by evaporating a V_2O_5/TiO_2/water/formamide suspension and investi-

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gated its behaviour for the oxidation of *o*-xylene using a reactor with external product recirculation. They found, at lower temperatures, in the range 573–663 K, a decrease in activity and phthalic anhydride selectivity for increasing V_2O_5 loading. In this temperature range, total oxidation product selectivity increased with V_2O_5 content, but for higher temperatures, catalysts showed an opposite behaviour.

The present paper is part of a complete study of the *o*-xylene to phthalic anhydride oxidation reaction that will include also the analysis of the transient regime (in Part 2) (17), the study of the heavy organic residue (in Part 3) (18), and the mathematical modelling of the kinetic results (in Part 4) (19).

V_2O_5/TiO_2 (anatase) samples were prepared by wet impregnation (0.6, 1, 5 wt.% V_2O_5/TiO_2) and a grafting technique using $VO(O\text{-}i\text{-}(C_4H_9)_3$, and characterized by BET surface area measurement, X-ray diffraction (XRD), laser Raman spectroscopy (LRS), FTIR, X-ray photoelectron spectroscopy (XPS), and temperature-programmed reduction (TPR). Kinetic studies have been performed in order to obtain a better understanding of the reaction mechanism. *o*-Xylene oxidation has usually been studied at higher temperatures to avoid deposition of tar and low volatility polymers on the catalyst (6, 20). In this paper, experimental conditions that allow the formation of such deposits (i.e., lower reaction temperatures and shorter contact times (9) were also used to obtain more information about the role of different surface structures and experimental conditions in their formation.

o-Tolualdehyde, a significant intermediate species in *o*-xylene oxidation (1, 2), was used as reactant, allowing a better understanding of its role in the oxidation mechanism and in the reaction steps responsible for the formation of polymeric deposits. The influence of the composition of the catalyst for both *o*-xylene and *o*-tolualdehyde oxidations was studied.

EXPERIMENTAL

Catalyst Preparation

The support (supplied by Tioxide International plc) was the anatase modification of TiO_2 and its characteristics are given in Table 1.

TABLE 1

Chemical Composition of the Anatase Support

Component	Content (Wt.%)
TiO_2	98.86
P_2O_5	0.57
K_2O	0.24
Nb_2O_5	0.27
Al_2O_3	0.04
SiO_2	0.02

Catalysts containing 0.6, 1, and 5 wt.% V_2O_5 were prepared by wet impregnation, using an aqueous solution of NH_4VO_3 (Fluka) in oxalic acid (1 *M*). The blue solution obtained after heating was added to the anatase support, and the slurry evaporated; the thick paste obtained was dried (12 h at 393 K) and calcined (4.5 h at 723 K).

A catalyst containing a monolayer of V_2O_5 on the TiO_2 support was prepared by grafting as described by Bond *et al.* (21). The support was wetted with deionised water and dried under flowing N_2 (12 h at 393 K). A solution of $VO(O\text{-}i\text{-}C_4H_9)_3$ in toluene was added and the resulting suspension was stirred at 348 K for 5 h. The solid was filtered under N_2 flow, washed with pure solvent and dried (1 h, 393 K); it was then hydrolysed, dried (393 K, 18 h), and calcined (723 K, 5 h).

Catalyst Characterization

The BET surface areas were measured using a Ströhlein Area Meter instrument. X-ray diffraction patterns were obtained with a Philips diffractometer using Cu $K\alpha$ radiation. Raman spectra were recorded on a Spex Ramalab spectrometer, the 514.5 nm line from an argon-ion laser being adjusted to 100 mW power. Infrared spectra were recorded on a Perkin–Elmer Fourier Transform spectrometer to which a minicomputer was attached. Samples were placed on the sample holder in the form of a fine powder and a 2 cm^{-1} resolution was used. XPS measurements were performed on a Kratos ES 300 electron spectrometer equipped with an Al $K\alpha$ anode and the V $2p_{3/2}$ binding energies were referenced to the C 1*s* peak.

The study of the reducibility of the catalysts was performed in a conventional TPR apparatus using a 40 cm^3 min^{-1} (STP) flow of 5 mol% H_2/Ar and a 5 K min^{-1} heating rate.

Catalytic Measurements

o-Xylene and *o*-tolualdehyde oxidations were carried out in a conventional flow apparatus at atmospheric pressure; the feed mixtures were obtained by injecting the organic reactant into the air flow using a B. Braun pump. The catalyst bed (0.5 g) was diluted (1 : 3) with inert quartz to avoid adverse thermal effects and placed in a tubular steel reactor fitted with a thermowell located at the centre into which a thermocouple was inserted. Kinetic measurements were performed for temperatures (T_R), contact times (W/F), and organic reactant concentrations in the ranges 533–633 K, 1.6×10^{-5}–2.3×10^{-4} kg_{cat} dm^{-3} h, and 0.3–8 mol%, respectively. The reactor outlet was maintained at 443 K to prevent condensation of products and it led into a multicolumn Shimadzu GC-14A gas chromatograph equipped with thermal conductivity and flame ionization detectors. Total oxidation products were analysed by the TCD detector using a 1.5-m Porapak R column. Organic reactants and selective oxidation products were separated on a 3 m length column of 20% silicone 550 on Chromosorb W and sensed by an FID detector. Before each experiment the catalyst was kept for 1 h at 673 K under flowing air, after which it was cooled to the reaction temperature. After stabilization, the organic reactant was fed to the system.

Selectivities to oxidation products were calculated as moles of product (or for CO_2, mole/8) per mole of *o*-xylene converted. The fraction of this reactant which disappears but is *not* detected as either selectively oxidised products or CO_2 is termed the *residual selectivity* S_R; in Part 3 (18) the amount of residue remaining on the surface will be quantitatively determined by a modified TPO (temperature-programmed oxidation) method which we have developed (22), and its chemical characteristics as indicated by FTIR and mass spectrometry will be described. The amount of residue remaining *on* the surface is less than that expected from the value of S_R because some of it volatilises and condenses in the cooler exit line (9). Kinetic experiments were frequently repeated to ensure reproducibility of the measurements, which was shown to be good (23). Use of a very sensitive FID detector for the glc analysis under steady state conditions enabled results of high reliability to be obtained. Checks on carbon balances were performed and at very high conversions (obtained by using high reaction temperature and high W/F) a satisfactory carbon balance between reactor inlet and outlet was observed (±5%). At lower conversions, the on-line gas-chromatographic analysis gave results that were always consistent. Although in most experiments the conversion exceded 40%, repetition of some, covering the whole range of conversion, has shown good reproducibility. S_R values are largest at low conversions, because there the *o*-xylene concentration is highest, and are lowest at high conversion where the residue is chiefly converted to CO_2 (see below). The column used was capable of separating maleic anhydride from other components, but none was detected under our experimental conditions. Further details concerning the preparation and characterization of the catalysts, the apparatus, and analytical procedure are provided elsewhere (23).

RESULTS AND DISCUSSION

Catalyst Characterization

The X-ray diffraction patterns confirmed that the Tioxide support contained only anatase.

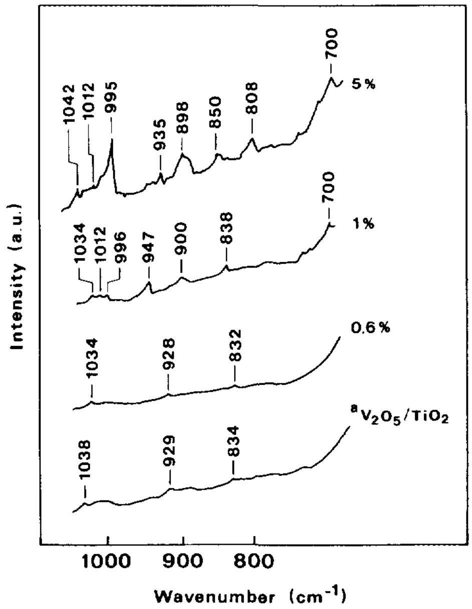

FIG. 1. Raman spectra of V_2O_5/TiO_2 catalysts (^{a}catalyst prepared by grafting).

Raman spectra (Fig. 1) were recorded in the range 690–1110 cm^{-1} since for lower wavenumbers a strong absorption, ascribed to TiO_2, complicates the interpretation of the spectra. A band at 995–996 cm^{-1} ascribed to the symmetrical stretching mode of the $V{=}O$ bond in crystalline V_2O_5 (14, 24, 25), was detected for 1 and 5% V_2O_5/TiO_2. Bands at 1034–1042, 928–947, and 832–850 cm^{-1}, detected for all samples, may correspond to new VO_x species formed on the catalyst surface. Wachs (26) associates Raman bands at 920 and 850 cm^{-1} to the symmetric stretching of VO_x clusters and a band at 1036 cm^{-1} has been ascribed to the $V{=}O$ bond stretching vibration in surface species (25). A band at about 1035 cm^{-1} has been also ascribed to dehydrated surface VO_x species on TiO_2 whereas hydrated species would exhibit bands at 920 and 850 cm^{-1} (26).

FTIR spectra are presented in Fig. 2 and represent the difference between the spectra of the catalysts and the support. Bands in the range 2020–1975 cm^{-1} are due to overtones and summation bands of the stretching modes of $V{=}O$ groups in crystalline V_2O_5 (1020 cm^{-1} (strong), 980–985 cm^{-1} (shoulder)) (27–30); these bands can be detected with 5% V_2O_5/TiO_2. Bands at 965–970 cm^{-1} cannot be caused by crystalline V_2O_5. An absorption at 940 cm^{-1} (26, 31) has been attributed to the symmetric stretch of $V{=}O$ bonds in VO_x clusters, a band at about 980 cm^{-1} being ascribed to the stretching frequency of VO_x surface species (32, 33). According to Wachs (26), dehydrated surface VO_x species on TiO_2 exhibit an infrared band at 1035 cm^{-1}, whereas hydrated species would show bands at 990 and 940 cm^{-1}.

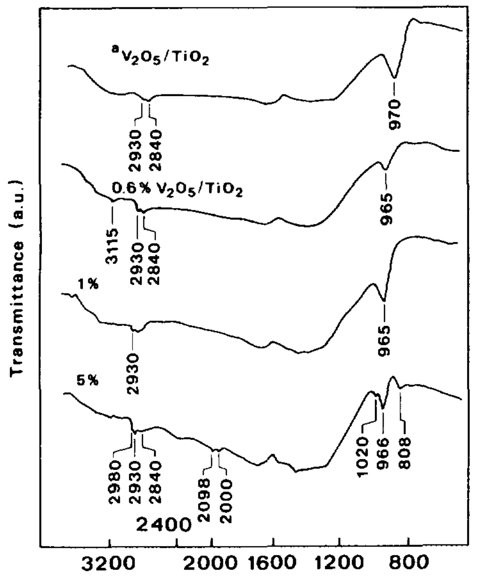

FIG. 2. FTIR spectra of V_2O_5/TiO_2 catalysts after subtraction of the support spectrum (^{a}catalyst prepared by grafting).

From XPS measurements a binding energy of 517.1 eV was observed for the V $2p_{3/2}$ peak. The comparison of this value with others reported in the literature for a number of vanadium oxides (34, 35) showed that this corresponds to V(V).

TPR results are presented in Table 2. The 0.6% V_2O_5/TiO_2 and the V_2O_5/TiO_2 prepared by grafting show only one peak, whereas samples containing 1 and 5% V_2O_5/TiO_2 present a peak and a shoulder. According to Bond *et al.* (21), the first peak can be attributed to VO_x monolayer species; these are more reducible than pure V_2O_5, which shows peaks at 938, 975, and 1050 K. The shoulder detected for samples with higher V_2O_5 contents is probably associated with small crystallites of V_2O_5 (21). For samples prepared by wet impregnation, the temperatures corresponding to the TPR peaks show an increase with the V_2O_5 content, which is in agreement with the literature (21).

TABLE 2

Properties of V_2O_5/TiO_2 Catalysts

Sample	V_2O_5 content^a (wt.%)	S_{BET} (m^2 g^{-1})	TPR peaks (K)
TiO_2	—	8.5	—
0.6% V_2O_5/TiO_2	0.6	8.7	737
1% V_2O_5/TiO_2	1.1	7.5	742, 812^b
5% V_2O_5/TiO_2	4.8	6.8	782, 821^b
V_2O_2/TiO_2^{c}	0.8	9.2	732

[a] Obtained by TPR.
[b] Shoulder.
[c] Prepared by grafting technique.

Catalytic Measurements

For o-xylene oxidation, o-tolualdehyde, phthalide, phthalic anhydride, and carbon dioxide were obtained as products; for o-tolualdehyde oxidation the last three were found. The fraction of reactant not detected as oxidised products is denoted by the residual selectivity (S_R) and has been attributed to the formation of heavy organic compounds, which can condense at the reactor outlet or remain on the catalyst surface (6, 9, 20).

For 1% V_2O_5/TiO_2 a complete kinetic study involving different temperatures (T_R), contact times (W/F), and organic reactant concentrations was performed. In Figs. 3 and 4, conversions and selectivities as function of W/F and organic reactant concentration are plotted, indicating that the catalytic behaviour is strongly dependent on the experimental conditions used. Results showed that S_R attained higher values at lower T_R and lower W/F, decreasing rapidly for increasing T_R and W/F. For these conditions, other processes besides reaction between adsorbed molecules are favoured. Wachs and Saleh (6) studying the o-xylene oxidation over a 7% V_2O_5/TiO_2 catalyst found that S_R can reach 20% in the range 593–693 K. Bond and König (9) obtained for the same reaction, over a 1.7% V_2O_5/TiO_2 catalyst, at 547 K and for a total flow rate of 32.4 cm^3 min^{-1} (STP), a residual selectivity of 36%. At lower T_R and lower W/F, no S_R values have been published. In fact, the experimental conditions generally used tend to prevent the formation of heavy organic by-products (6, 9, 20).

Higher phthalic anhydride selectivity (S_{PA}) was obtained at increasing T_R, increasing W/F, and decreasing reactant concentrations; o-tolualdehyde selectivity (S_T) showed an opposite behaviour. Phthalide was obtained in very low concentrations and no strong variations of phthalide selectivity (S_P) were observed. Higher CO_2 selectivity (S_{CO_2}) was obtained at higher T_R and W/F but no significant variations with the operating conditions were detected, suggesting that several sources must be considered for CO_2 formation. Results show that S_{PA} and S_R have opposed behaviours, increasing S_R values corresponding to decreasing S_{PA}. On the other hand, an increase in conversion is always accompanied by an increase in S_{PA} and a decrease in S_R.

For o-tolualdehyde oxidation (Figs. 5 and 6), higher S_R and S_P values were obtained at lower T_R, lower W/F, and higher reactant concentrations, S_{PA} and S_{CO_2} showing behaviour similar to those observed for o-xylene. However, higher S_{CO_2} values were detected for o-tolualdehyde oxidation. As with o-xylene oxidation, S_R and S_{PA} showed oppo-

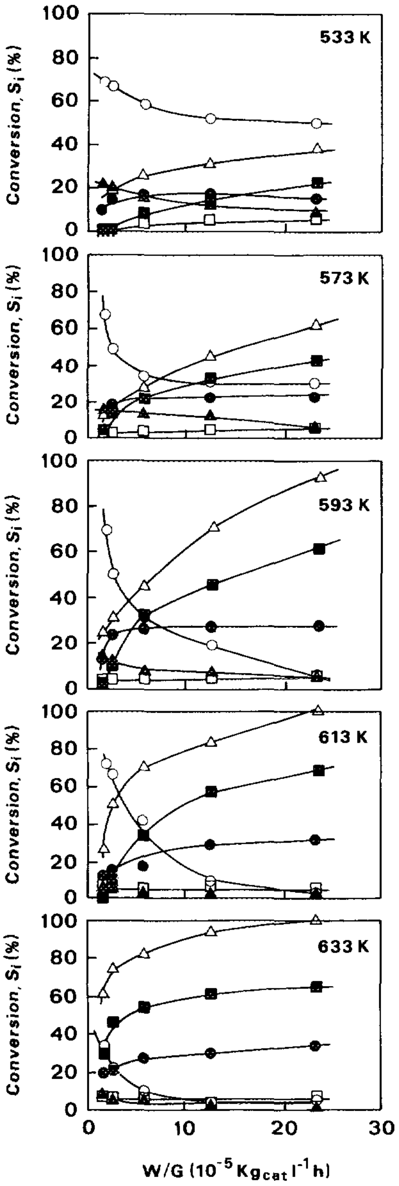

FIG. 3. Oxidation of *o*-xylene, steady state conversion and selectivity (S_i) versus *W/F* at different temperatures. C_{xylene} = 0.7 mol%. Conversion (△), *o*-tolualdehyde (▲), phthalide (□), phthalic anhydride (■), carbon dioxide (●) and residual (○) selectivity.

site behaviour. This can be ascribed to the deposition of an organic residue over the active sites that are important for the oxidation reaction. Residual selectivities obtained using *o*-tolualdehyde were lower than those for *o*-xylene oxidation, showing that adsorbed *o*-xylene molecules are involved in the formation of heavy compounds.

CO_2 can be formed by the oxidation either of adsorbed intermediates that can lead to selectivity oxidised products or of heavy organic compounds (i.e., the "residue") firmly attached to the surface. On interrupting the reactant organic flow, formation of the products of selective oxidation (*o*-tolualdehyde, phthalide, and phthalic anhydride) and the appearance of the reactant in the effluent ceased immediately, but CO_2 continued to be formed (Fig. 7) for periods of 1 h or more. We attribute these prolonged periods of CO_2 formation, with both *o*-xylene and *o*-tolualdehyde as reactants, to the slow oxidation of the residue rather than oxidation of the intermediates to the selective products, which must be in dynamic equilibrium with the products if the reaction is to proceed. Visual integration of the curves shown in Fig. 7 suggests that (i) more residue is formed

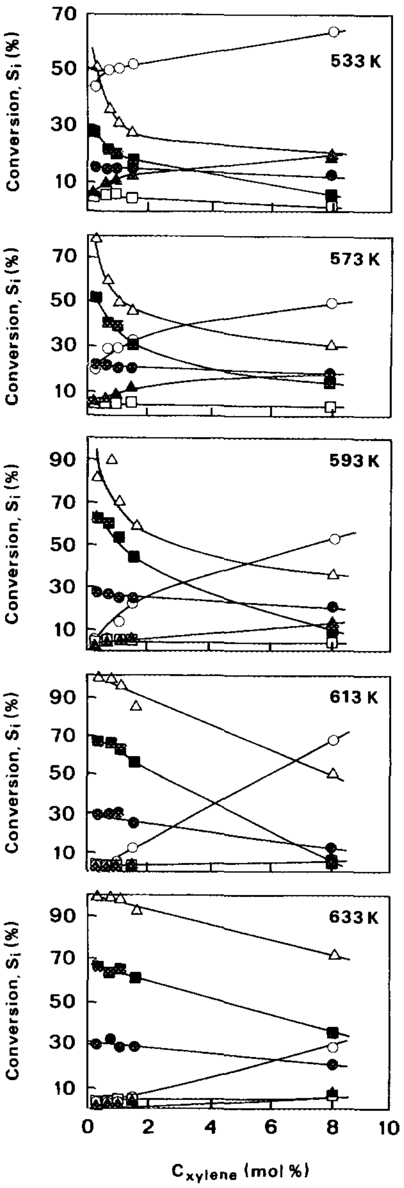

FIG. 4. Oxidation of *o*-xylene, steady state conversion and selectivity (S_i) versus *o*-xylene concentration at different temperatures. W/F = 2.3×10^{-4} kg_{cat} dm^{-3} h. Symbols as in Fig. 3.

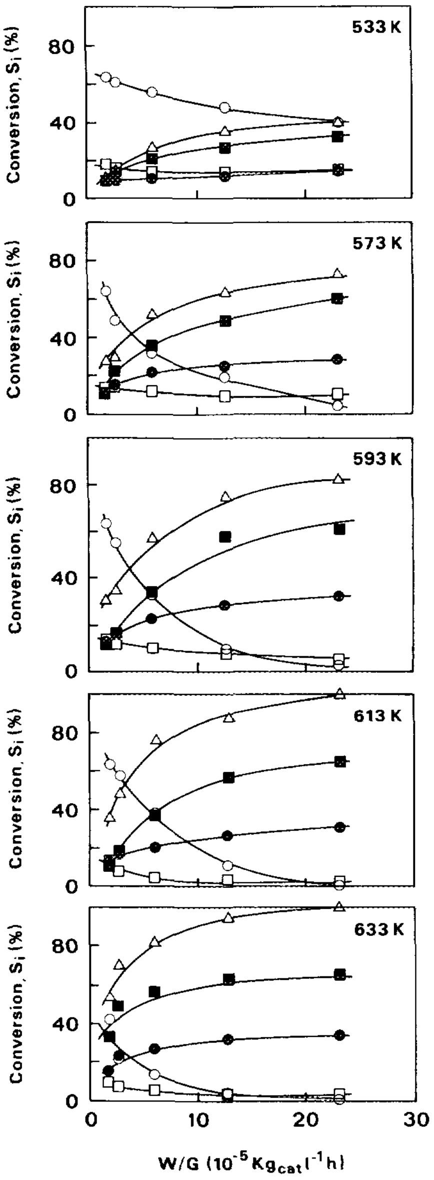

FIG. 5. Oxidation of o-tolualdehyde, steady state conversion and selectivity (S_i) versus W/F at different temperatures. $C_{\text{tolualdehyde}}$ = 0.5 mol%. Symbols as in Fig. 3.

from o-xylene than from tolualdehyde under equivalent conditions and (ii) more is formed (especially in the case of o-xylene) at the low conversion (i.e., shorter contact time). These observations are in line with our other results. The higher initial concentrations of CO_2 and their more rapid decrease with time at the longer contact time (Fig. 7) are therefore, respectively, a consequence of the higher value of S_{CO_2} and of the lower value of S_R which pertain during the prior steady state reaction under this condition. It is, however, unwise to use the integral areas under these curves to estimate the total amount of residue formed, since it is unlikely that all will be oxidised at the reaction temperature, however long the time (9); TPO to 800 K (18) will give more reliable values.

Conversions and selectivities found for o-xylene and o-tolualdehyde oxidation using other catalysts are plotted in Figs. 8–10. For both reactions, the variation of selectivity and activity with the experimental conditions is generally similar to that found for 1% V_2O_5/TiO_2. Higher S_R values were obtained at lower W/F and T_R, while S_{PA} showed an opposite behaviour. For o-xylene oxidation, S_P showed generally low constant values while S_T decreased with T_R.

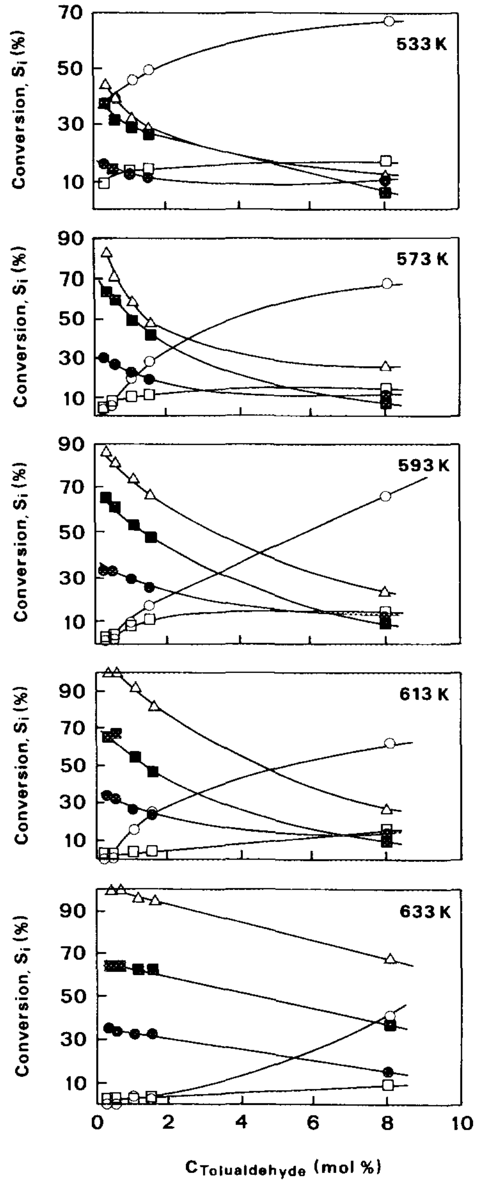

FIG. 6. Oxidation of o-tolualdehyde, steady state conversion and selectivity (S_i) versus o-tolualdehyde concentration at different temperatures. $W/F = 2.3 \times 10^{-4}$ kg$_{cat}$ dm^{-3} h. Symbols as in Fig. 3.

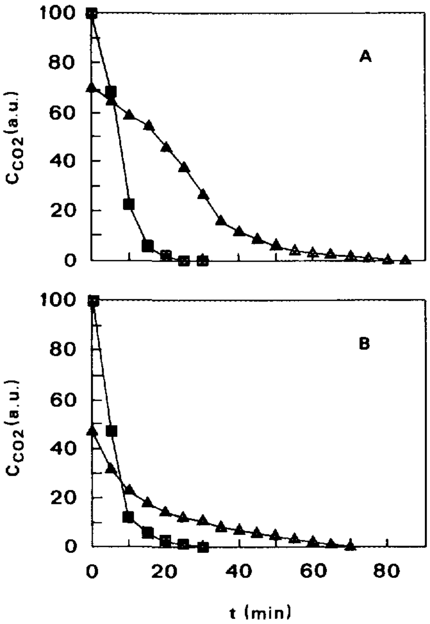

FIG. 7. Concentration of CO$_2$ (C_{CO_2}) versus time after interruption of the organic reactant flow for o-xylene (A) and o-tolualdehyde (B) oxidations. T_R = 533 K. C_{xylene} = 0.7 mol%. $C_{tolualdehyde}$ = 0.5 mol%. $W/F = 2.3 \times 10^{-4}$ kg$_{cat}$ dm^{-3} h (■), $W/F = 5.8 \times 10^{-5}$ kg$_{cat}$ dm^{-3} h (▲).

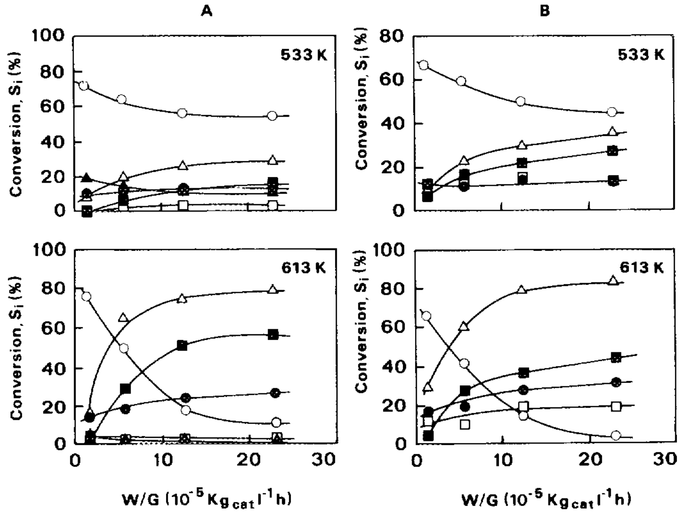

FIG. 9. Oxidation of o-xylene (A) and o-tolualdehyde (B) over 5% V$_2$O$_5$/TiO$_2$, conversion and product selectivities (S_i) obtained for steady state versus W/F at different temperatures. C_{xylene} 0.7 mol%. $C_{tolualdehyde}$ = 0.5 mol%. Symbols as in Fig. 3.

Using o-tolualdehyde as reactant, S_P showed higher values, the variation depending on the operating conditions, on the preparation method, and on the catalyst composition. For both reactants, an increase in S_{CO_2} was observed at increasing temperatures. As with 1% V$_2$O$_5$/TiO$_2$, a decrease in conversion was always accompanied by a decrease in S_{PA} and an increase in S_R.

The comparative analysis of kinetic results shows that the catalyst prepared by grafting presents generally higher S_{PA}, lower S_R, and lower S_{CO_2} values. However, for o-xylene oxidation, at lower T_R, this sample gave enhanced o-tolualdehyde and phthalide formation. The superior behaviour shown by this catalyst can be associated with the formation of a more complete VO$_x$ monolayer on the support.

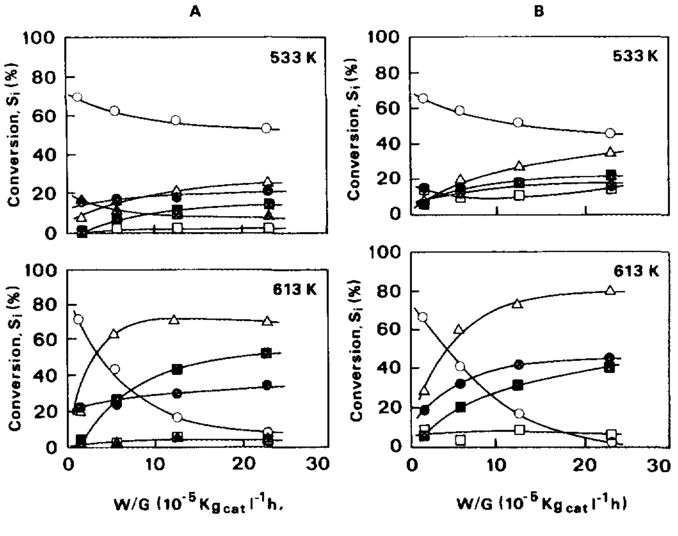

FIG. 8. Oxidation of o-xylene (A) and o-tolualdehyde (B) over 0.6% V$_2$O$_5$/TiO$_2$, conversion and product selectivities (S_i) obtained for steady state versus W/F at different temperatures. C_{xylene} 0.7 mol%. $C_{tolualdehyde}$ = 0.5 mol%. Symbols as in Fig. 3.

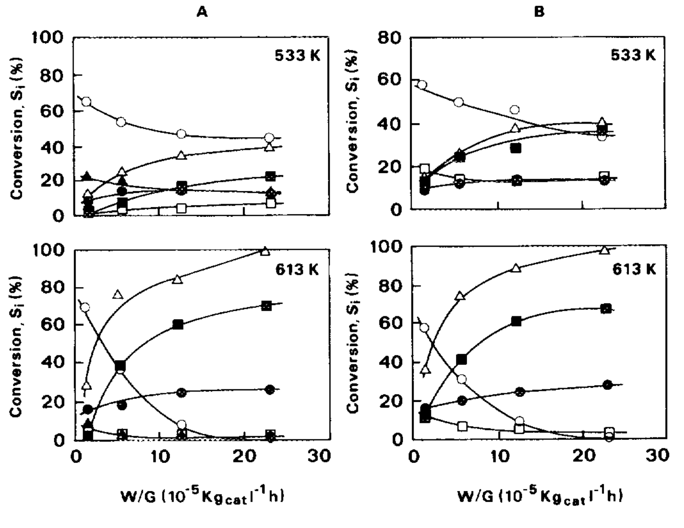

FIG. 10. Oxidation of o-xylene (A) and o-tolualdehyde (B) over V$_2$O$_5$/TiO$_2$ prepared by grafting, conversion and product selectivities (S_i) obtained for steady state versus W/F at different temperatures. C_{xylene} = 0.7 mol%. $C_{tolualdehyde}$ = 0.5 mol%. Symbols as in Fig. 3.

The series of catalysts prepared by wet impregnation had V_2O_5 concentrations between 0.6 and 5%, corresponding to about 0.7 to 6 monolayer equivalents. Results show that, except for low W/F, higher S_R values were obtained for 5% V_2O_5/TiO_2, suggesting that the formation of heavier compounds can be associated with the presence of crystalline V_2O_5 formed above monolayer coverage. At low W/F, 0.6% V_2O_5/TiO_2 gave enhanced formation of heavier by-products, and in general it exhibited the highest S_{CO_2}, showing that the formation of total oxidation products may be favoured by the presence of uncoated support. Strong Lewis acid sites, present on the TiO_2 surface (36), can be responsible for a stronger interaction between aromatic molecules and the surface, enhancing the breaking of carbon–carbon bonds and making the desorption of molecules more difficult; the reaction between adsorbed species with consequent formation of heavier compounds would then be facilitated. The presence of crystalline V_2O_5 does not significantly affect CO_2 formation since no significant variation in S_{CO_2} was detected as the V_2O_5 concentration was increased to 5%. This can be attributed to the absence of strong Lewis acid sites on the surface of crystalline V_2O_5 (37).

CONCLUSIONS

The present study of the *o*-xylene oxidation has shown that, besides phthalic anhydride, the formation of by-products must be considered. This reaction can proceed by the three following paths: selective oxidation (A), formation of heavy compounds (B), and formation of CO_2 (C), their relative importance being dependent on the catalyst characteristics and experimental conditions used. The same active sites seem to be involved in paths A and B, but the heavy organic compounds formed are not precursors of the selective oxidation products.

There is no preferential source for CO_2 formation; depending on the experimental conditions used, CO_2 can be obtained from the polymeric residue deposited on the catalyst or from adsorbed intermediates. The formation of a polymeric residue from reactant or/and intermediate adsorbed molecules is enhanced at lower temperatures and lower contact times.

Superior catalytic behaviour is associated with the presence of a VO_x monolayer on the support surface. This takes the form of oxovanadium species having a weaker V=O bond than that at the surface of crystalline V_2O_5, thus permitting higher selectivity and greater activity. For higher and lower V_2O_5 contents than that corresponding to a monolayer, both crystalline V_2O_5 and uncoated TiO_2 seem to have negative effects on the catalytic behaviour, increasing, respectively, residual and CO_2 selectivity. The catalyst prepared by grafting, having only a VO_x monolayer, exhibited the best performance.

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