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REACTION NETWORK AND KINETICS OF O-XYLENE OXIDATION TO PHTHALIC ANHYDRIDE OVER V_2O_5/TiO_2 (ANATASE) CATALYSTS

Ramzi Y. SALEH and Israel E. WACHS*

Intermediates Technology Division, Exxon Chemical Company, Annandale, New Jersey 08801, U.S.A.

*Department of Chemical Engineering, Whitaker Laboratory #5, Lehigh University, Bethlehem, PA 18015, U.S.A.

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ABSTRACT

The reaction network of o-xylene oxidation to phthalic anhydride over V_2O_5/TiO_2 (anatase) catalysts was determined in the present investigation. The detailed o-xylene conversion/product selectivity data obtained demonstrate that phthalic anhydride is not produced from the direct oxidation of o-xylene over V_2O_5/TiO_2 (anatase) catalysts, but indirectly via a series of consecutive reaction steps involving o-tolualdehyde and phthalide intermediates. The maleic anhydride by-product is produced from the over-oxidation of phthalic anhydride. The influence of the two reactive sites in V_2O_5/TiO_2 (anatase) catalysts, surface vanadium oxide monolayer and V_2O_5 crystallites, upon the o-xylene oxidation reaction were obtained for moderate amounts of vanadium oxide by varying the crystalline V_2O_5 content of the catalysts. The initial reaction step of the partial oxidation of o-xylene to o-tolualdehyde occurs almost exclusively over the surface vanadium oxide monolayer. The o-tolualdehyde intermediate is directly converted to phthalic anhydride primarily over the surface vanadium oxide monolayer and to phthalide over both the surface vanadium oxide monolayer and the V_2O_5 crystallites. The partial oxidation of phthalide to phthalic anhydride mostly occurs over the monolayer of surface vanadium oxide. The over-oxidation of phthalic anhydride to maleic anhydride also occurs primarily over the monolayer of surface vanadium oxide. The non-selective formation of the combustion products, CO and CO_2, primarily occurs from the direct oxidation of o-xylene over the monolayer of surface vanadium oxide. The turnover rate for o-xylene oxidation over V_2O_5/TiO_2(anatase) catalysts is determined for the first time, and found to be $\sim 1 \times 10^{-3}$ molecules $site^{-1}$ s^{-1} for the experimental conditions used in the present study. The apparent activation energy for the conversion of o-xylene to all products is found to be $\sim$32 kcal $mole^{-1}$.

INTRODUCTION

The complex reaction network of o-xylene oxidation to phthalic anhydride over V_2O_5/TiO_2 (anatase) catalysts has been the subject of several recent investigations [1-7]. A generalized reaction scheme for o-xylene oxidation which includes all the probable pathways is presented in Figure 1. The various reaction steps proposed by different investigators are also shown in Figure 1 [1-7]. Some investigators propose that the desired phthalic anhydride product can only be formed by a series of reaction steps via o-tolualdehyde and phthalide intermediates (reaction steps 1,2 and 3, or 1 and 9) [2,4,6], and other investigators propose that phthalic

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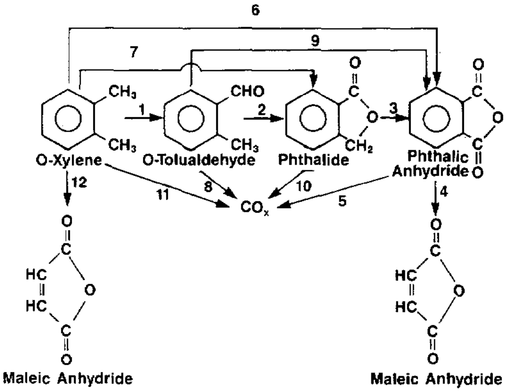

	Reaction Steps											
Investigators	1	2	3	4	5	6	7	8	9	10	11	12
Herten & Froment	X		X			X	X	X	X	X	X	
Van Hove & Blanchard	X	X	X	X	X			X	X			
Calderbank et al.	X	X	X		X	X					X	
Wainwright & Foster	X	X	X	X				X			X	
Yabrov & Ivanov	X	X	X		X	X	X	X	X	X	X	
Skrzypek et al.	X	X	X		X	X			X		X	X

FIGURE 1 Generalized reaction network for o-xylene oxidation over V_2O_5/TiO_2 (anatase) catalysts and the various reaction steps proposed by different investigators.

anhydride can be formed directly in one step from the oxidation of o-xylene (reaction step 6) [1,3,5,7]. Similar reaction paths have been proposed for the formation of the maleic anhydride byproduct: series reaction (reaction steps 1,2,3,4) or direct one step reaction (reaction step 12). The major difficulty in comparing the above results is that they were performed under very different experimental conditions. Some of these reaction studies were performed with V_2O_5/TiO_2 catalysts containing different kinds of promoters and different types of carriers. Several of these studies were also performed under non-isothermal conditions in commercial size tubular reactors where heat and mass transfer limitations may have affected the observed results. In order to resolve some of these issues we decided to examine the oxidation of o-xylene to phthalic anhydride over unpromoted V_2O_5/TiO_2 (anatase) catalysts, without a carrier, and under isothermal reaction conditions.

EXPERIMENTAL

The unsupported V_2O_5/TiO_2 (anatase) catalysts were prepared as previously described [8]. The TiO_2 (anatase) was obtained from Mobay Corporation, and possessed a surface area of $\sim$9 m^2 g^{-1}. The TiO_2 (anatase) support was found to contain 0.15 wt% K, 0.10 wt% P, 0.10 wt% Al and 0.16 wt% Si as determined by atomic absorption. The V_2O_5/TiO_2 (anatase) catalysts were prepared by dissolving V_2O_5 in an aqueous solution of oxalic acid and impregnating the titania support. The excess water was allowed to evaporate at $\sim$65°C. The catalysts were subsequently dried at 110°C and calcined in oxygen for 2 h at 450°C.

The performance of the V_2O_5/TiO_2 (anatase) catalysts for the oxidation of o-xylene was examined in the reactor unit previously described [8]. All catalysts were examined for this reaction with 1.25 mole% o-xylene in air, at a space velocity of 2760 h^{-1} and between 320 and 370°C. Changes in conversion were obtained by varying the reaction temperature. Air at the desired flow rate was passed through an o-xylene generator immersed in a temperature controlled water bath. A slip stream of the o-xylene/air feed was analyzed by a calibrated on-line multicolumn gas chromatograph equipped with a thermal conductivity detector. The gas chromatograph analyzed for all gases and organic components. After the desired o-xylene concentration was established, the feed was diverted to the reactor immersed in a molten salt (DuPont Hi Tech) bath. A slip stream of the reactor effluent was analyzed by the gas chromatograph for o-xylene conversions and the reaction products. The main reaction products observed were phthalic anhydride, tolualdehyde, phthalide, maleic anhydride, CO, CO_2 and water. Other products, including citraconic anhydride and benzoic acid, were ignored because they were present in very small quantities. At each temperature the reactor effluent was typically analyzed three to five times followed by several feed analyses. The carbon balance was always within 5%. The reactor was usually blanketed with N_2 during startup and overnight while the feed was being analyzed. The reactor (0.5 in. o.d., 316 stainless steel) was fitted with a 0.125 in. thermowell located at the center. A thermocouple inserted in the thermowell monitored the temperature throughout the catalyst bed. The feed was preheated to the salt bath temperature and entered the reactor from the bottom. The reactor was packed with 2 cm^3 of catalyst (corresponding to 1.96 g of V_2O_5/TiO_2 (anatase) having a particle diameter of 0.4 - 0.7 mm) diluted with 8 cm^3 of 0.5 mm glass beads. This catalyst dilution ratio was found to give an isothermal profile along the length of the catalyst bed. The remaining reactor volume was filled with 3 mm glass beads (2 cm^3 at the top and 2 cm^3 at the bottom). Blank runs showed the reactor walls and beads to be inert with respect to o-xylene oxidation at the temperature range investigated.

RESULTS AND DISCUSSION

The product selectivity as a function of o-xylene conversion for an unsupported 7% V_2O_5/TiO_2(anatase) catalyst under isothermal conditions is presented in Figure 2. The conversion was varied by changing the temperature of the catalyst bed (see Figure 6). At very low conversions of o-xylene, approaching zero % conversion, the major reaction products are o-tolualdehyde, CO_x (CO_2 and CO), and a tar by-product. Tar formation at low conversions of o-xylene over V_2O_5/TiO_2 (anatase) catalysts was also reported by Bond et al. [6]. In this low conversion region phthalide and maleic anhydride are not present and the phthalic anhydride selectivity approaches zero % as the conversion of o-xylene approaches zero. As the conversion of o-xylene is increased to ∿20%, the selectivity to o-tolualdehyde and the tar byproduct decreases very rapidly with o-xylene conversion, and the selecti-

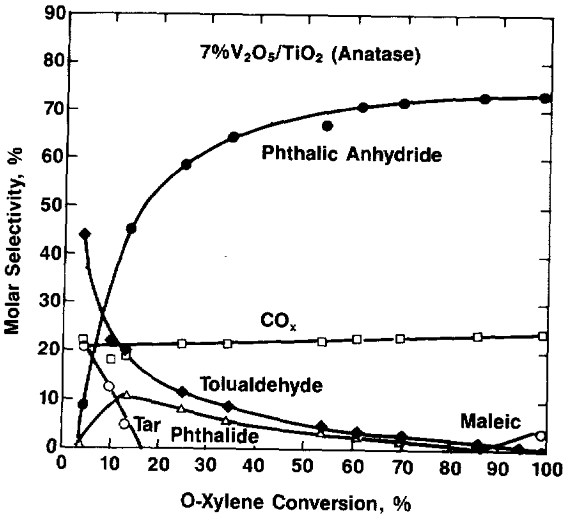

FIGURE 2 The product selectivity as a function of o-xylene conversion for 7% V_2O_5/TiO_2(anatase) catalyst.

vity to phthalic anhydride and phthalide increases with o-xylene conversion. The behavior of the o-xylene reaction products with conversion suggest that o-tolualdehyde, CO_x and the tar byproduct are the primary products of o-xylene oxidation, and that phthalic anhydride, phthalide and maleic anhydride are the secondary products which are not derived directly from the o-xylene reactant. Further increase in the conversion of o-xylene increases the selectivity towards phthalic anhydride, and decreases the selectivity towards phthalide. The maximum in the phthalide selectivity with increasing o-xylene conversion suggests that phthalide is an intermediate in the reaction that leads to phthalic anhydride formation. However, phthalide is not the only intermediate responsible for phthalic anhydride production since at very low conversions, where phthalide is not present, some phthalic anhydride is present in the product stream. This suggests that phthalic anhydride can be produced directly from the partial oxidation of o-tolualdehyde. Studies of o-tolualdehyde oxidation over V_2O_5/TiO_2 catalysts found that phthalide and phthalic anhydride are both directly produced from o-tolualdehyde [2]. Maleic anhydride formation is only observed at very high conversions of o-xylene and most probably results from the over-oxidation of phthalic anhydride. The response of the o-xylene partial oxidation products to o-xylene conversion is consistent with the behavior expected for a series of first-order consecutive reaction steps [9,10]. The phthalide intermediate, however, is probably produced in a parallel reaction step since phthalic anhydride can be produced independently of phthalide at low conversions of o-xylene (additional evidence for this parallel reaction path will be provided below when the V_2O_5 content of the catalyst is varied). The constant selectivity towards CO_x as a function of o-xylene conversion

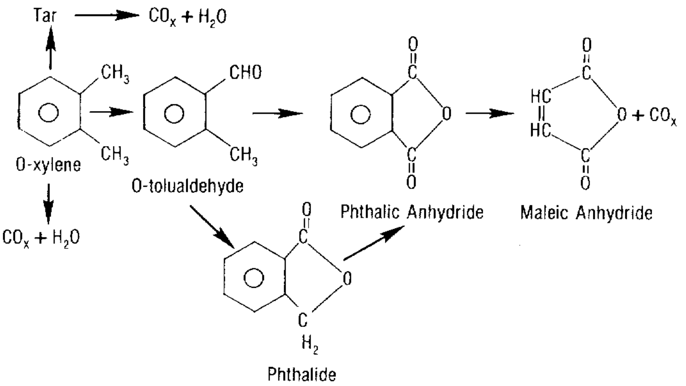

FIGURE 3 Reaction network for o-xylene oxidation to phthalic anhydride over V_2O_5/TiO_2 (anatase) catalysts.

suggests that almost all the CO_x is produced directly from o-xylene and that very little CO_x is produced from the partially oxidized intermediates. This is substantiated by the significantly higher selectivities for the oxidation of o-tolualdehyde over V_2O_5/TiO_2 catalysts [2]. Similar kinetic results were obtained with supported V_2O_5/TiO_2 catalysts, under moderately non-isothermal conditions, and by varying conversion via residence time of the gases in the reactor.

The detailed o-xylene conversion/product selectivity data obtained in the present investigation clearly demonstrates that phthalic anhydride, as well as maleic anhydride, is not produced from the direct oxidation of o-xylene over V_2O_5/TiO_2 (anatase) catalysts, but indirectly via a series of consecutive reaction steps. The kinetic results of the present study suggest that reaction network in Figure 3 for the oxidation of o-xylene to phthalic anhydride over V_2O_5/TiO_2 (anatase) catalysts. The present findings agree with the most probable reaction network proposed by Wainwright and Foster in their comprehensive review article on phthalic anhydride synthesis [4]. These findings are also consistent with the reaction networks proposed by Vanhove and Blanchard [2] and Bond and Konig [6] based on their experimental findings. An examination of the experimental apparatus employed by these authors, as described in the literature, to study the oxidation of o-xylene over V_2O_5/TiO_2 (anatase) catalysts suggests that their experimental conditions minimized residence time of the reaction products and non-isothermal conditions. The results of Herten and Froment [1], Calderbank et al. [3], Yarbov and Ivanov [5], at Skrzypek et al. [7] suggest that phthalic anhydride can be produced directly from the oxidation of o-xylene. These studies, however, used integral fixed bed reactors [1,7], spinning catalyst-basket reactors [3] and fluidized catalyst microreactors operating close to the continuous stirred tank reactor regime [5]. It is, therefore, not surprising that these studies observed phthalic anhydride and maleic anhydride at low conversions of o-xylene. The long residence time of the partial oxidation products in the spinning catalyst-basket

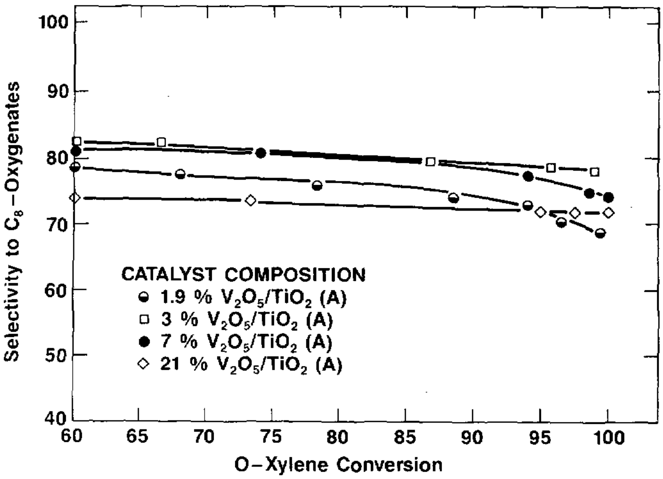

FIGURE 4 Influence of V_2O_5 content of V_2O_5/TiO_2 (anatase) catalysts upon the C_8-oxygenate (o-tolualdehyde, phthalide and phthalic anhydride) selectivity.

[3] and fluidized microreactor [5] would result in the further conversion of these intermediate products to phthalic anhydride and/or maleic anhydride [10]. Reaction on the walls of these reactors could further exacerbate this situation. The presence of external diffusion gradients in temperature and reactant concentrations are known to be present in highly exothermic reactions, such as o-xylene oxidation, conducted in integral fixed bed reactors [10], and the resulting effect would be to further convert the partial oxidation products. The presence of external diffusion gradients in the investigations employing integral fixed bed reactors [1,7] are most likely responsible for the presence of phthalic anhydride and/or maleic anhydride at low conversions during o-xylene oxidation over V_2O_5/TiO_2 (anatase) catalysts.

Recent characterization studies have revealed that two types of vanadium oxide are present in V_2O_5/TiO_2 (anatase) catalysts calcined at moderate temperatures (350-575°C) [6,8,11-18]. These investigations showed that TiO_2 (anatase) modifies the properties of the supported vanadium oxide phase by forming a monolayer of surface vanadium oxide species coordinated to the TiO_2 support as well as small crystallites of V_2O_5. The relative amount of surface vanadium oxide and crystalline V_2O_5 depends on the vanadium oxide content and the surface area of the TiO_2 support. For the TiO_2 (anatase) support used in the present study, a monolayer of surface vanadium oxide corresponds to $\sim$1.9% V_2O_5/TiO_2 (anatase) [8]. Below monolayer coverage, only the surface vanadium oxide species are present on the TiO_2 (anatase) support. Above monolayer coverage, small crystallites of V_2O_5 are also present on the support in addition to the monolayer of the surface vanadium oxide species. Thus, increasing the vanadium oxide content of V_2O_5/TiO_2 (anatase) catalysts above monolayer increases the amount of vanadium oxide present as V_2O_5

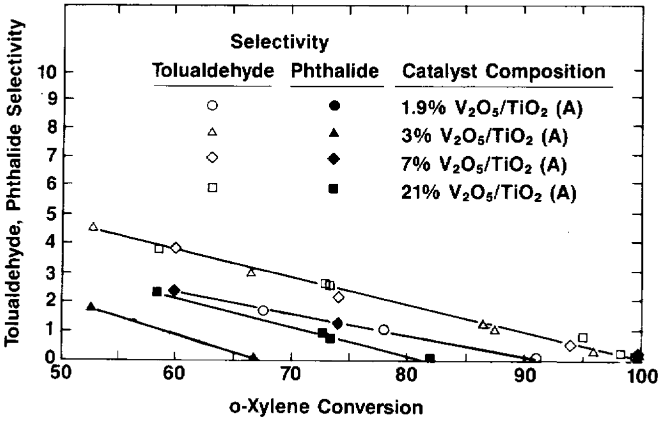

FIGURE 5 Influence of V_2O_5 content of V_2O_5/TiO_2 (anatase) catalysts upon the o-tolualdehyde and phthalide selectivities.

crystallites. The previous studies also demonstrated that the surface vanadium oxide was the active site for the partial oxidation of hydrocarbons and that it possesses a higher activity and selectivity than crystalline V_2O_5 for the oxidation of o-xylene [8,13,18]. V_2O_5/TiO_2 (anatase) catalysts possessing less than a complete monolayer of surface vanadium oxide, however, exhibit very inferior catalytic performance (o-xylene conversion and phthalic anhydride selectivity) because the exposed titania sites result in undesirable reactions (combustion of the reaction intermediates and possibly carbon deposition). Moderate amounts of crystalline V_2O_5 in V_2O_5/TiO_2 (anatase) catalysts do not significantly affect the catalytic performance (o-xylene conversion and phthalic anhydride selectivity) of such catalysts because of the low effective surface area and poor catalytic activity of this phase. The effect of V_2O_5 content upon the C_8-oxygenate selectivity during o-xylene oxidation over V_2O_5/TiO_2 (anatase) catalysts is shown in Figure 4. The 1.9%, 3% and 7% V_2O_5/TiO_2 (anatase) catalysts exhibit very similar selectivities at partial conversion of o-xylene. Below monolayer coverage there is a dramatic drop in selectivity [8]. The slight improvement in selectivity above monolayer coverage, greater than 1.9% V_2O_5/TiO_2 (anatase), suggests that the surface vanadium oxide monolayer does not effectively cover all the exposed titania sites and that slightly higher vanadium oxide contents are necessary to assure complete coverage of the few remaining titania sites. The differences in the catalytic performance of these samples become somewhat more pronounced as complete conversion of o-xylene is approached due to the increased severity of the reaction conditions. Significant amounts of crystalline V_2O_5, 21% V_2O_5/TiO_2 (anatase) sample, decrease the catalytic performance because the V_2O_5 crystallites become kinetically significant and intrinsically possess a lower selectivity than the underlying surface vanadium oxide monolayer [8,13,18].

Additional insights into the reaction network of o-xylene oxidation to phthalic anhydride over V_2O_5/TiO_5 (anatase) catalysts are also obtained from reaction studies in which the V_2O_5 content of the catalyst is varied. The influence of V_2O_5 content upon the o-tolualdehyde and phthalide selectivities are presented in Figure 5 as a function of o-xylene conversion. At a given conversion of o-xylene, the o-tolualdehyde selectivity in the product stream is slightly lower for the catalyst containing approximately a monolayer of surface vanadium oxide species, 1.9% V_2O_5/TiO_2 (anatase), than the catalysts containing crystalline V_2O_5 in addition to the surface vanadium oxide monolayer, 3%, 7% and 21% V_2O_5/TiO_2 (anatase). These results suggest that the crystallites slightly retard the conversion of o-tolualdehyde to phthalic anhydride and phthalide since the catalysts are being compared at the same conversion of o-xylene. The phthalide selectivity in the product stream is also sensitive to the content of V_2O_5 crystallites, and increases with V_2O_5 content. These observations are in agreement with the observation made by Chandrasekharan and Calderbank that the reaction intermediates are less evident for V_2O_5/TiO_2 (anatase) catalysts than unsupported, crystalline V_2O_5 catalysts [19]. For the catalyst containing approximately a monolayer of surface vanadium oxide species, 1.9% V_2O_5/TiO_2 (anatase), the phthalide intermediate was not observed over the range examined. Bond and Konig did detect phthalide formation with their vanadium oxide monolayer catalyst, and these differences may be related to the specific nature of the titania support and its associated impurities [6]. The phthalide intermediate, however, was detected for the catalyst containing small amounts of crystalline V_2O_5 in addition to the surface vanadium oxide monolayer, 3% V_2O_5/TiO_2 (anatase). The catalysts containing higher amounts of crystalline V_2O_5 in addition to the surface vanadium oxide monolayer, 7% V_2O_5/TiO_2 (anatase) and 21% V_2O_5/TiO_2 (anatase), exhibit much higher concentrations of phthalide in the product stream. The slight decrease in phthalide selectivity upon increasing the vanadium oxide content from 7% to 21% V_2O_5 may be related to the slightly lower C_8-oxygenate selectivity of the 21% V_2O_5/TiO_2 (anatase) catalyst. The 3% and 7% V_2O_5/TiO_2 (anatase) samples exhibit identical o-tolualdehyde selectivity, but differing phthalide selectivity. This suggests that in the presence of V_2O_5 crystallites the o-tolualdehyde to phthalic reaction step is enhanced relative to the o-tolualdehyde to phthalic anhydride reaction step. The strong dependence of the phthalide selectivity upon the V_2O_5 crystalline content supports the earlier statement that the phthalide intermediate is probably produced in a parallel reaction step during o-xylene oxidation over V_2O_5/TiO_2 (anatase) catalysts. The CO_x selectivity is fairly constant with the V_2O_5 content and suggests that CO_x formation is primarily associated with the monolayer of surface vanadium oxide for moderate amounts of crystalline V_2O_5 in V_2O_5/TiO_2 (anatase) catalysts. The maleic anhydride selectivity observed at high o-xylene conversions is also independent of V_2O_5 content and suggests that its formation is primarily associated with the monolayer of surface vanadium oxide.

TABLE 1

O-xylene oxidation reaction steps and their corresponding reactive sites for moderate amounts of crystalline V_2O_5 in V_2O_5/TiO_2 (anatase) catalysts.

Reaction step	Most Probable reactive sites
o-xylene → o-tolualdehyde	Surface vanadium oxide monolayer
o-tolualdehyde → phthalic anhydride	Surface vanadium oxide monolayer
o-tolualdehyde → phthalide	Surface vanadium oxide monolayer and V_2O_5 crystallites
phthalide → phthalic anhydride	Surface vanadium oxide monolayer
phthalic anhydride → maleic anhydride and CO_x	Surface vanadium oxide monolayer
o-xylene → CO_x	Surface vanadium oxide monolayer

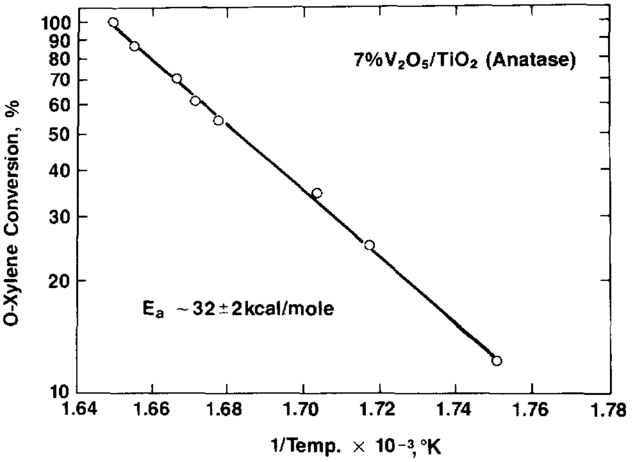

FIGURE 6 Arrhenius plot for o-xylene conversion with temperature for the 7% V_2O_5/TiO_2 (anatase) catalyst.

The above study reveals that the two sites in V_2O_5/TiO_2 (anatase) catalysts affect the o-xylene oxidation reaction network. The initial reaction step of the partial oxidation of o-xylene to o-tolualdehyde can be performed by either the surface vanadium oxide monolayer or the V_2O_5 crystallites [8,13]. The significantly higher activity of the surface vanadium oxide monolayer than the V_2O_5 crystallites for the conversion of o-xylene [8,13], however, suggests that the partial oxidation of o-xylene to o-tolualdehyde occurs almost exclusively over the surface vanadium oxide monolayer. The o-tolualdehyde intermediate is converted to either phthalic anhydride or phthalide [2]. The V_2O_5 crystallites appear to slightly retard the conversion of o-tolualdehyde and enhance the relative formation

TABLE 2

Apparent activation energies for the conversion of o-xylene to products over V_2O_5/TiO_2 (anatase) catalysts.

Investigators	Apparent activation energies/kcal mole^{-1}
Herten and Froment (1968)	16
Calderbank et al. (1977)	26 at 370-440°C 14 at 440-550°C
Wainwright and Hoffmman (1977)	27
Bond and Konig (1982)	27
Skrzypek et al. (1985)	20-26
Saleh and Wachs (1986)	32

of phthalide compared to phthalic anhydride. Thus, the partial oxidation of o-tolualdehyde to phthalic anhydride appears to primarily occur over the surface vanadium oxide monolayer and the partial oxidation of o-tolualdehyde to phthalide is associated with both the surface vanadium oxide monolayer and the V_2O_5 crystallites. The phthalide intermediate is further oxidized to phthalic anhydride and this step apparently can be performed by either the surface vanadium oxide monolayer or the V_2O_5 crystallites. The higher activity and effective surface area of the surface vanadium oxide monolayer compared to V_2O_5 crystallites suggests that the partial oxidation of the phthalide intermediate to phthalic anhydride is mostly associated with the surface vanadium oxide monolayer. Similarly, the over-oxidation of phthalic anhydride to maleic anhydride is associated with the surface vanadium oxide monolayer. The fairly constant CO_x selectivity with o-xylene conversion and V_2O_5 content suggests that CO_x is primarily produced from the direct oxidation of o-xylene over the monolayer of surface vanadium oxide for moderate amounts of crystalline V_2O_5 in V_2O_5/TiO_2 (anatase) catalysts. The origin of this non-selective reaction step, unfortunately, is currently not well understood. The above reaction steps and their most probable corresponding reactive sites are listed in Table 1.

An Arrhenius plot for the conversion of o-xylene to all reaction products for the 7% V_2O_5/TiO_2 (anatase) catalyst is presented in Figure 6. An apparent activation energy of 32 ± 2 kcal mole^{-1} is determined for the conversion of o-xylene over this catalyst. Previously reported apparent activation energies for the conversion of o-xylene over V_2O_5/TiO_2 (anatase) catalysts are listed in Table 2 and range from 13-27 kcal mole^{-1}. Diffusion gradients can be present in highly exothermic reactions such as o-xylene oxidation, and these gradients have been shown to mask the intrinsic kinetics to yield apparent activation energies that are significantly lower [10]. The somewhat lower apparent activation energies for o-xylene conversion reported by Herten and Froment [1], Calderbank et al. [3] and Skrzpek et al. [7] suggest that diffusion gradients may have been present in the reactor systems used by these investigators. The promoters present in some of these catalysts, however, may also have partially influenced some of the determined apparent activation energies. Interestingly, the same investigators that reported somewhat lower apparent activation energies also claimed that phthalic anhydride and/or maleic anhydride were present at low conversions of o-xylene over V_2O_5/TiO_2 (anatase) catalysts (see earlier discussion on reaction network). The kinetic studies that appeared to minimize residence time of the reaction products and non-isothermal conditions (references 4,6 and the present study) report high apparent activation energies, 27-32 kcal $mole^{-1}$, for o-xylene conversion and the absence of phthalic anhydride and/or maleic anhydride at low conversions of o-xylene over V_2O_5/TiO_2 (anatase) catalysts.

Turnover rates (the number of molecules reacted per active site per second) are routinely measured for many different metallic catalysts because selective chemisorption techniques have been developed to determine the number of surface atoms [20]. The advantage of using the turnover rate is that it permits an easy comparison between the work of different investigators, and consequently has significantly contributed to the progress of catalysis by metals. The selective chemisorption techniques, unfortunately, usually do not work with metal oxides and the number of exposed sites in metal oxide catalysts are not generally known. The number of exposed sites, however, can be determined for supported metal oxide catalysts containing oxide monolayers and have been applied in the case of supported vanadium oxide catalysts. Murakami et al. determined the turnover rates for a number of reactions over V_2O_5/Al_2O_3 and V_2O_5/TiO_2 catalysts [21]. The information and experimental conditions presented above also allow us to determine the turnover rate for the oxidation of o-xylene over V_2O_5/TiO_2 (anatase) catalysts. The number of active vanadium oxide sites is given by the monolayer of surface vanadium oxide since the oxidation of the o-xylene molecule occurs almost exclusively over the monolayer. The total number of vanadium sites in the monolayer corresponds to $\sim 2.5 \times 10^{20}$ sites for our experimental conditions of 1.96 gms of 1.9% V_2O_5/TiO_2 (anatase). The total amount of o-xylene converted for our experimental conditions corresponds to 3×10^{17} o-xylene molecules/sec at 60% conversion which is achieved at 325°C (see Figure 6). From these figures one obtains a turnover rate of $\sim 1 \times 10^{-3}$ o-xylene molecules $site^{-1}$ s^{-1} for the present experimental conditions. The present study reports the first determination of the turnover rate for o-xylene oxidation over V_2O_5/TiO_2 (anatase) catalysts. The turnover rates measured for the supported vanadium oxide monolayer catalysts agree very well with the turnover rates measured for metal catalysts [20].

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