Applied Catalysis, 15 (1985) 339–352
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

THE INTERACTION OF VANADIUM PENTOXIDE WITH TITANIA (ANATASE): PART I. EFFECT ON O-XYLENE OXIDATION TO PHTHALIC ANHYDRIDE

ISRAEL E. WACHS, RAMZI Y. SALEH[a], SHIRLEY S. CHAN and CLAUDIO C. CHERSICH

Corporate Research-Science Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey 08801, U.S.A.

[a]Intermediates Technology Division, Exxon Chemical Company Baton Rouge, Louisiana 70821, U.S.A.

(Received 23 July 1984, accepted 8 November 1984)

ABSTRACT

Two types of vanadia are present in active V_2O_5/TiO_2(anatase) catalysts: a surface vanadia species coordinated to the TiO_2 support and crystallites of V_2O_5. The surface vanadia is the active site in V_2O_5/TiO_2(anatase) catalysts for the oxidation of o-xylene to phthalic anhydride. The TiO_2(anatase) support must be covered by a complete monolayer of the surface vanadia species since exposed titania sites lead to complete combustion of the partial oxidation products. The surface vanadia species possess a higher activity and selectivity than crystalline V_2O_5 for this oxidation reaction. Moderate amounts of crystalline V_2O_5 do not significantly affect the catalytic performance of V_2O_5/TiO_2(anatase) because of the low effective surface area and poor catalytic activity of this phase. The unique properties of the surface vanadia species are related to the vanadia-titania interaction.

INTRODUCTION

Interactions with a support can dramatically change the properties of metals or metal oxides [1,2]. For example, V_2O_5 supported on TiO_2(anatase) is a superior catalyst for the selective oxidation of hydrocarbons than unsupported V_2O_5 [3-7]. Furthermore, o-xylene is only selectively oxidized to phthalic anhydride when V_2O_5 is supported on TiO_2(anatase) [8]. The mechanism by which TiO_2(anatase) modifies the properties of the supported V_2O_5 phase is not well understood [6-11]. Vejux and Courtine argue that the special properties of V_2O_5/TiO_2(anatase) arise from the close structural similarities between V_2O_5 (and lower oxides) and TiO_2(anatase) [9]. Inomata et al. attribute this phenomenon to the selective exposure of the (010) face of V_2O_5 at the surface of V_2O_5/TiO_2(anatase) [11]. Bond et al. claim that a monolayer of surface vanadia species is formed on the TiO_2(anatase) support, and is responsible for the catalytic behavior [7]. Kozlowski et al. attribute the behavior to the intrinsic disorder of surface vanadia species on the TiO_2(anatase) surface [10]. To better understand the interaction of V_2O_5 with the surface of TiO_2(anatase), this supported oxide system was characterized with laser Raman spectroscopy (LRS), x-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD), temperature programmed reduction (TPR), and catalytic performance for o-xylene oxidation to phthalic anhydride.

0166-9834/85/$03.30

EXPERIMENTAL

Both low surface area and high surface area TiO_2(anatase) were used as supports in the present investigation. Low surface area anatase possessing 8-9 m^2/g was obtained from Mobay Corporation. High surface area anatase was prepared by hydrolysis of titanium isopropoxide with subsequent calcining at 550°C for two hours. The resultant TiO_2 had a surface area of ~80 m^2/g. This study primarily deals with the low surface area TiO_2(anatase) and only brief reference to the high surface area TiO_2(anatase) support will be made. The impurities present in the TiO_2(anatase) supports were determined by atomic absorption. The high surface area TiO_2 was found to contain 0.21% Al, 0.24% Sn and 0.08% Ca, and the Mobay anatase was found to contain 0.15% K, 0.10% P, 0.10% Al and 0.16% Si (all compositions are in weight percent). The presence of K and P on the surface of Mobay anatase was confirmed by XPS measurements.

X-ray diffraction patterns were obtained with a Philips diffractometer using Cu Kα radiation and a diffracted beam monochromator. X-ray diffraction examination confirmed that both the high surface area TiO_2 and low surface area TiO_2 contained only the anatase phase (rutile was not present in the XRD patterns).

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 TiO_2 support. The excess water was allowed to evaporate at ~65°C. The catalysts were subsequently dried at 110°C and calcined in oxygen at 450°C for two hours. The V_2O_5 content of the samples was varied from 0.7 to 21.0 wt.% V_2O_5. Unsupported V_2O_5 possessing a surface area of 4-5 m^2/g was obtained from Alfa Corp.

X-ray photoelectron spectroscopy measurements were made with a Leybold-Heraeus LHS-10 electron spectrometer. The x-ray source was obtained from an aluminum anode operated at 12kV and 25 mA, and the binding energies of the V $2p_{3/2}$ signals were referenced to the Ti $2p_{3/2}$ peak at 458.5 eV [12]. In situ XPS measurements could also be performed with this unit as described elsewhere [13].

A detailed description of the multi-channel laser Raman spectrometer is given elsewhere [13]. An argon ion laser (Spectra Physics, Model 165) was tuned to the 514.5 nm line for excitation. The laser power at the sample location was set at 40 mW. The Raman spectrometer was a triple monochromator (Instruments SA, Model DL203) that was coupled to an optical multi-channel analyzer (Princeton Applied Research, Model OMA2). This optical multi-channel analyzer system could deliver a spectrum about a factor of 100 faster than the conventional scanning spectrometer and averaging capability permitted measurements on samples of weak signals. The overall resolution was about 6 cm^{-1}.

The reducibility of the vanadia catalysts was determined by temperature programmed reduction. About 10-100 mg of sample was supported on a fritted disc in a quartz tube (1/4" OD). The samples were reduced by a 10% H_2/Helium mixture flowing at 50 cc/min. The samples were heated at 1°C/sec by a nickrome wire wrapped around the quartz tube. The maximum reduction temperature was maintained at 700°C in order to avoid any solid state reactions between V_2O_5 and TiO_2(anatase). The hydrogen consumption during the TPR experiment was monitored with a UTI-100C mass spectrometer.

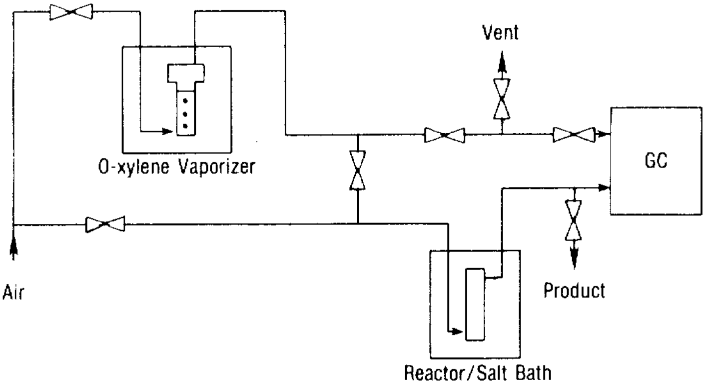


Figure 1 Schematic of Reactor Unit for the Oxidation of O-Xylene to Phthalic Anhydride.

The performance of the unsupported V_2O_5 and V_2O_5/TiO_2(anatase) catalysts for the oxidation of o-xylene was examined in the reactor unit schematically illustrated in Figure 1. All catalysts were examined for this reaction with 1.25 mole % o-xylene in air, at a space velocity of 2760 hr^{-1}, and between 320-380°C. Air at the desired flow rate was passed through the o-xylene generator immersed in a water bath. Thermostatically controlled water circulated to the generator bath and maintained the temperature to within 0.1°C. 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 the molten salt (DuPont Hi Tech) bath. The temperature of the salt bath could be maintained to within 1°C. A slip stream of the reactor effluent was analzyed 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 acid 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 start up and overnight while the feed was being analyzed. The reactor (0.5" OD, 316 stainless steel) was fitted with 0.125" 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 cc of catalyst (corresponding to 1.92 gm of V_2O_5/TiO_2(anatase) having a particle diameter of 0.4-0.7 mm) diluted with 8 cc 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 cc at the top and 2 cc 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

The Mobay TiO_2(anatase) support did not undergo structural changes during the vanadia impregnation and calcination (450°C-2 hrs.) steps. The surface areas of the V_2O_5/TiO_2(anatase) catalysts were constant at 8-9 m^2/g, and x-ray diffraction analysis only exhibited the anatase phase (rutile was not present in the XRD patterns).

X-ray diffraction, however, does not have sufficient sensitivity to provide much information about the supported vanadia. A V_2O_5 phase is detected by XRD for the V_2O_5/TiO_2(anatase) samples containing at least 7% V_2O_5. The V_2O_5 XRD peaks are barely detectable for the 7% V_2O_5/TiO_2(anatase) sample and their relative intensities deviate from that of bulk V_2O_5. This observation suggests that the small V_2O_5 crystallites, ~100Å, present on the TiO_2(anatase) surface are distorted. More information about the state of the supported vanadia phase over the entire range of vanadia content was provided by laser Raman spectroscopy. The advantage provided by laser Raman spectroscopy is that LRS, unlike XRD, can detect very small crystallites of V_2O_5 as well as amorphous states of vanadia [14,15].

The laser Raman spectra of unsupported V_2O_5 and TiO_2(anatase) are presented in Figure 2 in the range ~750-1250 cm^{-1}. The bulk V_2O_5 exhibits a sharp Raman peak at 997 cm^{-1} which is associated with the symmetrical stretching mode of the terminal oxygen atom (V=O) [16]; additional bulk V_2O_5 Raman bands lie below 750 cm^{-1}. TiO_2(anatase) possesses a weak second-order feature at 794 cm^{-1} in the same region; the major anatase Raman bands appear at 144, 199, 399, 520, and 643 cm^{-1} [16]. The very strong TiO_2(anatase) Raman bands below 750 cm^{-1} complicates the detection of vanadia Raman bands in this region. Thus, the Raman data in the present study was limited to the region ~750-1250 cm^{-1}.

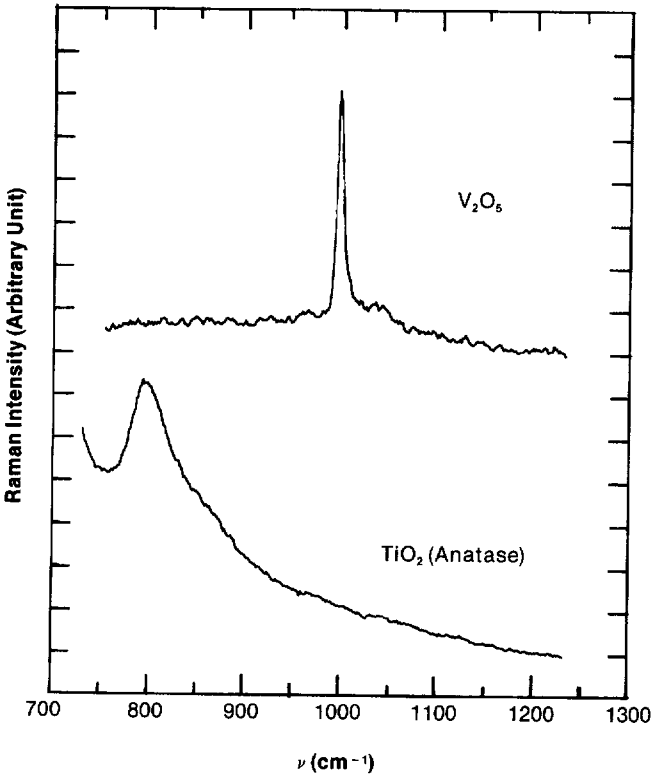


Figure 2 Laser Raman Spectra of Unsupported V_2O_5 and TiO_2(Anatase).

The laser Raman spectra of a series of V_2O_5/TiO_2(anatase)-Mobay samples are shown in Figure 3 as a function of V_2O_5 content. These spectra were corrected for the TiO_2(anatase) background. The Raman spectrum of the 3% V_2O_5/TiO_2(anatase) sample is dominated by a sharp peak at 997 cm^{-1} which is associated with the V=O bond of crystalline V_2O_5 [16]. As the loading of V_2O_5 on TiO_2(anatase) is lowered, the sharp feature associated with V_2O_5 crystallites is replaced by a broad Raman band between 850-1000 cm^{-1}. This broad band is due to a surface vanadia species coordinated to the TiO_2(anatase) surface [15]. The broadening reflects the disordered state (change in distribution of the density of states) of the surface vanadia species on TiO_2(anatase). The amount of vanadia required to achieve a monolayer of the surface vanadia species on the TiO_2(anatase) surface may be estimated from the area occupied per $VO_{2.5}$ unit of bulk V_2O_5 (0.105 nm^2) [17] and for the TiO_2(anatase) used in the present study this would correspond to approximately 1.3% V_2O_5/TiO_2(anatase) [17]. The lowest loading of vanadia that

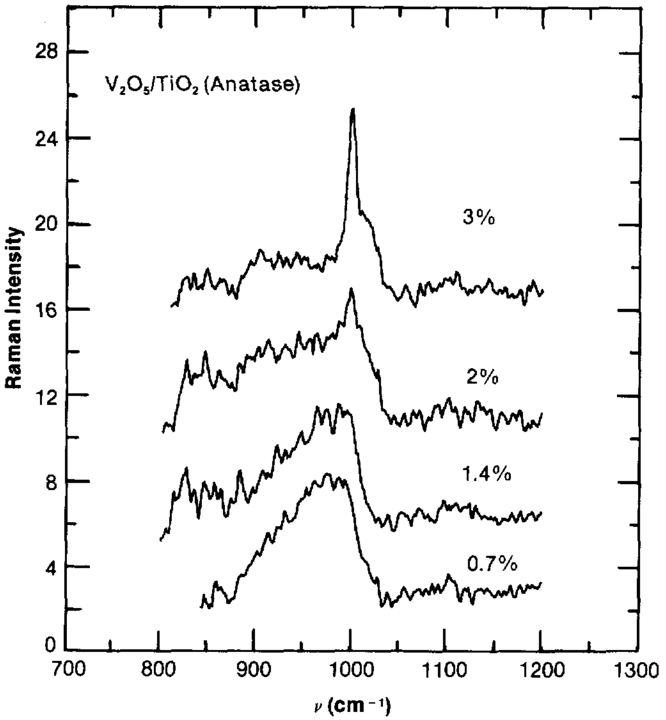


Figure 3 Laser Raman Spectra of Low Surface Area V_2O_5/TiO_2(Anatase) as a Function of V_2O_5 Content (all spectra corrected for TiO_2(anatase) background).

exhibits the crystalline V_2O_5 Raman feature at 997 cm^{-1} is 2% V_2O_5/TiO_2(anatase). Thus, it appears that approximately a monolayer of the surface vanadia species is formed on the TiO_2(anatase) surface prior to the formation of V_2O_5 crystallites. At V_2O_5 loadings exceeding ~1.9% V_2O_5/TiO_2(anatase) small crystallites of V_2O_5 are present on the anatase support in addition to the monolayer of the surface vandia species. Thus, two states of vanadia can be present in V_2O_5/TiO_2(anatase) samples calcined at 450°C.

The laser Raman spectra of the high surface area V_2O_5/TiO_2(anatase) samples are presented in Figure 4. The Raman spectra of these samples are dominated by a broad band between 850-1000 cm^{-1}. Comparison of the 3% V_2O_5/TiO_2(anatase) samples from Figure 3 and Figure 4 shows that the state of vanadia on TiO_2(anatase) is also dependent on the surface area of the TiO_2(anatase) support. The high surface area anatase support (~80 m^2/g) is able to accommodate about an order of magnitude more of the surface vanadia species than the low surface area anatase support (8-9

m^2/g) before a vanadia monolayer is achieved. Thus, the relative amounts of the surface vanadia species and the crystalline V_2O_5 on TiO_2(anatase) depend on the surface area of the TiO_2(anatase) support and the content of vanadia. All subsequent data will be limited to the V_2O_5/TiO_2(anatase)-Mobay samples.

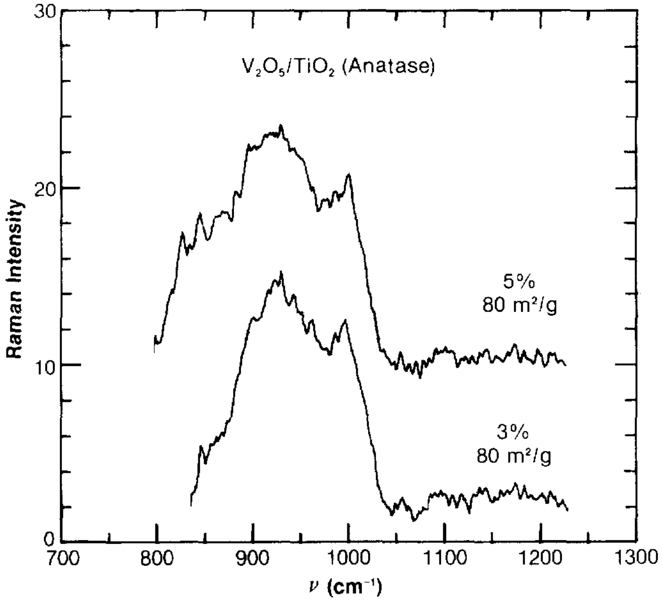


Figure 4 Laser Raman Spectra of High Surface Area V_2O_5/TiO_2(Anatase) as a Function of V_2O_5 Content (all spectra corrected for TiO_2(anatase) background).

The Raman intensities of the surface vanadia species in Figure 3 (i.e., 0.7% vs. 1.4%) do not scale with vanadia content. This is related to the increase in the sample color with increasing vanadia content. The white TiO_2 support became strongly colored with increasing vanadia content which increased the optical absorbance of the samples. The increase in the optical absorbance of the samples with increasing vanadia content is apparent from the strong suppression of the anatase support Raman bands. This suggests that as the vanadia content of the samples increased the Raman scattering occurred from a progressively thinner layer located near the front surface of the pressed disc.

X-ray photoelectron spectroscopy of the V_2O_5/TiO_2(anatase) samples revealed that the supported vanadia is present as V^{+5}. The XPS V $2p_{3/2}$ binding energies of the V_2O_5/TiO_2(anatase) samples (low surface area anatase) are presented in Table I. The measured V $2p_{3/2}$ binding energies, 517.3-517.4 eV, are independent of vanadia content and correspond to vanadium in the +5 oxidation state of V_2O_5.

TABLE I

Sample	V $2p_{3/2}$	O 1s
1.4% V_2O_5/TiO_2(anatase)[a]	517.4 eV	529.8 eV
7.0% V_2O_5/TiO_2(anatase)[a]	517.3 eV	529.9 eV
V_2O_5[b]	517.4 eV	530.2 eV

[a] Referenced to Ti $2p_{3/2}$ at 458.5 eV.

[b] Referenced to C 1s at 284.6 eV.

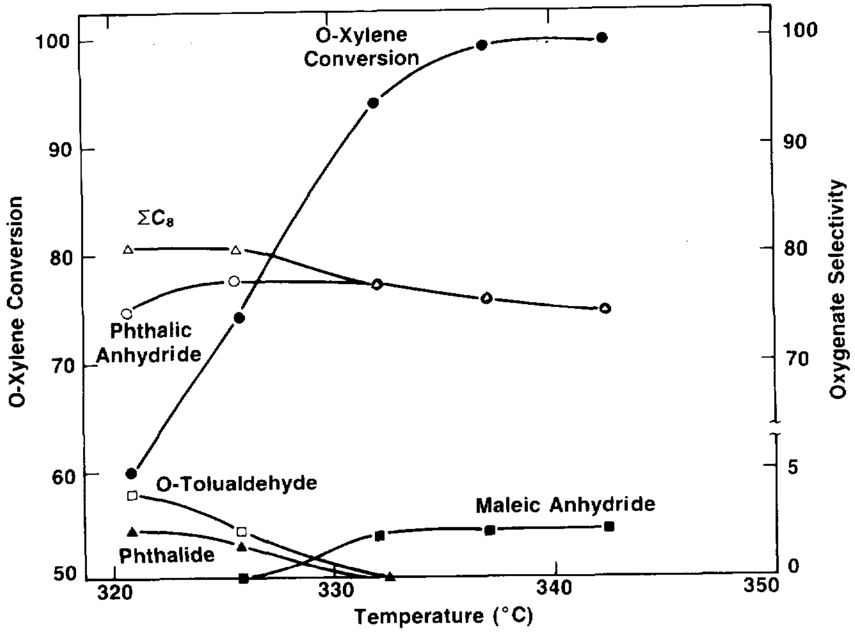


Figure 5 Conversion of O-Xylene and Selectivity Towards Various Oxidation Products as a Function of Catalyst Temperature for the 7% V_2O_5/TiO_2(Anatase) Sample.

This observation is in agreement with recent electron spin resonance (ESR) studies that concluded that the amount of V^{+4} in V_2O_5/TiO_2(anatase) catalysts calcined at 500°C is negligible [11]. In situ XPS reduction experiments with H_2 at 450°C demonstrated that the supported V^{+5} is readily reducible to V^{+3} (binding energy of 515.6 eV) [18]. The reduction behavior of the V_2O_5/TiO_2(anatase) samples and unsupported V_2O_5 was examined with the temperature programmed reduction method. The vanadia supported on titania was found to reduce more readily than unsupported V_2O_5.

The o-xylene oxidation reaction is a complex reaction that yields many different reaction products. The conversion of o-xylene and selectivity towards the various oxidation products as a function of catalyst temperature for the 7% V_2O_5/TiO_2(anatase) sample is presented in Figure 5. The reaction temperature was maintained above 320°C to prevent the formation of the tar-like reaction products which occur at lower temperatures and conversions, and can plug the gas chromatograph valves [7]. In this temperature range phthalic anhydride was the major C_8-oxygenate product, and tolualdehyde and phthalide accounted for only several percent of the reaction products. Tolualdehyde and phthalide were not present in the product stream as the conversion of o-xylene approached 100%. The only oxygenate by-product formed at these high conversions was maleic anhydride which most probably originated from the complete oxidation of phthalic anhydride.

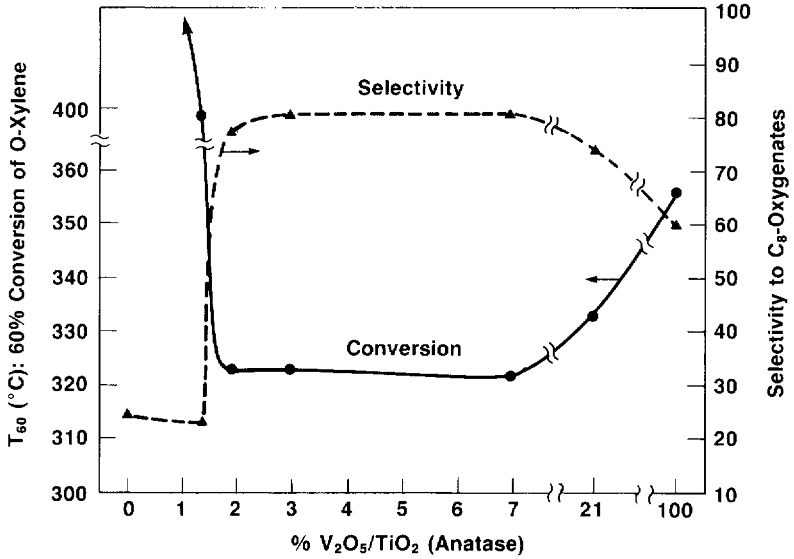
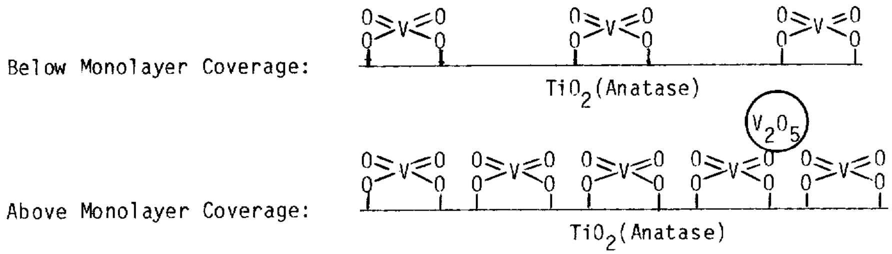


Figure 6 O-Xylene Activity and Selectivity Towards C_8-Oxygenates Over Unsupported V_2O_5 and V_2O_5/TiO_2(Anatase) Catalysts.

The unsupported V_2O_5 and the V_2O_5/TiO_2(anatase) catalysts were examined for their catalytic performance for o-xylene oxidation as shown in Figure 6. The reactivity, reflected in the temperature required to achieve 60% conversion (T_{60}), and selectivity of the V_2O_5/TiO_2(anatase) catalysts towards o-xylene oxidation are very sensitive to vanadia content. Below monolayer coverage of the surface vanadia species, 0 to ~1.9% V_2O_5/TiO_2(anatase), the activity for o-xylene oxidation and selectivity towards C_8-oxygenates increase markedly with increasing vanadia content. The catalyst containing a monolayer of the surface vanadia species, ~1.9% V_2O_5/TiO_2(anatase), is active and selective for the oxidation of o-xylene to the C_8-oxygenates. Above monolayer coverage of vanadia, ~1.9 to 7.0% V_2O_5/TiO_2(anatase), the activity and selectivity of this reaction are essentially not influenced by the vanadia content. However, as the vanadia content is further increased to 21% V_2O_5/TiO_2(anatase) the activity for o-xylene oxidation and selectivity towards C_8-oxygenates are diminished. The unsupported V_2O_5 catalyst displays very low activity and selectivity for this oxidation reaction. The conversion data was corrected for the lower surface area of the unsupported V_2O_5 catalyst, 4-5 m^2/g, relative to the V_2O_5/TiO_2(anatase) catalysts, 8-9 m^2/g, so that all catalysts were compared on a comparable surface area basis. The oxidation of o-xylene over the unsupported V_2O_5 catalyst under the chosen experimental conditions resulted in the formation of reaction products that plugged the unit. The V_2O_5/TiO_2(anatase) catyalysts did not plug the unit under the same experimental conditions. Thus, V_2O_5/TiO_2(anatase) catalysts containing a monolayer or more of vanadia are more active and selective for o-xylene oxidation to phthalic anhydride than unsupported V_2O_5.

DISCUSSION

The laser Raman spectroscopy data reveal that two states of vanadia are present in V_2O_5/TiO_2(anatase) catalysts calcined at 450°C: a surface vanadia species and crystalline V_2O_5. Furthermore, the formation of the surface vanadia species precedes the formation of crystalline V_2O_5. It appears that crystalline V_2O_5 formation occurs only after approximately a monolayer of the surface vanadia coordinated to the TiO_2(anatase) surface is present. Additional studies with high surface area TiO_2 further support this observation as shown in Figure 4. The preferred formation of the vanadia monolayer reflects the strong interaction between vanadia and the TiO_2(anatase) surface. However, different preparation techniques may yield some crystalline V_2O_5 prior to the completion of the vanadia monolayer. The interaction of vanadia with the TiO_2(anatase) surface sharply contrasts with the interaction of vanadia with the SiO_2 surface. For the V_2O_5/SiO_2 system crystalline V_2O_5 is present at extremely low coverages of vanadia, and reflects the weak interaction between vanadia and the SiO_2 surface [15]. The surface vanadia species coordinated to the TiO_2(anatase) surface are present in the +5 oxidation state. However, the coordination of the surface vanadia species cannot be assigned from the laser Raman data. Recent extended x-ray absorption fine structure (EXAFS) and x-ray absorption near edge structure (XANES) measurements of the surface vanadia species supported on TiO_2(anatase) by Kozlowski et al. concluded that the surface vanadium oxide has two terminal (1.65 ± 0.05Å) and two bridging bonds (1.90 ± 0.5Å) to oxygen, and exhibits intrinsic disorder [10]. The model of the V_2O_5/TiO_2(anatase) system that emerges is depicted below:



Below monolayer coverage, less than $\sim$1.9% V_2O_5/TiO_2(anatase), only the surface vanadia species are present on the TiO_2(anatase) surface. Above monolayer coverage, above $\sim$1.9% V_2O_5/TiO_2(anatase), small crystallites of V_2O_5 are also present on the support in addition to the monolayer of the surface vanadia species. The small V_2O_5 crystallites supported on TiO_2(anatase) are somewhat distorted in comparison to bulk, unsupported V_2O_5.

The model of the V_2O_5/TiO_2(anatase) system presented above is slightly oversimplified since it does not take into account the presence of impurities on the titania surface. A portion of the surface vanadia is undoubtedly complexed with some of the surface impurities present on the titania support. This may account for the present observation that the amount of vanadia required to achieve a monolayer on the TiO_2(anatase)-Mobay support was somewhat greater than that estimated from geometric considerations ($\sim$1.9% vs. 1.3% V_2O_5). Crystalline V_2O_5, however, is not present in V_2O_5/TiO_2 samples unless approximately a monolayer of surface vanadia has been formed on the titania support.

Both states of vanadia in V_2O_5/TiO_2(anatase) reduce more readily than unsupported V_2O_5. Similar observations were also made by Roozeboom et al. for vanadia supported on other oxides (Al_2O_3, SiO_2, etc.) [15]. The enhanced reduction of the small V_2O_5 crystallites is in agreement with reduction studies of V_2O_5 crystals in an optical microscope [19]. These studies found that the rate of reduction increased with decreasing thickness of the V_2O_5 crystal in the <u>c</u> direction. Apparently, crystallite dimensions affect the reducibility of crystalline V_2O_5, and small V_2O_5 crystallites supported on TiO_2(anatase) reduce more readily than bulk, unsupported V_2O_5. The enhanced reduction kinetics of the surface vanadia species must be related to the vanadia-support interaction. However, this is not unique to TiO_2 (anatase) because Roozeboom et al. found the same behavior on other oxide supports [15].

The catalytic studies demonstrated that the surface vanadia species are active and selective for the oxidation of o-xylene to phthalic anhydride because the V_2O_5/TiO_2(anatase) catalyst containing approximately a monolayer of the surface vanadia species is active and selective for this oxidation reaction (see Figure 6 for 1.9% V_2O_5/TiO_2(anatase)). The fraction of the surface vanadia that is complexed with the surface impurities on the TiO_2(anatase) support, however, would not be expected to contribute significantly to the oxidation of o-xylene because such impurities, especially potassium, are known to decrease the activity of V_2O_5/TiO_2(anatase) catalysts [5]. Below monolayer coverage, the oxidation activity is strongly dependent on the vanadia coverage on the support since TiO_2 is essentially inactive for the oxidation of o-xylene (see Figure 6). The selectivity, however, of o-xylene oxidation to C_8-oxygenates below monolayer coverage of vanadia is extremely low. This suggests that exposed titania sites may lead to complete combustion of the C_8-oxygenates since the TiO_2(anatase) support is not active for o-xylene oxidation under these conditions. This was confirmed by physically mixing TiO_2(anatase) with an active and selective V_2O_5/TiO_2(anatase) catalyst, and obtaining a lower product selectivity. Thus, the TiO_2(anatase) support must be covered by a complete monolayer of the surface vanadia species to be an active and selective catalyst for the oxidation of o-xylene to phthalic anhydride. Gellings et al. [20] reached similar conclusions during their investigation of toluene oxidation over V_2O_5/TiO_2 (50 m^2/g; 65% anatase; 35% rutile) catalysts, and Bond et al. [7] demonstrated that a V_2O_5/TiO_2(anatase) catalyst containing a monolayer of vanadia is active and selective for the oxidation of o-xylene to phthalic anhydride.

Above monolayer coverage of vanadia, ~1.9 to 7.0% V_2O_5/TiO_2(anatase), the activity and selectivity of the o-xylene oxidation reaction are essentially not influenced by the vanadia content. The minor role of the crystallized V_2O_5 phase for o-xylene oxidation is primarily a consequence of the low effective surface area of the crystallized V_2O_5 particles relative to the higher effective surface area of the monolayer of surface vanadia species on the TiO_2 support. However, as the vanadia content is further increased to 21% V_2O_5/TiO_2(anatase) the activity for o-xylene oxidation is diminished suggesting that the supported, crystalline V_2O_5 phase is not very active for this oxidation reaction. Thus crystalline V_2O_5, unsupported or supported on TiO_2, is not as effective as the surface vanadia species for the oxidation of o-xylene. Gasior and Machej [21] recently demonstrated that the (010) crystallographic plane of V_2O_5, the plane containing exposed V=O bonds, is more active and selective than the other V_2O_5 planes for the oxidation of o-xylene to phthalic anhydride. However, the maximum selectivity for phthalic anhydride over the unsupported V_2O_5 catalysts is still inferior to that obtained with active V_2O_5/TiO_2(anatase) catalysts.

The above data shows that TiO_2(anatase) modifies the properties of vanadia by forming a surface vanadia species coordinated to the TiO_2 support. The surface vanadia species possesses a higher activity and selectivity than unsupported, crystalline V_2O_5 for the oxidation of o-xylene to phthalic anhydride. The enhanced activity of the surface vanadia species is probably related to the enhanced reducibility of vanadia supported on TiO_2. The higher selectivity of the surface vanadia species than the crystalline V_2O_5 phase for the oxidation of o-xylene to phthalic anhydride is apparently intrinsic to the properties of the surface vanadia species on the TiO_2(anatase) support. The present study demonstrates that the surface vanadia coordinated to the TiO_2 support is the active site in V_2O_5/TiO_2(anatase) catalysts for o-xylene oxidation to phthalic anhydride. Bond et al. [7] and Gellings et al. [20] reached similar conclusions in their kinetic investigations of o-xylene oxidation and toluene oxidation over V_2O_5/TiO_2, respectively. In the present study, the catalytic performance of V_2O_5/TiO_2(anatase) for o-xylene oxidation was correlated to the states of vanadia on the TiO_2 support with laser Raman spectroscopy which demonstrated that the surface vanadia species is the active site for this oxidation reaction. Bond et al. also concluded that the optimum amount of vanadia in V_2O_5/TiO_2(anatase), for best catalytic performance, corresponded to a monolayer of the surface vanadia species, and that vanadia in excess of monolayer coverage was detrimental to catalytic performance [7]. The present study demonstrates that moderate amounts of crystalline V_2O_5 do not affect the catalytic performance of V_2O_5/TiO_2(anatase) catalysts for o-xylene oxidation to phthalic anhydride because of the low effective surface area and poor catalytic activity of this crystallized phase. Gellings et al. similarly demonstrated that moderate amounts of crystalline V_2O_5 do not effect the oxidation of toluene over V_2O_5/TiO_2 catalysts [20]. Furthermore, Bond et al. suggested that the nature of the surface vanadia species on the TiO_2(anatase) support is dependent on the catalyst preparation method [7]. The work in this laboratory and of Gellings et al. [15,20,22] using different preparation techniques has shown that the properties of the surface vanadia species are independent of the preparation method, but are intrinsic to the vanadia-titania interaction.

CONCLUSIONS

Two types of vanadia are present in active V_2O_5/TiO_2(anatase) catalysts: a surface vanadia species coordinated to the TiO_2 support and crystallites of V_2O_5. The surface vanadia is the active site in V_2O_5/TiO_2(anatase) catalysts for the oxidation of o-xylene to phthalic anhydride. The TiO_2(anatase) support must be covered by a complete monolayer of the surface vanadia species since exposed titania sites lead to complete combustion of the partial oxidation products. The crystalline V_2O_5 phase is not as effective for this oxidation reaction. Moderate amounts of crystalline V_2O_5 do not significantly affect the catalytic performance of V_2O_5/TiO_2(anatase) because of the low effective surface area and poor catalytic activity of this phase. Thus, the TiO_2(anatase) support modifies the properties of vanadia through the formation of a monolayer of surface vanadia species whose properties are related to the vanadia-titania interaction.

ACKNOWLEDGEMENTS

The experimental assistance of S. Cameron in obtaining the XPS data and J. Francis for providing the high surface area TiO_2(anatase) is greatly appreciated.

REFERENCES

1 S. J. Tauster, S. C. Fung, R. T. K. Baker, and J. A. Horsley, Science 211, 1121 (1981).
2 S. Soled, L. Murrell, I. Wachs, and G. McVicker, Div. Petrol. Chem., ACS 28, 1310 (1983).
3 D. Vanhove and M. Blanchard, Bull. Sci. Chim. Fr. 3291 (1971).
4 R. Grabowski, B. Grzybowska, J. Haber, and J. Sloczynski, Reaction Kinet. Catal. Lett., 2, 81 (1975).
5 G. C. Bond, J. Sarkany, and G. D. Parfitt, J. Catal. 57, 476 (1979).
6 Y. Murakami, M. Inomata, A. Miyamoto and K. Mori, "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980", p. 1344, Elsevier, Amsterdam (1981).
7 G. C. Bond and P. Konig, J. Catal. 77, 309 (1982).
G. C. Bond and K. Bruckman, Faraday Discussions, 72, 235 (1981).
8 M. S. Wainwright and N. R. Foster, Catal. Rev.-Sci. Eng. 19, 211 (1979).
9 A. Vejux and P. Courtine, J. Solid State Chem. 23, 93 (1978).
10 R. Kozlowski, R. F. Pettifer, and J. M. Thomas, J. Phys. Chem. 87, 5176 (1983).
11 M. Inomata, K. Mori, A. Miyamoto, T. Ul, and Y. Murakami, J. Phys. Chem. 87, 754 (1983).
12 C. D. Wagner, M. W. Riggs, L. E. Davis, J. Moulder, and G. E. Muilenberg, Handbook of X-Ray and Photoelectron Spectroscopy, Physical Electronics Industries (1979).
13 S. S. Chan, I. E. Wachs, and L. L. Murrell, J. Catal. (in press).
14 F. Roozeboom, J. Medema, and P. J. Gellings, Z. Phys. Chem. (Frankfurt am Main) 111, 215 (1978).
15 F. Roozeboom, M. C. Mittelmeijer-Hazeleger, J. A. Moulijn, J. Medema, V. H. J. de Beer, and P. J. Gellings, J. Phys. Chem. 84, 2783 (1980).
16 I. R. Beattie and T. R. Gilson, J. Chem. Soc. (A), 2322 (1969); Proc. Roy. Soc. A, 307, 407 (1968).
17 F. Roozeboom, T. Fransen, P. Mars, and P. J. Gellings, Z. Anorg. Allg. Chem. 449, 25 (1979).
18 R. J. Colton, R. J. Guzman, and J. W. Rabalais, J. Appl. Phys. 49, 409 (1978).
19 R. J. D. Tilley and B. G. Hyde, J. Phys. Chem. Solids 31, 1613 (1970).
20 A. J. Van Hengstum, J. G. Van Ommen, H. Bosch, and P. J. Gellings, Appl. Catal. 8, 369 (1983).
21 M. Gasior and T. Machej, J. Catal. 83, 472 (1983).
22 A. J. Van Hengstum, J. G. Van Ommen, H. Bosch, and P. J. Gellings, Appl. Catal. 5, 207 (1983).