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THE INTERACTION OF V_2O_5 WITH TiO_2(ANATASE): THE ACTIVE SITE FOR THE OXIDATION OF O-XYLENE TO PHTHALIC ANHYDRIDE

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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 surface vanadia species possess a higher activity and selectivity than crystalline V_2O_5 for this oxidation reaction. The unique properties of the surface vanadia species are related to the vanadia-titania interaction.

INTRODUCTION

V_2O_5 supported on TiO_2(anatase) is a superior catalyst for the selective oxidation of hydrocarbons than unsupported V_2O_5 (ref.1-5). For example, o-xylene is only selectively oxidized to phthalic anhydride when V_2O_5 is supported on TiO_2(anatase) (ref.6). The mechanism by which TiO_2(anatase) modifies the properties of the supported V_2O_5 phase is not well understood (ref.7-9). 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), temperature programmed reduction (TPR) and catalytic performance for o-xylene oxidation to phthalic anhydride.

EXPERIMENTAL

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 (Mobay Corporation; 8-9 m^2/g). The excess water was allowed to evaporate at ~65°C. The catalysts were subsequently dried at 110°C and calcined at 450°C for 2 hours. 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 12 kV 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 (ref.10). In situ XPS measurements could also be performed with this unit as described elsewhere (ref.11).

The Raman data were obtained with a multi-channel laser Raman spectrometer (ref.11). 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 OMA 2).

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 in a 10% H_2/helium mixture flowing at 50 cc/min. The samples were heated at 1°K/sec. by a nichrome 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 the TiO_2 support. The hydrogen consumption during the TPR experiment was monitored with a UTI mass spectrometer (100C).

The performance of the V_2O_5/TiO_2(anatase) catalysts for the oxidation of o-xylene (1.25 mole % in air; 2760 hr^{-1} space velocity) was examined in a fixed-bed reactor (0.5" OD; 316 stainless steel fitted with 0.125" thermowell at the center) in the temperature range 320-380°C. In order to maintain an isothermal profile the reactor was immersed in a molten salt bath (DuPont Hi Tech) and 1.92 gm of the V_2O_5/TiO_2(anatase) catalyst (0.4-0.7 mm diameter) was diluted with 4 parts of glass beads (0.5 mm diameter). The o-xylene feed was generated by bubbling air through o-xylene immersed in a water bath for control of the vapor pressure. An on-line multicolumn gas chromatograph, equipped with a thermal conductivity detector, was used for product analysis. The main products observed from the oxidation of o-xylene were phthalic anhydride, tolualdehyde, phthalide, maleic anhydride, CO, CO_2 and H_2O.

RESULTS AND DISCUSSION

The laser Raman spectra of a series of V_2O_5/TiO_2(anatase) samples are shown in Figure 1 as a function of vanadia 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

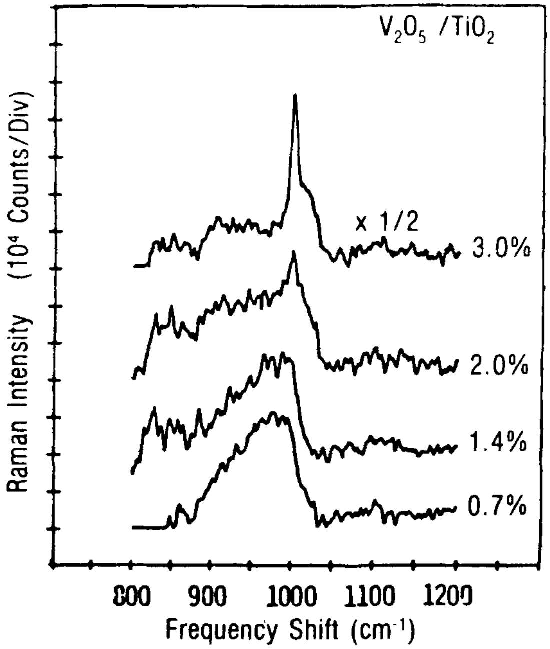
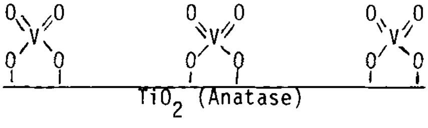


Fig. 1. Laser Raman Spectra of V_2O_5/TiO_2(Anatase) as a Function of V_2O_5 Content (Wt.%).

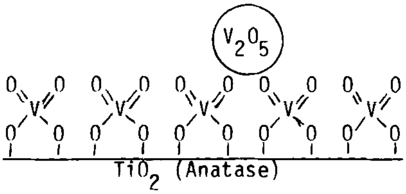
associated with the symmetrical stretching mode of the terminal oxygen atom (V=O) of crystalline V_2O_5 (ref.12). As the loading of V_2O_5 on TiO_2(anatase) is lowered, the sharp feature associated with V_2O_5 crystallites is replaced by a broad Raman band between 900-1000 cm^{-1}. This broad band is due to a surface vanadia species coordinated to the TiO_2(anatase) surface (ref.13). The broadening reflects the disordered state of the surface vanadia species on TiO_2(anatase). The amount of vanadia required to achieve a complete monolayer of the surface vanadia species on the TiO_2 support (8-9 m^2/g) may be estimated from the area occupied per $VO_{2.5}$ unit of crystalline V_2O_5 (0.105 nm^2) (ref.14), and corresponds to approximately 1.3% V_2O_5. The lowest loading of vanadia that exhibits the crystalline V_2O_5 Raman feature at 997 cm^{-1} is 2% V_2O_5/TiO_2(anatase). Thus, it appears that crystalline V_2O_5 formation occurs only after the TiO_2(anatase) surface is covered with a complete monolayer of the surface vanadia species. The preferred formation of the complete surface vanadia monolayer prior to the formation of crystalline V_2O_5 reflects the strong intraction between vanadia and the TiO_2(anatase) surface. At V_2O_5 loadings of 2% V_2O_5/TiO_2(anatase) and higher small crystallites of V_2O_5, not detectable by XRD until 7% V_2O_5/TiO_2(anatase), are present on the support in addition to the monolayer of the surface vanadia species.

The laser Raman spectroscopy data reveal that two states of vanadia can be present in V_2O_5/TiO_2(anatase) catalysts calcined at 450°C: a surface vanadia species and crystalline V_2O_5. The coordination of the surface vanadia species on TiO_2(anatase) 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 vanadia supported on TiO_2(anatase) concluded that the surface vanadia species has two terminal (1.65 ± 0.05Å) and two bridging bonds (1.90 ± 0.05Å) to oxygen and exhibits intrinsic disorder (ref.8). The model for the V_2O_5/TiO_2(anatase) system that emerges is depicted below.

Below Monolayer Coverage



Above Monolayer Coverage



Below monolayer coverage, less than 1.9% V_2O_5, only the surface vanadia species are present on the TiO_2(anatase) surface. Above monolayer coverage, above 1.9% V_2O_5, small crystallites of V_2O_5 are also present on the support in addition to the complete monolayer of the surface vanadia species.

The measured x-ray photoelectron spectroscopy V $2P_{3/2}$ binding energies for the V_2O_5/TiO_2(anatase) catalysts are independent of vanadia content, 517.3-517.4 eV, and correspond to vanadium in the +5 oxidation state. 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 (ref.9). In situ XPS reduction experiments with hydrogen at 450°C demonstrated that the supported V^{+5} is readily reducible to V^{+3} (binding energy of 515.6 eV (ref.15)). The reduction kinetics of the V_2O_5/TiO_2(anatase) samples and the unsupported V_2O_5 were examined with the temperature programmed reduction method. The TPR experiments reveal that the surface vanadia species and V_2O_5 crystallites supported on the TiO_2(anatase) surface reduce more readily than the unsupported, crystalline V_2O_5. Roozeboom et al. observed similar enhanced reduction for vanadia supported on a high surface area TiO_2 support (50 m^2/g; 65% anatase, 35% rutile) (ref.13).

The unsupported V_2O_5 and the V_2O_5/TiO_2(anatase) catalysts were examined for their catalytic performance for o-xylene oxidation. The reactivity and selectivity of the V_2O_5/TiO_2(anatase) catalysts towards o-xylene oxidation are very sensitive to vanadia content as shown in Figure 2. Below monolayer coverage of the surface vanadia species, 0 to 1.9% V_2O_5, the activity for o-xylene oxidation and selectivity towards C_8-oxygenates (phthalic anhydride, phthalide, and o-tolualdehyde) increase markedly with increasing vanadia content. The catalyst containing a monolayer of the surface vanadia species, 1.9% V_2O_5, is active and selective for the oxidation of o-xylene to the C_8-oxygenates. Thus, the surface vanadia species are active and selective for this oxidation reaction since crystalline V_2O_5 is not present in the 1.9% V_2O_5/TiO_2(anatase) catalyst. Furthermore, 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. Apparently exposed titania sites lead to complete combustion of the C_8-oxygenates since the TiO_2(anatase) support is not active for o-xylene oxidation (see Figure 2). Above monolayer coverage of vanadia, 1.9 to 7.0% V_2O_5, the activity and selectivity of this reaction are not as markedly influenced by the vanadia content. The relative insensitivity of this oxidation reaction to the presence of moderate amounts of crystalline V_2O_5 particles, 1.9 to 7.0% V_2O_5/TiO_2(anatase), suggests that the surface vanadia is the active site for the oxidation of o-xylene to phthalic anhydride. The minor role of the crystallized V_2O_5 phase 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 substantially diminished. At such high loadings of V_2O_5, the fraction of the vanadia present as surface vanadia is significantly lower than in the preceding catalysts, and the lower reactivity suggests that the supported, crystalline V_2O_5 phase is not very active for the o-xylene oxidation reaction. The unsupported V_2O_5 catalyst displays very low activity and selectivity for this oxidation reaction. The slightly 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, does not account for the much lower activity of the unsupported V_2O_5. Thus, crystalline V_2O_5 is not an effective catalyst for o-xylene oxidation.

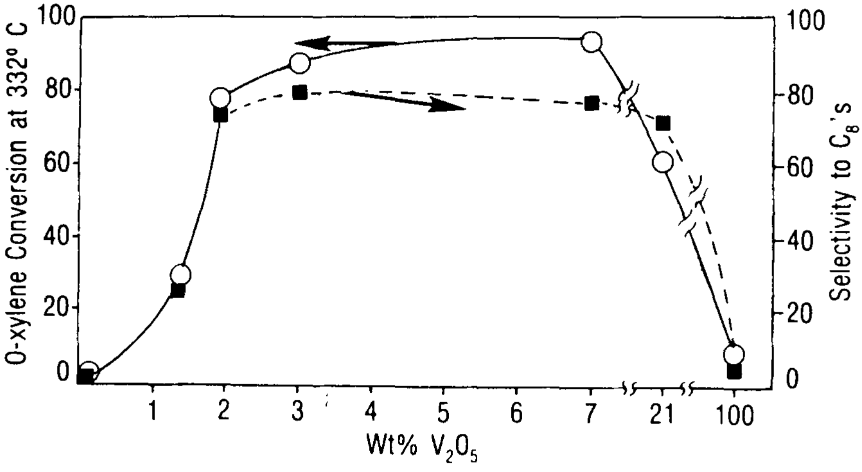


Fig. 2. Catalytic Performance of Unsupported V_2O_5 and V_2O_5/TiO_2(Anatase) Catalysts for the Oxidation of O-xylene.

The above data show that TiO_2(anatase) modifies the properties of V_2O_5 by forming a surface vanadia species coordinated to the TiO_2 support. The surface vanadia 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 for o-xylene oxidation to phthalic anhydride. Bond et al. reached similar conclusions in their kinetic investigation of o-xylene oxidation over V_2O_5/TiO_2(anatase) (ref.5). 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 unequivocally establishes the surface vanadia as 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, corresponds to a monolayer of the surface vanadia species, and that the presence of crystalline V_2O_5 is detrimental to catalytic performance. The present study demonstrates that moderate amounts of crystalline V_2O_5 do not adversely 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.

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 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 V_2O_5 through the formation of a monolayer of surface vanadia species whose properties are related to the vanadia-titania interaction.

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