

## The Interaction of $V_2O_5$ with $TiO_2$ (Anatase)

### II. Comparison of Fresh and Used Catalysts for *o*-Xylene Oxidation to Phthalic Anhydride

Two types of vanadia are present in fresh  $V_2O_5/TiO_2$ (anatase) catalysts calcined at 450°C: surface vanadia coordinated to the  $TiO_2$  support and small crystallites of  $V_2O_5$  (1, 2). The surface vanadia is the active site for the oxidation of *o*-xylene to phthalic anhydride (1, 3, 4). The surface vanadia is more active and selective than the  $V_2O_5$  crystallites for the *o*-xylene oxidation reaction (1). The unique properties of the surface vanadia species are related to the vanadia-titania interaction. The influence of the *o*-xylene oxidation reaction upon the two types of vanadia in  $V_2O_5/TiO_2$ (anatase) catalysts is examined here. The fresh and used  $V_2O_5/TiO_2$ (anatase) catalysts for *o*-xylene oxidation to phthalic anhydride were characterized by laser Raman spectroscopy, temperature-programmed reduction, and X-ray diffraction.

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, 9 m<sup>2</sup>/g). The excess water was evaporated at ~65°C, the catalysts were dried overnight at 110°C, and calcined in flowing oxygen at 450°C for 2 h. These fresh catalysts were examined for their catalytic performance for the oxidation of *o*-xylene (1.25 mole% in air) to phthalic anhydride in a fixed-bed reactor (320–350°C) for several days (1). The reactor was purged with nitrogen upon completion of the *o*-xylene oxidation reaction and removed from the salt bath at the reaction temperature. Independent thermal gravimetric analysis revealed that the  $V_2O_5/$

$TiO_2$ (anatase) system was stable in nitrogen environments up to 575°C. This removal procedure, as well as the subsequent handling in air, resulted in partial reoxidation of the used  $V_2O_5/TiO_2$ (anatase) catalysts. However, as shown below, the used catalysts were still sufficiently altered by the *o*-xylene oxidation reaction that significant differences existed between the fresh and used catalysts.

The Raman data were obtained with a multichannel laser Raman spectrometer (1). An argon-ion laser (Spectra Physics, Model 1650) 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 consisted of a triple monochromator (Instruments SA, Model DL203) that was coupled to an optical multichannel analyzer (Princeton Applied Research, Model OMA 2).

The reducibility of the vanadia catalysts was determined by temperature-programmed reduction. About 100 mg of sample was supported on a fritted disk in a quartz tube (¼ in. o.d.). The samples were reduced in a 10%  $H_2$ /helium mixture flowing at 50 cm<sup>3</sup>/min. The samples were heated at ~1°C/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-100C mass spectrometer.

X-Ray diffraction patterns were obtained

with a Philips diffractometer using  $\text{CuK}\alpha$  radiation and a diffracted-beam monochromator.

The  $\text{TiO}_2$  support of the  $\text{V}_2\text{O}_5/\text{TiO}_2(\text{anatase})$  catalysts was not altered by the *o*-xylene oxidation reaction. X-Ray diffraction analysis of the spent  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalysts exhibited the  $\text{TiO}_2(\text{anatase})$  phase, and  $\text{TiO}_2$  (rutile) was not present. The surface areas of the spent  $\text{V}_2\text{O}_5/\text{TiO}_2(\text{anatase})$  catalysts were also not affected by the reaction environment. However, some of the vanadia in the  $\text{V}_2\text{O}_5/\text{TiO}_2(\text{anatase})$  catalysts was reduced by the reaction environment because the spent catalysts possessed a much darker color than the fresh catalysts.

The laser Raman difference spectra, corrected for the  $\text{TiO}_2(\text{anatase})$  background, of fresh and spent 1.9%  $\text{V}_2\text{O}_5/\text{TiO}_2(\text{anatase})$  catalysts, containing approximately a monolayer of the surface vanadia species on the  $\text{TiO}_2$  support (1), are shown in Fig. 1. The fresh and spent catalysts exhibit the broad Raman band between 850 and 1050  $\text{cm}^{-1}$  characteristic of surface vanadia. The temperature-programmed reduction spectra of the same two catalysts are presented in Fig. 2. The fresh and spent catalysts ex-

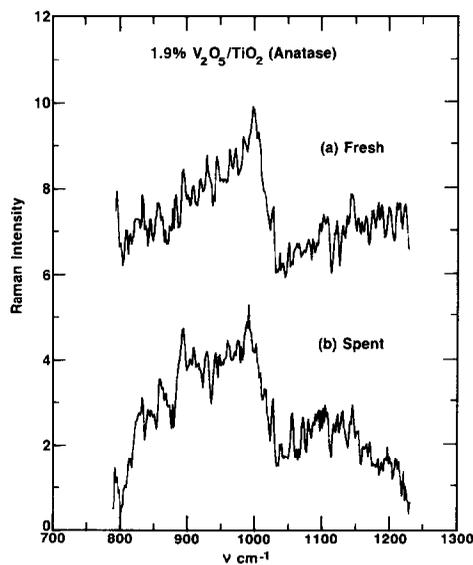


FIG. 1. Laser Raman difference spectra of 1.9%  $\text{V}_2\text{O}_5/\text{TiO}_2(\text{anatase})$  catalysts: (a) fresh and (b) spent.

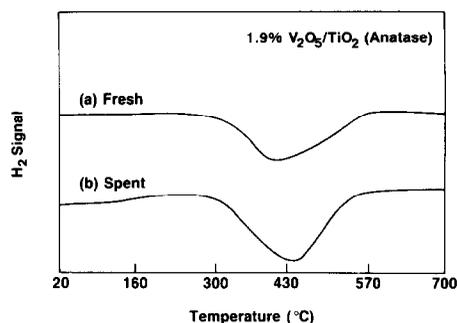


FIG. 2. Temperature-programmed reduction spectra of 1.9%  $\text{V}_2\text{O}_5/\text{TiO}_2(\text{anatase})$  catalysts: (a) fresh and (b) spent.

hibit the TPR peak at  $\sim 430^\circ\text{C}$  characteristic of surface vanadia. X-Ray diffraction of these 1.9%  $\text{V}_2\text{O}_5/\text{TiO}_2(\text{anatase})$  samples does not give rise to any vanadia XRD peaks since the surface vanadia phase is not crystalline. Thus, it appears that the surface vanadia species on the  $\text{TiO}_2$  support are essentially in the same state in the fresh and spent  $\text{V}_2\text{O}_5/\text{TiO}_2(\text{anatase})$  catalysts.

The laser Raman spectra, uncorrected for the  $\text{TiO}_2(\text{anatase})$  background, of fresh and spent 7.0%  $\text{V}_2\text{O}_5/\text{TiO}_2(\text{anatase})$  catalysts, containing both a monolayer of the surface vanadia species on the  $\text{TiO}_2$  support and crystallites of  $\text{V}_2\text{O}_5$ , are shown in Fig. 3. The laser Raman spectrum of the fresh 7.0%  $\text{V}_2\text{O}_5/\text{TiO}_2(\text{anatase})$  sample exhibits a small Raman band at 794  $\text{cm}^{-1}$  due to the anatase support, and a sharper Raman band at 997  $\text{cm}^{-1}$  associated with the symmetric stretch of terminal  $\text{V}=\text{O}$  in crystalline  $\text{V}_2\text{O}_5$  (5). The crystalline  $\text{V}_2\text{O}_5$  Raman bands at 704, 485, 307, and 287  $\text{cm}^{-1}$  are also observed for the 7.0%  $\text{V}_2\text{O}_5/\text{TiO}_2(\text{anatase})$  sample. The laser Raman spectrum of the spent 7.0%  $\text{V}_2\text{O}_5/\text{TiO}_2(\text{anatase})$  sample does not exhibit the sharp Raman band at 997  $\text{cm}^{-1}$  associated with crystalline  $\text{V}_2\text{O}_5$ . Crystalline  $\text{V}_2\text{O}_4$  and  $\text{V}_2\text{O}_3$  do not possess Raman bands in the region 750–1200  $\text{cm}^{-1}$ , and the very weak Raman signals from these vanadium oxide phases cannot be distinguished from the strong  $\text{TiO}_2(\text{anatase})$  Raman bands below 750  $\text{cm}^{-1}$  (6). The  $\text{TiO}_2(\text{anatase})$  band at 794  $\text{cm}^{-1}$  is weaker

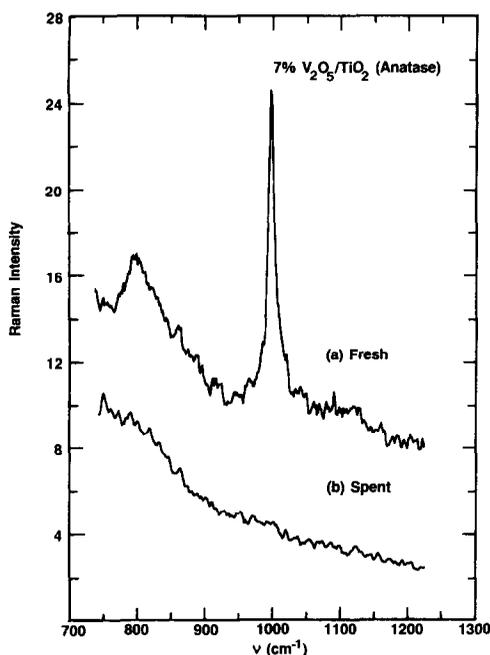


FIG. 3. Laser Raman spectra of 7.0%  $V_2O_5/TiO_2$ (anatase) catalysts: (a) fresh and (b) spent.

for the spent  $V_2O_5/TiO_2$ (anatase) catalyst than for the fresh  $V_2O_5/TiO_2$ (anatase) catalyst because of the increase in the optical absorbance of the darker spent catalyst which decreases the sampling depth of the catalyst wafer by the laser. The temperature-programmed reduction spectra of the same two catalysts are presented in Fig. 4. The fresh catalyst exhibits TPR peaks at  $\sim 350$  and  $\sim 430^\circ C$  characteristic of  $V_2O_5$  crystallites and surface vanadia, respectively (1). The spent catalyst exhibits TPR peaks at  $\sim 430$  and  $\sim 570^\circ C$ . The TPR peak at  $\sim 350^\circ C$ , which is characteristic of  $V_2O_5$  crystallites, is not present in the spent 7.0%  $V_2O_5/TiO_2$ (anatase) catalyst. The TPR peak at  $\sim 425^\circ C$  reveals that the surface vanadia is present in the spent catalyst, and the new TPR peak at  $\sim 500^\circ C$  is indicative of an additional state of vanadia. X-Ray diffraction of these 7.0%  $V_2O_5/TiO_2$ (anatase) samples exhibits the presence of crystalline  $V_2O_5$  in the fresh sample and significant amounts of  $V_2O_4$  for the spent sample. Thus, it appears that the crystallized vanadia phase in  $V_2O_5/TiO_2$ (anatase) catalysts is present as  $V_2O_5$  in fresh catalysts and is partially reduced in spent catalysts.

The above comparison of fresh and spent  $V_2O_5/TiO_2$ (anatase) catalysts for *o*-xylene oxidation to phthalic anhydride demonstrates that the vanadia in the spent catalysts is partially reduced by the reaction environment. Gasior and Grzybowska also found that the vanadium oxide in  $V_2O_5/TiO_2$ (anatase) catalysts is reduced during *o*-xylene oxidation (7). The more extensive reduction of the  $V_2O_5/TiO_2$ (anatase) catalysts in the present study is a consequence of the much higher concentration of *o*-xylene in air employed. The spent  $V_2O_5/TiO_2$ (anatase) catalysts remained reduced even though the spent samples had ample opportunity to be oxidized by the ambient environment prior to characterization. The analysis of the spent catalysts reveals that the crystalline vanadia phase is reduced by the *o*-xylene oxidation reaction conditions. The crystalline vanadia phase remained reduced in the ambient environment because elevated temperatures are required to activate the diffusion of oxygen atoms into the crystalline vanadia lattice. The surface vanadia species coordinated to the  $TiO_2$  support, however, were found to be oxidized in the spent  $V_2O_5/TiO_2$ (anatase) catalysts. The surface vanadia was most probably also partially reduced by the *o*-xylene

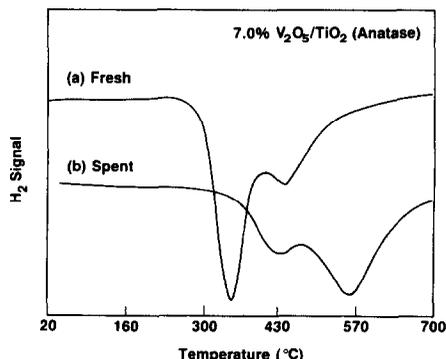


FIG. 4. Temperature-programmed reduction spectra of 7.0%  $V_2O_5/TiO_2$ (anatase) catalysts: (a) fresh and (b) spent.

oxidation reaction, but was oxidized by the ambient environment prior to characterization. The more facile oxidation of the surface vanadia is probably related to the fact that, unlike crystalline vanadia, every surface vanadia is exposed to the environment. The facile oxidation of the surface vanadia probably accounts for the fast redox cycle on this site during the oxidation of *o*-xylene to phthalic anhydride over  $V_2O_5/TiO_2$ (anatase) catalysts.

Two types of vanadia are present in fresh  $V_2O_5/TiO_2$ (anatase) catalysts calcined at 450°C: surface vanadia coordinated to the  $TiO_2$  support and small crystallites of  $V_2O_5$ . During the oxidation of *o*-xylene to phthalic anhydride the supported vanadia is partially reduced by the reaction conditions. The  $V_2O_5$  crystallites are partially reduced under the present experimental conditions. The surface vanadia species are most probably also partially reduced by the reaction environment, but are reoxidized by their exposure to air prior to the analysis.

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