Applications of Surface Science 20 (1984) 181–185
North-Holland, Amsterdam

COMMUNICATION

IN SITU CHARACTERIZATION OF SMALL V_2O_5 CRYSTALLITES SUPPORTED ON TiO_2(ANATASE)

Israel E. WACHS and Shirley S. CHAN *

Corporate Research – Science Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey 08801, USA

Received 21 June 1984; accepted for publication 20 August 1984

Many multicomponent oxide systems consist of one oxide phase supported on the surface of another oxide phase. Such oxide systems find applications as heterogeneous catalysts [1,2], photocatalysts [3], electrochemical electrodes [4], pigments [5], etc. To date, very few high temperature laser Raman studies have been conducted on the behavior of small oxide particles supported on a second oxide phase. In the present study, the behavior of small V_2O_5 crystallites supported on TiO_2(anatase) was examined in situ with laser Raman and X-ray photoelectron spectroscopies under oxidizing and reducing environments at elevated temperatures.

The V_2O_5/TiO_2(anatase) sample was prepared by dissolving V_2O_5 in an aqueous solution of oxalic acid, and impregnating the TiO_2 (Mobay, 8–9 m^2/g) support. The material was dried at ~ 65°C, heated overnight at 110°C, and calcined in flowing oxygen at 450°C for 2 h. The V_2O_5 content was adjusted to yield 7% V_2O_5 and 93% TiO_2 in the finished oxide.

X-ray diffraction patterns were obtained with a Philips diffractrometer using Cu Kα radiation and a diffracted beam monochromator.

The Raman spectrometer was a triple monochromator (Instruments SA, Model DL 203) coupled to an optical multi-channel analyzer (Princeton Applied Research, Model OMA2) equipped with an intensified photodiode array detector cooled to −15°C. 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 in the range 0.4–40 mW by adding or removing neutral density filters. A sample chamber was designed which was capable of sample spinning and in situ treatments. The sample was heated by a cylindrical heater coil surrounding the chamber, and the temperature was determined with an internal thermocouple. The chamber was capable of operating up to 600°C.

---

* Current address: Technical Center, The BOC Group, 100 Mountain Avenue, Murray Hill, New Jersey 07974, USA.

X-ray photoelectron spectroscopy (XPS) 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. In situ XPS reduction measurements could also be performed with this unit via a reactor furnace directly attached to the ultrahigh vacuum chamber. This arrangement allowed the transfer of the catalyst sample from the reactor to the XPS chamber in UHV. The base pressure of the XPS

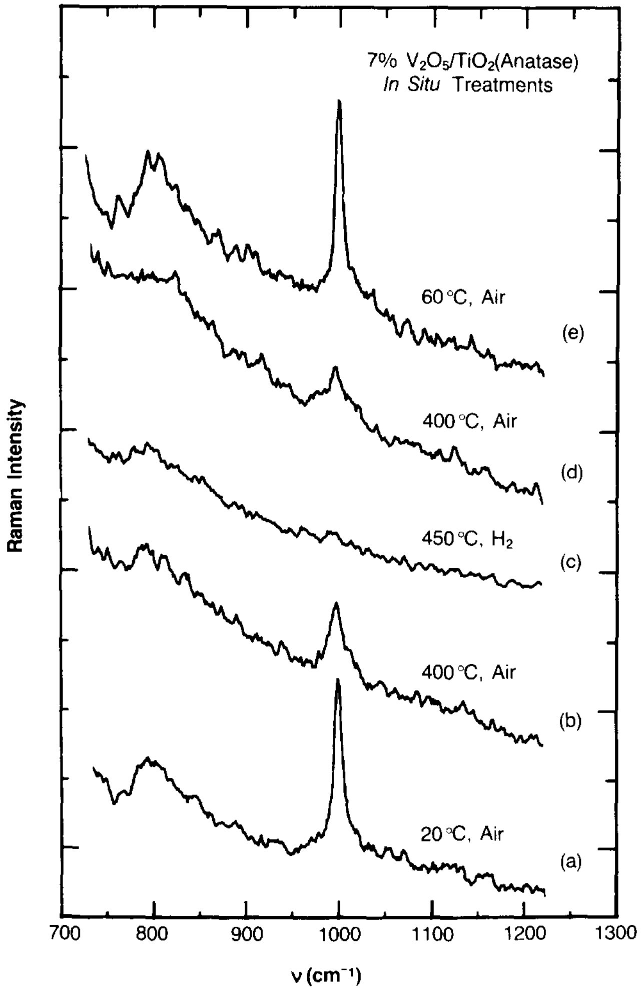

Fig. 1. In situ laser Raman spectra of 7% V_2O_5/TiO_2(anatase): (a) 20°C, Air; (b) 400°C, Air; (c) 450°C, H_2; (d) 400°C, Air; and (e) 60°C, Air.

chamber was usually in the 10^{-10} Torr range. The reduction of the V_2O_5/TiO_2 samples was performed by heating the samples in flowing H_2 (26 SCCM) in the reactor section, maintaining the samples at 450°C for 5 min, cooling the samples and transferring the catalysts in vacuum to the XPS chamber.

The small V_2O_5 crystallites could barely be detected with X-ray diffraction. The relative X-ray diffraction peak intensities of the V_2O_5 crystallites deviated from that of large V_2O_5 particles and suggested that the small V_2O_5 crystallites, ~ 100 Å, were somewhat distorted on the TiO_2(anatase) surface. The in situ laser Raman spectra of the V_2O_5 crystallites on the TiO_2(anatase) are shown in fig. 1 for the range 750–1250 cm^{-1}. Fig. 1a exhibits the laser Raman spectrum of the V_2O_5 crystallites on TiO_2(anatase) at room temperature. The laser Raman spectrum possesses a small, broad Raman band at 794 cm^{-1} due to TiO_2(anatase) [6], and a sharper Raman band at 997 cm^{-1}. The Raman band at 997 cm^{-1} is associated with crystalline V_2O_5, see fig. 2, and is due to the symmetric stretch of the terminal V=O in the crystalline V_2O_5 structure [6].

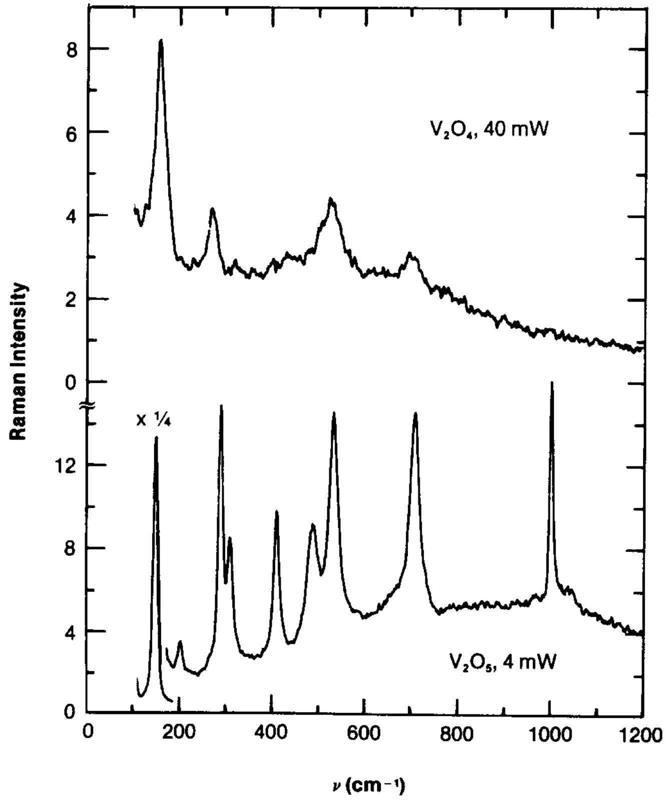

Fig. 2. Laser Raman spectra of V_2O_5 and V_2O_4.

This Raman band is unique to V_2O_5 and is not present in lower oxides of vanadia since they do not possess a terminal oxygen; see fig. 2 for Raman spectrum of V_2O_4. The crystalline V_2O_5 Raman bands at 704, 485, 307, and 287 cm^{-1} were also observed for the V_2O_5/TiO_2(anatase) sample.

Heating the V_2O_5/TiO_2 oxide system to 400°C in flowing air causes a decrease in intensity and broadening of the crystalline V_2O_5 Raman band at 997 cm^{-1}. The weak TiO_2(anatase) Raman band at 794 cm^{-1} also broadens at these elevated temperatures. These changes are due to thermal broadening of the Raman bands as a result of the change in the density of states at this elevated temperature. Moreover, the thermal effect does not shift the band frequency. The thermal broadening is especially pronounced for the V_2O_5 crystallites on the TiO_2(anatase) surface because of the close approach to the melting temperature of bulk V_2O_5 (T_m = 690°C). Replacing the flowing air with flowing hydrogen at 450°C completely removes the broad V_2O_5 Raman band at 997 cm^{-1}, see fig. 1c. Apparently the V_2O_5 crystallites on TiO_2(anatase) reduced to lower oxides of vanadium. Parallel in situ X-ray photoelectron spectroscopy studies confirmed the reduction of the V_2O_5 crystallites as shown in table 1. The V $2p_{3/2}$ binding energy for the unreduced V_2O_5/TiO_2(anatase) sample occurs at 517.3 eV and is consistent with vanadium in the +5 oxidation state [7]. Reduction of the V_2O_5/TiO_2(anatase) sample at 450°C yields a V $2p_{3/2}$ binding energy of 515.6, which is consistent with vanadium in the +3 oxidation state [7]. Bulk V_2O_3, however, is black and does not give rise to a Raman spectrum. Thus, the loss in the Raman band at 997 cm^{-1} upon reduction at 450°C is due to the reduction of the V_2O_5 crystallites to V_2O_3 crystallites on the TiO_2(anatase) surface.

Replacing the flowing hydrogen with flowing air at 400°C restores the broad Raman band at 997 cm^{-1}, see fig. 1d. Apparently the small V_2O_3 crystallites on TiO_2(anatase) are easily oxidized back to V_2O_5 crystallites. Cooling the V_2O_5/TiO_2(anatase) sample in flowing air back to 60°C restores the sharp V_2O_5 Raman band at 997 cm^{-1}, see fig. 1e, because of the reduction of thermal broadening at this milder temperature. Thus, the entire cycle of heating, reduction, reoxidation and cooling is reversible for V_2O_5 crystallites supported on TiO_2(anatase) over the temperature range investigated.

Table 1
XPS of V_2O_5 on TiO_2(anatase)

	V $2p_{3/2}$ (eV)	O 1s (eV)
Bulk V_2O_5 [a]	517.4	530.2
7% V_2O_5/TiO_2(anatase), 450°C, O_2 [b]	517.3	529.9
7% V_2O_5/TiO_2(anatase), 450°C, H_2 [b]	515.6	530.0

[a] Referenced to C 1s peak at 284.6 eV.

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

The behavior of small V_2O_5 crystallites supported on TiO_2(anatase) was examined in situ under oxidizing and reducing environments at elevated temperatures with laser Raman spectroscopy and X-ray photoelectron spectroscopy. At elevated temperatures, the small V_2O_5 crystallites on TiO_2(anatase) are readily reduced to V_2O_3 crystallites in hydrogen and reoxidized to V_2O_5 crystallites in flowing air. Similar studies with other supported oxide systems will provide much information about the properties of such small oxide crystallites and the influence of the support upon tbe behavior of oxide crystallites.

The authors greatly appreciate the assistance of S. Cameron in obtaining the XPS data and C.C. Chersich for the preparation of the V_2O_5/TiO_2(anatase) sample.

References

[1] Y. Murakami, M. Inomata, A. Miyamoto and K. Mori, in: Proc. 7th Intern. Congr. on Catalysis, Tokyo, 1980 (Elsevier, Amsterdam, 1981) p. 1344.

[2] I.E. Wachs, S.S. Chan, C.C. Chersich and R.Y. Saleh, in: Proc. 9th Canadian Symposium on Catalysis, Quebec, 1984 (Elsevier, Amsterdam, 1984) p. 275.

[3] L.V. Lyashenko, V.M. Belousov and F.A. Yampol'skaya, Kinetika Kataliz 23 (1982) 622.

[4] L.R. Faulkner, Chem. Eng. News 62 (2) (1984) 28.

[5] R.E. Day, Progr. Org. Coatings 2 (1973) 269.

[6] I.R. Beattie and T.R. Gilson, J. Chem. Soc. A (1969) 2322; Proc. Roy. Soc. (London) A307 (1968) 407.

[7] R.J. Colton, R.J. Guzman and J.W. Rabalais, J. Appl. Phys. 49 (1978) 409.