COMMUNICATION

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

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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 diffractometer using Cu Ka 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.

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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$_2$O$_5$/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$_2$O$_5$/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$_2$O$_5$ crystallites could barely be detected with X-ray diffraction. The relative X-ray diffraction peak intensities of the V$_2$O$_5$ crystallites deviated from that of large V$_2$O$_5$ particles and suggested that the small V$_2$O$_5$ crystallites, ~100 Å, were somewhat distorted on the TiO$_2$(anatase) surface. The in situ laser Raman spectra of the V$_2$O$_5$ 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$_2$O$_5$ 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$_2$O$_5$, see fig. 2, and is due to the symmetric stretch of the terminal V=O in the crystalline V$_2$O$_5$ structure [6].

![Laser Raman spectra of V$_2$O$_5$ and V$_2$O$_4$.](image)

Fig. 2. Laser Raman spectra of V$_2$O$_5$ and V$_2$O$_4$. 
This Raman band is unique to V$_2$O$_5$ 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$_2$O$_4$. The crystalline V$_2$O$_5$ Raman bands at 704, 485, 307, and 287 cm$^{-1}$ were also observed for the V$_2$O$_5$/TiO$_2$(anatase) sample.

Heating the V$_2$O$_5$/TiO$_2$ oxide system to 400°C in flowing air causes a decrease in intensity and broadening of the crystalline V$_2$O$_5$ 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$_2$O$_5$ crystallites on the TiO$_2$(anatase) surface because of the close approach to the melting temperature of bulk V$_2$O$_5$ ($T_m = 690°C$). Replacing the flowing air with flowing hydrogen at 450°C completely removes the broad V$_2$O$_5$ Raman band at 997 cm$^{-1}$, see fig. 1c. Apparently the V$_2$O$_5$ 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$_2$O$_5$ crystallites as shown in table 1. The V 2p$_{3/2}$ binding energy for the unreduced V$_2$O$_5$/TiO$_2$(anatase) sample occurs at 517.3 eV and is consistent with vanadium in the +5 oxidation state [7]. Reduction of the V$_2$O$_5$/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$_2$O$_3$, 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$_2$O$_5$ crystallites to V$_2$O$_3$ 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$_2$O$_3$ crystallites on TiO$_2$(anatase) are easily oxidized back to V$_2$O$_5$ crystallites. Cooling the V$_2$O$_5$/TiO$_2$(anatase) sample in flowing air back to 60°C restores the sharp V$_2$O$_5$ 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$_2$O$_5$ crystallites supported on TiO$_2$(anatase) over the temperature range investigated.

Table 1
XPS of V$_2$O$_5$ on TiO$_2$(anatase)

<table>
<thead>
<tr>
<th></th>
<th>V 2p$_{3/2}$ (eV)</th>
<th>O 1s (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk V$_2$O$_5$</td>
<td>517.4</td>
<td>530.2</td>
</tr>
<tr>
<td>7% V$_2$O$_5$/TiO$_2$(anatase), 450°C, O$_2$</td>
<td>517.3</td>
<td>529.9</td>
</tr>
<tr>
<td>7% V$_2$O$_5$/TiO$_2$(anatase), 450°C, H$_2$</td>
<td>515.6</td>
<td>530.0</td>
</tr>
</tbody>
</table>

$^a$ 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$_2$O$_5$ 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$_2$O$_5$ crystallites on TiO$_2$ (anatase) are readily reduced to V$_2$O$_3$ crystallites in hydrogen and reoxidized to V$_2$O$_5$ 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 the behavior of oxide crystallites.

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References