INFLUENCE OF THE OXIDE MATRIX ON THE ELECTRONIC STATE OF VANADIUM IONS

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ESCA spectra of V$_2$O$_5$, V$_2$O$_5$/TiO$_2$ and V$_2$O$_5$ dissolved in TiO$_2$ were recorded after oxidation and reduction. V$^{4+}$ ions have the same effective charge in reduced V$_2$O$_5$ and in TiO$_2$, whereas the effective charge of V$^{5+}$ ions in TiO$_2$ is higher than in V$_2$O$_5$, indicating enhanced electron acceptor properties.

The V$_2$O$_5$-TiO$_2$ system is well known for its activity and selectivity in the oxidation of o-xylene to phthalic anhydride. It has been found /1/ that a solid solution of V$_2$O$_5$ in TiO$_2$ is formed in the course of the preparation of the active catalyst. The question may be raised as to whether there is a difference in the electronic state of vanadium ions in V$_2$O$_5$ supported on TiO$_2$ and those dissolved in TiO$_2$ forming a solid solution, and whether this influences the behavior of these ions in redox processes. X-ray photoelectron spectroscopy was applied to answer this question.

EXPERIMENTAL

A Vacuum Generators ESCA-3 apparatus was used with X-ray excitation from the Al/1486.6 eV source. Powdered oxide samples were deposited from an acetone suspension of a finely ground powder onto the sample holder. The samples were
outgassed and then reduced progressively "in situ" in the spectrometer by heating in vacuum for different periods of time.

$V_2O_5$ spectra were calibrated against the Cls peak position (285.0 eV). It has been found for all samples containing titania that the Ti 2p$_{3/2}$ peak position is stable and unaffected by reducing conditions. The distance between Ti 2p$_{3/2}$ and 01s peaks was constant and amounted to 71.6±0.1 eV. Thus it seemed justified to use the Ti 2p$_{3/2}$ peak as reference, assuming its binding energy to be 459.4 eV /2/.

RESULTS AND DISCUSSION

Figure 1 shows spectra of V2p$_{3/2}$ and 01s electrons from a sample of a solid solution of $V_2O_5$ in TiO$_2$ recorded in the course of its gradual reduction by heating in vacuum. After reduction at 100–450 °C a new line appears on the lower BE side of the V2p$_{3/2}$ peak with a maximum at 527.2 eV. This value, after correction by 1.4 eV, allowing for the difference in the position of 01s peaks, taken as the reference, is in good agreement with the value of 515.7 eV quoted for VO$_2$ /3,4/. This indicates that V$^{4+}$ ions formed in the course of the reduction of a solid solution in TiO$_2$ are characterized by the same effective charge as when present in VO$_2$.

This is not the case with the oxidized samples (Fig. 2). The values of BE for both oxidized and reduced samples are summarized in Table 1.

It may be noticed that the spectrum of $V_2O_5$ supported on TiO$_2$ is identical to that of pure $V_2O_5$, indicating that the $V_2O_5$/TiO$_2$ sample consists of a heterogeneous mixture of $V_2O_5$ and TiO$_2$. In the case of a solid solution of V$^{5+}$ in TiO$_2$ the V2p BE value is higher than for V$^{5+}$ ions in $V_2O_5$ and amounts to 518.5 eV. This indicates that the effective charge of V$^{5+}$ ions incorporated into the TiO$_2$ lattice is higher than in the $V_2O_5$ lattice, pointing to a distinct matrix effect. It may be related to the fact that the metal-oxygen distances in TiO$_2$ are considerably longer than those in $V_2O_5$. 

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