IN SITU OBSERVATION OF THE THERMAL DECOMPOSITION OF DIVANADIUM PENTOXIDE V_2O_5 IN TEM

D.S. Su*, M. Hävecker, A. Blume, R. Schlögl

Department of Inorganic Chemistry, Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, D-14195 Berlin, Germany

The reduction behaviours and phase transition of vanadium oxides at various temperatures have been well studied previously [1,2]. This is due to the fact that reduction and phase transition are phenomena accompanied in almost all the catalytic process using vanadium oxide based catalysts. A great deal of work has been carried out to study the surface reduction of V_2O_5. For instance, a V_2O_5-V_6O_{13} transformation is reported at the V_2O_5 (001) surface by heating V_2O_5 (500°C) in O_2 atmosphere (5 x 10^{-4} Torr, 1h) [1]. Cleaved V_2O_5 (001) surface can also be reduced to the V_6O_{13} (001) surface by a long term exposure to an electron beam in a LEED chamber [2]. In the present work, we investigate the thermal decomposition of V_2O_5 in a specimen chamber of a transmission electron microscope (TEM) that allowing the *in situ* electron diffraction, high-resolution imaging and electron energy-loss spectroscopic characterisation of the transformation. For comparison, we studied also the thermal decomposition of V_2O_5 in sealed glass tube and in a thermal decomposition spectrometer (TDS).

A heating stage was used for the thermal decomposition of V_2O_5 in TEM. The high vacuum of the specimen chamber was kept beneath 10^{-7} Torr. The sample was heated to 200, 400, 500, and 600°C with a heating rate of 20°C/min and kept for one hour at each temperature, respectively. A Philips CM200 FEG electron microscope, operating at 200 kV and equipped with a GATAN imaging filter GIF100, was used. Thermal decompositions of the V_2O_5 in sealed glass tube were performed at 200, 400 and 550°C at 2 x 10^{-4} mbar for 12 h. Experiment in TDS was performed at 10^{-7} Torr with a heating rate of 20 K/min up to 600 °C.

The thermal decomposition in sealed glass tube proceeds very slowly. Even heating at 550 °C for 12 h causes only slightly change of the sample callous. However, the decomposition in TEM goes very fast. Fig. 1 shows the vanadium *L* and oxygen *O* edges, extracted from EEL-spectra recorded from V_2O_5 unheated and heated at 200, 400, 500, 600°C. The initial spectrum is typical for V_2O_5 in orthorhombic structure, characterised by the V *L*-edges at 519 and 526.7 eV and O *K*-edge above 530 eV. Heating the V_2O_5 sample two remarkable changes in the spectra can be noticed: the vanadium *L* edges shifted to lower energy and the integral intensity of oxygen *K* edge decrease indicating a preferable release of oxygen during the thermal decomposition. The peak energy of L_3 edge of vanadium shift to 518.3 eV at 400°C, which is very close to the peak position of VO_2 at 518.5 eV. The maximum of this peak shifts to 517.4 eV at 600°C, corresponding to the energy of the L_3 edge maximum of V_2O_3.

An electron diffraction pattern taken at 500°C from a thin sample flake is shown in Fig.2A. Before the heating, the diffraction pattern contains regularly arranged spots of single crystal V_2O_5. The pattern in Fig. 2A stems from randomly oriented crystallites

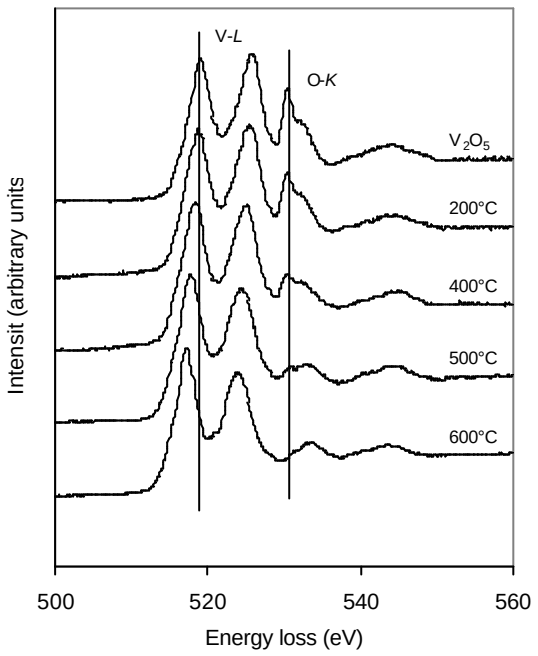

Fig.1 Vanadium L and oxygen K edges taking at various temperatures in a Philips CM200 FEG TEM, after background and multiple scattering correction

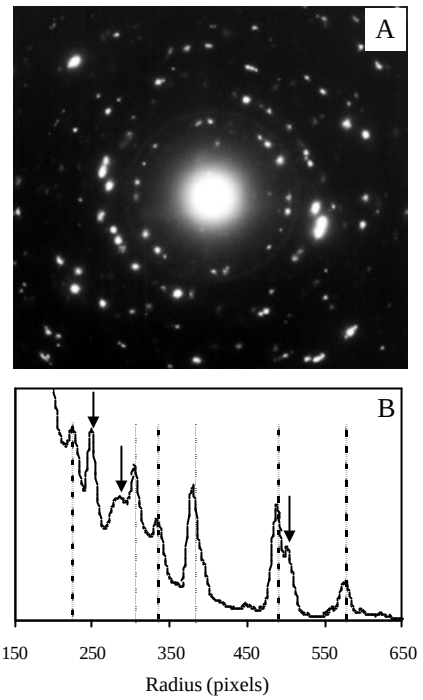

Fig. 2 Electron diffraction pattern (A) taken at 500°C and ist rotationally integrated profiles (B). Lined peaks are identified as from V_2O_3 and arrowed peaks are from VO_2.

formed through thermal decomposition. This indicates that the phase transition does not take place tropotactically. Fig.2B shows the rotationally integrated profile of this pattern. The peaks marked with lines can be identified as the ones of V_2O_3 in corundum structure and the peaks marked with arrows are the ones of VO_2 in rutile structure. No peaks due to V_2O_5 could be detectable. Therefore we have a mixture of V_2O_3 with VO_2 at 500°C. Further heating the sample to 600°C, the diffraction patterns from very thin crystallites can be identified uniquely as from V_2O_3, while the patterns from large crystallites still contain rest intensities from VO_2. With prolonged heating of the sample at 600°C to several hours, no further reduction of V_2O_3 could be observed. Therefore, we can conclude that under the given conditions, V_2O_5 undergoes a phase transformation via VO_2 into V_2O_3.

We present in this preliminary report on the thermal decomposition of V_2O_5 in low and high vacuum. In low vacuum, the decomposition proceeds very slowly. In high vacuum V_2O_5 undergoes a phase transformation to V_2O_3 via VO_2 in just few hours. TDS experiment confirms the loss of oxygen from the bulk of the sample.

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Reference
1. K. Devriendt, H. Poelman, L. Fiermans, Surf. Sci. 433-435 (1999) 734.
2. L. Fiermans, and J. Vennik, Surf. Sci. 9 (1968) 187.

Email: dangsheng@fhi-berlin.mpg.de