

Thermal decomposition of divanadium pentoxide V_2O_5 in vacuum

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Introduction

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 (5×10^{-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).

Experimental

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. Fine V_2O_5 crystals were dispersed onto a copper mesh grid covered with a holey carbon film and allowed to dry. 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 2×10^{-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.

Result

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 . Electron diffraction confirms that V_2O_5 undergoes a phase transformation via VO_2 into V_2O_3 . High-resolution images reveal the formation of single crystalline V_2O_3 nano-particles with quite different morphology. TDS results show the release of oxygen atoms from the heated samples.

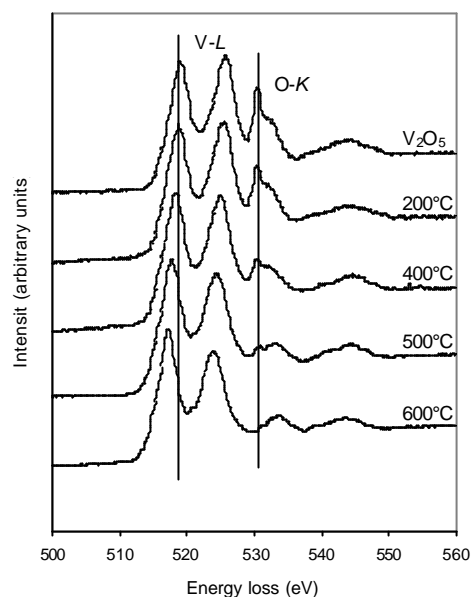


Fig.1 Vanadium L and oxygen K edges taking at various temperatures in a Philips CM 200 FEG electron microscope.

Summary

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. V_2O_3 nano-particles form which are single crystalline. TDS experiment confirms the loss of oxygen from the bulk of the sample.

Acknowledgement

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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.