



## Thermal decomposition of divanadium pentoxide $V_2O_5$ : Towards a nanocrystalline $V_2O_3$ phase

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### Abstract

Thermal decomposition of  $V_2O_5$  was studied by means of transmission electron microscopy (TEM) and electron energy-loss spectroscopy (EELS). Samples were heated in a specimen chamber of an electron microscope up to 600 °C in vacuum at  $10^{-7}$  Torr. TEM and EELS reveal a sequence of transformations from  $V_2O_5$  via  $VO_2$  to  $V_2O_3$ , which differs from the electron beam induced reduction of  $V_2O_5$ . The phase transformation does not proceed topotactically. Our observation reveals that the initial thermal decomposition of  $V_2O_5$  to  $V_2O_3$  is followed by a combination of diffusion, coalescence, and stabilisation processes. Our experiments open a new way for the preparation of single crystalline  $V_2O_3$  nanoparticles.

**Keywords:**  $V_2O_5$ ,  $V_2O_3$ , thermal decomposition, Reduction, TEM, EELS

### Introduction

The reduction behaviours and phase transitions of vanadium oxides at various temperatures have been well studied previously [1 - 7]. This is due to the fact that reduction and phase transition are phenomena accompanied in almost all catalytic processes 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 ( $5 \times 10^{-4}$  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]. The mechanism for the transformation of  $V_2O_5$  into  $V_6O_{13}$  occurring during the reduction is considered to be through ordering of oxygen vacancies: if every third oxygen layer in the  $V_2O_5$  structure is removed, shearing occurs from corner-linked to edge-linked octahedra [3]. The earlier investigations on the bulk reduction of  $V_2O_5$  were concentrated on the  $V_2O_5$  -  $H_2$  reactions for the syntheses of vanadium oxides with oxidation states lower than 5+ [8 - 10]. Recently,  $V_2O_5$  -  $H_2$  reductions were re-studied by in-situ X-ray diffraction with respects of reduction kinetics and the geometry of phase transitions at various tempera-

tures [11]. Thermal decomposition of a mixture of  $V_2O_3$  and  $V_2O_5$  was studied by Gillis by heating the sample at 600°C in vacuum for 8 days [5]. Phase transformations resulting in the co-existence of  $V_2O_5$ ,  $V_6O_{13}$ ,  $VO_2$  and  $V_3O_7$  were found. The thermal decomposition of bulk  $V_2O_5$  at temperature up to 400°C in vacuum was investigated by Tilley et al using TEM [4]. A number of new phases were reported, two of them being described as ordered super-lattices of anion vacancies in  $V_2O_5$ . These authors could not find any evidence for the occurrence of crystallographic shear that is said to be necessary for the phase transformation.

Electron beam induced reduction of  $V_2O_5$  differs from the  $V_2O_5$  -  $H_2$  reduction and from the thermal decomposition reported by Tilley et al. [4] and by Gillis [5]. High-resolution imaging [6] as well as electron diffraction and electron energy-loss spectroscopy (EELS) [7] reveal the  $V_2O_5$  - VO (in rock salt structure) transformation induced by high voltage electron beam irradiation in the TEM. However, different pathways for this transformation were observed: while Fan et al. reported that  $V_2O_5$  is firstly reduced to  $V_6O_{13}$  before VO is formed [6], Su et al. found that  $V_2O_5$  is reduced to VO via an unknown intermediate phase (with the averaged oxidation state of vanadium near 3+) [7]. More

recently, it was reported that if the electron beam induced reduction is performed at liquid helium temperature,  $V_2O_5$  can only be reduced to an amorphous phase with an average oxidation state of 4+ [12].

In the present work, we investigate the thermal decomposition of  $V_2O_5$  on a heating stage of TEM, allowing the simultaneous electron diffraction, high-resolution imaging and electron energy-loss spectroscopic characterisation of the transformation. The reasons for this work are as follows: first, we want to find out the reduction path of  $V_2O_5$  under a controlled temperature condition and compare it with the reduction induced by electron beam irradiation, both under the same vacuum condition. Second, the obtained knowledge about the reduction in a non-chemical ambient (high vacuum) can help us in understanding the phase transition in a more complicated chemical process. Third, the obtained results can serve as pre-knowledge for the preparation of vanadium oxide nanostructures useful as model systems for catalytic selective oxidation reactions.

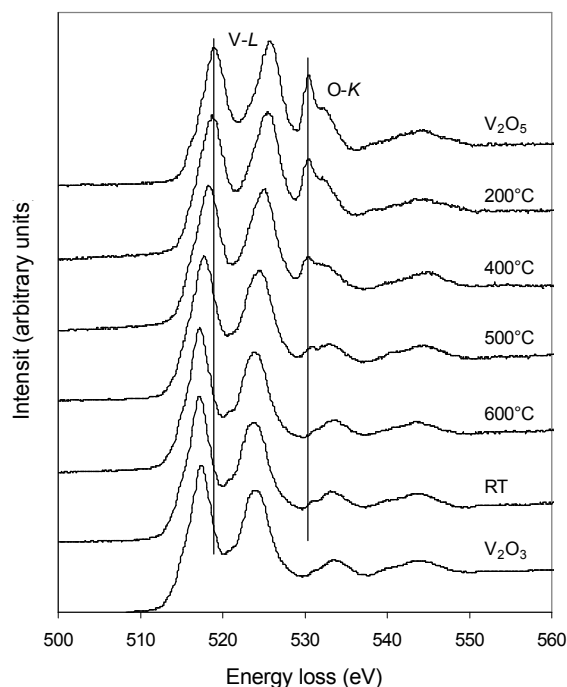
### Experimental

A GATAN heating stage was used for the thermal decomposition of  $V_2O_5$ . The high vacuum of the specimen chamber was kept at  $10^{-7}$  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.  $V_2O_5$  crystals, prepared by chemical vapour transport reaction [7, 8], were crushed gently in carbon tetrachloride. Due to the weakly bonded layer-structure [3], most of the crushed pieces were cleaved along the (001) plane. A drop of the solution containing the thin flakes was placed onto a copper mesh grid covered with a holey carbon film and allowed to dry. A Philips CM200 FEG electron microscope, operated at 200 kV and equipped with a GATAN imaging filter GIF100, was used. The imaging filter, operated in the spectroscopy mode, was used to record EEL-spectra. In order to obtain the near edge structures of vanadium and oxygen atoms, all the measured EEL-spectra were corrected for background and multiple scattering [9].

### Results

Fig. 1 shows the vanadium  $L$  and oxygen  $K$  edges, extracted from EEL-spectra recorded from  $V_2O_5$  unheated and heated at 200, 400, 500, 600°C. The initial spectrum (RT) is typical for  $V_2O_5$  in orthorhombic structure, characterised by the vanadium  $2p \rightarrow 3d$  transitions (V  $L$ -edge) at 519 and 526.7 eV and oxygen  $1s \rightarrow 2p$  transitions (O  $K$ -edge) above 530 eV. Heating the  $V_2O_5$  sample caused two remarkable changes in the spectra: the vanadium  $L$  edge shifted to lower energy and the integral intensity of oxygen  $K$  edges decreased, indicating a preferred release of oxygen besides possible  $V_xO_y$  evaporation during the thermal decomposition. The peak energy of  $L_3$  edge of vanadium shifted to 518.3 eV at 400°C, which is close to the peak position of  $VO_2$  at 518.5 eV. The maximum of this peak shifts to even lower energy loss with increasing temperature and reached 517.4 eV at 600°C, corresponding to the position of the  $L_3$  edge maximum of  $V_2O_3$ . The phase formed at 600°C is sta-

ble upon cooling down to room temperature. Fig. 1 also shows the vanadium  $L$  and oxygen  $K$  edges of the sample after cooling down to room temperature.

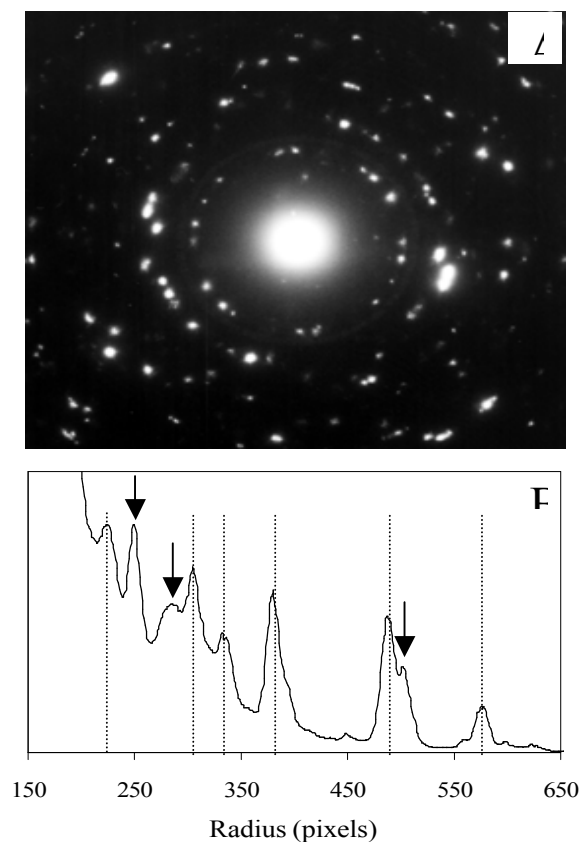


**Fig. 1** Vanadium  $L$  and oxygen  $K$  edges taken at various temperatures and after cooling down to room temperature (RT). For comparison, a reference spectrum from  $V_2O_3$  is included. The spectra are corrected for background and multiple scattering.

For comparison a reference spectrum of  $V_2O_3$  is included in Fig.1. The agreement of all the three spectra is obvious.

An electron diffraction pattern taken at 500°C from a thin sample flake is shown in Fig. 2A. Before the heating, the diffraction pattern contained regularly arranged spots of single crystalline  $V_2O_5$ . The pattern in Fig. 2A stems from randomly oriented crystallites formed through the thermal decomposition. This indicates that the phase transition did not occur topotactically. Fig.2B shows the rotationally integrated profile of this pattern. The profile contains both sets of peaks from  $VO_2$  and  $V_2O_3$ : the diffraction peaks marked with lines can be identified as the ones of  $V_2O_3$  in corundum structure, while the peaks marked with arrows indicate  $VO_2$  in rutile structure. No peaks due to  $V_2O_5$  were detected. This mixed phase can be quantitatively analysed by matching the measured EEL-spectrum with the composed spectrum using the known  $VO_2$  and  $V_2O_3$  samples, as revealed in Fig. 4. The best matching is obtained by a spectrum with the components of 36% from  $VO_2$  and 64% from  $V_2O_3$ . Further heating of the sample to 600°C produced a diffraction pattern from very thin crystallites of  $V_2O_3$ , in combination with a pattern from large crystallites containing intensities from  $VO_2$ . With prolonged heating of the sample at 600°C for several hours, no reduction of  $V_2O_3$  to other phases was observed. Therefore we conclude that under the given condi-

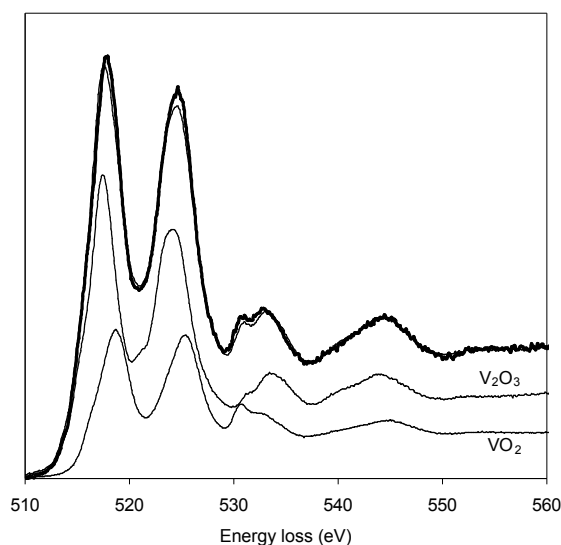
tions,  $V_2O_5$  undergoes a phase transformation via  $VO_2$  into  $V_2O_3$ .



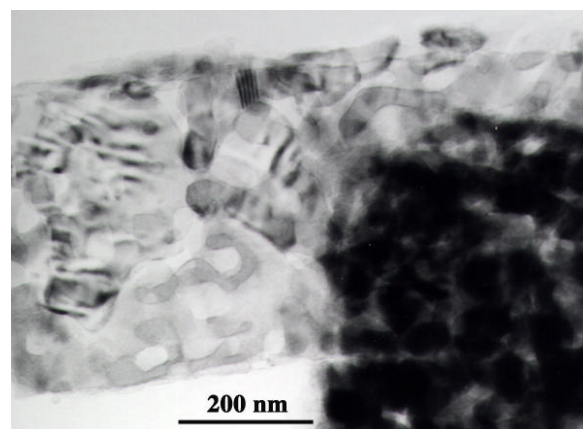
**Fig. 2** Electron diffraction pattern (A) taken at 500°C and its rotationally integrated profile (B). Lined peaks are identified as from  $V_2O_3$  and arrowed peaks are from  $VO_2$ .

The electron micrograph in Fig. 4 taken at 500°C shows how the morphology of the sample changes during the thermal decomposition. The decomposition proceeds faster for the initially thin  $V_2O_5$  particle (on the left side of the micrograph) than for the thick particle (at the right side of the micrograph). This micrograph reveals details of the decomposition steps: the nucleation and growth of the  $V_2O_3$  phase, determined by the atomic diffusion, and the formation of lattice defects during the phase transformation along microstructural defects of the parent  $V_2O_5$ . The intermediate defective state of the oxide is highly strained, as seen from the contrast in the electron micrograph (mainly on the left side). Since the diffusion occurs isotropically, at first the transformed phase forms spherical particles. Coalescence of the primary particles leads to worm-shaped objects. Spherical or worm-shaped particles exhibit a defect-rich surface and contain a high surface energy; stabilisation through reduction of surface defects and minimisation of the surface energy by a change of morphology should occur.

The electron micrograph in Fig. 5, taken after heating at 600°C, reveals the final stage of the phase transformation.

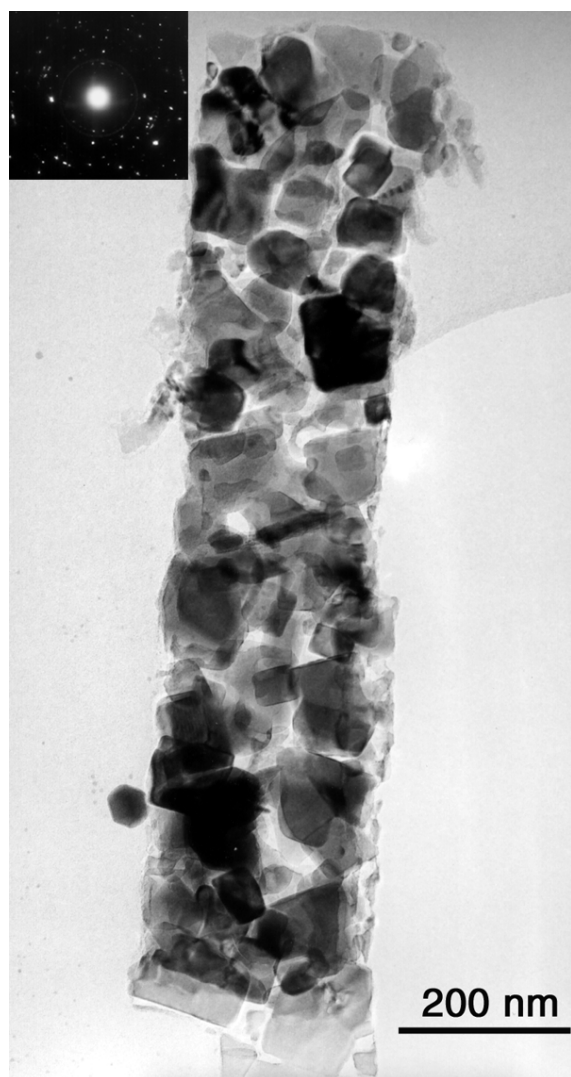


**Fig. 3** Matching of the measured EEL-spectrum at 500°C (bold line) with a composed spectrum with 36%  $VO_2$  component and 64%  $V_2O_3$  component.



**Fig. 4** Low magnification electron micrograph taken at 500°C showing the change of the morphology during the thermal decomposition.

that all these particles are single crystalline with well-ordered bulk and surface structures. Electron diffraction (inset) reveals again that all the formed  $V_2O_3$  nano-particles are random oriented.



**Fig. 5** Electron micrograph of a  $V_2O_5$  flake after heating at  $600^\circ\text{C}$ , showing the formation of  $V_2O_3$  nano-particles; the corresponding diffraction pattern is inserted.

## Discussion

We observed a thermal reduction of  $V_2O_5 - VO_2 - V_2O_3$ , which differs from the electron beam induced reduction under the same vacuum condition, by which  $V_2O_5$  was found to be reduced to VO in rock salt structure [7]. Thus, our results suggest that an electron beam damage cannot simply be conjectured to a bulk temperature equivalent and the effects of electron bombardment are complex and may operate quite differently from thermal decomposition of a bulk sample in vacuum.

Although we cannot observe a  $V_2O_5 - V_6O_{13}$  transformation directly, it is not likely to exclude such transform if it, as mentioned above, occurs only at the surface. Our method is bulk sensitive. Another reason could be that the *life* time of  $V_6O_{13}$  is too short and it can be rapidly reduced. Our experiment on the thermal decomposition of  $V_2O_5$  in a vacuum of  $10^{-4}$  Torr in a sealed glass tube shows that heating overnight at  $400^\circ\text{C}$  and  $550^\circ\text{C}$  respectively does not induce significant changes of  $V_2O_5$ . One reason for this different observation could be the high vacuum we have in the speci-

men chamber (at least  $10^{-7}$  Torr) in which the oxygen partial pressure is quite low. Furthermore, our experiment is performed under a dynamic vacuum condition (the chamber is pumped all the time).

Our observation suggests that no equilibrium in the system of  $V_2O_5$ ,  $V_6O_{13}$  and  $VO_2$  can be achieved under the given vacuum condition at high temperature, while an equilibrium in the system of  $V_2O_3$  is established. The obtained  $V_2O_3$  particles are stable and no further reduction could be observed. Considering that the preparation of vanadium oxide clusters as model catalysts is performed in ultra-high vacuum condition, our result may suggest that a direct evaporation of  $V_2O_5$  cannot result in the growth of vanadium clusters with an oxidation state higher than 4, simply due to the fact that  $V_2O_5$  reduces already at temperatures lower than the melting point.

Our observation reveals that the thermal decomposition of  $V_2O_5$  to  $V_2O_3$  is followed by a combination of diffusion, coalescence, and stabilisation processes, accompanied with the loss of oxygen from the very beginning. Since the diffusion occurs isotropically, the phase transformation does not proceed topotactically. The reduced phases are in spherical form and coalesce giving the worm-shaped contrast in electron micrograph (Fig. 3). The formation of  $V_2O_3$  nanoparticles in regular hexagonal or square form is the consequence of the surface energy minimisation of the coalesced particles. However, this is only possible due to the absence of gas phase oxygen or reductant gas ( $H_2$  or CO) otherwise the process could proceed fast.

The mechanism of  $V_2O_5 - V_6O_{13}$  reduction is explained as an ordering of oxygen vacancies in  $V_2O_5$ : if every third oxygen layer in the [010] direction is removed, shearing in [100] direction can lead the formation of  $V_6O_{13}$  [3]. Recently, it was pointed out that by further removing of oxygen atoms in every third oxygen layer and subsequent by shearing in the same direction,  $VO_2$  can be formed from  $V_6O_{13}$  by chemical reduction with hydrogen [10]. Lattices formed by such crystallographic shearing maintain the defined orientation relationship to the initial lattice. The resulted crystallite therefore should have a certain topotactical relationship to the initial crystals. The nano-particles shown in Fig. 6 are randomly oriented with respect to the initial  $V_2O_5$  single crystal. Our results suggest that in the absence of a chemical reductant such crystallographic shear mechanism cannot be applied to the  $V_2O_5 - V_2O_3$  or  $VO_2 - V_2O_3$  transformations. Further works on the reduction mechanism are needed.

## Summary

We present in this preliminary report on the thermal decomposition of  $V_2O_5$  in high vacuum heated up to  $600^\circ\text{C}$ . TEM and EELS reveal a sequence of transformations from  $V_2O_5$  via  $VO_2$  to  $V_2O_3$ . The thermal decomposition starts with the loss of oxygen, followed by diffusion and defect formation. In the absence of gas phase oxygen or reductant gas such as  $H_2$  or CO, the decomposition occurs slowly, allowing the coalesce and the stabilisation of the reduced phase. This leads to the formation of  $V_2O_3$  nano-particles in regular shapes, with minimised surface energy and perfect bulk and

surface structure. The rate of the reduction is related to the thickness of the crystal. The obtained results indicate that the thermal decomposition of V<sub>2</sub>O<sub>5</sub> occurs in a different way than the electron beam induced reduction of V<sub>2</sub>O<sub>5</sub> under the same vacuum condition. Our findings open a new way for the preparation of single crystalline V<sub>2</sub>O<sub>3</sub> nano-particles.

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