Electron beam induced amorphisation and recrystallisation of divanadium pentoxide crystals

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Abstact

Vanadium oxides are the main constituents of VPO catalysts. They are widespread used in selective oxidation processes and many efforts have already been made in the evaluation of the physical and chemical properties of vanadium oxides. In the present work we focused on the analysis of structural and electronical changes of such a system under electron exposure. Therefore single phase crystals were produced by the chemical vapor transport method. The investigated V_2O_5 crystallizes in the orthorhombic space group *Pmmn* [1] which was confirmed by XRD measurements.

At room temperature in an Philips CM200FEG electron microscope operating at 200 kV and equipped with a Gatan imaging energy-filter GIF100, the V_2O_5 crystals gave diffraction patterns that could be indexed in the orthorhombic structure. However, after prolonged electron radiation additional Bragg spots appeared (Fig. 1). These spots increased in intensity while the original pattern of the orthorhombic structure vanished. Electron energy-loss spectra (EELS) showed a decrease of the O 1s edge during electron exposure, indicating that the observed structural change is induced by a preferentially loss of oxygen (Fig. 2).

Because of the sensitivity of this material at room temperature further investigations were performed on the helium-cooled cryo-electron microscope SOPHIE [2] where the specimen is kept at a temperature of 4.2 K, operated at 200 kV. The diffraction patterns of the crystals were identical to that obtained at room temperature indicating that there is no phase transition of V_2O_5 at low temperatures (Fig.3). We obtained high resolution images of (001) orientation at 200 kV with sharp lattice fringes representing the well ordered structure of the crystals (Fig. 4). However, in contrast to the behavior at room temperature, the lattice fringes disappeared completely with increasing electron exposure until only an amorphous structure was left (Fig. 5). Diffuse rings due to the amorphous state were observed in the electron diffraction pattern.

We then transferred an extensive irradiated i.e. amorphous specimen from the SOPHIE microscope to the CM200FEG microscope and analyzed the same region again at room temperature. We found that the amorphous phase formed at 4 K was stable at room temperature. However, once the amorphous region was irradiated at room temperature an immediate recrystallization occurs. Interestingly the recrystallized sample produced the same diffraction pattern that was obtained when irradiating a V_2O_5 crystal in the CM200FEG microscope. In Fig. 5 the structural changes from the crystalline via the amorphous to the recrystallized state is shown by the corresponding diffraction pattern.

Summary

We observed structural changes of V_2O_5 crystals by means of electron diffraction pattern and high-resolution imaging. This changes could be explained by the loss of oxygen and the reduction of V^{5+} cations. Further work is needed to determine the final reduced state of V^{5+} and to explain the structural transitions at 4.2 K and at room temperature.

References

[1] ICSD Collection Code 60767

[2] Zemlin, F., Beckman, E. and v.d. Mast, K.D., Ultramicroscopy **63** (1996) 227-238.

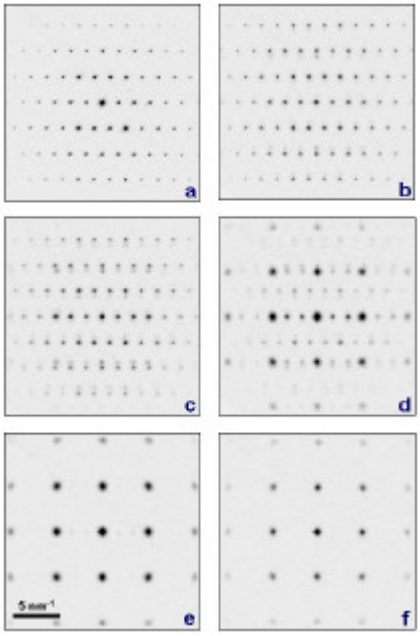

Fig. 1

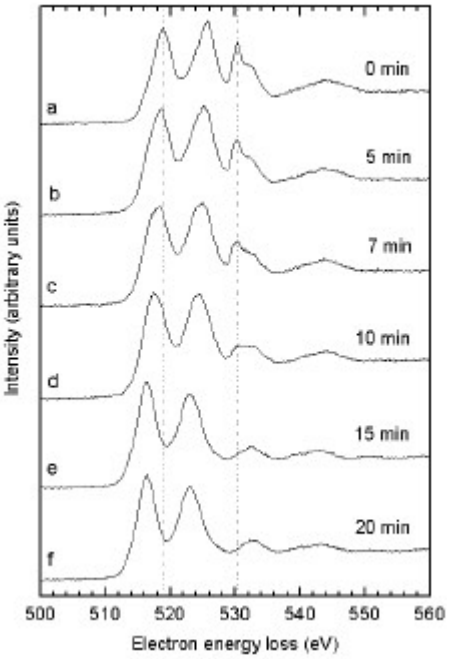

Fig. 2

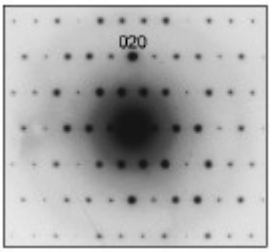

Fig. 3

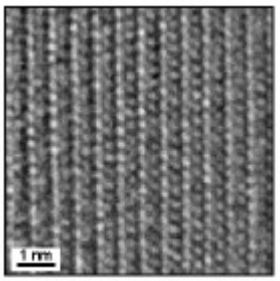

Fig. 4

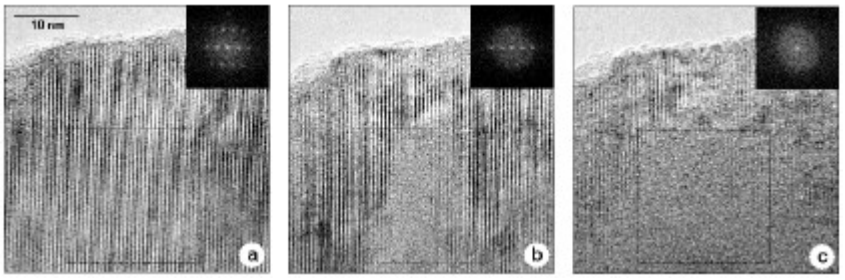

Fig. 5

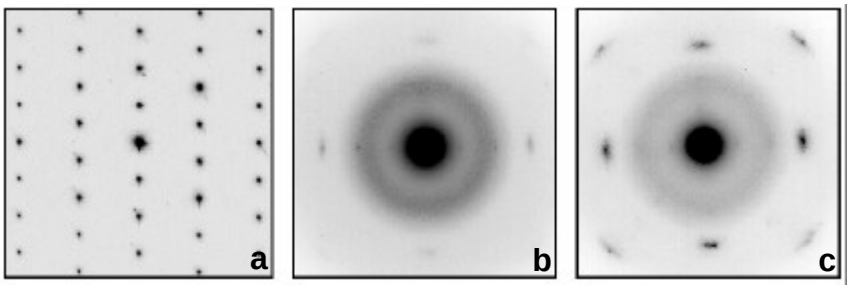

Fig. 6

Captions

Figure 1: Diffraction patterns of V_2O_5 as a function of irradiation time at room temperture.
Figure 1: V 2p and O 1s ELNES corresponding to the diffraction patterns as shown in Fig. 1.
Figure 3: Electron diffraction pattern of V_2O_5 along (001) at 4.2 K.
Figure 4: High resolution image of V_2O_5 at 4.2 K.
Figure 5: High resolution image series indicating the structural changes during electron exposure at 4.2 K. Insets show power spectra calculated from the outlined area.
Figure 6: Electron diffraction pattern of V_2O_5 (001) crystals. A, Original orthorhombic pattern of V_2O_5 at room temperature. B, Amorphous sample, irradiated extensively at 4.2 K, transferred and observed at room temperature. C, The same sample as in B after prolonged exposure to the electron beam at room temperature.