An analytical electron microscopic study on the chemical reduction of vanadium pentoxide

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1. Introduction

In the last years vanadium oxides have attracted special attention because of their outstanding structural flexibility combined with chemical and physical properties which are of interest for, e.g., catalytic and eletrochemical applications. In the present work, the reduction of vanadium cations in single crystal V_2O_5 by electron irradiation in an analytical transmission electron microscope (ATEM) is studied. Vanadium pentoxide, V_2O_5, is a widely used catalyst in a variety of chemical reactions and electrochromism.

2. Experimental

Single crystals were grown by a chemical vapor transport method. X-ray diffraction investigations identified the produced single crystals of V_2O_5 in the orthorhombic structure. For ATEM investigation, the V_2O_5 crystals were crushed gently in carbon tetrachloride. A drop of the solution containing fine flakes was placed onto a copper mesh grid covered with a holey carbon film and allowed to dry. A Philips CM 200 FEG electron microscope, operating at 200 kV and equipped with a GATAN imaging filter GIF100, was used.

3. Results

Fig.1 shows a series of EELS-spectra, taken with different irradiating times, corrected by background-subtraction and de-convolution. The initial spectrum (0 min) exhibits the characteristic 2*p*-edges of V and the 1*s*-edge of O in V_2O_5: the first and second peak, located at 519 and 526.7 eV, are attributed to the excitations from V $2p_{3/2}$ and V $2p_{1/2}$ core levels to the unoccupied V 3*d* bands, respectively. The third peak with shoulder can be assigned to the transitions from the O 1s core level to the unoccupied V 3*d* bands. Irradiating for 5 min produced already changes in the V 2*p* peaks and in the O 1*s*-edge: the spectral intensity of V $2p_{1/2}$ peak and the spectral intensity of the oxygen 1*s* electron transitions to the unoccupied V $3d(t_{2g})$ band begin to decrease (spectrum b). The fine shoulder at 517 eV appearing on the V $2p_{3/2}$ peak becomes more pronounced after 7 min irradiation (see spectrum c). With prolonged irradiation this shoulder shifts slightly to the left and after 20 min develops into the peak at 516.5 eV. Similar development can be observed on the V $2p_{1/2}$ peak which shifted from 526.7 to 523.1 eV after 20 min irradiation. The appearance of the shoulder and the broadening in width of V 2*p* peaks indicate that the spectra b, c, d, e in Fig. 1 are composed of unreduced V_2O_5 and of reduced vanadium cations. The significant change in O 1s-edge indicates the reduction, and the disappearing of the peak at 530 eV indicates the preferential loss of oxygen from the sample. The small peak at 532.4 eV developed after 20 min into a unique peak at 533 eV. After 20 min, the spectrum f is identical to the spectrum of VO; no further change in V and O core-level spectra could be observed.

3. Summary

We used EELS to characterise the oxidation states of vanadium cations in (001) orientated V_2O_5 crystals reduced by electron irradiation in an ATEM. The chemical shift of V $2p_{3/2}$ and V $2p_{1/2}$ peaks

observed in ELNES indicated that V^{5+} is reduced to V^{2+}. The final reduced state was found to be cubic VO.

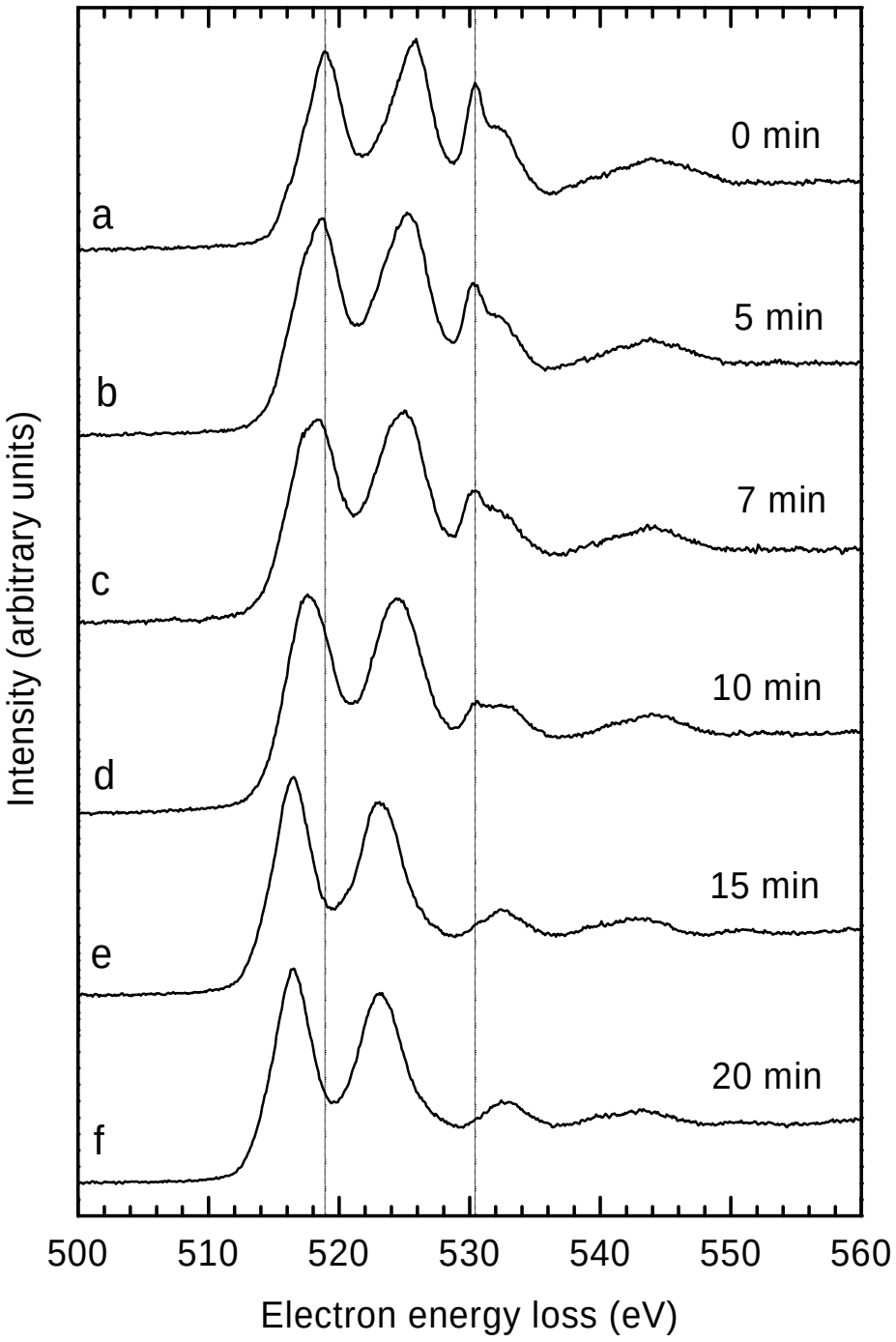

Fig. 1 EELS spectra of V 2*p* and O 1*s* as a function of irradiation time.

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Reference

1. D. S. Su, M. Wieske, E. Beckman, A. Blume, G. Mestl, R. Schlögl, to be published