



Electron beam induced changes in transition metal oxides

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Abstract

Electron beam induced changes in maximum valence transition metal oxides V_2O_5 , MoO_3 and TiO_2 (anatase) were studied by means of electron energy-loss spectroscopy and electron diffraction in a transmission electron microscope. For V_2O_5 , the observed chemical shifts of the L -edge reveal the reduction of V^{5+} to V^{2+} , while its structure changes from orthorhombic V_2O_5 to cubic VO. The orthorhombic MoO_3 can be reduced to a phase with an oxidation state lower than that in MoO_3 . This phase has a cubic or tetragonal structure with $a = c = 0.408$ nm. For TiO_2 (anatase), no noticeable changes in the intensity of the O K -edge can be observed. The main structure symmetry prevails during the electron irradiation.

Keywords: Transition metal oxides, Reduction, Oxidation state, Electron beam, Transmission electron microscopy

Introduction

High-voltage transmission electron microscopes (100 kV – 400 kV), equipped with electron energy-loss spectrometer (EELS), are widely used in structural and electronic analysis of solid state materials. Fast electrons interact with atomic nucleus (elastic) and atomic electrons (inelastic) that provide image contrast and structural information in electron microscopy. However, such interactions can also initiate destructive processes through which the structure/chemistry of the sample under investigation is changed. These electron beam induced structural changes, usually called radiation damage, cause artefacts in the electron micrograph or in the recorded EEL-spectrum. On the other hand, beam-induced changes in electron microscope provide a simple means to understand the phase transition and reduction behaviour of the studied materials in a non-chemical ambient (high vacuum).

In this short paper, we report our first observation of electron beam induced changes in typical transition metal oxides

V_2O_5 , MoO_3 and TiO_2 (anatase), studied by means of electron energy-loss spectroscopy (EELS) and of electron diffraction. In these three oxides, the metal atoms are in maximum valence. The energy-loss near edge structure (ELNES) of metal and oxygen atoms provide “fingerprints” of the changes in the oxidation state, in the chemical bonding and in the co-ordination of the detected species.

Experimental

Commercial powders of V_2O_5 , MoO_3 and TiO_2 from Fluka GmbH were used. For TEM investigations, all oxides were crushed gently in carbon tetrachloride and dispersed onto a holey carbon film supported by a copper mesh grid. A Philips CM200 FEG electron microscope, operating at 200 kV and equipped with GATAN imaging filters GIF100 for EELS measurement, was used. The high vacuum of the specimen chamber was kept lower than 10^{-7} Torr. All of the electron irradiation was performed at a current density of 3 A/cm^2 .

Results and discussion

1. V_2O_5

V_2O_5 crystallises in an orthorhombic structure with vanadium in the V^{5+} state. Vanadium L -edges and oxygen K -edges are used to monitor the electron irradiation induced electronic changes in (001) orientated V_2O_5 crystals. A series of results after different irradiation times is shown in Fig. 1.

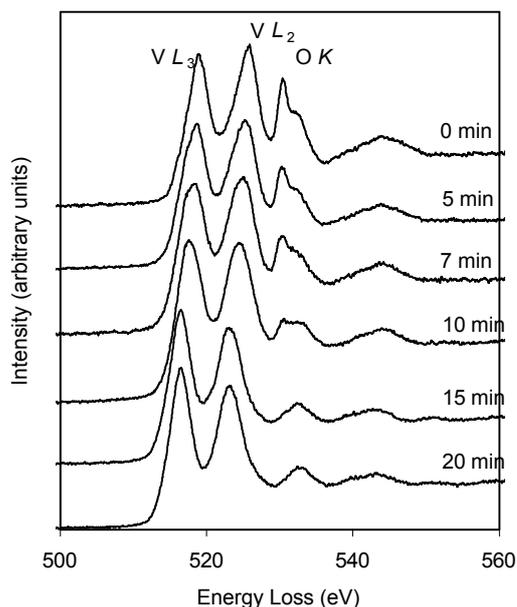


Fig. 1: V $2p$ and O $1s$ ELNES of V_2O_5 as a function of irradiation time. Spectra are offset for better distinction. The electron current density was 3 A/cm^2 .

The initial spectrum, characterised by the vanadium $2p \rightarrow 3d$ transition (V L -edge) and the oxygen $1s \rightarrow 2p$ transitions (O K -edge), shows a decrease of the intensity of the oxygen K signal with prolonged beam irradiation. Since this intensity is proportional to the number of oxygen atoms in the irradiated area, the decrease in intensity suggests a preferential loss of oxygen from the crystal lattice. The positions of the V L_3 peak shifts from 519 eV to lower energies, indicating a reduction of vanadium accompanied with the irradiation. After 20 min, the L_3 peak reaches to 516.5 eV, which, according to a relationship between L_3 -peak positions and oxidation states of vanadium in vanadium oxides [1], corresponds to a V^{2+} state. We conclude that vanadium is reduced from V^{5+} to V^{2+} .

The accompanying structural changes are revealed as changes in electron diffraction patterns. The patterns from initial V_2O_5 and from the final product are shown in Figs.2.

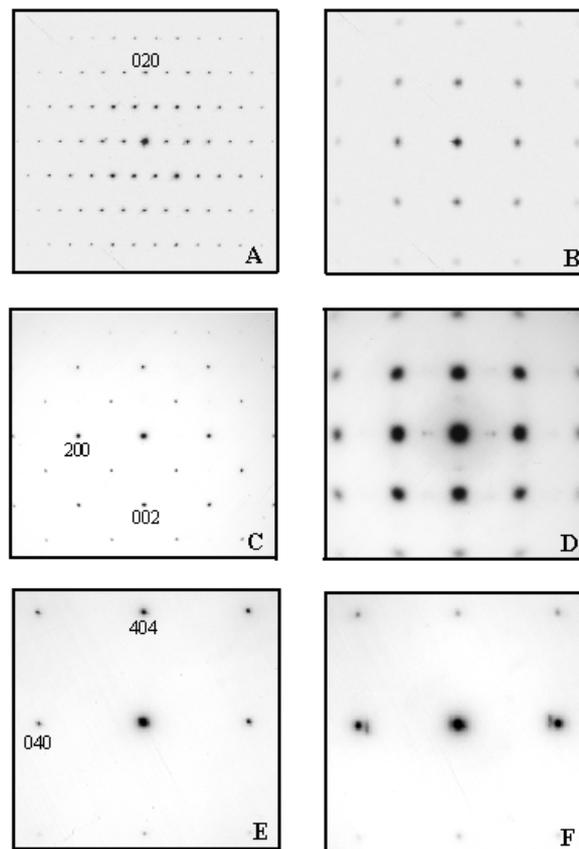


Fig. 2: Electron diffraction patterns. A: from 001-orientated V_2O_5 ; B: after 20 min irradiation; C: from 010-orientated MoO_3 ; D: after 50 min irradiation; E: from 10-1-orientated TiO_2 (anatase); F: after 30 min irradiation.

The lattice parameters determined from the diffraction pattern after 20 min irradiation are $a = b = 0.410 \text{ nm}$ which are in good agreement with the lattice parameter of VO (0.412 nm), supporting a structural change from orthorhombic V_2O_5 to cubic VO (vanadium in V^{2+} state).

2. MoO_3

In the orthorhombic structure of MoO_3 , molybdenum is in the Mo^{6+} state. Initially the main features of energy-loss spectra are the Mo M_{23} doublet peaks at about 400 eV (due to the transition of Mo $3p$ electrons to the unoccupied $4d$ states) and the O K doublet peaks at about 520 eV (due to transitions of O $1s$ electron to the co-valence mixed states derived from the O $2p$ and Mo $4d$ states). With electron irradiation we observe, however, a strong decrease of the intensity of O K -edge, as shown in Fig. 3, indicating also a preferential removal of oxygen atoms from crystal lattice.

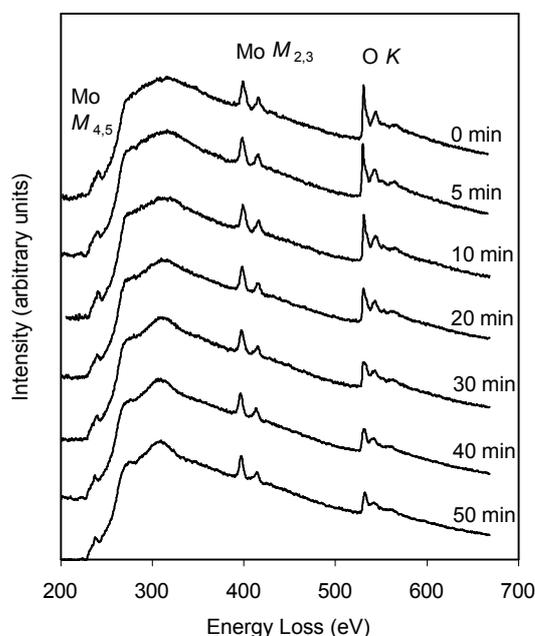


Fig. 3: Mo 3d and O 1s ELNES of MoO₃ as a function of irradiation time. Spectra are offset for distinction. The electron current density was 3 A/cm².

The maximum of *M*-edges shifts slightly towards lower energies, but not as significant as the corresponding chemical shifts of *V* *L*-edges. Comparison of the spectrum reduced by 60 min irradiation with that of pure MoO₂ and Mo indicates that the final states is lower than that of Mo⁴⁺. In situ characterisation of catalytic reaction of MoO₃ a final reduced phase of MoO₂ (Mo in Mo⁴⁺ state) was detected [2]. It was reported that under the electron beam MoO₃ could be reduced to metallic molybdenum [3]. Our observation, however, cannot confirm this finding since after 60 min of irradiation we can still detect oxygen signal, although the diffraction pattern changes to the one as from f.c.c. metal (Figs. 2). The lattice parameters, calculated from the diffraction patterns, are $a = c = 0.408$ nm. Among the known molybdenum oxides, no phases with such lattice parameters can be identified.

3. TiO₂ (anatase)

The ELNES characteristic of Ti in TiO₂ (anatase) are the two doublet peaks that stem from the electron transition from the Ti 2*p*_{3/2} and 2*p*_{1/2} to the Ti 3*d* orbitals which in turn split into *t*_{2g} and *e*_g orbitals due to the octahedral symmetry.

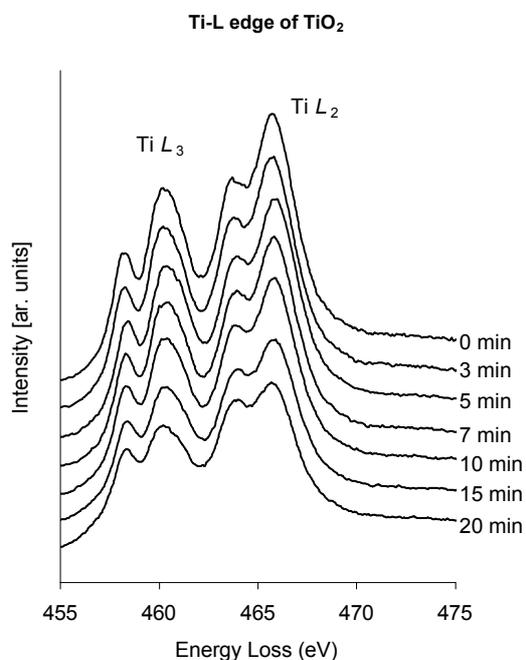


Fig. 4: Ti 2*p* ELNES of TiO₂ (anatase) as a function of irradiation time. Spectra are offset for distinction. The electron current density was 3 A/cm².

As shown in Fig.4, the shape of *L*_{2,3} edges changes slightly due to the electron irradiation, but no chemical shifts can be detected. Furthermore, no noticeable changes in the intensity of O *K*-edge can be observed (Fig. 5).

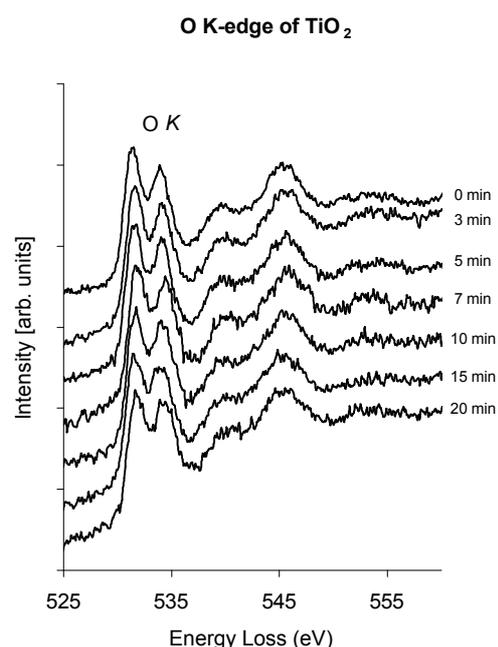


Fig. 5: O 1s ELNES of TiO₂ (anatase) at various irradiation times. Spectra are offset for distinction. The electron current density was 3 A/cm².

The electron diffraction patterns from initial anatase and after 30 min irradiation are shown in Figs.2. In contrast to other two oxides, the main symmetry prevails during the electron irradiation, with weak additional spots appear.

Conclusion

Our experiments reveal quite different behaviour of maximal valence transition metal oxides under electron beam irradiation. While TiO_2 (anatase) is quite electron beam-resistant, V_2O_5 and MoO_3 show dramatic change under electron beam. Orthorhombic V_2O_5 can be changed to cubic VO. MoO_3 can

be reduced to a phase with oxidation state less than that in MoO_2 . The results show how critical the electron bombardment is when transition metal oxide is studied in high-voltage electron microscope.

Acknowledgement

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