



KeyWords

XPS, V₂O₅ Single Crystal, Oxidation, Reduction, Surface Chemical Analysis

XPS surface analysis of V₂O₅ upon heating with EnviroESCA

This application note presents how EnviroESCA can be used to analyze samples during heating under near ambient pressure conditions using various gas atmospheres. Such investigations of surfaces at elevated temperatures and pressures are of paramount importance for catalysis in nature and industry.

Motivation

V₂O₅ is a transition metal oxide with interesting potential for technological applications [1]. It has been studied intensively by theoretical calculation and experimental techniques [2]. Polycrystalline films exhibit multicolored electrochromism allowing the use in electrochromic displays, color filters, and other optical devices [3]. In addition, bulk and thin films of V₂O₅ have been used as an oxidation catalyst [4]. As a functional inorganic material, V₂O₅ can be used in gas sensors [5]. Alkali metal doped or intercalated V₂O₅ is widely studied for applications in the field of catalysis, electrochromics, and energy storage [6]. In general, it has suitable structural and electronic properties allowing for reversible intercalation of small alkali metal (Na, Li) ions [7]. All these interesting properties are strongly related to oxygen vacancies leading to changes in the electronic structure and to crystal reorientations.



Fig. 1 Studied single crystal of vanadium pentoxide (V₂O₅)

Method

EnviroESCA utilizes X-ray Photoelectron Spectroscopy (XPS) as analytical technique. Here an electron beam is generated inside the X-ray source and focused on an aluminum X-ray anode. The deceleration of the electrons on the anode generates X-rays. This X-ray beam is monochromated and focused on the sample.

X-ray photons impinging the sample excite electrons in the material which are subsequently emitted with a specific kinetic energy determined by their binding energy and the photon energy of the X-rays. In case of solid samples only electrons from atoms down to a depth of about 10 nm are able to leave the surface.

These electrons propagate through the lens system of the Electron Analyzer into the hemisphere which acts as a spherical capacitor forcing the electrons onto circular paths with radii depending on their kinetic energy. The path of photoelectrons ends at an electron sensitive detector where the electrons are amplified and measured as intensity in counts per second. Sweeping the voltage of the spherical capacitor while measuring the number of electrons per second on the detector results in a photoelectron spectrum.

From these spectra a quantitative analysis of the atomic composition of the sample surface can be done.

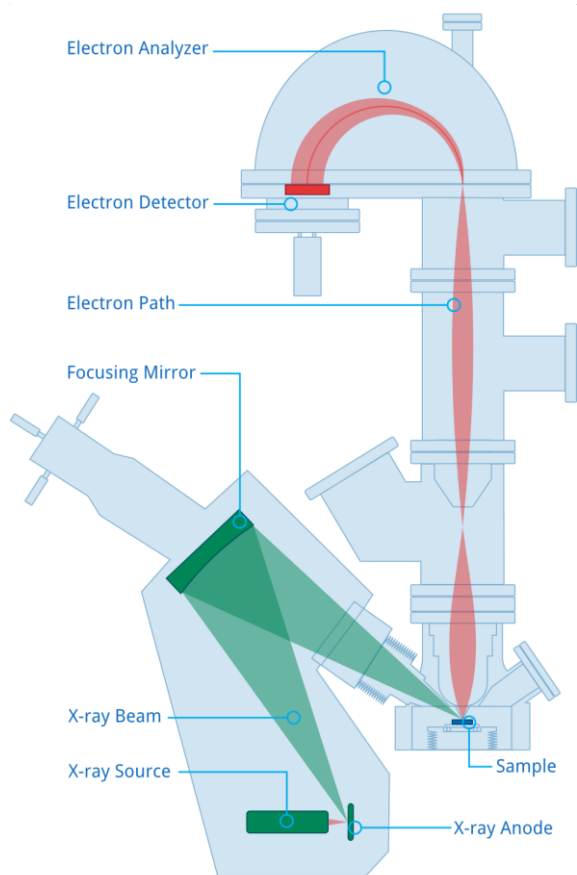


Fig. 2 XPS with EnviroESCA

Experimental Section

EnviroESCA can work under vacuum as well as near ambient pressure (NAP) conditions up to several dozens of mbar. Thus, it is very well suited to investigate surface reactions and catalytic processes at elevated pressures and temperatures.

In EnviroESCA an intrinsic charge compensation which we call Environmental Charge Compensation makes additional low energy electron or ion sources unnecessary.

The gas atmosphere that is surrounding the sample delivers all the free charges, when illuminated with the soft X-rays, that are needed to compensate for surface charging. As schematic illustration is shown in Fig. 3.

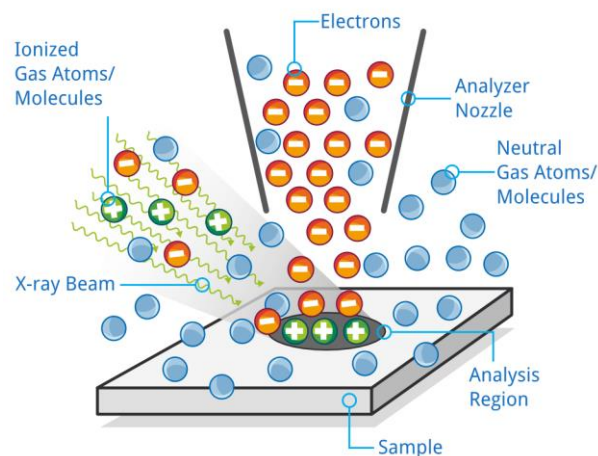


Fig. 3 Environmental Charge Compensation

The NAP XPS capability of EnviroESCA allows *in situ* studies of reactions at surfaces in different gas atmospheres. Here we present results of a surface chemical analysis of vanadium pentoxide (V_2O_5) single crystals.

First a freshly cleaved V_2O_5 crystal was heated gradually up to 500 °C under vacuum conditions. Second the same V_2O_5 sample was exposed at 300 °C to pure oxygen at 2 mbar. Finally the V_2O_5 sample was cooled down in the same atmosphere of oxygen.

Results

In a first survey spectrum of the V_2O_5 crystal taken at room temperature vanadium and oxygen are found as main elements. The elemental composition of 28 % vanadium and 72% oxygen indicates an almost ideal stoichiometry of the single crystals with all vanadium present as V^{5+} species. That fact is also reflected by characteristic V^{5+} positions of V 2p and O 1s photoemission lines located at 517.2 eV and 530.0 eV.[8-10]

Also some adventitious carbon was found that originates from the short exposure of freshly cleaved V_2O_5 to laboratory atmosphere during sample transfer.

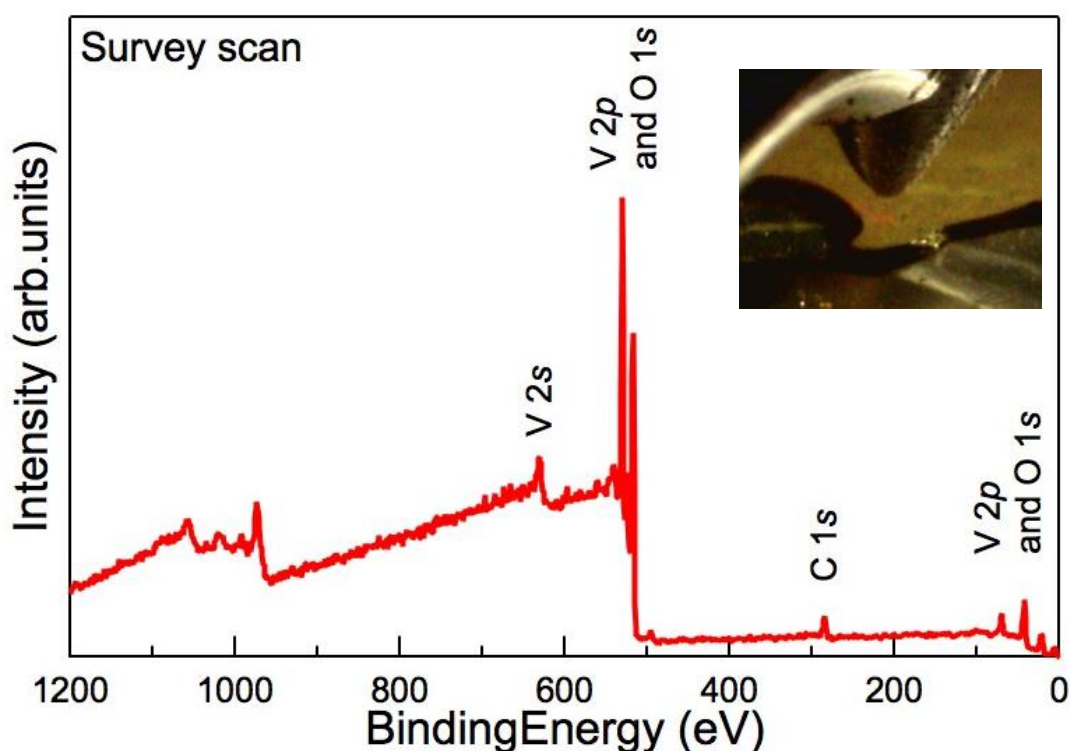


Fig. 4 Survey scan of a freshly cleaned V_2O_5 single crystal at room temperature under UHV conditions.

After initial characterization at room temperature the sample was heated successively to 500 °C in vacuum and O 1s and V 2p spectra were acquired every 100 °C. Spectra are normalized to the total area of V 2p and O 1s. And the V 2p splitting is fixed to 7.4 eV.

It is well known that V^{5+} oxide species are thermally reduced to V^{4+} at temperatures above 200 °C. That thermal reduction can be monitored easily by the V $2p_{3/2}$ peak as shown in Fig. 5. It is quite obvious that a second reduced vanadium species corresponding to V^{4+} is evolving with increasing temperatures. Figure 6 illustrates the evolution of that V^{4+} species during the heating experiment. At the same time amounts of V^{5+} and oxygen are reduced by thermal reduction of V_2O_5 .

It should also be mentined that V_2O_5 degrades slowly under X-ray illumination. Biesinger reported more than 15% conversion of V^{5+} to V^{4+} over 24 h using a 210 W source (15 mA, 14 kV).[10]

Such a X-ray induced redcution could be excluded here because X-ray exposure times were minimized by illuminating the V_2O_5 samples only with X-rays during measurements of combined V 2p and O 1s spectra, which take about 12 min.

After thermal induced reduction the possibility of re-oxidation of V^{4+} species by exposure to a pure oxygen atmosphere at 300°C was investigated *in situ* on a hot V_2O_5 crystal surface. Figures 5 shows that the difference between a hot V_2O_5 samples in UHV and in oxygen is characterized by significantly reduced amounts of V^{4+} species. And after cooling the V_2O_5 sample down to room temperature in oxygen at 2 mbar the initial V^{5+}/V^{4+} component ratio of the native crystal was restored almost completely. These results suggest a reversible reduction \leftrightarrow re-oxidation of V_2O_5 single crystal samples in oxygen atmospheres at elevated pressures and temperatures above 200 °C.

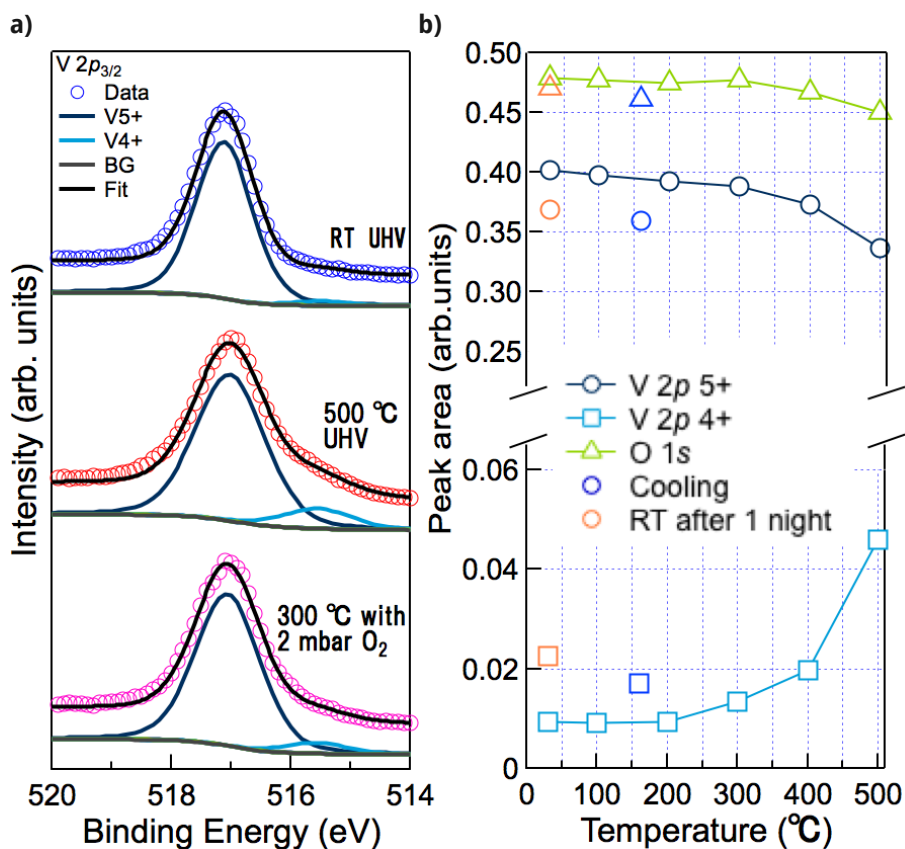


Fig. 5 Vanadium V 2p_{3/2} detail scans of V₂O₅ single crystal in UHV at room temperature (top) and after heating to 500 °C (middle) as well as in an oxygen atmosphere (2 mbar) at 300 °C (a). Development of V⁵⁺ and V⁴⁺ related V 2p_{3/2} peak components together with O 1s peak area during heating from room temperature up to 500 °C. Additional data from exposure to oxygen at 2 mbar during cool down and at room temperature are included (b).

Conclusion

The unique capabilities of EnviroESCA to work in near-ambient pressure conditions using different gas atmospheres at elevated pressures and temperatures allows *in situ* (and *operando*) surface characterization under conditions relevant for real world applications, e.g., in catalysis.

As an example V₂O₅ single crystals were studied in vacuum and in oxygen atmosphere at 2 mbar during heating to 500 °C. A significant amount of reduced vanadium species (V⁴⁺) was detected after thermal treatment. Successive exposure of the same V₂O₅ crystal to oxygen (2 mbar) induced re-oxidation of the V⁴⁺ species. Thus, a reversible reduction ↔ oxidation behavior of V⁵⁺ ↔ V⁴⁺ species in V₂O₅ single crystals in vacuum and oxygen at temperatures above 200 °C can be concluded from the presented data.

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We gratefully acknowledge Matthias Klemm and Siegfried Horn (Universität Augsburg) for providing V₂O₅ single crystal samples.