Ab-Initio Simulation of the Oxygen 1s Ionisation Near Edge Structure in Vanadium Pentoxide

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Introduction

Vanadium oxides are of considerable importance in many catalytic processes. The special chemistry of vanadium oxides results from the narrow d-states and their hybridization with the ligand p-orbitals. To gain detailed information about the overlap of the orbitals in vanadium pentoxide, the atom projected density of states (DOS) was calculated using the FP-LAPW (Full Potential Linearized Augmented Plane Wave) method [1]. EELS spectra from V_2O_5 single crystals were recorded and compared with the simulated ELNES (Energy Loss Near Edge Structure) spectra in order to support the interpretation of the different features.

Ab-initio calculation and experimental:

The program package WIEN97 (a FPLAPW package for calculating crystal properties) was used to calculate the atom projected density of states.The ELNES at the oxygen K-edge was simulated for the different oxygens (O1,O2,O3, Fig.1) via an extension to the WIEN97 program which permits to separate different contributions to the inelastic scattering cross section according to the character of the final state and an orientation dependent simulation of ELNES spectra [3]. A Philips CM200 FEG transmission electron microscope equipped with a Gatan GIF 200 spectrometer was used to acquire EELS spectra in image coupled mode. The microscope was operated at 200kV.

In Fig.2 the atom projected DOS of the vanadium 3d and vanadyl oxygen 2p orbitals are displayed. Due to the substantial hybridisation of the V 3d with the O 2p states, the distinct structure of the partial V-DOS is reflected by the partial oxygen density of states. Within a molecular orbital picture, the overlap of the particular V 3d with O 2p orbitals can be summarised for the three kinds of oxygen as in Table I which is in good agreement with the results of [2]. The smaller overlap with the ligand 2p states via π bonds is reflected by a reduced dispersion of the conduction bands below 4.5 eV and a higher density of states of the t_{2g} states (see Fig.2). On the other hand, the e_g levels (higher band) point towards the ligand and appear at higher energies because they form relatively stronger σ antibonding combinations with the O 2p orbitals. The simulation shown in Fig. 3 reveals the contribution of the different oxygens to the total oxygen edge as well as their contributions to the t_{2g} and e_g levels and is in good agreement with the EELS measurements (Fig. 4).

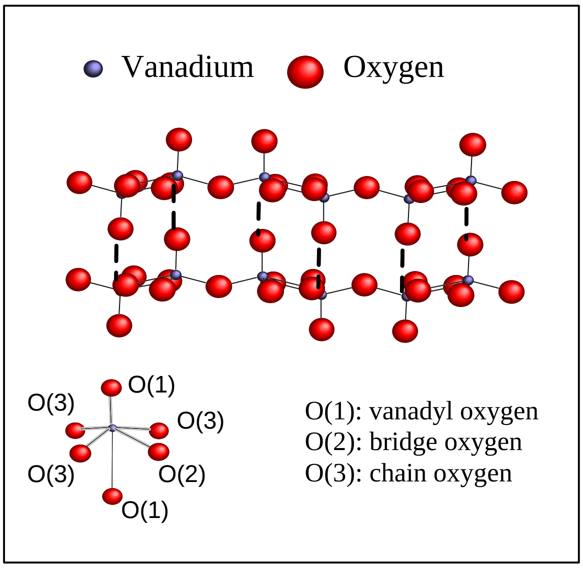

Fig.1: Crystal structure of V_2O_5

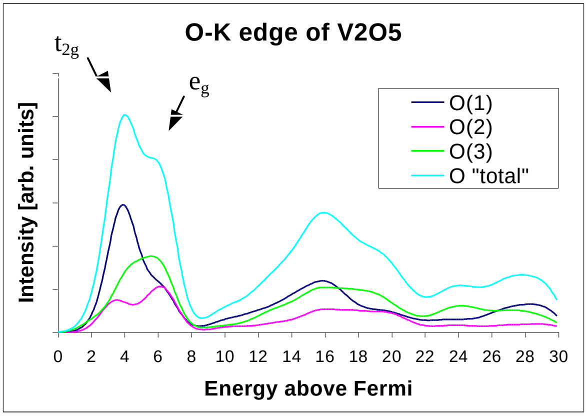

Fig.3: Contributions of the different oxygens to the total simulated oxygen K-edge

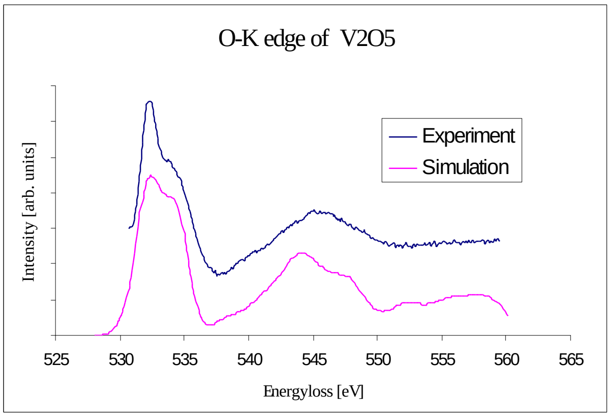

Fig.4: Comparison between simulation and EELS experiment.

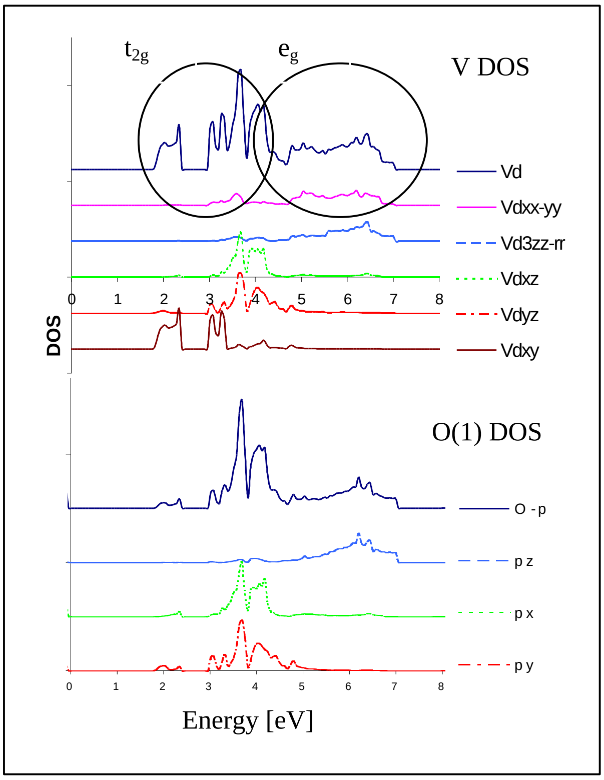

Fig.2: DOS: Conduction bands of vanadium d-orbitals and vanadyl-oxygen p-orbitals.

	O(1)	O(2)	O(3)
V $3d_{xy}$		$2p_x$, $2p_y$	$2p_y$
$3d_{xz}$	$2p_x$	$2p_z$	$2p_z$
$3d_{yz}$	$2p_y$	$2p_z$	
$3d_{x^2-y^2}$		$2p_x$, $2p_y$	$2p_x$
$3d_{3z^2-r^2}$	$2p_z$		

Table I:V3d-O2p orbital overlaps

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