Ab-initio band-structure calculations on a new polymorph of V_2O_5: A comparison between V_2O_5 and gamma-V_2O_5.

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Introduction

Vanadium oxides merit special attention because of their outstanding structural flexibility combined with chemical and physical properties which are of interest for catalytic and electrochemical applications. Specially V_2O_5 is an essential ingredient to heterogeneous catalysis and its electronic and structural properties have been widely studied. This work presents theoretical investigations of γ-V_2O_5, a polymorph of V_2O_5 which was first reported in 1991 [1]. The aim of the investigation is to compare the basic VO_5 units of the different structures and to relate them to differences in their electronic structure. A detailed understanding of the relation between geometric and electronic structure is essential since this basic unit is common to the industrial used VPO catalysts. The atom projected density of states (DOS) was calculated using the FP-LAPW (Full Potential Linearized Augmented Plane Wave) method [2]. In order to relate the theoretical results with experiments, the O-K ELNES (Energy Loss Near Edge Structure) was simulated and compared to EELS spectra recorded from V_2O_5 single crystals and γ-V_2O_5 nanorods [3].

Structure of γ-V_2O_5

The γ-V_2O_5 forms a layer type orthorhombic lattice with lattice constants *a = 9.946(0) Å, b = 3.585(0) Å* and *c = 10.042(0) Å*. The structure is set up by layers of edge and corner sharing VO_5 pyramids sticking out at both sides of the layer. As opposed to bulk V_2O_5, the double chains of edge sharing pyramids are tilted relatively to each other (Fig. 1). As a consequence, there exist two structurally different VO_5 pyramids. The first one can also be thought of as a bi-pyramidal (VO_6) by including the vanadyl oxygen from the adjacent layer. The second VO_5 pyramid is positioned in such a way that no oxygen atom lies in close vicinity of the basal plane. Each pyramid contains three structurally different oxygens, but in total, due to the linking via one common oxygen, there exist five different oxygens and two different vanadiums in γ-V_2O_5. The bonding distances in γ-V_2O_5 and V_2O_5 are summarised in Figure 2.

Ab-initio calculation and experimental:

The program package WIEN2k [4] was used to calculate the atom projected density of states.

The ELNES at the oxygen K-edge and the contributions of the different oxygens (O1-O5) was calculated via an extension to the WIEN2k program.

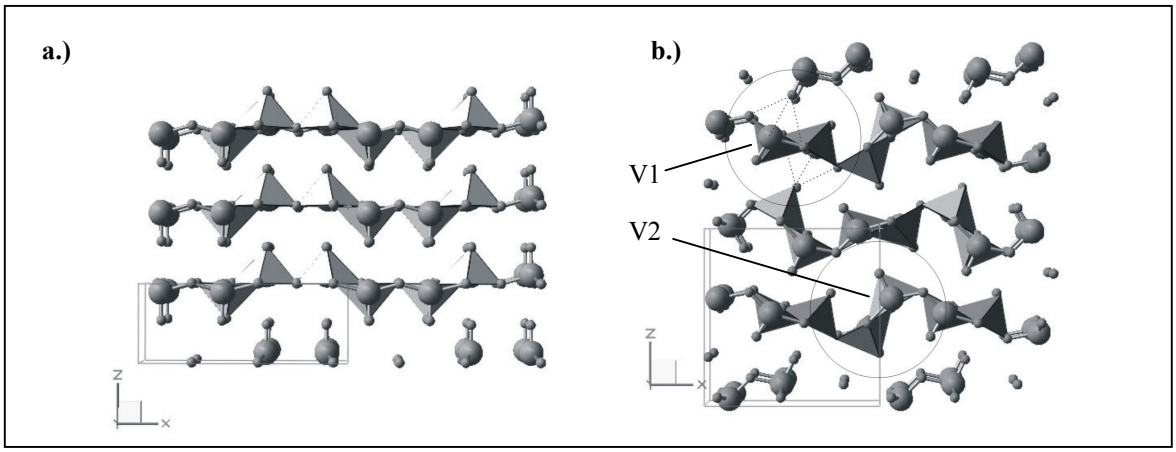
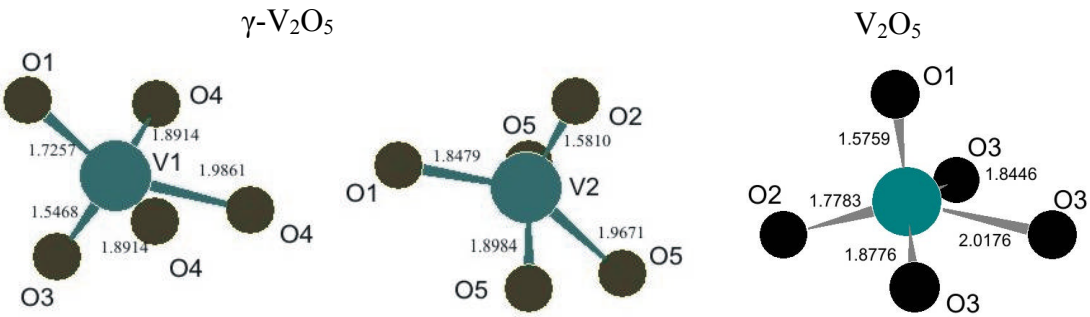


Fig. 1: Crystal structures of **a.)** bulk V_2O_5 and **b.)** γ-V_2O_5.
V1 and V2 indicate the two structurally different VO_5 pyramids in γ-V_2O_5.



Bond length	Vanadyl-Oxygen	Bridge-Oxygen	Chain-Oxygen
γ-V_2O_5	1.5468 Å (V1-O3)	1.7257 Å (V1-O1)	1.8914 Å, 1.9861 Å (V1-O5)
γ-V_2O_5	1.5810 Å (V2-O2)	1.8479 Å (V2-O1)	1.8984 Å, 1.9671 Å (V1-O4)
V_2O_5 (bulk)	1.5759 Å (V-O1)	1.7783 Å (V-O2)	1.8776 Å, 2.0176 Å (V-O3)

Fig.2: The three different VO_5 pyramids from which the atom projected density of states are compared and structural effects are discussed.

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