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Understanding the atomic force microscopy image of the V_2O_5 and $Li_{0.03}V_2O_5$(0 0 1) surface using ab initio calculations

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Abstract

Single crystals of V_2O_5 and $Li_{0.03}V_2O_5$ were imaged in ambient conditions by atomic force microscopy (AFM). Atomic-scale resolution images are compared with total electron-density plots of the surface calculated using the ab initio HartreeFock method. The calculated oxygen charge at the V_2O_5(0 1 0) surface suggests an increased local reactivity of the bridging oxygens with respect to electrophilic attacks by adsorbate molecules. The intercalation of lithium has no consequence on the reactivity of the surface. This is supported by results from electrostatic potentials calculated from the cluster charge distributions.

Keywords: AFM; V_2O_5; $Li_{0.03}V_2O_5$; Electronic structure

1. Introduction

V_2O_5 is a very important material that has been extensively used as cathode material in lithium batteries and industrial catalysts [1–3]. In particular, in heterogeneous catalyst, both when used alone and when activated on a suitable oxidic support. The catalytic properties of V_2O_5 base catalyst depend strongly on their ability to provide oxygens reactant in oxidation of hydrocarbons. In order to understand the atomistic mechanism, it is first necessary to acquire a detailed knowledge of the real space surface structure. The scanning probe microscopy is a powerful tool for acquiring such information. In most cases, observations are interpreted by assuming that filled-state images show the more electronegative atoms, and empty-state images the more electropositive atoms. Unfortunately, this qualitative argument often leaves ambiguities regarding the composition of the termination layer and the relative positions of surface atoms. In order to limit this ambiguity, we have proposed a method to overcome these difficulties by comparing experimental scanning probe microscopy images with calculated plots of the total surface electron-density. In AFM measurements, all the electrons of the surface atoms are involved in repulsive interactions with the tip, so that the AFM image of a sample surface is described by the total electron-density plot of the surface [4,5]. Such total electron-density plots, calculated using the extended Hückel tight-binding (EHTB) electronic band-structure method [6], have been necessary to explain the observed STM and AFM images of a large number of organic conducting salts, transition-metal chalcogenides and transition-metal halides [4,5]. In ambient conditions, our previous observations of V_2O_5(0 0 1) single crystal surface [7,8] give result which is some different from the ideal surface as observed by Smith et al. [9]; however, it is important to notice that sample used by Smith et al. was doped with Na and it is well known that some alkali atoms remain in the first layers of the bulk [10] and so surface behaviours can be modified. Accordingly, we were interested by the investigation of the clean and lithiated V_2O_5(0 0 1) single crystal surface in order to examine the influence of the simplest alkali atoms (here the lithium) on the catalytic properties of the (0 0 1) plane.

2. The geometric structure

The crystal lattice of vanadium pentoxide, V_2O_5, is characterized by a layer type orthorhombic structure with layers extending parallel to the (0 0 1) net plane [11–13] and unit cell parameters defined as $a = 11.51$ Å, $b = 4.37$ Å,

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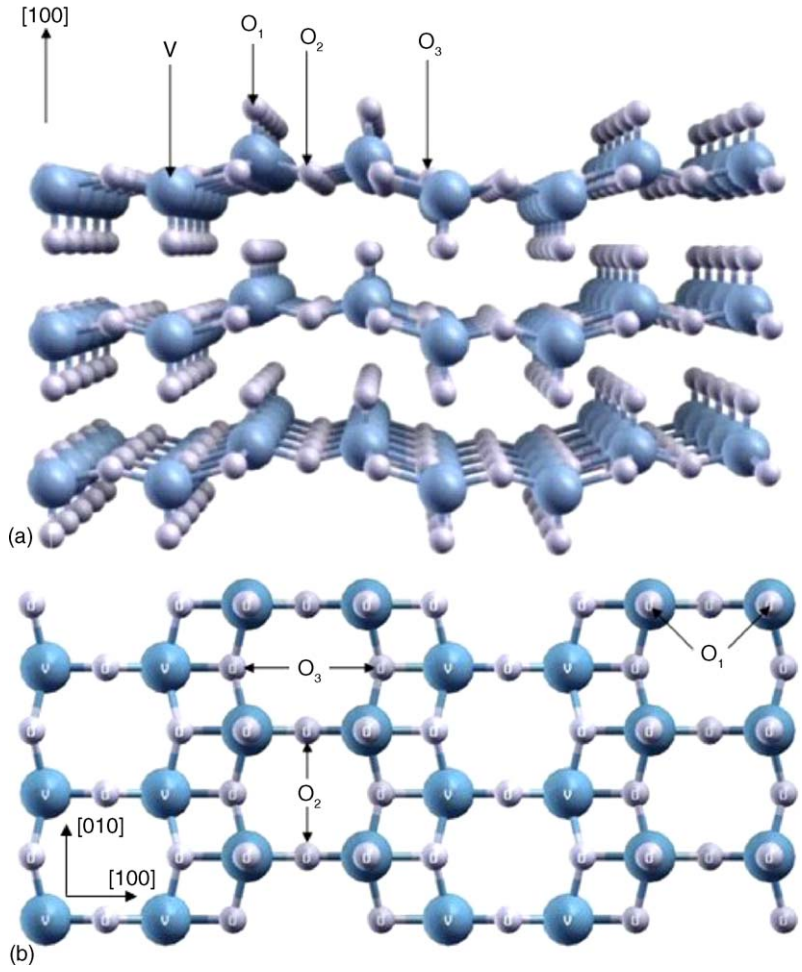

Fig. 1. (a) Perspective view of orthorhombic V_2O_5 crystal lattice, (b) and that projection on the (0 0 1) surface. The different types of oxygen atoms O_1, O_2 and O_3 are labelled.

$c = 3.56$ Å. The layers are characterized by periodic arrangements of edge and corner sharing VO_5 pyramids sticking out at both sides of the layer, see Fig. 1. There are three structurally different oxygen atoms, terminal (vanadyl) oxygens O_1 coordinated to one vanadium atom through a short bond (d(V–O) = 1.58 Å) and bridging oxygens O_2/O_3 coordinated to two or three vanadiums with V–O distances ranging between 1.78 and 2.02 Å. The interaction between the V_2O_5 layers is so small that the crystals cleave easily along the [0 0 1] direction. The $Li_xV_2O_5$ system can adopt many phases depending on temperature and lithium content x [14]. The α-$Li_xV_2O_5$ which has a low lithium content ($x < 0.1$) and the ε-$Li_xV_2O_5$ ($0.35 < x < 0.7$) are both stable at temperature below 400 °C. These two phases involve very little structural distortion of the bulk oxide.

3. Experimental procedure

3.1. Samples preparation

V_2O_5 and $Li_{0.03}V_2O_5$ single crystals have been grown by crystallization of the molten product. The powder of pure vanadium oxide was placed in a boat-shaped platinum crucible which was carried out in a quartz tube inside a furnace. A continuous purified oxygen stream was sent trough the tube. The temperature of the furnace was carried out at 50 °C/h up to a temperature higher than the melting point of the powder and kept at this temperature during 4 h to obtain a good diffusion of the different elements. In these conditions, single crystals lamella having a surface of about 20 mm × 3 mm and a thickness about 1 mm could be obtained. The faces of these obtained lamella were perfectly fat and highly reflecting. The X-ray diffraction patterns on the surface of the V_2O_5 single crystals show only the (0 0 1) peaks to appear indicating that these lamella are z-axis oriented (e.g. with the c-axis perpendicular to the surface).

3.2. AFM measurement

AFM measurements were performed in air using a Park Scientific Instruments Autoprobe CP Scanning Force Microscope that operates with an optical deflection sensor force. All imaging was performed with microfabricated Si_3N_4 cantilevers and microlever tips using a small repulsive force.