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Adsorption of CO on the $Ca_3Ru_2O_7$(001) surface

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ABSTRACT

The adsorption of CO molecules at the $Ca_3Ru_2O_7$(001) surface was studied using low-temperature scanning tunneling microscopy (STM) and density functional theory (DFT). $Ca_3Ru_2O_7$ can be easily cleaved along the (001) plane, yielding a smooth, CaO-terminated surface. The STM shows a characteristic pattern with alternating dark and bright stripes, resulting from the tilting of the RuO_6 octahedra. At 78 K, CO adsorbs at an apical surface O at the channel edge with a predicted binding energy of $E_{ads} = -0.85$ eV. After annealing at room temperature, the CO forms a strong bond ($E_{ads} = -2.04$ eV) with the apical O and the resulting carboxylate takes the place of the former surface O. This carboxylate can be decomposed by scanning the surface with a high sample bias voltage of $+2.7$ V, restoring the original surface.

1. Introduction

The surface chemistry of complex ternary transition metal oxides has emerged as an important research topic, since these materials are increasingly used in electrocatalysis and solid oxide fuel cells. A deeper understanding of surface properties on an atomic level is highly desirable. Surface-science investigations can deliver such insights, provided that appropriate model systems—single crystalline surfaces with a well-defined and known surface structure—are used. This is difficult for ternary materials, as the usual surface preparation method of sputtering and annealing affects the surface stoichiometry, which results in various, and often complex, surface reconstructions. An elegant way to prepare simple (1 × 1) terminated surfaces is cleaving appropriate layered materials. Here the Ruddelsden–Popper series $A_{n+1}Ru_nO_{3n+1}$ (A = Sr, Ca) has proven to be an ideal system, as high-quality crystals can be synthesized [1] and easily cleaved in ultrahigh vacuum (UHV) [2]. The original impetus to grow such crystals stems from their interesting physical properties including superconductivity, ferroelectricity, or magnetoresistance, which can be tuned by external parameters such as doping, fields, pressure, or temperature. Recent research [2–6] has shown that they are also ideal model systems for investigating surface reactivity at the atomic scale.

Up to now, surface-science studies have mostly focused on two specific materials, $Sr_3Ru_2O_7$ [2–4] and $Ca_3Ru_2O_7$ [5,6], with a similar electronic and geometric structure. The repeating unit consists of two vertically stacked perovskite $ARuO_3$ (A = Sr, Ca) cells with RuO_6 octahedra separated from the next unit by a rock-salt-like AO type interface. At this interface, the layered structure is easily cleaved [2], leading to large, pristine AO terminated (001) surfaces. The bulk structures of these two particular AO-terminated materials show small, but significant differences in the arrangement of the RuO_6 octahedra, which leads to distinct differences in their surface structures. While the RuO_6 octahedra are only rotated around the [001] axis in $Sr_3Ru_2O_7$ [7], they are both rotated and tilted in $Ca_3Ru_2O_7$ [8]. Therefore, the surface layer of $Sr_3Ru_2O_7$(001) is identical to that of a binary SrO oxide, albeit at a larger lattice constant, while the additional tilting leads to alternating wide/narrow channels with decreased/increased oxygen density along the [010] direction on a $Ca_3Ru_2O_7$(001) surface, see Fig. 1.

This distinct difference in the surface structure strongly influences the adsorption behavior of various small molecules including H_2O and O_2. As shown recently, water adsorbs in a dissociated configuration on both $Sr_3Ru_2O_7$ [4] and $Ca_3Ru_2O_7$ [5] at low coverage. The split-off proton forms a surface hydroxyl with an apical oxygen of a RuO_6 octahedron, holding the remaining OH_{ads} fragment adsorbed at an A–A cation bridge in place via formation of a hydrogen bond. However, on $Sr_3Ru_2O_7$, this OH_{ads} can hop around the surface hydroxyl with a low activation energy of 187 meV [4], while on $Ca_3Ru_2O_7$ the channels caused by the tilting of the octahedra prevent a hopping of the OH_{ads}

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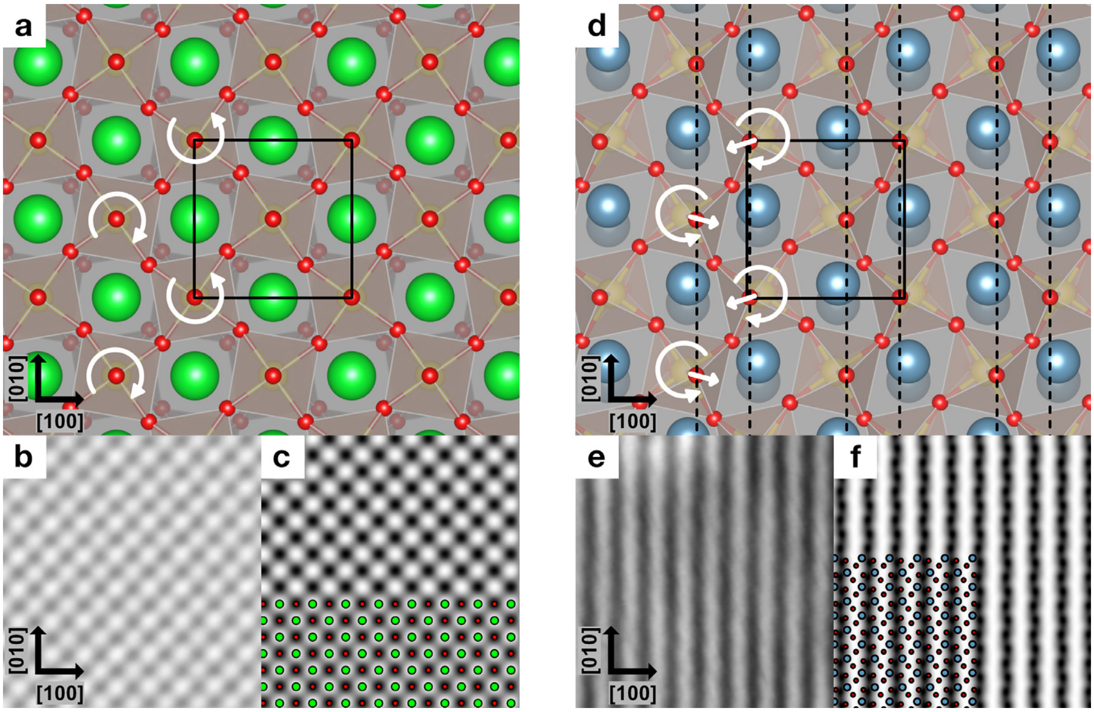

Fig. 1. Surface structure of $Sr_3Ru_2O_7$ and $Ca_3Ru_2O_7$. Ca - blue, Sr - green, Ru - yellow, O - red. **(a)**: $Sr_3Ru_2O_7$ surface structure with the (1 × 1) unit cell [2]. **(b)–(c)**: experimental and simulated STM, respectively. STM parameters: $V_s = +0.05\,V$, $I_t = 0.15\,nA$, $T = 78\,K$. **(d)**: $Ca_3Ru_2O_7$ surface with the (1 × 1) unit cell. The dashed lines indicate the characteristic wide and narrow channels caused by the tilting of the octahedra. **(e)–(f)**: experimental and simulated STM, respectively. STM parameters: $V_s = +0.8\,V$, $I_t = 0.1\,nA$, $T = 78\,K$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

fragment [5]. At higher water coverages, rows of dissociated H_2O are formed on $Sr_3Ru_2O_7$(001) along the [100] and [010] directions, which finally connect to cages and capture molecularly adsorbed water [4]. In contrast, on $Ca_3Ru_2O_7$(001) the higher reactivity of the surface results in only dissociative adsorption of water, and the resulting hydroxyl structures extend only along the preferred surface channels. Molecularly adsorbed water is found only in a second layer [5].

The adsorption behavior of oxygen also reflects the structural differences of the (001) surfaces of $Sr_3Ru_2O_7$ and $Ca_3Ru_2O_7$. In both cases, O_2 adsorbs as a superoxo O_2^- species by electron transfer from the valence band of the substrate [6,9]. At low coverages, the adsorbed O_2^- molecule sits at an A–A cation bridge site in a slightly tilted geometry. On $Ca_3Ru_2O_7$, the channel structure of the surface caused by the tilting of the octahedra results in a stark preference of the O_2^- to adsorb at wider channels where the octahedra are tilted away from each other, while the higher symmetry of the $Sr_3Ru_2O_7$ surface does not give preference to a specific A–A cation bridge site. This pattern persists at high coverage, where on $Ca_3Ru_2O_7$ a zig-zag pattern is formed that follows the wider channels [6]. On $Sr_3Ru_2O_7$ a similar zig-zag pattern of O_2^- adsorbed at Sr–Sr bridge sites is predicted, but without a directional preference [9].

The adsorption of CO molecules has so far only been studied on the $Sr_3Ru_2O_7$(001) surface [3]. There, the CO adsorbs weakly above an apical surface oxygen at liquid-nitrogen temperature. After heating the sample to 100 K, the CO is activated and forms a metal carboxylate. This occurs by breaking the surface Ru–O bond and forming a bent COO with C bound to the Ru atom beneath. Due to the high symmetry of the surface, the surface carboxylate can rotate by 90° with a calculated barrier of 0.44 eV, which can be overcome by scanning with the STM tip at +2.4 V sample bias voltage [3].

In this work we show that $Ca_3Ru_2O_7$(001) shows a similar behavior as $Sr_3Ru_2O_7$(001) with regard to CO adsorption, albeit with differences attributed to the specific surface symmetry. CO adsorbs weakly at 78 K, but activation either by annealing or manipulation with the STM tip causes the formation of the same Ru–COO carboxylate complex as on $Sr_3Ru_2O_7$(001). However, due to the tilting of the surrounding RuO_6 octahedra one rotational orientation of the carboxylate is preferred due to the reduced surface symmetry.

2. Methods

2.1. Experiment

We have used high-quality calcium ruthenate single crystals grown by the floating zone technique using a mirror-focused furnace [10]. Before insertion into the UHV, the samples were fixed on stainless-steel sample plates with conducting silver epoxy glue (EPO-TEK H21D, Epoxy Technology Inc.), and a metal stud was glued on top with another epoxy adhesive (EPO-TEK H77, Epoxy Technology Inc.). The crystals were cleaved in UHV at 110 K by removing the metal stub with a wobble stick. STM measurements were carried out in a UHV system consisting of a preparation chamber and an STM chamber with base pressures of 2×10^{-11} and 6×10^{-12} mbar, respectively. A low-temperature STM (commercial Omicron LT-STM) was operated at 78 K in constant-current mode using an electrochemically etched W-tip. For all STM measurements the bias voltage was applied to the sample; positive or negative bias voltages result in STM images of the unoccupied or occupied states, respectively. All STM images shown were corrected for distortions as described elsewhere [11]. CO was dosed to the STM head at a temperature of 78 K, with a leak valve in direct line of sight to the sample. Since CO not reaching the sample is efficiently pumped by the walls of the cryostat, the gas doses measured with a Bayard Alpert gauge are very inaccurate.

2.2. Computational methods

The DFT calculations were performed with the Vienna *Ab-Initio* Simulation Package (VASP) using the projector-augmented plane wave

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