Communication

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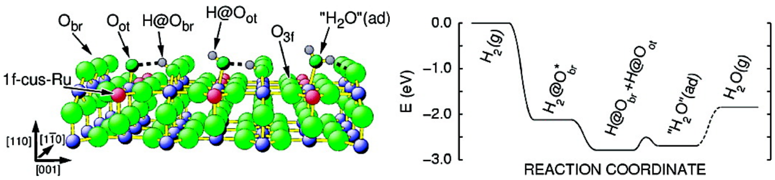

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Hydrogen Transfer Reaction on the Surface of an Oxide Catalyst

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Oxide catalysts are considered to be versatile in heterogeneous catalysis because of the presence of chemically distinct reactive centers on their surface, acting as either acidic or basic sites, and the intimate interplay of these centers in catalyzed reactions.[1] For instance, the model catalyst $RuO_2(110)$ exposes two kinds of active surface species that have shown to govern the interaction of the gas phase in contact with this surface.[2,3] These are the so-called 1f-cus-Ru atoms (1f-*cus* stands for 1-fold *c*oordinatively *u*nsaturated *s*ites: acidic sites) and the bridging O atoms O_{br} (basic sites), both of which are 1-fold undercoordinated with respect to the Ru and O atoms in bulk environment (cf. Figure 1).

Most of the molecules studied thus far on the $RuO_2(110)$ surface adsorb from the gas phase initially above the 1f-cus Ru atoms.[3] The CO molecule, for instance, adsorbs first on the 1f-cus-Ru site and then recombines with the bridging O atom to form CO_2 above room temperature.[2,4−8] In this oxidation reaction the bridging O atoms are consumed rather than serve as a reactive center. Quite in contrast, hydrogen molecules have shown to interact preferentially with the bridging O atoms, forming hydroxyl groups and a kind of water molecule.[9]

Here we will elucidate the cooperative interplay of the two active surface sites on $RuO_2(110)$ for a simple model reaction, namely the water formation over RuO_2 catalysts when supplying hydrogen and oxygen from the gas phase. Oxygen molecules adsorb dissociatively above the 1f-cus Ru atoms, forming on-top O atoms O_{ot}, while the incoming hydrogen molecules accommodate solely above the bridging O atoms. Subsequently, the on-top O species picks up sequentially two hydrogen atoms from the bridging O atoms—*hydrogen transfer reaction*—thereby forming adsorbed water above the 1f-cus-Ru atoms.

To study the water reaction on $RuO_2(110)$, we exposed the $RuO_2(110)$ surface to 50 L (1 L = 1.33×10^{-6} mbar•s) of D_2 at room temperature and recorded a thermal desorption (TD) spectrum of D_2O using a quadrupole mass spectrometer and a heating rate of 10 K/s. In a second experiment, we exposed the $RuO_2(110)$ surface to 50 L of D_2 at room temperature and then saturated the surface by on-top O. Both D_2O TD spectra are shown in Figure 2. Clearly, the production of D_2O is dramatically increased by a factor of 20 when on-top O is present on the surface. These experiments teach us two lessons: First, D_2 adsorbs on the stoichiometric $RuO_2(110)$ surface, barely removing oxygen from the oxide surface, and second, the presence of on-top O species is mandatory for efficient water production.

To determine the entrance channel of hydrogen, we reversed the sequence of the above adsorption experiment. We first saturated the $RuO_2(110)$ surface with on-top O, thereby blocking all the 1f-cus Ru atoms, and subsequently exposed the surface to 50 L of D_2. If hydrogen enters the surface only via the 1f-cus-Ru atoms, then blocking these sites by on-top O is to suppress the hydrogen adsorption and consequently the water formation. However, the amount of produced D_2O is not affected by the sequence of adsorption. Therefore D_2 adsorbs preferentially through the surface O atoms rather than via the 1f-cus Ru atoms, challenging recent DFT-based "predictions".[10]

Next we took TD spectra of D_2O and O_2 (Figure 3), exposing various D_2 doses: in each experimental run we exposed first the $RuO_2(110)$ surface to D_2 and saturated subsequently the surface with on-top O (by dosing 5 L of O_2 at room temperature). We notice that with increasing D_2 pre-exposure more D_2O is produced and less on-top O is left on the surface. The integral TD signals of D_2O and O_2 (integrated from 300 to 600 K) are complementary in that the sum of both TD signals is independent of the D_2 dose. From the shape of the TD traces we infer that the O_2 desorption proceeds with second-order kinetics consistent with that of two neighboring on-top O atoms that recombine to form O_2. Quite in contrast, the water signal follows first-order reaction kinetics with

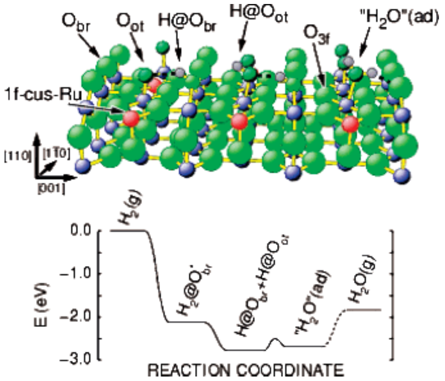

Figure 1. (Top) Ball and stick model of the $RuO_2(110)$ surface under oxidizing conditions. Oxygen atoms are indicated by large balls, while the Ru atoms are presented as small balls bridging O = O_{br}, on-top O = O_{ot}, 1-fold undercoordinated Ru site = 1f-cus Ru. (Bottom) Energy diagram of the water formation along the reaction path calculated from DFT. Hydrogen bonds are indicated by dashed lines, and the asterisk marks an unstable configuration. Without O_{ot} on the surface the binding energy of $H_2@O_{br}$ is only 0.3 eV. We estimate the error bars in the relative energies to be at most ca. 0.1 eV.

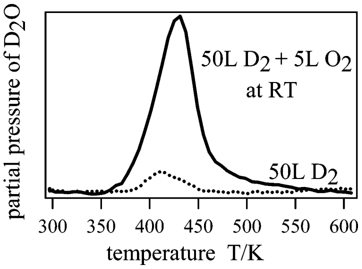

Figure 2. Temperature-programmed reaction of water D_2O by dosing only 50 L of D_2 (dotted line) and dosing first 50 L of D_2 and then 5 L of O_2 (solid line).

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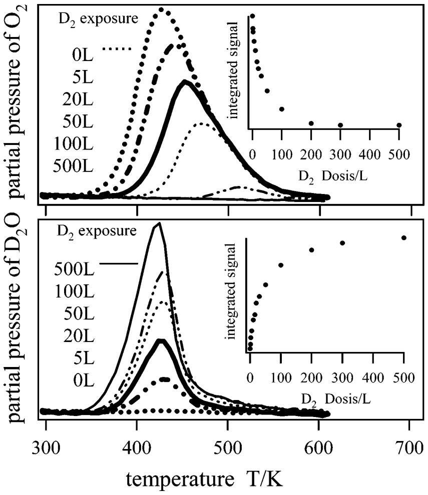

Figure 3. Predosing various D_2 doses (0−500 L) and postdosing 5 L of O_2 to saturate the surface with on-top O. (Top) Desorption of O_2 for various D_2 doses. (Inset) Temperature-integrated (300−600 K) O_2 TD spectra. (Bottom) Temperature-programmed D_2O reaction for various D_2 doses. (Inset) Temperature-integrated (300−600 K) D_2O TPR spectra.

a maximum at 420 K. This reaction order suggests that D_2O desorption is the rate-determining step. At a D_2 exposure of 500 L, no O_2 leaves the surface below a temperature of 600 K.

The last question we want to settle with mass spectrometry is whether both surface species—bridging O and on-top O—are equally capable in the accommodation of D_2. Exposing the stoichiometric RuO_2(110) surface to CO at room-temperature, we replaced all the bridging O atoms by bridging CO.[11] Subsequently, we saturated the 1f-cus Ru atoms by on-top O atoms (exposure of 5 L of O_2 at 200 K) and dosed 500 L of D_2. With mass spectrometry we followed the temperature-dependent production of D_2O, CO_2, and the O_2. No D_2O is detected, and most of the bridging CO molecules recombine with on-top O to form CO_2 identical to the case when no D_2 is post-exposed.[8,12] This experiment provides strong evidence that the on-top O species is hardly able to adsorb D_2. This finding is quite counterintuitive as we would have expected that the on-top O is much easier to polarize than bridging O atoms and therefore more prone to adsorbed D_2. Again the on-top O species on RuO_2(110) surprises by its inactive behavior.[13]

With DFT calculations[14] we studied the hydrogen transfer reaction from the bridging O atoms toward the on-top O atoms. In the first reaction step we started from a configuration where two hydrogen atoms sit on a single bridging O atom and no hydrogen atom is adsorbed on the on-top O species. Our DFT calculations indicate that there is no energy barrier for one hydrogen to shift to the on-top O site (cf. Figure 1). This means that the first hydrogen atoms move spontaneously from the bridging to the on-top O position. The reverse reaction is of course activated by the hydrogen adsorption energy (i.e., 0.7 eV per hydrogen atom). The final state of this reaction pathway is characterized by a hydrogen bond between the bridging O and the H atom now covalently attached to the on-top O atom.

The second reaction path modeled was the transfer of the second hydrogen atom from the bridging O to the on-top O atom.[15] In the initial state of this reaction, both the on-top and the bridging O atoms carry one hydrogen atom. The minimum energy configuration is characterized by the $O_{ot}H$ group that is inclined toward the next-row bridging O atom and a second hydrogen bond between the H atom from the bridging O atom and the on-top O atom. The reaction coordinate is again the separation of the on-top O species and the hydrogen atoms sitting on the bridging O atom. DFT calculations determined the energy barrier to be 0.28 eV. This activation barrier is still quite low compared to the desorption/reaction temperature of 420 K (cf. Figures 2 and 3). However, the resulting water molecule adsorbs quite strongly by 0.84 eV over the 1f-cus-Ru atoms, in agreement with a recent DFT study.[10] The strong adsorption of water is therefore consistent with the desorption temperature of 420 K and the observed first-order kinetics. The strong adsorption of water is also supported by a recent X-ray diffraction study[16] and HREELS measurements.[17] From our DFT calculations we infer that hydrogen bonding is important to lower the activation barriers for the hydrogen transfer reactions, similar to the well-known Grotthus effect,[18] where the fast diffusion of protons is explained in terms of structure diffusion.

The quintessential point is that the RuO_2(110) surface provides a nice example of a synergy effect in the catalyzed water reaction: The bridging O atoms harvest the hydrogen from the gas phase, while the on-top O atoms pick up those adsorbed hydrogen atoms from the bridging O atoms to form water. The mechanism of *hydrogen transfer* is mediated by the strong hydrogen bond. The hydrogen transfer is expected to play an important role for the whole class of catalyzed hydrogenation and dehydrogenation reactions of hydrocarbons over RuO_2.[19]

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