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Direct Imaging of Catalytically Important Processes in the Oxidation of CO over $RuO_2(110)$

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Ruthenium dioxide (RuO_2) reveals unique and promising redox properties, making RuO_2 a potential candidate for a versatile oxidation catalyst. Recently Zhang and Kisch[1] reported, for instance, that hydrated RuO_2 is a robust and efficient catalyst for room temperature oxidation of CO by humid air; recall that typical metal oxides do not tolerate humidity. In this contribution we present scanning tunneling microscopy (STM) data which directly image the catalytically important processes occurring on the RuO_2(110) surface after exposing the pristine surface to CO and O_2. The STM data are substantiated by density functional theory (DFT) calculations.

In the bulk rutile structure of RuO_2 the Ru atoms are 6-fold coordinated to oxygen atoms, while the O atoms are coordinated to three Ru atoms in a planar sp^2 hybridization. On the stoichiometric $RuO_2(110)$ surface two kinds of under-coordinated surface atoms are stabilized (cf. Figure 1a). These are the bridging oxygen atoms (O_{br}), which are coordinated only to two Ru atoms underneath (Ru−O bond length 1.94 Å), and the so-called 1f-cus-Ru atoms, i.e. 1-fold under-coordinated Ru atoms.[2] In Figure 1b we show an experimental 5 nm × 5 nm STM image of this surface taken at room temperature. Clearly, there are rows of protrusions visible along the [001] direction. STM simulations (cf. Figure 1c), using the Tersoff−Hamann model[3] within DFT, indicate that the bridging oxygen atoms are imaged as bright regions. This result is quite remarkable as for the $TiO_2(110)$ surface the observed protrusions in STM images were ascribed to 1f-cus-Ti atoms.[4] It demonstrates also that an interpretation of STM images needs additional information, such as provided by DFT calculations.

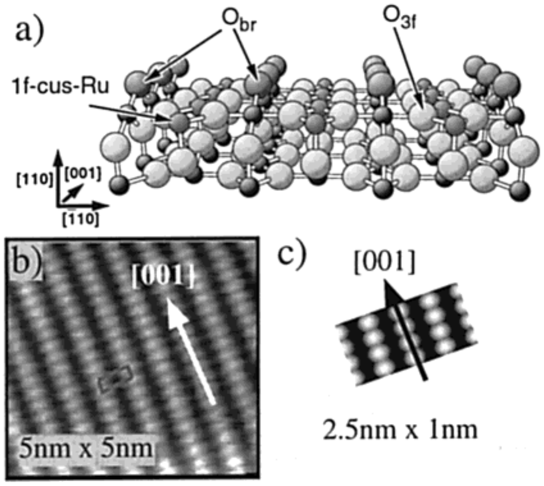

Figure 1. (a) Stick and ball model of the stoichiometric $RuO_2(110)$ surfaces. O and Ru atoms are shown as large and small balls, respectively. A bridge bonded O (O_{br}), a 3-fold coordinated O atom (O_{3f}), and a 1-fold under-coordinated Ru atom (1f-cus-Ru) are indicated. (b) Experimental STM image (constant current mode, taken at room temperature) of a stoichiometric $RuO_2(110)$ surface: 5 nm × 5 nm, $U = -0.01$ V, $I = 0.46$ nA. (c) STM simulation of the stoichiometric $RuO_2(110)$, using the Tersoff−Hamann model. The origin was set to the lateral position of Ru atoms attached to the O_{br} atoms. Therefore the bright spots seen in the simulated STM image are uniquely assigned to bridging O atoms.

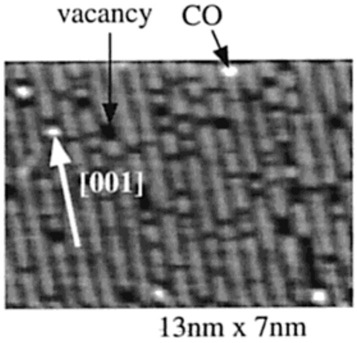

Figure 2. STM image (13 nm × 7 nm; constant current mode, room temperature) of the (partially) reduced $RuO_2(110)$ surface that was prepared by exposing 0.5 L of CO at 370 K. $U = -2.4$ V, $I = 5.0$ nA. The rows of bridging O atoms (bright rows) are interrupted by single and grouped vacancies. The single bright features are assigned to adsorbed CO molecules on the vacancies along the bridging O rows.

The extraordinarily high activity of stoichiometric $RuO_2(110)$ toward CO oxidation was demonstrated (on the atomic scale) to be controlled by the presence of 1-fold coordinatively unsaturated Ru sites (1f-cus-Ru).[5−7] We emphasize that not defects but rather the regular, under-coordinated surface atoms determine the activity of RuO_2. On the stoichiometric $RuO_2(110)$ surface, CO molecules adsorb strongly (adsorption energy exceeding 1.2 eV[8]) on-top of the 1f-cus-Ru atoms from where the actual oxidation reaction takes place via recombination with under-coordinated (and therefore weakly bound) bridging oxygen to form CO_2 (so-called Mars−van Krevelen mechanism[9]). Recent HREELS measurements[10] have confirmed and refined this view. The authors showed that CO exposure to $RuO_2(110)$ at room temperature removes the bridging oxygen, which is characterized by a vibrational loss at 69 meV.[11] DFT calculations identified the transition state of this reaction step.[12] If several neighboring bridging oxygen atoms have been removed, 2-fold coordinatively unsaturated Ru sites (2f-cus-Ru) are created offering two dangling bonds for the bonding with molecules from the gas phase. In Figure 2 this removal of bridging oxygens is verified by an STM image that was taken after the stoichiometric $RuO_2(110)$ surface had been exposed to 0.5 L of CO at 370 K. The bright rows reveal isolated vacancies and strings of vacancies. Occasionally isolated bright spots are visible in the vacancies along the bridging oxygen rows,

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(1) Zhang, L.; Kisch, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 3921.
(2) Kim, Y. D.; Seitsonen, A. P.; Over, H. *Surf. Sci.* **2000**, *465*, 1.
(3) Tersoff, J.; Hamann, D. R. *Phys. Rev. B* **1985**, *31*, 805.
(4) Diebold, U.; Anderson, J. E.; Ng, K.-O.; Vanderbilt, D. *Phys. Rev. Lett.* **1996**, *77*, 1322.
(5) Over, H.; Kim, Y. D.; Seitsonen, A. P.; Wendt, S.; Lundgren, E.; Schmid, M.; Varga, P.; Morgante, A.; Ertl, G. *Science* **2000**, *287*, 1474.
(6) Kim, Y. D.; Over, H.; Krabbes, G.; Ertl, G. *Top. Catal.* **2001**, *14*, 95.
(7) Böttcher, A.; Rogazia, M.; Niehus, H.; Over, H.; Ertl, G. *J. Phys. Chem. B* **1999**, *103*, 6267.
(8) Kim, Y. D.; Seitsonen, A. P.; Over, H. *Phys. Rev. B* **2001**, *63*, 115419.
(9) Mars, P.; van Krevelen, D. W. *Chem. Eng. Sci. Suppl.* **1954**, *3*, 41.
(10) Fan, C. Y.; Wang, J.; Jacobi, K.; Ertl, G. *J. Chem. Phys.* **2001**, *114*, 10058.
(11) Kim, Y. D.; Seitsonen, A. P.; Wendt, S.; Wang, J.; Fan, C. Y.; Jacobi, K.; Over, H.; Ertl, G. *J. Phys. Chem. B* **2001**, *105*, 3752.
(12) Liu, Z.-P.; Hu, P.; Alavi, A. *J. Chem. Phys.* **2001**, *114*, 5956.

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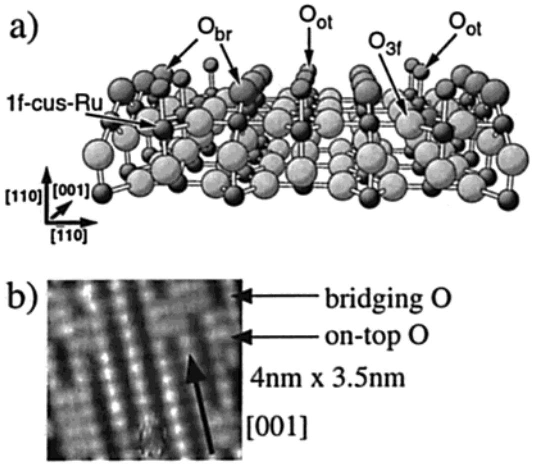

Figure 3. (a) Stick and ball model of the stoichiometric $RuO_2(110)$ surfaces covered with weakly bound oxygen (O_{ot}) in on-top position above the 1f-cus-Ru atoms. O and Ru atoms are indicated as large and small balls, respectively. (b) STM image (5 nm × 4 nm; constant current mode, room temperature) of the $RuO_2(110)$ surface that was exposed to 0.1 L of oxygen at room temperature. $U = 0.01$ V, $I = 0.46$ nA.

i.e. above the 2f-cus-Ru atoms. These features are assigned to adsorbed CO molecules in agreement with a recent HREELS study[13] and our DFT calculations. The adsorption energy of a single CO molecule substituting a bridging O atom is 1.73 eV. If all O_{br} atoms have been removed, CO molecules bridging the 2f-cus-Ru atoms or terminating the 1f-cus-Ru atoms are bound by 1.85 and 1.61 eV, respectively. The activation barriers for CO diffusion are of the order of 1 eV. Therefore, at room temperature the CO molecules can be imaged by STM.

An equally important process is the facile reoxidation of a (partially) reduced $RuO_2(110)$ surface by oxygen supply from the gas phase. A weakly held oxygen species was found to adsorb on-top of the 1f-cus-Ru atoms (cf. Figure 3a), and it has been argued that this species actuates the restoration of the reduced $RuO_2(110)$ surface.[11] The latter process is mandatory to keep the oxide catalyst active under reaction conditions. Oxygen molecules from the gas phase can efficiently dissociate on $RuO_2(110)$ with a sticking probability of 0.8 at room temperature.[14]

Exposing the stoichiometric $RuO_2(110)$ surface to oxygen at RT stabilizes a weakly held oxygen species that desorbs at about 450 K.[14] In Figure 3b we show an STM image of such a prepared $RuO_2(110)$ surface. Clearly additional bright features are visible in this image if compared to the stoichiometric surface (cf. Figure 1b). From the registry of these new features with respect to the bridging O atoms, the weakly held oxygen is inferred to adsorb on-top of the 1f-cus-Ru atoms. Another important aspect is that the protrusions in the STM image appear almost always as pairs or multiples of pairs, indicating that the mobility of the weakly held oxygen species is limited at room temperature. This observation supports the view that the molecular oxygen species is the precursor state for the dissociation process. At temperatures below 140 K molecular oxygen lies down on the $RuO_2(110)$ surface (as an intact entity), bridging two adjacent 1f-cus-Ru atoms.[11,15] On increasing the sample temperature, the molecular oxygen dissociates and forms terminal Ru−O bonds to the 1f-cus-Ru atoms. Since the diffusion barrier of on-top O species is so high (1.2 eV along the [001] direction as determined by DFT calculations) even at room temperature the on-top oxygen atoms are primarily grouped in pairs. However, if there is an adjacent vacancy in the rows of O_{br}, the diffusion barrier of on-top oxygen to migrate from the 1f-cus-Ru to the 2f-cus-Ru site is only 0.6 eV. Therefore this diffusion process is very likely at room temperature and correspondingly important for the restoration of a mildly reduced $RuO_2(110)$ surface.

Let us recapitulate the microscopic steps governing the catalytic activity of RuO_2 on the atomic scale. These steps were characterized in real-space with STM, which may pave the way to identify reaction processes in more complex reactions such as the partial oxidation reaction of alcohols. The reactants from the gas phase encounter strongly binding adsorption sites on the $RuO_2(110)$ surface in the form of the under-coordinated Ru atoms. For instance, CO adsorbs on the stoichiometric $RuO_2(110)$ surface by 1.2 eV (over the 1f-cus-Ru), while on the mildly reduced RuO_2-(110) surface the CO binding energy is 1.85 eV for the adsorption over 2f-cus-Ru atoms.[13] The RuO_2 surface provides an active oxygen species to react with CO, i.e. the under-coordinated (bridging) lattice oxygen atoms. The recombination of adsorbed CO with O_{br} creates vacancies, which were identified with STM. At room temperature, oxygen molecules from the gas phase can efficiently dissociate on $RuO_2(110)$ via the molecular precursor state. This leads to weakly bound O atoms, which absorb above the 1f-cus-Ru atoms and which are grouped in pairs as images in STM. This weakly held O species is important for the restoration of a mildly reduced $RuO_2(110)$ surface where bridging O atoms are removed due to recombination with CO molecules.

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(13) Wang, J.; Fan, C. F.; Jacobi, K.; Ertl, G. *Surf. Sci.* **2001**, *481*, 113.

(14) Böttcher, A.; Niehus, H. *Phys. Rev. B* **1999**, *60*, 14396.

(15) Seitsonen, A. P.; Kim, Y. D.; Over, H. Unpublished LEED and DFT calculations.