Direct Imaging of Catalytically Important Processes in the Oxidation of CO over RuO2(110)

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Ruthenium dioxide (RuO2) reveals unique and promising redox properties, making RuO2 a potential candidate for a versatile oxidation catalyst. Recently Zhang and Kisch‡ reported, for instance, that hydrated RuO2 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 RuO2-(110) surface after exposing the pristine surface to CO and O2. The STM data are substantiated by density functional theory (DFT) calculations.

In the bulk rutile structure of RuO2 the Ru atoms are 6-fold coordinated to oxygen atoms, while the O atoms are coordinated to three Ru atoms in a planar sp2 hybridization. On the stoichiometric RuO2(110) surface two kinds of under-coordinated surface atoms are stabilized (cf. Figure 1a). These are the bridging oxygen atoms (Obr), 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. 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 model1 within DFT, indicate that the bridging oxygen atoms are imaged as bright regions. This result is quite remarkable as for the TiO2(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.

The extraordinarily high activity of stoichiometric RuO2(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 RuO2. On the stoichiometric RuO2(110) surface, CO molecules adsorb strongly (adsorption energy exceeding 1.2 eV8) 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 CO2 (so-called Mars–van Krevelen mechanism9). Recent HREELS measurements10 have confirmed and refined this view. The authors showed that CO exposure to RuO2(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 RuO2(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.
i.e. above the 2f-cus-Ru atoms. These features are assigned to adsorbed CO molecules in agreement with a recent HREELS study\(^1\) 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.\(^1\) 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.\(^1\) Exposing the stoichiometric RuO\(_2\) (110) surface to oxygen at RT stabilizes a weakly held oxygen species that desorbs at about 450 K.\(^1\) 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.\(^1\) 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.\(^1\) 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) with a sticking probability of 0.8 at room temperature.\(^1\) Exposing the stoichiometric RuO\(_2\) (110) surface to oxygen at RT stabilizes a weakly held oxygen species that desorbs at about 450 K.\(^1\) 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.\(^1\) 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.

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