

# Atomic Scale Investigation of the Oxidation of CO on RuO<sub>2</sub>(110) by Scanning Tunneling Microscopy<sup>†</sup>

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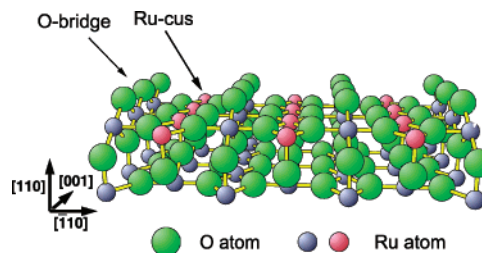
The reaction between adsorbed CO molecules and O atoms on epitaxially grown RuO<sub>2</sub>(110) was investigated by scanning tunneling microscopy. Two types of titration experiments were performed at 300 K, in which either CO was dosed on the stoichiometric oxide surface, or O<sub>2</sub> on the CO saturated surface. In both cases, reaction steps could be atomically resolved, and the surface mobility of adsorbed CO molecules and O atoms could be studied. CO molecules adsorbing on the stoichiometric surface react with bridge bonded O atoms at largely random positions. O<sub>2</sub> molecules adsorbing on the CO saturated surface react with cus-bonded CO molecules first at CO vacancies, and then also in a mainly random fashion. The statistical nature of the reaction is explained by the relatively high surface diffusion barriers, which are of the same size as the activation energies for the reactions.

## 1. Introduction

The oxidation of CO on the RuO<sub>2</sub>(110) surface has developed into a new model system for catalytic reactions on oxide surfaces. This breakthrough in understanding came with papers by Over et al. in 2000<sup>1</sup> and Fan et al. in 2001,<sup>2</sup> following pioneering work by Böttcher et al. in the late 1990s.<sup>3–6</sup> Initially, the interest in this system was stimulated by the unique catalytic properties of Ru, and it turned out that these are caused by the formation of an RuO<sub>2</sub> film at high oxygen pressures. However, RuO<sub>2</sub> has attractive features, such as metallic conductivity and the simple way in which single crystal, (110) oriented films can be prepared by surface oxidation of Ru(0001), that make it suitable for studying catalysis on oxides in general. In this paper, we present scanning tunneling microscopy (STM) experiments that were performed during reaction between CO molecules and O atoms on RuO<sub>2</sub>(110) and that aimed at an atomic scale analysis of the reaction mechanism. Previously published STM data of adsorbed CO and O mainly focused on the identification of the various species and on their adsorption sites.<sup>1,7–9</sup>

The essential structure elements of the stoichiometric RuO<sub>2</sub>-(110) surface (Figure 1) are [001]-oriented rows of O atoms (“O-bridge”), which reside on bridge positions with respect to the Ru atoms of the next layer, and rows of “coordinatively unsaturated Ru sites” (“Ru-cus”) between.<sup>1,10–12</sup> The equivalent Ru atoms in the bulk have one O atom on top, whereas at the surface they carry one perpendicular dangling bond each, rendering them a prominent role in the surface chemistry of RuO<sub>2</sub>(110).

The reaction between CO and O on RuO<sub>2</sub>(110) is currently understood as follows.<sup>1,2,7,9,13–18</sup> A CO molecule that adsorbs on the stoichiometric surface first binds to the dangling bond of an Ru-cus atom to form “CO-cus”. At 300 K, this species is



**Figure 1.** Structure model of the stoichiometric RuO<sub>2</sub>(110) surface. Indicated are the rows of topmost O atoms on bridge positions (“O-bridge”) and the coordinatively unsaturated Ru sites (“Ru-cus”).

not stable, the CO-cus reacts with a neighboring O-bridge atom to give CO<sub>2</sub>, which desorbs instantly. The created O-bridge vacancy can then be filled by another CO molecule, to give “CO-bridge”. In this way, all O-bridge atoms can be reacted off and replaced by CO-bridge molecules. An O<sub>2</sub> molecule adsorbing on the surface that has before reacted with CO and is covered by CO-bridge first dissociates at the dangling bonds of a pair of Ru-cus atoms to form two “O-cus”. The O-cus atoms can then react with neighboring CO-bridge molecules to give CO<sub>2</sub>, the vacancies on the bridge sites can be occupied by further O atoms, which restores the original structure of the stoichiometric surface. There are also conditions, where O-cus and CO-cus can exist simultaneously, in which case these two species directly react with each other.

This reaction scheme was mainly derived from titration experiments, in which CO was dosed on an O covered surface, or vice versa. For steady-state conditions, there are indications<sup>19,20</sup> that two reaction channels play a prominent role, namely the reaction between CO-cus molecules and O-bridge atoms and between CO-cus and O-cus.

In the present study, we have investigated these two processes by means of STM. The experiments were performed as titrations, by dosing CO on the stoichiometric surface, and by dosing O<sub>2</sub> on the CO-cus covered surface. We focus on microscopic questions that have remained open: What is the spatial distribution of the reaction? How mobile are the adsorbed CO

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molecules and O atoms during the reaction? These spatial effects are essential ingredients for a complete description of the reaction mechanism. STM investigations of other surface reactions, e.g., of the oxidation of CO on Pt(111),<sup>21</sup> have shown that the adsorbed reactants are not necessarily randomly distributed, but can cluster in islands because of adsorbate–adsorbate interactions, and that such effects can dominate the reaction kinetics. For adsorbed CO and O on RuO<sub>2</sub>(110) DFT calculations revealed adsorbate–adsorbate interactions of some 0.1 eV,<sup>15,20</sup> i.e., an order of magnitude smaller values than the respective adsorption energies. However, such energies are still large compared to  $kT$  at 300 K and hence possibly relevant for the surface distribution of the reactants. Nonrandomness may also be caused by reaction at defects.<sup>22</sup> For rutile TiO<sub>2</sub>(110), which is structurally identical to RuO<sub>2</sub>(110), an important role of defects has indeed been observed.<sup>23</sup>

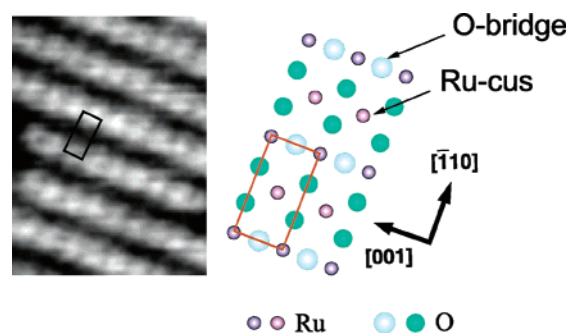
## 2. Experimental Section

The STM experiments were performed in an ultrahigh vacuum (UHV) system that was additionally equipped with Auger electron spectroscopy, optics for low energy electron diffraction, and an ion gun for sputtering. The STM was of the so-called “pocket size” type and was described in an earlier publication.<sup>24</sup> The base pressure in the UHV system was below  $1 \times 10^{-10}$  Torr. The Ru(0001) surface was prepared by sputtering/oxidation/annealing cycles as described elsewhere.<sup>25</sup> RuO<sub>2</sub>(110) films were prepared by dosing of  $2 \times 10^5$  L or  $1 \times 10^6$  L O<sub>2</sub> ( $1 \text{ L} = 1 \times 10^{-6}$  Torr  $\times$  s) on the Ru(0001) surface, at sample temperatures between 700 and 850 K.<sup>1,2</sup> The O<sub>2</sub> dosing was performed by means of a glass capillary gas shower that allowed to locally enhance the pressure in front of the sample to an estimated value of  $10^{-3}$  Torr, whereas the pressure in the chamber could be kept at  $1.2$  to  $2 \times 10^{-5}$  Torr. After preparation of the oxide film the sample was transferred into the STM.

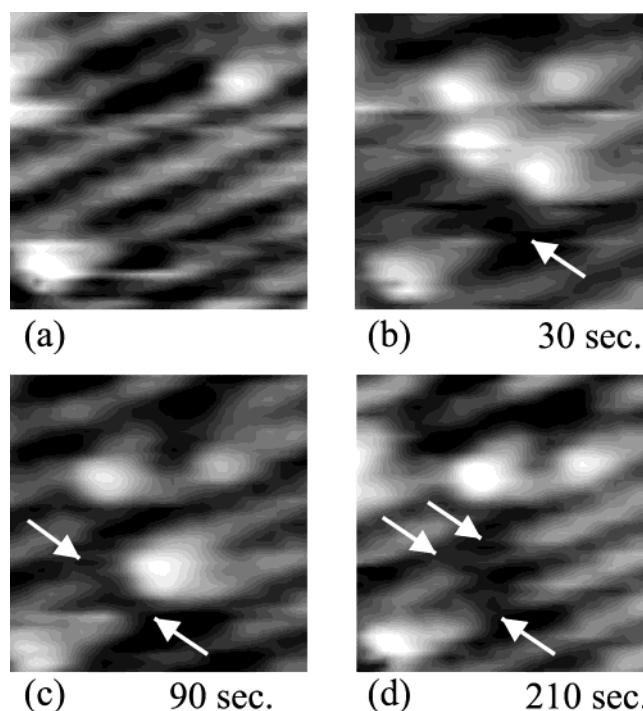
In the STM experiments, first a suitable area of the clean RuO<sub>2</sub>(110) surface was chosen. Then either small amounts of the respective gases were dosed in a step-by-step fashion, while the STM tip was withdrawn during each dosing step, or constant pressures of CO or O<sub>2</sub> were adjusted with the tip in tunneling distance. Data recorded under the latter conditions were included only when shadow effects of the tip could be ruled out, which was achieved by control experiments, in which the tip was retracted. STM images were recorded at room temperature.

## 3. Results

**3.1. Reaction of CO-cus with O-Bridge on the Stoichiometric RuO<sub>2</sub>(110) Surface.** STM images of the stoichiometric RuO<sub>2</sub>(110) surface showed bright rows, which, for high-resolution conditions, displayed an internal structure of close packed, bright oval spots (Figure 2). Similar data were obtained in previous STM investigations.<sup>1,7</sup> The period along the rows is approximately 3 Å, the distance between two rows about 6.5 Å, in good agreement with the dimensions of the unit cell of the RuO<sub>2</sub>(110) surface ( $3.11 \text{ Å} \times 6.38 \text{ Å}$ ). The rows in the STM data therefore reflect the row structure of the RuO<sub>2</sub>(110) surface (Figure 1 and model in Figure 2). Although it is not possible to directly allocate the bright oval spots to certain atoms or bonds on the surface, calculations of the  $E_F$ -LDOS have indicated that they represent the O-bridge atoms.<sup>8</sup> In this respect, the RuO<sub>2</sub> surface is different from the TiO<sub>2</sub> surface, where the O atoms appear dark.<sup>26</sup> The sample bias did not affect the contrast of the images. Sometimes, a contrast inversion was observed, which was mostly correlated with an unstable state of the tip, or occurred when the tip state changed during an adsorption experiment.

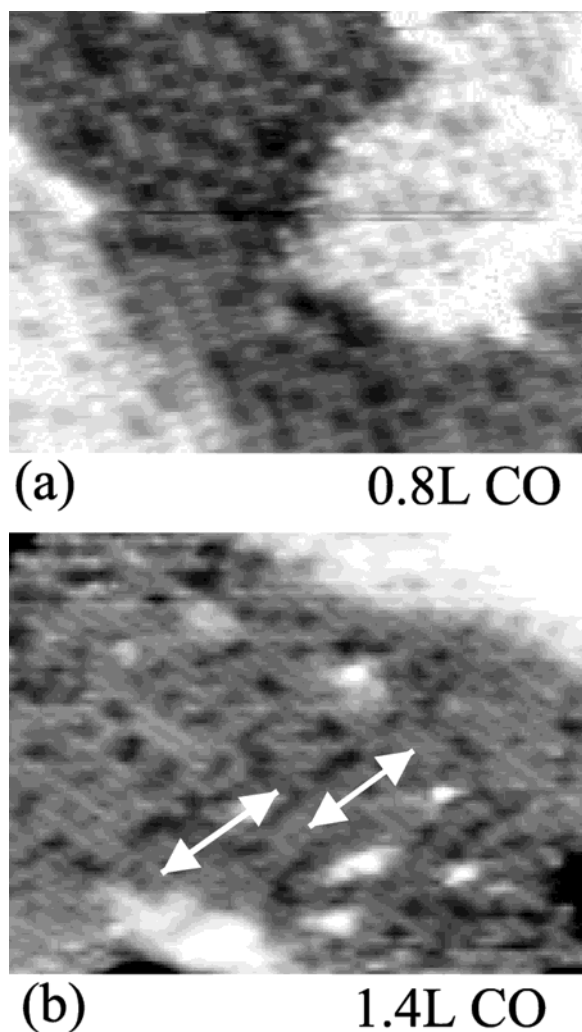


**Figure 2.** High-resolution image of the stoichiometric RuO<sub>2</sub>(110) surface. Tunneling voltage  $V = -0.6$  V, tunneling current  $I = 2.2$  nA, area  $27 \text{ Å} \times 40 \text{ Å}$ . ( $V$  is the sample potential with respect to the potential of the tip; same for the other STM data.) The rectangles in the image and in the top view model mark the unit cell of the stoichiometric RuO<sub>2</sub>(110) surface.



**Figure 3.** Series of STM images, recorded directly after dosing 0.3 L CO on the stoichiometric RuO<sub>2</sub>(110) surface. All frames are from the same surface area. (a) Stoichiometric RuO<sub>2</sub>(110) surface, (b) after 30 s, (c) after 90 s, (d) after 210 s. Bright rows are O-bridge, very bright dots occurring in (b) are interpreted as CO-cus molecules, dark sites as O-bridge vacancies created by the reaction (see arrows).  $V = -0.6$  V,  $I = 2.2$  nA,  $35 \text{ Å} \times 35 \text{ Å}$ .

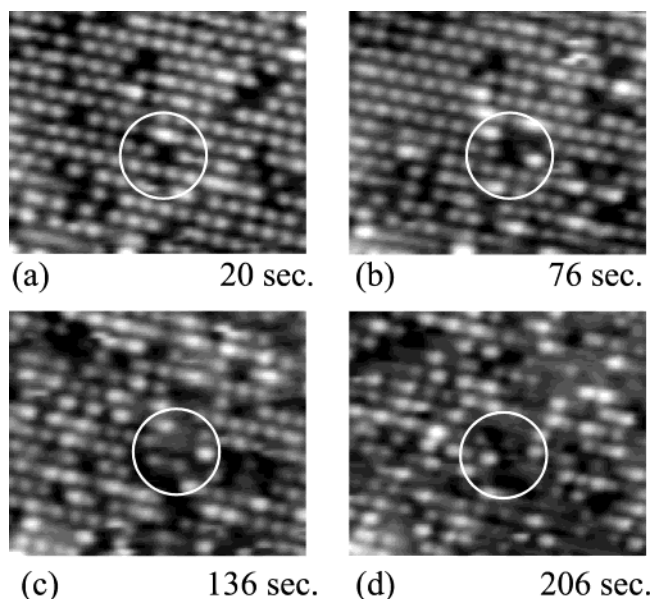
First, we present data that allow to verify the reaction scheme between the stoichiometric RuO<sub>2</sub>(110) surface and CO. The images of Figure 3 were recorded directly after dosing a small amount (0.3 L) of CO on the stoichiometric surface and are all from the same area of the surface. Figure 3a shows the row structure of the stoichiometric surface, the bright spot in the lower left corner is a defect that remained unchanged in the series and can serve as a marker of the scanning area. In the image recorded 30 s after the exposure (Figure 3b) one dark site appeared that is interpreted as an O-bridge vacancy created by the reaction (see arrow). In addition, three very bright spots appeared, located on sites between the bright rows. These are the positions of the Ru-cus atoms, suggesting that the features are three CO molecules, still bonded to the dangling bonds of the Ru-cus atoms between the unreacted O-bridge rows. The



**Figure 4.** STM images, recorded after exposures of 0.8 and 1.4 L of CO. (a) and (b) are from different surface areas. The data show the distribution of O-bridge vacancies (dark sites), created by reaction with CO, which is completely random in (a) and shows some preferential direction in (b) (arrows). (a)  $V = 0.6$  V,  $I = 2.2$  nA,  $115 \text{ \AA} \times 65 \text{ \AA}$ . (b)  $V = -0.6$  V,  $I = 2.2$  nA,  $195 \text{ \AA} \times 120 \text{ \AA}$ .

interpretation as CO-cus species is supported by the fact that they appear very bright in the STM images, similar to the well characterized, more stable CO-cus species that exists on the completely reacted surface, between rows of CO-bridge molecules.<sup>9</sup> 90 s after the exposure (Figure 3c) one of the bright spots disappeared, and a further dark site appeared at one of the neighboring bright rows (arrow). After 210 s, a second bright spot disappeared, and again a dark site appeared at a neighboring bright row (arrow). These observations are fully consistent with the above-described reaction mechanism. Obviously, the series shows the reaction between CO-cus and O-bridge to give CO<sub>2</sub>, which desorbed and left O-bridge vacancies behind, which were imaged as dark sites. Because the reaction was directly monitored, ambiguities about the interpretation of the various features in the STM data can be ruled out here.<sup>8</sup>

The distribution of reacted sites on larger areas is shown in Figure 4. In Figure 4a, recorded after adsorption of 0.8 L of CO and showing a surface area with terraces, the dark sites do not show any order, such as a regular distribution along the rows, or any clustering. The distribution indicates that the reaction between CO-cus molecules and O-bridge atoms occurs at random positions along the O-bridge rows. Sometimes some row formation of dark sites in  $[\bar{1}10]$  direction was observed



**Figure 5.** STM images recorded during adsorption of O<sub>2</sub> on the CO saturated surface. Bright dots are CO-cus molecules in a 2-fold periodic arrangement along  $[001]$ , dark sites in (a) are vacancies. The circle marks the development of one vacancy.  $P_{\text{O}_2} = 2 \times 10^{-8}$  Torr; the time elapsed after the start of the exposure is indicated.  $V = 0.6$  V,  $I = 2.2$  nA,  $160 \text{ \AA} \times 180 \text{ \AA}$ .

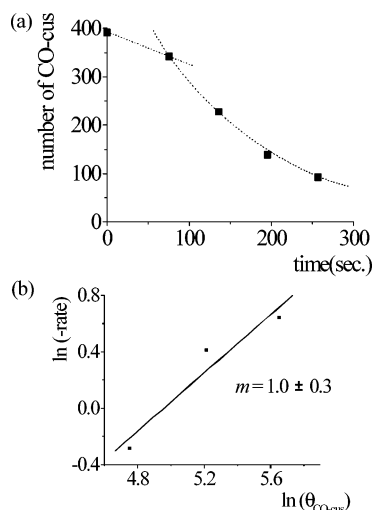
(Figure 4b, recorded after 1.4 L CO). This observation suggests the operation of some correlation effects for the reaction perpendicular to the O-bridge rows, e.g., some destabilization of O-bridge atoms on the rows parallel to a reacted row, but this trend is weak and the general appearance of the distribution is still largely a random one. There was also no correlation of the reaction sites with steps or other defects.

To draw conclusions about reaction sites the mobility of O-bridge sites has to be known, because subsequent hopping events after the reaction could smear out the original distribution. However, successively recorded images of partially reacted surfaces show an almost static distribution; the occasional hopping events correspond to a hopping rate of the order of magnitude of  $10^{-5} \text{ s}^{-1}$ . Assuming a pre-exponential factor of  $10^{13} \text{ s}^{-1}$  this value corresponds to an activation barrier for the diffusion of O-bridge atoms of  $E_{\text{diff,O-bridge}}^* = 1.0$  eV, which is not unreasonable considering the calculated value of  $E_{\text{diff,O-bridge}}^* = 1.2$  eV.<sup>7</sup> We conclude that the O-bridge atoms are immobile on the time scale of the reaction and that the distribution of vacancies evidences a statistical reaction probability.

**3.2 Reaction of O-cus with CO-cus on the CO-Bridge Covered RuO<sub>2</sub>(110) Surface.** The second reaction, between O-cus and CO-cus, was investigated by adsorption of O<sub>2</sub> on the CO covered surface. On the stoichiometric surface, a CO-cus layer cannot be prepared at 300 K, because CO-cus would react with O-bridge. However, as was shown previously, CO-cus can be stabilized (with respect to desorption)<sup>9</sup> if the surface has before reacted with CO and is saturated with CO-bridge molecules. At 300 K the CO-cus molecules occupy every other Ru-cus atom ( $\Theta_{\text{CO-cus}}$  at saturation is 0.5), which creates a characteristic chain structure with a 2-fold period in  $[001]$  direction in the STM images (Figure 5a). The bright dots have been shown to be due to the CO-cus molecules,<sup>9</sup> the dark sites can thus be interpreted as CO-cus vacancies.

In the experiment (Figure 5), the surface was first saturated with CO and then exposed to a constant O<sub>2</sub> pressure; the series shows the same surface area. It is seen that on the whole area,





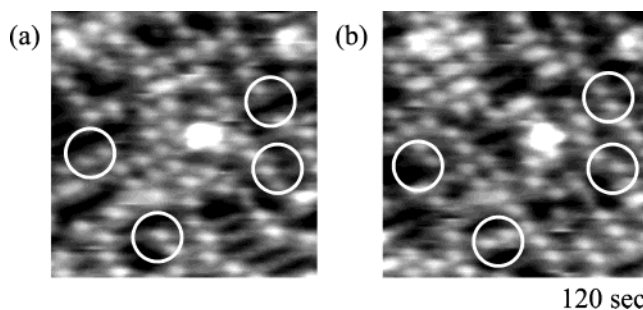
**Figure 6.** Analysis of the reaction between CO-cus and O-cus. (a) Time evolution of  $\Theta_{\text{CO-cus}}$ . (b) Double logarithmic plot of the data from (a).

the bright dots decreased and black and gray sites appeared. The circle shows the evolution of the area around one vacancy. After 76 s (Figure 5b), additional black sites had formed next to the vacancy, indicating that CO-cus molecules at these sites were preferentially reacted off, so that new vacancies were created. After 136 s (Figure 5c) some of the black sites that first appeared around the vacancy turned gray.

The initial reaction at vacancies can be easily explained by the established reaction model according to which an  $\text{O}_2$  molecule first dissociates before it reacts. The entire process therefore requires sites with at least two neighboring empty Ru-cus atoms, which in the 2-fold periodic CO-cus chains exist at the vacancies (three empty Ru-cus atoms), but not in the chains themselves (one empty Ru-cus atom). The gray features can be explained by O atoms adsorbed on empty Ru-cus atoms that were created by the reaction.

After the nucleation period the reaction does no longer show spatial correlation effects. In Figure 5c, the surface has started to form black and gray sites also on other parts, but there were also many defects before that may have acted as nucleation centers. At this stage, the reaction is mainly random.

By quantitative analysis of the entire time series, the reaction kinetics could be extracted. The plot of the coverage of CO-cus molecules vs exposure time (Figure 6a) shows a kink at approximately 70 s, after which  $\Theta_{\text{CO-cus}}$  decreases more quickly. This change of the reaction rate is apparently connected with the transition from the nucleation stage at defects to the random reaction on the entire surface. A double logarithmic plot of the rate after the kink vs  $\Theta_{\text{CO-cus}}$  shows a straight line with slope  $1.0 \pm 0.3$  (Figure 6b), indicating that the reaction follows a first-order kinetics with respect to  $\Theta_{\text{CO-cus}}$ . For a Langmuir–Hinshelwood reaction mechanism between O-cus and CO-cus one expects a second-order rate law according to  $-\text{d}\Theta_{\text{CO-cus}}/\text{d}t = k \cdot \Theta_{\text{CO-cus}} \cdot \Theta_{\text{O-cus}}$  (which is based on the assumption that the two reacting species are randomly distributed). However, at the  $\text{O}_2$  pressure of the experiment the impingement rate of oxygen was much greater than the reaction rate (the time to build up one monolayer of O-cus atoms was 25 s, given a sticking coefficient of unity), so that the equation may be simplified to a pseudo-first-order kinetics with respect to  $\Theta_{\text{CO-cus}}$ . This result is in agreement with the experimental finding. The kinetics is thus consistent with the impression of a random reaction probability in the second stage of the reaction. The pseudo-first-order rate constant  $k$ , obtained from these data,



**Figure 7.** Successive STM images of the partially CO-cus covered surface ( $\Theta_{\text{CO-cus}} \approx 0.25$ ), the bright dots represent CO-cus molecules. Some locations are indicated where CO molecules have hopped.  $V = -0.6$  V,  $I = 2.2$  nA.  $63 \text{ \AA} \times 63 \text{ \AA}$ .

is  $4.5 \pm 0.8 \times 10^{-3} \text{ s}^{-1}$ , which, with a pre-exponential factor of  $10^{13} \text{ s}^{-1}$ , corresponds to an activation energy of  $E_{\text{react}}^* = 0.9$  eV. This value agrees well with calculated activation energies, for which values of 0.62 eV<sup>27</sup> and 0.89 eV<sup>20</sup> have been reported.

Also in this case, the mobility of the preadsorbed reactant (CO-cus) was determined (the bridge sites were completely covered by CO). Successively recorded STM images (Figure 7, with  $\Theta_{\text{CO-cus}} = 0.22$ ) showed several hopping events per frame. The hopping rates depended on  $\Theta_{\text{CO-cus}}$  and varied between 90 and  $400 \times 10^{-5} \text{ s}^{-1}$  (the maximum occurred at approximately  $\Theta_{\text{CO-cus}} = 0.25$ ), but on the average CO-cus is 2 orders of magnitude more mobile than O-bridge at 300 K. By again assuming Arrhenius behavior and a preexponential factor of  $10^{13} \text{ s}^{-1}$  an activation energy of approximately  $E_{\text{diff,CO-cus}}^* = 0.9$  eV is obtained, in agreement with the published calculated value of 0.9 eV.<sup>15</sup> The CO-cus hopping rate and the activation energy are hence similar to the above obtained values for the CO-cus + O-cus reaction, and it is possible that the CO-cus distribution can change during the reaction. Closer inspection of the reaction series in Figure 5 indeed shows that several changes in the CO-cus configuration occurred. Such rearrangement processes probably play some role for the observed kinetics after the nucleation period. A reaction order of unity means that each CO-cus molecule has the same reaction probability, which, because of the 2-fold period of the molecules, requires fluctuations along the chains to create two neighboring empty Ru-cus atoms for the dissociative adsorption of  $\text{O}_2$ .

#### 4. Discussion

The STM data show that both investigated reactions on the  $\text{RuO}_2(110)$  surface, the reaction between O-bridge and CO-cus and the reaction between O-cus and CO-cus, are largely random processes, i.e., each particle has more or less the same reaction probability. Only in the initial stage of the latter reaction, when the surface is saturated with CO-cus molecules, do vacancies play a role, which can be simply explained by the site pairs required for  $\text{O}_2$  dissociation. With this exception, the  $\text{RuO}_2(110)$  surface is thus a surprisingly good example of the Langmuirian checker board model, according to which catalyst surfaces consist of equal sites that are statistically occupied by the reactants. By contrast, reactions on metal surfaces often show considerable deviations from this model, in particular because the adsorbed particles form islands, and reactions take place at the perimeters of the islands.<sup>21</sup> Such effects appear largely absent here, although calculations revealed appreciable interactions between adsorbed O atoms and CO molecules.<sup>15,20</sup> What is the reason for this different behavior? An obvious difference between the  $\text{RuO}_2(110)$  surface and the metal surfaces is the

much more directed chemical bonds on the oxide. Diffusion barriers are therefore of the same size as the activation energies for the reaction. Our estimated diffusion barrier of 1.0 eV for the O-bridge atoms can be related to calculated barriers for the reaction between O-bridge and CO-cus, for which values between 0.7 and 1.3 eV have been reported,<sup>17,18,20</sup> and the estimated diffusion barrier of 0.9 eV for the CO-cus molecules has the same value as the barrier for the reaction between O-cus and CO-cus. Hence, the adsorption layer on RuO<sub>2</sub>(110) is almost static during the reaction (apart from the local fluctuations within the CO-cus chains), so that lateral interactions do not lead to the large scale rearrangement effects occurring in the very mobile adsorbate layers on metal surfaces.

## 5. Conclusions

Two reactions that are expected to play an important role in the oxidation of CO on the RuO<sub>2</sub>(110) surface were investigated by time-resolved STM experiments at 300 K.

The reaction of CO molecules with O-bridge atoms on the stoichiometric surface was monitored on the atomic scale and was found to proceed according to the established reaction model. The CO molecules first adsorb on Ru-cus atoms, and then react with neighboring O-bridge atoms, creating vacancies in the O-bridge rows. The reaction largely occurs at random positions, defects do not play a role, and there are no significant contributions of islands of the reactants. The statistical nature of the reaction was explained by the large diffusion barrier of the O-bridge atoms (a value of  $E_{\text{diff,O-bridge}}^* = 1.0$  eV was estimated), which is similar to calculated activation barriers for the reaction, so that the configuration is largely static during the reaction.

The reaction of CO-cus with O-cus was investigated by O<sub>2</sub> titration on the CO-cus covered surface. On the saturated surface, where CO occupies every other Ru-cus atom, the reaction starts at CO-cus vacancies, because the O<sub>2</sub> molecules need two neighboring sites for dissociation. In the later stage, the reaction is mainly random, because the CO-cus molecules display some mobility on the partially reacted surface, allowing O<sub>2</sub> molecules to adsorb. Consistently with the largely random reaction probability in this stage, a reaction order of 1 with respect to  $\Theta_{\text{CO-cus}}$  was obtained. Island effects do not play a role, which is again explained by a relatively large diffusion barrier compared to the reaction barrier (for CO-cus a value of

$E_{\text{diff,CO-cus}}^* = 0.9$  eV was estimated, for the reaction between CO-cus and O-cus  $E_{\text{react}}^* = 0.9$  eV).

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