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Catalytic activity of RuO_2(1 1 0) in the oxidation of CO

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Abstract

The primary reason why the RuO_2(1 1 0) surface is much more active in the oxidation of CO than the corresponding metal Ru(0 0 0 1) surface is correlated with the weaker oxygen bonding on RuO_2(1 1 0) compared to chemisorbed oxygen on Ru(0 0 0 1). The RuO_2(1 1 0) surface stabilizes at least two potentially active oxygen species, i.e., bridging O and on-top O atoms. Together with various adsorption sites for CO during the reaction, the CO oxidation reaction over RuO_2(1 1 0) becomes quite complex. Using the techniques of temperature programmed reaction and desorption in combination with state-of-the-art density functional theory calculation we studied the CO oxidation reaction over RuO_2(1 1 0) in the temperature range of 300–400 K. We show that the CO oxidation on RuO_2(1 1 0) surface is not dominated by the recombination of CO with on-top O, although the binding energy of the on-top O is 1.4 eV lower than that of the bridging O atom.

Keywords: RuO_2(1 1 0); Oxidation; CO

1. Introduction

The catalytic activity of transition metal surfaces for the CO oxidation is determined by a delicate interplay of the binding energy of oxygen on the surface and the ability of the surface to dissociate molecular oxygen [1]. This behavior is reflected by the well-known volcano curve for transition metals, revealing that the highest activity is encountered with transition metals with half-filled d-bands, where the dissociation probability is not too low and the adsorption energy is not too high [2]. Accordingly, ruthenium—due to its very high binding energy of oxygen—is a poor catalyst for the CO oxidation reaction under UHV conditions.

In a series of surface science studies it has been demonstrated that Ru turns into a very efficient oxidation catalyst under high pressures of the reactants and oxidizing conditions [3–6]. Under such reaction conditions the metallic Ru transforms into the oxide RuO_2 [5]. To a first approximation the high activity of RuO_2 was traced back to the relatively low adsorption energy of surface O atoms together with the high adsorption energy of CO [7]. Both ingredients are considered equally important for the high catalytic activity of RuO_2 since the first supplies an active O species for the CO oxidation reaction, while the second ensures a high CO concentration on the surface under reaction conditions. It is worthwhile

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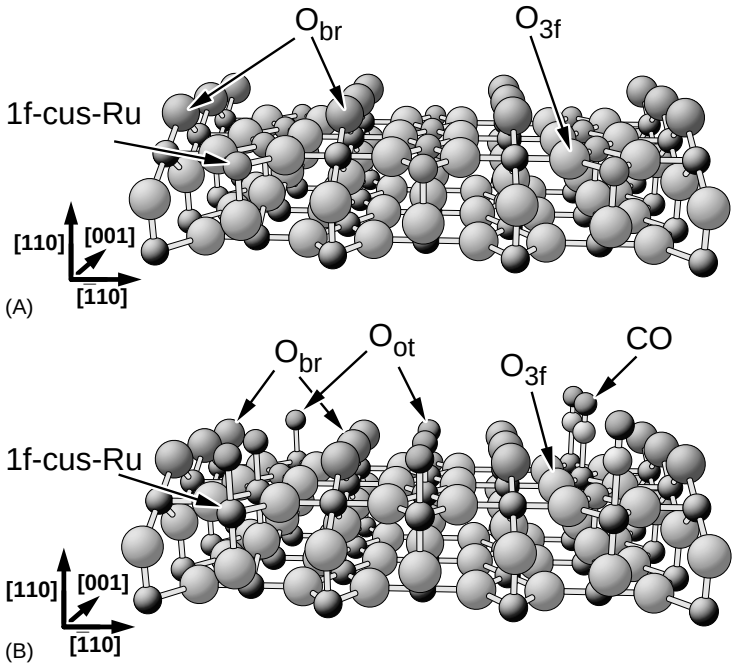

Fig. 1. (A) Ball and stick model of the clean $RuO_2(1\,1\,0)$ surface. Large balls represent oxygen and small balls the ruthenium atoms of $RuO_2(1\,1\,0)$. The bridge-bonded O_{br} and 3-fold coordinated O species O_{3f} are indicated. (B) Stick and ball model of on-top oxygen (O_{ot}) and on-top CO (CO_{ot}) on $RuO_2(1\,1\,0)$ surface.

to mention that the dissociative sticking coefficient of oxygen on $RuO_2(1\,1\,0)$ is as high as 0.7 [8] and does therefore not represent the rate limiting step for a stoichiometric feed gas $CO : O_2 = 2 : 1$.

Since $RuO_2(1\,1\,0)$ stabilizes at least two potentially active oxygen species, namely bridging O and on-top O atoms (O_{br} and O_{ot} in Fig. 1), and offers various adsorption sites for CO during the reaction, the CO oxidation reaction over $RuO_2(1\,1\,0)$ is quite complex. In this contribution, we present results from temperature programmed reaction (TPR), respectively, desorption (TPD) experiments under ultrahigh vacuum (UHV) conditions and density functional theory (DFT) calculations. Even in the presence of on-top O atoms on the $RuO_2(1\,1\,0)$ surface, the CO molecules sitting above the one-fold under-coordinated Ru atoms (1f-cus Ru in Fig. 1) recombine efficiently with bridging O atoms (O_{br} in Fig. 1). This finding is in sharp contrast with a recent HREELS study which favors the recombination between the on-top O species and on-top CO as the dominating reaction step [9].

2. Experimental and theoretical details

The TPD and TPR experiments were performed in a UHV chamber equipped with low energy electron diffraction (SPA-LEED) optics, a quadrupole mass spectrometer, and facilities for surface cleaning.

The Ru(0 0 0 1) sample was cleaned by argon ion bombardment at 1 keV followed by cycles of oxygen exposure and thermal annealing to 1000 K in order to remove surface carbon. Final traces of oxygen were removed by flashing the surface to 1530 K, resulting in a sharp (1×1) LEED pattern.

The ultra-thin $RuO_2(1\,1\,0)$ film was produced by exposing a well-prepared single crystal Ru(0 0 0 1) to high doses of oxygen at sample temperatures above 600 K (typical oxygen dose: $6 \times 10^{+6}$ L (Langmuir); $1\,\mathrm{L} = 1.33 \times 10^{-6}$ mbar s) [10]. The actual oxidation step of Ru proceeds via an autocatalytic reaction as discussed in more detail in Ref. [28]. A glass capillary array was used to dose such high amounts of oxygen. The local oxygen pressure at the sample is

estimated to be about 1×10^{-2} mbar. After the background pressure in the UHV chamber had reached a value below 10^{-9} mbar the contamination by residual oxygen adsorption was removed by briefly heating the sample to 600 K. The sample was then cooled down to 150 K. For all TPD and TPR experiments the heating rate was 4.5 K/s. The weakly held on-top oxygen species was produced by exposing a few Langmuirs of O_2–RuO_2(1 1 0) at room temperature [8,11].

First principle calculations were performed in the framework of DFT using the generalized gradient approximation of Perdew et al. [12] for the exchange-correlation functional. We used a plane wave basis set with an energy cut-off of 60 Ry and ab initio pseudopotentials in the fully separable form for O, C and Ru [13]. The RuO_2(1 1 0) surface was modeled by five double layers of RuO_2 with a (2×1) unit cell (super cell approach). Consecutive slabs were separated by a vacuum region of about 16 Å. CO and O adsorption on RuO_2(1 1 0) were modeled by placing CO on both sides of the RuO_2(1 1 0) slab. We relaxed the positions of all the O, C and Ru atoms. The reaction coordinate was defined as the O–CO separation between the reacting particles. The transition state for a particular reaction pathway and the corresponding activation barriers were searched with a constrained minimization technique [14]. The transition state is identified with the CO–O distance where the forces on the atoms vanish and the energy reaches a maximum along the reaction coordinate.

3. Results and discussion

3.1. Recapitulation of relevant properties of RuO_2(1 1 0)

In the bulk structure of RuO_2 (rutile structure) 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. The RuO_2(1 1 0) surface exposes two kinds of under-coordinated surface atoms (cf. Fig. 1A), namely the bridging oxygen atoms, which are coordinated to only two Ru atoms underneath, and the so-called 1f-cus Ru atoms, i.e., 1-fold coordinatively unsaturated Ru sites [10].

Exposure of the RuO_2(1 1 0) surface to oxygen at room temperature produces a weakly held oxygen species [8] that adsorbs directly above the 1f-cus Ru atom in terminal position (cf. O_{ot} in Fig. 1B) [10] and desorbs already at 450 K. High-resolution core-level photoelectron spectroscopy measurements corroborates the adsorption site of the weakly held oxygen species [19]. The $Ru3d_{5/2}$ core level of 1f-cus Ru shifts significantly to higher binding energies which observation is consistent with an oxidation state of Ru beyond that of the 1f-cus Ru and bulk Ru [20].

CO adsorption on the bare RuO_2(1 1 0) proceeds via the 1f-cus Ru atoms in terminal position (cf. Fig. 1B). At temperatures below 200 K this CO species is stable on the surface (the binding energy is 1.2 eV, DFT calculations) [15], while at higher temperatures (say around room temperature) the CO molecules recombine with neighboring bridging O atoms to form CO_2 [5,16,17],[1] thus creating vacancies in the rows of bridging O atoms [17]. Further CO molecules can strongly adsorb into these vacancies (1.7–1.8 eV, DFT calculations) [18], thereby substituting the bridging O atoms.

3.2. Oxidation of CO over RuO_2(1 1 0): general remarks

Under steady state reaction conditions (CO/O_2 ratio in the gas feed of 2:1 and a sample temperature being between 350 and 400 K) both reactants adsorb initially over the 1f-cus Ru atoms [11,15]. CO adsorbs molecularly in an upright position above the 1f-cus Ru atoms [15]. Molecular oxygen adsorbs dissociatively above the 1f-cus Ru atoms, requiring two neighboring vacant 1f-cus Ru sites [11]. We may note that the chosen surface temperature is low enough to prevent the surface from restructuring (see Ref. [21] for further details). This temperature window was also explored in recent steady state reaction experiments by Wang et al. [9].

At temperatures around 350 K adsorbed CO molecules can readily recombine with O atoms on the surface to form CO_2 [9]. In principle there are two potentially active oxygen species, i.e., the on-top O and the bridging O atoms (cf. Fig. 1B). If CO recombines with the bridging O atoms, vacancies are formed in the bridging O rows [17]. The diffusion barriers for on-top O and on-top CO along the 1f-cus Ru rows are

[1] Movies of the recombination of CO and undercoordinated O from RuO_2(1 1 0). http://www.iki.fi/~apsi/Science/movies/.

quite high with 1.0 eV, while diffusion perpendicular to the 1f-cus Ru rows into O-bridge vacancies is activated by only 0.7 eV [22]. From the calculated diffusion barriers it is likely that both, CO molecules and on-top O atoms, hop from the 1f-cus Ru atoms into the O_{br} vacancies even at temperatures around 350 K. CO molecules in such vacancies (bridging CO molecules) are by 0.5 eV more strongly bound than on-top CO molecules above 1f-cus Ru atoms [18] so that self-poisoning of the RuO_2(1 1 0) catalyst may occur.

Altogether, we have to consider four essentially different reaction pathways between CO and O on the RuO_2: first, the recombination of CO sitting above the 1f-cus Ru atoms with bridging O and on-top O atoms; second, the recombination of bridging CO molecules with bridging O and on-top O atoms.

3.3. Recombination of on-top CO with bridging O atoms on RuO_2(1 1 0)

To study this reaction pathway, we exposed the stoichiometric RuO_2(1 1 0) surface to small amounts of CO (say 0.25 and 0.5 L) at 170 K. This low sample temperature prevents CO oxidation during exposure. Subsequently we run a temperature programmed reaction experiment, monitoring both CO and CO_2 signals. These measurements are displayed in Fig. 2. The initial CO/CO_2 conversion probability of this process is as high as 80% [21]. In determining the CO/CO_2 conversion probability, we integrated the CO and CO_2 TD traces from 250 up to 400 K and corrected the quotient for the cracking pattern of CO_2 and the relative sensitivity of the mass spectrometer to CO and CO_2.[2] Assuming a frequency factor of 10^{13} Hz, transition state theory estimates the experimental activation energy of 0.9 eV for the reaction between on-top CO and bridging O in the temperature range around 300 K.

The initial state and the transition state of the modeled DFT reaction pathway are depicted in Fig. 3. The activation energy was determined to be 0.71 eV. This value is lower than that of Liu et al. [23] who calculated a value of 1.15 eV. The experimental value for the activation energy of 0.9 eV is in between these

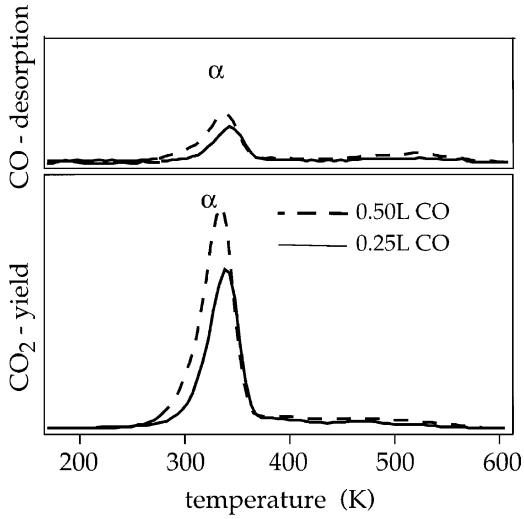

Fig. 2. Temperature programmed reaction experiments. The evolution of CO and CO_2 are shown as a function of temperature when the stoichiometric RuO_2(1 1 0) surface has been exposed to 0.25 and 0.5 L CO at 170 K. Only a single desorption state α is discernible.

two theoretical values. The atomic geometry of the transition state (cf. Fig. 3) shows that both on-top CO and the bridging O atoms are drawn to each other from their initial positions. In order to determine whether the activation of the CO molecule or that of the active O species imposes the rate-determining step, we decomposed the total activation barrier into three contributions. Two of them are due to the variation in the binding energy of the reactants, CO and active O, when moving from the initial to the transition state while keeping the other reactant at the equilibrium position and the third contribution comes from the difference of the interaction energies between the reactants in the initial and the transition state. This approach was recently applied by Liu and Hu [24] for studying the general trends in the activation barriers of catalytic reactions on transition metal surfaces. According to our DFT calculations, the binding energies of CO and bridging O atoms on the RuO_2(1 1 0) surface are thereby reduced by 1.67 and 0.43 eV, respectively [22]. These values give evidence that the activation of CO is the rate-determining step for the recombination of on-top CO with bridging O. It is interesting to note that the energy penalty of CO in the transition state is even higher than the adsorption energy in the equi-

[2] The parameters of the mass spectrometer were set in a way that the sensitivity to CO and CO_2 are identical. The portion of detected CO is 10% when only CO_2 is offered. The CO is due to cracking of CO_2.

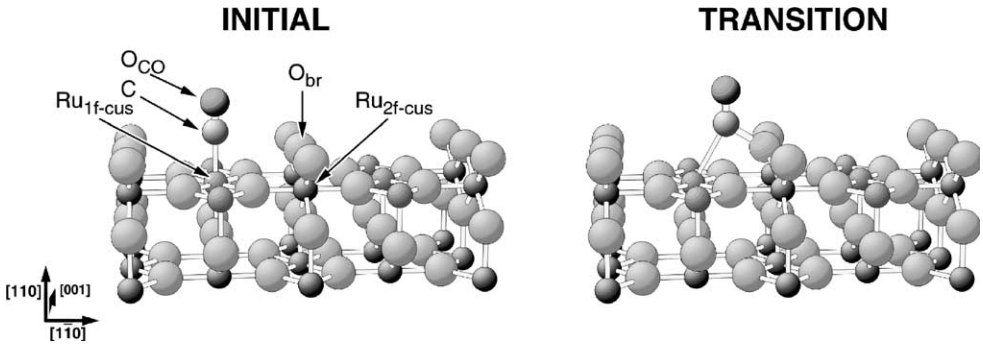

Fig. 3. A sketch of the initial and transition state for the CO oxidation over the stoichiometric $RuO_2(1\,1\,0)$ surface. In the initial state CO molecules are sitting above in 1f-cus Ru atoms in upright position. The active oxygen is the bridging oxygen O_{br}.

librium position. Of course, the high energy penalty of CO is compensated by the attractive interaction between CO and the active oxygen species in the transition state which amounts to about 1.5 eV. The strong attraction in the transition state has been explained by the interaction of the lone pair orbital of oxygen with the CO molecules [23]. One of the lone pair orbitals is aligned towards the on-top CO molecule.

3.4. Recombination of bridging CO with bridging O on $RuO_2(1\ 1\ 0)$

As mentioned above, the recombination of on-top CO molecules with bridging O atoms creates vacancies in the bridging O rows. Since the adsorption energy of CO in such vacancies is by 0.5 eV higher than in the on-top position, CO molecules populate partially the bridging O vacancies. A quite promising reaction route would be that such bridging CO molecules react with neighboring bridging O atoms.

In Fig. 4, we present temperature programmed reaction data, elucidating this point. We exposed first the stoichiometric $RuO_2(1\,1\,0)$ surface to 2.25 L CO at 170 K, and then run the temperature ramp to 600 K. Both spectra are dominated by the features in the temperature region of 230–380 K (Fig. 4: α and β state). The appearance of the β state is explained by CO–CO repulsion at higher coverages. In the low temperature region on-top CO molecules either desorb, or they recombine with bridging O atoms to form CO_2, thereby generating vacancies in the bridging O rows. CO can migrate into these vacancies (thereby increasing the binding energy by 0.5 eV). These CO molecules are

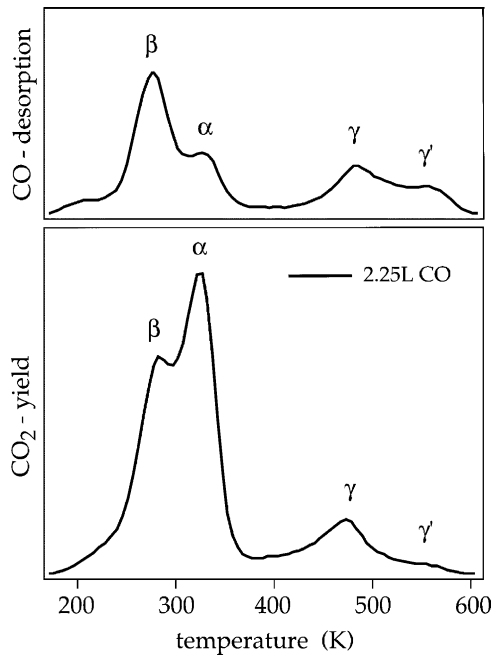

Fig. 4. Temperature programmed reaction experiments. The temperature dependent CO and CO_2 evolution are shown when the stoichiometric $RuO_2(1\,1\,0)$ surface was exposed to 2.25 L CO at 170 K. Besides the α states (cf. Fig. 2) also a low temperature β state appears and the high temperature states γ and γ′. From the saturation behavior of CO we conclude that the CO species in the state γ and γ′ are populated only when vacancies in the bridging O rows are formed with substantial concentration. Accordingly, CO in such vacancies forming the γ and γ′ states in the CO TD spectrum. The γ CO_2 reaction state is formed by recombination of bridging CO with adjacent bridging O atoms.

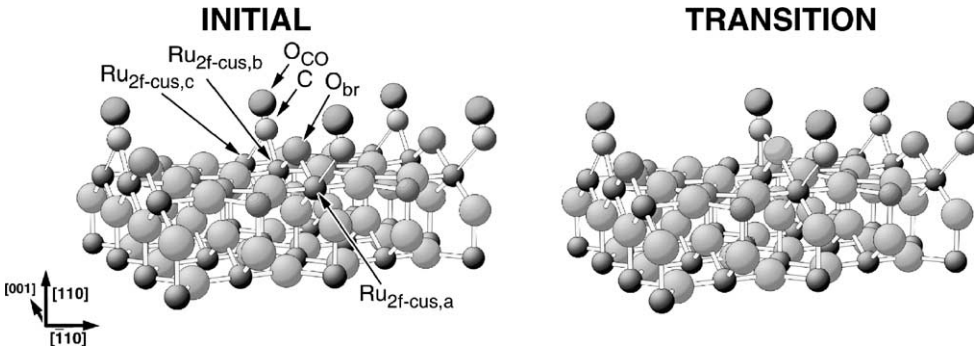

Fig. 5. A sketch of the initial and transition state for the CO oxidation over the partially reduced $RuO_2(1\,1\,0)$ surface. In the initial state CO molecules are sitting above in the vacancies of the bridging O rows. The active oxygen atoms are the bridging oxygen O_{br} adjacent to the bridging CO molecules.

characterized by the desorption states γ and γ′ at temperatures between 450 and 550 K (cf. Fig. 4). But these CO molecules can also recombine with bridging O atoms as indicated by the (CO_2) reaction state γ at 480 K. From the data in Fig. 4 it is obvious that the activation barrier for this reaction path should be significantly higher than for the recombination of on-top CO with bridging O (cf. Fig. 2, maximum reaction rate occurs at about 330 K). Assuming a frequency factor of 10^{13} Hz, we estimate the experimental activation energy for the reaction of bridging CO with bridging O in the temperature range around 500 K to be 1.4 eV.

This experimental estimation of the activation energy is supported by our DFT calculations (cf. Fig. 5 for the geometries of the initial and the transition state). The activation barrier for the recombination of bridging CO with bridging O is 1.30 eV, i.e., by 0.6 eV higher than the recombination of on-top CO with bridging O. This high activation energy is experimentally reconciled by the higher temperature of the γ state of 480 K in Fig. 4 (CO_2 yield). The DFT calculations indicate that O_{br} and CO_{br} both suffer from a substantial energy penalty (O_{br}: 0.39 eV, CO_{br}: 1.02 eV) which is imposed when both species are brought from the initial to the transition state. The attractive interaction between O_{br} and CO_{br} amounts only to 0.11 eV, resulting in a high activation barrier for this reaction pathway. The reason for the low interaction energy between O_{br} and CO_{br} in the transition state is seen in the fact that none of the lone pairs of oxygen is directed to the CO molecule.

3.5. Reaction of bridging CO with on-top oxygen on $RuO_2(1\,1\,0)$

In Section 3.4 we saw that the bridging CO molecule will not react with neighboring bridging O atoms as long as the sample temperature does not exceed 400 K. Keeping the sample temperature in the range of 350 K may therefore lead to self-poisoning of the RuO_2 catalyst by strongly chemisorbed bridging CO molecules. Fig. 6 indicates, however, that the bridging CO molecule can easily be removed by on-top O. Here we mildly reduced the $RuO_2(1\,1\,0)$ surface by dosing 5 L CO at 370 K. This procedure ensures that all the bridging O atoms are replaced by CO molecules [18]. A sample temperature of 370 K is high enough so that after this reduction step no CO molecule is sitting above the 1f-cus Ru atoms. Subsequently we saturated this surface by 1 L $^{36}O_2$ at 170 K, thus labeling the on-top O by ^{18}O. In Fig. 6 we show the production rate of CO_2 with $m/e = 46$, i.e., characteristic for the recombination of ^{28}CO with ^{18}O. Maximum $^{46}CO_2$ yield occurs at about 330 K which is significantly lower than for the reaction between bridging CO and bridging O. Therefore, under reaction conditions, where on-top O is partly present on the surface, strongly adsorbed bridging CO molecules are easily removed, thus preventing the catalyst from self-poisoning even at temperatures around 350 K. In the temperature region up to 400 K the CO_2 trace in Fig. 6 is virtually identical to that in Fig. 2. This may suggest that the rate-determining steps in both reactions are identical. In other words, an exchange

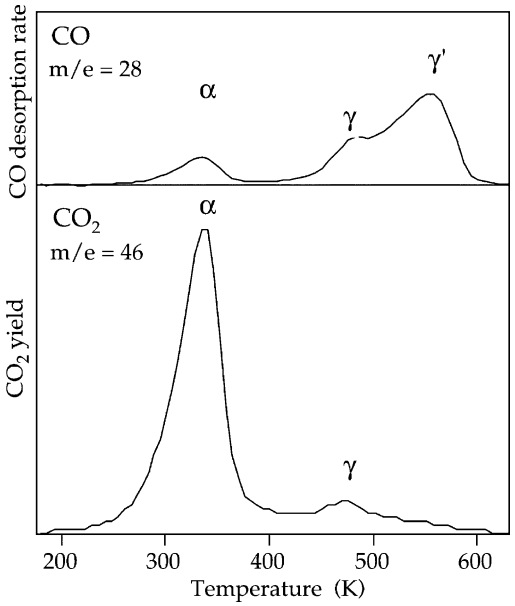

Fig. 6. Temperature programmed reaction experiments of CO and CO_2 evolution are shown. First, the RuO_2(1 1 0) surface was reduced by 5 L CO at 370 K, resulting in a surface where the bridging O atoms are replaced by bridging CO molecules without populating the 1f-cus Ru atoms with CO molecules. Subsequently the surface was exposed to 1 L $^{18}O_2$ at 170 K, leading to a surface where the 1f-cus Ru atoms are occupied by on-top oxygen. After this preparation we run a temperature ramp from 170 to 600 K, monitoring the CO_2 signal ($m/e = 46$). The $m/e = 44$ signal is negligible. Clearly, maximum CO_2 production occurs at 330 K.

reaction between bridging CO and on-top O may take place that precedes the actual recombination step between CO and O. From a thermo-dynamical point of view this exchange reaction is highly favorable since the system gains about 1 eV in adsorption energy.

3.6. Reaction of on-top CO and on-top oxygen on RuO_2(1 1 0)

To study this reaction pathway we varied the coverage θ of on-top O on the stoichiometric RuO_2(1 1 0) surface from 80 to 10% (in steps of 10%) and subsequently saturated the surface with CO in each case (CO coverage: $(1 - \theta)$). Both the signals of CO and CO_2 were simultaneously recorded by the mass spectrometer. As indicated in Fig. 7 the total (i.e., temperature integrated signal from 170 to 600 K) CO_2 TD signal as a function of the on-top O coverage

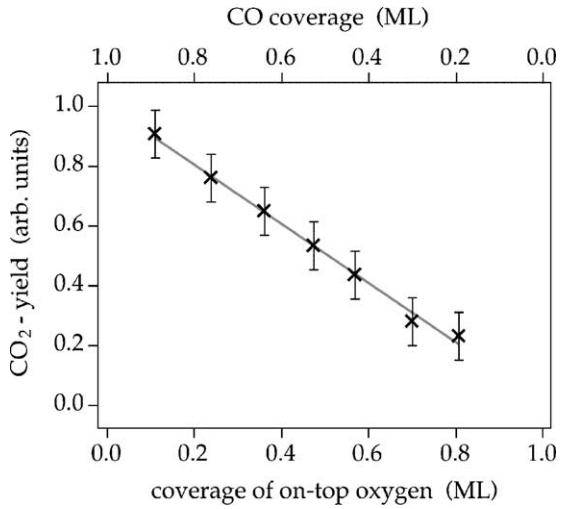

Fig. 7. The total CO_2 yield from RuO_2(1 1 0) surface as a function of the on-top O coverage. The stoichiometric RuO_2(1 1 0) surface was pre-covered with various amounts of on-top oxygen and subsequently saturated with CO. The total CO_2 yield was determined by integrating the CO_2 and CO traces over a temperature region of 170–600 K.

indicates a strictly linear relationship. This result is quite surprising as it suggests that the CO_2 yield depends solely on the total CO coverage accommodated at the surface, i.e., $(1 - \theta)$ with θ being the coverage of on-top O. Note that if on-top CO reacts exclusively with on-top O, then one would expect to find a parabolic dependence (i.e., $(1-\theta)\theta$) on the coverage θ of on-top O. We consider this observation as a first indication that a reaction between on-top CO and on-top O is not the dominating recombination mechanism at that surface. One possible explanation of the linear relationship in Fig. 7 is that adsorbed CO molecules are reacting exclusively with bridging O atoms. Accordingly, the CO_2 yield depends linearly on the CO coverage.

We estimated the CO/CO_2 conversion probability of on-top CO and on-top O to be only 45% for small CO coverages increasing monotonously to 80% at high CO coverages, i.e., when no on-top O is present on the RuO_2(1 1 0) surface. Under our experimental conditions the CO/O recombination reaction on the surface is in competition with CO desorption (branching reaction). A lower CO/CO_2 conversion probability suggests a higher CO desorption rate due to a destabilization of CO induced by the on-top O.

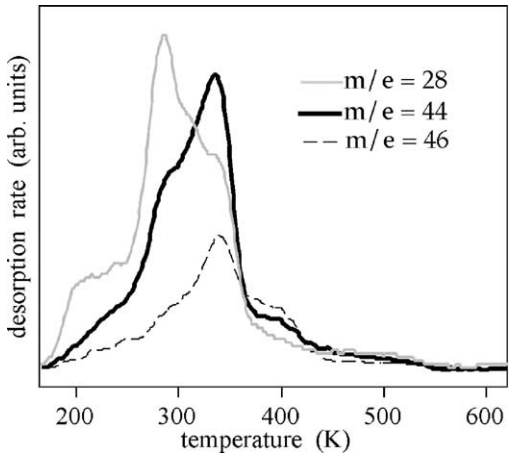

Fig. 8. The RuO_2(1 1 0) surface prepared by $^{16}O_2$ was first exposed to 0.2 L $^{18}O_2$ at room temperature and then saturated by exposing 3 L $^{12}C^{16}O$ at 170 K; the on-top O coverage corresponds to 0.2 ML. The CO_2 spectra for $m/e = 44$ ($^{12}C^{16}O^{16}O$) are compared to that of $m/e = 46$ ($^{12}C^{16}O^{18}O$). The 'not-reacted' CO ($m/e = 28$) is also shown.

In a further experiment we prepared various pre-coverages of on-top ^{18}O by directly exposing various doses of $^{18}O_2$ at room temperature. Subsequently, the ^{18}O pre-covered surface was saturated with $^{12}C^{16}O$ at low temperatures. In Fig. 8 we present the CO_2 spectra for $m/e = 44$ ($^{12}C^{16}O^{16}O$) in comparison with that of $m/e = 46$ ($^{12}C^{16}O^{18}O$) when we first expose 0.2 L $^{18}O_2$ at room temperature and then saturate the surface by exposing 3 L $^{12}C^{16}O$ at 170 K; the on-top ^{18}O coverage corresponds to 0.2 ML. The $m/e = 44$ spectrum is associated with on-top CO that recombines with bridging ^{16}O. At first glance the $m/e = 46$ spectrum seems to be related to the recombination of on-top CO with on-top ^{18}O. But this assignment is questionable since the shapes of the CO_2 TD traces of $m/e = 44$ and 46 are very much alike, suggesting that the rate-determining step in both recombination processes should be identical. Together with the results shown in Fig. 7 we favor an interpretation where the on-top CO reacts with bridging ^{18}O. We should note that an exchange reaction between on-top O and bridging O has been identified on RuO_2(1 1 0) by isotope labeling experiments [25]. Furthermore, the total yield of ($^{12}C^{16}O^{18}O$) as a function of the on-top ^{18}O coverage shows a maximum at 0.2 ML and drops then steeply to a third of the maximum value for on-top O coverages beyond 0.4 ML. This latter finding is consistent with a recombination of on-top CO with exchanged bridging ^{18}O atoms [25].

DFT calculations [26] determined the activation barrier for the recombination of on-top CO with on-top O. The activation energy (0.68 eV) is almost degenerate with the activation energy for the reaction of on-top CO with bridging O (0.71 eV). Already this result is quite surprising since the well-known Bronsted-Evans-Polanyi relationship [27] predicts that the on-top O species is much more active than bridging O atoms due to its lower adsorption energy (the adsorption energy difference is 1.4 eV).

3.7. Reaction mechanism of the CO oxidation reaction over RuO_2(1 1 0)

With the findings presented in Sections 3.2–3.6 we are now able to discuss the microscopic reaction mechanism for the CO oxidation over RuO_2(1 1 0) depending on the chosen reaction temperature. Assuming that the CO/O_2 ratio in the gas feed is less than about 2, the CO oxidation at 350 K is approximated and summarized in the following way:

$$CO + cus \leftrightarrow CO_{ot} \quad (cus = 1f\text{-}cus\text{-}Ru\ site) \tag{1}$$

$$\tfrac{1}{2}O_2 + cus \rightarrow O_{ot} \quad (O_2\ desorption\ is\ insignificant\ at\ 350\ K) \tag{2}$$

$$O_{ot} + V_{Obr} \rightarrow O_{br} + cus \quad (V_{Obr} = vacancies\ in\ the\ bridging\ O\ rows) \tag{3}$$

$$CO_{ot} + O_{br} \rightarrow CO_2 + cus + V_{Obr} \tag{4}$$

$$CO_{ot} + O_{ot} \rightarrow CO_2 + 2\,cus \tag{5}$$

Under these reaction conditions reaction (4) is important for the CO oxidation reaction on RuO_2(1 1 0). Alternative reaction pathways proposed in Ref. [9] are not important under the chosen reaction conditions. In particular the recombination between bridging O and bridging CO can be safely ignored at 350 K. According to Section 3.6 the reaction of on-top CO with on-top O is not dominating the CO oxidation reaction. Therefore, the explanation [9] why the pressure gap of the CO oxidation reaction on the RuO_2(1 1 0) is bridged is questionable. We suggest that the on-top

oxygen serves predominantly as a source for replenishing the consumed oxygen in the bridging O rows (3).

If we consider also strongly reducing conditions, i.e., CO/O_2 ratios larger than 2, then recombination between bridging CO and on-top O becomes important:

$$CO_{br} + O_{ot} \rightarrow CO_2 \quad (6)$$

If the reaction temperature is increased to 450 K, the direct recombination of bridging CO and bridging O is possible:

$$CO_{br} + O_{br} \rightarrow CO_2 \quad (7)$$

4. Conclusion

The $RuO_2(1\,1\,0)$ surface is much more active in the oxidation of CO than the corresponding metal Ru(0 0 0 1) surface since the under-coordinated oxygen atoms of RuO_2 are much more active than chemisorbed oxygen on Ru(0 0 0 1). In addition, the binding energy of CO on $RuO_2(1\,1\,0)$ is quite high so that at normal reaction temperatures the CO concentration on the $RuO_2(1\,1\,0)$ surface is sufficiently high. The $RuO_2(1\,1\,0)$ surface provides at least two potentially active oxygen species, namely the bridging O atoms (O_{br}) and the on-top O atoms (O_{ot}). During the CO oxidation reaction various adsorption sites for CO become available. This renders the CO oxidation over $RuO_2(1\,1\,0)$ a quite complex reaction. For a reaction temperature of 350 K, we have demonstrated that the recombination of on-top CO with bridging O is also in the presence of on-top O an efficient reaction route to from CO_2. On-top oxygen, although by 1.4 eV more weakly bound to the surface than bridging O atoms, is clearly not more active than bridging oxygen. This finding is in sharp contrast to recent HREELS measurements [16].

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