The oxidation of CO on $RuO_2(110)$ at room temperature

C. Y. Fan, J. Wang, K. Jacobi, and G. Ertl

View Online   Export Citation

ARTICLES YOU MAY BE INTERESTED IN

Interaction of CO with the stoichiometric $RuO_2(110)$ surface
The Journal of Chemical Physics **119**, 9729 (2003); https://doi.org/10.1063/1.1614205

Structure sensitivity in oxide catalysis: First-principles kinetic Monte Carlo simulations for CO oxidation at $RuO_2(111)$
The Journal of Chemical Physics **143**, 204702 (2015); https://doi.org/10.1063/1.4936354

Chlorine evolution reaction electrocatalysis on $RuO_2(110)$ and $IrO_2(110)$ grown using molecular-beam epitaxy
The Journal of Chemical Physics **150**, 041726 (2019); https://doi.org/10.1063/1.5051429

The oxidation of CO on RuO$_2$(110) at room temperature

C. Y. Fan, J. Wang, K. Jacobi,[a] and G. Ertl

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany

RuO$_2$(110) surfaces were prepared by exposing Ru(0001) to 10^7 L of O$_2$ at 700 K. Postexposure of O$_2$ at 300 K resulted in an additional oxygen species (O-cus) adsorbed on coordinatively unsaturated Ru atoms (Ru-cus). The surface was then exposed to CO at 300 K and studied by thermal desorption spectroscopy (TDS) and high-resolution electron energy loss spectroscopy (HREELS). It is demonstrated that CO is oxidized at 300 K through reaction with both the O-cus as well as with surface O-atoms held in bridge positions (O-bridge). Although—at room temperature—CO adsorbs intermediately on the Ru-cus atoms, it is stable only at the Ru atoms underneath the O-bridge after the latter has been reacted off. At room temperature only surface oxygen takes part in the CO oxidation and the oxygen-depleted surface can be restored by O$_2$ exposure, so that under steady-state flow conditions an oxygen-deficient surface will exist whose stoichiometry will be determined by the ratio of partial pressures. © *2001 American Institute of Physics.*
[DOI: 10.1063/1.1350817]

I. INTRODUCTION

The oxidation of CO is efficiently catalyzed by platinum group metal surfaces. Among them, Ru exhibits a peculiar behavior. Under ultrahigh vacuum (UHV) conditions it is an extraordinarily poor catalyst in CO oxidation, while its activity under high pressure and oxidizing conditions turned out to be superior to the other platinum group metals[1] which are active in CO oxidation under UHV as well as high pressure conditions.[2] However, more recently *oxygen-rich* Ru(0001) surfaces have been prepared which contain an oxygen amount equivalent to at least three oxygen monolayers (ML).[3,4] Recently, Over *et al.*,[5] by combining scanning tunneling microscopy (STM) images, low-energy electron diffraction (LEED) intensity analysis, and density functional theory (DFT) calculations demonstrated that the *oxygen-rich* surface consists in fact of patches of Ru(0001)–(1×1)–O and RuO$_2$(110). They found that the active phase of oxygen is on the RuO$_2$(110) domains, whereas the (1×1)–O regions are inactive for CO oxidation.[5,6] Interestingly, RuO$_2$ powder (with some content of water) prepared from aqueous solution was recently reported to catalyze CO oxidation, even at 295 K.[7] In the present report it will be demonstrated that such activity can also be observed with a well-defined RuO$_2$(110) single-crystal surface, whereby identification of the various surface species by means of vibrational spectroscopy provides detailed insights into the mechanism of this remarkable reaction.

The structure of the clean RuO$_2$(110) surface is sketched in Fig. 1. According to the recent structure determination,[5,8] RuO$_2$(110) exposes rows of coordinatively unsaturated Ru atoms (Ru-cus), twofold coordinated bridge oxygen (O-bridge) and threefold coordinated layer oxygen (O-layer), all along the [001] direction. The Ru atoms underneath the O-bridge atoms are called Ru bridge in the following. From electronic structure calculations, Over *et al.*[5] could give convincing arguments that the Ru-cus atom is the chemically active surface entity as it exhibits a charge accumulation normal to the surface like a dangling bond. By oxygen postexposure to the *oxygen-rich* phase at 300 K, a weakly bound **atomic** oxygen species can be prepared[9] which was shown recently to be bonded to Ru-cus[10,11] and is called O-cus for this reason. Thus, the chemical activity of the RuO$_2$(110) surface is different from that of TiO$_2$(110), for which it is believed that a molecular oxygen species can be stabilized around an O-bridge vacancy and atomic oxygen, adsorbed at Ti-cus, is not observed.[12]

The spectroscopic data were obtained with titration-type experiments by using high-resolution electron loss spectroscopy (HREELS). Due to its metallic conductivity RuO$_2$(110) is an ideally suited oxide surface since the HREEL spectra are not dominated by Fuchs–Kliewer phonons. HREELS is the ideal tool to identify adsorbed species on a flat, single-crystal surface. We will show that we can prepare a Ru(0001) surface, fully covered by RuO$_2$(110), by applying a high oxygen dose. By comparison with the DFT calculations, the stretching modes of O-bridge and O-cus have been identified already.[10,11] So, we can discriminate between different oxygen surface species, which interact with CO, by measuring the HREEL spectra after exposing O$_2$ and CO to the RuO$_2$(110) surface.

It is found that the reaction may proceed via two reaction channels in which CO reacts first with O-cus and then with O-bridge. Furthermore, the oxygen consumed in the CO oxidation reaction can fully be restored at room temperature.

II. EXPERIMENT

The experiments were performed in an ultrahigh vacuum (UHV) apparatus consisting of two separable chambers which were connected through a valve to allow sample preparation in a separate chamber. The upper chamber, with
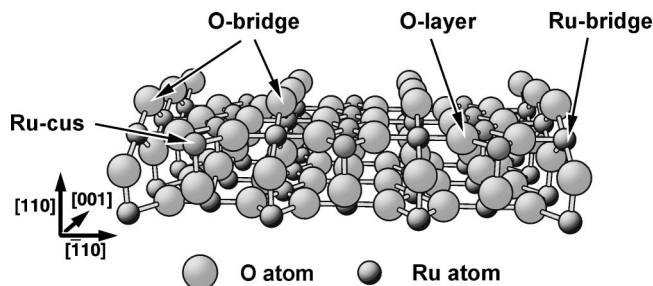
---

[a]Electronic mail: jacobi@fhi-berlin.mpg.de

FIG. 1. Ball-and-stick model of the RuO$_2$(110) surface in perspective view.
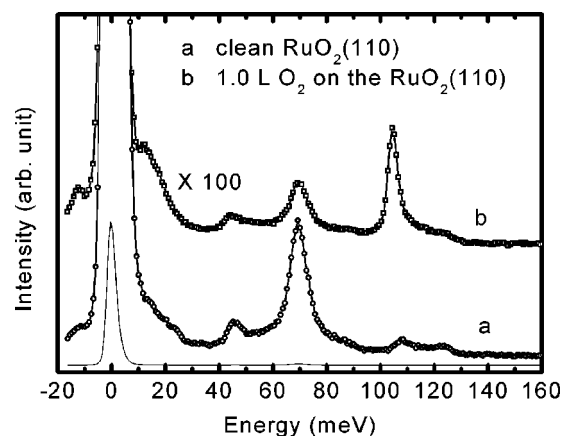

FIG. 2. HREEL spectra for a primary electron energy of 3 eV in specular geometry at an incidence angle of 60°. (a) RuO$_2$(110) surface after preparation at 700 K; (b) after an additional dose of 1.0 L O$_2$ at 300 K showing a loss due to O-cus at 103 meV.

a base pressure of 4×10^{-11} mbar, was used for preparation and contained facilities for low-energy electron diffraction (LEED), thermal desorption spectroscopy (TDS), gas dosing, and sputtering. The lower chamber with a base pressure of 2×10^{-11} mbar housed a high-resolution electron energy loss (HREEL) spectrometer. The HREEL spectra were taken at an angle of incidence of 60° relative to the surface normal in specular geometry. The primary energy was 3 eV and the resolution 2.7–3.6 meV.

The RuO$_2$(110) surface was prepared epitaxially on a Ru(0001) surface following recent recipes.[4,5] The Ru(0001) sample was mounted using W wires in narrow slits at the edges of the sample and heated by electron bombardment from the backside. The NiCr/Ni thermocouple was spot-welded to the top edge of the sample. Cleaning of the sample was achieved by repeated cycles of sputtering and annealing and checked by LEED and HREELS. The RuO$_2$(110) surface was produced by exposing 1×10^7 L of O$_2$ at a sample temperature of 700 K. A glass capillary array doser was used at a distance of about 15 mm from the sample, yielding an enhancement of the pressure at the sample surface by a factor of about 30. This procedure resulted in a surface which was covered by a thin, single-crystalline layer of RuO$_2$(110) (ordered in patches of three different domains, rotated laterally by 120°) as checked by LEED in accordance with Refs. 5 and 10. It has already been shown that for a smaller exposure of about 1×10^6 L at 600–800 K the surface is composed of patches of the (1×1)–O phase and of 2 nm thick RuO$_2$(110) platelets.[5] In our case we used larger doses (typically 10^7 L) so that the surface was completely covered by RuO$_2$(110). The preparation could be repeated after sputter cleaning the Ru(0001) substrate.

III. RESULTS AND DISCUSSION

A. The CO oxidation on RuO$_2$(110)

In Fig. 2 we present HREEL spectra of the bare RuO$_2$(110) surface, as prepared by oxidation at 700 K followed by cooling down *in vacuo* (curve a) and after an exposure of 1 L O$_2$ at 300 K (curve b). The details of these spectra have been discussed elsewhere[10,11] and can be summarized as follows: On the bare RuO$_2$(110) surface, the most intense vibrational loss at 69 meV is due to the stretching mode perpendicular to the surface of the topmost oxygen atoms in bridge positions (O-bridge, see Fig. 1). There are no larger Ru(0001)–(1×1)O patches on the surface because its characteristic oxygen stretching mode at 81 meV[13] is not

observed. This means that, besides LEED, HREELS also proves the surface to be almost completely covered by RuO$_2$(110). After subsequent O$_2$ exposure at 300 K, a new, intense feature appears at 103 meV which is identified as the vibration mode of O-cus, the weakly bound oxygen atoms on the Ru-cus sites (see Fig. 1).[10,11] The peak of O-bridge at 69 meV decreased in intensity due to screening through O-cus. It has been shown that the theoretical binding energy of O-cus is only 3.2 eV, in accordance with the desorption temperature in TDS of only 450–500 K.[10] The binding energy of O-bridge is 4.6 eV, i.e., higher in agreement with its higher desorption temperature (1060 K).

For the experiment described in the following, first, 1.0 L O$_2$ was exposed to the bare RuO$_2$(110) surface, followed by several doses of CO. Figure 3 exhibits the according HREEL spectra. With increasing CO exposure the loss peak at 103 meV continuously decreases. No CO-induced feature is observed for CO exposures of less than about 1 L, suggesting that the intermediately adsorbed molecules react rapidly with the O-cus species. The presumably formed CO$_2$ is not stable at 300 K and desorbs immediately. The decrease of the loss at 103 meV is accompanied by a recovery of the 69 meV loss intensity due to a reduced screening. Figure 4 shows the intensity (Gaussian peak areas) of the oxygen loss peaks at 69 and 103 meV and of the CO stretch mode as function of CO exposure. The O-cus intensity decreases continuously—first slowly and later more quickly—up to an exposure of about 1.9 L. At about 1.2 L the first losses of chemisorbed CO are observed. Interestingly, after about 70% of O-cus has been reacted off, O-bridge is also attacked. After an exposure of 2.4 L, both topmost oxygen species, O-cus and O-bridge, are removed almost completely. During the removal of O-bridge an increasing amount of CO is chemisorbed at the surface. There are two CO stretch modes observed which will be discussed in a forthcoming paper.[11]

The reactions of CO with O-cus and O-bridge are independent from each other, as shown by the next experiment in which we exposed the bare RuO$_2$(110) to 0.4 L CO. Figure 5 shows that most of the O-bridge has been removed, i.e., the
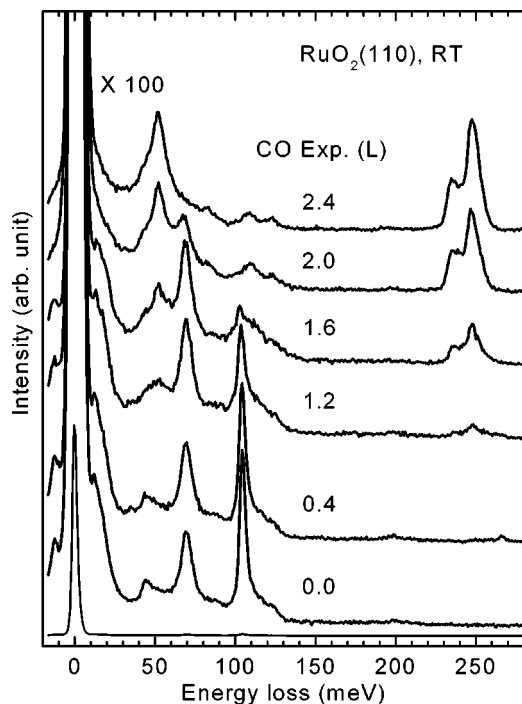
FIG. 3. HREEL spectra for $RuO_2(110)$ saturated with the weakly bonded oxygen O-cus (exposure 1.0 L O_2) and different exposure of CO at 300 K. Parameter as for Fig. 2.

reaction with O-bridge is not affected by an eventually preceding reaction with O-cus.

From these findings we can derive the following model: There are two independent reaction channels for the CO oxidation:

(1) If there is O-cus on the surface, CO reacts according to

$$CO_{ad} + O\text{-cus} \rightarrow CO_2\uparrow. \tag{1}$$

This is the main oxidation channel as long as O-cus is present. To react with O-cus, CO has to be adsorbed at a Ru-cus site. This is concluded from our data because the reaction rate is slow at the begin-
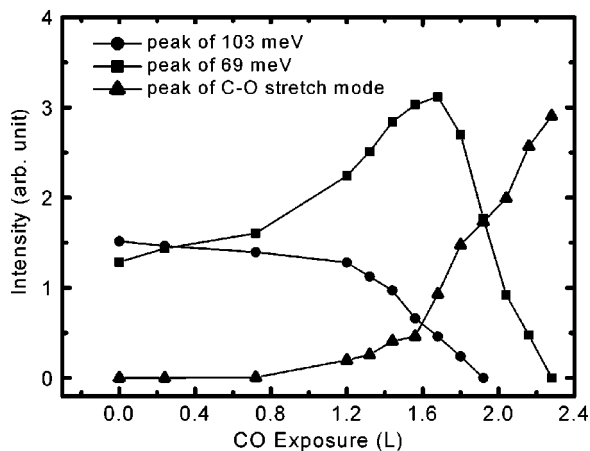

FIG. 4. Variation of the HREELS intensities with CO exposure for the loss peaks of O-bridge at 69 meV, of O-cus at 103 meV, and of the CO stretch modes. The data were collected from a sequence of spectra similar to those in Fig. 3.
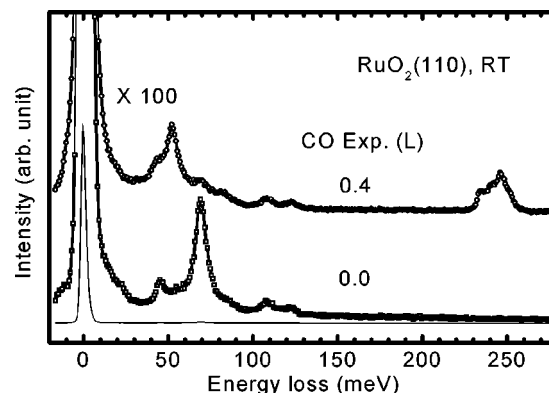

FIG. 5. HREEL spectra for the $RuO_2(110)$ surface after preparation at 700 K and after an exposure of 0.4 L CO at 300 K. Parameter as for Fig. 2.

ning when nearly all Ru-cus sites are occupied by O-cus. As the number of O-cus atoms decreases, more Ru-cus sites become available and the reaction rate increases. Probably, this reaction was observed on the *oxygen-rich* surface recently.[9]

(2) If most O-cus is reacted off, the second oxidation channel opens up

$$CO_{ad} + O\text{-bridge} \rightarrow CO_2\uparrow, \tag{2}$$

i.e., on the bare $RuO_2(110)$ surface the bridge oxygen can also react with CO. Also in reaction (2), CO has to adsorb at a Ru-cus site first. This is concluded since reaction (2) does not operate if the Ru-cus sites are blocked by O-cus, as in the present case or also by N_2.[10]

It is interesting to note that CO is not stable on the Ru-cus site at 300 K. Only in the course of reaction (2), i.e., when O-bridge is being removed, CO is stabilized at the surface. We conclude from this observation that CO is rather held at the Ru-bridge site, i.e., the Ru atom under the removed bridge oxygen. This is presumably also the species seen in STM images after CO exposure at 300 K, which upon increasing the temperature reacts further with oxygen atoms from the bulk lattice.[5] This conclusion is supported by comparison with HREELS data taken at 85 K, where CO adsorbed on Ru-cus is stable.[11]
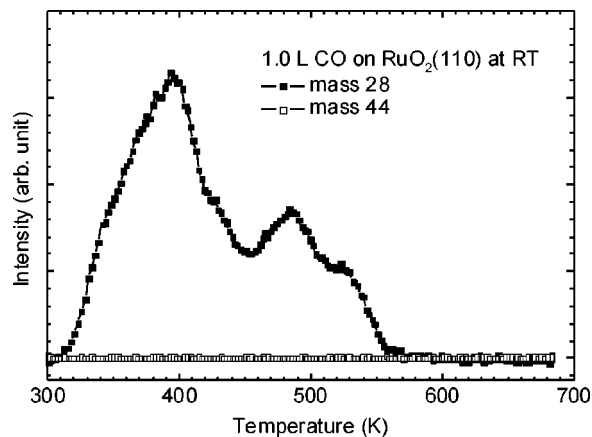

FIG. 6. TD spectra from the bare $RuO_2(110)$ surface for CO (mass 28) and CO_2 (mass 44) following CO adsorption at 300 K.
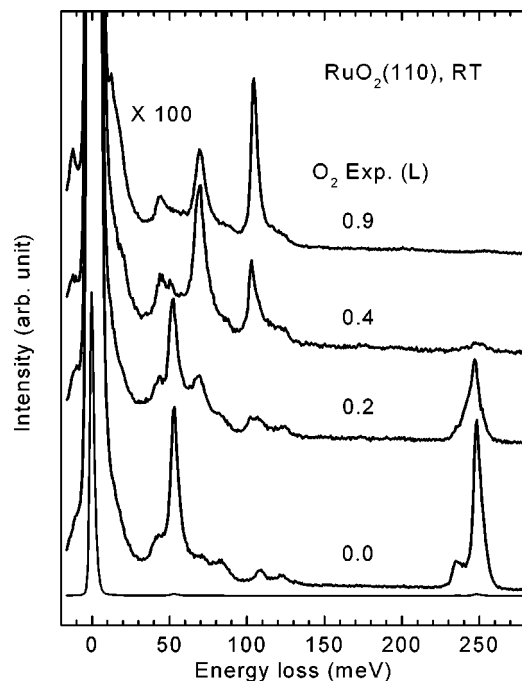
J. Chem. Phys., Vol. 114, No. 22, 8 June 2001

The oxidation of CO on RuO$_2$(110)   10061

FIG. 7. HREEL spectra of a RuO$_2$(110) surface after reaction with 1.0 L CO at 300 K and for additional exposure of O$_2$ at 300 K. Parameter as for Fig. 2.
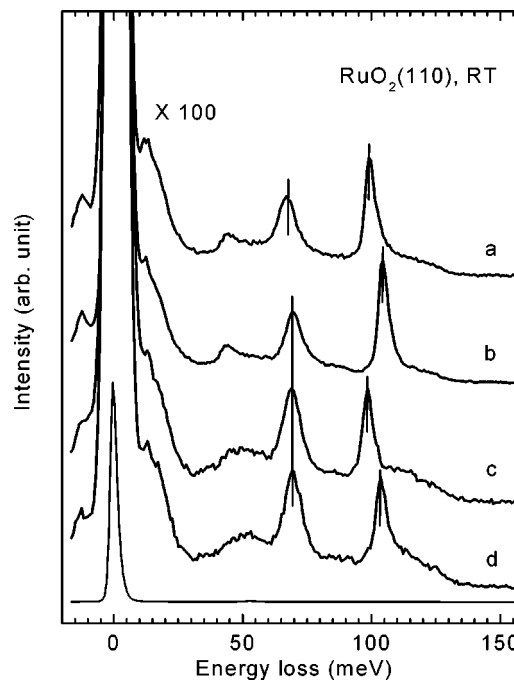

FIG. 8. HREEL spectra for differently prepared and reacted RuO$_2$(110) surfaces as indicated. Parameter as for Fig. 2. The following gas exposures were applied to the bare RuO$_2$(110) surface, i.e., to the surface prepared at 700 K and cooled to 300 K: curve a: first 1.0 L CO and then 1.0 L ^{18}O$_2$; curve b: first 1.0 L CO and then 0.9 L ^{16}O$_2$; curve c: first 1.0 L ^{18}O$_2$ and then 1.2 L CO; curve d: first 1.0 L ^{16}O$_2$ and then 1.2 L CO.

Furthermore, TDS also supports our conclusion that CO is adsorbed on Ru-bridge at 300 K. Figure 6 shows the TD spectra for CO and CO$_2$ after CO adsorption on the bare RuO$_2$(110) surface (i.e., with all O-bridge filled up, but without O-cus). The TD spectrum of CO exhibits a main peak at 400 K. Furthermore, desorption of CO occurs without any CO$_2$ formation. This is in accordance with our model, as there is no further surface oxygen available after an exposure of 1.0 L CO; all bridge oxygen atoms have been reacted off and the bulk does not supply oxygen via diffusion at 300 K.

B. Restoring of the RuO$_2$(110) surface

The O-bridge species on the surface can completely be removed during the CO oxidation. So, the question arises of whether the state of the surface from before the oxidation reaction can be restored. We performed HREELS measurement after O$_2$ was exposed to the CO-covered RuO$_2$(110) surface. Figure 7 shows the result. First, O$_2$ reacts with the CO, which covers the RuO$_2$(110) surface. Second, after CO is removed, the oxygen can restore the bridge site oxygen and then adsorb on Ru-cus, thus restoring O-cus. When we compare the uppermost curve of Fig. 7 with curve b of Fig. 2 and the bottom curve of Fig. 3, we recognize that the RuO$_2$(110) surface is almost completely restored by dosing 0.9 L O$_2$. It is known that, after the CO-covered RuO$_2$(110) surface is briefly heated to 600 K, the subsequently recorded STM image exhibits the formation of holes in the originally perfect RuO$_2$ surface.[5] The RuO$_2$ surface with many holes can only be restored when the surface is exposed to O$_2$ at elevated temperatures or is simply heated to 700 K.[11] Remarkably, in our experiments, dosing O$_2$ at RT can remove all CO and restore the former CO-covered surface after-

wards. It shows that the surface is not partially damaged during CO oxidation at RT. This means that only surface oxygen—either weakly adsorbed as O-cus or from the lattice as O-bridge—takes part in the CO oxidation reaction. Interestingly, the state of the surface is readily shifted between an oxidized and a reduced one by varying the relative oxygen exposure, establishing a remarkable surface redox system. Also, we expect that under steady-state flow conditions an oxygen-deficient surface will exist whose stoichiometry will be determined by the ratio of partial pressures.

So far, we have interpreted the results shown in Figs. 3–6, assuming that CO reacts first with O-cus, when O-cus and O-bridge are both on the surface, and then with O-bridge, when O-cus is removed almost completely. Interestingly, another reaction sequence is conceivable in which CO would always react with O-bridge, which would then be rapidly replaced by an O-cus. In order to exclude such a reaction sequence we have performed a number of isotope experiments, as shown in Fig. 8. In these experiments we always start with the bare RuO$_2$(110) surface, i.e., with all O-bridge sites filled up but without any O-cus on the surface. An exposure of 1.0 L CO for curves a and b of Fig. 8 will remove the O-bridge completely. A following exposure of 1.0 or 0.9 L O$_2$ restores O-bridge and O-cus. The fact that this is the case is recognized from the isotope shift of 2.5 meV for O-bridge and 4.0 meV for O-cus if we expose ^{18}O$_2$ instead of ^{16}O$_2$. For curve a in Fig. 8, both O-bridge and O-cus are occupied by ^{18}O and both stretching frequencies have experienced an isotope shift to lower energy. Curve b in Fig. 8 shows the same restoration performed with ^{16}O. For

curve c (^{18}O) and d (^{16}O) we have first filled the O-cus state with 1.0 L O_2. An exposure of 1.2 L of CO will empty the O-cus state by about 50%. If CO would react always with O-bridge, the O-bridge loss peak in curve c would be isotope shifted to smaller energy as it would be filled up with ^{18}O from the Ru-cus site after reaction with CO. This is not the case, so our interpretation of the CO reaction sequence—first with O-cus and then with O-bridge—is verified.

There is a further question to be answered by the isotope experiment. We have seen in Figs. 3–5 that the loss peak of O-bridge (69 meV) disappeared after exposing CO. Instead of removing O-bridge through reaction with CO to CO_2, one may wonder whether the energy loss due to O-bridge is shielded by CO. This possibility is excluded by the experiment of curve a in Fig. 8. If O-bridge had not been removed, it would not have been restored by O^{18}.

IV. CONCLUSION

Our results supply further evidence that the coordinatively unsaturated Ru surface atoms (Ru-cus) are the chemical active entities at the $RuO_2(110)$ surface as pointed out by Over *et al.*[5] We confirm that CO is oxidized at 300 K over $RuO_2(110)$ in accordance with the quoted report on the reactivity of (hydrated) $RuO_2(110)$ powder.[7] Two reaction channels are identified as the reactions of CO with atomic oxygen weakly bonded to Ru-cus (O-cus) and with the bridge oxygen (O-bridge). Although—at room temperature—CO interacts in a transition state with Ru-cus it is stationarily adsorbed only at Ru-bridge, the Ru atom underneath O-bridge. During a reaction with a high enough O_2 supply, the CO oxidation reaction will occur involving O-cus, but O-bridge can serve as a redundant source during high CO-pressure

transients. For the exposure values studied, only surface oxygen takes part in the CO oxidation and the oxygen depleted surface can be restored by O_2 exposure at room temperature. The system $RuO_2(110)+O_2+CO$ turned out to be a remarkable surface redox system operating at 300 K. We expect that under steady-state flow conditions an oxygen-deficient surface will exist whose stoichiometry will be determined by the ratio of partial pressures. The full kinetics will have to be elucidated in future experiments.

[1] H.-I. Lee and J. M. White, J. Catal. **63**, 261 (1980); V. I. Savchenko, G. K. Boreskov, A. V. Kalinkin, and A. N. Salanow, Kinet. Katal. **24**, 983 (1984).

[2] N. W. Cant, P. C. Hicks, and B. S. Lennon, J. Catal. **54**, 372 (1978); C. H. F. Peden, in *Surface Science of Catalysis*, edited by D. J. Dwyer and F. M. Hoffmann, ACS Symposium Series 483 (American Chemical Society, Washington, DC, 1992), p. 143.

[3] A. Böttcher, H. Niehus, S. Schwegmann, H. Over, and G. Ertl, J. Phys. Chem. B **101**, 11185 (1997).

[4] A. Böttcher, M. Rogozia, H. Niehus, H. Over, and G. Ertl, J. Phys. Chem. B **103**, 6267 (1999).

[5] H. Over, Y. D. Kim, A. P. Seitsonen, S. Wendt, E. Lundgren, M. Schmid, P. Varga, A. Morgante, and G. Ertl, Science **287**, 1474 (2000).

[6] Y. D. Kim, H. Over, G. Krabbes, and G. Ertl, Top. Catal. (in press).

[7] L. Zang and H. Kisch, Angew. Chem. Int. Ed. Engl. **39**, 3921 (2000).

[8] Y. D. Kim, A. P. Seitsonen, and H. Over, Surf. Sci. **465**, 1 (2000).

[9] A. Böttcher and H. Niehus, Phys. Rev. B **60**, 14396 (1999).

[10] Y. D. Kim, A. P. Seitsonen, S. Wendt, J. Wang, C. Fan, K. Jacobi, H. Over, and G. Ertl, J. Phys. Chem. (in press).

[11] J. Wang, C. Y. Fan, K. Jacobi, and G. Ertl, Surf. Sci (in press).

[12] M. A. Henderson, W. S. Epling, C. L. Perkins, C. H. F. Peden, and U. Diebold, J. Phys. Chem. B **103**, 5328 (1999).

[13] P. He and K. Jacobi, Phys. Rev. B **55**, 4751 (1997).