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Distinct Reaction Mechanisms in the Catalytic Oxidation of Carbon Monoxide on Rh(110): Scanning Tunneling Microscopy and Density Functional Theory Studies

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By means of scanning tunneling microscopy measurements and density functional theory calculations, we identify the reaction mechanism for the oxidation of carbon monoxide to carbon dioxide on the Rh(110) surface at 160 K, which appears to be completely different than the one active at room temperature. The reasons for these different behaviors are determined. Our results demonstrate that even for a very simple catalytic reaction, the microscopic mechanism can dramatically change with temperature, following pathways that differ for nucleation sites and surface propagation and involve different surface moieties.

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The unequivocal determination of reaction mechanisms of catalytic reactions is a long-standing yet elusive goal of catalysis research [1]. The determination of a set of rate equations, which correctly describes the sequence of the elementary steps leading to formation of a product, is generally hampered by the neglect of one or more intermediate steps and species or by other atomic-scale phenomena which are undetectable by the macroscopic probing of chemical kinetics.

The possible existence of parallel branches of the reaction, which may proceed through different mechanisms in different regimes, adds to the complexity of the problem. The identification and characterization of these branches which often play an important role in catalytic processes are therefore of high general interest. Recently, scanning tunneling microscopy (STM) has brought about major breakthroughs in both of these problems. Ertl and coworkers have been able to obtain a kinetic description of a chemical reaction based solely on the underlying atomic processes [2] and to identify a dual path mechanism for catalytic oxidation of hydrogen on a platinum surface [3]. In the latter case, the two different mechanisms were explained by the strongly temperature dependent lifetime of H_2O, the *reaction product*. In this Letter we report on a new case of a dual path reaction, namely CO + O on Rh(110), where we find, by means of STM measurements and density functional theory (DFT) calculations, two mechanisms related to the temperature dependent lifetime of the *reacting species*.

The adsorption of oxygen and carbon monoxide on the Rh(110) surface and their reaction have been widely studied [4]. Several ordered phases form upon oxygen adsorption, most of which involve a missing row reconstruction [5]. The reactivity of the adsorbed layers appears to be strongly affected by the structure [6]. Detailed studies have been carried out particularly on the $c(2 \times 8)$ oxygen layer, taken as a prototype case as it consists of a mixture of terraces and furrows created by a (1×4) missing row reconstruction. In particular, STM measurements at 300 K after reaction with CO [7], x-ray photoelectron spectroscopy (XPS), and mass spectroscopy (MS) studies during reaction at temperatures down to 200 K [8] have been reported on this surface.

The room temperature (RT) STM results [7] showed that the reaction nucleates at steps and proceeds along the terraces in a quasi-one-dimensional way, without crossing the furrows. The reason for this behavior was suggested to be the fact that the steps represent the only free Rh sites available for adsorption of CO which then enables the reaction to initiate. The MS and XPS results indicate a vigorous reaction at RT and above, where after a dose of 10 L of CO about 90% of the oxygen in the $c(2 \times 8)$ structure is removed at 350 K. At 200 K, about 25% of the oxygen layer is quickly removed, while that remaining stays on the surface even after long CO exposures. In the latter case, XPS showed the presence on the surface of a CO species—not present at room temperature—strongly affected by the coadsorbed oxygen, i.e., with an O 1s binding energy more than 1 eV higher than the highest value for CO on the clean Rh(110) surface. This different behavior and the detection of different species hinted that different mechanisms are involved in the reaction at different temperatures.

In this Letter we present a joint experimental and theoretical investigation of the reaction mechanism at low temperature (LT). By STM measurements we find that at 160 K the one-dimensional process is inactive, and the reaction follows a new path which does not nucleate at steps nor propagate along the narrow Rh terraces. On the basis of the STM results and DFT calculations we propose a detailed model for the new LT mechanism, which appears

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to be completely different from the RT one. The new path allows for the reaction to take place anywhere along the close-packed rows. At the same time, however, only part of the oxygen overlayer can be reacted off via this pathway, since it requires a specific chemisorbed oxygen species as one of the reactants.

The measurements were performed in an Omicron variable temperature STM. The $c(2 \times 8)$ structure was prepared by dosing 15 L of oxygen on the clean Rh surface at 620 K, until a sharp diffraction pattern was obtained. STM images were acquired in constant current mode before and after exposing the surface to carbon monoxide. The sample surface quality was good; i.e., terraces 20–60 nm wide were observed over large areas of the sample. No oxygen vacancies were observed in the $c(2 \times 8)$ structure, which showed the characteristic zigzag —Rh-O— chains with no point defects.

The DFT calculations of the CO adsorption and the CO_2 formation at the O-covered Rh(110) surface were performed using for the exchange-correlation (XC) interaction the generalized gradient approximation (GGA) in the RPBE form [9]. Slabs with $c(2 \times 6)$-missing-row and $p(2 \times 2)$ surface cells and six Rh(110) layers were used for the study of the reaction in the furrows and at the terraces, respectively. The former slabs were used instead of the $c(2 \times 8)$ in order to reduce the calculation time. Ultrasoft pseudopotentials and a plane wave basis were employed, and the surface Brillouin zone was sampled at 8 and 16 **k** points for the two surface cells, respectively.

We start with a discussion of the CO adsorption sites based on the STM results. Figure 1(a) shows the surface ~40 min after exposure to 0.2 L of CO on the oxygen $c(2 \times 8)$ surface at 160 K. The bright features are attributed to CO molecules which are present all over the surface. Closer examination reveals that two species of CO are present on the terraces, distinguished by different levels of contrast, Fig. 1(b). Less bright molecules, denoted CO_A, are found at the borders of the terraces, and when found in groups, have a periodicity in the $[1\bar{1}0]$ direction equal to that of the oxygen atoms, i.e., twice the Rh-Rh atom distance. We suggest that these are molecules adsorbed on Rh sites as shown in Fig. 2(a), left, where the molecule is coordinated to three Rh atoms, two of which are in the upper surface layer, Rh_A. When two rows of molecules in this state occur on opposite sides of a terrace, the rows are in antiphase, just as the oxygen atoms are. This proves that the oxygen atoms are still present in between the CO_A molecules and act as a template for the adsorption sites. This model is consistent with the XPS results [8,10] indicating two states of CO at LT, one of which (with a strong core level shift) can be assigned to CO_A, adsorbed next to three oxygen atoms. The brighter objects in Fig. 1(b) are assigned to CO_B molecules adsorbed at oxygen vacancy sites, mostly located towards the center of the terraces [Fig. 2(a), right]. This interpretation is in agreement with previous LT XPS results [8], which indicate the presence of a CO species with a core level binding energy similar to CO on the clean surface. The occurrence of the CO_B molecules at oxygen vacancy sites signifies that oxygen has been reacted off the surface at 160 K.

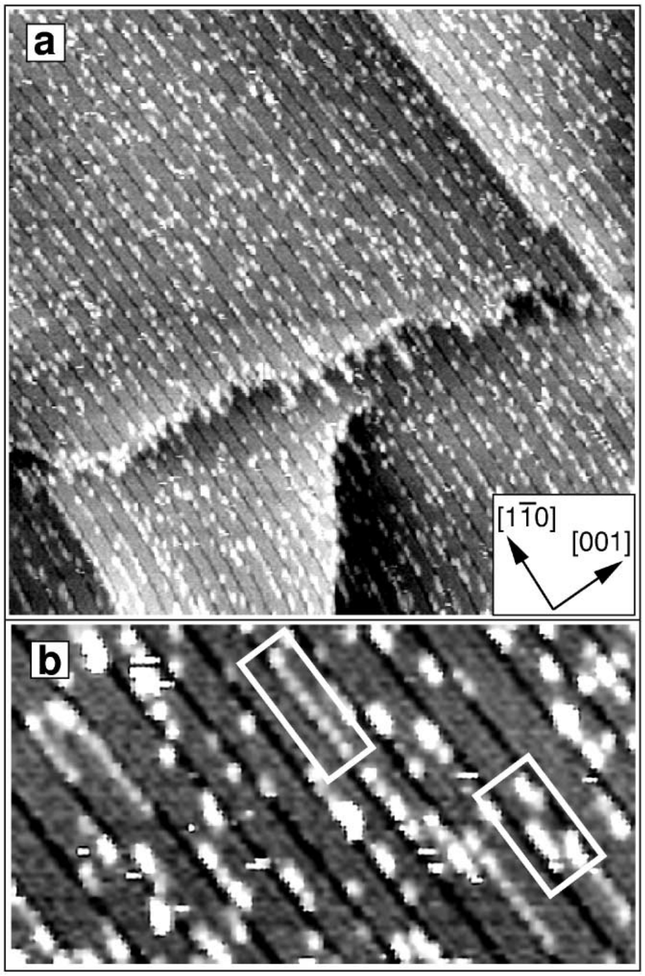

FIG. 1. (a) A 70 nm × 70 nm STM image of the $c(2 \times 8)$-O/Rh(110) after dosing 0.2 L of CO at 160 K. Tip voltage and current: -0.100 V, 1 nA. The straight features in the top right and lower left are steps parallel to the $[1\bar{1}0]$ direction. Two other steps are visible in the lower part of the figure, one roughly parallel to the [001] direction and the other emerging from a dislocation. (b) A 22 nm × 14 nm image of a zone in (a) showing details of the CO molecules. Examples of types CO_A and CO_B (see text) are marked.

In our DFT studies we find a number of stable CO adsorption configurations. In particular, the CO_A and CO_B species identified in the STM studies described above are found to be highly stable. CO_A is associated with a chemisorption bond of 1.0 eV, while CO_B shows a chemisorption bond of 1.4 eV. The CO_A molecule is tilted by 29° towards the furrow [see Fig. 2(a)], which nicely explains why these molecules are observed in the images slightly protruding towards the furrows. According to our calculations, the CO_A molecules are indeed adsorbed in threefold sites on the side of the Rh_A rows, while the CO_B molecules are adsorbed in twofold sites on the Rh_A rows. The CO_A

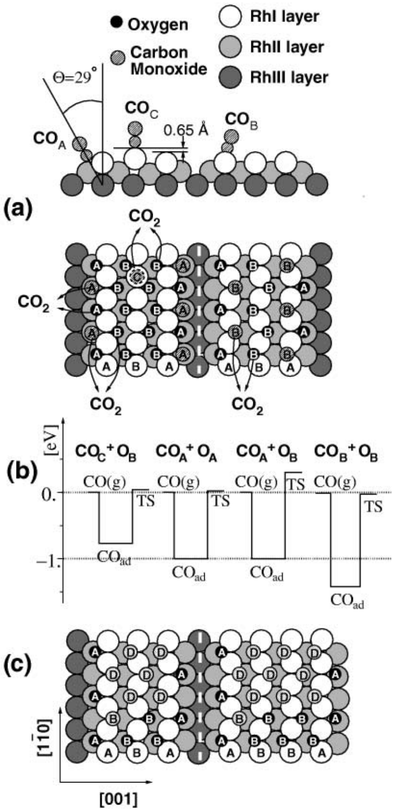

FIG. 2. (a) Schematic side and top view models of the overlayer structure imaged at LT. Left side: CO_A adsorbed near oxygen atoms. Right side: CO_B adsorbed on an empty site left by reaction of CO_C with O_B. (b) Reaction energetics for the four CO + O pathways indicated in (a). (c) Schematic top view model of the reaction front at high temperature. Left side: a $c(2 \times 8)$ terrace, with CO_D molecules reacting with O_B atoms. Right side: same model for a $c(2 \times 10)$ terrace.

molecules are thereby bound closer to the surface than the CO_B, which is consistent with the finding in the STM study of a brighter contrast for the CO_B molecules.

The DFT studies also predict another stable CO adsorption configuration, the CO_C depicted in Fig. 2(a), left. It is bound atop a first layer Rh atom on the fully oxygen covered terrace. The Rh atom right beneath the CO molecule relaxes by some 0.65 Å towards the CO. Although this Rh atom is already coordinated to two oxygen atoms, a sizable chemisorption bond, 0.8 eV, is calculated for the CO_C. However, from previous theoretical work for CO adsorption on transition metal surfaces [9], we believe that GGA based DFT studies may overestimate the binding energy of CO. With the present XC functional, which has the least overestimate of many GGAs, the overbinding may still be of the order of half an eV. Since differences in adsorption energies are known to be more accurate than absolute adsorption energies [9], we choose to focus on the relative binding energies in the three surface sites, CO_A, CO_B, and CO_C. First of all, CO_B is by far the most stable CO configuration, and it should be observed whenever oxygen vacancy sites are present. The more weakly bound CO_A and CO_C, which do not require oxygen vacancies, may, however, be observed at low enough temperatures. Since CO_A is 0.2 eV more stable than CO_C, we may well be working at a temperature where only the CO_A is long-lived enough to be imaged, the CO_C existing as a mobile precursor.

Turning to the LT reaction mechanism, the STM images yield information only on the initial and final stages of the reaction. Details of the reaction mechanism can be inferred from the DFT results. According to the calculations, the formation of an oxygen vacancy is more unfavorable by 0.4 eV at the sides of the terraces (O_A) than within them (O_B). A mobile oxygen vacancy will therefore always move to O_B, where it will be imaged by STM as CO_B after CO adsorption.

In Fig. 2(a) we indicate the CO and O species involved in the four most stable CO + O reaction pathways, as determined by the DFT studies, and Fig. 2(b) shows the energetics along these reaction pathways. One low energy pathway is found for the $CO_C + O_B$ reactions while three high energy pathways are found for the $CO_A + O_A$, $CO_A + O_B$, and $CO_B + O_B$ reactions. The energy barriers along the four pathways are 0.8, 1.0, 1.3, and 1.4 eV, respectively. These findings suggest that the $CO_C + O_B$ reaction will be the only pathway with a significant reaction rate at 160 K. This means that O_B can be reacted off at any place inside the terraces. The energetics of the CO adsorption now suggests that CO adsorption as CO_B at the oxygen vacancy will be very likely consistent with our STM observations of such CO species.

We note that the $CO_C + O_B$ reaction is a highly confined reaction configuration—the CO_C reactant involves a Rh atom with two adjacent O atoms and the O_B reactant is yet another adsorbed O atom nearby, as the reaction barrier with an adjacent O atom is about 0.2 eV higher. This reaction pathway thus requires three oxygen atoms to be configured in a particular way, and will cease to exist as the oxygen overlayer becomes diluted via the $CO_C + O_B$ reaction itself.

At RT, our STM images show a completely different mechanism of the reaction. As previously reported [7], it predominantly nucleates at steps, and propagates along the narrow terraces of the $c(2 \times 8)$ structure, Fig. 3. The reacted, CO-covered areas are clearly visible but the CO molecules are not imaged sharply. In the present image they have a spiky structure in the direction of the tip movement, resembling Christmas garlands. This is most likely due to the excitation of vibrational and/or translational motion of the molecules by the tip. Nevertheless, it can clearly be seen that the highest intensity, and therefore the preferred site of the molecule, is near the central line of the $c(2 \times 8)$ terraces. Also there are some strips of $c(2 \times 10)$ terraces with four rows of Rh atoms instead of three (indicated by an arrow). On these the CO molecules preferentially occupy the two central lines, and the amplitude of vibration/hopping is reduced. This means that in this reaction mechanism the CO molecules titrate the central

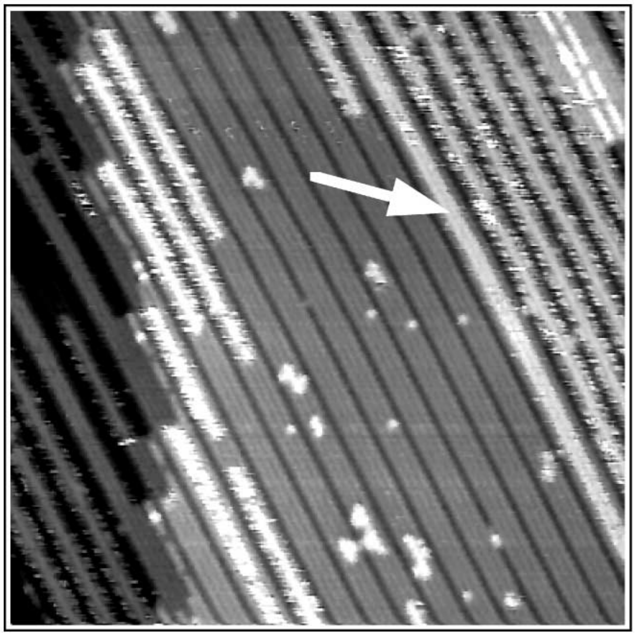

FIG. 3. A 34 nm × 34 nm STM image of the $c(2 \times 8)$-$O/Rh(110)$ after dosing 2 L of CO at 300 K. Tip voltage and current: -0.1 V, 1 nA. Arrow indicates a $c(2 \times 10)$ type terrace. Bright "Christmas garland" lines are reacted regions occupied by CO_D.

oxygen [O_B in Fig. 2(c)] starting from the step edges, and leave the central row(s) of Rh atoms free of oxygen so that CO can adsorb on it. This CO, which we denote CO_D, has a different adsorption site from those observed at LT, in agreement with XPS observations [8]. While the CO_B is completely surrounded by oxygen atoms, the CO_D mostly has CO neighbors. If all central oxygen is replaced by CO_D via the room temperature reaction, the model predicts that after complete reaction 0.25 ML of oxygen is left on the $c(2 \times 8)$ surface. This is in fair agreement with XPS results which report a final coverage of 0.36 ML. While we cannot model the $CO_D + O_B$ reaction in our finite surface unit cells, we expect the pathway and the barrier for this reaction to be similar to that of the $CO_B + O_B$ reaction. The one-dimensional reaction front now results from a mere geometrical requirement that the CO_D and the O_B need to be adjacent for the reaction to occur. The quenching at high temperatures of the LT channel can be explained in terms of the lowering of the lifetime of the CO_C species responsible for this reaction.

In summary, our model for the reaction is as follows. At LT the CO arrives from the gas phase and is adsorbed into a short lived state, CO_C, from which it diffuses on the surface without being imaged. On the terraces, either it gets trapped in the CO_A state on the edge of the terraces or it reacts from the CO_C state with an O_B atom to leave an empty site where the CO_B can adsorb. The overall reaction appears to nucleate homogeneously on the surface, but since it requires a configuration involving three adsorbed oxygen atoms it stops working as the oxygen coverage is decreased.

At RT the reaction starts at steps and a reaction front moves one dimensionally within each strip of Rh terrace. In this case the reaction is radically different since it requires only one CO molecule and one oxygen atom. The O_B atoms at the center of the terraces are cleaned off by CO_D molecules until very little oxygen is left on the surface.

In conclusion, direct imaging of this prototypical catalytic reaction on Rh(110) indicates that two competing mechanisms cause very different pathways for the reaction at RT and LT. By combining STM results, DFT calculations, and previous photoemission data, a consistent picture emerges in which the sites of the individual atoms and molecules involved in the reaction are identified. The influence of the temperature on the overall mechanism is complex, as it affects the reaction in several ways: (a) by changing the lifetime of CO_C on the surface, quenching therefore the LT reaction channel at RT; (b) by changing the CO surface mobility; (c) by changing the reaction rate (both in the LT and RT channels), according to the respective activation energies. The interplay of these effects in different temperature regimes gives rise to alternative processes, which differ for nucleation site, surface propagation, and surface moieties involved.

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