Enhanced reactivity of adsorbed oxygen on Pd(111) induced by compression of the oxygen layer

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The reaction between O atoms and CO molecules on Pd(111) was investigated by scanning tunneling microscopy (STM). CO was dosed on the (2×2)O-covered surface at temperatures between 100 and 190 K, and the structure changes were monitored by STM. CO adsorption causes compression of the (2×2)O overlayer into islands of the (2×1)O structure, followed by reaction of the O atoms to give CO_2. The (2×2)O overlayer does not react with CO at temperatures up to 180 K, whereas the (2×1)O phase reacts at temperatures as low as 136 K. The analysis of the reaction kinetics reveals an activation energy for the O+CO reaction of 0.4 eV and a reaction order of 1 with respect to the O coverage.

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I. INTRODUCTION

In kinetic models of surface catalytic reactions it is mostly assumed that the adsorbed particles react independently of each other. Only under this condition can one formulate kinetic equations that depend in a simple way on the coverages. However, this neglect of correlations between the particles for the kinetics is questionable, in particular at the high pressures of applied catalysis where coverages may be high. There are indeed many indications for significant interactions between adsorbed particles. It is found that adsorption energies usually vary with coverage, as is observed, e.g., by thermal desorption spectroscopy (TDS).[1] In the majority of cases, adsorbed particles form islands at some coverage, and involvement of islands in surface reactions have been reported.[2–4] In this paper, we present investigations by scanning tunneling microscopy (STM) on the reaction between CO molecules and O atoms on Pd(111). We find a strongly enhanced reactivity caused by a compression of the oxygen adlayer by repulsive interactions with the coadsorbed CO molecules.

That interactions between O and CO play a particularly important role on Pd(111) has been recognized in the early work on this system.[5] In the absence of CO, oxygen forms a (2×2)O structure. Adsorption of CO on this phase (at a lowered temperature, e.g., at 200 K, to avoid immediate reaction to give CO_2) leads to phase transitions, first to a $(\sqrt{3}x\sqrt{3})R30°$ O structure, then to a (2×1)O structure. The formation of these higher density oxygen phases, obviously caused by repulsive interactions between O and the adsorbed CO molecules, is a unique feature of the Pd(111) surface. In contrast, on the close-packed surfaces of Pt, Rh, Ni, and Ru, the CO molecules can occupy sites within the (2×2)O unit cells.[6] Density functional theory (DFT) calculations and low energy electron diffraction (LEED) investigations support the interpretation of these phase transitions on Pd(111) as a result of repulsive interactions.[7] It was furthermore observed that the activation energy for the CO+O reaction on Pd(111) changes with temperature. Molecular beam experiments revealed a change of the activation energy by a factor of 2 at around 450 K,[8] and a LEED study showed similar changes

between 400 and 240 K.[9] These findings can be explained by the different coverages at high and low temperatures, so that the repulsions and also the activation energies are different.

In a recent publication we have treated the structural aspects of the CO-induced phase transitions of the O layer on Pd(111).[10] Here, we concentrate on the reaction between O and CO on this surface. We find that the reaction takes place at temperatures as low as 130 K, and that the lowered activation energy can be directly correlated with the formation of the compressed (2×1)O phase.

II. EXPERIMENTAL

The experiments were performed in an ultrahigh vacuum chamber that, together with the preparation of the (111) oriented Pd single crystal, was described in detail before.[10] The home-built, variable temperature STM used for the experiments was also described previously.[3] To prepare the initial oxygen layer, the sample was dosed at 2×10^{-7} Torr O_2 for 50 s at temperatures between 230 and 300 K, and then cooled in the STM to temperatures between 100 and 190 K for the individual measurements. To monitor structure changes as a function of time, CO was dosed with the tip in tunneling contact, during recording of the STM images. Such dosing experiments are often hampered by shadowing of the scanned surface area under the tip.[10] Therefore, for time-dependent measurements, it had to be verified that the surface processes were not limited by the CO impingement rate. Arguments that the CO adsorption was fast enough were the observation of the $(\sqrt{3}x\sqrt{3})R30°$ CO structure or of higher coverage CO structures between the O islands (corresponding to local coverages of $\Theta_{CO} \geq 0.33$), and checks that the measured reaction rate did not depend on the CO pressure.

III. RESULTS AND DISCUSSION

Figure 1 shows an experiment performed at 143 K in a constant CO pressure of 2×10^{-8} Torr. All STM images of the series are from the same area. The scanning lines run in x direction. The direction in which the images were recorded in y is indicated by white arrows. The hexagonal structure
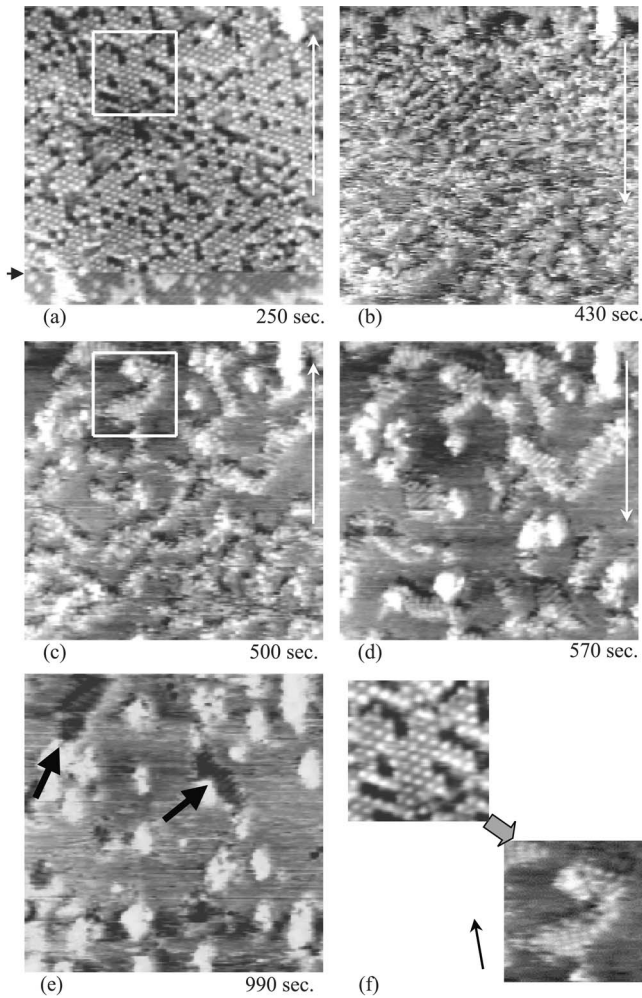
(a) 250 sec. (b) 430 sec.

(c) 500 sec. (d) 570 sec.

(e) 990 sec. (f)

FIG. 1. Series of STM images recorded during CO dosing on the (2×2)O-covered surface. $T = 143$ K, $p_{CO} = 2 \times 10^{-8}$ Torr, all images are from the same area. Indicated is the time elapsed since the start of the CO dosing. Tunneling voltage (V_T) 0.3 V, tunneling current (I_T) 2.2 nA, 240 Å×240 Å. The two close-ups in (f) show details from the marked areas in frames (a) and (c).

FIG. 2. STM image of (2×1)O islands (bright areas). This state was prepared by dosing 1 L ($= 1 \times 10^{-6}$ Torr s) of CO on the completely (2×2)O-covered surface at 170 K and slowly letting it warm up to 180 K. V_T, 0.4 V; I_T, 0.7 nA; 120 Å×120 Å.

stripes are rotated by approximate 120° angles with respect to each other. We have shown before that this structure is the (2×1)O phase; the stripes correspond to the twofold periodicity of this structure.[10] (The very bright features are unidentified defects.) In the next frame [Fig. 1(e)] the tip changes again, and the (2×1)O islands are imaged dark, corresponding to "normal contrast."[10] At the same time some of the islands have disappeared, showing that oxygen has started to react off. The CO_2 molecules, formed by the reaction, desorb immediately after formation and are not resolved. Figure 1 thus shows the CO-induced (2×2)O-to-(2×1)O phase transition and the start of the reaction after the transition. The close-ups from Figs. 1(a) and 1(c) [Fig. 1(f)] illustrate the compression of the (2×2)O layer into (2×1)O islands that have a two times higher oxygen density than the (2×2)O structure.

The intermediate $(\sqrt{3} x \sqrt{3})R30°$ O phase was not resolved here, in contrast to STM experiments performed at 170 to 190 K.[10] Possibly the disordered state in Fig. 1(b) has local $\sqrt{3}$ structure elements, but at the low temperature the O atoms are apparently not mobile enough to form an ordered $(\sqrt{3} x \sqrt{3})R30°$ O structure in the time period before the (2×1)O phase develops. CO structures between the O islands are not resolved here, but under the conditions of the experiment a local CO coverage of 0.5 has been observed.

The (2×1)O islands approximately cover half of the area initially covered by the (2×2)O phase.

This result is more clearly seen in Fig. 2, showing the surface after CO dosing on the completely (2×2)O-covered surface. Here, the temperature was 170 K during adsorption and it slowly increased to 180 K in the course of the experiment. The striped (2×1)O islands cover about 50% of the surface. Because the density of oxygen atoms in the (2×1)O islands is two times higher than in the (2×2)O layer [Fig. 1(f)], it can be concluded that there is no significant reaction before or during the (2×2)O-to-(2×1)O phase transition, even at temperatures of up to 180 K. Only the (2×1)O islands after the transition are reactive. The (2×1)O islands were found reactive at temperatures as low as 136 K.

A surprising observation in the reaction stage [Figs. 1(d) and 1(e)] is that the islands do not shrink continuously. In

resolved in the beginning [lower part of Fig. 1(a)] is the (2×2)O structure, which has many vacancies in this experiment. In the lower part of Fig. 1(a) the image contrast reverses, after which a hexagonal structure of bright dots appears. Following our previous analysis this situation represents "inverted contrast" conditions,[10] where the O atoms appear bright (with a metallic tip they appear dark). The inversion is likely caused by the adsorption of a CO molecule or an O atom on the tip apex. In the following three frames [Figs. 1(b)–1(d)] the tip remains unchanged, so that bright dots can be interpreted as O atoms. In Fig. 1(b) the surface disorders completely. As indicated by the many streaks in the x direction the fuzzy appearance of the surface is mainly a dynamic effect, caused by structure changes on a shorter time scale than the frequency of the scan lines. In Fig. 1(c) these processes stop at the upper half of the frame. In Fig. 1(d) a new structure has developed from the disordered state. The structure forms islands displaying a characteristic striped pattern, and closer inspection shows that the
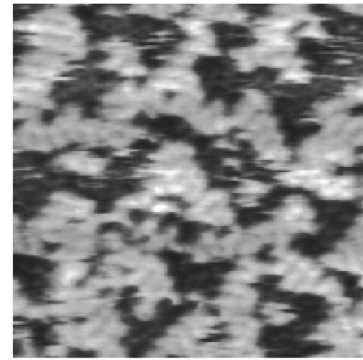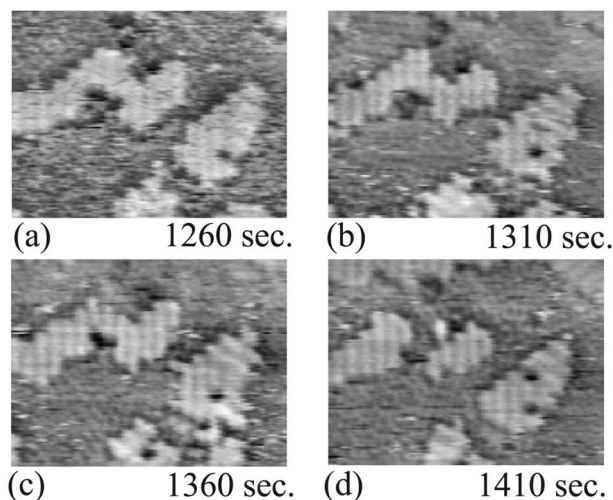
(a) 1260 sec. (b) 1310 sec.

(c) 1360 sec. (d) 1410 sec.

FIG. 3. STM images showing the discrete nature of the reaction of the (2×1)O islands. CO was dosed on the Pd(111) surface covered with (2×1)O islands (striped patches). $T = 185$ K, $p_{CO} = 3 \times 10^{-9}$ Torr, all images are from the same area. V_T, 2.2 V; I_T, 0.7 nA; 120 Å $\times$ 90 Å.

Fig. 1(e), while most islands have completely disappeared, some islands have not even shrunk noticeably (arrow marks). This effect was observed repeatedly. Figure 3 shows an example with better resolution. At the low CO pressure in this experiment (3×10^{-9} Torr) the reaction was slow and could be monitored more easily. The series shows two islands with the characteristic striped pattern of the (2×1)O structure. In the first three frames the islands display some fluctuations at the perimeters, but do not become markedly smaller. Then, in Fig. 3(d), the left island suddenly shrinks in the center part of the image, whereas the right island does not change. This discontinuous behavior was found to be typical. Islands remain unchanged for some time, and then suddenly shrink or completely disappear in the next image, whereas other islands remain unaffected. Although the reaction is clearly dominated by the presence of islands, it does not proceed by a continuous removal of O atoms from the island perimeters. It rather progresses in a statistical, stepwise manner.

To investigate the kinetics, the shrinking area covered by islands was determined quantitatively. In these experiments freshly prepared tips were used and great care was taken to avoid mechanical contact with the sample. Longer used tips were found unsuitable because they become increasingly blunt by occasional surface contact, and, although atomic resolution is still achieved by "mini tips," the display pronounced shadowing effects in the dosing experiments. The (2×1)O islands were prepared by dosing an amount of CO onto the (2×2)O-covered surface that did not yet start the reaction. Then the tip was stabilized and a sufficiently large area was chosen to average over the statistical reaction discontinuities of single islands. CO was dosed onto the (2×1)O covered surface while the same area was continuously scanned until the islands had reacted off. Figure 4 shows one of such measurements at 144 K. The (2×1)O phase was prepared by exposing the initial (2×2)O adlayer to 7 L CO [Fig. 4(a)]. The series shows the evolution of the

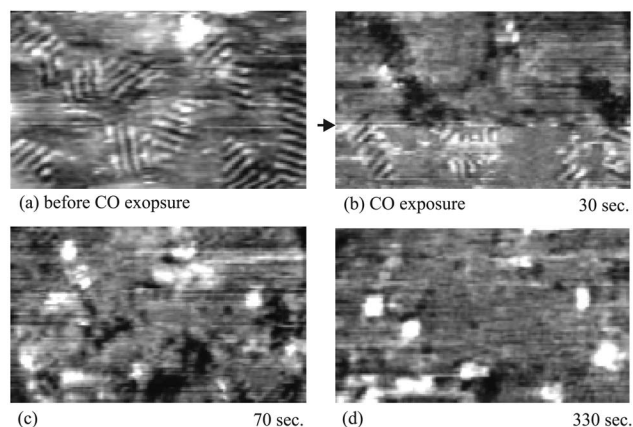(a) before CO exposure (b) CO exposure 30 sec.

(c) 70 sec. (d) 330 sec.

FIG. 4. STM images recorded during reaction of the (2×1)O islands at $T = 144$ K. At $t = 0$ CO dosing with $p_{CO} = 2 \times 10^{-7}$ Torr was started. All images are from the same area. V_T, 2.2 V; I_T, 0.7 nA; 130 Å $\times$ 80 Å.

adlayer at the same area. In the beginning [Fig. 4(a)], the (2×1)O islands are imaged with their characteristic stripe pattern. Then a CO pressure of 2×10^{-7} Torr was adjusted, defining $t = 0$. The state of the tip changes shortly thereafter [arrow in Fig. 4(b)], after which the islands are imaged dark. Before $t = 0$, the boundary of the islands show some mobility, such as in Fig. 3 (not shown). After starting the exposure to CO [Figs. 4(b)–4(d)] the islands become smaller and, after approximately 350 s, have eventually disappeared.

These data were analyzed, and the result is shown in Fig. 5. Figure 5(a) shows that before $t = 0$ there are only small changes of $\Theta_{(2 \times 1)}$, indicating that no reaction occurs. After the CO dosing is started, $\Theta_{(2 \times 1)}$ decreases immediately. Similar observations as these at 144 K were made at 136 K. Below 130 K no compression of the (2×2)O into the (2×1)O structure occurred and no reactions were detected.

To determine the kinetics of the reaction it was assumed that the reaction rate can be described by an equation of the form $-d\Theta_{(2 \times 1)}/dt = k\Theta_{(2 \times 1)}^m \Theta_{CO}^n$. Using the fact that the CO adsorption was much faster than the reaction Θ_{CO} in this equation can be regarded as constant. With this assumption a double-logarithmic plot of the reaction rate $\ln[-d\Theta_{(2 \times 1)}/dt]$ vs $\ln \Theta_{(2 \times 1)}$ should yield a straight line with slope m, the reaction order with respect to the O coverage. As can be seen in Fig. 5(b) the data scatter somewhat in this double-logarithmic plot, but a straight line with $m = 1.14 \pm 0.38$ can be fitted. The same analysis for the data of Fig. 1 gave $m = 0.96 \pm 0.32$. By assuming $m = 1$ and a Θ_{CO} of the order 1 and integrating, one obtains $\Theta_{(2 \times 1)} = \Theta_{(2 \times 1)}^{(0)} e^{-kt}$, so that the reaction constant is obtained by plotting $\ln \Theta_{(2 \times 1)}$ vs t [Fig. 5(c)]. The resulting value for the reaction constant, $k = 0.78 \pm 0.04 \times 10^{-2}$ s^{-1}, corresponds, with a preexponential factor of 10^{13} s^{-1}, to an activation energy for the reaction of $E_a = 0.43$ eV. Results for an experiment at 136 K are $m = 1.78 \pm 0.31$, $k = 0.93 \pm 0.11 \times 10^{-2}$ s^{-1}, and $E_a = 0.41$ eV. Although the data set is too small for a final conclusion, it appears that the reaction order is close to unity, and that a reaction order of $m = 0.5$ can be ruled out. A half-order reaction with respect to the O coverage had been found for the
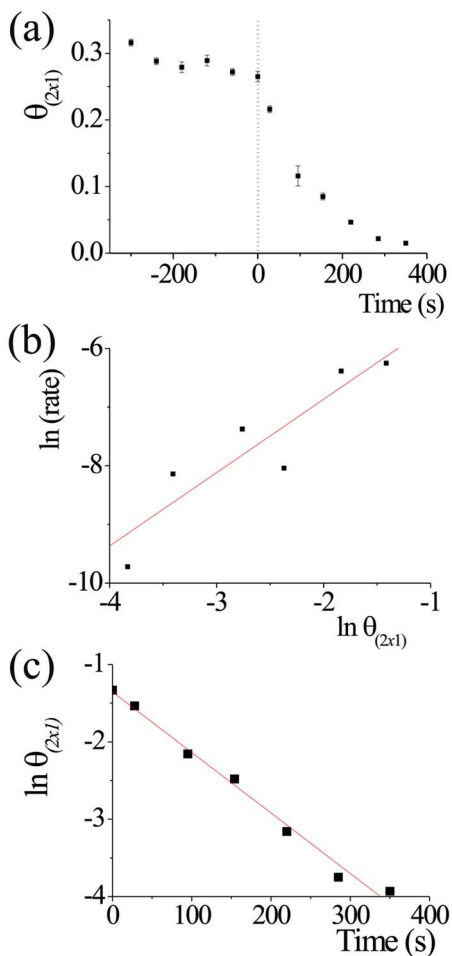
FIG. 5. (Color online) (a) Time evolution of the (2×1)O coverage from the series of Fig. 4. (b) Plot of $\ln[-d\Theta_{(2\times1)}/dt]$ vs $\ln \Theta_{(2\times1)}$ for the data from (a) for $t \geq 0$. (c) Plot of $\ln \Theta_{(2\times1)}$ vs t for the data of (a) for $t \geq 0$.

CO oxidation on Pt(111) and was explained by the reaction at the perimeters of O islands. (Given the islands have a compact shape, the island perimeter length is proportional to the square root of the island area and thus also to the overall coverage, hence $m=0.5$[2,3]). Although the (2×1)O islands on Pd(111) appear sufficiently compact the kinetics does not reveal the result expected for a reaction at the island perimeters.

The activation of oxygen during the low-temperature reaction can be explained by the compression of the O layer into the (2×1)O structure. Following recent work the (2×1) phase is a pure oxygen structure;[7,10] a mixed (2×1)O/CO structure, with one O atom and one CO molecule per unit cell, which was assumed in the older work,[5,11] can almost certainly be ruled out. DFT calculations have shown that the compression of the oxygen layer is connected with a lowering of the O binding energy, from 1.15 eV in the

(2×2)O structure to 0.84 eV in the (2×1)O structure.[7] The data presented here show that this reduced binding energy of the O atoms quite directly transforms into a lower activation energy for the reaction with CO. For the reaction between about 350 and 450 K, a value of $E_a=0.6\pm0.1$ eV was found by molecular beam experiments,[8] and TDS data revealed $E_a=1.0\pm0.3$ eV for the reaction at 240 K.[9] Under these conditions the (2×1)O structure does not form. The value of $E_a=0.4$ eV that was extracted from the STM data for the reaction of the (2×1)O structure is thus reasonable, considering the calculated 0.3 eV energy upshift caused by the compression of the O atoms into the (2×1)O phase.[7] A similar trend towards lower activation energy with increasing O coverage has also been found by DFT calculations in a comparative study on (3×2)O and (2×2)O structures on Pd(111).[12]

An interesting aspect is the reaction order with respect to $\Theta_{(2\times1)}$ that seems too high for a reaction at the island perimeters. A value of $m=1$ may suggest that all O atoms are accessible for the reaction, irrespective of their positions in the (2×1)O islands. One may speculate that impinging CO molecules transiently occupy sites in the interior of the islands, where they then react with O atoms. In this way one could explain the finding by angular-resolved TDS that at low temperatures the angular distribution of the desorbing CO_2 product was extremely peaked normal to the surface.[9] This collimation had been explained by the geometrically constrained transition state of the reaction in the mixed (2×1)O/CO phase. Although the present structure model of the (2×1) phase assumes a pure O structure, this explanation could still be valid if the mixed O/CO sites in the interior of the islands are only transiently occupied. Another possible explanation for the reaction order could be the observed discontinuities in the reactions of the island that point to a more complex reaction mechanism. This may preclude a simple rate equation for the kinetics.

IV. CONCLUSIONS

In conclusion, the data presented here reveal a direct correlation between structure and reactivity: Formation of the (2×1)O structure, which is induced by the repulsive action of coadsorbed CO, is a necessary condition for the low-temperature reaction of oxygen on Pd(111). This conclusion is valid for the whole temperature range between 130 and 180 K. The discontinuous progress of the reaction and the reaction order of 1 suggest that the reaction is not limited to the island perimeters.

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