

## CO Oxidation on Pt(110): Scanning Tunneling Microscopy Inside a High-Pressure Flow Reactor

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(Received 19 March 2002; published 9 July 2002)

We have used a novel, high-pressure high-temperature scanning tunneling microscope, which is set up as a flow reactor, to determine simultaneously the surface structure and the reactivity of a Pt(110) model catalyst at semirealistic reaction conditions for CO oxidation. By controlled switching from a CO-rich to an O<sub>2</sub>-rich flow and vice versa, we can reversibly oxidize and reduce the platinum surface. The formation of the surface oxide has a dramatic effect on the CO<sub>2</sub> production rate. Our results show that there is a strict one-to-one correspondence between the surface structure and the catalytic activity, and suggest a reaction mechanism which is not observed at low pressures.

DOI: 10.1103/PhysRevLett.89.046101

PACS numbers: 68.37.Ef, 82.65.+r

Much of the present-day fundamental understanding of heterogeneous catalysis has been obtained by studying simplified model catalysts at well-defined, but strongly nonrealistic conditions, such as ultrahigh vacuum (UHV) or very low gas pressures [1]. Yet, there lies an enormous pressure gap of at least 9 orders of magnitude between the low pressures used in model experiments (10<sup>-9</sup> bar) and the pressures applied in practical catalysis (>1 bar). It has been suggested that the presence of reactants at a high pressure can have a dramatic effect on the surface structure and composition, and thereby the performance of a catalyst [2–6].

The scanning tunneling microscope (STM) makes it possible to determine the surface structure on an atomic scale, not only in UHV, but also at elevated pressures [6,7]. Insertion of a STM inside a flow reactor should make it possible to determine simultaneously (changes of) the surface structure and the catalytic activity of a single crystal surface. However, the detection of the small quantities of reaction product from the typical small surface area of the model catalyst requires a reactor volume smaller than the size of a typical STM. For this reason, we have developed a dedicated, high-pressure, high-temperature scanning tunneling microscope [8,9]. The STM is combined with a flow reactor in such a way that only the STM tip is inside the gold-plated high-pressure cell. The rest of the STM is separated from the reactor cell by a tiny flexible O-ring, which serves as a leak tight seal, but allows the scanning motion. In this way, we have reduced the reactor volume to only 500 μl, and avoided exposure of the entire STM to the reactants. The STM can operate at pressures from vacuum to 5 bars at temperatures of 300–425 K and a flow of 0–10 ml/min, which corresponds to 1/3 of the reactor volume per second. As we operate this so-called “Reactor-STM” in a flow mode, we can image the surface and simultaneously determine the reaction rate by means of on-line mass analysis with a quadrupole mass spectrometer of the gas leaving the reactor. With this instrument, we can directly observe the effects of controlled changes in the gas mixture. The Reactor-STM is integrated in a standard UHV system, which allows state-of-the-art surface prepa-

ration and prereaction and postreaction analysis by traditional surface science diagnostics [e.g., low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES)].

The selected model system for the experiments shown here was the oxidation of CO on a platinum single crystal surface [10,11], Pt(110). Our Pt(110) sample was prepared in UHV, until a clean surface was obtained with the familiar (1 × 2) “missing-row reconstruction” as shown by the LEED pattern. After preparation, the sample was transferred to the Reactor-STM. At low pressures, CO is known to lift the missing-row reconstruction of Pt(110) and stabilize the unreconstructed (1 × 1) surface [12]. We find that also high pressures of CO remove the (1 × 2) reconstruction.

The CO-exposed, unreconstructed surface forms the starting configuration of our experiment, which is summarized in Fig. 1. The lower part of Fig. 1 shows a selection of STM images from an STM movie [13], which we recorded at a rate of 65 s/image, while simultaneously monitoring the composition of the gas mixture leaving the flow reactor. The thermal drift of the STM was such that we could not image the same area on the surface over the full duration of the experiment, but we have checked that our STM observations were always characteristic for the behavior of the entire surface. The upper part of Fig. 1 shows the partial pressures of the two reactants, CO and O<sub>2</sub>, and the signal of the reaction product, CO<sub>2</sub>.

Figure 1A shows the surface at  $t = 0$  s, in the initial CO flow of 3.0 ml/min at 0.5 bar and at 425 K. The signals of O<sub>2</sub> and CO<sub>2</sub> at  $t = 0$  s correspond to the base levels for these masses. Several flat terraces and monatomic steps ( $d_{\text{step}} = 0.139$  nm) can be observed in the STM images, but the terraces were all imaged with stripes, parallel to the STM scan direction (left to right), which is characteristic for a high surface mobility. At  $t = 502$  s, we closed the CO valve and opened the O<sub>2</sub> valve to establish a flow of 3.0 ml/min O<sub>2</sub>. The total pressure remained at 0.5 bar. The O<sub>2</sub> signal in the mass spectrum increased almost instantly and the presence of O<sub>2</sub> in the reactor gave rise to a modest production of CO<sub>2</sub> (rate  $R_{\text{low}}$ ). The CO partial

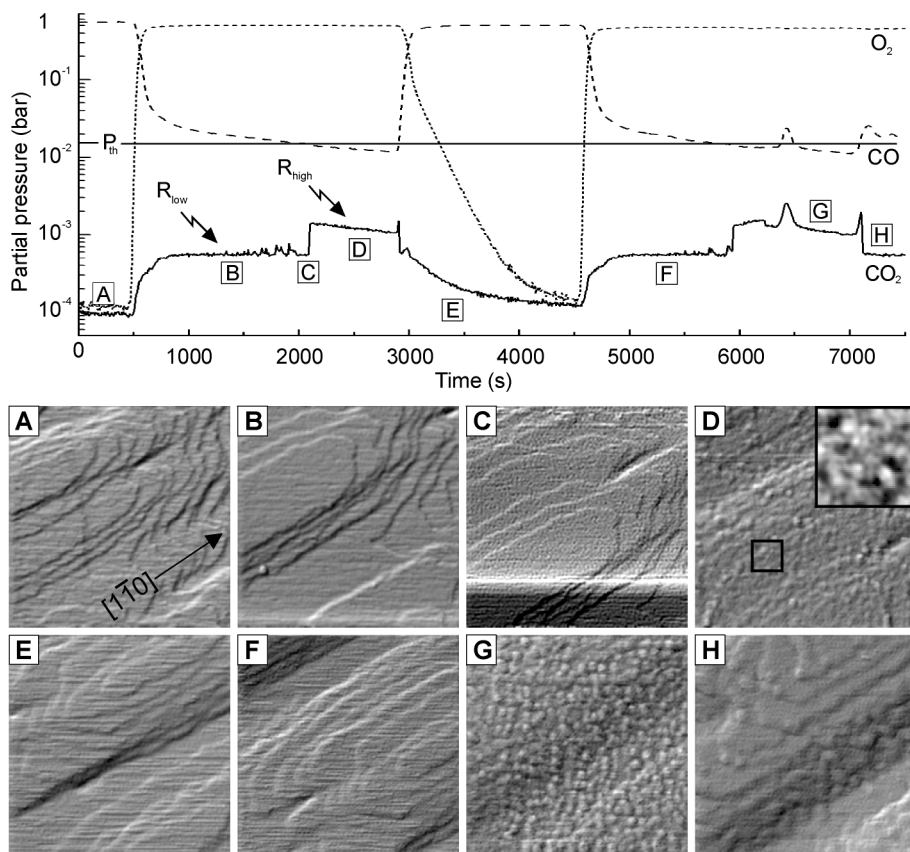


FIG. 1. (Upper panel) Mass spectrometer signals of O<sub>2</sub>, CO, and CO<sub>2</sub> [21], measured directly from the reactor cell. The mass spectra were recorded simultaneously with the STM movie. Labels (A)–(H) correspond to the STM images in the lower panel. R<sub>low</sub> and R<sub>high</sub> denote the low and high CO<sub>2</sub>-production rate branches (see text). P<sub>th</sub> indicates the threshold value of the CO pressure at which the rate switched from R<sub>low</sub> to R<sub>high</sub> and the surface changed simultaneously from smooth to rough. (Lower panel) STM images of 210 × 210 nm<sup>2</sup> from an STM movie [13] of a Pt(110) surface at a temperature of 425 K in a 3.0 ml/min flow of mixtures of CO and/or O<sub>2</sub> at 0.5 bar (65 s/image, I<sub>t</sub> = 0.2 nA, V<sub>t</sub> = 80 mV). The images were differentiated to enhance the contrast. Images (A), (B), (E), (F), and (H) show flat terraces separated by steps of the Pt lattice. This corresponds to the metallic, CO-covered surface (see text). Image (C) shows the change of the surface during the step in activity (the image was built up from bottom to top). The bright scan lines and the change in slope are the result of extra thermal drift due to the increased, exothermic reaction. Images (D) and (G) show the rough surface consisting of protrusions, with heights of 0.2–0.4 nm, and pits (see inset). These are formed during the high activity stage. There is a direct correspondence between the buildup of the roughness and the total amount of produced CO<sub>2</sub>.

pressure was not reduced to zero immediately, but after a rapid initial drop it decayed slowly, reflecting the long time constant of the entire gas handling system. The STM images show that the surface did not change when the O<sub>2</sub> was introduced as is illustrated by Fig. 1B. Although the CO pressure decreased steadily, the CO<sub>2</sub> signal was constant. Around  $t = 1800$  s several instabilities in the CO<sub>2</sub> production could be observed, which finally at  $t = 2109$  s were followed by an abrupt increase in the CO<sub>2</sub> signal by a factor of 3 (rate R<sub>high</sub>) and a minute, downward step in the CO signal. The sudden increase in reactivity coincided with a change of the surface (Fig. 1C). The change in contrast in the lower part of Fig. 1C is due to a change in thermal drift, which is the result of the increased exothermic reaction (the image was built up from bottom to top). The upper three-fourths of the image shows the surface with the higher activity. The surface appears to be less

smooth, and the stripes along the fast scan direction have disappeared. A similar change in appearance was also observed when we exposed the Pt surface to a high pressure of O<sub>2</sub> only. After the increase in reactivity, a characteristic roughness developed gradually on a time scale of several minutes (Fig. 1D). This roughness, which took the shape of small protrusions with heights of 0.2–0.4 nm (not corresponding to integer multiples of  $d_{\text{step}}$ ) and average apparent widths of 4–7 nm, and pits in the surface, appeared only when the surface was exposed to both O<sub>2</sub> and CO. After the sudden increase at  $t = 2109$  s, the CO<sub>2</sub> production slowly decreased, proportional to the CO signal (note the log scale). At  $t = 2913$  s, we switched back to a CO-rich flow. The CO<sub>2</sub> signal dropped to R<sub>low</sub> and the protrusions and pits disappeared from the surface (Fig. 1E). Immediately after this, the CO<sub>2</sub> signal decayed slowly, together with the decreasing O<sub>2</sub> pressure. The end point of this first

cycle was a smooth surface, similar to the one we started with (Fig. 1A), and which we associated with the CO-covered, unreconstructed Pt surface. The second cycle started off similar to the first one. After the surface had switched to the rough state, at  $t = 5952$  s, we briefly increased the CO pressure at  $t = 6441$  s. This was accompanied by a peak in the CO<sub>2</sub> production rate. During this brief period of higher reaction rate, the roughness increased even faster (Fig. 1G). After the second CO peak, at  $t = 7108$  s, the surface smoothed again; the protrusions left behind Pt adatom islands and at the location of the pits there were vacancy islands (Fig. 1H), which subsequently decayed, as can be observed in the STM movie [13]. During the experiment, we have routinely imaged parts of the surface, which had not been scanned previously. In this way, we have checked that the surface was not affected by the presence of the Pt/Ir STM tip. In addition, by repeating the experiment at the same conditions, but using a different sample (e.g., Ru), we have verified that the reaction kinetics were characteristic for the Pt surface, which excludes significant contributions of reactions taking place on the reactor walls or on the STM tip.

The switching behavior of the catalytic activity is further illustrated by Fig. 2a, which shows that the CO<sub>2</sub> data points of Fig. 1, plotted versus CO pressure, fall on two different branches, namely, a low reaction rate branch ( $R_{\text{low}}$ ), and a high rate branch ( $R_{\text{high}}$ ). Figure 2b shows similar CO<sub>2</sub> production branches from a separate experiment, performed at a higher oxygen pressure (1.25 bars). The switching from one branch to the other is completely correlated with the switching of the Pt(110) surface between the smooth and the rough states.  $R_{\text{low}}$  does not depend on  $P_{\text{CO}}$ , which is not surprising if the surface is mainly covered with CO. By contrast, under O<sub>2</sub>-rich conditions,  $P_{\text{CO}_2}$  is proportional to  $P_{\text{CO}}$ . The fact that this high-reactivity branch does not depend on the oxygen pressure implies that the surface is saturated with oxygen. We see that on each branch the reaction rate depends only on the concentration of the minority reactant. The roughening of the surface, which accompanied the CO<sub>2</sub> production, had no effect on the reactivity.

The observed bistability has been a key element in the oscillatory behavior of CO oxidation on Pt single crystals [14] and on polycrystalline Pt [15], Pd, and Ir [16] at atmospheric pressures. Clearly, the switching is not an effect limited to platinum or to the specific (110) face. This indicates that it is not related to some delicate restructuring [e.g., transformation from a (1 × 1) to a (1 × 2) structure]. Instead, it should be related to a switching in the surface composition, e.g., from a CO-covered surface to either a platinum surface covered with chemisorbed oxygen or a platinum oxide. We conclude, in contrast to earlier work [15], that the oxygen-rich phase is a thin surface oxide layer, on the basis of the following arguments. Since the buildup of the roughness did not affect the reactivity, the reaction was not taking place at “special sites” on the

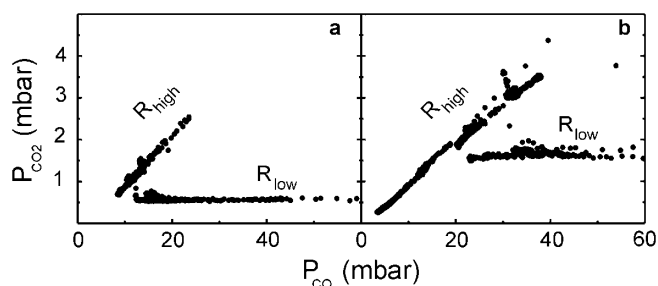


FIG. 2. CO<sub>2</sub> production versus CO pressure for (a) a constant oxygen pressure of 0.5 bar, and (b) a constant oxygen pressure of 1.25 bars. The branch ( $R_{\text{high}}$ ), which depends linearly on  $P_{\text{CO}}$  but not on  $P_{\text{O}_2}$ , corresponds to the oxidic surface. The branch ( $R_{\text{low}}$ ), which depends on  $P_{\text{O}_2}$  but not on  $P_{\text{CO}}$ , corresponds to the metallic surface.

rough surface. This also implies that the surface directly after the switch to a higher reactivity (Fig. 1C, upper part) and the rough surface, observed later on (Fig. 1D), had the same composition. It further shows that the protrusions, the pits, and the flat regions on the surface all have the same composition. As already mentioned, the heights of individual protrusions in the oxygen-rich flow did not correspond to integer multiples of the Pt monatomic step height. However, immediately after switching back to a CO-rich flow, we have observed the protrusions to be reduced to Pt-adatom islands. Clearly, the protrusions were not *just* platinum, but did *contain* platinum. From this, we conclude that the protrusions, and therefore the entire surface, are oxidized in the oxygen-rich flow [3].

We can now interpret the stages in Fig. 1 as follows. In the starting situation, in a CO flow at  $t = 0$  s, we observe a metallic, CO-saturated Pt surface. As soon as O<sub>2</sub> is introduced, a modest fraction of the oxygen reacts with the adsorbed CO. There is an excess of CO, which makes the CO<sub>2</sub> production rate ( $R_{\text{low}}$ ) depend primarily on the O<sub>2</sub> pressure and not on the CO pressure. When the CO pressure drops below a particular value,  $P_{\text{th}}$  (indicated by the horizontal line in the upper part of Fig. 1), the surface oxidizes. Probably, the determining factor is the ratio  $\theta_{\text{CO}}/\theta_{\text{O}}$  between the surface coverages of CO and O, rather than just the CO pressure. The dramatic increase in the CO<sub>2</sub> production rate clearly indicates that this oxidized surface is catalytically more active than the metallic surface. The gradual formation of the roughness, after the surface had switched to this oxidized state, suggests that CO molecules react with the oxygen of the platinum oxide to produce CO<sub>2</sub>. In this way, the surface is continuously reduced and (re)oxidized during the reaction. Such a so-called Mars-Van Krevelen redox mechanism [17] has been postulated for the partial oxidation of methane on platinum [18] and has also been proposed for CO oxidation on RuO<sub>2</sub> [19]. We speculate that the roughness is formed by the oxidation of Pt atoms, which diffuse out of the temporarily reduced parts of the oxide [20]. The number of displaced Pt atoms is orders of magnitude smaller than the

number of CO<sub>2</sub> molecules produced. This shows that the roughness should be regarded as a mere by-product of the catalytic reaction. If the CO pressure is increased again above  $P_{th}$ , the oxide is reacted away completely, leaving behind a CO-covered metallic surface, which brings the reaction rate down to  $R_{low}$ . Initially, the resulting surface has vacancy islands and Pt adatom islands, originating from the pits and the protrusions on the oxide, but they decay rapidly, to restore the smooth surface. The oxidation and reduction transitions of the surface are reversible, albeit with significant hysteresis.

In summary, we have followed the evolution of a catalyst under semipractical reaction conditions with a scanning tunneling microscope, and correlated the observed structures with the catalytic activity. During CO oxidation on Pt(110) at atmospheric pressures, the surface switches reversibly between a metallic state and an oxidic state with a higher catalytic activity, depending on the applied pressures. Our results show that the presence of the gas phase at high pressures can stabilize surface structures (e.g., surface oxides), which are not present at low pressures, but can play an important role in real catalysis. To our knowledge, these are the first experiments of this type. We expect them to be of great value for obtaining a fundamental understanding of practical, heterogeneous catalysis.

We acknowledge A. W. Kleyn, B. E. Nieuwenhuys, and M. D. Ackermann from Leiden University, and G. J. Kramer and H. P. C. E. Kuipers from Shell Global Solutions for their helpful comments. This work is supported by the Dutch Technology Foundation (STW) and the Dutch Organization for Scientific Research (NWO).

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