Transient Experiments on CO₂ Formation by the CO Oxidation Reaction over Oxygen-Rich Ru(0001) Surfaces

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Reactive scattering of CO molecules at oxygen-rich Ru(0001) surfaces with concentrations equivalent up to 16 monolayers and sample temperatures between 300 and 700 K led to the identification of two distinct reaction channels in the transient CO₂ rate. The first reaction channel is related to the recombination of CO molecules with oxygen atoms already located on the surface. The second reaction channel, which can be observed at sample temperatures above about 400 K, is controlled by the diffusion of oxygen atoms from the near-surface region toward the surface.

1. Introduction

The oxidation of carbon monoxide is efficiently catalyzed by platinum group metal surfaces. Due to the simplicity and the practical importance of this reaction for automotive exhaust control, it has been one of the most extensively studied heterogeneous reactions, both under idealized ultrahigh vacuum (UHV) and under high-pressure conditions. For the cases of Pt, Rh, and Pd general agreement has been reached that both oxygen and CO chemisorb on the surface prior to the actual oxidation step,[1] i.e., the so-called Langmuir−Hinshelwood mechanism (LH) is operational. Consequently, these catalysts are most active under steady-state conditions where the CO coverage is about as high as the O coverage regardless of whether the reaction takes place under UHV or high-pressure environment.[2]

By contrast, ruthenium behaves distinctively differently. Under UHV conditions Ru is known to be an extraordinarily poor catalyst in CO oxidation,[3] while the activity under high-pressure and oxidizing conditions turned out to be superior to the other platinum group metals.[4−6] High reaction rates over Ru(0001) were observed when the oxygen coverage was about one monolayer (ML) and the CO coverage was negligibly small.[5] Theoretical DFT work so far revealed no conclusive evidence for the reaction mechanism.[7]

Recent experiments[6] demonstrated that the reaction rates were even higher by up to 2 orders of magnitude when the oxygen coverage exceeds about 3 ML, i.e., when at least 2 ML of oxygen are located in the subsurface region. The high conversion rates of CO at oxygen-rich Ru(0001) surfaces were determined by titration experiments. An oxygen-precovered Ru(0001) surface with a specific oxygen load up to 20 ML oxygen was postexposed to high CO doses (at fixed sample/reaction temperature). Subsequently, the oxygen content left at the surface was determined by a thermal desorption experiment. Assuming

that one CO₂ molecule was formed for each oxygen atom removed from the surface, the number of removed oxygen atoms normalized to the number of impinging CO molecules yields the mean CO/CO₂ conversion probability. As the CO titration experiments ran over several minutes and the amount of removed oxygen was several monolayers, these measurements provided only conversion rates averaged over both the CO exposure time and the O coverage. The actual mean conversion rate at a sample temperature of 700 K and a 7 ML precoverage of O at the Ru(0001) surface for example was found to be about 1%. This high conversion probability prompted supplementary molecular beam experiments in which the reaction product, CO₂, which evolves from an oxygen precovered surface under the impact of a molecular beam of CO, can be directly followed by mass spectrometry. Transient measurements led to the conclusion that there are two distinct reaction channels which govern the CO₂ production: One component results from the recombination of CO with an active species of on-surface oxygen, and the second component is controlled by oxygen diffusion toward the surface.

2. Experimental Section

The experiments were conducted in a UHV chamber[8] which contains standard facilities for surface characterization and preparation such as ultraviolet photoelectron spectroscopy (UPS), quadrupole mass spectrometry (QMS), and low-energy electron diffraction (LEED). The base pressure was better than 1×10^{-10} mbar. The UHV chamber is connected to a two-stage molecular beam source, which is able to produce a CO molecular beam with well-defined translational energy. The molecular beam can be mechanically modulated with a chopper of varying frequency ranging from 160 to 350 Hz. The scattered beam is analyzed by a mass spectrometer in specular direction; the total scattering angle is 45°. This particular geometry was also chosen for the reactive scattering experiments because it allows a high reproducibility of the sample position in front of the QMS and with respect to the incoming CO beam.

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The Ru(0001) sample was prepared by repeated cycles of Ar$^+$ ion sputtering (5 μA/2 kV/2 $\times$ 10^{-5} mbar Ar) and baking the sample at 1100 K in an oxygen atmosphere of 10^{-7} mbar for 10 min. Final annealing of the sample to 1550 K removes the residual oxygen on the surface. The high O concentration in the near-surface region of Ru(0001) was produced by dosing several 10^6 of Langmuirs of molecular oxygen (Messer Griesheim, purity 99.998%). The actual uptake of oxygen on Ru(0001) depends critically on the sample temperature and is most efficient above 500 K when oxygen penetration sets in.[6,8] To introduce such high O$_2$ doses into the UHV system, the chamber was backfilled with 10^{-3}–10^{-2} mbar of oxygen. A very efficient pumping system, in particular a large-area liquid nitrogen cooled sublimation pump, ensures the base pressure of 1 $\times$ 10^{-10} mbar to be restored within 15 min. The reproducibility of the oxygen content of the O-rich Ru(0001) surfaces was better than 5% when identical parameters for the preparation were chosen, such as the O$_2$ partial pressure, the sample temperature, and the exposure time.

The supersonic CO beam was produced by an adiabatic expansion of the CO gas (Messer Griesheim, purity: 99.997%, H$_2$ concentration < 1 ppm) from the stagnation chamber with a CO pressure of 1–4 bar through a 20 μm wide nozzle into a chamber of low pressure of 10^{-4}–10^{-3} mbar. This produces a collimated CO beam (diameter at the sample: 7 mm) with a quite narrow velocity distribution and a molecular flux of 0.6 $\times$ 10^{14} and 3.6 $\times$ 10^{14} molecules/cm^2 s for CO pressures of 1 and 4 bar in the nozzle, respectively. The CO$_2$ product, which comes off the surface after reactive scattering, is analyzed with a mass spectrometer positioned in specular direction to the CO beam with an acceptance angle of about 15°.

3. Results

Figure 1 presents measurements of the time evolution of the CO$_2$ flux from a Ru(0001) surface precovered with various amounts of oxygen ranging from 2.3 to 7.5 ML and which is exposed to a molecular beam of CO. The incoming CO flux was set to be 3.6 $\times$ 10^{14} molecules/cm^2 s and the sample temperature was kept at 450 K. At time zero the CO flux was switched on within 0.5 s by removing a beam flag. The CO$_2$ signal in the QMS rises steeply within 4 s to a high value, reaches a maximum, falls rapidly first and then slowly to zero. The CO$_2$ evolution is dominated by a strong and narrow peak during the first 10 s. After about 10 s a smaller CO$_2$ flux is leaving the surface which, however, continues over about 200 s (delayed component). After about 200 s the CO$_2$ signal has dropped to the background level. For a 2 ML-O precovered Ru(0001) surface the CO$_2$ production is infinitely small, consistent with previous experiments.[6] With increasing oxygen content the total amount of CO$_2$ produced as well as the maximum flux from the dominating peak increase. The dominating peak can be rationalized within the Langmuir–Hinshelwood mechanism. Similar to the CO titration experiments of the oxygen precovered Ag(110) surfaces,[9] the steep increase in the CO$_2$ rate during the first 4 s is the result of a rapid increase of the CO coverage with time in combination with a high concentration of active oxygen species at the surface, i.e., the CO$_2$ rate first parallels the CO uptake. Since the active oxygen species becomes gradually consumed under the impact of the CO beam, the CO$_2$ rate, which is proportional to the product of CO and O coverages for the Langmuir–Hinshelwood mechanism, goes through a maximum and decreases subsequently. Accordingly, one might attribute the first component of CO$_2$ to the recombination of CO with an active on-surface oxygen
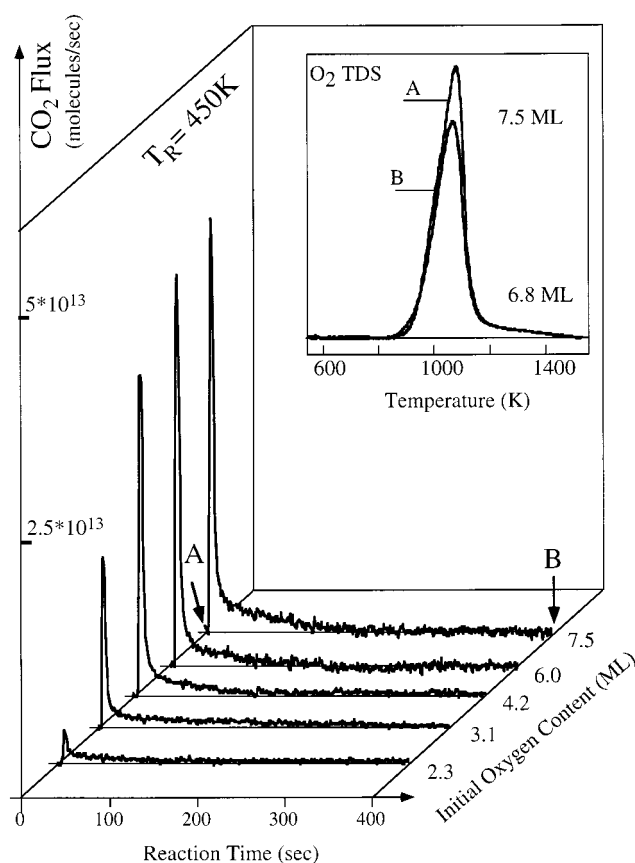

Figure 1. The flux of CO$_2$ molecules is monitored as a function of the titration time during exposure of various oxygen-rich Ru(0001) surfaces to the CO molecular beam; the sample was kept at 450 K. The CO flux within the molecular beam was 3 $\times$ 10^{14} molecules/cm^2 s and the nozzle temperature was 295 K. The inset displays the total reaction yield for the 7.5 ML-O case by comparing the O$_2$-TD spectra taken before (A) and after (B) exposing the sample to the CO beam for 400 s. About 0.7 ML O are reacted off by incident CO molecules.

species and tentatively assign the delayed component to the recombination of CO with oxygen originating from the near-surface region. The on-surface contribution depends critically on the total amount of oxygen as the major peak increases markedly with the O coverage. Recent LEED measurements revealed for the oxygen-rich Ru(0001) surfaces beyond the (1 $\times$ 1)-O the formation of an oxide-type additional ordered surface structure.[10] Therefore, the first component in the CO oxidation reaction might be related to the reaction of CO with oxygen from this oxide-type surface whose concentration increases with the total O amount accommodated at the surface.

The integrated CO$_2$ flux from this first component is in all cases smaller than 0.3 ML, thus being compatible with an on-surface oxygen reaction (which should be always smaller than 1 ML, the maximum concentration of on-surface oxygen). In the inset of Figure 1, the O$_2$ thermal desorption spectra of a 7.5 ML-O precovered Ru(0001) is shown before and after exposing it to the CO beam for 600 s at a sample temperature of 450 K. The difference amounts to 0.7 ML. The time dependence of the CO$_2$ flux for the case of a 7.5 ML precovered Ru(0001) surface indicates that after 200 s practically no further CO is converted into CO$_2$. This means that only about 0.7 ML oxygen is removed from the surface by CO oxidation and 6.8 ML oxygen are still left at the surface. If we tentatively attribute buried oxygen as being responsible for the delayed component, we can interpret these data in a way that only oxygen atoms from the outermost few Ru layers are able to reach the surface
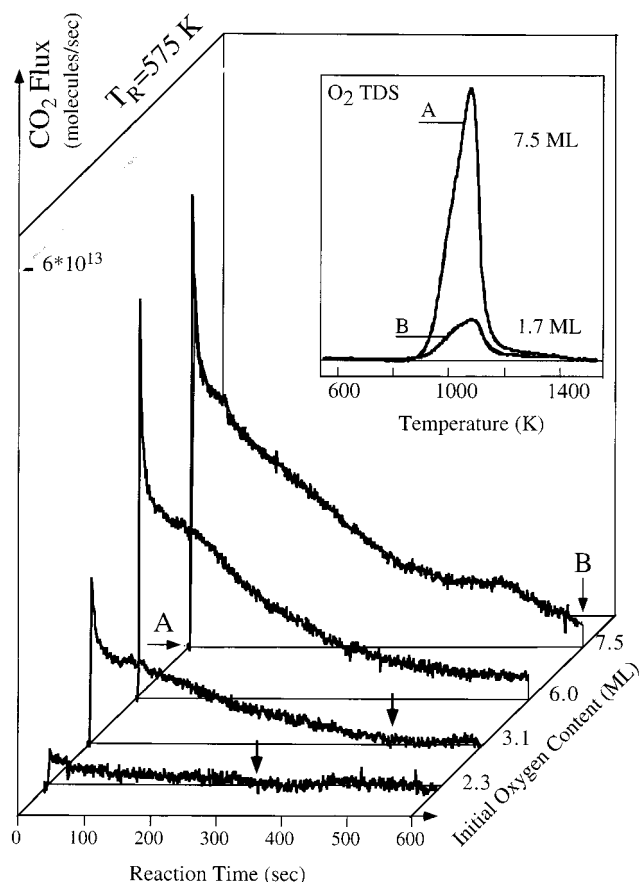
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Figure 2. The flux of CO_2 molecules is shown as a function of the titration time during exposure of various oxygen-rich Ru(0001) surfaces to the CO molecular beam; the sample temperature was kept at 575 K. The CO flux within the molecular beam was 3×10^{14} molecules/cm^2 s and the nozzle temperature was 295 K. The inset displays the total reaction yield for the 7.5 ML-O case by comparing the O_2-TD spectra taken before (A) and after (B) exposing the sample to the CO beam for 400 s. About 5.8 ML O are removed by incident CO molecules.

Figure 3. A comparison of the total amount of oxygen removed by CO titration with a CO molecular beam and the total CO_2 yield obtained by time integration of CO_2 traces in Figure 2 as a function of the O precoverage. Since both dependencies are identical, the CO_2 flux can be calibrated by assuming that every removed oxygen atom has left the surface as CO_2.

by diffusion where they can recombine with CO to form CO_2; the higher the reaction temperature the more extended is the slab from which oxygen atoms are able to reach the surface. Conversely, this provides a rough estimate for the oxygen content in the near surface region (say between the top four Ru layers) of about 0.7 ML for a 7.5 ML oxygen precovered Ru-(0001) surface.

One way to support the interpretation of the delayed reaction channel as being actuated by oxygen below the surface is to look at the reaction behavior at a higher sample (reaction) temperature, e.g., 575 K, as a function of the initial oxygen content. These measurements are collected in Figure 2. It is obvious that now the delayed component is governing the time evolution of the CO_2 flux. Even after 600 s CO_2 is still produced at the surface albeit with low rate. From the thermal desorption of O_2 after exposing the 7.5 ML-O surface to the CO beam for 600 s, it turns out that now 5.8 ML oxygen are removed by CO oxidation. To quantify the CO_2 flux formed at the surface, the total amount of removed oxygen for various O precoverages (cf. Figure 3) is compared to the integrated CO_2 flux as a function of the O precoverage. The data are practically identical if properly scaled, thus confirming that O atoms are exclusively removed from the surface via CO oxidation. On the other hand, the agreement also allows us to calibrate roughly the CO_2 flux coming from the surface and therefore to scale the CO fluxes in Figures 1, 2, and 4; note that the uncertainties can, however,
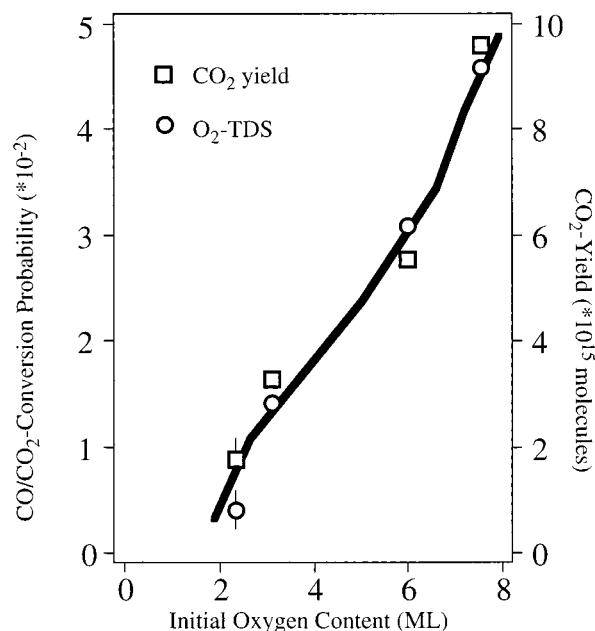
easily exceed 50%. From this analysis the initial conversion probability of an impinging CO molecule to become oxidized at a 7.5 ML-O precovered Ru(0001) surface can be estimated to be as high as 10% at a sample temperature of 575 K, a value which is significantly higher than (but not conflicting with) the averaged conversion probability of 1% as found in ref 6. The actual turnover rate might therefore be very high under strongly oxidizing conditions. The difference of the integral conversion rates as derived from the time-integrated CO fluxes of Figures 1 and 2 for two sample temperatures provide a very rough estimate for the apparent activation barrier for this reaction of about 0.3 eV. The integral conversion rate is dominated by the delayed component, which in turn is controlled by O diffusion from the subsurface region to the surface. Hence, the apparent activation barrier for CO oxidation might be related to the activation energy for subsurface-O diffusion. This value is rather low, in particular, when compared to typical values found in other metal oxides.[11] It is important to mention that phase-sensitive measurements (using a modulated CO beam and lock-in technique) showed that the incoming CO beam and the outgoing CO_2 flux are completely dephased. From the used chopper frequency of 160 Hz the residence time of CO on the surface can be estimated to be larger than 1 ms at sample temperatures of 450 and 575 K, thus being again consistent with a Langmuir–Hinshelwood mechanism.

To underline the importance of the O diffusion toward the surface controlling the CO oxidation reaction rates, the CO_2 flux is monitored (cf. Figure 4) from a 16 ML O containing Ru(0001) surface under the impact of a constant CO flux of 3.6×10^{14} molecule/cm^2 s but for various sample temperatures. While the first reaction channel is already open above 350 K, the diffusion-controlled CO oxidation reaction becomes significant only above 450 K. The total CO_2 yield as a function of the sample temperature is shown in the inset of Figure 4. At a sample temperature of about 500 K the total CO_2 yield increases steeply by a factor of 10. This temperature is identical to the onset temperature for O penetration into the subsurface region
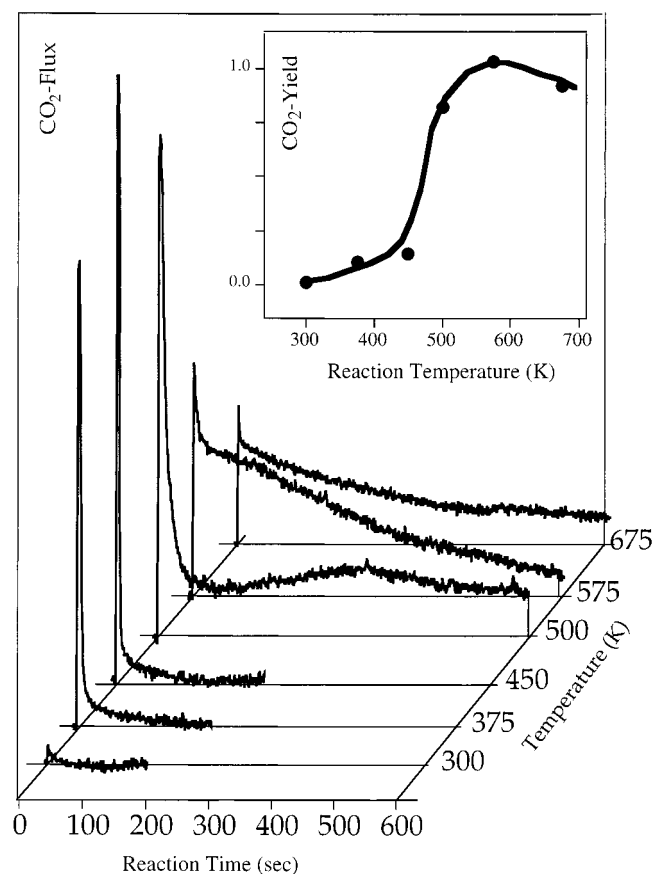
Figure 4. The CO_2 flux as a function of the titration time during the exposure of a 16 ML O precovered Ru(0001) surface to a CO beam (flux 3×10^{14} molecules/cm^2 s) for various sample temperatures. The inset displays the total CO_2 yield dependent on the sample/reaction temperature. The steep increase at about 500 K is attributed to the onset of oxygen diffusion from the near-surface region toward the surface.

when exposing the clean Ru(0001) surface to large amounts of oxygen (cf. Figure 1 in ref 6) and therefore lends further support to the interpretation of a O diffusion-controlled CO oxidation reaction in the delayed component. Another interesting aspect of these measurements is the decreasing CO_2 flux from the first component with increasing sample temperature. It seems that for the first reaction channel the residence time of CO on the surface becomes too short at elevated sample temperatures to be efficiently converted into CO_2. This interpretation is in line with the thermal desorption behavior of CO over oxygen-rich Ru(0001) surfaces which indicate a desorption states at 350 (cf. Figure 5). As the temperature behavior contrasts with that of the delayed component, one may suggest that the actual recombination step is different. Besides the O diffusion, which process is facilitated at elevated temperatures, the actual reaction with CO occurs on a much shorter time scale in the delayed component so that the rate is, in fact, determined by the combination of O supply from the bulk (which increases with temperature) and the actual surface concentration of CO (which decreases with temperature), thus leading to the low positive value of the apparent activation energy.

In Figure 6 the CO flux dependence of the first reaction channel shows that the peak profile of this component changes in a way which is characteristic for a Langmuir−Hinshelwood mechanism. With decreasing CO flux the CO_2 flux from the first component decreases and broadens so that the total CO_2 yield is conserved (cf. inset of Figure 6). The steep initial rise in the CO_2 formation rate is related to the accumulation of CO
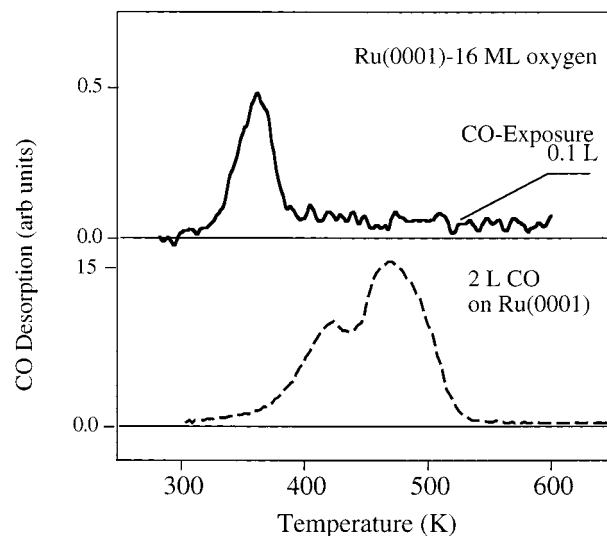

Figure 5. Thermal desorption spectrum of CO when a 16 ML-O precovered Ru(0001) surface is exposed to 1 L of CO (top) compared to the clean Ru(0001) surface (bottom) which was exposed to 2 L of CO. It should be noted that CO molecules do not adsorb on the (1 × 1)-O phase of Ru(0001) for sample temperatures above 50 K.[6]
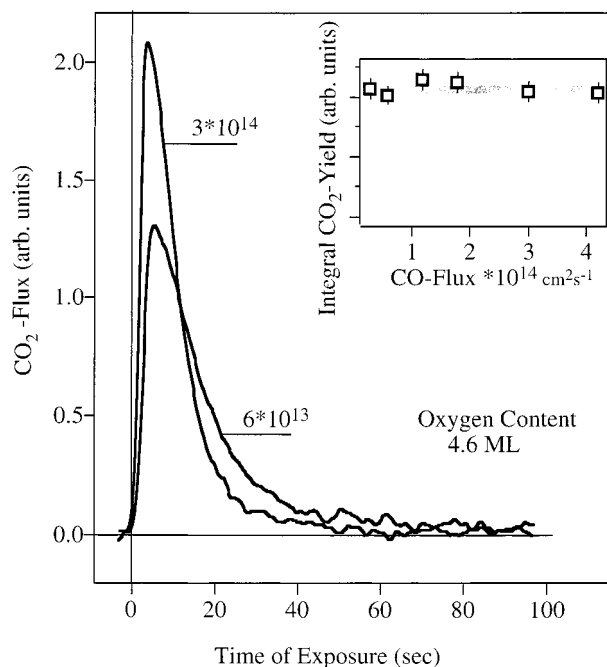

Figure 6. Surface titration curves of a Ru(00001)−4.6 ML-O surface (sample temperature: 295 K) from a CO beam with fluxes of 0.6 × 10^{14} molecules/cm^2 s and 3 × 10^{14} molecules/cm^2 s. At the chosen sample temperature the first reaction channel is dominating the titration curves. The total CO_2 yield as shown in the inset is constant over a range of CO fluxes from 0.6 × 10^{14} molecules/cm^2 s to 4.3 × 10^{14} molecules/cm^2 s. This reaction behavior is indicative of a Langmuir−Hinshelwood mechanism.

on the surface, while the distinctively slower decline reflects the depletion of the active oxygen species on the surface. Both processes are accelerated when the driving CO flux is increased. Since the total yield of this reaction component should be related to the total amount of active oxygen on the surface, the total amount of CO_2 should be conserved. The actual concentration of active on-surface oxygen for the case of a 4.6 ML-O precovered Ru(0001) surface is estimated to be about 0.3 ML.

In a last set of experiments the first reaction channel of the CO titration is further elucidated (cf. Figure 7). The chosen
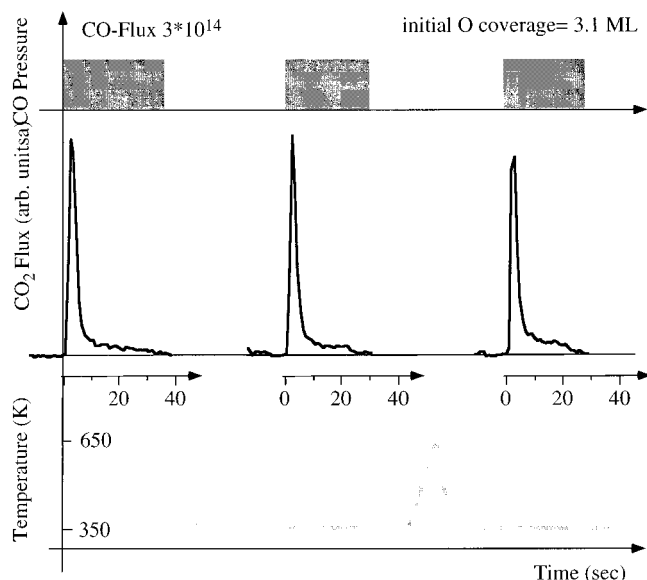
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Figure 7. A Ru(0001)−3.6 ML-O surface kept at 350 K is exposed to a CO beam (flux: 3×10^{14} molecules/cm^2 s) for periods of 40 s separated by periods where the beam is switched off. Between consecutive CO pulses, the sample was annealed to 650 K to reactivate the surface. The protocols for the incident CO flux and the sample temperature are shown in the upper and lower panels. The CO$_2$ response from the surface is shown in the middle panel.

reaction temperature of 350 K is far below the onset of O diffusion toward the surface. The Ru(0001) surface is precovered by about 3 ML oxygen and exposed to the CO beam with a flux of 3×10^{14} molecules/cm^2 s. The transient behavior of the CO$_2$ flux leaving the surface is shown in Figure 7. We see the typical steep increase, which is followed by a sharp decrease after 5 s. After 40 s CO$_2$ is no longer produced, and obviously, all the active on-surface oxygen has been consumed. Annealing the sample to 650 K for several seconds and cooling again to 350 K populates the surface again by O diffusion from the near-surface region; note that sufficient mobility of oxygen is ensured for sample temperatures above 550 K. As verified in the next CO titration run (cf. Figure 7), the active state of the surface is indeed restored by this treatment. The incident CO molecule

converts to CO$_2$ at the O precovered Ru(0001) surface, revealing almost the same transient reaction rate as before. This kind of CO$_2$ production/activation cycles could be repeated several times.

4. Summary

Using a molecular beam technique, transient CO titration experiments of oxygen-rich Ru(0001) surfaces revealed two distinct reaction channels. For both channels the CO oxidation reaction occurs via the Langmuir−Hinshelwood mechanism. At sample temperatures below 350 K CO oxidation proceeds through an active on-surface oxygen species which is consumed during the titration experiment. Subsequent annealing of the surface to 650 K is able to restore the active state of the surface via diffusion of subsurface oxygen to the surface. CO titration experiments at temperatures above 500 K are dominated by a second reaction channel, which is governed by oxygen diffusion from the near-surface region toward the surface.

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