Role of Atomic Step Defect Sites on the Catalytic Oxidation of Carbon Monoxide: Comparison between Ru(001) and Ru(109) Single-Crystal Surfaces

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A comparison of the reactivity of chemisorbed oxygen with chemisorbed CO on Ru(109) and Ru(001) surfaces to produce CO_2 shows that the atomically stepped Ru(109) surface provides active oxygen species, whereas the Ru(001) surface is inactive. Using Auger spectroscopy and low-energy electron diffraction, it is found that the activity of Ru(109) is caused by the local high oxygen coverages achieved at the Ru step sites where the O/Ru ratio is 1.3 ± 0.3. The O/Ru(109) surface, saturated with CO, produces an inhomogeneous CO layer as observed by infrared spectroscopy, whereas O/Ru(001) produces a single terminally bound CO species.

1. Introduction

The atomically smooth Ru(001) surface exhibits low activity for the oxidation of CO under low-pressure conditions, despite its high catalytic activity under high-pressure conditions.[1−4] The inertness of the surface under low-pressure conditions is thought to be due to the limited coverage of oxygen atoms, which may be achieved, and the lack of a surface ruthenium oxide phase. The dissociation of O_2 on Ru(001) leads to a mixed phase overlayer containing 2×2 domains (0.25 ML) and 2×1 domains (0.5 ML), yielding an overall saturation coverage of 0.5 ML when complete conversion to the 2×1 domain structure occurs at the O_2 exposure used in the work to be reported here.[6,7] In this coverage range, the O atoms are nonreactive for CO oxidation.[5,8,9]

Chemisorbed oxygen layers grown on Ru(001) to higher coverages at high oxygen exposures are active for CO oxidation.[1,10] These oxygen coverages exceed 0.5 ML and are produced at high oxygen chemical potentials achieved either by high O_2 pressures or by NO_2 exposures, at high adsorption temperatures.[10] In this high oxygen coverage regime, it has been suggested that "active and labile" $O(a)$ species exist together.[10] Reaction with CO occurs either through a Langmuir−Hinshelwood mechanism or through an Eley−Rideal mechanism.[1] Recent studies indicate that at high oxygen coverages, surface ruthenium oxide layers form on Ru(001), which contain labile $O(a)$ atoms,[11−13] leading to facile CO_2 formation.[11,13]

In this Article, we present our observation of catalytic CO oxidation on the stepped Ru(109) surface under UHV conditions. An appreciable amount of CO_2 desorption occurs from coadsorbed CO and atomic oxygen layers on the stepped Ru(109) surface, but not on the flat Ru(001) surface. Here, we compare the activity of Ru(001) and Ru(109) single crystals for CO oxidation, working in the low oxygen exposure regime. Ru(109) contains atomic steps of 2-Ru atom height, separated by 9-atom wide Ru(001) terraces.[14] It is found that high local oxygen coverages are formed on the atomic steps, producing active oxygen species for CO oxidation, which do not exist on the narrow Ru(001) terraces between the Ru steps.

2. Experimental Section

The Ru(001) crystal had a miscut angle of $\leq 0.5°$. The Ru-(109) crystal was produced by cutting at an $11.5°$ angle with respect to the (001) plane, in the $\langle 100 \rangle$ azimuth. Both single crystals were used in the same apparatus and underwent careful cleaning by Ar^+-ion bombardment and by high-temperature treatment in O_2 to remove traces of carbon using procedures previously employed in this laboratory.[14,15] The absence of impurity carbon was assured using an analysis of the Ru (LMM) Auger line shape, described previously.[14,15] The cleaned crystal was also free of oxygen down to the typical Auger detection limit of a few %. The LEED pattern of the clean Ru(001) crystal was of hexagonal symmetry, while that of Ru(109) exhibited triple-split LEED beams indicative of a regularly stepped crystal composed of double height steps, as previously described.[14]

Controlled CO and O_2 exposures were carried out using a capillary array effusive doser[16] up to saturation coverage. CO coverages and CO_2 yields were measured by temperature-programmed desorption using an apertured quadrupole mass spectrometer (QMS) (UTI 100C). Oxygen coverages were measured using the O(KLL)/Ru(LMN) Auger ratio. Significant electron stimulated desorption of adsorbed oxygen did not occur under the measurement conditions employed.

Infrared reflection absorption spectroscopy measurements were performed with a Mattson-Cygnus FTIR spectrometer (model 4236)[17] using parallel-polarized radiation at a spectroscopic resolution of 2 cm^{-1} and acquiring data with 2000 scans.
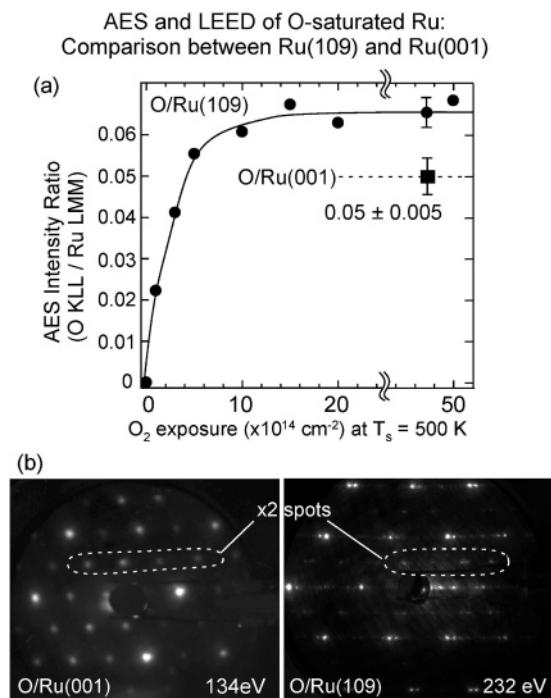
The base pressure in the UHV chamber was kept to less than 1×10^{-10} mbar, and the main residual gases were H_2 and CO.

3. Results

Figure 1a shows a comparison of the O(KLL)/Ru(LMM) ratio for both crystals as adsorption occurs to saturation in the low-pressure regime up to exposures of 5×10^{15} O_2/cm^2 at a crystal temperature, T_S, of 500 K. The results indicate that the stepped Ru(109) surface exhibits a higher saturation coverage of oxygen, as compared to Ru(001). The measured Auger intensity ratio

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Figure 1. (a) Auger spectroscopy intensity ratio of O/Ru for both Ru crystals and (b) corresponding LEED patterns.

$(O(KLL)/Ru(LMM))$ at the saturation oxygen coverage is 0.065 ± 0.005 on Ru(109), while it is 0.050 ± 0.005 on Ru(001).

Figure 1b shows the LEED patterns for the oxygen-saturated surfaces on both crystals. In both cases, the "×2" LEED beams indicate the production of 2 × 2 symmetric oxygen adlayers on Ru(001),[18] as well as on the (001) terraces of the Ru(109) surface. The periodic multiplet beams from the Ru(109) surface are characteristic of the regular stepped structure as discussed elsewhere.[14]

Figure 2 compares the CO and CO_2 desorption spectra obtained from coadsorbed CO and O(a) layers on Ru(109) and Ru(001), respectively. Prior to achieving saturation CO exposure at 85 K, we exposed both crystals to O_2 at an exposure of 2 × 10^{15} O_2/cm^2 at 500 K, producing saturation oxygen coverage in the low-pressure regime. For Ru(109), both CO and CO_2 production are observed below 400 K. We estimate that a few percent of the surface CO undergoes reaction. In contrast, no CO_2 is observed for the same experiment on Ru(001), which is consistent with other reports.[5,19]

Figure 3 compares the infrared spectra for CO adsorption on saturated oxygen-covered Ru crystals. For Ru(109), the CO exhibits multiple absorption bands in the range $2030-2100$ cm^{-1}, and two distinct bands at 2068 and 2084 cm^{-1} emerge at the highest coverage. All of these species are assigned as terminally bonded CO on the oxygen-saturated surface. Another small absorption band is observed at 1858 cm^{-1} and is assigned to bridge-bonded CO on the oxygen-saturated surface.[5,8] In contrast to the multiple species observed on Ru(109), only a single carbonyl stretching mode is observed on Ru(001), which shifts from 2068 to 2079 cm^{-1} as the CO coverage is increased on the oxygen-saturated surface.

4. Discussion

The Auger spectroscopy measurements of oxygen adsorption at 500 K provide definite evidence that the average saturation oxygen coverage on Ru(109) exceeds that achieved on Ru(001) by about 30%. The "×2" spots from the LEED measurements
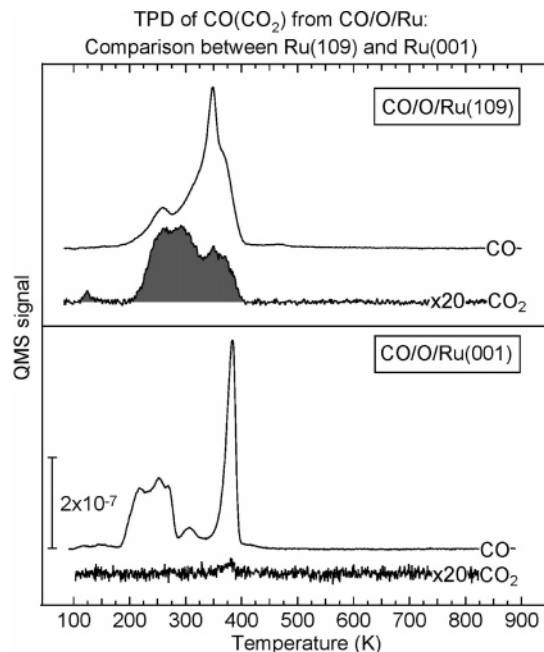

Figure 2. Comparison of TPD spectra of CO (mass 28) and CO_2 (mass 44) obtained from coadsorbed CO and O on both Ru single-crystal surfaces. Saturated oxygen layers were prepared by the O_2 exposure of 2 × 10^{15} O_2/cm^2 at 500 K, followed by saturation CO exposure at 85 K.
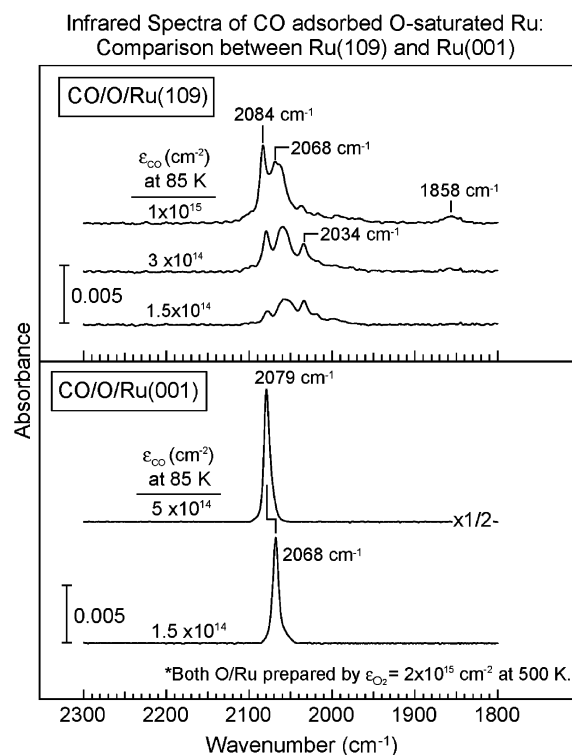
Figure 3. Infrared spectra of $^{12}C^{16}O$ taken at 85 K from CO adsorbed on both oxygen-saturated Ru surfaces.

in Figure 1b indicate that both the Ru(109) terraces and the Ru(001) surface become saturated up to 0.5 O/Ru in the low oxygen exposure regime. By assuming that the saturation oxygen coverage of 0.5 O/Ru is achieved on Ru(001), we measured the "average oxygen coverage" achieved on Ru(109) to be 0.65 ± 0.05. Because the same maximum oxygen coverage of 0.5 O/Ru can be achieved on the Ru terraces of Ru(109), we conclude that the additional oxygen present on the Ru(109) surface is present on the doubled height atomic steps, producing

Schematic of O Chemisorbed Layers on Ru(109)
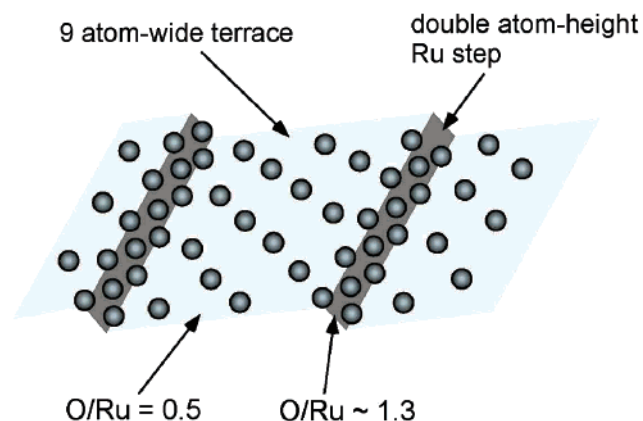
Figure 4. Schematic of oxygen chemisorbed layers formed on the stepped Ru(109) single-crystal surface following O_2 adsorption at 500 K.

a high local oxygen coverage on the Ru steps. The measured 30% excess oxygen on Ru(109), as compared to Ru(001), indicates that on the 2-atom height step sites, the O/Ru ratio reaches 1.3 ± 0.3. Figure 4 shows a schematic diagram of the O adsorption conditions on the step and terrace sites of Ru(109).

This model involving high local saturation coverages of oxygen on the atomic step sites suggests that the "active" $O(a)$ species are produced in these high coverage regions just as is seen for high coverage oxygen layers produced under high-pressure conditions on Ru(001).[10] There is also the possibility that the active $O(a)$ species are from the local surface RuO_2 layers formed on the Ru step sites.[20] It is likely that CO molecules, adsorbed on the oxygen-saturated terraces of Ru-(109), react with the active chemisorbed oxygen species on the step sites by a Langmuir–Hinshelwood mechanism, leading to CO_2 production on Ru(109). This finding is identical to an earlier finding for CO oxidation on Pt(335), where it was shown that the reaction involves step-bound oxygen atoms reacting with terrace-bound CO molecules.[21]

The observation of multiple CO stretching modes for CO on oxygen saturated Ru(109) indicates that the stepped surface provides inhomogeneous Ru sites capable of adsorbing CO amidst the oxygen-covered sites. By analogy to O/Ru(001), the CO bands at 2068 and 2034 cm^{-1} are related to CO molecules adsorbed on $O(2 \times 1)$ and $O(2 \times 2)$ surface phases on the terrace sites.[5,8] The discrete CO band at 2084 cm^{-1} is related to CO molecules adsorbed on Ru sites with the high coverage oxygen layers as seen previously.[5] In contrast to this behavior, the more homogeneous O/Ru(001) surface adsorbs only one CO species, whose frequency shifts upward slightly as coverage increases as a result of dipolar interactions between the CO molecules. At the low CO exposure of 1.5×10^{14} CO/cm^2, the CO modes at 2030–2085 cm^{-1} observed for both Ru surfaces exhibit higher frequencies than those ($\sim$2010 cm^{-1}) observed for CO on clean Ru(109) and Ru(001) as a result of the outward negative electric field produced by the electronegative O atoms. This upward shift in the CO stretching mode frequency is of the order of 20–70 cm^{-1}.

5. Summary

The catalytic oxidation of CO on Ru single-crystal model catalyst surfaces has revealed the following behavior:

(1) No reactivity occurs for a saturated oxygen layer, covered with CO, on Ru(001) under conditions where the maximum oxygen coverage achieved corresponds to the low oxygen coverage regime, which is near 0.5 O/Ru.

(2) For the atomically stepped Ru(109) surface, the production of a high local oxygen coverage (1.3 ± 0.3 O/Ru) on the step sites is inferred from the average saturation coverage ratio (0.65 ± 0.05 O/Ru) achieved.

(3) The stepped Ru(109) surface exhibits reactivity between $O(a)$ and $CO(a)$ to produce CO_2 in the temperature range 200–400 K. This reactivity is related to the high local oxygen coverage on the step sites, where active oxygen species are present.

(4) A Langmuir–Hinshelwood reaction, involving CO bound to oxygen-covered terrace sites and active $O(a)$ species present in the local high coverage regions of the step sites, is postulated to occur.

(5) CO adsorption on the O/Ru(109) surface produces an inhomogeneous layer exhibiting multiple CO stretching frequencies; in contrast, CO adsorbed on the O/Ru(001) surface is homogeneous, exhibiting a single CO vibrational mode.

(6) These results imply that defect sites on Ru catalysts are capable of adsorbing oxygen to high local coverage, producing active $O(a)$ species for CO oxidation. Such active oxygen species may also be produced on non-defective Ru(001) surfaces if the oxygen coverage is raised to high levels by a high-pressure and a high-temperature oxidation.

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