Oxidation of a Single Carbon Monoxide Molecule Manipulated and Induced with a Scanning Tunneling Microscope

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A carbon monoxide molecule (CO) was positioned with a scanning tunneling microscope (STM) at various distances from an oxygen atom (O) on the Ag(110) surface at 13 K. At the closest separation, carbon dioxide (CO_2) production was induced by tunneling electrons. Direct reaction of a CO desorbed from the STM tip with an O atom on Ag(110) illustrates another catalytic oxidation mechanism. Inelastic electron tunneling spectroscopy with the STM was used to monitor the vibrations of CO in its different environment.

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The formation of the CO_2 molecule by the catalytic oxidation of CO at metal surfaces is one of the simplest reactions and serves as a model for heterogeneous catalysis. On the practical side, it is an important reaction in automobile emission control, air purification, and chemical sensing. Nearly all available surface science techniques [1–6] have been applied to identify and characterize the elementary steps of this reaction. A microscopic understanding of this reaction, however, is still lacking because it is difficult to probe the states of the reactants during the reaction. It is believed that the oxidation occurs with the CO molecules and O atoms coadsorbed on the surface. Direct reaction of an incident particle with an adsorbate in a single encounter is regarded as having negligible contribution to catalytic reactions. Such a mechanism has been attributed to some gas-surface reactions, such as the impingement of an atomic hydrogen beam with adsorbed chlorine atoms on Au(111) [7].

The scanning tunneling microscope (STM) has allowed us to visualize chemistry at the spatial limit. In this paper, we demonstrate the use of the STM to illuminate the different pathways for the catalytic oxidation of CO. The unique capabilities of the STM have enabled the manipulation [8], dissociation [9,10], and synthesis [11,12] of single molecules. In addition, vibrational analysis of CO by inelastic electron tunneling spectroscopy with the STM (STM-IETS) [13] provided insights into its adsorbed state and interactions with the adsorbed O atoms.

Experiments were carried out using a homemade, variable temperature STM [14], housed inside an ultrahigh vacuum chamber with a base pressure of 2×10^{-11} Torr. The Ag(110) sample was cleaned by cycles of 500 eV Ne ion sputtering and 693 K annealing [15]. The STM tip was made by electrochemical etching of polycrystalline tungsten wire and further cleaned *in situ* by Ne ion sputtering and annealing. Field emission and light physical contacts with the surface reshaped the tip. The O_2 molecules were adsorbed on the sample at 45 K via a capillary doser in order to ensure molecular chemisorption. The O_2 coverage was below 0.01 monolayer (ML). The sample and the STM were then cooled to 13 K for the adsorption of CO (<0.001 ML) and subsequent experiments. A CO molecule can be transferred to the tip, enabling atomically resolved imaging [11].

Oxygen atoms were prepared by dissociating single O_2 molecules with tunneling electrons [10]. The dissociation of O_2 was accomplished by placing the tip over a single O_2 and raising the sample bias to +470 mV with the feedback turned off. The two O atoms were found along the $[1\bar{1}0]$ direction and separated by one (Fig. 1A), two (Fig. 4A), or three (not shown) lattice spacings (lattice constant is 2.89 Å along the $[1\bar{1}0]$).

Figure 1 shows a series of STM topographical images, recorded during the manipulation and reaction of a CO with one of the two O atoms. The CO and O atoms are imaged as depressions (Fig. 1A). The CO was moved toward the O atoms by repeatedly applying sample bias pulses (+240 mV) over the CO (from Fig. 1A to 1B) since the CO does not always move toward the O atoms. However, the O-CO-O complex is eventually formed (Fig. 1C). As the CO approaches the O atoms, the composite images (Fig. 1B and 1C) show increasing depressions. With an additional sample bias pulse over the CO in the complex, formation of CO_2 was induced and the product quickly desorbed, leaving the remaining O atom on the surface (Fig. 1D).

Vibrational spectra (Fig. 1E) were obtained by STM-IETS over the CO (*) along the reaction pathways (I, II, and III). The spectra reveal a peak (dip) at positive (negative) bias [13,14], which is assigned to the hindered rotation mode. The vibrational assignment is supported by isotopic shift [16]. The voltage position of the peak is higher in magnitude by 2 mV from that of the dip. This asymmetry may be due to changes in the interaction between the CO and the surface under different bias polarities [17]. No significant differences in the line shape and position of the peak or dip are observed between spectra I and II as well as for isolated CO molecules. However, the mode shows an up-shift of 4 meV, a decrease in intensity, and a line shape broadening for the O-CO-O complex (III).

In order to gain further insight into the reaction pathway, atomically resolved topographical images were taken with

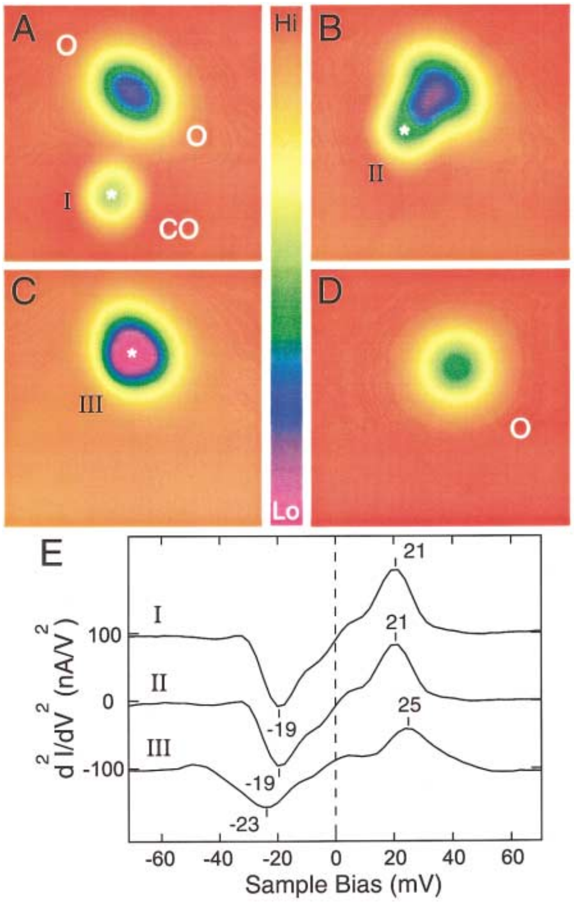

FIG. 1 (color). STM topographical images obtained with a bare tip, 70 mV sample bias, and 1 nA tunneling current, showing the manipulation of a CO molecule toward two O atoms coadsorbed on Ag(110) at 13 K and the corresponding vibrational spectra taken over the CO. (A) A single CO molecule and two O atoms. (B) The CO was moved toward O atoms by applying sample bias pulses (+240 mV) after positioning the tip over it. This movement prevented the measurement of C-O stretch (267 meV [11]). (C) The CO was moved to the closest distance from the two O atoms to form the O-CO-O complex. (D) An additional voltage pulse applied to the CO side of the complex led to an image of the remaining O atom on the surface. Scan area of (A)–(D) is 29 Å × 29 Å. (E) Single molecule vibrational spectra obtained by STM-IETS for CO at positions marked by $*$'s in (A)–(C). The spectra displayed are averages of multiple scans from -70 mV to $+70$ mV and back down and subtracting the background spectra taken over clean Ag(110). Dwell time of 300 ms per 2.5 mV step and 7 mV rms bias modulation at 200 Hz were used for recording the spectra. The line markers indicate the positions of the vibrational features. The energies for these positions were determined by fitting the spectra in the region of a peak or a dip to Gaussian functions. The relative conductance changes, $\Delta\sigma/\sigma$, where $\sigma = dI/dV$, are 9%, 9%, and 5% for the hindered rotation mode at positive sample bias in spectra I, II, and III, respectively.

a CO-terminated tip. The bare tip was positioned over a CO and with the feedback remaining on, the CO was transferred to the tip by controlling the sample bias voltage and tunneling current [11]. The increase in the spatial resolution can be attributed to the more localized wave function of the molecule-terminated tip. Images of isolated CO and the two O atoms are shown in Figs. 2A and 2B, respectively. The image in Fig. 2C corresponds to Fig. 1B and is seen as a composite of Figs. 2A and 2B. Recalling further the similarity in the vibrational spectra of CO in Fig. 2A and 2C, it can be concluded that no significant interactions exist between the CO and the two O atoms. Resolving the underlying substrate atoms led to the adsorption sites shown in Fig. 2D. In the intertwined image of the complex (Fig. 2E), interactions between CO and the two O atoms (Fig. 2F) are suggested, which is further supported by the changes in the vibrational spectra (Fig. 1E).

The spatial distribution of the STM-IETS intensity can be probed by recording simultaneously the topographical (Fig. 3A) and vibrational (Fig. 3C) images [11,13,15]. To gain further insights into the structure of the O-CO-O complex, vibrational microscopy image was taken at a sample

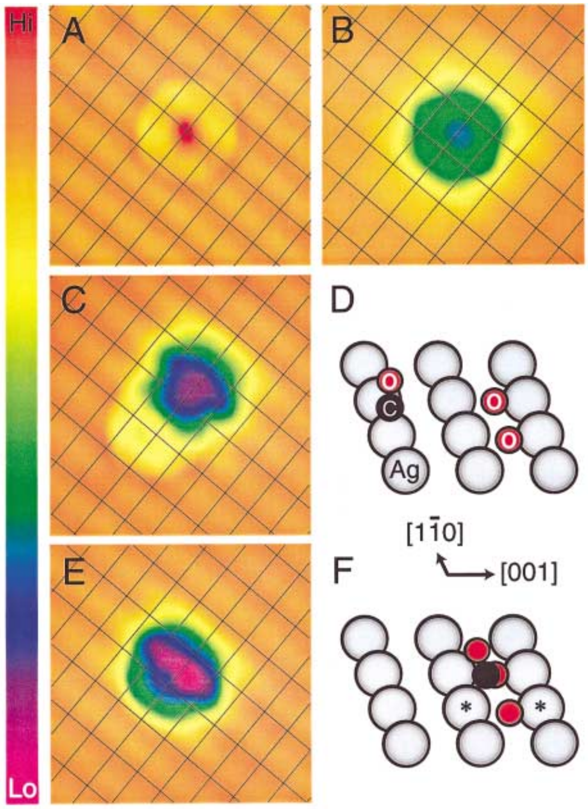

FIG. 2 (color). STM topographical images obtained with a CO-terminated tip, 70 mV sample bias, and 1 nA tunneling current. (A) Isolated CO molecule (adsorbed on atop site), (B) two O atoms (adsorbed on the nearest fourfold hollow sites along the [1$\bar{1}$0] direction), (C) CO and two O atoms separated by 6.1 Å along the [001] direction, and (E) O-CO-O complex. (C) and (E) correspond to Figs. 1B and 1C, respectively. Grid lines are drawn through the silver surface atoms. Scan area of (A)–(C) and (E) is 25 Å × 25 Å. Schematic diagrams for adsorption geometries of (C) and (E) are shown in (D) and (F), respectively; a linear atop and a tilted off-site CO are implicated. The black (red) circles represent carbon (oxygen) atoms and the large gray circles are silver atoms. The sizes of the circles are scaled to the atomic covalent radii.

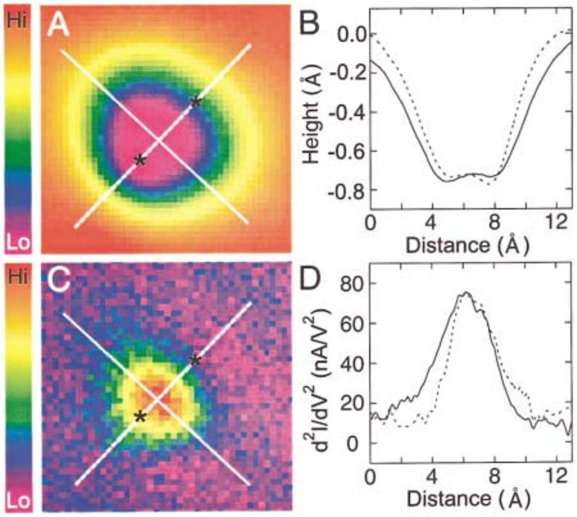

FIG. 3 (color). Comparison of the topographical image of the O-CO-O complex and the spatial distribution of STM-IETS intensity for the hindered rotation mode of CO. (A) Topographical image taken with a bare tip, 70 mV sample bias, and 1 nA tunneling current. (B) Cross sections of (A) taken along the $[1\bar{1}0]$ (solid line) and the [001] (dashed line) directions. (C) Vibrational image obtained simultaneously with (A) for the hindered rotation of CO at 25 mV sample bias. (D) Cross sections of (C) taken along the two directions. The raw data, 14 Å × 14 Å, are shown with a resolution of 0.3 Å per pixel. Two Ag atoms shown in Fig. 2F are marked by "∗" in both topographical and vibrational images.

bias of 25 mV (corresponding to the hindered rotation energy) with a bare tip. Cross sections along the $[1\bar{1}0]$ (solid line) and the [001] (dashed line) directions reveal quantitative variations in the topography and vibrational intensity (Figs. 3B and 3D). The highest intensity of the vibration occurs not on the atop location but at the center of the topographical image (between two Ag atoms (∗) along the [001] direction). This spatial distribution indicates that the CO in the complex is between the two Ag atoms along the [001] direction. The CO may also be tilted (Fig. 2F) by the repulsive interaction between the O atom of CO and adsorbed O atoms, as suggested for a transition state in CO oxidation on the Ru(0001) surface [18].

The observed changes in the vibrational energy and line shape can be induced by the electrostatic (Stark effect) and chemical (chemical shift) interactions between coadsorbed species [19–21]. Stark shift is related to changes in the CO electronic levels induced by external electric fields, resulting in charge redistribution. According to the calculations [20,21], the O atoms on Ag(110) induce a positive field at the CO, leading to a decrease in the hindered rotation energy. This is in contrast to the observed 4 meV up-shift, implying the interaction is chemical in origin.

The chemical shift arises from electron correlations between the CO molecule and the O atoms, either directly (O-CO-O) or mediated by the substrate (CO-Ag-O, O). In the latter case, we expect the electronegative O atoms to weaken the CO-Ag bond by reducing the electron back-donation from metal orbitals to the CO $2p^*$ antibonding orbital [22]. The weakening of the CO-Ag bond would lead to a redshift in the hindered rotation, in contrast to the observation. On the other hand, the direct interaction of CO with O atoms in the O-CO-O complex can enhance the binding of CO to the surface, hence a blueshift. Density functional theory calculations for the oxidation of CO on the Rh(111) surface [23] revealed that the presence of CO near an O atom weakens the O-metal bond. This activates the O atoms [18,23] and one of the O p orbitals becomes available for forming a new bond with the CO, i.e., CO 5σ or 1π interacting with O $2p$.

Direct transfer of a CO molecule from the tip to an adsorbed O atom illustrates another oxidation pathway. The topographical image of two O atoms obtained with a CO-terminated tip reveals occupation of fourfold hollow sites separated by two lattice constants. The tip was positioned over one of the O atoms (∗ in Fig. 4A) followed by the application of a +470 mV pulse with the feedback turned off. A rescan of the same area (Fig. 4C) showed the remaining O atom on the surface. This O image and the lack of resolution of substrate atoms are consistent with the absence of CO on the tip. Tunneling current during the pulse (Fig. 4B) showed two step rises. In contrast, only one step rise in current was recorded when the CO was transferred from the tip to the Ag(110) surface; the transferred CO was found on an atop site below the tip. The threshold bias voltage for transfer onto an O atom (~440 mV) was comparable to that for a Ag surface atom.

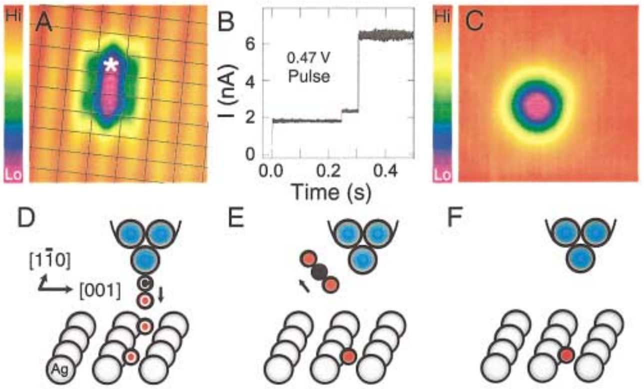

FIG. 4 (color). Reaction of a CO molecule released from a CO-terminated tip with an O atom adsorbed on the surface. (A) STM topographical image, taken with a CO-terminated tip, of two O atoms (on the fourfold hollow sites) separated by two lattice spacings (2 × 2.89 Å) along the $[1\bar{1}0]$ direction. Grid lines are drawn through the silver surface atoms resolved with the CO-terminated tip. (B) Tunneling current during a +470 mV sample bias pulse with the CO-terminated tip over one of two O atoms (denoted by "∗"). Two current rises (at 250 and 310 ms) indicate the moment of desorption and reaction of CO from the tip and the moment of desorption of CO_2 into vacuum. (C) STM topographical image of the same area rescanned after the pulse, showing CO on the tip has reacted away (substrate atoms no longer resolved). Scan area of (A) and (C) is 25 Å × 25 Å. (D), (E), and (F) are the schematic diagrams for (A), (B), and (C), respectively.

Atomic oxygen on Ag(110) reacts readily with gaseous CO to produce CO_2 [24,25]. The reaction is exothermic and may lead to product desorption. Tunneling electrons may also induce the desorption of the CO_2 product. In Fig. 4B, the first current rise at 250 ms after the initiation of the voltage pulse indicates the onset of the reaction. A continuous evolution is envisioned from reactants to products. An O-C-O intermediate is formed in the junction as the CO is detached from the tip and reacts with the O atom. The smaller scan height for the CO-terminated tip compared to the bare tip [26] could lead to this current increase. The second current rise at 310 ms indicates the conversion of O-C-O to CO_2 which desorbs. A distribution of time intervals between these two current rises has been measured. The duration of the intervals ranges from 5 to 90 ms in 38 current traces and follows an exponential distribution, using 10 ms bin width. Desorption of an O atom due to collision with the CO released from the tip is not likely since the binding energy of an O atom is 3.14 eV [27]. However, lateral movement of O atom on Ag(110) was induced with a bare tip and a sample bias greater than 3 V.

The O-CO-O complex was proposed as a possible intermediate for CO oxidation on Ag(110) [24]. The formation of this complex was also achieved by transferring a CO from the tip between two nearest neighbor O atoms as well as by lateral movement of an adsorbed CO [28]. The O-CO-O complex was not formed when the two O atoms are farther apart, such as next nearest neighbor sites (Figs. 4A and 4D). An O-CO complex was not found when an adsorbed CO was moved toward a single O atom, but CO_2 production was observed when the CO was released from the tip [28]. A reaction barrier is implicated for an adsorbed CO toward a single O atom. Similarly no reaction was observed when the CO-terminated tip was physically moved over and increasingly closer to an adsorbed O atom. Since CO is bonded to the tip via the C, a repulsive interaction of CO with adsorbed O is expected. The release of CO from the tip and the reaction with an adsorbed O necessarily involve a rotational motion of the CO [11,29]. The combined imaging, manipulation, and spectroscopic capabilities of the STM provide direct visualization of reaction pathways at the single molecule level.

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