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Surface Chemistry

Real-Space Investigation of Non-adiabatic CO_2 Synthesis**

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Heterogeneous catalysis on surfaces is of utmost importance to applied problems and interesting in fundamental sciences. Apart from thermal reactions, chemistry induced by femtosecond lasers has aroused increasing interest in recent years.[1] This excitation source might trigger reactions that are not possible thermally, for example, the formation of carbon dioxide from carbon monoxide and oxygen on a Ru(0001) surface.[2] Thereby, the possibility of a reaction in a specific environment is indispensable for an improved understanding of such surface chemistry. A significant advance in surface studies concerned with femtosecond reactions is the development of a technique that allows resolution of the dynamics at surfaces on the length scale of molecules, rather than measuring the averaged response of an ensemble of surface sites. A combined femtosecond laser–scanning tunneling microscope (fs-STM) facilitates such single-molecule femtochemistry in real space. A fs-STM was used in an approach that images the nuclear motion of single molecules.[3,4] The first study pinpointed a qualitative difference in diffusion direction for laser-assisted motion of CO molecules on a Cu(110) surface to thermal diffusion.[3] A quantitative study of diffusion of CO molecules on Cu(111) allowed us to determine non-adiabatic energy barriers.[4] Diffusion as investigated in references [3,4] is, however, only one step in a surface reaction and the synthesis of a new species from two reactants should be the ultimate goal for real space studies.

Herein, we present STM results of femtosecond-laser-induced synthesis of CO_2 from coadsorbed CO and O_2 molecules—among the simplest reactions that is frequently used as a model system in heterogeneous catalysis. The reaction is also of technological relevance in control of automobile emissions, air purification, and chemical sensing. We have chosen CO and O_2 molecules on Cu(111), because femtosecond irradiation of CO and O_2 molecules coadsorbed on Pt(111) showed CO_2 desorption with an enhanced quantum efficiency as compared to nanosecond irradiation indicative of non-adiabatic processes.[5] Cu(111) is preferred over Pt(111) because of the higher absorbance at the wavelength of our laser (400 nm). We first prepare the reactants, CO and O_2 molecules, next to each other and identify this molecule arrangement by a functionalized tip. Illumination by 40 fs–400 nm pulses leads to CO_2 synthesis with a transient motion of the CO_2 molecules from the mixed overlayer over several tens of nanometers onto the bare terrace, for which we propose a cannonball mechanism. Our study presents the first real space observation of single molecules produced non-adiabatically.

We prepare the reactants by depositing the molecules at a temperature at which CO molecule is immobile[4] but oxygen is mobile[6] so as to bring the two reactants in close proximity and avoid segregation. At the right deposition ratio, each randomly distributed CO molecule is surrounded by a large number of oxygen molecules as shown in Figure 1 for codeposition with a ratio of O_2/CO = 12:1. The brindle parts are completely covered by molecules; the nearly homogeneous parts represent the copper surface with a small number of CO molecules. At first sight, the molecules have formed a nonordered layer that is always found in the smaller corners of large terraces or completely wets small terraces. This corroborates the expected high mobility of the oxygen molecules at 17 K. Owing to the immobility of CO molecules at the deposition temperature, few circular depressions representative for CO molecules are found on the terraces

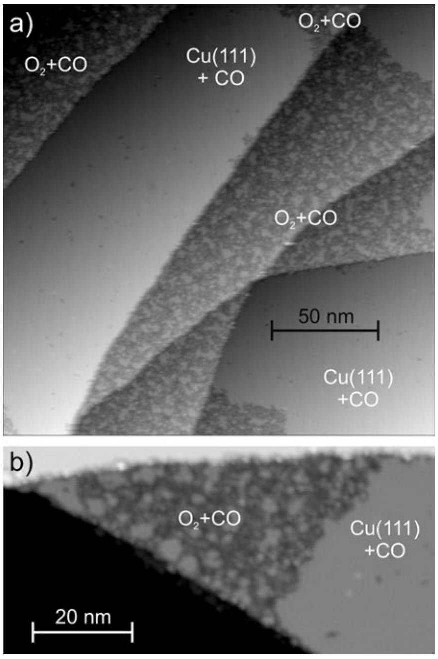

Figure 1. Oxygen molecules (O_2) coadsorbed with carbon monoxide molecules (CO) on Cu(111): a) Large-scale image, tunneling bias: 96 mV, tunneling current: 4.7 pA, measurement temperature: 5.8 K. b) Small-scale image of the corner of one terrace covered with molecules, 96 mV, 3.1 pA, 5.0 K.

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(arrow in Figure 2 a). These cover approximately 0.12 % of the free terrace.

The brindle parts consist of darker and brighter (white) patches, none of them with a higher apparent height than the bare copper terraces (Figure 1 b). Picking up one of the molecules, most probably oxygen, with the tip by approaching the tip with increased voltage to the mixed overlayer changes the apparent height of the surface covered with molecules (cf. for CO imaged with CO[7]). This allows resolution of individual molecules within the wetting layer (Figure 2). Two types of structures are found (Figure 2 b–d). Note a few brighter spots with an apparent height of 80 pm above the surface. These are molecules in the second layer of unknown identity and will be disregarded for the remainder of this article.

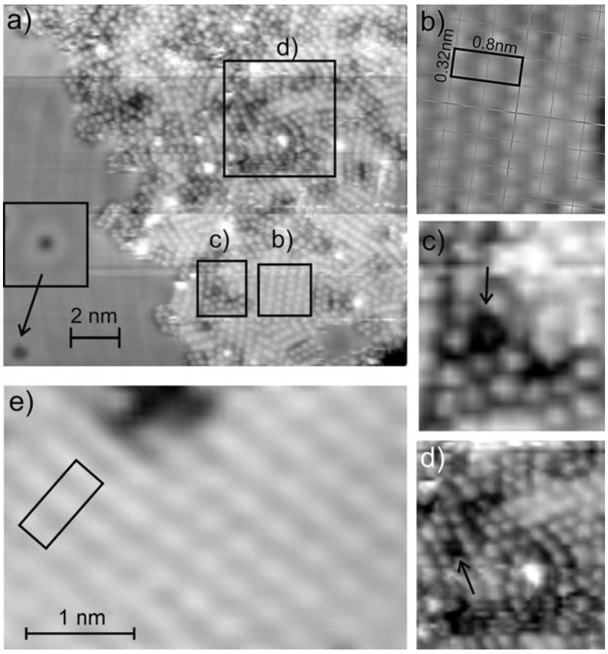

Figure 2. a–d) High-resolution image of mixed overlayer with modified tip, 167 mV, 17 pA, 5.5 K; rectangles (b) to (d) are magnified in (b–d); inset on left-hand side shows CO molecule to scale from adsorption of CO only (b,c) 3.8 times magnified; c(4×2) unit cell is indicated in (b) and (d) twice magnified; arrows point to CO molecules; note that some patches of c(4×2) oxygen molecules are too small to lead to a measurable white patch in the large-scale images. e) High-resolution image on O_2 monolayer with regular tip, −1 V, 0.19 nA, 5 K; black on top is defect within layer; rectangle has same size as in (b).

In the originally brighter patches all molecules are imaged with the same apparent height (Figure 2 b). The structure is best described by a centered rectangular unit cell with $a \approx 0.3$ nm and $b \approx 0.8$ nm. The same unit cell is observed after adsorption of oxygen only (Figure 2 e). The centered rectangular structure is reminiscent of a c(2×4) structure of oxygen molecules observed before on Ag(100) with different lattice size.[6] Theory predicts that oxygen molecules adopt on Cu(111) an orientation, in which their molecular axes are parallel to the surface (di-σ configuration).[8] The parallel adsorption is corroborated by the slightly ellipsoidal form of the protrusions, if imaged with the functionalized tip (Figure 2 b).

Within the originally darker regions few even darker *circular* protrusions are observed (Figure 2 c,d). Their existence leads to a local disturbance of the regular arrangement of the surrounding oxygen molecules. We attribute those circular protrusions to the single CO molecules consistent with the deposition ratio of the molecules. Thus, the CO molecules are indeed surrounded by oxygen molecules and we have prepared an ideal starting position for CO_2 synthesis.

We now retract the tip und illuminate the tip-sample gap with the femtosecond laser. The nonresonant laser light is expected to be absorbed by the metal when it produces energetic electrons that can attach to the adsorbed molecule and thus trigger reactions.[1]

The two images in Figure 3 a demonstrate that a direct comparison of the situation before and after illumination can be performed for exactly the same part of the terrace. After laser illumination the former (quasi) clean terrace now shows many additional dark depressions (Figure 3 a). The additional dark spots cover 1.2 % of the total bare terraces in the example shown, that is, ten times the CO coverage before illumination. Furthermore, changes to the structure within the molecular overlayer are observed, for example, in the magnified region in Figure 3 a, where the brighter (oxygen) areas retract.

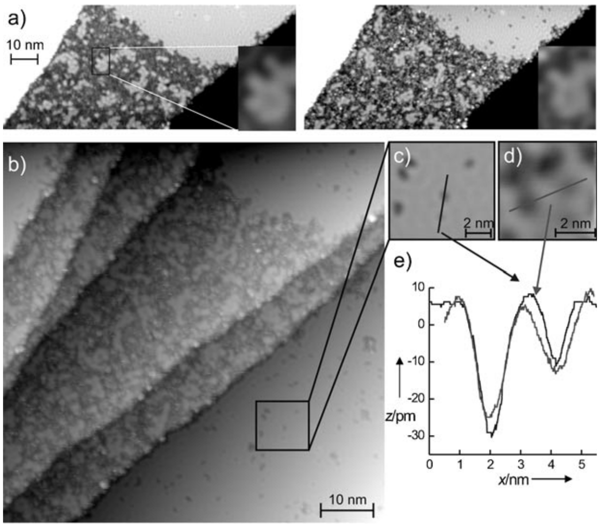

Figure 3. Laser excitation of O_2/CO mixture on Cu(111): a) Left: before laser excitation; 6.5 K; Right: after laser excitation with 4.27 J m^{-12}, 5×10^8 pulses; 5.7 K; 92 mV, 4.7 pA; zoom-ins show the mixed layer with enhanced contrast: b) Large-scale image after excitation with 3.78 J nm^{-2}, 1.5×10^9 pulses, 3.3 pA, 96 mV, 5.7 K. c) Zoom-in on terrace where indicated in (b). d) Image from experiment with co-adsorption of CO_2 and CO on Cu(111). e) Line scans where indicated in (c) and (d). Note that images were taken with different regular tips. Similar tip states are ensured by the similar apparent width and depth of the CO molecules.

Are the additional depressions induced by laser-induced electron excitation indeed CO_2 molecules as anticipated? In principle we could also envisage them to result from diffusion or fragmentation of either of the reactants. However, the additional depressions can not be the result of CO diffusion, because they are imaged with 35 pm, which is considerably deeper than the CO molecules (Figure 3e). In addition, they show a slightly elliptic form and cluster into larger islands; both observations are in contrast to CO molecules.[4]

To exclude that we simply see an induced diffusion of O_2 molecules onto the terrace or their dissociation, we have excited the same spot of the surface several times with the same laser fluence (and an increasing number of pulses, Figure 4). The STM images Figure 4b,c show that the newly produced depressions stay stationary during the next pulses, which excludes them from being simply diffusing species. Furthermore, the number of newly produced molecules per square nanometer and pulse decreases with each illumination (Figure 4d) and is always recovered, when we move tip and laser spot to a new region of the sample. This outcome can only be explained by a reaction, which decreases with the number of O_2/CO pairs within the mixed overlayer available for reaction.

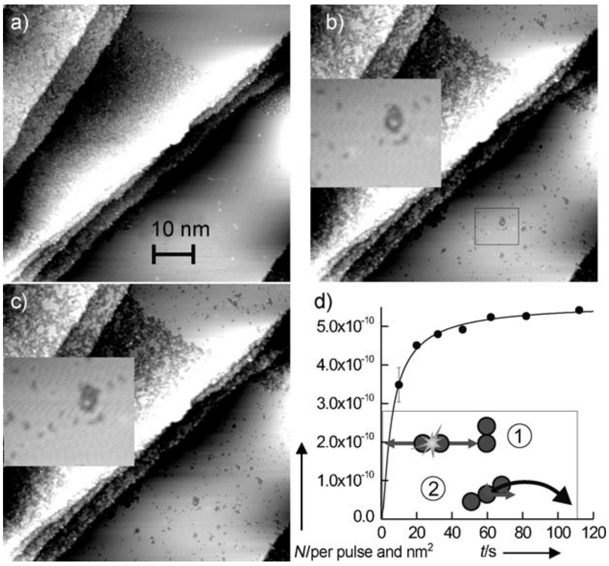

Figure 4. Decrease of CO_2 formation: Series of STM images showing additional protrusions on the terrace after laser excitation of O_2/CO on Cu(111): 5.3 J m^{-12}; 96 mV, 3.3 pA: (a) and (b) 1.0×10^8 pulses, (b) and (c) 1.2×10^8 pulses; insets in (b) and (c) are magnifications of the area indicated by a rectangle in (b). d) Total number of produced molecules N on terrace during an illumination time t for an excitation with 5.35 J m^{-12}, normalized to pulse and nm^2; line serves to guide the eye. Inset: sketch of CO_2 formation via a hot-adatom mechanism; arrows represent momenta.

Though the larger depressions do not appear upon illumination of CO molecules only on Cu(111),[4] they could still be explained by an oxygen-catalyzed CO dissociation. To univocally substantiate our claim that we produced CO_2, we coadsorbed CO_2 and CO molecules. A line scan through a pair of CO_2 and CO molecules reproduces a line scan along the femtosecond-produced species and CO (Figure 3c–e). Note that we compare images, in which the CO molecule is imaged with the same apparent height and width at similar tunneling parameters. This comparison ensures that the tip states, which are known to influence these values, are similar in both cases. The femtosecond-laser-induced depressions on the formerly bare terrace are thus identified as CO_2 molecules. The clustering of the CO_2 molecules can be explained based on their relatively large quadrupole moment. The total number of new molecules reflects approximately the number of available CO molecules within the mixed overlayers (between 1 and 2 % ML in both cases).

To ensure the nonthermal origin of the CO_2 reaction, we keep the pulse energy low enough so that the transient surface temperature stays far below the threshold of thermal reaction. The temperatures transiently reached by the electron and phonon system are 910 K and 46 K, respectively, as calculated by the two temperature model[9] for 5.35 J m^{-12} absorbed laser fluence on Cu(111). The phonon temperature is decreased to below 30 K after 100 ps and to below 20 K after 500 ps. The measured rates can never be obtained at 46 K within this short time interval under the assumption of the experimentally determined activation energy for dissociation of approximately 0.8 eV.[10] A thermal reaction is thus excluded and we conclude that the energetic electrons induce the reaction.

As a reaction mechanism, we propose the hot-adatom mechanism based on the fact that CO_2 does not desorb.[11] In this mechanism (schematically depicted in Figure 4d, inset), the oxygen molecule is dissociated and hot oxygen atoms (dissociation barrier 0.2 eV and energy release 2.4 eV per molecule[8]) are emitted in direction of the molecular O_2 axes, that is, in parallel to the surface. These atoms attack CO molecules and the nascent CO_2 retains the momentum of the hot atoms through the reaction, which gives an additional energy as a result of its exothermicity. In addition, there is a repulsive force normal to the surface because of the larger adsorption distance of CO_2 as compared to the reactants and a rotational motion from the change in adsorption angle from perpendicular (CO) to parallel (CO_2) to the surface. In total, a cannonball trajectory is thus achieved (cf. for chlorine dissociation[12]). This allows the product molecules to escape from the mixed layers to the bare terraces. Even on terraces as broad as 160 nm, we find an equal distribution of CO_2 molecules, thus a transient motion of 100 nm is a lower limit of the observed motion (Figure 4b,c).

Note that the mixed layer does not get completely homogeneous at saturation. A possible explanation is that the oxygen molecules are unable to rearrange at 6 K to the centered rectangular unit cell observed after O_2 adsorption only (Figure 1e), and thus the disorder induced by the CO molecules is maintained after the CO is lost through reaction. Alternatively, it is also possible that the reaction takes place only for specific arrangement of the environment of the O_2/CO pairs and thus the mixed layer remains mixed. We are, however, unable to determine the nature of these pairs and their immediate vicinity because molecular resolution is not possible with the laser system attached to the STM.

Our study opens a new field of surface chemistry by utilizing a combination of low-temperature STM and femtosecond laser illumination for the analysis of non-equilibrium synthesis from coadsorbed reactants in close proximity. For less exothermic reactions it is envisioned to unravel the reaction probability and the jump length in dependence of local environment. Other processes besides the cannonball mechanism revealed here are expected to be discovered in future.

Experimental Section

The measurements were performed with a custom-built low-temperature scanning tunneling microscope in ultra-high vacuum with femtosecond laser excitation.[13] The femtosecond laser system is based on a Ti:Sa oscillator (*Femtosource scientific XL*). It delivers 30 fs (FWHM) pulses at 796 nm (band width 40 nm) with a pulse energy of >30 nJ at 10.67 MHz repetition rate. The pulses are frequency doubled to provide higher excitation energy and higher photon absorption in Cu(111). In a parallel set-up we determine that $\tau_{400nm} \approx (40 \pm 5)$ fs and the Gaussian profile of the elliptical laser spot as 10 μm × 30 μm (FWHM) at the sample.

The Cu(111) surface is cleaned by repeated cycles of Ne^+ sputtering and annealing. CO, O_2, and CO_2 molecules are brought to the surface from selectively increased background pressure to the sample held at 17 K. At the deposition temperature also the oxygen molecules stay intact (dissociation threshold at ≈170 K[14]). Measurements are performed between 5 K and 7 K. Prior to illumination, the tip is retracted by more than 200 nm in perpendicular direction to the sample and by more than 1 μm in parallel to the sample perpendicular to the laser plane.

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[1] C. Frischkorn, M. Wolf, *Chem. Rev.* **2006**, *106*, 4207 – 4233.
[2] M. Bonn, S. Funk, C. Hess, D. N. Denzler, C. Stampfl, M. Scheffler, M. Wolf, G. Ertl, *Science* **1999**, *285*, 1042 – 1045.
[3] L. Bartels, F. Wang, D. Möller, E. Knoesel, T. F. Heinz, *Science* **2004**, *305*, 648 – 651.
[4] M. Mehlhorn, K. Morgenstern, *Phys. Rev. Lett.* **2010**, *104*, 076101.
[5] a) F.-J. Kao, D. G. Busch, D. Gomes da Costa, W. Ho, *Phys. Rev. Lett.* **1993**, *70*, 4098 – 4101; b) S. Deliwala, R. J. Finlay, J. R. Goldmann, T. H. Her, W. D. Mieher, E. Mazur, *Chem. Phys. Lett.* **1995**, *242*, 617 – 622.
[6] S. Messerli, S. Schintke, K. Morgenstern, J. Nieminen, W.-D. Schneider, *Chem. Phys. Lett.* **2000**, *328*, 330 – 336.
[7] L. Bartels, G. Meyer, K. H. Rieder, *Surf. Sci. Lett.* **1999**, *432*, L621 – L626.
[8] Y. Xu, M. Mavrikakis, *Surf. Sci.* **2001**, *494*, 131 – 144.
[9] S. I. Anisimov, B. Rethfeld, *Proc. SPIE-Int. Soc. Opt. Eng.* **1996**, *3093*, 192 – 203.
[10] F. H. P. M. Habraken, E. P. Kiefer, G. A. Bootsma, *Surf. Sci.* **1979**, *83*, 45 – 59.
[11] T. Yamanaka, Y. Inoue, T. Matsushima, *J. Chem. Phys.* **1999**, *110*, 2597 – 2605.
[12] U. Diebold, W. Hebenstreit, G. Leonardelli, M. Schmid, P. Varga, *Phys. Rev. Lett.* **1998**, *81*, 405 – 408.
[13] M. Mehlhorn, H. Gawronski, L. Nedelmann, A. Grujic, K. Morgenstern, *Rev. Sci. Instrum.* **2007**, *78*, 033905.
[14] T. Sueyoshi, T. Sasaki, Y. Iwasawa, *Surf. Sci.* **1996**, *365*, 310 – 318.