Heterogeneous Catalysis

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High-Pressure Scanning Tunneling Microscopy of a Silver Surface during Catalytic Formation of Ethylene Oxide**

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The pressure-gap problem of heterogeneous catalysis designates the question in how far it is valid to expand a reaction mechanism derived with the methods of surface science under ultra-high vacuum (UHV) conditions to the more than 10 orders of magnitude higher pressures of practical catalysis. The main reason for the problem is that at the pressures of practical catalysis most surface analysis techniques cannot be applied.

One of the few techniques that can be used under these conditions is scanning tunneling microscopy (STM), in principle offering the chance to image the surface of an operating catalyst with atomic resolution.[1] Using STM we have investigated the ethylene epoxidation over silver, a prime example for the pressure-gap problem. The reaction is a large-scale industrial process, by which 15 million tons of ethylene oxide (EtO) are produced from ethylene and O_2 per year.[2] The reaction is performed at 490 to 550 K and 10 to 30 bar on promoted, Al_2O_3-supported Ag catalysts, giving EtO with a selectivity of about 80%. Surprisingly, despite of more than 40 years of research the reaction mechanism is still heavily debated.[3] The basic step, the attachment of an O atom to the π bond of an ethylene molecule on the Ag surface, seems to be simple. However, there is strong evidence that this step requires a special "active form" of oxygen, the nature of which has remained mysterious.

It has so far not been possible to prepare the active form of oxygen in a typical surface science experiment. If one adsorbs O_2 at low pressures on an Ag(111) single crystal at room temperature the molecules dissociate. The O atoms induce a reconstruction, a structure change of the topmost Ag layer, on which the O atoms occupy favorable adsorption sites.[4] X-ray photoelectron spectroscopy (XPS) of oxygen adsorbed on the reconstructed Ag(111) surface and also on polycrystalline Ag foils shows an O 1s peak at a binding energy (BE) between 528.1 and 528.4 eV[5] (in the following "528 eV species"). If one anneals an Ag sample covered with this oxygen species in the presence of ethylene exclusively the total oxidation products CO_2 and H_2O are formed.[3f,5a] Hence, in a surface science experiment not even the right product is formed.

On the other hand, after treating Ag samples with O_2 or O_2/ethylene mixtures at high pressures and temperatures a different oxygen species, with BE(O 1s) = 530.1 to 530.6 eV, was observed in X-ray photoelectron spectra[5a,b,6] (in the following "530 eV species"). When a sample covered with this species (possibly together with the 528 eV species) was heated in the presence of ethylene EtO formation could be detected.[3f,5a,6b] Meanwhile it has been achieved to observe the 530 eV species by in situ XPS under steady-state reaction conditions close to 1 mbar.[3c] This species may thus be the active form of oxygen.

Applying STM and XPS we have investigated the active oxygen on Ag(111). We describe, firstly, a method by which the active oxygen species can be prepared in UHV. Secondly, we have observed the same species by STM under O_2/ethylene reaction mixtures at 1 mbar and at a temperature of 470 K. Under these conditions we detect formation of EtO. This may be an important step toward closing the pressure gap for one of the oldest problems in heterogeneous catalysis.

The experiments were performed with a UHV chamber connected to a high-pressure cell with the scanning tunneling microscope.[1c] Under UHV, STM images of the clean Ag(111) surface show the typical step/terrace morphology of uncovered, close-packed metal surfaces (Figure 1a), with curved monatomic steps. On a smaller scale characteristic "fringes" at the steps are visible (Figure 1b) caused by fluctuations of the step atoms at elevated temperatures.

In the UHV experiments NO_2 was used as oxygen source because of its roughly six orders of magnitude higher sticking coefficient on Ag(111) than O_2.[7] NO_2 dissociates on the Ag surface into O atoms and NO, the NO desorbs. When NO_2 was dosed, typically in portions of 360 L ($1\,L = 1.3 \times 10^{-6}$ mbar s) at 500 K, the structure of the well-known (4 × 4)O reconstruction of the Ag(111) surface appeared,[4b,c] the step/terrace morphology was unchanged, and in X-ray photoelectron spectra an O 1s peak was observed at 528.3 eV. This is the 528 eV species known from previous work.[5,6b] Annealing to somewhat above the desorption temperature of oxygen from the (4 × 4)O phase at about 580 K[5c] removed the (4 × 4)O structure and the peak at 528.3 eV, as expected. However, when this adsorption and annealing procedure was repeated several times a new O 1s peak appeared in the X-ray photoelectron spectra at a BE of 530.7 eV and a second component at 530.2 eV (Figure 1c, top). Obviously, in each adsorption/desorption cycle some oxygen had remained on the sample. The relative intensities of the 530.7 and 530.2 eV peaks depended on several parameters such as temperature

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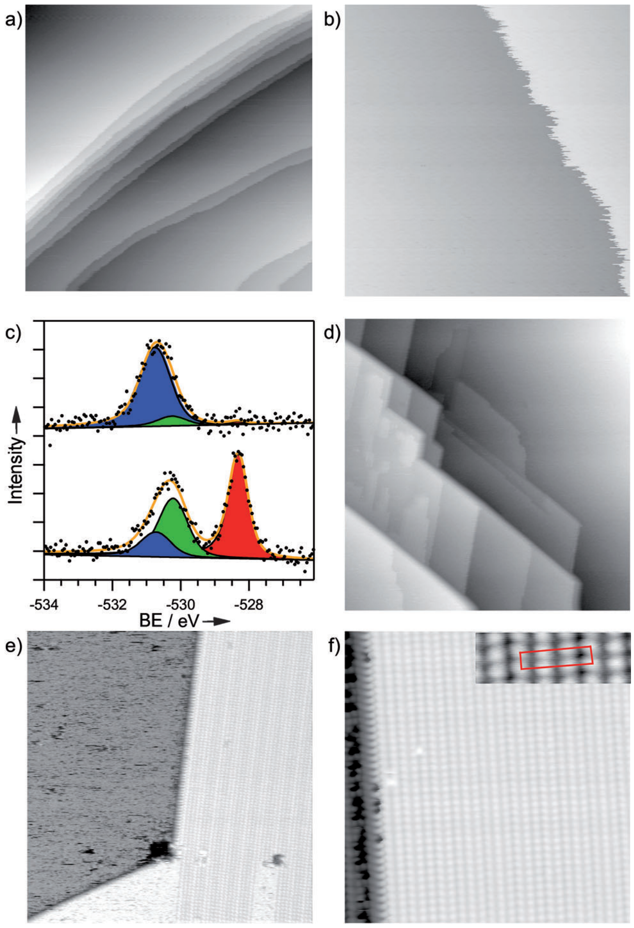

Figure 1. Ag(111), clean and covered by reactive oxygen. a) STM image of clean Ag(111), 2000 Å×2000 Å, −1.1 V, 0.3 nA, at 300 K and b) 700 Å×700 Å, +1.0 V, 1.0 nA at 470 K. c) Top: XPS of O 1s, recorded after repeatedly dosing 360 L of NO_2 at 500 K and annealing at 625 K; bottom, XPS recorded after an additional 370 L NO_2 dose at 500 K; blue: O 1s at 530.7 eV, green 530.2 eV, red: 528.3 eV. Intensities are referenced to Ag $3d_{5/2}$. d–f) STM images of the Ag(111) surface covered by the 530 eV oxygen species: d) 3000 Å×3000 Å, +1.0 V, 0.03 nA, e) 480 Å×480 Å, +1.1 V, 0.1 nA, and f) detail and inset with $(7\times\sqrt{3})$rect unit cell, 200 Å×200 Å, +0.7 V, 0.4 nA.

and preparation procedure. For example, before the annealing step at 580 K (the 528 eV species was still present), the peak at 530.2 eV was higher than the 530.7 eV peak (Figure 1c, bottom).

The O 1s binding energy of the new state is the same as that of the active 530 eV oxygen species reported,[5a,b,6a,b] and recently a similar splitting into two components was reported.[6c] It appears that we have found a way of preparing the 530 eV species in UHV, without having to apply the pressures of 1 mbar and higher used in previous work.

STM images of the surface covered by the 530 eV species show a completely changed morphology. Most of the steps are straight now—they run along the $[11\bar{2}]$ direction—and there is a significant fraction of multiple steps (Figure 1d). On a smaller scale (Figure 1e) one can identify two phases, one with extended, regular stripes, the second disordered. On the disordered areas dark features form short streaks or groups of streaks indicating mobile structure elements. The area covered by the stripe phase scaled with the peak intensity of the 530 eV species, so that the disordered phase must contain less oxygen. However, the O 1s binding energies of both phases are identical, suggesting similar local Ag/O configurations.

A surface fully covered by the stripe phase showed a sharp diffraction pattern of a $(7\times\sqrt{3})$rect superstructure in low-energy electron diffraction (LEED), and a $(7\times\sqrt{3})$rect unit cell can be identified in the STM images (Figure 1f). The stripes run along the $[11\bar{2}]$ direction, like the oriented steps. Perpendicular to the stripes one can see a modulation (Figure 1e), which is caused by the mismatch between the three stripes and seven substrate lattice constants per $(7\times\sqrt{3})$rect unit cell.

Stripe phases of oxygen on Ag(111) have been reported before, but these were oriented into the perpendicular $[1\bar{1}0]$ direction and contained the 528 eV oxygen species.[8] Moreover, the maximum coverage of the 530 eV species we could prepare was $\Theta \approx 1$ according to the O 1s intensity, three times higher than that of the 528 eV species.[4,8] This high coverage speaks against the previous idea that the 530 eV species is formed by adsorbed O atoms on the unreconstructed Ag(111) surface.[5b,6a] The 530 eV species forms a new type of surface phase.

The special preparation procedure suggests that the bulk or the near-surface region of the Ag crystal becomes loaded by dissolved O atoms, and when the oxygen solubility is exceeded the 530 eV phase precipitates at the surface. This can also explain why this species has been observed before only after dosing at high pressures, or under reaction conditions. It can also explain the many previous indications that bulk-dissolved O atoms play a role in the EtO formation.[3a,e,f,k] A contribution by the Ag bulk is also consistent with the high oxygen desorption temperatures and broad peaks connected with the 530 eV species in temperature-programmed desorption experiments, and similar desorption characteristics have been observed before for highly oxygen-loaded Ag samples.[3m] (Depending on preparation conditions we observed peak temperatures between 630 and 850 K.) The special role of Ag as catalyst for the EtO synthesis would thus be linked to the known solubility or the high diffusion coefficient of O atoms in Ag.[9]

To test the chemical reactivity of the 530 eV species titration experiments were performed. Dosing with ethylene at pressures of 5×10^{-7} and 1×10^{-6} mbar at 450 K led to a linear decrease of the O 1s intensity of the 530 eV species (Figure 2a and b). Dosing with CO did not lead to a measurable reaction. The titration of the 530 eV species with ethylene was also monitored by STM under similar conditions (Figure 2c–f); a movie is available as Supporting Information. At the beginning one can see a large domain with the typical stripe structure of the 530 eV species, the rest is the disordered structure. During dosing, the stripe domain shrinks until it has completely disappeared at the end of the series, where only the disordered structure remains. At the same time the step/terrace morphology changes. An atomic step that initially (Figure 2c) is at the left side has moved to the right side (Figure 2f). Such morphology changes are typically observed in surface reactions in which phases with

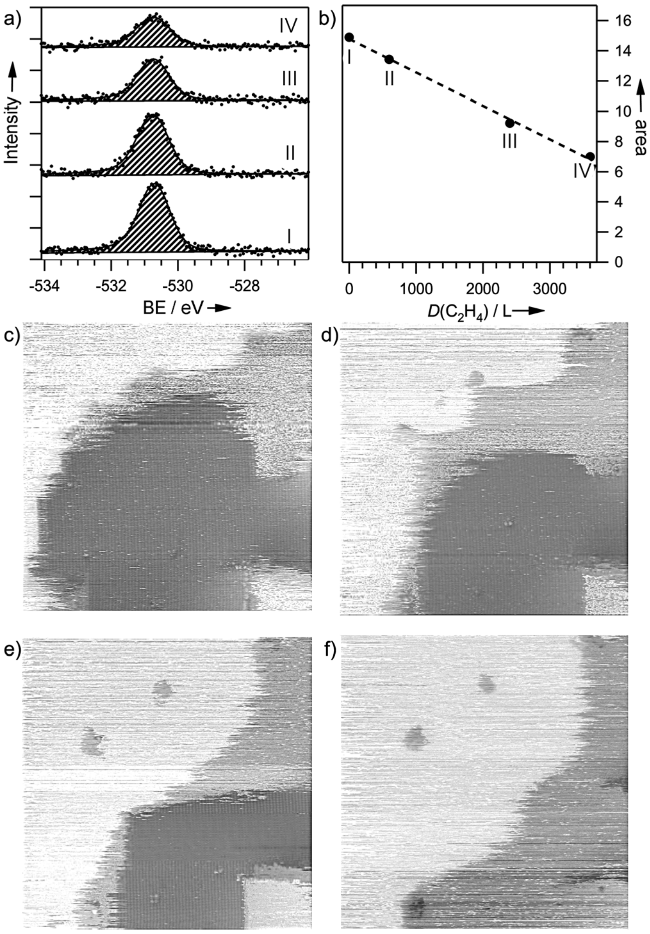

Figure 2. Titration of the reactive oxygen by ethylene. a) XPS of O 1s during titration of the 530 eV species by ethylene at 450 K (intensities referenced to Ag $3d_{5/2}$) and b) O 1s intensity as a function of ethylene dosage (D). c–f) STM images recorded at 696, 1565, 2087, and 2609 s, during dosing of the 530 eV species with ethylene, p(ethylene) = 5×10^{-7} mbar, at 358 K. 600 Å×600 Å, +0.7 V, 0.1 nA.

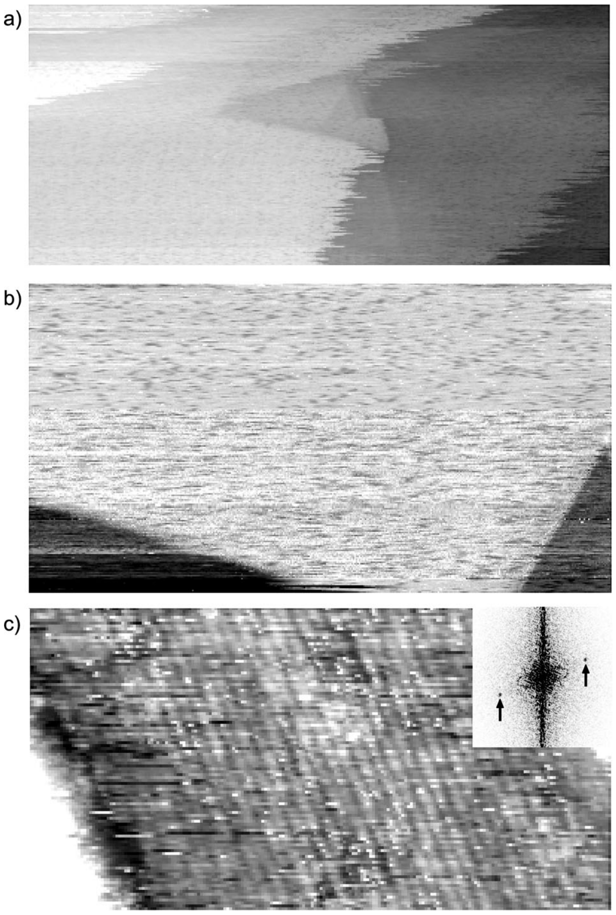

Figure 3. STM of the Ag(111) surface under reaction conditions. The reaction gas mixture was 0.5 mbar of ethylene and 0.5 mbar of O_2, T = 470 K. a) 1000 Å×450 Å, +1.0 V, 0.3 nA; b) 490 Å×260 Å, +1.0 V, 3.0 nA; c) 250 Å×130 Å, +1.0 V, 1.0 nA. Inset: Fourier transform of the image.

different densities of the substrate metal are involved. In any case, the 530 eV species does in fact react with ethylene. It is not yet proven that this gives EtO, but because of the low reaction probability EtO could not be detected by quadrupole mass spectrometry (QMS) in the gas phase in these titration experiments.

The steady-state STM experiments in reaction gas mixtures were difficult because of tip instabilities and thermal drift. Experiments were repeated many times to secure reproducibility, and we are able to present unfiltered data. Large-scale images (Figure 3 a) show defined terraces and partially fringed step edges as on the clean surface, but there are also partially straight steps as on the surface covered by the 530 eV species (also Figure 3 b). On a smaller scale one can see that the terraces are covered by disordered, dark features that appear as short streaks, indicating mobility (Figure 3 b). The appearance is very similar to the disordered phase of the 530 eV species prepared in UHV (Figure 1 e, left side). Occasionally also small areas with stripes were found (Figure 3 c). The Fourier transform gives a periodicity of 6.3 Å, in reasonable agreement, considering thermal drift, with the stripe periodicity of the $(7\times\sqrt{3})$rect structure of $1/3\times20.2$ Å = 6.7 Å. These observations evidence that the 530 eV oxygen species actually exists under these conditions.

The question was, of course, if this state of the surface produces EtO. Detection of EtO under the conditions of the steady-state STM experiment by QMS was a massive problem because of the small surface of the single crystal, the extremely low reaction probability of the ethylene molecules, and cross sensitivities of the EtO mass fragments with byproducts, in particular CO_2, and with ethylene. We have performed extensive experiments with a test reactor to identify conditions under which EtO could be safely detected.[10] The method finally obtained uses switches between low and high temperatures to subtract a background signal and the $m/z = 43$ molecular fragment for detection of EtO. The procedure was then successfully transferred to the STM cell. In contrast to the test reactor experiments only the sample was heated to avoid blank reactions at the large inner surfaces of the STM cell. The back side and the “brim” of the hat-shaped crystal were covered by the sample holder so that the sputter-cleaned (111) front made up for the largest part of the “free” surface. Figure 4 a shows one period of the temperature modulation of the sample. The QMS signals

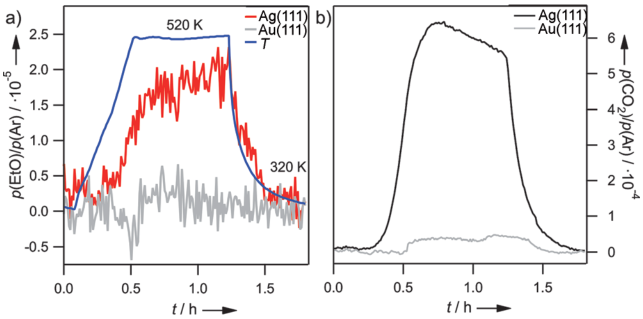

Figure 4. Product gas analysis by QMS in the STM cell. a) Temperature program (blue) and EtO signal at $m/z=43$ with Ag(111) sample (red) and blank reaction with a Au(111) sample (gray), 0.5 mbar ethylene, 0.5 mbar O_2, 1.5 mbar Ar. b) CO_2 signal at $m/z=44$ (black) and blank reaction (gray).

measured in the low-temperature periods at 320 K, where the sample was inactive, were used to subtract a background.

In the high-temperature phase at 520 K (Figure 4a) the background-corrected EtO signal, measured with an Ag(111) crystal in the STM cell, was clearly above the noise level [Ar was used as reference gas for quantification]. The CO_2 signal (Figure 4b) was much higher, that is, the selectivity was low, but this had to be expected at the relatively low pressures compared to the industrial process.[3d] To check if blank reactions, at the sample holder or other components of the scanning tunneling microscope, were sufficiently low the Ag(111) sample in the scanning tunneling microscope was replaced by an (inactive) Au(111) sample and the same temperature and pressure conditions were applied. As the data show, both, the EtO as well as the CO_2 signal, were then much lower. The catalytic formation of EtO on Ag(111) under the conditions of the STM experiment has thus been demonstrated.

In conclusion, we have found for one of the most controversially discussed reactions in heterogeneous catalysis a way to prepare the long-sought active oxygen species under UHV conditions. This makes it accessible to the full arsenal of surface science techniques. STM experiments performed in situ, under conditions where EtO formation could be detected, showed the same structural features, indicating that this species does, in fact, participate in the EtO formation. There is evidence that the active oxygen phase is connected with the dissolution of O atoms in the Ag bulk or near surface region, which may explain the unique role of Ag as catalyst for this particular reaction.

Experimental Section

The experiments were performed with a UHV chamber and an attached small cell (operation pressure between 10^{-10} mbar and 1 bar) that housed the scanning tunneling microscope.[1c] A transfer rod was used to move the sample from the UHV chamber to the STM cell without contact to air. The UHV chamber was equipped with an XP spectrometer with monochromatic X-ray source, a QMS, and LEED optics. The Ag(111) sample was prepared in the UHV chamber by Ar sputtering and annealing. In the UHV experiments NO_2 (99.0 Vol %) was used as oxygen source. For the reaction experiments the STM cell was filled with O_2 (99.995 Vol %) and ethylene (99.95 Vol %) under pressure control by a baratron. The sample was heated with IR laser light from the backside. STM data were recorded at elevated pressures and temperatures of the reaction. For the turnover measurements additionally Ar (99.990 Vol %) was fed in as reference gas. The product composition was analyzed by QMS.

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