Communications

Two-Dimensional Adatom Gas Bestowing Dynamic Heterogeneity on Surfaces

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Almost 80 years ago Taylor coined the concept of "active sites" in heterogeneous catalysis, suggesting that adsorbate bond cleavage or formation occurs preferentially at specific arrangements with low-coordinate surface atoms.[1] The identification of such active sites is decisive for understanding surface reaction mechanisms, the corresponding rate-limiting steps, and the design of advanced catalysts with improved efficiency or selectivity.[2–5] With the advent of modern surface science techniques, detailed insight into the features of active sites was obtained. Notably, structural defects at terraced surfaces such as steps, kinks, vacancies, and dislocations could be directly associated with centers of locally increased catalytic activity, and corresponding theoretical calculations provided much insight into the underlying chemistry.[6–12] However, in these studies the catalyst and the active sites are generally described in terms of static configurations. This is a severe restriction in view of the generally elevated operating temperatures (ca. 400–1000 K) in industrial processes, where catalysts are frequently subject to morphological changes. Only recently an example of the dynamic formation

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of active sites was conclusively demonstrated; they were encountered in the form of thermally fluctuating one-dimensional -O-Ag-O-Ag- chains that strongly accelerate the catalytic oxidation of CO on a Ag(110) surface.[13] It is thus timely to consider the intriguing case that highly mobile adsorbed atoms, arising from evaporation at atomic step edges, may act as dynamic active sites in heterogenous catalysis. Based on the fact that increased catalytic activity often correlates with reduced coordination number, such adatoms are in principle species of extreme efficiency. Indeed, immobilized individual metal atoms supported on various nonmetallic substrates have been proven to operate as single-site catalysts.[14–16]

The existence of adatoms as an intrinsic property of real surfaces can be rationalized within the scope of the terrace–step–kink (TSK) model, which comprises their main defects. As illustrated in Figure 1, the arrangement of steps and kinks
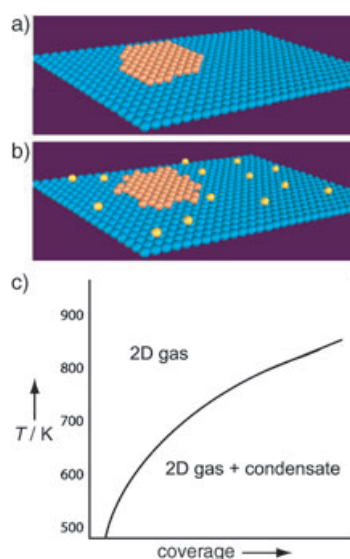

Figure 1. Island–terrace morphology of a surface covered by an island of adatoms. a) Static situation at low temperature. b) On thermal activation, island edges start fluctuating and emitting atoms from kink sites. A dilute 2D adatom lattice gas exists on the terraces. c) Schematic diagram of 2D adatom gas phase and condensed phase (islands) coexisting at elevated temperatures for metal-on-metal systems.

is static when fluctuations and atom-exchange processes are frozen, while on thermal activation adatoms start to evaporate from kink sites of the steps and are transported to terraces (Figure 1a and b).[17] These thermal adatoms form a two-dimensional (2D) lattice gas, whose surface concentration c_a strongly depends on temperature, chemical nature and symmetry, and step–terrace morphology of the substrate. On the basis of ultrahigh-vacuum (UHV) studies on a variety of systems,[18–21] c_a must be appreciable for many materials at elevated temperatures. At 700 K the 2D vapor pressure of the catalytically important metals Pd, Cu, and Ag results in adatom densities ranging between 1 and 6% on the surfaces of Mo and W (Figure 1c).[18,22] Although the decisive role of adatoms in the formation of reconstructions,[23–25] orienta-

tional ordering of adsorbed organic species,[26–28] and synthesis of metallosupramolecular complexes[28,29] at surfaces has been recognized, their elusive nature poses a challenge in identifying their impact as dynamic active sites.

Our combined scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) studies aim at discriminating the chemical activity of mobile adatoms from that of substrate terraces or static surface defects, such as step edges or kinks. The experiments were conducted under well-defined conditions in two UHV systems equipped with standard facilities for surface and thin-film preparation, which incorporated a home-built STM and a photoelectron detector, respectively. The individual adatoms in the 2D gas phase are highly mobile and cannot be resolved by STM, rather they usually appear as flicker noise in the STM measurements. The XPS measurements were carried out at the HE-SGM beamline at the BESSY II synchrotron in Berlin. Specifically, we considered the deprotonation of a carboxy group by copper. For this purpose, molecules of commercially available trimesic acid (1,3,5-benzenetricarboxylic acid, $C_6H_3(COOH)_3$, TMA, see structural model in Figure 2a) were deposited on a Ag(111) substrate by organic molecular beam epitaxy (OMBE). An electron-beam evaporator was used to deposit small amounts of Cu. The controlled codeposition of Cu and TMA allows the role of Cu adatoms to be identified.

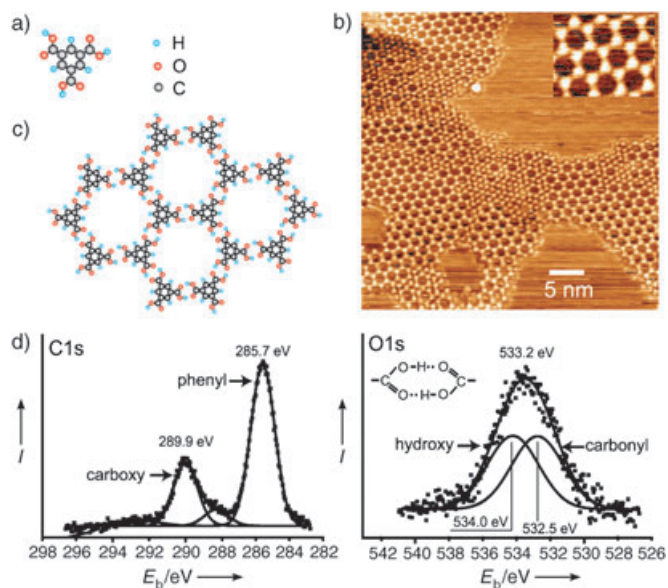The morphology of the pure TMA molecular films is controlled by the temperature of the Ag substrate. In particular, it is possible to fabricate hydrogen-bonded open networks by deposition on a substrate at a temperature below 340 K. This TMA supramolecular layer is illustrated by the STM image in Figure 2b, taken from a sample prepared by TMA deposition on a substrate at 120 K followed by warming to room temperature. The corresponding model in Figure 2c shows how dimerization of the self-complementary carboxylic groups accounts for the dominant planar honeycomb domains.[27,30] The XPS data shown in Figure 2d substantiate this interpretation. In the C 1s region two well-separated peaks are identified at 285.7 and 289.9 eV, which are distinctive features of the six carbon atoms in the phenyl ring and the three carbon atoms in the carboxy groups, respectively.[31] Accordingly, the broad O 1s signal (full width at half-maximum (fwhm) 4.0 eV at 533.3 eV) can be deconvoluted into two equal-height peaks at 532.5 and 534.0 eV, assigned to oxygen in carbonyl and hydroxy groups, respectively.[31] These findings prove that the carboxy groups are not affected by the presence of Ag under the employed conditions (i.e., temperatures below 340 K).

To address the reactivity of coadsorbed Cu, TMA molecules were deposited on the cold Ag(111) surface (120 K), and subsequently small amounts of Cu atoms (0.05 monolayers (ML)) were added. The molecules remained unaffected at the low deposition temperature, as evidenced by the corresponding XPS measurements, where again the characteristic peaks of the carboxy groups were resolved both for the C 1s and O 1s levels. However, since regular honeycomb networks are not expected to evolve at 120 K due to the limited molecular mobility at low temperatures,[32] the Cu atoms are highly dispersed in an irregular organic matrix, where they interact only weakly with the nearby TMA molecules.[33] Their chemical activity becomes apparent on increasing the substrate temperature. While the details of the respective processes could not be elucidated with the present experimental means, in view of their dynamic behavior involving rapid chemical transitions and structural reorganizations in the adsorbed layer, the pertinent net outcome could be conclusively addressed, that is, the spectroscopic data show dramatic changes in the TMA carboxy groups above 200 K. The analysis of the XPS chemical shifts clearly reveals the formation of a tricarboxylate species at 300 K, that is, complete deprotonation of the carboxylic groups which is associated with the presence of Cu adatoms definitely takes place (see Figure 3a). The carboxy C 1s peak at 289.9 eV disappeared, and the new single peak at 288.7 eV is characteristic for carboxylate carbon.[31] In the O 1s region a narrowed peak at 530.9 eV (fwhm = 1.8 eV) is detected instead of the broad peak at 533.2 eV. The symmetric peak reflects the two equivalent oxygen atoms in a carboxylate moiety. These findings are substantiated by STM topographic data (Figure 3b) showing complete inhibition of honeycomb network formation, since the underlying hydrogen-bonding motif is absent. Instead, TMA molecules aggregate in disordered agglomerates containing bright protrusions, which are Cu islands formed in the annealing process. This formation of islands reflects appreciable surface mass transport and movement of Cu adatoms. Since carboxy groups are still present after Cu deposition prior to sample annealing, it is concluded

Figure 2. Hydrogen-bonded TMA supramolecular layer. a) Structural model of the TMA molecule. b) Assembly of extended hydrogen-bonded TMA honeycomb networks on Ag(111) following submono-layer deposition on the substrate at 120 K and warming to room temperature. c) Model of the hydrogen-bonded nanoporous supramolecular TMA layer with hydrogen-bond-mediated dimerization of self-complementary carboxy groups. d) XPS data to testify the integrity of the organic molecules (photon energy 400 eV for C, 670 eV for O spectrum). The C 1s position of the phenyl ring and carboxy groups and the convoluted O 1s signal with contributions from carbonyl and hydroxy groups, respectively, are indicated. E_b = binding energy.
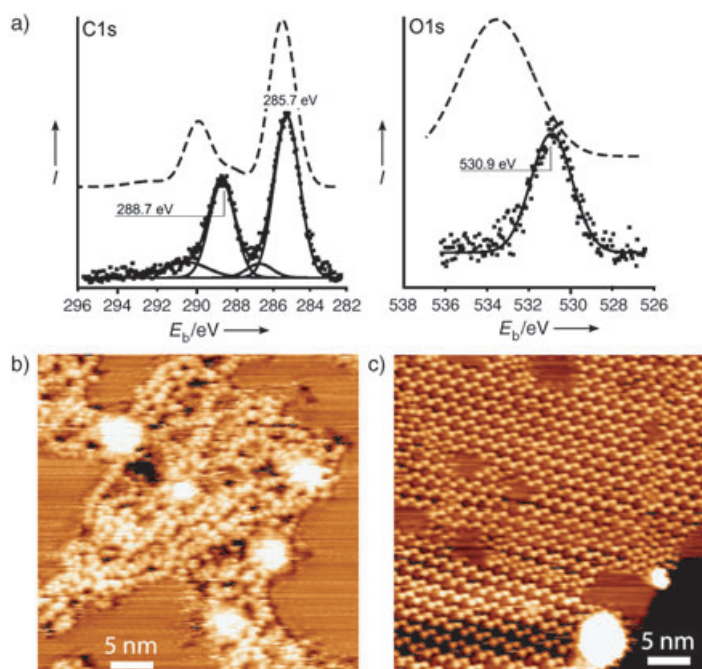
Figure 3. a) XPS data (solid curves) monitoring the chemical changes occurring during warming to 300 K of an intermixed TMA/Cu layer grown at low temperature on Ag(111) (photon energy 400 eV for C, 670 eV for O spectrum). For comparison, spectra of the protonated species are shown as dashed curves. The formation of a TMA tricarboxylate species is reflected by the distinct chemical shift of the higher energy C 1s peak and the characteristic narrowing of the O 1s peak. b) STM image of irregular TMA agglomerates coexisting with Cu islands when TMA and Cu codeposited at 120 K are annealed to room temperature. c) In the presence of predeposited condensed 2D Cu islands deprotonation on warming is negligible, and regular hydrogen-bonded TMA honeycomb networks evolve.

that the deprotonation reaction is not triggered by the impact of Cu in the deposition process; rather it must be mediated by thermal activation and Cu adatoms during warming. The corresponding temperatures are in a range for which recombinative desorption of molecular hydrogen occurs (e.g., on Ag(111) at $T = 190$ K[34]), a process which is similarly believed to be operative in the present scenario. Furthermore, we performed a series of experiments with varying TMA coverage (0.20, 0.25, 0.40, and 0.45 ML) while keeping the Cu concentration constant. The total amount of Cu condensed in the islands proved to be independent of the TMA coverage and corresponded to the quantity of Cu deposited on a clean surface. This demonstrates the absence of formation of Cu–TMA complexes, observed under similar conditions on a Cu(100) substrate.[29] Accordingly, no evidence for Cu^{II} species in a carboxylate is found in the Cu $2p_{3/2}$ XP spectrum, and high-resolution STM images reveal a homogenous character of the islands typical for metals. Consequently, the Cu active sites are not consumed in the deprotonation reaction. The resulting coupling of trimesate to the Ag(111) surface is in agreement with similar bonding schemes encountered with related systems, such as terephthalate layers on Cu(100).[35]

To clarify whether the boosting of chemical reactivity correlates with the highly dispersed Cu adatoms, control experiments were performed in which Cu was made available in a 2D condensed form by predepositing the same amount of Cu at room temperature on the clean Ag surface. Subsequently the substrate was cooled to 120 K and TMA was added. After warming to room temperature, the formation of perfect honeycomb structures coexisting with the Cu islands was observed, as shown by the STM image in Figure 3 c. The underlying hydrogen bonding implies that TMA deprotonation does not occur in the presence of pregrown Cu islands, with the possible exception of molecules at step edges. The same behavior was encountered with pregrown Cu islands in control experiments in which TMA was codeposited at 300 K. The minute reactivity reflects the fact that the 2D adatom concentration in the presence of Cu islands at room temperature is much smaller than in the highly dispersed state obtained by low-temperature deposition in an organic matrix. Only at elevated temperatures can a 2D Cu gas with appreciable density be expected, but in the present system the chemical activity of the substrate then comes into play. Moreover, in TMA deposition at elevated temperatures both high molecular diffusivity and rotary motions may interfere.

The major difference in the scenarios is that in the first case TMA molecules experience an environment of Cu adatoms whose density is much higher than that of a 2D condensed submonolayer Cu/Ag(111) system. Hence the mobile Cu adspecies have a high probability of coming into contact with the carboxy groups during the warm-up phase, before they eventually aggregate into islands. By contrast, in the second case the Cu adatom density is in thermodynamic equilibrium with the Cu islands and thus much smaller (the 2D vapor pressure is minute at the employed temperature of 120 K); hence, the probability that deprotonation of postdeposited TMA can be mediated by mobile active sites is strongly reduced. Notably, the atomic steps of the Cu island themselves also do not interfere in a significant way. The sharp distinction between the two cases demonstrates that Cu condensation must be associated with drastically decreased chemical reactivity. Consequently, the rate of deprotonation depends on the Cu adatom density, and Cu adatoms are the decisive element mediating carboxy deprotonation, that is, this mobile species is the true active site in this surface chemical reaction.

Our findings reveal that adatom active sites interfering in a surface chemical reaction may be decisive for reaction pathways and formation of final products. Many catalytic surface reactions are run under reaction conditions for which the density of the intrinsic 2D adatom gas of a catalytically active metal is in the percent range. It is likely that these highly mobile atoms are not only the active sites in deprotonation reactions but also promote many other elementary processes. Our observations thus suggest that thermally activated formation and mobility of active sites is of general relevance in surface chemistry and may bestow a dynamic heterogeneity on catalysts.

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