Single atoms are the most active: Cu-catalyzed carboxylic deprotonation

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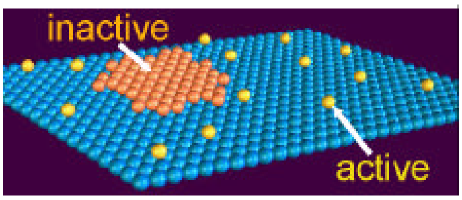
Almost 80 years ago Taylor coined the concept of 'active sites' in heterogeneous catalysis suggesting that adsorbate bond cleavage or formation occurs preferentially at specific arrangements with low-coordinated surface atoms. The identification of such active sites is decisive for the understanding of surface reaction mechanisms, the corresponding rate-limiting steps, and the design of advanced catalysts with improved efficiency or selectivity. Here we demonstrate a new paradigm in this field: the function of highly mobile adsorbed atoms (adatoms) as *dynamic* active sites in surface chemical reactions. In view of the appreciable two-dimensional vapour pressure of many metal catalysts at typical reaction temperatures (>400 K), these findings indicate that mobile adatom deserve general consideration in surface chemical reactions and can bestow dynamic heterogeneity to materials.

Combined scanning tunnelling microscopy and X-ray photoelectron spectroscopy studies reveal that the deprotonation reaction of carboxylic groups of 1,3,5-benzenetricarboxylic acid molecules (trimesic acid, TMA, cf. figure 1A) adsorbed at the Ag(111) surface readily occurs in the presence of a diluted 2-D Cu adatom gas at the surface, while negligible reaction rates occur under similar conditions with Cu in the form of 2-D condensed islands. We demonstrate the function of highly mobile adsorbed atoms (adatoms) as dynamic active sites in surface chemical reactions, as illustrated by scheme 1.



Scheme 1

The hydrogen-bonded open networks can be fabricated by deposition of TMA on a cold substrate (T = 120 K) followed by warming to room temperature, as shown by the STM image in figure 1B. The corresponding model in figure 1C shows how the dimerization of the self-complementary carboxylic groups accounts for the dominating planar honeycomb domains. The XPS data shown in figure 1D prove that the carboxylic groups are protonated.

In order to address the reactivity of coadsorbed Cu, TMA molecules and small concentrations of Cu atoms (0.05 ML) were sequentially deposited on the cold Ag(111) surface (120 K). Under these conditions, the molecules remain protonated at 120K, as evidenced by the corresponding XPS measurements. The chemical activity of the Cu atoms becomes apparent upon increasing the substrate temperature. The spectroscopic data show dramatic changes in the TMA carboxylic groups above 200K. The analysis of the XPS chemical shifts clearly reveals the formation of a tricarboxylate species at 300K, i.e., there is definitely a complete deprotonation of the carboxylic groups which is associated with the presence of Cu adatoms (cf. figure 2A). These findings are substantiated by STM topographic data (reproduced in figure 2B) showing complete inhibition of honeycomb network formation since the underlying H-bond motif is absent. Rather, TMA molecules aggregate in disordered agglomerates containing bright protrusions, which are Cu islands formed in the annealing process. Since carboxylic groups are still present after Cu deposition before the sample warm-up, it is concluded 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 warm-up.

In order to clarify whether the boost of chemical reactivity correlates with the highly dispersed Cu adatoms, control experiments were performed, where Cu was offered in a 2-D condensed form by predepositing the same amount of Cu at room-temperature on the clean Ag surface. Subsequently the substrate was cooled down to 120 K and TMA was added. Following warm-up to room temperature, strikingly the formation of perfect honeycomb structures coexisting with the Cu islands was observed, as shown by the STM image in figure 2C. The underlying hydrogen bonding implies that TMA deprotonation does not occur in the presence of pre-grown Cu islands.

The sharp distinction between the two cases demonstrates that the Cu condensation must be associated with a drastically decreased chemical reactivity. Consequently the deprotonation reaction rate depends on the Cu adatom density, and Cu adatoms are the decisive element mediating carboxylic deprotonation, i.e., this mobile species represents the true active site in this surface chemical reaction. Since the two-dimensional vapour pressure of metals is appreciable at typical reaction temperatures (>400 K), the findings indicate that activation by a mobile adatom gas is of general relevance in catalysis and bestows a dynamic heterogeneity to materials.

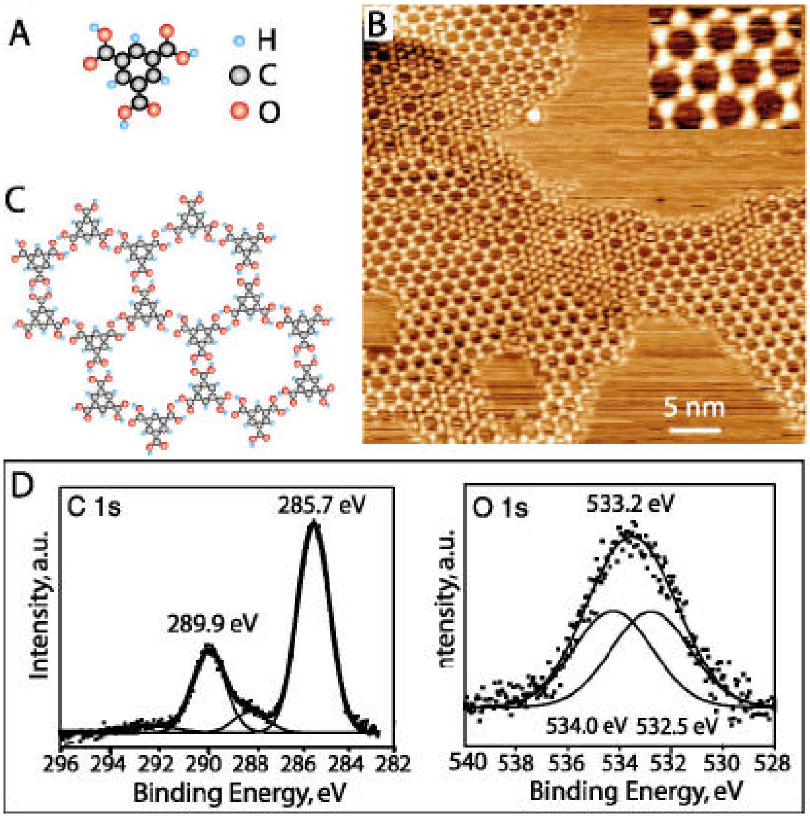


Figure 1. **A** Structural model of the 1,3,5-benzenetricarboxylic acid $C_6H_3(COOH)_3$ (TMA) molecule. **B** Assembly of extended hydrogen-bonded TMA honeycomb networks on Ag(111) following sub-monolayer deposition on the 120 K-cooled substrate and warm-up to room temperature. **C** Model of the hydrogen-bonded nanoporous supramolecular TMA layer with hydrogen-bond mediated dimerization of self-complementary carboxylic groups. **D** XPS data testify the integrity of the organic molecules (photon energy 400 eV for carbon, 670 eV for oxygen spectrum). Indicated are the C 1s position of aromatic ring and carboxylic group, and the convoluted O 1s signal with contributions from carbonyl and hydroxyl groups, respectively.

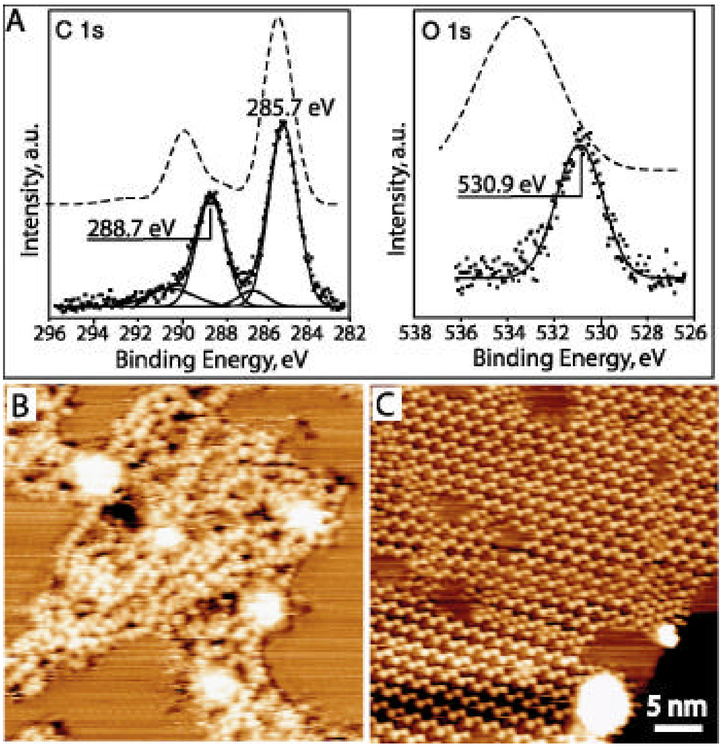


Figure 2. **A** XPS data (solid curves) monitoring the chemical changes occurring in the 300 K warm-up of an intermixed TMA/Cu layer grown at low temperature on Ag(111) (photon energy 400 eV for carbon, 670 eV for oxygen spectrum). For comparison, spectra of the protonated species are shown as dashed 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 120 K co-deposited TMA and Cu are annealed to room temperature. **C** In the presence of pre-deposited condensed 2-D Cu islands deprotonation in warm-up is negligible, and regular hydrogen-bonded TMA honeycomb networks evolve.