In situ observation of the on-surface thermal dehydrogenation of a linear alkane on Pt(111)

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Rising global living standards are fueling a surge in demand for organic chemicals and polymers, including everyday products as detergents or solvents, as well as critical products like medicines or plastics precursors and additives. In this context of ever-increasing demand, alkanes constitute a crucial carbon source for chemical industry. These saturated hydrocarbon chains provide an ideal carbon scaffold to which other functional groups can be added to produce value-added chemicals. However, their inherently inert C(sp^3)-H bonds introduce high energy barriers to the process and reduce the selectivity towards the desired products. For this reason, the thermal dehydrogenation of alkanes, yielding the more reactive alkenes with the mediation of a catalyst, arises as an interesting strategy to unlock the full economic and chemical utility of these otherwise unreactive molecules.

Platinum-based catalysts are among the most widely used materials in chemical industry due to the high selectivity of this metal towards C-H bond cleavage. In this work, we focus our attention on the linear *n*-octane (*n*-C_8H_{18}) deposited on a catalytic Pt(111) model surface with the goal of investigating the thermal dehydrogenation of this medium-length molecule from the fundamental point of view. We profit from the spatial resolution of Scanning Tunneling Microscopy (STM) to characterize the morphology of the dehydrogenated products. On the other hand, for a precise chemical analysis, we employ Synchrotron Radiation X-ray Photoelectron Spectroscopy (SR-XPS) at the SuperESCA beamline in Elettra. The complementary information provided by *ab initio* calculations and STM-image simulation allows for atomistic determination of the dehydrogenation mechanism.

In Fig. 1 we present our main results for a saturated monolayer of *n*-octane after thermal treatment between 77 and 900 K. Our STM and SR-XPS results indicate the existence of three dehydrogenation stages in terms of adsorbate morphology and chemical state. Below 330 K (Fig. 1 a,d,g), STM images show that *n*-octane appears as elongated features that are randomly distributed over the surface mainly following the three main crystallographic directions. The corresponding high-resolution C 1s XPS spectrum (Fig. 1 g) shows four different contributions related to the -CH_3 ends of the molecule (283.4 eV), the inner -CH_2- atoms (283.95 eV) and the remnants of a dense phase that desorbs at 240 – 280 K. Additionally, the simultaneous excitation of the C-H stretching mode upon photoionisation produces a visible vibrational replica of the -CH_2- contribution (284.35 eV). Density Functional Theory (DFT)-based simulations indicate that at this stage *n*-octane physisorbs to the surface without chemical modification, aligned with the high symmetry directions of the Pt(111) and with the carbon backbone plane slightly tilted with respect to the surface. Simulated STM images from this configuration reproduce the experimentally observed features (Fig. 1 d).

After annealing at 330 – 600 K, STM images (Fig. 1 b) show adsorbates with a similar random distribution to the previous stage. However, molecules develop a bright protrusion at one of their ends. In the corresponding C 1s spectrum (Fig. 1 h), we observe the full desorption of the remnants of the dense layer and the transfer of intensity from the -CH_3 component to a new narrow one at 283.7 eV, with a final 1 : 1 intensity ratio. We assign this component with the formation of a C-Pt bond, in agreement with our DFT results. Accordingly, *n*-octane undergoes a highly-regioselective C-H bond cleavage at one of its -CH_3 ends and the radical stabilizes by forming a covalent bond with a Pt atom from the surface. We detect the hydrogen released in the process in Thermal Program Desorption (TPD) experiments. In addition, STM simulations from this chemisorbed configuration reproduce the experimentally observed adsorbate morphology (Fig. 1 e).

Annealing above 600 K results in a drastic change of the adsorbate morphology. The surface appears covered by lobed structures with irregular shapes (Fig. 1 c). In some cases, their sizes surpass that of a single *n*-octane molecule (compare with Fig. 1 a), pointing to molecular aggregation favored by the thermal diffusion of the adsorbates. The C-1s spectrum (Fig. 1 i) shows an intensity reduction of the -CH_2- contributions and an increase of the contribution at 283.4 eV. This is due to the dehydrogenation of some of the inner carbon atoms in the carbon backbone, generating unsaturated double bonds and hydrogen, as detected in TPD experiments. The binding energy of the photoelectrons from C=C and -CH_3 carbon atoms coincides. Our *ab initio* calculations predict a rapid dehydrogenation at the 3rd and 4th C atoms, yielding a double bond between them. The simulated STM images reproduce the morphology of the smallest features observed in the experiment (Fig. 1 f, which correspond to non-aggregated adsorbates.

To sum up, we have investigated the thermal dehydrogenation mechanisms of *n*-octane on a Pt(111) model surface at the atomic scale. The reaction starts from a physisorbed disordered state. In a first step, above 330 K, a C-H bond is cleaved at one of the -CH_3 ends and the molecule chemisorbs forming a C-Pt bond with the surface. At 600 K, diffusion favors molecular aggregation and further dehydrogenation yields unsaturated bonds in their carbon backbone. In our original article, we also provide information about the calculated energy barriers of the proposed reactions and the possibility to reproduce the TPD spectra of the released hydrogen. Our investigations of the surface-catalyzed dehydrogenation of linear alkanes provide new insights into the atomistic mechanisms of this industrially relevant reaction.

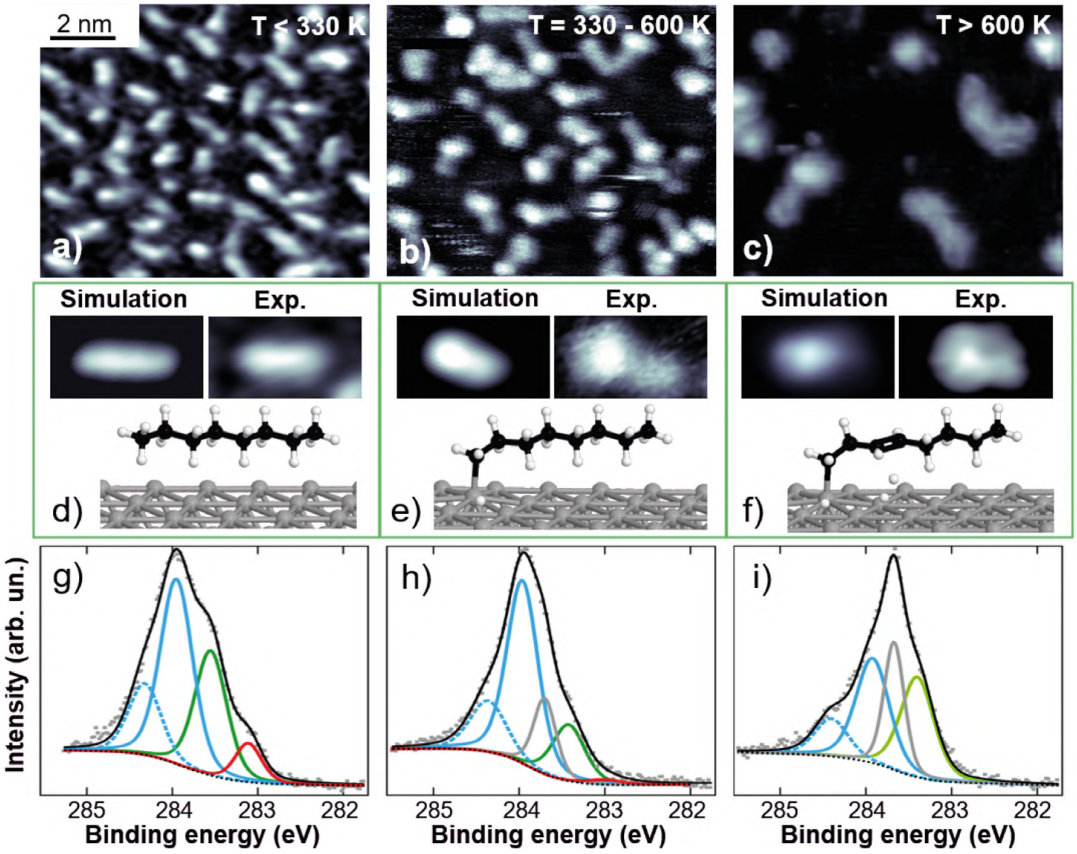

Figure 1. (a) STM images obtained after deposition of *n*-octane at room temperature, after annealing at 400 K (b) and after annealing at 675 K (c). DFT-based simulations of the physisorbed configuration, the chemisorbed configuration, and after the formation of double-bonds are shown respectively in panel (d, e, f). In each case, a simulated and an experimental STM image of an individual molecule/adsorbate are provided for comparison. High-resolution C 1s XPS spectra are displayed in panels (g,h,i).

Acknowledgments

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Original paper

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