Adsorption, cyclo-dehydrogentaion and graphene formation from large molecular precursors on catalytic surfaces

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Surface science techniques have shown their capability to follow in-situ chemical reactions on catalytic surfaces [1,2]. In this talk we will review the main mechanisms and strategies used to create new molecular structures and networks out of polycyclic molecular precursors.

In particular we have studied the adsorption [3], cyclodehydrogentaion [4] and graphene formation [5,6] processes from C60H30 and C57N3H33, achiral polycyclic aromatic hydrocarbons (PAH), on different single-crystal transition metal surfaces by means of thermal under-vacuum annealing. The landing side of the molecule on a Pt(111) surface induces two chiral molecular forms on the surface, as seen by in-situ scanning tunneling microscopy (STM) images. We show that the surface becomes enantioselective "recognizing" the landing side of an individual molecule. Thus, molecules adsorbed "right" or "left"-hand are differently split in two adsorption geometries, accordantly shifted [3]

Moreover, after annealing the adsorbed layer, a highly efficient (~100%) dehydrogenation mechanism leads to a cyclodehydrogenation processes leading to the formation of fullerene C60 and for the first time triazafullerene C57N3 from their corresponding planar polycyclic aromatic precursors by a surface catalyzed process [4]. We have visualized the whole process by in-situ STM, X-Ray Photoemission spectroscopy, thermal desorption spectroscopy and DFT calculations. A 2D layer is formed. This layer is amorphous and weakly bound to the surface.

The process is catalyzed very efficiently by Pt surfaces, which favors dehydrogenation, very poorly by Cu surfaces and it is mostly unsuccessful on Au surfaces. On this last surface a 2D layer is formed. This layer is amorphous and weakly bound to the Au underneath. Finally, extra annealing leads to molecular decomposition and to the formation of multiphase-graphene [5,6], where many different superstructures and Moirés can be found on the surface.

Another question that will be touch is the capability for inducing dehydrogenation reaction of the oxide surfaces. These surfaces when reduced, present an electronic state within the gap, which could catalyze some reaction of large cyclic organic molecules.

References

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Figures
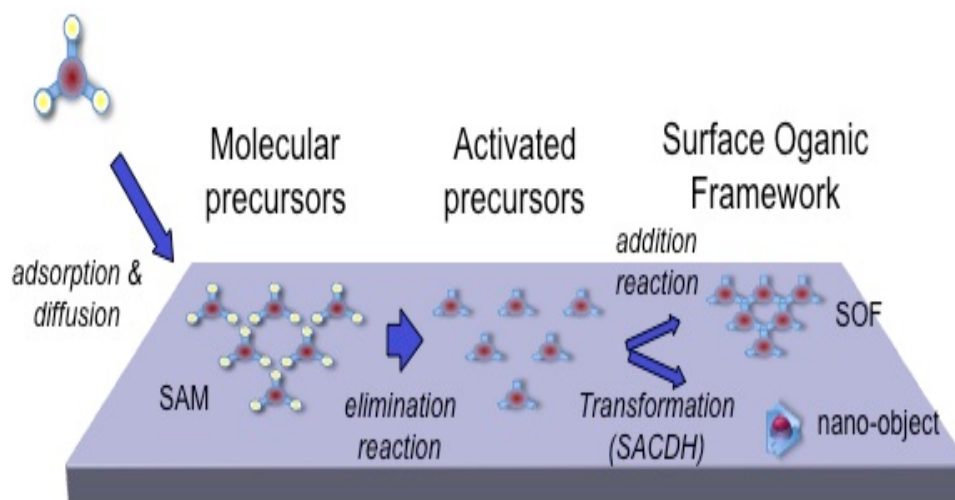
Schematic and simplified representation of an on-surface synthesis process. The deposited molecular precursors arrive to the surface and diffuse on it. In some cases, they could form an ordered SAM, which provides a pre-organization of the system. After a thermal treatment activated species can be formed. These species could lead either to surface organic frameworks (SOF) or being individually transformed into other different molecular species (nano-object), after for example, a surface assisted cyclodehydrogenation (SACDH) reaction.