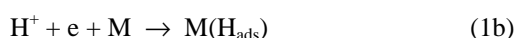


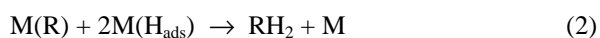
**Towards Molecular-Level Understanding of
Electrocatalytic Hydrogenation.
Part 1. Behavior of Benzene at Pt(111)**

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Electrocatalytic hydrogenation (ECH) involves *in-situ* generation of electro-adsorbed hydrogen, $M(H_{ads})$, by water reduction in basic electrolytes (Eq. (1)) or by proton discharge in acidic electrolytes:



where M represents the electrode surface and H_{ads} is the electro-adsorbed hydrogen species. Following the generation of adsorbed H , the reaction with an adsorbed organic molecule, $M(R)$, takes place (Eq. (2)) [1].



There are numerous advantages resulting from the *in-situ* generation of adsorbed hydrogen such as: (i) the mild hydrogenation conditions (low temperatures, from 20 to 100C, and low pressure, atmospheric or up to a few atmospheres) resulting in higher chemoselectivity; (ii) elimination of the utilization of pressurized molecular hydrogen and associated complex manipulations; and (iii) the possibility of using catalysts that have a low activity in classical catalytic hydrogenation (due to inefficient molecular hydrogen dissociation).

In order to develop highly chemoselective, efficient electrohydrogenation as well as new and active electrocatalysts, it is necessary to: (i) identify the nature of the electro-adsorbed H species active in the process (H_{UPD} versus H_{OPD}) [2,3]; (ii) evaluate the strength and nature of the adsorption of the organic molecule at the electrode, $M(R)$; (iii) understand and identify various experimental factors which affect the adsorption of these species and their mutual interactions at the electrode's surface; and (iv) identify the mechanism of reaction between $M(H)$ and $M(R)$ (Eq. (2)).

As a first step towards the molecular-level comprehension of electrocatalytic hydrogenation, we analyze the behavior of benzene at a Pt(111). In particular, we examine the chemisorption behavior of benzene in the potential region corresponding to the under-potential deposition of H , UPD H . We study the relation between H_{UPD} and benzene surface coverages, and their respective evolution upon the repetitive electrode cycling. The modification of benzene coverage is discussed in terms of possible surface processes that might lead to its hydrogenation.

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