

Catalytic Surfaces under a Pressure of Gas: Insights from Simulations

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Introduction

Heterogeneous catalysis involves two partners: a chemical reaction with reactants, intermediate and products and a solid catalyst with a surface and specific sites where the catalytic reaction occurs. In textbooks, the catalyst is viewed as a more or less rigid substrate, presenting a heterogeneity of structures (terraces, steps, defects). On some of these surface structures (the active site) the catalytic reaction takes place with a large rate. The active site might be designed by a complex chemical procedure, such as the deposit of small clusters on a specific support, or the construction of a well-defined organometallic complex attached to the solid substrate. In any case, in this view, the active site is constructed a priori, before the surface meets the reactants, and is unchanged during the catalytic act.

This approach has been challenged for many years already as being too simplistic. Several catalytic reactions require an activation time, during which the catalytic activity is progressively attained and the surface structure of the catalysts is changed. In this case one should not speak of a catalyst, but of a catalyst's precursor, the active site being constructed in situ during the reaction. Such an approach is appealing but extremely complex to characterize, since in situ (or operando) spectroscopic techniques are required.

Materials and Methods

Theoretical chemistry is an adequate approach to obtain insights in these two complementary faces of heterogeneous catalysis, although it has been until now mainly used to understand how the structure of the surface site can control the catalytic reaction. In this paper, Density Functional theory will be combined with in Situ XPS (at pressure of 1 mbar) in order to study the near-surface region of palladium under various hydrogenation conditions for a set of reacting alkynes and alkenes on a palladium surface.

Results and Discussion

Under the reduced pressure conditions of 1 mbar, alkynes are hydrogenated to alkenes while alkene feeds are transformed to alkanes, just as at more realistic conditions. However the structure of the catalytic surface is strongly dependent on the nature of the reactant. We show that a PdC carbide surface phase is formed during alkyne hydrogenation, while this PdC phase is absent for alkenes. Density functional theory allows to understand the stability of the PdC phase on a model Pd(111) surface, as a function of the carbon chemical potential. The carbon chemical potential in turn is controlled by the type of reactant, which is the source of carbon, and by the temperature and pressure. The stable surface termination is hence dependent in a subtle way on the gas phase composition: For acetylene subsurface carbon formation is thermodynamically favored, while this is not the case for ethene.

Substituents on the molecules and the respective molecule/hydrogen pressure ratio allow modulating this effect.

This PdC surface phase has a strong influence on the hydrogenation activity and selectivity. Experiment shows that the alkyne hydrogenation is selective towards alkene only in conditions where the PdC phase is present. From the calculations we show that the hydrogen and hydrocarbon adsorptions are strongly affected, hence explaining the observed selectivity.

Significance

All the data clearly indicate that the (near-)surface state of the palladium catalyst is a strong function of the experimental hydrogenation conditions. Understanding such interplays will allow designing heterogeneous catalysts to a desired reaction. The present study clearly demonstrates the significance of combining theory and experimentation in bringing new insights on the structure of active site in realistic catalytic conditions and on their specific reactivity

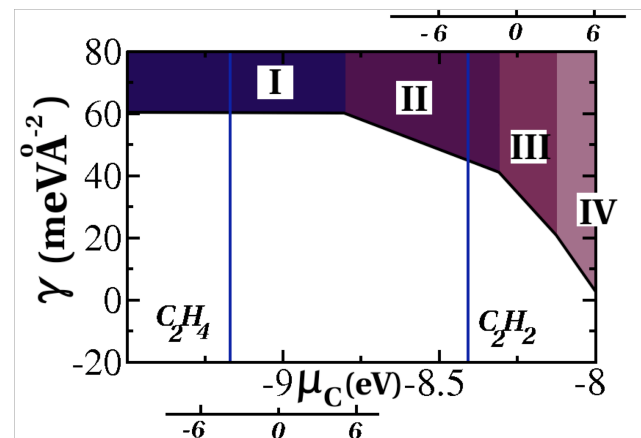


Figure 1. Surface free energy for the most stable surface structures as a function of carbon chemical potential μ_C . Structure **I** is the pure Pd(111) surface, **II** shows a 1/3 ML C content in the first interlayer, **III** a 2/3 ML C content distributed among first and second interlayers, and **IV** a 1 ML C distributed in the first three interlayers. Vertical lines indicate the μ_C value for the acetylene (right line) and ethylene (left line) dissociation into C and H₂, at pressure conditions employed in XPS (10⁻⁴, and 10⁻³ atm for $p_{C_2H_x}$ and p_{H_2}).

References

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2. D. Teschner, J. Borsodi, A. Wootsch, Zs. Révay, M. Hävecker, A. Knop-Gericke, S. David Jackson, R. Schlögl, *Science* **2008**, 320, 86.