

Structure And Reactivity Of Metal Surfaces: Combining First Principles Calculations With Experimental Data.

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The understanding at a molecular scale of the reactive elementary steps on the surface of a solid catalyst is of large importance in the field of heterogeneous catalysis, in the perspective of the knowledge-based design of new and improved catalytic systems. There are however crucial preliminary questions: what is the structure of the catalyst's surface ? Is the chemical nature of the active surface modified in the pressure and temperature conditions of catalysis ?

These surfaces might be of complex nature, especially in the case where two elements are present, as for the surfaces of binary alloys or for the metal surfaces in the presence of a gas phase pressure, e.g. oxygen. Their structural determination from a single method is hence a hard task. In this lecture we will show on two examples how a combination between experimental characterisation and DFT calculations can give important insights in the structure and reactivity of solid catalytic systems. First, the combination of spectroscopy, crystallography, microscopy and total energy calculations allow to construct realistic models of catalytic surfaces. Then quantum theory can provide key information on reaction pathways, transition states, and elementary reaction rates. This opens the way to a detailed kinetic modelling of the reactivity from the elementary reaction rates.

The first example concerns the structure and reactivity for hydrogenation of a model bimetallic catalyst, created by the deposit of Pd layers on a Ni(110) substrate. The nanostructure formed by the deposit was determined by a tight combination of Grazing Incidence X-Ray Diffraction on the Grenoble synchrotron and intensive DFT calculations. The final model relaxes the compressive strain of the Pd layer by formation of a periodic array of edge dislocations initiated at vacancies at the interface (figure 1). It also shows a strong pairing-row reconstruction, hence forming new reactive sites with a Pd metallic coordination not seen on a usual Pd (110) surface [1,2]. The calculated hydrogenation reaction pathways show reduced barriers on these new sites at the deposit surface, and the global kinetic model results in an increased catalytic activity, in very good agreement with the measurements [3].

The second example deals with the structure of a silver catalyst in a pressure of oxygen, and of its activity for ethene epoxidation. The structure of the surface in realistic conditions was obtained by a combination of Scanning Tunneling Microscopy (STM), of simulations of the images and of first principle atomistic thermodynamics. Such an approach allows to calculate the Free energy of the surface as a function of temperature and pressure and to build a phase diagram (figure 2), which shows that in the realistic conditions, a surface oxide is formed [4]. The reactivity of this surface oxide will be detailed [5,6].

References

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Figure 1

Structure of a 4 ML deposit of Pd on a Ni(110) surface (Pd dark, Ni light).

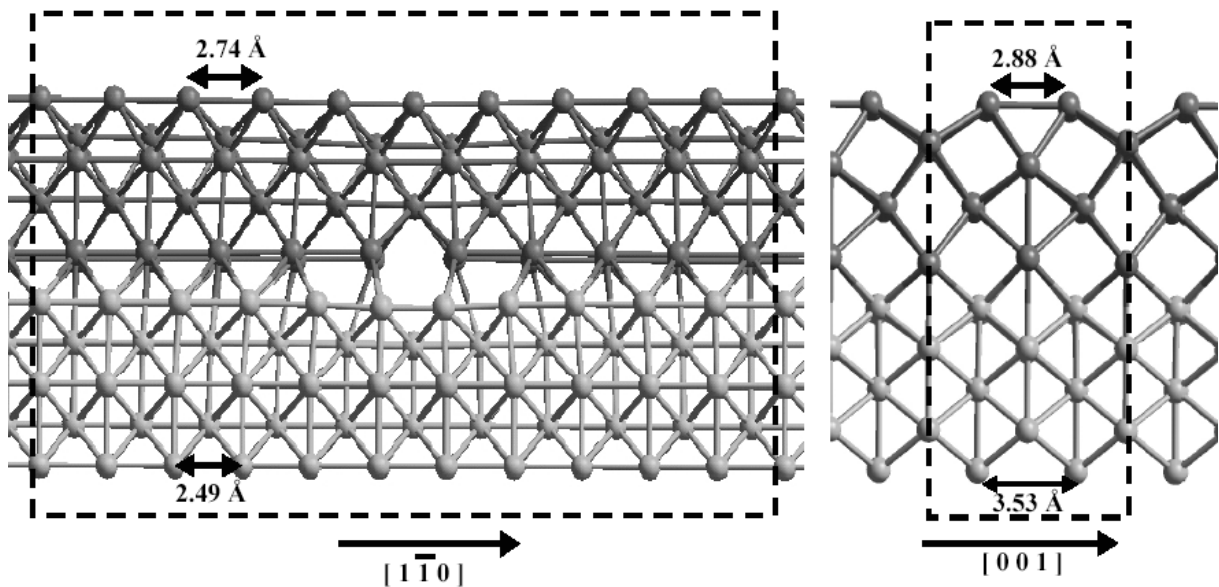


Figure 2:

Thermodynamic diagram calculated by DFT showing the stability domains of:

- bare silver surface (grey)
- silver with oxygen adatoms (yellow)
- thin oxide layer (red)

Note the different surface structures obtained in UHV and in the industrial conditions of the reaction (INDUSTRY).

