

# Rational Catalyst Design Applied to the Selective Hydrogenation of Acetylene

Felix Studt<sup>1,2</sup>, Frank Abild-Pedersen<sup>1,2</sup>, Thomas Bligaard<sup>1</sup>, Rasmus Z. Sørensen<sup>3</sup>,  
Arkadii Kustov<sup>3</sup>, Claus H. Christensen<sup>3</sup>, Jens K. Nørskov<sup>1\*</sup>

<sup>1</sup>Center for Atomic-scale Materials Design, Department of Physics, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

<sup>2</sup>Computational Materials Design ApS, DK-2800 Kgs. Lyngby, Denmark

<sup>3</sup>Center for Sustainable and Green Chemistry, Department of Chemistry, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

\*norskov@fysik.dtu.dk

## Introduction

Solid surfaces are used extensively to catalyze chemical transformations in industrial production, in environmental processes, and in energy conversion.[1] It has long been the ambition of research in heterogeneous catalysis and in surface science to develop methods that would allow the design of catalysts on the basis of insight. In particular, it would be desirable if one could use quantum chemical methods to perform a first screening of possible catalysts for a given reaction, since that would be considerably less demanding than the usual laboratory methods involving synthesis, characterization and test of new materials. There has been a few attempts at using theoretical methods to guide the search for better catalysts, but progress is hampered by the demand for a large number of high-accuracy calculations for complex systems. We introduced a new catalyst screening strategy which allows us to use a single descriptor to obtain an overview of reactivity trends. We illustrate the approach by applying it to the identification of new interesting catalysts for the selective hydrogenation of acetylene.[2]

## Materials and Methods

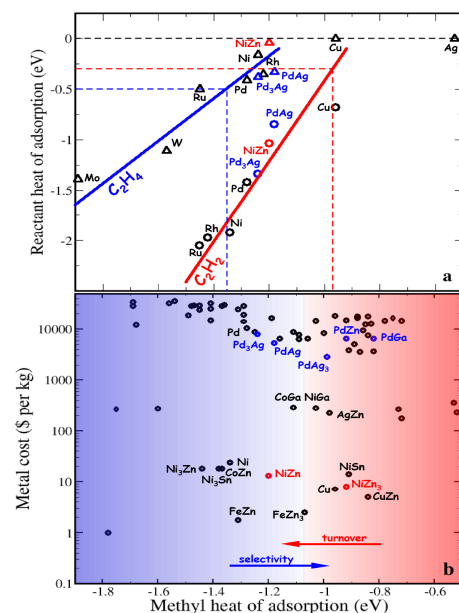
The surfaces in this study are modeled by a (2x2) surface unit cell with a slab thickness of three layers in the direction perpendicular to the surface. The RPBE functional[3] in the general gradient approximation is used to describe exchange and correlation effects. The method and setup of the density functional theory calculations are described in ref [4].

## Results and Discussion

In an effort to identify selective hydrogenation catalysts based on less expensive and more available metals than the industrially used Pd-Ag alloys, density functional theory calculations were performed that identified relations of heats of adsorption of hydrocarbon molecules and fragments on metal surfaces. This analysis not only verified the facility of known catalysts but identified Ni-Zn alloys as alternatives. Experimental studies demonstrated that these alloys were indeed selective for the hydrogenation of acetylene.[2]

## Significance

We show that one can use computational screening procedures for the discovery of new catalyst materials.



**Figure 1(top)** Adsorption energies of acetylene( $C_2H_2$ ) and ethylene ( $C_2H_4$ ) plotted against the binding energies of methyl ( $CH_3$ ). The adsorption energies are defined as the total energy of the adsorbed species minus the total energy of the surface and minus the total energy of the species in vacuum. The solid lines show the predicted acetylene(red line) and ethylene(blue line) adsorption energies from scaling. The dotted lines define the interesting region where the ethylene binding energy is less than the barrier for further hydrogenation(blue) and where the reactivity of the acetylene hydrogenation step equals  $1 \text{ s}^{-1} \text{ site}^{-1}$  (red). **(bottom)** Price of the investigated binary intermetallic alloys in 2006 prices plotted against the methyl binding energies. Gradients have been added to show the smooth transition between regions with low and high selectivity(blue) and high and low reactivity(red).

## References

1. Somorjai, G. A. in "Introduction to Surface Chemistry and Catalysis", New York, 1994.
2. Studt, F., Abild-Pedersen, F., Bligaard, T., Sørensen, R.Z., Christensen, C.H., Nørskov, J.K. *Science* 320, 1320 (2008).
3. Hammer, B., Hansen, L.B., Nørskov, J.K. *Phys. Rev. B* 59, 7413 (1999).
4. Bligaard, T., Nørskov, J.K., Dahl, S., Matthiesen, J., Christensen, C.H., Sehested, J. *J. Catal.* 221, 206 (2004).