



Surface Science Perspectives

The unhappy marriage of transition and noble metal atoms: A new way to enhance catalytic activity? (A perspective on: “When adding an unreactive metal enhances catalytic activity: NO_x decomposition over silver–rhodium bimetallic surfaces” by O.R. Inderwildi, S.J. Jenkins, D.A. King)

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Coinciding with the birth of modern single-crystal surface science in the 1960s was the formal birth of density-functional theory (DFT) for solving the electronic structure problem. Since then and, in particular, since the pioneering studies of Lang and Kohn [1], DFT has proved an important ally to experimental surface science in helping to advance understanding of the electronic structure and catalytic activity of metal surfaces. Although, far from a panacea for all physical problems in this domain (or any other), no other theoretical approach has provided as much basic understanding of the electronic structures and properties of metal surfaces. Notable, more recent, contributions to our understanding advanced by the application of DFT have been the identification of trends in surface energies, work functions and surface reconstructions (see, for example, Refs. [2,3]), the recognition of the centre of a metal's *d* band as a useful descriptor of many catalytic activity problems [4], the identification of Brønsted–Evans–Polanyi relationships between activation and reaction energies for dissociative adsorption reactions [5,6], and the realization of the possible role thin surface metal-oxide films play in heterogeneous catalysis [7,8]. In an article in this issue of Surface Science Inderwildi, Jenkins, and King extract insight from the results of DFT calculations into a new and potentially important way of controlling the catalytic activity of transition metal surfaces [9]. Specifically, they reveal, through studies of NO on Rh and Rh–Ag alloy surfaces, that the reactivity of a transition metal surface alloyed with inert noble metal atoms can exceed that of the original transition metal surface. Of course alloys of transition and noble metals are not new to heterogeneous catalysis (see, for example, Refs. [10–15]), nor is the suggestion that small increases in adsorption energy may be observed on such surfaces [11,16], but the finding that an adsorbate can bind *much* more strongly to the noble-transition metal bimetallic than it can to either of the monometallic substrates is new, hitherto unappreciated, and of potential importance to many future catalytic studies.

The background to Inderwildi's work is the enhanced catalytic activity of Rh–Ag particles in NO reduction catalysis reported by Kotsifa et al. [17]. Specifically, Kotsifa et al. observed a significant increase in the selective catalytic reduction of NO by propylene when a few percent of Ag was added to their supported Rh catalyst particles. Inderwildi et al. addressed this issue through the application of DFT to the adsorption and dissociation of NO on (111) surfaces of Rh, Ag, and Rh–Ag alloys. Certainly the models employed are simplified versions of Kotsifa's catalytic system, a necessary limitation of computationally expensive electronic structure calculations. This is of little concern, however, since the conclusions reached by Inderwildi et al. have relevance far beyond the specific catalytic system considered. Their key finding is

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that NO molecules adsorb significantly more strongly on Rh–Ag surfaces than they do on either pure Rh or pure Ag surfaces; increases in adsorption energy compared to pure Rh on the order of 20–40% are found depending on the substrate model and exchange-correlation functional employed. This indicates that the properties of the alloy surface are not a mixture of the properties of Rh and Ag, but instead genuinely bimetallic in character. There are always question marks about the absolute accuracy of DFT predictions of adsorption energies (see, for example, Refs. [18,19]). However, the relative enhancement in the adsorption energy, predicted with two different exchange-correlation functionals, is at ≥ 0.5 eV per molecule a comfortably large increase to be beyond legitimate doubt. The authors also find that the barrier to NO dissociation through a transition state involving just Rh atoms at the alloy surface is reduced compared to the dissociation barrier through an equivalent transition state on pure Rh(111), again pointing to an enhanced reactivity of the alloy surface.

An explanation for the observed behavior could be found by the authors through analysis of the electronic structures that lay behind their density-functional calculations. Specifically an increase in the Rh d densities of states just below the Fermi level was identified as being important to the enhanced reactivity of the bimetallic surfaces. And, indeed, a correlation between the computed adsorption energy on the various substrates investigated and the number of Rh d states within a window of 2 eV below the Fermi level was identified. The crucial build-up in Rh d states, it is argued, arises because the Ag atoms interrupt the pattern of d orbital overlap between the Rh atoms. Implicit in this argument is the assumption that Rh atoms bond less effectively to Ag atoms than they do to other Rh atoms. This seems reasonable since the Ag d band rests several eV below the Rh d band. Thus, in somewhat abstract terms, the Rh atoms in the bimetallic surface are less happy, i.e., less stable, than Rh atoms at a pure Rh surface and can be thought of as having a reduced “effective coordination”, resembling in some respects Rh atoms at steps or other defect sites. The effect of strain in the lattice due to the presence of atoms of different sizes is well known to be of importance to the reactivity of alloy surfaces (see, for example, Refs. [16,20]). However, it is interesting to note that Inderwildi et al. demonstrate that strain effects alone are not sufficient to explain their observations.

Inderwildi’s paper is also important because it raises questions that are likely to prompt numerous follow-up studies. For example, it will be interesting to see if the observed behavior extends to other adsorbates and other transition-noble metal bimetallics. Inderwildi et al. report already a step down this road with results for NO on a RhCu surface and, indeed, NO also bonds more strongly to this surface than it does to pure Rh. Along these lines one can envisage a whole host of other studies involving various atomic and molecular adsorbates where small or moderate changes in adsorbate-substrate binding may have an important tailored impact on specific catalytic systems. Indeed, recent reports of high-throughput density functional studies of transition metal alloy catalysts are a potential *existing* source of such information (see, for example, Refs. [11,13,21]). In addition, model systems with lower surface concentrations of noble metals in the bimetallic alloy – computed in larger unit cells to those employed by Inderwildi et al. – would be of interest since these would allow the spatial dependence of this effect to be explored. It is not yet known how long range these effects are and how far away from a noble metal impurity “normal” reactivity of the substrate transition metal atoms is recovered. In this context I refer the interested reader to a related discussion recently given by Greeley and Mavrikakis [22]. Other issues to explore in more detail in the future are the influence of strain with regard to the observed behavior and its impact upon surface segregation. Finally, if one were able to construct a substrate resembling one of those explored by Inderwildi et al. with, for example, a low concentration of surface substitutional noble metal atoms in an otherwise perfect transition metal surface, then the enhanced binding of adsorbates to the substrate would be observable with any number of experimental surface science probes (infra-red spectroscopy, temperature programmed desorption, photoelectron spectroscopies, scanning tunneling microscopy, etc.). With scanning tunneling microscopy, for example, it may be possible to observe adsorbates congregating at the transition metal atoms adjacent to the noble metal impurities.

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