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When adding an unreactive metal enhances catalytic activity: NO_x decomposition over silver–rhodium bimetallic surfaces

O.R. Inderwildi *, S.J. Jenkins, D.A. King

University of Cambridge, Department of Chemistry, Lensfield Road, Cambridge CB2 1EW, United Kingdom

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Abstract

Recent experiments indicate unexpectedly high catalytic activity for decomposition of NO_x species over Ag–Rh nanoparticles, but the crucial role played by the coinage metal remains unclear. We have therefore performed *ab-initio* density functional calculations aimed at elucidating key features of NO surface chemistry on Ag, Rh, and Rh–Ag alloy substrates. Through investigation of thermochemistry and reaction barriers, and analysis of the alloy density of states, we explain the paradox that addition of an unreactive coinage metal can *radically enhance* the activity of a transition metal catalyst.

Keywords: Density theory calculations; Bimetal; Alloy; NO decomposition; Emission control catalysis

Legislation in industrial countries is increasingly aimed at reduction of green house gas (GHG) emissions, owing to the severe environmental problems the world has to face if the atmospheric GHG concentration keeps rising [1]. Internal combustion engines, mainly in automobiles, are one of the major emission sources of the key GHG CO_2. A possibility to reduce the CO_2 emission of automotive engines is to increase their fuel-efficiency, which can be achieved by operating under lean (i.e. oxygen-rich) conditions. However, under these oxygen-rich conditions it is difficult to reduce pollutants such as nitrogen oxides (NO_x, $x = 1,2$). A catalyst that decomposes harmful NO_x gases, and converts them into harmless dinitrogen (N_2) in the presence of excess oxygen, would therefore be highly desirable.

Rhodium-based catalysts have in general a high potential of fulfilling this goal [2–4] and, furthermore, an distinctively enhanced catalytic NO_x reduction activity of silver–rhodium nanoparticles was reported recently by Kotsifa et al. [5]. This motivated us to study the surface chemistry of NO on different silver–rhodium bimetals/alloys. Whilst it has been shown recently that coinage metals can be catalytically active when they are supported by oxides [6–8], or promoted by electronegative co-adsorbates [9], little is known about the influence of coinage metals on the reactivity of platinum-group metals. This, combined with the relatively low cost of coinage metals compared to reactive metals such as rhodium, makes coinage/non-coinage bimetallic catalysis an important topic. It seemed to us initially puzzling that addition of a less-reactive metal to an already active metal should enhance its activity. It has, however, been hinted that large contents of coinage metal (e.g. 75%) may very slightly increase the heat of adsorption of CO on platinum-group metals [10], but crucially the influence of coinage metals on dissociation barriers is not discussed in those early studies.

In this work, the decomposition of NO on rhodium, silver and various bimetallic rhodium–silver systems was studied by means of density functional theory (DFT) calculations. The decomposition of NO is the crucial step in the catalytic reduction of nitrous oxides since it is rate determining: The conversion of nitrous dioxide can be neglected

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* Corresponding author. Fax: +44 1223 336536.
E-mail address: ori20@cam.ac.uk (O.R. Inderwildi).

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since it is known to deoxygenate readily on rhodium surfaces. Other important steps in the catalytic cycle of the NO_x reduction, such as the removal of oxygen by oxidation of CO and hydrocarbons have activation barriers far below the barrier for N–O cleavage [11].

DFT calculations herein were carried out using the CASTEP computer code [12] and the generalised gradient approximation (GGA) as proposed by Perdew et al. was applied [13] (henceforth referred to a PW91), combined with Vanderbilt ultrasoft pseudopotentials [14]. Adsorption energies were also calculated using the revised GGA-PBE (RPBE) functional as proposed by Hammer et al. [15]. Results presented here were obtained from spin-unpolarised calculations, but tests with spin-polarised functionals indicate that this is perfectly adequate for the present system (i.e. when spin-polarised electronic configurations were employed for the initial step in the self-consistency cycle, the spin degree of freedom spontaneously relaxed to an unpolarised configuration).

The planewave basis set was truncated at a kinetic energy of 340 eV and the Brillouin zones was sampled with a k-point mesh with a k-point spacing of 0.05 Å^{-1} as generated by the Monkhorst–Pack scheme [16]. The surface was modelled using a four-layer slab with the lower three layers fixed at their positions in the bulk and the uppermost layer mobile. Periodic boundary conditions were used to model an extended surface. A 10-Å vacuum region was placed between the periodically-repeated slabs to ensure that the adsorbate and the subsequent slab do not interact. The transition state of the surface reaction was located on the potential energy surface (PES) by performing linear synchronous and quadratic synchronous transit calculation with conjugate gradient refinements [17]. All transition states were converged using this procedure until a root-mean-squared gradient of less than 0.15 eV/Å was reached.

The primitive cells of bulk Rh, bulk Ag and a model Rh_3Ag alloy were optimised; the computed lattice constants of 3.85 Å for rhodium and 4.12 Å for silver are in good agreement with the experimental values (Rh: 3.80 Å, Ag: 4.09 Å). The lattice constant of the Rh_3Ag alloy is a hybrid of the two constituent metals with a distance of 3.91 Å From these optimised bulk structures {1 1 1} surfaces were cleaved. All other bimetals were pre-optimised as surfaces with the lowest layer constrained and the uppermost three layers mobile. After the optimisation only the uppermost was mobile for subsequent optimisations relevant to adsorption and reaction of NO on these surfaces.

On (1×1)-$Rh_3Ag\{111\}$, NO is most stable in the fcc-threefold positions; the calculated PW91 adsorption energy is extraordinarily high at 3.70 eV in case of the fcc position; the hcp-threefold site is only slightly less stable with an adsorption energy of 3.56 eV. The atop position is the least stable position with an adsorption energy of 2.37 eV. However, in comparison to other metals this adsorption energy is still very high. A stable bridged species could not be identified, nor could a stable position in which NO is even partially bonded to Ag. In comparison, the calculated PW91 adsorption energy of NO on a (2×2)-Rh{1 1 1}[1] elementary cell is 2.63 eV. The adsorption energy is hence 41% higher on the alloy than on the pure rhodium, according to our DFT calculations. The adsorption energy of NO on Ag{1 1 1} is also significantly lower (0.38 eV/PW91) than on the alloy. These results indicate alloy properties differing radically from a simple interpolation of those of its constituents. It is known, however, that the PW91 functional often overestimates molecular adsorption energies. We therefore recalculated the adsorption energies using the RPBE functional, which is known to produce more accurate heats of adsorption [15], based on the geometries derived from optimisations using PW91. It appears that the resulting difference is not so high as for PW91, but the bonding is still significantly stronger on the alloy (Ead is 27% higher on Rh_3Ag than on Rh, or 3.29 eV versus 2.59 eV). Moreover, the adsorption energy on the alloy is once again much higher than on either of the pure metals. This supports our assertion that the theoretically-generated alloy exhibits genuine bimetallic properties, different from the properties of its constituents. Since it is known that in coinage/platinum-group bimetals the coinage metal segregates to the surface, a further bimetal ($Rh_{15}Ag\{111\}$) with a silver content of 25% in the top layer and 0% in the lower layers (6.25% overall silver content) was generated. Again in this case the adsorption energy is significantly increased in comparison to the pure rhodium surface (PW91: 24.4%, RPBE: 21.1%). An overview of the different energies is given in Table 1.

But it is not only the adsorption properties of the bimetallic species that differ from the pure metals; the *reactivity* of these bimetallic systems is also significantly altered. The transition states of NO decomposition were calculated, starting from the NO adsorbed in an fcc-threefold position on Rh{1 1 1}, $Rh_3Ag\{111\}$ and $Rh_{15}Ag\{111\}$. Two different decomposition pathways are possible: (A) one in which the oxygen atom is located in an hcp-threefold position after decomposition and, (B): one in which the oxygen atom is ultimately located in an fcc-threefold position.

Pathway A: In pathway A the oxygen atom is located in an almost Rh-atop position in the transition state (Fig. 1a). Table 1 gives an overview over the molecular and dissociative adsorption energies as well as the activation barriers and energies of reactions, the most exothermic/least endothermic reaction and the lowest activation barrier are printed in bold. It can be seen from this table that the decompositon via path A is thermochemically as well as kinetically more likely on either silver–rhodium bimetal than on pure rhodium according to both PW91 and RPBE calculations. Pure silver is neglected in this comparison, because it is well-known that NO decomposition activity is significantly weaker on this metal [18]. Again, the bimetallic surface seems to be more active than either of the equiv-

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[1] The (2×2) primitive cell of Rh{1 1 1} contains four surface atoms and is therefore equivalent to the (1×1) primitive cell of $Rh_3Ag\{111\}$ which consists of three rhodium and one silver atom.