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CO adsorption on a Au/Ni(111) surface alloy—a DFT study

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Abstract

The adsorption of CO on a Au/Ni(111) surface alloy has been investigated using *ab initio* density-functional calculations. We show that, in contrast to a Au adatom on a Ni(111) surface, a Au impurity binds CO only very weakly. In addition, the impurity induces a reduction of the adsorption energies which is strictly localized to its immediate neighbourhood. The consequences for possible reaction scenarios are discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The modification of the chemical reactivity of a metal by surface-alloying with a second element, with the aim of improving the catalytic properties of the material, is a timely and challenging field of research. Gold-doped Ni surfaces have received much attention since the development of a novel steam-reforming catalyst with improved resistance against carbidization of the surface [1]. However, the material continues to be of timely interest, as demonstrated by the recent work of Lahr and Ceyer [2] on CO oxidation on Au/Ni surface alloys, and the studies of Vestergaard *et al* [3] and Zhdanov *et al* [4] on CO-mediated removal of Ni atoms from the topmost layer of a Au/Ni(111) surface alloy.

Au and Ni are immiscible in the bulk, due to a substantial size mismatch of about 16% (the nearest-neighbour distances in face-centred cubic Au and Ni are 2.88 and 2.49 Å, respectively [5]). Hence the central questions are under which conditions surface alloying can occur, and further, how the presence of Au adatoms on the surface or of Au atoms in substitutional sites in the surface layer modifies the adsorption properties. Very recently, we have presented an *ab initio* density-functional study of surface alloying and CO adsorption on Au/Ni(111) [6]. A first important result of this study was that alloying Au into a Ni(111) surface (exchanging a Au adatom against a Ni atom from the surface layer) is an activated endothermic process with an activation energy of 1.7 eV and a heat of reaction of 0.44 eV. If surface alloying

takes place, it is driven by entropic effects. Because of the higher stability of the adatom over an impurity atom, CO adsorption was studied for a Au adatom on Ni(111). The main result was that reduction of the adsorption energy is restricted to the immediate vicinity of the Au adatom: at an adatom concentration of 0.1 monolayer (ML), the impurity-induced reduction of the adsorption energy is smaller than 0.2 eV/molecule for 44% of the hollow sites able to accommodate a CO molecule and smaller than 0.5 eV/molecule for 77% of all sites. On the other hand, the Au adatom binds CO much more strongly than a Au(111) surface and represents a local potential-energy minimum.

In the present work we extend these investigations to a Au impurity in a substitutional site on a Ni(111) surface. This is motivated by the fact that a number of experimental studies suggest the simultaneous presence of adatoms and substitutional impurities on a Au-doped Ni surface [7–10]. This phenomenon is closely related to the competition between short-range order and phase separation in bulk Au–Ni alloys [11–13]: chemical interactions favour ordering based on heterocoordination of Au by Ni; strain-induced interactions drive phase separation.

CO adsorption on Au/Ni(111) surface alloys has been studied both theoretically and experimentally. On the basis of temperature-programmed desorption studies, Holmblad *et al* [14] conclude that the binding energy of a CO molecule is reduced by about 0.3 eV/molecule as the Au concentration in the surface layer increases from 0 to 0.7 ML. Vestergaard *et al* [3] performed DFT calculations of CO adsorption for Au/Ni(111) surface alloys with different Au concentrations and concluded that Au atoms bind the CO about 1 eV more weakly than the Ni atoms, but stopped short of analysing the potential-energy surface for CO adsorption. This is precisely the aim of our study.

2. Methodology

Our calculations have been performed using the Vienna *ab-initio* simulation package VASP [15, 16]. Electronic exchange and correlation are described in the generalized gradient approximation, using the functional proposed by Perdew, Burke and Ernzerhof (PBE) [17]. The plane-wave basis-set contained a component with a kinetic energy of $E_{\text{cut}} = 400$ eV. The substrate was modelled by slabs consisting of four nickel layers with a surface periodicity of $p(3 \times 3)$, separated by about 20 Å of vacuum. The upper two layers of the surface have been allowed to relax, while the remaining layers were fixed at their bulk-like positions. A single Au atom substituted one Ni atom from the surface, and a single CO molecule was adsorbed per surface cell; this yields a coverage of 0.11 ML of CO molecules. For all further details we refer to our previous work (which is hereafter referred to as I) [6].

3. Results and discussion

The geometry of the Au-doped surface has been described in detail in I. Due to its much larger size, the centre of the substituted Au atom is located about 0.5 Å above the average location of the Ni atoms in the surface layer and the three nearest-neighbour Ni atoms relax slightly outwards. For the mapping of the potential-energy surface of CO on the alloy surface, the lateral coordinates of the C atom were fixed at the high-symmetry sites (hollow, bridge, on-top) defined in figure 1, while the height of the CO molecule, its angles relative to the surface normal, and the coordinates of the Ni atoms in the two top layers were allowed to relax. Table 1 compiles the adsorption energies, CO bond-lengths and height of the C atom of the molecule relative to the Ni atoms, calculated for all hollow (fcc and hcp), bridge, and top sites in the (3×3) surface cell.

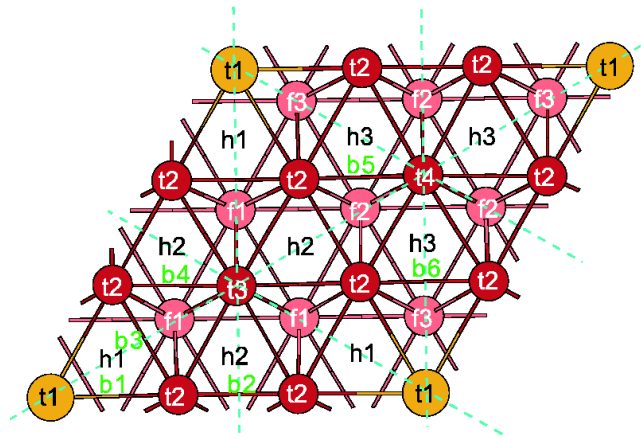


Figure 1. The $p(3 \times 3)$ surface cell used for studying the adsorption of CO in the vicinity of a substitutional Au impurity (located at position t1) in the Ni(111) surface. The figure serves to define the nomenclature for the sites for which the adsorption energy and geometry of CO has been calculated. The dotted lines indicate the mirror symmetries of the surface.

Table 1. CO adsorption in the vicinity of a substitutional Au impurity in a Ni(111) surface: adsorption energy (E_{ads}), change of adsorption energy relative to a clean Ni surface (ΔE_{ads}), C–O bond-length (d_{CO}), and height of the C atom above the Ni surface ($z_{\text{Ni-C}}$).

Site	E_{ads} (eV)	ΔE_{ads} (eV)	d_{CO} (Å)	$z_{\text{Ni-C}}$ (Å)
f1	2.09	−0.04	1.195	1.31
f2	2.16	+0.03	1.193	1.32
f3	1.17	−0.96	1.187	1.41
h1	1.18	−0.95	1.187	1.41
h2	2.16	+0.03	1.193	1.33
h3	2.10	−0.04	1.194	1.31
b1	0.96	−1.01	1.176	1.45
b2	2.01	+0.04	1.184	1.43
b3	1.81	−0.16	1.187	1.42
b4	2.00	+0.03	1.186	1.41
b5	2.00	+0.03	1.185	1.41
b6	1.82	−0.15	1.187	1.41
t1(Au)	0.36		1.154	2.00 ^a
t2	1.61	+0.00	1.163	1.74
t3	1.70	+0.09	1.162	1.73
t4	1.69	+0.08	1.162	1.74

^a Height of the C atom above the Au impurity.

The reference values for the adsorption energy are the binding energies of CO on a clean Ni(111) surface (2.13 eV in fcc or hcp hollows, 1.97 eV in bridge, and 1.61 eV in top sites). The lowest adsorption energy of $E_{\text{ads}} = 0.36$ eV is calculated for a CO molecule on top of the Au atom. This is very close to the experimental adsorption energy on a Au(111) surface of $E_{\text{ads}} = 0.40$ eV, and to the value of 0.32 eV calculated by Gajdos *et al* [18] (note that in this paper a slightly different GGA functional has been used—but the differences in the adsorption energies calculated with the PBE functional used in our study and the Perdew–Wang [19] functional used by Gajdos and Hafner never exceed a few 0.01 eV), but much

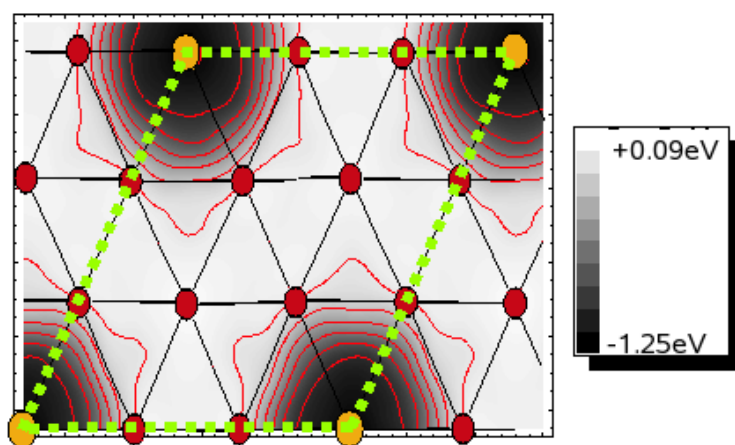


Figure 2. Contour plot of the impurity-induced changes of the adsorption energy of CO in the vicinity of a substitutional Au atom in a Ni(111) surface. The contour interval is 0.2 eV; the last contour line around the impurity is drawn for $\Delta E_{\text{ads}} = 0$.

lower than the binding energy of CO on a Au adatom on Ni(111) ($E_{\text{ads}} = 1.16$ eV). The CO molecule adsorbed on the Au atom is located 2.00 \AA above the metal atom—this shows that in this position it is only weakly physisorbed. At the bridge-sites connecting the impurity to the nearest Ni neighbours (b1), the adsorption energy is 0.96 eV, i.e. reduced by 1.01 eV compared to a bridge position on a clean Ni(111) surface; on the hollow sites h1 and f3 surrounding the impurity the adsorption energy is 1.18 and 1.17 eV, respectively, corresponding to a reduction by 0.96 eV. At the bridge sites next to these hollows (b3, b6) the influence of the impurity is already much weaker (the adsorption energy is reduced by only 0.15 eV); on all other sites the impurity-induced change in the adsorption energy varies only between -0.04 and $+0.09$ eV. On the sites with the largest distance from the impurity, the adsorption energies are even slightly enhanced (as already noted in the presence of a Au adatom). The impurity-induced changes in the adsorption energies are summarized in figure 2 in the form of a contour-line plot—this demonstrates that the effect is strongly localized.

The changes in the adsorption energies are accompanied by small changes in the adsorption geometry. In contrast to the situation with a Au adatom (where CO atoms adsorbed close to Au undergo a strong tilting), on the surface alloy CO is always adsorbed in a nearly upright position. Only at the sites b1 linking the Au atom to its nearest Ni neighbours is the adsorbed CO molecule tilted 13° from the surface normal towards the Au atom. In the threefold hollows surrounding Au (h1, f3) a very weak tilting of 3° – 5° away from the impurity is observed. For adsorption in a threefold hollow, the reduction of the binding energy is accompanied by a change of the height of the C atom above the surrounding Ni atoms by up to 0.1 \AA ; on the bridge and top sites the variation is distinctly smaller. Changes in the CO bond lengths are rather modest.

A further difference between the potential-energy surface of CO on a Ni(111) surface with a Au adatom and on a Au/Ni(111) surface alloy is that a CO molecule adsorbed on an adatom sits in a local potential-energy minimum, surrounded by barriers of about 0.28 eV located at the top and hollow positions surrounding the adatom (see I for details). In contrast, a CO molecule adsorbed on a Au impurity occupies a global maximum on the potential-energy surface and there is no barrier against diffusion to a hollow site, where it is strongly adsorbed. This is illustrated in figure 3 for a diffusion path along the long diagonal of the cell shown in figure 1.

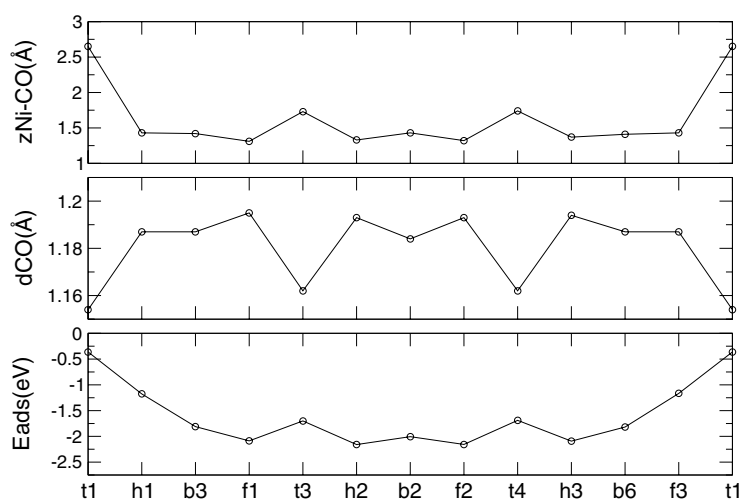


Figure 3. Potential-energy profile, Co-bond length and adsorption height of a CO atom adsorbed on a Au/Ni(111) surface alloy, along a path connecting two Au atoms—cf figure 1.

Note that also far from the impurity the barrier for diffusion between two hollows across a bridge is only 0.16 eV, as on the clean Ni surface.

Hence any molecule impinging on the alloy surface close to the impurity will immediately diffuse to the strongly attractive sites far from the impurity. As shown in figure 2, out of the 18 hollow sites in our surface cell, six will be blocked for CO adsorption by the presence of the Au impurity such that the effective coverage (calculated with respect to the available binding sites in the threefold hollows) is increased from 0.11 to 0.166 ML. As analysed in detail by Eichler [20], at higher coverages CO/Ni(111) forms superstructures based on hollow- and bridge-adsorbed CO. It is also important to emphasize that the difference between the binding energy of CO at adatoms and at impurities leads to a further stabilization of Au adatoms over surface impurities at higher partial pressures of CO.

It is also interesting to explore the electronic origin of the striking differences of the adsorption behaviour of a Au atom in adatom and impurity sites. Figure 4 shows the electronic density of states (DOS) of a Au(111) surface, of a Au adatom and of a Au impurity on Ni(111). For the adatom the change relative to the Au surface consists mainly in a pronounced band-narrowing; the centre of gravity of the d-band DOS remains essentially at the same binding energy of about 3 eV. For the surface impurity the much stronger hybridization with the Ni substrate leads to a strong repulsion between the d bands; the peak in the d DOS of the Au impurity is shifted to a binding energy of 5 eV. A further important difference is that while on the pure Au surface and for the Au impurity in a Ni surface the Au d states are very efficiently screened by the s electrons spilling out of the surface, the d states of the adatom are only weakly screened and able to provide a covalent binding of the molecules via the familiar mechanism of $5\sigma-d_{z^2}$ and $2\pi^*-d-t_{2g}$ interactions (see [18] and [20] for a more detailed discussion). Hence while for the adatom the presence of a hybridization-induced d-DOS close to the Fermi energy leads to an at least partially covalent character of the Au–CO binding, due to the d-band shift of the impurity the binding mechanism consists only of a weak polarization-induced interaction.

Our results are also relevant for the interpretation of catalytic reactions on the Au/Ni(111) surface. In their recent report on CO oxidation catalysed by Au-doped Ni(111), Lahr and Ceyer [2] tentatively attribute the production of CO₂ at temperatures above 125 K to the reaction

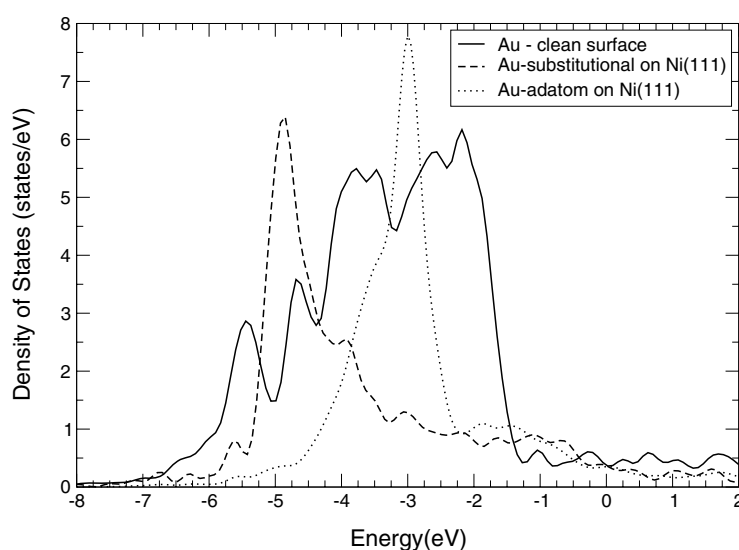


Figure 4. Electronic density of states of a Au(111) surface and local density of states of a Au adatom and of a Au impurity on a Ni(111) surface.

between CO and O bound to Au impurities in the Ni surface. Our results shed some doubt on this conclusion: We find that the reactivity of Au atoms present as substitutional impurities in the Ni surface is rather small and comparable to that of atoms in a clean Au(111) surface. Certainly, the form of the potential energy surface around a substitutional Au atoms excludes the existence of CO bound to the impurities. Au adatoms on Ni(111) bind CO molecules much more strongly, although CO bound on top of an adatom is only metastable. Kinetic modelling studies of a wide range of molecular reactions catalysed by metals [21] have shown that the optimum catalysts have intermediate binding energies of -1.1 ± 0.3 eV. Hence pure Ni(111) surfaces bind CO too strongly for an efficient activation of the molecule, while binding to Au atoms in a Au/Ni(111) surface alloy is much too weak. Binding to Au adatoms and to sites in the vicinity of a Au impurity on the other hand occurs at energies within the range for an optimal reactivity. However, it must be left to future studies to develop an atomistic model for CO oxidation on Au-doped Ni(111) surfaces.

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