

A density-functional theory study of the adsorption of CO molecules on Au/Ni(111)

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2006 J. Phys.: Condens. Matter 18 10825

(<http://iopscience.iop.org/0953-8984/18/48/009>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 14:41

Please note that [terms and conditions apply](#).

A density-functional theory study of the adsorption of CO molecules on Au/Ni(111)

Konstantinos Termentzidis, Jürgen Hafner and Florian Mittendorfer

Institut für Materialphysik, Universität Wien and Center for Computational Material Science, Sensengasse 8, A-1090 Wien, Austria

E-mail: kostas.termentzidis@univie.ac.at and juergen.hafner@univie.ac.at

Received 22 August 2006, in final form 11 October 2006

Published 17 November 2006

Online at stacks.iop.org/JPhysCM/18/10825

Abstract

The adsorption of carbon monoxide in the vicinity of an isolated Au adatom on a Ni(111) surface has been studied using *ab initio* density-functional theory (DFT). Our detailed investigations of the potential-energy surface for the binding of CO atoms show that for bonding sites in which the molecule binds at least to one Ni nearest neighbour of the Au adatom, the adsorption energy is reduced by up to 1.2 eV. At larger distances from the impurity, the adsorption energies are almost unchanged. On the other hand, binding to the Au adatom is much stronger than on a flat Au surface. These results are discussed in relation to the electronic structure of the Au-doped Ni surface.

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

1. Introduction

One of the goals of surface science is to design surfaces with tailor-made properties, e.g. with a capacity to bind a molecular species just strongly enough to initiate a catalytic reaction without, however, inducing a dissociative reaction that would poison the catalyst. It is well known that alloying can modify the catalytic activity and selectivity of a metal significantly and that alloy catalysts represent a promising route towards novel catalysts with superior properties compared with elementary metals [1, 2]. During recent years, density-functional studies of alloy surfaces [3] have been developed to a point at which realistic predictions of the reactivity governed by the interplay of electronic and geometric effects have become possible.

One of the first examples of the design of a novel alloy catalyst inspired by theoretical concepts and *ab initio* calculations was the development of a novel steam-reforming catalyst [4] based on gold-doped Ni. Clean Ni surfaces are known to show a good performance as a steam-reforming catalyst because of the ability to readily dissociate CH₄. However, it is also well known that the activity of Ni catalysts rapidly deteriorates because Ni binds C atoms too strongly, resulting in carbide formation and graphitization of the surface. Various

attempts have been made to reduce the Ni–C bond strength, e.g. by a selective poisoning of the surface with sulfur [5]. Doping the surface with a sub-monolayer amount of Au turned out to be much more successful. The Au/Ni system belongs to the bimetallic systems which do not mix in the bulk [6] (the segregation energy at the close-packed Ni(111) surface is [7] $\Delta E_{\text{seg}} = -0.69$ eV), but form stable surface alloys in the outermost surface layer [8]. Only a small fraction of Au atoms incorporated into the outermost Ni layer induces a substantial modification of the surface reactivity: (i) DFT calculations show that the chemisorption energy of C on Ni(111) is reduced by almost 2 eV/atom if the C atom binds to a site next to a Au impurity, and even next-nearest-neighbour sites are still significantly destabilized [4]. (ii) Again according to DFT calculations [9], the dissociation barrier for CH₄ is increased by 0.17 and 0.39 eV/molecule for a Ni atom with one or two Au neighbours, respectively. (iii) Temperature-programmed desorption studies [10] have shown that the binding energies of CO and D₂ decrease by approximately 0.26–0.31 eV/molecule as the Au concentration in the surface layer increases from 0 to 0.7 ML. (iv) Scanning-tunnelling microscopy studies combined with DFT calculations have demonstrated that CO binding is excluded at the threefold hollows next to a Au atom. These results show that the doping of the Ni surface will strongly reduce the tendency to carbide formation and graphitization, while the barrier for methane dissociation is only modestly increased [11].

There are, however, certain aspects that are still incompletely understood. For example, it has recently been reported that at high pressure CO induces a tendency to reverse surface alloying [12]. Au is the noblest of all metals, and its low-index surfaces show a very low reactivity. Nanoparticles of gold, deposited on inert substrates, on the other hand, have been found to be very reactive and to show catalytic activity at or even below room temperature [13]. The intention of the present work is to study the chemical reactivity at a Au adatom adsorbed on a Ni(111) surface and its influence on the surrounding Ni atoms via the simulated adsorption of CO molecules.

2. Methodology

In this work the adsorption of CO on clean Ni(111) and on the system Au/Ni(111) has been studied using density-functional theory (DFT). The calculations were performed using the Vienna *ab initio* simulation package VASP [14–17], which performs a variational solution of the Kohn–Sham equations in a plane-wave basis set.

The electron–ion interaction is described using ultrasoft pseudopotentials [20, 21]; atomic pseudo-charge densities are transformed to all-electron charge densities according to the projector-augmented-wave (PAW) method introduced by Blöchl [18] as modified by Kresse and Joubert [19]. Electronic exchange and correlation are described in the generalized-gradient approximation, using the functional proposed by Perdew, Burke and Ernzerhof (PBE) [22]. The plane-wave basis set contained components with a kinetic energy of up to $E_{\text{cut}} = 270$ eV for calculations of the clean metal surface, and with $E_{\text{cut}} = 400$ eV for studying CO adsorption. Convergence with respect to the basis set was checked very carefully in an extended study of CO adsorption on transition-metal surfaces [25].

The substrate was modelled by slabs consisting of four Ni layers with a periodicity of $p(3 \times 3)$ in the surface plane, separated by about 20 Å of vacuum. The upper two layers of the surface were allowed to relax, while the remaining layers were fixed at their bulk-like positions. A single Au atom and a single CO molecule were adsorbed per surface cell; this yields a coverage of 0.11 ML of Au atoms and of CO molecules. For the Brillouin zone integrations a $5 \times 5 \times 1$ Monkhorst–Pack grid [23] was used. To locate transition states and for the determination of reaction barriers, the nudged-elastic-band method [24] was used. With

Table 1. Adsorption energies (E_{ads} , in eV/atom) and geometries (relaxation of Ni–Ni interlayers distances and shortest Ni–Au distance) for Au adatoms on Ni(111) at a coverage of 0.11 ML.

Au/Ni(111)	Top	hcp	fcc	Bridge
E_{ads} (eV)	2.04	2.83	2.84	2.31
d_{1-2} (%)	5.7	2.4	1.9	−1.0
d_{2-3} (%)	−0.3	−1.1	−1.4	−0.2
d_{NiAu} (Å)	2.3	2.6	2.4	2.5

this computational setup, differences in adsorption energies are converged at the level of a few meV/molecule.

For mapping the potential-energy surface of CO on Au/Ni(111), the in-plane coordinates of the carbon atom were fixed at positions corresponding to on-top, bridge, and hollow sites. Spin-polarized calculations were performed for the system Au/Ni, while only non-magnetic calculations were used for studying CO adsorption on Au/Ni. A recent extended DFT study of CO adsorption on close-packed metal surfaces [25] has demonstrated that spin polarization has only a minimal influence on the adsorption properties.

3. Au adsorption on Ni(111)

Although gold does not form bulk alloys with nickel at ordinary temperatures [6] and surface segregation is favoured by an exothermic segregation energy [7] of $\Delta E_{\text{seg}} = -0.69$ eV, at elevated temperatures the formation of surface alloys on Ni(111) [27] and Ni(110) [8, 28] surfaces has been reported. Photoelectron spectroscopy [29, 30] of ultrathin bimetallic Au/Ni films vapour deposited on Y-doped ZrO_2 revealed a pronounced tendency of the Au atoms to segregate to the surface. Temperature-programmed desorption (TPD) studies of adsorbed CO showed a strong shift of the TPD peaks to lower temperatures even at the lowest Au/Ni ratios.

We have studied the adsorption of an isolated Au atom in a $p(3 \times 3)$ surface cell of Ni(111). The most stable adsorption site is the fcc hollow, which is favoured by 10 meV/atom over the hcp hollow. Adsorption on an on-top site is locally stable, but is disfavoured by about 0.8 eV/atom, whereas the bridge site represents only a saddle point. Details of the calculated adsorption geometries are compiled in table 1, together with adsorption energies with respect to gas-phase Au ($E_{\text{ads}} > 0$ meaning exothermic adsorption). The presence of the Au adatom induces a slight outward relaxation of the top Ni layer, in contrast to the clean Ni(111) surface [26] which shows a very modest inward relaxation by -0.9% . The Au-induced outward relaxation of the top layer is modest for the stable location of Au in the threefold hollows, where it is accompanied by a contraction of the distance between the Ni subsurface layers. The presence of the Au adatom induces only a very modest change in the structure of the surface layer: nearest-neighbour Ni atoms relax laterally by about 0.01 Å; the buckling of the surface layer is ≤ 0.01 Å. For the metastable location of the Au atom in an on-top position, a more pronounced outward relaxation and a stronger surface buckling is found.

In addition we have calculated, using the nudged-elastic-band method [24], the potential-energy profile for the exchange reaction between a Au adatom and a Ni atom from the top layer. The initial configurations had a Au atom in an fcc hollow of a clean Ni(111) surface; in the final configuration, Au occupied a substitutional site in the Ni(111), while one of the Ni atoms was expelled to an adatom position in a threefold hollow next to the Au impurity. The reaction coordinate measures the distance between these two configurations; all coordinates perpendicular to the reaction path are allowed to relax. The resulting potential-energy profile is shown in figure 1. We find that surface alloying is an activated and endothermic process. The energy cost for the exchange process is 0.44 eV—this is substantially lower than the bulk

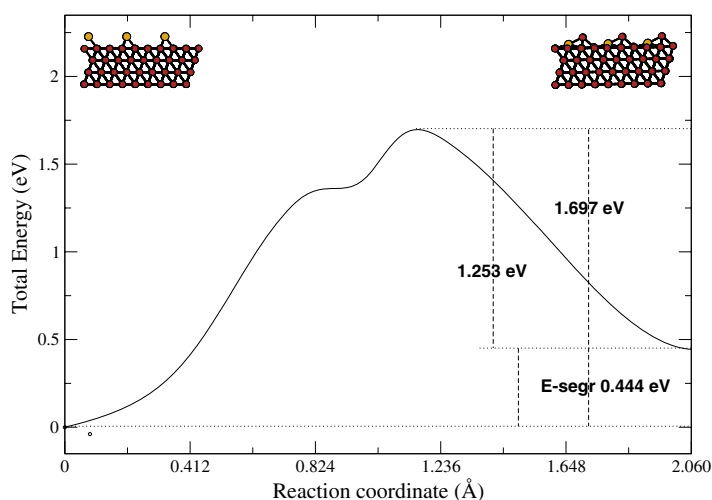


Figure 1. Potential-energy profile for the exchange between a Au adatom and a Ni surface atom on Ni(111). The inset shows the initial and final configurations.

segregation energy of 0.69 eV calculated by Ruban *et al* [7]. The activation energy for the exchange process is 1.70 eV. In the final configuration, the Au atom protrudes from the Ni surface. The centre of the Au atom is located at about 0.65 Å above the Ni surface. The six nearest-neighbour Ni atoms in the surface relax by about 0.14 Å away from the Ni atom and they are pushed slightly deeper into the surface by 0.015 Å. This distortion of the Ni surface accounts for a substantial part of the endothermic energy of formation of a Au surface impurity.

Our results suggest that the surface alloying observed at elevated temperatures [8] is entropy driven. This conclusion agrees with the findings of Ozolins *et al* [32] which show that Ni–Au alloys have a large configurational and nonconfigurational (vibrational) entropy of formation. As a Au impurity is only loosely anchored in the Ni surface layer, we can expect the vibrational contribution to the entropy to be even larger for a surface impurity than in the bulk.

The presence of a Au impurity induces a change in the d-band position of the neighbouring Ni atoms; see figure 2. For Ni atoms that are nearest neighbours to the Au adatom, the peak in the density of states (DOS) immediately below the Fermi energy is reduced, and due to the hybridization with the Au d states, the DOS is enhanced at a binding energy of about -3 eV. Hence the centre of gravity of the d band is locally shifted to higher binding energies. The changes are the same for the spin-polarized and the paramagnetic DOS. Both effects—the reduction of the DOS near E_F and the shift of the d-band centre—lead to a reduced chemical reactivity of the Ni atom. However, already for next-nearest neighbours to the adatom, the local DOS is almost unchanged with respect to the clean surface. The centre of gravity of the d-band DOS of the Au adatom is located at ~ -3 eV; compared to a clean Au(111) it is shifted by ~ 0.3 eV to lower binding energies. The d band of the adatom is rather narrow, but due to the hybridization with the Ni d states, a significant d-band DOS is also found between -2 eV and the Fermi energy.

4. CO adsorption on Au/Ni(111)

4.1. CO adsorption on clean Ni(111)

To obtain detailed information about the reference system, the adsorption of CO on a clean Ni(111) surface at a coverage of $\Theta = 0.11$ ML has been studied, complementing earlier

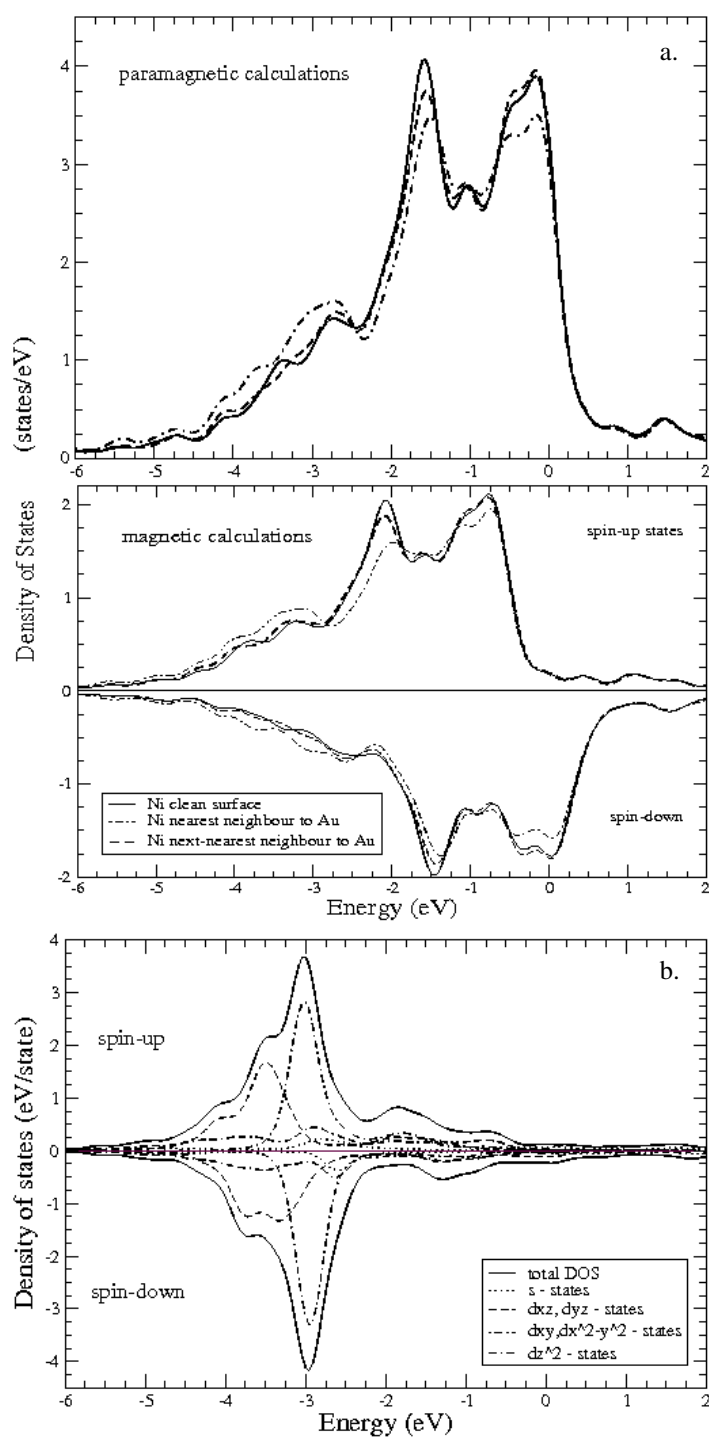


Figure 2. (a) Spin-polarized and paramagnetic electronic density of states (DOS) of the d band for a Ni atom on a clean Ni(111) surface and for Ni atoms in nearest- and next-nearest-neighbour positions to a Au adatom on Ni(111). (b) Local electronic DOS of a Au adatom.

Table 2. Adsorption energy (E_{ads}), length of the CO bond (d_{CO}), Ni–C distance ($d_{\text{Ni–C}}$), and vertical distance of the C atom in the CO molecule from the surface ($z_{\text{Ni–C}}$), for all adsorption sites.

Site	E_{ads} (eV)	d_{CO} (Å)	$d_{\text{Ni–C}}$ (Å)	$z_{\text{Ni–C}}$ (Å)
fcc	2.13	1.20	1.94	1.36
hcp	2.13	1.20	1.94	1.36
Bridge	1.97	1.19	1.87	1.45
Top	1.61	1.16	1.74	1.84

investigations at higher coverages ($\Theta \geq 0.25$ ML) [25, 33]. Our results are compiled in table 2. The most favourable adsorption site for CO is the fcc hollow with an adsorption energy of 2.13 eV/molecule, which is only 2 meV larger than for adsorption in an hcp hollow. Adsorption in bridge and on-top sites is less favourable by 0.15 eV/molecule and 0.52 eV/molecule, respectively. The adsorption energies calculated in this low-coverage limit are substantially higher than those reported for 0.25 ML coverage. The difference is largest ($\Delta E_{\text{ads}} = 0.18$ eV/molecule) for adsorption in a threefold hollow, and only very modest ($\Delta E_{\text{ads}} = 0.04$ eV/molecule) for on-top adsorption. The results of Gajdos *et al* [25] have been calculated with a different exchange–correlation functional (PW91) proposed by Perdew *et al* [34], which produces, however, very similar results to our PBE functional. A revised variant of the PBE functional (RPBE) has been designed by Hammer *et al* [35], with the aim of improving the prediction of molecular adsorption energies. While the RPBE functional indeed reduces the adsorption energy of CO on Ni(111) by 0.46 eV/molecule compared to the results achieved with the PW91 functional and hence largely improves agreement with experiment ($E_{\text{ads}} = 1.44$ eV/molecule (theor.), 1.32 eV/molecule (exp.)), the results for adsorption on noble metal surfaces are disappointing. For the Au(111) surface one finds using the PW91 functional $E_{\text{ads}} = 0.32$ eV/molecule (theor.), 0.40 eV/molecule (exp.), while the RPBE functional predicts CO adsorption to be endothermic by -0.12 eV/molecule (for details see [25]). Hence, for the transition-metal surfaces the difference in the adsorption energies predicted by the PW91 (or PBE) and the RPBE functionals consists in an almost constant shift to lower (and hence more realistic) values. For the noble metals PW91 and PBE correctly predict exothermic adsorption, whereas using RPBE the CO molecule does not bind at all: the prediction is qualitatively wrong. For this reason, the present study was performed using the unmodified PBE functional [22].

The stronger adsorbate–surface interaction at reduced coverage leads also to a slightly more pronounced stretching of the C–O bond length compared to its value in the gas-phase molecule ($d_{\text{CO}} = 1.14$ Å), whereas the surface–adsorbate distances were found to be hardly coverage dependent.

4.2. CO adsorption on Au/Ni(111)

For the investigation of CO adsorption in the vicinity of a Au adatom adsorbed in a threefold (fcc) hollow site of the Ni(111) surface, we used the $p(3 \times 3)$ surface cell shown in figure 3. For the mapping of the potential-energy surface of CO on the Au/Ni(111) surface, the lateral coordinates of the C atom were fixed at the high-symmetry sites (hollow, bridge, on-top) defined in figure 3, 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. As the interaction between the CO molecule and the Au atom is repulsive, we have in addition frozen the lateral coordinates of the adatom—this must be considered in an analysis of the potential-

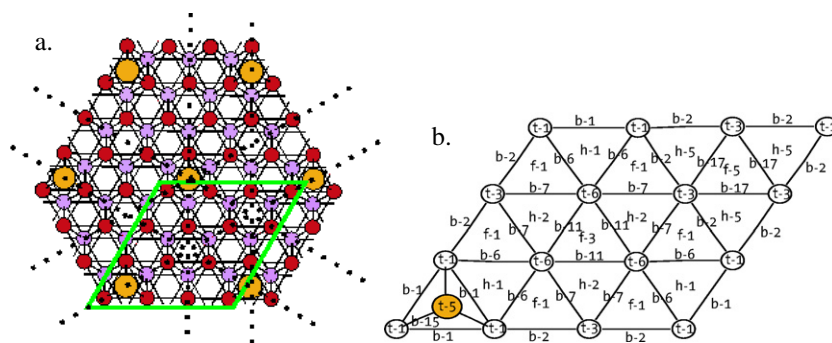


Figure 3. (a) The Au/Ni(111) surface for a coverage of 0.11 ML. Dark circles represent Ni atoms in the surface layer, light circles subsurface Ni atoms. The large dots represent the Au adatoms. Dotted lines mark mirror symmetries in the $p(3 \times 3)$ surface cell, which is marked by the parallelogram. (b) The $p(3 \times 3)$ surface cell used for studying the adsorption of CO in the vicinity of a Au adatom on Ni(111). The Au atom is placed into a threefold hollow next to the corner of the surface cell (position t5). The figure serves to define the nomenclature for the sites for which the adsorption energy and geometry of CO has been calculated.

Table 3. CO adsorption in the vicinity of a Au adatom on 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}), height of the C atom above the Ni surface ($z_{\text{Ni-C}}$), and tilt angle relative to the surface normal (θ).

Site	E_{ads} (eV)	ΔE_{ads} (eV)	d_{CO} (Å)	$z_{\text{Ni-C}}$ (Å)	θ (deg)
f1	1.66	−0.46	1.21	1.34	10
f3	2.15	+0.03	1.20	1.37	0
f5	2.09	−0.04	1.20	1.34	0
h1	0.88	−1.25	1.15	3.47	80
h2	2.08	−0.04	1.20	1.36	0
h5	1.93	−0.20	1.20	1.34	4
b1	1.11	−0.87	1.16	3.96	32
b2	1.58	−0.40	1.20	1.44	8
b6	0.87	−1.10	1.22	1.50	36
b7	1.84	−0.13	1.19	1.45	0
b11	1.96	−0.02	1.19	1.48	0
b15	1.10	−0.87	1.15	3.96	35
b17	1.93	−0.05	1.19	1.44	0
t1	0.88	−0.74	1.15	3.55	87
t3	1.55	−0.06	1.16	1.80	0
t5	1.16	−0.45	1.16	4.08	0
t6	1.41	−0.20	1.17	1.86	7

energy surface. In any case, our calculations have demonstrated that mobility of the adatom is restricted by a diffusion barrier of ~ 0.53 eV (see table 1).

Details of the adsorption energies and adsorption geometries are compiled in table 3. To facilitate the interpretation of the data, contour plots of the adsorption energies and of the difference in the adsorption energies on clean Ni(111), induced by the presence of the Au adatom, are given in figures 4 and 5.

Due to the presence of the Au adatom the adsorption energies of CO are reduced by up to about -1.25 eV/molecule. As expected, the sites in the centre of the cell, at the largest distance from the Au atom, are least affected. On the fcc site f3 located in the centre of the

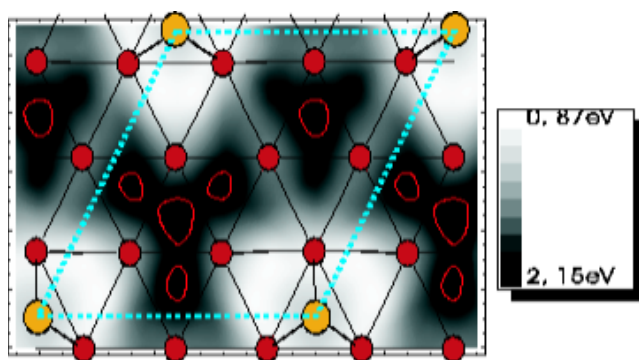


Figure 4. Contour plot of the adsorption energies of a CO molecule in the vicinity of a Au adatom on a Ni(111) surface (located in the lower left corner of the $p(3 \times 3)$ surface cell). The bright line encloses the spots with $E_{\text{ads}} \geq 2$ eV/molecule.

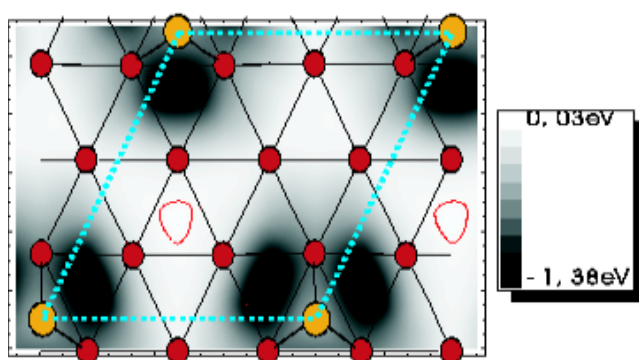


Figure 5. Same as figure 4, but showing the difference in the adsorption energies induced by the presence of the Au adatom. The line encloses sites with $\Delta E_{\text{ads}} \geq 0$ eV.

cell, the adsorption energy is even slightly increased by 0.03 eV, and on the surrounding bridge (b11) and hexagonal hollow (h2) sites, the adsorption energy is decreased only by -0.02 and -0.04 eV, respectively. At these sites, the adsorption geometries (CO bond length, adsorbate–surface distance) are also almost unchanged with respect to the clean Ni(111) surface. A rather modest change in the adsorption properties is also found for the group of adsorption sites around the f5 centre of symmetry (hollow f5, bridge b17, hollow h5). The reduction of the CO binding is strongest (-0.2 eV) in the vicinity of the Au atom (hollow h5), where the Ni substrate atoms share bonds with CO as well as Au. On the f5 and b17 sites, the change in the adsorption energy is only -0.04 eV/molecule, and the adsorption geometry is also almost unchanged.

The other extreme is found at the site of the Au atom and in its immediate environment. Since the adsorption energies of Au and CO on clean Ni(111) are comparable, a relaxation of the lateral coordinates of the Au atom, with the C atom in a fixed position, would lead to a displacement of Au such that the CO–Ni binding can be optimized. Since this is not the effect we want to study, the Au atom was fixed in the hollow. On top of the Au atom (position t5), the adsorption energy of CO is 1.16 eV/molecule. CO is adsorbed in an upright configuration: the Au–C distance is about 1.8 Å. This means that CO adsorption on an isolated Au adatom on Ni(111) is much stronger than on a close-packed Au(111) surface (where the adsorption energy is only 0.32 eV/molecule). This confirms the enhanced chemical reactivity of Au

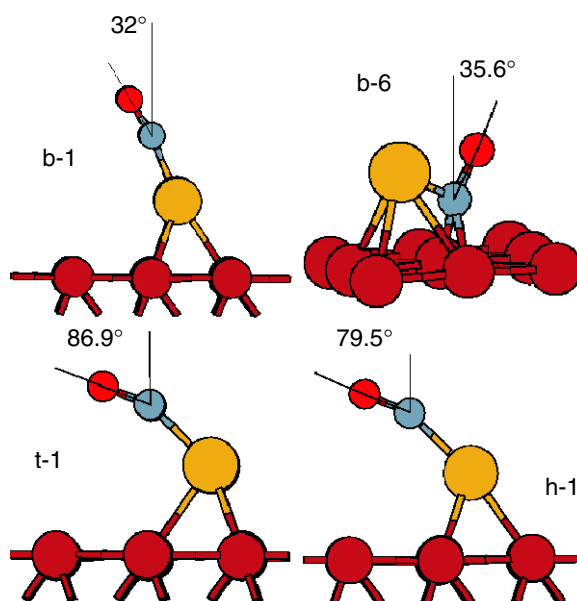


Figure 6. Adsorption geometries in the immediate vicinity of the Au adatom on Ni(111).

nanoparticles, even if they are supported on a metallic surface. Note that binding of CO on top of the adatom is at least locally stable, with surrounding barriers of nearly 0.3 eV located at the surrounding on-top (t1), hollow (h1) and bridge (b6) sites.

The b15 bridge sites connect the Au adatom and the nearest-neighbour Ni atoms. The CO binding energy on these sites is about 1.1 eV; the axis of the CO molecule is tilted away from the surface normal by about 35°. Some typical bonding geometries in the vicinity of the Au atom are shown in figure 6. A molecule placed into the b1 bridge sites cannot really bind to the Ni atoms, because they are screened by the extended electron density around the Au. The next sites are CO on top of one of the Ni atoms binding to the Au adatom (sites t1). In this case the adsorption energy is only about half as large as on top of a Ni atom on a clean surface, the Ni–C distance is strongly increased, and in equilibrium the CO molecule lies almost parallel to the Ni surface. Again this reflects the fact that the Ni atom is screened by the Au adatom.

Bonding in the ‘threefold’, respectively ‘twofold’, sites h1 and b6 is most strongly affected by the impurity—the adsorption energy is decreased by -1.1 to -1.2 eV/molecule. The binding energy in the threefold hollow h1 is strongly reduced, because two of the substrate atoms binding to the adsorbate bind also to the impurity. The molecule drifts to a large distance from the surface and adopts a position parallel to the surface (see figure 6). Binding in the b6 bridge has a rather special character: in this location the CO molecule binds to two substrate atoms (one is a first-nearest, the other a second-nearest neighbour to the Au atom) and to the adatom. Hence in this configuration the molecule binds in a pseudo-threefold site. The adsorption energy is about as strong as in the h1 site, but the molecule approaches the surface much more closely and undergoes only a moderate tilt with respect to the surface normal. Hence, in configuration h1 the molecule binds rather to the Au adatom screening the neighbouring adsorption sites than to the Ni surface. However, the binding to the isolated Au atom is more than twice as strong as on a Au(111) surface. Remarkably, the elongation of the C–O bond is largest for this tilted b6 geometry. The reason is that due to the tilted geometry,

interactions forbidden in an upright geometry (e.g. the interaction between the d_{z^2} orbital of Ni and the $2\pi^*$ antibonding orbital of the CO molecule) can weaken the intramolecular bond. The situation is similar to that for the tilted adsorption of CO on Fe(100) surfaces [31].

Holmblad *et al* [10] have used TPD spectroscopy to investigate the influence of Au impurities on the desorption energy of CO from Ni(111) surfaces. For coverages up to 0.1 ML, the TPD spectra show a broadening of the peak located at about 315 K, with only a very moderate shift of the peak position. For coverages above 0.15 ML, a side peak at about 180 K begins to grow, while the main peak gradually fades out. For coverages above about 0.6 ML, no CO is adsorbed. Our results provide an explanation for the bimodal structure of the TPD spectrum, the high- and low- T peaks corresponding to adsorption in Au-free and Au-contaminated parts of the Ni surface.

5. Conclusions

We have demonstrated that the presence of a Au adatom leads to a strong local reduction of the adsorption energy of CO. On a clean Ni(111) surface, CO adsorbs in a threefold hollow with an adsorption energy of 2.13 eV/molecule. At an adatom concentration of ~ 0.1 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 ≤ 0.5 eV/molecule for 77% of all sites. If the Au adatom is placed into a fcc hollow of the surface, the adsorption energy of CO in the neighbouring hcp hollows sharing two Ni atoms with the adatom (site h1) is reduced by -1.25 eV; in the nearest fcc hollow sharing a single Ni atom with the adatom (site f1), the reduction is only -0.46 eV. In the hcp hollow neighbouring the Ni–Au bond (site h5), the adsorption energy is reduced only by -0.20 eV. In all other hollow sites in the $p(3 \times 3)$ surface cell, the adsorption energy is almost unchanged. Hence the doping of a Ni surface with Au has a very local influence on the adsorption properties. This agrees also with the analysis of the local electronic densities of states: already for next-nearest Ni atoms, Au-induced changes are very small. The reduction of the adsorption energy is a direct consequence of the reduced Ni DOS and of the shift of the d-band centre to higher binding energies, in accordance with the Hammer–Nørskov model [36]. On the other hand, the Au adatom binds a CO molecule much more strongly than a Au(111) surface. On all noble metal surfaces, CO adsorption is very weak, because the low-lying d band suppresses any formation of covalent adsorbate–substrate bonds through the interaction of the d states with the 5σ and $2\pi^*$ molecular orbital of CO (see also the detailed discussion in [25]). For the Au adatom, the presence of a substantial d-band DOS at energies of -2 to -1 eV below the Fermi energy leads to a contribution to the adsorption bonding similar to that on transition-metal surfaces. A CO molecule adsorbed at the Au adatom site is located in a local potential-energy minimum surrounded by barriers resulting from the strong reduction of the adsorption energy at the hollow, bridge and on-top sites closest to the adatom. Adsorption at these sites is unstable (in accordance with the STM observations) as there is no barrier against diffusion into a more attractive site.

Acknowledgment

This work has been supported by the Austrian Science Funds through the Science College ‘Computational Materials Science’ (Project No. W004).

References

- [1] Sinfelt J H 1983 *Bimetallic Catalysts: Discoveries, Concepts, and Applications* (New York: Wiley)
- [2] Ponec V 1983 *Adv. Catal.* **31** 149

- [3] Groß A 2006 *Top. Catal.* **37** 29
- [4] Besenbacher F, Chorkendorff I, Clausen B S, Hammer B, Molenbroek A M, Nørskov J K and Stensgaard I 1998 *Science* **279** 1913
- [5] Rostrup-Nielsen J R 1984 *J. Catal.* **85** 31
- [6] Massalski T B (ed) 1987 *Binary Alloy Phase Diagrams* (Metals Park, OH: American Society for Metals)
- [7] Ruban A V, Skriver H L and Nørskov J K 1999 *Phys. Rev. B* **59** 15990
- [8] Pleth Nielsen L, Besenbacher F, Stensgaard I, Laegsgaard E, Engdahl C, Stoltze P, Jacobsen K W and Nørskov J K 1993 *Phys. Rev. Lett.* **71** 754
- [9] Kratzer P, Hammer B and Nørskov J K 1996 *J. Chem. Phys.* **105** 5595
- [10] Holmblad P M, Hvolbaek-Larsen J and Chorkendorff I 1996 *J. Chem. Phys.* **104** 7289
- [11] Lauritsen J V, Vang R T and Besenbacher F 2006 *Catal. Today* **111** 34
- [12] Vestergaard E K, Vang R T, Knudsen J, Pedersen T M, An T, Laegsgaard E, Stensgaard I, Hammer B and Besenbacher F 2005 *Phys. Rev. Lett.* **95** 126101
- [13] Lopez N and Nørskov J K 2002 *J. Am. Chem. Soc.* **124** 11262
- [14] Kresse G and Hafner J 1993 *Phys. Rev. B* **48** 13115
- [15] Kresse G and Furthmüller J 1996 *Comput. Mater. Sci.* **6** 15
- [16] Kresse G and Furthmüller J 1996 *Phys. Rev. B* **54** 11169
- [17] Detailed information on VASP may be found on the web site: <http://cms.mpi.univie.ac.at/vasp>
- [18] Blöchl P 1994 *Phys. Rev. B* **50** 17953
- [19] Kresse G and Joubert D 1999 *Phys. Rev. B* **59** 1758
- [20] Vanderbilt D 1990 *Phys. Rev. B* **41** 7892
- [21] Kresse G and Hafner J 1994 *J. Phys.: Condens. Matter* **6** 8245
- [22] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
- [23] Monkhorst H J and Pack J D 1972 *Phys. Rev. B* **13** 5188
- [24] Mills G, Jónsson H and Schenter G K 1994 *Surf. Sci.* **324** 305
- [25] Gajdos M, Eichler A and Hafner J 2004 *J. Phys.: Condens. Matter* **16** 1141
- [26] Mittendorfer F, Eichler A and Hafner J 1999 *Surf. Sci.* **423** 1
- [27] Pleth Nielsen L, Besenbacher F, Stensgaard I, Laegsgaard E, Engdahl C, Stoltze P, Jacobsen K W and Nørskov J K 1995 *Phys. Rev. Lett.* **74** 1159
- [28] Jacobsen J, Pleth Nielsen L, Besenbacher F, Stensgaard I, Laegsgaard E, Rasmussen T, Jacobsen K W and Nørskov J K 1995 *Phys. Rev. Lett.* **75** 489
- [29] Zafeiratos S and Kennou S 2001 *Appl. Surf. Sci.* **173** 69
- [30] Zafeiratos S and Kennou S 2002 *J. Phys. Chem. B* **106** 41
- [31] Stibor A, Kresse G, Eichler A and Hafner J 2002 *Surf. Sci.* **99** 507
- [32] Ozolins V, Wolverton C and Zunger A 1998 *Phys. Rev. B* **57** 6427
- [33] Eichler A 2003 *Surf. Sci.* **526** 332
- [34] Perdew J P, Chevary J A, Vosko S H, Jackson K A, Pedersen M R, Singh D J and Fiolhais C 1992 *Phys. Rev. B* **46** 6671
- [35] Hammer B, Hansen L B and Nørskov J K 1999 *Phys. Rev. B* **59** 7413
- [36] Hammer B and Nørskov J K 2000 *Adv. Catal.* **45** 71