Carbon monoxide adsorption on a nickel iron surface: bonding and electronic structure computational study

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Carbon monoxide adsorption on a nickel iron surface: bonding and electronic structure computational study

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CO adsorption on the FeNi(111) surface has been studied by density functional theory calculations. The CO molecule presents its most stable geometry in an intermediate position between the bridge Ni site and the top Fe site. Ni–C (1.94 Å) and Fe–C (2.09 Å) interactions occur after molecular adsorption. The main interactions occur involving C s–metal p and C p–metal d orbitals. The new interactions weaken the metal bonding. As a consequence, the strength of local metal bonds decreases by 15% from the original bulk value.

Keywords: carbon monoxide; iron; nickel; computational

1. Introduction

It is crucial to understand the chemisorption of small gas molecules on transition-metal surfaces in order to determine the mechanism of heterogeneous catalysis at the molecular level. In the case of carbon monoxide (CO) on transition-metal surfaces, CO is present in almost all catalytic processes, either as a reactant or contamination; therefore, it is one of the most extensively studied systems in surface chemistry and physics due to its technological importance as well as its structural simplicity. Great effort has been made to better understand the properties of the CO substrate using experimental and theoretical approaches.

There are several studies of CO adsorption on pure transition metals on various surfaces. Jiang and Carter [1] found a barrier in order to obtain a dissociative process consistent with the carburization of Fe at high temperature. In a more recent study, Scheijen et al. [2], using a plane-wave basis code (VASP), studied the adsorption of CO on a Th(100) surface on a variety of pure metals and Fe\textsubscript{3}Mo and Fe\textsubscript{3}Cr alloys; they concluded that CO is the most stable at four-fold hollow sites with the CO axis tilted from the normal surface by 47–58°. In addition, there are studies on CO adsorption on metallic monolayers supported on Pt, Cu, Fe, and Ni [3].

On the other hand, bimetallic surfaces play a decisive role in heterogeneous catalysis. Due to the particular arrangement of the different atoms at the surface, new reaction pathways can be opened and both the activity and selectivity of the catalyst can be improved. Various concepts for the specific reaction properties of bimetallic surfaces have been discussed in the literature, the most important of which are the electronic ligand effect and the geometric ensemble effect.

Using the periodic slab density functional theory, CO adsorption, diffusion, and dissociation energetics on a monolayer of Al covering Fe(100) [Al/Fe(100)] has been investigated. The author predicted that a weakly chemisorbed state of CO existed on Al/Fe(100), with CO adsorbing on the four-fold hollow site in a very tilted fashion. The dissociation of CO starting from this weakly adsorbed state has a barrier that is approximately 0.70 eV lower than that on Fe(100) [4].

Infrared reflection absorption spectroscopy (IRRAS) was used to investigate CO adsorption on sub-monolayer (ML)-thick Fe deposited Pt(111). CO exposure to a clean Pt(111) surface at room temperature yielded linear-bonded and bridge-bonded CO–Pt bands. The CO–Pt band intensities decreased steeply with increasing Fe thickness [5].

IRRAS measurements were conducted on CO adsorption on Pt(111) bimetallic surfaces with various thicknesses of deposited Ni, i.e. Ni\textsubscript{x}/Pt(111) (x, Ni thickness in nanometers). CO exposure to the clean Pt(111) surface at 323 K engenders linearly bonded and bridge-bonded CO–Pt bands. The 343 K deposited Ni\textsubscript{0.1nm}/Pt(111) gives rise to a new band in addition to the CO–Pt(111) bands. The new band is most

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prominent for Ni$_{0.3nm}$/Pt(111), on which the bridge-bonded CO on the Ni admetal layer appear [6].

The adsorption behavior of CO on bimetallic Ni/Cu(110) surfaces has been studied experimentally by thermal-desorption spectroscopy and theoretically by DFT calculations. Adsorption of CO at 180 K on such a bimetallic surface yields three new adsorption states with adsorption energies between that of CO on clean Cu(110) and clean Ni(110). DFT calculations showed that CO adsorption on nickel dimers consisting of insurface and adjacent subsurface atoms can best explain the experimental data observed. The result shows that CO adsorption is determined by local geometric effects rather than by long-range electronic effects [7].

The adsorption of CO on a Au/Ni(111) surface alloy has been investigated using ab initio density-functional calculations. In contrast to a Au adatom on a Ni(111) surface, a Au impurity only binds CO very weakly. In addition, the impurity induces a reduction in the adsorption energies that is strictly localized to its immediate neighborhood [8].

The materials used for industrial processes are generally Fe- and Ni-based alloys that offer high corrosion and creep resistance. However, when the material is exposed to gases containing carbon, e.g. CO, it can absorb the carbon [9]. The resistance to thermal cycling is reduced and cracks might develop in the material.

The interaction of carbon monoxide with nickel–iron alloys has been studied on Ni(111)–Fe surfaces by means of ellipsometry and Auger electron spectroscopy, and by means of infrared spectroscopy on γ-Al$_2$O$_3$-supported Ni$_x$Fe catalysts. The nickel-to-iron ratio of the alloy affects the interaction with CO. Surfaces contaminated with carbon and oxygen show a lower heat of adsorption [10].

A combination of flow reactor studies and electron microscopy techniques was used to investigate the way in which the composition of iron–nickel alloy particles influences the growth characteristics of carbon deposits formed during the decomposition of ethane at temperatures above 815–865°C. Major differences in alloy selectivity patterns were evident, with the amount of catalytically produced solid carbon being significantly higher on a Fe–Ni (5:5) powder than on a Fe–Ni (8:2) sample. Examination of the deposit revealed the existence of two types of structures, carbon nanofibers and a graphite shell-like material, both containing associated metal particles [11].

The decomposition of a C$_2$H$_4$/CO/H$_2$ reactant mixture over a series of Fe/Ni catalysts has been studied and the analysis revealed that the addition of CO to a C$_2$H$_4$/H$_2$ feed results in a substantial increase in the decomposition of the olefin over all bimetallic powders, with the effect being most pronounced on iron-rich systems. The major product from this series of Fe/Ni catalysts was found to be solid carbon in the form of various filamentous structures [12].

In spite of the studies reported in the literature, there is little information concerning CO adsorption on Fe/Ni alloys at the quantum level. In this paper we study CO chemisorption on the FeNi(111) surface by means of the Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) calculations. We analysed the electronic structure and
Figure 2. Total DOS for the CO/FeNi(111) system (left), and the projected DOS for CO neighboring Fe (middle) and Ni (right) atoms.

Figure 3. Total DOS for the clean FeNi(111) surface (left), total DOS for the CO/FeNi(111) system (middle), and projected DOS for CO on the FeNi(111) surface (right).
bonding after the adsorption phenomena. The computational model and calculations are described in the next section.

2. Results and discussion

2.1. Geometric structure calculations

Our calculations were performed with a DFT-based code using a Linear Combination of Atomic Orbitals and considering pseudopotentials for the core electrons as implemented in the SIESTA code [13–20]. The interaction between the CO molecule and the FeNi(111) surface was studied using a two-dimensional slab of finite thickness, so as to better simulate the semi-infinite nature of the metallic surface. A five-layer slab (FCC arrangement) was used as a compromise between computational economy and reasonable accuracy. Spencer et al. [21–23] and Jiang and Carter [24,25] have shown that such a slab is thick enough to be used in the study of an adsorption process. In our case, the difference between the results using a three-layer slab and a five- or seven-layer slab is less than 0.02 eV and 0.008 Å for the adsorption energy and bond length, respectively.

Initial metal bond lengths were taken at the bulk value of 2.54 Å and the distance between planes was 2.074 Å. The initial geometry for CO was taken from literature data: C–O = 1.13 Å [26]. Seven adsorption sites were selected on the FeNi(111) surface for the present study (see Figure 1(top)). The CO molecule was approximated vertically on the FeNi(111) plane, the carbon being the nearest atom to the surface. A geometry optimization was performed applying relaxation calculations. Table 1 shows the C–surface distances and the relative minimum energy corresponding to the CO location for each adsorption site by SIESTA calculations. Sites 1, 2, 5 and 6 present a local minimum energy, showing the optimum localization of the molecule at these sites. On the other hand, sites 3, 4 and 7 are not stable and correspond to transition states, since CO relaxes to other sites when initially set at these sites. Finally, the most stable location for CO

Table 2. Atomic orbital occupations and net charges for CO neighboring Fe and Ni atoms.

<table>
<thead>
<tr>
<th>Adsorption site</th>
<th>C–surface distance (Å)</th>
<th>Relative energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.80</td>
<td>0.580</td>
</tr>
<tr>
<td>2</td>
<td>1.84</td>
<td>0.410</td>
</tr>
<tr>
<td>3</td>
<td>1.41</td>
<td>0.190</td>
</tr>
<tr>
<td>4</td>
<td>1.21</td>
<td>0.000</td>
</tr>
<tr>
<td>5</td>
<td>1.44</td>
<td>0.278</td>
</tr>
<tr>
<td>6</td>
<td>1.39</td>
<td>0.232</td>
</tr>
<tr>
<td>7</td>
<td>1.39</td>
<td>0.069</td>
</tr>
</tbody>
</table>

Figure 4. COOP curves for Fe–C and Ni–C interactions.
on the FeNi(111) surface corresponds to an intermediate position between sites 1 and 4, where the C atom is positioned in the middle of two Ni atoms and a neighbouring Fe atom. A schematic view of the location of CO is shown in Figure 1(bottom). For the final configuration, we found a C–O distance of 1.21 Å and a C–surface distance of 1.36 Å, in agreement with the results presented in the literature for CO adsorption on both Fe and Ni single crystal surfaces, respectively [1,27–29].

2.2. Electronic structure calculations

We calculated the density of states (DOS) and the crystal orbital overlap population (COOP) curves for the CO/FeNi(111) system in order to analyse the adsorbate–surface interactions. Figure 2(left) shows the DOS plots for the CO/FeNi(111) system. The metal d states form a 5 eV bandwidth. A substantial number of s and p states penetrate the d band (see Figure 2(middle and right)). The dispersion of s and p bands is much larger than the d band, reflecting the greater overlap between s and p orbitals and the more contracted nature of the d orbitals. If we compare the DOS plots for CO/FeNi(111) (Figure 3(middle)) with the isolated FeNi(111) total DOS (Figure 3(left)), the most noticeable differences are the three small peaks that appear at about −6 eV, −10 eV and −22 eV, respectively, that correspond to the C and O states from the CO molecule after adsorption. The small contribution of CO to the total DOS is due to its low concentration. For a major view, Figure 3(right) presents a plot of CO states after adsorption.

We also calculated the atomic orbital occupation and the OP values for the atoms that participate in the absorbate–substrate interaction (see Table 2). The C (of the CO molecule) bonds with the nearest-neighbor Ni and Fe surface atoms, yielding Ni–C (1.94 Å) and Fe–C (2.09 Å) OP values of 0.246 and 0.185, respectively. If we compare these new interactions with the metal–metal interaction (isolated FeNi matrix), the Ni–C and Fe–C interactions have OP values that correspond to 25% and 20% of the metallic bond OP, respectively. The COOP curves for the new interactions are shown in Figure 4; such curves mainly correspond to bonding interactions. Substrate–adsorbate interactions mainly involve the s and p orbitals of Ni, the populations of which decrease 9.53% and increase 16.46%, respectively, compared with the clean surface, whereas the Ni d orbital populations decrease to about 0.11% (see Table 2). On the other hand, the Fe orbital occupations are modified and the major changes are noticed in the s, p and d atomic orbitals, the populations of which decrease 9.78%, increase 5.24% and decrease 0.93%, respectively, after CO adsorption. Hybridization of the C impurity states with the Fe–Ni band can be observed at energies of −6 eV, −10 eV and −22 eV (see Figure 3). The main interactions occur involving C s–metal p and C p–metal d orbitals (see Table 3). It is reasonable for d orbitals to be involved in the surface bonding since the role of d states is critical, defining the adsorption site and the adsorption geometry. Bonding between C and the metal arises because of the nearness of the C valence levels to the s–d band of the Fe and Ni atomic levels and because of the availability of C 2p orbitals for better bonding interactions with metallic d orbitals [30]. This is in agreement with the expectation that p orbitals of the carbon are important participants in the frontier molecular orbitals. The lobes of these orbitals are well oriented and have the possibility of overlapping with the metal s and, especially, with p and d metal orbitals.

In general, electron transfer from CO to Fe and Ni nearest neighbors is observed, therefore the slab surface layer is negatively charged with regard to the bulk due to CO interaction (see Table 2). A large

<table>
<thead>
<tr>
<th>Bond</th>
<th>OP</th>
</tr>
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<tbody>
<tr>
<td>C 2s–Fe 4s</td>
<td>0.034</td>
</tr>
<tr>
<td>C 2s–Fe 4p</td>
<td>0.104</td>
</tr>
<tr>
<td>C 2s–Fe 3d</td>
<td>0.039</td>
</tr>
<tr>
<td>C 2s–Ni 4s</td>
<td>0.045</td>
</tr>
<tr>
<td>C 2s–Ni 4p</td>
<td>0.154</td>
</tr>
<tr>
<td>C 2s–Ni 3d</td>
<td>0.042</td>
</tr>
<tr>
<td>C 2p–Fe 4s</td>
<td>0.034</td>
</tr>
<tr>
<td>C 2p–Fe 4p</td>
<td>0.033</td>
</tr>
<tr>
<td>C 2p–Fe 3d</td>
<td>0.094</td>
</tr>
<tr>
<td>C 2p–Ni 4s</td>
<td>0.039</td>
</tr>
<tr>
<td>C 2p–Ni 3d</td>
<td>0.115</td>
</tr>
<tr>
<td>C 2p–Ni 4p</td>
<td>0.065</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Bond</th>
<th>OP</th>
</tr>
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<tbody>
<tr>
<td>Fe_nn–NN</td>
<td>0.803&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ni_nn–NN</td>
<td>0.845&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Fe_nn–NN</td>
<td>0.941&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ni_nn–NN</td>
<td>0.989&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>For CO/FeNi(111).
<sup>b</sup>For FeNi(111).

nn, nearest neighbor to C.
NN, up to the third nearest neighbor in the metallic surface.
Figure 5. COOP curves for Fe–NN and Ni–NN interactions before CO adsorption.

Figure 6. COOP curves for Fe–NN and Ni–NN interactions after CO adsorption.
bonding OP between C and both Ni and Fe atoms appears, whereas the Ni–Ni, Fe–Fe and Ni–Fe OPs decrease. After CO adsorption, the strength of the Ni–NN and Fe–NN bonds (NN: metallic atoms up to the third nearest neighbor) decreases to about 15% (see Table 4). A detrimental effect on the metal bonds is observed after CO adsorption on the FeNi(111) surface. Figure 5 shows a plot of the Fe–NN and Ni–NN bonds before CO adsorption. If we compare the latter figure with Figure 6, which shows the same interactions after CO adsorption, the changes in the Fe–NN and Ni–NN overlap populations after CO adsorption can be seen. Integration of the COOP curves up to the Fermi level gives smaller metal–metal overlap populations for the chemisorption system compared with the clean surface, thus confirming weakening of the metal bond after adsorption. We conclude that the Ni–C and Fe–C interactions mainly occur at the expense of the metallic bonds.

3. Conclusions

We have analysed theoretically the adsorption of CO on FeNi(111) by SIESTA calculations. Different configurations were initially selected in order to establish the preferential adsorption site and the corresponding molecule–surface distance. Ni–C and Fe–C interactions occur, mainly with the participation of the C s–metal p and C p–metal d orbitals. As a consequence, weakening of the metal bond by 15% after CO adsorption is observed. A detrimental effect on the metal bonds is observed after CO adsorption on the FeNi(111) surface and can be associated with alloy embrittlement by a decohesion mechanism.

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References


Appendix A: Computational methods

We performed calculations within the framework of the density functional theory (DFT) [13]. The exchange-correlation potential \( V_{XC} \) is considered within the generalized gradient
approximation (GGA) proposed by Perdew et al. [14], and the self-consistent total energy method, as implemented in the SIESTA Package code [15,16], was used. This implementation has been applied successfully in the study of several kinds of interactions [17]. The electron–ion interactions are treated by means of norm-conserving pseudo-potentials in agreement with the Troullier–Martins procedure [18]. For the basis set we use a double-zeta basis set plus polarization functions (DZP). The atomic orbitals were slightly excited (0.01 Ry) in order to limit the range of the pseudo-atomic basis orbitals [19].

We used a uniform grid in real space with a mesh cut-off of 450 Ry. The Brillouin zone was sampled, and total energy was converged with respect to the number of $k$ points resulting in the diagonal Monkhorst–Pack matrix ($7 \times 7 \times 1$) [20].

In order to understand the interactions between the atoms, we used the concept of COOP (crystal orbital overlap population) curves. The COOP curve is a plot of the overlap population-weighted DOS (density of states) versus energy. Integration of the COOP curve up to the Fermi level ($E_F$) gives the total overlap population of the bond specified and is a measure of the bond strength.