Catalytic Promotion and Poisoning: All-Electron Local-Density-Functional Theory of CO on Ni(001) Surfaces Coadsorbed with K or S

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The adsorption of CO on Ni(001) and its coadsorption with K or S as studied with our all-electron full-potential linearized-augmented-plane-wave method show that (i) K modifies the electrostatic potential in the surface layer, produces an increased occupation of the CO antibonding $2\pi^*$ states, and facilitates the dissociation of CO; (ii) in contrast, S interacts more covalently with the Ni surface and neighboring CO molecules thereby deactivating the surface and inhibiting CO dissociation.

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Chemisorption and dissociation of CO on a transition-metal catalyst are the initial stages in the synthesis of hydrocarbons from CO and H_2 (Fischer-Tropsch synthesis).[1] It has been observed that the addition of potassium increases the dissociation rate of CO molecules and strengthens the Ni-C bond[2,3] thus promoting the formation of higher hydrocarbons. Sulfur, on the other hand, is well known to act as a poison to catalysts.[4] On the basis of the effective-medium theory, Nørskov, Holloway, and Lang[5] suggested that the mechanism underlying the promotion and poisoning of the catalytic process on transition metals is electrostatic in nature. Experimental evidence from extensive studies of CO and K coadsorbed on Ni(001)[6] also supports this type of long-range interaction, i.e., that the principal effect of the coadsorbed alkali metal is to modify the electrostatic potential in the surface region. On the other hand, studies based on the coadsorption of CO and K on Cu(001)[7,8] and Ru(0001)[7] attributed a local nature to the promotion mechanism which is dominated by the direct interaction between K and CO, rather than being due to a substrate-mediated indirect interaction. Similarly, there exist controversial pictures of the role of sulfur poisoning: From an experimental study of chemical modification of chemisorptive and catalytic properties of nickel it was concluded[4] that each adsorbed sulfur atom affects about ten neighboring surface Ni atoms, i.e., the poisoning effect is of a long-range nature. In contrast, from a vibrational characterization of CO adsorbed on sulfur-modified Ni(001) surfaces Gland *et al.*[9] concluded that the S-CO interaction is predominantly local. On the other hand, a recent theoretical study[10] of S adsorbed on Rh(001) surfaces shows long-range features. Thus, the electronic origin of catalytic promotion and poisoning, although a key element in the understanding of catalysis, cannot be considered as settled at this point. So far, theoretical attempts to gain insight into the interaction mechanism between CO and metal surfaces have been mostly limited to cluster approaches.[11-14] While appealing, one of the major drawbacks of the cluster approach is its difficulty in accounting for the metallic nature of the substrate and, hence, describing long-range electrostatic effects in the metal-vacuum interface region.

In this Letter, we present the first all-electron local-density-functional studies of (i) a $c(2\times2)$ CO overlayer chemisorbed on Ni(001) (denoted by CO/Ni) and (ii) the promotion and poisoning of the CO adsorption process caused by coadsorption of K [(CO+K)/Ni] and S [(CO+S)/Ni], respectively. The surface is modeled by a single-slab geometry and the local-density-functional one-particle equations are solved self-consistently by use of the full-potential linearized-augmented-plane-wave (FLAPW) method.[15] Comparing the charge density between CO/Ni and the superposition of Ni(001) and free molecular CO, we find a depletion of the Ni-C-O σ-like charge and an increase in the antibonding $2\pi^*$ population (i.e., "σ donation and π back donation"). This confirms and refines the generally accepted picture of the interaction between CO and the transition-metal surfaces.[16] The effect of the K coadsorption is to change significantly the surface dipole layer which causes a 2-eV shift of the CO molecular orbitals to larger binding energies with respect to E_F, and additional antibonding $2\pi^*$ molecular orbitals become occupied. Moreover, we find evidence that the electronic density in the C-O σ-bonding region is further reduced. This coadsorption with K facilitates the dissociation of the CO molecule. In contrast, the coadsorption of S leaves the work function essentially unchanged and does not cause pronounced shifts of the molecular one-electron energies. Although this does not exclude electrostatic effects, there is evidence for covalent interactions between S and CO and, maybe more importantly, between S and the Ni substrate.

In this study, the CO molecules are assumed to form a dense $c(2\times2)$ overlayer with the molecules perpendicular to the surface, adsorbed in a top-site geometry. We use a C-O bond distance of 1.18 Å and a C-Ni bond length of 1.96 Å.[17] The high-coverage limit of coadsorbed K and S is modeled by the placement of the K or S atoms between the CO molecules in the form of a $c(2\times2)$ overlayer at a height of 3.14 Å with respect to the surface Ni atoms. The Ni substrate is represented by a three-layer film with adsorbed layers on both sides.

Before discussing the modifying effects of K and S we first highlight the results obtained for an unsupported CO monolayer and a pure $c(2\times2)$ CO overlayer on the Ni(001) surface. To help clarify the effects, we show in Fig. 1 the charge density of the 5σ and $2\pi^*$ orbitals [Figs. 1(a) and 1(b)] and the C partial density of states [Fig. 1(c)] of an unsupported array of CO molecules with the same spacing between the molecules as in the $c(2\times2)$ structure on the Ni(001) surface. That significant interactions occur between the molecules can be seen from the bandwidths of up to 1 eV found for the occupied states and 2 eV for the antibonding $2\pi^*$ states. Upon chemisorption onto Ni(001), the 5σ orbital interacts strongly and hybridizes with the band states of the substrate [cf. Fig. 1(d)]. New bonding states are formed between 6 and 7 eV below E_F whose character is a mixture of CO 1π and 5σ molecular states hybridized with localized Ni d_{z^2}-like character; its antibonding partner is formed just above E_F (marked by an arrow in Fig. 1(d)]. The net effect in the redistribution of charge upon chemisorption is a loss of electronic charge in the C-O bonding region and also from C-Ni σ-like antibonding derived states (cf. Fig. 2). The electrons from these states are transferred into states of π symmetry (cf. Fig. 2) leading to a partial occupation of the antibonding $2\pi^*$ states [cf. Fig. 1(b)] and of bonding states

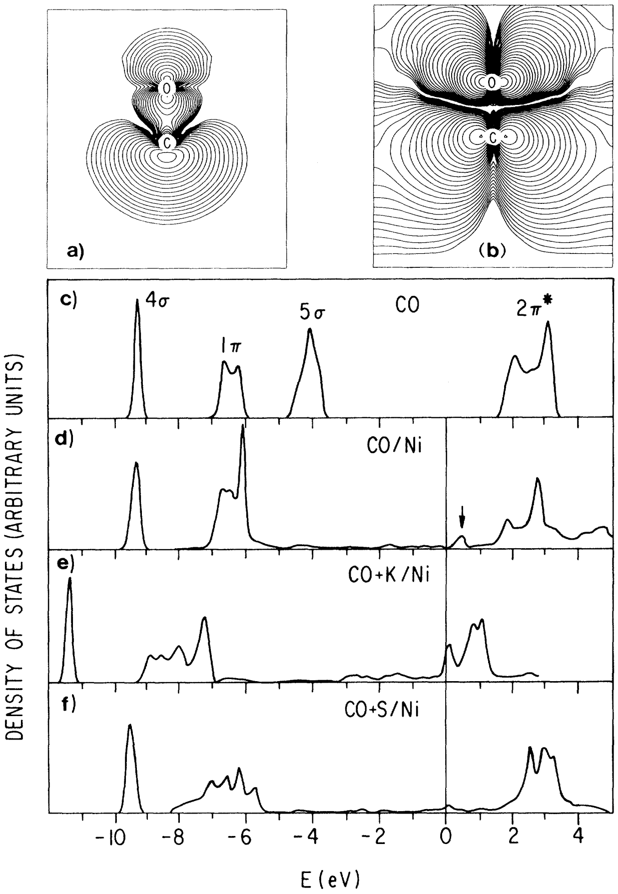

FIG. 1. Charge densities of (a) 5σ and (b) $2\pi^*$ states in an unsupported film of CO molecules. Partial densities of states, projected onto C spheres, for (c) unsupported CO film, (d) CO/Ni, (e) (CO + K)/Ni, and (f) (CO + S)/Ni.

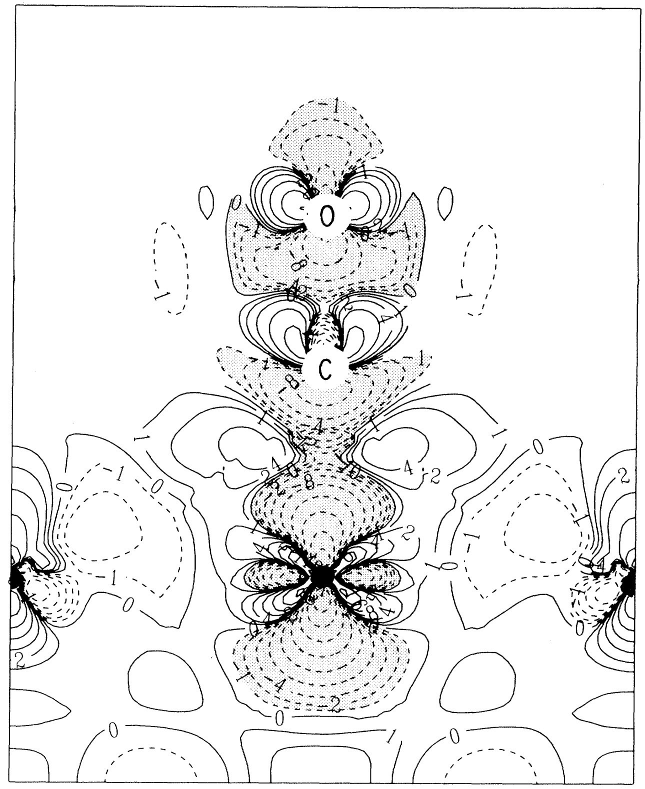

FIG. 2. Charge-density difference (in units of 10^{-3} e/a.u.^{3}) between CO/Ni and unsupported CO plus clean Ni all in the (110) plane perpendicular to the surface. For emphasis, some regions of negative density have been shaded.

between the C and Ni atom. The net effect is, therefore, a weakening of the C-O bond and the formation of a C-Ni bond. An alternative way of interpreting the increase of π-like charge between C and Ni (cf. Fig. 2) would be as a metallic screening of the loss of σ-like charge in the C-Ni bond axis. Thus, the present results for CO chemisorbed on Ni confirm and refine the generally accepted picture[16] of σ donation and π back donation.

Consider now the results obtained for a (CO + K)/Ni system. The promotion mechanism underlying the coadsorption of K can be seen from a plot of the difference in charge density between (CO + K)/Ni and CO/Ni shown in Fig. 3(a). There is an increase of the molecular $2\pi^*$ antibonding character [cf. Fig. 1(b)], together with a further depletion of the C-O bonding charge. We find that the main effect of K coadsorption onto CO/Ni is a shift of molecular single-particle energies to larger binding energies with respect to E_F [see Fig. 1(e)]. The electronic origin of these shifts lies in the K-induced modification of the electrostatic potential in the surface region: The alkali-metal valence electrons are polarized towards the transition-metal surface leading to a dipole layer which raises all electronic levels (including the Fermi level) of the substrate with respect to the vacuum level, i.e., it reduces the work function,[18] Φ. Thus, Φ (= 6.0 eV) for $c(2\times 2)$CO/Ni(001) is reduced to 1.9 eV when an additional $c(2\times 2)$ layer of K is coadsorbed. As a result of the location of the CO molecule within the surface dipole layer, the K-induced energy shift of the molecular levels is less pronounced and results in a relative shift to larger binding energies as referred to E_F of the substrate: the C $1s$ and O $1s$ core levels by 0.34 and 1.25 eV, respectively, the CO 4σ and 1π levels by 2 eV, and the 5σ states by less than 2 eV [cf. Fig. 1(e)]. In particular, the $2\pi^*$ states, which are mostly unoccupied without K, become partially occupied [the peak about 0.1 eV above E_F in Fig. 1(e) is of $2\pi^*$ character]. This leads to the weakening of the C-O bond and enhances the dissociation of the CO molecule. Besides this electrostatically driven mechanism, we find evidence for direct interaction between the alkali-metal $3p$ electrons and the molecular 1π states which manifests itself by a pronounced broadening of the CO 1π-derived band from 1 to 2 eV.

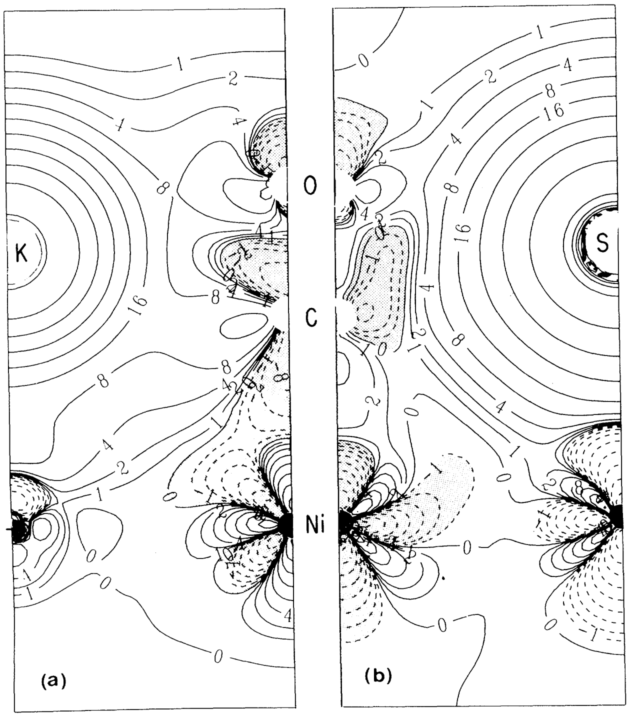

FIG. 3. As in Fig. 2, charge-density difference between (a) (CO + K)/Ni and CO/Ni and (b) (CO + S)/Ni and CO/Ni, each shown in half-cut views for easy comparison.

In contrast, the coadsorption of S slightly increases the work function (from 6.0 to 6.2 eV) indicating a small transfer of electronic charge towards the S sites. Furthermore, S-induced shifts in the molecular levels are small [less than 0.5 eV; cf. Fig. 1(f)]. The 1π/5σ band [around −7 eV, Fig. 1(f)] is markedly broadened from 1 eV for CO/Ni to 2.5 eV for (CO + S)/Ni. This may be taken as evidence for direct S-CO interactions (a similar but weaker broadening is induced by K coadsorption). Importantly, S is found to interact strongly with the Ni substrate leading to a depopulation of Ni d_{z^2}-like states [cf. Fig. 3(b)]. This S-Ni bonding leads to site blocking and to a deactivation of the Ni surface. The S-induced changes in the charge distribution in the Ni-C-O bonding region are found to be opposite to those induced by K (cf. Fig. 3): Ni-d_{z^2}-derived states are depopulated near the C atom. It is interesting to note, however, that near the O atom both K and S lead to similar charge rearrangements.

In conclusion, in these first model studies we have considered the physically unattainable high-coverage limit of K and S adsorbates in an atop site in order to make the calculation tractable even on present supercomputers. Among the interesting results obtained, we found that the changes in the electronic structure of CO chemisorbed on Ni(001) induced by the catalytic modifers K and S are of a complex nature and thus a simple classification into long-range versus short-range effects may not be significant. This investigation reveals that the catalytic promotion of K is dominated by electrostatically driven interactions which cause a shift of the molecular energy levels to larger binding energy and a larger occupation of the antibonding $2\pi^*$ levels, thus facilitating the dissociation of CO. In contrast, the poisoning effect of S is of a more complex nature involving covalent bonding between S and the Ni surface accompanied by a small transfer of electronic charge towards the S atoms (site blocking and deactivation of the surface) as well as direct interactions between S and adjacent CO molecules which tend to inhibit the dissociation of CO.

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