SURFACE SCIENCE LETTERS

LCAO-TYPE CALCULATIONS OF THE EFFECT OF K AND Cl ATOMS ON THE DISSOCIATION OF CO AT THE Ni(111) SURFACE

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Using an LCAO-type formalism, we calculate potential energy surfaces for the dissociation of CO over the Ni(111) surface and this surface in the presence of K and Cl additives. The observed increase (decrease) of the activation barrier for dissociation in the presence of Cl (K) arises due to differences in the population of the CO $\widetilde{2\pi}^*$ orbital for a stretched CO molecule.

For important reactions such as oxidation and hydrogenation of carbon monoxide, transition metals are used as catalyst [1–3]. Both reactions seem to take place via a dissociation of CO prior to its re-association with other adsorbed fragments. Depending on the reaction conditions, the dissociative adsorption of CO may become rate-determining [1] and is therefore of special interest. In a study performed on Ni surfaces it has been shown that adsorption of electro-positive elements such as K or Na strongly enhances the dissociative adsorption of CO [4]. On the other hand, the presence of electro-negative additives such as Cl or S inhibits the dissociation of CO [5]. Similar effects have been observed for these additives on a variety of transition metal surfaces [2].

The purpose of this letter is to obtain microscopic understanding of the way these atoms influence the dissociative adsorption of CO. Using an LCAO-type method, we calculate potential energy surfaces for the CO dissociation at the Ni(111) surface without and with K and Cl impurities.

Calculations are performed for small clusters consisting of four Ni atoms with one adsorbed CO molecule. In the case of additives, one K or Cl atom is used as substitutional impurity. The geometry of the cluster is shown in the inset of fig. 1. For calculating the total energy, we use the Atom Superposition and Electron Delocalization (ASED) technique [6]. Here, the total energy consists of two parts. The binding part, due to electron delocalization, is given by the extended Hückel one-electron energy. The atom superposition part is a sum of repulsive interatomic interactions. In previous calculations [7], this

a

b
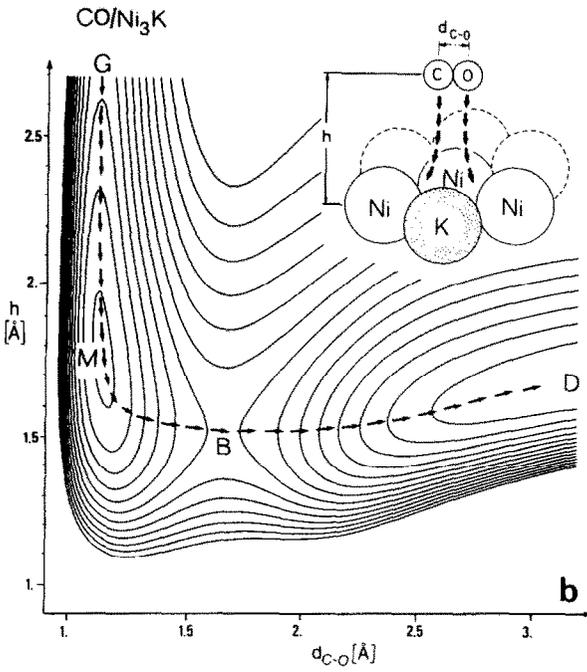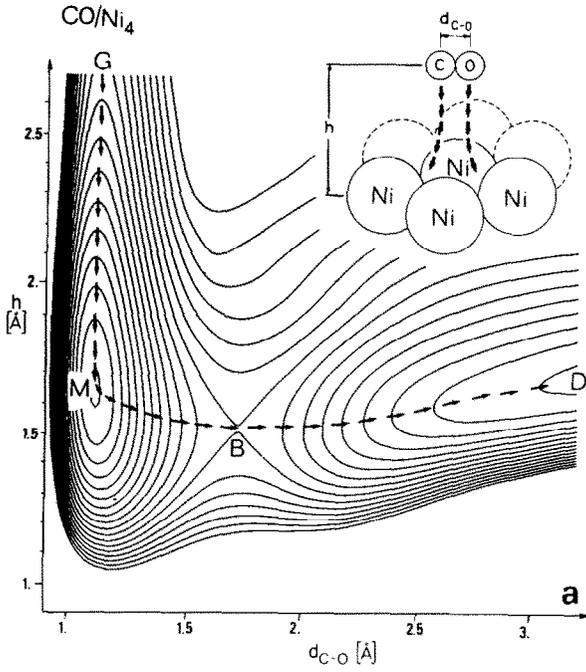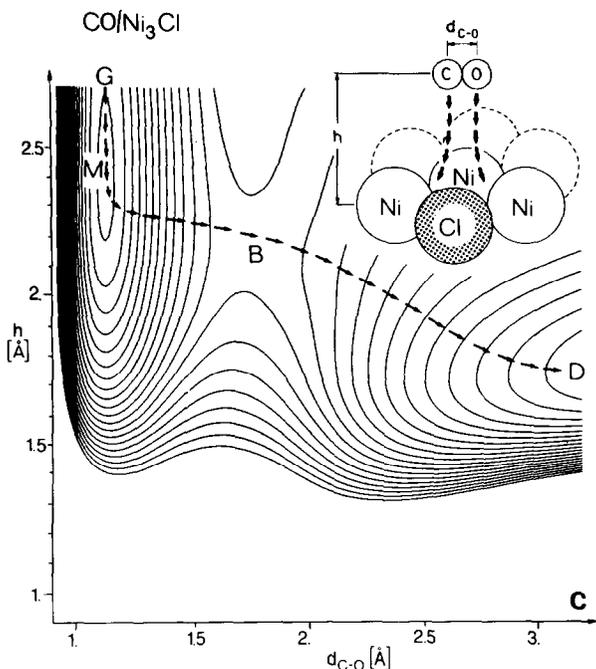
Fig. 1. Total energy contour plots for the dissociation of CO over Ni_4, Ni_3K and Ni_3Cl clusters. The equi-distant contours are separated by 0.2 eV. Preferential dissociation path (marked by arrows): gas (G), molecular precursor state (M), activation barrier (B), dissociated state (D). The cluster geometry is shown in the inset figures.

method predicted successfully the equilibrium geometry and the force constants for various adsorbed molecules.

A summary of parameters used in the calculation is given in table 1. Values for the ionization potentials are based on experimental data [9]. Slater-type orbital exponents have been calculated previously [10]. Upon adsorption on a Ni surface, the C and O levels shift by 1.5 eV upwards due to the presence of the metal electrons [11]. Using these parameters in order to describe the equilibrium adsorption of CO on Ni_4, we obtain a level spectrum which looks very similar to observed photoemission spectra [12]. Concerning the unfilled levels, the CO $2\pi^*$ induced resonance is ~ 2 eV broad and centered ~ 2.4 eV above E_F, which compares well with recent inverse photoemission data [13].

In our calculation the CO molecule is assumed to come down and to dissociate parallel to the surface. This assumption does not contradict the fact that the molecularly adsorbed CO stands perpendicular to the surface [14]. We rather speculate that the parallel adsorption geometry might be a precursor state for the CO dissociation in contrast to the perpendicular geometry for the

Table I

Atomic parameters used in the calculations: principal quantum number (n), ionization potential (IP) in [eV] and orbital exponents (ζ); double zeta basis (with orbital coefficients C) has been used for Ni d levels

Atom	s			p			d					
	n	IP	ζ	n	IP	ζ	n	IP	ξ_1	ξ_2	C_1	C_2
C [a]	2	18.5	1.658	2	9.76	1.618						
O [a]	2	26.98	2.246	2	12.12	2.227						
Ni [b]	4	7.64	1.800	4	3.99	1.500	3	10.00	5.750	2.000	0.568	0.629
K	4	4.34	0.874									
Cl	3	24.54	2.356	3	13.01	2.039						

[a] Ref. [7].

[b] Ref. [8].
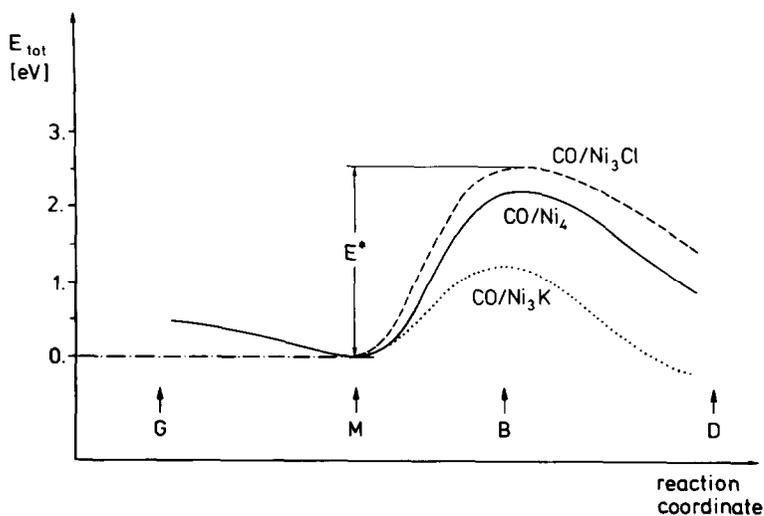
Fig. 2. Total energy changes as a function of the reaction coordinate along the preferential dissociation paths in fig. 1. E^* is the activation barrier for dissociation.

stable molecular adsorption state. The resulting potential energy surfaces for CO/Ni_4, CO/Ni_3K and CO/Ni_3Cl are presented in fig. 1 in the form of contour plots. The preferential dissociation paths are marked by arrows and the changes in the total energy along these trajectories are shown in fig. 2.

High above the surface the CO molecule is neutral, with an equilibrium bond length $d_{C-O} = 1.1$ Å. Molecular adsorption with a slightly increased bond length takes place at a height $h \approx 1.6$ Å. In this state, on all the substrates CO is slightly negatively charged ($Q \lesssim 0.2$ electron), with a $\widetilde{2\pi}^*$ occupancy below 0.5 electron. For Ni the d-band is nearly full ($n_d \approx 9.8$) and the sp-band is nearly empty ($n_{sp} \approx 0.3$). The relatively weak CO–metal bond in this geometry results mainly from the stabilization of the $\widetilde{5\sigma}$ orbital due to its hybridization with substrate sp and d levels (both of comparable importance).

In order to dissociate, CO has to overcome a dissociation barrier E^* at $h \approx 1.5$ Å and $d_{C-O} \approx 2$ Å. The magnitude of E^* is of special importance for the dissociation probability which is given by the Arrhenius law as $a \sim \exp(-E^*/kT)$. With respect to its magnitude on a pure Ni substrate ($E^* = 2.2$ eV), this barrier is slightly increased in the presence of Cl ($E^* = 2.5$ eV) and strongly decreased in the presence of K ($E^* = 1.2$ eV). These changes can be understood within the donation–backdonation mechanism for the CO–substrate bond [15]. According to this model, the CO bond is weakened upon adsorption as a result of partial filling of the lowest unoccupied $2\pi^*$ orbital due to hybridization with substrate d orbitals. This picture is justified by our calculation. Upon stretching the CO bond, the covalent splitting between the

CO π orbitals decreases and $2\pi^*$ approaches E_F. In the neighborhood of the activation barrier ($d_{C-O} = 2$ Å, $h = 1.5$ Å), the occupancy of this orbital has increased to $n_{2\tilde{\pi}^*} = 1.9$ on the Ni$_4$ substrate. A K impurity in the neighborhood of the CO provides an additional electron and – via the Ni 3d orbitals – increases the $2\tilde{\pi}^*$ filling to $n_{2\tilde{\pi}^*} = 2.1$. In an analogous way, a Cl impurity decreases this occupancy to $n_{2\tilde{\pi}^*} = 1.5$. In a similar calculation it has been shown that the above described effects of K and Cl impurities strongly decrease if such atoms are no nearest neighbor of the adsorbed molecule.

Having crossed the activation barrier, the CO molecule dissociates and reaches the minimum total energy for $d_{C-O} \geq 3$ Å. The C–O hybridization decreases in favor of that between the constituent C and O atoms, and the substrate. In this geometry, for the parameters chosen, there is a transfer of 0.5 –1 electron towards the C atom and 1–1.5 electron towards the O atom. These charge transfers seem exaggerated and make a total energy estimate uncertain, unless a self-consistent level readjustment is performed in this region.

In this paper, the K and Cl atoms have been chosen as substitutional impurities in order to separate best electronic from steric effects. It would be interesting to extend these calculations to the case of chemisorbed impurities. Concerning the parameter choice, also note that the effective Coulomb field of the K, Cl impurities will shift the CO levels (by ≤ 1 eV) in addition to the shift estimated for the metal surface. Since we expect this shift to be nearly constant for the dissociating molecule, it should not change the form of the potential energy surfaces and thus our conclusions.

In summary, we calculated potential energy surfaces for the dissociative adsorption of CO on clean Ni(111) surfaces and such with substitutional K and Cl impurities. It has been shown that the activation energy for dissociation increases in the case of Cl and decreases in the case of K additives. These changes are in agreement with changes in the catalytic activity and are caused by population changes of the $2\pi^*$-derived orbitals for a stretched CO molecule on these surfaces.

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