

## Molecular orbital studies on the CO/Ni chemisorption system in presence of alkali additives and steps

S K SAHA and B C KHANRA\*

Saha Institute of Nuclear Physics, 92 Acharya Prafulla Chandra Road, Calcutta 700009, India

MS received 11 October 1985; revised 8 January 1986

**Abstract.** The atom superposition and electron delocalization molecular orbital theory has been used to study the effect of alkali additives and steps on the dissociative chemisorption of CO molecule on Ni(001) surface. We have found that with increasing concentration of alkali atoms the CO bond length increases, the CO bond strength weakens and the CO dissociation barrier decreases. The results are in qualitative agreement with experimental results. The steps have also been found to reduce the dissociation barrier quite significantly compared with the reduction by alkali additives.

**Keywords.** Alkali additives; molecular orbitals; dissociation barrier; carbon monoxide.

PACS No. 82-65

### 1. Introduction

The role of additives and lattice imperfections on the catalytic activity of transition metals is of interest in view of its technological and scientific importance. Alkali metal compounds are frequently used along with the transition metal catalysts to alter their reactivity and selectivity in many heterogeneous reactions such as synthesis of ammonia, hydrogenation of carbon monoxide, steam reforming and hydrogenolysis etc (Bonzel 1984). Again, the presence of lattice imperfections like steps, kinks and voids etc is known to influence the catalytic activity more strongly than the plane surface (Somorjai 1979; Toyoshima and Somorjai 1979). With a view to understanding the role of alkali metals in actual heterogeneous reactions a large number of model experiments have been carried out (for detailed references see Bonzel 1984; Hegde and Ayyoob 1985). For a very typical system like CO chemisorption on alkali-covered Ni surfaces (say), it has been found that with increase in alkali coverage there is an increase in the probability of CO dissociation (Campbell and Goodman 1982; Kiskinova 1981). In order to understand this phenomenon we undertook an MO calculation and the results are presented in this paper. The system considered is CO/Ni in the presence of alkali additives, electronegative additives and steps. The key questions addressed are: How does the increasing concentration of chemical additives affect the bonding and the dissociation probability of CO on Ni(001) surface? How does the presence of a crystalline irregularity like steps influence the dissociation probability of CO molecule on the nickel surface?

---

\* To whom all correspondence should be addressed.

## 2. Theoretical model

For the subject of our interest we need to use either the *ab initio* Hartree Fock (HF) MO theory (Roothan 1951) or some of its approximate form like the complete neglect of differential overlap (CNDO) theory (Pople *et al* 1965) or the atom superposition and electron delocalization (ASED) theory (Anderson 1974, 1975). It is well known that the *ab initio* HF MO theory, though better than its other approximate forms, involves computation of a large number of integrations which makes itself prohibitively costly for studying chemisorption of molecules on transition metal surfaces. The only chemisorption systems so far studied by this *ab initio* HF theory, therefore, are very small systems, involving CO and a few transition metal atoms (Cederbaum *et al* 1975; Bagus and Hermann 1976; Hermann and Bagus 1977; Ellis *et al* 1977; Bagus and Hermann 1979; Rosén *et al* 1979, 1980; Bagus *et al* 1981). For systems of larger dimensions and involving more than two types of atoms as in our co-adsorption problem we consider it more convenient to use the ASED theory than the *ab initio* HF or CNDO theory. Particularly, except charges on the molecular orbitals or on the atoms, the ASED type calculations can give information about the bonding geometry and the energy levels etc as correctly as the HF method but with much less computer time. Given below is a brief outline of the ASED theory.

### 2.1 ASED theory

The ASED theory is an approximation to the non-iterative HF Roothan's MO theory (Roothan 1951). In the ASED theory the total energy is approximated as the sum of the orbital energies due to electron delocalization and atom-atom pairwise repulsive energies due to atom superposition. The total chemisorption system is considered as a superposition of  $n$  rigid atoms and the molecular orbitals are formed as usual from a linear combination of atomic orbitals. The coefficients are obtained by solving the secular equations  $(H - SE)C = 0$ ,  $S$  being the overlap matrix. Diagonal matrix elements of the Hamiltonian are approximated as the measured atomic ionization potentials and the off-diagonal matrix elements are approximated by

$$H_{ij} = 1.125 (H_{ii} + H_{jj}) \exp(-0.13 R),$$

where  $R$  is the internuclear separation. The rest of the calculations is straightforward.

This theory has previously been found to be successful in predicting various properties of chemisorption systems (Ray and Anderson 1983; Tománek and Bennemann 1983). In our study we have considered a nine-atom cluster from Ni(001) surface. The atomic parameters for the Ni atoms are taken from the work of Tománek and Bennemann (1983). The effect of alkali additives has been simulated by adjusting the ionization potentials of Ni atoms. This is possible since the adsorption of alkali through charge transfer from alkali to Ni atoms reduces the ionization potential of Ni atoms (Gerlach and Rhodin 1970).

## 3. Results and discussion

### 3.1 CO on preadsorbed alkali/Ni surface

Our calculations show that the CO molecule is most favourably bonded to the Ni(001) surface at the four-fold site with its axis normal to the surface and the carbon atom

pointing towards the surface. The detailed results are summarized in table 1. It is seen that with increasing concentration of alkali atoms the CO bond length increases and the CO stretching force constant decreases facilitating thereby the dissociation of the CO molecule on the Ni(001) surface. This is physically understandable since the bonding of CO to transition metals is known to occur through the donation of electrons from the  $5\sigma$  orbital of CO to the partially unoccupied  $d$  orbitals of the metal and back-donation from the metal  $d$  orbitals to the  $2\pi^*$  antibonding orbitals of CO molecule. The latter effect weakens the CO bond. The addition of alkali adsorbates to a transition metal surface enhances the backdonation of electrons to the CO  $2\pi^*$  orbital by reducing the difference in levels of the  $2\pi^*$  orbital and the  $d$  orbitals of the metal. This weakens the CO bond further and lowers the dissociation barrier. Tománek and Bennemann (1983) used this ASED model for CO chemisorption on clean Ni(111) surface and found the barrier height of the order of 2.2 eV, while in our present calculation it is found to be 2.78 eV. This suggests that Ni(111) surface may be more reactive than the Ni(001) surface. The results presented in table 1 are qualitatively consistent with the experimental results of Kiskinova (1981) and Kiskinova and Goodman (1981). Similar calculations on the effect of electronegative metal additives like Cl, Br and I etc on the CO dissociation on Ni surface give the results as shown in table 2. With addition of these additives the changes in the physical quantities are found to be of the opposite sign when compared to those due to the alkali additives. This is because the electronegative metal additives reduces the back-donation of electrons

**Table 1.** Calculated results for the CO/Ni chemisorption system in presence of alkali additives.

Decrease in ionisation potential (eV) of Ni due to alkali additives	CO bond length (Å)	CO stretch force constant (mdyne/Å)	Dissociation barrier (eV)
0.25	1.23	3.6	2.53
0.50	1.26	3.3	2.22
0.75	1.33	1.36	1.94
1.00	1.42	1.20	1.68

**Table 2.** Results with electronegative additives.

Increase in ionization potential (eV) of Ni due to alkali additives	CO bond length (Å)	CO stretch force constant (mdyne/Å)	Dissociation barrier (eV)
0.25	1.164	10.31	2.88
0.50	1.156	10.57	3.13
0.75	1.152	10.74	3.32
1.00	1.146	10.86	3.46

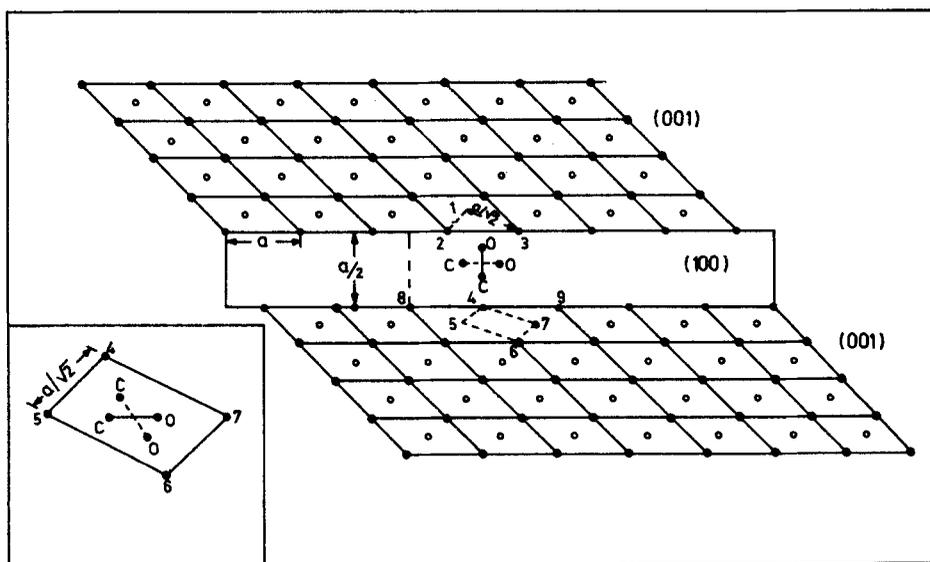
from metal  $d$  band to the CO  $2\pi^*$  orbital and thus raises the dissociation barrier.

### 3.2 CO on steps

We have also studied the chemisorption of CO on stepped surface. The step geometry considered in this work is shown in figure 1. The two terraces are in the Ni(001) surface separated by a step height  $a/2$  in the (100) surface, where  $a$  is the lattice parameter of Ni. In reality, steps, terraces and kinks of known direction and orientation can be created by cutting single crystals in various directions. In this work, however, we have considered the idealized geometry as shown in figure 1. We have considered the nine-atom cluster from two terraces and one step. For various orientations of CO on the terraces and on the step we have calculated the barrier height for CO dissociation. We were particularly interested in two chemisorption sites, one at the centre of the terrace unit cell formed by the atoms numbered 4, 5, 6 and 7 (see inset in figure 1) and the other on top of the atom No. 4. While on the former site the barrier for dissociation of the molecule parallel to the terrace is 2.76 eV, the barrier for dissociation of the molecule at the second site (above atom No. 4) parallel to the step height is 1.304 eV. Though for the idealized geometry considered in this work the numerical values obtained and quoted above need not be taken at their face values, their differences seem to suggest that the probability of dissociation of a CO molecule is higher on the step than on the terrace.

## 4. Conclusion

Within the limitations of MO calculations where one cannot consider a large number of steps or terraces (for enormous increase in computation time) the present study



**Figure 1.** Schematic diagram of a step geometry for Ni. Inset: the unit cell in the terrace formed by the atoms numbered 4, 5, 6 and 7.

nevertheless shows that in catalysis the presence of steps is sometimes as important as the presence of alkali additives.

## References

- Anderson A B 1974 *J. Chem. Phys.* **60** 2477  
Anderson A B 1975 *J. Chem. Phys.* **62** 1187  
Bagus P S and Hermann K 1976 *Solid State Commun.* **20** 5  
Bagus P S and Hermann K 1979 *Surf. Sci.* **89** 588  
Bagus P S, Hermann K and Seel M 1981 *J. Vac. Sci. Technol.* **18** 435  
Bonzel H P 1984 *J. Vac. Sci. Technol.* **A2** 866  
Campbell C T and Goodman D W 1982 *Surf. Sci.* **123** 413  
Cederbaum L S, Domcke W, von Niessen W and Brenig W 1975 *Z. Phys.* **B21** 381  
Ellis D E, Baerends E J, Adachi H and Averill F W 1977 *Surf. Sci.* **64** 649  
Gerlach R L and Rhodin T N 1970 *Surf. Sci.* **19** 403  
Hegde M S and Ayyoob M 1985 *Proc. Indian. Nat. Sci. Acad.* **A51** 256  
Hermann K and Bagus P S 1977 *Phys. Rev.* **16** 4195  
Kiskinova M P 1981 *Surf. Sci.* **111** 584  
Kiskinova M P and Goodman D W 1981 *Surf. Sci.* **108** 64  
Popple J A, Santry D P and Segal G A 1965 *J. Chem. Phys.* **43** S129  
Ray N K and Anderson A B 1983 *Surf. Sci.* **125** 803  
Roothan C C J 1951 *Rev. Mod. Phys.* **23** 69  
Rosén A, Baerends E J and Ellis D E 1979 *Surf. Sci.* **82** 139  
Rosén A, Grundevik P and Morovic T 1980 *Surf. Sci.* **95** 477  
Somorjai G A 1979 *Surf. Sci.* **89** 496  
Tománek D and Bennemann K H 1983 *Surf. Sci.* **127** L111  
Toyoshima I A and Somorjai G A 1979 *Catal. Rev.* **19** 105