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Theoretical Studies on the Disproportionation of Carbon Monoxide on Nickel Clusters

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In the framework of CNDO (Complete neglect of differential overlap method, VOIP (Valence orbital ionization potential) has been evaluated using the method of Anno and Sakai and for exchange integrals Wolfsberg-Helmholtz approximation has been used. With these the problem of parametrization with reference to transition metals becomes rather less troublesome. In its present form the method has been used for studying the disproportionation of carbon monoxide on a nickel cluster having five atoms. A large number of theoretical models were devised, which are based upon various mechanistic possibilities; for each of these, bond energies between different atoms were calculated and plotted against the distance, with an aim of studying the formation and desorption of CO_2. The present studies suggest that this reaction may follow a dissociative path, where in the first step one molecule of CO dissociates, leaving adsorbed carbon and oxygen on the Ni surface, followed by subsequent reaction of this adsorbed oxygen with another molecule of CO from the gas phase or it may follow disproportionation.

At higher temperatures the exposure of crystalline nickel surface to carbon monoxide results in the buildup of carbon. Below 180°C also the buildup of carbon can be brought about by using electrons of sufficiently high energy.[1–4] The adsorption of CO and the subsequent buildup of carbon on the catalyst surface is of great importance since these are the key steps in methanation:

$$3H_2 + CO \rightarrow CH_4 + H_2O$$

and Fischer–Tropsch synthesis. Although Auger data and flash desorption results show 10—20% overlayers of carbide like carbon on the surface following the reaction,[5] but the overall mechanism is not understood very clearly.

The proceeding of a chemical reaction may be described well by the splitting of one and formation of other bonds and consequently the changes in various bond energies may be expected to throw interesting light on the disruption (weakening) and formation of various bonds. The CNDO method as described here may, therefore, be expected to become a good method for studying the course of a reaction mainly because the bond energy is explicity defined in its framework.

Method

The local core matrix elements U_{ii} have been estimated from the atomic data using the following expression.

$$U_{ii} = I_{\mathrm{p}}(i) - (N-1)\,\gamma_{\mathrm{ss}} - M\gamma_{\mathrm{sd}} \tag{1}$$

Where $I_{\mathrm{p}}(i)$ is the valence state ionization potential, N denotes the total number of electrons in the valence s and p orbitals and M represents the number of electrons in the d orbital.

The I_{p}'s have been evaluated by using the method of Anno and Sakai.[6]

The exchange integral H_{ij} was calculated with the Wolfsberg-Helmholtz[7] approximation,

$$H_{ij} = KS_{ij}\,(H_{ii} + H_{ij})/2. \tag{2}$$

Thus in the present work only K, which is a dimensionless parameter, has been empirically assigned a value of 1.50. The electronic configuration $3d^{M}4s^{2}$ or $3d^{M}4s4p$ was considered for the ground state of the nickel atom. The orbital exponents suggested by Veigele et al.[8] were used for nickel and the Slater values were used for C and O.

The bond energies between atoms A and B were evaluated by the following equation,

$$\begin{aligned} E_{\mathrm{AB}} = \sum_{\gamma}^{\mathrm{A}}\sum_{\mathrm{S}}^{\mathrm{B}} (2P_{\mathrm{rs}}\,\beta_{\mathrm{rs}} - 1/2P_{\mathrm{rs}}^{2}\,\gamma_{\mathrm{AB}}) + (Z_{\mathrm{A}}Z_{\mathrm{B}}R_{\mathrm{AB}}^{-1} \\ - P_{\mathrm{AA}}V_{\mathrm{AB}} - P_{\mathrm{BB}}V_{\mathrm{BA}} + P_{\mathrm{BB}}P_{\mathrm{AA}}\gamma_{\mathrm{AB}}). \end{aligned} \tag{3}$$

E_{AB} is not identical with the bond energy and in fact represents a simple two-center energy decomposition scheme within the framework of zero differential overlap approximation. In the present communication we use this as a parameter for our theoretical studies. All the terms in Eq. 3 have their usual meaning. The method in the present form has been found to produce satisfactory results[9] on various properties of diatomic molecules of the first transition series and has also been successful in giving valuable information about the mechanism of oxidation of carbon monoxide on nickel clusters.[10] The present method has also been successfully applied to the chemisorption of CO on Ni clusters.[11]

Results and Discussion

At present there are following two main streams in the discussion of mechanism of the carbon deposition on the nickel surface exposed to carbon monoxide at high temperatures and by bombardment with electrons of sufficiently high energy.

1. Dissociative Mechanism: It is claimed that the dissociation of CO is the first step resulting in the formation of Ni–C and Ni–O bonds (2Ni+CO→Ni–C+Ni–O) followed by the CO_2 formation (Ni–O+CO→CO_2).

2. Disproportionation Mechanism: It predicts the reaction between two CO molecules on the surface (2 CO→$CO_2(g)+C_{ad}$).

Disproportionation is thermodynamically favorable but there is evidence[13] that the dissociative adsorption is also possible.

For our studies we have visualized three different possibilities for this reaction.

(i) Reaction between two adsorbed CO molecules [Models (1) and (2)].

$$CO_{ad} + CO_{ad} \rightarrow CO_2(g) + C_{ad}.$$

(ii) Reaction between two CO molecules, one of which is in chemisorbed state and the other reacts from the gas phase [Model (6)].

$$CO_{ad} + CO(g) \rightarrow CO_2(g) + C_{ad}.$$

(iii) Dissociation of CO to adsorbed C_{ad} and O_{ad} species followed by a reaction of adsorbed O_{ad} with CO either from the gas phase [Model (5)] or in an adsorbed state [Model (3)] and [Model (4)].

$$CO \rightarrow C_{ad} + O_{ad}.$$

$$O_{ad} + CO(g) \rightarrow CO_2(g) \text{ (Eley-Rideal)}$$

$$O_{ad} + CO_{ad} \rightarrow CO_2(g) \text{ (Langmuir-Hinshelwood)}$$

Based on the above three theoretically possible mechanisms, different models involving Ni_5 cluster were designed (Fig. 1) and in these models horizontal and tilted (30°) forms of adsorbed CO have also been included besides the familiar vertical form. For all these models the energy of interaction E_{int} of a CO molecule to the rest of cluster was calculated by using the following definition.

$$E_{int} = E_t - E_a \tag{6}$$

Where E_t is the total energy of the system containing all the atoms as shown in each model and E_a is the total energy of the system which has one molecule of CO less than the original model. The bond energy of

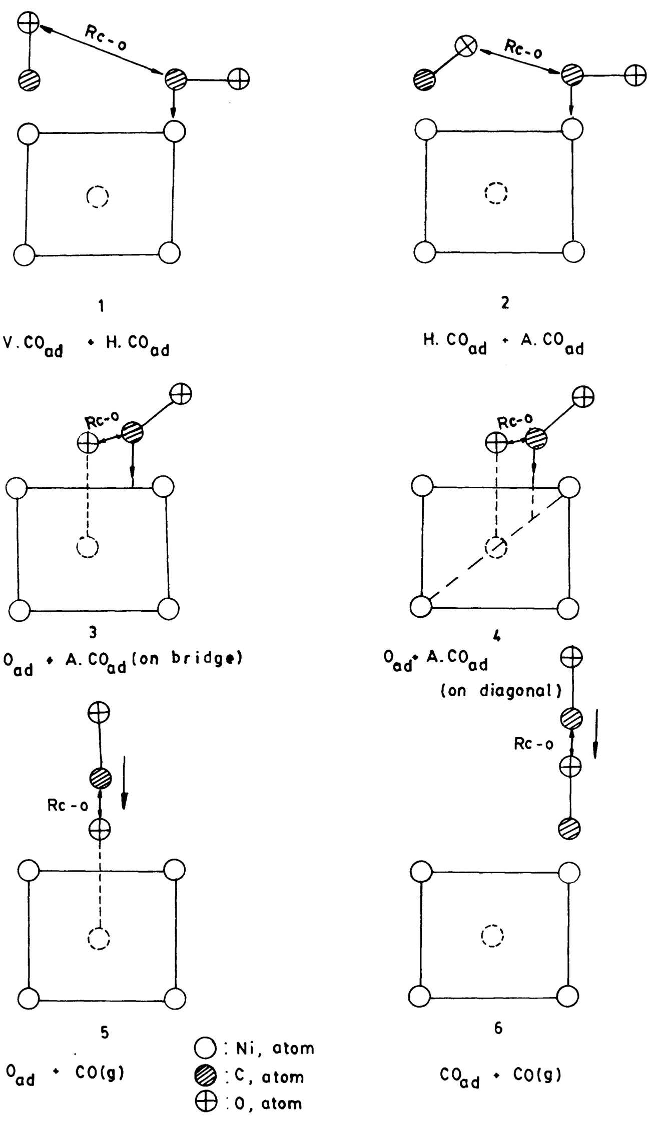

Fig. 1. Models used for studying the disproportionation of carbon monoxide on a 5-atom nickel cluster.

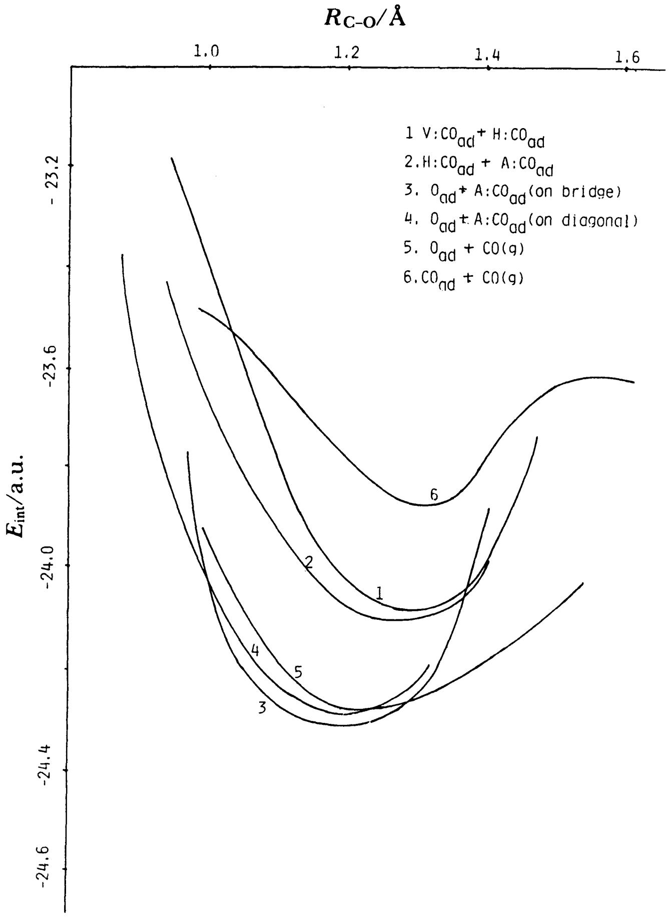

Fig. 2. Plot of E_{int} against R_{C-O}.

CO bond (the new bond which is being formed and is essential for the formation of CO_2) i.e. $E_{C\text{-}O}$ as well as sum of the bond energies of all the Ni–C and Ni–O bonds i.e. $\sum E_{Ni\text{-}C}+\sum E_{Ni\text{-}O}$ have also been calculated. All these energies have been plotted against $R_{C\text{-}O}$ i.e. the distance between C and O atoms involved in the new bond formation. The plots of E_{int} and $E_{C\text{-}O}$ against $R_{C\text{-}O}$ are good indices on the formation on CO_2, and plots of $\sum E_{Ni\text{-}O}+\sum E_{Ni\text{-}C}$ vs. $R_{C\text{-}O}$ may give information regarding the desorption of the CO_2 molecules.

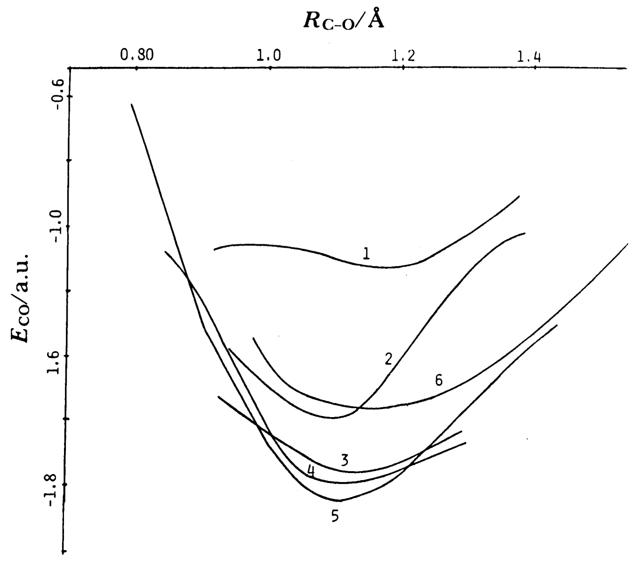

Fig. 3. Plot of $E_{C\text{-}O}$ against $R_{C\text{-}O}$.

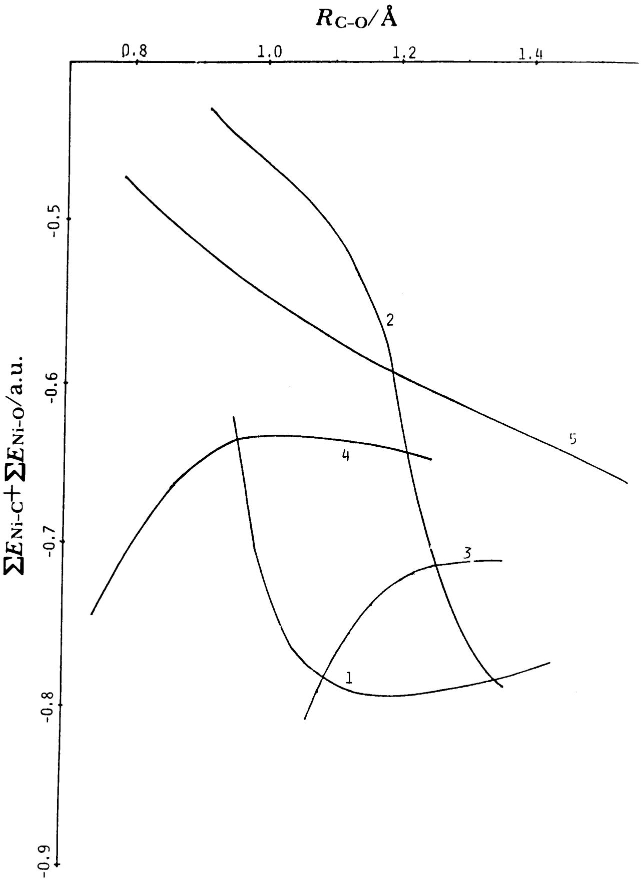

Fig. 4. Plots of $\sum E_{Ni\text{-}C}+\sum E_{Ni\text{-}O}$ vs. $R_{C\text{-}O}$.

Studies on Ni_5 Cluster: In Fig. 2, the interaction energy E_{int} of CO with the rest of the cluster has been plotted against $R_{C\text{-}O}$, and it seems that models (2), (3), (4), and (5), all of which represent a dissociation path, may be mechanistically more probable.

Figure 3 contains the plots of $E_{C\text{-}O}$ vs. $R_{C\text{-}O}$ and a comparative study of various curves shows that models (2), (3), (4), and (5) represent a pathway for the reaction which is more favorable for the formation of CO_2.

A study of Fig. 4 which includes plots of $\sum E_{Ni\text{-}C}+\sum E_{Ni\text{-}O}$ against $R_{C\text{-}O}$ reveals that as far as the possibility of desorption of CO_2 is concerned models (2) and (5) may be comparatively better suited.

On the basis of the qualitative studies of Ni_5 it seems that models (2) and (5), representing disproportionation and dissociative path respectively, are the only two suitable paths for the reaction under study.

Conclusion

The qualitative studies presented in this paper on Ni_5 cluster have shown that there are following two plausible mechanisms for this reaction.

1. Disproportionation Mechanism: It has been proposed that the disproportionation reaction occurs between two CO molecules adsorbed on the top of two adjacent Ni atoms. However, our studies are in favor of the scheme with one of these being adsorbed horizontally parallel and the other one tilted at an angle of about 30° to the surface.

$$CO \rightarrow H:CO_{ad} \text{ (Horizontally adsorbed)}$$

$$CO \rightarrow A:CO_{ad} \text{ (Tilted at an angle } 30^\circ\text{)}$$

$$H:CO_{ad} + A:CO_{ad} \rightarrow CO_2(g) + C_{ad}$$

The studies of Keim et at.[12] based on ellipsometry and Auger electron spectroscopy suggest disproportionation of the absorbed CO on Ni (100) surface due to bombardment by electrons of very high energy. Our studies presented here suggest that the disproportionation involves a reaction between a horizontally adsorbed CO molecule with a tilted CO molecule adsorbed on an adjacent site (Model 2).

2. Dissociative Mechanism: It is proposed that in the first step the CO molecule dissociates leaving O adsorbed at a four fold symmetrical site, which finally reacts with another molecule of CO from the gas phase to leave adsorbed C and simultaneously form CO_2 which desorbs immediately (Model 5)

$$CO \rightarrow C_{ad} + O_{ad}$$

$$O_{ad} + CO(g) \rightarrow CO_2(g)$$

A dissociative mechanism has also been proposed by Madden and Ertl[4] on the basis of their LEED and AES studies and by Caputi et al.[13] on the basis of their kinetic studies.

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