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Disproportionation of Carbon Monoxide on the Surface of Titanium and Vanadium Clusters

Arun Kumar SRIVASTAVA,* Kamla Kant TEWARI, and Isao KOJIMA†
Department of Chemistry, University of Allahabad, Allahabad, India
†Analytical Chemistry Division, National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305
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In the framework of CNDO (Complete Neglect of Differential Overlap method) VOIP (Valance Orbital Ionization Potential) has been evaluated using the method of Anno and Sakai and for exchange integrals Wolfsberg–Helmholtz approximation has been used. The method has been used for studying the disproportionation of carbon monoxide on titanium and vanadium clusters having two atoms respectively. A large number of theoretical models were designed, based upon various mechanistic possibilities. The bond energies between different atoms have been plotted against the distance, for the purpose of studying the formation and desorption of CO_2. The present studies suggest that the disproportionation of CO on titanium cluster may follow a dissociative path while in case of vanadium cluster this reaction may follow a disproportionation, where disproportionation involves a reaction between a 'bridge site' adsorbed CO molecule with a gas phase CO molecule.

The catalytic properties of transition metal surfaces have motivated much of the surface science research into the chemisorption of atoms and molecules.[1] The interaction of CO with metal surfaces has attracted much attention since it is considered to be a model system for understanding molecular chemisorption. The CO molecule usually bonds vertically to the surface through the carbon atom. However, there are strong-chemisorption (e.g. Nickel) and weak-chemisorption (e.g. Copper) limits, and cases of tilted and lying down molecules are also reported.[2,3] Chemisorption of carbon monoxide with Fe has been studied in detail[4–9] and anomalously low stretching mode in electron energy loss experiment has been observed.

It is thought that molecular specie is a precursor to dissociation and is important in catalytic behavior of iron.[8] Several theoretical models have been suggested to describe the chemisorption of CO.[10–14] Experimental studies based on LEED, UPS, XPS, AES, EELS,[15] and spin polarized photoemission have been reported.[16] Titanium and vanadium are known to be highly reactive transition metals relevant to problems of technological importance such as hydrogen storage[17] and also as active ingredient in some complex catalysts.[18] The adsorption of CO and subsequent build-up of carbon on the catalyst surface is of great importance since these are the key steps in methanation and Fischer–Tropsch synthesis. UPS and AES[19,20] studies have concluded that CO is dissociated on the clean titanium film at room temperature. Lee and coworkers[21] have performed molecular orbital calculation for studying molecular and dissociative chemisorption of CO on several metal surfaces.

The proceeding of a chemical reaction may be described by the splitting and formation of various bonds and therefore the changes in various bond energies may be expected to give useful information on the mechanism of the reaction. In CNDO framework the bond energy is explicitly defined and consequently the method as described here is much simpler than ab-initio method and has already been shown to be quite useful for making comparative studies.[22–24] Here we report our CNDO results on disproportionation of CO on titanium and vanadium clusters.

Method

The CNDO method is widely used and retains the main features of electron repulsion introduced by Pople, Santry, and Segal.[25] In this method the involvement of many parameters makes it less useful for the transition metal system. An effort has been made by Srivastava and Miyazaki[22,23] to reduce the number of parameters in the CNDO technique.

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

$$U_{ii} = -I_p(i) - (N-1)\gamma_{ss} - M\gamma_{sd}.$$

Here $I_p(i)$ 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 d-orbital. The I_p's have been calculated by using the method of Anno and Sakai,[26] where valence orbital ionization potential (VOIP) was calculated with the help of a quadratic equation as given below:

$$\text{VOIP} = A_0 + A_1Z + A_2Z^2,$$

where Z is the atomic number, A_0 and A_1 were evaluated with the help of the following expressions,

$$A_0 = a_0 + a_1M + a_2M^2,$$

$$A_1 = b_0 + b_1M.$$

Values of a_0, a_1, a_2, b_0, and b_1 have been taken from Ref. 26. The exchange integral H_{ij} has been calculated with the help of Wolfsberg–Helmholtz approximation.[27]

$$H_{ij} = K\,S_{ij}(H_{ii} + H_{jj})/2.$$

The electronic configuration $3d^m4s^2$ or $3d^m4s4p$ was assumed for the ground state of titanium and vanadium atoms. Thus in the present work only $K(=1.5)$ has been used as an empirical parameter. The bond energy has been evaluated from the following expression.

$$E_{AB}=\sum_{\mu}^{A}\sum_{\nu}^{B}(2P_{\mu\nu}\beta_{\mu\nu}-1/2P_{\mu\nu}^{2}\gamma_{AB})$$
$$+(Z_AZ_BR_{AB}^{-1}-P_{AA}V_{AB}-P_{BB}V_{BA}+P_{AA}P_{BB}\gamma_{AB}),$$

where all the terms have their usual meaning.

Results and Discussion

Theoretically one can predict the following mechanisms for the disproportionation of CO on the surface of titanium and vanadium.

1. Dissociative Mechanism. It claims that the dissociation of CO is first step with the formation of Ti–C and Ti–O bonds.

$$2\mathrm{Ti}+\mathrm{CO}\rightarrow\mathrm{Ti{-}C}+\mathrm{Ti{-}O}$$

followed by

$$\mathrm{Ti{-}O}+\mathrm{CO}\rightarrow\mathrm{CO_2}$$

Similarly for vanadium formation of V–C and V–O bonds is the first step.

2. Disproportionation. It predicts reaction between the CO molecules on the surface

$$(2\mathrm{CO}\rightarrow\mathrm{CO_2(g)}+\mathrm{C_{ad}}),$$

where (g) refers to a gas phase species and (ad) to an adsorbed or surface species.

Here three different possibilities have been considered for this reaction.

(i) Reaction between two adsorbed CO molecules (Model-D)

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

(ii) Dissociation of CO to adsorbed C_{ad} and O_{ad} species follow by a reaction of adsorbed O_{ad} with CO either from the gas phase (Model-B) or in an adsorbed state (Model-A and Model-C)

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

(iii) Reaction between adsorbed CO and another CO molecule from the gas phase (Model-E)

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

Based upon the above three theoretically possible mechanisms different models involving Ti_2 and V_2 clusters were designed as shown in Fig. 1. 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:

$$E_{int}=E_t-E_a,$$

where E_t is the total energy of the system containing all the atom 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.

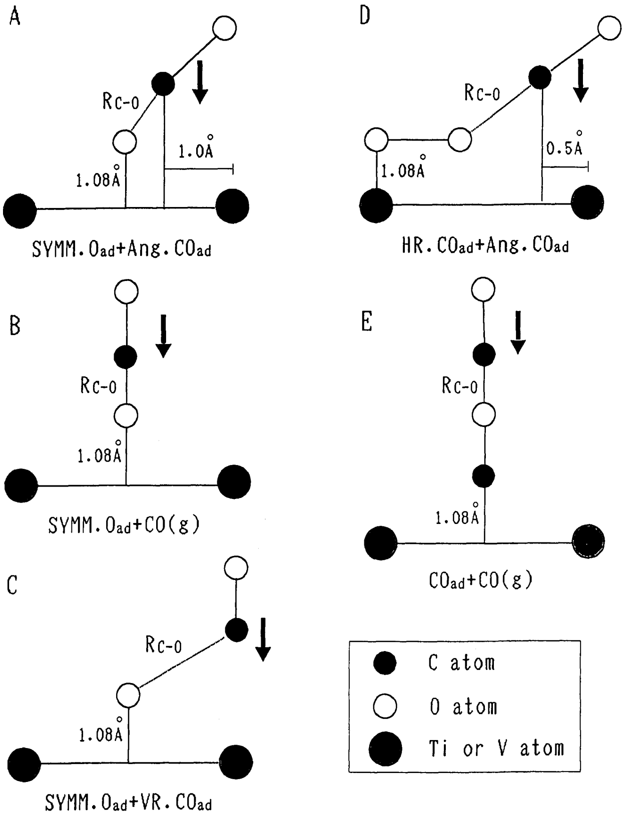

Fig. 1. Disproportionation of CO on Ti_2 or V_2 clusters.

The bond energy of CO bond (the new bond which is being formed and is essential for the formation of CO_2) i.e. E_{C-O} as well as the bond energies of the adsorbed C–O bond and Metal–O bonds were calculated. All these energies have been plotted against R_{C-O} i.e. distance between C and O atoms involved in the new bond formation. The plots of E_{int} and E_{C-O} against R_{C-O} are expected to throw light upon the formation of CO_2 and plot of $E_{metal-O}$ vs. R_{C-O} may give information regarding the desorption of the CO_2 molecules.

(a) Disproportionation of CO on Titanium Cluster (Ti_2). In Fig. 2 the energy of interaction E_{int} of carbon monoxide with rest of the cluster has been plotted against R_{C-O} and it seems that Model-C which represents a dissociative path, may be mechanistically more probable.

Figure 3 contains the plots of E_{C-O} vs. R_{C-O}. A comparative study of various curves shows that Model-C represents a pathway for the reaction which is more favorable for the formation of CO_2.

Figure 4 presents the plot of bond energy E_{Ti-O} against bond distance R_{C-O}. A close study of these curves reveals that as far as the possibility of desorption of CO_2 is concerned Model-C may be comparatively better suited.

Figure 5 presents the plot of $E_{C-O_{ad}}$ i.e. bond between O_{ad} and C against R_{C-O}.

On the basis of the qualitative studies on Ti_2 cluster, it

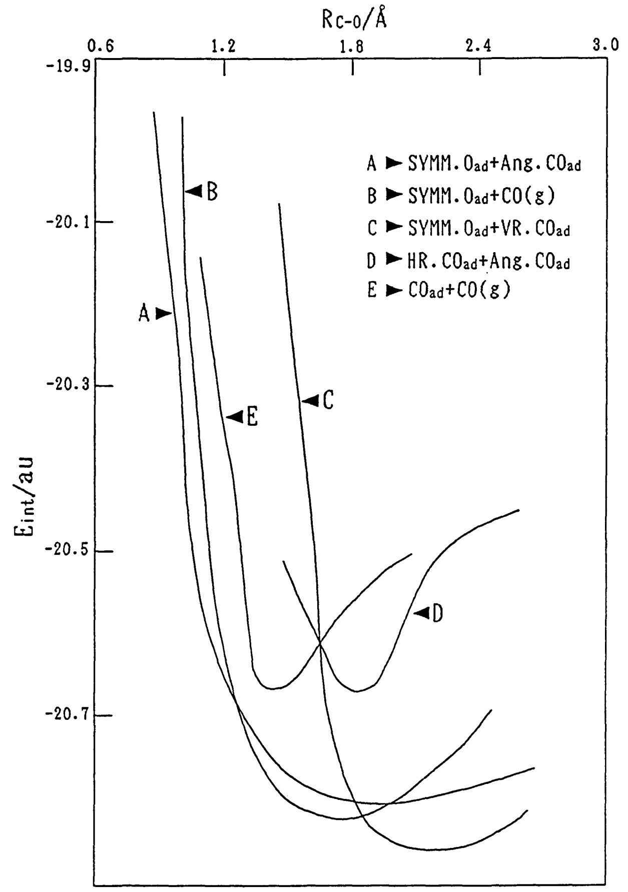

Fig. 2. Interaction energy E_{int} against R_{C-O} involving a Ti_2 cluster.

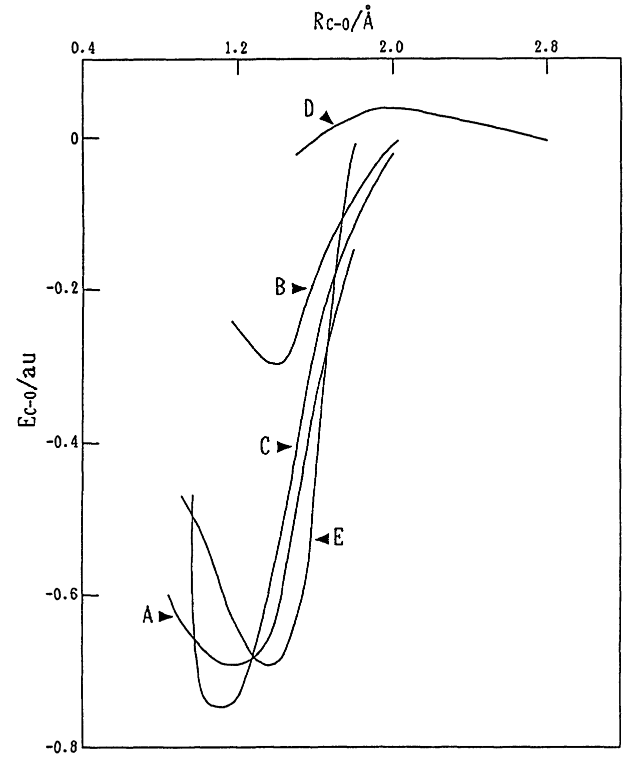

Fig. 3. Energy of C–O bond i.e. E_{C-O} against R_{C-O} involving a Ti_2 cluster.

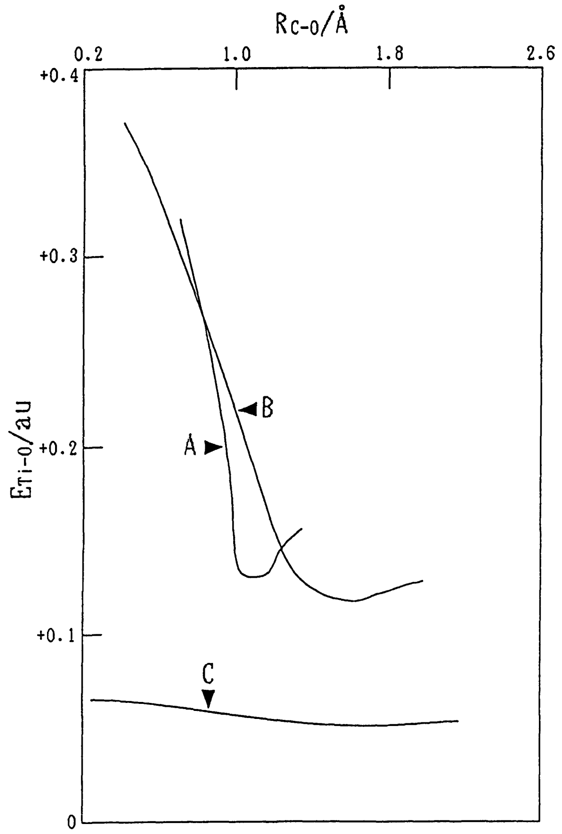

Fig. 4. Bond energy of Ti–O bond i.e. E_{Ti-O} against R_{C-O} involving a Ti_2 cluster.

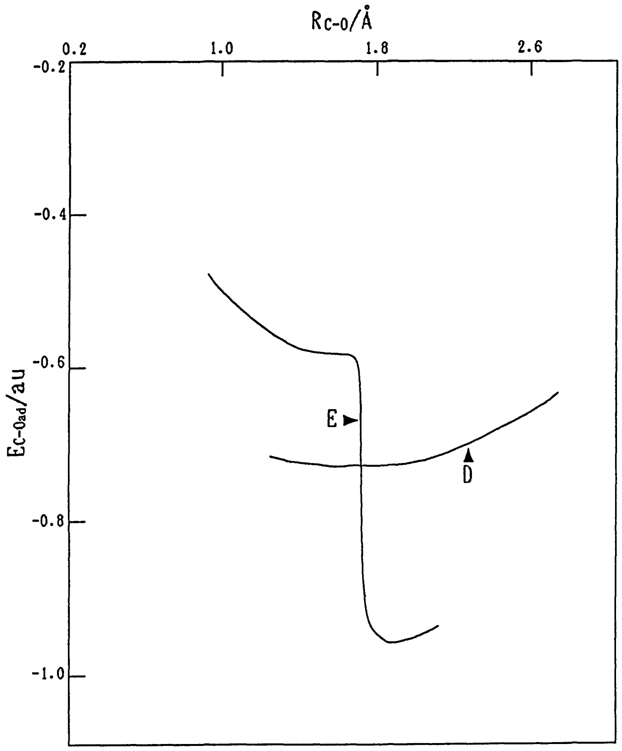

Fig. 5. Energy of C–O_{ad} bond i.e. $E_{C-O_{ad}}$ against R_{C-O} involving a Ti_2 cluster.

seems that Model-C, representing the dissociative path is the only suitable path for the reaction under study. Our findings are in good agreement with the findings of Srivastava et al.[23] The dissociative mechanism for this reaction may be as given below:

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

$$O_{ad} + V : CO_{ad} \rightarrow CO_2.$$

A similar dissociative mechanism has also been proposed by Madden and Ertl,[28] on the basis of their LEED and AES studies.

(b) Disproportionation of CO on Vanadium Cluster (V_2). The energy of interaction E_{int} of carbon monoxide with rest of the cluster has been plotted against R_{C-O} in Fig. 6. From these curves it may be concluded that the Model-E represents a more suitable path for this reaction.

The plots of E_{C-O} against R_{C-O} are given in Fig. 7. A close scrutiny of these curves suggests that Model-E represents a pathway for the reaction which is more favorable for the formation of CO_2.

Plots of E_{V-O} vs. R_{C-O} are given in Fig. 8. It is interesting to note that curves A, B, and C, based upon Models-A, B, and C, respectively, show a strengthening of V–O bond, thus in case of these models there seems to be virtually no possibility of CO_2 desorption after its formation.

From Fig. 9 the weakening of C–O bond is evident in case of Model-E. So it can be concluded that the Model-E may be more favorable for the desorption of

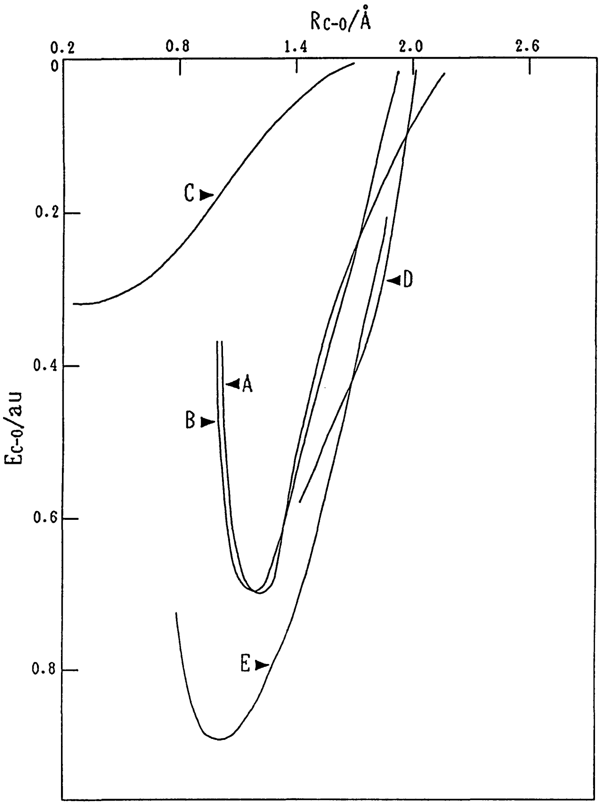

Fig. 7. Energy of C–O bond i.e. E_{C-O} against R_{C-O} involving a V_2 cluster.

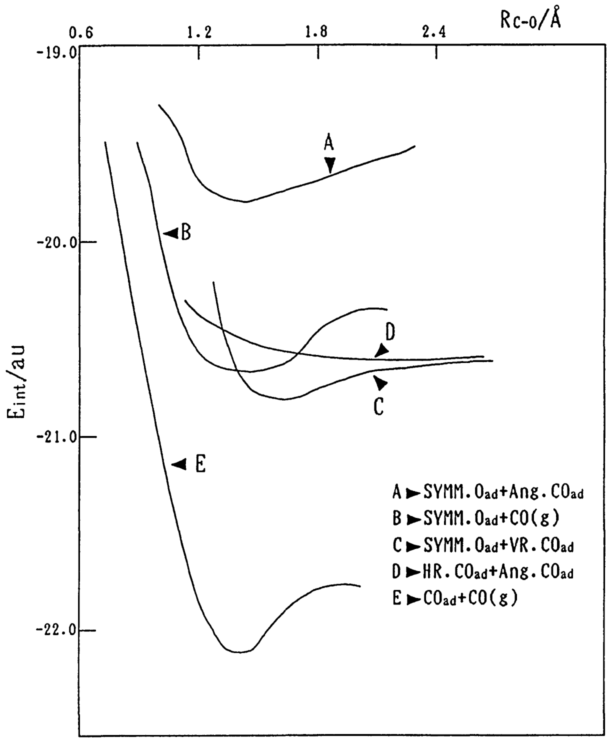

Fig. 6. Interaction energy E_{int} against R_{C-O} involving a V_2 cluster.

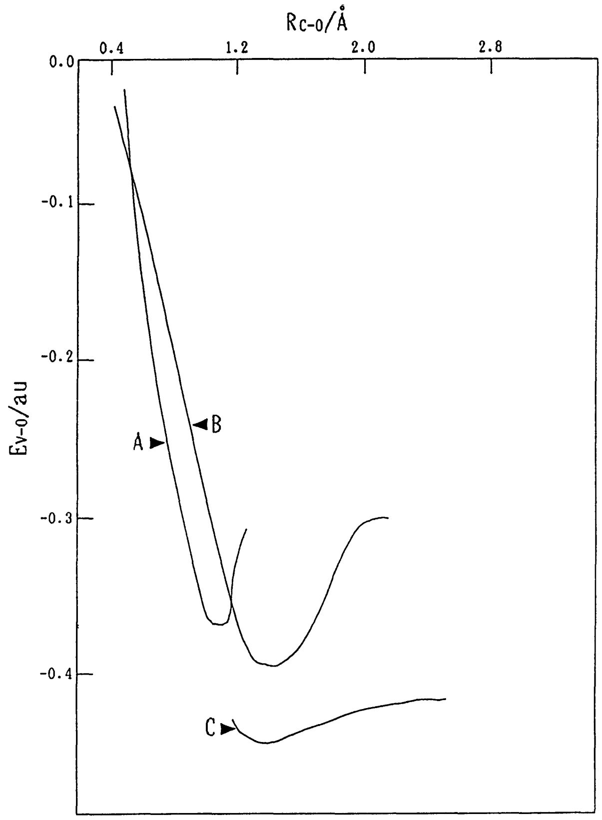

Fig. 8. Bond energy of V–O bond i.e. E_{V-O} against R_{C-O} involving a V_2 cluster.

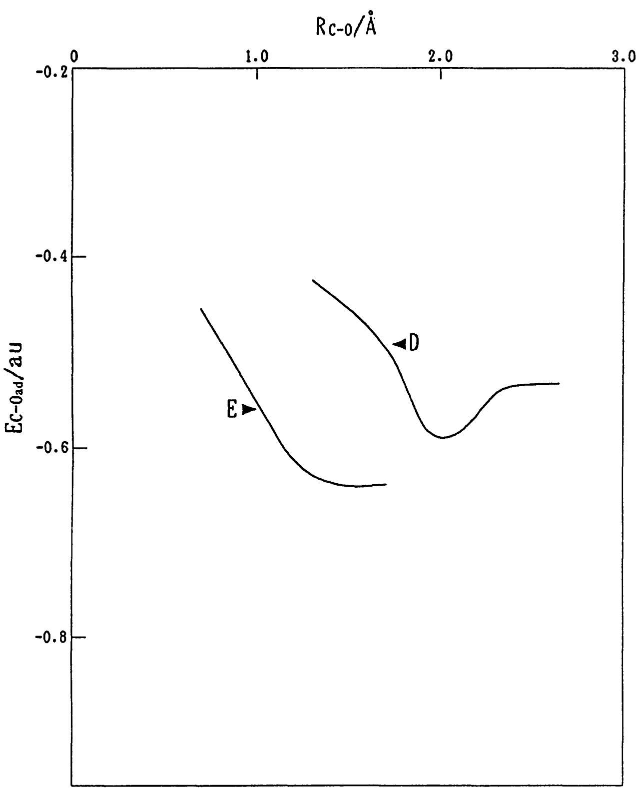

Fig. 9. Energy of C–O_{ad} bond i.e. $E_{C\text{-}O_{ad}}$ against $R_{C\text{-}O}$ involving a V_2 cluster.

CO_2.

Thus on the basis of our qualitative results, it can be suggested that Model-E offers a more suitable course for the reaction under study. The qualitative studies on V_2 cluster have shown that the following mechanism may be suggested for this reaction:

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

A similar disproportionation mechanism has also been proposed by Keim et al.[29] on the basis of their ellipsometry and AES studies.

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References

1) D. A. King and D. P. Woodruff, "The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis," Ellsevier, New York (1988), Vols. 1—4.

2) E. W. Plummer and W. Eberhardt, *Adv. Chem. Phys.*, **49**, 50 (1982).

3) H. J. Freund and M. Neumann, *Appl. Phys.*, **A47**, 3 (1988).

4) D. W. Moon, S. L. Bernasek, D. J. Dwyer, and J. L. Gland, *J. Am. Chem. Soc.*, **107**, 4363 (1985).

5) R. S. Saiki, G. S. Herman, M. Yamada, J. Osterwalder, and C. F. Fadley, *Phys. Rev. Lett.*, **63**, 283 (1989).

6) D. W. Moon, D. J. Dwyer, and S. L. Bernasek, *Surf. Sci.*, **1985**, 163.

7) F. Jona, K. O. Legg, H. D. Shih, D. W. Jepsen, and P. M. Marcus, *Phys. Rev. Lett.*, **40**, 1466 (1978).

8) D. W. Moon, S. Cameron, F. Zaera, W. Eberhardt, R. Carr, S. L. Bernasek, J. L. Gland, and D. J. Duzyer, *Surf. Sci.*, **180**, L123 (1987).

9) C. Bnndorf, B. Nieber, and B. Kruger, *Surf. Sci.*, **177**, L907 (1986).

10) G. J. Blyholder, *J. Phys. Chem.*, **68**, 2772 (1964).

11) B. Gumhalter, K. Wandelt, and Ph. Avouris, *Phys. Rev. B*, **37**, 8048 (1988).

12) E. Greuter, D. Heshelt, and E. W. Plummer, *Phys. Rev. B*, **27**, 7117 (1983).

13) C. R. Fischer, L. A. Bruke, and J. L. Whitten, *Phy. Rev. Lett.*, **45**, 344 (1982).

14) I. Kojima, A. K. Srivastava, and E. Miyazaki, *J. Chem. Phys.*, **84**, 4455 (1986).

15) J. Paul, S. D. Cameron, D. J. Dwyer, and F. M. Hoffmann, *Surf. Sci.*, **177**, 121 (1986).

16) N. B. Brookes, A. Clarkes, and P. D. Hohson, *Phys. Rev. Lett.*, **63**, 2764 (1989).

17) G. Alefeld and J. Volkl, "Hydrogen in Metals," Springer, Berlin (1978), Vols. I and II.

18) H. Morisaki, T. Watanabe, M. Iwase, and K. Yayama, *Appl. Phys. Lett.*, **29**, 338 (1976).

19) D. E. Eastman, *Solid State Commun.*, **10**, 933 (1972).

20) M. P. Hooker and J. T. Grant, *Surf. Sci.*, **62**, 21 (1977).

21) T. H. Lee and J. W. Rabalais, *Surf. Sci.*, **77**, 223 (1978).

22) A. K. Srivastava, I. Kojima, and E. Miyazaki, *Bull. Chem. Soc. Jpn.*, **59**, 3375 (1986).

23) A. K. Srivastava, E. Miyazaki, and I. Kojima, *Indian J. Chem., Sect. A*, **25**, 987 (1986).

24) A. K. Srivastava, I. Kojima, and E. Miyazaki, *Bull. Chem. Soc. Jpn.*, **62**, 3666 (1989).

25) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, 5129 (1965).

26) T. Anno and Y. Sakai, *Theor. Chim. Acta*, **18**, 208 (1970).

27) M. Wolfberg and C. Helmholtz, *J. Chem. Phys.*, **20**, 837 (1952).

28) H. H. Madden and G. Ertl, *Surf. Sci.*, **35**, 211 (1973).

29) E. G. Keim, F. Labohm, O. L. G. Gizeman, G. A. Bootsma, and J. W. Geus, *Surf. Sci.*, **112**, 52 (1981).