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Articles

MO Study of CO Chemisorption and Oxidation on a Pt(100) Surface

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Using an atom superposition and electron delocalization molecular orbital (ASED-MO) method, we have investigated the vibrational and chemisorptive properties of adsorbates on a Pt(100) surface during CO oxidation. The calculated vibrational stretching frequency for a predicted structure of $[CO\cdots O]^*$ complex is 1642 cm^{-1}. The CO bond stretches by 0.05 Å when adsorbed on one-fold site, and is tilted by 30 Å from the surface normal. We find the decrease in CO vibrational frequency on going from the one-fold to the high coordination sites. Binding at the two-fold site is predicted to be favored for $Pt_{18}(100)$ and at the 1-fold site for $Pt_{23}(100)$. From the calculations of the steric interactions, we have found that pre-adsorbed oxygen modifies the surface so that CO is adsorbed on the one-fold site ordered in a $(\sqrt{2}\times\sqrt{2})R45°$. Our results are in good agreement with recent experimental findings of Hong *et al.* [*J. Phys. Chem.* **1993**, *97*, 1258].

Introduction

Chemisorption of carbon monoxide on Pt surfaces has received considerable attention since the early days of Langmuir[1]. Recently, P. Gardener *et al.*[2] have studied infrared spectra of CO adsorbed on a Pt(100) surface. At the initial adsorption, two vibrational bands at 1864 cm^{-1} and 2062 cm^{-1} have been assigned to CO adsorbed on two-fold and one-fold sites, respectively. As the exposure is increased, both vibrational bands shift to higher frequencies. They explained this observation on that the $(\sqrt{2}\times\sqrt{2})R45°$ structure like Figure 1(a), which is often referred to the *c* (2×2) structure, rapidly fades away upon further exposure, and eventually transformes into a well ordered *c* (4×2) structure like Figure 1(b) at saturation.

The oxidation reaction of CO to CO_2 on group VIII metals is one of the most thoroughly studied heterogeneous catalytic reactions to date[3-10]. However, the structure for the reaction intermediate complex are still not well known. Ray and Anderson[11] calculated theoretically binding energies, bond length and charges of CO molecules on a Pt(111) surface, and predicted the Langmuir-Hinshelwood complex geometry for the oxidation reaction of CO. More recently, Hong and Richardson[12] reported spectroscopic measurements of the complex formed during the reaction of CO and O_2 on a Pt(100) surface. In their results, three bands were observed in the infrared spectra at 400 and 430 K. The first band at ~1630 cm^{-1} was assigned to a complex involving adsorbed CO and oxygen. The second and the third bands at ~2087 and 1880 cm^{-1} were assigned to CO adsorbed on the one-fold and the two-fold sites ordered in a $(\sqrt{2}\times\sqrt{2})R45°$ adlayer, respectively. Alternative assignments might be that the band at 1630 cm^{-1} is from CO adsorbed on the high coordination site (four-fold site in this model) on the surface[13], or is from CO adsorbed on or near a surface contaminant. Thus, it is interesting to examine whether the band at 1630 cm^{-1} re-

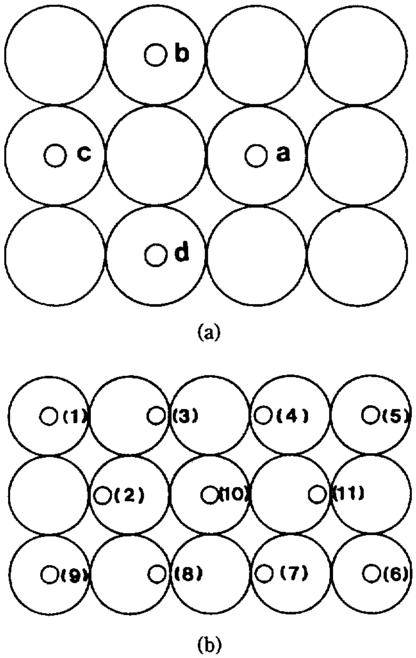

Figure 1. The structures for CO on Pt(100); (a) The *c* (2×2) structure at $\theta=0.5$, the positions of adsorbed CO molecule have expressed as a, b, c and d. (b) The *c* (4×2) structure at $\theta=0.75$; The sites of adsorbed eleven CO molecules are consisted of six asymmetric two-fold and five one-fold sites. The positions of adsorbed CO molecule have expressed as the numbers of 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11. The five one-fold sites to CO adsorbed are CO(1), CO(5), CO(6), CO(9), CO(10), and the six asymmetric two-fold sites are CO(2), CO(3), CO(4), CO(7), CO(8), CO(11). Intermolecular distance for CO(1)-CO(2) is 3.46 Å and for CO(1)-CO(3) is 3.70 Å.

Table 1. Atomic Parameters: Principal Quantum Number (n), Valence State Ionization Potential (IP), Orbital Exponents (ξ) and Respective Coefficient (C) -d only-used to produce results in Table 2; for all Adsorption Studies, Pt Ionization Potentials are increased by 1.5 eV and O and C Ionization Potentials are decreased by 1.5 eV; Further discussion is in ref. 25

Atom	s			p			d					
	n	Ip	ξ	n	Ip	ξ	n	Ip	C_1	$ξ_1$	C_2	$ξ_2$
C[a]	2	20.00	1.66	2	11.26	1.618						
O[a]	2	28.48	2.25	2	13.62	2.227						
Pt[a]	6	9.00	2.55	6	4.96	2.250	5	9.60	0.6567	6.013	0.5765	2.39

[a] Ref. 11.

Table 2. Calculated Bond Lengths (R_e), Vibrational Energies (ω_e) and Dissociation Energies (D_e) for Pt_2 and CO

Molecule	R_e (Å)	ω_e (cm^{-1})	D_e (kcal/mole)
Pt_2	2.45(2.34)[a]	252(218)[a]	94.08(85.4)[b]
CO	1.11(1.13)[a]	2221(2169)[a]	220(257)[b]

[a] Ref. 18. [b] From thermodynamical measurements (ref. 19).

sults from the [CO···O]* complex or the CO adsorbed on the high coordination site.

In this paper, we have calculated vibrational stretching frequencies for the reaction intermediate complex and compared them with the experimental and characterized theoretically the structure of [CO···O]* complex formed during CO oxidation on a Pt(100) surface. We also investigated the vibrational frequencies of CO in the presence of preadsorbed oxygen and discussed roles of oxygen. We have chosen the Pt(100) modeled by clusters and used the atom superposition and electron delocalization molecular orbital(ASED-MO) theory[11,12,14-16].

Theoretical Method

The ASED-MO theory is a semiempirical approach for determining approximate molecular structures, force constants, bond strengths, electronic spectra, and reaction energy surfaces, and orbitals starting with experimental atomic valence ionization potentials and corresponding Slater orbitals. This theory identifies two energy terms for the chemical bond formation. One is a pairwise atom-atom repulsion energy called E_R. The other is an attractive energy due to electron delocalization and bond formation. This energy is approximated by a one-electron molecular orbital energy, E_{MO}, obtained by diagonalizing a Hamiltonian similar to the extended Huckel:

$$E=E_R+E_{MO} \tag{1}$$

$$H_{ii}^{aa}=-\mathrm{VSIP}_i^a \tag{2}$$

$$H_{ij}^{aa}=0 \tag{3}$$

$$H_{ij}^{ab}=1.125\ (H_{ii}^{aa}+H_{jj}^{bb})S_{ij}^{ab}\ \exp(-0.13R^{ab}) \tag{4}$$

In Eq. (2) the VSIP are the atomic valence state ionization potentials, and in Eq. (4) S_{ij} is the overlap intergral between atomic orbitals i and j on atoms a and b, and R^{ab} is the internuclear distance in Å unit. For further details, the literature[17] may be consulted. The parameters in the theory are given in Table 1. Predicted bond distances, vibrational frequencies and dissociation energies for these system (Pt_2 and CO) are given in Table 2. The calculated values for the bulk systems are in reasonable agreement with experimental data[18,19]. To produce reasonable frequencies and charge transfers in this adsorption study, Pt ionization potentials[11] are increased by 1.5 eV and O and C ionization potentials are decreased by 1.5 eV to mimic self-consistency.

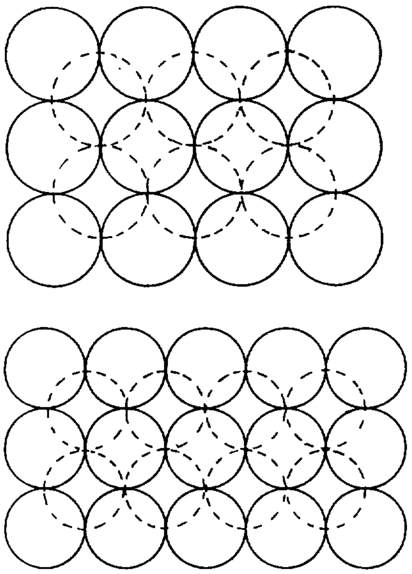

Figure 2. 18-atom cluster models of Pt(100) and 23-atom cluster. Clusters are bulk superimposable with Pt-Pt nearest neighbor distances of 2.77 Å.

J. P. Biberian[22] has proposed the patterns of structure as in Figure 1. In order to use these patterns for CO molecules, we model the Pt(100) surfaces with 18-atom and 23-atom clusters shown in Figure 2. The clusters are bulk superimposable with Pt-Pt nearest neighbor distance of 2.77 Å. The patterns of the c (2×2) structure at the coverage of $\theta=0.5$ and the c (4×2) structure at $\theta=0.75$ are shown in Figure 1(a) and 1(b), respectively. For Figure 1(a), four CO molecules are located in the one-fold sites with a, b, c, d-positions. For Figure 1(b), the eleven CO molecules are consisted of six asymmetric two-fold sites and of five one-fold sites. The five one-fold sites for CO adsorption are CO(1), CO(5), CO(6), CO(9), CO(10)-positions, and the six asymmetric two-fold sites are CO(2), CO(3), CO(4), CO(7), CO(8), CO(11)-positions. Intermolecular distances for CO(1)-CO(2) and CO(1)-CO(3)

Table 3. Calculated Binding Energies (BE), Heights (h), Bond Lengths (R), Charges (q), and Mulliken Overlaps for CO on Pt_{18} and Pt_{23} (Parentheses) Models of Pt(100) Surface

	1-fold (top site)	2-fold (bridged site)	high-coordination
BE (eV)	1.98(1.86)^a	2.00(1.75)^a 1.86^b	1.46(1.32)^a
h (Å)	2.03(2.03)	1.64(1.64) 1.83^b	1.24(1.24)
R (Å)	1.11(1.11)	1.13(1.13) 1.12^b	1.14(1.14)
C-$O_{overlap}$	1.53(1.53)	1.44(1.44) 1.49^b	1.36(1.39)
Pt-$C_{overlap}$	0.70(0.70)	0.86(0.84) 0.72^b	0.92(0.88)
q	0.47(0.50)	0.26(0.33) 0.42^b	0.13(0.20)

[a] See ref. 11, 21, 23 for the further discussion. [b] These are calculated results for a single asymmetric two-fold site (2-position).

are 3.46 Å, and 3.70 Å, respectively.

In the present calculations, the structure optimizations for the CO adsorption and oxidation have been carried out using the Pt_{18} cluster model. In addition, the Pt_{23} model has only been carried out to investigate the CO adsorption in the c (4×2) arrangement.

For the vibrational analysis, we have calculated the vibrational frequencies using an elementary formula for force constant, $k_e=(\Delta E/\Delta R^2)_e$, where ΔR increments are 0.01 Å for the C-O and the Pt-C bonds. The bending frequency has been calculated using the formula $k_{\theta_e}=360°/2\pi R(\Delta E/\Delta\theta)_e$, where $\Delta\theta$ increments are 1° for the CO bond in a plane perpendicular to the surface.

Results and Discussion

CO adsorption on Pt(100) surface. The results for the adsorbed CO are given in Table 3. It can be seen that the adsorbed CO molecule can occupy the one-fold, the two-fold, and the high coordination sites; their binding energies in the Pt_{18} cluster model are 1.98, 2.00, and 1.46 eV, respectively. The one-fold and the two-fold sites are equally favored for CO adsorption on the Pt_{18} cluster, in agreement with experimental studies at low coverages for unreconstructed structures.[21,22] For the Pt_{23} cluster, the binding energies are 1.86, 1.75, and 1.32 eV, respectively. It indicates that the one-fold site is also favored for the larger cluster. These results are in reasonable agreement with the cluster size effects discussed by Anderson.[11,23]

Table 4 shows the calculated and the observed vibrational, ω_e (cm^{-1}), for adsorbed CO on the Pt_{18} and the Pt_{23} (parentheses) clusters. For the Pt_{18} cluster, the calculated vibrational for the one-fold, the two-fold, and the high coordination sites are 2057, 1827, and 1723 cm^{-1}, respectively. For the Pt_{23} cluster, the vibrational are 2059, 1837, and 1725 cm^{-1}, respectively. For the asymmetric two-fold sites, the calculated CO vibration energy is 1952 cm^{-1}. This frequency is worth to note because the asymmetric two-fold sites are found in the c (4×2) arrangement. In order to form the c (4×2) arrangement, we must use the Pt_{23} cluster. In this case, the binding energy and the vibrational energy of the asymmetric two-fold site on a clean surface have been found larger than those of the two-fold site as shown in Table 3, and 4. Although we have not been able to explain completely the band shift suggested by P. Gardner *et al.*, we suggest the possibility of shifting to higher frequency. However, the calculated C-O vibrational energies are very close to the experimental results.[2,12] The C-O vibrational energies decrease on going from the one-fold to the high-coordination sites. Table 3 lists the optimized CO bond length and the C-O overlap population. Noteworthily as the Pt-C overlap population increases on going from the one-fold to high coordination sites, the C-O overlap population decreases and CO bond length increases. Thus, the C-O vibrational energies depend on the overlap population and the bond strength.

As mentioned earlier by Ray[11], with the valence electronic configuration $4\sigma^2 1\pi^4 5\sigma^2 \pi^0$, all CO molecules bind to the clean Pt(100) surface vertically with C atom closest to the surface. The bond is formed by electron transfer from the 5σ orbital of CO to metal orbitals and electron back-donation from occupied metal orbitals to unoccupied antibonding π orbital of CO. Thus on going from the one-fold to the high coordination sites, C-O bond strength decreases as shown in Table 3. These results are in reasonable agreement with the discussion of Ray *et al*[24]. However, part of the calculated bond stretchings for the two-fold site, the high coordination and the asymmetric two-fold are results of atomic ionization po-

Table 4. Calculated and Observed Vibrational Energies, ω_e (cm^{-1}), for Adsorbed Carbon Monoxide on Pt_{18} and Pt_{23} (Parentheses) Models of Pt(100) Surface

	1-fold (top site)		2-fold (bridged site)		high coordination	
	Cal	Exp	Cal	Exp	Cal	Exp
ω_e(C-O)stretch	2057(2059)	2087^a	1827(1837)	1880^a	1723(1725)	
		2062^b		1864^b		
			1952^c	1950^d		
ω_e(Pt-C)stretch	762(765)		975(636)		480(473)	
			669^c			

[a] Ref. 12. [b] Ref. 2. [c] Calculated value for asymmetric two-fold site (2-position). [d] Experimental value for asymmetric two-fold site. (see ref. 2).

tential shifts introduced for mimic self-consistency. With these parameters, the bond length of the free CO is stretched by 0.03 Å from the value in Table 2. Thus on the one-fold site a 0.03 Å shrinking has occurred, despite the π mixing. This is a result of stabilizing the 5σ orbital, which is antibonding in behavior[24]. In other words its energy rises as CO bond length decreases.

The steric interactions of adsorbed species. Lateral interactions of adsorbed species have been considered in studying CO adsorption and the role of oxygen on surface. Pt_{18} cluster has been used for the calculation of CO interaction. The calculation shows a single CO binds to the one-fold site (a-position in Figure 1(a)) with 1.98 eV, and b, c, d-positions shown in Figure 1(a) with 1.84 eV, 1.86 eV, and 1.84 eV, respectively. This small difference of binding energy between a-position and edge sites (b, c, d-positions) illustrates small edge effects. Four CO's have been found to bind in the *c* (2×2) arrangement as shown in Figure 1(a) with an average energy of 1.83 eV. The calculated position of one-fold site as shown in Table 3, 4 is a-position in Figure 1(a).

The Pt_{23} cluster has been used to examine CO interaction in the *c* (4×2) arrangement. The calculation shows a single CO binds to the one-fold site (the center of this cluster, 10-position) with 2.12 eV, also illustrating small edge effects, and four CO's (1, 5, 6, 9-positions in Figure 1(b)) are located at the same site with a binding energy of 1.86 eV. The binding energies of the asymmetric two-fold site for a single CO (2, 11-positions in Figure 1(b)) are 1.86 eV, and four CO's are located at the same site (3, 4, 7, 8-positions in Figure 1(b)) with a binding energy of 1.89 eV, respectively. On Pt_{23} cluster, the calculated positions of the one-fold and the asymmetric two-fold sites as shown in Table 3, 4 are CO(1)-position and CO(2)-position. Eleven CO's have been found to bind in the *c* (4×2) arrangement as shown in Figure 1(b) with an average energy of 1.69 eV. In order to demonstrate the role of oxygen, we have compared binding energies and bond lengths for the *c* (4×2) arrangement and the *c* (2×2). In the former arrangement the CO molecules occupy the five one-fold sites and the six asymmetric two-fold sites of the Pt_{23} cluster. In the latter arrangement only the one-fold site is occupied. To find the arrangement for oxidation of CO the surface, $Pt_{18}(CO)_3$ cluster has been used to examine the interaction between CO and O. When the three CO's bind in the arrangement as in Figure 3(a), the average binding energy per CO is calculated to be 1.61 eV. When two molecules of CO are moved from the asymmetric two-fold site to the one-fold site as in Figure 3(b), the average binding energy of CO increases by 0.17 eV. Comparing the average binding energies of CO in the *c* (2×2) arrangements as in Figure 1(a) and Figure 3(b), the average binding energy of CO in Figure 3(b) decrease by 0.05 eV. This illustrates the small edge effect. However, these results suggest the possibility of making up the *c* (2×2) arrangement.

In case of the pre-adsorbed oxygen, the average binding energy per CO molecule is calculated to be 1.73 eV as in Figure 3(d). When the three CO's bind in the arrangement as in Figure 3(c), the binding energies of CO(1) on a $Pt_{18}(O)$ cluster, CO(2) on a Pt_{18} (CO(1)+O), CO(3) on a Pt_{18} (CO(1) CO(2)+O) are calculated to be 1.64 eV, 1.58 eV, and −4.19 eV, respectively, and the average binding energy per CO is −0.32 eV. This negative value implies that the CO(3) is desorbed from the surface due to strong repulsion between the adsorbed oxygen and CO(3). If we calculate the CO binding energies in case of coadsorption of O in the *c* (4×2) structure of CO, we might obtain such results as one obtained in the arrangement as in Figure 3(c). However, a part of strong repulsions is a result of the lateral interactions of the adsorbed species. These results suggest that pre-adsorbed oxygen modifies the surface so that CO is favored on the one-fold site as in Figure 1(a), and these are in agree-

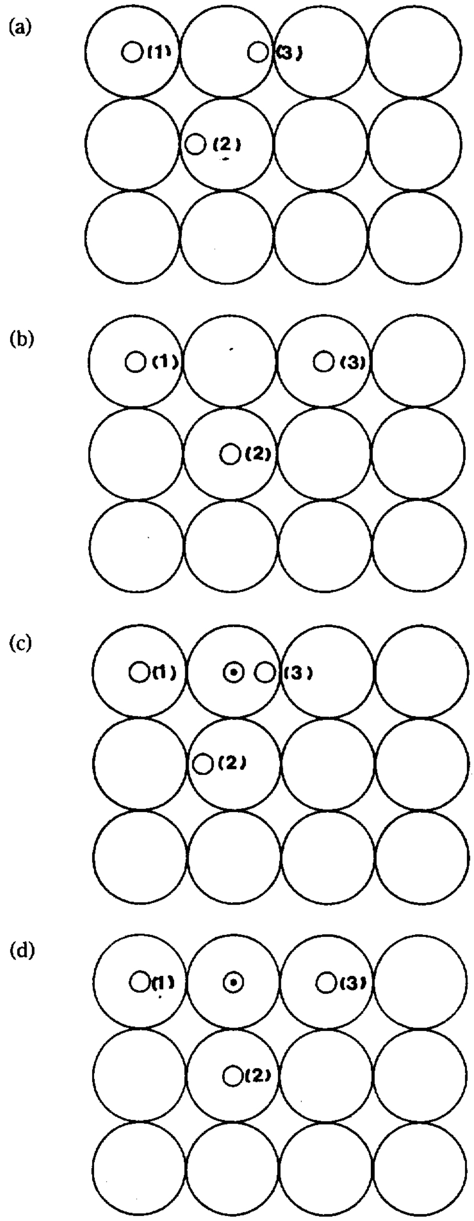

Figure 3. (a) CO molecular positions in part of modified *c* (4×2) arrangement overlayer on $Pt_{18}(100)$. (b) Each CO molecule on asymmetric two-fold sites shifts to open up an oxygen adsorption site. (c) In case of pre-adsorbed oxygen, the arrangement of three CO molecules on 1, 2, 3-positions. The number of positions are same numbers as shown in Figure 2(b). (d) In case of pre-adsorbed oxygen, the arrangement of adsorbed three CO molecules on one fold sites. ⊙; Oxygen.

Table 5. Calculated Binding Energies (BE), Heights (h), Charge (q) and Mulliken Overlaps for O Atom on Pt_{18} Model

	1-fold (top site)	2-fold (bridged site)	high coordination
BE (eV)	4.81[a]	5.10[a]	2.28[a]
h (Å)	1.54[b]	0.80[b]	0.93[b]
$Pt\text{-}O_{overlap}$	1.16	1.70	0.88
q	−0.39	0.22	−0.72

[a] See ref. 23 for the further discussion. [b] Heights optimized to nearest 0.01 Å.

Table 6. Calculated Results for Adsorbed CO and O on $Pt_{18}(100)$ Surface Models

	1-fold[a] (top site)	2-fold[b] (bridged site)
Pt-C overlap	0.70	0.84
Pt-O overlap	1.16	0.86
C-O overlap (C=O molecule)	1.53	1.43
C···O overlap	0	0
CO charge	0.44	0.28
O charge	−0.41	0.24
BE (eV) of CO on $Pt_{18}O$	1.79	1.36

[a] CO and O are on top of adjacent Pt atom (CO-O neighbor distance is 2.77 Å); CO is vertical with C end down at a height of 2.03 Å; O atom is at a height of 1.54 Å. [b] CO and O are on bridged of adjacent Pt atoms (CO-O neighbor distance is 2.77 Å); CO is vertical with C end down at a height of 1.64 Å; O atom is a height of 0.80 Å.

Table 7. Calculated Activation Energy for the Reaction $CO_{ads} + O_{ads} \rightarrow CO_{2\ ads}$ on a Pt(100) Surface; O is at a 1-fold site (1.75 Å) and C of CO is at two-fold site (1.91 Å); CO bond is tilted 30° from the vertical. (see Figure 5)

	Pt_{18} cluster
Activation energy (eV)	1.55[a]
Pt-O overlap	0.45
Pt-C overlap	0.21
$C\text{-}O_{(1)}$ overlap (C=O molecule)	1.26
$O_{(2)}\cdots C$ overlap	0.78

[a] See ref. 11. for the discussion.

ment with the suggestion by Hong, *et al.* Now we are much interested in predicting the structure of [CO···O]* complex for the CO oxidation, we have studied the oxidation of adsorbed CO only on Pt_{18} cluster with simplicity.

Oxidation of adsorbed CO on Pt(100) surface covered with oxygen. A theoretical study for the chemisorption of O atoms on Pt(111) has been carried out by Ray and Anderson[11]. Their calculation shows that atomic oxygen interacts strongly with Pt(111) surface, and the one-fold adsorption site is the most favorable for the O atom. In this calculation as shown in Table 5 and in Table 3, the two-fold site is the most favorable for O atom adsorption on Pt(100) surface. The distances of oxygen from the surface are optimized to nearest 0.01 Å. In order to demonstrate O-position theoretically in Table 6, we have calculated the binding energies of CO on the surface when oxygen is located at the one-fold site, the binding energies of CO for the one-fold site of adjacent Pt atom (CO-O neighbor distance is 2.77 Å) and for the two-fold (CO-O neighbor distance is 1.39 Å) are 1.79 eV and −1.54 eV, respectively. While the oxygen is located at the two-fold site, the binding energies of CO for the one-fold site (CO-O neighbor distance is 1.39 Å) and for two-fold site (CO-O neighbor distance is 2.77 Å) are −0.16 eV and 1.36 eV, respectively. The negative value of binding energy means that CO molecule is not bound to Pt surface because of the repulsion between the oxygen and the carbon monoxide. Thus, we find that the adsorption of CO and O on the one-fold site is the most stable arrangement. Comparing the results of Table 3, 5, and 6, the binding energy of CO on an oxygen covered surface is smaller than that of CO on a clean surface. However, the electronic structures of adsorbed species are nearly similar in Pt_{18}/CO, Pt_{18}/O, and $Pt_{18}/CO+O$. These tendencies are in agreement with previous studies.[11,23]

Table 7 shows the calculated activation energy for reaction and the reduced overlap population. The caculated activation energy is in reasonable agreement with ref. 11. It is of interest to note that (see Tables 6 and 7), on going from the adsorbed reactants to the $[CO_{(1)}\cdots O_{(2)}]^*$ complex, the Pt-C and $C\text{-}O_{(1)}$ (in carbon monoxide) reduced overlap populations decrease while that for $C\cdots O_{(2)}$ increases. This can be attributed to the gradual weakening of Pt-C bond and the formation of a new O-C bond. The structures are shown in Figure 4(a), (b) and (c). The adsorbed reactants (carbon monoxide and oxygen) are shown in Figure 4(a). The reaction intermediate complex for the oxidation of CO is shown in Figure 4(b). The CO adlayer has been removed by reacting with adsorbed oxygen. The side view of the reaction intermediate complex is shown in Figure 4(c). Figure 5 shows the plot of an energy versus the reaction coordinate. ΔE is the energy change for CO passing through the reaction intermdiate complex, forming CO_2 products over the Pt_{18} cluster. The O, CO and CO_2 are bound to the one-fold site. The intermediate complex is reached when the CO adlayer is transformed to the two-fold site, and the $C\text{-}O_{(1)}$ bond is tilted by 30° from the surface normal and stretched by 0.05 Å. The activation energy is 1.55 eV. Table 8 shows the calculated vibrational energies (ω_e) for the reaction intermediate complex on the Pt(100) surface, 1642 cm^{-1} for $C\text{-}O_{(1)}$ stretching, 406 cm^{-1} for $C\text{-}O_{(1)}$ bending, and 451 cm^{-1} for Pt-C stretching, respectively. The calculated $C\text{-}O_{(1)}$ stretching energy is quite close to the experimental value[12]. Pt-C stretching energies decrease compared with Table 4 while the $C\text{-}O_{(1)}$ distance increases, and the vibrational energy of $C\text{-}O_{(1)}$ bending is less than that of $C\text{-}O_{(1)}$ stretching.

Oribital correlation diagram for oxidation of carbon monoxide is shown in Figure 6. The energy levels for the free reactants (CO and oxygen) are in the first column and those for the adsorbed reaction intermediate complex are in the third column. The second column is for a free complex structure in the adsorbed reaction intermediate complex. Compared with the energy level of σ_p-bonding orbital in carbon

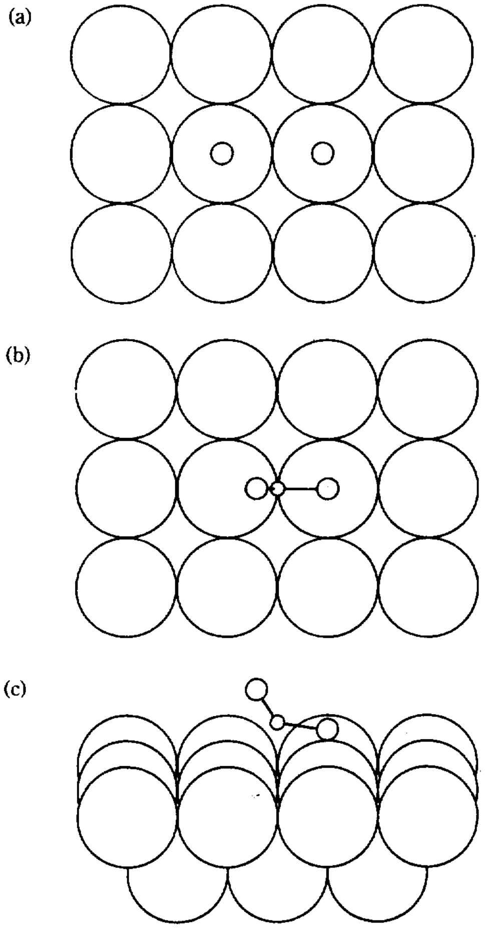

Figure 4. (a) The topview of carbon monoxide and oxygen on one fold site (reactants). (b) The topview of $[CO_{(1)}\cdots O_{(2)}]^*$ complex for oxidation of CO; The CO adlayer is removed by reacting with adsorbed oxygen; The CO molecule is located in two-fold site. (c) the side view of the complex; $CO_{(1)}$ bond is tilted 30° from vertical.

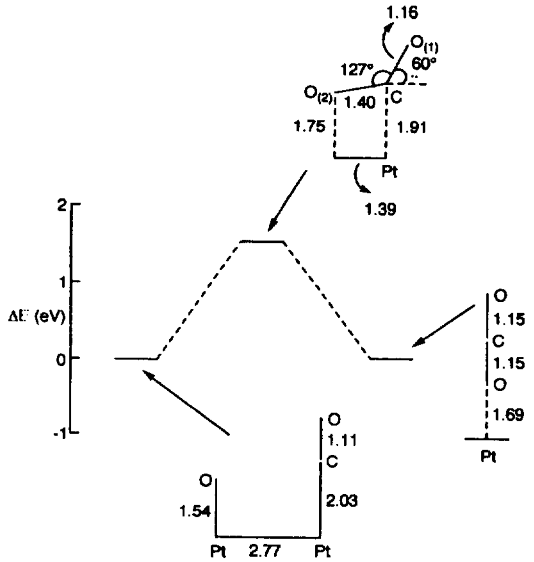

Figure 5. An energy versus reaction coordinate plot for the reactants studied. ΔE is the change for CO passing through a complex, forming CO_2 products over Pt_{18} cluster. The CO and CO_2 are bound to the one-fold site.

Table 8. Calculated Vibrational Energies, ω_e (cm^{-1}) for a Complex on the Pt(100) Surface. (see Figure 5)

	Adsobed	Exp
	cal	
ω_e(C-$O_{(1)}$) stretch	1642	1630[a]
ω_e(C-$O_{(1)}$) bend	406	
ω_e(Pt-C) stretch	451	

[a] Ref. 12.

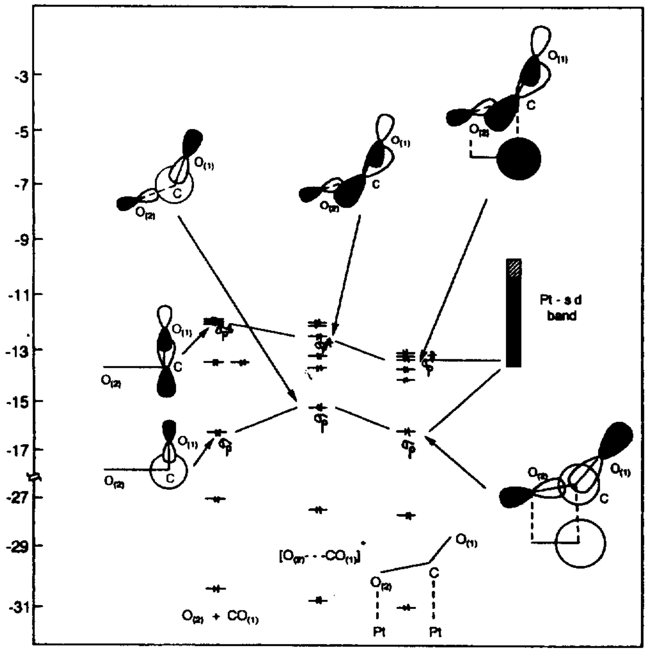

Figure 6. Orbital correlation diagram for oxidation of carbon monoxide complex. The $[CO_{(1)}\cdots O_{(2)}]^*$ column of levels is calculated for a free complex structure in adsorbed reaction intermediate complex.

monoxide, the energy level in the free transition-state structure increases by 0.77 eV. This result is largely from the destabilization of the $CO_{(1)}$ orbital that is caused by increasing the $CO_{(1)}$ distance by 0.05 Å. On the surface this orbital is stabilized (third column) by mixing with the $Pt_{s\text{-}d}$ band orbitals. The $CO_{(1)}$ σ^*_p orbital is greatly stabilized by the stretch and migrating carbon monoxide. The net result is a strong $C\cdots O_{(2)}$ σ combination activation. The CO_2 molecule is found to adsorb on the Pt(100) surface vertically at a height of 1.69 Å on the top of a Pt atom, the binding energy is 1.76 eV for Pt_{18} cluster. These results are close to those calculated previously for the Pt(111) surface[11].

Conclusion

We have calculated the following terms by using ASED-MO theory.

The order of stable binding sites for CO on the Pt_{23}(100) cluster is the one-fold, the two-fold, the high coordinate site, and on the Pt_{18}(100) cluster is the two-fold, the one-fold, the high coordination sites.

The calculated vibrational energies for the one-fold, the two-fold, and the high coordinate sites are in good agreement with the experimental values.

We find that the adsorption of CO and O on the one-fold site is the most stable arrangement.

If oxygen is adsorbed on the one-fold site, the adsorbed oxygen modifies the surface so that CO is adsorbed on the one-fold site ordered in $(\sqrt{2}\times\sqrt{2})R45°$.

The calculated vibrational energies for complex $[CO_{(1)}\cdots O_{(2)}]^*$ are 1642 cm^{-1} for $C\text{-}O_{(1)}$ stretching, 406 cm^{-1} for $C\text{-}O_{(1)}$ bending, and 451 cm^{-1} for Pt-C stretching.

The complex $[CO_{(1)}\cdots O_{(2)}]^*$ is reached when the CO adlayer is transformed to two-fold site, and the $CO_{(1)}$ bond is tilted by 30° from the surface normal. The heights of $O_{(2)}$ and C from surface plane are 1.75 Å and 1.91 Å, respectively. The calculated bond angle and the bond length are 127° for $CO_{(1)}$, $CO_{(2)}$, 1.16 Å for $C\text{-}O_{(1)}$, and the distance for $C\text{-}O_{(2)}$ is 1.40 Å.

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