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CO ADSORPTION ON (111) AND (100) SURFACES OF THE Pt_3Ti ALLOY.

EVIDENCE FOR PARALLEL BINDING AND STRONG ACTIVATION OF CO.

by

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Abstract

An ASED-MO study has been made of CO adsorption on a 40 atom cluster model of the (111) surface and a 36 atom cluster model of the (100) surface of the Pt_3Ti alloy. Parallel binding to high coordinate sites associated with Ti and low CO bond scission barriers are predicted for both surfaces. The binding of CO to Pt sites occurs in an upright orientation. These orientations are a consequence of the nature of the CO π donation interactions with the surface. On the Ti sites the π orbitals donate to the nearly empty Ti 3d band and the antibonding counterpart orbitals are empty. On the Pt sites, however, they are in the filled Pt 5d region of the alloy band, which causes CO to bond in a vertical orientation by 5σ donation from the carbon end.

1. Introduction

The high heat of formation of the Pt$_3$Ti alloy[1] has been
attributed to the strong interaction between the d orbitals of both
metals.[2] Understanding of this intermetallic bond has been the
focus of a number of investigations in the recent past.[3-6] These
studies have examined modifications of the electronic and the
chemisorptive properties of this alloy compared with the pure
metals. Such effects, often called 'ligand effects', are con-
sidered to be the cause of the change in the catalytic activity of
Pt$_3$Ti compared with the activity of the pure Pt metal. The Pt$_3$Ti
bulk structure is the fcc Cu$_3$Au-type structure as shown by X-ray
diffraction analysis.[4] Superlattice LEED patterns observed by
Bardi and Ross[5] showed that the (111) and the (100) surfaces of
Pt$_3$Ti are the simple terminations of the bulk structures in planes
normal to the [111] and [100] directions respectively. The {111}
planes are all equivalent, consisting of alternating atomic rows of
(50% Pt + 50% Ti) and 100% Pt as shown in Fig. 1. For the {100}
planes, however, there are two possible inequivalent regular termi-
nations when the crystal is cut normal to the [100] direction.
These planes alternately have (50% Pt + 50% Ti) and 100% Pt compo-
sitions (see Fig. 2). Bardi and Ross[5] have established that the
clean annealed surface has the (50% Pt + 50% Ti) composition and not
the 100% Pt composition. Using dynamical LEED intensity analysis,
they later determined that the (100) surface plane has a relaxed
structure with the surface Pt atom plane lying ~0.5 Å above the
surface Ti atom plane.[7] Relaxation of the (111) surface has not
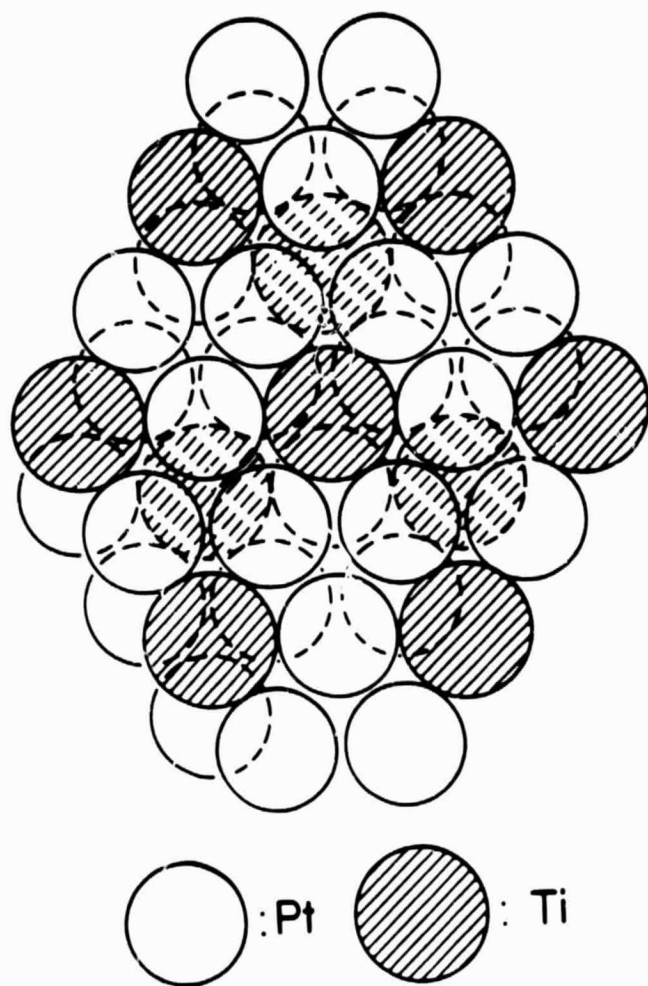yet been examined to our knowledge.

Fig. 1. $Pt_{30}Ti_{10}$ cluster model for the (111) surface of the Pt_3Ti
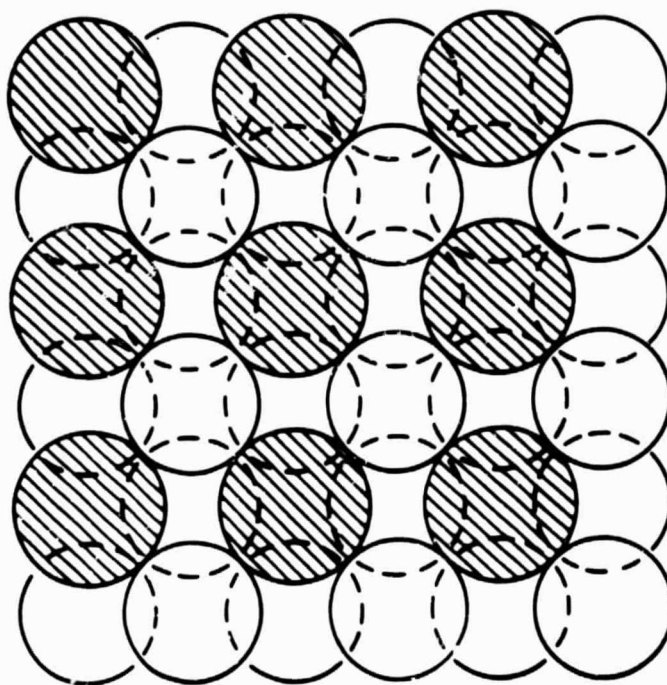alloy. The bulk lattice parameter of 3.906 Å was used in all
the calculations.

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Fig. 2. $Pt_{27}Ti_9$ cluster model for the (100) surface of the alloy.
The top layer has 50% Pt + 50% Ti, and the bottom layer
has 100% Pt composition.

Bardi et al.[4] have studied the chemisorption of CO and H_2 on a polycrystalline Pt_3Ti alloy. They concluded from thermal desorption measurements that CO adsorbs with reduced binding energy to the alloy compared to pure platinum, and attributed this difference to the 'ligand effect'.

In this paper we have examined CO adsorption and dissociation on the (111) and the (100) surfaces of the alloy by using cluster models. We use the atom superposition and electron delocalization molecular orbital (ASED-MO) technique, the usefulness of which has been demonstrated in our previous CO adsorption studies on Pt(111),[8] potassium promoted Pt(111),[9] negatively charged Ru(001),[10] and Cr(110) surfaces,[11] and the reader is referred to those works for further discussion of the ASED-MO theory. The parameters used in the present study are given in Table I. Platinum, carbon and oxygen parameters are the same ones used in past studies of CO binding to Pt(111) surfaces (Refs. 8,9). Titanium parameters are the metallic ones.

The clusters used for modeling the single crystal alloy surfaces are assigned low spin. We use bulk lattice parameter of 3.906 Å but the surface atoms are relaxed to the nearest 0.05 Å from their bulk positions, in a direction perpendicular to the surface plane, for the minimum energy. The CO bond length is optimized to the nearest 0.01 Å, the heights of CO above the surface and its lateral displacements are optimized to the nearest 0.05 Å, and the tilt of CO from the horizontal is optimized to the nearest 1 deg.

2. Results and Discussion

2.1 CO Adsorption on the (111) Surface

We have used a two-layer thick 40 atom cluster consisting of 30 Pt and 10 Ti atoms as shown in Fig. 1, for modeling the (111) surface of the Pt_3Ti alloy. The top layer has 16 Pt and 7 Ti atoms, and the bottom layer has 14 Pt and 3 Ti atoms. On relaxing only Ti atoms in the top layer, it is found that they move down 0.55 Å from their bulk positions. The binding site and the binding orientation of a single CO molecule is then studied on this relaxed surface. The calculated results are given in Table II. It is evident from the calculated binding energies that the binding of CO to the Ti sites is favored over its binding to the Pt sites. On the Ti sites, the binding energies of CO bonded end-on as well as side-on are very close. When CO is terminally bonded through the oxygen end it is 0.16 eV more stable than when bonded through carbon. When CO binds to Ti in the lying-down orientation it is 0.06 eV less stable than when bound through the oxygen end. While these energies are approximate, they suggest CO can bind to the alloy through oxygen, as indicated experimentally by the O 1s binding energies for CO adsorbed on $Pt_3Ti(111)$.[12]

In the reclined orientation the O-end of CO lies about 0.2 Å from the 1-fold Ti site and the C-end orients towards the neighboring 3-fold hollow site. The CO axis is tilted 7 deg relative to the surface plane (see Fig. 3). It may be noted that CO binds standing up through carbon on the 1-fold site of the Pt(111) surface (Ref. 8 and references therein). For comparison purposes we have also calculated the binding energy of CO on the 1-fold site of Pt on a Pt_{40} cluster (28 unpaired electrons) having
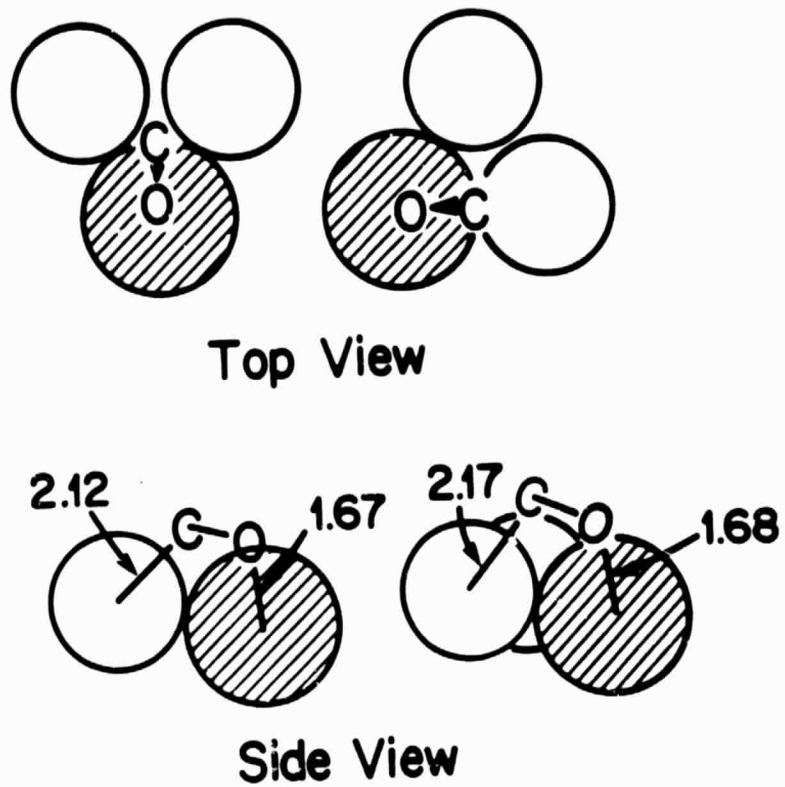
Top View

Side View

Fig. 3.   The lying-down orientations of CO on the Ti site of the 40 atom alloy cluster model of Fig. 1.

the same structure as the $Pt_{30}Ti_{10}$ cluster, but using the Pt bulk nearest neighbor distance of 2.77 Å. We find the structure is nearly the same as on the 1-fold Pt site of the alloy. The height being 2.05 Å and the CO internuclear distance being 1.16 Å (compare to Table II). The binding energy to the surface, however, is 0.29 eV greater on the Pt_{40} cluster compared to the same site on the alloy cluster. On the $Pt_{30}Ti_{10}$ cluster, the binding energy of CO in the perpendicular orientation on the 3-fold site having a Ti atom underneath in the second layer is calculated to be 0.12 eV greater than the same orientation on the 1-fold site. But it is still 0.17 eV less stable than the 1-fold site of the $Pt_{40}(111)$ cluster. This decrease in the binding energy of CO on the surface Pt atoms of the alloy compared to the pure Pt, as well as the change in the site preference from the 1-fold atop to the high-coordinate site is due to the ligand effects in the alloy. It may, however, be noted that the reduction in CO binding energy on the alloy surface would occur only if the Ti sites are blocked. In fact, this was observed experimentally: initially adsorbed CO leads to the blocking of the Ti sites by oxygen ions formed from its dis-ssociation and the carbon appears to go into the bulk.[12] Sub-sequently, CO will adsorb only on the Pt sites with a presumably weakened adsorption energy.

The lying-down binding configuration for CO on the Ti sites is similar to the Cr(110) surface where theory[11] and experiment[13] agree that the CO binds side-on on the high-coordinate site. In a second di-σ like lying-down orientation for CO on the $Pt_{30}Ti_{10}$ cluster model, the CO axis is tilted by 25 deg from the surface plane (Fig. 3). This orientation is 0.2 eV less stable than the

first orientation discussed previously. The lying-down orientation in which the carbon end points towards the 3-fold hollow allows the carbon to bind to two surface Pt atoms, accounting for its stability.

The energy level correlation diagram for CO adsorbed on the Ti atom in the lying-down orientation with the carbon end towards the 3-fold hollow surface site is shown in Fig. 4. It may be seen that CO binds to the surface by means of 5 σ and π donation bonds to the filled titanium band region. The antibonding counterparts are high lying and empty, so the donation results in a small positive charge of 0.17 on CO. Overall, three donation bonds to the surface and two back-donation bonds from the metal to the π^* orbitals of CO. These orbital stabilizations are all stronger than they are for the upright orientation where the orbital overlaps with surface orbitals are reduced because only the carbon atom is involved. CO binds parallel to the Cr(110) surface according to experimental analysis[13] and the reason is the same as above, as we have recently shown.[11] When more d electrons are present in the transition metal, the situation may change. In the case of Ru(001) the anti-bonding counterparts to the π donation bonds are half-filled. As a consequence CO binds perpendicular to the surface but when the surface is charged cathodically by coadsorbed potassium, the back donation to the π^* orbitals becomes stronger and the reclined orientation becomes favored.[10] Experimental studies show these two orientations.[14] Platinum has a nearly filled d band and since the antibonding counterpart orbitals to the π donation orbitals are doubly occupied, the resulting closed-shell repulsion causes CO to stand upright with the resulting bonding to the surface consisting
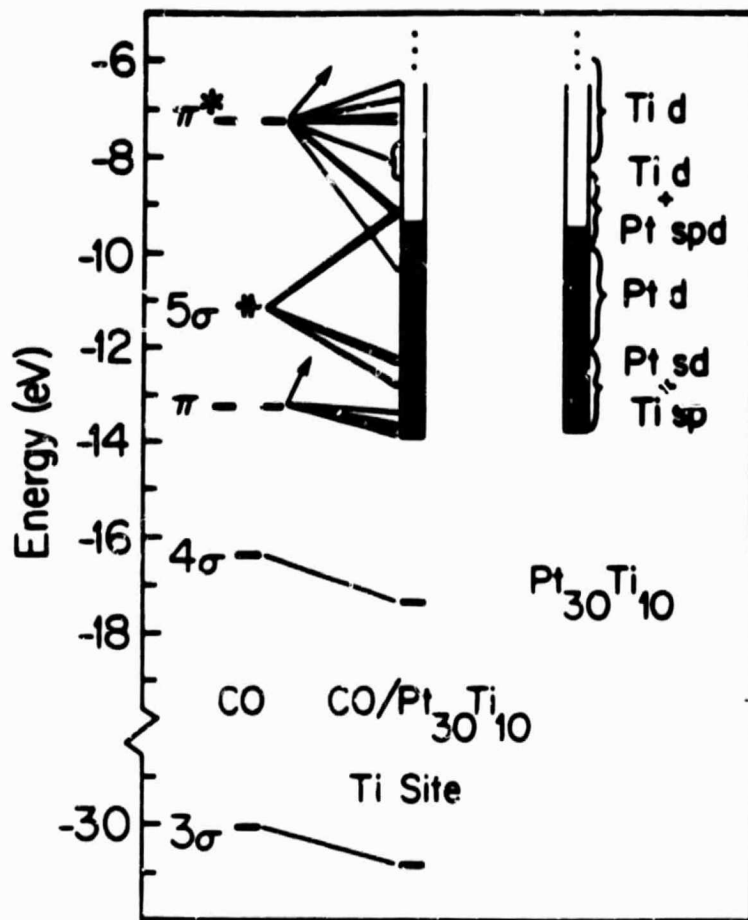
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Fig. 4. Energy level correlation diagram for CO adsorbed in the lying-down orientation on the Ti site of the $Pt_{30}Ti_{10}$ cluster model of the (111) surface. The C-end orients towards the 3-fold hollow surface site. The correlation lines are drawn for orbitals having 0.04 or more electron on CO.

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in a strong 5 σ donation and weak back-donations to the π^* orbitals with a resulting small positive net charge on CO.[8] In this case, cathodic shifting of the d band causes CO to move from the 1-fold site to 2- and 3-fold sites where the back-donation to the π^* orbitals is enhanced and substantial charge is transferred to CO.[9]

It is easily understood why parallel binding of CO over two Pt atoms on the (111) surface of the alloy is very weak (0.89 eV). In this case, as shown in Fig. 5, the antibonding counterparts to the donation bonds lie in the filled platinum band region and the resulting closed-shell repulsion causes CO to stand upright.

The tilted side-on bonding configuration with the carbon end towards the 3-fold hollow site may be considered as a precursor state for the dissociation of CO on this surface. When stretched by 0.55 Å on this site, it reaches its transition state with an activation barrier of 0.74 eV, showing strong activation con- sistent with the experimental observation of dissociation at near-ambient temperature.[12] Figure 6 shows the orbital sta- bilizations for CO in its transition state. As the CO bond is stretched, the π^* orbitals shift down, thus increasing the inter- action with the filled Pt-Ti d bands. This gives rise to increased charge transfer to the π^* orbitals.

2.2 CO Adsorption on the (100) Surface

We model the (100) surface of the Pt_3Ti alloy by employing a 36 atom cluster (Fig. 2). The top layer contains 9 Ti and 9 Pt atoms and represents the (50% PT + 50% Ti) truncation as discussed in the Introduction. The bottom layer has 18 Pt atoms and models the 100% Pt truncation. On relaxing the top layer atoms, it is found that
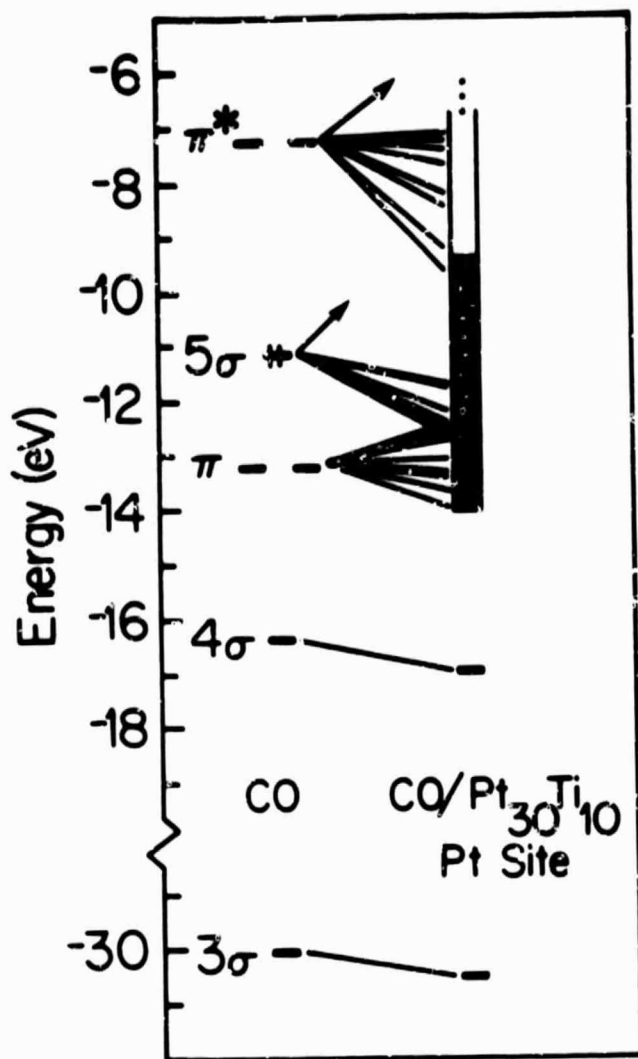
Fig. 5. Same as in Fig. 4 for CO in the side-on orientation
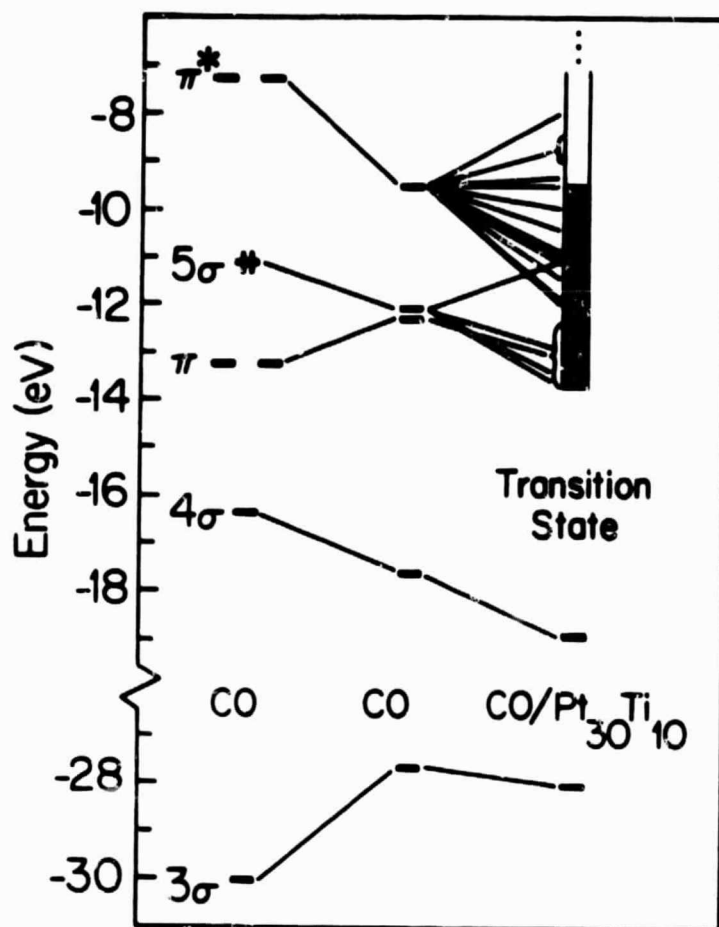bridging two Pt atoms on the (111) surface of the alloy.

Fig. 6. Same as in Fig. 4 for CO in the transition state on the
(111) surface of the alloy. The second column shows the
energy levls of CO having the transition state structure
but without the cluster.

7B

the Ti atoms move down by 0.65 Å and the Pt atoms move up by 0.05 Å from their bulk positions. The calculated relative displacement of the Pt and the Ti atoms on the surface plane (0.7 Å) is quite close to the value of ~0.5 Å estimated by Ross and coworkers using dynamical LEED intensity analysis.[7] The adsorption of CO is then studied on this relaxed surface. Figure 7 shows all the binding sites and the binding orientations studied on the 36-atom cluster model. The calculated results are presented in Table III. Evidently the binding of CO on the Ti site in the side-on configuration is distinctly favored over the other sites and orientations. In this orientation the oxygen end of the CO molecule lies 0.29 Å from the top of the Ti atom and the carbon end lies 0.45 Å towards the Ti site from the center of the neighboring 4-fold hollow site. The next site in terms of the decreasing binding energy is the 4-fold hollow site on which the carbon and the oxygen ends of CO point towards the surface Pt atoms.

The CO orbital stabilizations on the most stable lying-down configuration are similar to those shown in Fig. 4 for the (111) surface. Since the bond length for the adsorbed CO on the Ti site in the side-on orientation is 0.03 Å longer than it is on a similar site of the (111) surfaces, there is greater back donation to the π^* orbitals of CO. This results in a Mulliken charge of -0.06 on CO.

We have also calculated the CO bond scission barrier for CO adsorbed on the most stable site on the (100) surface. When the CO bond is stretched by 0.55 Å from its equilibrium value it reaches its transition state with a barrier of 0.91 eV which is similar to that calculated for the (111) surface.
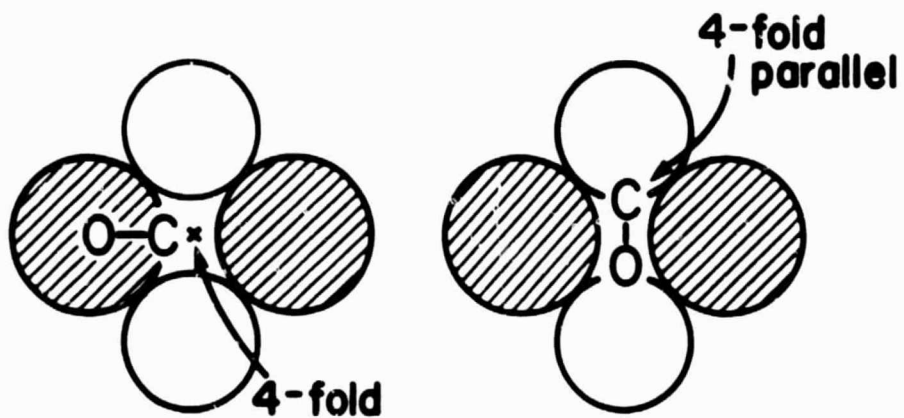
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Fig. 7. Adsorption sites studied on the cluster model of Fig. 2. The cross symbol (x) represents perpendicular orientation on this site.

3. Summary

We have made a theoretical study of CO adsorption on the (111) and (100) surfaces of the Pt_3Ti alloy. On the clean surfaces, binding of CO on the Ti sites is favored compared to the binding on the Pt sites. On the (111) surface the terminally bonded CO through oxygen on the 1-fold Ti site, and the side-on bonded CO with the carbon end oriented towards the 3-fold hollow surface site and the oxygen end nearly on the 1-fold Ti site, are comparable in stability. In the lying-down orientation, bonding to the surface is a result of the 5σ and π donation interactions, the antibonding counterparts of both are high-lying and empty. When CO lies down on the Pt sites, the antibonding counterparts of the π donation orbitals are occupied leading to a closed-shell type interaction and the bonding to the surface is due to 5σ donation bond. A qualitative understanding of this difference in stability for CO binding on the Ti and the Pt sites in the lying-down configuration is given in Fig. 8. When CO bonds on the Ti sites, the interaction of CO π orbitals occurs with the high-lying Ti d band region of the Pt/Ti d band. The antibonding orbitals are pushed up further and lie in the empty Ti d band region resulting into a bond order of two due to π interactions. This is shown on the left side of Fig. 8. When CO bonds parallel on the Pt sites, the CO π orbitals interact with the Pt d band region near the bottom of the Pt/Ti d band and therefore their antibonding counterparts lie in the filled Pt/Ti d band. This reduces the net bond order due to π interaction, to zero. This is shown on the right side of Fig. 8. The same explanation holds true for the favored lying-down configuration of CO on the (100) surface of the alloy.
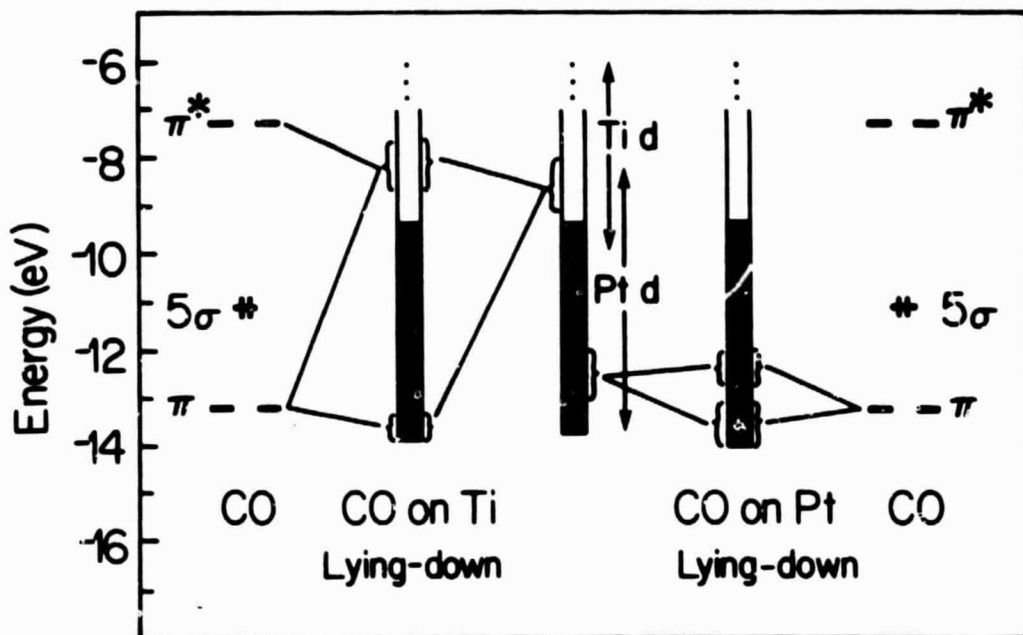
Fig. 8. Qualitative correlation diagram for CO in the lying-down
orientation on the Ti and the Pt sites, on the (111)
surface.

We calculate CO bond scission barriers of 0.74 e^v and 0.91 eV on the (111) and the (100) alloy surfaces respectively, showing considerable bond activation of the lying-down CO molecules.

Acknowledgement

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Table I. Atomic parameters used in the calculations[a]: Principal quantum number (n), ionization potentials (IP) in eV, Slater orbital exponents (ξ) and respective coefficients (C) for double-ξ d functions

Atom				p			d					
	n	IP	ξ	n	IP	ξ	n	IP	ξ_1	C_1	ξ_2	C_2
Pt	6	10.50	2.550	6	6.46	2.250	5	11.10	6.013	0.6562	2.396	0.5711
Ti	4	6.82	1.500	4	4.85	1.200	3	8.00	4.55	0.4206	1.400	0.7839
C	2	18.50	1.658	2	9.76	1.618						
O	2	26.98	2.146	2	12.12	2.127						

[a]Atomic parameters for Pt, C, and O are the same as used earlier in our previous CO adsorption studies on Pt(111).[8,9] The ionization potentials for Ti are taken from W. Lotz, J. Opt. Soc. Am. 60, 206 (1970), and the Slater exponents are taken from J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, J. Chem. Phys. 36, 1057 (1962). The 4s and 4p exponents are determined as in our past studies of first row transition metals and the 4p ionization potential is determined from the lowest 4s → 4p excitation energy.

Table II. Binding site and orientation, binding energy (BE), bond length (R_{CO}), heights (h), and the tilt relative to the surface plane, for CO adsorbed on the $Pt_{30}Ti_{10}$ cluster model of the (111) surface.

Binding site	Orientation	BE(eV)	$R_{CO}(\mathring{A})$	$h_C(\mathring{A})$	$h_O(\mathring{A})$	Tilt (deg)
1-fold Pt	Perpendicular through C	1.54	1.16	2.00	3.16	–
	Perpendicular through O	1.52	1.16	2.91	1.75	–
1-fold Ti	Perpendicular through C	2.77	1.15	1.90	3.05	
	Perpendicular through O	2.93	1.14	2.74	1.60	–
3-fold[a]	Perpendicular through C	1.66	1.21	1.50	2.71	–
Ti	Lying down[b] (C-end towards the 3-fold hollow)	2.87	1.18	1.25	1.11	7
	Lying down[c] (C-end towards the 1-fold Pt)	2.67	1.16	1.60	1.11	25
Bridging Pt atoms	Parallel	0.89	1.18	1.95	1.95	-

[a]This is the site between three Pt atoms having a Ti atom underneath in the second layer. The 3-fold site with a hole underneath is found to be less stable by 0.3 eV.

[b]see Fig. 3.

[c]see Fig. 3.

Table III. Binding site and orientation, binding energy (BE), bond length (R_{CO}), and heights (h), for CO adsorbed on the $Pt_{27}Ti_9$ cluster model of the (100) surface.

Binding site	Orientation	BE(eV)	R_{CO}(A)	h_C(A)	h_O(A)
1-fold Pt	Perpendicular through C	2.72	1.17	2.00	3.17
	Perpendicular through C	2.57	1.16	2.91	1.75
1-fold Ti	Perpendicular through C	2.96	1.15	1.85	3.00
	Perpendicular through O	3.05	1.14	2.79	1.65
Ti	Parallel[a]	3.93	1.21	1.50	1.50
4-fold	Perpendicular through C	2.99	1.21	1.05	2.26
	Perpendicular through O	1.52	1.15	2.05	0.90
4-fold	Parallel	3.71	1.16	1.55	1.55

[a]In this orientation the C-end lies 0.45 Å towards the Ti atom from the 4-fold surface site and the O-end lies 0.29 Å from the 1-fold site of the Ti atom.

Figure Captions

Fig. 1. $Pt_{30}Ti_{10}$ cluster model for the (111) surface of the Pt_3Ti alloy. The bulk lattice parameter of 3.906 Å was used in all the calculations.

Fig. 2. $Pt_{27}Ti_9$ cluster model for the (100) surface of the alloy. The top layer has 50% Pt + 50% Ti, and the bottom layer has 100% Pt composition.

Fig. 3. The lying-down orientations of CO on the Ti site of the 40 atom alloy cluster model of Fig. 1.

Fig. 4. Energy level correlation diagram for CO adsorbed in the lying-down orientation on the Ti site of the $Pt_{30}Ti_{10}$ cluster model of the (111) surface. The C-end orients towards the 3-fold hollow surface site. The correlation lines are drawn for orbitals having 0.04 or more electron on CO.

Fig. 5. Same as in Fig. 4 for CO in the side-on orientation bridging two Pt atoms on the (111) surface of the alloy.

Fig. 6. Same as in Fig. 4 for CO in the transition state on the (111) surface of the alloy. The second column shows the energy levls of CO having the transition state structure but without the cluster.

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Fig. 7.   Adsorption sites studied on the cluster model of Fig. 2.
         The cross symbol (x) represents perpendicular orientation
         on this site.

Fig. 8.   Qualitative correlation diagram for CO in the lying-down
         orientation on the Ti and the Pt sites, on the (111)
         surface.