

Articles

Comparison of Adsorption Properties of Adsorbates on Pt(111) and Pt(111)/ γ -Al₂O₃ Surface in the Ethylene Hydrogenation Reaction: MO-Theory

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Using an atom superposition and electron delocalization molecular orbital (ASED-MO) method, we have compared adsorption properties of adsorbates on the Pt(111) surface with the Pt(111)/ γ -Al₂O₃ surface in the ethylene hydrogenation reaction. In two-layer thick model systems, the calculated activation energy of the hydrogenation by the surface platinum hydride is equal to the energy by the hydride over supported platinum γ -alumina. The transition structure on platinum is very close to the structure on the supported platinum/ γ -alumina surface. Hydrogenation by the surface hydride on platinum can take place easily because the activation energy is about 0.5 eV less than hydrogenation by ethylidene. On supported platinum/ γ -alumina the activation energy of the hydride mechanism is about 0.61 eV less than that of ethylidene mechanism. In one-layer thick model systems, the activation energy of hydrogenation by ethylidene is about 0.13 eV less than the activation energy of hydride reaction. The calculated activation energy by the hydride over the supported platinum γ -alumina is 0.24 eV higher than the platinum surface.⁶ We have found from this result that the catalytic properties of one-layer thick model systems have been influenced by the support but the two-layer thick model systems have not been influenced by the support.

Introduction

The adsorption properties of adsorbates in ethylene hydrogenation on the metal surface is well understood on the basis of many experimental¹⁻⁵ and theoretical studies.⁶ However, little is known about those properties on the supported metal surface because it is difficult to prepare well dispersed crystalline metal layers on a support.

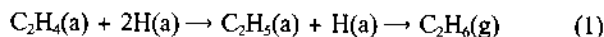
The interest in the supported metal catalysts^{7,8} and ethylene hydrogenation on those catalyst surfaces is growing. Che *et al.*^{7b} has suggested that the variations in catalytic behavior may be due to a combination of the particle size effect and the support effect. It is not easy to examine the support effect since we have to consider layer-thickness and particle size. We have used the models of one-space and two-metal atomic layers on the support to investigate the effect of the support on the ethylene hydrogenation reaction.

G. C. Bond⁷ has observed that Pt/ γ -Al₂O₃ catalyst (EUROPT-3) is extremely active for the hydrogenation of mixtures of ethylene and acetylene. The activation energy to form ethane is 40.7 kJ mol⁻¹ at near room temperature.⁷ Somorjai³ has measured the activation energy on a Pt(111) surface at near room temperature to be 45 kJ mol⁻¹. It is interesting to note that the difference of activation energy on two surface systems is below 10 percent.

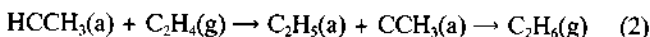
There are basically two objectives for the research on the supported metal catalysts: (i) the discovery of improved catalysts and (ii) the better understanding of phenomena already known. We have already made a theoretical study of binding at the Pt(111)/ γ -Al₂O₃(111) interface⁹ and of the ethylene hydrogenation mechanism on the Pt(111) surface.⁶ In previous studies,⁶ the activation energy has been 0.91 eV on the CCH₃-covered Pt₁₅; the overestimate of the H bind-

ing energy to the surface has suggested the possibility that the activation energy might be lower, perhaps approaching the experimental of 0.47 eV; the hydrogenation of the ethyl radical by adsorbed H will proceed easily with an activation energy of about 0.5 eV less than the hydrogenation by ethylidene.

This work composes to adsorption properties of adsorbates on the Pt(111) and the Pt(111)/ γ -Al₂O₃(111) surface in an ethylene hydrogenation reaction at near room temperature, using the atom superposition and electron delocalization molecular orbital (ASED-MO) theory.^{6,9-12} As studied in ref. 6, we used two different mechanisms for ethylene hydrogenation reactions. The first type is ethylene hydrogenation by the surface metal hydride on the ethylidyne (CCH₃) covered surface. The surface metal hydride transfers to adsorbed ethylene to form adsorbed ethyl radicals which are subsequently hydrogenized to ethane.



The second type is ethylene hydrogenation by surface ethylidene.



In this paper, we have compared the adsorption properties of adsorbates on the Pt(111) and the Pt(111)/ γ -Al₂O₃ surface. The adsorbates we used are by ethylidyne (CCH₃), ethylidene (HCCH₃), ethyl radical, and ethylene. We have calculated the activation energies of ethylene hydrogenation, transition state structures, the binding energy of adsorbates, and adsorbed ethyl radical structures.

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 ER. The other is an attractive energy due to electron delocalization by a one-electron molecular orbital energy, EMO, obtained by diagonalizing a Hamiltonian similar to the extended Huckel Hamiltonian:

$$E = E_R + E_{MO} \quad (3)$$

For calculations on the Pt(111) surface we have modeled Pt₂₅ and Pt₂₃ clusters as shown in Figure 1. Figure 1 shows a 25-platinum atom cluster and a 23-platinum atom cluster orientation with two-layer thickness. Clusters are bulk superimposable with Pt-Pt nearest neighbor distance of 2.77 Å. On Pt(111)/γ-Al₂O₃ surface we have modeled four clusters of Pt₂₅Al₉O₃₃, Pt₂₃Al₉O₃₃, Pt₁₅Al₉O₃₃, and Pt₁₃Al₉O₃₃ as shown in Figure 2. Figure 2 shows their views. As studied in ref 9, the oxygen anions of γ-alumina surface are bound with the platinum cluster in these models. Optimal distances in which the oxygen anions are in contact with Pt surface are 1.76 Å for the Pt₂₅Al₉O₃₃ cluster, 1.84 Å for the Pt₂₃Al₉O₃₃, 1.98 Å for Pt₁₅Al₉O₃₃, and 1.98 Å for Pt₁₃Al₉O₃₃, respectively. In this paper, we have named a supported platinum two-layer thick model Pt₂₅Al₉O₃₃ SP25, a supported platinum two-layer thick model Pt₂₃Al₉O₃₃ SP23, a supported platinum one-layer thick model Pt₁₅Al₉O₃₃ SP15, and a supported platinum one-layer thick model Pt₁₃Al₉O₃₃ SP13. Generally in this work angles are optimized to the nearest 1° and the distance to the nearest 0.01 Å. Theory parameters

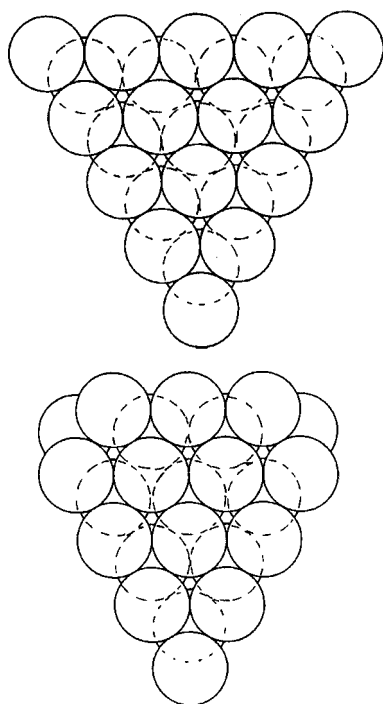


Figure 1. Pt₂₅ and Pt₂₃ cluster models of the Pt(111) surface. Clusters are bulk superimposable with a Pt-Pt nearest neighbor distance of 2.77 Å.

are given in Table 1.

Results and Discussions

In previous studies,^{9(a,c)} it has been found that the interfacial bond of platinum-alumina may be possible by a charge-transfer mechanism from the platinum surface to the partially empty O-2p band. The smaller is the net charge per platinum atom, and the greater is the charge-transfer from the platinum surface. The greater is the charge-transfer from the platinum surface to the partially empty O-2p band, and the stronger is the binding energy in a cluster. Alemany^{9b}

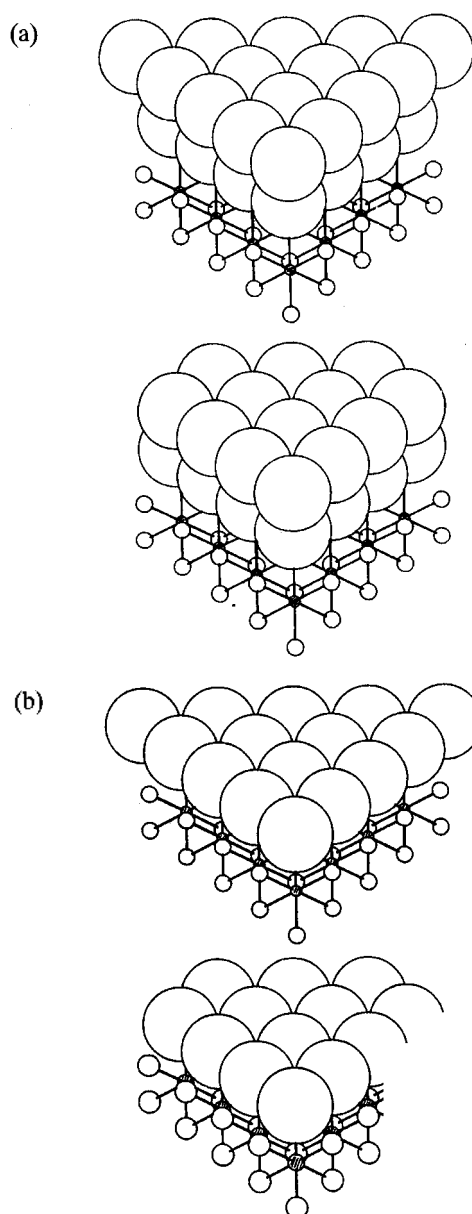


Figure 2. (a) The side views of Pt₂₅Al₉O₃₃ cluster and Pt₂₃Al₉O₃₃ cluster. The optimal distance at which the oxygen anions of alumina are in contact with the Pt surface is 1.76 Å for the Pt₂₅Al₉O₃₃ cluster and 1.84 Å for the Pt₂₃Al₉O₃₃ cluster. (b) The side views of Pt₁₅Al₉O₃₃ cluster and Pt₁₃Al₉O₃₃ cluster. The optimal distances are 1.98 Å. The large circles are platinum; medium circles are oxygen; hatched small circles are aluminium.

Table 1. Parameters used in calculations: Principal Quantum Numbers, *n*, Diagonal Hamiltonian Matrix Elements, *H*(eV), Orbital Exponent, ζ (au), and Linear Coefficients, *C*, for Double Zeta ζ d-Orbital

Atom	s			p			d					
	<i>n</i>	<i>H</i>	ζ	<i>n</i>	<i>H</i>	ζ	<i>n</i>	<i>H</i>	ζ_1	<i>C</i> ₁	<i>C</i> ₂	ζ_2
Pt ^a	6	-10.00	2.550	6	-5.96	2.250	5	-10.60	6.013	0.65620	0.57110	2.396
Al ^b	3	-12.62	1.521	3	-7.99	1.504						
O ^b	2	-26.48	1.746	2	-11.62	1.727						
C ^a	2	-19.00	1.658	2	-10.26	1.618						
H ^a	1	-12.60	1.200									

^a ref 6. ^b ref 13.

has assumed that the interactions at the interface in metals-ceramics is crucial in determining the extent of dispersion of catalytically active metal on the inactive support. The bonding of a metal to a ceramic is also important in the formation of seals in such catalysts. In this calculation, the net charge per platinum is 0.355 for SP25, 0.419 for SP23, 0.554 for SP15, and 0.599 for SP13. The binding energy per oxygen atom is 0.836 eV for SP25, 0.801 eV for SP23, 0.175 eV for SP15, and 0.172 eV for SP13. The interfacial bond of platinum-alumina in the supported platinum two-layer thick models is much stronger than that in the one-layer thick models. It means that the supported platinum two-layer thick model can play more important roles in the formation of seals in this catalyst than the one-layer thick model can.

It has been pointed out in ref. 6 that ethylidyne is an inactive spectator. The binding energies of ethylidyne are reduced, on going from the center of the cluster to the edge. In this calculation, a single CCH₃ over Pt₂₅ cluster is bound to the center with 5.98 eV and to the edge with 5.02 eV. The binding energy over SP25 is 5.03 eV at the center and 4.44 eV at the edge. The binding energy over SP15 is 6.14 eV at the center, and 5.63 eV at the edge. These results show the small magnitude of edge effects. In order to elucidate ethylene hydrogenation, we have used similar surface models introduced in the previous study.⁶ The ethylene has been found to be repelled by the (2×2) CCH₃-covered surface, and chemisorbed weakly on the open site of the surface in the previous study.⁶ Ethyl radical, CH₂CH₃, is placed in 1-fold coordination and a hydrogen atom is abstracted by a surface Pt atom. The catalytic properties for the adsorbed ethyl radical are shown in Table 2. Figure 4a, b shows the detailed structure of the ethyl radical. The binding energies of the ethyl radical are 1.60 eV over CCH₃-covered Pt₂₅, 1.52 eV over CCH₃-covered SP25 surface, and 1.69 eV over CCH₃-covered SP15 surface. The Pt-C distances from carbon of the adsorbed ethyl radical to the platinum surface on each cluster are 2.19 Å, 2.21 Å, and 2.18 Å, respectively (see Figure 4a). This Pt-C distance is referred to by the height. The Pt-C overlap populations are 0.45, 0.43, and 0.48, respectively. We have found from these results that the binding energies and heights depend on the Pt-C overlap population. Ethyl radicals are adsorbed in the one-fold site on two-layer thick models (CCH₃-covered Pt₂₅ and SP25). The bond lengths are 1.16 Å for an ethylene-like C-H bond and 1.20 Å for an ethane-like C-H bond. The angle of C-C-Pt is 116°, and the angle of H-C-Pt is 117°. All of the CCH angles of adsorbed ethyl radicals are 107 degrees. The ethyl radical is also adsorbed on the

top site on the CCH₃-covered SP15 surface. In this case the bond lengths are 1.17 Å for an ethylene like C-H bond, the CCpt angle is 117°, the HCpt angle is 120°, and the CCH angle is 106°. In transition states with respect to the dehydrogenation, there is no change in heights. The Pt-C distances of ethane-like species are 2.94 Å for Pt₂₅, 2.96 Å for SP25, and 2.74 Å for SP15 as shown in Table 3 (see Figure 4b). The calculated activation energy over the CCH₃-covered Pt₂₅ is 0.81 eV which is equal to the value over the CCH₃-covered SP25. However, it was 1.15 eV over the CCH₃-covered SP15 surface. These results mean that the catalytic properties on the two-layer thick models are similar to the Pt₂₅ cluster. However, the CCH₃-covered SP15 surface is different from the CCH₃-covered SP25 and Pt₂₅ surfaces. The difference of the C-H bond distance between the transition state is 0.63 Å for Pt₂₅, 0.54 Å for SP25, and 0.68 Å for SP15 (Tables 2 and 3). In the two-layer thick models, the angle (∠CCH) between the C-H bond and the C-C bond increases from 107° to 110°, the CCpt angle decreases from 116° to 115°, and the HCpt angle decreases from 117° to 116° (see Tables 2 and 3). On the CCH₃-covered SP15 surface, the CCH angle increases from 106° to 114°, the CCpt angle decreases from 117° to 108°, and the HCpt angle decreases from 120° to 117°. Comparing the activation energy of the CCH₃-covered SP25 surface with the CCH₃-covered SP15 surface, the activation energy is lower than the CCH₃-covered SP15 surface by 0.34 eV. The electronic aspects of the activation may be understood by using an energy level correlation diagram on the (CCH₃)₃γ-Al₂O₃ (Figure 3). Energy levels for the adsorbed ethyl radical are in the first column and those for the transition state are in the third column. The second column is calculated for a free radical in the transition structure. As pointed out in ref.

Table 2. Calculated Binding Energies (BE), Heights (h), Bond Lengths, Angles in Degrees (°), and Reduced Overlap Population (Pt-C overlap) for Adsorbed Ethyl Radical

	CH ₂ CH ₂ / (CCH ₃) ₃ Pt ₂₅	CH ₂ CH ₂ / (CCH ₃) ₃ Pt ₂₅ Al ₆ O ₃₃	CH ₂ CH ₂ / (CCH ₃) ₃ Pt ₁₅ Al ₆ O ₃₃
BE (eV)	1.60	1.52	1.69
^a h (Å)	2.19	2.21	2.18
C-C (Å)	1.78	1.78	1.78
^a C-H (Å)	1.16 ^b (1.20 ^c)	1.16 ^b (1.20 ^c)	1.17 ^b (1.20 ^c)
^a ∠CCpt (°)	116	116	117
^a ∠HCpt (°)	117	117	120
^a ∠CCH (°)	107	107	106
Pt-C _{overlap}	0.45	0.43	0.48

^a See Figure 4a. ^b Ethylene-like C-H bond. ^c Ethane-like C-H bond.

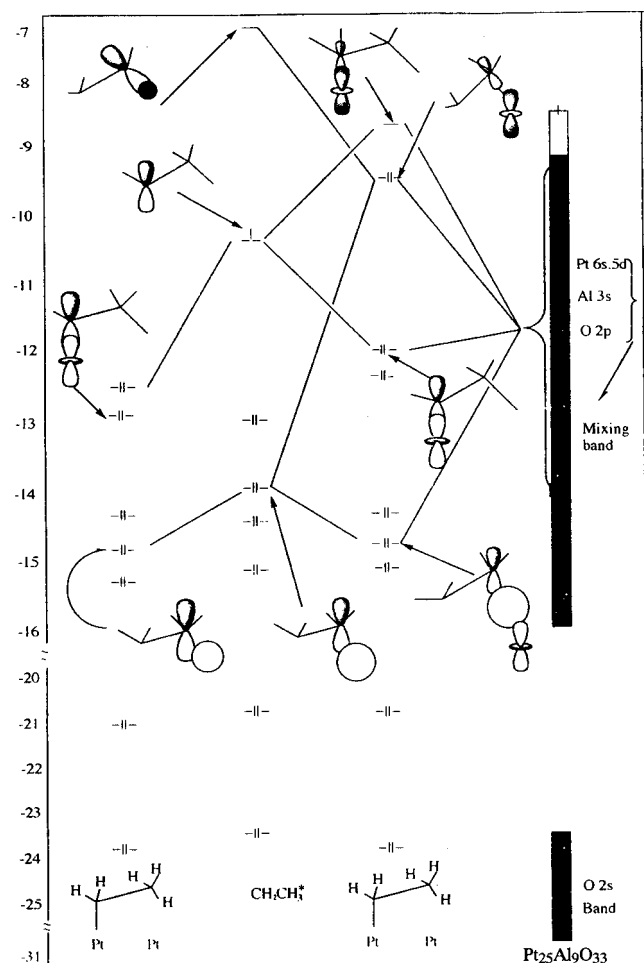


Figure 3. Orbital correlation diagram for ethyl radical dehydrogenation/ethylene hydrogenation transition state on the $(\text{CCH}_3)_3\text{Pt}(111)/\gamma\text{-Al}_2\text{O}_3$ surface. The C_2H_5^* column of levels has the surface removed.

6, destabilization of the C-H orbital must be caused by increasing the C-H distance. On the surface this orbital is stabilized (third column) by mixing with the band orbitals (Pt 6s, 5d, Al 3s, O 2s-mixing band orbital). The antibonding counterpart is doubly occupied, giving the overall interaction in a form of closed-shell repulsion. The $\text{C-H}\sigma^*$ -orbital is greatly stabilized by the stretch (second column) and can be mixed with antibonding interaction and stabilizes the antibonding counterpart. The net result is a strong C-H σ donation activation. This result is in reasonable agreement with the previous studies.⁶

The next examination is hydrogenation *via* α -H transfer from ethylidene. It has already been concluded in earlier studies⁶ that at $c(2\times 2)$ ethylidene coverage an equilibrium of the form allows also the possibility of only a very small concentration of CHCH_3 on the cluster surfaces. In the previous study,⁶ it was found that ethylidene is bound to a 2-fold site on a surface cluster. When ethylene approaches the surface, an ethylene molecule may bind to the surface through one C while the other C receives the α -H from ethylidene. In this study, we have used similar models to those introduced in the previous study.⁶ Ethylene hydrogenation by transfer of an α -H is modeled by using a

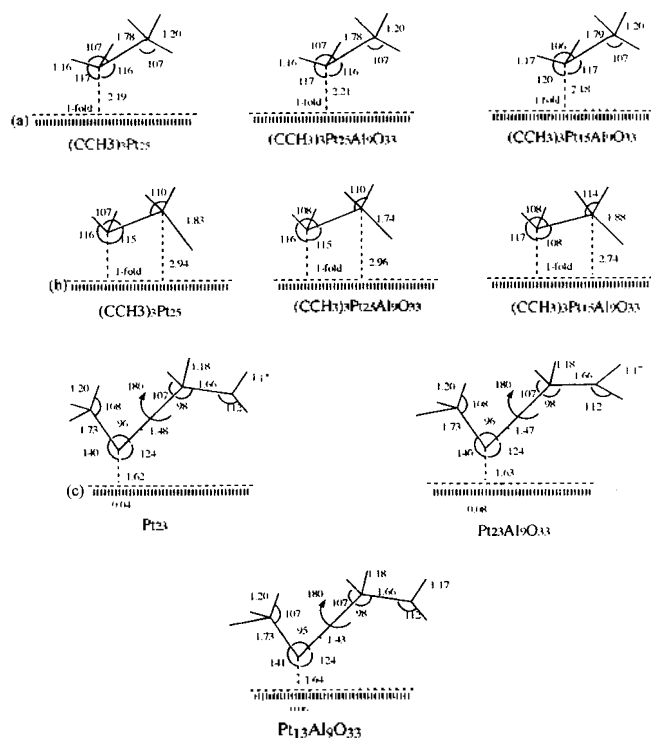


Figure 4. Structure details: distances in angstroms and angles in degrees. (a) Adsorbed ethyl radical structures on a 1-fold site of $(\text{CCH}_3)_3\text{Pt}_{25}$, $(\text{CCH}_3)_3\text{Pt}_{25}\text{Al}_9\text{O}_{33}$, and $(\text{CCH}_3)_3\text{Pt}_{15}\text{Al}_9\text{O}_{33}$. (b) Ethyl radical dehydrogenation/ethylene hydrogenation transition state on $(\text{CCH}_3)_3\text{Pt}_{25}$, $(\text{CCH}_3)_3\text{Pt}_{25}\text{Al}_9\text{O}_{33}$, and $(\text{CCH}_3)_3\text{Pt}_{15}\text{Al}_9\text{O}_{33}$. (c) Transition state for α -H transfer from adsorbed ethylidene on Pt_{23} , $(\text{CCH}_3)_3\text{Pt}_{23}\text{Al}_9\text{O}_{33}$, and $(\text{CCH}_3)_3\text{Pt}_{13}\text{Al}_9\text{O}_{33}$.

Table 3. Calculated Activation Energies (E_{act}), Angles in Degrees ($^\circ$), and Bond Lengths (\AA) for Transition State obtained from Ethyl Radical Dehydrogenation

	$\text{CH}_2\text{CH}_3/(\text{CCH}_3)_3\text{Pt}_{25}$	$\text{CH}_2\text{CH}_3/(\text{CCH}_3)_3\text{Pt}_{25}\text{Al}_9\text{O}_{33}$	$\text{CH}_2\text{CH}_3/(\text{CCH}_3)_3\text{Pt}_{15}\text{Al}_9\text{O}_{33}$
E_{act} (eV) ^a	0.81	0.81	1.15
$^b\text{C}\cdots\text{H}$ (\AA)	1.83	1.74	1.88
$^b\text{Pt-C}$ (\AA)	2.94	2.96	2.74
$^b\angle\text{CCPt}$ ($^\circ$)	115	115	108
$^b\angle\text{HCPT}$ ($^\circ$)	116	116	117
$^b\angle\text{CCH}$ ($^\circ$)	$107^\circ(110^d)$	$108^\circ(110^d)$	$108^\circ(114^d)$

^a Activation energy obtained from ethyl radical dehydrogenation.

^b See Figure 4b. ^c Ethylene like C-H bond part. ^d Ethane-like C-H bond part.

two-layer thick Pt_{23} cluster, SP23, and SP13. In the calculated transition state on the surfaces in Table 4, the $\text{H}_\alpha\text{-C}$ bond of adsorbed ethylidene is stretched by 0.33 \AA , 0.32 \AA , and 0.28 \AA on the surface, respectively. The transition distances are 2.89 \AA for Pt_{23} , 2.93 \AA for SP23, and 2.89 \AA for SP13. Figure 4c shows the transition states on the Pt_{23} cluster, SP23, and SP13. Bond angles around the ethylene C accepting the α -H are tetrahedral within a few degrees. The ethane-like C-H bond length is 0.01 \AA longer than the ethylene-like bond. The ethylene C-C distances are increased by 0.13 \AA . They are over halfway to the single bond value. The CCH_3 are unchanged but C-C bonds are tilted by 40° from the surface normal in the two-layer thick model sys-

Table 4. Calculated Activation Energies (E_{act}), Angles in Degrees ($^\circ$), and Bond lengths (\AA) for Transition state obtained by ethylene hydrogenation

	Pt ₂₃	Pt ₂₃ Al ₉ O ₂₃	Pt ₁₃ Al ₉ O ₂₃
E_{act} (eV) ^a	1.31	1.42	1.03
$C_\alpha \cdots H$ (\AA) ^b	1.48	1.47	1.43
$C_\alpha-C$ (\AA) ^c	2.89	2.93	2.89
Pt-C _α (\AA) ^d	1.62	1.63	1.64
$\angle CC_\alpha C$ ^e	96	96	95

^a Activation energy obtained by ethylene hydrogenation on a surface ethylidene. ^b It means that the hydrogen of α -carbon of the ethylidene stretches in order to form ethylene hydrogenation. ^c The distance between α -carbon of the ethylidene and carbon of ethylene; it means transition state distance in ethylene hydrogenation. ^d The distance between α -carbon of ethylidene and platinum surface. ^e The angle ($\angle CC_\alpha C$) between CC bond of ethylidene and carbon of ethylene.



tems, and are tilted by 39° in SP13. The CCH_3 fragment height for Pt₂₃ is decreased from 1.72 \AA to 1.62 \AA , from 1.73 \AA to 1.63 \AA for SP23, and from 1.71 \AA to 1.64 \AA for SP13 during ethylene hydrogenation. The activated energies are 1.31 eV on Pt₂₃, 1.42 eV on SP23, and 1.03 eV on SP13. In this mechanism, it is interesting that the activation energy has related to the binding energy for a single CCH_3 over each cluster surface which has been discussed above. The stronger is the binding energy of a single CCH_3 , the lower is the activation energy as the possibility of eq 4. The hydrogenation of the adsorbed ethyl radical by adsorbed H on the Pt₂₃ surface will proceed easily with an activation energy of about 0.5 eV less than the hydrogenation by ethylidene, and about 0.61 eV on the CCH_3 -covered SP25 surface. On the CCH_3 -covered SP15 cluster surface the reaction will not proceed easily because the activation energy is about 0.12 eV greater than the hydrogenation by ethylidene. As discussed in the previous study,⁶ it means that ethylene hydrogenation also takes place over H-covered metal surface even in two-layer thick model systems and ethylidyne is an inactive spectator. However, ethylidyne is activated on the SP13 cluster, which allows the possibility of eq 4. In the previous study⁶, the activation energy was 0.91 eV on the CCH_3 -covered Pt₁₅ cluster surface and it was 1.49 eV on the Pt₁₃ cluster. These results are very interesting since it implies variations of catalytic behavior by support.

G. C Bond¹⁴ has proposed that the lattice vibrational modes (*i.e.*, phonons) of the substance acting on the catalyst and a facet of solid state of the catalyst properties may determine the catalytic behavior. Then activation energies are the same values in two-layer thick model systems which are 0.81 eV as shown in Table 3, because the transition state (Figure 4b) is bound to the same site on the surface. However the activation energy over the CCH_3 -covered SP15 cluster is 0.34 eV higher than that of the CCH_3 -covered SP25. Vibrational modes (*i.e.*, phonons) of the ethyl radical acting on the CCH_3 -covered SP15 differs from the modes of the ethyl radical acting on the CCH_3 -covered SP25. The activation energy on the Pt₂₃ cluster is 0.11 eV lower than SP23 (Table 4) because adsorption sites are different on

these surfaces. The CCH_3 fragments have shifted latterly toward the 3-fold site by 0.04 \AA for the Pt₂₃ cluster, 0.08 \AA for the SP23 cluster, and 0.06 \AA for SP13.

Conclusions

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

a) The adsorption property of adsorbates on a Pt(111) is similar to that of adsorbates on Pt(111)/ γ -Al₂O₃(111) in two-layer thick model systems.

b) The supported platinum two-layer thick models can play more important roles in the formation of seals in this catalyst than the supported one-layer thick models, since the interfacial bond of platinum-alumina in the supported platinum two-layer thick models is much stronger than that in the supported one-layer thick models.

c) The supported platinum one-layer thick model has been influenced by the support.

d) The hydrogenation of the adsorbed ethyl radical by adsorbed H on SP25 proceeds with the lowest activation energy.

These conclusions can be generally applied to the catalytic hydrogenation of ethylene over other transition-metal surfaces.

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