Adsorption of CO$_2$ and H$_2$ on Cu and Zn Micro-Cluster Surfaces Studied by Quantum Chemistry and Theory of Absolute Reaction Rates

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Received August 9, 2011; revised September 10, 2011; accepted October 11, 2011

Abstract

Statistical mechanics and semi-empirical molecular orbital theory (PM6) are used to calculate the surface coverage of CO$_2$ and H$_2$ molecular species chemically adsorbed on the surface of Cu and Zn micro clusters. The calculation shows that CO$_2$ is adsorbed well both on the surface of Cu and Zn micro clusters. Although H$_2$ is adsorbed well on the surface of Zn micro clusters, H$_2$ absorption on the surface of Cu micro clusters is much more limited in the pressure range of 20 - 100 atm and temperature range of 200 - 1000 K. Reaction rates are also estimated for some chemical adsorption process of H$_2$ gas using theory of absolute reaction rates. It is found that the values of the reaction rate calculated in the present paper agree reasonably well with the experimental values.

Keywords: Surface Reaction, CO$_2$, Hydrogen, Global Warming, Catalyst

1. Introduction

In view of the social awareness of the global climate change supposedly due to anthropogenic carbon dioxide (CO$_2$) emissions [1], Sustainability Science Consortium was established in August 2010 in Japan for the purpose of better cooperation among various fields such as physics, chemistry, engineering, biology, economics, politics, quality control etc. Since the reduction of fossil fuel burning is becoming an urgent issue, various types of alternative, renewable energy resources have been proposed, such as solar energy, biomass, wind power, wave power, etc [2]. Among others, Research Institute of Innovative Technology for Earth proposed a “Global CO$_2$ Recycle System”, in which a solar power station in a desert will generate electric power, and hydrogen gas will be produced using this electric power. Carbon dioxide gas recycled from industrialized countries will be carried to the desert by using, for example, a liquefied CO$_2$ gas tanker. The chemical reaction of CO$_2$ gas with hydrogen gas will be used to form methanol. The methanol will be conveyed return back to industrialized countries using a methanol tanker, and will be used as fuel [3-5]. Namura shipbuilding Co. Ltd. has already constructed a methanol tanker which is now used practically in industry. In Mojave Desert in California in U.S.A., Solar Energy Generating Systems is in operation and electric power is produced therein.

Methanol can be formed through the inhomogeneous chemical reaction of CO$_2$ gas with H$_2$ gas catalyzed by the surface of Cu and Zn alloy, as studied by ab initio quantum chemistry [6] and by experiments [3,4,7]. The purpose of the present paper is to describe our calculation results on the surface coverage of CO$_2$ and H$_2$ molecular species chemically adsorbed on the surface of Cu and Zn micro clusters. It is well known that ab initio quantum chemical calculations give quantitative value of molecular parameters such as chemical bonding energies, frequencies of molecular normal vibrations, and activation energies of chemical reactions. In general, chemical reaction rate, $K$, is given by

$$K = A \exp(-E_a/R_0 T),$$

where $E_a$ is the activation energy, $T$ is the temperature, $R_0$ is the gas constant, and $A$ is a constant called frequency factor. Quantum chemical calculation gives the value of $E_a$. The theory of absolute reaction rates [8], which is based on the statistical mechanics, can be employed to derive a mathematical formula for the frequency factor, $A$.
Generally, a catalytic surface has surface sites, on each of which a single gaseous molecule can adsorb. In the present paper, we use the approach of quantum chemical calculation to obtain quantitative values of molecular constants of chemical species on surface sites. Statistical mechanical technique \[9\] gives a mathematical formula which describes surface coverage, \(\theta\) (total number of adsorbed molecules/total number of surface sites), as a function of the temperature \(T\) and the gas pressure \(p\). In the present paper, we calculate quantitative value of \(\theta\) by coupling the quantum chemical values of molecular constants with the mathematical formula of statistical dynamics.

Theory of absolute reaction rates \[8\] was used to model inhomogeneous surface reactions more than 20 years ago \[10\]. The numerical accuracy of the calculations, however, was not very high, because of the limited performance of computers. In addition, quantum chemical calculation of molecular parameters was very difficult when complex chemical systems or heavy metal elements were involved in inhomogeneous surface reactions. Accurate molecular parameters are indispensable for making quantitative calculations of statistical mechanics.

Today, remarkably improved computer performance has made it possible to carry out quantum chemical calculations of considerably large chemical systems. Ab initio quantum chemical calculations can possibly give reliable molecular parameters if sufficient resources are available. Semi-empirical quantum chemical calculations, on the other hand, are simplified and approximate calculations. They can be implemented using ordinary personal computers, giving reasonably accurate molecular parameters. Until recently, however, only light elements have been covered, with little coverage of heavy metal elements. In 2007, PM6 was introduced as a platform for semi-empirical molecular orbital calculation \[11-13\] and is now commercially available (Ryoka system Inc.). Computer program named WinMostar (Tencube Co.) can be suitably used to visualize the result of the calculation given by PM6, showing molecular structures on personal computers. PM6 solves the Schrödinger equation that incorporates an approximate, semi-empirical Hamiltonian, simplified by introducing fitting parameters. More than 9000 experimental data and numerical results of ab initio molecular orbital calculations have been used to optimize and to determine the parameters of PM6. As for previously developed semi-empirical molecular orbital theories, AM1 (developed in 1985) uses 200 data, and PM3 (developed in 1989) uses 500 data to determine the parameters in Hamiltonians. Both AM1 and PM3 have been used by chemists for more than 20 years. When compared with AM1 or PM3 methods, PM6 gives numerical values of formation/bonding energy of chemical compounds with higher accuracy and predicts stable/semi-stable structures of chemical species with higher accuracy. PM6 covers almost all of the elements in the periodic table including heavy metal elements such as Cu and Zn as well as light elements such as H, C, O, etc. The web sites of open MOPAC (http://openmopac.net/manual/index_accuracy.html and http://openmopac.net/MOPAC2009brochure.pdf) show that the average unsigned error of heat of formation of PM6 is around 8 kcal/mol, and the accuracy of PM6 is as good as the accuracy of B3LYP 6-31G(d), a sophisticated code developed for super-computer calculations. Empirical molecular orbital theory such as extended Hückel calculation is used in material science for qualitative discussion \[14\]. In contrast, semi-empirical molecular orbital theory gives much more accurate quantitative values of molecular parameters. As PM6 covers open shell calculations, reaction intermediates or radicals can also be treated using the same framework. PM6 has already been used for the study of molecular properties such as polycyclic aromatic hydrocarbons and fullerenes \[15\], molecular orbital study of the interaction between MgATP and the myosin motor domain \[16\], and frontier orbital theory study of some aminopyrimidine derivatives and their interaction with an iron surface \[17\].

In the present paper, PM6 molecular orbital calculation, the theory of absolute reaction rates, as well as the technique of statistical mechanics are used systematically to simulate CO\(_2\) and H\(_2\) adsorption on the surface of Cu and Zn micro clusters. As the result, surface coverage of these molecular species is calculated numerically as a function of the temperature and the gas pressure. In addition, rough estimation of the reaction rate of gas phase H\(_2\) molecules with adsorbed CO\(_2\) chemical species is made by using the theory of absolute reaction rates. The rate of chemical adsorption of hydrogen molecule on a Zn site in a CuZn catalyst is also estimated by using the theory of absolute reaction rates, and compared with experimental data \[4\]. It is found that values of reaction rates calculated in the present paper agree with reasonable accuracy with experimental values.

2. Theory

2.1. CO\(_2\) Molecules Adsorbed on the Surface of a Cu\(_9\) Cluster

We use a conventional statistical mechanical technique and simulate a system in which linear molecules are adsorbed on a surface of a “bulk” metal. Here the “bulk” metal treated in the present paper consists of several metal atoms, and the structure of the cluster is optimized using PM6 calculation. In this section, we treat a Cu\(_9\)
cluster and a CO2 molecule. This Cu9 cluster consists of 9 Cu atoms. We adopt a catalytic chemical reaction model [6] wherein non-dissociative chemical adsorption of CO2 on Cu surface is assumed. In other words, we adopt a chemical structure in which each of the two O atoms of the adsorbing CO2 molecule is assumed to contact a Cu atom of the Cu9 cluster.

The free energy of adsorbed CO2 molecule is given by [9],

\[ F(N) = -(kT) \log[N_0!/(N!(N_0-N)!)] 
- (kTN) \log[G\exp[\mu/(kT)]] \]

where \( N \) is the number of adsorbed CO2 molecules, \( k \) is the Boltzmann’s constant, \( T \) is the temperature of the system, \( N_0 \) is the total number of the surface sites of the metal cluster, Cu9, and \( G \) is the spin parameter of the adsorbed molecule. In this case, the spin parameter \( G = G_1 \) is given by

\[ G_1 = (2S_C + 1)(2S_O + 1) (2S_O + 1). \]

Here suffix 1 specifies the particular case of CO2/Cu9, and \( S_C \) is the nuclear spin of C atom,

\[ S_C = 0, \]

and \( S_O \) is the nuclear spin of O atom,

\[ S_O = 0. \]

In Equation (2), \( V \) is the partition function for vibration of a molecule (in this case, CO2) adsorbed on the metal cluster (Cu9) cluster. Thus, the partition function, \( V = V_1 \), is given by

\[ V_1 = V_{Cu9} + CO2/V_{Cu9}. \]

Here \( V_{Cu9} (= V_{metal}) \) is the partition function for vibration of the Cu9 cluster given by

\[ V_{metal} = \Pi_{metal} [1/\exp(h\nu_i(2kT)) - \exp(-h\nu_i(2kT))]. \]

In Equation (7), \( \nu_i \) stands for the frequency of the \( i \)’th normal vibration of Cu9 cluster. In Equation (6), \( V_{Cu9 + CO2} (= V_{metal + molecule}) \) is the partition function for vibration of the CO2 + Cu9 (molecule + metal) cluster,

\[ V_{metal + molecule} = \Pi_{metal + molecule} [1/\exp(h\nu_i(2kT)) - \exp(-h\nu_i(2kT))], \]

where \( \nu_i \) is the frequency of the \( i \)’th normal vibration of the CO2 + Cu9 (molecule + metal) cluster. In Equation (2), the heat of adsorption \( \omega = \omega_h \) is given by

\[ \text{CO}_2(\text{gas}) \rightarrow \text{CO}_2(\text{adsorbed}) + \omega_h. \]

The chemical potential of an adsorbed molecular species (CO2) is defined by

\[ \mu \text{ (adsorbed)} = \langle \partial F/N \rangle \text{ F(N).} \]

By inserting Equation (2) into Equation (10) and using l’Hôpital’s rule, we obtain

\[ \mu \text{ (adsorbed)} = -(kT) \log[\Pi_{metal} \Pi_{molec_vibration} \exp[\mu/(kT)]] 
+ (kT) \log[N/(N_0-N)]. \]

The chemical potential of an isolated CO2 molecule, on the other hand, is given by [9]

\[ \mu \text{ (gas)} = (kT) \log[h^\nu/[[2\pi mkT]^{1/2}(kT)]] 
- (kT) \log\{\exp(\nu)/(kT)\}, \]

where \( m \) is the mass of a CO2 molecule, and \( p \) is the pressure of the CO2 gas, and \( j \) is given by

\[ j = 0.5 \ g_{nuc} r_d(T) V_{molec_vibration}(T) \]

where

\[ g_{nuc} = (2S_C + 1)(2S_O + 1) (2S_O + 1), \]

and \( r_d(T) \) is given by

\[ r_d(T) = 8\pi^2 I kT/h^2, \]

where \( I \) is the moment of inertia of a CO2 molecule, and \( V_{molec_vibration}(T) \) is given by

\[ V_{molec_vibration}(T) = \Pi_{molec_vibration} [1/\exp(h\nu_i(2kT)) - \exp(-h\nu_i(2kT))]. \]

where \( \nu_i \) is the frequency of the \( i \)’th normal vibration of a CO2 molecule. The values of \( \nu_i, I, \) and \( \omega_i \) are calculated using PM6 molecular orbital calculation.

The condition of the thermal equilibrium between a CO2 gas molecule and an adsorbed CO2 molecule is given by

\[ \mu \text{ (adsorbed)} = \mu \text{ (gas)}. \]

By inserting Equations (11) and (12) into Equation (17), one obtains

\[ N/(N_0-N) = A p, \]

where \( A \) is given by

\[ A = [h^\nu/[[2\pi mkT]^{1/2}(kT)]](j^{-1}G_1V_1) \exp[\omega_h/(kT)]. \]

Surface coverage. \( \theta = \theta_{CO2} \) is defined by

\[ \theta = N/N_0. \]

From Equations (18) and (19), the surface coverage \( \theta \) is given by

\[ \theta = Ap/(1 + Ap). \]

2.2. H2 Molecules Adsorbed on the Surface of a Cu9 Cluster

Next, we consider a system in which a H2 molecule is adsorbed on a Cu9 cluster. We assume a case in which the H2 molecule dissociates when adsorbed on the cluster surface. The free energy of an adsorbed system is given
by Equation (2), where \( N \) is the number of H atoms adsorbed on the surface, \( N_0 \) is the total number of the surface sites of the Cu\(_9\) cluster, and \( G = G_2 \) is given by

\[
G_2 = (2S_H + 1),
\]

where \( S_H \) is the nuclear spin of H atom,

\[
S_H = 1/2,
\]

and \( \hbar \omega \) is the heat of adsorption:

\[
H(\text{gas}) \rightarrow H(\text{adsorbed}) + \hbar \omega,
\]

and \( V = V_2 \) is given by

\[
V_2 = V_{\text{Cu}_9+\text{H}}/V_{\text{Cu}_9},
\]

where \( V_{\text{Cu}_9} \) is the partition function for vibration of Cu\(_9\) cluster given by Equation (7). In Equation (25), \( V_{\text{Cu}_9+\text{H}} \) is the partition function for vibration of \( H + \text{Cu}_9 \) cluster written as Equation (8), with \( m_i \) indicating the frequency of the \( i \)’th normal vibration of \( H + \text{Cu}_9 \) cluster.

The chemical potential of an adsorbed H atom is defined by Equation (10). Thus we use Equation (11) to obtain the chemical potential of an adsorbed H atom, where \( G_2 \), \( V_2 \), and \( \hbar \omega \) are used instead of \( G_1 \), \( V_1 \), and \( \hbar \omega \), respectively. The chemical potential of an isolated H\(_2\) molecule is given by [9]

\[
\mu(\text{gas}) = (kT) \log \left( (2\pi mkT)^{3/2} (kT) \right) - (kT) \log (p) - 2\hbar \omega,
\]

where \( \hbar \omega \) is the heat of dissociation of the reaction

\[
H(\text{gas}) \rightarrow (1/2) H_2(\text{gas}) - \hbar \omega.
\]

In Equation (26), \( m \) is the mass of a H\(_2\) molecule, \( p \) is the pressure of the H\(_2\) gas, \( j \) is given by Equation (13), where

\[
g_{\text{nuc}} = (2S_H + 1)(2S_H + 1),
\]

\( r_\text{A}(T) \) is given by Equation (15), where \( I \) indicates the moment of inertia of a H\(_2\) molecule, and

\[
V_{\text{molec_vibration}}(T) = 1/ \left( \exp(hn/(2kT)) - \exp(-hn/(2kT)) \right),
\]

where \( n \) is the frequency of the vibration of a H\(_2\) molecule. The values of \( v_i \) (the frequency of the \( i \)’th normal vibration of Cu\(_9\) cluster), \( I \) and \( \omega \) are calculated using PM6 molecular orbital calculation.

The condition of the thermal equilibrium between H\(_2\) gas and the adsorbed H is given by

\[
2\mu(\text{adsorbed}) = \mu(\text{gas}).
\]

By substituting Equation (11) (with \( G_2 \), \( V_2 \) and \( \hbar \omega \), respectively, instead of \( G_1 \), \( V_1 \) and \( \hbar \omega \)) and Equation (26) into Equation (30), we obtain

\[
N/(N_0 - N) = A p^{0.5},
\]

where

\[
A = [h^{1.5} / (2\pi m kT)^{3/2} (kT)^{0.5}]
\]

\[
j^{0.5} G_2 V_2 \exp[(\hbar \omega / kT)] \exp(- \hbar \omega A(kT)).
\]

Surface coverage is defined by

\[
\theta_{H2} = N/N_0.
\]

From Equations (31) and (33), \( \theta_{H2} \) is given by

\[
\theta_{H2} = A p^{1/2} / (1 + A p^{1/2}).
\]

A system in which a H\(_2\) molecule is adsorbed on a Zn\(_7\) cluster can be calculated in a similar way.

### 2.3. General Theory of Surface Reaction Rates

When a surface reaction occurs between Cu\(_9\)Zn and H\(_2\), for example, an activated complex is generally formed in a transition state. Figure 1 shows (a) the initial state, (b) the transition state and (c) the final state of the reaction

\[
\text{Cu}_9\text{Zn} + \text{H}_2 \rightarrow \text{Cu}_9\text{ZnH}_2.
\]

Here the chemical structure of an activated complex has been obtained from the PM6 calculation as follows. First we choose two atoms (Zn and H atoms, in the case of Figure 1); these two atoms, each being selected from the two molecules, interact with each other in the reaction process. The total energy of the compound is calculated as a function of the distance between the two selected atoms. In other words, the distance between the two atoms is used as the reaction coordinate. When the total energy takes a maximum at a certain distance (0.22 nm, in the present example), the compound corresponding to this distance is regarded as the activated complex.

Reaction rate of the total system can be calculated by using the theory of absolute reaction rates [8]. In this theory, the velocity, \( v \), of the translational motion (thermal motion) of the activated complex along the reaction coordinate is given by

\[
v = (kT/2\pi m \delta)^{1/2}.
\]

The mean time, \( \tau \), in which an activated complex changes to the final reaction product is given by

\[
\tau = \delta u,
\]

where \( \delta \) is the typical length of the transition state. Here we assume \( \delta = 0.10 \text{ nm} \).

Let us consider a system in which powder of the catalytic material (powdered CuZn catalyst) is used. In an experiment [4] of methanol formation from H\(_2\) and CO\(_2\), the catalytic powder is formed in a shape of cylinder (\( 6 \times 3 \times 3 \text{ mm} \)). We assume that the volume of a grain of the powder, \( V_{\text{grain}} \), is equal to 27 mm\(^3\) (0.003 \times 0.003 \times 0.003 \text{ m}^3) and the surface area of one grain of the powder, \( S_{\text{grain}} \), is equal to 54 mm\(^2\) (6 \times 0.003 \times 0.003 \text{ m}^2).
Then, the total surface area of unit volume (1 m³) of the grain of the catalyst is given by

\[ S_{\text{total}} = S_{\text{grain}}/V_{\text{grain}}. \]  

(38)

The number of the final reaction product formed in a unit time is given by

\[ N = n/\tau, \]  

(39)

where \( n \) is the total number of the activated complexes in the system and is given by

\[ n = \theta V S_{\text{total}}/s, \]  

(40)

where \( \theta \) is the surface coverage of the activated complex, \( V \) is the total volume of the catalyst powder, and \( s \) is the area of a unit surface site. That is, \( V S_{\text{total}}/s \) is the total number of the surface sites of the experimental system. In the present paper, we assume \( s = 1.0 \times 10^{-20} \text{ m}^2 \).  

By inserting Equation (40) into Equation (39), \( N \) is calculated to be

\[ N = \theta S_{\text{total}}/V/\tau. \]  

(42)

The surface coverage of the activated complex can be calculated in a way similar to the case of that of a stable molecular species on a surface. It should be noted, however, that for a stable molecular species on a surface, any frequencies of normal vibration modes have positive values. For an activated complex, on the other hand, one frequency of a normal vibration is usually negative as is the case of the present calculation. This negative frequency corresponds to the translational motion along the reaction coordinate. The partition function for translational motion, \( Z_{\text{trans}} \), is given by

\[ Z_{\text{trans}} = (2\pi mkT)^{1/2} \delta h, \]  

(43)

where \( m \) is the mass of the activated complex. This \( Z_{\text{trans}} \) is used as the contribution of the negative frequency of vibration to the partition function of the activated complex. In the field of catalytic engineering, the following quantity

\[ R = N/V, \]  

(44)

is usually used as the quantity representing the reaction rate. By inserting Equation (42) into Equation (44), \( R \) is given by

\[ R = \theta S_{\text{total}}/(s \tau). \text{ (molecules·m}^{-3}·\text{s}^{-1}) \]  

(45)

2.4. Reaction Rate of H₂ Adsorption on Zn Sites of CuZn Surface

As shown in Subsection 2 - 3, theoretical value of the reaction rate \( R \) is calculated in relation to the surface coverage \( \theta \). In the present paper, first, we apply the theory to the case in which a H₂ molecule approaches to the

Figure 1. Reaction path of Cu₉Zn + H₂ → Cu₉ZnH₂: (a) Initial state (distance between Zn and H is 0.328 nm); (b) Activated complex (distance between Zn and H is 0.22 nm); and (c) reaction product (distance between Zn and H is 0.20 nm). Large and small red circles, respectively, indicate the Zn and H atoms employed to determine the reaction coordinate. (a) Initial State; (b) Activated Complex; (c) Reaction Product.
Zn site of a Cu9Zn cluster:

\[ \text{H}_2 + \text{Cu}_9\text{Zn} \rightarrow \text{Cu}_9\text{ZnH}_2 \]  \hspace{1cm} (46)

To calculate the value of \( R \), we calculate \( \theta \) of the activated complex system as follows. The free energy of the activated complex system is given by Equation (2), where \( N \) is the number of \( \text{H}_2 \) molecules in activated complexes, \( N_0 \) is the total number of the surface sites of the Cu9Zn cluster, and \( G_3 \) (instead of \( G \)) is given by

\[ G_3 = (2S_{H1} + 1) (2S_{H2} + 1), \]  \hspace{1cm} (47)

and \( V_3 \) (instead of \( V \)), the partition function for vibration of \( \text{H}_2 \) in an activated complex on the Cu9Zn cluster, is given by

\[ V_3 = V_{\text{Cu}_9\text{Zn} + \text{H}_2} V_{\text{Cu}_9\text{Zn}} \]  \hspace{1cm} (48)

where \( V_{\text{Cu}_9\text{Zn}} \) is the partition function for vibration of Cu9Zn cluster given by Equation (7), where, \( \omega_i \) is the frequency of the \( i \)‘th normal vibration of Cu9Zn cluster, and \( V_{\text{Cu}_9\text{Zn} + \text{H}_2} \) is the partition function for vibration of the total activation complex of \( \text{H}_2 + \text{Cu}_9\text{Zn} \) cluster:

\[ V_{\text{Cu}_9\text{Zn} + \text{H}_2} = Z_{\text{trans}} N_{\text{Cu}_9\text{Zn} + \text{H}_2} \{ \exp(h\omega_i/(2kT)) - \exp(-h\omega_i/(2kT)) \} \} \]  \hspace{1cm} (49)

Here, \( Z_{\text{trans}} \) is the partition function of translational motion along the reaction coordinate, which has negative vibration frequency, (see Equation (43)), \( \nu_i \) is the frequency of the \( i \)‘th normal vibration of Cu9Zn cluster, whose frequency is positive, and \( \omega_i \) in Equation (2) is, in this case, the heat of adsorption, \( \omega_n \), which is given by

\[ \text{H}_2 (\text{gas}) \rightarrow \text{H}_2 (\text{activated complex}) + \omega_n \]  \hspace{1cm} (50)

The chemical potential of \( \text{H}_2 \) in the activated complex is defined by Equation (10), where \( F(N) \) is the free energy of the activated complex system described above. Thus we obtain Equation (11) as the chemical potential of \( \text{H}_2 \) in an activated complex, by replacing \( G_1, V_1 \), and \( \omega_n \) with \( G_3, V_3 \), and \( \omega_n \), respectively. The chemical potential of an isolated \( \text{H}_2 \) molecule, on the other hand, is given by Equation (26). In this case, \( \omega_n \) equals to zero, since the activated complex is \( \text{H}_2 \) molecular specimen and not dissociated H atoms on the surface.

The condition of the thermal equilibrium between a \( \text{H}_2 \) gas molecule and \( \text{H}_2 \) molecular specimen in the activated complex is given by Equation (17). The value of \( N/(N_0 - N) \) is given by Equation (18), where \( A \) is given by Equation (19). In this Equation (19), \( G_3, V_3 \), and \( \omega_n \) are used instead of \( G_1, V_1 \), and \( \omega_n \), respectively. \( m \) is the mass of a \( \text{H}_2 \) molecule, \( J \) is given by Equation (13) with \( g_{\text{mac}} \) is given by Equation (28) and \( V_{\text{molec vibration}} \) is given by Equation (29). Surface coverage \( \theta_{\text{H2 activated}} \) is defined by Equation (20), and is given by Equation (21). The reaction rate \( R_{\text{calc}} \) of \( \text{H}_2 \) adsorption is given by Equation (45) \( (R = R_{\text{calc}}) \), where \( \theta_{\text{H2 activated}} \) is used instead of \( \theta \).

### 3. Results and Discussion

#### 3.1. \( \text{CO}_2 \) Molecules Adsorbed on the Surface of a \( \text{Cu}_9 \) Cluster

The value of \( \theta_{\text{CO2}} \) of \( \text{CO}_2 \) molecules chemically adsorbed on a Cu surface has been numerically calculated in the temperature range 200 - 1000 K and in the pressure range 20 - 100 atm. The value of \( \theta_{\text{CO2}} \) is 1.0, irrespective of the temperature and gas pressure:

\[ \theta_{\text{CO2}} = 1.0 \times 10^0. \]  \hspace{1cm} (51)

Thus, all the Cu surface sites adsorb \( \text{CO}_2 \) molecules, with virtually no vacant sites remaining on the surface. As mentioned before, we adopt a non-dissociative chemisorption model of \( \text{CO}_2 \) on Cu surface [6]. Equation (51) shows that the surface coverage of such adsorbing \( \text{CO}_2 \) is considerably high (near 1.0) under the experimental conditions considered here. This means that such non-dissociative adsorbing \( \text{CO}_2 \) is thermodynamically stable. This result is consistent with the catalytic reaction model given in Ref.6.

#### 3.2. \( \text{H}_2 \) Molecules Adsorbed on the Surface of a \( \text{Cu}_9 \) Cluster

The value of \( \theta_{\text{H2}} \), the coverage of H atoms chemically adsorbed on a Cu surface has been calculated in the temperature range of 200 - 1000 K and in the pressure range 20 - 100 atm. Table 1 shows the result of this numerical calculation. Under these temperature and pressure conditions, it is found that almost all of the Cu9 surface sites are vacant. Thus, H atoms are rarely adsorbed on the Cu surface. This is in good accordance with the statement in Ref.18 that “dissociative chemisorption of \( \text{H}_2 \) molecules is not found in experiments”.

Under the same temperature and pressure conditions, the surface coverage of H atoms chemically adsorbed on a Zn surface is calculated. In the calculation, a Zn9 cluster and a \( \text{H}_2 \) molecule are involved. Table 2 shows the result of this numerical calculation. Under these temperature and pressure conditions, considerable numbers of \( \text{H}_2 \) are adsorbed on the Zn surface.

#### 3.3. \( \text{CO}_2 \) and \( \text{H}_2 \) Molecules Co-Adsorbed on the Surface of a \( \text{Cu}_9 \) Cluster

In this part, we consider the case in which \( \text{CO}_2 \) and \( \text{H}_2 \) molecules are co-adsorbed on the surface of a Cu9...
Table 1. Surface coverage of H atoms chemically adsorbed on a Cu surface calculated as a function of H$_2$ gas pressure and temperature.

<table>
<thead>
<tr>
<th></th>
<th>200 K</th>
<th>400 K</th>
<th>600 K</th>
<th>800 K</th>
<th>1000 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 atm</td>
<td>$1.37 \times 10^{-46}$</td>
<td>$4.01 \times 10^{-25}$</td>
<td>$5.79 \times 10^{-18}$</td>
<td>$2.27 \times 10^{-14}$</td>
<td>$3.33 \times 10^{-12}$</td>
</tr>
<tr>
<td>40 atm</td>
<td>$1.94 \times 10^{-46}$</td>
<td>$5.67 \times 10^{-25}$</td>
<td>$8.19 \times 10^{-18}$</td>
<td>$3.21 \times 10^{-14}$</td>
<td>$4.71 \times 10^{-12}$</td>
</tr>
<tr>
<td>60 atm</td>
<td>$2.38 \times 10^{-46}$</td>
<td>$6.94 \times 10^{-25}$</td>
<td>$1.00 \times 10^{-17}$</td>
<td>$3.93 \times 10^{-14}$</td>
<td>$5.77 \times 10^{-12}$</td>
</tr>
<tr>
<td>80 atm</td>
<td>$2.75 \times 10^{-46}$</td>
<td>$8.01 \times 10^{-25}$</td>
<td>$1.16 \times 10^{-17}$</td>
<td>$4.53 \times 10^{-14}$</td>
<td>$6.67 \times 10^{-12}$</td>
</tr>
<tr>
<td>100 atm</td>
<td>$3.07 \times 10^{-46}$</td>
<td>$8.96 \times 10^{-25}$</td>
<td>$1.30 \times 10^{-17}$</td>
<td>$5.07 \times 10^{-14}$</td>
<td>$7.45 \times 10^{-12}$</td>
</tr>
</tbody>
</table>

Table 2. Surface coverage of H atoms chemically adsorbed on a Zn surface calculated as a function of H$_2$ gas pressure and temperature.

<table>
<thead>
<tr>
<th></th>
<th>200 K</th>
<th>400 K</th>
<th>600 K</th>
<th>800 K</th>
<th>1000 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 atm</td>
<td>$1.00 \times 10^0$</td>
<td>$9.98 \times 10^{-1}$</td>
<td>$9.16 \times 10^{-1}$</td>
<td>$5.83 \times 10^{-1}$</td>
<td>$2.93 \times 10^{-1}$</td>
</tr>
<tr>
<td>40 atm</td>
<td>$1.00 \times 10^0$</td>
<td>$9.99 \times 10^{-1}$</td>
<td>$9.39 \times 10^{-1}$</td>
<td>$6.64 \times 10^{-1}$</td>
<td>$3.70 \times 10^{-1}$</td>
</tr>
<tr>
<td>60 atm</td>
<td>$1.00 \times 10^0$</td>
<td>$9.99 \times 10^{-1}$</td>
<td>$9.50 \times 10^{-1}$</td>
<td>$7.07 \times 10^{-1}$</td>
<td>$4.18 \times 10^{-1}$</td>
</tr>
<tr>
<td>80 atm</td>
<td>$1.00 \times 10^0$</td>
<td>$9.99 \times 10^{-1}$</td>
<td>$9.56 \times 10^{-1}$</td>
<td>$7.36 \times 10^{-1}$</td>
<td>$4.53 \times 10^{-1}$</td>
</tr>
<tr>
<td>100 atm</td>
<td>$1.00 \times 10^0$</td>
<td>$9.99 \times 10^{-1}$</td>
<td>$9.61 \times 10^{-1}$</td>
<td>$7.57 \times 10^{-1}$</td>
<td>$4.81 \times 10^{-1}$</td>
</tr>
</tbody>
</table>

3.4. CO$_2$ and H$_2$CO$_2$ Co-Adsorbed on a Cu Surface

In this subsection, we discuss the co-adsorption of CO$_2$ and H$_2$CO$_2$ on a Cu surface. As described in Sec.3-1, a Cu surface is nearly saturated with CO$_2$ when it is exposed to pure CO$_2$ gas. Here we investigate whether H$_2$CO$_2$ and CO$_2$ can be co-adsorbed on the surface of a Cu$_9$ cluster when CO$_2$ gas and H$_2$ gas coexist. In this case, the condition of thermal equilibrium is given by the equations

$$ \mu (\text{CO}_2 \text{gas}) + \mu (\text{H}_2 \text{gas}) = \mu (\text{H}_2\text{CO}_2 \text{adsorbed}) \quad (53) $$

$$ \mu (\text{CO}_2 \text{gas}) = \mu (\text{CO}_2 \text{adsorbed}) \quad (52) $$

Solving these equations, the values of $N_{\text{CO}_2 \text{adsorbed}}/(N_0 - N_{\text{H}_2\text{CO}_2 \text{adsorbed}})$ and $N_{\text{H}_2\text{CO}_2 \text{adsorbed}}/(N_0 - N_{\text{CO}_2 \text{adsorbed}})$ can be obtained, where $N_0$ is the total number of the surface sites of the Cu$_9$ cluster, $N_{\text{CO}_2 \text{adsorbed}}$ is the total number of adsorbed CO$_2$ molecules, and $N_{\text{H}_2\text{CO}_2 \text{adsorbed}}$ is the total number of adsorbed H$_2$CO$_2$ molecules.

Table 3 summarizes the result of present calculation, showing the surface coverage of co-adsorbed CO$_2$ and H$_2$CO$_2$. The temperature range is 600 - 1000 K and the total pressure range is 60 - 100 atm, with the condition that the partial pressure of CO$_2$ equals to that of H$_2$. From Table 3, it is seen that most of Cu surface sites adsorb CO$_2$ molecules but much less H$_2$CO$_2$ molecules at 600 K. At 1000K, on the other hand, considerable amounts of both CO$_2$ and H$_2$CO$_2$ are adsorbed on the Cu surface. In a previous quantum chemical calculation [6], it was suggested that dioxomethylene (H$_2$CO$_2$) adsorbed on a Cu cluster surface might play an important role in the catalytic formation of methanol from H$_2$ and CO$_2$. The surface coverage of H$_2$CO$_2$ obtained from the present work strongly supports the catalytic chemical reaction model proposed in Ref.6.

3.5. Reaction Rate of H$_2$ Adsorption on Zn Sites of CuZn Surface

Reaction rate, $R_{\text{calc}}$, of H$_2$ adsorption on Zn sites of CuZn surface is calculated in the temperature range of 400 - 600 K and in the gas pressure range of 60 - 100 atm.
Numerical values of $R_{\text{calc}}$ are shown in Table 4. The value of $R_{\text{calc}}$ can be approximately given by

$$R_{\text{calc}} = (1.5 \times 10^{12}) P_{\text{H}_2} \cdot \exp(-E_{\text{calc}}/R_0 T),$$

(molecules-m⁻³-s⁻¹) \hspace{1cm} (54)

where $P_{\text{H}_2}$ is the pressure of $H_2$ gas (Pa) and $E_{\text{calc}}$ is given by

$$E_{\text{calc}} = 80 \text{ kJ mole}.$$ \hspace{1cm} (55)

It is known that the inverse shift reaction,

$$CO_2 + H_2 \rightarrow CO + H_2O,$$ \hspace{1cm} (56)

plays an important role in the methanol formation from $H_2$ and $CO_2$ using a CuZn catalyst [4]. The rate constant of this inverse shift reaction was experimentally obtained to be [4]

$$R_{\text{exp}} = (1.1 \times 10^{36}) f_{\text{H}_2} \cdot \exp(-E_{\text{exp}}/R_0 T),$$

(molecules-m⁻³-s⁻¹) \hspace{1cm} (57)

where $f_{\text{H}_2}$ is the fugacity of $H_2$ gas (Pa), and $E_{\text{exp}}$ was given by

$$E_{\text{exp}} = 121 \text{ kJ mole}.$$ \hspace{1cm} (58)

The experiment [4] was carried out around the temperature 503 - 521 K and the gas pressure 100 atm ($H_2$ gas plus $CO_2$ gas). It should be noted that Equation (57) includes the fugacity of $H_2$ gas, $f_{\text{H}_2}$, but does not include the fugacity of $CO_2$ gas, $f_{\text{CO}_2}$. This situation is in good agreement with the result of the present paper that the surface is nearly saturated with $CO_2$ chemical species when $H_2$ gas and $CO_2$ gas coexist in the experimental range of pressure and temperature (see Equation (51)). The values of $R_{\text{exp}}$ [4] and $R_{\text{calc}}$ are compared in Table 4. The values of frequency factor and activation energy calculated in the present paper are considerably different from those obtained experimentally. The present values of and $R_{\text{calc}}$, however, agree well with the values of $R_{\text{exp}}$ (see Table 4) in the range where experiment was carried out (503 - 521 K). This shows that the reaction in which a Zn site on a Cu$_9$Zn catalyst surface adsorbs $H$ chemical species is one of the rate determining steps in the inverse shift reaction given by Equation (56).

### 3.6. Reaction Rate of Chemical Adsorption of $H_2$ Gas on $CO_2$ Chemical Species on Cu$_9$ Cluster

Finally we estimate the reaction rate, $R_{\text{calc}}$, of chemical adsorption of $H_2$ gas on $CO_2$ chemical species on Cu$_9$ cluster. In other words, we estimate the rate of gas phase $H_2$ reaction with $CO_2$ chemical species. As a result, $H_2CO_2$ would be formed on the surface. This estimation is calculated in the temperature range of 400 – 600 K and in the gas pressure range of 60 - 100 atm. The value of $R_{\text{calc}}$ is approximately given by

$$R_{\text{calc}} = (1.49 \times 10^{31}) P_{\text{H}_2} \cdot \exp(-E_{\text{calc}}/R_0 T),$$

where $P_{\text{H}_2}$ is the pressure of $H_2$ gas (Pa) and $E_{\text{calc}}$ is given by

$$E_{\text{calc}} = 299 \text{ kJ mole}.$$ \hspace{1cm} (60)

This activation energy, $E_{\text{calc}}$, is much larger than that of the inverse shift reaction given in Equation (58). The value of the frequency factor, $1.49 \times 10^{31}$, is much smaller than the frequency factor of the inverse shift reaction (see Equation (57)). Therefore, the quantitative value of reaction rate of chemical adsorption of $H_2$ gas on $CO_2$ chemical species on Cu$_9$ cluster is much smaller.

### Table 3. Surface coverage of CO$_2$ chemical species and H$_2$CO$_2$ chemical species co-adsorbed on a Cu surface calculated as a function of gas pressure and temperature.

<table>
<thead>
<tr>
<th></th>
<th>600 K</th>
<th>1000 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total pressure</td>
<td>CO$_2$</td>
<td>$H_2CO_2$</td>
</tr>
<tr>
<td>60 atm</td>
<td>$1.0 \times 10^6$</td>
<td>$3.76 \times 10^{-7}$</td>
</tr>
<tr>
<td>80 atm</td>
<td>$1.0 \times 10^6$</td>
<td>$5.01 \times 10^{-7}$</td>
</tr>
<tr>
<td>100 atm</td>
<td>$1.0 \times 10^6$</td>
<td>$6.27 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

### Table 4. Reaction rate (molecules-m⁻³-s⁻¹) of $H_2$ adsorption on Zn sites of CuZn surface. Experimental values ($R_{\text{exp}}$) are taken from Ref.(4), while the calculated values ($R_{\text{calc}}$) are from the present calculation.

<table>
<thead>
<tr>
<th></th>
<th>400 K</th>
<th>500 K</th>
<th>600 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total pressure</td>
<td>$R_{\text{exp}}$</td>
<td>$R_{\text{calc}}$</td>
<td>$R_{\text{exp}}$</td>
</tr>
<tr>
<td>60 atm</td>
<td>$5.4 \times 10^{26}$</td>
<td>$1.6 \times 10^{28}$</td>
<td>$7.8 \times 10^{29}$</td>
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<tr>
<td>80 atm</td>
<td>$7.2 \times 10^{26}$</td>
<td>$2.1 \times 10^{28}$</td>
<td>$1.0 \times 10^{30}$</td>
</tr>
<tr>
<td>100 atm</td>
<td>$9.0 \times 10^{26}$</td>
<td>$2.6 \times 10^{28}$</td>
<td>$1.3 \times 10^{30}$</td>
</tr>
</tbody>
</table>

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than the corresponding value of the inverse shift reaction. This indicates that the direct chemical adsorption of H₂ gas on CO₂ chemical species on Cu₉ cluster plays little role in the inverse shift reaction.

4. Conclusions

In the present paper, surface coverage values have been calculated for several catalytic surfaces in relation to the formation of methanol. The calculation of the surface coverage of an activated complex gives the estimation of the surface reaction rate. It has been shown that a surface reaction is simulated by combining PM6 semi-empirical molecular orbital calculation, statistical dynamics and theory of absolute reaction rates. Comparison with experimental results has indicated that the present PM6 calculation gives reasonable value of hydrogen adsorption rate from a quantitative point of view. In a future work, more extensive calculations are desirable to obtain a more comprehensive set of reaction rate constants including the intermediates for the methanol synthesis process on various catalytic surfaces.

5. Acknowledgements

The authors would like to thank Mr. Masao Kikuchi at Jica Expert Conference in Kanagawa (JECK) for his suggestions in metallurgical engineering aspects, and Mr. Norio Chida of Tencube Co. for providing the WinMoster software.

6. References