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Adsorption of CO_2 and H_2 on Cu and Zn Micro-Cluster Surfaces Studied by Quantum Chemistry and Theory of Absolute Reaction Rates

Shin'ichiro Okude[1], Hiroaki Kuze[2*]
[1]*Yokohama-Totsuka Research Institute of Science and Technology*, *Mie Laboratory*, *Mie*, *Japan*.
[2]*Center for Environmental Remote Sensing*, *Chiba*, *Japan*.
[*]*E-mail*: *YRX*02226@*nifty.com*
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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 activetion energies of chemical reactions. In general, chemical reaction rate, K, is given by

$$K = A \exp(-E_a/R_0T), \quad (1)$$

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, θ (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 θ 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 CO_2 molecule. This Cu_9 cluster consists of 9 Cu atoms. We adopt a catalytic chemical reaction model [6] wherein non-dissociative chemical adsorption of CO_2 on Cu surface is assumed. In other words, we adopt a chemical structure in which each of the two O atoms of the adsorbing CO_2 molecule is assumed to contact a Cu atom of the Cu_9 cluster.

The free energy of adsorbed CO_2 molecule is given by [9],

$$F(N) = -(kT)\log[N_0!/(N!(N_0 - N)!)] - (kTN)\log\{GV\exp[\omega/(kT)]\} \quad (2)$$

where N is the number of adsorbed CO_2 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, Cu_9, and G is the spin parameter of the adsorbed molecule. In this case, the spin parameter $G = G_1$ is given by

$$G_1 = (2S_C + 1)(2S_O + 1)(2S_O + 1). \quad (3)$$

Here suffix 1 specifies the particular case of CO_2/Cu_9, and S_C is the nuclear spin of C atom,

$$S_C = 0, \quad (4)$$

and S_O is the nuclear spin of O atom,

$$S_O = 0. \quad (5)$$

In Equation (2), V is the partition function for vibration of a molecule (in this case, CO_2) adsorbed on the metal cluster (Cu_9 cluster). Thus, the partition function, $V = V_1$, is given by

$$V_1 = V_{Cu9 + CO2}/V_{Cu9}. \quad (6)$$

Here V_{Cu9} ($= V_{metal}$) is the partition function for vibration of the Cu_9 cluster given by

$$V_{metal} = \Pi_{metal}\{1/[\exp(h\nu_i/(2kT)) - \exp(-h\nu_i/(2kT))]\}. \quad (7)$$

In Equation (7), ν_i stands for the frequency of the i'th normal vibration of Cu_9 cluster. In Equation (6), $V_{Cu9 + CO2}$ ($= V_{metal + molecule}$) is the partition function for vibration of the $CO_2 + Cu_9$ (molecule + metal) cluster,

$$V_{metal + molecule} = \Pi_{metal + molecule}\{1/[\exp(h\nu_i/(2kT)) - \exp(-h\nu_i/(2kT))]\}, \quad (8)$$

where ν_i is the frequency of the i'th normal vibration of the $CO_2 + Cu_9$ (molecule + metal) cluster. In Equation (2), the heat of adsorption $\omega = \omega_1$ is given by

$$CO_2(gas) \rightarrow CO_2(adsorbed) + \omega_1 . \quad (9)$$

The chemical potential of an adsorbed molecular species (CO_2) is defined by

$$\mu(adsorbed) = (\partial/\partial N)F(N). \quad (10)$$

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

$$\mu(adsorbed) = -(kT)\log\{G_1V_1\exp[\omega_1/(kT)]\} + (kT)\log\{N/(N_0 - N)\}. \quad (11)$$

The chemical potential of an isolated CO_2 molecule, on the other hand, is given by [9]

$$\mu(gas) = (kT)\log\{h^3/[(2\pi mkT)^{3/2}(kT)]\} - (kT)\log j + (kT)\log p , \quad (12)$$

where m is the mass of a CO_2 molecule, and p is the pressure of the CO_2 gas, and j is given by

$$j = 0.5\, g_{nuc}\, r_e(T)\, V_{molec\_vibration}(T) \quad (13)$$

where

$$g_{nuc} = (2S_C + 1)(2S_O + 1)(2S_O + 1), \quad (14)$$

and $r_e(T)$ is given by

$$r_e(T) = 8\pi^2 I\, kT/h^2 , \quad (15)$$

where I is the moment of inertia of a CO_2 molecule, and $V_{molec\_vibration}(T)$ is given by

$$V_{molec\_vibration}(T) = \Pi_i\{1/[\exp(h\nu_i/(2kT)) - \exp(-h\nu_i/(2kT))]\}, \quad (16)$$

where ν_i is the frequency of the i'th normal vibration of a CO_2 molecule. The values of ν_i, I, and ω_1 are calculated using PM6 molecular orbital calculation.

The condition of the thermal equilibrium between a CO_2 gas molecule and an adsorbed CO_2 molecule is given by

$$\mu(adsorbed) = \mu(gas). \quad (17)$$

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

$$N/(N_0 - N) = A\, p, \quad (18)$$

where A is given by

$$A = \{h^3/[(2\pi mkT)^{3/2}(kT)]\}(j^{-1}G_1V_1)\exp[\omega_1/(kT)] \quad (19)$$

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

$$\theta = N/N_0. \quad (20)$$

From Equations (18) and (20), the surface coverage θ is given by

$$\theta = Ap/(1 + Ap). \quad (21)$$

2.2. H_2 Molecules Adsorbed on the Surface of a Cu_9 Cluster

Next, we consider a system in which a H_2 molecule is adsorbed on a Cu_9 cluster. We assume a case in which the H_2 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

$$G_2 = (2S_H + 1), \tag{22}$$

where S_H is the nuclear spin of H atom,

$$S_H = 1/2, \tag{23}$$

and $\omega = \omega_2$ is the heat of adsorption:

$$H(gas) \rightarrow H(adsorbed) + \omega_2 , \tag{24}$$

and $V = V_2$ is given by

$$V_2 = V_{Cu9+H}/V_{Cu9}, \tag{25}$$

where V_{Cu9} is the partition function for vibration of Cu_9 cluster given by Equation (7). In Equation (25), V_{Cu9+H} is the partition function for vibration of H + Cu_9 cluster written as Equation (8), with ν_i indicating the frequency of the i'th normal vibration of H + 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 ω_2 are used instead of G_1, V_1, and ω_1, respectively. The chemical potential of an isolated H_2 molecule is given by [9]

$$\mu(\text{gas}) = (kT)\log\{(h^3)/[(2\pi\, mkT)^{3/2}(kT)]\} - (kT)\log j + (kT)\log(p) - 2\omega_3, \tag{26}$$

where ω_3 is the heat of dissociation of the reaction

$$H(gas) \rightarrow (1/2)H_2(gas) - \omega_3. \tag{27}$$

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

$$g_{nuc} = (2S_H + 1)\,(2S_H + 1), \tag{28}$$

$r_e(T)$ is given by Equation (15), where I indicates the moment of inertia of a H_2 molecule, and

$$V_{molec\_vibration}(T) = 1/\{\exp(h\nu/(2kT)) - \exp(-h\nu/(2kT))\}, \tag{29}$$

where ν is the frequency of the vibration of a H_2 molecule. The values of ν_i (the frequency of the i'th normal vibration of Cu_9 cluster), I and ω_3 are calculated using PM6 molecular orbital calculation.

The condition of the thermal equilibrium between H_2 gas and the adsorbed H is given by

$$2\mu(\text{adsoped}) = \mu(\text{gas}). \tag{30}$$

By substituting Equation (11) (with G_2, V_2 and ω_2, respectively, instead of G_1, V_1 and ω_1) and Equation (26) into Equation (30), we obtain

$$N/(N_0 - N) = A \cdot p^{0.5}, \tag{31}$$

where,

$$A = \{h^{1.5}/[(2\pi\, m\, kT)^{3/4}(k\,T)^{0.5}]\} \; j^{-0.5}\, G_2\, V_2 \exp[\omega_2/(kT)] \exp[-\omega_3/(kT)]. \tag{32}$$

Surface coverage is defined by,

$$\theta_{H2} = N/N_0. \tag{33}$$

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

$$\theta_{H2} = Ap^{1/2}/(1 + Ap^{1/2}). \tag{34}$$

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_9Zn 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

$$Cu_9Zn + H_2 \rightarrow Cu_9ZnH_2. \tag{35}$$

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, u, of the translational motion (thermal motion) of the activated complex along the reaction coordinate is given by

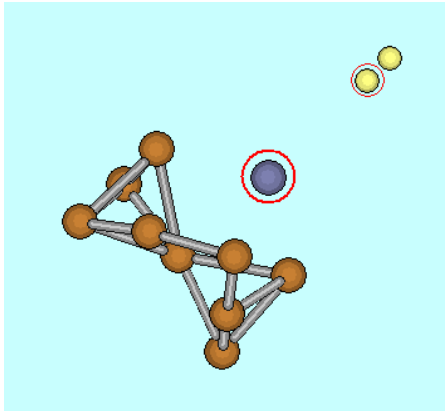
$$u = (kT/2\pi m)^{1/2} . \tag{36}$$

The mean time, τ, in which an activated complex changes to the final reaction product is given by

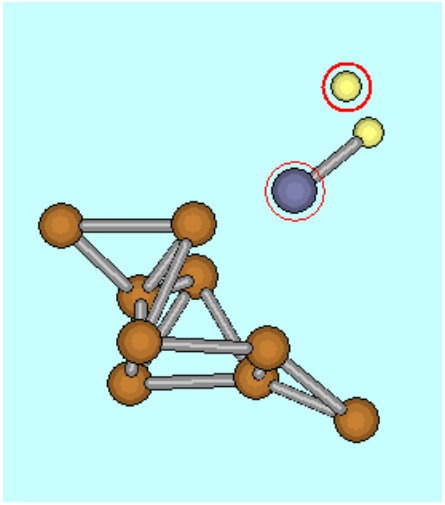
$$\tau = \delta/u, \tag{37}$$

where δ is the typical length of the transition state. Here we assume $\delta = 0.10$ nm.

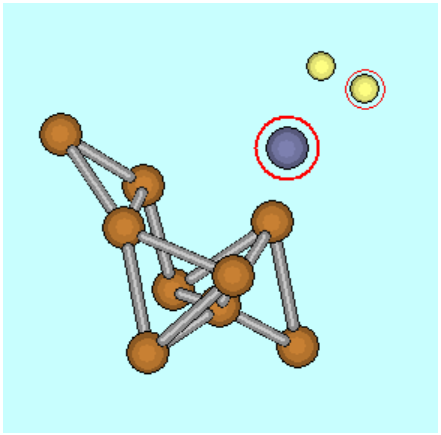
Let us consider a system in which powder of the catalytic material (powdered CuZn catalyst) is used. In an experiment [4] of methanol formation from H_2 and CO_2, the catalytic powder is formed in a shape of cylinder (ϕ3 mm × H3 mm). We assume that the volume of a grain of the powder, V_{grain}, is equal to 27 mm^3 (0.003 × 0.003 × 0.003 m^3) and the surface area of one grain of the powder, S_{grain}, is equal to 54 mm^2 (6 × 0.003 × 0.003 m^2).



(a)



(b)



(c)

Figure 1. Reaction path of $Cu_9Zn + H_2 \rightarrow Cu_9ZnH_2$: (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.

Then, the total surface area of unit volume (1 m^3) of the grain of the catalyst is given by

$$S_{\text{total}} = S_{\text{grain}}/V_{\text{grain}} . \quad (38)$$

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

$$N = n/\tau, \quad (39)$$

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

$$n = \theta V S_{\text{total}}/s, \quad (40)$$

where θ 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

$$s = 1.0 \times 10^{-20}\ \text{m}^2. \quad (41)$$

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

$$N = \theta S_{\text{total}} V/(s\tau). \quad (42)$$

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_{trans}, is given by

$$Z_{\text{trans}} = (2\pi\, mkT)^{1/2}\ \delta/h , \quad (43)$$

where m is the mass of the activated complex. This Z_{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

$$R = N/V, \quad (44)$$

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

$$R = \theta S_{\text{total}}/(s\ \tau). \ (\text{molecules}\cdot\text{m}^{-3}\cdot\text{s}^{-1}) \quad (45)$$

2.4. Reaction Rate of H_2 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 θ. In the present paper, first, we apply the theory to the case in which a H_2 molecule approaches to the

Zn site of a Cu_9Zn cluster:

$$H_2 + Cu_9Zn \rightarrow Cu_9\,ZnH_2. \quad (46)$$

To calculate the value of R, we calculate θ 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 H_2 molecules in activated complexes, N_0 is the total number of the surface sites of the Cu_9Zn cluster, and G_3 (instead of G) is given by

$$G_3 = (2S_H + 1)\ (2S_H + 1), \quad (47)$$

and V_3 (instead of V), the partition function for vibration of H_2 in an activated complex on the Cu_9Zn cluster, is given by

$$V_3 = V_{Cu9Zn+H2}/V_{Cu9Zn}, \quad (48)$$

where V_{Cu9Zn} is the partition function for vibration of Cu_9Zn cluster given by Equation (7), where, ν_i is the frequency of the i'th normal vibration of Cu_9Zn cluster, and $V_{Cu9Zn+H2}$ is the partition function for vibration of the total activation complex of $H_2 + Cu_9Zn$ cluster:

$$V_{Cu9Zn+H2} = Z_{trans}\ \Pi_{Cu9Zn+H2}\{1/[\exp(h\nu_i/(2kT)) - \exp(-h\nu_i/(2kT))]\}. \quad (49)$$

Here, Z_{trans} is the partition function of translational motion along the reaction coordinate, which has negative vibration frequency, (see Equation (43)), ν_i is the frequency of the i'th normal vibration of $Cu_9 + H_2$ cluster whose frequency is positive, and ω in Equation (2) is, in this case, the heat of adsorption, ω_4, which is given by

$$H_2\ (gas) \rightarrow H_2\ (activated\ complex) + \omega_4. \quad (50)$$

The chemical potential of 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 H_2 in an activated complex, by replacing G_1, V_1, and ω_1 with G_3, V_3, and ω_4, respectively. The chemical potential of an isolated H_2 molecule, on the other hand, is given by Equation (26). In this case, ω_3 equals to zero, since the activated complex is H_2 molecular specimen and not dissociated H atoms on the surface.

The condition of the thermal equilibrium between a H_2 gas molecule and 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 ω_4 are used instead of G_1, V_1, and ω_1, respectively, m is the mass of a H_2 molecule, j is given by Equation (13) with g_{nuc} is given by Equation (28) and $V_{molec\_vibration}(T)$ is given by Equation (29). Surface coverage $\theta_{H2\_activated}$ is defined by Equation (20), and is given by Equation (21). The reaction rate R_{calc} of H_2 adsorption is given by Equation (45) ($R = R_{calc}$), where $\theta_{H2\_activated}$ is used instead of θ.

3. Results and Discussion

3.1. CO_2 Molecules Adsorbed on the Surface of a Cu_9 Cluster

The value of θ_{CO2} of 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 θ_{CO2} is 1.0, irrespective of the temperature and gas pressure:

$$\theta_{CO2} = 1.0 \times 10^0. \quad (Cu\ surface,\ 200 - 1000\ K,\ 20 - 100\ atm) \quad (51)$$

Thus, all the Cu surface sites adsorb CO_2 molecules, with virtually no vacant sites remaining on the surface. As mentioned before, we adopt a non-dissociative chemical absorption model of CO_2 on Cu surface [6]. Equation (51) shows that the surface coverage of such adsorbing CO_2 is considerably high (near 1.0) under the experimental conditions considered here. This means that such non-dissociative adsorbing CO_2 is thermodynamically stable. This result is consistent with the catalytic reaction model given in Ref.6.

3.2. H_2 Molecules Adsorbed on the Surface of a Cu_9 Cluster

The value of θ_{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 Cu_9 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 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 Zn_9 cluster and a H_2 molecule are involved. **Table 2** shows the result of this numerical calculation. Under these temperature and pressure conditions, considerable numbers of H_2 are adsorbed on the Zn surface.

3.3. CO_2 and H_2 Molecules Co-Adsorbed on the Surface of a Cu_9 Cluster

In this part, we consider the case in which CO_2 and H_2 molecules are co-adsorbed on the surface of a Cu_9

Table 1. Surface coverage of H atoms chemically adsorbed on a Cu surface calculated as a function of H_2 gas pressure and temperature.

	200 K	400 K	600 K	800 K	1000 K
20 atm	1.37×10^{-46}	4.01×10^{-25}	5.79×10^{-18}	2.27×10^{-14}	3.33×10^{-12}
40 atm	1.94×10^{-46}	5.67×10^{-25}	8.19×10^{-18}	3.21×10^{-14}	4.71×10^{-12}
60 atm	2.38×10^{-46}	6.94×10^{-25}	1.00×10^{-17}	3.93×10^{-14}	5.77×10^{-12}
80 atm	2.75×10^{-46}	8.01×10^{-25}	1.16×10^{-17}	4.53×10^{-14}	6.67×10^{-12}
100 atm	3.07×10^{-46}	8.96×10^{-25}	1.30×10^{-17}	5.07×10^{-14}	7.45×10^{-12}

Table 2. Surface coverage of H atoms chemically adsorbed on a Zn surface calculated as a function of H_2 gas pressure and temperature.

	200 K	400 K	600 K	800 K	1000 K
20 atm	1.00×10^{0}	9.98×10^{-1}	9.16×10^{-1}	5.83×10^{-1}	2.93×10^{-1}
40 atm	1.00×10^{0}	9.99×10^{-1}	9.39×10^{-1}	6.64×10^{-1}	3.70×10^{-1}
60 atm	1.00×10^{0}	9.99×10^{-1}	9.50×10^{-1}	7.07×10^{-1}	4.18×10^{-1}
80 atm	1.00×10^{0}	9.99×10^{-1}	9.56×10^{-1}	7.36×10^{-1}	4.53×10^{-1}
100 atm	1.00×10^{0}	9.99×10^{-1}	9.61×10^{-1}	7.57×10^{-1}	4.81×10^{-1}

cluster. In a previous theoretical calculation [6], it was shown that formate (HCO_2 adsorbed on Cu cluster surface) plays an important role in the catalytic formation of methanol from H_2 and CO_2. PM6 calculation in the present paper shows that HCO_2 adsorbed on Cu_9 cluster has a negative charge of –0.872. This negative charge makes a formate molecule chemically stable on a Cu surface. On a Zn surface, on the contrary, HCO_2 is unstable, and it is dissociated into atoms. This behavior is based on the result of present calculation, namely a Zn surface adsorbs H atoms well (see **Table 2**), but on a Cu surface virtually no adsorption of H atoms takes place (**Table 1**). These results suggest that on the surface of a CuZn metal alloy catalyst, it is likely that Cu surface sites play an important role in adsorbing CO_2, and Zn surface sites in adsorbing H, leading to the formation of HCO_2 on Cu surface sites.

3.4. CO_2 and H_2CO_2 Co-Adsorbed on a Cu Surface

In this subsection, we discuss the co-adsorption of CO_2 and H_2CO_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_2CO_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

$$\mu(\mathrm{CO_2\ gas}) = \mu(\mathrm{CO_2\ adsorbed}), \quad (52)$$

$$\mu(\mathrm{CO_2\ gas}) + \mu(\mathrm{H_2\ gas}) = \mu(\mathrm{H_2CO_2\ adsorbed}). \quad (53)$$

Solving these equations, the values of $N_{\mathrm{CO2\ adsorbed}}/(N_0 - N_{\mathrm{H2CO2\ adsorbed}})$ and $N_{\mathrm{H2CO2\ adsorbed}}/(N_0 - N_{\mathrm{CO2\ adsorbed}})$ can be obtained, where N_0 is the total number of the surface sites of the Cu_9 cluster, $N_{\mathrm{CO2\ adsorbed}}$ is the total number of adsorbed CO_2 molecules, and $N_{\mathrm{H2CO2\ adsorbed}}$ is the total number of adsorbed H_2CO_2 molecules.

Table 3 summarizes the result of present calculation, showing the surface coverage of co-adsorbed CO_2 and H_2CO_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_2CO_2 molecules at 600 K. At 1000K, on the other hand, considerable amounts of both CO_2 and H_2CO_2 are adsorbed on the Cu surface. In a previous quantum chemical calculation [6], it was suggested that dioxomethylene (H_2CO_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_2CO_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_{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_{calc} are shown in **Table 4**. The value of R_{calc} can be approximately given by

$$R_{calc} = (1.5 \times 10^{32})\, P_{H2} \cdot \exp(-E_{calc}/R_0T), \quad (\text{molecules}\cdot\text{m}^{-3}\cdot\text{s}^{-1}) \quad (54)$$

where P_{H2} is the pressure of H_2 gas (Pa) and E_{calc} is given by

$$E_{calc} = 80 \text{ kJ/mole}. \quad (55)$$

It is known that the inverse shift reaction,

$$CO_2 + H_2 \rightarrow CO + H_2O, \quad (56)$$

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]

$$R_{exp} = (1.1 \times 10^{36}) f_{H2} \cdot \exp(-E_{exp}/R_0T), \quad (\text{molecules}\cdot\text{m}^{-3}\cdot\text{s}^{-1}) \quad (57)$$

where f_{H2} is the fugacity of H_2 gas (Pa), and E_{exp} was given by

$$E_{exp} = 121 \text{ kJ/mole} \quad (58)$$

The experiment [4] was carried out around the temperature 503 - 521 K and the gas pressure 100 atom (H_2 gas plus CO_2 gas). It should be noted that Equation (57) includes the fugacity of H_2 gas, f_{H2}, but dose not include the fugacity of CO_2 gas, f_{CO2}. 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_{exp} [4] and R_{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_{calc}, however, agree well with the values of $R_{exp.}$ (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_9Zn 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_{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_{calc} is approximately given by

$$R_{calc} = (1.49 \times 10^{31}) P_{H2} \exp(-E_{calc}/R_0T), \quad (59)$$

where P_{H2} is the pressure of H_2 gas (Pa) and E_{calc} is given by

$$E_{calc} = 299 \text{ kJ/mole}. \quad (60)$$

This activation energy, E_{calc}, is much larger than that of the inverse shift reaction given in Equation (58). The value of the frequency factor, 1.49×10^{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_2CO_2 chemical species co-adsorbed on a Cu surface calculated as a function of gas pressure and temperature.

	600 K		1000 K	
Total pressure	CO_2	H_2CO_2	CO_2	H_2CO_2
60 atm	1.0×10^{0}	3.76×10^{-7}	7.24×10^{-1}	2.76×10^{-1}
80 atm	1.0×10^{0}	5.01×10^{-7}	6.63×10^{-1}	3.37×10^{-1}
100 atm	1.0×10^{0}	6.27×10^{-7}	6.11×10^{-1}	3.89×10^{-1}

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

	400 K		500 K		600 K	
Total pressure	R_{exp}	R_{calc}	R_{exp}	R_{calc}	R_{exp}	R_{calc}
60 atm	5.4×10^{26}	1.6×10^{28}	7.8×10^{29}	2.0×10^{30}	1.0×10^{32}	5.4×10^{31}
80 atm	7.2×10^{26}	2.1×10^{28}	1.0×10^{30}	2.7×10^{30}	1.3×10^{32}	7.1×10^{31}
100 atm	9.0×10^{26}	2.6×10^{28}	1.3×10^{30}	3.4×10^{30}	1.7×10^{32}	9.0×10^{31}

than the corresponding value of the inverse shift reaction. This indicates that the direct chemical adsorption of H_2 gas on CO_2 chemical species on Cu_9 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.

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