Tight-Binding Quantum Chemical Molecular Dynamics Study of CO Adsorption on Pt (111) Surface

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Recently, we have successfully developed a novel tight-binding quantum chemical molecular dynamics program 'Colors', based on our original tight-binding approximation. This program is over 5000 times faster than the conventional first-principles molecular dynamics approach. In this paper, we present the results on the interaction of CO over Pt(111) surface, using the above tight-binding quantum chemical molecular dynamics method. Our simulation result predicts the preference site of the CO adsorption on the Pt (111) surface which is in good agreement with the experimental results. The vibration dynamics of the CO on the Pt(111) surface and the change of the Pt-Pt distance by the CO adsorption were investigated and discussed.
Key words: CO adsorption, Pt (111) surface, tight-binding quantum chemical molecular dynamics

1. INTRODUCTION

Transition metals, especially precious metals such as Rh, Pd and Pt, play essential role in automobile exhaust catalyst, as the active ingredients of so-called three-way catalyst (TWC), which can simultaneously decrease the amount of the pollutants, viz., carbon monoxide, hydrocarbons and NOx. Understanding the nature of CO adsorption to precious metals is an important issue that transcends surface chemistry [1], inorganic and organometallic chemistry [2], and even biochemistry [3]. This technological importance led to an enormous effort directed towards the understanding of the rather simple catalytic oxidation of CO on Pt, and especially most experimental work were concentrated on the (111) surface [4-9].

On the other hand, in recent years computational methods have become a powerful research tool for understanding the chemical reactions. For example, quantum chemical calculations provide information at electronic/atomic level. For example, density functional theory (DFT) calculation was employed to investigate the energetics and charge density state of CO on Pt (111) surface [10-14]. However, these studies were performed at 0 K and only static information was achieved. On the other hand, first-principles molecular dynamics calculation based on DFT methods demand huge computational costs, and hence only small model (~30 atoms; much smaller number for transition metals) can be simulated.

In this regard, recently we have successfully developed a novel quantum chemical molecular dynamics program 'Colors' [15-20], based on our original tight-binding theory. This program is over 5000 times faster than the regular first-principles molecular dynamics programs, and it can simulate large model systems, which can not be accomplished by the conventional first-principles molecular dynamics method. Hence, the chemical reaction dynamics and electron transfer dynamics on large catalyst model can be clarified by the above new program. In this paper, we applied the tight-binding quantum chemical molecular dynamics method to the interaction of CO over Pt (111) surface and the dynamics behavior of CO on the surface is well analyzed and discussed.

2. METHOD

2.1 Tight-binding quantum chemical molecular dynamics

The tight-binding quantum chemical molecular dynamics calculations were performed using our originally developed "Colors" code. In this program, the total energy and the force for each atom are expressed by Eqs. (1) and (2), respectively.

$$E = \sum_{i=1}^{n} m_i v_i^2 / 2 + \sum_{k=1}^{occ} \varepsilon_k + \sum \sum_{i>j} Z_i Z_j e^2 / R_{ij}$$
$$+ \sum \sum_{i>j} E_{rep}(R_{ij}) \tag{1}$$

$$F_i = \sum_{j \neq i}^{n} \sum_{k=1}^{occ} C_k^T \left(\partial H / \partial R_{ij}\right) C_k + \sum_{j \neq i}^{n} \sum_{k=1}^{occ} \varepsilon_k C_k^T \left(\partial S / \partial R_{ij}\right) C_k$$

$$- \sum_{j \neq i} Z_i Z_j e^2 / R_{ij}^2 + \sum_{j \neq i} \partial E_{rep}(R_{ij}) / \partial R_{ij} \quad (2)$$

where Z_i is the atomic charge, e is the elementary electric charge, and r_{ij} is the interatomic distance. In the Eq. (1), the first term refers to the kinetic energy, the second term is the summation of the eigenvalues of all occupied orbitals calculated by the tight-binding calculation, and the third term represents the Coulombic interaction. The last term corresponds to the short-range exchange-repulsion energy. The short-range exchange-repulsion term, $E_{rep}(R_{ij})$ is represented by Eq. (3).

$$E_{rep}(R_{ij}) = b_{ij} \ exp \ [(a_{ij} - r_{ij}) / b_{ij}] \quad (3)$$

Here, the parameters a_{ij} and b_{ij} represent the size and stiffness of atoms, respectively.

2.2 First-principles parameterization

In a similar way to the previous tight-binding quantum chemical molecular dynamics method, we used various parameters in "Colors", viz., the valence state ionization potential of atomic orbital i ($I_i = -H_{ii}$) and the Slater exponent of atomic orbital i (ζ_i). These parameters were determined by the first-principles density functional calculations for various charges and spin states of the atoms. On the basis of the improvement in the Wolfsberg-Helmholz formula by Anderson [21] and Calzafferi et al. [22], we used the following expression for H_{rs}:

$$H_{rs} = \frac{1}{2} K_{rs}(H_{rr} + H_{ss}) S_{rs} \quad (4)$$

$$K_{rs} = 1 + (\kappa_{rs} + \Delta^2 - \Delta^4 \kappa_{rs}) \exp\left[-\delta_{rs}(R_{ij} - d_0)\right] \quad (5)$$

$$\Delta = (H_{rr} - H_{ss}) / (H_{rr} + H_{ss}) \quad (6)$$

where, κ, δ, and d_0 are parameters for the tight-binding Hamiltonian, and κ_{rs} and δ_{rs} were determined for each pair of atomic orbitals to improve the accuracy in the chemical bonding calculations. In the conventional tight-binding calculations, the total orbital energy is calculated by:

$$E = \sum_{k=1}^{occ} \varepsilon_k \quad (7)$$

where ε_k is the orbital energy. Taking into account the work by Anderson [21,23] and Anderson and Hoffman [24], to improve the accuracy in the total valence electron energy, we introduced the following term for individual atoms with a different charge on the basis of the total electron energy of the same atom with the same charge calculated by the density functional theory method (E_{DFT}):

$$\Delta E_i = E_{DFT} - \sum_{k=1}^{occ} \varepsilon_k \quad (8)$$

ΔE_i is calculated for all the simulated atoms with

different charges and used to correct the total orbital energy in the tight-binding calculations. The dynamic behaviors of the quantum chemical molecular dynamics simulation results were visualized using our New-RYUGA program [25].

First-principles density functional calculations were performed by the Amsterdam density functional (ADF) program [26], in order to determine the parameters for the tight-binding quantum chemical molecular dynamics calculations. Energies were calculated using the generalized gradient approximation (GGA) with Becke's exchange and Perdew correlation functions. The triple zeta plus polarization functions (TZpp) basis sets were used.

3. RESULTS AND DISCUSSION

The tight-binding quantum chemical molecular dynamics calculations of the CO molecular adsorption on the Pt (111) surface were performed for 2000 steps with a time step of 0.2 fs at 300 K. Three-dimensional periodic boundary condition was applied. Verification of the accuracy of the parameters is mentioned in ref. [27]. Simulation cell has the dimension of $a = 8.32$ Å, $b = 9.61$ Å, $c = 15.00$ Å, $\alpha = \beta = \gamma = 90°$. Calculation model for the CO adsorption on the Pt (111) surface is shown in Fig. 1. In this calculation, the bottom layer of the Pt (111) surface was fixed. CO molecule is placed on the on-top site of the Pt atom and initial distance of the surface Pt atom and C atom is set to be 2.00 Å.

Fig. 2 presents the snapshots of the quantum chemical molecular dynamics simulation. CO molecule adsorbed on the on-top site of the Pt atom until 500 step, and then the CO molecule moved to the bridge site between two Pt atoms at 1000 step. Finally the CO molecule moved to another bridge site. Several experimental studies indicate that CO prefers low-coordination sites on the Pt (111) surface, such as on-top or bridging site on the Pt atoms [28-29]. On the contrary, the previous DFT results indicate that CO prefers the 3-fold site on the Pt (111) surface [11, 30]. Our
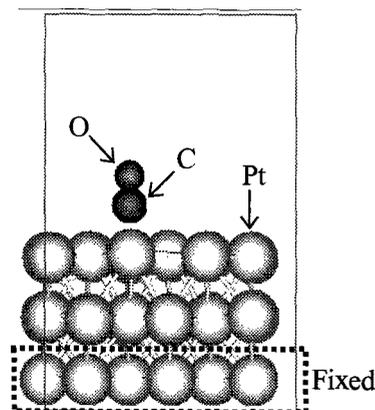
Figure 1. calculation model for the CO adsorption on the Pt (111) surface.
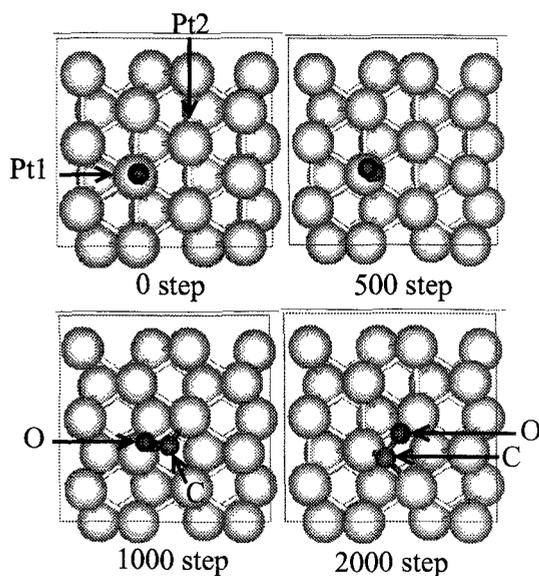
Figure 2. Dynamics behavior of CO adsorption and diffusion on Pt (111) surface (top view).
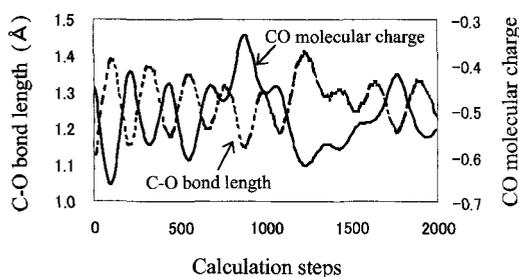
Figure 3. Change in the C-O bond length and the charge of CO molecule (black line: CO charge, dotted line: C-O bond length)
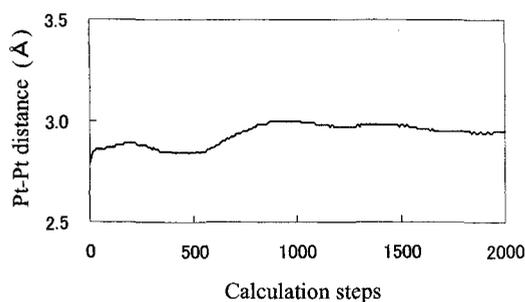
Figure 4. Change in the distance of Pt1 and Pt2 atoms (see figure 2: Pt1 is the initial adsorption site of the CO molecule and Pt2 is neighboring atom of the Pt1)

simulation result strongly supports the above experimental results on the low-coordinate preference of the CO molecule. Additionally, our simulation shows that the CO molecule takes bent structure on the bridge site, while the CO molecule takes linear structure on the on-top site.

Fig. 3 shows the change in the C-O bond length and the charge of the CO molecule. This figure shows that the CO molecule vibrate and the CO bond length changes from 1.15 Å to 1.40 Å on the Pt (111) surface at 300 K, while the C-O bond length of the CO molecule in the gas phase is 1.13 Å. This result shows that the CO molecule is activated on the Pt (111) surface. Moreover, this figure indicates that the C-O bond length is well correlated with the CO molecular charge and the C-O bond is elongated with the increment of the negative charge of the CO molecule. It is well known that the back-donation of electrons leads to the activation of CO molecule, since the LUMO of CO molecule is anti-bonding orbital.

Fig. 4 shows the change in the bond length of surface Pt1-Pt2 atoms. The positions of the Pt1 and Pt2 atoms are shown in Fig. 2. Pt1 is the initial adsorption site of the CO molecule and Pt2 is neighboring atom of the Pt1. The Pt1-Pt2 bond was slightly elongated until 200 step since the CO molecule adsorbed on the on-top site of the Pt (111) surface. Here, initial Pt1-Pt2 bond length was 2.80 Å. After 500 step, the significant elongation of Pt1-Pt2 bond was observed and the maximum bond length was found at about 1000 step. This is caused by the change of the CO adsorption site from the on-top site to the bridge site.

4. CONCLUSION

We performed a tight-binding quantum chemical molecular dynamics simulation and successfully analyzed the electronic states dynamics of the CO adsorption on the Pt (111) surface. Our tight-binding quantum chemical molecular dynamics calculation strongly supported the previous experimental results on the low-coordinate preference of the CO adsorption. We also successfully analyzed the activation and the dynamic vibration properties of the CO molecule caused by the electron transfer from the Pt (111) surface and the change in the adsorption site. Finally, the present studies indicate the possibility of the further applications of our original tight-binding quantum chemical molecular dynamics method to evaluate various adsorption and activation dynamics of molecules, which gives important information for the catalytic reaction on electronic and atomic level.

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