Development of New Molecular Simulation Software for Catalytic Reaction Engineering

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ABSTRACT

Recently, computational chemistry made great impacts on the catalysts research and development. On the other hand, the construction of new research field "Catalysis Reaction Engineering" by the merge of "Catalysis Chemistry" and "Catalysis Engineering" is strongly demanded. Static first-principles calculation has been employed to clarify the catalytic reaction, while molecular dynamics method has been employed to elucidate transport phenomena. However, the above methods cannot simulate both the catalytic reaction and transport phenomena at the same time, since the first-principles calculation cannot deal with the transport phenomena and molecular dynamics method cannot deal with the catalytic reaction. However, in order to establish new research field "Catalytic Reaction Engineering", both the catalytic reaction and transport phenomena should be simulated at the same time. Hence, recently we have succeeded in the development of new simulation program, which realizes the simulations of both the catalytic reaction and transport phenomena for the first time. This new simulation program is based on our original tight-binding quantum chemical molecular dynamics method. This program enables us to establish new research field "Theoretical Catalytic Reaction Engineering". The objective of this review is the introduction of the concept of "Theoretical Catalytic Reaction Engineering" and the characteristics of our new simulation program. Moreover, various successful applications of our new simulation program to the wide range of catalyst systems are also summarized.

KEYWORDS
Molecular Simulations, Catalytic Reaction Engineering, Catalytic Reaction Dynamics, Transport Phenomena, Quantum Chemical Molecular Dynamics

INTRODUCTION

The construction of new research field "Catalysis Reaction Engineering" by the merge of "Catalysis Chemistry" and "Catalysis Engineering" is strongly demanded. However, there are very few approaches for the construction of "Catalysis Reaction Engineering" field because of its difficulty. On the other hand, recently, computational chemistry made great impacts on the design and development of new catalysts. Especially, the first-principles quantum chemical calculation is powerful tool to clarify the catalytic reaction, activity, selectivity, and other information and hence it greatly contributes to "Catalysis Chemistry" on electronic and atomic level. However, since the first-principles calculation can investigate only the static states at 0 K, it cannot simulate the transport phenomena. Hence, this approach cannot contribute to "Catalysis Engineering". On the
other hand, molecular dynamics approach is frequently employed to elucidate the diffusion, adsorption, molecular sieve effect, etc., and greatly contributes to "Catalysis Engineering". However, since the molecular dynamics approach cannot consider the electronic states of the system, it cannot investigate the catalytic reaction. Hence, this approach cannot contribute to "Catalysis Chemistry". The above discussion indicates that there is no previous approach for the construction of new research field "Catalytic Reaction Engineering" in the computational chemistry area.

Hence, recently we intend to construct "Catalysis Reaction Engineering" field in the computational chemistry area by the development of new software, which can simulate both the catalytic reaction and transport phenomena. Although first-principles molecular dynamics method is one of the most promising methodologies to construct "Catalysis Reaction Engineering" field, it requests huge computational costs and then only a small model can be employed. Hence, the realistic catalyst model including active metals, supports, and additives cannot be simulated by the first-principles molecular dynamics method. Therefore, we have recently succeeded in the development of new tight-binding quantum chemical molecular dynamics method, which is more than 5,000 times faster than the traditional first-principles molecular dynamics method. This program was based on our original tight-binding theory, which enables us to simulate both the catalytic reaction and transport phenomena on large catalyst model at reaction temperatures. Moreover, we have successfully applied the above tight-binding quantum chemical molecular dynamics simulator to various catalyst systems. Hence, the objective of the present paper is the introduction of the development of new simulation program, which can simulate both the catalytic reaction and transport phenomena. Furthermore, our successful applications of the above new simulation program were also summarized.

**DEVELOPMENT OF NEW SIMULATION PROGRAM**

Tight-binding quantum chemical molecular dynamics program “Colors” is based on our original tight-binding theory and enables us to simulate both the catalytic reaction and transport phenomena of large catalyst systems at the reaction temperatures. In the tight-binding quantum chemical molecular dynamics program, the total energy is given by Eq. (1).

\[
E = \sum_{i=1}^{n} \frac{m_i v_i^2}{2} + \sum_{k=1}^{\text{occ}} e_i + \sum_{i} \sum_{j \neq i} Z_i Z_j e^2 / R_{ij} + \sum_{i} \sum_{j \neq i} E_{\text{rep}} (R_{ij})
\]  

(1)

The first, second, third, and fourth terms represent the kinetic energy, the total orbital energy of valence electrons, the Coulombic interaction energy, and the short-range exchange-repulsion interaction energy, respectively. \(m\) and \(v\) are a mass and velocity of an atom, \(Z\) is an atomic charge, \(e\) is the elementary electric charge, and \(R\) is an interatomic distance. The short-range exchange-repulsion term, \(E_{\text{rep}} (R_{ij})\) is given by the following equation;

\[
E_{\text{rep}} (R_{ij}) = b_{ij} \exp \left( \frac{a_{ij} - R_{ij}}{b_{ij}} \right)
\]  

(2)

where \(a\) and \(b\) represent the size and stiffness of the atoms, respectively. The force is described by Eq. (3).

\[
F_i = \sum_{j \neq i} \sum_{k=1}^{\text{occ}} C_k \frac{\partial H}{\partial R_{ij}} C_k + \sum_{j \neq i} \sum_{k=1}^{\text{occ}} e_k C_k \frac{\partial S}{\partial R_{ij}} C_k
\]

\[
- \sum_{j \neq i} \frac{Z_i Z_j e^2}{R_{ij}^2} + \sum_{j \neq i} \frac{\partial E_{\text{rep}} (R_{ij})}{\partial R_{ij}}
\]

(3)
where $H$ is the Hamiltonian matrix, $S$ is the overlap integral matrix, $C$ is the eigenvector matrix, and $C^T$ is the transformation matrix of the eigenvector matrix. We employed various parameters in the Hamiltonian to accelerate the calculation speed. We also succeeded in the development of new parameterization procedure based on the density functional theory (DFT) calculations in order to realize high accuracy. Further details regarding the first-principles parameterization can be seen elsewhere (Elanany et al., 2003).

The above new simulation program realizes 5,000 times acceleration compared to the traditional first-principles molecular dynamics method. It indicates that 10 years calculation by the first-principles molecular dynamics method can be finished within only one day by using our tight-binding quantum chemical molecular dynamics method. Hence, it can be applied to the large catalyst systems including active metals, supports, and additives.

RESULTS AND DISCUSSION

Methanol Synthesis Reaction on Cu/ZnO Catalyst

Cu/ZnO is a most famous catalyst for the methanol synthesis reaction, and a large amount of experimental results for the Cu/ZnO catalyst were accumulated. However, the atomistic understanding of both the catalytic reactions and transport phenomena on the Cu/ZnO catalysts are strongly demanded in order to design highly active and selective catalysts. Hence, we applied our tight-binding quantum chemical molecular dynamics program to the methanol synthesis process from CO$_2$ and H$_2$ on the Cu/ZnO catalyst at reaction temperatures (Kubo, et. al., 2004).

Fig. 1 shows the dynamics of the ultrafine Cu particle on the ZnO surface calculated by our new simulator. Finally, the formation of the hemispherical ultrafine Cu particle was observed on the ZnO support. It is interesting to see that the average charge of the Cu atoms on the ZnO support is +0.10, which indicates that the ZnO support strongly influences the electronic states of the ultrafine Cu particle. The above information cannot be obtained by the traditional first-principles molecular dynamics simulator, since it requests large computational costs and cannot be applied to such large catalyst system. Hence, we confirmed that only our new simulator can calculate the huge simulation model, including both the ultrafine metal particle and metal oxide supports.

Fig. 2 shows the catalytic reaction dynamics of the formation process of methanol molecule from formaldehyde intermediate and H$_2$ molecule on the Cu/ZnO catalysts at 500 K. Here, the reaction site is magnified for good understanding, although the electronic-states dynamics of all the atoms in Fig. 1 were calculated. We successfully observed the formation of methanol molecule

![Figure 1. Dynamic behaviour of ultrafine Cu particle on ZnO support simulated by our tight-binding quantum chemical molecular dynamics simulator.](image-url)
through metoxy intermediate and then the desorption of the methanol molecule was also detected. The formation of methanol molecule from formaldehyde intermediate through metoxy intermediate was suggested by the previous experiments. Since our simulation results are in good agreement with the experimental observation, we confirmed that our new simulator is accurate enough and a powerful tool to clarify both the catalytic reaction and transport phenomena at reaction temperatures.

Propylene Polymerization Reaction on Ziegler-Natta Catalyst

Polypropylene is one of the most important polymeric materials. The development of new catalysts to produce polypropylene with high quality has been very important research field and a lot of efforts have been already done. Ziegler-Natta catalyst is the most famous industrial catalyst in the production of polypropylene. Especially, the atomistic control of the selectivity is strongly demanded in the polypropylene synthesis. Hence, in the present study, we applied our tight-binding quantum chemical molecular dynamics program to the propylene polymerization reaction on the 4-fold-activated Ti site/MgCl₂(100) surface and discussed the catalytic reaction mechanism.

Fig. 3 shows the insertion process of the first propylene to the 4-fold-activated Ti site on the MgCl₂(110) surface. Our results show that a π-complex can be formed in a barrierless way when the propylene is oriented at the specific position as shown in Fig. 3(b). There is no steric hindrance between the ethyl group in the incoming propylene and the growing polymer chain. Thus, a stable π-complex is generated in Fig. 3(b). Fig. 3 (c) and (d) show the transition state and final product of the propylene insertion process. This result indicates that our new simulator can directory predict the final product from the initial structure through the transition state. This is very important characteristic of our new simulator, which realizes the detailed discussion of the reaction mechanism, activity, and selectivity. The energy difference between the final product (Fig. 3(d)) and the initial structure (Fig. 3(a)) is 13.5 kcal/mol. The lower energy in Fig. 3(d) indicates that the stable structure of the growing polymer chain was formed after the insertion process. This value is quite reasonable compared to the previous works. Moreover, it was found that the stereoselectivity

Figure 2. Catalytic reaction dynamics of the formation process of methanol from formaldehyde on Cu/ZnO catalyst at 500 K.
is a consequence of the local geometry of the active site carrying the growing chain. These results support the reaction mechanism of the propylene insertion process proposed by experiments.

The above results indicate that our new simulator can directly predict the final product and transition state from the initial structure. Moreover, the energetics during the whole catalytic reaction process can be discussed accurately. Hence, we confirmed that our new simulator is very effective and useful to design and develop practical catalysts in industries.

**Temperature Programmed Desorption Process on Zeolites**

Zeolites have been extensively studied because of their wide range applications such as catalysts, molecular sieves, adsorbents, and so on. Detailed characterization for the nature of acidic sites in zeolites remains a significant issue in order to understand their structure/activity relationship. Experimentally, temperature programmed desorption (TPD) technique is employed to evaluate the acidic properties of zeolites. However, the traditional first-principles calculation cannot simulate the TPD measurement directly, since it can only simulate the static states at 0 K. Hence, we applied our quantum chemical molecular dynamics approach to the NH$_3$ desorption process in H-mordenite for the first time, to the best of our knowledge (Elanany, et al., 2004). The temperature of the simulation system is increasing with the rate of 4 K/10 steps.

Fig. 4 shows the snapshots taken from the dynamic simulation of ammonia desorption in H-mordenite. At the beginning of the simulation, the ammonium ion is stabilized by three hydrogen bonds (Fig. 4(a)). There is an electrostatic interaction between NH$_4^+$ and oxygen atoms around Al site. However, at the end of the simulation, NH$_3$ diffuses away from the acidic site leaving the proton attached to the framework. Fig. 5 displays the bond distance analysis during the quantum chemical molecular dynamics simulation of NH$_3$ desorption in H-mordenite. As can be seen at 1260 step (~ 540 K) ammonia desorption is taking place from the Bronsted acid site in main channel. The calculated desorption temperature is quite reasonable compared to the experimental results (Katada, et al., 1997).

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**Figure 3.** Insertion process of the first propylene to 4-fold-activated Ti site on the MgCl$_2$(110) surface: (a) Initial structure, (b) π-complex, (c) transition state, and (d) final product.
This result indicates that our new simulator is very powerful tool to evaluate the chemical properties of catalysts related to the dynamic behaviours. Although most of the chemical properties of catalysts are related to both the chemical reaction and transport phenomena, there is no appropriate simulator to evaluate the chemical properties related to dynamic behaviours previously. However, the simulation results by our simulator can be directory compared to the experimental dynamic behaviour and chemical properties. It indicates that our new simulator succeeded in innovating new research filed "Catalyst Reaction Engineering" in the computational chemistry area.

Other Applications

Moreover, we have also applied our new tight-binding quantum chemical molecular dynamics method to various catalyst systems, such as support effect (Jung, et al., 2003), third-component effect, sol-gel process (Elanany, et al., 2003), lanthanocene catalyst (Luo, et al., 2003), Pd membrane, hydrogen storage materials, and so on. The catalytic reaction dynamics at reaction

(a)                                                                 (b)

Figure 4. Quantum chemical molecular dynamics simulation of NH₃ desorption in H-mordenite: (a) Initial structure and (b) final structure.

Figure 5. Change in the N-H bond distance of NH₄⁺ ion in H-mordenite during the quantum chemical molecular dynamics simulation. Temperature is increasing with rate of 4 K/10 steps.
temperatures were clarified and discussed well by employing large catalyst models. Hence, the applicability and effectiveness of our new simulator to wide-range of catalysis field were strongly confirmed.

CONCLUSIONS

In the present paper, we introduced our new tight-binding quantum chemical molecular dynamics program for both the catalytic reaction and transport phenomena. Moreover, some successful applications of our tight-binding quantum chemical molecular dynamics program to the large-scale catalyst system including active metals, supports, and additives were reviewed. We confirmed the effectiveness and applicability of our tight-binding quantum chemical molecular dynamics program for the simulation of both the catalytic reaction and transport phenomena on electronic and atomic level. Finally, we concluded that our new simulation program successfully innovate new research field "Theoretical Catalytic Reaction Engineering" for the first time and it would significantly contribute to the practical catalyst design and development in the industries.

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REFERENCES