

Multi-scale Theoretical Study of Sintering Dynamics of Pt for Automotive Catalyst

Ai Suzuki, Ryo Sato, Katsuyoshi Nakamura, Kotaro Okushi, Hideyuki Tsuboi,
Nozomu Hatakeyama, Akira Endou, Hiromitsu Takaba, Momoji Kubo,
Mark C. Williams and Akira Miyamoto

Tohoku University

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ABSTRACT

The capability of theoretical durability studies to offer an efficient alternative methodology for predicting the potential performance of catalysts has improved in recent years. In this regard, multi-scale theoretical methods for predicting sintering behavior of Pt on various catalyst supports are being developed. Various types of Pt diffusions depending on support were confirmed by the micro-scale ultra accelerated quantum chemical molecular dynamics (UA-QCMD) method. Moreover, macro-scale sintering behavior of Pt/ γ -Al₂O₃, Pt/ZrO₂ and Pt/CeO₂ catalyst were studied using a developed 3D sintering simulator. Experimental results were well reproduced. While Pt on γ -Al₂O₃ sintered significantly, Pt on ZrO₂ sintered slightly and Pt on CeO₂ demonstrated the highest stability against sintering.

1. INTRODUCTION

A longstanding problem, affecting many applications that use highly dispersed metal nanoparticles, is loss of active surface area in the metal components as a result of sintering. This is a particularly pernicious problem in applications in which catalysts have to experience high temperatures. This sintering causes a decrease in the catalytic activity.

Especially, the lifetime of a vehicle catalyst is important in maintaining low exhaust gas emissions. Mid-life catalyst durability performance has been experimentally examined in an engine dyno evaluations. In general, such a traditional confirmation of catalyst performance is done preparing many kinds of prototypes of catalysts, and using plenty of fuel in continuous evaluation tests.

Whereas, so far, little work has been devoted to the theoretical evaluation of catalyst sintering behavior.

Supported precious metals, such as platinum (Pt), rhodium (Rh), and palladium (Pd), are used to facilitate many industrial catalytic processes. Pt in particular is found at the core of catalysts for three-way (CO and hydrocarbon oxidation/NO_x reduction) conversions within car exhausts.

On the other hand, the most widely used ceramic materials as a support material in three-way catalysts (TWC) for the controls of notorious emissions from mobile sources are alumina, Al₂O₃, ceria, CeO₂ and zirconia, ZrO₂. Al₂O₃ has the advantages in its high hardness and wear resistance. Especially, γ -Al₂O₃ with large surface area and good thermal stability is widely used as a support material⁽¹⁾.

Ceria acts as an oxygen storage/release component by shifting their oxidation conditions between CeO₂ and CeO_{2-x} under reaction conditions due to high availability of surface oxygen, thus allowing oxygen storage and release to occur easily. However, the oxygen storage/release capacity (OSC) and durability of pure ceria are still inadequate for practical use in TWC.

ZrO₂ additions increase the fracture toughness of ceramic materials although it has low surface area compared to other supports, especially, addition of ZrO₂ into the CeO₂ lattice, as a Ce-Zr mixed oxides, have been found to be effective in strongly preventing the ceria from sintering and promoting the OSC^{(2),(3)}. In order to develop more efficient and durable TWC, it is really meaningful to investigate and clarify the relationship between supported precious metal, Pt and support material. Therefore, we selected above three typical TWC support materials and tried to theoretically

investigate what happened to its structure along with the thermal dynamics of Pt and its correlation with each support material.

In this paper, we report the results of an alternative methodology to experimental durability testing schemes (4), (5). We investigated the thermal durability of supported precious metals, represented as Pt, from micro scale to macro scale perspective. We focused not only microscopically on thermal diffusion dynamics of Pt at high temperatures, but also performed macroscopic long-term realistic time scale and particle-based sintering process simulation using a three-dimensional sintering simulator.

2. THEORETICAL STUDY ON DURABILITY

2.1 CLASSIFICATION OF THEORETICAL STUDY AND OUR CONCEPT OF MULTI-SCALE THEORETICAL SIMULATION

For theoretically studying thermal durability of catalysts, the factors of “time” and “temperature” are important ones. Although they are necessary to consider, too much variation exists in the way they are considered using theoretical methodology. Fundamental “scale” or “scope” of calculation is also important. Covering large scope of scale, i.e., μm scale, is phenomenologically important in understanding the rough trends of catalyst performance. On the other hand, focusing on limited scope, i.e. nm scale, is very useful for investigating and understanding the physics behind each phenomenon. First, we introduce some kinds of theoretical methodology which are shown in Table 1. Static Monte Carlo methods cannot perform real-time scale calculations. Molecular dynamics methods can include temperature, but time scales in this method are too short to trace aging phenomenon since a real-time scale is needed in actual durability tests. Some researchers perform particle-based surface evolution dynamics, but the models are often unrealistically simple. Ab initio quantum chemical methodology is suitable for the case where accurate calculation is desired. However, due to its heavy computational load, it cannot be applied to the large atomic scale, or to thermal dynamics. This situation forces us to conduct calculations using models composed of too few atoms, and it is too few to model realistic catalyst structure.

Table 1: Specifications for theoretical methods

Methods	Specifications
static Monte Carlo	Non real-time
molecular dynamics	Too short real-time
particle based-surface evolving dynamics	Unrealistically simple model
first principles quantum chemistry	• Too small numbers of atoms to compare realistic structure • Difficult to perform thermal dynamics

In summary, we try to perform theoretical studies by introducing “time” and “temperature” as important factors in considering thermal durability. In order to trace a series of phenomena affecting catalyst durability and include physical mechanisms, we try to understand continuously from micro to macro “scale” perspective. Our concept can be achieved by multi-scale simulation which is conducted by different scale models which is shown in Fig. 1.

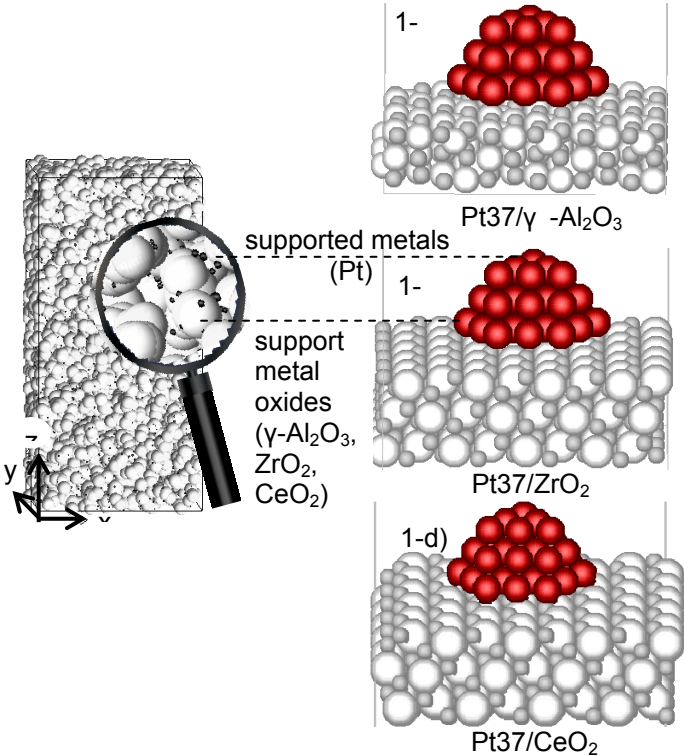


Fig. 1-a) Three-dimensional porous model for sintering simulation and micro-scale model of 1-b) Pt37/ γ -Al₂O₃, 1-c) Pt37/ZrO₂ and 1-d) Pt37/CeO₂ for Ultra Accelerated Quantum Chemical Molecular Dynamics

2.2 ULTRA ACCELERATED QUANTUM CHEMICAL MOLECULAR DYNAMICS (UA-QCMD) METHOD

We used our in-house code for ultra accelerated quantum chemical molecular dynamics (UA-QCMD) to investigate the adsorbed electronic and structural and diffusional characteristics of Pt on the surface of support metal oxides under high temperature conditions. We were also able to visualize the diffusion trajectories undergone in this system. UA-QCMD enables one to perform quantum chemical molecular dynamics (QCMD) calculations by reflecting binding energy and charges based on quantum calculations. Calculation of the electronic condition based on quantum chemistry was performed by Tight-Binding quantum chemical molecular dynamics.

Since high-level quantum mechanical calculations in the combined quantum mechanical/molecular

mechanical (QM/MM) approach are computationally intensive, it is very time consuming to do the full dynamical simulations. This means that semi-empirical QM methods have to be employed. To achieve the required accuracy, it is possible to use parameters optimized for the system of interest.

M. Elstner et al. developed new approach, called the self-consistent charge density functional tight binding (SCC-DFTB) method ⁽⁶⁾. Moreover, Q. Cui and M. Elstner implemented a QM/MM approach based on an approximate density functional theory, the SCC-DFTB method and tested on a number of systems ⁽⁷⁾.

Our novel UA-QCMD simulator consists of two parts. The first part is an original tight-binding (TB) simulator. In this simulator, an electronic structure calculation is performed by solving the Schrödinger equation $\mathbf{H}\mathbf{C}=\epsilon\mathbf{S}\mathbf{C}$ ($\mathbf{H}$, $\mathbf{C}$, ϵ , and $\mathbf{S}$ refer to the Hamiltonian matrix, eigenvector, eigenvalue, and overlap integral matrix, respectively) with the diagonalization condition $\mathbf{C}^T\mathbf{S}\mathbf{C}=\mathbf{I}$ ($\mathbf{I}$ refers to the unit matrix). To determine the off-diagonal elements of $\mathbf{H}$, H_{rs} , the following corrected distance-dependent Wolfsberg-Helmholz formula ⁽⁸⁾ was used:

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

To solve the Schrödinger equation in this simulator, parameters for $\mathbf{H}$ are used. In electronic structure calculations using the TB simulator, the total energy of a system is obtained using the following equation:

$$E = \sum_{k=1}^{occ} n_k \epsilon_k + \sum_{i=1}^N \sum_{j=i+1}^N \frac{Z_i Z_j e^2}{r_{ij}} + \sum_{i=1}^N \sum_{j=i+1}^N E_{ij}^{repul}(r_{ij}) \quad (2)$$

where the first, second, and third terms on the right-hand side refer to the molecular orbital (MO) energy, Coulombic energy, and exchange-repulsion energy, respectively. The first term on the right-hand side of eq 2 is rewritten as follows:

$$\sum_{k=1}^{occ} n_k \epsilon_k = \sum_{k=1}^{occ} \sum_r n_k (C_{kr})^2 H_{rr} + \sum_{k=1}^{occ} \sum_r \sum_s n_k C_{kr} C_{ks} H_{rs} \quad (3)$$

where the first and second terms on the right-hand side refer to the monoatomic contribution to the binding energy and the diatomic contribution to the binding energy, respectively (n_k is the number of electrons occupied in the k th molecular orbital). The binding energy calculated from the second term of eq 3 is used for the determination of the D_{AB} parameter in the Morse-type two-body interatomic potential function described in the following equation:

$$E_{AB} = D_{AB} \{ \exp[-2\beta_{AB}(R_{AB} - R_{AB}^*)] - 2 \exp\{-\beta_{AB}(R_{AB} - R_{AB}^*)\} \} \quad (4)$$

where E_{AB} , D_{AB} , β_{AB} , R_{AB} , and R_{AB}^* are the interatomic potential energy between atoms A and B, the binding energy between atoms A and B, the factor for the potential curve, the interatomic distance between atoms A and B, and the equilibrium interatomic distance between atoms A and B, respectively.

To set $\mathbf{H}$ and $\mathbf{S}$ in our TB simulator, the exponent of a Slater-type atomic orbital (AO), ⁽³⁾ denoted as ζ_r , and valence-state ionization potentials (VSIPs) for the valence shell of an AO of Al, Zr, Ce, Pt, and O atoms are necessary. The former parameters are used to calculate the $\mathbf{S}$ matrix and H_{rs} in eq 1. The latter ones are used for the diagonal element of $\mathbf{H}$ (H_{rr} or H_{ss} in eq 1). In our TB simulator, these are represented by the polynomial functions of atomic charges. ζ_r and H_{rr} are calculated by the polynomial functions of atomic charges described by eqs 5 and 6, respectively. In eqs 5 and 6, Z_i corresponds to the atomic charge on atom i . The parameters regarding ζ , i.e., a_0 , a_1 , a_2 , a_3 , a_4 , and a_5 in eq 5, and regarding H_{rr} , i.e., b_0 , b_1 , b_2 , b_3 , b_4 , and b_5 in eq 6, were adjusted to reproduce the binding energies and electronic structures of each reactant obtained by first principles calculations; these are summarized in Tables 2 and 3, respectively.

$$\zeta_r = a_0 + \sum_{k=1}^5 a_k (Z_i)^k \quad (5)$$

$$H_{rr} = b_0 + \sum_{k=1}^5 b_k (Z_i)^k \quad (6)$$

The second part of our methodology involves the classical MD simulator. Details of this method are described elsewhere ^{(9), (10)}. To reflect the Morse-type function and the atomic charges into during the MD simulation process, TB calculations are performed at the beginning and at successive intervals during the MD simulation process.