Development of Three Dimensional Kinetic Monte Carlo (3D-KMC) Grain Growth Simulator Based on Tight Binding Quantum Chemical Molecular Dynamics and Its Application to the Analysis of Thermal Grain Growth of CeO_2 and Rh/ CeO_2

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The electronic configuration between the interface of supported Rh and CeO_2 (111) surface was investigated by Tight Binding based Ultra Accelerated Quantum Chemical Molecular Dynamics method (TB-UAQCMD) at 1073 K. Time courses of bond energies of Rh-O (-Ce) plots for 5000 fs showed gradual increases of bond strength between oxygen and rhodium atoms in the uppersurface of the CeO_2 (111). This caused the anchoring effect of Rh-O (-Ce) bonds in the form of Rh-O (-Ce). Therefore total energies of the Ce-O bonds in the Rh/ CeO_2 were found to become more stable than that in the pure CeO_2 . The activation energy of grain growth of Rh/ CeO_2 nanoparticles was estimated by this deviation in these Ce-O bond energies. Experimentally observed suppression in the grain growth of Rh/ CeO_2 nanoparticles relative to those without Rh was quantitatively reproduced by three dimensional Kinetic Monte Carlo method (3D-KMC).

Keywords: Tight-binding (TB), Ultra accelerated quantum chemical molecular dynamics (UA-QCMD), Three-dimensional Kinetic Monte Carlo (3D-KMC), CeO_2 , Rh

1 Introduction

Ceria is widely used as a catalytic support with noble metals (Pt, Pd and Rh) for oxygen reduction reaction of fuel cells and purification of vehicle exhaust gases. Especially for the combination of Rh- CeO_2 , it is effective for the decomposition of N_2O and methanol [1]. Several first-principle models to investigate interfaces between noble metals and CeO_2 were presented by B. Li [2] and Z. Lu [3]. However, only a small number of atoms was composed in these cluster models for noble metals which have many orbitals including 4d and 5d due to large computational load. In addition, real supported noble metals, such as Pt and Rh were confirmed by Transmission Electron Microscopy (TEM) or High Resolution Transmission Electron

Microscopy (HRTEM) [4–7] to be exposed (111) facet on the CeO_2 surface. In order to reflect the fact in the models for theoretical investigation, the supported Rh cluster was modeled by a larger number of atoms to form about 1 nm size. The state of Rh on CeO_2 was quantum chemically investigated under realistic temperature, the same as the catalyst utilization temperature, at 1073 K. The grain growths of pure CeO_2 and Rh/ CeO_2 also confirmed whether the three dimensional Kinetic Monte Carlo (3D-KMC) simulation can quantitatively reproduce experimental magnitude of grain growth.

2 Methodologies

2.1 Quantum chemical molecular dynamics

Both "time" and "temperature" are essential factors for thermal durability of catalysts, and mobility and sinterability of catalysts are affected in the catalyst performance. However, it is not sufficient to depend only on conventional theoretical methodologies. They have individual shortcomings. For example, Static Monte Carlo methods cannot consider real-time scale. Molecular dynamics methods can consider 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. *Ab initio* quantum chemical methodology can evaluate electronic properties with relatively high accuracy, but only with smaller cluster sized molecules due to its heavy computational load, it cannot be applied to the large atomic scale, nonetheless, thermal dynamics. For this situation, in order to trace a series of phenomena affecting catalyst durability and include physical mechanisms, we try to continuously reflect microscopic characteristics into macroscopic perspectives. This modeling concept can be achieved by performing simulations of multi-scale models with each model having different scales. The investigation in the nm-scale area, such as interface between supported Rh and CeO₂ (111) facet was conducted by the ultra accelerated quantum chemical molecular dynamics (UA-QCMD) method. The results of UA-QCMD were introduced into the diffusion parameters which determine the diffusion of supports in particle based 3D-KMC method. It was applied to the simulation of grain growth of both CeO₂ and Rh supported CeO₂ nanoparticles. Both methods UA-QCMD and 3D-KMC considered temperature.

2.2 Quantum chemical analysis

Since *ab initio* quantum chemical calculations are computationally intensive, it is very time consuming to perform the thermal dynamics simulations. This means that semi-empirical QM methods have to be employed. To achieve the required accuracy, it is possible to use parameters, for example, the exponent of a Slater-Type atomic orbital (AO) and valence-state ionization potentials (VSIPs). By this technique, without heavy computational load, the UA-QCMD can calculate the electronic configuration to investigate the affinity of Rh catalyst on the surface of ceria support (111) facet under the temperature, 1073 K. UA-QCMD has proved to be a very successful technique for a detailed understanding of diffusion or aggregation processes involving metal clusters, allowing us to explore cluster evolu-

tion and understand the behavior of supported and unsupported metal clusters at the atomic level by reflecting binding energy and charges based on quantum calculations. The electronic configuration of catalysts was calculated after UA-QCMD simulation by original Tight Binding Quantum Chemical (TBQC) calculation.

Dynamics of atoms were carried out using the following potential functions, which were employed to consider the ionic, covalent interactions among atoms.

$$U = \sum_i \sum_{j>1} \left[\frac{Z_i Z_j e^2}{R_{ij}} + f_0 (b_i + b_j) \exp\left(\frac{a_i + a_j - R_{ij}}{b_i + b_j}\right) \right] + \sum_i \sum_{j>1} D_{ij} [\exp\{-2\beta_{ij}(R_{ij} - R_0)\} - 2\exp\{-\beta_{ij}(R_{ij} - R_0)\}] \quad (1)$$

The first term corresponds to the Coulomb potential, and the second term corresponds to the short-range exchange repulsion potential (f_0 is the constant for unit adjustment, a is the size, and b is the stiffness), which gives a good account of the repulsive interactions arising from the overlap of electronic clouds. Z_i and Z_j are the charges of atoms, e is the elementary charge, and R_{ij} is the internuclear distance. The third

term in eq. (1) corresponds to the Morse-type potential which represents covalent interactions, where D_{ij} is the bond energy, β_{ij} is the form factor, and R_0 is the bond length at minimum energy. Using the described potentials, a classical molecular dynamics (MD) simulation [8] was performed. This system can solve the equation of motion for large sets of atoms. In this MD simulator, a Verlet algorithm [9] is employed to integrate equations of motion. Moreover, the temperature scaling method was implemented in the system, which is similar to the Woodcock algorithm [10]. UA-QCMD simulations were carried out with a 0.1 fs of integration time for the equations of motions.

Our UA-QCMD method consists of two parts. The first part is an TBQC calculation. The second part of our methodology involves the classical MD simulator [8]. To reflect the Morse-type function and the atomic charges into during the MD simulation process, TBQC calculations are performed at the beginning and after UA-QCMD simulation. In this method, 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, eigenvalues, and overlap integral matrix, respectively) with the diagonalization condition ($\mathbf{C}^T\mathbf{S}\mathbf{C} = \mathbf{I}$; $\mathbf{I}$ refers to the identity matrix). In order to determine the off-diagonal elements of $\mathbf{H}$, H_{rs} , the corrected distance-dependent Wolfsberg-Helmholz formula, eq. (2) was used:

Table 1. Coefficients of a single zeta parameters in a Slater-type atomic orbital in eq. (6)

Element	AO	s_0	s_1	s_2	s_3	Coefficient
O	s	2.145	0.0802	0.0185	0.0007	1.0
	p	1.9664	0.5181	1.0817	1.1475	1.0
Rh	s	1.449	1.0	0.0	0.0	1.0
	p	1.50	1.0	0.0	0.0	1.0
	d	2.939	1.0	0.0	0.0	1.0
Ce	s	1.9165	1.1446	0.0	0.0	1.0
	p	1.8592	1.9970	0.0	0.0	1.0
	d	2.2319	1.1768	0.0	0.0	1.0
	f	3.0582	1.3363	0.0	0.0	1.0

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

In the TBQC scheme, the total energy of a system, E is expressed by using the following equation,

$$E = \sum_{k=1}^{occ} n_k \varepsilon_k + \sum_i \sum_{j>1} \frac{Z_i Z_j e^2}{R_{ij}} + \sum_i \sum_{j>1} (b_i + b_j) \exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right) \quad (3)$$

Summing up the values of b_i , b_j and a_i , a_j , we can modify the eq. (3) as follows;

$$E = \sum_{k=1}^{occ} n_k \varepsilon_k + \sum_i \sum_{j>1} \frac{Z_i Z_j e^2}{R_{ij}} + \sum_i \sum_{j>1} b_{ij} \exp\left(\frac{a_{ij} - R_{ij}}{b_{ij}}\right) \quad (4)$$

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. (4) is rewritten as follows:

$$\sum_{k=1}^{occ} n_k \varepsilon_k = \sum_{k=1}^{occ} \sum_r n_k (C_{kr})^2 H_{rr} + \sum_{k=1}^{occ} \sum_r \sum_s n_k C_{kr} C_{ks} H_{rs} \quad (5)$$

where the first and second terms on the right-hand side refer to the one-electron contribution to the binding energy and the two-electrons contributions to the binding energy, respectively (n_k is the number of electrons in the k -th molecular orbital). A binding energy calculated from the second term of eq. (5) is used for the determination of the D_{ij} parameter in eq. (1).

In order to set the Hamiltonian matrix, $\mathbf{H}$ and overlap integral matrix, $\mathbf{S}$ in the TBQC scheme, exponents of a Slater-type AO, denoted as ζ_r , and VSIPs for the valence shell of calculation atoms must be optimized. The former parameters are used to calculate the $\mathbf{S}$ matrix and H_{rs} in eq. (2). The latter ones are used

for the diagonal element of $\mathbf{H}$ (H_{rr} or H_{ss} in eq. (2)).

The relationship between H_{rr} and VSIP of the r -th AO of the i -th atom (I_r^i) is described as, $H_{rr} = -I_r^i$. These two parameters in the TBQC scheme, were represented by the polynomial functions of atomic charges. The ζ_r and H_{rr} were calculated by the polynomial functions of atomic charges described below by eq. (6) and (7), respectively.

$$\zeta_r = s_0 + \sum_{k=1}^3 s_k (Z_i)^k \quad (6)$$

$$H_{rr} = h_0 + \sum_{k=1}^4 h_k (Z_i)^k \quad (7)$$

In eq. (6) and eq. (7), Z_i corresponds to the atomic charge on atom i . The parameters regarding ζ_r , i.e., s_0 , s_1 , s_2 and s_3 in eq. (6), and those regarding H_{rr} , i.e., h_0 , h_1 , h_2 , h_3 , h_3 and h_4 in eq. (7), were adjusted to reproduce the binding energies and electronic structures of each reactant obtained by first principles calculations; these are summarized in Tables 1 and 2, respectively.

2.3 3D-KMC method

Diffusion of supported nanoparticles as well as support particles was simulated by an originally developed 3D-KMC program [11]. In this study, the program named *SINTA polygon* was applied to simulate the grain growth process of the polygon shaped model. A schematic flowchart of the 3D-KMC algorithm of grain growth of ceria support was added as Figure 6. As shown in Figure 6, it was enabled by repeating a series of events for the involved number of nanoparticles in the supports with a determined number of steps. The coordinates output by the system are then used to map the process of the grain growth of Rh/CeO₂ nanoparticles. This enables comparison of the characteristics of the grain growth process of CeO₂ support nanoparticles with experimental results. During the simulation a diffusion direction is randomly generated while the diffusion

Table 2. Coefficients of the H_{rr} parameters in eq. (7)

Element	AO	h_0	h_1	h_2	h_3	h_4
O	s	-28.6066	-15.0328	-1.4510	-0.4949	0.0419
	p	-14.2851	-14.8159	-1.6244	0.0154	0.0434
Rh	s	-8.0526	-4.40	0.0	0.0	0.0
	p	-3.5500	-0.50	0.0	0.0	0.0
	d	-8.4292	-7.60	0.0	0.0	0.0
Ce	s	-6.2303	-1.4425	0.0	0.0	0.0
	p	-1.5612	-0.0986	0.0	0.0	0.0
	d	-8.0356	-2.7249	0.0	0.0	0.0
	f	-8.7929	-2.8099	0.0	0.0	0.0

Table 3. Energy validation for quantum chemically calculated total binding energies of cluster model of Rh55. The calculated energy by TB-QC was compared with experimental total energies [13].

Element	TB-QC	Experiment	TB-QC/Experiment
Rh55	-7512.99	-7320.60	1.02

Figure 1. Snapshot of the results of UA-QCMD simulation at 1073.15 K of CeO_2 periodical model and its atomic trajectories

length for one 3D-KMC step, l , is calculated as $l = \sqrt{D(r)\Delta t}$, where $D(r)$ and Δt are the diffusion coefficient given as a function of particle size and the real-scale diffusion time per one 3D-KMC step, respectively. At the initial stage of grain growth, both metals and oxygens in the metal oxide can diffuse, meet and nucleate into larger atomic islands.

$$D_S(r) = D_{S0}(2r_S)^{-n} \exp\left(-\frac{E_S}{RT}\right) \quad (8)$$

T , R and n denote the absolute temperature, the gas constant, and particle size dependent coefficient of diffusion of supports, respectively. D_{S0} denotes the pre-factor of diffusion coefficient of the support. The nanoparticle size of the CeO_2 support in the unit of m, r_S at a certain time was reflected into eq. (8) and $n = 1.0$. The diffusion coefficients of CeO_2 support in eq. (8) were determined as $D_{S0} = 35 \text{ m}^2/\text{s}$ and $E_S = 458 \text{ kJ/mol}$ [12] based on experimental data [12].

3 Results and Discussion

3.1 CeO_2 (111) surface with and without Rh

Experimentally estimated enthalpy of Rh₅₅ [13] for supported metal cluster model as shown in the state in 0 fs of Figure 3 (a) at 298 K was -7320.6 kcal/mol as noted in Table 3. Total binding energy obtained by Tight Binding quantum chemical calculation was $-7512.99 \text{ kcal/mol}$ for Rh₅₅. This calculated energy was found to closely agree with experimentally measured enthalpies and determined parameters for eq. (6) and (7) were energetically validated. Figure 1 shows two snapshots of the structures of UA-QCMD simulation from 0 fs to 5000 fs with the atomic trajectories of ceriums and oxygens at 1073.15 K of CeO_2 . This calculation was conducted under the NPT ensemble (The pressure is 101.325 kPa, atmospheric pressure) with the time step of 1.0 fs/step. The size of the CeO_2 model was $x = 1.988 \text{ nm}$ and $y = 1.91 \text{ nm}$ under the periodic boundary condition. The CeO_2 crystal structure maintained its structure at

Figure 2. Snapshot of the results of UA-QCMD simulation at 1073.15 K (a) $\text{CeO}_2(111)$ facet and (b) its electronic configuration.

Figure 3. Snapshot of the results of UA-QCMD simulation at 1073.15 K (a) Rh55/ $\text{CeO}_2(111)$ and (b) its electronic configuration. Numerical values are bond lengths in the unit of Å.

Figure 4. Time course of Rh-O bond energies, bond population and bond length obtained from UA-QCMD simulation at 1073.15 K.

Figure 5. Time course of total energies of Ce-O all bonds in CeO_2 obtained from UA-QCMD simulation at 1073.15 K.
 (a) Total energies of Ce-O bonds in $\text{CeO}_2(111)$ and $\text{Rh}_{55}/\text{CeO}_2(111)$.
 (b) Deviation percentage of Ce-O bonds in $\text{CeO}_2(111)$ and $\text{Rh}_{55}/\text{CeO}_2(111)$.

1073 K by determined parameters as shown in Tables 1 and 2 for eq. (6) and (7). Figure 2 (a) shows the snapshots of $\text{CeO}_2(111)$ surface from 0 fs to 5000 fs obtained by UA-QCMD simulation at 1073 K. Figure 2 (b) shows its electronic configuration. The calculation condition was the same as for the calculation shown in Figure 1. The oxygen and cerium atoms composed of oxygen

termination O-Ce-O bonds in the uppermost layer were drastically moved. On the other hand, Figures 3 (a) and (b) show the snapshots of the $\text{Rh}_{55}/\text{CeO}_2(111)$ structures from 0 fs to 5000 fs with electronic configurations obtained by UA-QCMD simulation. The size of $\text{Rh}_{55}/\text{CeO}_2$ model was $x=1.988$ nm and $y=1.91$ nm under the periodic boundary condition. The initial

Figure 6. Algorithm of grain growth of nanoparticles

position of Rh₅₅ cluster was more than 2.6 Å from the upper surface of the CeO₂ (111) surface. A snapshot after 5000 fs in Figure 3 (a) gave a sample of penetration of a part of the Rh into the ceria which confirmed S. Imamura's experiment [1]. In Figure 4, time courses of Rh-O bond energies, bond population and bond length obtained from UA-QCMD simulation at 1073.15 K were shown. A solid triangle shows average bond energy of Rh-O, and its value became gradually larger from -50 kcal/mol at 0 fs to -130 kcal/mol at 5000 fs. Open circle shows the length between Rh and O, and its value became gradually closer to 2.8 Å (A Rh₅₅ cluster was far enough apart from the top of CeO₂ surface) at 0 fs to 2.0 Å at 5000 fs. Open square shows bond population of Rh-O, and its value became gradually larger from 0.18 at 0 fs to 0.48 at 5000 fs. After 5000 fs, the bond length of Rh-O (-Ce) was about 2.0 Å. The bonding strength of Rh-O (-Ce) (-130 kcal/mol) is much greater than either Rh-Rh (-27.75 kcal/mol) or Ce-O (-67 kcal/mol). Thus the stable Rh-O-Ce bond structure was formed.

Next, the thermal diffusion of oxygen and cerium atoms to compose O-Ce-O bonds in the uppermost surface of CeO₂ (111) surface was investigated. Additionally, the degree to which energetical stability was provided was investigated as Figure 5 (a) and (b). Figure 5 (a) shows the difference in total energies of all Ce-O bonds in pure CeO₂ (111) and Rh/CeO₂ (111) from 0 fs to 5000 fs. These results were obtained from the UA-QCMD

simulations as shown in Figures 2 and 3. As shown in Figure 5 (b), total energies of Ce-O bonds in Rh/CeO₂ were stabilized about 7–8% compared with pure CeO₂.

3.2 Grain growth of CeO₂ with and without Rh

In order to demonstrate the particle based phenomena based on the nano-scale characteristics, 3D-KMC simulation was conducted. The E_s in eq. (8) for Rh/CeO₂ was estimated as eq. (9);

$$E_s = E_{s(\text{CeO}_2)} + E_{s(\text{CeO}_2)} \times \frac{E(\text{Rh} / \text{CeO}_2) - E(\text{CeO}_2)}{E(\text{CeO}_2)} \quad (9)$$

Here, $E(\text{CeO}_2)$ and $E(\text{Rh} / \text{CeO}_2)$ corresponds to total energies of all Ce-O bonds in CeO₂ (111) and Rh₅₅/CeO₂ (111) surface, respectively in UA-QCMD simulations. The E_s for Rh/CeO₂ was estimated as 505 kJ/mol derived from the UA-QCMD calculation result shown in Figure 2 and 3.

S. Sato and K. Tomishige [14] found by TEM micrograph that the shape of calcined CeO₂ particles up to 1000 °C was flat and smooth with exposing many stable (111) facets. Z. L. Wang and X. Feng found that the evolution of CeO₂ nanoparticle shapes proceeded from truncated octahedral to octahedral with exposing (111) facets [15]. It turns out that there are 14 and 8 facets for truncated octahedral and octahedral shapes, respec-

Figure 7. Time evolution of grain growth process of CeO_2 nanoparticles which have dodecahedral facets at 1073 K estimated by 3D-KMC simulation.

The model size is $x=0.1\ \mu\text{m}$, $y=0.1\ \mu\text{m}$ and $z=0.1\ \mu\text{m}$.

Figure 8. The model of thermal grain growth simulation of 5 wt.% Rh/CeO_2 nano particles

(a) Particle based periodic boundary condition model for 3D-KMC simulation.

The model size is $x=0.1\ \mu\text{m}$, $y=0.1\ \mu\text{m}$ and $z=0.1\ \mu\text{m}$.

(b) Enlarged illustration of supported noble metals on dodecahedral facets of particle based model

(c) Supported noble metal cluster on $\text{CeO}_2(111)$ facet on periodic boundary condition.

(d) Time evolution of grain growth of 5 wt.% Rh/CeO_2 nanoparticles at 1073 K.

tively. K. Kaneko also found that CeO_2 nanocrystals were truncated at the corners exposing (111) octahedral facets and at the edges (220) dodecahedral facets [16]. Therefore CeO_2 nanoparticles were modeled dodecahedral facets which means facet number of 14 and 8 facets in order to agree with TEM results as mentioned above. A nanoparticle CeO_2 model ($x=0.1\ \mu\text{m}$, $y=0.1\ \mu\text{m}$ and $z=0.1\ \mu\text{m}$) has dodecahedral facets as shown in Figure 7 and 8. P. Bera confirmed that the average sizes of CeO_2 crystallites are in the range of 25–35 nm [17]. Therefore the sizes of nanoparticles were set about 25 nm. Figure 7 shows the time evolution of grain growth of CeO_2 nanoparticles at 1073 K

obtained by 3D-KMC simulation. O. Pozdnyakova found that most of the ceria particles were in the form of CeO_2 (fluorite structure) with (110), (111) and (001) orientation [18]. N. Ichikawa and S. Sato found that the (111) facet is predominant on large CeO_2 particles, whereas the (100) and (110) facets are exposed on small particles [19]. N. Zouvelou estimated that the stability of orientation of particles was of the following order; (111)>(110)>(100) [11]. Therefore a Rh cluster was supported on CeO_2 (111) facet as shown in Figure 3 and Figure 8 (c). Figure 8 (a) shows the model of thermal grain growth simulation for 5 wt. % Rh/CeO_2 nanoparticles. The density of Rh is

Figure 9. Time-course of agglomerated crystallite size of CeO₂ and Rh/CeO₂ at 1073 K by 3D-KMC simulation based on the result of UA-QCMD.

12.41 g/cc. A nanoparticle Rh/CeO₂ model was set to be $x=0.1$ μm , $y=0.1$ μm and $z=0.1$ μm . Rh nanoparticles were supported on flat and smooth CeO₂ surfaces as shown in Figure 8 (b). Figure 8 (d) shows the grain growth of Rh/CeO₂ at 1073 K every hour for 3 h simulated by 3D-KMC. Simulated grain growth for 3 h at 1073 K for pure CeO₂ was increased to 346.5 Å. Whereas that of Rh/CeO₂ was increased no further than 100 Å. These simulated results agreed with the quantitatively experimental results that S. Hosokawa found that the Rh supported CeO₂ had suppressed grain growth compared to pure CeO₂ [20]. As shown in Figure 9, the experimentally measured crystallite size was 360 Å for pure CeO₂ calcined at 1073 K for 3 h. This was much larger than the size of CeO₂ supported with Rh, 95 Å.

4 Conclusion

The formation of Rh-O-Ce bonds is the key factor which caused the difference in the magnitude of grain growth between CeO₂ and Rh/CeO₂. Bond population, bond length and bond energy of Rh-O obtained from UA-QCMD simulations at 1073 K showed the formation of Rh-O (-Ce) bonds in the upper surfaces of CeO₂ (111). This was caused by anchoring of Rh atoms through Rh-O-Ce bonds on the CeO₂ support. This caused the energetic difference of Ce-O bonds in the CeO₂ surfaces with and without Rh. It could reflect into the 3D-KMC simulation as the diffusion parameters. By introducing quantum chemical characteristics into the 3D-KMC method, experimentally observed suppression of grain growth in Rh/CeO₂ relative to pure CeO₂ could be quantitatively reproduced.

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