

2P03

## Ultra accelerated quantum chemical molecular dynamics study of surface reduction process of CeO<sub>2</sub>(111) and CeO<sub>2</sub>(110) by H<sub>2</sub>

OMd. Khorshed Alam<sup>1</sup>, Farouq Ahmed<sup>1</sup>, Ai Suzuki<sup>2</sup>, Hideyuki Tsuboi<sup>1</sup>, Nozomu Hatakeyama<sup>1</sup>, Akira Endou<sup>1</sup>, Hiromitsu Takaba<sup>1</sup>, Momoji Kubo<sup>1</sup> and Akira Miyamoto<sup>2,1</sup>

<sup>1</sup>Grad. Sch. Eng., Tohoku Univ. (6-6-11-1302 Aoba, Aramaki, Aoba-ku, Sendai 980-8579)

<sup>2</sup>NICHE, Tohoku Univ. (6-6-11-1302 Aoba, Aramaki, Aoba-ku, Sendai 980-8579)

### 【Introduction】

Ceria is an important catalyst in various industrial and environmental applications such as a three-way automotive exhaust catalyst (TWC) [1]. To understand the catalytic properties of both pure ceria and metal/CeO<sub>2</sub> materials, it is imperative to examine the redox surface chemistry. Recently, these materials have generated great interest in the solid oxide fuel cells as an alternative electrolyte for a lower temperature operation [2]. In particular, the defect chemistry of CeO<sub>2</sub> subjected to a H<sub>2</sub> atmosphere has been studied by various experimental techniques; such as temperature programmed reduction (TPR) and nuclear magnetic resonance (NMR). Hence in the present study, we applied our in house code for ultra accelerated quantum chemical molecular dynamics (UA-QCMD) to simulate (111) and (110) surfaces of ceria to investigate the reduction mechanisms of the surface by hydrogen that causes water desorption creating oxygen vacancy on the surfaces.

### 【Method】

Ultra accelerated quantum chemical molecular dynamics (UA-QCMD) code used in this study. The first part is tight-binding (TB) and second part is classical molecular dynamics (MD) New-Ryudo. From the TB calculation we obtained two body potentials and charges that were updated for MD simulation. The combination of Colors and New-Ryudo were repeated for number of times for accuracy.

### 【Results and Discussion】

To study the interaction of H<sub>2</sub> on ceria surfaces, we consider here the ceria (111) surface. As the initial structure, a single H<sub>2</sub> molecule was placed on the free surface above the Ce and O atoms and maintained distance between H<sub>2</sub> and the surface was 6.5 Å. In the present study, a high temperature of 873 K was used and the corresponding mean velocity about 2700 m/s was given to the H<sub>2</sub> molecule. Due to MD simulation after 130 fs H<sub>2</sub> come close to the ceria surface as shown in Fig.1 (b). After 1403 fs strong interaction occurred between the H<sub>2</sub> and the surface oxygen. This stage hydrogen molecule dissociates and the dissociated H atoms formed O-H groups on the surface as shown in Fig.1(c). Due to the simulation mutual interaction observed between the O-H groups. During the simulation structural change was observed as shown in Fig.1(c) and (d). The Ce-O<sub>surf</sub> bond completely broke after 2803 fs for (111) surface and 380 fs for the (110) surface. The loosely bound O<sub>surf</sub> come out and leads to water formation as shown in Fig.1 (d) creating oxygen vacancy on the ceria surface. The bond lengths and bond energies between O to H(a) and to H(b) are about 1.00 Å and -104 kcal/mol respectively. The reduction mechanisms of the CeO<sub>2</sub>(111) and (110) surfaces by H<sub>2</sub> have been elucidated by UA-QCMD.

It was found that the reduction of the CeO<sub>2</sub> surface take place via stepwise mechanisms adsorption/dissociation of H<sub>2</sub> with formation of OH species and desorption of H<sub>2</sub>O along with the reduction of Ce<sup>4+</sup> and the formation of an oxygen vacancy. According to our findings, less stable (110) surface is energetically more favorable.

### 【Reference】

[1] H.C. Yao, Y.F. Yu Yao J.Catal. 86 (1984), 254.

[2] H. Hibino, A. Hashimoto, T. Inoue, J. Tokuno, J. Yoshida, S. Sano, M. Science, 288 (200), 2031.

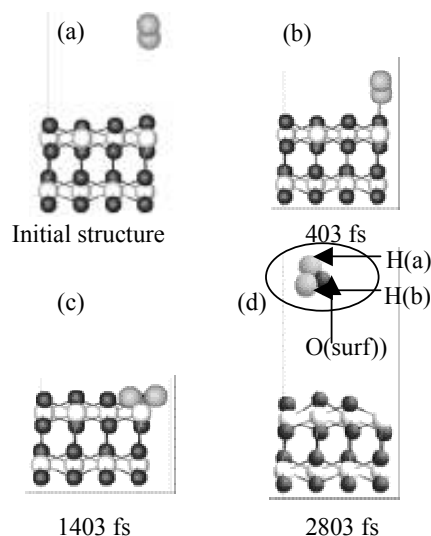


Fig.1 (a) Initial structure (b) Snap shot at 130 fs where H<sub>2</sub> molecule come close to the surface (c) H<sub>2</sub> dissociated on the surface (d) Water formation creating oxygen vacancy on the surface.