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Doping of ceria surface with Ti and its catalytic activity: a Quantum Chemical Molecular Dynamics Study

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Introduction: Ceria is an important catalyst in various industrial and environmental applications such as a three-way automotive exhaust catalyst (TWC). To understand the catalytic properties of both pure and doping CeO_2 materials, it is imperative to examine the redox surface chemistry. Recently, experimental work has shown that many metal dopants enhance the oxygen vacancy formation energy and reactivity of ceria. Doping of ceria with other metallic elements, such as Zr, has been shown to enhance thermal stability and to promote catalytic activity [1]. In the present study, we study doping effect of Ti on ceria surface and to investigate the structural distortion, vacancy formation energy and redox behavior of ceria.

Method:

We use density functional theory (DFT) and UA-QCMD for this purpose. UA-QCMD simulator consists of two parts. The first part is tight binding (TB) and the second part is molecular dynamics (MD) [2]. Using TB we obtained two body potentials and charges that were updated to perform MD simulation.

Results and Discussion:

We start by describing the atomic structure of the ceria (111) surface with introduction of the one Ti dopant. In the undoped ceria (111) surface, the surface Ce-O distances are equivalent 2.35 Å and the subsurface Ce-O distances are similar to bulk. Ti doped ceria average Ti-O distance is 1.98Å. The valence band has mostly O2p character with some contribution from Ce4f5d. Density of states (DOS) for the Ti doped ceria is obviously affected by the doping. Metal induced gap states appear below the empty Ce 4f states and the Fermi level is pinned the gap states. By analyzing DOS for Ti doped ceria, we find that the MIGS composed of mainly of Ti 3d and O 2p states. To analyze dynamical behavior of Ti doped ceria we consider here doped ceria surface with H_2. Distance bet-ween H_2 to surface is 5.8 Å, and the calculated temperature of this system was 573 K. In MD simulation after 100 fs H_2 adsorbed and dissociated on the surface by forming O-H bonds as shown in Fig.1 1(c). Due to UA-QCMD simulation mutual interaction occurred and a oxygen vacancy formed on the surface shown in Fig. 1 (d). The vacancy formation energy is 2.98 eV. Detailed results of this reaction dynamics will be discussed in the conference.

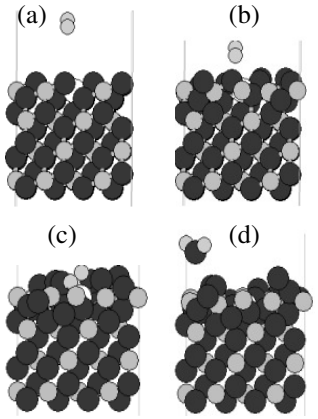

Fig.1 (a) Surface model of Ti doped ceria, (b, c) Snap shots after 40 and 100 fs respectively (d) Oxygen vacancy formation after 190 fs due to MD simulation.

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2) Md.K.Alam, A.Miyamoto, J.Phys.Chem.C, 113, 7723 (2009)