

STM Study of the Redox Properties of CeO(111)

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Abstract: Cerium dioxide (CeO_2 , ceria), has attracted a large attention due to its applications in automotive technology and various industrial processes like automotive exhaust catalysis, water-gas shift (WGS) reactions, fuel cells etc¹⁾. The wide range of applications is originated from the ability of cerium ions to change the oxidation states from Ce^{4+} to Ce^{3+} in a reversible way²⁾. Since in many catalytic processes ceria may come in contact with hydrogen, study of the reduction of the ceria is of great technological importance. Hydroxyls on oxide surfaces have attracted attention of intensive experimental and theoretical research^{3,4)}. However, none of the reported study provided an atomic scale characterization of the defects and hydroxyl species on ceria surface after exposed to molecular or atomic hydrogen.

All experiments were carried out in the ultra-high vacuum (UHV) condition (base pressure below 1×10^{-8} Pa) equipped with variable temperature STM (Omicron LT-STM), low-energy electron diffraction (LEED) optics, a hemispherical analyzer (Omicron EA125HR), and a Mg/Al twin anode x-ray source (Omicron DAR400) and standard facility for surface cleaning. The Ru(0001) single crystal (8 mm diameter and 2 mm thick, Mateck), used as substrate for $\text{CeO}_2(111)$ thin film, was cleaned by repetitive cycles of Ar^+ sputtering (1 KeV) followed by annealing (1073 K) in O_2 (5×10^{-5} Pa) to remove hydrocarbons and finally flashing to 1423 K to remove the oxides. Clean Ru(0001) was confirmed by LEED, XPS and STM. $\text{CeO}_2(111)$ thin film was prepared by evaporating Ce to the heated Ru substrate (1060 K) at 0.22 - 0.35 $\text{\AA}/\text{min}$ in O_2 environment (5.5×10^{-5} Pa) by EB heating of the Ta crucible containing pieces of Ce metal (Ce foil from Alfa Aesar, 99.9%).

A reduction of $\text{CeO}_2(111)/\text{Ru}(0001)$ surface by atomic hydrogen has been investigated using scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). We observed a formation of oxygen hydroxyl trimers (Figure 1) and vacancy trimers (figure 2) on the stoichiometric $\text{CeO}_2(111)$ surface when it was exposed to atomic hydrogen at room temperature. The interaction of atomic hydrogen with the surface oxygen atom results the formation of hydroxyl species which diffuse on the surface as hydrogen diffusion until they are stabilized by formation of trimers. The trimers were located atop sites of the oxygen atoms in the top most surface layer. Mobile hydrogen (means hydrogen hopping from one oxygen site to another oxygen site) interacts with hydroxyl (hydrogen bonded with oxygen atom of topmost surface) to be desorbed as H_2O leaving vacancy on the surface. Vacancy trimer is the result of the desorption of three H_2O molecules which is shown in Figure 2. Vacancy trimers and hydroxyl trimers on the surface were not same in numbers and not observed in close vicinity. Hence, our STM observation supports that active atomic hydrogen make bond with surface oxygen to form hydroxyl which diffuses over the surface (as H diffusion) and some hydroxyls interact with mobile hydrogen to be desorbed as H_2O leaving the vacancy on the surface at room temperature (Figure 3).

XPS data shows an increase of $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratio and hydroxyl species with the increasing amount of atomic hydrogen. After flash annealing at 645 K $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratio and hydroxyl species on the surface shows the decrease with the repetition of the flash annealing cycle. The decrease of $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratio and the number of hydroxyl species after flash annealing indicate the desorption as molecular hydrogen through the interaction between mobile hydrogen and hydroxyls.

Figure 1

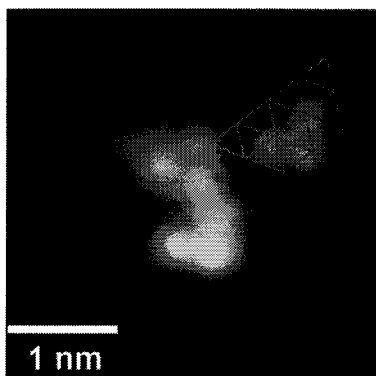


Figure 2

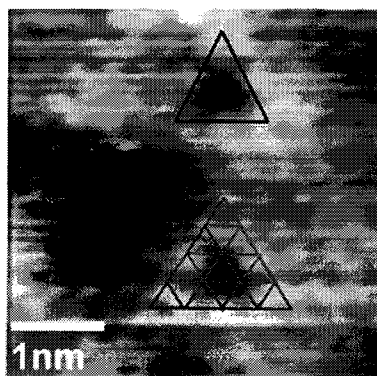


Figure 3

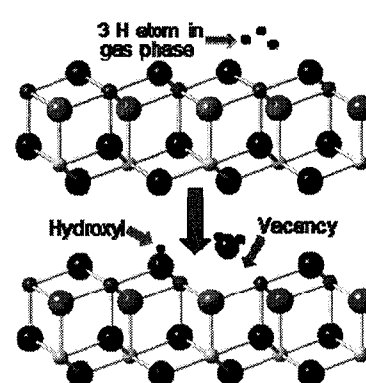


Fig 1: STM image of OH trimer on $\text{CeO}_2(111)$ Fig. 2: STM image of the vacancy trimer on $\text{CeO}_2(111)$, and Fig 3: Schematic model of the reduction reaction of atom-H on $\text{CeO}_2(111)$.

Hydroxyl trimers and vacancy trimers were found to be stable products. It can be speculated that an atomic hydrogen impinges on the surface and makes bond with an oxygen atom at the top most surface to form hydroxyl which diffuses over the surface (as H diffusion). Actually, in the STM image, no monomers or dimers were observed. It means that a hydroxyl diffuses over the surface and makes a hydroxyl trimer to be stabilized. This process might be quite faster than scanning speed of STM at room temperature. Since STM visualized only hydroxyl trimers in image obtained at 150 K, we conclude that the stable state of the hydroxyls over the oxide layer of $\text{CeO}_2(111)$ surface is achieved by the formation of trimers. Adsorbates can be trimerized by the interaction between them or by hydrogen bonding though the detail inner structure of hydroxyl trimer is yet to be understood. On the other hand, as known very well, the surface vacancy plays a key role in the surface chemistry of oxides. The vacancy site assumes to be preferred for additional reaction of hydroxyl formation. As a result, vacancy trimer would be created which was the most dominant defect on $\text{CeO}_2(111)$ surface after atomic hydrogen dosing.

Since surface hydroxyls are believed to be a key ingredient for catalytic reaction on metal oxide surface, hydroxylated reduced $\text{CeO}_2(111)$ surface will be intriguing for catalytic reaction study. Hence, our study will create a new insight of the surface hydroxyls for future catalytic study on $\text{CeO}_2(111)$ surface.

References:

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論文審査の結果の要旨

CeO₂(セリア)は様々な用途に用いられる触媒であるが、その最大の特徴は、セリウム原子の価数が比較的容易に変化するため、酸素原子の供給・受容の両方が可能なことである。そのため、酸化・還元の両用途に使用される。しかしながらその原子レベルでの触媒作用の詳細は未だ明らかにされていない。その理由には、良好な単結晶試料が入手しにくく、大きなバンドギャップを持った半導体であり電子を用いる分光手法が使用困難である点などが挙げられる。

本論文では、セリアをルテニウム(0001)表面上にエピタキシャルに成長させる手法に注目し、膜成長の条件を最適化することによって世界的に見ても優れた基板としての特性を持った試料の作成に成功した。これらの作成手法の新規性は高く評価される。その試料は、単結晶試料に比較して欠陥密度などで優れた性質を有すだけでなく、走査型トンネル顕微鏡(STM)やX線光電子分光法(XPS)などの手法を用いた解析を可能とした。その試料を用いて、セリア表面での欠陥構造に注目し、結晶構造のエネルギー安定性からその生成・消滅過程を明らかにした。セリア(111)表面の結晶構造を反映した、六角形と三角形の欠陥構造を原子レベルで解明した。またSTMやXPSを用いて水素吸着構造を原子レベルで明らかにした。水素吸着は還元作用の素過程と考えられ、その原子レベルでの解明は、触媒作用の基礎的理解に必須である。セリア(111)表面を水素原子に露出することにより、OHの3量体が形成され、それが安定なユニットとして表面を拡散すること、それらが合体することにより、酸素原子が表面から引き抜かれ欠陥が生じることを明らかにした。またXPS測定でCe³⁺/Ce⁴⁺の比率を測定することによって、セリウム原子の価数変化の測定に成功している。このことによりOHの3量体が水として脱離する過程を明確に示した。これらの研究は触媒過程の基礎的な理解に必須であり、博士論文としての価値を有すると考える。これらの実験は、自立して研究活動を行うに必要な高度の研究能力と学識を有することを示している。Syed Mohammad Fakuruddin Shahed 提出の博士論文は、博士(理学)の学位論文として合格と認める。