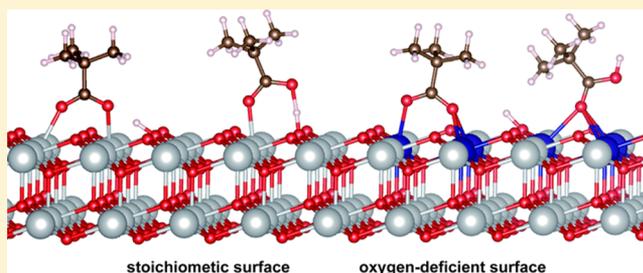


Theoretical Study of Trimethylacetic Acid Adsorption on CeO₂(111) Surface

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S Supporting Information

ABSTRACT: Trimethylacetic acid (TMAA) adsorption on stoichiometric and oxygen-deficient CeO₂(111) surfaces was investigated using density functional theory that accounts for the on-site Coulomb interaction via a Hubbard term (DFT +U) and long-range dispersion correction. Both the molecular state and dissociative state (TMAA → TMA⁻ + H⁺) were identified on stoichiometric and oxygen-deficient CeO₂(111) surfaces. For the stoichiometric surface, two thermodynamically favorable configurations with adsorption energies of the order of −30 kcal/mol are identified; one is a molecule adsorption state, and the other one is a dissociative state. For the oxygen-deficient surface, dissociative states are more favorable than molecular states. The most favorable configuration is the dissociative adsorption of TMAA with the adsorption energy of the order of −77 kcal/mol. The dissociated TMA moiety takes the position of oxygen vacancy, forming three Ce–O bonds. The signature vibrational frequencies for these thermodynamically stable structures are reported as well as their electronic structures. The effects of long-range dispersion interactions are found to be negligible for geometries but important for adsorption energies.

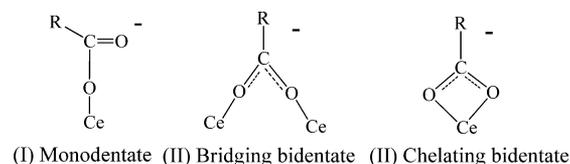


1. INTRODUCTION

CeO₂ is an important material with wide applications, including use as a catalyst and electrolyte and in solar cells because of its ability to accommodate varying charge states and facilitate relatively facile surface oxidation–reduction that allows it to mediate oxygen concentration. It is well-known that the concentration of Ce³⁺ ions increases with the reduction of the size of CeO₂ nanoparticles, and consequently oxygen exchange and redox reactions occur easily.¹ Because of this unique property, CeO₂ nanoparticles have been recently identified for a wide range of biomedical applications in which the ligand–nanoparticle interactions are of paramount importance in controlling the required properties.² For instance, CeO₂ nanoparticles coated with appropriate ligands can work as effective drug carrier and delivery agents.^{3,4} Because their efficiency depends on the binding stability of the nanoparticles with the ligands, it is vital to understand the chemistry between the anchoring groups on ligands and the surfaces of CeO₂ nanoparticles. One of the most commonly used anchoring groups is carboxylate; thus, the chemical adsorption of carboxylic acids on the nanoparticle surface is of great interest. Because of the complexity of nanoparticle surfaces, researchers have been using solid surfaces to study various facets of CeO₂ nanoparticle surfaces. Carefully designed experimental studies have been undertaken on the adsorption of carboxylic acids and carboxylates, such as formic acid, acetic acid, and formate, on the CeO₂(111) surface,^{5–7} which has

been determined both theoretically⁸ and experimentally⁹ to be the most stable low-index surface. The three general adsorption modes being studied are monodentate, bridging bidentate, and chelating bonding, shown in Scheme 1.^{10,11}

Scheme 1. Adsorption Mode of Carboxylate on Ceria Surface



However, concerning the most stable configuration of carboxylic acid on the CeO₂(111) surface, varying results were reported. Stubenrauch et al.⁵ studied the reactions of formic and acetic acids on CeO₂(111) and CeO₂(100) surfaces using temperature-programmed desorption (TPD) and high-resolution electron loss spectroscopy (HREELS). They found that carboxylic acids were dissociated on both surfaces to form surface carboxylates and hydroxyl groups and identified

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