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Effect of transition metal Fe adsorption on CeO_2 (110) surface in the methane activation and oxygen vacancy formation: A density functional theory study

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ABSTRACT

Methane activation and oxygen vacancy formation over transition metal Fe adsorption on CeO_2 (110) are studied by using the method of density functional theory (DFT) + U method. A set of model configurations are generated by placing Fe at five surface sites, viz., O-top site, O-bridge site, Ce-bridge site, Ce-top and double oxygen-bridge sites. The study shows that the energetically most favorable configuration is Fe adsorption at the double oxygen-bridge site. Based on the calculated surface, subsurface and the second oxygen vacancies formation energy with (or without) Fe adsorption, it shows that the Fe adsorption is in favor of the surface, subsurface and second oxygen vacancies formation. For the surface and subsurface oxygen vacancy on the Fe/CeO_2 (110) surface, the main factor responsible for lowering of E_{vac} is that the adsorption induces structural distortions, whereas, for the second oxygen vacancy, half can be attributed to the large structural relaxation, half can be attributed to the electronic effects. After calculating and discussing about the CH_4 activation on CeO_2 (110) and Fe/CeO_2 (110) surface with (or without) the surface or subsurface oxygen vacancies at the possible adsorption sites, the results show that when the CH_4 adsorbed on the Fe/CeO_2 (110) with the surface oxygen vacancy at the Ce_1 and Ce_2 sites, the CH_4 decomposed into the $CH_{(ads)}$ and $H_{(ads)}$, its belongs to the chemical absorption, whereas, when the CH_4 adsorbed on the other possible sites, the mentioned phenomenon is not occurred, its belongs to the physical absorption. This study reveals the correlation between surface reducibility and catalytic activity for methane oxidation on cerium-based materials, which might be beneficial in developing improved catalysts for methane combustion.

1. Introduction

Ceria (CeO_2) based compounds have been used in a variety of applications [1–3,6–9] due to their unique properties and extensive applications as active supports in metal-based catalysts for oxidation reactions [1], for instance, owing to their ability to cycle oxygen through redox processes and high oxygen ion mobility, it is widely used in three-way automotive catalysts [2], preferential CO oxidation [3–5], catalytic oxidation of hydrocarbons [6], the water gas shift (WGS) reaction, high oxygen storage capacity (OSC) and as solid electrolytes in solid oxide fuel cells (SOFCs) [7–9]. It is also used to help to improve mechanical and thermal stability as well as activity and selectivity of catalysts in catalysis [10,11]. The ability cycle oxygen efficiently for ceria originates from that they readily

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release (uptake) oxygen through redox processes involving the tetravalent (Ce^{4+}) and trivalent (Ce^{3+}) transformation, minimize thermal sintering, and promote metal activity and dispersion [12].

Previous experimental and theoretical investigations have suggested that loading small quantities of a transition metal M on CeO_2 could significantly enhance the reducibility of Ce^{4+} to Ce^{3+} and catalytic reactivity of CeO_2 [13–15]. For example, Cui et al. [15] thought that the metal dispersion on a CeO_2 matrix could make the materials with novel structural and (or) electronic properties. Hosokawa et al. [16] suggested that the M–O–Ce structure played an important role in M/CeO_2 catalysts, and believed that it was a key factor for high catalytic reactivity. It was suggested that the electronic properties and the oxidation states of the adsorbed metal ion also was an important factor to decide the performance of CeO_2 supported catalysts. For instance, Fu et al. [17] thought that the positively charged Au which resulted from transfer of an electron from atomic Au to Ce was main responsible for Au/CeO_2 with high catalytic activity. Similarly, the conclusion was confirmed by Škoda et al. [18] who investigated the interaction of Au with CeO_2 (111) layers using XPS. Chen et al. [19] investigated the charge transfer and format ion of Ce^{3+} upon adsorption of metal atom M (M = Cu, Ag, Au) on CeO_2 (100) surface, found that the adsorption was accompanied by an electron charge transfer between neutral metal atom and neighboring Ce^{4+} cation. Over the past few years, a lot of researches were aimed to study the interaction of the metal particle with the ceria support to explain the enhanced catalytic activity of transition metal/ceria catalysts, however, most of these studies have focused on the adsorption of metal ions on the CeO_2 (111) surface, which is the most stable surface amongst the low-index ceria surfaces [20]. The studied metal adsorbates that were Cu [21–24], Ag [21,24], Au [21,24,25], Pt [26], Pd [27], Rh [28] and Ni [23]. All these metal atoms adsorbed strongly on the (111) surface and were found to be oxidized. Alternatively, very few studies have investigated the interaction of transition-metal adsorbates with the (110) surface in the past. There were only several papers about it, for example, Yang et al. [29] studied that the oxygen vacancy pair defected on CeO_2 (110) and found that it was more reactive than CeO_2 (111). Carrasco et al. [30] showed that the Ni/CeO_2 system had an exceptional activity and selectivity for both WGS and ethanol steam reforming reactions. Nolan [31] studied the adsorption of a series of 3rd row transition metals (V, Cr, Fe), d^{10} metals (Cu, Ag and Au) and trivalent cations (Al, Ga, In, La) on CeO_2 (110) surface. It was found that all the transition metals were oxidized (Cu, Ag and Au to their +1 oxidation states, V and Cr to their +3 oxidation states, Fe to its +2 oxidation state) with the partial reduction of an equivalent number of lattice Ce^{4+} ions to Ce^{3+}. It was found that the d^{10} metals adsorbed more strongly on the (110) surface compared to other transition metals. Li et al. [32] have studied that Ni on the CeO_2 (110) and (100) surfaces: adsorption vs. substitution effected on the electronic and geometric structures and oxygen vacancies, and found that Ni adsorbate and substituent on the (110) surface were both found to induce significant structural distortions, and Ni adsorbate increased the energy required to create an oxygen vacancy while a Ni dopant reduced it. Chen et al. [5] have investigated the mechanisms for the oxidation of CO catalyzed by Fe-modified CeO_2 surfaces using periodic density functional theory calculations corrected for the on-site Coulomb interaction by a Hubbard term (DFT + U), it was found that the Fe^{3+} dopant in ceria lead to strong structural distortions, smaller oxygen vacancy formation energies drive CO oxidation, compared to the undoped system.

Through above review, we know, though the researchers have studied the loading small quantities of a transition metal M on CeO_2 in theory and experiment of catalytic performance and its related reduction properties, transition metal Fe adsorption on CeO_2 (110) surface effect on the methane activation and oxygen vacancy formation has been less systematical investigations, and the atomic and electronic levels understanding of the correlation between redox properties and hydrocarbon oxidation activity with changes are still not well understood. Herein, we use density functional theory, with the inclusion of an on-site coulombic interaction (DFT + U), to examine the energetics of dissociative methane adsorption and oxygen vacancy formation over ceria surfaces with the addition of Fe adsorption. These results provide insight into the relationship between composition, surface reduction and catalytic activity of ceria-based materials. It also provides an important information on the oxidation states of the adsorbed metal and the surface, which can be probed experimentally. We report the energies of oxygen vacancy formation for different location, the preferred adsorption modes and sites for methane adsorption, and the methane adsorption energy. Each result is discussed in the context of changes in electronic as well as structural features. It is expected that our results can provide insight into properties of relevance to the catalytic performance of ceria-based materials, and provide a useful basis of comparison for experimental studies focused on catalyst designs for methane oxidation.

This paper is organized as follows. The computational details are outlined in Section 2. Section 3 details discusses the major theoretical predictions, and it can be divided into three parts, first, the structural and electronic properties of Fe adsorb on CeO_2 (110) p(2 × 2) surface, second, the charge effect and transition metal Fe adsorption on CeO_2 (110) that affect the formation of oxygen vacancies, third, the methane (CH_4) adsorb on the clean and transition metal Fe adsorption on CeO_2 (110) p(2 × 2) surface. The most significant conclusions from this study are summarized in Section 4.

2. Model and computational details

The bulk of CeO_2 is geometry optimized by implementing in the Cambridge Serial Total Energy Package (CASTEP) program, based on the spin-polarized density functional theory (DFT) + U method [33], the GGA [34] is used along with ultrasoft pseudopotentials to represent the atoms. Specifically, for geometric optimization, the Perdew–Burke–Ernzerhof potential for solids (PBEsol) is used [35]. Here the cerium 5s, 5p, 5d, 4f, and 6s, and the oxygen 2s and 2p electrons are treated as valence electrons [36]. The gradient-corrected exchange and correlation functionals of the Perdew–Burke–Ernzerhof potential for solids (PBEsol) [35] with the Ce 4f state treated with on-site correction for Coulomb interaction (DFT + U) are also used in the calculations based on generalized gradient approximation (GGA) [34,37,38]. Here, we choose 5.0 eV [37] for the U term to describe Ce 4f state. The plane-wave basis set cutoff energy is 500 eV [39,40]. The convergence tolerance of energy charge, maximum force and stress are 5×10^{-6} eV, 0.01 eV/nm and 0.02 GPa, respectively [41]. Geometry optimization of the bulk model in each case is optimized to minimize the total energy using the Broyden, Fletcher, Goldfarb, Shanno (BFGS) method [42]. The Brillouin zones integration is performed by using 4 × 4 × 4 Monkost–Pack grid [39] for the geometry optimization and calculated electronic structure properties of the CeO_2, and a 2 × 2 × 1 Monkost–Pack grid [43,4] for the geometry optimization of the CeO_2 surface. The lattice constants of the cubic bulk CeO_2 is 5.4234 Å, this is in good agreement with the other calculation [44] and experiment [45], and it is also in good agreement with our earlier work [46,47]. In order to know the surface stability of CeO_2, we also calculate the surface energy, and the surface energies are evaluated by the following:

$$E_{\text{surface}} = \frac{(E_{\text{slab}} - nE_{\text{bulk}})}{2S}, \tag{1}$$

where E_{slab} and E_{bulk} are the total energy of the slab and the total energy of the CeO_2 bulk, respectively, n is the ratio between the atoms of the slab and those of the bulk, and S is the area of the