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Catalytic Activity of Single-Atom Copper Modified Reconstructed Cerium Dioxide (100) Surface for Ammonia Oxidation: A DFT+U Study

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Abstract

Ammonia has been proposed as a potential carbon-free energy source. However, a highly active catalyst is required for ammonia oxidation to promote the combustion rate. In this study, the single-atom copper catalyst loaded on the reconstructed cerium dioxide (100) surface with the pocket-like structure (Cu_1/CeO_4-t-p) is constructed for ammonia oxidation, and the catalytic process is investigated using the density functional theory calculations corrected by on-site Coulomb interactions (DFT+U). The adsorptions of ammonia and oxygen, the dissociation of ammonia and the oxidation of the dissociated ammonia species are systematically examined.

Key words: ammonia oxidation, reconstructed cerium dioxide (100) surface, single-atom copper catalyst, density functional theory.

1. Introduction

Cerium dioxide (CeO_2) has been widely used in many important catalytic reactions like CO oxidation [1] and water-gas shift reaction [2]. It is generally believed that the excellent catalytic performance of CeO_2 is related to the highly localized $4f$ orbital of the Ce elements and the remarkable activity of the lattice oxygen [3]. Among the various low-index surfaces of cerium dioxide, experimental studies have shown that the $CeO_2(100)$ surface has higher reactivity and oxygen storage capacity than its (110) and (111) counterparts [4, 5]. Notably, $CeO_2(100)$ is a common polar surface with high surface energy, which often undergoes the reconstruction to increase the surface stability. The scanning tunneling microscopy (STM) and high-resolution transmission electron microscopy (HRTEM) studies have revealed that the exposed (100) surface at CeO_2 nanocubes is not fully cerium or oxygen terminated [6]. The theoretical work conducted by Capdevila-Cortada *et al.* [7] showed that the $CeO_2(100)$ surface with CeO_4 termination (CeO_4-t) has lower surface energy than the oxygen (O-t) or cerium termination (Ce-t). Zhou *et al.* [8] have proposed a series of more stable reconstructed CeO_4-t $CeO_2(100)$ surfaces with pocket-like structure, and they also showed that these surfaces have superior affinity toward the adsorption and dispersion of single metal atoms.

Ammonia has been proposed as a potential carbon-free energy source due to its high energy density and zero carbon dioxide emission [9]. However, compared with common fossil fuels, the application of ammonia as fuel faces the challenges like high ignition temperature, low combustion rate and the emission of NO_x [10, 11]. Therefore, it is essential to design the catalysts for ammonia oxidation with high efficiency. At the same time, recent progresses in single-atom catalysts have drawn great attention. Various copper single-atom catalysts have been prepared and applied in many catalytic processes due to their high reactivity and selectivity [12]. Moreover, several CeO_2 supported single-atom copper catalysts have also been reported. For example, Rabee *et al.* [13] prepared the CeO_2 supported single-atom Cu catalysts modified by Fe for the reverse water gas shift reaction; Huang *et al.* [14] developed the single-atom Cu catalysts at CeO_2 for electrocatalytic reduction of CO_2. Considering the high reactivity of $CeO_2(100)$, we expected that the excellent ammonia oxidation activity could be achieved by loading atomic copper on the $CeO_2(100)$ surface.

In the present work, we conducted the density functional theory calculations corrected by on-site Coulomb interactions (DFT+U) to systematically investigate the catalytic processes of ammonia oxidation on the single-atom copper modified reconstructed

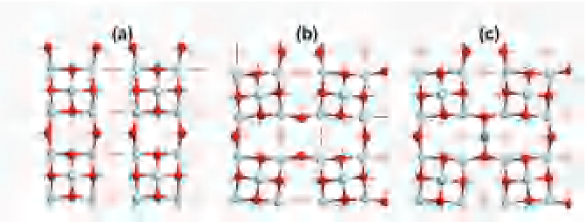

Figure 1. Top view of (a) CeO_4-t (b) CeO_4-t-p (c) Cu_1/CeO_4-t-p $CeO_2(100)$ surfaces. Red: O; light grey: Ce; orange: Cu; blue dashed circle: CeO_4 unit.

$CeO_2(100)$ surface. Detailed characteristics of the adsorptions and reactions within the possible ammonia oxidation pathways were carefully studied. It has been generally found that the localized $4f$ electron and the oxygen storage capacity of CeO_2 are both favorably involved in the reaction processes.

2. Computational methods and models

All the spin-polarized DFT+U calculations were carried out using Vienna *ab initio* Simulation Package (VASP) [15]. Electronic exchange and correlation were treated within the generalized gradient approximation (GGA) by using Perdew-Burke-Ernzerhof (PBE) functional [16]. The project-augmented wave method [17] with an energy cutoff of 450 eV was employed to describe the interaction between atomic cores and electrons.

Throughout all the calculations, the on-site Coulomb interaction correction with an effective U of 5.0 eV for Ce $4f$ orbitals was applied to describe the localized electronic states, which was consistent with our previous study [8]. The transition states (TS) were located by a constrained optimization method [18] and were verified when (i) all forces on the relaxed atoms vanish and (ii) the total energy is a maximum along the reaction coordination, but it is a minimum with respect to the rest of the degrees of freedom. All the calculations of structural optimization and transition states optimization were converged until the Hellman-Feynman forces on each ion were less than 0.05 eV/Å.

The lattice parameter of CeO_2 unit cell was optimized using a Γ-centered 5×5×5 k-point mesh, and the result of $a = b = c =$ 5.486 Å was obtained, which was consistent with the experimental value [19] of $a = b = c =$ 5.411 Å. For model construction, we first built the CeO_4-t surface (Figure 1a) from the $p(4 \times 4)$ slab cell. The clean CeO_4-t-p surface (Figure 1b) was then built by adjusting the positions of the surface O_{2c} on the CeO_4-t surface according to our previous study [8].

The model of single-atom copper catalyst (Cu_1/CeO_4-t-p, see Figure 1c) was further built by adding a copper atom into the position between two surface O_{2c} of the clean CeO_4-t-p surface. The CeO_4-t-p and the Cu_1/CeO_4-t-p surfaces were simulated with slabs containing 9 atomic layers. To prevent the interactions between the slabs, the vacuum layer of about 12 Å was set between neighboring slabs. It needs to be mentioned that the thermal stability of the single-atom Cu catalyst built in this way is also an important issue, which will be in-depth studied in our future work.

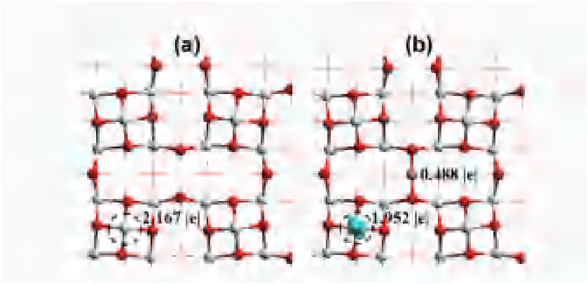

Figure 2. Calculated spin charges (top view, in blue) and Bader charges of (a) CeO_2-t-p and (b) Cu_1/CeO_2-t-p surfaces.

The adsorption energy (E_{ads}) of adsorbates (NH_3 and O_2) on the reconstructed $CeO_2(100)$ surfaces was defined as:

$$E_{\mathrm{ads}} = -(E_{\mathrm{mol/slab}} - E_{\mathrm{slab}} - E_{\mathrm{mol}})$$

where $E_{\mathrm{mol/slab}}$ is the calculated energy of the surface slab with adsorbates, E_{slab} is the calculated energy of the clean surface slab, and E_{mol} is the calculated energy of the isolated molecule. The oxygen vacancy formation energy (E_{vac}) was defined as:

$$E_{\mathrm{vac}} = E_{\mathrm{slab/vac}} + 0.5\, E_{O_2} - E_{\mathrm{slab}}$$

where E_{slab} is the calculated energy of the clean surface slab, $E_{\mathrm{slab/vac}}$ is the calculated energy of the surface slab with a single oxygen vacancy, and E_{O_2} is the calculated energy of a single O_2 molecule.

3. Results and discussion

3.1 Electronic structure of CeO_4-t-p and Cu_1/CeO_4-t-p surface

To learn the effect of single-atom copper modification on the CeO_4-t-p surface, we performed the electronic structure calculation. Figure 2 shows the calculated spin charge densities and Bader charges of the CeO_4-t-p and Cu_1/CeO_4-t-p surfaces.

The existence of a localized electron at the surface CeO_4 unit was clarified by the typical charge distribution of a $4f$ electron, and the Bader charge analysis also showed that the Ce of this CeO_4 unit was reduced to Ce^{3+}. In addition, the Bader charge of the anchored single Cu was calculated to be 0.488 $|e|$, which is close to that of Cu in the bulk Cu_2O (0.539 $|e|$). These results indicated that the oxidation state of Cu is +1 and the lost electron of Cu transfers to one surface Ce.

3.2 Formation of oxygen vacancies on Cu_1/CeO_4-t-p surfaces

The superior oxygen storage capacity of CeO_2 is closely related to the formation of oxygen vacancies and we systematically calculated the vacancy formation energies (E_{vac}) of the lattice oxygen with different coordination numbers, and the results are showed in Figure 3.

On the Cu_1/CeO_4-t-p surface, the O_{2c} (2-fold coordination O) gave very small E_{vac} of 1.04 eV, while the O_{3c} (3-fold coordination O) gave larger E_{vac} of 1.85 eV. Compared with the E_{vac} of O_{2c} and O_{3c} on CeO_4-t surface (1.27 and 2.06 eV, respectively) and