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
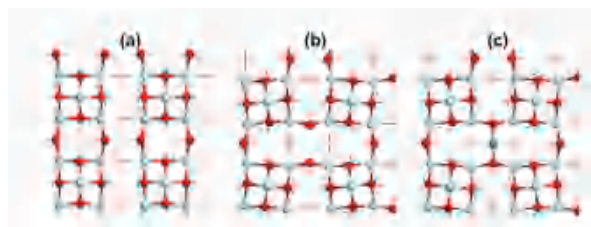
Figure 1. Top view of (a) CeO$_4$-t (b) CeO$_4$-t-p (c) Cu$_1$/CeO$_4$-t-p CeO$_2$(100) surfaces. Red: O; light grey: Ce; orange: Cu; blue dashed circle: CeO$_4$ unit.

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.

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.
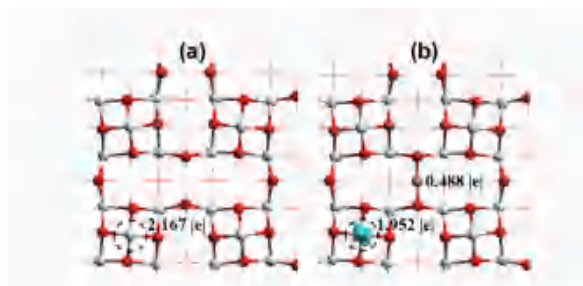
The adsorption energy (E_{ads}) of adsorbates (NH$_3$ and O$_2$) on the reconstructed CeO$_2$(100) surfaces was defined as:

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

where $E_{mol/slab}$ 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:

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

where E_{slab} is the calculated energy of the clean surface slab, $E_{slab/vac}$ 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$_2$O (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