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Interfacial synergistic effect of the Cu monomer or CuO dimer modified $CeO_2(1\,1\,1)$ catalyst for CO oxidation

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ABSTRACT

The synergistic effect at the interface of the bilayer Cu monomer or CuO dimer modified $CeO_2(1\,1\,1)$ catalyst for CO oxidation is investigated with density functional theory calculation. Important factors related to the synergistic effect such as interfacial ionicity, electron transfer, and charge partitioning of the Cu modifications are analyzed in detail for better understanding and control of this catalyst system.

1. Introduction

In light of the current demand for environmentally benign technologies, fuel cell systems are of interest to researchers and consumers as they offer an efficient means of power production. H_2-fuel Polymer Electrolyte Membrane Fuel Cells (PEMFC) are currently under investigation for stationary and mobile applications due to the safety, lower cost and wider availability of bio-methanol [1–4]. These devices rely on the auto-thermal reforming process of hydrocarbons or alcohol to produce gaseous H_2 fuel. The H_2-enriched gas streams from this process are usually contaminated with CO at ~500 ppm which, if fed directly to a PEMFC, can rapidly poison the Pt anodes of the fuel cell. Because of the intolerance of these devices to CO, purification methods such as the Preferential Oxidation of CO (PROX) or Water Gas Shift (WGS) reactions are required to reduce the CO concentration to less than 10 ppm and minimize the deactivation of the PEMFC [5–8]. Research has shown that yttria-stabilized zirconia, γ-alumina or ceria supported Cu nanoparticle catalysts can achieve competitive levels of activity, stability and selectivity compared to Pt and Pd catalysts [9–11]. Furthermore, Cu catalysts have the advantage of being a base metal that is widely available at low cost compared to precious metal catalysts such as Au [12]. However, to date, the metal/support interaction, active sites, and reaction mechanisms responsible for PROX activity over Cu/CeO_2 catalysts are not well established in relation to its possible contribution towards the synergistic effect.

Metallic Cu and its oxides are thought to promote the CO adsorption on CeO_2 *via* electron transfer between copper oxides and CeO_2 support in which CeO_2 can stabilize the dispersed Cu or CuO species and aid CO activation at the interface [5]. Moreover, recent experimental and theoretical studies also point out that CO oxidation capability is related to the oxidation state of highly ionic CuO dimer and the electron behavior for the synergistic effect oxygen-bridged CuO dimers modified on the CeO_2 surface [13,14]. However, the mechanisms for the enhanced catalytic activity are unclear as it is difficult to probe intrinsic interfaces and surface reactions experimentally. In this regard, computational methods such as density functional theory (DFT) can provide a new electronic understanding of the interface of the Cu modified CeO_2 system. DFT is a quantum mechanical method that can monitor the changes in electronic and physical structure of catalyst systems. For instance, the DFT approach has been applied to similar systems such as the pure Cu surface [15], Cu_2O [15,16] and Cu doped CeO_2 [17]. Yet, its application towards Cu monomer or CuO dimer modified $CeO_2(1\,1\,1)$ system to identify the critical details of the synergistic effect between these two dissimilar materials towards CO adsorption is absent in the literature. In fact, recent studies of metal dopants on metal-oxide supports do not address how it is possible that electronic or structural effects at the catalyst interfacial boundary can contribute to the synergistic effect [18–22].

In this work, we aim to identify the key fundamental details regarding the synergistic effect at the interface formed between the Cu monomer or oxygen-bridged CuO dimer and $CeO_2(1\,1\,1)$

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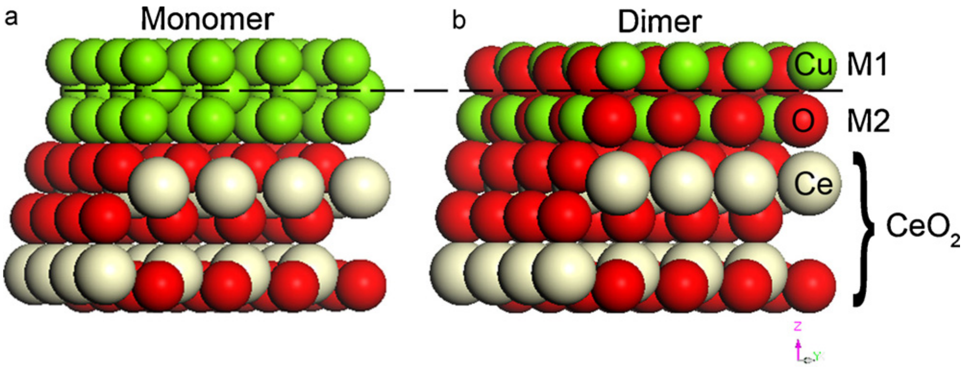

Fig. 1. Geometry optimized (2 × 2) CeO_2(1 1 1) catalyst modified with: (a) Cu monomer and (b) CuO dimer, where green, red, white colours represent copper, oxygen and cerium respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

(Fig. 1). In particular, we will address the following questions: (i) How does Cu monomer or CuO dimer modification affect CO adsorption? (ii) How do these modifications affect the electron spin/charge at the interface? (iii) How does the electron transport between the Cu monomer or CuO dimer modification and CeO_2 surface contribute to the synergistic effect? These questions will be addressed based on the DFT calculated adsorption energies, electron spin/charge, total density of states (TDOS), electron density difference, and physical structure. These questions are obviously related to the mechanistic details underlying how the synergistic effect promotes CO oxidation, which is helpful to the optimum design and control of catalyst structure and activity for this system.

2. Computational method

Our DFT calculations are performed by CASTEP (CAmbridge Serial Total Energy Package) with the GGA (generalized gradient approximation) scheme. PBE (Perdew, Burke and Ernzerhof) [23] exchange correlation functional is used for all spin unrestricted total energy calculations. Spin polarized calculations are performed due to the net *f* spin states on Ce. A plane wave kinetic energy cutoff of 370 eV is used with an applied thermal broadening of 0.1 eV. The Brillouin-zone integration for the unit cell is performed through a 6 × 6 × 1 Monkhorst-pack grid with 18 irreducible *k*-points. The upper and lower portions of the Cu monomer or CuO dimer in this modified CeO_2(1 1 1) system are identified as M1 and M2 as shown in Fig. 1a and b. Our model incorporates 3D periodic boundary conditions with a 15 Å vacuum gap. CeO_2(1 1 1) is selected to be the crystallographic plane because it is the most stable face [24]. To test the validity of the simulation parameters, the calculated lattice parameter for CeO_2 is $a = 5.46$ Å which is comparable with the experimental value of $a = 5.41$ Å [25]. The calculated energy gaps for O2p–Ce4*f* and O2p–Ce5d are 2.1 and 5.3 eV respectively which are comparable to the corresponding ab initio calculated values of 2.3 and 5.1 eV reported in the literature [26]. These comparisons show that the simulation parameters are valid and the starting model is acceptable for further modification with the Cu bilayer and CO adsorption. It is reported that DFT calculation using the GGA technique has a difficulty in describing the electronic behavior of narrow *f*-band materials such as ceria. Despite this shortcoming, findings presented here are unaffected as the DFT+U is only vital for the calculation of reduced CeO_2 surfaces with oxygen vacancies and for the quantitative analysis of bandgaps [27].

3. Results and discussion

3.1. Energy analysis of CO adsorption on the Cu modified CeO_2(1 1 1) catalyst

To study the adsorption strength of CO on Cu monomer and CuO dimer modified CeO_2(1 1 1), the CO adsorption energies E_{COads} are calculated according to: $E_{\mathrm{COads}} = (E_{\mathrm{Bulk}} + E_{\mathrm{CO}}) - E_{\mathrm{Total}}$, where E_{Bulk} is the energy of the isolated Cu modified CeO_2(1 1 1), E_{CO} is the energy of the isolated CO, and E_{Total} is the total energy of CO and Cu modified CeO_2(1 1 1) combined [25]. The calculated adsorption energies for CO on the clean, Cu monomer and CuO dimer modified CeO_2(1 1 1) surface are 0.02, 1.47 and 0.87 eV respectively. Such result shows a 41% decrease of CO stabilization energy from Cu monomer to CuO dimer modified CeO_2(1 1 1) surface, *i.e.*, CO is more stable on the Cu monomer modified CeO_2(1 1 1) surface. In addition, the adsorption of CO on clean CeO_2 surface is much weaker than those on Cu modified CeO_2 surfaces.

3.2. Structural analysis of the Cu modified CeO_2(1 1 1) catalyst after CO adsorption

Our structural analysis shows that Cu monomer and CuO dimer modifications lead to similar Cu–O distances but slightly different Ce–O distances at the interface of the Cu modification and CeO_2. The atomic distances between Cu and O atoms in the Cu monomer and CuO dimer modified CeO_2 catalyst are 1.911 and 1.909 Å respectively. The average Ce–O bond lengths are 2.372 and 2.426 Å for the Cu monomer and CuO dimer modified CeO_2(1 1 1) respectively. The larger Ce–O bond in the latter can cause the Cu^{2+} ions to donate electron density to both Ce and O atoms and increase the ionic characteristic of the interface. In addition, the complex orbital interactions due to contracted Ce4*f* orbitals in CeO_2 could cause the distortion of Ce–O and Cu–O bonds. It is known that bonds formed with Ce are short and stable due to the ineffectiveness of shielding nuclear charge by the 4*f* orbitals. The contraction of 4*f* orbitals exposes 5s/p orbitals and decreases its atomic radius, which stabilizes its surrounding environment through bond length shortening. Upon Cu modification, the interaction with the Cu3d orbital disrupts the screening of nuclear charge in Ce atom, which leads to Ce–O bond expansion at the interface. In addition, when CO molecule is adsorbed on the surfaces, the average bond lengths for C–O and C–Cu are 1.15 and 1.84 Å respectively which are consistent with the corresponding literature values of 1.15 and 1.9 Å for covalent CO adsorption on Cu oxides [28]. This result suggests that the interfacial boundary induces a minor structural effect on the M1 adlayer that is involved with covalent CO bonding. From