

CO oxidation mechanism on Pd-doped CeO₂ catalysts: A DFT+U study

Bing Liu¹, Zhen Zhao^{1*}, Jian Liu¹, Xue-Qing Gong², Aijun Duan¹, Guiyuan Jiang¹

¹State Key Laboratory of Heavy Oil, College of Science, China University of Petroleum-Beijing, Beijing 102249, P. R. China

²State Key Laboratory of Chemical Engineering, Key Laboratory for Advanced Materials, Research Institute of Industrial Catalysis and Centre for Computational Chemistry, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, P.R. China

*corresponding author: zhenzhao@cup.edu.cn

Introduction

Ceria (CeO₂), which possesses cubic fluorite type of structure, has attracted intense attention in recent decades due to its excellent performance for the use in energy and environmental fields. The most important application of ceria is for automotive emission control as a major component of three-way catalysts (TWC), due to its remarkable redox properties and oxygen storage capacity (OSC). It has been suggested that the dopant atom weakens the surrounding oxygen bond of the doped oxide, which acts as a better oxidant, and thus facilitates CO oxidation. Substitution of noble metal ions like Pd²⁺ and Pt²⁺ into CeO₂ is also reported to further enhance the OSC and catalytic activities of the Ce-based catalysts. To further illustrate the role of Pd species in the catalyst and CO oxidation mechanism, density functional theory (DFT) calculations have also performed.

Materials and Methods

All the DFT calculations were performed using the Vienna ab-initio simulation package (VASP) with the employment of a plane wave basis set. To accurately treat highly localized Ce 4f-orbitals, we conducted spin-polarized DFT+U calculations with a value of U=5.0 eV applied to the Ce 4f state. The projector-augmented wave (PAW) method was used to represent the core-valence interaction. The plane wave energy cutoff was 400 eV. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was used in the calculations. Gaussian smearing method with the width of 0.05 eV was used. The Brillouin zone was sampled at the Γ -point. The convergence criteria for the energy and force were set to 10⁻⁵ eV and 0.02 eV/Å. The transition state (TS) of the surface reaction was searched using the constrained optimization scheme, which has been used in many previous DFT studies. The TS was verified using vibrational frequency analysis (only one negative mode is present at the TS). The energy barrier (E_{bar}) was determined as the energy difference between the corresponding transition- and initial-states.

Results and Discussion

1. CO adsorption

It is widely believed that the mechanism of CO oxidation at ceria or doped ceria surfaces follows the so-called Mars-van Krevelen-type catalytic cycle, in which CO reacts with lattice oxygen of ceria to form CO₂ and leave an oxygen vacancy, and then the gas-phase oxygen replenishes the vacancy to complete the reaction cycle. However, it needs to be mentioned that, within the Mars-van Krevelen type catalytic cycle, the elementary steps of CO oxidation by lattice oxygen may still follow the Langmuir-Hinshelwood or Eley-Rideal mechanism. In the Langmuir-Hinshelwood mechanism, the CO molecule adsorbs firstly on the ceria surface before undergoing the oxidation, whereas in the Eley-Rideal mechanism, the CO

molecule directly attacks the surface oxygen from the gas phase. Gong *et al.* [1] proposed that Eley-Rideal mechanism is feasible for CO oxidation on pure CeO₂. Fabris *et al.* [2] studied the CO oxidation on Au-doped CeO₂ and proposed that this process also follows Eley-Rideal mechanism.

To illuminate the mechanism of CO oxidation studied in this work, we first calculated the adsorption of CO at the O, Ce and Pd sites on the surface of Pd-CeO₂(111). All the calculated adsorption energies are lower than 0.15 eV, close to that (0.18 eV) for the CO physisorption on the pure CeO₂(111) surface. Thus, it indicates that the reaction of CO at this surface is unlikely to occur via the Langmuir-Hinshelwood mechanism, and direct CO reaction with a surface O appears to be the only feasible pathway.

2. Catalytic cycle for CO oxidation and catalyst regeneration

Following the Eley-Rideal (ER) mechanism, the complete reaction pathway for CO oxidation and catalyst regeneration was systematically calculated and it is illustrated in Fig. 1. As one can see, the whole pathway consists of three steps: (A) reaction of the first CO molecule with one lattice oxygen on the stoichiometric Pd-CeO₂(111) surface, leading to the formation one desorbed CO₂ and an O vacancy (Fig. 1A); (B) adsorption of molecular O₂ at the O vacancy, giving rise to the adsorbed O₂ species on the surface (Fig. 1B); and (C) reaction of another CO molecule with this adsorbed O₂ species, forming CO₂ and regenerating the stoichiometric Pd-CeO₂(111) surface (Fig. 1C).

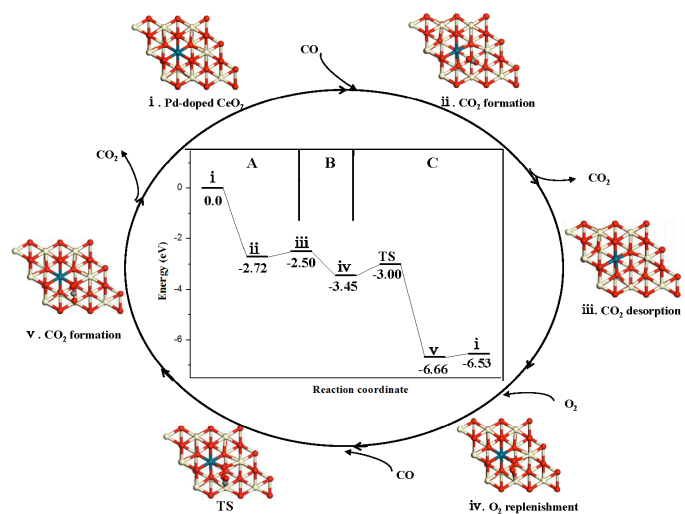


Figure 1. The reaction energy profiles with intermediate structures for CO oxidation process.

The result of Bader charge analysis for the catalytic cycle is presented in Fig. 2. When the oxygen vacancy is formed after the first step, Pd is reduced from +1.36 to +0.92 (Fig. 2b), while the charges on cerium are nearly unchanged, suggesting that no Ce⁴⁺ is reduced to Ce³⁺. This is different from the case of pure CeO₂ that the electrons left by missing O always

localize at Ce atoms, reducing them from Ce^{4+} to Ce^{3+} . After adsorption at the O vacancy, the adsorbed O_2 was determined to be spin unpolarized, which indicates the formation of peroxide (O_2^{2-}) species. Meanwhile, Pd is reoxidized from +0.92 to +1.36. These results then clearly show that the presence of a Pd dopant makes itself, instead of Ce, an electron acceptor/donor during the oxygen vacancy formation and O_2 replenishing.

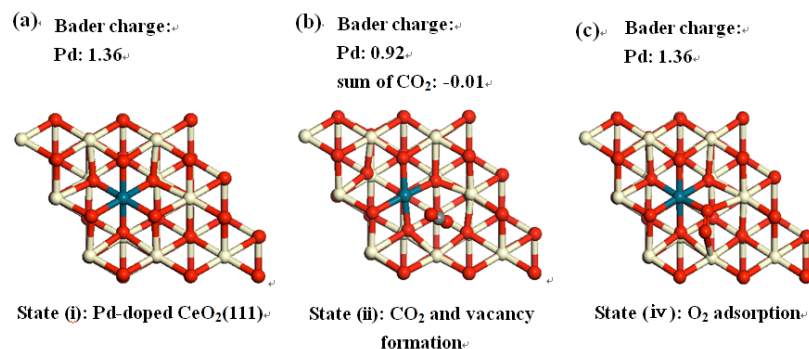


Figure 2. The Bader charge analysis in the reaction pathway.

3. Origin of the high activity of Pd-doped Ce-based catalyst

Based on the above analysis, the origin of the high activity of Pd-doped ceria lies in the following facts: (1) The geometric distortion and electron deficit effects induced by Pd dopant lead to the promotion of O vacancy formation regardless of whether it occurs near the Pd dopant site or far away from it, and thus enhance the activity of surface lattice oxygen atoms. (2) Pd doped into the ceria lattice can sustain a full catalytic cycle for CO oxidation and catalyst regeneration, which is highly exothermic (more than 6 eV) and with a low energy barrier. Thus, the Pd doped catalysts have well-balanced thermodynamics and kinetics for CO oxidation. (3) The presence of a Pd dopant induces the Pd instead of Ce acting as an electrons acceptor/donor during the oxygen vacancy formation and O_2 replenishing. Consequently, Pd dopant alters the reaction product and pathway to prevent the formation of stable carbonate species on the surface of catalysts and reduces the effect of carboxylate poisoning and enhances the activity toward CO_2 formation.

Significance

High-performance doped oxide catalyst should keep a good balance between the oxygen vacancy formation and the replenishment by O_2 molecule adsorption at the vacancy site to maintain the catalytic redox cycle. On one hand, it must weaken the binding of surface lattice oxygen with the surface to facilitate its reaction with the gas-phase reactant. On the other hand, this surface distortion must not be so pronounced that the reduced surface relaxes too significantly to be restored by adsorption of O_2 molecules. An over-facilitated oxygen vacancy formation process may result in difficulty in the oxygen species healing process, decreasing the efficiency of the catalyst.

References

1. Chen, F.; Liu, D.; Zhang, J.; Hu, P.; Gong, X.; Lu, G. *Phys. Chem. Chem. Phys.* **2012**, *14*, 16573
2. Camellone, M. F.; Fabris, S. *J. Am. Chem. Soc.* **2009**, *131*, 10473.
3. Shapovalov, V.; Metiu, H. *J. Catal.* **2007**, *245*, 205.
4. Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169.
5. Liu, Z. P.; Hu, P. *J. Am. Chem. Soc.* **2003**, *125*, 1958.