

Adsorption of CO on M-doped(M = Ca, Ce and Pr) Monoclinic Zirconia(111) Surface: A First-Principles Study

Hongchun Luo¹, Chunhua Zeng^{1,2,*}, Dong Tian², Hua Wang², and Yunchang Fu¹

¹ Faculty of Science, Kunming University of Science and Technology,

² Center of Metallurgical Energy Conservation and Emission Reduction

Abstract. Structures and catalytic activities of CO molecule on monoclinic $ZrO_2(111)$ (M = Ce, Ca and Pr) surface has been studied by using density functional theory (DFT). Calculations indicate that on the stoichiometric $ZrO_2(111)$ surface, the preferential adsorption structure is the Zr-CO configuration. The adsorption energy of the Zr-CO configuration is larger for the M-doped $ZrO_2(111)$ (M = Ce, Ca and Pr) surface than for the stoichiometric one. The adsorption energy of the Zr-CO configuration is -0.73eV for the Pr-doped surface, -0.67eV for the Ce-doped surface, -0.41eV for the Ca-doped surface, -0.35eV for the stoichiometric $ZrO_2(111)$ surface. Pr-doped enhances electron which transfer from the monoclinic $ZrO_2(111)$ Surface to the antibonding states of CO, giving rise to strong ionic bonding between the adsorbed CO and Zr cation. Carbon monoxide adsorbed on Pr-doped monoclinic $ZrO_2(111)$ surface is the most stable. The investigation on catalytic behavior of M-doped monoclinic $ZrO_2(111)$ surface toward CO oxidation reveals that Pr doping largely enhanced catalytic activity.

1 Introduction

Adsorption and activation of carbon monoxide on the surface of transition metal is important for many catalytic processes involving carbon monoxide[1], such as carbon monoxide methane, water gas shift reaction to prepare hydrogen[2], synthetic methanol and other important chemical processes. One of the most simple catalytic reactions is the oxidation of carbon monoxide in the vehicle exhaust emissions control, and it has a wide range of applications. With the development of carbon monoxide sensor, some of the metal oxide have been found to have good gas sensing properties for carbon monoxide, such as Ca-doped $LaFeO_3$, ZrO_2 and $LaFeO_3$ [3]. Adsorption of CO on the zirconia is very important, because it involves a lot of middle process of catalytic reaction. And it is found that the adsorption capacity of carbon monoxide on pure zirconia is very poor, doping is an effective way to improve the adsorption capacity of carbon monoxide on the zirconia[4]. There are theoretical researchs show that the adsorption capacity of carbon monoxide improved by using Ca doping $LaFeO_3$ [5]. Experimental studies show that Ce doping zirconia can also increase the adsorption capacity of carbon monoxide on the zirconia[6]. Many experiments studies have been found that doping can improve the adsorption and catalytic activity of carbon monoxide, such as Cu doping CeO_2 [7], Pt doping CeO_2 [8], Rh doping CeO_2 [9] and Ti doping CeO_2 [10], Li doping MgO [11].

In this article, we studied the adsorption of carbon monoxide molecules on the monoclinic $ZrO_2(111)$ surface by using density functional theory. We mainly considered the three positions, oxygen top, Zirconium top, Zirconium Bridge, and found that the most stable adsorption site is zirconium top. We also studied the structural changes of doped zirconia(111) surface, the adsorption of carbon monoxide on several metal ions(Ce, Ca and Pr) doping can change. We modify zirconia(111) surface by doping metal ions, trying to raise adsorption capacity of carbon on monoxide zirconia(111) surface.

2 Calculation methods

All of the calculations were performed with the density functional theory (DFT) which provided by the pro-program with SIESTA. It were further checked by using the pseudo potential plane-wave CASTEP code. Perdew-Burke-Ernzerh of (PBE) generalized gradient approach (GGA) has been used to describe exchange-correlation potential[12]. Cut off energy of 300eV was used in all our calculations. A Gaussian smearing of 0.01eV was used for monoclinic $ZrO_2(111)$ surface. The Monkhorst-Pack k-point mesh for the Brillouin zone sampling with a $3 \times 3 \times 1$ mesh was used in all our calculations. The energy of convergence criterion was chosen as 1.0×10^{-6} eV/atom. The convergence criterion of optimal geometry for the energy, force, and displacement were 2.0×10^{-5} eV, 5.0×10^{-2} eV and 2.0×10^{-3} Å. Charge transfer was calculated by Milliken Population Analysis (MPA)[13]. We used three monoclinic ZrO_2 layers in the model, the vacuum layer is 10Å to avoid the atomic interaction between layers. In the calculation process, the bottom layer is fixed, and other layers allowed to relax. The optimized structure of monoclinic ZrO_2 is shown in Fig.1(a). The unit cell is optimized to be close to the experimental value of band gap, the band gap we got through calculation is 4.021eV as in Fig.2, this is in good agreement with

the experimental results. The experimental value of band gap is measured to be 4.2 eV [14], and 4.5 eV [15, 16]. We obtained the lattice constant that is ($a=5.1454\text{\AA}$, $b=5.2075\text{\AA}$, $c=5.3107\text{\AA}$ and $\beta=90.23^\circ$) by theoretical calculation. This is in accordance with the experimental lattice parameters ($a=5.151\text{\AA}$, $b=5.212\text{\AA}$, $c=5.317\text{\AA}$ and $\beta=90.23^\circ$) [17]. It can be seen that our theoretical calculations are in good agreement with the experiments studies. The next calculation is based on the optimization structure.

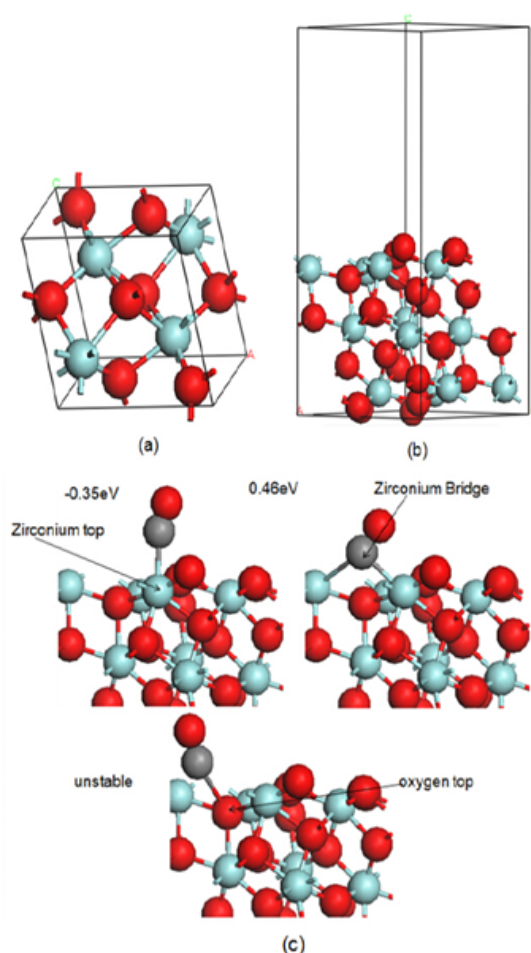


Fig.1 Optimized crystal structure: (a) pure monoclinic ZrO_2 and (b) monoclinic $ZrO_2(111)$ surface. Red ball indicates the O atom, and the silver ball represent Zr atom. (c) Is the optimized of carbon monoxide molecules adsorbed on the pure monoclinic $ZrO_2(111)$ surface Zirconium top, Zirconium Bridge and oxygen top, respectively. The most stable adsorption site is zirconium top.

The adsorption energy can be expressed as the following equation:

$$E_{ads} = E_{(slab+CO)} - (E_{slab} + E_{CO}).$$

Where $E_{(slab+CO)}$ is the total energy of the adsorbate-substrate system, E_{slab} is the energy of clean monoclinic $ZrO_2(111)$ surface, E_{CO} is the energy of free CO.

3 Results and Discussions

The optimized structure of monoclinic ZrO_2 is shown in Fig.1(a), Fig.1(b) is the optimized crystal structure for monoclinic $ZrO_2(111)$ surface. Fig.3 is the optimized adsorption structure that carbon monoxide adsorbed on the monoclinic $ZrO_2(111)$ surface. The model contains 36 atoms, there are 12 Zr atoms and 24 O atoms. In this paper, we studied the effect of doping on the oxidation of

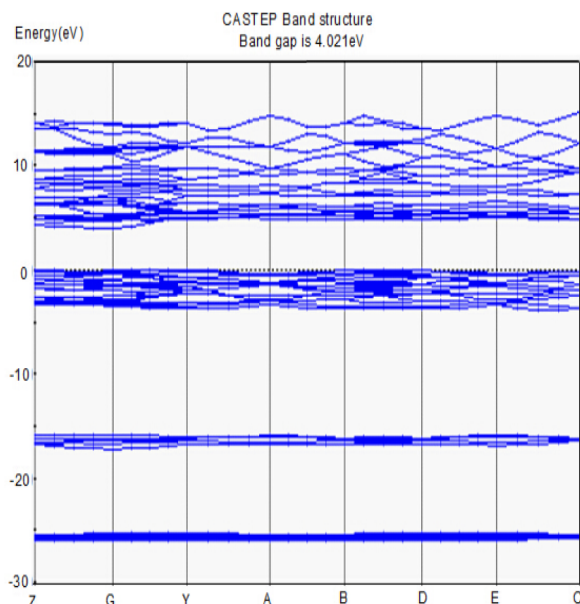


Fig.2 The band structure of monoclinic zirconia. The band gap we got through the calculation is 4.021eV, the Fermi level is the position of zero energy.

carbon monoxide by replace the second layers atomic. We first calculate the carbon monoxide molecules adsorbed on the monoclinic $ZrO_2(111)$ surface, we mainly considered three position: oxygen top, zirconium top, zirconium bridge, it showed in fig.1(c). The adsorption energy are -0.35 eV and is 0.46 eV for Zr top site and Zr bridge site, respectively. When we put the carbon monoxide molecules in oxygen top, we found that the carbon monoxide molecules away from the oxygen top and ran to the place that close to the zirconium top. It indicates that the oxygen top is very unstable, the most stable adsorption site is zirconium top. In the following, we only considered that the carbon monoxide molecules adsorbed on zirconia top site. The adsorption energy are -0.35eV, -0.41eV, -0.67eV and -0.73eV for pure monoclinic $ZrO_2(111)$ surface, Ca-doped $ZrO_2(111)$ surface, Ce-doped $ZrO_2(111)$ surface and Pr-doped $ZrO_2(111)$ surface, respectively. We found that the Ca-doping is little effect on the adsorption energy, on the contrary, doping noble metal (Ce, Pr) lead to the the adsorption energy increase.

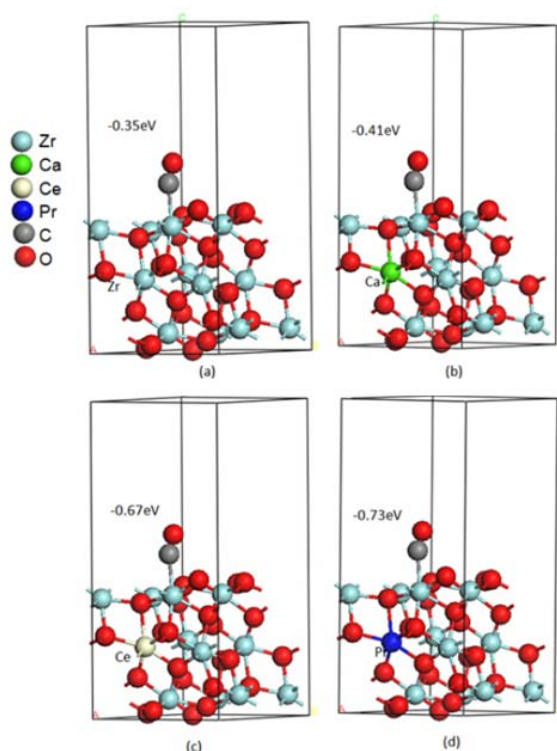


Fig.3 The optimized structure: (a) carbon monoxide adsorbed on the surface of monoclinic $ZrO_2(111)$, (b), (c) and (d) are the optimized structure of carbon monoxide on M-doped $ZrO_2(111)$ (M = Ca, Ce, and Pr), respectively.

Table 1. The obtained results of adsorption energy E_{ads} and Mulliken Charges Q_{co} (e) for carbon monoxide adsorbed undoped and doped monoclinic $ZrO_2(111)$ surface, Ca-doped, Ce-doped and Pr-doped.

	E_{ads} (eV)	Q_{co} (e)
Pure monoclinic ZrO_2 surface (Zr-CO)	-0.35	+0.02
Ca doping surface (Zr-CO)	-0.41	+0.04
Ce doping surface (Zr-CO)	-0.67	+0.03
Pr doping surface (Zr-CO)	-0.73	+0.03

In order to understand the microstructure, we analyzed the density of states (DOS). We found that the density of states of carbon monoxide move to the left after adsorption on pure $ZrO_2(111)$ surface in Fig.4. A similar phenomenon has been found in the study of carbon monoxide adsorbed on $LaFeO_3(010)$ surface [3]. The 4σ , 1π and 5σ orbitals of carbon monoxide all decreased after CO adsorbed on the pure $ZrO_2(111)$ surface. The energy of each orbital of carbon monoxide are reduced, and it becomes more stable. This is quite consistent with the density of states of carbon monoxide on Pd-doped $-Fe_2O_3(001)$ surface. The biggest change we found was the 5σ orbitals of carbon monoxide. The 5σ orbitals reduce a lot, and the width increase is very obvious. This means that outer electrons of carbon monoxide have a strong interaction with the zirconia(111) surface, and carbon monoxide is activated

on the monoclinic $ZrO_2(111)$ surface. Through the Fig.4 and Fig.5, we found that for the most stable adsorption of carbon monoxide the density of states move to the left is more obvious. It can be seen that the density of states of carbon monoxide the outermost electron orbits on Ca-doped zirconia(111) surface is the highest, and farthest from Fermi level, on Pr-doped zirconia(111) surface is the lowest, closest Fermi level in fig.4. By comparing fig.4 and fig.5, we found the trend is in agreement with the adsorption energy in Table 1, indicates that the density of states shifts toward to lower energy level.

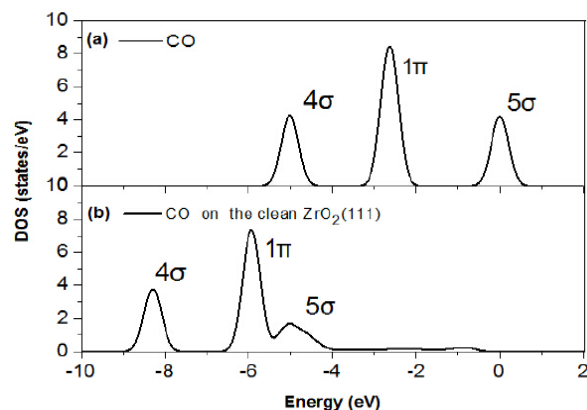


Fig.4 Total density of states (TDOS) of (a) the free CO, and (b) CO adsorbed on undoped monoclinic $ZrO_2(111)$ surface, the position of zero energy is Fermi level.

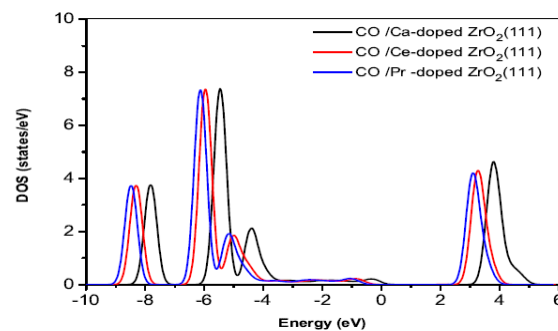


Fig.5 Density of states of CO adsorbed on doped monoclinic $ZrO_2(111)$ surface, respectively, black line represent the Ca-doped $ZrO_2(111)$ surface, red line represent the Ce-doped and blue line represent the Ca-doped $ZrO_2(111)$ surface.

In order to have the further insight into the bonding mechanism of the Zr-CO configuration, we analyse the density of the state (DOS) of the adsorbed CO. In fig.6(a), it shows the total density of states of Zr site at three situations. CO is adsorbed with the Zr-CO configuration and CO adsorption for pure and Pr-doped monoclinic $ZrO_2(111)$ surface, respectively. The density of states of Zr-4d, the band of Zr on Pr-doped monoclinic $ZrO_2(111)$ surface shift toward lower energy comparing with un-doped monoclinic $ZrO_2(111)$ surface in fig.6(b). The Zr-4d orbitals is the mainly contribution to density of states of the Zr. Fig.7(a) shows the density of states of Zr-4p (a) and Zr-5s (b), the band of Zr-4p on Pr-doped monoclinic $Zr(111)$ surface also shift toward lower energy. This is the reason that the DOS of CO and Zr-4d, Zr-4p

have a strong hybridization between them. But the rule of Zr-5s is very poor, it indicates that adsorption and doping have little effect on the inner electron layer.

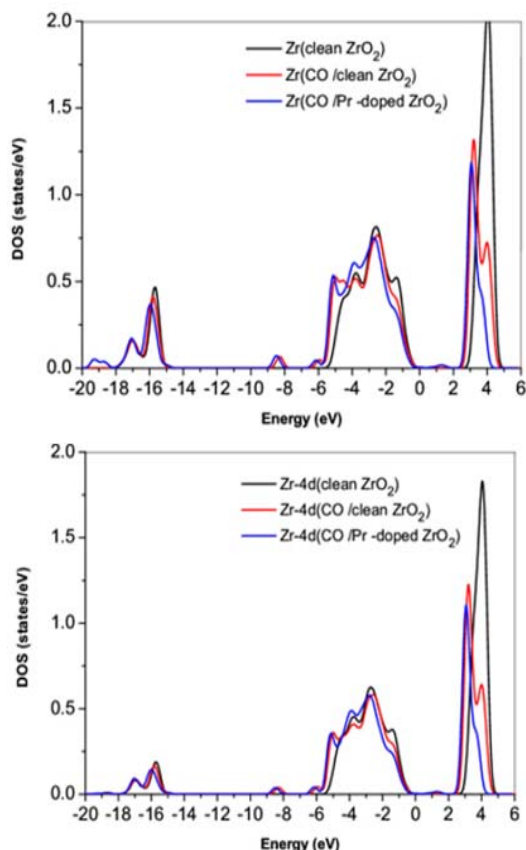


Fig.6 Total and partial density of states of Zr site on which CO is adsorbed with the Zr-CO configuration before and after CO adsorption for the pure and Pr-doped monoclinic $ZrO_2(111)$.

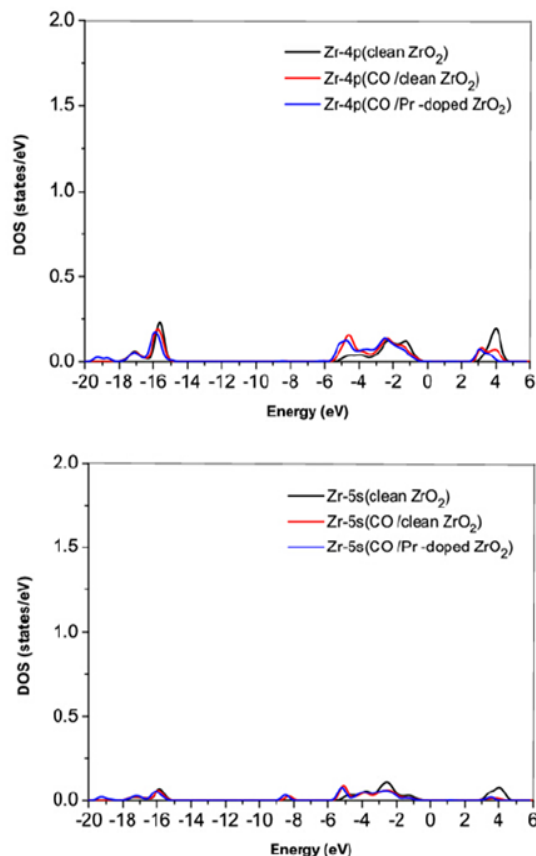


Fig.7 Partial density of states of Zr site on which CO is adsorbed with the Zr-CO configuration before and after CO adsorption for the pure and Pr-doped monoclinic $ZrO_2(111)$ surface.

4 Conclusion

In this paper, the detailed geometrical and orbital-decomposed electronic structures of CO adsorbed on un-doped and doped monoclinic $ZrO_2(111)$ surface have been investigated by using the first-principle. The band gap we got through the calculation is 4.021eV as in Fig.2, which is in good agreement with the experimental results. The adsorption energy of CO on pure monoclinic $ZrO_2(111)$ surface is -0.35eV, -0.41eV for Ca-doped $ZrO_2(111)$ surface, -0.67eV for the Ce-doped $ZrO_2(111)$ surface and -0.73eV for Pr-doped $ZrO_2(111)$ surface. The most stable adsorption of carbon monoxide is on Pr-doped $ZrO_2(111)$ surface. By comparing the density of states (DOS) of the free CO with CO adsorbed on un-doped monoclinic $ZrO_2(111)$ surface. We found that the density of states shifts toward lower energy level after adsorption. A similar phenomenon has been found in the study of carbon monoxide adsorbed on $LaFeO_3(010)$ surface[3]. By analysing the density of states (DOS) of Zr site at three situation. The band of Zr on Pr-doped monoclinic $ZrO_2(111)$ surface shift toward lower energy compare to un-doped monoclinic $ZrO_2(111)$ surface. Comparing to the DOS of CO adsorbed on doped monoclinic $ZrO_2(111)$ surface, The energy of carbon monoxide on Pr-doped monoclinic $ZrO_2(111)$ surface is the lowest. This is in

good agreement with the results that carbon monoxide adsorbed on Pr-doped monoclinic ZrO₂(111) surface is the most stable. The investigation on catalytic behavior of M-doped monoclinic ZrO₂(111) surface toward CO oxidation reveals that Pr doping largely enhanced catalytic activity.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant No. 11305079), and (Grant No. 11104120), and the introduction of talent capital group fund project of Kunming University of Science and Technology (under KKZ3201407030).

References

- [1] Chen, M. S. Goodman, D. W. Science. **306**, 252(2004).
- [2] D. Andreeva, V. Idakiev, T. Tabakova, L. Ilieva, P. Falaras, A. Bourlinos, A. Travlos. Catal.Today. **72**, 51(2002) .
- [3] Lihui Sun, Jifan Hu, Hongwei Qin, Ming Zhao, and Kai Fan, J.Phys.Chem.C. **115**, 5593(2011).
- [4] Eva-Maria Kock, Michaela Kogler, Thomas Bielz, Bernhard Klotzer, and Simon Penner. J. Phys. Chem. C. **117**, 17666(2013).
- [5] Kim, D. Kim, K. Bull. Korean Chem. **15**, 616(1994).
- [6] Gopalakrishnan, M. Faga, I. Miletto, S. Coluccia, G. Caputo, S. et al. Applied Catalysis B. **234**, 138(2013).
- [7] Bera, P. Priolkar, K. R. Sarode, P. R. Hegde, M. S. Emura, S. Kumashiro, R. Lalla, N. P. Chem. Mater. **14**, 3591(2002).
- [8] Baidya, T. Gayen, A. Hegde, M. S. Ravishankar, N. Dupont, L. J. Phys. Chem. B **110**, 5262(2006).
- [9] Bera, P. Gayen, A. Hegde, M. S. Lalla, N. P. Spadaro, L. Frusteri, F. Arena, F. J. Phys. Chem. B. **107**, 6122(2003).
- [10] Gayen, A. Priolkar, K. R. Sarode, P. R. Jayaram, V. et al. Chem. Mater. **248**, 2317(2004).
- [11] Zamora, M. Lopez, T. Gomez, R. Asomoza, M. Melendez, R. Catal. Today. **289**, 107(2005).
- [12] Perdew, J. P. Chevary, J. A. Vosko, S. H. Jackson, K. A. et al. Phys. Rev. B **46**, 6671(1992).
- [13] Mulliken, R. S. J. Chem. Phys. **23**, 1833(1955).
- [14] D. W. McComb, Phys. Rev. B. **54**, 7094(1996).
- [15] E. Elizalde, J. M. Sanz, F. Yubero, L. Galan, Surf. Interface Anal. **16**, 213(1990).
- [16] J. Frandon, B. Brouseau, F. Pradal, Phys. Status Solidi B. **98**, 379(1980).
- [17] R. H. French, S. J. Glass, F. S. Ohuchi, Y. N. Xu, W. Y. Ching, Phys. Rev. B **49**, 5133(1994).