A Comparative Study of Monoclinic ZrO_2(111) and γ-Al_2O_3(100) Supported Ce_2O_4

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Introduction

Metal oxides are used as either active components or support in industrial catalysis. The interplay between the active oxides and support controls the activity and selectivity of the catalyst toward a reaction. Due to the complexity of the supported metal oxide catalysts and difficulty in manipulating and characterizing the oxide overlayers, our understanding of such systems at atomic level is limited.

In this study, first-principles density functional theory (DFT) calculations were used to study Ce_2O_4 supported on ZrO_2(111) and γ-Al_2O_3(100). ZrO_2 and γ-Al_2O_3 represent reducible and irreducible oxides, respectively. CO and CO_2 were selected as probing molecules to measure the acidity/basicity and redox properties of the support and supported Ce_2O_4. We anticipate that such a comparative study will provide some insights into the effect of supports on the catalytic activity of Ce_2O_4.

Materials and Methods

All calculations were carried out using the VASP code [1], a DFT program package with plane wave as basis set. The interaction between ions and electrons was described using the projector augmented wave method.[2] The nonlocal exchange-correlation energy was evaluated by the PBE functional [3]. The on-site Coulomb interactions of Ce atoms were corrected using the DFT + U method with U = 5.0. A cutoff energy of 400 eV was applied to the plane wave basis set. Spin-polarization was included in all calculations. The atomic structures were considered converged when forces on the unconstrained atoms were less than 0.05 eV/Å.

The surface of ZrO_2 used in this study was built on the basis of the monoclinic model. The lattice parameters from our optimization (a = 5.160 Å, b = 5.236 Å and c = 5.319 Å, α = β = 90º and γ = 99.64º) are very close to the experimental values (a = 5.151, b = 5.212, c =5.317, α = β = 90º and 99.23º) [4]. For γ-Al_2O_3, we used the non-spinel model that was proposed by Digne et al.[5]

Results and Discussion

CO adsorbs at the Ce site of Ce_2O_4 supported on both ZrO_2 and γ-Al_2O_3 in an upright configuration. The calculated C-O stretching frequencies are slightly higher than that of CO adsorbed on CeO_2(111), attributed to a relatively low coordination number of Ce in the supported cluster. CO molecules can also interact with two oxygen atoms of the supported Ce_2O_4 cluster, forming a CO_3^{2-} species, as shown in figure 1(a) and (b). This process is highly exothermic, with an energy gain of 4.39 eV on the γ-Al_2O_3-supported Ce_2O_4 cluster. The same process on the ZrO_2-supported Ce_2O_4 cluster is much less exothermic, with an energy gain of only 0.55 eV. In both cases, the Ce sites were reduced upon the formation of CO_3^{2-} species.

CO_2 can adsorb on the O sites of Ce_2O_4 supported on both ZrO_2 and γ-Al_2O_3, resulted in a surface CO_3^{2-}. The structure and vibrational frequencies of the CO_3^{2-} species are shown in Figure 1(c) and (d).

Significance

In this work, we compared the effect of different supports on the activity of Ce_2O_4, probed by CO and CO_2 adsorption. The insights from this study help us to establish some key factors that will determine the activity of the supported oxide catalysts.

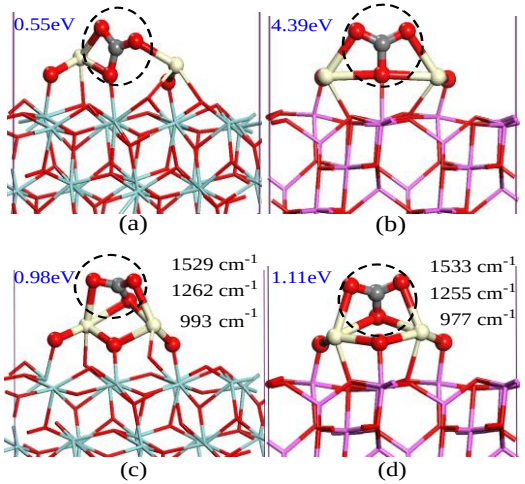

Figure 1. Side view of (a) and (b): CO reactive adsorption on ZrO_2- and γ-Al_2O_3- supported Ce_2O_4 clusters, respectively; (c) and (d): CO_2 adsorption on ZrO_2- and γ-Al_2O_3- supported Ce_2O_4 clusters. The CO_3^{2-} species were circled and adsorption energies were labeled. Vibrational frequencies in the structures formed from CO_2 adsorption were included.

References

1. Kresse, G.; Furthmuller, J. Vasp, the guide, (2007).
2. Kresse, G.; Joubert, D. *Phys. Rev. B 59*, 1758 (1999).
3. Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett. 77*, 3865 **(**1996).
4. Stefanovich, E. V.; Shluger, A. L.; Catlow, C. R. A. *Phys. Rev. B, 49*, 11560 (1994).
5. Digne, M.; Sautet, P.; Raybaud, P.; Euzen, P.; Toulhoat, H. *J.Catal.* 226,54 (2004).