

Periodic density functional theory study of ethylene hydrogenation over Co_3O_4 (1 1 1) surface: The critical role of oxygen vacancies



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ARTICLE INFO

Article history:

Received 18 January 2016

Received in revised form 22 February 2016

Accepted 24 February 2016

Available online 27 February 2016

Keywords:

Heterogeneous catalysis

Ethylene hydrogenation

Oxygen vacancy

Cobalt oxide

DFT

ABSTRACT

Recently, metal oxides are attracting increasing interests as hydrogenation catalyst. Herein we studied the hydrogenation of ethylene on perfect and oxygen defective Co_3O_4 (1 1 1) using periodic density functional theory. The energetics and pathways of ethylene hydrogenation to ethane were determined. We have demonstrated that (i) H_2 dissociation on Co_3O_4 is a complicated two-step process through a heterolytic cleavage, followed by the migration of H atom and finally yields the homolytic product on both perfect and oxygen defective Co_3O_4 (1 1 1) surfaces easily. (ii) After introducing the surface oxygen vacancy, the stepwise hydrogenation of ethylene by atomic hydrogen is much easier than that on perfect surface due to the weaker bond strength of OH group. The strength of O–H bond is a crucial factor for the hydrogenation reaction which involves the breakage of O–H bond. The formation of oxygen vacancy increases the electronic charges at the adjacent surface O, which reduces its capability of further gaining electrons from adsorbed atomic hydrogen and then weakens the strength of O–H bond. These results emphasize the importance of the oxygen vacancies for hydrogenation on metal oxides.

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1. Introduction

Heterogeneous catalytic hydrogenation is widely used in catalysis. Noble metals such as Pt, Ir, Rh, Pd are commonly used hydrogenation catalysts [1]. Due to the limited abundance of noble metals, intense efforts have been done to search for low-cost alternatives. Raney nickel and supported Ni are often used as hydrogenation catalysts but harsh operation conditions are the major bottleneck for its practical application [2]. Recently, increasing interests have been drawn to metal oxides. The activity of metal oxide for olefin hydrogenation is first studied over Cr_2O_3 [3], followed by ZnO [4,5], Co_3O_4 [6,7] and etc. Recent studies also show that CeO_2 exhibits good activity for the selective hydrogenation of acetylenic compounds and nitroaromatics [8–11]. More recently, nanoscale Co_3O_4 and Fe_2O_3 are reported to be highly active and selective for hydrogenation of nitroarenes under mild conditions [12,13]. Hydrogenation of ethylene is an often used model reaction for understanding the hydrogenation of olefins and aromatics. The generally accepted ethylene hydrogenation mechanism involves

the dissociation of H_2 on catalyst surface followed by sequential addition of H atoms to the adsorbed ethylene [14]. There are lots of literatures about theoretical studies on metal catalysts, but metal oxides are rarely reported. The detailed hydrogenation mechanism over oxides is not fully interpreted yet. Therefore, a thorough understanding of hydrogenation mechanism over oxides in atomic level is essential and useful.

Crystal defects have significant effect on the catalytic performance of catalyst [15–18]. Specifically, under hydrogenation reaction conditions, oxygen vacancies are common characteristics. It is already reported that the creation of oxygen vacancies on the Ga_2O_3 surface promotes H_2 dissociation compared with perfect surface [19]. Oxygen vacancy on the In_2O_3 (1 1 0) surface assists CO_2 activation and hydrogenation and also stabilizes the key intermediates involved in CO_2 hydrogenation [20]. Recently, we have proved that oxygen-deficient tungsten oxide is a versatile and efficient hydrogenation catalyst, and density functional theory (DFT) calculations attributes it to the formation of oxygen vacancy activating H_2 very easily, both in kinetics and thermodynamics [21,22].

Co_3O_4 has attracted a great deal of attention in heterogeneous catalysis. In particular, Co_3O_4 is an efficient catalyst for CO oxidation [23], methane combustion [24] and oxidative dehydrogenation [25]. Spinel-type Co_3O_4 is readily accessible and contains two

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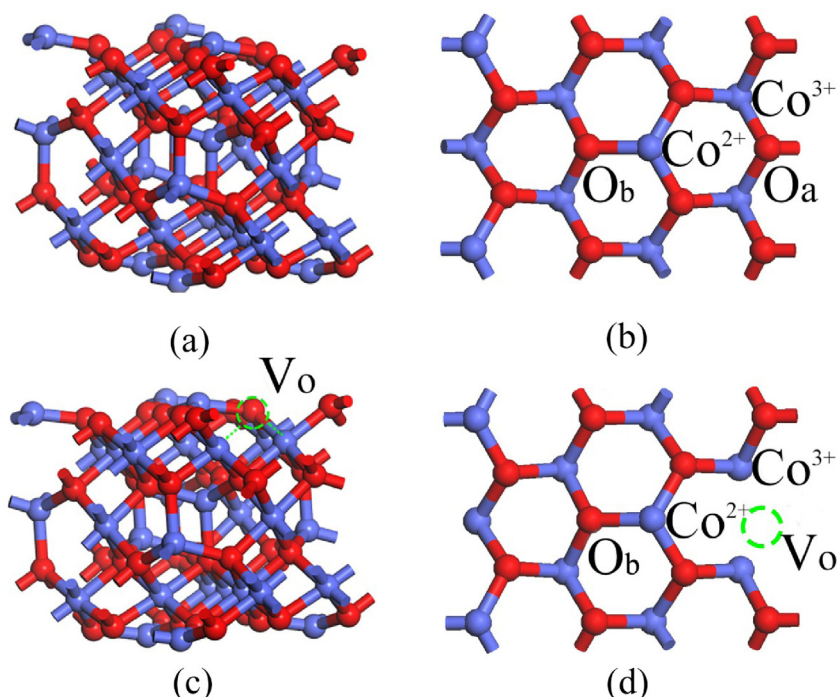


Fig. 1. (a) Side and (b) top view of perfect Co_3O_4 (1 1 1) surface. (c) Side and (d) top view of oxygen defective Co_3O_4 (1 1 1) surface. Red and blue spheres represent O and Co atoms, respectively. Green dotted ball stands for O vacancy site. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

different oxidation states of cobalt ions, Co^{2+} located in the tetrahedral sites and Co^{3+} located in the octahedral sites. The purpose of the present work is to gain a deeper insight into the hydrogenation mechanism on metal oxides. For this, we have systematically studied the H_2 dissociation and stepwise addition of H atoms to ethylene on perfect Co_3O_4 (1 1 1) surface using density functional theory calculations corrected by on-site Coulomb interactions (DFT+U). Besides, to find out the important role of oxygen vacancies, we have investigated the same process on oxygen defective Co_3O_4 (1 1 1) surface. Interestingly, the results show that H_2 dissociation on Co_3O_4 is a complicated two-step process through a heterolytic cleavage followed by the transfer of H atom and finally yields the homolytic product. The adsorption strength of H atoms on oxygen defective surface is weakened, which influences reaction behavior of H atoms included in subsequent ethylene hydrogenation. The findings in the present study not only clarify the importance of oxygen vacancies for hydrogenation on metal oxides but also give new insights in designing efficient oxide-based hydrogenation catalysts.

2. Computational methods and models

All the spin-polarized calculations in this work were performed using Vienna Ab-initio Simulation Package (VASP) [26,27] with the projector-augmented wave method [28,29]. The Perdew–Burke–Ernzerhof functional of generalized gradient approximation was employed as exchange–correlation function [30,31]. Semi-empirical dispersion correction proposed by Grimme [32] (DFT-D2) was carried out to include van der Waals interaction. The Kohn–Sham equation was solved using a plane wave basis set with a cutoff energy of 650 eV to describe the valence electrons. The DFT+U method [33] was employed in order to describe the strongly correlated character of the Co-3d orbitals correctly. This approach depends on the difference $U_{\text{eff}} = U - J$, simply denoted as U. $U = 3.3$, originated from a fit to the reaction energy of CoO oxidation to Co_3O_4 and band gap, was used for all models [34]. To locate transition states (TS), the Climbing Image Nudged Elastic

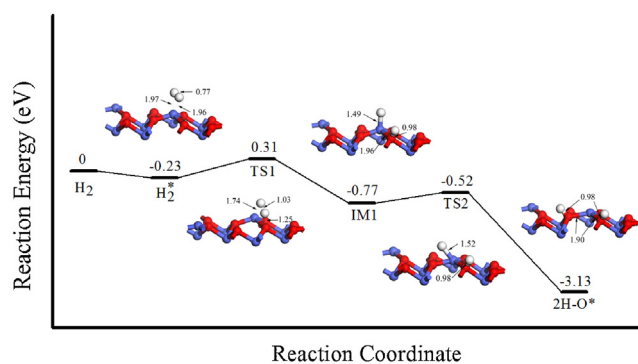


Fig. 2. Energy profile of H_2 heterolytic dissociation and H atom migration on perfect Co_3O_4 (1 1 1) surface with the structures of related states.

Band [35] (CI-NEB) algorithm was employed. Each transition state was confirmed by vibrational frequency analysis.

The optimized lattice constant of bulk Co_3O_4 obtained by fitting total energies to Birch–Murnaghan equation of state [36] was 8.09 Å, in good agreement with experiment value of 8.09 Å [37]. Co_3O_4 (1 1 1) surface was selected as the model catalyst because it is the predominant and naturally occurring surface and has been widely studied experimentally [38]. Ferstl et al. studied the interaction of CO and O_2 with Co_3O_4 (1 1 1) films grown on Ir (100) [39]. What's more, Co_3O_4 (1 1 1) nano-sheets were used as catalyst for methanol decomposition [40]. Because of the structural complexity of Co_3O_4 , there are six types of possible (1 1 1) surface terminations. However, Co_3O_4 (1 1 1) films terminated by Co^{2+} are energetically preferred under all conditions based on DFT computations [41]. Furthermore, it was reported that Co_3O_4 (1 1 1) thin films deposited on Ir (100) were terminated by tetrahedrally coordinated Co ions [42,43]. Therefore, only the Co^{2+} -terminated surface was considered in the present work.

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