Hydrogenation of ethene catalyzed by Ir atom deposited on γ-Al$_2$O$_3$(001) surface: From *ab initio* calculations

Yongchang Chen [b], Zhaolin Sun [a,b], Lijuan Song [a,*], Qiang Li [a], Ming Xu [a]

[a] *Liaoning Key Laboratory of Petrochemical Engineering, Liaoning ShiHua University, Fushun, Liaoning 113001, China*
[b] *School of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China*

ABSTRACT

Ethene hydrogenation reaction, catalyzed by an iridium atom adsorbed on γ-Al$_2$O$_3$(001) surface, is studied via *ab initio* calculations based on density functional theory (DFT). The catalyzed reaction process and activation energy are compared with the counterparts of a reaction occurs in vacuum condition. It is found that the activation energy barrier is substantially lowered by the adsorbed Ir atom on the γ-Al$_2$O$_3$(001). The catalyzed reaction is modeled in two steps: (1) Hydrogen molecular dissolution and then bonded with C$_2$H$_4$ molecular. (2) Desorption of the C$_2$H$_6$ molecular from the surface.

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1. Introduction

The developments of chemical industries are always closely related with the development of catalysts. Catalyzed chemical reactions at solid surfaces are studied intensively in the past decades. Many techniques from surface physics have been used to study the elementary processes involved in heterogeneous catalysis [1]. Recently, supported metal atoms or clusters become more and more important in heterogeneous catalysis, because of their intrinsic different physical properties from bulk metal or metal surfaces [2]. The catalytic efficiency of supported metal clusters as catalyst is related with not only the size, geometry and distribution of the metal cluster, the support itself also play important role in the catalysis reaction [3].

Among various oxides as catalyst supports, γ-Al$_2$O$_3$ is studied extensively because of its application as both a catalyst and catalyst support [4,5]. γ-Al$_2$O$_3$ possesses a defective spinel structure [6], while certain tetragonal distortion is observed when samples are prepared with different preparation conditions [7–10]. In the defective spinel structure, vacancies at octahedral Al sites are required in order to satisfy the stoichiometry of Al$_2$O$_3$ [11–13]. As a catalyst or catalyst support, the surface properties of γ-Al$_2$O$_3$ have also been studied by many researchers [14,15]. Recently, we have show that a dense Al–O(001) layer, containing both octahedral aluminum and oxygen atoms, are stable at various external

O$_2$ pressures and temperature ranges [16]. With this stable surface model, we also calculated the binding energies and electronic structures of Ir atom deposited on the γ-Al$_2$O$_3$(001) surface [17], and the results show that top sites of O atoms are energetically most favorable sites for Ir adsorption. As a continuous work of our previous studies, in the current Letter the catalytic effect of γ-Al$_2$O$_3$ supported iridium atoms are investigated by means of *ab initio* calculations within the DFT.

Catalytic reactions are always very complicated and an accurate knowledge of the reaction mechanisms is usually difficult to be obtained experimentally. To the best of our knowledge, a general mechanism on the catalysis of the supported metal clusters is still not available in literature. Generally, most catalysts for hydrogenation reaction contain transition or noble metals [18,19]. The catalyzed hydrogenation reaction of C$_2$H$_4$ to C$_2$H$_6$ is simple but industrially very relevant. However, the catalytic mechanism of this simple reaction is still unclear from the atomic level. Recently, Chan and Radom [20] studied the zeolite-catalyzed hydrogenation of ethene from density functional theory, from which they proposed a three stage reaction mechanism. However, the details on atomic movement in the reaction process were not revealed. In the present work, the ethene hydrogenation reaction catalyzed by Ir atom adsorbed on the γ-Al$_2$O$_3$(001) is studied in details.

2. Computational details

As a continuous work of our previous studies, the structural models of γ-Al$_2$O$_3$(001) and Ir adsorption on the surface are constructed according to our previous results. Please refer to Refs. [16,17] for details. An eleven layer slab model with thick Al–O

* Corresponding author. Tel.: +86 413 6860658; fax: +86 413 6860658.
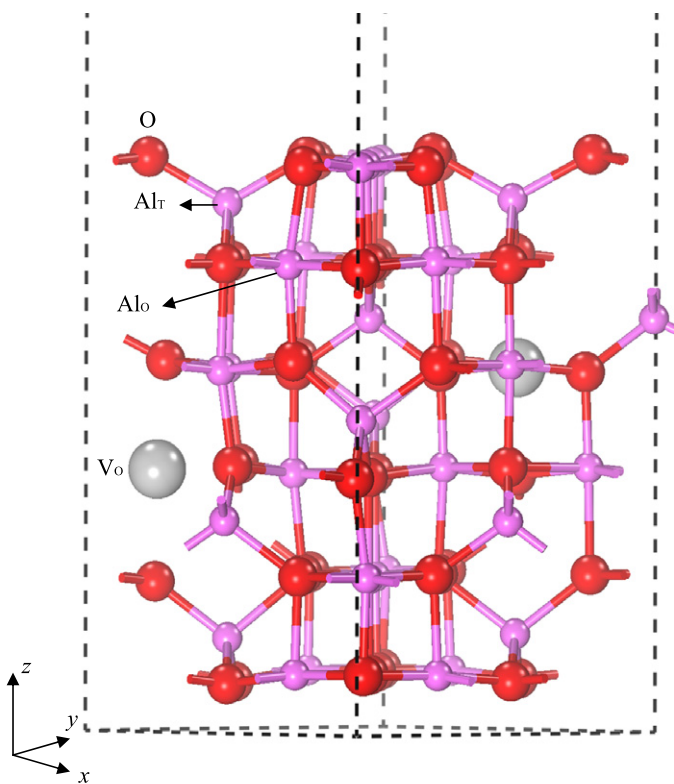*E-mail addresses:* chenyc828@yahoo.com.cn (Z. Sun), chenyc828@foxmail.com
(L. Song).

Fig. 1. Schematic view of the relaxed structure of the bare γ-Al$_2$O$_3$(001) slab model. The red (middle sized), purples (small) and grey (largest) spheres present O atoms, Al atoms, and octahedral vacancies, respectively. Al$_T$ and Al$_O$ denotes tetrahedral and octahedral Al atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this Letter.)

layers exposed on both side of the slab has been constructed, as shown in Fig. 1. The stoichiometry of the slab is restricted to Al$_2$O$_3$, with 2 octahedral site vacancies in the middle of the slab. An Ir atom is adsorbed on the top of a surface O atom, which was shown to be energetically most favorable in Ref. [17].

All calculations are performed with DACAPO code [21,22], which is an *ab initio* simulation package based on the DFT and the plane-wave pseudopotential method [23]. The exchange and correlation energies were treated via the spin-polarized generalized gradient approximation (GGA) with the Perdew–Wang (PW91) exchange correlation functional [24,25]. The valence electron wave functions and the augmented electron density are expanded in the plane-wave basis sets with cutoff energies of 25 and 40 Ry, respectively. The Monkhorst–Pack [26] type $3 \times 3 \times 1$ k-points mesh is used for sampling in the irreducible Brillouin zone. For relaxation of ethene and ethane molecule adsorbed at the Ir atom on the surface, atoms in the middle 3 layers were fixed while all the other atoms were fully relaxed until the final forces on all the relaxed atoms were smaller than 0.05 eV/Å. The ethene hydrogenation reaction on the iridium adsorbed γ-Al$_2$O$_3$(001) surfaces was simulated by using the NEB method [27,28].

3. Results and discussions

For comparison purpose, the hydrogenation reaction of ethene (C$_2$H$_4$) in a vacuum was simulated, which is taken as reference for a non-catalytic reaction. The initial state was constructed as one ethene molecule and one separated hydrogen molecule (H$_2$). The distance between them is far enough to ensure that the interaction between them is negligible. The final state is a single ethane (C$_2$H$_6$) molecule. The total energy of the final state is about 1.8 eV lower than that of the initial state, indicating that the hydrogena-
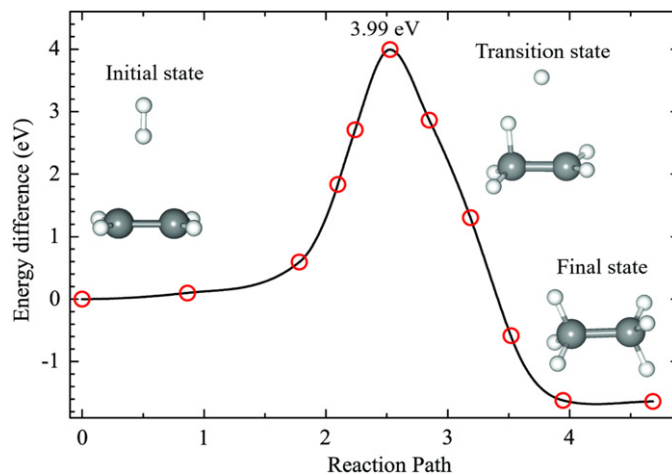

Fig. 2. Reaction energy barrier of the hydrogenation of ethene in vacuum condition. The initial, transition and final states are shown in this figure, and the grey (large) and white (small) spheres present C and H atoms, respectively.

tion reaction is thermodynamically favorable. As described in Section 2, the simulation was performed by using the NEB method.

Fig. 2 shows the total energy changes of the gas phase system along the optimized reaction path. The reaction reaches its transition state when the H$_2$ bond is broken, with one H atom bonds with one C atom while the other remains single. The evaluated energy barrier for hydrogenation of ethene in vacuum is 3.99 eV, which is quite large and the reaction is difficult to happen even under high temperature. A catalytic reaction is required to realize the reaction of hydrogenation of ethane. In the following context, we show how Ir adsorbed at γ-Al$_2$O$_3$(001) catalyzes this reaction.

In order to simulate the catalytic behavior of the γ-Al$_2$O$_3$(001) supported Ir atoms with the NEB method, reasonable initial and final states should be built and optimized. The final state is simple (see Fig. 3c), which is defined as an ethane molecule in the vacuum layer of the slab. The Ir atom is located at most favorable site on the γ-Al$_2$O$_3$(001) surface. In our previous study, we have shown that the energetically most favorable sites are the top sites of the O atoms at the dense Al–O layer of the γ-Al$_2$O$_3$(001) surface [17]. The ethane molecule is far away from the surface, which makes sure that the interaction between them is negligible.

For the initial state, an ethene molecule was first put on the top of the Ir atom. Different geometries of the molecule have been tried and the results show that the system is energetically most favorable when the ethene molecule plane is horizontal and parallel to the surface plane (see Fig. 3a). In the following context, we call it as "π-bonded" initial state just for simple description of the geometry. One H$_2$ molecule was then put in the vacuum of the slab and located far enough from the surface to ensure that the interaction between the H$_2$ molecule and the surface is small. Due to the small surface area of our model, we did not choose the initial H$_2$ molecule geometry by adsorbing on the Al$_2$O$_3$ surface. As the ethene molecule is initially "π-bonded" to the Ir atom and the energy of the system is most favorable, it can be understood that the product of the hydrogenation reaction could also have strong interaction with the Ir atom and the system energy is low. Therefore, we put an ethane molecule at the surface with the same way of putting the ethene molecule on the surface. Relaxation of the system with an ethane molecule on the top of the Ir atom shows that the C–C bond breaks and the resulted two methyl groups are bonded with the Ir atom, as shown in Fig. 3b. The energy of the relaxed system is even about 0.2 eV lower than the initial state, and therefore we choose it as the middle state of the Ir catalyzed process of the ethene hydrogenation reaction. This assumption is consistent with Argo et al.'s proposal on the