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Periodic DFT study of the deep oxidation in the oxidative dehydrogenation of ethane over V_2O_5 (001)

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ABSTRACT

The mechanism of the deep oxidation in ethane oxidative dehydrogenation (ODH) over V_2O_5 (001) was investigated by periodic DFT. In ethane ODH over V_2O_5 (001), acetaldehyde formation is the main side reaction. Desorbed acetaldehyde can be further easily oxidized to acetic acid. However, before they can desorb from the surface, most of the acetaldehyde species are oxidized to CO_x . The oxidation product CO_x mainly comes from the oxidation of acetaldehyde.

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1. Introduction

The oxidative conversion of lower alkanes to alkenes is one of the most challenging and industrially important problems in catalytic chemistry [1–15]. Due to its abundant availability and for economic reasons, efforts have been devoted to the oxidation of ethane to ethene in the presence of molecular oxygen as an oxidant, which is thermodynamically favorable and does not lead to the formation of coke. Unfortunately, the yield of ethene on most catalysts is not satisfactory due to side reactions leading to CO_x . So, a better understanding of the mechanism of ethane ODH, especially the mechanism of the deep oxidation of ethane to CO_x , will provide useful guidelines for improved catalyst design. Most investigations so far were on catalyst design and the physicochemical properties of the catalytic materials, while only a few studies were on the mechanistic aspects of ethane ODH [12]. Oyama et al. [16] investigated ethane oxida-

tion on vanadium oxide experimentally, and reported that the main products are acetaldehyde, ethene, CO, and CO_2 , and that there are large drops in activation energies for the 100% V_2O_5 sample. In addition, the 100% V_2O_5 sample gave a much higher selectivity to deep oxidation products throughout the temperature range. In our previous study [17], we reported the first detailed periodic density functional theory (DFT) study of the ethane ODH reaction over the V_2O_5 (001) surface and showed that ethane ODH over V_2O_5 (001) followed a similar mechanism to propane. The first C–H bond activation at the terminal oxygen O(1) site is the rate limiting step and it leads to the ethoxide intermediate, which forms ethene by a second C–H bond breaking, with energy barriers of 142.5 and 132.1 kJ/mol at O(1) and bridge oxygen atom O(2) sites, respectively. The acetaldehyde byproduct of ethane ODH is formed at the O(1) site by the dehydrogenation of the ethoxide species with a lower energy barrier than ethene formation (128.7 vs 142.5 kJ/mol).

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Acetaldehyde formation is an exothermic process and its high stability on the surface leads to the deep oxidation to CO_x . However, the total oxidation reactions, that is, the deep oxidation of ethene and the sequential oxidation of acetaldehyde, which lead to CO_x and lower the selectivity of ethene have not been studied and discussed before.

In this study, we examined the whole ethane ODH process over V_2O_5 (001). In addition to ethene deep oxidation to CO_x , the other pathway of acetaldehyde oxidation was also investigated in detail. The factors that are important in increasing the selectivity of ethene are systematically discussed.

2. Computational details

All total energy DFT calculations were carried out using the SIESTA package with numerical atomic orbital basis sets and Troullier-Martins norm-conserving pseudopotentials [18,19]. The exchange-correlation functional utilized was from the generalized gradient approximation method, known as GGA-PBE [20]. A double- ξ plus polarization (DZP) basis set was employed. The orbital-confining cutoff radii were determined using an energy shift of 0.01 eV. The energy cutoff for the real space grid used to represent the density was 150 Ry. To further speed up the calculations, the Kohn-Sham equations were solved by an iterative parallel diagonalization method that utilized the ScalAPACK subroutine pdsygvx with a two dimensional block cyclic distributed matrix [21]. The Broyden method was employed in the geometry relaxation, which was performed until the maximum force on each relaxed atom was less than 0.5 eV/nm. Unless specific stated, the V_2O_5 (001) surface was modeled as a one layer slab, and all the atoms were allowed to relax. A (1×3) unit cell (1.154×1.081 nm) was used to model the surface. The vacuum region was 2 nm. This slab model has been previously used to study the ODH of ethane and propane and its reliability has been verified [17,22]. Only the Γ -point was used to sample the Brillouin zone in our calculations. Spin-polarization was included in all the calculations. A previous study showed that this electronic structure method used has the accuracy to provide reliable relative energies [17].

A constrained minimization scheme was employed to find the transition states (TSs) on the potential energy surface [23,24]. A TS was considered identified when (1) the forces on the atoms vanish and (2) the energy is a maximum along the reaction coordinate but a minimum with respect to all the other degrees of freedom. The energy barrier was determined as the energy difference between the saddle point and the initial state.

The adsorption energy (E_{ads}) was calculated as:

$$E_{\text{ads}} = E_{(\text{adsorbate-substrate})} - (E_{\text{adsorbate}} + E_{\text{substrate}})$$

and a negative E_{ads} indicates an exothermic process.

3. Results and discussion

The mechanism of the ODH of ethane over the V_2O_5 (001) surface has been investigated in our previous work [17]. The first C–H bond cleavage leading to an ethoxide intermediate is the rate limiting step. The most probable pathway for the C–H bond activation takes place at the O(1) ($\text{V}=\text{O}$) site with an activation

energy of 146.7 kJ/mol. Ethene is formed more easily at O(2) than at O(1) with energy barriers of 132.1 kJ/mol and 142.5 kJ/mol, respectively, through a second C–H bond breaking from the ethoxide intermediate. The acetaldehyde byproduct of ethane ODH is formed at the O(1) site by the dehydrogenation of ethoxide, with a lower energy barrier than that of ethene formation (128.7 vs 142.5 kJ/mol). Acetaldehyde formation is exothermic, and its high stability on the surface leads to its further oxidation to CO or CO_2 .

3.1. Ethene oxidation

Oyama et al. [16] investigated ethane oxidation on 100% V_2O_5 samples and reported that the conversion of ethane at 800 K was 8.0%, which increased to 18% at 875 K. The selectivity to ethene decreased from 26% to 21% in this temperature range, the selectivity to acetaldehyde was stable at 0.2%, and CO_x selectivity increased with temperature to >79% at 870 K. With increasing temperature, the sequential oxidation of ethene contributes to the formation of CO_x , which lowers the selectivity to ethene. Our DFT calculation of the reaction pathway for the oxidation of ethene over V_2O_5 (001) is shown in Figure 1. Through transition state TS1, one of the carbon atom in ethene bonds with the lattice O(1) site to form intermediate IM1. The distance between the O(1) site and the carbon atom is reduced from 0.166 nm in TS1 to 0.147 nm in IM1. Then, one hydrogen atom of IM1 migrates to the nearby lattice O(1) site via TS2, and the C–H bond is activated and broken to form an OH group and a CH_2CHO^* species on the surface. The energy barrier of the rate determining step was calculated to be 104.5 kJ/mol, and the whole C–H bond activation process is exothermic by

Fig. 1. Reaction pathways of ethene oxidation to form CH_2CHO^* .

35.1 kJ/mol. Our previous work [22] showed that this surface vinyloxy species CH_2CHO^* can be easily oxidized to CO_x . Obviously, the oxidation of ethene is easy over V_2O_5 (001) and if ethene does not desorb in time, it will undergo further oxidation to CO_x , which lowers the selectivity of ethene.

3.2. Acetaldehyde oxidation before desorption

From our previous mechanism study of ethane ODH over V_2O_5 (001) [17], acetaldehyde is the major byproduct. It is formed at the O(1) site via the dehydrogenation of ethoxide with a lower energy barrier than ethene formation. The high stability of acetaldehyde on the surface leads to its further oxidation to CO_x , which accounts for the low selectivity of ethene. In this work, we first investigated the oxidation mechanism of acetaldehyde before it desorbs. Starting from the surface acetaldehyde derived from the dehydrogenation of adsorbed ethoxide, a hydrogen atom of the carbonyl group is abstracted by a nearby lattice O(1) via TS3 with an energy barrier of 118.3 kJ/mol to yield a surface CH_3CO^* species (Fig. 2). The methyl hydrogen atom of acetaldehyde can also be abstracted by an O(1) atom through TS4 with a calculated energy barrier of only 48.9 kJ/mol. Obviously, this acetaldehyde oxidation pathway is more favorable because of the lower energy barrier for the formation of the CH_2CHO^* species.

Our previous study [17] showed that the formation of acetaldehyde and ethene are competitive reactions, especially at the O(1) site. The oxidation of ethoxide to form acetaldehyde is easier than that of ethene because it has a lower energy barrier by 13.8 kJ/mol. As compared to the oxidation of ethene, which

has been discussed above in detail, acetaldehyde deep oxidation is easier due to the relatively lower energy barrier for the dehydrogenation of acetaldehyde to form CH_2CHO^* and O^*H . (48.9 kJ/mol for acetaldehyde vs 104.5 kJ/mol for ethene). In addition, the desorption of acetaldehyde would deprive the surface of a lattice O(1) atom, and it needs the higher desorption energy of 72.7 kJ/mol, which is higher than the energy barrier of acetaldehyde oxidation. So, before acetaldehyde molecules can desorb from the surface, most of these will be oxidized to surface CH_2CHO^* . These results account for why although acetaldehyde is easier to form than ethane, its selectivity is much lower than that of ethene (0.2% vs 26%) in the experiments at 800 K over 100% V_2O_5 [16].

3.3. Acetaldehyde oxidation after desorption

Although most of the acetaldehyde molecules are oxidized to form surface CH_2CHO^* before desorption, a small amount desorb and remove a lattice O(1) atom. Will these desorbed species undergo further oxidation to produce CO_x also? In order to obtain a better understanding of this, we also explored the oxidation channel of desorbed acetaldehyde over V_2O_5 (001). When the carbonyl of the acetaldehyde molecule in the gas phase attacks the lattice O(1), a stable insertion product, which is the acetic acid species, is formed (shown in Fig. 3) through TS5. In the transition state (TS5), the distance between the carbon and hydrogen atoms in the carbonyl is elongated to 0.157 nm (the normal C–H bond length is 0.114 nm), which suggested that the activated C–H bond is almost broken. At the same time, the distances between the lattice O(1) and the car-

Fig. 2. Reaction pathways of acetaldehyde oxidation to form CH_2CHO^* and CH_3CO^* .

Fig. 3. Reaction pathways of acetaldehyde oxidation to form acetic acid.

bon atom and hydrogen atom are shortened to 0.134 and 0.130 nm, respectively, which suggested that a carboxyl group is forming. The process of acetaldehyde oxidation to form acetic acid was calculated to be exothermic by 77.7 kJ/mol with a barrier of only 13.8 kJ/mol. Even though a small amount of acetaldehyde species desorbed from the surface, another surface lattice O(1) atom can easily oxidize these to form acetic acid, which also contributes to the low selectivity of acetaldehyde.

In our previous theoretical study on propane deep oxidation, we found that the oxidation of propane can produce acetic acid, and that the oxidation of acetic acid is not easy, which is in agreement with a previous experiment [25] in which Lin et al. investigated propane ODH over Mo-V-Te-Nb-O catalyst and found that other than carbon oxides, acetic acid was a major byproduct. These experimental results also implied that acetic acid is stable and does not undergo further oxidation easily. Although Oyama et al. [16] did not report this species in their experiments on ethane ODH over vanadium oxide, from our results, we suggest that there would be a small amount of acetic acid in the product since the amount of desorbed acetaldehyde was small.

3.4. Complete reaction mechanism of ethane ODH

We summarize the energy profiles of ethane ODH and the deep oxidation reaction in Fig. 4. The ethene formation mechanism and the deep oxidation of acetic acid (CH_3COOH) and vinyl oxide (CH_2CHO^*) have been discussed in our previous works [17,22]. Starting from the adsorbed ethoxide at O(1) site formed after the first C–H bond of ethane is broken, the pathway that a methylene hydrogen atom is abstracted by a nearby lattice O(1) to yield surface acetaldehyde is more feasible with an energy barrier that is lower by 13.8 kJ/mol than the reaction of methyl hydrogen atom transfer to produce ethene. Acetaldehyde would be the main byproduct of ethane ODH over V_2O_5 (001) if it does not undergo further oxidation.

Although the desorption of ethene is very easy with a desorption energy of only 16.3 kJ/mol, the oxidation of ethene to

Fig. 4. Energy pathways of ethane total oxidation process occurred on V_2O_5 (001) surface.

form surface CH_2CHO^* is also rather feasible with the rate determining energy barrier of 104.5 kJ/mol, which is lower than that of ethane by 42.2 kJ/mol. This explains that as the temperature increased, the conversion of ethane increased while the selectivity of ethene decreased. The decrease of ethene selectivity at higher temperature is due to its further oxidation to CO_x .

As an easily formed intermediate in ethane ODH over V_2O_5 (001), acetaldehyde is very easily further oxidized to form surface CH_2CHO^* with an energy barrier of only 48.9 kJ/mol. Our previous investigation [22] showed that this surface vinyl oxide species CH_2CHO^* can be oxidized to formaldehyde and CO, and both sequential oxidation reactions of these species easily give CO_2 . From its desorption energy of 72.7 kJ/mol, it can be concluded that most acetaldehyde will suffer deeper oxidation to produce CO_x before desorption. In addition, desorbed acetaldehyde is very easily transformed to acetic acid by carbonyl oxidation. These explain the fact that the selectivity of acetaldehyde is low (only 0.2%) throughout the temperature range (800–870 K) [16].

Overall, a clear picture of ethane ODH and the deep oxidation reaction over V_2O_5 (001) is obtained from our calculations. The undesirable acetaldehyde formation pathway and the further oxidation of ethene are the two main factors that decrease the selectivity to ethene. To achieve a high selectivity to ethene, these undesirable pathways must be suppressed.

4. Conclusions

We performed periodic DFT calculations to find the total oxidation pathways of ethane over the V_2O_5 (001) surface, and the main results are summarized below. (1) Acetaldehyde formation is the main side reaction in ethane ODH over V_2O_5 (001). (2) Ethene can be easily oxidized to form the surface

Graphical Abstract

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Periodic DFT study of the deep oxidation in the oxidative dehydrogenation of ethane over V_2O_5 (001)DAI Guoliang, LI Zhenhua, WANG Wenning, LIU Jing, FAN Kangnian*
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In ethane ODH over V_2O_5 (001), acetaldehyde formation is the main side reaction, and it can be further easily oxidized to acetic acid. CO_x mainly comes from the oxidation of acetaldehyde.

CH_2CHO^* species with an energy barrier of 104.5 kJ/mol, which can undergo further oxidation to produce CO_x . (3) Before they can desorb from the surface, most of the acetaldehyde molecules are oxidized to CO_x . (4) The amount of desorbed acetaldehyde is small, and most of these are very easily oxidized to acetic acid. The sequential oxidation of acetic acid is difficult, and there would be a small amount of acetic acid in the product.

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乙烷在 V_2O_5 (001)表面深度氧化反应机理的周期性密度泛函理论研究戴国梁^a, 李振华^a, 王文宁^a, 刘 晶^b, 范康年^{a,*}^a复旦大学化学系, 上海市分子催化和新材料重点实验室, 上海 200433^b华中科技大学煤燃烧国家重点实验室, 湖北武汉 430074

摘要: 采用周期密度泛函理论研究了 V_2O_5 (001)表面乙烷深度氧化过程. 结果表明, 乙醛是主要的副产物, 且脱附态的乙醛能很容易被氧化成乙酸, 但多数乙醛在从表面脱附前已被氧化成 CO_x . 显然, 在乙烷氧化脱氢反应的最终产物 CO_x 主要来源于乙醛.

关键词: 深度氧化; 乙烷; 氧化脱氢; 周期密度泛函

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