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Article

Activity and selectivity of propane oxidative dehydrogenation over $\text{VO}_3/\text{CeO}_2(111)$ catalysts: A density functional theory study

Chang Huang[†], Zhi-Qiang Wang[†], Xue-Qing Gong^{*}

Key Laboratory for Advanced Materials, Centre for Computational Chemistry and Research Institute of Industrial Catalysis, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, China

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ABSTRACT

The oxidative dehydrogenation (ODH) of propane on monomeric VO_3 supported by $\text{CeO}_2(111)$ ($\text{VO}_3/\text{CeO}_2(111)$) is studied by periodic density functional theory calculations. Detailed energetic, structural, and electronic properties of these reactions are determined. The calculated activation energies of the breaking of the first and second C–H bonds of propane on the $\text{VO}_3/\text{CeO}_2(111)$ catalyst are compared, and it is found that both the unique structural and electronic effects of the $\text{VO}_3/\text{CeO}_2(111)$ catalyst contribute to the relatively easy rupture of the first C–H bond of the propane molecule during the ODH reaction. In particular, the so-called new empty localized states that are mainly constituted of O 2p orbitals of the ceria-supported VO_3 species are determined to be crucial for assisting the cleavage of the first C–H bond of the propane molecule. Following this they become occupied and the remaining C–H bonds become increasingly difficult to break owing to the increasing repulsion between the localized 4f electrons at the Ce cations, resulting in the adsorption of more H and other moieties. This work illustrates that CeO_2 -supported monomeric vanadium oxides can exhibit unique activity and selectivity for the catalytic ODH of alkanes to alkenes.

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1. Introduction

Light alkenes are of paramount importance in chemical industries as they are raw materials for numerous bulk and fine chemical products. Light alkenes are usually obtained directly from high-temperature pyrolysis of the corresponding alkanes. As these processes require massive energy and the catalysts used are easy to coke, their applications are typically strictly determined by the economic profits between the alkenes and highly purified alkanes, which are in turn affected by the oil price in the global market. In comparison with these conventional nonoxidative routes, the so-called oxidative dehydro-

genation (ODH) of alkanes to olefins is a promising alternative approach because this reaction is not confined by the chemical equilibrium in pyrolysis and the oxygen used here can prevent coke formation [1–3]. However, one important problem for this process is the strong oxidation of alkenes, which decreases the productivity of the desired olefin product. Therefore, it is required to design catalysts that increase the selectivity toward dehydrogenation products instead of in particular oxygen-containing molecules or carbon oxides.

Supported vanadium oxides are known to be one of the best catalysts for the ODH reactions of alkanes as they can exhibit a high thermal stability and excellent selectivity [4–12]. As a car-

^{*} Corresponding author. Tel: +86-21-64252623; Fax: +86-21-64253457; E-mail: xgong@ecust.edu.cn

[†] These authors contributed equally to this work.

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rier of the catalyst, reducible CeO_2 has been found to be much better than irreducible SiO_2 and Al_2O_3 [13–18]. It is widely believed that the ODH reaction of alkanes on ceria-supported vanadium catalysts proceeds via the Mars–van Krevelen mechanism and the rate-determining step should be the first C–H bond cleavage [19–22]. Moreover, the presence of highly dispersed vanadium oxides is also crucial to achieve better activity and selectivity [5,23–27]. Therefore, it is very desirable to understand the structure and corresponding catalytic activity of such ceria-supported vanadia catalysts. Indeed, tremendous efforts have been devoted to resolving their structure–activity relationship. By using high-resolution scanning tunneling microscopy (STM), some studies found that vanadium oxide species were highly dispersed as monomers on the ceria support under very low vanadium loadings, indicating that a strong interaction existed between the vanadia and ceria surfaces [28]. Moreover, subsequent studies highlighted that the ODH activity of VO_x/CeO_2 was affected by the loading of vanadium, with the VO_x monomers yielding much better performances than other larger oligomers, whereas vanadia supported on irreducible oxides, such as SiO_2 , exhibited the opposite result [17,18].

In an early work, Shapovalov et al. [29] studied the atomic structures of supported monomeric VO_x . They performed density functional theory (DFT) calculations to examine the properties of isolated VO_x ($x = 1\text{--}4$) clusters on rutile $\text{TiO}_2(110)$ and $\text{CeO}_2(111)$ surfaces. They proposed that the redox reactions occurring over the VO_x/CeO_2 catalysts should follow the Mars–van Krevelen mechanism because the oxidized substances take oxygen from VO_x , which is then oxidized by the gas-phase oxygen. Recently, Liu et al. [18] and Wu et al. [30,31] conducted DFT calculations to illustrate the catalytic activities of supported vanadia/ceria catalysts for the ODH reactions of alcohols. They found that the so-called characteristic new empty localized states (NELS) were crucial for the oxidation of methanol to formaldehyde. In particular, it was proposed that the presence of the NELS in the supported monomeric vanadia/ceria catalysts such as $\text{VO}_3/\text{CeO}_2(111)$ could drastically increase the hydrogen adsorption energy. Moreover, they are determined to be the most active species for the ODH reactions.

Though the ODH reactions of alcohols over supported vanadia/ceria catalysts have been studied in detail, the mechanism for the ODH of alkanes to olefins is still unclear, particularly regarding the detailed role of the catalytically active VO_x species in the ceria-supported system and its unique performance for this specific catalytic reaction. Therefore, with the aim to gain a deeper insight into the alkane ODH mechanism, in this study, we investigate the conversion of propane to propene mainly on the characteristic VO_3 cluster supported on $\text{CeO}_2(111)$ surface. Its catalytic activity and particularly the electronic effect of the NELS on the reaction selectivity are carefully examined and discussed.

2. Computational details

Spin-polarized DFT + U calculations were performed with the GGA-PW91 functional by using the Vienna Ab Initio Simula-

tion Package (VASP) [32,33]. The project-augmented wave (PAW) [34] method was used to describe the electron–core interaction, with Ce (5s, 5p, 6s, 5d, 4f), C and O (2s, 2p), and H (1s) electrons being treated as valence electrons. The on-site Coulomb interaction correction was necessary for the appropriate description of the localized 4f orbitals/electrons and related electronic and geometric properties of ceria. As suggested by Nolan and coworkers [35,36], in this work, the U value was set as 5 eV. The wavefunctions were expanded in the planewave basis set with a kinetic energy cut-off of 400 eV. The calculated lattice parameter of bulk ceria using the DFT + U method (5.445 Å) was in good agreement with the experimental value (5.411 Å) [37].

The $\text{CeO}_2(111)$ surface was modeled using a 12-atomic-layer slab, which represents a $p(3 \times 3)$ lateral cell, with the bottom three layers being fixed to the bulk parameters and other layers being allowed to fully relax. To avoid interactions between neighboring slabs, they were separated by a vacuum gap larger than 10 Å. The Brillouin-zone integration was performed with a $2 \times 2 \times 1$ Monkhorst–Pack grid for each surface. Transition states of the surface reactions were located by using the constrained optimization scheme [38]. The adsorption energy (E_{ads}) was calculated as follows:

$$E_{\text{ads}} = -(E_{\text{total}} - E_{\text{substrate}} - E_{\text{gas-phase adsorbate}})$$

where E_{total} is the calculated total energy of the adsorption system, $E_{\text{substrate}}$ is the energy of the clean substrate, and $E_{\text{gas-phase adsorbate}}$ is the energy of the gas-phase molecule.

3. Results and discussion

3.1. Monomeric VO_3 supported on $\text{CeO}_2(111)$ surface

To understand the mechanism of the ODH reactions of propane, it is important to know and build the structures of the $\text{VO}_x/\text{CeO}_2(111)$ catalysts. In the recent years, the atomic structures of supported VO_x species have been clarified with the assistance of DFT calculations. The identified most stable configurations of VO_x for given compositions ($x = 2\text{--}4$) have been well illustrated by different groups [29–31]. The calculated phase diagrams at an oxygen pressure of 0.21 atm show that VO_4 is the most stable species below 520 K, whereas VO_2 is the most stable one within a higher temperature range of 520–950 K. At ~520 K, these three different species are in close competition in terms of the stability. Particularly, supported VO_3 has a rather high H adsorption energy [31], indicating the unique role of VO_3 in the dehydrogenation processes. It is also interesting to note the existence of several different types of oxygen atoms on the $\text{VO}_3/\text{CeO}_2(111)$ catalyst, which may have different chemical activities.

The detailed structure of the supported $\text{VO}_3/\text{CeO}_2(111)$ catalyst is illustrated in Fig. 1. We can see that there are mainly three types of active oxygen atoms in this configuration, i.e., (1) singly coordinated terminal oxygen $\text{O}_{\text{V=O}}$, which is a terminal oxygen, (2) two-fold coordinated oxygen $\text{O}_{\text{V-O-Ce}}$, which bridges the V and Ce cations, and (3) three-fold coordinated oxygen $\text{O}_{\text{Ce-O-Ce}}$, which is simply a top-surface lattice O besides the adsorbed VO_3 . To identify the type of oxygen atom responsible for

Fig. 1. Top view of the calculated $\text{VO}_3/\text{CeO}_2(111)$ catalyst (insert: side view). The balls in dark blue represent V atoms, whereas those in cyan represent Ce atoms. Four different types of O atoms are labelled: the balls in yellow represent two types of oxygen atoms, namely, $\text{O}_{\text{V}=\text{O}}$ and $\text{O}_{\text{V}-\text{O}-\text{Ce}}$, at VO_3 , balls in green represent top-surface oxygen atoms $\text{O}_{\text{Ce}-\text{O}-\text{Ce}}$ on $\text{CeO}_2(111)$, and those in red are sub-surface oxygen atoms O_{sub} in $\text{CeO}_2(111)$.

the propane ODH reaction, we first modeled propane adsorption at these different sites on the $\text{VO}_3/\text{CeO}_2(111)$ surface.

3.2. C_3H_8 adsorption on the supported VO_3

The molecular adsorption of propane on the supported VO_x in different catalysts has been well investigated in previous studies [39–43]. It is widely believed that similar to methane, propane can only be weakly adsorbed on various catalysts. Therefore, the ODH reaction of propane to propylene may prefer to follow an Eley–Rideal type mechanism and breaking of the first C–H bond of the propane molecule can be considered as the rate-determining step.

In principle, the breaking of the first C–H bond can occur in the methyl ($-\text{CH}_3$) or methylene ($-\text{CH}_2$) group of the propane molecule, so that the corresponding adsorbed products are *n*-propoxide or *i*-propoxide species, respectively. It can be learned from the thermodynamic data that the C–H bond energy in the methyl group is higher than that in the methylene group (420 vs. 401 kJ/mol) [42]. In an early theoretical study, Gilardoni et al. [44] by performing DFT calculations also showed that the formation of *i*-propoxide was both thermodynamically and kinetically favored. Thus, in this work we only focused on the activation of the C–H bond, which leads to the formation *i*-propoxide.

In Fig. 2, we illustrate the calculated structures of dissociatively adsorbed propane in two possible configurations. As one can see, in the calculated structure shown in Fig. 2(a), *i*-propoxide is present on the surface $\text{O}_{\text{Ce}-\text{O}-\text{Ce}}$ and a H binds to the nearby $\text{O}_{\text{V}-\text{O}-\text{Ce}}$ of the supported VO_3 . In comparison, in the calculated structure shown in Fig. 2(b), the surface sites of

Fig. 2. Side view of the calculated dissociatively adsorbed C_3H_8 in two different configurations (a, b) on $\text{VO}_3/\text{CeO}_2(111)$. The H atoms are in white and C in dark grey color.

these two species are interchanged. The adsorption energies corresponding to these two dissociative adsorption configurations were determined to be 2.78 and 3.08 eV, respectively. The calculated adsorption energies indicate that the dissociative adsorption structure with the C_3H_7 moiety located at $\text{O}_{\text{V}-\text{O}-\text{Ce}}$ and H at a nearby surface $\text{O}_{\text{Ce}-\text{O}-\text{Ce}}$ is energetically favorable to form. From the side views of the two adsorption structures it is inferred that more favorable H bonding between $\text{H}-\text{O}_{\text{Ce}-\text{O}-\text{Ce}}$ and $\text{O}_{\text{V}-\text{O}-\text{Ce}}$ in the structure depicted in Fig. 2(b) compared with that between $\text{H}-\text{O}_{\text{V}-\text{O}-\text{Ce}}$ and $\text{O}_{\text{Ce}-\text{O}-\text{Ce}}$ in the structure presented in Fig. 2(a) may account for the difference in their stabilities. Moreover, we understand from the work of Wu et al. [30] that H adsorption at $\text{O}_{\text{Ce}-\text{O}-\text{Ce}}$ is also slightly stronger than that at $\text{O}_{\text{V}-\text{O}-\text{Ce}}$.

3.3. Activation of the C–H bonds in propane

In Fig. 3, we illustrate the calculated energy profiles for the formation of the two dissociative adsorption structures discussed above. It can be seen that these two dissociative adsorption processes are quite similar. They are both initiated by a weak propane adsorption (IS, $E_a = 0.18$ eV), following which the C–H bond breaking occurs in the methylene group (TS1 and TS2), resulting in an adsorbed H and a C_3H_7 radical in the gas phase (IM1 and IM2). The C_3H_7 radical then binds with different O atoms in the final state (FS1 and FS2). Significantly, it can be easily noticed that the calculated barrier for such C–H bond breaking is 0.26 eV in the first process (Fig. 3(a)), whereas it is as low as 0.12 eV in the second process (Fig. 3(b)).

The above results show that in agreement with the Bronsted–Evans–Polanyi relationship, both the dissociative adsorption energy and activation energy for the evolution of the propane molecule in path B are better than those in path A. For the breaking of the first C–H bond of the propane molecule at the interface of VO_3 and $\text{CeO}_2(111)$, the H is preferably left at the surface oxygen of the $\text{CeO}_2(111)$ support close to VO_3 and *i*-propoxide is formed at the interfacial oxygen of the supported VO_3 . In addition, we also believe that the high catalytic activity of the $\text{VO}_3/\text{CeO}_2(111)$ catalyst toward the first C–H breaking

Fig. 3. Calculated two reaction pathways for breaking the first C–H bond in C_3H_8 on $VO_3/CeO_2(111)$. (a) Path A; (b) Path B.

process in the propane ODH reaction is mainly owing to its unique electronic effect, which strongly favors the capture of a H atom, as we have discussed in a recent work [30]. In particular, the NELS being largely constituted of O 2p orbitals of the supported VO_3 are strongly involved in this first C–H bond breaking process similar to the manner in the oxidation of methanol to formaldehyde [30].

Similar to the complete propane ODH reaction, the second C–H bond is also needed to be broken in the adsorbed C_3H_7 to obtain the target product of propylene. In Fig. 4, we present the calculated reaction profiles for the further C–H bond activation of the dissociatively adsorbed propane. As one can see from the calculated structures, to break the second C–H bond, the *i*-propoxide at the supported VO_3 leaves one H atom of a methyl group to a nearby free O_{V-O-Ce} . From the calculated results, one can clearly find that the activation energy for the breaking this second C–H bond (1.81 eV) is much higher than that for the first one (0.12 eV). As a direct product, a C_3H_6 species is formed on the supported VO_3 (IM3). We then calculated and compared the energetics of the two possible pathways for the further

evolution of this intermediate state. As one can see from Fig. 4, C_3H_6 desorption as a propene molecule is much more favorable than the further breaking of the third C–H bond on the surface.

In Table 1, we list the calculated barriers for the first and second C–H bond breaking processes discussed above. We also list the calculated results of the same processes for propane and ethane on $V_2O_5(001)$ reported in previous studies by Fan and co-workers [45,46]. As it can be seen from the table, the calculated reaction barriers for both the first and second C–H bond breaking processes on the clean $V_2O_5(001)$ are quite high. More significantly, the first C–H bond typically appears to be more difficult to break than the second one for both propane and ethane; this is in agreement with the regular order of the bond strengths. Most interestingly, from our calculations, we can find that on the supported $VO_3/CeO_2(111)$ system, the first C–H bond breaking step is actually very easy to occur, which has an activation barrier of only 0.12 eV. In contrast, the second C–H bond breaking step is relatively significantly difficult with a barrier of 1.81 eV. To better understand the reason for the reversed activities toward C–H bond activation in alkanes, we conducted further electronic analyses for this interesting catalyst.

The partial electronic density of states (PDOS) for the five oxygen atoms constituting the NELS at $VO_3/CeO_2(111)$ were calculated (Fig. 5). It can be clearly seen from Fig. 5(a) that for the system with weakly adsorbed C_3H_8 on the clean $VO_3/CeO_2(111)$ surface, there is a high sharp peak above the Fermi level. As we have explained in a recent study [30], this corresponds to the empty states constituted mainly by the (empty) 2p orbitals of the O ions of the supported VO_3 as they

Fig. 4. Calculated reaction profiles for breaking more C–H bonds of C_3H_7 (continuing from the profile in Fig. 3(b)).

Table 1

Calculated lowest activation energies for the first (ΔE_{H1}) and second C–H bonds (ΔE_{H2}) of propane at $VO_3/CeO_2(111)$ and those for alkanes in the literature.

	$\Delta E_{H1}/\text{eV}$	$\Delta E_{H2}/\text{eV}$
C_3H_8 at $VO_3/CeO_2(111)$	0.12	1.81
C_3H_8 at $V_2O_5(001)$ [42]	1.18	0.96
C_2H_6 at $V_2O_5(001)$ [43]	1.48	1.34

Fig. 5. Calculated PDOS and side views of the key states in the first C–H bond breaking step for C_3H_8 on $\text{VO}_3/\text{CeO}_2(111)$. (a) C_3H_8 adsorption; (b) IM2; (c) FS2. The PDOS were calculated for the five oxygen atoms labelled as $\text{O}_{\text{V}=\text{O}}$, $\text{O}_{\text{V}-\text{O}-\text{Ce}}$, and $\text{O}_{\text{Ce}-\text{O}-\text{Ce}}$ in Fig. 1. The occupied states in the PDOS are filled in gray (spin-up) and black (spin-down), respectively, and the empty states are unfilled. Fermi levels (E_{F}) are marked by the red dash line.

fail to take enough electrons from the vanadium atom, which has five valence electrons only. Such unique NELS are located below the unoccupied $4f$ states of the ceria support in energy, which are then obviously more powerful in capturing electrons compared with the localized $4f$ states of the surface Ce cations. This is the simple reason for the very low activation barrier for the first C–H bond breaking process in the calculated propane ODH reaction. In comparison, such unique NELS are crucial for the H abstraction from propane, and in addition, we find that the NELS disappear immediately after the first C–H bond breaks on the $\text{VO}_3/\text{CeO}_2(111)$ surface. As it can be obviously seen from Fig. 5(b) and (c), the NELS practically vanish when the first H atom adsorbs on the O atom of CeO_2 and C_3H_7 radical remains in the gas phase, whereas there are nearly no NELS when the C_3H_7 radical adsorbs on an O of VO_3 . Therefore, these results clearly indicate that without the assistance of NELS, the breaking of the second C–H or any additional C–H bonds would be very difficult.

In fact, we also calculated the spin-polarized charge density (Fig. 6) of the important structures for the $\text{VO}_3/\text{CeO}_2(111)$ catalyst during the propane ODH reaction. It is well recognized that the unique NELS practically vanish when the first H atom adsorbs on the O atom of CeO_2 . Consistent with the radical nature of the C_3H_7 species in IM2, we determined the existence of a spin electron at this species (Fig. 6(a)). Interestingly, we then found that after the radical species binds to $\text{O}_{\text{V}-\text{O}-\text{Ce}}$, this spin electron transfers to the surface and localizes at one Ce cation. Thus, owing to the disappearance of the NELS, the $4f$ states capture the spin electron, converting the Ce cation to Ce^{3+} . Furthermore, for the system with co-adsorbed C_3H_6 and two H, which is a result of the second C–H bond breaking process (FS2, Fig. 4), we can observe that two spin electrons are localized at

Fig. 6. Calculated spin-polarized charge densities (in purple) of the important structures for the $\text{VO}_3/\text{CeO}_2(111)$ catalyst during the propane ODH reaction.

two Ce cations and one spin electron remains in the double bond of C_3H_6 (Fig. 6(c)). These results clearly indicate that the Ce $4f$ orbitals would be the only empty states to accommodate the transferred electrons from H and other moieties during the further dissociation of C_3H_7 , and the obvious repulsions between the crowded localized $4f$ electrons may strongly inhibit further dissociation of other adsorbents like C_3H_6 .

Finally, it needs to be mentioned that as another important VO_x species on $\text{CeO}_2(111)$, the VO_4 cluster can form via O_2 adsorption on VO_2 , which forms after the VO_3 species results in water formation and desorption. Moreover, the $\text{VO}_4/\text{CeO}_2(111)$ catalyst contains more NELS than VO_3 , which can capture altogether three extra electrons. Therefore, such NELS of VO_4 may be effective in the two successive C–H bond breaking processes of propane, and in particular, they should be able to significantly reduce the barrier for the breaking of the C–H bond in the adsorbed C_3H_7 . Nevertheless, the further dissociation of C_3H_6 would still be inhibited without their assistance.

4. Conclusions

In summary, we present a comprehensive theoretical study of the mechanism for the oxidative dehydrogenation reaction of propane over VO_3 supported on $\text{CeO}_2(111)$. We propose that the extraordinary catalytic performance of $\text{VO}_3/\text{CeO}_2(111)$ for breaking the first C–H bond of propane is mainly owing to the unique new empty localized states, which can capture one electron easily. After the disappearance of the NELS, it is difficult for the $\text{VO}_3/\text{CeO}_2(111)$ catalyst to break the second C–H bond of propane because the less favorable empty $4f$ states of Ce cations become a reservoir for the other electron. Therefore, this work illustrates that the varied abilities of the involved NELS and Ce- $4f$ in the different C–H bond breaking processes contribute to both the specific activity and selectivity of supported VO_x/CeO_2 catalysts for the ODH reactions of alkanes.

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Graphical Abstract

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Activity and selectivity of propane oxidative dehydrogenation over VO₃/CeO₂(111) catalysts: A density functional theory study

Chang Huang, Zhi-Qiang Wang, Xue-Qing Gong *

East China University of Science and Technology

The new empty localized states of VO₃/CeO₂(111) can assist the breaking of the first C–H bond of the propane molecule, following which they become occupied and the remaining C–H bonds become increasingly difficult to break.

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VO₃/CeO₂(111) 催化剂上丙烷氧化脱氢反应活性和选择性的密度泛函理论研究

黄昶[†], 王志强[†], 龚学庆^{*}

华东理工大学化学与分子工程学院, 计算化学中心, 结构可控先进功能材料及其制备教育部重点实验室, 上海 200237

摘要: 低碳烯烃一直以来都是化工行业非常重要的基础原料, 一般采用烷烃直接热裂解制得, 但该方法耗能很大, 经济价值有限. 近年来, 人们开始尝试利用氧化脱氢反应 (ODH) 方法制备低碳烯烃, 并取得了巨大的研究进展, 其中稀土氧化物负载钒氧化物催化剂具有良好的低碳烷烃氧化脱氢性能. 本文分析了前人对于钒氧化物负载在 CeO₂ 表面的计算研究结果, 并选取了最具代表性的 VO₃/CeO₂(111) 作为烷烃 ODH 制烯烃的模型催化剂, 详细研究了丙烷在该催化剂体系中发生 ODH 反应机理. 通过使用密度泛函理论, 对丙烷在 VO₃/CeO₂(111) 催化剂上断裂第一根和第二根碳氢键的反应过程进行了理论模拟, 并对比了丙烷制丙烯中碳氢键断裂先后的活化能及 VO₃/CeO₂(111) 催化剂材料自身的电子性质. 结果表明, 该催化剂的电子结构在丙烷氧化脱氢反应中扮演关键角色. 在丙烷分子断裂第一根碳氢键的反应过程中, 会产生两个自由电子, 对其电子结构分析发现, 其中的一个自由电子会局域在由 VO₃/CeO₂(111) 催化剂中五个相关氧原子的 2p 轨道所形成的新发生局域空轨道 (NELS) 上, 这个独特的新发生局域空轨道只能接受一个电子, 另一个电子则会通过丙基在 CeO₂ 表面发生吸附将电子传递到 CeO₂ 表面的 Ce 原子上; 当丙烷分子进一步发生第二根碳氢键断裂反应时, 同样会产生两个新的局域电子, 其中一个电子局域在 Ce 的 4f 轨道上, 此时 CeO₂ 表面存在两个局域电子, 相互排斥, 导致该催化剂上丙烷断裂第二根碳氢键所需的活化能远高于第一根碳氢键. 综上, 本文对 VO₃/CeO₂(111) 催化剂上低碳烷烃 ODH 反应独特的催化活性和选择性给出了较为细致的分析和解释.

关键词: 氧化脱氢; 丙烷制丙烯; C–H 键活化; 氧化铈负载钒基催化剂; 密度泛函理论计算

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*通讯联系人. 电话: (021)64252623; 传真: (021)64253457; 电子信箱: xgong@ecust.edu.cn

[†]共同第一作者.

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