DFT studies on the activation of C–H bonds on V/P mixed oxides

Gang Fu *, Ruming Yuan, Pei Wang, Huilin Wan #

State Key Laboratory for Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, Fujian, China

ARTICLE INFO

Article history:
Received 2 April 2015
Accepted 17 June 2015
Published 20 September 2015

Abstract

We carried out DFT calculations on the activation of C–H bonds on V/P mixed oxides. A set of oxo clusters, $V_xP_{10-x}$ ($x = 0–4$), used as model catalysts showed that the PO–H bond was stronger than the VO–H bond and the proton was preferentially bonded to the P=O bond. However, for alkane activation, the P=O was not the active site as expected because the activation requires a large reorganization energy. In addition, the results showed that the P=O bond played a role in the activation of intermediates with a more acidic C–H bond, such as 2-butene and 2,5-dihydrofuran.

© 2015, Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Published by Elsevier B.V. All rights reserved.

Keywords:
Density functional theory
Selective oxidation
Light alkanes
H atom abstraction
Vanadium/Phosphorus mixed oxide
Cluster model

1. Introduction

'Conventional' and 'unconventional' (such as shale gas, coal bed gas, etc.) natural gas are abundant on our planet. Natural gas is a gas mixture consisting of light alkanes (C1–C4) which has a higher hydrogen to carbon ratio than oil and coal. Thus, developing efficient strategies for the conversion of these 'cheap' and 'clean' resources to liquid fuel or value added chemicals is a challenge.

Currently, the well-established technology uses an indirect route: (1) production of syngas (CO + H2) by the steam reforming of natural gas and (2) conversion of syngas into value added products through processes such as Fischer-Tropsch synthesis [1,2]. However, this technology is chemically inelegant [3] since alkanes are firstly over-oxidized to CO, only to be then reduced to the desired products. In contrast, a direct route, e.g., selective oxidation of light alkanes, in principle, would proceed more efficiently and cost effectively. In addition to the well-known industrial process of the oxidation of $n$-butane to maleic anhydride, some other important examples under active investigation are methane partial oxidation (MPO), oxidative dehydrogenation (ODH), and oxidation of propane to acrylonitrile [4].

Effective catalysts for the selective oxidation of alkane are multi-component oxides composed of more than two elements of which at least one is a transition metal with a variable valence (most often V, Mo or Fe) and another is a main group non-metal element (such as P, S, Se, or Te) [5]. There are a number of successful catalysts varying from binary vanadium phosphorus oxides (VPO) to the more complicated four-component MoVTeNbO x catalysts [5]. The former is used commercially in the manufacture of maleic anhydride, while the latter has shown promise in the oxidation of propane to acrylic acid.

* Corresponding author. Tel: +86-13625012808; Fax: +86-592-2183047; E-mail: gfu@xmu.edu.cn
# Corresponding author. Tel: +86-592-2182651; Fax: +86-592-2183047; E-mail: hlwan@xmu.edu.cn

This work was supported by the National Natural Science Foundation of China (21373167, 21133004), the Program for Innovative Research Team in Chinese Universities (IRT_14R31), and the Fundamental Research Funds of Central Universities.

Much effort has been made to understand the chemical and structural properties of their key elements and how they function. It is widely accepted that the high valence transition metal oxo bond (M=O) was involved in alkane activation, while the non-metal oxo bond (NM=O) may not be involved in the initial activation [6]. However, recent theoretical works have disclosed that the NM=O bond could be more active than the M=O bond towards alkane C–H bond activation [7–10]. Xu et al. [7,8] suggested that the H atom is preferentially adsorbed on the Te=O moiety rather than the V=O or Mo=O moieties on the M1 phase of MoVTeNbOx catalysts. Goddard et al. [9,10] pointed out that in VOPO4, the P=O moiety can activate the C–H bond in n-butane. Clearly, these pictures are in sharply contrast to the traditional view that the active center is the M=O moiety.

In previous works [11–14], we investigated the activation of light alkanes on single component transition metal oxides, such as MoO3, V2O5, Cr2O3 and WO3. We proposed that the activation of a C–H bond proceeded via the H abstraction mechanism and emphasized the role of the O–H bond strength in determining the reactivity of the metal oxide. In this contribution, we would compare the reactivity of the V=O and P=O moieties in V/P mixed oxides to discuss their intrinsic difference by density functional theory (DFT).

2. Computational details

We chose neutral heteronuclear o xo clusters (V4–xP2O10, x = 1–3) as model catalysts (Fig. 1). For comparison, homonuclear V4O10 and P4O10 clusters were also considered. Similar cluster models have been successfully applied to the modeling of a variety of transition metal oxide catalyzed systems [15–18].

The quantum calculations were performed at the level of B3LYP/6–311+G(2d, 2p) [19–23]. Geometries were fully optimized and vibrational frequencies were analytically computed in order to confirm that a local minimum has no imaginary frequency and that a transition state (TS) has only one imaginary frequency. The zero point energy correction has been included with no empirical scaling. The energetics were re-optimized. Our calculations showed that no significant changes were found for the optimized geometries as compared to those from B3LYP. From the energetic aspect, BEs of the alkane C–H bond were calculated to be almost equal with these two methods. However, M06 underestimated BE(OH) by 5–8 kcal/mol as compared with B3LYP. As a result, the barrier predicted by M06 was 4–7 kcal/mol higher than that by B3LYP. Nevertheless, all the key points deduced from B3LYP were further confirmed by M06.

All calculations were carried out with the Gaussian 09 package [29].

3. Results and discussion

3.1. Comparison of the electronic properties of the V=O and P=O moieties V/P mixed oxides

C–H bond activation by oxo species (X=O; X is a transition metal or non-metal) usually proceeds through a H abstraction process leading to the forming of an O–H bond and breaking of a C–H bond, shown in Eq. (1).

\[ \text{X}=\text{O} + \text{H–R} \rightarrow \text{X}–\text{O}–\text{H} + \text{R} \]  \hspace{1cm} (1)

The reaction enthalpy (\(\Delta H\)) can be evaluated by simply calculating the difference of their binding energies (BEs):

\[ \Delta H = \text{BE}(\text{C–H}) - \text{BE}(\text{O–H}) \]  \hspace{1cm} (2)

For a hydrocarbon, the BE of the C–H bond is constant and the reaction is critically dependent on the strength of the O–H bond. Based on the Hammond postulate, a stronger O–H bond formed has a more rapid reaction between the hydrocarbon and X=O. As shown in Table 1, the BE(O–H) for the V=O moiety varies in a narrow range (67.4 to 69.8 kcal/mol) for V4O10 and...

---

**Huilin Wan** (Xiamen University) received the Catalysis Achievement Award (the Dayu Zhang Award) in 2011 presented by The Catalysis Society of China. Professor Huilin Wan graduated from Department of Chemistry, Xiamen University in 1966, and completed his graduate study in the same university in 1966. He was a visiting scholar at Department of Chemistry, Massachusetts Institute of Technology (1982.3-1983.4). In 1997, he was elected member of the Chinese Academy of Science. Currently, he is the director of the Academic Committee on Science & Engineering at Xiamen University, director of the Academic Committee of State Key Laboratory of Physical Chemistry of Solid Surfaces and member of the Advisory Panel of National Basic Research Program of China (973 Program) of the Ministry of Science and Technology. His research interests include (1) selectively oxidative conversion of light alkanes; (2) in situ and dynamic spectroscopic characterization; and (3) theoretical modeling of catalytic reactions and mechanisms. He has published more than 350 papers, and won 2 National Natural Science Awards of the third class, two and three Science and Technology Progress Awards of the Education Ministry of the first and the second class, respectively, and 15 national patents.
the V/P mixed oxides. In contrast, the BE (O–H) for the P\textsubscript{4}O\textsubscript{10} moiety was predicted to be as low as 18.4 kcal/mol. This appeared to be due to that the pure P oxide is hard to reduce as its lowest unoccupied molecular orbital (LUMO) has a dominant P–O σ\* character, which is high lying. However, BE [O–H] was significantly enhanced for the V/P mixed oxides. To our surprise, the calculated BE for the PO–H moiety was even 6–10 kcal/mol stronger than that of the VO–H bond, indicating that the P=O moiety could be superior to the V=O moiety in the C–H bond activation. It should be noted that upon PO–H bond formation, the P atom maintained its valence of +5, while the nearby V was reduced from +5 to +4, which was shown in Eq. (3).

\[
\begin{align*}
\text{V} & \text{ P} \text{ O} \text{ (H)} \quad \text{V} \text{ O} \text{ (H)} \\
\text{V} & \text{ P} \text{ O} \text{ (H)} \quad \text{V} \text{ O} \text{ (H)} \\
\end{align*}
\]

(3)

In terms of proton-coupled electron transfer (PCET) [30–32] theory, a H atom can be viewed as a combination of an electron and a proton such that both the electron affinity (EA) and the proton affinity (PA) contribute to the strength of an O–H bond. Table 1 also listed the EAs of the different oxides, and the PAs for the different oxo moieties. We can see that for V\textsubscript{3}O\textsubscript{10}, the EA and PA were calculated as 103.4 and 178.0 kcal/mol, respectively. In contrast, P\textsubscript{4}O\textsubscript{10} have a very low EA (58.2 kcal/mol) and a weak PA (162.6 kcal/mol), leading to a weak PO–H bond. As compared with V\textsubscript{4}O\textsubscript{10} and P\textsubscript{4}O\textsubscript{10}, V/P mixing enhanced not only the EA but also the PA. The general trends can be summarized as follows: (1) the EA increased with the increase of the ratio of P, while the PA showed the opposite trend; (2) for an oxo group, the PA can be correlated with the NBO charge of the terminal oxygen \((R^2 = 0.956)\); (3) the EA correlated well with the NBO charge of V \((R^2 = 0.999)\); (4) for a given mixed oxide, the PA of the P=O moiety was favored over that of the V=O moiety by about 20 kcal/mol, which made it a better H abstractor rather than the V=O moiety.

Why do V/P mixed oxides have larger EAs and PAs compared to the pure counterparts, such as V\textsubscript{4}O\textsubscript{10} and P\textsubscript{4}O\textsubscript{10}. We proposed that the properties of the V and P centers were correlated well with the NBO charge of V \((R^2 = 0.999)\); (4) for a given mixed oxide, the PA of the P=O moiety was favored over that of the V=O moiety by about 20 kcal/mol, which made it a better H abstractor rather than the V=O moiety.

### Table 1
Predicted electronic properties of V\textsubscript{x}P\textsubscript{y}O\textsubscript{z} \((x = 0–4)\) clusters (energy in kcal/mol and NBO charge in a.u.).

<table>
<thead>
<tr>
<th>V/P oxide</th>
<th>EA</th>
<th>Charge of V</th>
<th>BE(O–H)</th>
<th>Charge of O</th>
<th>PA</th>
<th>BE(O–H)</th>
<th>Charge of O</th>
<th>PA</th>
</tr>
</thead>
<tbody>
<tr>
<td>V\textsubscript{4}O\textsubscript{10}</td>
<td>103.4</td>
<td>1.036</td>
<td>69.8</td>
<td>-0.238</td>
<td>178.0</td>
<td>77.4</td>
<td>-0.995</td>
<td>191.4</td>
</tr>
<tr>
<td>V\textsubscript{3}PO\textsubscript{10}</td>
<td>105.9</td>
<td>1.048</td>
<td>67.7</td>
<td>-0.230</td>
<td>170.4</td>
<td>76.1</td>
<td>-0.986</td>
<td>183.2</td>
</tr>
<tr>
<td>V\textsubscript{2}P\textsubscript{2}O\textsubscript{10}</td>
<td>109.7</td>
<td>1.068</td>
<td>67.4</td>
<td>-0.222</td>
<td>162.3</td>
<td>75.3</td>
<td>-0.980</td>
<td>174.0</td>
</tr>
<tr>
<td>VP\textsubscript{3}O\textsubscript{10}</td>
<td>116.1</td>
<td>1.100</td>
<td>69.1</td>
<td>-0.220</td>
<td>153.1</td>
<td>18.4</td>
<td>-0.975</td>
<td>162.6</td>
</tr>
<tr>
<td>VP\textsubscript{4}O\textsubscript{10}</td>
<td>119.0</td>
<td>1.120</td>
<td>69.8</td>
<td>-0.218</td>
<td>143.2</td>
<td>18.4</td>
<td>-0.975</td>
<td>162.6</td>
</tr>
<tr>
<td>VP\textsubscript{5}O\textsubscript{10}</td>
<td>121.9</td>
<td>1.140</td>
<td>70.5</td>
<td>-0.216</td>
<td>134.3</td>
<td>18.4</td>
<td>-0.975</td>
<td>162.6</td>
</tr>
<tr>
<td>VP\textsubscript{6}O\textsubscript{10}</td>
<td>124.8</td>
<td>1.160</td>
<td>71.2</td>
<td>-0.214</td>
<td>125.4</td>
<td>18.4</td>
<td>-0.975</td>
<td>162.6</td>
</tr>
<tr>
<td>VP\textsubscript{7}O\textsubscript{10}</td>
<td>127.7</td>
<td>1.180</td>
<td>71.9</td>
<td>-0.212</td>
<td>116.5</td>
<td>18.4</td>
<td>-0.975</td>
<td>162.6</td>
</tr>
<tr>
<td>VP\textsubscript{8}O\textsubscript{10}</td>
<td>130.6</td>
<td>1.200</td>
<td>72.5</td>
<td>-0.210</td>
<td>107.6</td>
<td>18.4</td>
<td>-0.975</td>
<td>162.6</td>
</tr>
<tr>
<td>VP\textsubscript{9}O\textsubscript{10}</td>
<td>133.5</td>
<td>1.220</td>
<td>73.2</td>
<td>-0.208</td>
<td>98.7</td>
<td>18.4</td>
<td>-0.975</td>
<td>162.6</td>
</tr>
<tr>
<td>VP\textsubscript{10}O\textsubscript{10}</td>
<td>136.4</td>
<td>1.240</td>
<td>73.9</td>
<td>-0.206</td>
<td>90.8</td>
<td>18.4</td>
<td>-0.975</td>
<td>162.6</td>
</tr>
</tbody>
</table>

*EA = ΔH(X=O) – ΔH(X=O–H).*

*BE(O–H) = ΔH(X=O) + ΔH(H) – ΔH(X–O–H).*

*PA = ΔH(X=O) + ΔH(H+) – ΔH(X–O–H–).*

### Table 2
Activation barrier, reaction enthalpy, and the imaginary frequency of the TS for H abstraction from a methylene C–H bond of n-butane by V\textsubscript{x}P\textsubscript{y}O\textsubscript{z} \((x = 0–4)\) clusters.

<table>
<thead>
<tr>
<th>V/P oxide</th>
<th>(\Delta H^*) [kcal/mol]</th>
<th>(\Delta E) [kcal/mol]</th>
<th>Imaginary frequency [cm(^{-1})]</th>
<th>P=O</th>
</tr>
</thead>
<tbody>
<tr>
<td>V\textsubscript{4}O\textsubscript{10}</td>
<td>25.3</td>
<td>25.3</td>
<td>1821.7</td>
<td>17.7</td>
</tr>
<tr>
<td>V\textsubscript{3}PO\textsubscript{10}</td>
<td>27.4</td>
<td>26.2</td>
<td>1781.8</td>
<td>19.0</td>
</tr>
<tr>
<td>V\textsubscript{2}P\textsubscript{2}O\textsubscript{10}</td>
<td>27.7</td>
<td>25.6</td>
<td>1698.8</td>
<td>19.8</td>
</tr>
<tr>
<td>VP\textsubscript{3}O\textsubscript{10}</td>
<td>26.0</td>
<td>23.7</td>
<td>1606.6</td>
<td>23.6</td>
</tr>
</tbody>
</table>

*Reaction heat is estimated according to Eq. (2).*
The barrier was as high as 78.6 kcal/mol. For the V/P mixed oxides, the following trends can be noted: (1) the barrier of H abstraction by the V=O moiety decreased with the increase of the ratio of P; (2) there was only a small difference in the barrier for H abstraction by the P=O moiety, which varied from 23.0 to 24.3 kcal/mol; (3) the P=O moiety was only 0.7–1.3 kcal/mol more active than the V=O moiety, which was far less than the difference in the strength between the PO–H and the VO–H bond (6–10 kcal/mol). The last point was further confirmed by M06, which predicted that the differences in the barrier and reaction enthalpy were 1.4–2.7 and 8–13 kcal/mol, respectively.

Why was the P=O moiety less active than expected? To answer this question, we further considered H abstraction from a range of light alkanes (C1–C4), representing the primary, secondary, tertiary C–H bond respectively, by the P=O moiety and compared these with those by the V=O moiety. For this, V2P2O10 was chosen as the model as the ratio of V/P is equal to 1, consistent with formula of VPO catalysts. The calculated barriers were summarized in Table 3. For a given C–H bond, H abstraction by the P=O moiety was always favored over that by the V=O moiety although the difference between them was quite small (0.7–1.3 kcal/mol). Fig. 3 plotted the correlation of the calculated barrier versus the calculated enthalpy of the different C–H bonds (Polanyi correlation [30]). We found that the barrier of H abstraction by the V=O moiety correlated well with the enthalpy (R² = 0.996) with a slope of 1.19. For the case of the P=O moiety, good linearity (R² = 0.999) with a similar slope (1.23) was observed but the intercept differed by 6.2 kcal/mol. Interestingly, a similar linear correlation was also obtained by using M06 in which the difference in the intercept was in-

<table>
<thead>
<tr>
<th>Light alkane</th>
<th>C–H bond energy</th>
<th>V=O</th>
<th>Imaginary frequency (cm⁻¹)</th>
<th>P=O</th>
<th>Imaginary frequency (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃–H</td>
<td>103.3</td>
<td>36.0</td>
<td>1891.5i</td>
<td>34.8</td>
<td>1686.9i</td>
</tr>
<tr>
<td>C₂H₅–H</td>
<td>98.7</td>
<td>30.2</td>
<td>1830.7i</td>
<td>29.0</td>
<td>1510.6i</td>
</tr>
<tr>
<td>(CH₃)₂CH–H</td>
<td>95.0</td>
<td>25.6</td>
<td>1710.2i</td>
<td>24.7</td>
<td>1518.0i</td>
</tr>
<tr>
<td>(CH₃)(C₂H₅)CH–H</td>
<td>95.1</td>
<td>25.6</td>
<td>1698.8i</td>
<td>24.3</td>
<td>1382.5i</td>
</tr>
<tr>
<td>(CH₃)₃C–H</td>
<td>92.3</td>
<td>22.5</td>
<td>1626.0i</td>
<td>21.8</td>
<td>1386.5i</td>
</tr>
</tbody>
</table>

Fig. 2. Optimized TS structures for n-butane activation by V₄–PₓO₁₀ (x = 0–4) clusters (bond length in Å).

Fig. 3. Plot of the calculated H abstraction barrier versus reaction enthalpy.
creased to 11.3 kcal/mol. This means that at the same bond enthalpy, more energy was required for the P=O moiety than the V=O moiety for the hydrocarbon to pass through the barrier. Hence, there was an intrinsic difference in the reactivity of the two moieties.

In the classical Marcus model [33,34], the potential energy surface can be approximated by parabolas, and the intersection of these parabolas represents a transition state (Fig. 4). There are two main factors that affect the barrier, namely, the stability of the product and sharpness of the curves. The first is related to the enthalpic driving force. Clearly, a more stable product indicates a more favorable reaction. To estimate the sharpness of the curve, we use the energy change of the $V_xP_xO_{10}$ moiety from the reactant structure to the TS structure at the reactant electronic state. In this case, single point calculations were performed and the zero point energy and thermal correction were not included. Our calculations showed that only 9.6 kcal/mol was required for V=O, while P=O required 18.2 kcal/mol. This indicated that P=O underwent more distortion during the process. The sharpness of curve is also related to the reorganization energy ($\lambda$). In our case, only the electron transfer between R–H and the V/P mixed oxide was considered since the Marcus theory is based on an outer sphere electron transfer. Our calculations showed that $\lambda_R$ was the same for abstraction by V=O and P=O as they involved the same vertical excitation with the reactant structure. The difference between these two processes was in the $\lambda_P$. Here, we extracted the $V_xP_xO_{10}$ moieties from the product structures, and used the energy difference between the anion and neutral clusters of $V_xP_xO_{10}$ to estimate $\lambda_P$. Again, single point calculations were performed. Our calculations showed that for P=O, $\lambda_P$ varied from 128 to 140 kcal/mol, which were 21–23 kcal/mol higher than that for V=O. Thus, the small difference in the barrier could be understood by that abstraction by P=O had a more favorable reaction enthalpy but involved a larger reorganization energy. It should be pointed out that besides the enthalpic driving and reorganization energy, the electronic coupling at the intersection zone, i.e., $|H_{AB}|$, would also affect the barrier. The influence of the interaction energy and orbital interaction were included in the $|H_{AB}|$ term.

### 3.3. Comparison of the reactivity of V=O and P=O for the activation of different C–H bonds

For the selective oxidation of n-butane to maleic anhydride, the olefinic mechanism is widely accepted [35] where n-butane is consecutively oxidized to 2-butene, butadiene, 2,5-dihydrofuran, crotonolactone, and finally MA. During this process, eight H atoms are removed consecutively. To investigate the reactivity of the V=O and P=O moieties for the different kinds of C–H bonds, we extended our scope to include 2-butene, 2,5-dihydrofuran and crotonolactone.

Figure 5 displayed the optimized H abstraction TS structures for the key intermediates. Fig. 6 depicted the differences...
in the barrier with the V=O and P=O moieties. For n-butane, the difference in the barrier was only 1.3 kcal/mol, indicating that the V=O and P=O moieties were competitive in the initial activation. In contrast, the P=O moiety played a determining role when 2-butene and 2,5-dihydrofuran were involved as the gap between the barriers was increased to 6–7 kcal/mol. Subsequently, the difference in the barrier for crotonolactone was reduced to 2.5 kcal/mol, indicating that the V=O moiety became competitive again.

The variation in the energy differences can be explained by the nucleophilicity of the terminal O atom. NBO analysis showed that the O atom in the P=O moiety was a better nucleophile than that of the V=O moiety (−1.0 a.u. versus −0.2 a.u.) (Table 1). Thus, the P=O moiety would be preferentially attacked by a substrate with a more acidic C–H bond. According to Evens’ pKa [36] values, the allylic C–H bond has a stronger acidity than that of the alkylic C–H bond (43 versus 50) such that 2-butene and 2,5-dihydrofuran were easier to be activated by the P=O moiety rather than by the V=O moiety. For crotonolactone, the electrostatic repulsion between the substrate and the oxide should be taken into account, which would destabilize the TS on the P=O moiety more than that on the V=O moiety.

4. Conclusions

The activation of C–H bonds on V/P mixed oxides was studied by hybrid density functional theory (B3LYP). H abstraction can be viewed as a proton-coupled electron transfer. For V/P mixed oxides, V$^{5+}$ can act as the electron acceptor while either the V=O or P=O moiety can serve as the proton acceptor. Preferential protonation on the P=O group made the PO–H bond 6–10 kcal/mol more stable than the VO–H bond. For alkane activation, the H abstraction barrier on both the V=O and P=O moieties correlated well with the reaction enthalpy but the intercept of the linear regression differed by 6 kcal/mol. This indicated that the P=O moiety was not as active as expected from the strength of the PO–H bond. The difference between the V=O and P=O moieties were due to the reorganization energy. For the V=O moiety, the change from the reactant structure to the TS structure underwent more distortion, resulting in a larger reorganization energy. The O in the P=O moiety was more nucleophilic than that of the V=O moiety such that it would be preferentially attacked by substrates with a more acidic C–H bond, such as 2-butene and 2,5-dihydrofuran. In contrast, when the C–H bond had weak acidity, e.g., n-butane, both the V=O and P=O moieties can perform the activation.

References


Graphical Abstract

DFT studies on the activation of C–H bonds on V/P mixed oxides

Gang Fu *, Ruming Yuan, Pei Wang, Huilin Wan *

Xiamen University

DFT calculations on the activation of C–H bonds on V/P mixed oxides with a set of oxo clusters, $V_{x}P_{y}O_{z}$ ($x, y = 0–4$), showed that the PO–H was stronger than the VO–H as the proton was preferentially bonded to the P=O bond. For alkane activation, the P=O bond was not as active as expected because the activation requires a large reorganization energy. The P=O bond played a role in the activation of intermediates with a more acidic C–H bond, such as 2-butene and 2,5-dihydrofuran.
关键词表明活化能的差距增加为反应的能垒不仅取决于反应焓变，还与内部重组能有关。

这些理论研究可以加深我们对复合氧化物催化剂上活性位点的认识，并为催化剂的理性设计提供理论支撑。