This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
The Roles of Surface Structure, Oxygen Defects, and Hydration in the Adsorption of CO\textsubscript{2} on Low-Index ZnGa\textsubscript{2}O\textsubscript{4} Surfaces: A First-Principles Investigation

Chuanyi Jia \textsuperscript{a,b}, Weiliu Fan \textsuperscript{a)\ast}, Xiufeng Cheng \textsuperscript{b)}, Xian Zhao \textsuperscript{b)}, Honggang Sun \textsuperscript{b)}, Pan Li \textsuperscript{b)}, and Na Lin \textsuperscript{b)}

\textit{a) School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100 China}

\textit{b) State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100 China}

\textbf{ABSTRACT:} The effects of the surface atomic and electronic structure, oxygen defects, and hydration on CO\textsubscript{2} adsorption on ZnGa\textsubscript{2}O\textsubscript{4} (100), (110), and (111) surfaces was studied using density functional theory (DFT) slab calculations. For the perfect (100) surface, the most stable adsorption state involved the Zn–O–Ga bridge site, with an adsorption energy of 0.16 eV. In the case of the (110) and (111) surfaces, the strongest binding occurred on the Zn–O bridge sites, with much lower adsorption energies of -0.22 eV and -0.35 eV, respectively. In addition, the perfect surfaces showed CO\textsubscript{2} activation ability, but dissociation adsorption could not proceed. The oxygen vacancies on these three surfaces (1) made the metal sites beside them carry less positive charge and further reduced the adsorption energies on these metal sites, and (2) created efficient adsorption sites that allowed even dissociative adsorption. The most favorable molecular and dissociative adsorption states both involved the O\textsubscript{3c} vacancy site of the (100) surface, and these two processes were spontaneous with adsorption energies of 0.74 eV and 0.80 eV, respectively. When H\textsubscript{2}O molecules are

\textsuperscript{\ast} To whom all correspondences should be addressed. Tel: 86-531-88366330, Fax: 86-531-88364864, E-mail: fw1@sdu.edu.cn.
present on the perfect and defective surfaces, the generation of hydrogen bonds between H$_2$O and CO$_2$ would slightly enhance the stability of adsorption (except for that on the (111)-Vo$_{3e}$ surface), making it energetically favorable. However, the co-adsorption of H$_2$O could also increase the energy barriers for the decomposition reactions on the defective surfaces, making them kinetically unfavorable. Furthermore, the oxygen vacancy defects showed good activity for H$_2$O adsorption and decomposition, as well. Thus, when H$_2$O and CO$_2$ were both present in the adsorption system, H$_2$O would compete with CO$_2$ for the oxygen vacancy sites and further decrease the amount of CO$_2$ adsorption and decomposition. These findings have important implications regarding the decomposition of CO$_2$ on the ZnGa$_2$O$_4$ surfaces and can provide theoretical guidance for chemists to efficiently synthesize ZnGa$_2$O$_4$ catalysts.

1. INTRODUCTION

With the increasing greenhouse effect and energy crises,$^{1-3}$ there has been increased interest in the development of environmentally clean and safe processes that can be used to expand our energy infrastructure. Because CO$_2$ produced by human activities is the chief greenhouse gas, it will be of great concern to find a way to remove this compound from the atmosphere. Therefore, there is considerable impetus to investigate the potential usefulness of carbon dioxide as a reactant in hydrocarbon synthesis.

Recently, researchers have studied the conversion of CO$_2$ over various modified or
unmodified forms of catalysts,\textsuperscript{4-7} among which semiconductor photocatalysts have got much attention for their potential applications in green energy and environmental cleanup.\textsuperscript{8-12} It have been three decades since photocatalytic reduction of CO\textsubscript{2} to formic acid, formaldehyde, methanol, and methane as the main products was first demonstrated.\textsuperscript{13} From then on, many efforts have been devoted to developing efficient photocatalysts for the reduction of CO\textsubscript{2}. The structure dependence of the reaction rates and the selectivity of heterogeneous catalytically active sites are growing into new popular fields of study.\textsuperscript{14,15} Moreover, surface defects and hydration are often considered to be important for heterogeneous catalysis as well, since these particular factors also play important roles in the reactant-surface binding and the formation of bonds between the surface atoms and CO\textsubscript{2} molecules.\textsuperscript{16-20} However, many of the previous studies were focused on the addition of transition metals or co-catalysts to improve the catalytic efficiency.\textsuperscript{21-27} The morphology, defects, and hydration of the catalyst, however, have rarely been considered. To gain more understanding of the influences of these factors, we need to carry out further research to determine the relationship between the microstructure and reaction activity of the catalysts.

As a typical ternary oxide, zinc gallate (ZnGa\textsubscript{2}O\textsubscript{4}) has good activity for water splitting, pollutants degradation, and so on.\textsuperscript{28-32} Recently, well-designed ZnGa\textsubscript{2}O\textsubscript{4} catalysts were also found to show good photocatalytic activity for the reduction of CO\textsubscript{2} to renewable hydrocarbon fuel (CH\textsubscript{4}) in the presence of water vapor.\textsuperscript{33} Therefore, the interaction of CO\textsubscript{2} with ZnGa\textsubscript{2}O\textsubscript{4} surfaces is a subject of great interest, not only for fundamental research but also for industrial engineering. However, because of the
great complexity of the ZnGa$_2$O$_4$ surface structure, a clear and general picture of the interaction between CO$_2$ molecules and the ZnGa$_2$O$_4$ surfaces is not yet available. Moreover, some former studies indicated that dissociative adsorption, CO$_2$ → CO + O, was particularly crucial for the process of CO$_2$ decomposition.$^{34-38}$ Therefore, identifying the reaction mechanisms (especially the mechanism of dissociative adsorption) and the effect of the surface structure, defects, and hydration on CO$_2$ activation and decomposition will have important implications regarding the photoreduction of CO$_2$ on ZnGa$_2$O$_4$ catalysts.

In our present work, the structure sensitivity and the effects of the oxygen vacancy defects and hydration of ZnGa$_2$O$_4$ catalysts were studied by comparing the adsorption of CO$_2$ on the perfect, reduced, and hydrated (100), (110), and (111) surfaces of low-index ZnGa$_2$O$_4$. The majority of this work is aimed at gaining a theoretical understanding of the CO$_2$ adsorption on the ZnGa$_2$O$_4$ surfaces and of the detailed chemistry occurring on its surfaces.

**COMPUTATIONAL DETAILS AND MODELS**

All calculations were performed in the framework of the periodic density functional theory (DFT) by using code from the Cambridge Sequential Total Energy Package (CASTEP).$^{39}$ The interactions between ion cores and valence electrons were dealt by the ultrasoft pseudopotential.$^{40}$ For Zn, the 3$d$ and 4$s$ states were treated as valence states, whereas for Ga, the 3$d$, 4$s$, and 4$p$ states were treated as valence states. The Perdew’s and Wang’s 1991 (PW91) functional within the generalized gradient approximation (GGA)$^{41,42}$ was chosen to describe the exchange correlation energy.
The energy cutoff of the plane-wave basis set was chosen to be 300 eV to expand the
Kohn-Sham wave functions for the valence electrons. The convergence test for the
energy cutoff was shown in the Supporting Information (Figure S1). The
Monkhorst-Pack grids of $2 \times 2 \times 1$ $\mathbf{k}$-point were used to cover the irreducible
Brillouin zone (the test for the $\mathbf{k}$-point for each surface was shown in Table S1). The
maximum force for the convergence criteria of the structural optimization and energy
calculation was chosen to be 0.05 eV/Å (our calculations indicated that smaller
maximum force had little effect on the adsorption states, as shown in Table S2). For
the self-consistent field (SCF), maximum stress and maximum displacement were
separately chosen to be $2 \times 10^{-6}$ eV/atom, 0.1 GPa and $2 \times 10^{-3}$ Å.

Among the three low-index ZnGa$_2$O$_4$ surfaces, the (100) and (111) surfaces were
modeled using a $2 \times 2$ supercell with dimensions of 11.97 Å $\times$ 11.97 Å $\times$ 27.50 Å and
11.97 Å $\times$ 11.97 Å $\times$ 29.16 Å, respectively. Sixteen ZnGa$_2$O$_4$ molecular units in each
slab were distributed in seven layers. The supercell for the (110) surface included a $2$
$\times$ 1 surface unit cell and six atomic layers with twelve molecular units, resulting in a
supercell size of 8.46 Å $\times$ 11.97 Å $\times$ 27.62 Å. The vacuum regions separating the
slabs were all set to widths of 20 Å, which is enough distance to screen the
self-interaction effects of the periodic boundary conditions. On these three surfaces,
the adsorbates (H$_2$O and CO$_2$) and all of the atoms in the three topmost layers were
allowed to relax, whereas to simulate the bulk effects the rest layers in the bottom
were fixed. To further observe the charge transfers and population analyses, we also
performed the Mulliken populations on the equilibrium structure, which was carried out
by using a projection of the plane-wave states onto a linear combination of atomic
orbital basis sets.\textsuperscript{43, 44}

The binding energies of the adsorbed CO\textsubscript{2} and H\textsubscript{2}O are defined as
\[ E_{\text{ad}}^{\text{CO}_2} = (E_{\text{sur}/\text{CO}_2} - E_{\text{sur}} - E_{\text{CO}_2}), \]
\[ E_{\text{ad}}^{\text{H}_2\text{O}} = (E_{\text{sur}/\text{H}_2\text{O}} - E_{\text{sur}} - E_{\text{H}_2\text{O}}) \]

where
\[ E_{\text{sur}} \] is the total energy of the bare slab of the surface,
\[ E_{\text{CO}_2} \] is the total energy of free CO\textsubscript{2},
\[ E_{\text{sur}/\text{CO}_2} \] is the total energy of the slab with the adsorbed CO\textsubscript{2} molecule on the
surface,
\[ E_{\text{H}_2\text{O}} \] is the total energy of free H\textsubscript{2}O,
\[ E_{\text{sur}/\text{H}_2\text{O}} \] is the total energy of the slab with the adsorbed H\textsubscript{2}O molecule on the
surface.

This means that a positive \( E_{\text{ad}} \) value will lead to an exothermic adsorption
reaction. Moreover, in order to determine accurate activation barriers for the reaction,
we performed the complete LST/QST approach to search for transition states as well.

3. RESULTS AND DISCUSSION

3.1. CO\textsubscript{2} Adsorption on the Dry Perfect ZnGa\textsubscript{2}O\textsubscript{4} (100), (110), and (111)
Surfaces. Firstly, we studied the adsorption of CO\textsubscript{2} on the dry perfect ZnGa\textsubscript{2}O\textsubscript{4}
surfaces. In Figure 1, it can clearly be seen that the Zn\textsubscript{2c} (2-fold-coordinated Zn), Zn\textsubscript{3c}
(3-fold-coordinated Zn), Ga\textsubscript{3c} (3-fold-coordinated Ga), Ga\textsubscript{4c} (4-fold-coordinated Ga),
and Ga$_{5c}$ (5-fold-coordinated Ga) metal atoms on these three ZnGa$_2$O$_4$ surfaces were coordinately unsaturated and carried positive charges (seen in Figure 1). As pointed out in our previous work,$^{45}$ this would make them strong Lewis acids that can adsorb CO$_2$ by interacting with its O atoms,$^{46}$ whereas the surface O atoms (O$_{3c}$ or O$_{4c}$), which carry negative charges, would be strong Lewis bases adsorbing the C atoms of CO$_2$. Moreover, because the surface structures and the charges carried by the surface
atoms were different from each other for the different surfaces, their adsorption behaviors would be different, as well. To further understand the correlation of the surface atomic and electronic structures with catalytic activity, detailed calculations and discussion of the interactions between CO$_2$ molecules and the surfaces of the ZnGa$_2$O$_4$ catalyst are presented in the flowing sections.

After considering all the possible adsorption states, we obtained five models of the interaction between CO$_2$ and the surface, as shown in Figure 2. In this paper, they are labeled as (a) CO$_2$ perpendicular to the surface, (b) only the C atom adsorbed on the surface metal atom to form a monodentate carbonate species, (c) both the O$_a$ and C atoms interacting with the surface atoms to generate a bidentate carbonate species, (d) two O atoms of CO$_2$ binding with two metal atoms and the C atom binding with an O atom to form a bridge geometry, and (e) only the two O atoms of CO$_2$ binding with two metal atoms to form a bridge geometry. In these adsorption configurations, the two oxygen atoms of the adsorbed CO$_2$ are labeled as O$_a$ and O$_b$ if they were not in equivalent positions. Different sites on the perfect ZnGa$_2$O$_4$ surfaces, including Zn, Ga, Zn–O, Ga–O, Ga–Ga, and Zn–O–Ga sites, were examined for CO$_2$ adsorption. The results showed that the CO$_2$ molecule had a tendency to keep a linear structure when it interacted with the perfect ZnGa$_2$O$_4$ surfaces; if we put a bent structure on these surfaces, it would return to the linear structure after optimization.
Figure 2. All the possible models of adsorbed CO$_2$ on the ZnGa$_2$O$_4$ surfaces.

Comparing the adsorption energies of all the sites on each surface, we found that the most stable ones were model (d) on the (100) surface (100, Zn-Ga-d), model (c) on the (110) surface (110, Zn-c), and model (c) on the (111) surface (111, Zn-c), as shown in Figure 3. The adsorption energies and key structural parameters of these three models are shown in Table 1, and the remaining less stable structures on each surface are provided in the Supporting Information (Figure S2-S4). For configuration (100, Zn-Ga-d), CO$_2$ was adsorbed across the Zn–O–Ga bridge site. The distances between O$_b$ and Zn$_{2c}$, O$_a$ and Ga$_{5c}$, and C and O$_{4c}$ were 2.66 Å, 3.03 Å, and 3.13 Å, respectively. Therefore, both oxygen atoms and the carbon atom in CO$_2$ could interact with the surface, and all these interactions enhanced the stability of the adsorption state. Moreover, the main adsorption site Zn$_{2c}$ on the (100) surface protruded above the surface, which could lead to steric hindrance preventing the CO$_2$ molecule from reaching the surface. However, for configurations (110, Zn-c) and (111, Zn-c), it can be seen that the main interactions between the CO$_2$ molecule and the surface happened between one oxygen atom of CO$_2$ and the surface Zn$_{3c}$ atom, and these configurations were less stable than configuration (100, Zn-Ga-d), since the interactions were weaker. The stability of Zn-Ga-d adsorption on the (110) and (111)
Figure 3. Top (left) and side (right) views of the most stable CO$_2$ molecular adsorption state on each surface. (100, Zn-Ga-d): the CO$_2$ molecule adsorbed by the Zn and Ga sites on the (100) surface (the d adsorption type in Figure 2); (110, Zn-c): the CO$_2$ molecule adsorbed by the Zn site on the (110) surface (the c adsorption type in Figure 2); (111, Zn-c): the CO$_2$ molecule adsorbed by the Zn on the (111) surface (the c adsorption type in Figure 2).
Table 1. Structural Parameters, Adsorption Energies and Mulliken Charges of CO$_2$ Adsorbed in the Most Stable Configurations on Each Perfect ZnGa$_2$O$_4$ Surface.

<table>
<thead>
<tr>
<th>Configurations</th>
<th>$E_{\text{ads}}$ (eV)</th>
<th>C-O$_a$ bond(Å)</th>
<th>C-O$_b$ bond(Å)</th>
<th>O$_a$-C-O$_b$ angle(°)</th>
<th>C</th>
<th>O$_a$</th>
<th>O$_b$</th>
<th>CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100,Zn-Ga-d)</td>
<td>-0.16</td>
<td>1.178</td>
<td>1.185</td>
<td>178.5</td>
<td>0.77</td>
<td>-0.42</td>
<td>-0.45</td>
<td>-0.10</td>
</tr>
<tr>
<td>(110,Zn-c)</td>
<td>0.22</td>
<td>1.176</td>
<td>1.185</td>
<td>178.8</td>
<td>0.78</td>
<td>-0.42</td>
<td>-0.46</td>
<td>-0.10</td>
</tr>
<tr>
<td>(111,Zn-c)</td>
<td>0.35</td>
<td>1.187</td>
<td>1.178</td>
<td>178.7</td>
<td>0.77</td>
<td>-0.47</td>
<td>-0.42</td>
<td>-0.12</td>
</tr>
<tr>
<td>CO$_2$-mol</td>
<td>—</td>
<td>1.180</td>
<td>1.180</td>
<td>180.0</td>
<td>1.00</td>
<td>0.50</td>
<td>0.50</td>
<td>0.00</td>
</tr>
</tbody>
</table>

The reason that these two adsorption states are quite unstable is the specific atomic and electronic structures of these two surfaces. From Figures S2 and S3, we can see that the Ga$_{4c}$ and Zn$_{3c}$ atoms on the (110) surface are both located below the surface level, and similarly, the Zn$_{3c}$ and O$_{4c}$ atoms on the (111) surface are located below the surface level, as well. As such, the CO$_2$ molecules must overcome more steric hindrance to reach these surfaces, which would significantly reduce the strength of the interactions between the CO$_2$ molecules and the surface atoms. Moreover, the differences among the charges carried by the surface metal atoms are important reasons that the Zn-Ga-d adsorption on these two surfaces is less stable. As shown in Figure 1, the charges carried by Zn$_{3c}$ and Ga$_{4c}$ on the (110) surface were 0.79 |e| and 1.14 |e|, respectively, which are less than the corresponding charges on the Zn$_{2c}$ (0.85 |e|) and Ga$_{5c}$ (1.16 |e|) atoms on the (100) surface. This means that the acidity of the metal atoms on the (110) surface is weaker than that on the (100) surface, which further made the adsorption on the (110)
surface less stable. For the (111) surface, although the charge on the Zn_{3c} (0.93 |e|) atom was a little higher than the charge on the Zn_{2c} atom on the (100) surface, the charge on the Ga_{3c} (0.69 |e|) was much less than that on the Ga_{5c} atom. Therefore, the total interaction strengths between these two metal atoms on the (111) surface and the CO_2 was less than those on the (100) surface.

The above results indicate that the surface atomic and electronic structure would play an important role in the interaction between CO_2 and the ZnGa_2O_4 catalyst. The adsorption energies of CO_2 on the (100), (110), and (111) surfaces were -0.16 eV, 0.22 eV, and 0.35 eV (seen in Table 1), respectively, which means that only CO_2 adsorption on the (100) surface was exothermic and thermodynamically favorable. In addition, the perfect ZnGa_2O_4 surfaces showed CO_2 activation ability, but the CO_2 molecule could not decompose on them. Therefore, there must be other factors that have obvious effects on CO_2 adsorption and activation, among which the oxygen vacancy (Vo) defects and hydration are considered as common factors here.

Oxygen vacancy is an intrinsic defect in metal oxides, and it usually shows good activity for CO_2 adsorption, as shown by many experimental and theoretical studies.\textsuperscript{47-49} Meanwhile, when water is adsorbed on the metal oxide surface it can significantly influence the nature of the surface sites and further affects the subsequent adsorption and decomposition of CO_2 molecules as well.\textsuperscript{19} Thus, in the following two sections we further discuss the effect of oxygen vacancy and hydration on CO_2 adsorption and decomposition on ZnGa_2O_4 (100), (110), and (111) surfaces.

3.2. CO_2 Adsorption and Dissociation on Dry (100), (110), and (111) Surfaces
with Oxygen Vacancy Defects. In this section, we further explore the CO$_2$ adsorption on the dry ZnGa$_2$O$_4$ surfaces with oxygen vacancy defects. As shown in Figure 4, there is a total of five kinds of oxygen vacancy defects on these three surfaces: O$_{3c}$ and O$_{4c}$ vacancies on the (100) surface, an O$_{3c}$ vacancy on the (110) surface, and O$_{3c}$ and O$_{4c}$ vacancies on the (111) surface. Our previous study showed that the generation of oxygen vacancy defects causes significant charge redistribution that reduces the positive charges carried by the metal atoms beside them as compared to those on clean surfaces. This change would decrease the acidity of these metal atoms and further decrease the stability of the adsorption states of CO$_2$ on these sites.

In the following sections, we would discuss in detail the changes in the adsorption behavior on the defective (100), (110), and (111) surfaces.

![Figure 4](image.png)

Figure 4. All the possible oxygen vacancy defects on the (100), (110) and (111) surfaces.

Firstly, we compared all of the adsorption energies of different configurations in the presence of an oxygen vacancy defect (Vo$_{3c}$ or Vo$_{4c}$) on the (100) surface and obtained
the most stable configurations, as shown in Figure 5. We found that when such a surface vacancy presented on the surface, it could modify the energy for configurations in which CO$_2$ is adsorbed on the perfect surface at the sites near the vacancy. The presences of an oxygen vacancy defect will significant decrease the adsorption energies as well (Figure 5, (100-Vo$_{3c}$, Zn-Ga-d) and (100-Vo$_{4c}$, Zn-Ga-d)). This can be explained by the decrease in the charges on the metal atoms near the vacancy, which would decrease the acidity of the metal atoms. Moreover, we also found that the O$_{3c}$ vacancy was an active site for CO$_2$ adsorption (Figure 5-(100-Vo$_{3c}$-mol)) and decomposition (Figure 5-(100-Vo$_{3c}$-dis)). The adsorption
on O$_{3c}$ and O$_{4c}$ vacancy defective ZnGa$_2$O$_4$ (100) surface. (100-Vo$_{3c}$, Zn-Ga-d): the CO$_2$ molecule adsorbed by the Zn and Ga sites on the (100)-Vo$_{3c}$ surface (similar to (100, Zn-Ga-d) state in Figure 3); (100-Vo$_{3c}$-mol): the molecular adsorption on the oxygen vacancy site of the (100)-Vo$_{3c}$ surface; (100-Vo$_{3c}$-dis): the dissociative adsorption on the oxygen vacancy site of the (100)-Vo$_{3c}$ surface; (100-Vo$_{4c}$, Zn-Ga-d): the CO$_2$ molecule adsorbed by the Zn and Ga sites on the (100)-Vo$_{4c}$ surface (similar to (100, Zn-Ga-d) state in Figure 3); (100-Vo$_{4c}$-mol): the molecular adsorption on the oxygen vacancy site of the (100)-Vo$_{4c}$ surface.

energies of these two configurations were both much higher than those of the other sites on the defective or perfect surfaces (Figure 3 and 5). This suggests that the generation of O$_{3c}$ vacancy defects could promote CO$_2$ adsorption and decomposition on the (100) surface. Because dissociative adsorption has a higher adsorption energy than molecular adsorption, dissociative adsorption on the (100)-Vo$_{3c}$ surface would be more favorable thermodynamically. On the (100)-Vo$_{4c}$ surface, the molecular adsorption state on the O$_{4c}$ vacancy site, however, was quite unstable because of the large steric hindrance caused by the Zn and Ga atoms near the vacancy, and dissociative adsorption could not occur on this surface. In fact, our calculation indicated that the CO$_2$ molecule tended to stay far away from the surface rather than dissociate on it. Thus, the (100)-Vo$_{4c}$ surface would not be a good surface for CO$_2$ adsorption and decomposition. For the defective (110) and (111) surfaces, a detailed discussion was performed in the Supporting Information. We found that the molecular adsorption on the oxygen vacancy site is much easier to happen than the dissociative
adsorption on the (110)-O$_{3c}$, (111)-O$_{3c}$, and (111)-O$_{4c}$ surfaces, and the dissociative adsorption states are all less stable than the state on the (100)-O$_{3c}$ surface as well. Therefore, compared to the (100)-O$_{3c}$ surface, CO$_2$ decomposition on these three surfaces would be less favorable thermodynamically.

Having studied the favorable dissociated structures, we now turn to exploring the dissociative adsorption mechanism of CO$_2$ on the defective surfaces. The potential energy profiles and the structures of the transition states are both shown in Figure 6. For the reaction process on the (110)-Vo$_{3c}$ surface, the molecularly adsorbed CO$_2$ dissociated into adsorbed CO$_a$ and O$_b$ atoms through a transition state TS1, with an

Figure 6. Potential energy profiles for the dissociation of CO$_2$ on the O$_{3c}$ or O$_{4c}$ vacancy defective Zn$_2$Ga$_2$O$_4$ (100), (110), and (111) surfaces. Structures of the
transition states (TS1-4) are shown beside the potential energy profiles, respectively. See Figures 3 for color coding.

activation barrier of 0.62 eV. In TS1, the distance between C and Zn$_{2c}$ increased to 2.40 Å from 2.32 Å in the (100)-Vo$_{3c}$-mol configuration, the angle of CO$_2$ was 108.7°, and the C–O$_a$ and C–O$_b$ bond lengths were 1.20 Å and 2.02 Å, respectively. Moreover, because the product (100)-Vo$_{3c}$-dis was more stable than the reactant (100)-Vo$_{3c}$-mol (0.06 eV higher), the decomposition of CO$_2$ on the (100)-Vo$_{3c}$ surface would be exothermic. For the other three defective surfaces, only the molecular adsorption state on the (110)-Vo$_{3c}$ surface was exothermic (i.e., the (100)-Vo$_{3c}$-mol state was more stable than the free CO$_2$ + slab), and the other two states on the (111)-Vo$_{3c}$ and (111)-Vo$_{4c}$ surfaces were both endothermic. This suggests that spontaneous molecular adsorption on the defective (111) surface is difficult. In contrast to the situation on the (100)-Vo$_{3c}$ surface, all of the products on these three surfaces were less stable than the reactants, so the decomposition of CO$_2$ on them would be endothermic. In addition, comparison of the results of the potential energy profiles in Figure 6 shows that the lowest energy barrier (0.62 eV) and reaction energy (-0.06 eV) were both found on the (100)-Vo$_{3c}$ surface, whereas the highest energy barrier (5.02 eV) and reaction energy (1.24 eV) were both found on the (111)-Vo$_{3c}$ surface. This provides further kinetics-based proof of our conclusions that the (100)-Vo$_{3c}$ surface would be the best surface for CO$_2$ decomposition and that the activity of these surfaces decreases in the order (100)-Vo$_{3c}$ > (110)-Vo$_{3c}$ > (111)-Vo$_{4c}$ > (111)-Vo$_{3c}$. Therefore, if we want to synthesize a ZnGa$_2$O$_4$ catalyst for CO$_2$ decomposition, we should let the catalyst
expose more (100) surface and generate more oxygen vacancy defects on it.

3.3. CO$_2$ Adsorption on the Hydrated Perfect (100), (110), and (111) Surfaces.

After considering the various possible initial structures, we obtained the most stable structure for each surface, as shown in Figure 7. In this simulation, the hydrated

![Figure 7](Image)

Figure 7. Top (left) and side (right) views of the most stable CO$_2$ adsorption structures and energies on the hydrated perfect ZnGa$_2$O$_4$ (100), (110), and (111) surfaces. E(t):
the total adsorption energies of the CO₂ and H₂O; E(CO₂): the adsorption energies of the CO₂, which is defined as E(t)-E(H₂O) (E(H₂O) is shown in Figure S8). Surfaces were created by adsorbing water molecules on the perfect ZnGa₂O₄ surfaces. The adsorption energy and structure for each hydrated perfect surface are provided in Figure S8. Comparing the three adsorption energies of CO₂ (E(CO₂) in Figure 7), we find that the most stable states are on the (100) surface in this case, as well. Moreover, the presence of the coadsorbed H₂O on these three surfaces makes the overall adsorption process more thermodynamically favorable than that on the clean surfaces (seen in Table 1). This can be explained by the special structures of the coadsorbed states. In Figure 7, the distances between the hydrogen atoms (Hₐ) of the adsorbed H₂O molecules and the oxygen atoms (Oₐ) of the CO₂ molecules were 2.23 Å, 2.36 Å, and 1.97 Å, respectively, which are small enough to generate hydrogen bonds (less than 2.50 Å). Therefore, hydration enhances the stability of the CO₂ adsorption states.

Next, we compared CO₂ adsorption on the dry defective ZnGa₂O₄ surfaces with that on the hydrated perfect ZnGa₂O₄ surfaces to help clarify which surface modification had a greater effect on CO₂ adsorption and activation. Although protonation of the adsorbed CO₂ made the overall adsorption process thermodynamically favorable, the changes in the CO₂ adsorption energies on the (100), (110), and (111) surfaces were very small (0.03 eV, 0.02 eV, and 0.03 eV, respectively). On the other hand, the most stable CO₂ molecular adsorption states on the dry defective surface in the (100-VO₃c-mol), (110-VO₃c-mol), and (111-VO₄c-mol) configurations had adsorption energies of -0.74 eV, -0.43 eV, and 0.20 eV, respectively,
which were much more stable than the adsorption states on clean surfaces. Therefore, surface oxygen defects enhanced the CO$_2$ adsorption much more than hydration. To further examine the effect of the preadsorbed water on CO$_2$ adsorption on the defective surfaces, we calculated CO$_2$ adsorption behavior on the hydrated defective surfaces as well.

3.4. CO$_2$ Adsorption and Dissociation on the Hydrated (100), (110), and (111) Surfaces with Oxygen Vacancy Defects. In this section, we calculate the stability of CO$_2$ adsorption on the hydrated defective surfaces with oxygen vacancies, as well as the effect of water on CO$_2$ adsorption on the defective surfaces. Because the stable adsorption states all involved the vacancy defect sites, we mainly discuss the changes in the molecular and dissociative adsorption behaviors on these sites. Furthermore, our calculations also indicated that the adsorption behaviors on the other sites were similar to those on the hydrated perfect surfaces. The adsorption energy and structure for each hydrated defective surface are provided in Figure S9.

For the (100) surface, the coadsorption of CO$_2$ and H$_2$O would significantly enhance the stability of the adsorption state, especially for the (100-VO$_\text{3c}$-Hy-mol) state, as shown in Figure 8. This can be explained by the specific structure of the (100-VO$_\text{3c}$-Hy-mol) state. In the (100-VO$_\text{3c}$-Hy-mol) state, the length of the H$_a$–O$_a$ hydrogen bond is 1.81 Å, which is much shorter than the hydrogen bond in (100-VO$_\text{3c}$-Hy-dis) (2.26 Å). This means that the interactions between the H$_a$ and O$_a$ atoms in the (100-VO$_\text{3c}$-Hy-mol) state are much stronger than in the (100-VO$_\text{3c}$-Hy-dis). This suggests that the strength of the hydrogen bond will play an
Figure 8. Top (left) and side (right) views of the CO$_2$ molecular and dissociation adsorption structures and energies on the oxygen vacancy sites of the hydrated defective ZnGa$_2$O$_4$ (100), (110), and (111) surfaces. $E(t)$: the total adsorption energies.
of the CO$_2$ and H$_2$O; E(CO$_2$): the adsorption energies of the CO$_2$, which is defined as E(t)-E(H$_2$O) (E(H$_2$O) is shown in Figure S9).

important role in the stability of the coadsorption state. As was the case for the dry Vo$_{4c}$ defective (100) surface, the CO$_2$ adsorption states on the hydrated (100) surface with Vo$_{4c}$ defects were quite unstable. In particular, our calculations indicate that the H$_2$O and CO$_2$ coadsorption could not happen on the Vo$_{4c}$ defect site, and the H$_2$O and CO$_2$ molecules had a tendency to remain far away from the surface rather than adsorbing onto it. This implies that spontaneous coadsorption on the Vo$_{4c}$ defective site is impossible.

In our previous work,$^{45}$ we pointed out that the oxygen vacancies were also good sites for H$_2$O adsorption and decomposition and that the dissociation adsorption energy of H$_2$O on the defective (100) surface is -0.79 eV, which is similar to the dissociation adsorption energy of CO$_2$ on the hydrated defective (100) surface (-0.86 eV). Therefore, hydration would compete with CO$_2$ adsorption and decomposition for the oxygen vacancy sites if both H$_2$O and CO$_2$ were present in the gas phase. Comparing the adsorption energies for CO$_2$ (E(CO$_2$)) in Figure 6, we further find that the molecular absorption (reactant) on the (100-Vo$_{3c}$-Hy) surface is more favorable thermodynamically. This would make the decomposition of CO$_2$ on the (100-Vo$_{3c}$-Hy) surface endothermic, which is disadvantageous for the decomposition of CO$_2$. Moreover, the transition states for dissociative adsorption on the hydrated defective (100) surface also show that the coadsorption of H$_2$O increases the energy barrier for the decomposition of CO$_2$, as shown in Figure 9. This provides further kinetics-based
proof for our conclusion that the hydrated defective (100) surface is not good for CO\textsubscript{2} decomposition, as compared to the dry defective (100) surface.

Next, for the (110)-Vo\textsubscript{3c} and (111)-Vo\textsubscript{4c} surfaces, the generation of hydrogen bonds between H\textsubscript{a} and O\textsubscript{a} could enhance the stability of the adsorption states, as well. However, because the molecular adsorption and dissociative adsorption of H\textsubscript{2}O\textsuperscript{45} are much more stable than the adsorption of CO\textsubscript{2}, there would be significant competition between H\textsubscript{2}O and CO\textsubscript{2} for the vacancy sites, which is quite disadvantageous for the

Figure 9. Potential energy profiles for the dissociation of CO\textsubscript{2} on the hydrated O\textsubscript{3c} or O\textsubscript{4c} vacancy defective Zn\textsubscript{2}Ga\textsubscript{2}O\textsubscript{4} (100), (110), and (111) surfaces. Structures of the transition states (TS7 and TS8) are shown beside the potential energy profiles, respectively. See Figures 7 for color coding.
decomposition of CO₂. Moreover, the transition states shown in Figure 9 also indicate that the coadsorption of H₂O could increase the energy barriers of the decomposition of CO₂ on these two surfaces and make them even more kinetically unfavorable. Finally, for the (111)-Vo₃c surface, unlike for the other surfaces, the coadsorption of H₂O even made the CO₂ molecular adsorption and dissociative adsorption states less stable than on the dry defective surface, in addition to increasing the energy barrier for the decomposition reaction (seen in Figure 9). The CO₂ molecular adsorption and dissociative adsorption configurations in Figure 8 show that the distances between Ha and Oa were 3.23 Å and 3.68 Å, respectively, which were too long to generate hydrogen bonds. This further confirms our conclusion that the generation of a hydrogen bond was the key factor that made the coadsorption state more stable than on the dry surfaces.

Thus, it was found that the coadsorption of H₂O can enhance the stability of the CO₂ adsorption state on defective ZnGa₂O₄ surfaces (except for the (111)-Vo₃c surface). However, because the oxygen vacancy defects can also adsorb H₂O molecules (on some surfaces, the adsorption states of H₂O are much more stable than the adsorption states of the CO₂), there will be strong competition between them. Therefore, the presence of H₂O will decrease the availability of surface oxygen vacancy sites for CO₂ activation and decomposition.Combining this competition with the kinetic effects (the coadsorption of H₂O can increase the energy barrier for the decomposition of CO₂), we can conclude that the presence of water will have a negative effect on the catalytic activity of ZnGa₂O₄ catalysts toward CO₂ conversion.
Therefore, if we want to use ZnGa$_2$O$_4$ to catalyze CO$_2$ decomposition into CO and O$_2$, we should be sure that the reaction system is in a dry environment. Furthermore, if we want to use ZnGa$_2$O$_4$ to catalyze the reaction between CO$_2$ and H$_2$O yielding hydrocarbons, we need to separate and remove water from the product stream to maintain the high activity of the catalysts.

4. CONCLUSIONS

In the present work, the effect of water and oxygen vacancies on CO$_2$ adsorption on the low-index ZnGa$_2$O$_4$ (100), (110), and (111) surfaces has been studied using DFT slab calculations. The results show that CO$_2$ adsorption on the low-index ZnGa$_2$O$_4$ surfaces is a structure-sensitive reaction and that the surface atomic and electronic structure, oxygen vacancies, and hydration all play important roles in the reaction parameters. On the dry perfect surface, only the CO$_2$ molecular adsorption on the (100) surface was exothermic and thermodynamically favorable. The dry perfect surface showed CO$_2$ activation ability, but dissociative adsorption could not proceed.

A defective ZnGa$_2$O$_4$ surface was created by removing a surface O$_{3c}$ or O$_{4c}$ atom from the dry perfect surface. We found that the presence of oxygen vacancies could promote CO$_2$ activation and decomposition on the low-index ZnGa$_2$O$_4$ (100), (110), and (111) surfaces. The oxygen vacancy sites also provided active sites for CO$_2$ decomposition, and the most stable dissociative adsorption state involved the (100)-Vo$_{3c}$ surface. Accordingly, a high oxygen vacancy density should improve the CO$_2$ adsorption and activation and, thereby, improve the catalytic activity of ZnGa$_2$O$_4$.
catalysts for CO₂ conversion. Our results also indicate that because of the generation of hydrogen bonds, the coadsorption of H₂O and CO₂ could enhance the stability of the adsorption state (except the (111)-Vo₃c surface). However, the coadsorption of H₂O would increase the energy barrier for the decomposition of CO₂. Furthermore, because the oxygen vacancy defects also show good activity for H₂O adsorption and decomposition, the H₂O molecules would compete with CO₂ molecules for the oxygen vacancy sites. Therefore, if we want to synthesize a ZnGa₂O₄ catalyst for CO₂ conversion, we need to expose the (100) surface more than the other surfaces and generate more vacancy defects. In addition, separating and removing water from the product stream will help to maintain high activity of ZnGa₂O₄ catalysts.

**Supporting Information**

The structures and energies of the less stable states on the (100), (110), and (111) surfaces, the top views of the optimized structures of the defective ZnGa₂O₄ (100), (110) and (111) surfaces, CO₂ adsorption structures and energies on the vacancy defective ZnGa₂O₄ (110) and (111) surfaces, the adsorption structures and energies of H₂O on the perfect and defective (100), (110), and (111) surfaces, the molecular and dissociative adsorption structures and energies of H₂O on the oxygen vacancy sites of the (100), (110), and (111) surfaces. This material is available free of charge via the Internet at http://pubs.acs.org.

**Acknowledgment**
This work is supported by the 973 Program of China (Grant No. 2009CB930103 and 2010CB933504), National Natural Science Foundation of China (Grant No. 21173131), Independent Innovation Foundation of Shandong University (Grant No. 2012TS212).

References


Table of Contents

CO₂ adsorption and decomposition on low-index perfect, oxygen vacancy defective, and hydrated ZnGa₂O₄ (100), (110) and (111) surfaces were investigate.
The structure sensitivity and the effects of the oxygen vacancy defects and hydration of ZnGa$_2$O$_4$ catalysts are studied by comparing the adsorption of CO$_2$ on the perfect, reduced, and hydrated (100), (110), and (111) surfaces of low-index ZnGa$_2$O$_4$ to gain a theoretical understanding of the CO$_2$ adsorption on the ZnGa$_2$O$_4$ surfaces and of the detailed chemistry occurring on its surfaces.