Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

The Roles of Surface Structure, Oxygen Defects, and Hydration in the Adsorption of CO_2 on Low-Index $ZnGa_2O_4$ Surfaces: A First-Principles Investigation

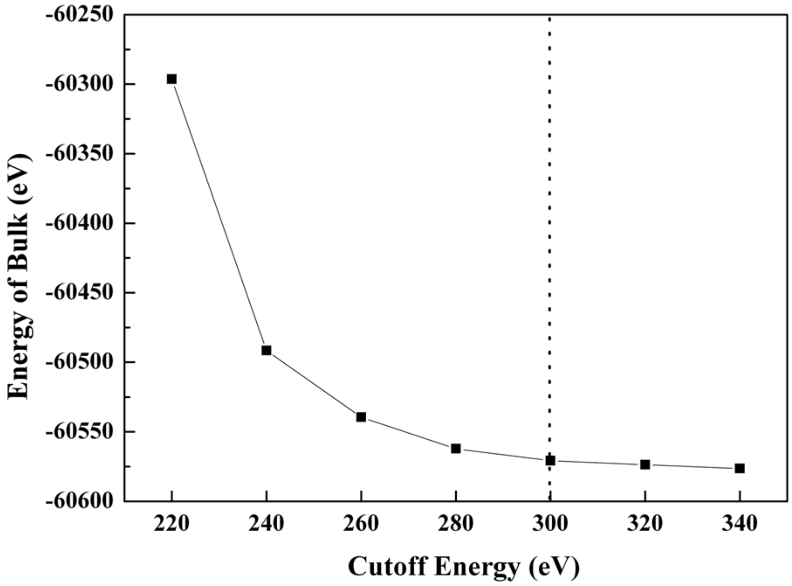
Chuanyi Jia [a,b)], Weiliu Fan [a)] *, Xiufeng Cheng [b)], Xian Zhao [b)], Honggang Sun [b)], Pan Li [b)], and Na Lin [b)]

a) School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100 China

b) State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100 China

*Corresponding author. E-mail: fwl@sdu.edu.cn.

1. The tests for the computational details



---

* To whom all correspondences should be addressed. Tel: 86-531-88366330, Fax: 86-531-88364864, E-mail: fwl@sdu.edu.cn.

Figure S1. The convergence tests for the cutoff energy.

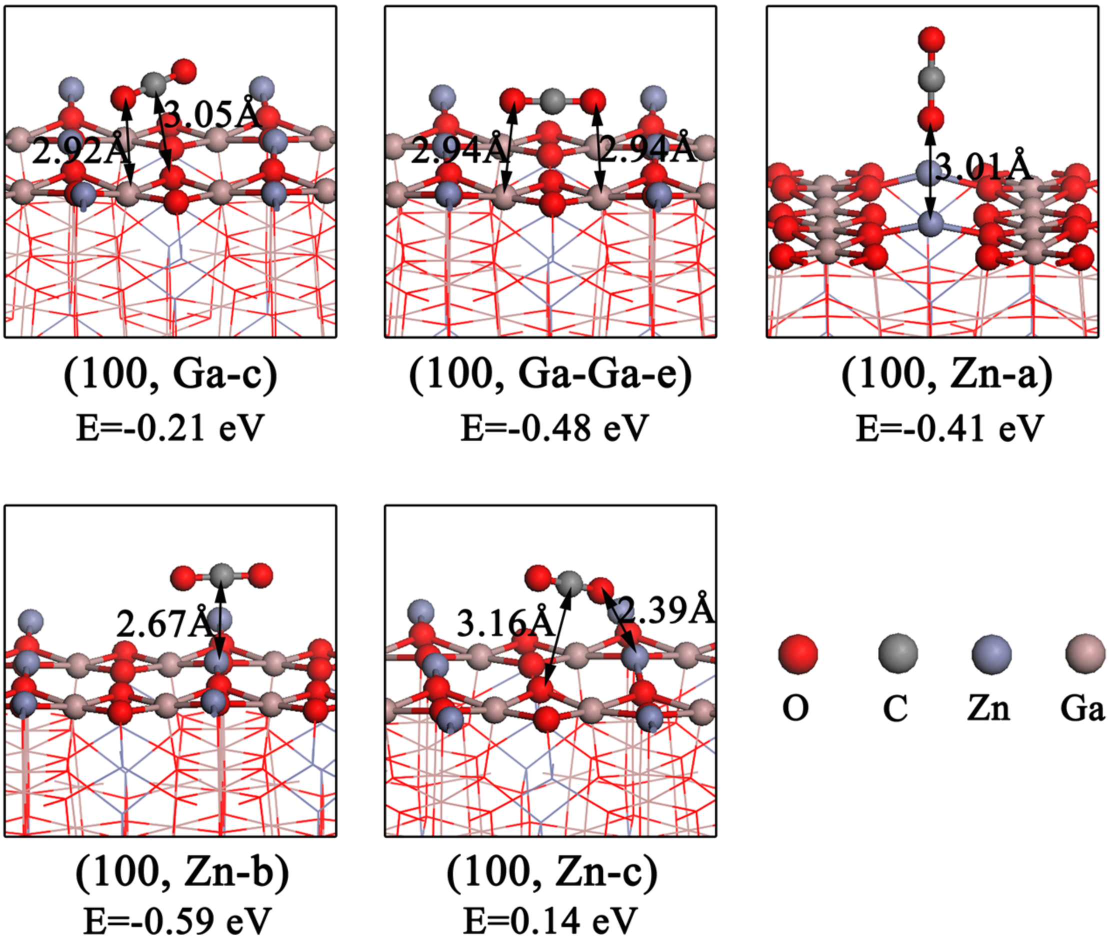
Adsorption State	K-point	Adsorption Energy (eV)
(100, Zn-Ga-d)	2×2×1	0.159
	3×3×1	0.162
	4×4×1	0.164
(110, Zn-c)	2×2×1	-0.217
	3×3×1	-0.215
	4×4×1	-0.211
(111, Zn-c)	2×2×1	-0.354
	3×3×1	-0.350
	4×4×1	-0.351

Table S1. The adsorption energies of the most stable adsorption state on (100), (110) and (111) surfaces with different K-points.

Force State	0.05 (eV/Å) /eV	0.02 (eV/Å) /eV	Δ E/eV
(100,Zn-Ga-d)	-122147.0348523	-122147.0252197	-0.0096326
(110,Zn-c)	-91867.0749803	-91867.0758926	0.0009123
(111,Zn-c)	-122141.0002567	-122141.0007771	0.0005204

Table S2. The adsorption energies of the states on the (100), (110) and (111) surfaces with different convergence forces (0.05 eV/Å and 0.02 eV/Å).

2. The data and figures for the Stoichiometric surfaces



(100, Ga-c)
E=-0.21 eV

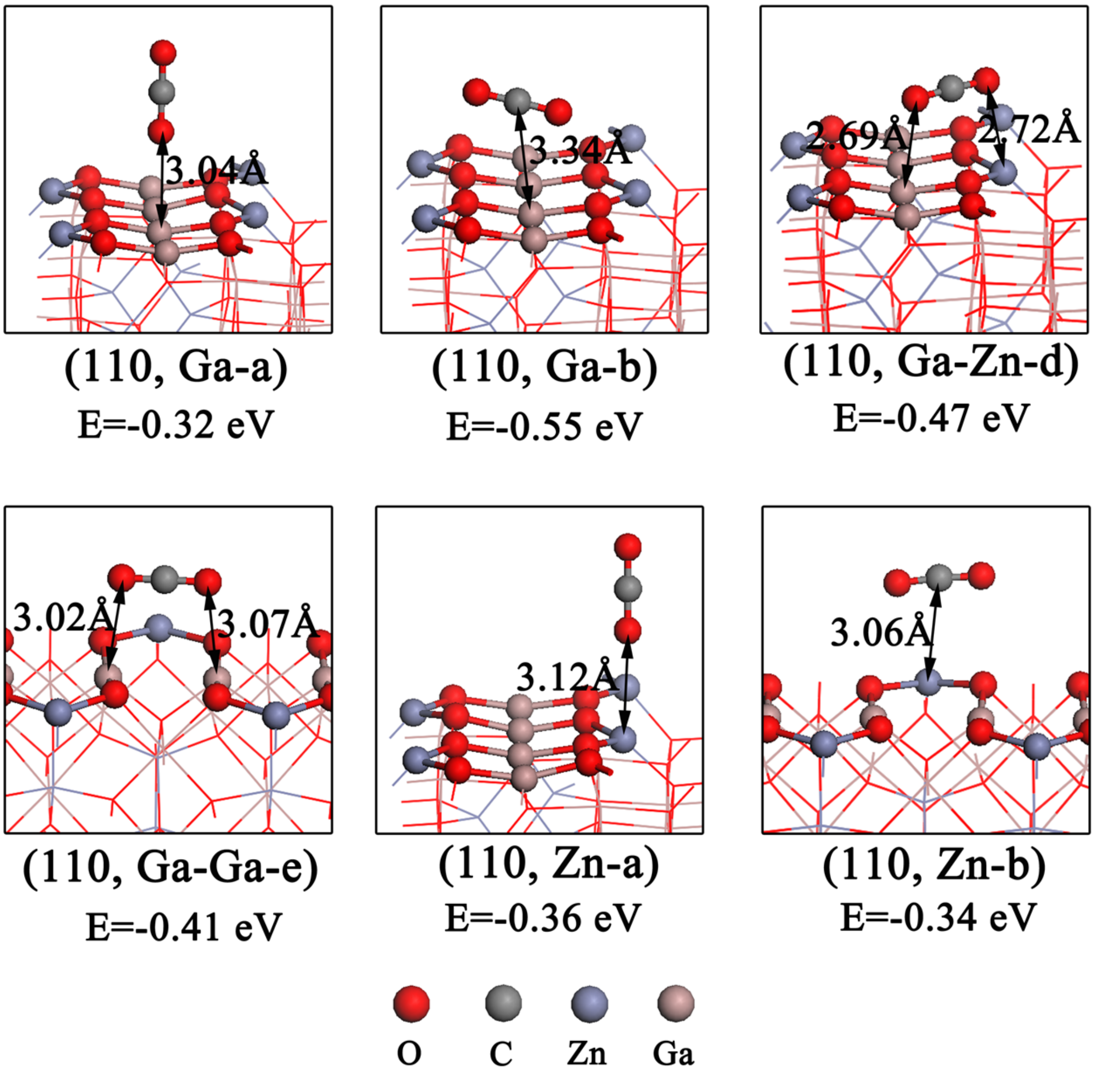
(100, Ga-Ga-e)
E=-0.48 eV

(100, Zn-a)
E=-0.41 eV

(100, Zn-b)
E=-0.59 eV

(100, Zn-c)
E=0.14 eV

Figure S2. The structures and energies of the less stable states on the (100) surface.



(110, Ga-a)
E=-0.32 eV

(110, Ga-b)
E=-0.55 eV

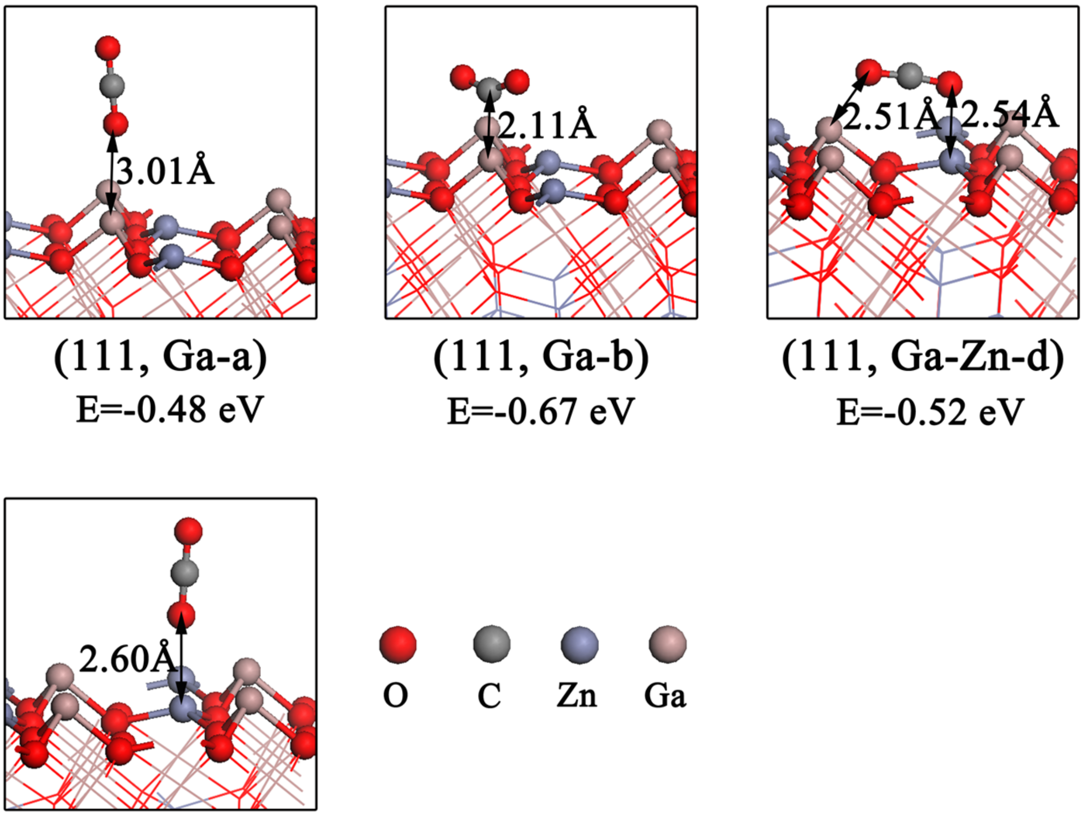
(110, Ga-Zn-d)
E=-0.47 eV

(110, Ga-Ga-e)
E=-0.41 eV

(110, Zn-a)
E=-0.36 eV

(110, Zn-b)
E=-0.34 eV

Figure S3. The structures and energies of the less stable states on the (110) surface.



(111, Ga-a)
E=-0.48 eV

(111, Ga-b)
E=-0.67 eV

(111, Ga-Zn-d)
E=-0.52 eV

(111, Zn-a)
E=-0.46 eV

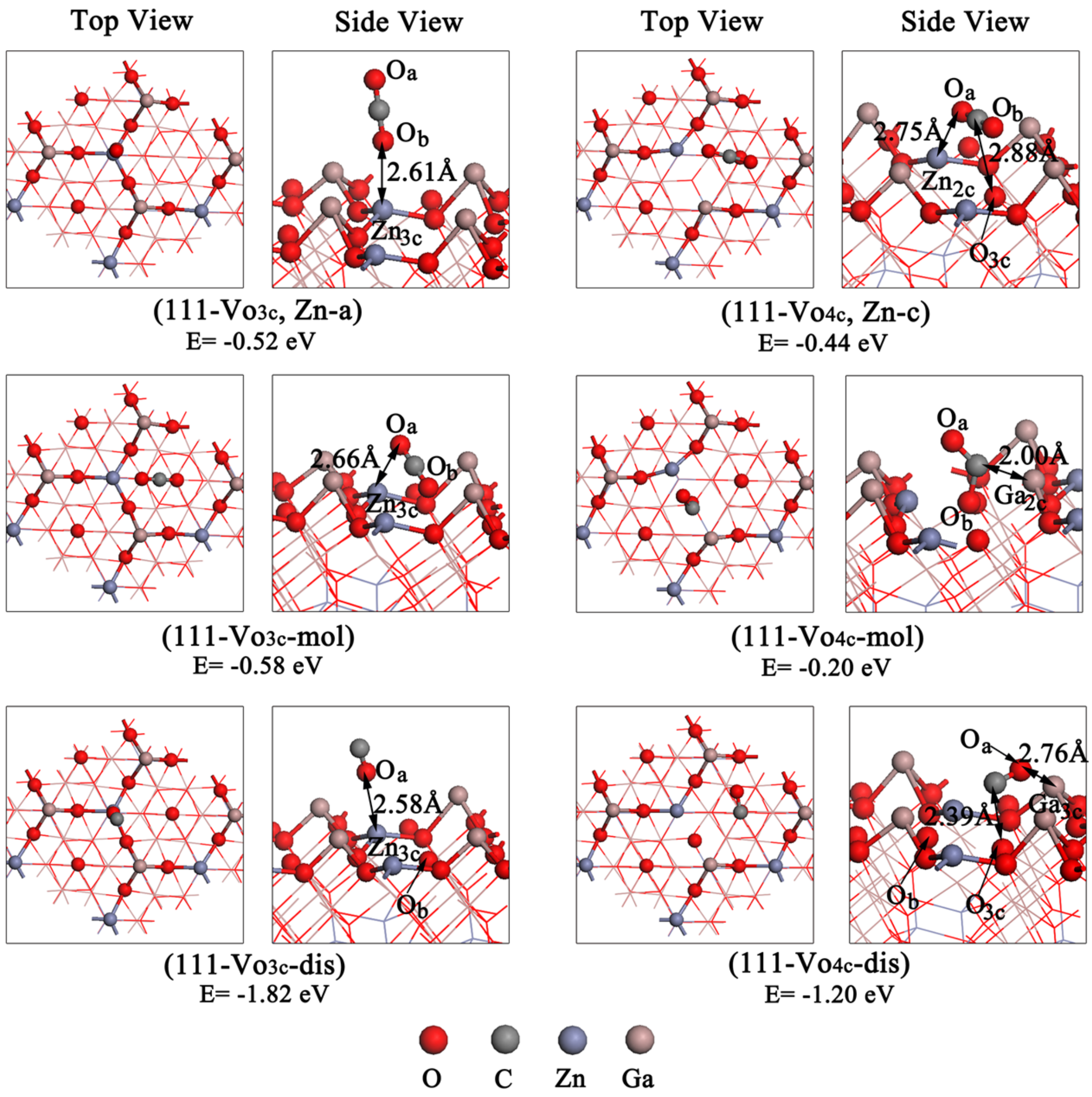
Figure S4. The structures and energies of the less stable states on the (111) surface.

3. The adsorption behaviors and the data and figures for the oxygen vacancy defective (110) and (111) surfaces

After comparing various adsorption states on the (110) surface with an O_{3c} vacancy defect, we obtained three typical stable states, as depicted in Figure S5. As was the case for the (100) surface, the decrease in the charges on the metal atoms near the oxygen vacancy would make molecular adsorption on the (110) surface less stable. From Figure S5, it can be seen that the molecular adsorption on the oxygen vacancy site is much more stable than the dissociative adsorption on the defective (110)

Figure S5. Top (left) and side (right) views of CO_2 adsorption structures and energies on O_{3c} vacancy defective $ZnGa_2O_4$ (110) surface. **(110-Vo$_{3c}$, Zn-c)**: the CO_2 molecule adsorbed by the Zn site on the **(110)-Vo$_{3c}$** surface (similar to **(110, Zn-c)** state in Figure 3); **(100-Vo$_{3c}$-mol)**: the molecular adsorption on the oxygen vacancy site of the **(110)-Vo$_{3c}$** surface; **(110-Vo$_{3c}$-dis)**: the dissociative adsorption on the oxygen vacancy site of the **(110)-Vo$_{3c}$** surface.

surface. Thus, on the **(110)-Vo$_{3c}$** surface, molecular adsorption would be more favorable thermodynamically. For the (111) surface, as shown in Figure S6, the generation of O_{3c} or O_{4c} vacancies would make the molecular adsorption on the metal atoms beside them become less stable, as well. Although the CO_2 molecules could be decomposed on the **(111)-Vo$_{3c}$** and **(111)-Vo$_{4c}$** surfaces, the adsorption states were quite unstable (with much lower adsorption energies). Therefore, molecular adsorption would be much more likely on the defective (111) surfaces. In addition, the dissociative adsorption states on the vacancy sites of these three surfaces are all less stable than the states on the **(100)-O_{3c}** surface. After a detailed comparison of the surface atomic and electronic structure (seen in Figure S7) between these five defective surfaces, we find two main reasons leading to this consequence. One is that the main adsorption site Zn_{2c} on the **(100)-O_{3c}** surface is higher than the surface level, so CO_2 molecule will suffer less steric hindrance effect when it is adsorbed on this surface (This also explains the phenomenon that the Zn_{3c} atom on the **(111)-O_{3c}** surface carried similar positive charges to the Zn_{2c} atom on the **(100)-O_{3c}** surface but the adsorption state on it is less stable than the state on the **(100)-O_{3c}** surface). The



(111-Vo3c, Zn-a)
E= -0.52 eV

(111-Vo4c, Zn-c)
E= -0.44 eV

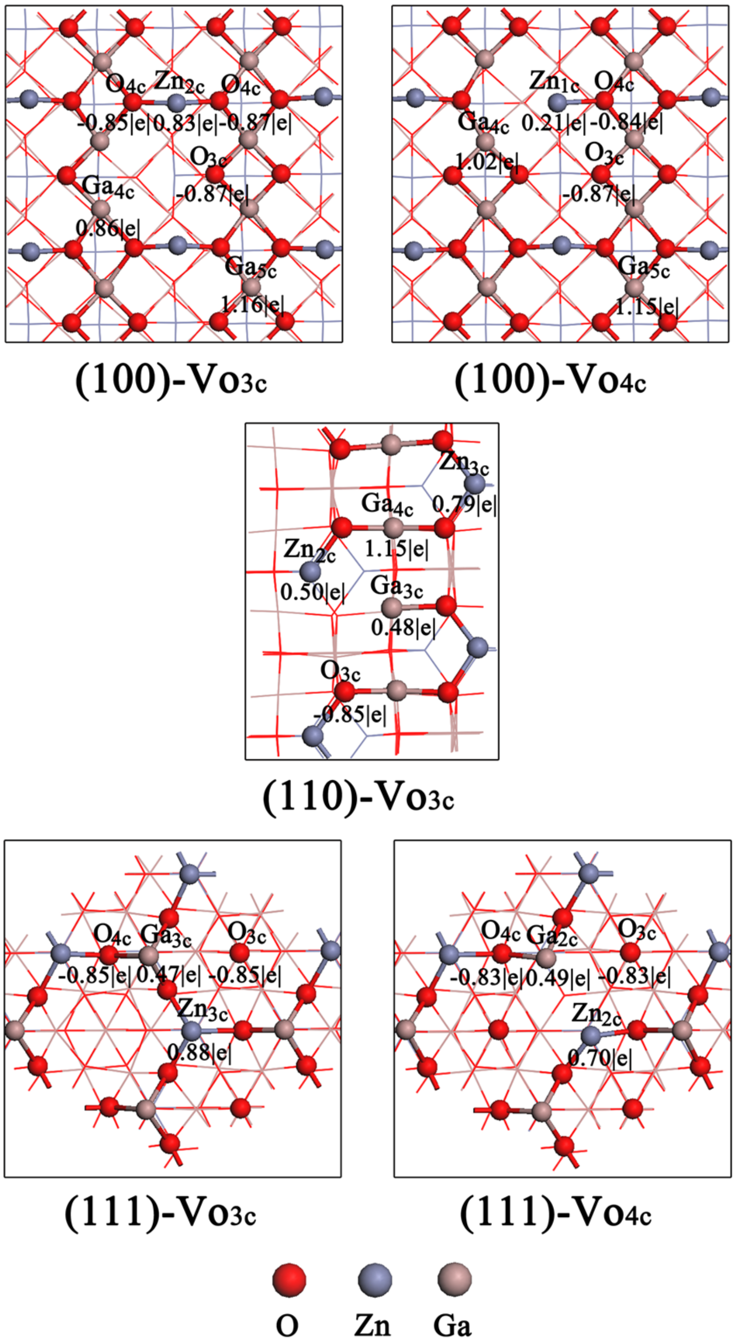
(111-Vo3c-mol)
E= -0.58 eV

(111-Vo4c-mol)
E= -0.20 eV

(111-Vo3c-dis)
E= -1.82 eV

(111-Vo4c-dis)
E= -1.20 eV

Figure S6. Top (left) and side (right) views of CO_2 adsorption structures and energies on O_{3c} and O_{4c} vacancy defective $ZnGa_2O_4$ (111) surface. **(111-Vo$_{3c}$, Zn-c)**: the CO_2 molecule adsorbed by the Zn site on the **(111)-Vo$_{3c}$** surface (similar to **(111, Zn-c)** state in Figure 3); **(111-Vo$_{3c}$-mol)**: the molecular adsorption on the oxygen vacancy site of the **(111)-Vo$_{3c}$** surface; **(111-Vo$_{3c}$-dis)**: the dissociative adsorption on the oxygen vacancy site of the **(111)-Vo$_{3c}$** surface; (**111-Vo$_{4c}$, Zn-c**): the CO_2 molecule adsorbed by the Zn site on the **(111)-Vo$_{4c}$** surface (similar to (**111, Zn-c**) state in Figure 3); **(111-Vo$_{4c}$-mol)**: the molecular adsorption on the oxygen vacancy site of the **(111)-Vo$_{4c}$** surface.



(100)-Vo$_{3c}$ (100)-Vo$_{4c}$

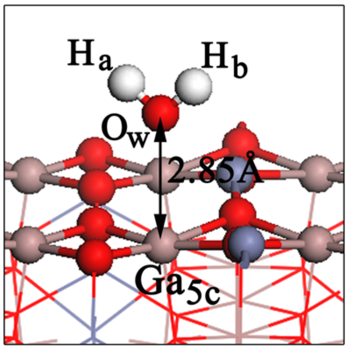
(110)-Vo$_{3c}$

(111)-Vo$_{3c}$ (111)-Vo$_{4c}$

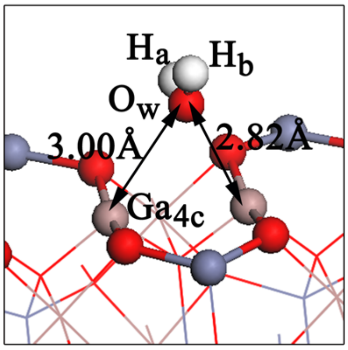
Figure S7. The top views of the optimized structures of the defective ZnGa$_2$O$_4$ (100), (110) and (111) surfaces. The Mulliken charges carried by surface sites are labeled on each surface as well.

other is that the main adsorption site Zn$_{2c}$ on the **(100)-O$_{3c}$** surface carried more positive charges, which can generate a larger interaction between the surface metal atom and the oxygen atom in CO_2 (That is why the Ga_{3c} atom on the **(100)-O_{4c}** surface is also higher than the surface level but the adsorption state on it is less stable than the state on the **(100)-O_{3c}** surface).

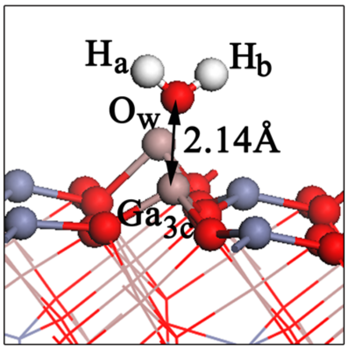
3. The data and figures for the hydrated surfaces



(100-Hy)
E= -0.10 eV



(110-Hy)
E= 0.25 eV



(111-Hy)
E= 0.40 eV

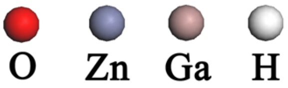
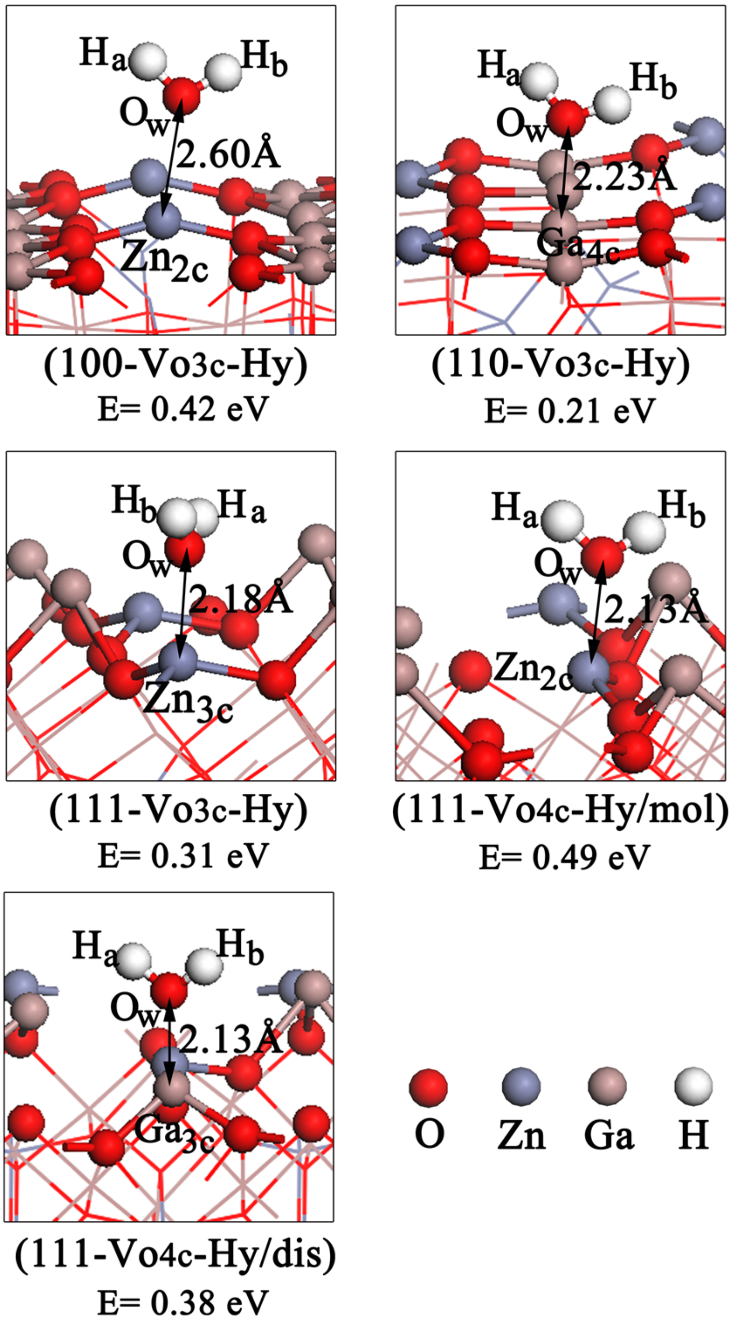


Figure S8. The adsorption structures and energies of H_2O on the perfect (100), (110), and (111) surfaces.



(100-Vo3c-Hy)
E= 0.42 eV

(110-Vo3c-Hy)
E= 0.21 eV

(111-Vo3c-Hy)
E= 0.31 eV

(111-Vo4c-Hy/mol)
E= 0.49 eV

(111-Vo4c-Hy/dis)
E= 0.38 eV

Figure S9. The adsorption structures and energies of H_2O on the defective (100), (110), and (111) surfaces.