

Electronic Supplementary Information (ESI)

Ti₂CO₂ MXene: A Highly Active and Selective Photocatalyst for CO₂ Reduction

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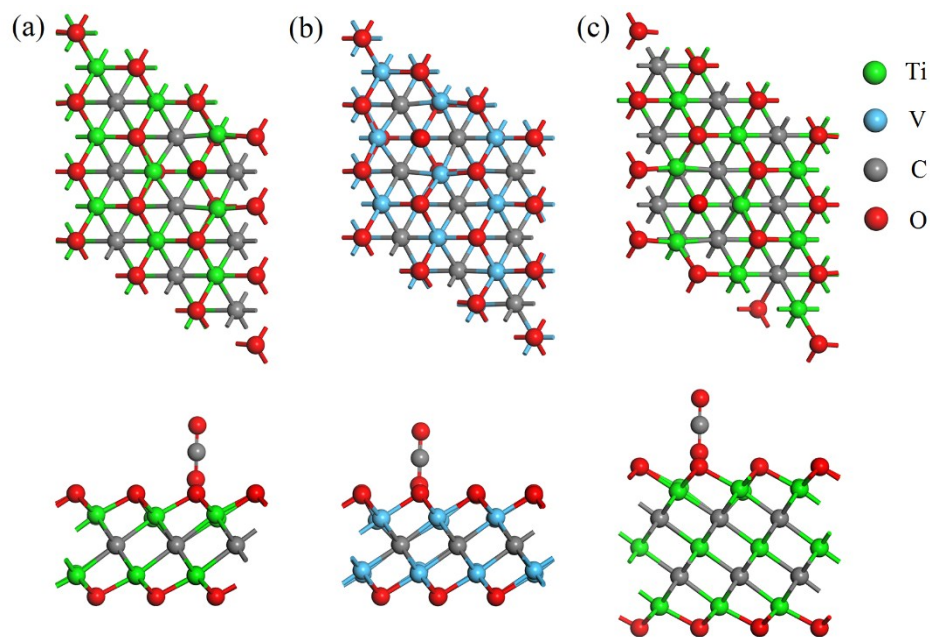


Fig. S1. Top (up) and side (down) view of the optimized energetically most favorable structures of CO₂ adsorbed at the O_v in (a) Ti₂CO₂, (b) V₂CO₂ and (c) Ti₃C₂O₂ monolayers.

Table S1. The adsorption energies E_{ads} (eV) of CO₂ at O_v on Ti₂CO₂, V₂CO₂ and Ti₃C₂O₂ monolayer and the average atomic charge a.c. ($|e|$) of the oxygen atoms adsorbed in O_v and the metal atoms around O_v.

	E_{ads}	a.c. (O)	a.c. (M)
Ti ₂ CO ₂	-0.67	-1.15	1.76
V ₂ CO ₂	-0.35	-1.14	1.60
Ti ₃ C ₂ O ₂	-0.73	-1.14	1.78

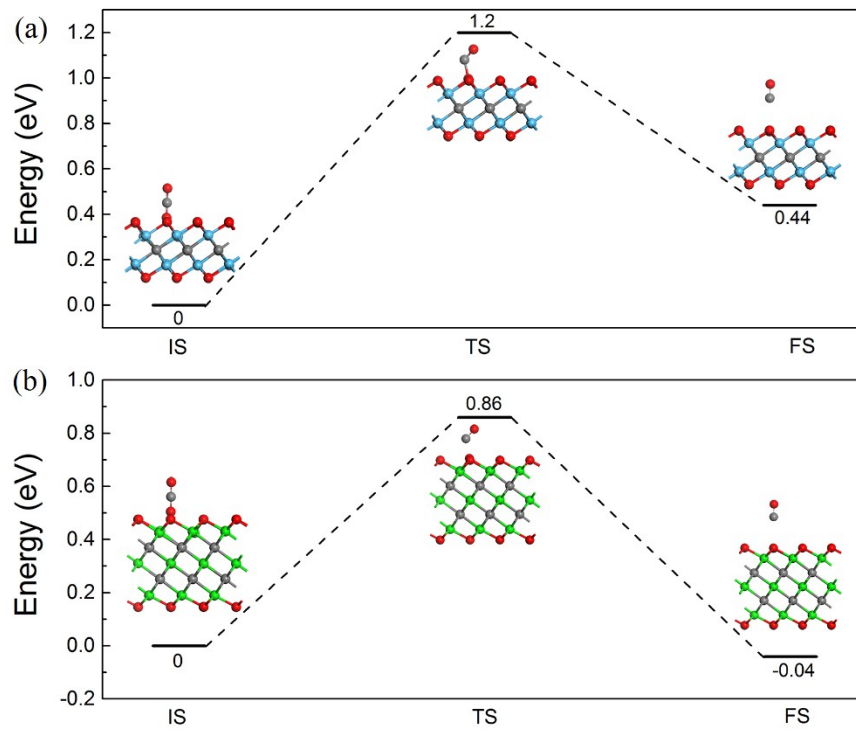


Fig. S2. Reaction pathway (i) at O_v in (a) V₂CO₂ and (b) Ti₃C₂O₂ monolayer.

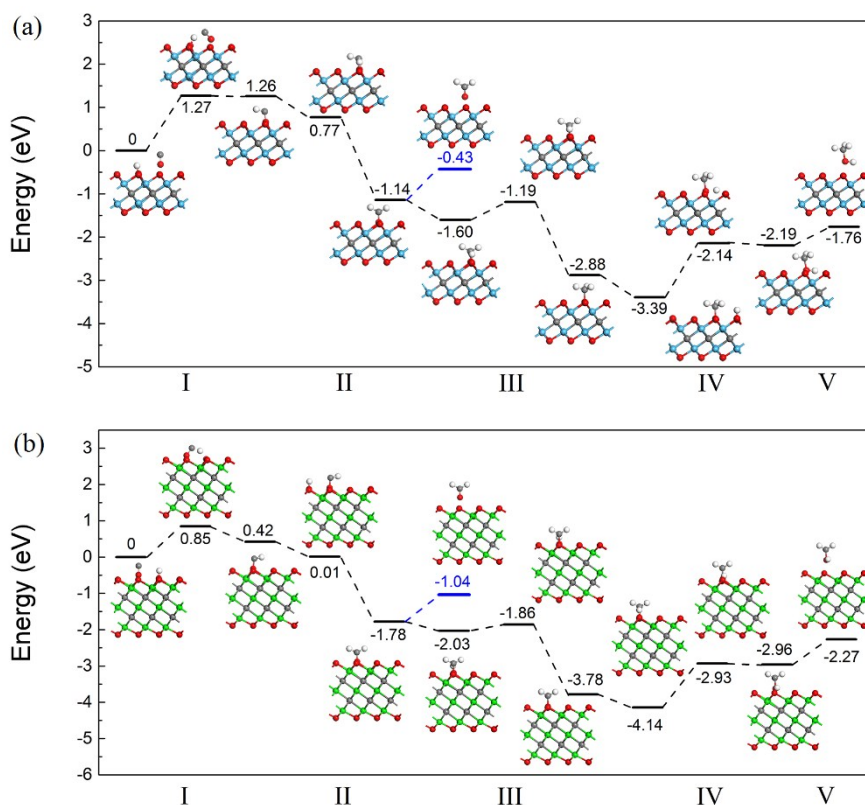


Fig. S3. Reaction pathway of hydrogenation of CO at O_v in (a) V_2CO_2 and (b) $Ti_3C_2O_2$ monolayers.

I: $CO \rightarrow HCO$; II: $HCO \rightarrow HCHO$, the blue lines represent the desorption of formaldehyde; III: $HCHO \rightarrow CH_3O$; IV: $CH_3O \rightarrow CH_3OH$; V: the desorption of methanol.

For V_2CO_2 , in the first step, the CO molecule is also adsorbed at O_v vertically and then the adsorbed proton approaches the C atom to form HCO by overcoming an energy barrier of 1.27 eV. Then, the HCO is further hydrogenated to HCHO without any energy barrier. The process of the desorption of formaldehyde is exothermic by 0.71 eV. In process III, the third proton approaches the C atom by overcoming an energy barrier of 0.17 eV with an exothermic process. In process IV, an energy barrier of 1.25 eV should be overcome. At the final step, the methanol is released with a barrier of 0.43 eV.

For $Ti_3C_2O_2$, the overall energy barrier of the reduction of CO_2 to formaldehyde is 0.85 eV, while to catalyze the further reduction to CH_3OH , an energy barrier of 1.21 eV should be overcome.

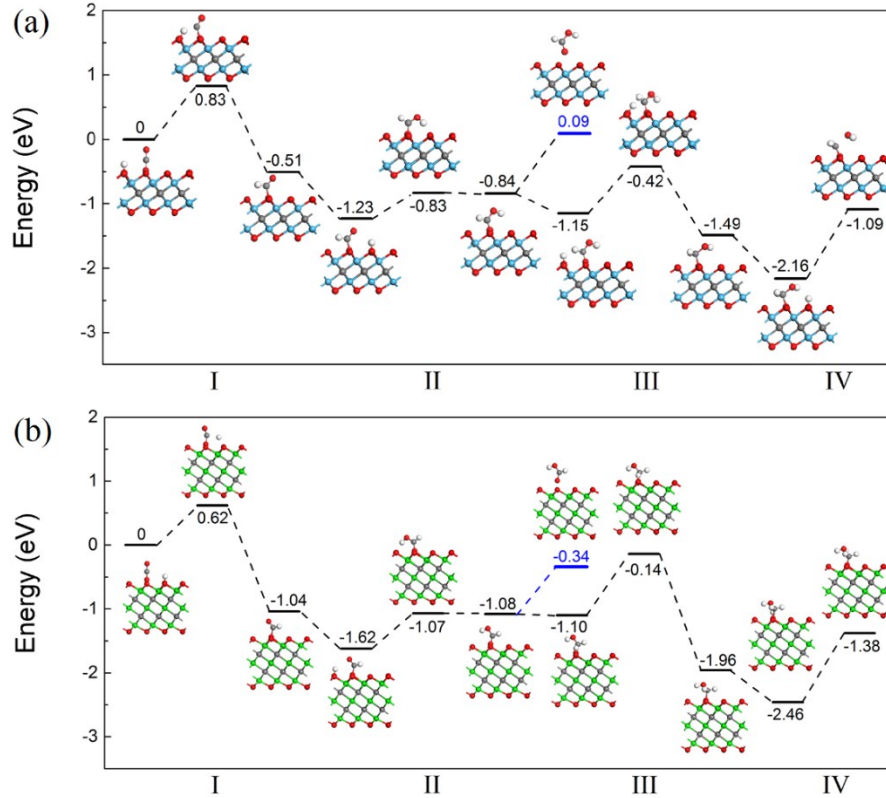


Fig. S4. Reaction pathway of hydrogenation of CO_2 at O_v in (a) V_2CO_2 and (b) $\text{Ti}_3\text{C}_2\text{O}_2$ monolayer.

I: $\text{CO}_2 \rightarrow \text{HCOO}$; II: $\text{HCOO} \rightarrow \text{HCOOH}$; the blue lines represent the desorption of formic acid; III: $\text{HCOOH} \rightarrow \text{H}_2\text{COOH}$; IV: $\text{H}_2\text{COOH} \rightarrow \text{HCHO} + \text{H}_2\text{O}$.

For V_2CO_2 , the energy barrier to form HCOO is higher than that on Ti_2CO_2 (0.83 eV) in process I. In the next process, the second proton approaches the C atom by overcoming an energy barrier of 0.4 eV. Then the desorption of the HCOOH needs a high energy value of 0.93 eV. In process III, an energy barrier of 0.73 eV should be overcome for the further hydrogenation of HCOOH . At the final process, a very high energy barrier of 1.07 eV should be overcome, indicating that it is extremely difficult to realize in experiments.

For $\text{Ti}_3\text{C}_2\text{O}_2$, an overall barrier of 0.62 eV should be overcome to form HCOOH . The desorption process of the HCOOH is exothermic by 0.74 eV. However, the further hydrogenation of HCOOH is extremely difficult due to a high energy barrier of ~ 1 eV.