Suppporting Information

for

The Effect of Sulfur Doping on the $ZrTiO_4$ (111) Surface toward CO_2RR into Chemically Valuable Products: A Density Functional Theory Study

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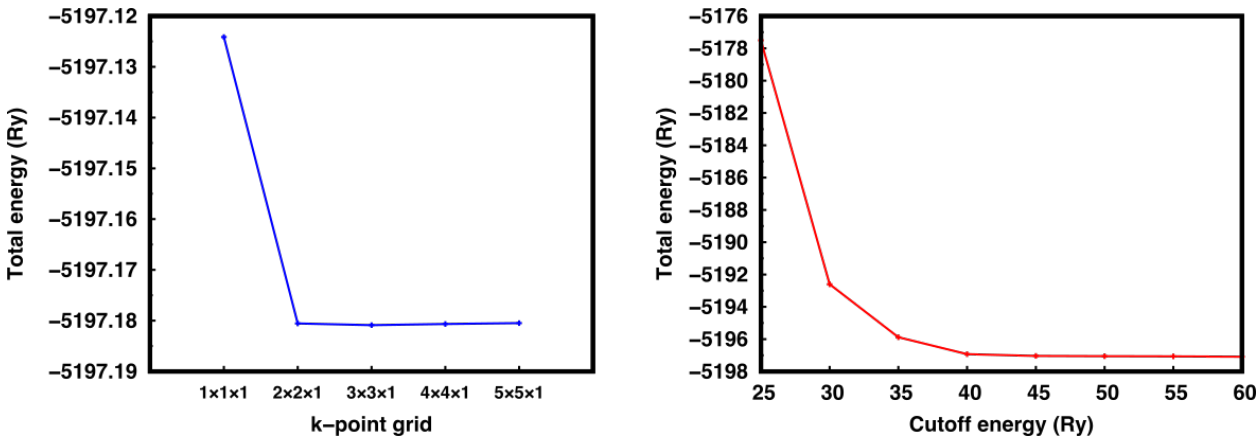


Fig. S1 Total energy of $ZrTiO_4$ versus k-point grid and cut-off energy.

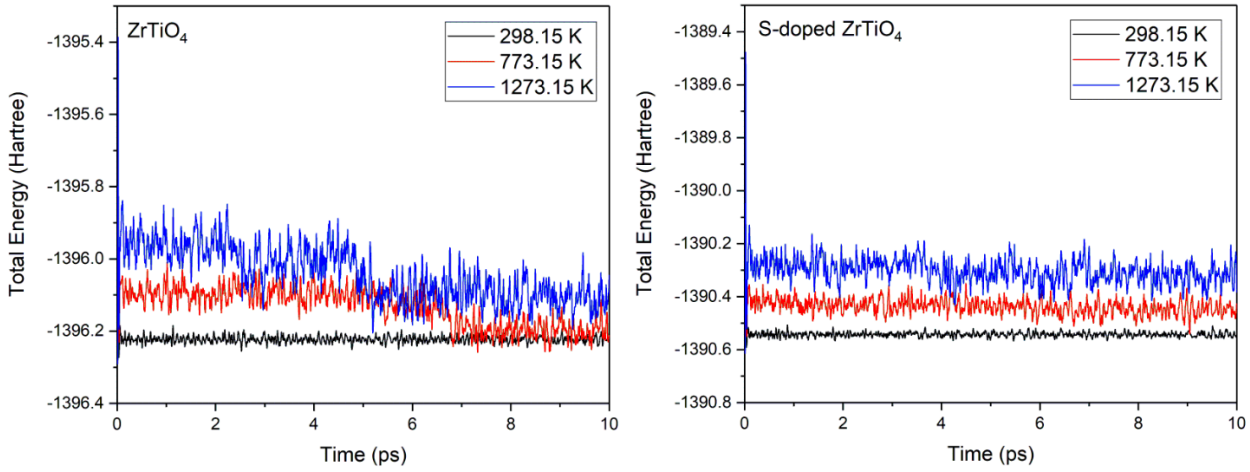


Fig. S2 Total energy of pristine and S-doped $ZrTiO_4$ during molecular dynamics.

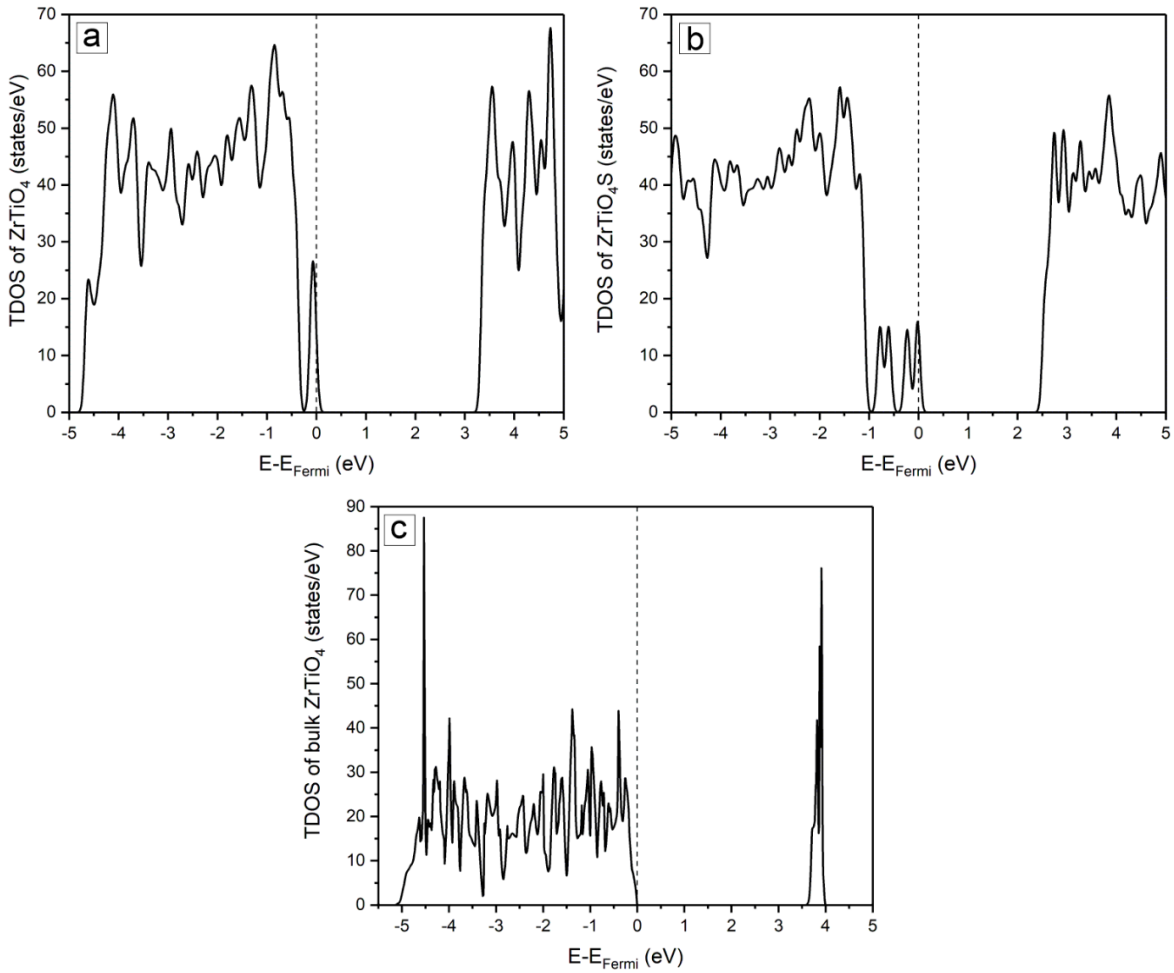


Fig. S3 TDOS for (a) $ZrTiO_4$, (b) S-doped $ZrTiO_4$, and (c) bulk $ZrTiO_4$..

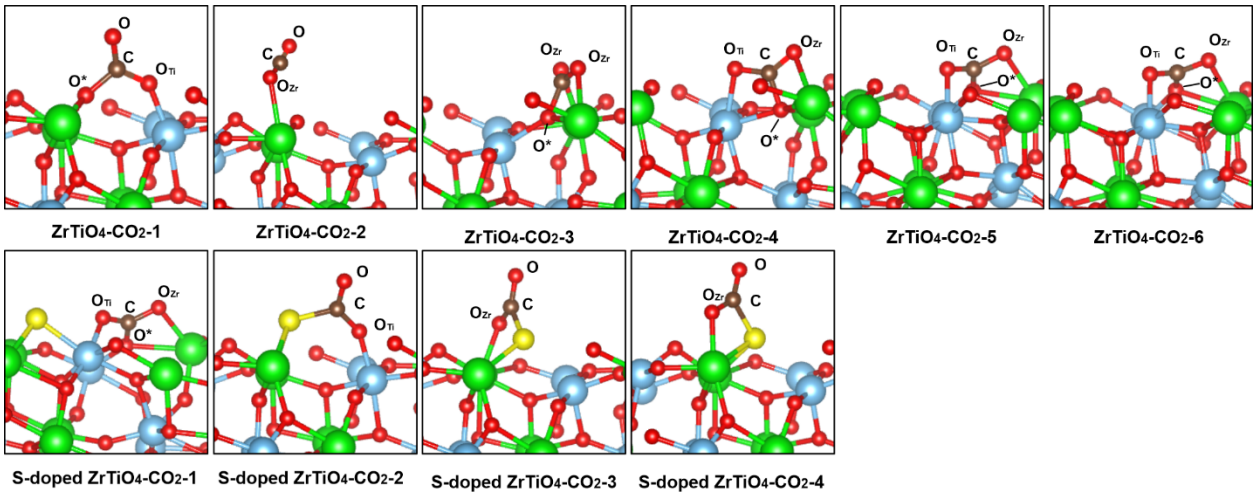


Fig. S4 Optimized geometries of CO_2 adsorbed on pristine and S-doped $ZrTiO_4$ surfaces.

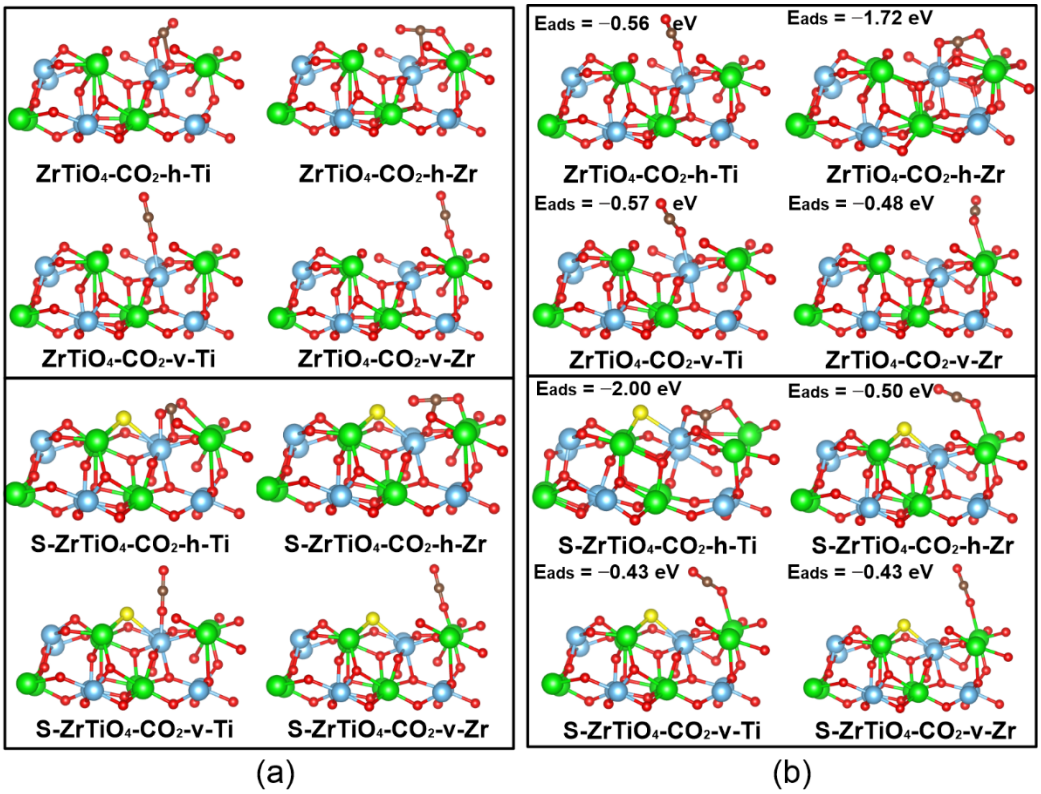
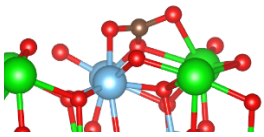
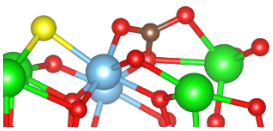
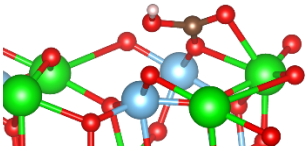
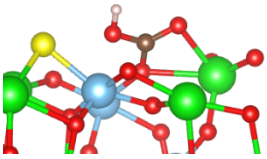
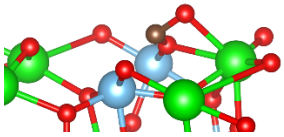
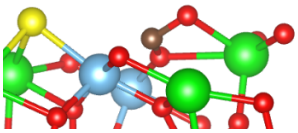
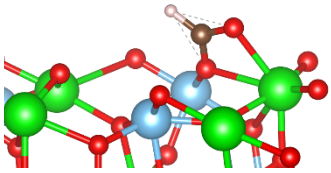
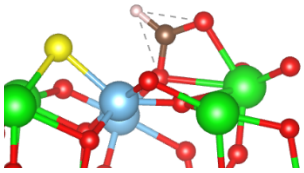
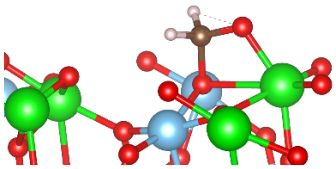
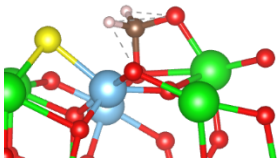
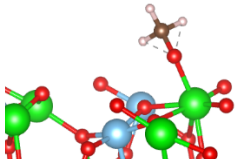
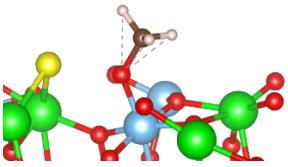
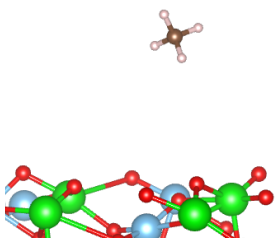
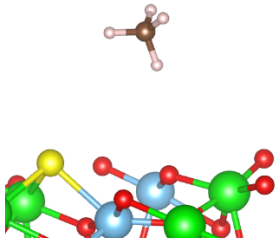
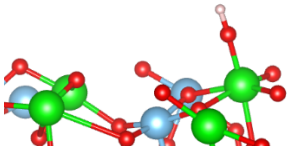
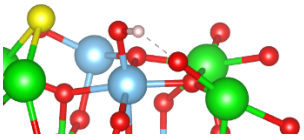
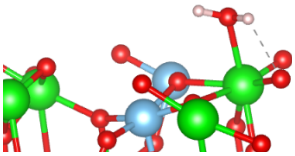
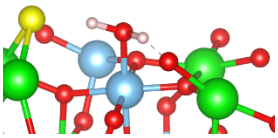
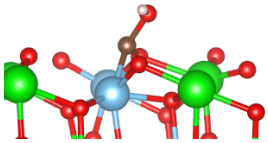
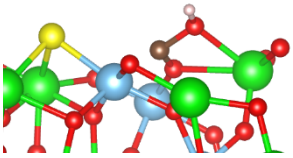
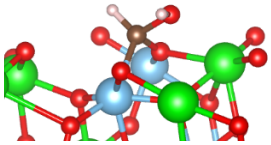
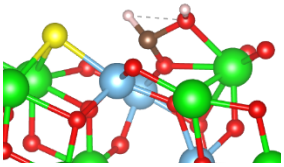
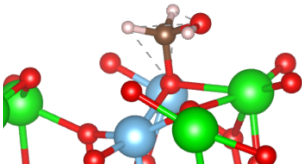
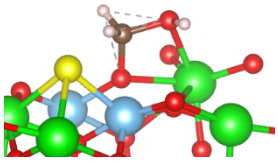
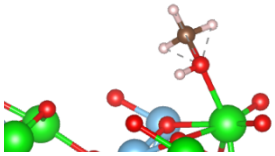
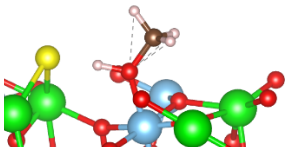
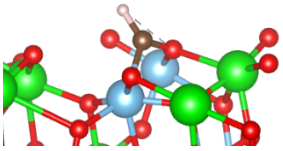
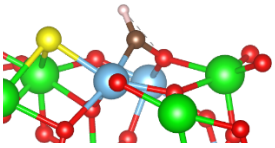
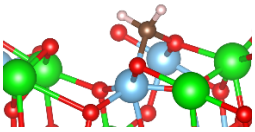
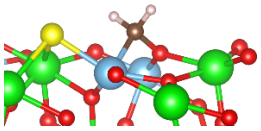


Fig. S5 CO_2 adsorption in horizontal and vertical configurations: (a) before and (b) after geometry optimization.

Intermediate	Optimized geometry	
	$ZrTiO_4$	S-doped $ZrTiO_4$
*CO_2		
*COOH		
*CO		
*CHO		
*CH_2O		
*CH_3O		
*O + CH_4		

*OH		
*OH_2		
*COH		
*CHOH		
*CH_2OH		
*CH_3OH		
*CH		
*CH_2		

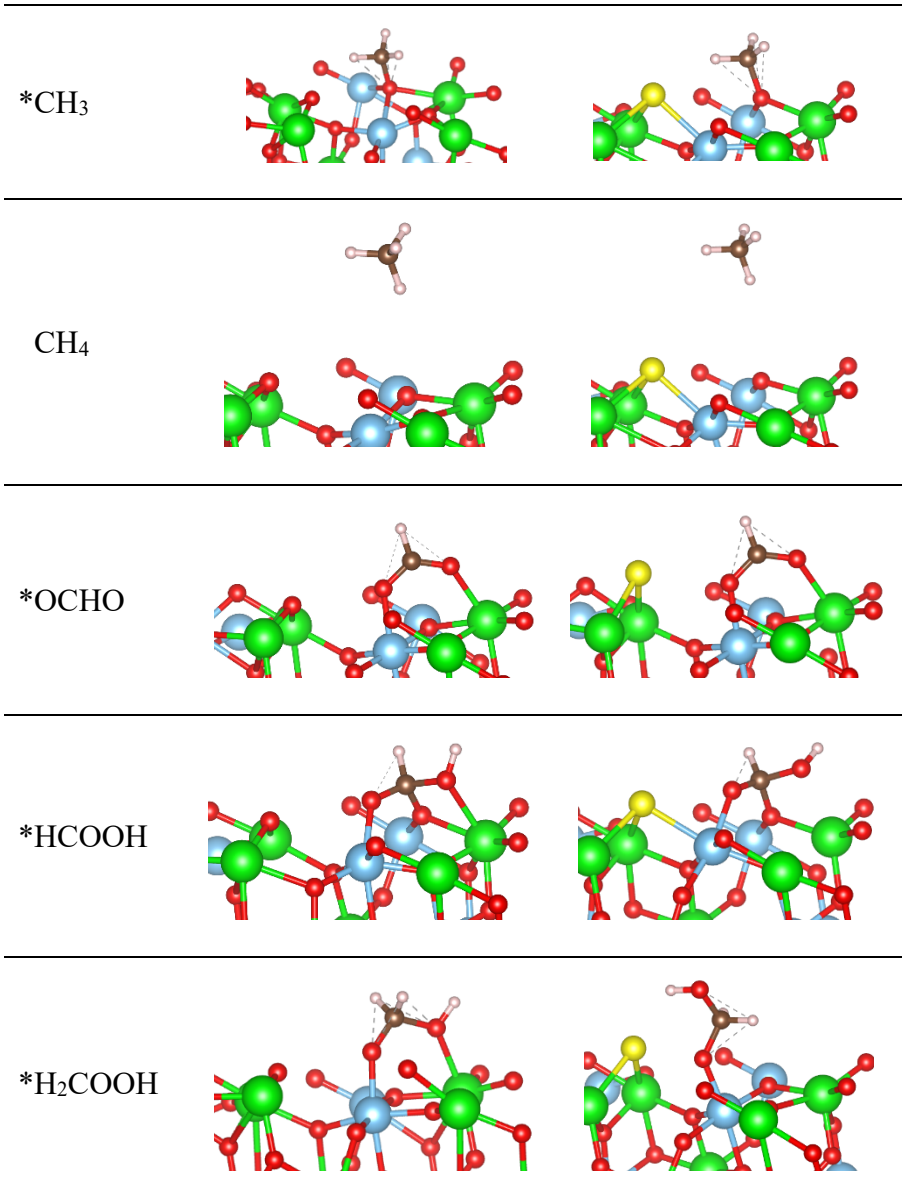


Fig. S6 Optimized geometries of the CO_2RR intermediates on the $ZrTiO_4$ and S-doped $ZrTiO_4$.

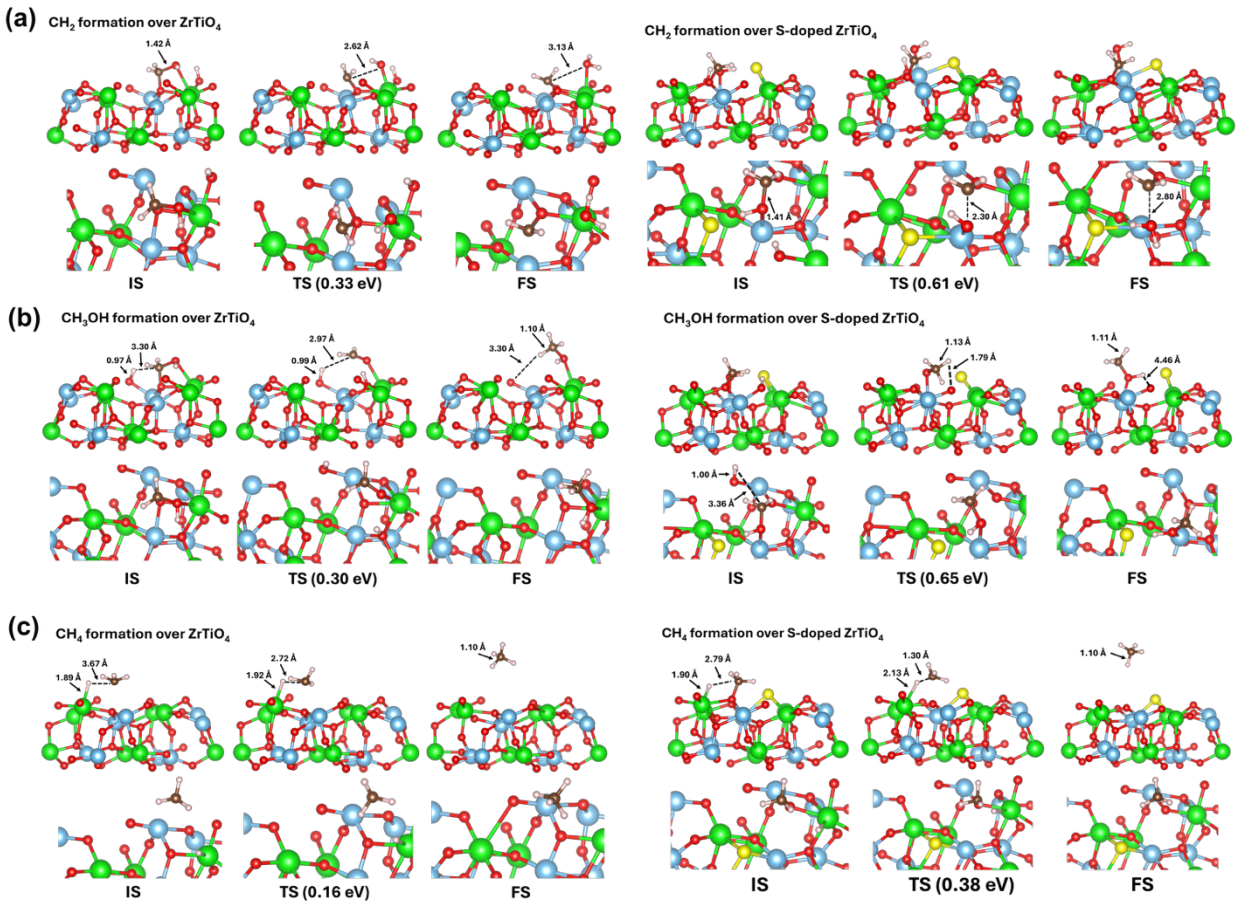


Fig. S7 Initial strutcure (IS), transition structure (TS), and final structure (FS) of (a) CH_2 (b) CH_3OH (c) CH_4 formation over pristine and S-doped $ZrTiO_4$ catalysts

Table S1 Adsorption energy of CO_2 over S-doped $ZrTiO_4$ as a function of the vacuum length.

Vacuum length (Å)	Adsorption energy (eV)
10	-1.9651283
15	-1.9608292
20	-1.9594082

Table S2 Physical properties of the adsorbed CO_2 on the $ZrTiO_4$ in various position

Position	E_{ads} (eV)	Bond Length (Å)		CO_2 Bond Angle (°)	Atomic Charge O*	C
1	−1.41	C–O*	1.384	126.730	−1.222	2.138
		$C–O_{Ti}$	1.306			
		C–O	1.206			
2	−0.50	C–O*	2.430	174.165	−1.240	2.173
		$C–O_{Zr}$	1.183			
		C–O	1.157			
3	−0.57	C–O*	1.389	128.946	−1.258	2.135
		$C–O_{Zr}$	1.253			
		$C–O_{Zr}$	1.256			
4	−0.30	C–O*	1.396	134.212	−1.229	2.117
		$C–O_{Ti}$	1.261			
		$C–O_{Zr}$	1.248			
5	−1.73	C–O*	1.320	125.540	−1.239	2.176
		$C–O_{Ti}$	1.273			
		$C–O_{Zr}$	1.270			
6	−1.73	C–O*	1.322	125.934	−1.240	2.185
		$C–O_{Ti}$	1.275			
		$C–O_{Zr}$	1.268			

Table S3 Physical properties of the adsorbed CO_2 on the S-doped $ZrTiO_4$ in various position

Position	E_{ads} (eV)	Bond Length (Å)		CO_2 Bond Angle (°)	Atomic Charge		
					O*	S	C
1	−1.97	C–O*	1.315	124.018	−1.264		2.208
		C–O_{Ti}	1.268				
		C–O_{Zr}	1.272				
2	−0.77	C–S	1.833	127.122		−0.526	1.608
		C–O_{Ti}	1.299				
		C–O	1.205				
3	−0.39	C–S	1.885	130.951		−0.644	1.686
		C–O_{Zr}	1.288				
		C–O	1.201				
4	−0.69	C–S	1.878	130.829		−0.638	1.682
		C–O_{Zr}	1.298				
		C–O	1.198				