

Supporting Information:

Tuning the Lewis acidity of ZrO₂ for efficient conversion of CH₄ and CO₂ into acetic acid

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Supporting method

Temperature-programmed desorption measurements

Temperature-programmed desorption measurements of NH_3 (NH_3 -TPD) was performed on an automated chemisorption analyzer (TP5076 TPD/TPR) equipped with a TCD. Before each TPD experiments, 200 mg of sample was charged into the quartz tube and flushed with N_2 at 500 °C for 1 h following by cooling down to 40°C. Ammonia was adsorbed by exposing sample to a 10% NH_3/Ar (30 mL/min) for 1h at 40°C and then purged with helium at this temperature for 30 min to desorb physically adsorbed ammonia. Desorption of ammonia was carried out in flowing He (30 mL/min) by increasing the temperature to 700 °C with a heating rate of 10°C/min.

For CO-TPD, 200 mg of sample was first pretreated in N_2 at 500°C for 1 h following by cooling down to 40°C. The sample was exposed in a flow of 5%CO/Ar (30 mL/min) for 1h at 40°C and then purged with helium at this temperature for 30 min. Finally, the sample was heated to 700°C (for CO desorption) with a heating rate of 10 K·min⁻¹ in He flow (30 mL·min⁻¹).

For CO_2 -TPD, 200 mg of sample was first pretreated in N_2 at 500°C for 1 h following by cooling down to 40°C. The sample was exposed in a flow of 20% CO_2/Ar (30 mL/min) for 1h at 40°C and then purged with helium at this temperature for 30 min. Finally, the sample was heated to either 900°C for CO_2 desorption or 700°C with a heating rate of 10°C·min⁻¹ in He flow (30 mL·min⁻¹).

Sulfate species on SZ would be decomposed to produce sulfur oxides at high temperatures. To distinguish the contribution of decomposed products of SZ during the TCD measurements, temperature-programmed decomposition measurements were also performed. The sample was pretreated in N_2 at 500°C for 1h, cooled down to 40°C and heated to 900°C with a heating rate of 10 °C·min⁻¹ in He flow (30 mL·min⁻¹). The corresponding temperature-programmed decomposition curves are shown as dashed lines in Fig. 7a.

Table S1. Physicochemical properties of various catalysts.

Sample	Sulfur content ^a (wt %)	Sulfur content ^b (wt %)	BET surface area ^c (m ² /g)	Pore size ^d (nm)	Pore volume ^d (cm ³ /g)
ZrO ₂	--- ^e	--- ^e	38.99	17.1	0.167
SZ-1	5.83	10.14	47.42	5.73	0.068
SZ-2	8.17	12.82	7.06	10.7	0.019
SZ-3	10.72	15.52	3.29	10.7	0.009

^a Analyzed by ICP-OES.

^b Analyzed by XPS.

^c Calculated by N₂ sorption data.

^d Calculated using the BJH formalism from the N₂ adsorption (or desorption) branch isotherm.

^e Sulfur was not detected.

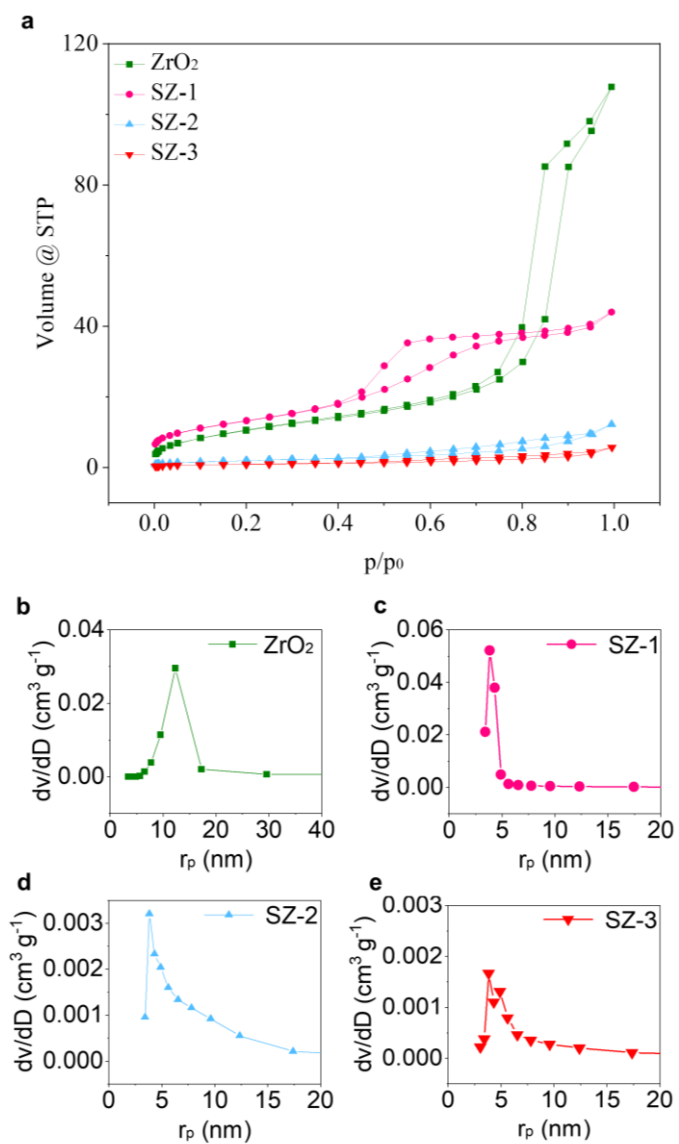


Fig. S1 N₂ adsorption-desorption isotherm curves (a); BJH pore size distribution curves (b-e).

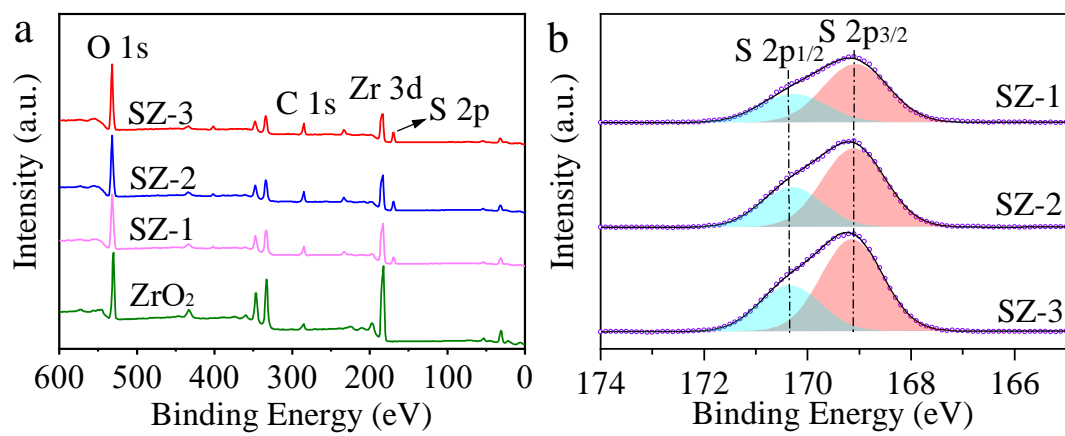


Fig. S2 Survey (a) and S 2p (b) XPS spectra of ZrO₂ and SZ catalysts.

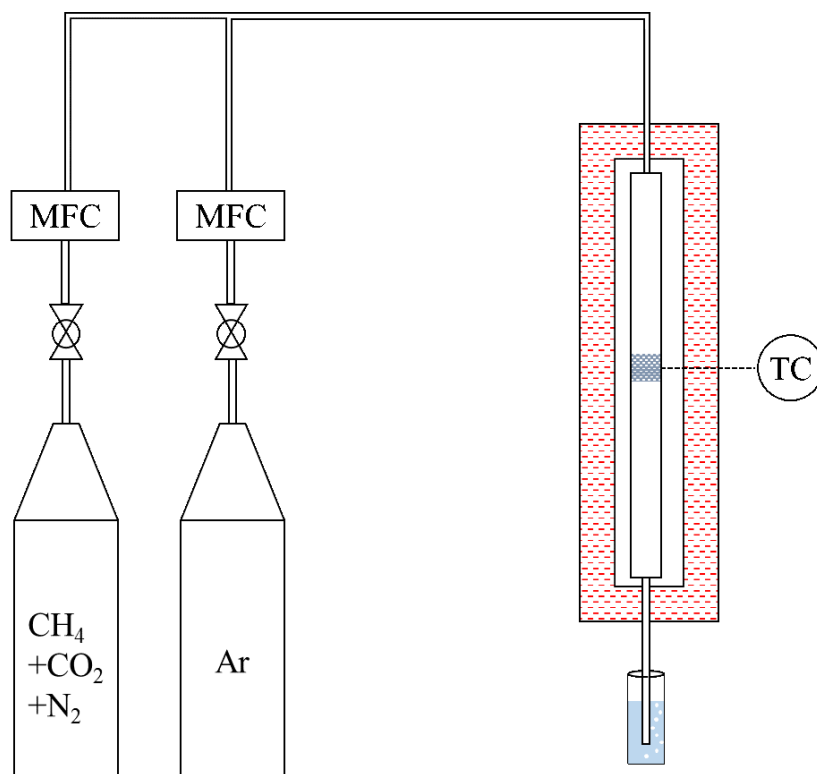


Fig. S3 The schematic of reactor for conversion of CH_4 and CO_2 into acetic acid.

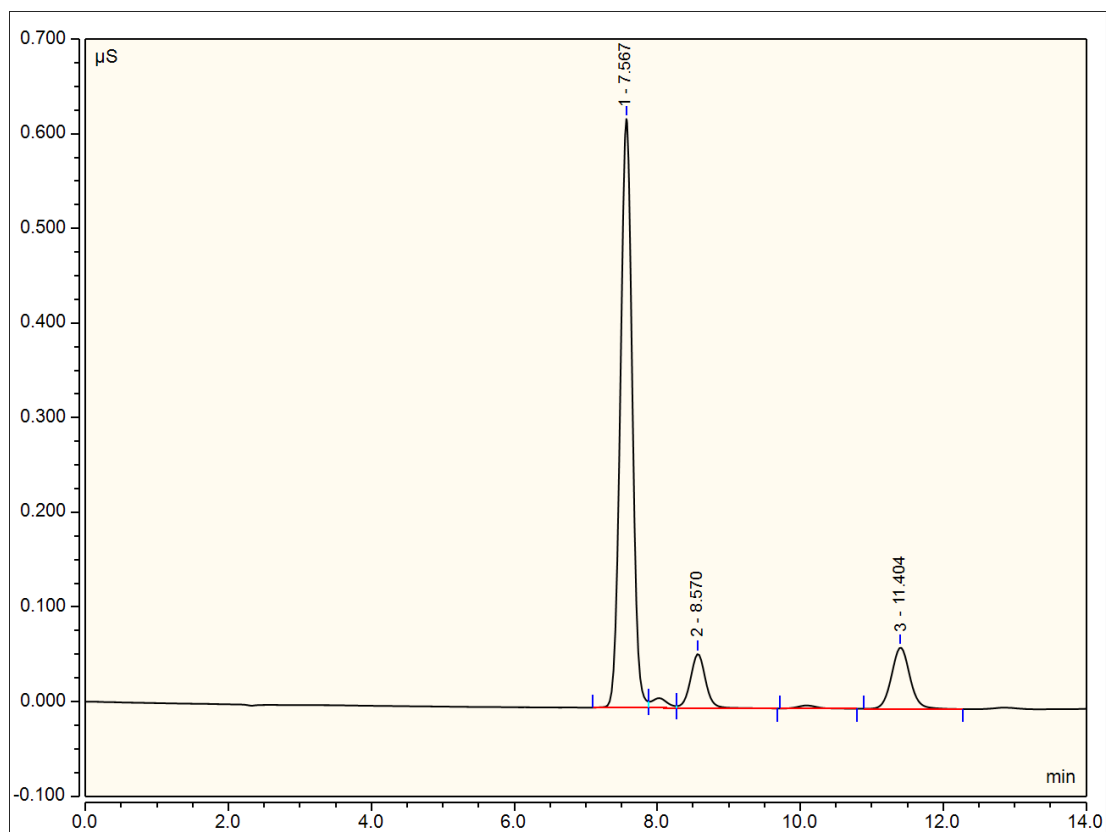


Fig. S4 A typical ion chromatography spectrum obtained from the co-conversion of CH_4 and CO_2 on SZ-3. The main chromatographic peaks with the retention time at 7.567, 8.570 and 11.404 min were identified as fluoride, acetate and formate ion, respectively.

Table S2. Catalytic performance of various catalysts.

Entry	Catalysts	Acetic acid/ μg	Formic acid/ μg	Total products/ μg
1	ZrO ₂ ^a	0.0248	0.003	0.0278
2	SZ-1 ^a	0.1697	0.0624	0.2321
3	SZ-2 ^a	0.2423	0.0552	0.2975
4	SZ-3 ^a	0.3557	0.0687	0.4244
5	SZ-3 ^b	0	0	0
6	SZ-3 ^c	0.0849	0.1812	0.2661

^a Reaction conditions: 1 atm, 500 °C, CH₄: CO₂: N₂=45: 45: 10, 3000 cm³h⁻¹g_{cat}⁻¹

^b Reaction conditions: 1 atm, 500 °C, pure CO₂, 3000 cm³h⁻¹g_{cat}⁻¹

^c Reaction conditions: 1 atm, 500 °C, pure CH₄, 3000 cm³h⁻¹g_{cat}⁻¹

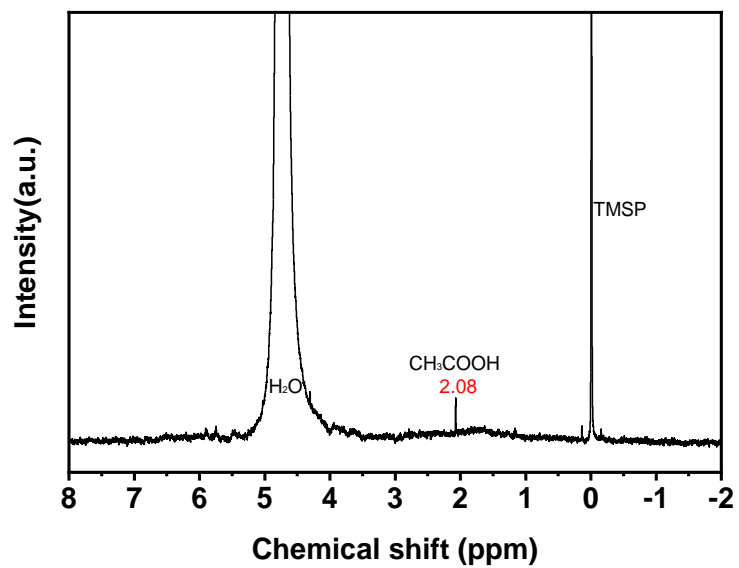


Fig. S5 ^1H NMR spectrum obtained from the co-conversion of CH_4 and CO_2 on SZ-3. Chemical shift of 2.08 ppm proves the formation of acetic acid.

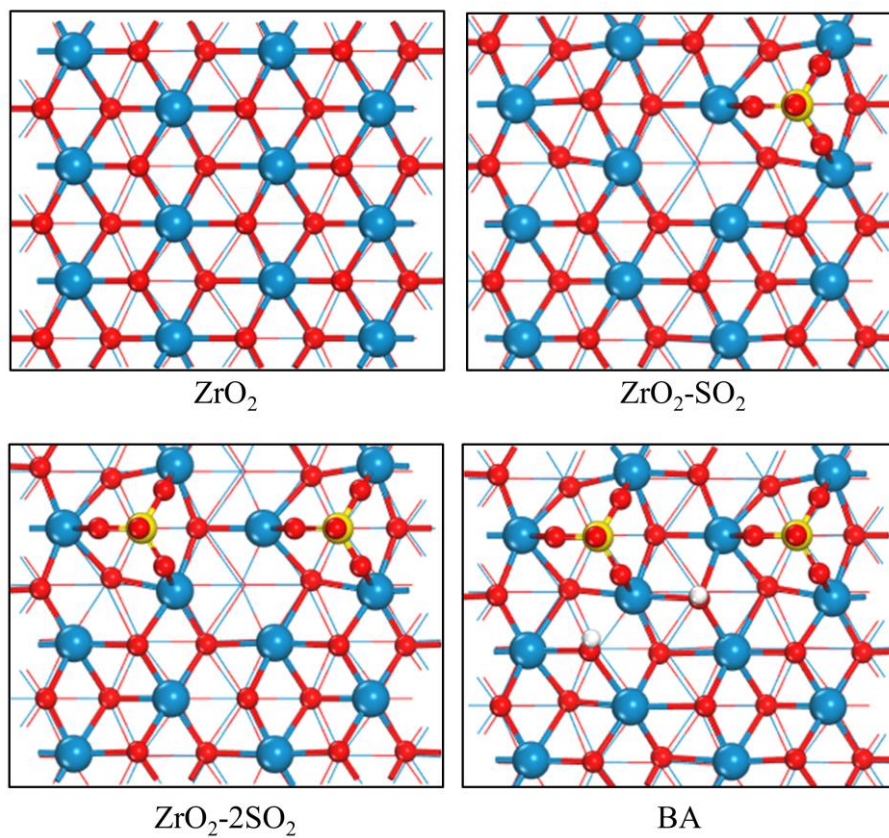


Fig. S6 Structural models of ZrO_2 , ZrO_2-SO_2 , ZrO_2-2SO_2 and BA in the DTF calculations.

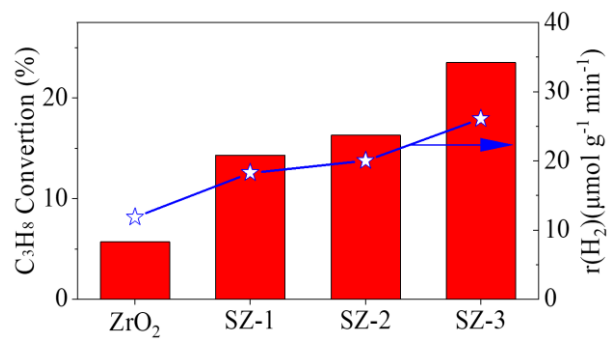
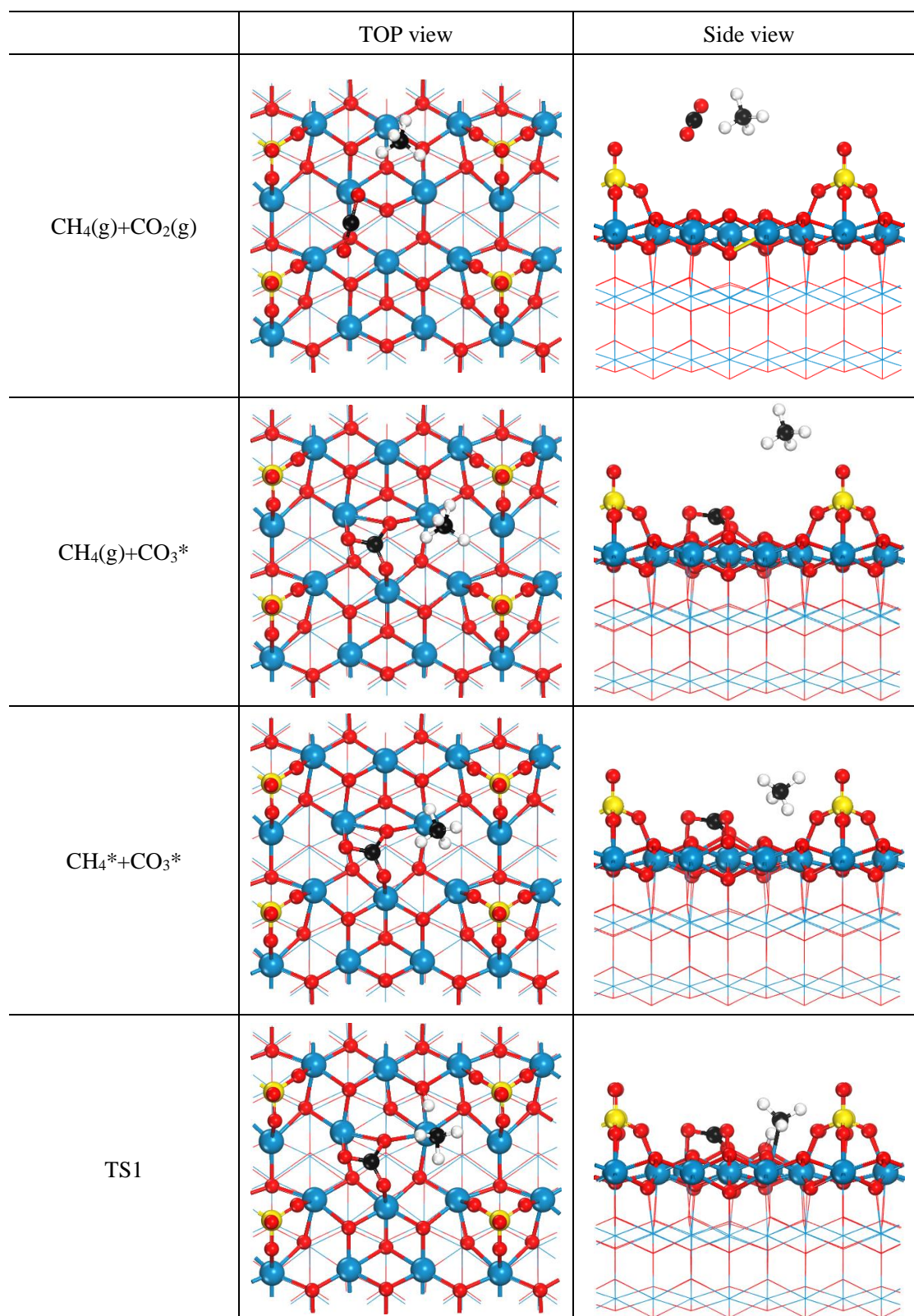
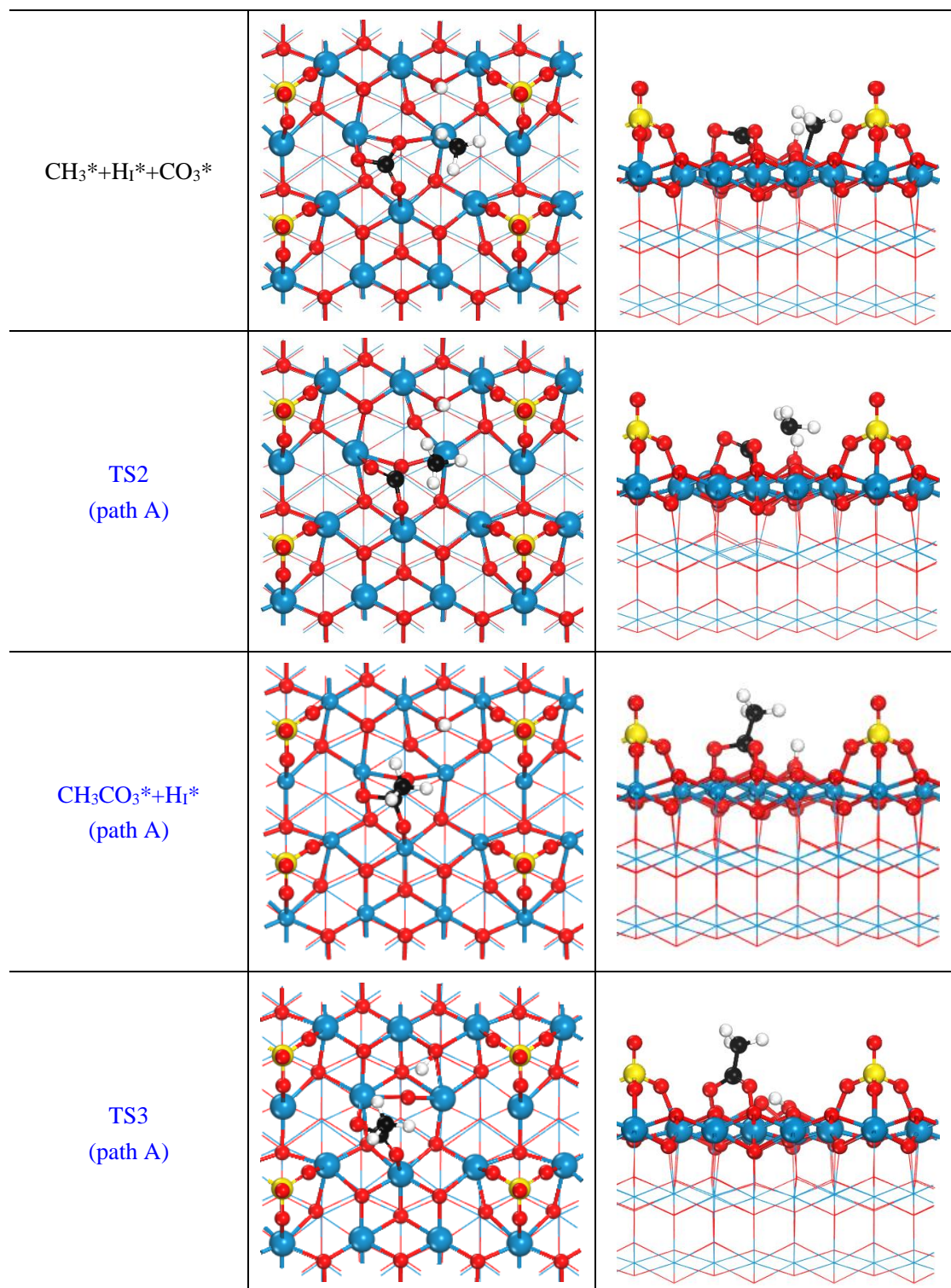
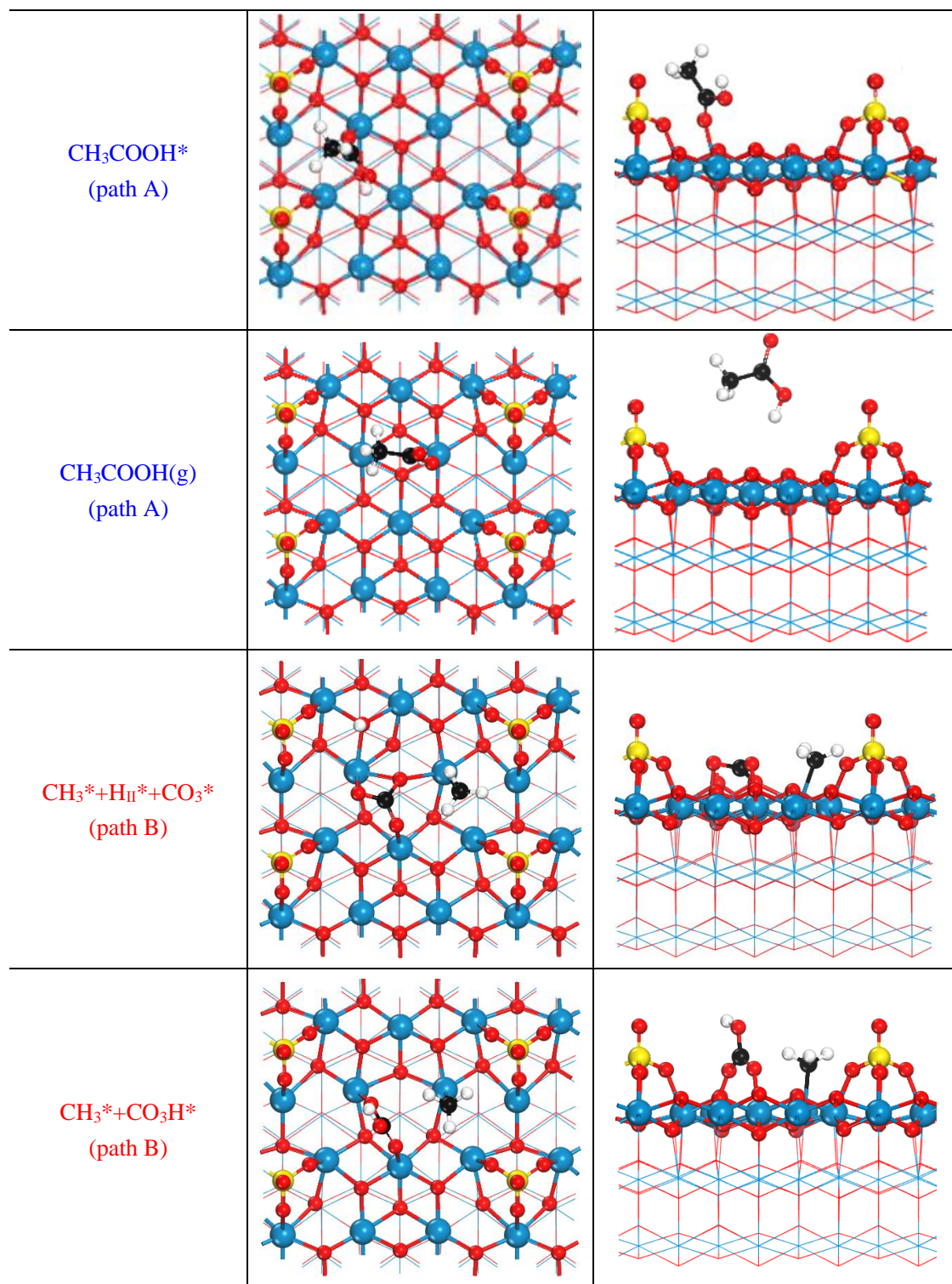


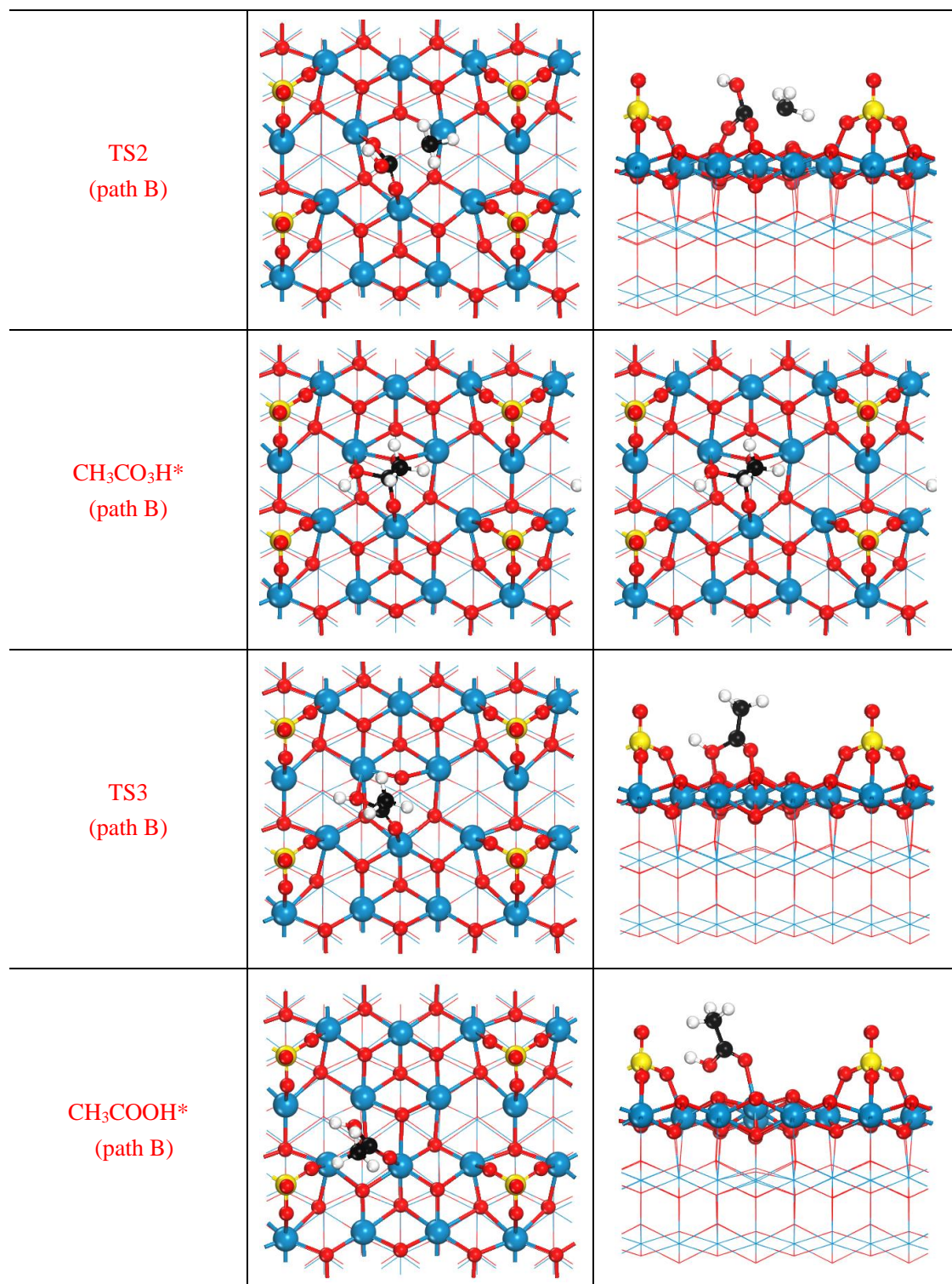
Fig. S7 PDH reaction over all catalysts. Reaction condition: $T=550^{\circ}\text{C}$, $P=1\text{ atm}$, $t=10\text{ min}$, $\text{C}_3\text{H}_8:\text{N}_2=20:80$, $GHSV=3000\text{ cm}^3\text{h}^{-1}\text{g}_{\text{cat}}^{-1}$.

Table S3. Configurations for conversion CH_4 and CO_2 into acetic acid on $\text{ZrO}_2\text{-2SO}_2$.

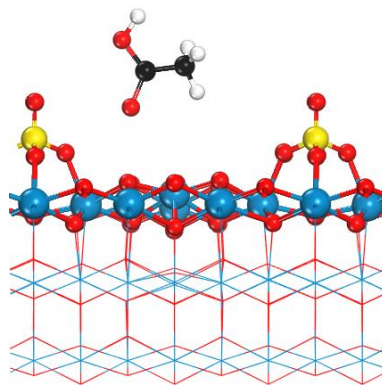
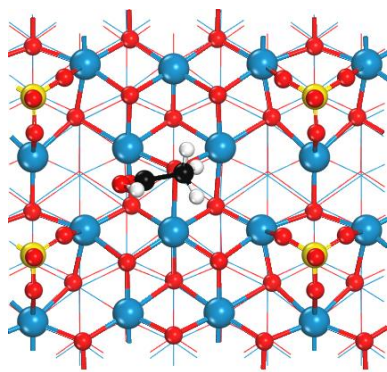








$\text{CH}_3\text{COOH}(\text{g})$
(path B)



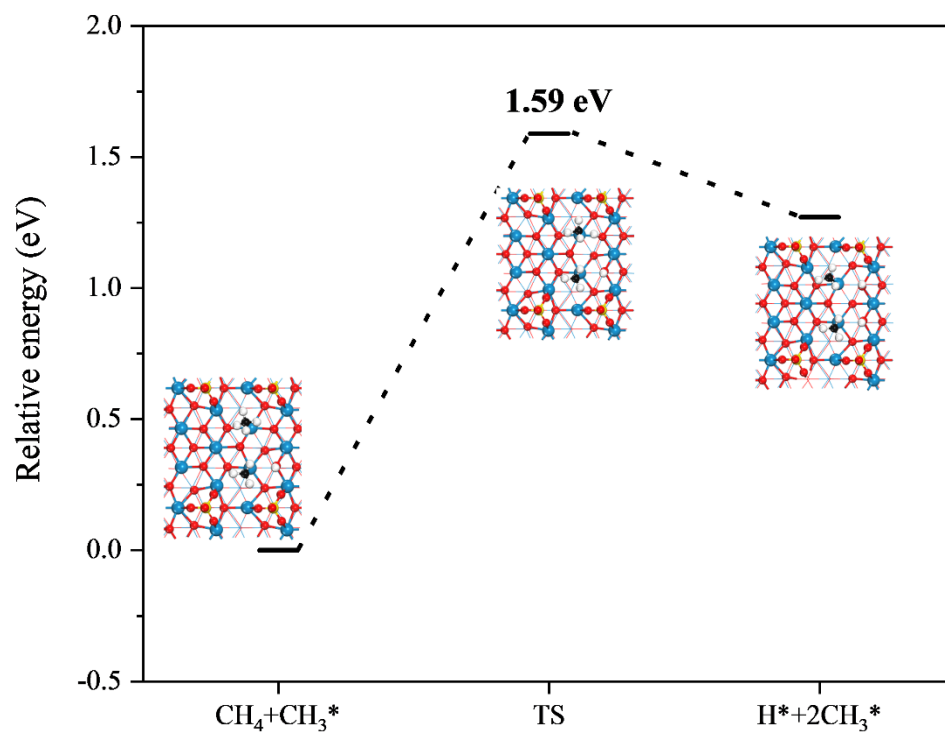


Fig. S8 Results for the second CH₄ dissociation on ZrO₂-2SO₂ after the activation of first CH₄.