

Supporting information

Enhanced surface Lewis acidity of ZrO₂ by –HSO₄ for efficient CF₄ decomposition

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1. Characterization of catalysts

X-ray diffraction (XRD) patterns were obtained by using a STADIP automated transmission diffractometer, operated at 36 kV and 20 mA by using CuK α 1 radiation. The XRD patterns were scanned in the 2 Theta range of 15-90°.

The transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) images were obtained by JEOL 3010 operated at 200 kV. The finely ground sample was dispersed in ethanol and then dropped onto a copper grid for TEM and EDX testing.

The Brunauer-Emmett-Teller (BET) surface area and pore size distribution of the catalysts were determined by N₂ adsorption-desorption analysis using AUTOSORB IQ. Prior to measurements, the samples were degassed at 300 °C for 6 h, at a rate of 10 °C/min.

ICP-OES tests of all samples were performed by an Agilent 5110 spectrometer. Prior to testing, the samples were completely dissolved by sonication in a 5% concentration of HF solution. Then, the F ions in the test liquid were evaporated at room temperature.

NH₃ (or CF₄)-temperature programmed desorption (TPD) was performed by using a PCA-1200 on a chemisorption analyzer equipped with a thermal conductivity detector (TCD). The chemisorption analyzer was PCA-1200 from Beijing Builder electronic technology Co., Ltd. For each experiment, the weighed sample (100 mg) was pretreated at 600 °C (10 °C/min) for 2 h under Ar (30 mL/min) and cooled to room temperature. Then the NH₃ (or CF₄) gas (30 mL/min) was introduced instead of Ar at this temperature for 1 h to ensure the saturation adsorption of NH₃ (or CF₄). The sample was then purged with Ar for 1 h (30 mL/min) until the signal returned to the baseline as monitored by a TCD. The desorption curve of NH₃ (or CF₄) was acquired by heating the sample from room temperature to 800°C (10 °C/min) under Ar with the flow rate of 30 mL min⁻¹.

Pyridine-infrared (py-IR) spectra of samples were analyzed by a Thermo IS-50 Fourier Transform infrared (FTIR) spectrometer. The sample was heated at 600 °C for 5 h, and

cooled to room temperature. Then, vacuumized to 10^{-3} Torr, samples were exposed to pyridine vapour (3000 Pa) at 100 °C for 1 h, followed by reevacuation for 1 h, and lower the temperature to take out our samples. After this step, the sample was analyzed by FTIR.

In situ IR spectra of sample was also analyzed by a Thermo IS-50 FTIR spectrometer. Self-supported wafer was prepared from catalyst powder (ca. 10 mg). The wafer was loaded into an *in situ* IR thermal catalytic cell with CaF_2 windows and pretreated under Ar flow at 650 °C for 2 h. Then regulated to the target temperature to obtain a background spectrum which should be deducted from the sample spectra. As for the transient reactions with CF_4 and H_2O , after the background spectra at appointed temperatures under Ar flow was obtained, the catalyst was exposed to 1 mL min^{-1} 20% $\text{CF}_4/\text{Ar} + \text{H}_2\text{O}$ (50 mL Ar passing through water bottle) at 580 °C and meanwhile the reaction process was recorded as a function of time.

2. Computation detail

All our investigations in this study are based on density functional theory, as implemented in the Vienna ab initio simulation package (VASP)[1,2]. The exchange-correlation potential is treated with the Perdew-Burke- Ernzerhof (PBE) formula by using the projected augmented wave (PAW) method within the generalized gradient approximation (GGA)[3]. The cut-off energy for all calculations was set to be 450 eV. All the positions of atoms are fully relaxed until the Hellmann-Feynman forces on each atom are less than 0.01 eV/Å. Meanwhile, a k-points Γ -centered mesh is generated for Brillouin zone samples. The DFT-D3 method proposed by Grimme was adopted to describe the van der Waals interactions, which has been shown to accurately describe chemisorption and physisorption properties on layered material. In addition, A vacuum region of about 15Å was used to decouple the periodic replicas.

[1]. Kresse, Georg, and Jürgen Hafner. "Ab initio molecular dynamics for liquid metals." Physical Review B 47.1 (1993): 558.

- [2]. Kresse, Georg, and Jürgen Furthmüller. "Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set." *Physical review B* 54.16 (1996): 11169.
- [3]. Perdew, John P., Kieron Burke, and Matthias Ernzerhof. "Generalized gradient approximation made simple." *Physical review letters* 77.18 (1996): 3865

3. Results

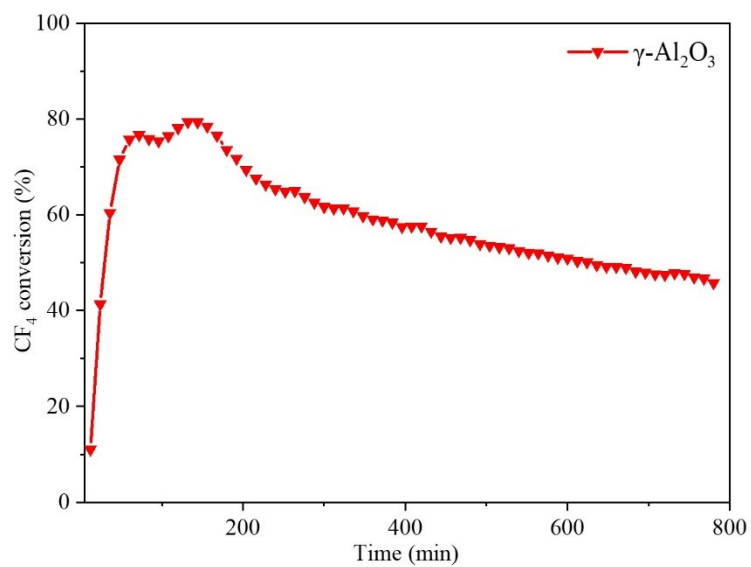


Figure S1. The CF₄ decomposition test of $\gamma\text{-Al}_2\text{O}_3$ under 650 °C.

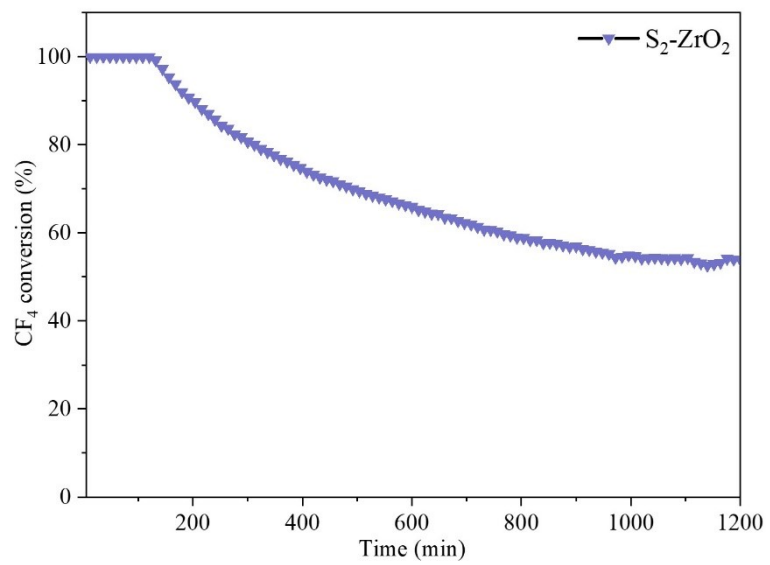


Figure S2. The stability test of the best catalyst S₂-ZrO₂ under 650 °C.

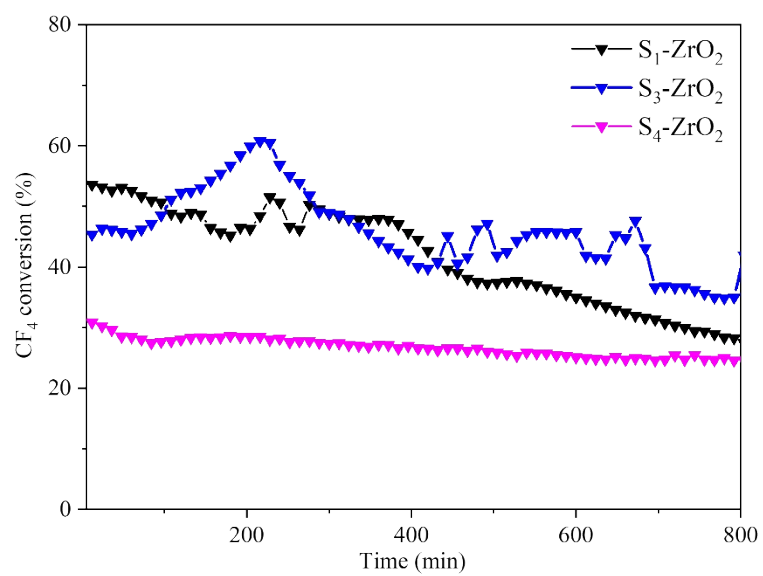


Figure S3. The stability test of S₁-ZrO₂, S₃-ZrO₂ and S₄-ZrO₂ catalysts under 650 °C.

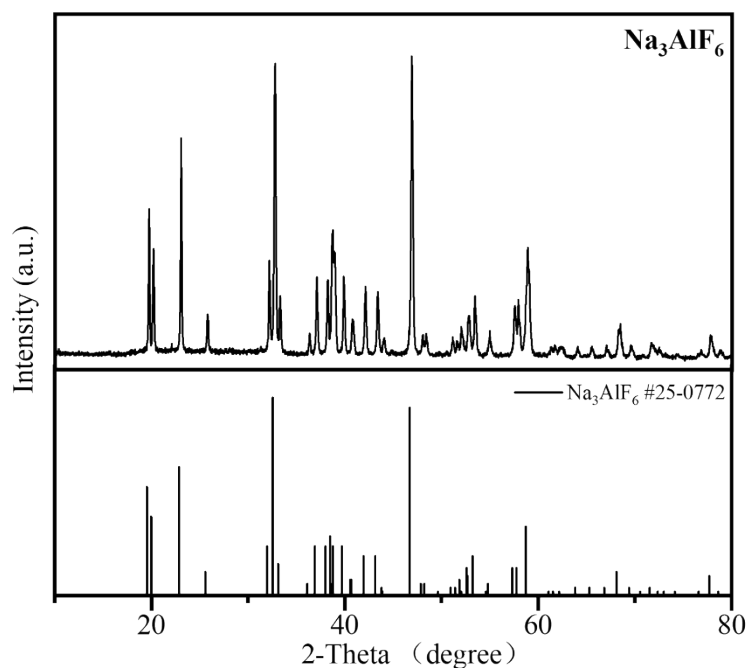


Figure S4. The XRD pattern of the obtained Na_3AlF_6 by recycling HF.

The F ion contents in the solution were quantified by employing the F ion selective electrode method. After decomposition of CF_4 with the $\text{S}_2\text{-ZrO}_2$ catalyst at $650\text{ }^\circ\text{C}$ for 10 h, the amount of F ion in solution was about 350 mg L^{-1} . As shown in Fig. S4, the XRD pattern showed that the F ions were successfully resourced as electrolytic aluminum industry raw materials of Na_3AlF_6 with a rate of 99.6%. The residual F ions in the solution decreased to $\sim 1.4\text{ mg L}^{-1}$, which is below to the World Health Organization's guideline for drinking water (1.5 mg L^{-1}).

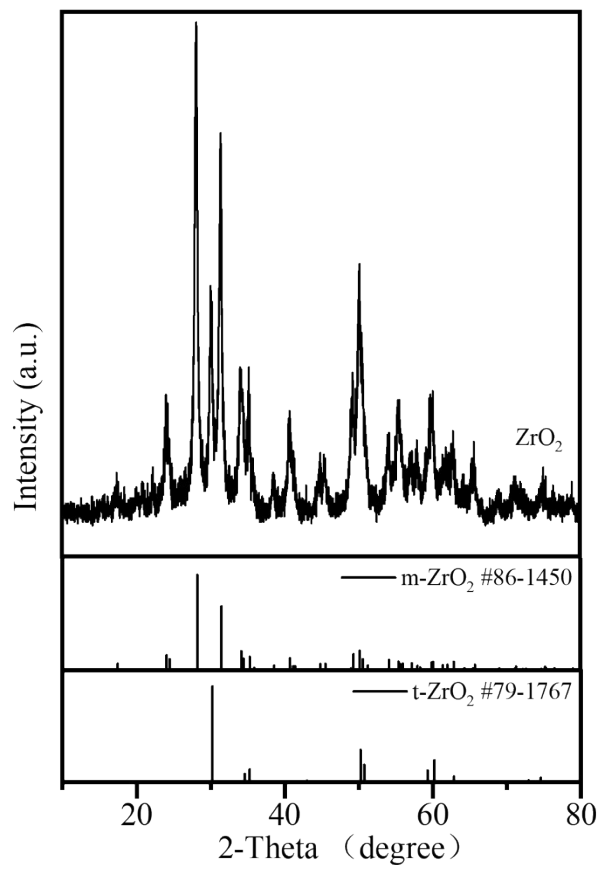


Figure S5. The XRD pattern of ZrO₂.

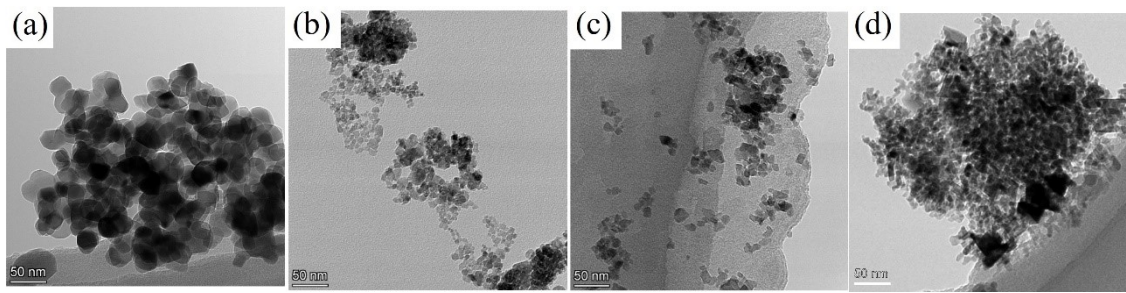


Figure S6. TEM images of (a) ZrO₂, (b) S1-ZrO₂, (c) S₃-ZrO₂ and (d) S₄-ZrO₂.

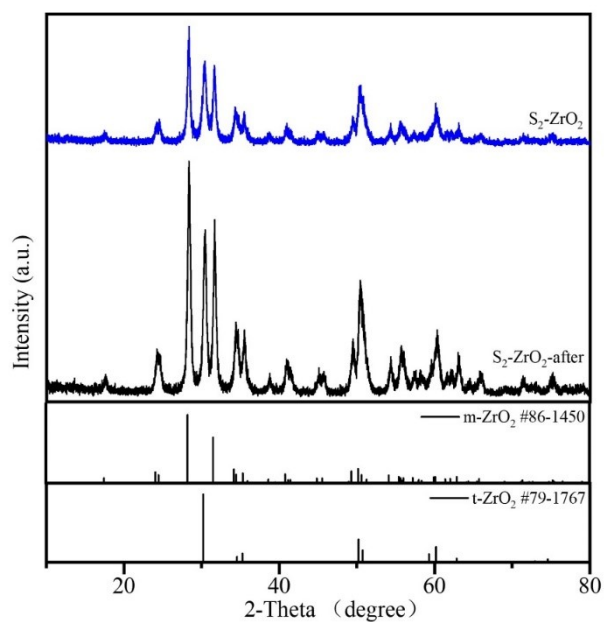


Figure S7. The XRD pattern of $S_2\text{-ZrO}_2$ and $S_2\text{-ZrO}_2\text{-after}$.

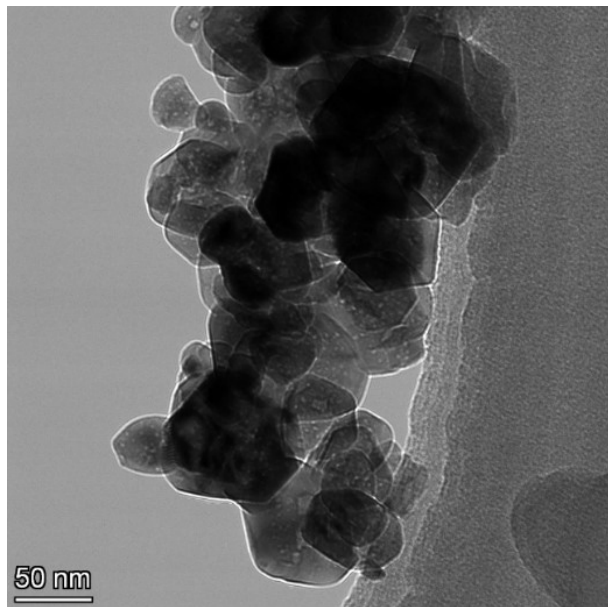


Figure S8. TEM image of S₂-ZrO₂-after.

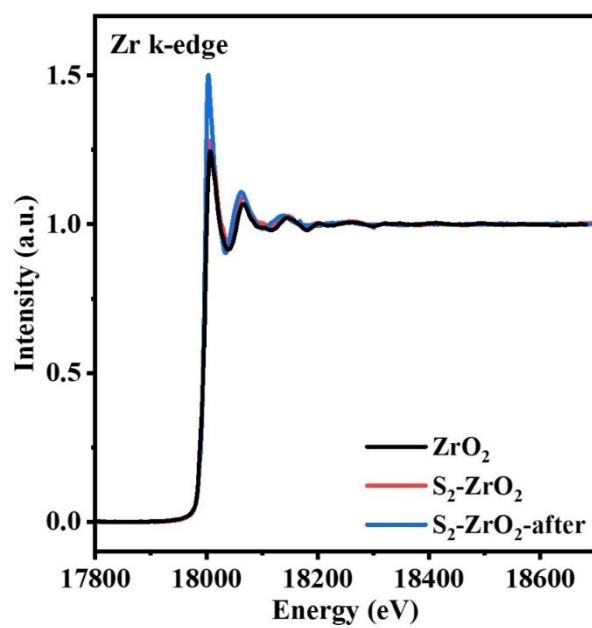


Figure S9. The Zr K-edge XANES spectra of ZrO_2 , $\text{S}_2\text{-ZrO}_2$ and $\text{S}_2\text{-ZrO}_2\text{-after}$.

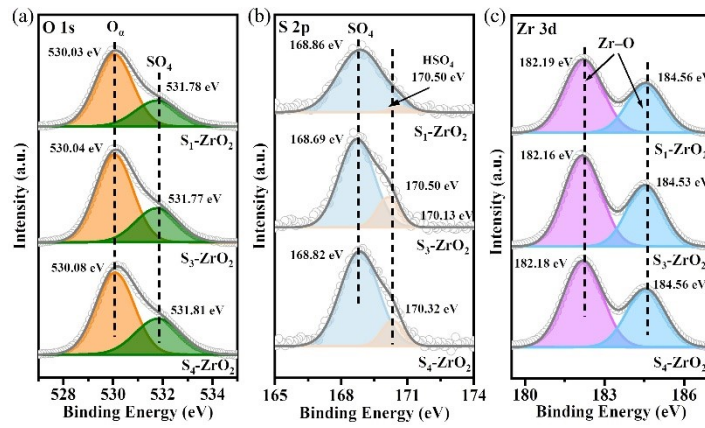


Figure S10. XPS spectra of (a) O 1s, (b) S 2p and (c) Zr 3d for S₁-ZrO₂, S₃-ZrO₂ and S₄-ZrO₂ catalysts.

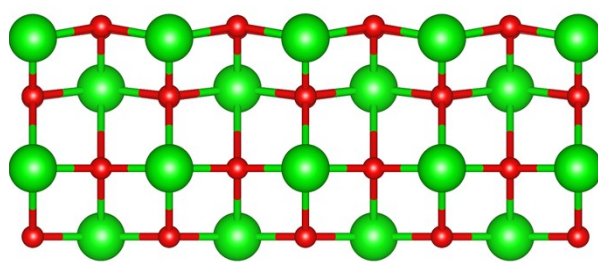


Figure S11. The calculation model of ZrO₂.

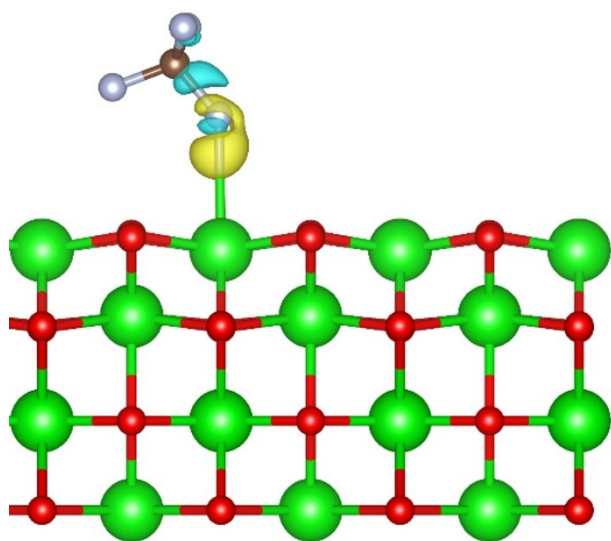


Figure S12. The calculation model of ZrO_2 with CF_4 .

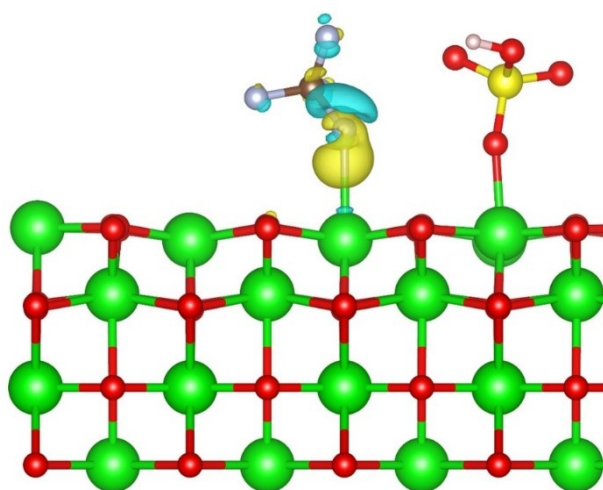


Figure S13. The calculation model of S-ZrO₂ with CF₄.

Table S1. Physical properties and S content of ZrO₂ and S_n-ZrO₂ samples.

Sample	SA (m ² /g)	PV (cm ³ /g)	APR	S content (wt.%)
ZrO ₂	18.60	0.13	24.1	-
S ₁ -ZrO ₂	67.08	0.1	5.93	1.074
S ₂ -ZrO ₂	67.13	0.15	8.99	1.226
S ₃ -ZrO ₂	60.26	0.17	11.61	3.691
S ₄ -ZrO ₂	64.11	0.2	12.72	4.486

Table S2. Physical properties and S content of S₂-ZrO₂-after.

Sample	SA (m ² /g)	PV (cm ³ /g)	APR	S content (wt.%)
S ₂ -ZrO ₂ -after	20.30	0.06	11.94	0.317

Table S3. Fitting Results of Zr K-edge EXAFS Data.

Sample	R_{Zr-O}	N_{Zr-O}	R_{Zr-Zr}	N_{Zr-Zr}	R_{Zr-S}	N_{Zr-S}
S_2-ZrO_2	2.15	4.48	3.43	6.63	3.51	1.33
S_2-ZrO_2 -after	2.16	7.44	3.48	3.6	-	-

Table S4. The surface elements content with different states from XPS determination.

Sample	Atomic concentration / %			
	Zr 2d	O 1s	S 2p	
			-HSO ₄	-SO ₄
S ₁ -ZrO ₂	24.84	54.85	0.64	2.72
S ₃ -ZrO ₂	24.62	56.11	0.64	2.90
S ₄ -ZrO ₂	23.74	54.62	0.74	3.16