

Supporting Information

Sulfate-modified iron oxide catalyzed epoxidation of styrene with CO₂ activated hydrogen peroxide in water

Fangchao Wang^{a,b}, Wei Yang^a, Ding Ding^a, Hongyi Cui^{a,b}, Guoying Zhang^{a,*}

^a State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Institute of Coal Chemistry, Chinese Academy of Sciences, 030001 Taiyuan, P. R. China

^b University of Chinese Academy of Sciences, 100049 Beijing, P. R. China

E-mail: zhanggy@sxicc.ac.cn

Preparation of α -Fe₂O₃: FeSO₄•xH₂O (10 g, Aladdin) was dissolved in deionized water (75 mL), stirring at 90 °C for 20 min. After complete dissolution, add 18 mL of ammonia (25-28 wt %, Macklin) dropwise. After that, the gray-green precipitate was stirred at 90 °C for 4 h and aged at room temperature for 10 h. Then filtered, washed with a large amount of deionized water, and dried overnight at 120 °C. The dried samples were calcined at 600 °C under air atmosphere for 2 h to obtain α -Fe₂O₃, denoted as Fe₂O₃ (2S). In order to examine the properties of α -Fe₂O₃ prepared from other iron salts FeCl₂•4H₂O (Alfa Aesar), FeCl₃ (Energy Chemical), Fe(NO₃)₃•9H₂O (Alfa Aesar) etc. were obtained with the same substance ratios and preparation steps, which were denoted as Fe₂O₃ (2C), Fe₂O₃ (3C), Fe₂O₃ (3N) respectively. Other metal oxides such as MnO₂, Ni₂O₃, Co₃O₄, CuO, ZrO₂, Al₂O₃, MgO, ZnO, etc. were prepared in a similar way as α -Fe₂O₃.

Preparation of sulfate-modified iron oxide

Iron oxide modified with sulfate was produced by grinding a mixture of Fe₂O₃ and (NH₄)₂SO₄ (3A Materials), followed by roasting. 100 mg of Fe₂O₃ (2S) and 800 mg of ammonium sulfate were fully ground in a mill for 10 min, followed by calcining at 600 °C for 2 h under air atmosphere, denoted as FS-8. Different mass ratios of ammonium sulfate-modified iron oxides prepared in the same way were denoted as FS-x, with x denoting the number of ammonium sulfate mass multiples used. Also, substances containing sulfate, ammonium, and sulfur elements were used to modify Fe₂O₃ in the same way as (NH₄)₂SO₄ was used to modify Fe₂O₃. (NH₄)₂SO₄ modifies other metal oxides as well as other ammonium salts, and (NH₄)₃PO₄ modifies Fe₂O₃ in the same way as described above. When modifying Fe₂O₃ with H₂SO₄ (Sinopharm Chemical Reagent), Fe₂O₃ was impregnated with varying concentrations of H₂SO₄ in equal volumes. The mixture was then left to stand at room temperature for 10 hours and dried at 120 °C for 10 hours. Finally, it was calcined at 600 °C for 2 hours under an air atmosphere.

Catalyst Characterization

N₂ physisorption at -196 °C was measured using a porosity analyzer (Quantachrome). Prior to measurement, the samples were degassed at 300 °C for 3 h under high vacuum.

The Brunauer–Emmett–Teller surface area (BET) was determined in the P/P_0 range of 0.05-0.30 of the adsorption branches of the isotherm.

Powder XRD patterns were recorded using a D8 ADVANCE A25 (Bruker) equipped with a Cu $K\alpha$ radiation source (40 kV, 40 mA). The data were collected at a resolution of 0.02° and a count time of 0.3 s at each point.

SEM analysis was performed using a ZEISS Sigma 300 (ZEISS) microscope operated at 10 kV of accelerating voltage. Energy Dispersive Spectrometry (EDS) results were collected in scanning SEM mode with OXFORD Xplore. TEM analysis was performed using a FEI Tecnai G2 F20 (FEI) microscope at accelerating voltages of 200 kV.

XPS analyzes were performed on a Thermo Scientific K-Alpha (Thermo Scientific) scanning XPS system using monochromatic Al $K\alpha$ (1486.6 eV) X-rays focused at a $400\ \mu\text{m}$ spot and scanned over an area of $400\ \mu\text{m} \times 400\ \mu\text{m}$. The photoelectron take-off angle was 45° and the pass energy in the analyzer was set at 150.0 eV for survey scans and 50.0 eV to obtain high-energy resolution spectra for the C 1s, O 1s, S 2p and Fe 2p regions. Charge referencing to the unfunctionalized saturated carbon (C-C) C 1s peak at 284.8 eV was applied for all XPS spectra.

FTIR spectra were collected on a Bruker Tensor II instrument in the range of 4000-400 cm^{-1} with KBr pellets. Raman spectra were collected on Horiba LabRAM HR Evolution in the range of 50-2000 cm^{-1} .

Py-IR experiments were carried out using a Tensor 27 FTIR spectrometer (Bruker). Prior to adsorption, the catalysts were degassed in a $500\ ^\circ\text{C}$ vacuum for 1 hour and cooled to $30\ ^\circ\text{C}$, and the corresponding spectra were collected as background. When Py reached adsorption saturation, samples were vacuumed at $150\ ^\circ\text{C}$, $250\ ^\circ\text{C}$ and $350\ ^\circ\text{C}$ for 30 min respectively. The corresponding spectra used for quantification were recorded, after samples had been cooled to $30\ ^\circ\text{C}$. The Py-IR spectral bands at about $1450\ \text{cm}^{-1}$ and $1540\ \text{cm}^{-1}$ are assigned to the adsorption of Py on the Lewis acid and Brønsted acid sites, respectively.

NH_3 -TPD of catalysts were measured by using a chemisorption instrument with a TCD detector (Micromeritics AutoChem II 2920). Firstly, catalyst purge of He at $400\ ^\circ\text{C}$ for 1 h. Next, after adsorbing 5 % NH_3/He at room temperature for 60 min, the catalyst was

purged with He at 50 °C for 30 min to remove the physisorbed NH₃. Lastly, when the baseline was stable, the NH₃ desorption program was run at a heating rate of 10 °C min⁻¹ from 50 to 500 °C with He flow.

EPR experiments were carried out on a EMXPLUS10/12 (Bruker) spectrometer. Add 500 μL of TEMP (Macklin, 97%) to the reaction system and react for 1.5 h under standard conditions. Then, add 3 mL of ethyl acetate and stir to extract. Dilute the supernatant 500 times and use for EPR testing. The microwave frequency was 9.86 GHz. The microwave power was 2 mW. The modulation amplitude was 2 G. The modulation frequency was 100 kHz. The experimental temperatures applied was room temperature.

Catalytic Activity Evaluation

In a typical reaction, styrene (120 μL, 1.04 mmol, Energy Chemical), 6 mg of 3.8 % mol sulfate-modified Fe₂O₃, 160 mg of 50 % mol TBAB (Aladdin), and 0.6 mL of 6 equiv. H₂O₂ (30 wt.%, Sinopharm Chemical Reagent) were mixed in a 5 mL glass bottle. The bottle was then placed in an autoclave and filled with 1.5 MPa CO₂ after three exchanges. After the reaction, the system was evacuated and refilled with CO₂ three times, and then immersed in a preheated metal bath (35 °C) for 1.5 hours. After the reaction was completed, the products were extracted with ethyl acetate and analyzed by gas chromatography (FULI ,9790II) equipped with SH-5 column and FID detector, using *n*-hexadecane (Energy Chemical) as an internal standard. In the catalyst stability test, the catalysts were reused without any treatment. After the previous reaction, the reaction mixture was centrifuged or filtered to recover the catalyst, which was washed with ethyl acetate, followed by drying in a vacuum oven at 120 °C and used for the next test.

Styrene conversion (X), Styrene oxide yield (Y) were calculated using the following equations:

$$X (st) = \frac{1.04 - n(st)}{1.04} \times 100 \% \quad (1-1)$$

$$Y(so) = \frac{n(so)}{1.04} \times 100 \% \quad (1-2)$$

$n(st)$ and $n(so)$ were calculated by the external standard method with the addition of n -hexadecane to the post-reaction solution.

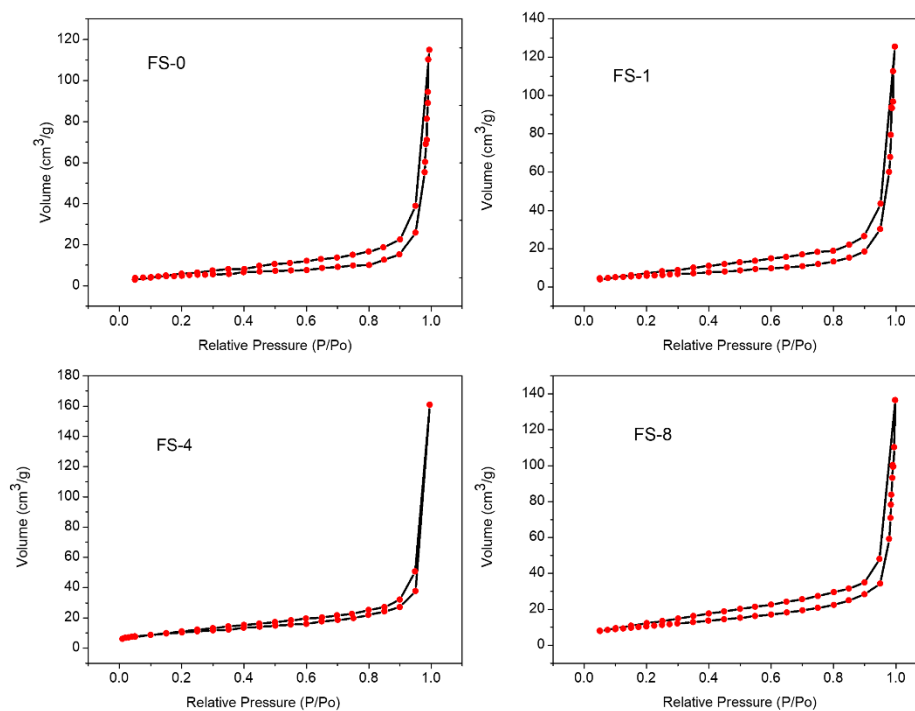


Fig. S1 N₂ adsorption-desorption isotherms for FS-0, FS-1, FS-4 and FS-8 samples.

Tab. S1 Surface area and pore diameter for FS-0, FS-1, FS-4 and FS-8 samples

Sample	Surface area (m ² g ⁻¹)	Pore Diameter (nm)
FS-0	17	3.41
FS-1	21	3.06
FS-4	37	3.05
FS-8	37	3.06

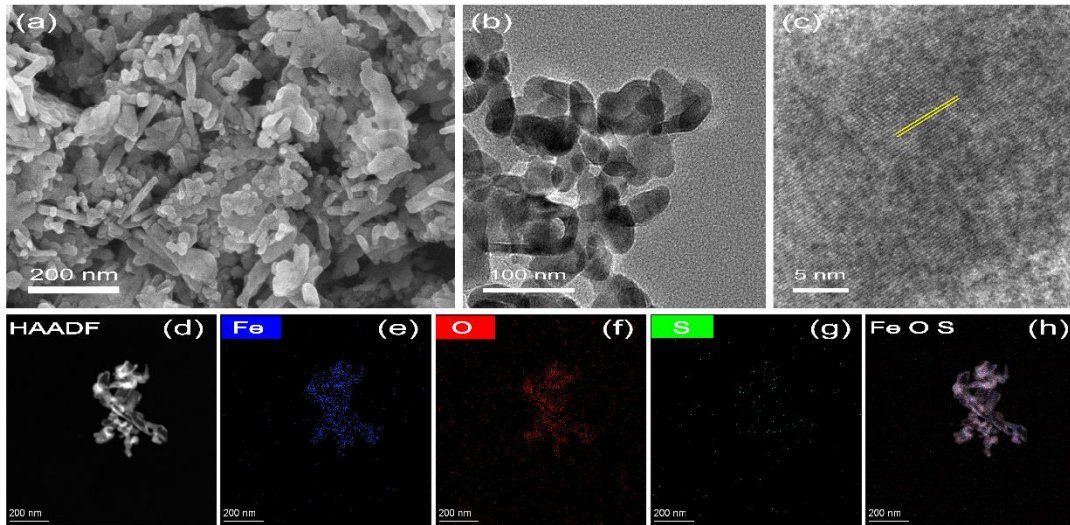


Fig. S2 (a) SEM image, (b) (c) TEM image, (d) TEM-EDS elementary mapping for (e) Fe, (f) O, (g) S, (h) Fe O S of FS-0.

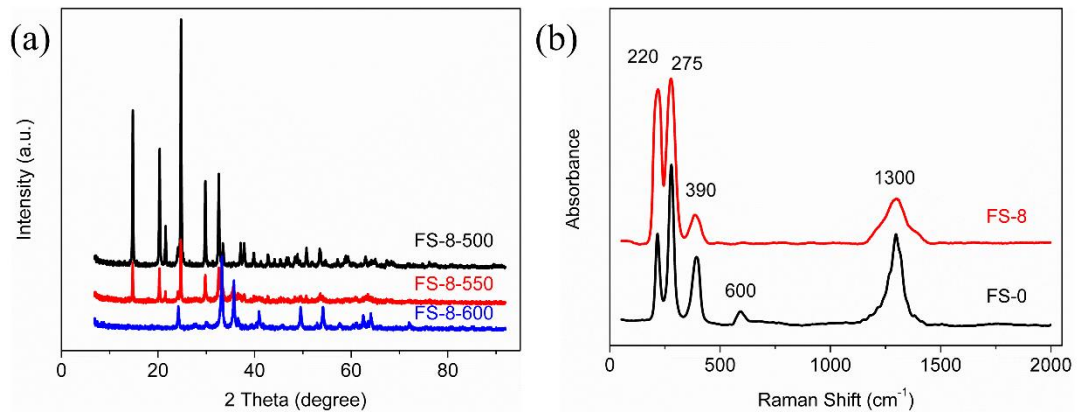


Fig. S3 (a) XRD patterns of FS-8 roasted at 500, 550 and 600 °C for 2 hours. (b) Raman spectra of FS-8 and FS-0

Tab. S2 Ratio of Brønsted and Lewis acids contents calculated by Py-IR for FS-0, FS-8 and ammonium sulfate-modified ZrO₂ samples at 150 °C, 250 °C and 350 °C

Sample	Acid ratio (B/L)		
	150 °C	250 °C	350 °C
FS-0	0.12	0.13	0.17
FS-8	0.07	0.09	0.12
ZRS-8	0.19	0.18	0.19

Tab. S3 Reaction performance of iron oxide modified with different amounts of ammonium sulfate

Entry	Sample	Conv. (St) %	Yiel. (So)%	Yiel. (BzH)%
1	FS-0	24	6	< 5
2	FS-1	56	23	6
3	FS-2	92	58	7
4	FS-4	97	53	7
5	FS-8	96	59	5
6	FS-12	97	57	6
7	FS-16	94	48	6

Reaction condition: 1.04 mmol Styrene, 6 mg catalyst, 0.5 mmol TBAB, 0.6 mL 30% H₂O₂, 1.5 MPa CO₂, 35°C and 1.5 h

Tab. S4 Reaction performance of ammonium sulfate modification of iron oxides with different precursors, ammonium sulfate modification of different metal oxides and iron oxides modified with different ammonium salts

Entry	Sample A	Sample B	Conv. %	Yiel. %
1	Fe ₂ O ₃ (2S)	(NH ₄) ₂ SO ₄	96	59
3	Fe ₂ O ₃ (2C)	(NH ₄) ₂ SO ₄	4	< 5
4	Fe ₂ O ₃ (3C)	(NH ₄) ₂ SO ₄	90	43
5	Fe ₂ O ₃ (3N)	(NH ₄) ₂ SO ₄	8	< 5
6	Fe ₂ O ₃ (2S)	(NH ₄) ₂ PO ₄	97	60
7	Fe ₂ O ₃ (2S)	(NH ₄) ₂ CO ₃	25	< 5
8	Fe ₂ O ₃ (2S)	NH ₄ Cl	29	6
9	Fe (OH) ₃	(NH ₄) ₂ SO ₄	92	53
10	MnO ₂	(NH ₄) ₂ SO ₄	21	7
11	Ni ₂ O ₃	(NH ₄) ₂ SO ₄	35	trace
12	Co ₃ O ₄	(NH ₄) ₂ SO ₄	24	trace
13	CuO	(NH ₄) ₂ SO ₄	9	< 5
14	ZrO ₂	(NH ₄) ₂ SO ₄	23	< 5
15	Al ₂ O ₃	(NH ₄) ₂ SO ₄	8	trace

Reaction condition: 1.04 mmol Styrene, 0.038 mmol catalyst, 0.5 mmol TBAB, 0.6 mL 30% H₂O₂, 1.5 MPa CO₂, 35°C and 1.5 h

Tab. S5 Reaction performance of ZnO, MgO prepared from different precursor salts

Entry	Sample	Conv. %	Yield %
1	MgO (S)	89	55
2	MgO (C)	25	< 5
3	ZnO (S)	90	43
4	ZnO (C)	65	19
5	ZnO (N)	23	< 5

Reaction condition: 1.04 mmol Styrene, 4 mmol% ZnO (S) and 5 mmol% MgO (S), 0.5 mmol TBAB, 0.6 mL 30% H₂O₂, 1.5 MPa CO₂, 35°C and 1.5 h

Tab. S6 Reaction performance of iron oxides modified with different sulfur-containing compounds

Entry	Sample	S source	Conv. %	Yield %
1	FS-8	(NH ₄) ₂ SO ₄	96	59
2	FS-ZG	water evaporation	96	57
3	FS-AHS	NH ₄ HSO ₄	91	52
4	FS-Na	Na ₂ SO ₄	10	10
5	FS-K	K ₂ SO ₄	30	5
6	FS-SA	H ₂ SO ₄	95	57
7	FS-PTSA	C ₅ H ₅ NO ₃ S	94	51
8	FS-STPC	C ₇ H ₈ O ₃ S	97	53
9	FS-PS	C ₁₂ H ₁₀ O ₂ S	35	< 5
10	FS-DS	C ₁₂ H ₈ O ₂ S	35	5
11	FS-DMSO	C ₂ H ₆ OS	31	7
12	FS-S	S	53	14
13	FS-TU	CH ₄ N ₂ S	22	7
14	FS-CD	CS ₂	37	13

Reaction condition: 1.04 mmol Styrene, 0.038 mmol catalyst, 0.5 mmol TBAB, 0.6 mL 30% H₂O₂, 1.5 MPa CO₂, 35°C and 1.5 h

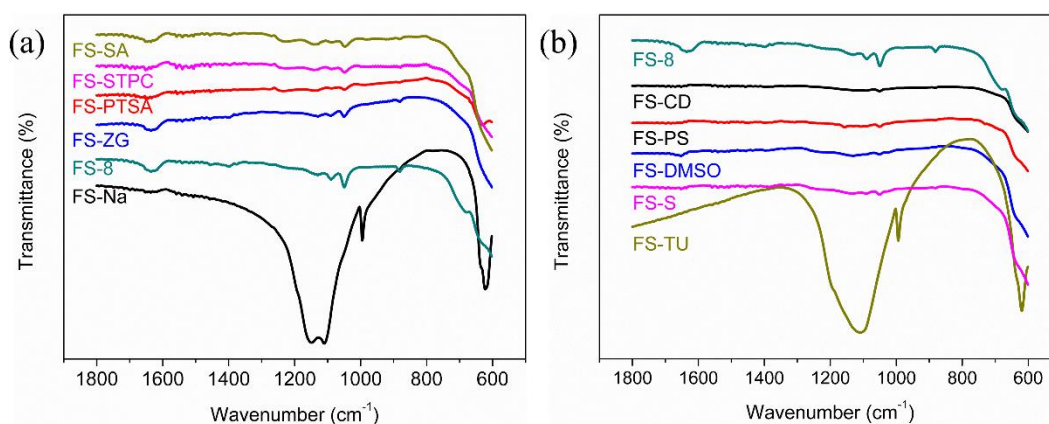


Fig. S4 FT-IR spectra of iron oxides modified with different sulfur-containing compounds

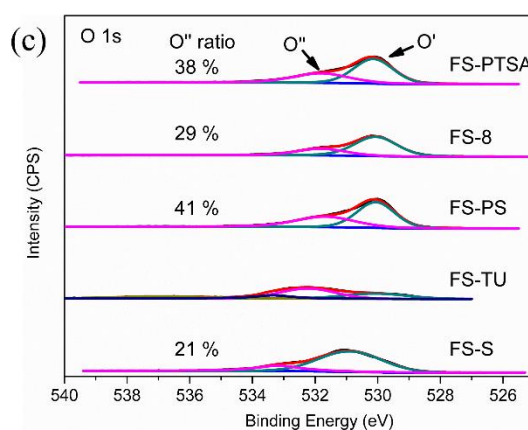
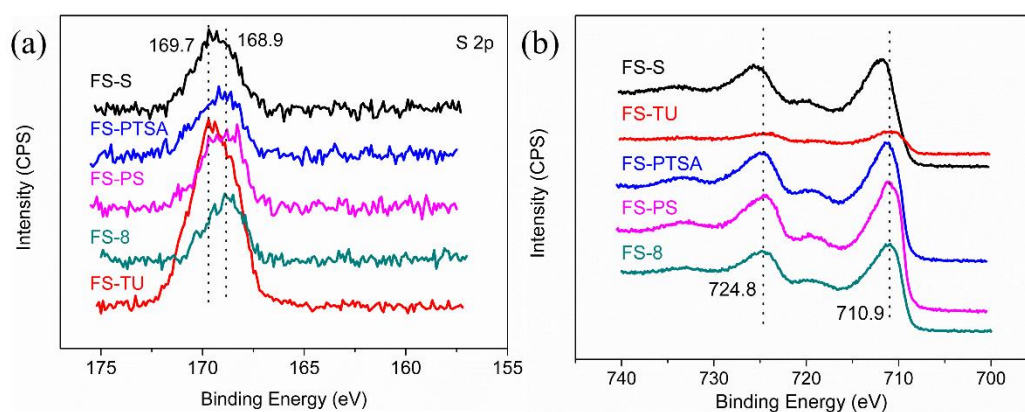


Fig. S5 XPS patterns of iron oxides modified with different sulfur-containing compounds

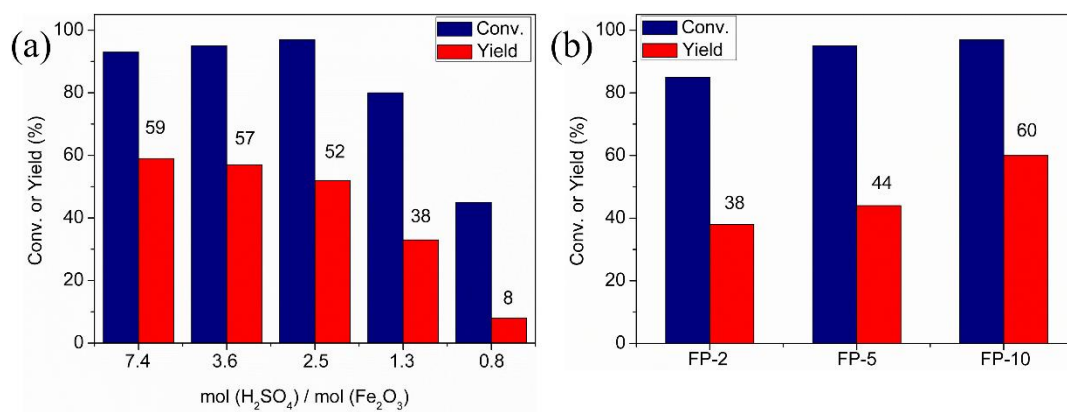


Fig. S6 Reaction performance of Iron oxides modified with different amounts of (a) sulfuric acid and (b) ammonium phosphate

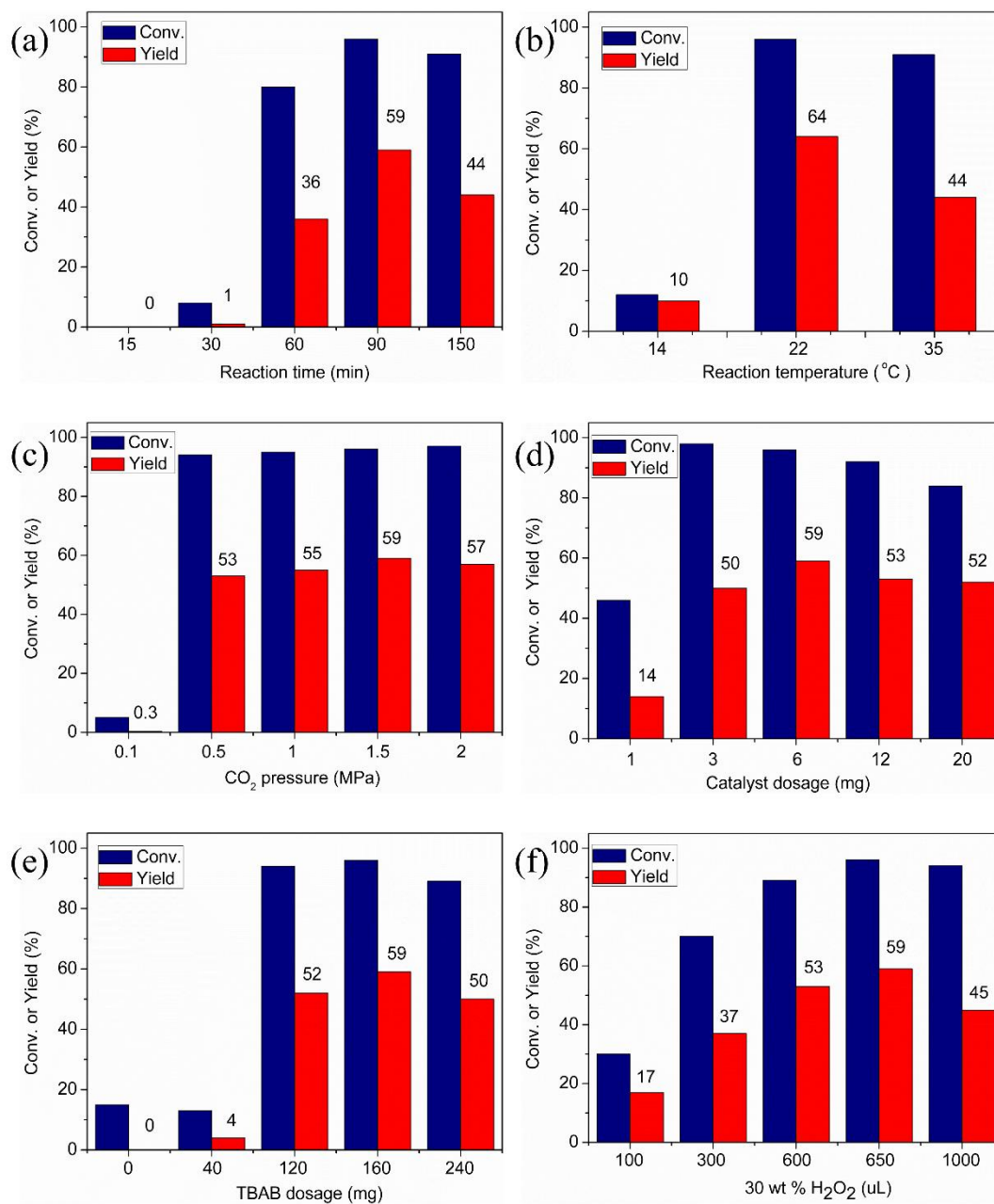


Fig. S7 Reaction performance of FS-8 at different (a) reaction times; (b) reaction temperatures; (c) CO_2 pressure; (d) catalyst dosage; (e) TBAB dosage and (f) H_2O_2 dosage

Tab. S7 Reaction performance when deviation from the optimized conditions

Entry	Deviation from the optimized conditions	Conv. %	Yiel. %
1	none	96	59
2	without catalyst, 5 h	38	6
3	without catalyst, 50 h	79	trace
4	without TBAB, 48 h	41	trace
5	0.1 MPa CO ₂	5	trace
6	Add 1mL H ₂ O	37	trace
7	Add 1mL CH ₃ OH	22	trace
8	Add 1mL CH ₃ CN	30	11
9	Add 1mL C ₃ H ₇ NO	55	< 5
10	Add 1mL C ₄ H ₈ O ₂	18	12
11	Add 1mL C ₆ H ₁₂	31	18
12	Add 0.1 ml H ₂ O	90	53
13	Add 0.3 ml H ₂ O	57	23
14	Add 0.6 ml H ₂ O	5	< 5
15	Add 0.6 ml H ₂ O & 160 mg TBAB	32	18

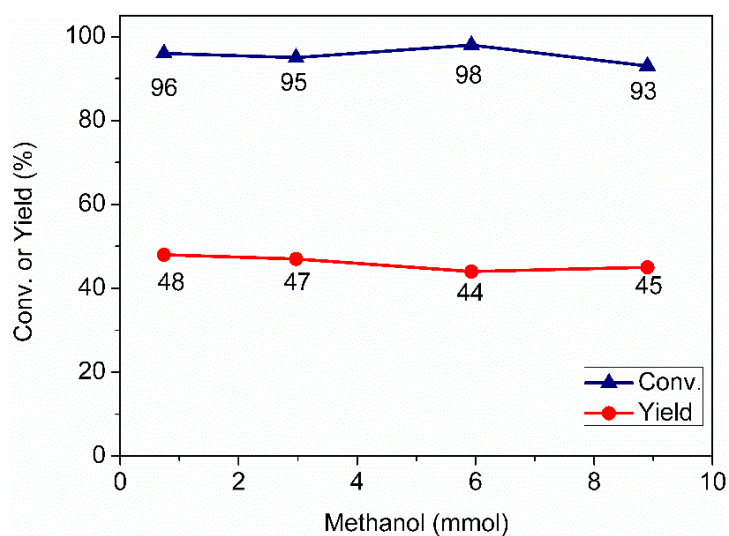


Fig. S8 The conversion of styrene and yield of styrene oxide when adding different amounts of methanol

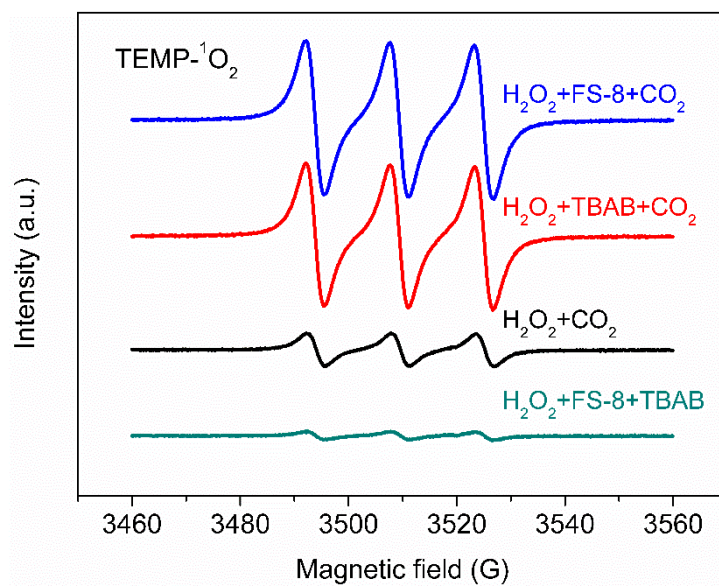


Fig. S9 EPR spectra under different reaction conditions

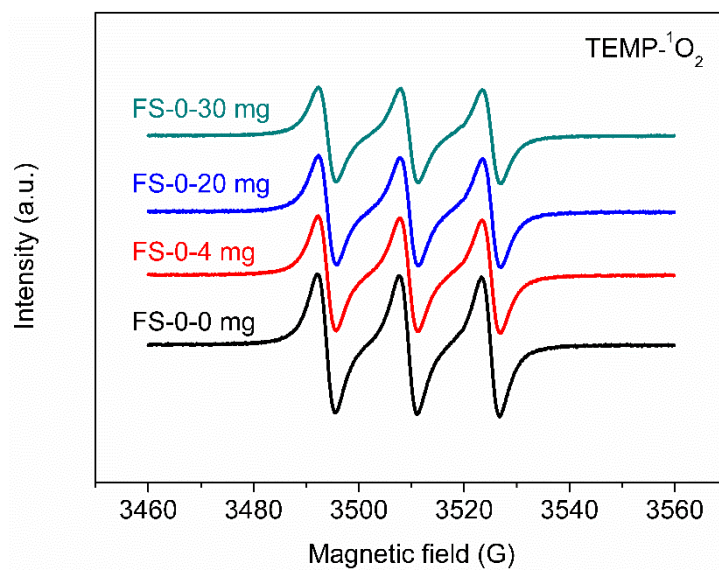


Fig. S10 EPR spectra under different FS-0 dosage

Tab. S8 Reaction performance when using NH_4CO_3 , $(\text{NH}_4)_2\text{CO}_3$, NaHCO_3 and Na_2CO_3 to replace CO_2

Entry	Sample	Amount mmol	Conv. %	Yiel. %
1	NaHCO_3	0.07	3	trace
2	NaHCO_3	0.18	21	< 5
3	NaHCO_3	1.10	23	< 5
4	NH_4HCO_3	0.06	15	trace
5	NH_4HCO_3	0.19	21	< 5
6	NH_4HCO_3	1.00	31	8
7	Na_2CO_3	1.08	15	trace
8	$(\text{NH}_4)_2\text{CO}_3$	1.02	22	< 5
9 ^a	NaHCO_3	1.10	38	trace
10 ^a	NH_4HCO_3	1.00	29	trace

Reaction condition: 1.04 mmol Styrene, 6 mg FS-8, 0.5 mmol TBAB, 0.6 mL 30% H_2O_2 , 35°C and 1.5 h

^a without FS-8, 10 h

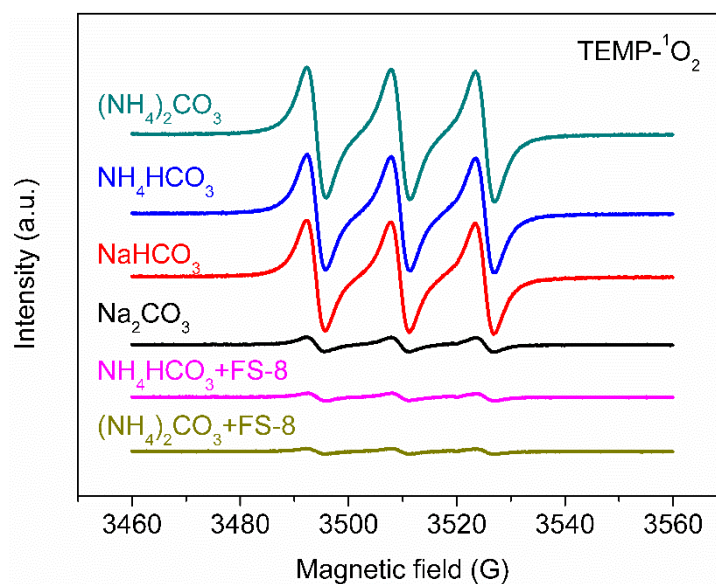


Fig. S11 EPR spectra when using NH_4CO_3 , $(\text{NH}_4)_2\text{CO}_3$, NaHCO_3 and Na_2CO_3 to replace CO_2

Tab. S9 Reaction performance of FS-8 catalysts at different initial pH

Entry	Sample	Amount mmol	pH	Conv. %	Yiel. %
1	-	-	6	96	59
2	NH ₄ OH	~ 0.3	9	88	55
3	NH ₄ OH	~ 0.9	10	81	38
4	H ₂ SO ₄	~0.04	1	18	5
5	NH ₄ HSO ₄	~0.1	2	90	42
6	(NH ₄) ₂ SO ₄	~0.09	5	96	61
7	NH ₄ HCO ₃	~0.1	8	91	67
8	(NH ₄) ₂ CO ₃	~0.07	9	92	60

Reaction condition: 1.04 mmol Styrene, 6 mg FS-8, 0.5 mmol TBAB, 0.6 mL 30% H₂O₂, 1.5 MPa CO₂, 35°C and 1.5 h

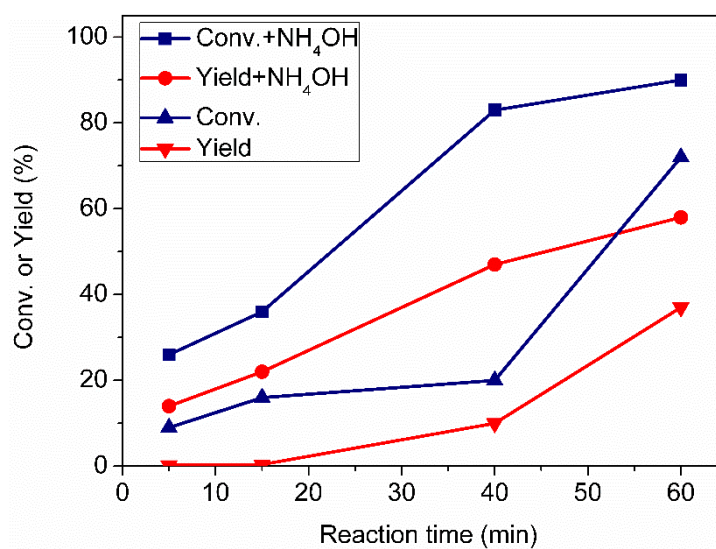


Fig. S11 Effect of the addition of 20 μ L ammonia on the catalytic performance of FS-8 under standard reaction conditions

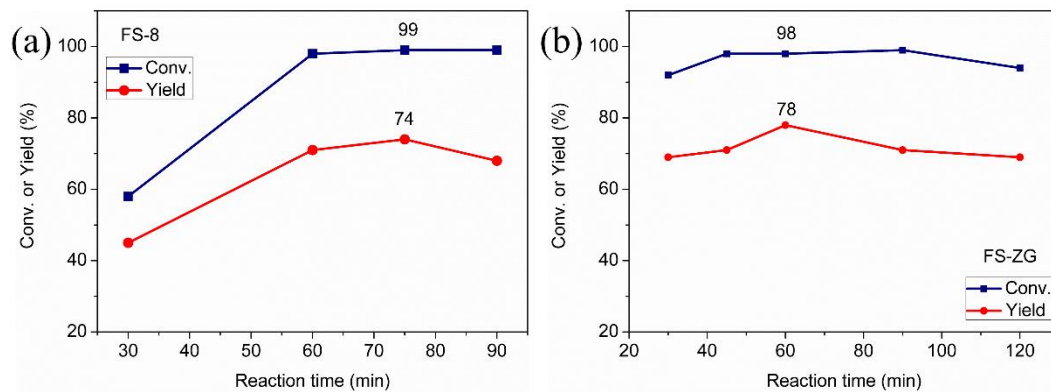


Fig. S12 Catalytic performance of FS-8 and FS-ZG when using TBAF and ammonia as a replacement for TBAB

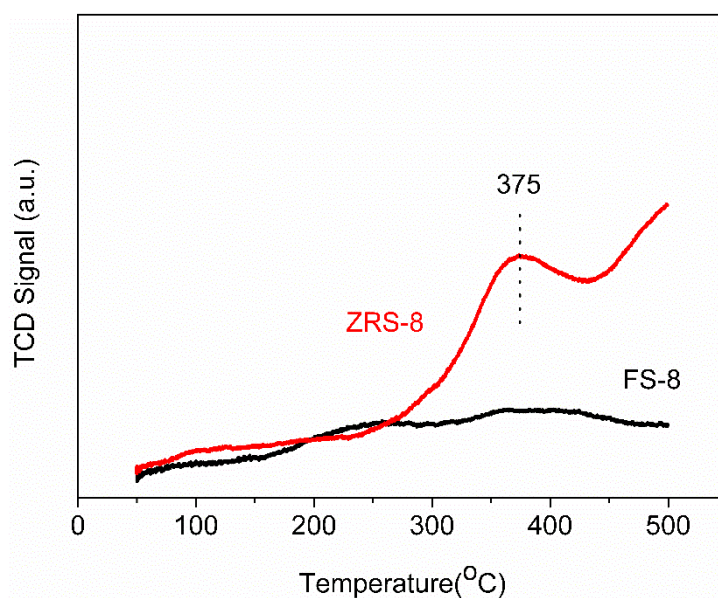


Fig. S13 NH₃-TPD patterns of FS-8 and ammonium sulfate modified zirconium oxide

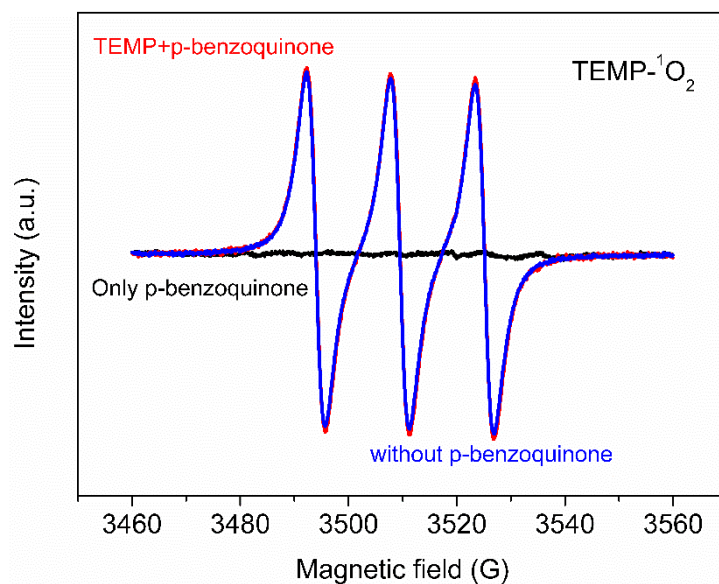

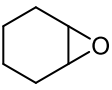
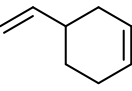
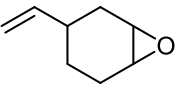
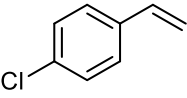
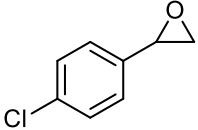
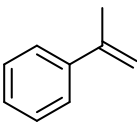
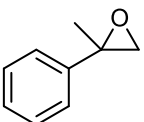
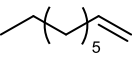
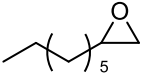
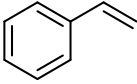
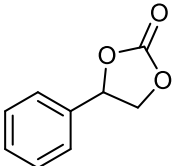


Fig.S14 EPR spectra when using 10 mg p-benzoquinone with TEMP (red), only p-benzoquinone(black) and without p-benzoquinone(blue)

Tab. S10 Reaction performance of FS-8 catalysts with different olefin substrates

Entry	Starting alkene	Product	Yield ^a (%)
1			25
2			11
3			52
4			17
5			trace
6 ^b			48(20°)

Reaction condition: 1.00 mmol Olefine, 6 mg FS-8 catalyst, 0.5 mmol TBAB, 0.6 mL 30% H₂O₂, 1.5 MPa CO₂, 35°C and 1.5 h

^a calculated by the external standard method with the addition of n-hexadecane to the post-reaction solution

^b 12 h

^c without catalyst

Tab. S11 Reaction performance of recycled TBAB

Entry	Catalyst	RE TBAB mg	Conv. %	Yield %
1	FS-8	160	97	55
2	-	160	30	< 5
3	FS-8	120	98	50
4	FS-8	80	34	< 5

Reaction condition: 1.04 mmol Styrene, 6 mg FS-8 catalyst, 0.6 mL 30% H₂O₂, 1.5 MPa CO₂, 35°C and 1.5 h

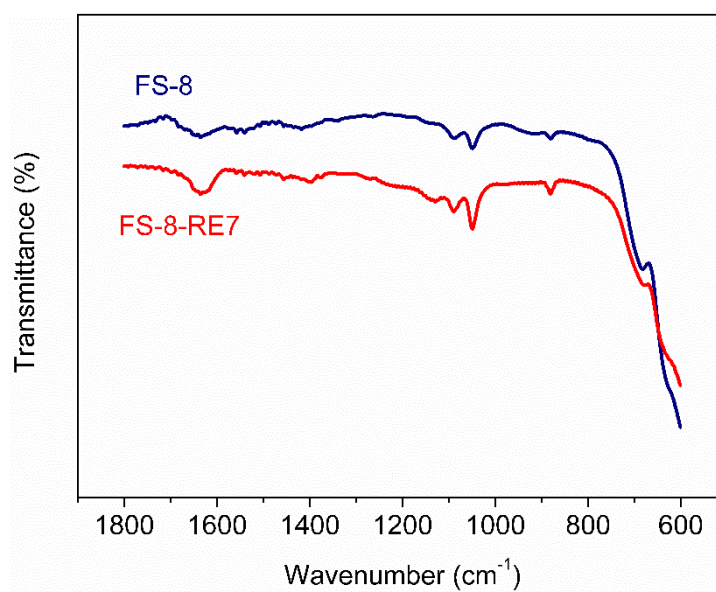


Fig.S15 FT-IR spectra of FS-8 before and after 7 cycle reactions

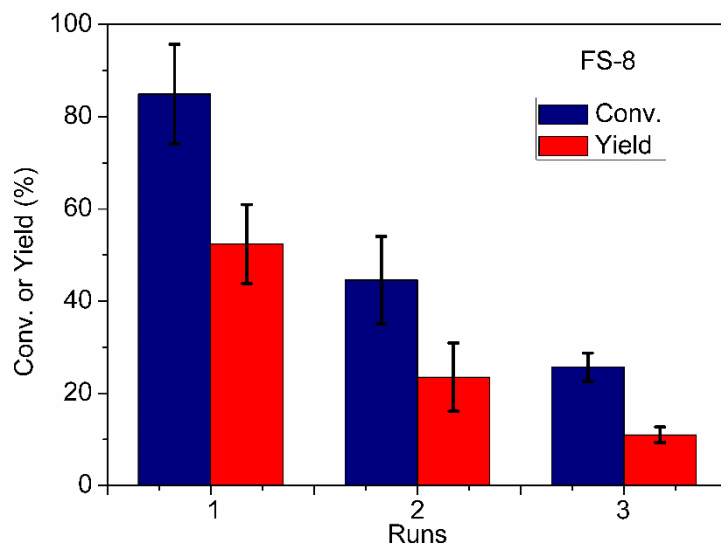


Fig.S16 Catalyst reuse performance when washed with ethyl acetate and water

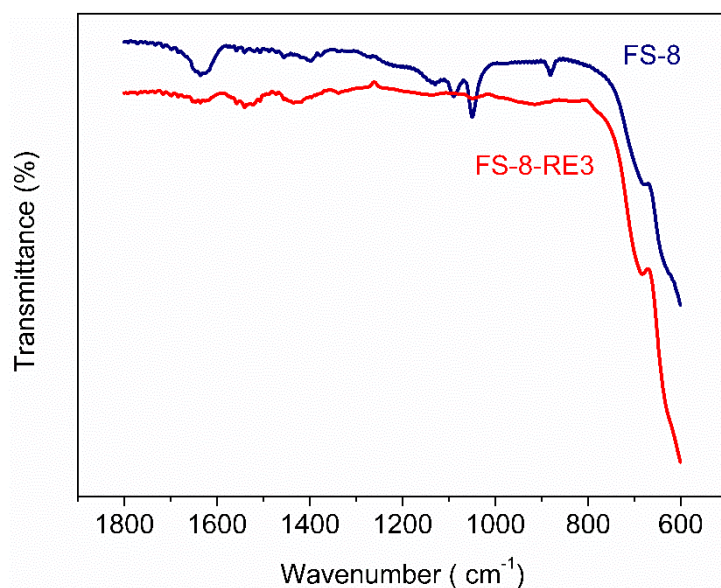


Fig.S17 FT-IR spectra of FS-8 before and after 3 cycle reactions when washed with ethyl acetate and water