

Supporting Information

Thermochemical conversion of CO₂ into CH₄ using oxygen deficient NiFe₂O_{4-δ} with unique selectivity

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S1. Experimental information

Preparation of catalysts

Synthesis of NiFe₂O₄ nanospheres was carried out by a simple solvothermal method. In a typical synthesis process, 2mmol NiCl₂·6H₂O and 4mmol Fe(NO₃)₃·9H₂O were dissolved in 60 ml EG with vigorous stirring. When the solution became clear, 1.6 g (40 mmol) NaOH were added under continuous stirring. The mixture was then transferred into a Teflon-lined stainless-steel autoclave of 80 mL capacity. The sealed tank was heated to and maintained at 200 °C for 10 h in an oven and then air-cooled to room temperature (RT). The resulting black precipitates were collected by filtration and washed with de-ionized water and pure ethanol for several times, and finally dried in a vacuum oven at 60 °C for 5 h.

Characterization

The phase structures of samples were characterized by the Powder X-ray diffraction (XRD) patterns using a PANalytical X'Pert diffractometer with Ni-filtered Cu K α radiation ($\lambda=0.15406\text{nm}$) from 10 to 80°. X-Ray tube voltage and current were set at 35 kV and 25 mA. The step width was 0.04° at an acquisition time of 0.5 s per step. The morphology of the sample was obtained using scanning electron microscopy (SEM; Hitachi S-4800). High-resolution scanning electron microscopy (HRSEM) images were taken on a Hitachi S-4800 ultrahigh-resolution scanning electron microscope operated at 20 kV equipped with a cold field emission gun (FEG) and an in-lens electron optics. An energy dispersive X-ray spectrometer (EDS) detector attached to the SEM (S-3400N, Hitachi) was used to measure the element composition and distribution with the X-Flash Detector 4010 (Burker, ALX). Transmission electron microscopy (TEM) images were obtained by a FEI Tecnai G2 F20 with a beam energy of 300 keV. X-ray photoelectron spectroscopy (XPS) was performed on the Thermo Scientific ESCALab 250Xi using 200 W monochromated Al K α radiation ($h\nu = 1,486.6\text{ eV}$). The 500 μm X-ray spot

was used for XPS analysis. The base pressure in the analysis chamber was about 3×10^{-10} mbar. Typically, the hydrocarbon C1s line at 284.8 eV from adventitious carbon is used for energy referencing. XPS data were analysed using Thermo Scientific Avantage Data System software (version 5.957), and a SMART background was subtracted before peak deconvolution and integration. The surface area SBET was calculated by the Brunauer-Emmett-Teller (BET) method in the P/P0 range 0.05-1. The thermal analysis were characterized by the Thermal Gravimetric Analyzer under air condition and the heating rate is $10^{\circ}\text{C}/\text{min}$. UV-vis diffuse reflectance spectra of the samples were measured in the range of 200-800nm using SHIMADZU UV-3600 using spectral purity BaSO_4 as the reference.

Catalytic measurements

The thermocatalytic reduction of CO_2 was carried out with 100 mg of the powdered thermocatalytic, which was uniformly placed at the bottom of a Pyrex glass cell. The thermocatalytic activity evaluation was performed at 350°C , which kept through the heating jacket in out of the reactor and the temperature control device. Vacuumed the reactor with the vacuum up to empty the air inside the reactor and then CO_2 (99.999 wt %) passed through the reactor at a flow rate of 27 mL/min for 5min. The reaction was in a gas tight system, distilled water(0.3 mL) was injected into the system when the temperature above 120°C . In a period of insulation for 5h, took samples per hour and qualitatively analyzed by GS-Tek (Echromtek A90) and quantitatively analyzed by gas chromatograph equipped with a hydrogen flame detector (FID). The quantification of CH_4 yield was based on the external standard and the use of calibration curve.

Analytical determinations

Detection and quantification of CH_4 were carried out by using a Echromtek A90 chromatograph equipped with a capillary column (HP-PLOTQ), a thermal conductivity detector (TCD) and a flame ionization detector (FID). Pure N_2 (99.999 wt %) was used as carrier gas. A chromatographic ramp reported in literature was chosen. Under these conditions a good separation of the peaks of products can be achieved and water can be effectively removed from the column. The quantification of CH_4 yield was based on the external standard and the use of calibration curve.

S2.data about the studies of oxygen vacancy

2.1 D-value

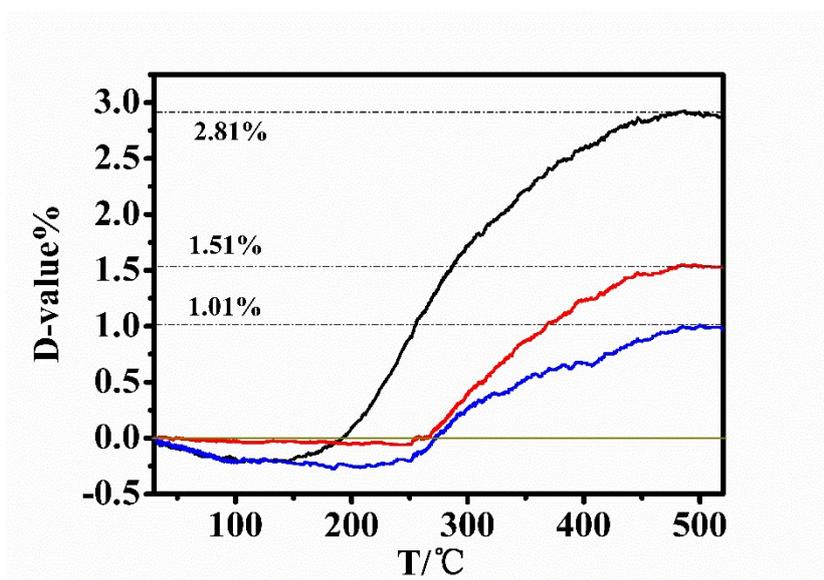


Fig.S2.1 The TGA differential spectra of NFO samples with standard NFO-S. * NFO-S was standard NiFe_2O_4 without oxygen vacancies.

2.2 BET

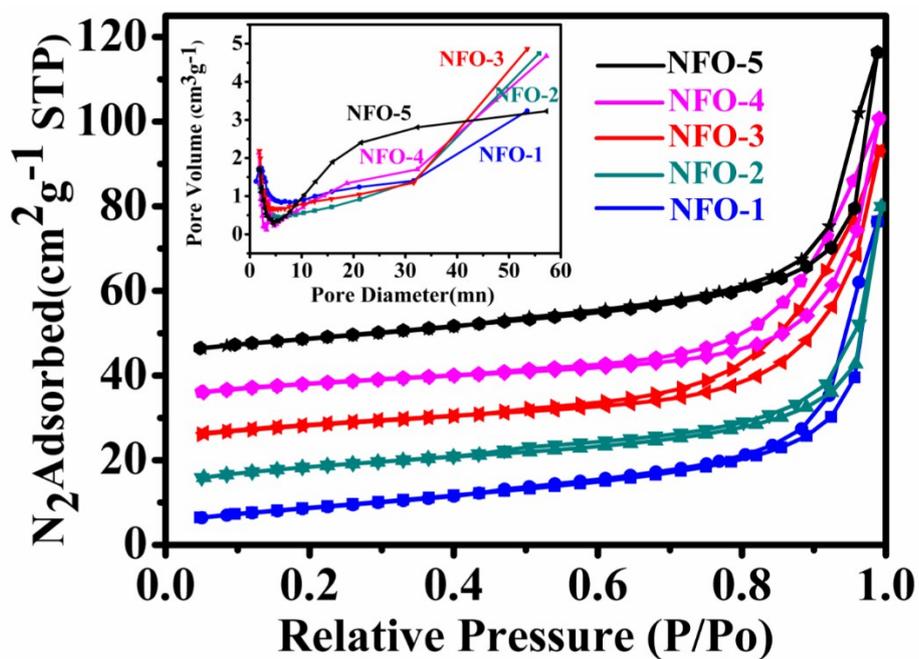


Fig. S2.2 N₂ adsorption-desorption isotherm of the 5 different kinds samples (NiFe₂O₄ NFO-1, NFO-4, NFO-5, NFO-6, NFO-7). (For a better visibility, the N₂ physisorption isotherms are shifted along the Y-axis with 0, 10, 20, 30, 40.)

2.3 UV-Vis

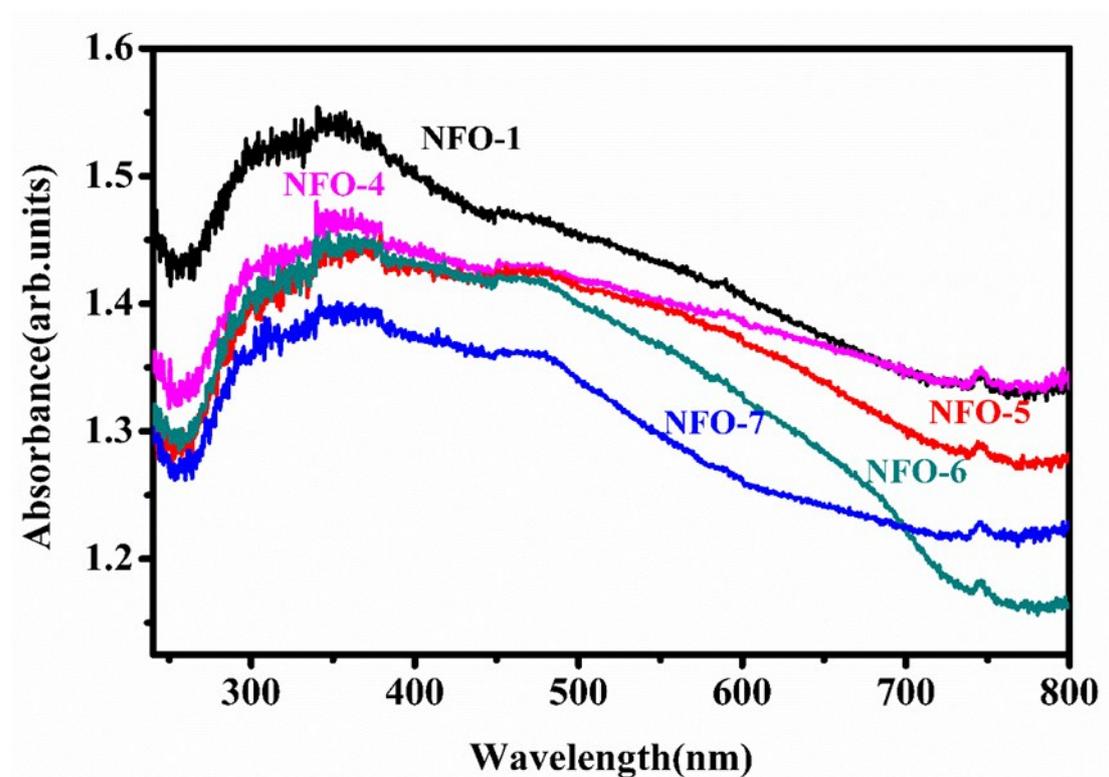


Fig. S2.3 UV-Vis diffuse absorption spectra (Kubelka–Munk function) for the 5 different kinds samples.

2.4 SAXS

The Fig.S2.4 shown the all NFO samples were without mesoporous structure.

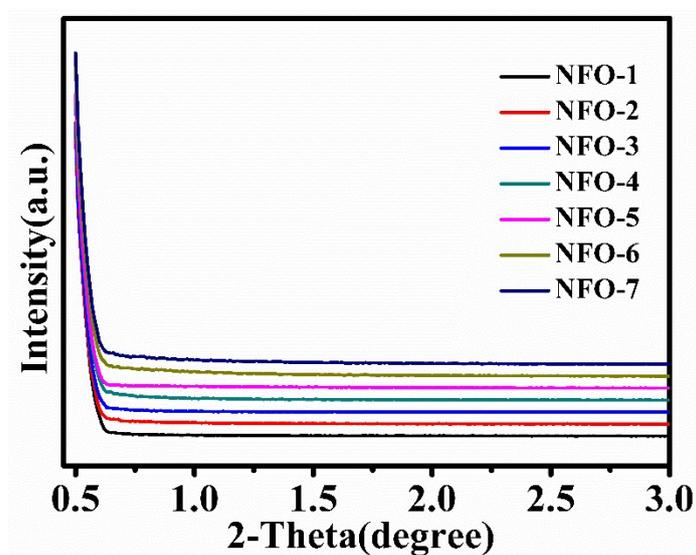


Fig. S2.4 SAXS of all samples

S3.the studies of CO₂ about selectivity and yield of the thermal catalysis

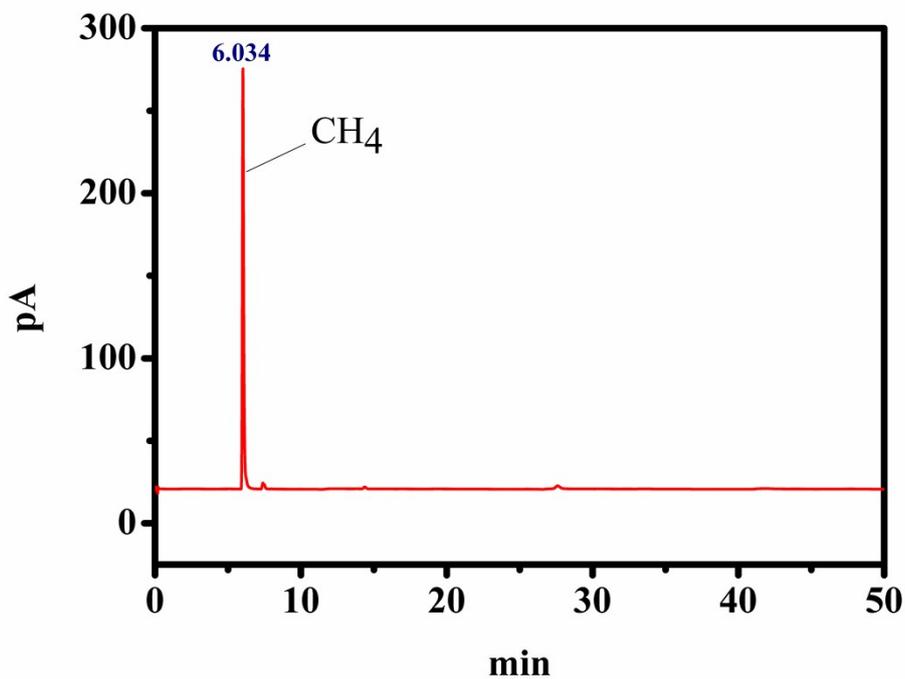
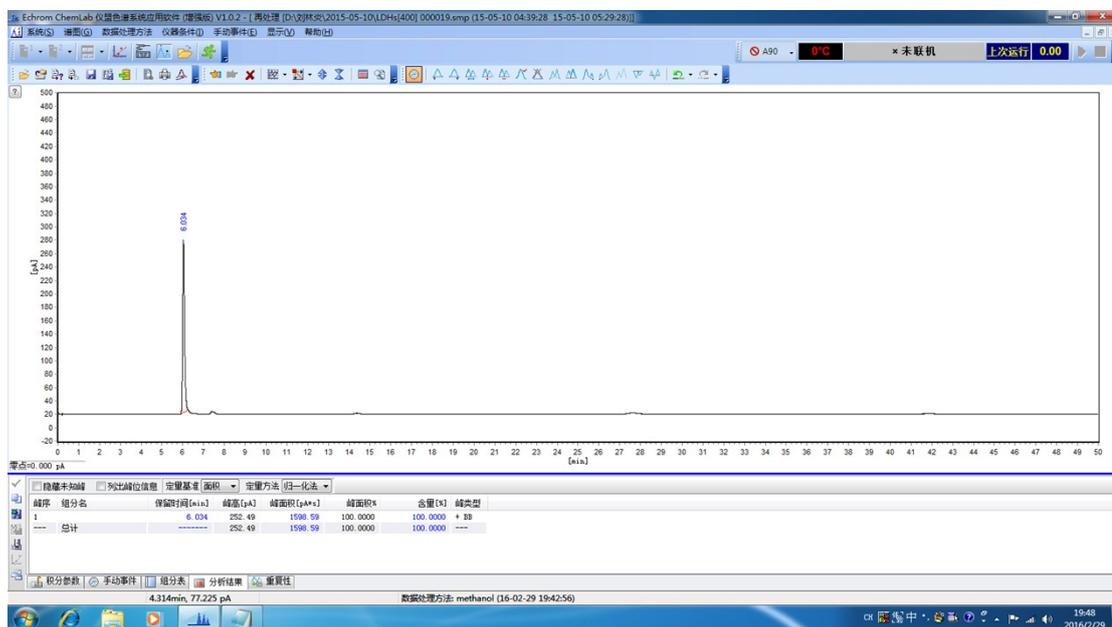


Fig. S3 Gas chromatogram of CH₄ produced over NiFe₂O₄ catalyst. And only CH₄ was generated.

The yield and TON of Calculation:

For example: CO₂: V(input)=130ml, n=130ml/22.4mol=5803.5714umol;

Catalyst: m=100mg, n=0.1g/234.39 (g/mol) =426.64uoml.

Reactor volume=210ml

The quantification of CH₄ yield was based on the external standard and the use of calibration curve. The average area of CH₄ (100%) is 756900 (V=0.5ml). At the same conditions, the average area of CH₄ evolved from NFO-5 is 2883.89 under thermocatalytic conditions after 5h (**Every time, the volume of taking samples injected into the system is V=0.5ml (The volume of gas is mingle gas volume.)**). The total volume of CH₄ (100%) evolved from NFO-5 is 80.105ul under thermocatalytic conditions through mathematical computation.

Yield (Moles of product (CH₄) per 100 moles of carbon dioxide) =
80.105ul/22.4/5803.5714*100=6.16193%

TON (Turnover number = number of moles of product per mol of catalyst precursor.)=80.105ul/22.4/426.64uoml=0.83821.

Table. S3 The yield and TON of thermal reduction of CO₂ with H₂O vapor to CH₄ over NFO catalyst

Time(h)	Yield ^[a] (%)			TON ^[b]			Selectivity (%)
	NFO-5	NFO-6	NFO-1	NFO-5	NFO-6	NFO-1	
1	3.22751	1.88009	0.81832	0.43904	0.25575	0.11132	99.9
2	4.93169	2.4508	1.18536	0.67086	0.33338	0.16124	99.9
3	5.90405	3.58223	1.37479	0.80313	0.48729	0.18701	99.9
4	6.0503	3.80694	1.60554	0.82302	0.51786	0.2184	99.9
5	6.16193	4.06305	1.75511	0.83821	0.5527	0.23875	99.9

^[a] Moles of product (CH₄) per 100 moles of CO₂.

^[b] Turn over number=number of moles of product per moles of catalyst precursor.

S4.the studies of water splitting into hydrogen

In the same method of catalytic measurements, the CO₂ was not added in a Pyrex glass cell. That is to say, only water and catalyst were used in a Pyrex glass cell. The thermocatalytic activity evaluation was performed at 350°C, which kept through the heating jacket in out of the reactor and the temperature control device. In a period of insulation for 5h, took samples per hour and qualitatively analyzed by GS-Tek (Echromtek A90) and quantitatively analyzed by gas chromatograph equipped with a thermal conductivity detector (TCD). The H₂ yield was based on the external standard and the use of calibration curve.

4.1 hydrogen-producing

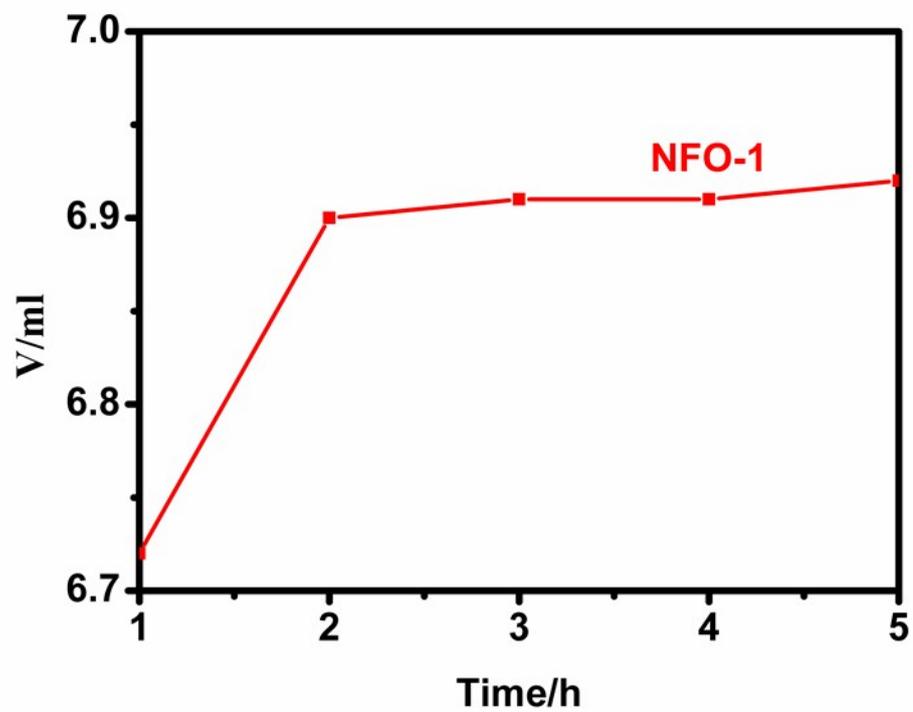


Fig. S4 H₂ generation over the NFO-1 under heating.