Supplementary Information

Synergistic photocatalysis-Fenton reactions for selective conversion of methane to methanol at room temperature

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Experimental procedures

Materials

The commercial TiO_2 (P25), Fe_2O_3, NiO, CuO, ZnO and WO_3 catalysts are supplied by Macklin. $FeCl_2 \cdot 4H_2O$ was purchased from Macklin. H_2O_2 (30%) was supplied from Shanghai Lingfeng Chemical Reagent Co., Ltd. CH_4 (>99.99%) was supplied by Air Liquide. All of the chemicals above were used as received without further purification.

Characterizations

The crystal structure of the samples were measured by X-ray diffraction (XRD, SHIMADZU XRD-6100) with Cu Kα radiation (λ=1.54 Å) in the 2θ range from 10° to 80°. The data was recorded at a scan rate of 5° / min. The morphology of TiO_2 was observed by transmission electron microscopy (TEM, FEI Tecnai G2 F20). Electron spin resonance (ESR) spectra of radical spin-trapped by 5,5-dimethyl-1-pyrroline N-

oxide (DMPO) were measured by a spectrometer (Bruker A300). In a typical measurement, 20 mg catalyst was dispersed in 20 ml deionized water. Then 2 ml 0.01M $FeCl_2$ solution was added in the above suspension, followed by stirring for 5 min. After that, 200 μl H_2O_2 was added in the suspension. 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was used as the trapping regent for both hydroxyl radicals (•OH) and superoxide radicals ($•O^-_2$) detection. The ESR signals were collected after irradiation for 5 min (a xenon lamp with AM 1.5G filter was used as solar light source).

Conversion of methane

The Photocatalysis-Fenton reaction for conversion of methane was carried out in an autoclave of 130 ml volume equipped with a quartz window. A 300 W Xenon lamp (PLS-SXE 300, Perfect light) with AM 1.5G filter was used to provide solar light source. In a typical experiment, 20 mg catalyst were dispersed in 20 ml deionized water to form a suspension. Then, 2 ml $FeCl_2$ (0.01 M) solution was added into the above suspension, followed by stirring for 5 min. Subsequently, 200 μl H_2O_2 (30%) was added to the suspension (In these experiments of controlling H_2O_2 / Fe^{2+} ratios, the H_2O_2 dosages varied according to Fe^{2+} concentration). Thereafter, the above suspension was placed into the reactor (see Figure S1). Then, the reactor was purged with methane for several times to replace initial air. After that, 3 MPa methane was injected into the reactor. The Photocatalysis-Fenton reaction was then carried out under solar light irradiation and the temperature of the suspension was maintained at 30 ℃.

After reaction for 1 h, the reactor was cooled in an ice bath for 1h. Subsequently, the gas in the reactor was injected into a gas chromatography to detect CO_2 and CO. Nevertheless, no CO_2 or CO were detected by the gas chromatography (KE CHUANG, GC 2002) equipped with two flame ionization detectors (FID1 and FID2) and one thermal conductivity detector (TCD). FID1 and TCD were connected to a TDX-01 column (2m × 3mm). The FID2 was connected to a GDX-502 column (4m × 3mm). The suspension in the reactor was then filtered and collected. The products (CH_3OH, CH_3CHO) in the solution collected from the suspension were analyzed with the gas chromatography mentioned above. Formic acid (HCOOH) in the solution was analyzed with a high performance liquid chromatography (SHIMADZU, Essentia CTO-16) equipped with a RSpak KC-811 6E column (Shodex) using 0.1% H_3PO_4 solution as mobile phase.

Selectivity and conversion rate calculation

The selectivity of methanol is calculated by the following equation:

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$$\text{Selectivity (\%)} = \frac{N(CH_3OH)}{N(HCOOH) + N(CH_3OH) + N(CH_3CHO)} \times 100\%$$

$$\text{Conversion rate (\%) of methane} = \frac{\text{moles of } CH_4 \text{ consumed}}{\text{moles of initial } CH_4} \times 100\%$$

Here, mole of CH_4 consumed= N (HCOOH) + N (CH_3OH) + 2N (CH_3CHO)”

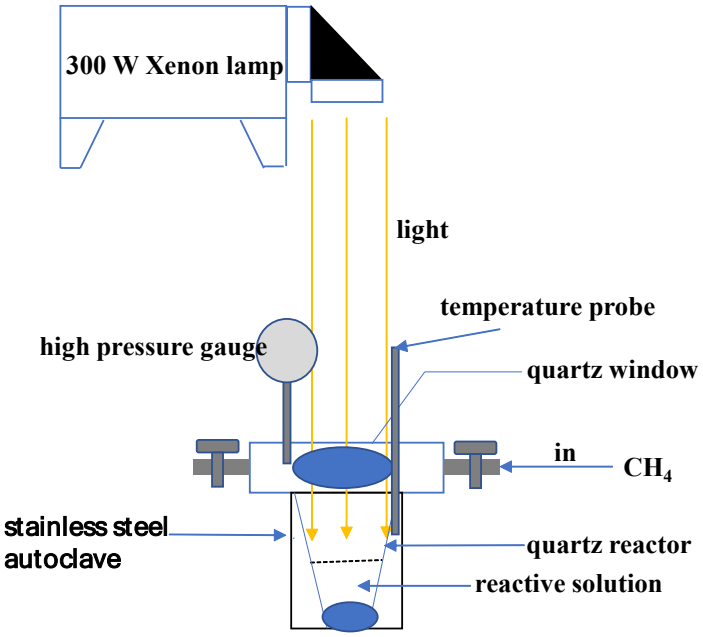

Fig. S1. Schematic reactor of conversion of methane.

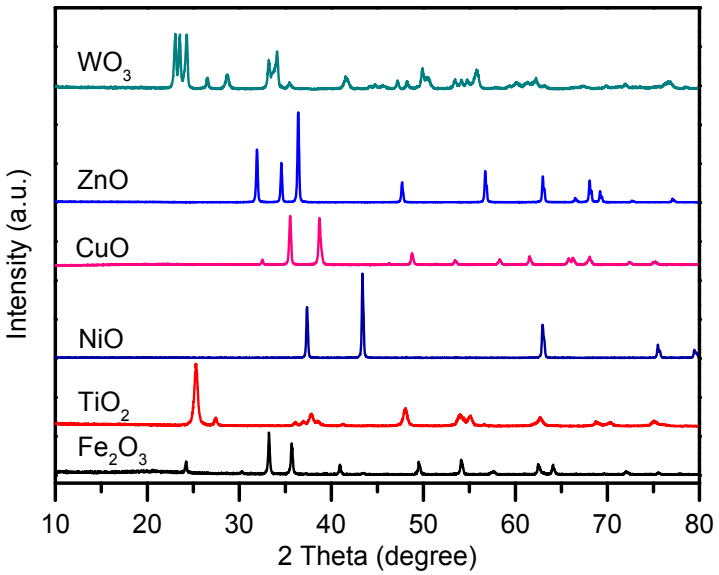

Fig. S2. XRD patterns of different catalysts.

Table S1. Conversion rates of methane in different PCFR, PCR, PFR, and FR processes.

Reactions	Products (μmol g^{-1} h^{-1})			Selectivity (%)	Conversion rates (%)
	HCOOH	CH_3OH	CH_3CHO	CH_3OH	CH_4
PCFR	34	471	53	84	0.39
PCR	64	64	0	50	0.08
PFR	0	165	59	74	0.15
FR	0	39	26	60	0.06

Table S2. Conversion rates of methane with different metal oxide semiconductor catalysts.

Catalysts	Products (μmol g^{-1} h^{-1})			Selectivity (%)	Conversion rates (%)
	HCOOH	CH_3OH	CH_3CHO	CH_3OH	CH_4
Fe_2O_3	101	71	30	35	0.15
TiO_2	34	471	53	84	0.39
NiO	300	52	32	14	0.27
CuO	454	151	38	23	0.43
ZnO	0	0	38	0	0.05
WO_3	871	350	92	27	0.89

Table S3. Comparison of conversion of methane to methanol in different reactive processes over various catalyst reported.

Catalysts	Methods	Temperature and pressure	Generation rates of CH_3OH (μmol g^{-1} h^{-1})	Selectivity of CH_3OH (%)	Ref.
La/WO_3	[a]**PCR:** mercury lamp, UVC-visible light	55 ℃, 0.1MPa	32	47	1
WO_3	**PCR:** mercury lamp, UVC-visible light	55 ℃, 0.1MPa	55.5	38	2
$BiVO_4/V_2O_5$	**PCR:** 450 W Hg lamp, UVC-visible light	70 ℃, 0.1MPa	10.7	29.5	3
$g\text{-}C_3N_4@Cs_{0.33}WO_3$	**PCR:** 300 W Xe lamp,	25 ℃, 0.1MPa	4.38	51.5	4
$BiVO_4$	**PCR:** 450 W mercury lamp,UVC-visible ligh	25 ℃, 0.1MPa	21	50	5
$BiVO_4$	**PCR:** 350 W Xe arc lamp, AM 1.5	65 ℃, 0.1MPa	134	85	6
$FeOOH/WO_3$	**PCR:** 300 W Xe lamp, visible light	25 ℃, 0.1MPa	211	91	7
Cu/MOR	[b]**TDR:** high temperature	200 ℃, 0.7MPa	0.204mol/ Cu (mol)	97	8
Cu-ZSM-5	**TDR:** high temperature	200 ℃, 0.1MPa	13	/	9, 10
TiO_2	[c]**PCFR:** 300 W Xe lamp, AM 1.5	30 ℃, 3 MPa	471	83	this work

Abbriviations: [a]PCR, photocatalytic reaction; [b]TDR, thermodynamic reaction; [c]PCFR: photocatalysis-Fenton reaction

Table S4. Conversion rates of methane with different H_2O_2/Fe^{2+} ratios.

Ratios of H_2O_2/Fe^{2+}	Products (μmol g^{-1} h^{-1})			Selectivity (%)	Conversion rates (%)
	HCOOH	CH_3OH	CH_3CHO	CH_3OH	CH_4
0	0	0	0	0	0
10	0	162	0	100	0.10
20	34	471	53	84	0.39
50	53	325	180	58	0.47
120	179	294	189	44	0.48

References:

1. K. Villa, S. Murcia-López, J. R. Morante and T. Andreu, *Appl Catal B*, 2016, **187**, 30-36.
2. K. Villa, S. Murcia-López, T. Andreu and J. R. Morante, *Appl Catal B*, 2015, **163**, 150-155.
3. S. Murcia-López, M. C. Bacariza, K. Villa, J. M. Lopes, C. Henriques, J. R. Morante and T. Andreu, *ACS Catal*, 2017, **7**, 2878-2885.
4. Y. Li, J. Li, G. Zhang, K. Wang and X. Wu, *ACS Sustainable Chem. Eng*, 2019, **7**, 4382-4389.
5. S. Murcia-López, K. Villa, T. Andreu and J. R. Morante, *ACS Catal*, 2014, **4**, 3013-3019
6. Zhu W, Shen M, Fan G, ACS Appl. Nano Mater. 2018, 1, 6683−6691
7. J. Yang, J. Hao, J. Wei, J. Dai and Y. Li, *Fuel*, 2020, **266**.
8. V. L. Sushkevich, D. Palagin, M. Ranocchiari and J. A. van Bokhoven, *Science*, 2017, **356**, 523-527.
9. P. J. Smeets, M. H. Groothaert and R. A. Schoonheydt, *Catal Today*, 2005, **110**, 303-309.
10. A. A. Latimer, A. Kakekhani, A. R. Kulkarni and J. K. Nørskov, *ACS Catal.*, 2018, **8**, 6894-6907.