Electronic Supplementary Material (ESI) for Chemical Science.

Supporting information for

High-yield Production of Liquid Fuels in CO_2 Hydrogenation on a Zeolite-free Fe-based Catalyst

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Experimental Section

Sample preparation. *Carbon template synthesis*. Carbon template was first synthesized via hydrothermal synthesis. To be specific, sucrose of 11.4 g was dissolved in deionized water of 60 mL and stirred 1.0 h at room temperature. After that, above mentioned solution was transferred into a Teflon-lined stainless steel autoclave, followed by one-pot hydrothermal synthesis at 160 °C for 10 h. Obtained black sample was filtered and washed several times with distilled water, and finally dried at 120 ^{o}C for 6h (marked as C). *Fe-based catalyst synthesis*. 1.0 mmol $Zn(NO_3)_2·6H_2O$, 2.0 mmol $Fe(NO_3)_3·9H_2O$, and 0.1 mmol KNO_3 were added to a certain amount of deionized water (5mL) and stirred evenly. Then, 0.36g C template was added to the above solution and stirred for 0.5 h. The resulting sample was treated with ultrasound for 0.5 h to enable the C template to fully absorb metal ions repeatedly. After adequate ultrasonic absorption, the mixtures containing solution and C template were directly fed into the muffle furnace. The following heat treatment process was as follows: from room temperature to 120 °C with a rate of 1 °C/min and kept for 6 h, then to 700 °C with a rate of 2 °C/min and kept for 2 h, and finally being cooled to room temperature in air atmosphere conditions. The final sample was marked as KZFe. For KZFe-Co catalyst, 1.0 mmol $Zn(NO_3)_2·6H_2O$, 2.0 mmol $Fe(NO_3)_3·9H_2O$, 0.1 mmol KNO_3, and x mmol $Co(NO_3)_2·6H_2O$ (x=0.05, 0.1, 0.2, 0.4) were added to a certain amount of deionized water (5mL) and stirred evenly. The remaining preparation steps were the same as those of KZFe catalyst. The obtained samples were labelled as KZFe-2.5Co, KZFe-5.0Co, KZFe-10.0Co, and KZFe-20.0Co. Besides, same addition amount of C template was replaced by SiO_2 to obtain a reference KZFe-SiO_2 catalyst. In addition, 2.0 mmol $Fe(NO_3)_3·9H_2O$, and 0.1 mmol KNO_3 were added to a certain amount of deionized water (5mL) and stirred evenly. Then, 0.36g C template was added to the above solution and stirred for 0.5 h. The remaining steps are the same as the preparation of KZFe catalyst, marked as KFe. If the impregnation precursor solution contains only Zn^{2+} or Co^{2+} ions, the resulting catalyst was labeled Z and Co, respectively. If only Zn^{2+} and Fe^{3+} (molar ration: 1:2) are present in the precursor solution, the resulting spinel catalyst is labeled ZFe. KFe+Z was fabricated by physical mixing of KFe and Z catalyst. Similar, KZFe+Co was prepared by physical mixing of KZFe and Co catalyst.

Catalyst characterization. N_2 physisorption was performed on a Micromeritics analyzer. Prior to analysis, the catalysts were vacuum dried at 200 ^{o}C for 6h to remove the physical adsorbed water. The molar ratios of as-prepared catalysts were measured by inductively coupled plasma mass spectrometry (ICP-MS) using Thermo Fisher iCAP Q ICP-MS. Powder XRD spectra of the catalysts were characterized by a Rigaku SmartLab 9KW using Cu-Ka irradiation. Scans were recorded in the 2θ range of 10-90^{o} with a step size of 0. 2 ^{o}/s. X-ray photoelectron spectroscopy (XPS) analysis was obtained using Thermo Fisher Scientific ESCALAB 250Xi multifunctional X-ray photoelectron spectroscope. High-resolution transmission electron microscopy (HR-TEM) for spent catalyst was obtained by a JEM 2100F at 200kV equipped with energy-dispersive X-ray spectroscopy (EDS) mapping (Super X instrument). The CO_2 temperature-programmed adsorption (CO_2-TPD) and H_2-temperature-programmed reduction (H_2-TPR) properties of the fresh catalysts were determined by a BELCAT-II-T-SP characterization system. Sample of 50 mg was first pretreated at 150 °C with He for 1 h. Then a 5 vol% H_2/Ar gas mixture (30 mL/min) was fed into the reactor when the temperature was cooled to 50 °C. Finally, the H_2-TPR curves were recorded from 50 to 700 °C with a heating rate of 10 °C/min. In terms of CO_2-TPD, 50 mg of sample was first reduced at 400 °C in H_2 gas flow (30 mL/min) for 2h. Then, the temperature was decreased to 50 °C in He gas flow (30 mL/min). 10 vol% CO_2/Ar gas mixture was then introduced into the reactor for 1 h. Then He was introduced into the reactor to remove gas phase CO_2. The CO_2-TPD trace was recorded from 50 to 700 °C with a heating rate of 10 °C/min. The extended X-ray absorption fine structure (EXAFS) experiments were conducted at the Beijing Synchrotron Radiation Facilities (BSRF), Beijing, China. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra were recorded on a NEXUS 470 FTIR spectrometer. Before test, the sample was in situ reduced at 400 °C under 5 vol% H_2 in Ar (50 mL/min) for 2 h and then switched to He for 0.2 h (50 mL/min). After that, the reaction gas was introduced into the reaction cell for reaction. Finally, at 1.0 MPa, 320 °C, 20 mL/min of mixture gas as 24 vol% CO_2/70 vol% H_2/6 vol% Ar passed through and DRIFT spectra were recorded.

Catalytic performance test. CO_2 hydrogenation performances were conducted in a fixed-bed stainless steel reactor using 0.2 g as-prepared catalyst. Before reaction, the as-prepared catalysts of 0.2 g were in situ reduced at 400 °C for 10 h in a pure H_2 flow of 40 mL/min. After that, the temperature was dropped to 320 °C. Subsequently, $CO_2/H_2/Ar$ (24.5 vol% /71.8 vol% /3.7 vol %) was fed into the reactor, and the pressure gradually increased to 2.0 MPa. N-octane as solvent was equipped to capture the long-chain hydrocarbons in the effluents. The collected long-chain hydrocarbons were analyzed by an off-line gas chromatograph using a flame ionization detector (FID). CO_2 conversion, CO selectivity, and hydrocarbons selectivity were calculated according to equation (1), (2), and (3), respectively. The carbon balance data is between 90% and 110%.

$$\mathrm{CO_2\ conversion\ (\%)} = \frac{CO2\ inlet - CO2\ outlet}{CO2\ inlet} \times 100\% \qquad (1)$$

$$\mathrm{CO\ selectivity\ (\%)} = \frac{CO\ outlet}{CO2\ inlet - CO2\ outlet} \times 100\% \qquad (2)$$

$$\mathrm{C_i\ hydrocarbon\ selectivity\ (C\text{-}mol\ \%)} = \frac{Mole\ of\ Ci\ hydrocarbons}{Mole\ of\ total\ hydrocarbons} \times 100\% \qquad (3)$$

Table S1 Catalyst molar ratio determined by ICP-OES.

Entry	Catalyst	Co/Fe (%)	Zn/Fe(%)
1	KZFe	0	50.6
2	KZFe-2.5Co	2.2	47.0
3	KZFe-5.0Co	4.8	52.8
4	KZFe-10.0Co	9.2	52.5
5	KZFe-20.0Co	19.3	52.8

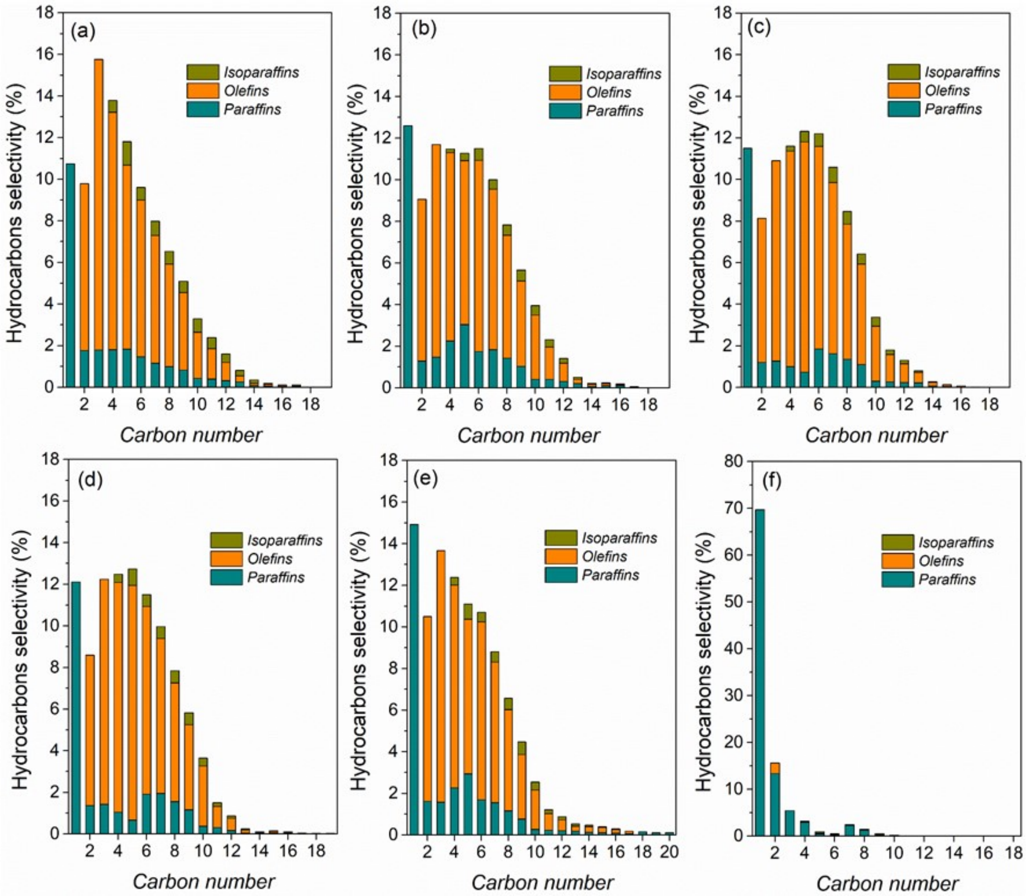

Figure S1 Detailed hydrocarbons distribution over (a) KZFe, (b) KZFe-2.5Co, (c) KZFe-5.0Co, (d) KZFe-10.0Co, (e) KZFe-20.0Co, (c) KZFe-SiO_2 catalyst.

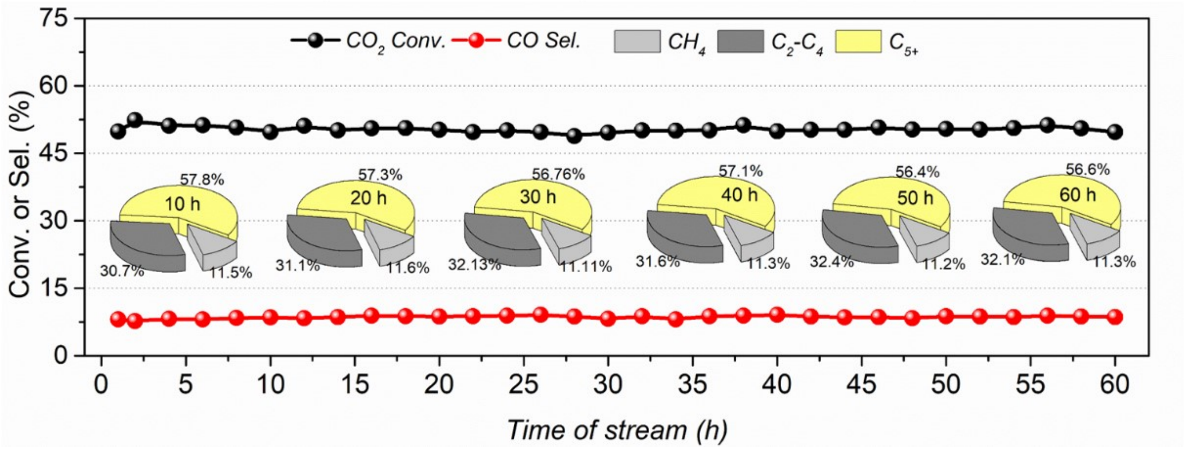

Figure S2 CO_2 hydrogenation stability over the KZFe-5.0Co catalyst at 320 °C, 2.0 MPa, 6000 mL g^{-1} h^{-1}.

Table S2 Catalytic performances of CO_2 hydrogenation over different catalysts. [a]

Entry	Catalyst	CO_2 conv.(%)	CO sel.(%)	Hydrocarbon selectivity (%)		
				CH_4	C_2 - C_4	C_{5+}
1	Co	57.7	1.4	90.2	9.8	0
2	Z	0	0	0	0	0
3	ZFe	34.7	20.1	25.4	53.9	20.7
4	KFe	36.7	25.1	15.6	49.0	35.4
5	KFe+Zn(PM)	33.2	26.7	17.9	45.8	36.3
6	KZFe+5.0Co(PM)	34.5	26.1	28.7	45.7	25.6

Reaction conditions: 320 ^{o}C, 2.0 MPa, 6000 mL g^{-1} h^{-1}.

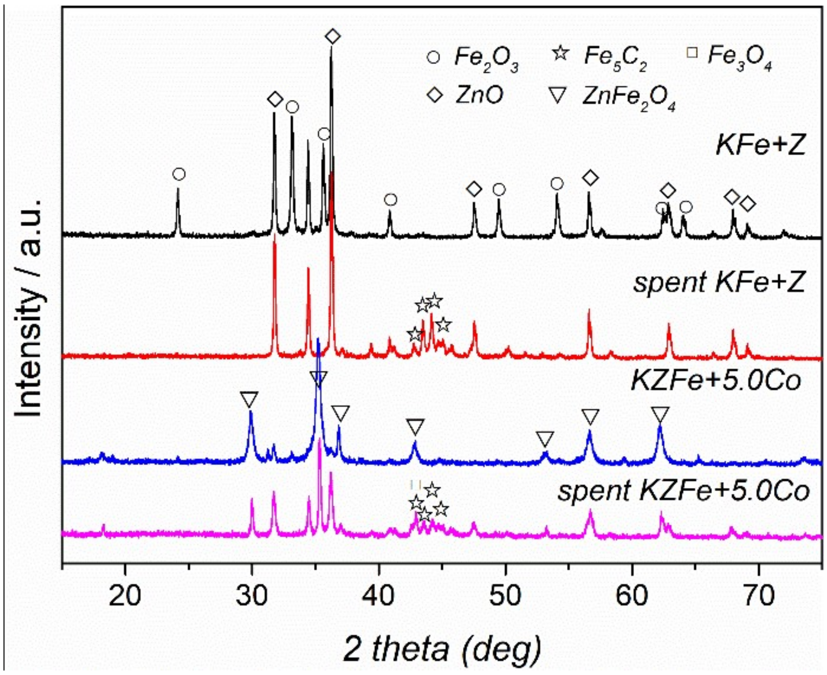

Figure S3 Powder XRD patterns of as-prepared and spent KFe+Z, and KZFe+5.0Co.

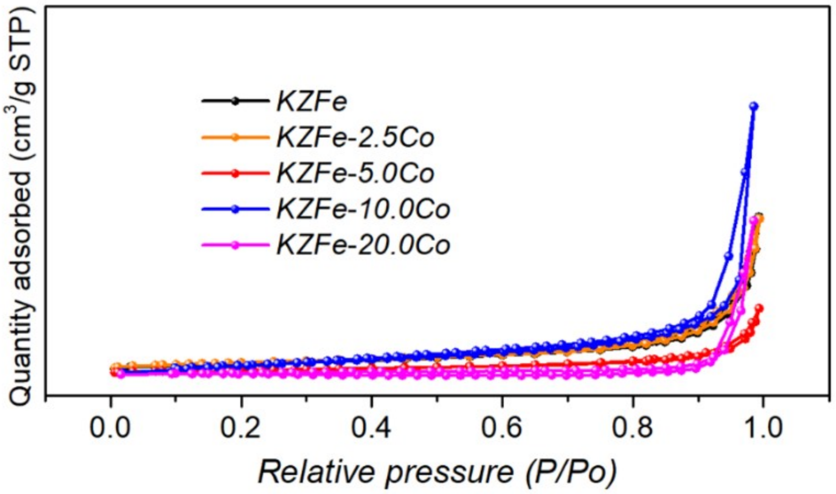

Figure S4 N_2 adsorption-desorption isotherms of different catalysts.

Table S3 Surface area of as-prepared catalysts.

Entry	Catalyst	Surface area / (m^2/g)[a]
1	KZFe	20.7
2	KZFe-2.5Co	27.0
3	KZFe-5.0Co	13.0
4	KZFe-10.0Co	26.3
5	KZFe-20.0Co	2.9

[a] Determined by BET curves.

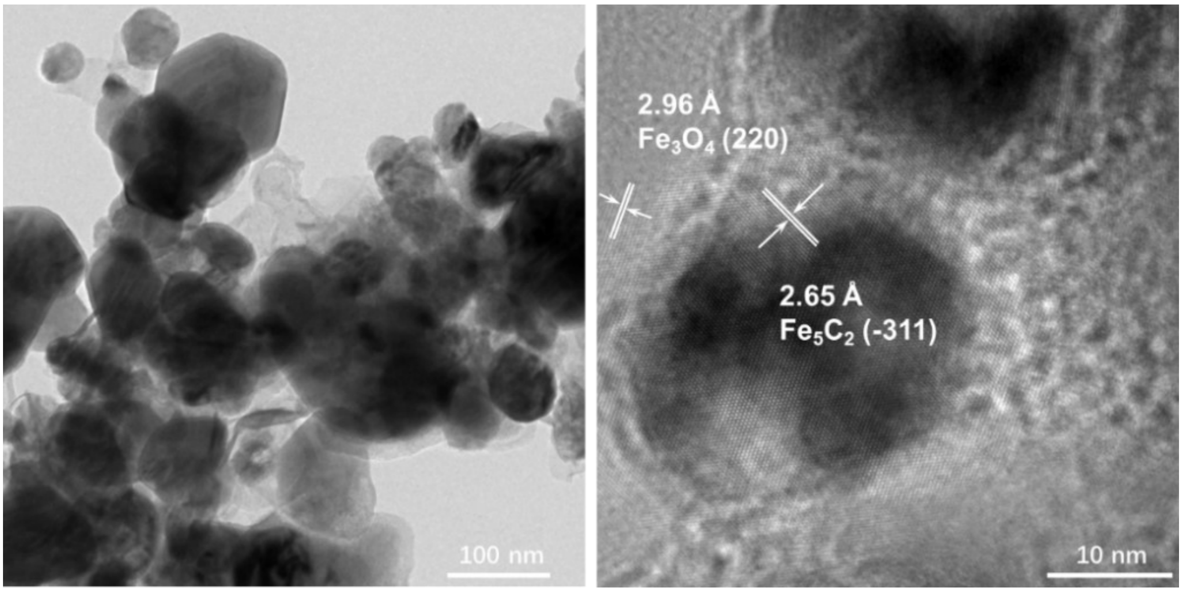

Figure S5 TEM images of spent KZFe catalyst.

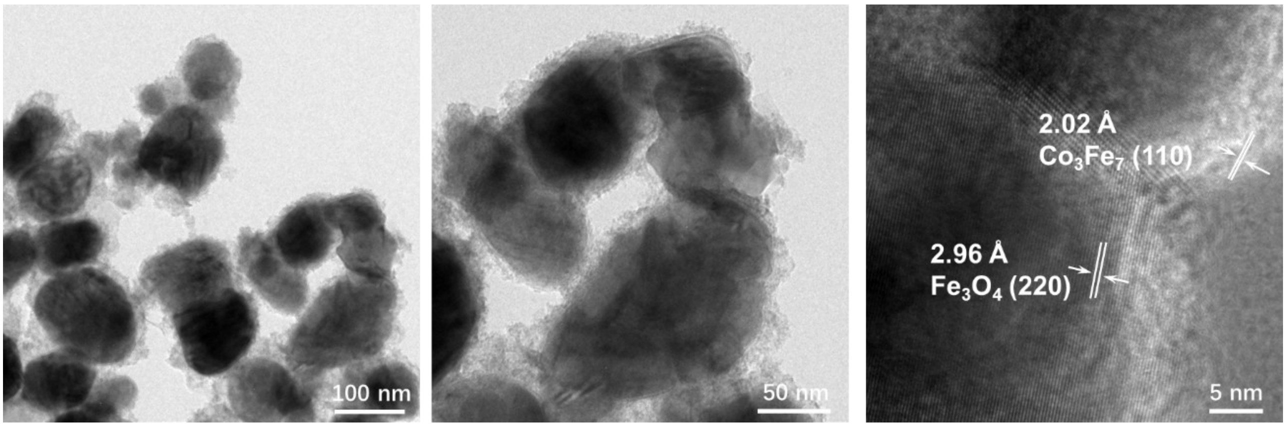

Figure S6 TEM images of spent KZFe-2.5Co catalyst.

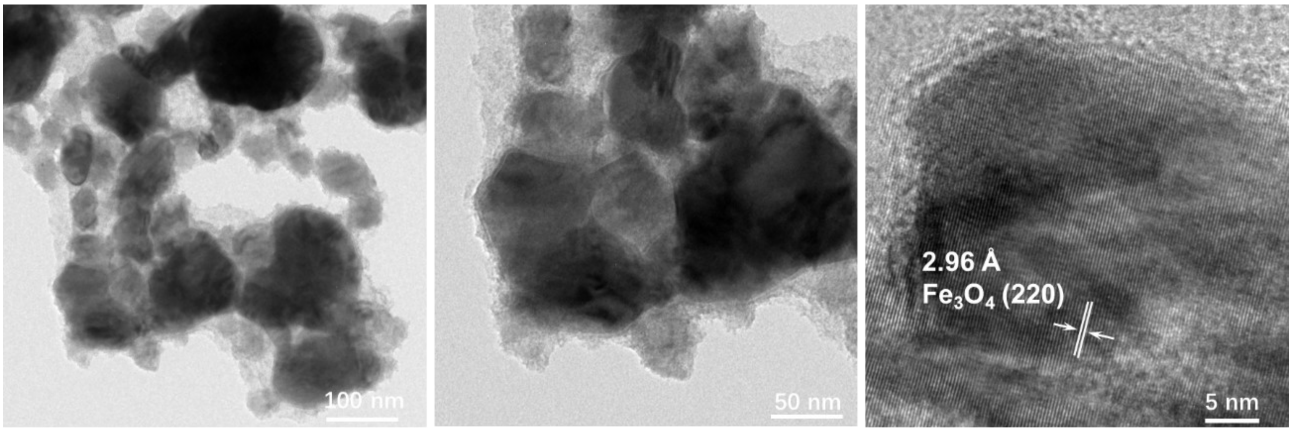

Figure S7 TEM images of spent KZFe-10.0Co catalyst.

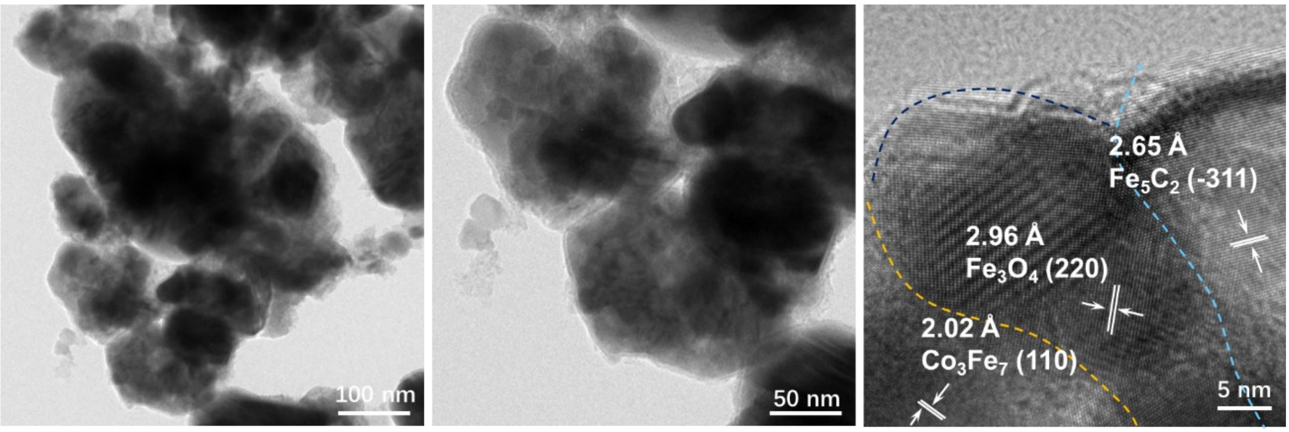

Figure S8 TEM images of spent KZFe-20.0Co catalyst.

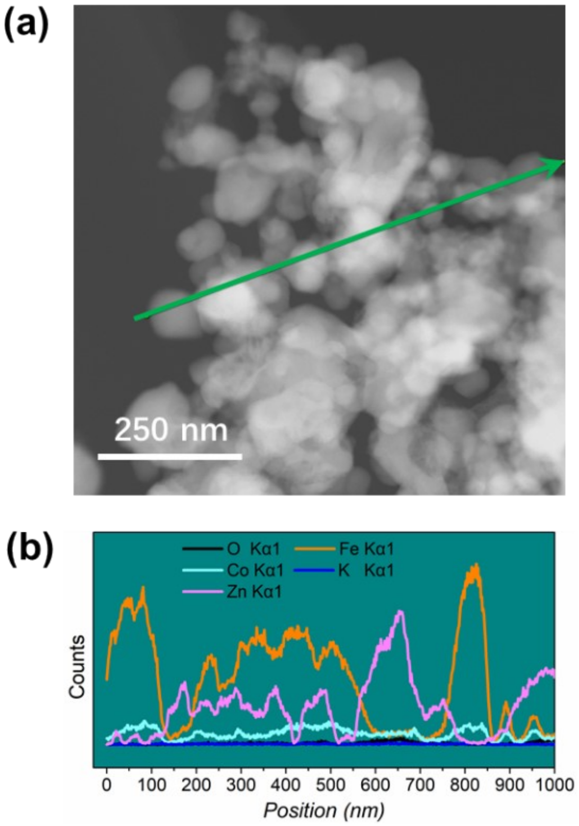

Figure S9 Line scanning of spent KZFe-5.0Co catalyst after reaction.

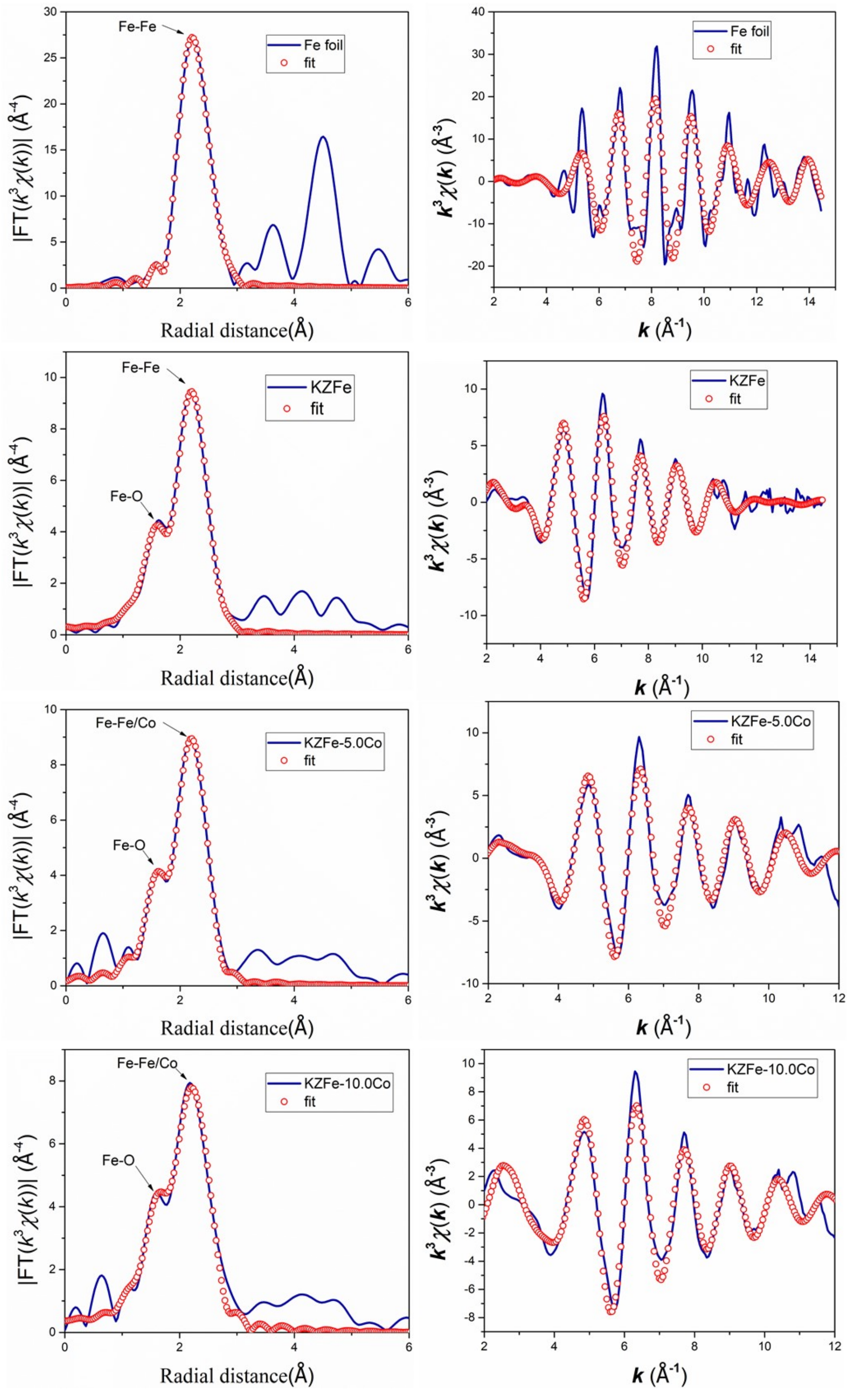

Figure S10 Fourier transforms of the k3-weighted EXAFS spectra and fitted curves (circles) of different catalysts at the Fe K-edge.

Table S4 EXAFS fitting parameters at the Fe K-edge for various samples（S_0^2=0.762）

Sample	Shell	CN^a	R(Å)^b	σ^2(Å^2)^c	ΔE_0(eV)^d	R factor
Fe foil	Fe-Fe	8*	2.47±0.01	0.0038±0.0007	6.2±1.1	0.0018
	Fe-Fe	6*	2.86±0.01	0.0049±0.0011		
KZFe	Fe-O	1.8±0.4	1.93±0.01	0.0066±0.0026	4.4±1.0	0.0041
	Fe-Fe/Co	10.0±0.9	2.58±0.01	0.0152±0.0009		
	Fe-Co	2.2±0.7	2.60±0.01	0.0132±0.0011		
	Fe-Fe	8.0±1.0	2.48±0.01	0.0132±0.0011		
KZFe-5.0Co	Fe-O	1.5±0.5	1.96±0.03	0.0055±0.0039	4.4±1.4	0.0034
	Fe-Fe/Co	8.5±0.6	2.58±0.01	0.0140±0.0014		
	Fe-Fe	4.0±0.3	2.53±0.07	0.0061±0.0114		
	Fe-Co	3.1±0.8	2.67±0.06	0.0061±0.0114		
KZFe-10.0Co	Fe-O	3.3±0.5	2.01±0.03	0.0129±0.0075	8.3±3.1	0.0109
	Fe-Fe/Co	6.8±0.7	2.61±0.02	0.0129±0.0024		
	Fe-Fe	5.9±0.3	2.57±0.04	0.0138±0.0129		
	Fe-Co	2.0±0.4	2.61±0.05	0.0138±0.0129		

$^a CN$, coordination number; $^b R$, distance between absorber and backscatter atoms; $^c \sigma^2$, Debye-Waller factor to account for both thermal and structural disorders; $^d \Delta E_0$, inner potential correction; R factor indicates the goodness of the fit. $S0^2$ was fixed to 0.762, according to the experimental EXAFS fit of Fe foil by fixing CN as the known crystallographic value. Fitting range: $3.0 \leq k$ (/Å) ≤ 12.5 and $1.5 \leq R$ (Å) ≤ 3.0 (Fe foil); $3.0 \leq k$ (/Å) ≤ 12.0 and $1.0 \leq R$ (Å) ≤ 3.0 (Fe-1 and Fe-1-a); $3.0 \leq k$ (/Å) ≤ 11.2 and $1.0 \leq R$ (Å) ≤ 3.0 (Fe-2, Fe-2-a, Fe-3 and Fe-3-a). A reasonable range of EXAFS fitting parameters: $0.700 < S_0^2 < 1.000$; $CN > 0$; $\sigma^2 > 0$ Å^2; $|\Delta E_0| < 10$ eV; R factor < 0.02.

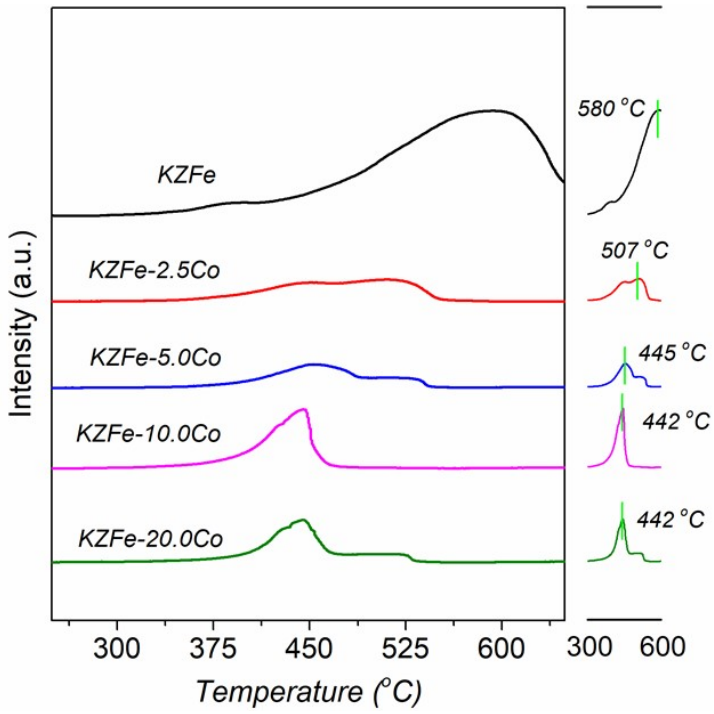

Figure S11 H_2-TPR profiles of different catalysts.

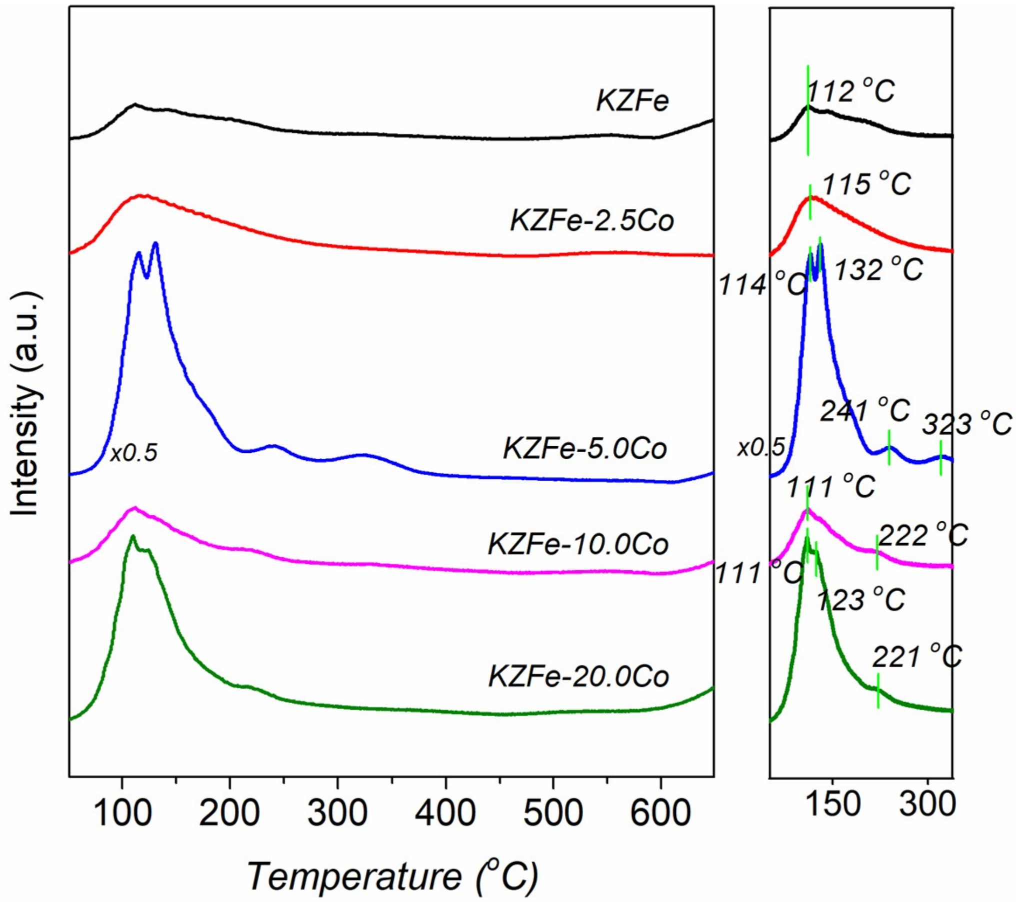

Figure S12 CO_2-TPD profiles of different catalysts.

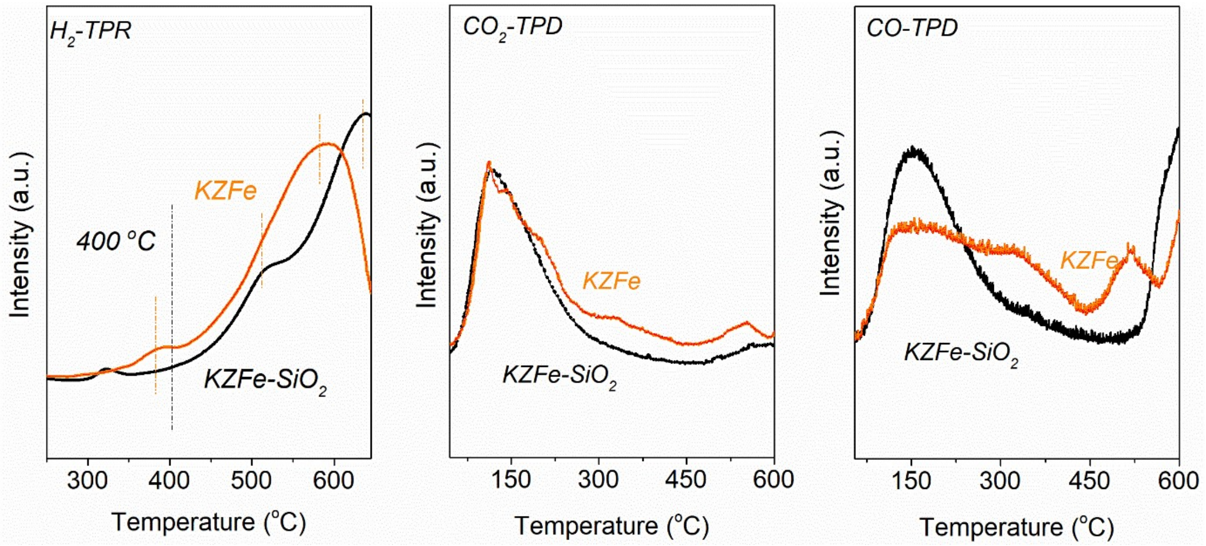

Figure S13 H_2-TPR, CO_2-TPD, and CO-TPD profiles of different catalysts.

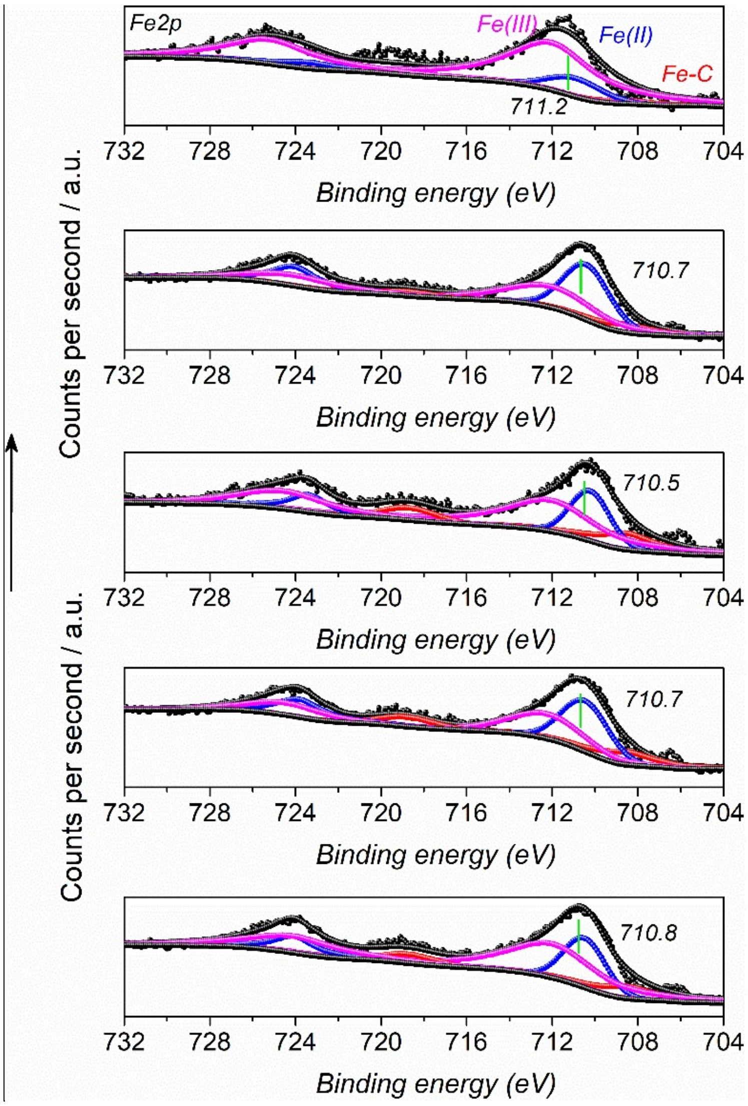

Figure S14 Fe2p spectra of different spent catalysts. From top to bottom, they correspond to KZFe, KZFe-2.5Co, KZFe-5.0Co, KZFe-10.0Co, and KZFe-20.0Co catalysts, respectively.

Table S5 Surface phase composition of spent catalysts. [a]

Entry	Catalyst	Fe(III)	Fe(II)	Fe-C
1	KZFe-SiO_2	91.7	7.3	1.0
2	KZFe	83.3	13.2	3.5
3	KZFe-2.5Co	41.8	47.1	11.1
4	KZFe-5.0Co	55.4	26.9	17.7
5	KZFe-10.0Co	38.8	42.6	18.6
6	KZFe-20.0Co	58.5	28.3	13.2

[a] Determined by XPS results.

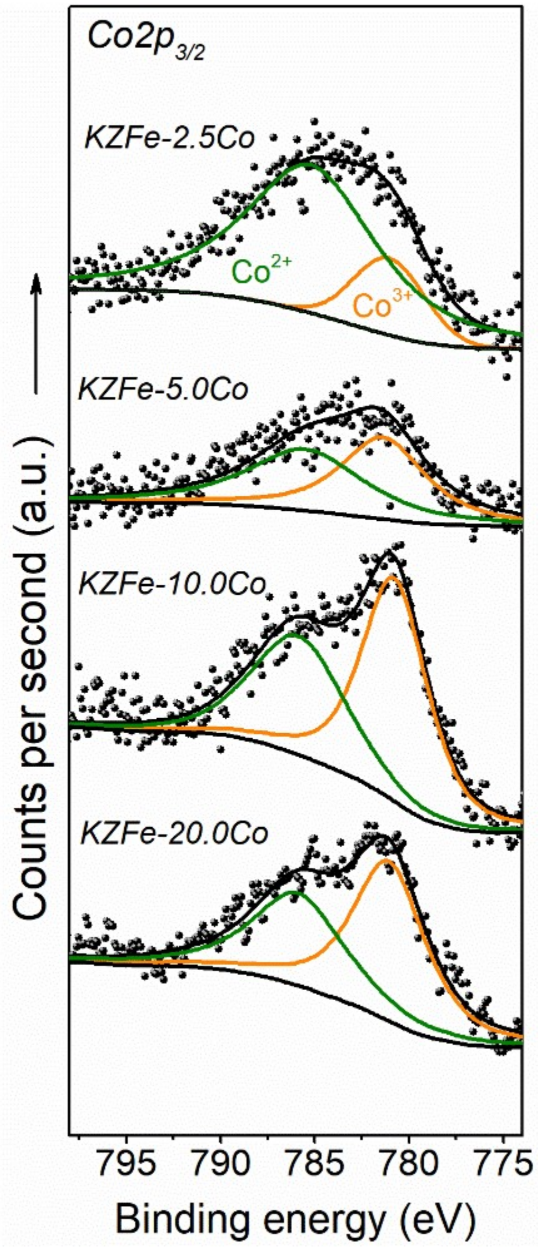

Figure S15 Co2p$_{3/2}$ spectra of different spent catalysts.

Table S6 Surface Co^{2+} phase composition of spent catalysts. [a]

Entry	Catalyst	Co^{2+} / (Co^{2+}+ Co^{3+})
1	KZFe-2.5Co	0.83
2	KZFe-5.0Co	0.51
3	KZFe-10.0Co	0.42
4	KZFe-20.0Co	0.43

[a] Calculated from $Co2p_{3/2}$.

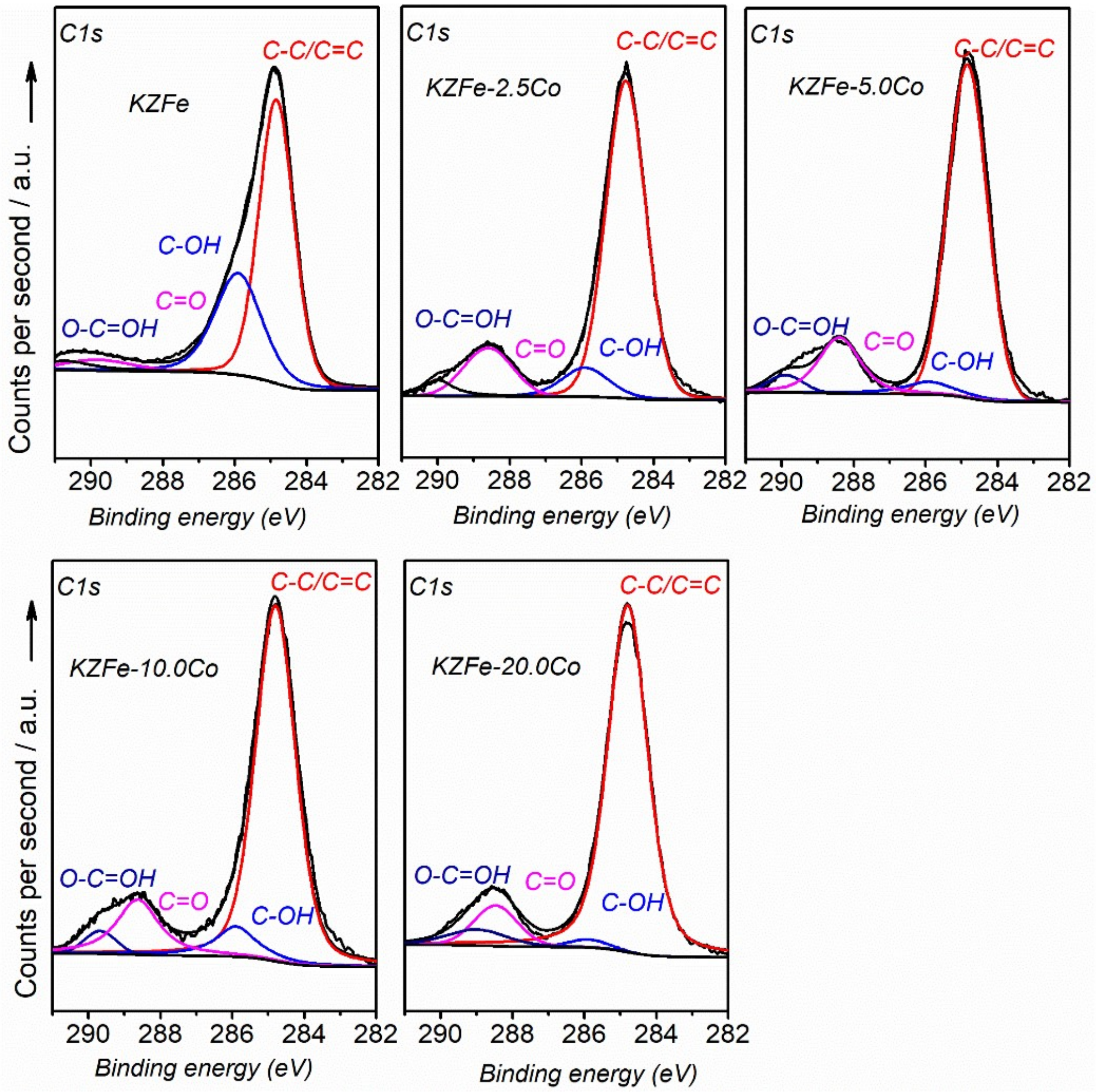

Figure S16 C1s spectra of different spent catalysts.

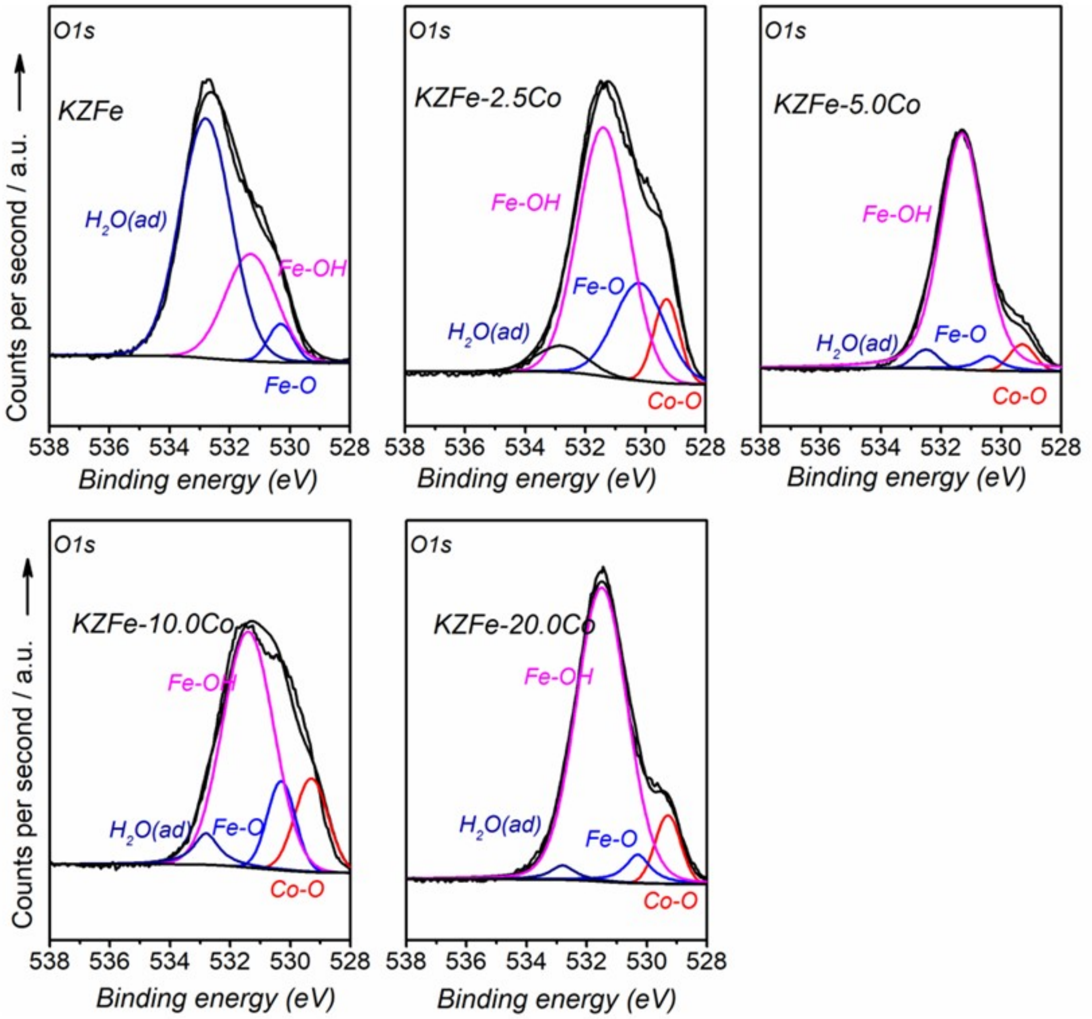

Figure S17 O1s spectra of different spent catalysts.

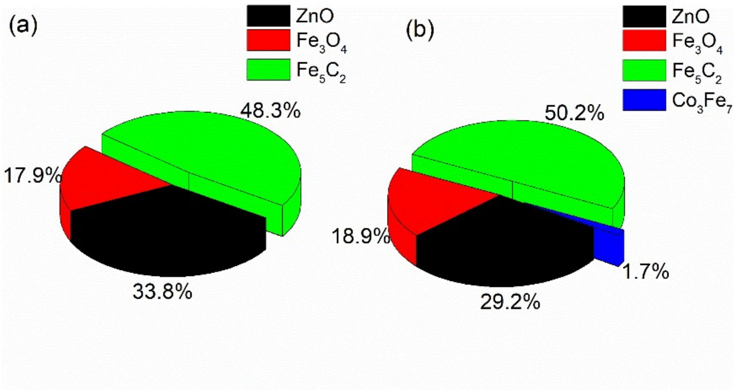

Figure S18 Phase composition determined from refinement of XRD data, (a) KZFe and (b) KZFe-5.0Co after 8h reaction.