Supporting information for

Microwave-Assisted Carbon-Confined Iron Nanoparticles for Steering CO_2 Hydrogenation to Heavy Hydrocarbons

Lisheng Guo [a, b]*, Peipei Ai [b], Xinhua Gao [c], Hao Wu [a], Xianbiao Wang [a], Yasuharu Kugue [d], Jiaming Liang [d], Weizhe Gao [d], Xiaoyu Guo [d], Jian Sun [e]*, Song Sun [a]*, Noritatsu Tsubaki [d]*

[a] School of Chemistry and Chemical Engineering, Anhui University, Hefei, Anhui 230601, China

[b] State Key Laboratory of Clean and Efficient Coal Utilization, Taiyuan University of Technology, Taiyuan 030024, Shanxi, China

[c] State Key Laboratory of High-efficiency Utilization of Coal and Green Chemical Engineering, College of Chemistry & Chemical Engineering, Ningxia University, Yinchuan 750021, China

[d] Department of Applied Chemistry, School of Engineering, University of Toyama, Gofuku 3190, Toyama 930-8555, Japan

[e] Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

Corresponding authors: lsguo@ahu.edu.cn; sunj@dicp.ac.cn; suns@ustc.edu.cn; tsubaki@eng.u-toyama.ac.jp

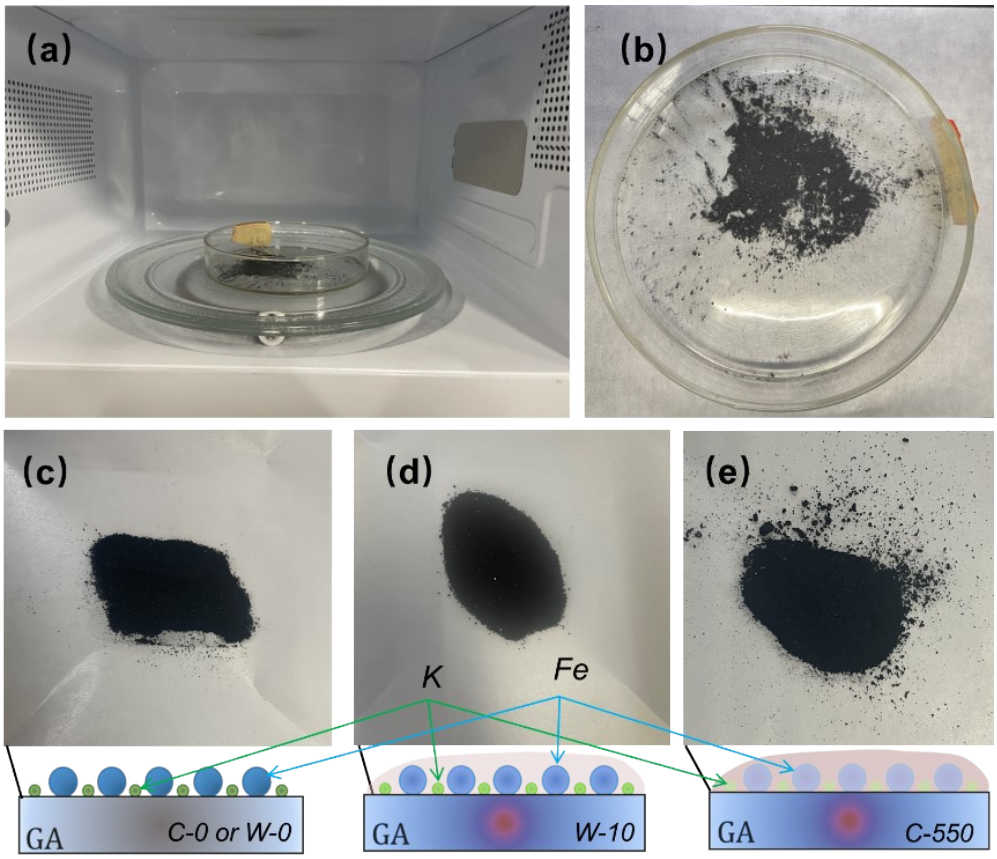

Fig. S1 Details and schematic diagram of K-Fe/GA preparation processes. (a) Sample in the microwave oven; (b) sample in petri dish; (c) Sample without any heating treatment; (d) Sample with microwave heating treatment (10s); (e) Sample with calcination heating treatment (550 ^{o}C for 5h).

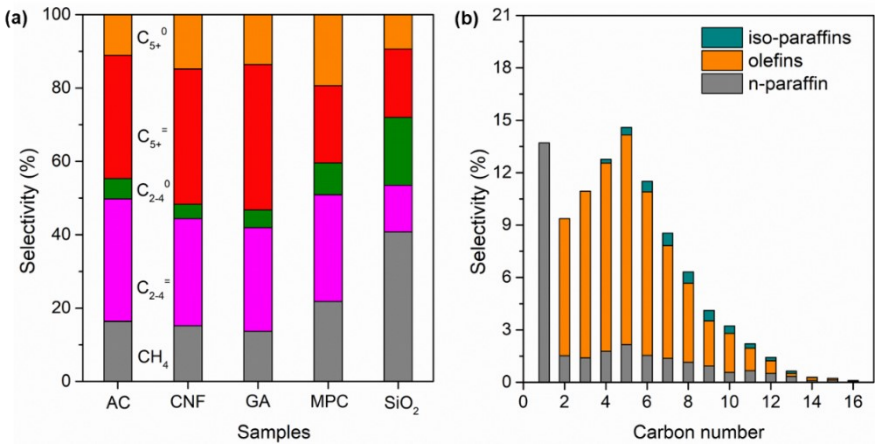

Fig. S2 (a) Selectivity distribution of different types of hydrocarbon products; (b) Detailed product distribution over K-Fe/GA-W-10 sample.

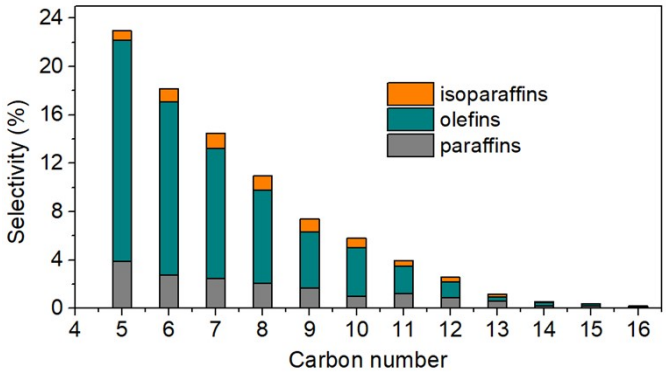

Fig. S3 Liquid hydrocarbon (C_{5+}) distribution determined by GC analysis.

Table S1 CO_2 conversion and product selectivity from different catalysts.

Catalyst	HT [a]	GHSV [b]	H_2/CO_2	P/MPa	T/°C	CO_2 Conv.	CO Sel.	CO-free HCs Sel. (mol-%)		
								CH_4	C_2-C_4	C_{5+}
K-Fe/SiO_2-W-60	60s	4800	2.5	2.0	320	5.6	59.8	83.8	16.2	0
K-Fe/SiO_2-W-300	300s	4800	2.5	2.0	320	6.4	58.9	73.3	26.7	0

All the conversion and selectivity data are collected at a stable 6-8 h on stream; a. represents the heating time (HT) over 100 °C during catalyst preparation; b. unit in mL g_{cat}^{-1} h^{-1}.

Table S2 CO_2 conversion and product selectivity from different catalysts.

Catalyst	HT [a]	GHSV [b]	H_2/CO_2	P/MPa	T/°C	CO_2 Conv.	CO Sel.	CO-free HCs Sel. (mol-%)		
								CH_4	C_2-C_4	C_{5+}
K-Fe/AC-W-10(2.5K)	10s	4800	2.5	2.0	320	26.3	40.2	16.4	38.9	44.7
K-Fe/GA-W-10(5.0K)	10s	4800	2.5	2.0	320	23.1	42.9	13.7	33.1	53.2
K-Fe/AC-W-10(7.5K)	10s	4800	2.5	2.0	320	26.2	45.1	10.7	30.6	58.6
K-Fe/AC-W-10(10.0K)	10s	4800	2.5	2.0	320	27.2	39.3	15.1	37.5	47.4

All the conversion and selectivity data are collected at a stable 6-8 h on stream; a. represents the heating time (HT) over 100 °C during catalyst preparation; b. unit in mL g_{cat}^{-1} h^{-1}.

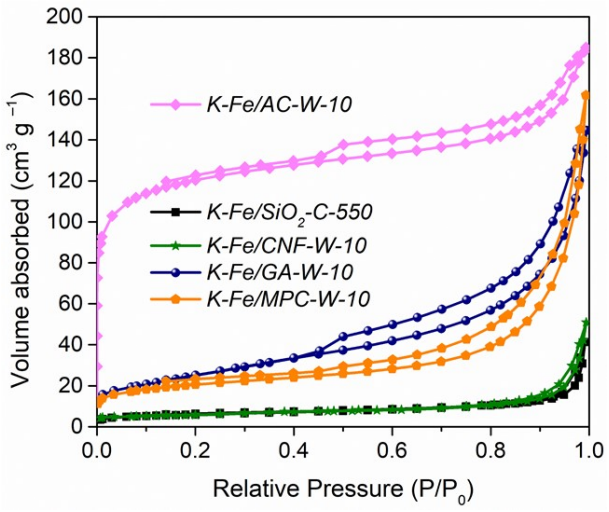

Fig. S4 BET profiles of as-prepared samples.

Table S3 Surface areas of different iron-based catalysts.

Samples	Surface area (m^2/g)
K-Fe/SiO_2-C-550	20
K-Fe/AC-W-10	375
K-Fe/CNF-W-10	19
K-Fe/GA-W-10	91
K-Fe/MPC-W-10	69

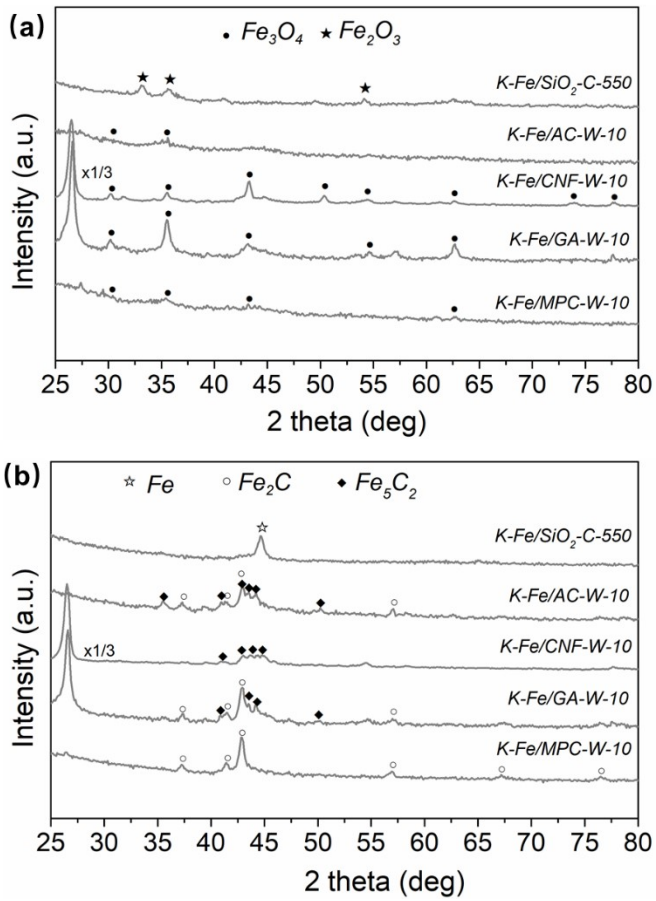

Fig. S5 Ex situ XRD patterns of as-prepared samples (a) and spent samples (b).

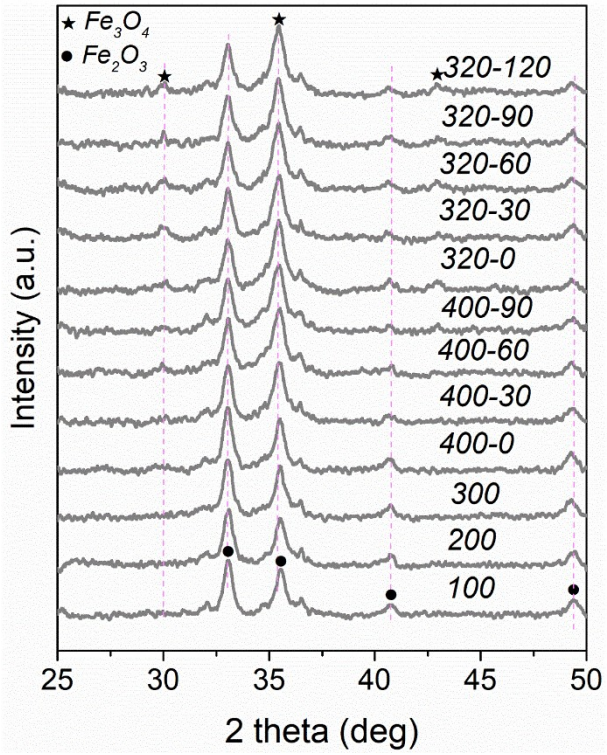

Fig. S6 In situ XRD patterns of K-Fe/SiO_2-C-550 sample.

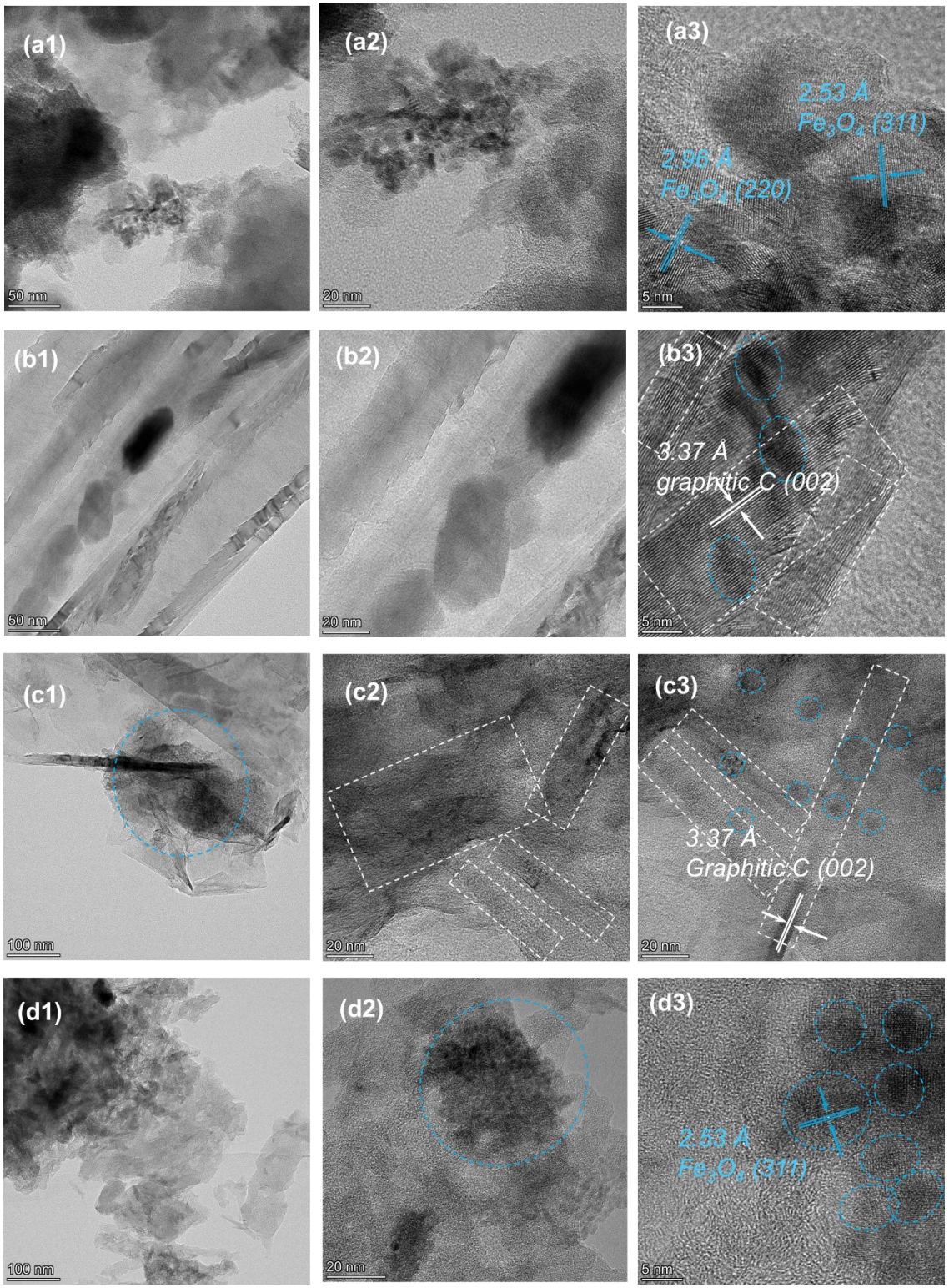

Fig. S7 TEM and HR-TEM images of as-prepared samples, (a) K-Fe/AC-W-10, (b) K-Fe/CNF-W-10, (c) K-Fe/GA-W-10, and (d) K-Fe/MPC-W-10. (The regions in Blue Circle are iron species, while the regions in White Square are carbon layers.)

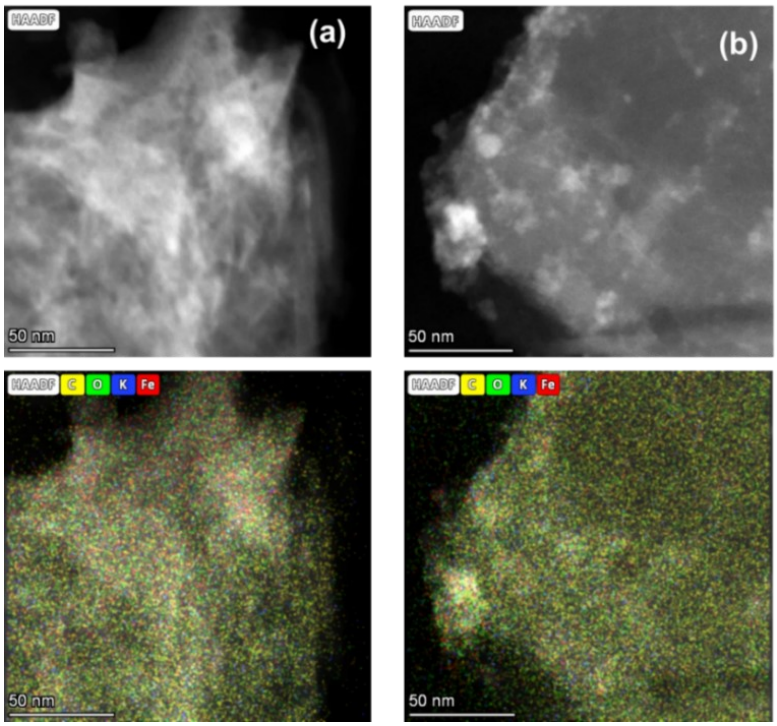

Fig. S8 HAADF-TEM images and the corresponding elemental mapping images of K-Fe/GA-W-0 (a), and (b) K-Fe/GA-W-10 catalysts.

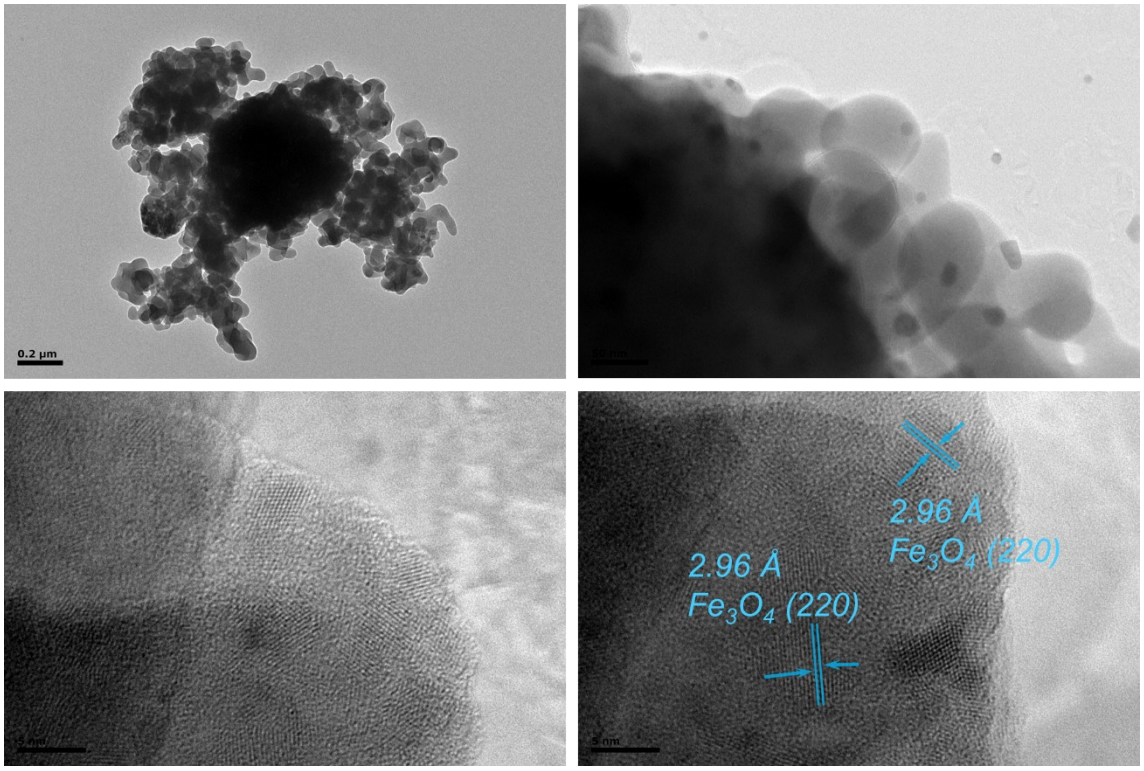

Fig. S9 TEM and HR-TEM images of spent K-Fe/SiO_2-C-550 sample.

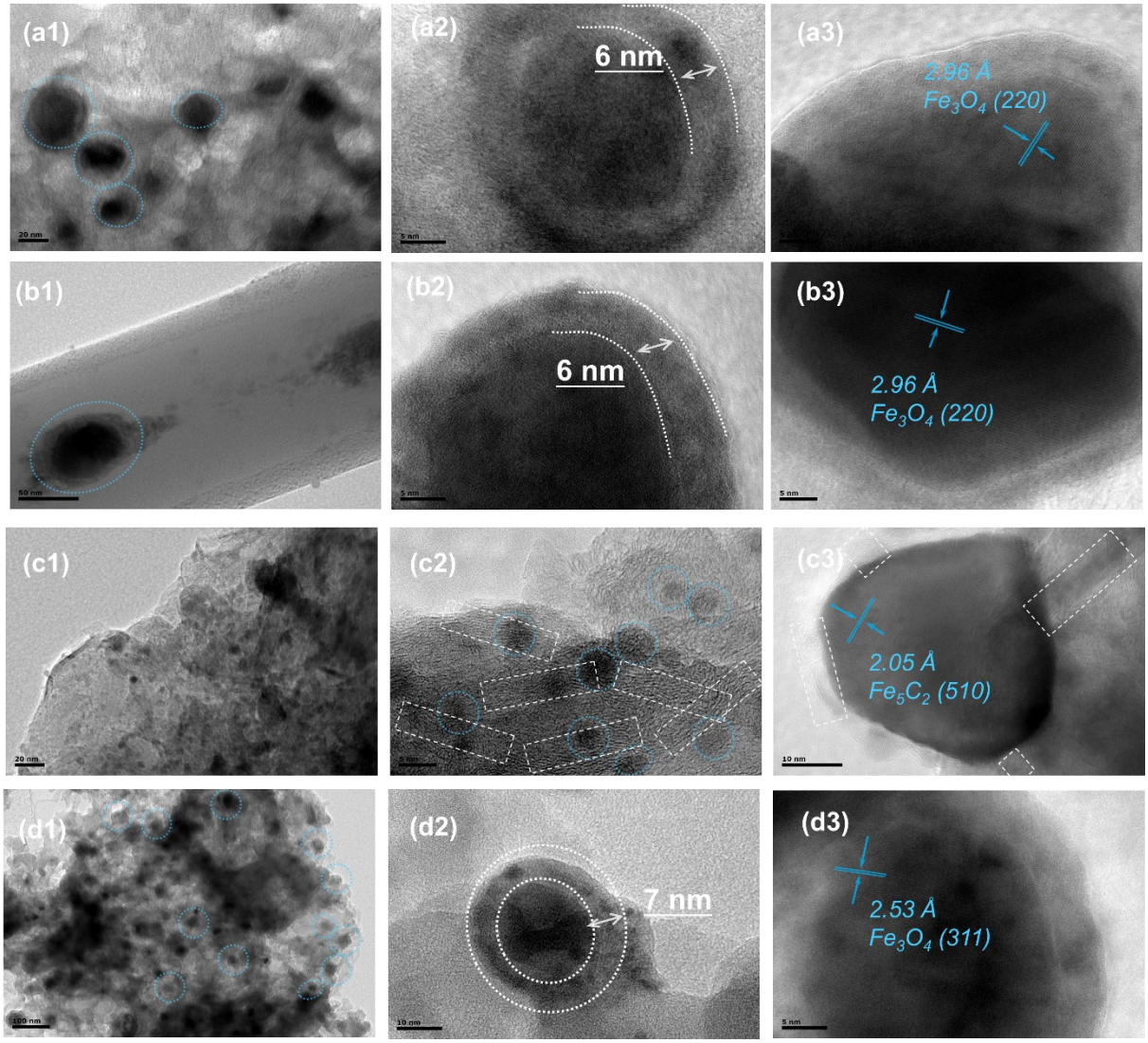

Fig. S10 TEM and HR-TEM images of spent samples, (a) K-Fe/AC-W-10, (b) K-Fe/CNF-W-10, (c) K-Fe/GA-W-10, and (d) K-Fe/MPC-W-10.

Table S4 Particle size based on FWHM data.

Operations	Particle size based on FWHM data (A)			
	K-Fe/AC-W-10	K-Fe/CNF-W-10	K-Fe/GA-W-10	K-Fe/MPC-W-10
100-0	38~54	~264	~154	67~107
200-0	157~187	~214	~150	78~118
300-0	134~151	~230	~132	107~159
400-0	~249	~178	~155	~191
400-30	~262	~128	~217	~186
400-60	~273	~246	~235	~180
400-90	~262	~242	~236	~192
320-0	~284	~194	~120	~190
320-30	~198	~219	~36	~167
320-60	74~132	~124	~23	51~133
320-90	52~135	~80	~56	33~119
320-120	55~135	~82	~52	24~120

Notes: The reduction temperature was raised from room temperature to 400 ^{o}C and reduced for 90 min in H_2 atmosphere, then the reaction gas was switched to reaction and phase changes was in situ detected. In terms of 320-120, 320 represents 320 ^{o}C and 120 stands for 120 min at 320 ^{o}C.

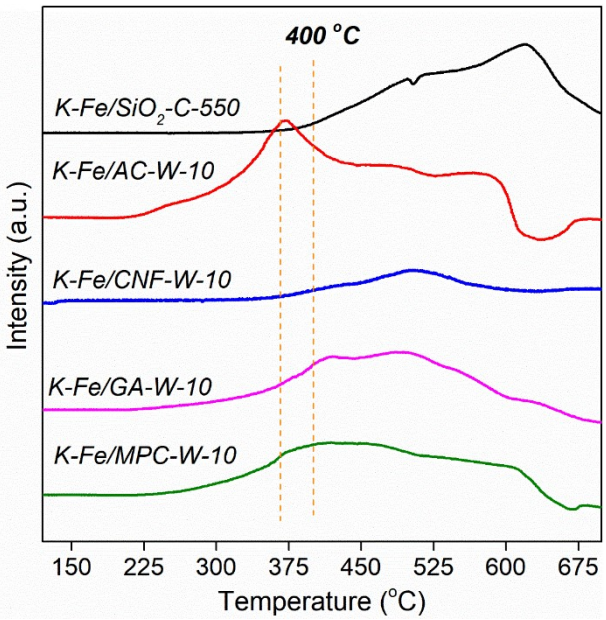

Fig. S11 H_2-TPR profiles of different samples.

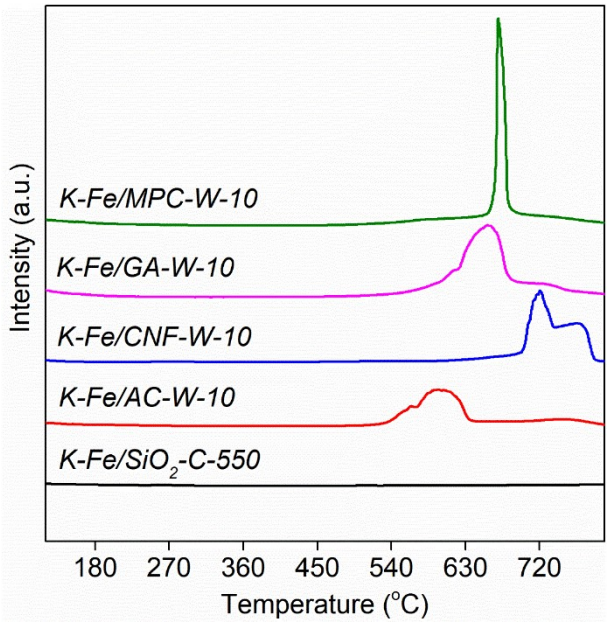

Fig. S12 CO_2-TPD profiles of different samples.

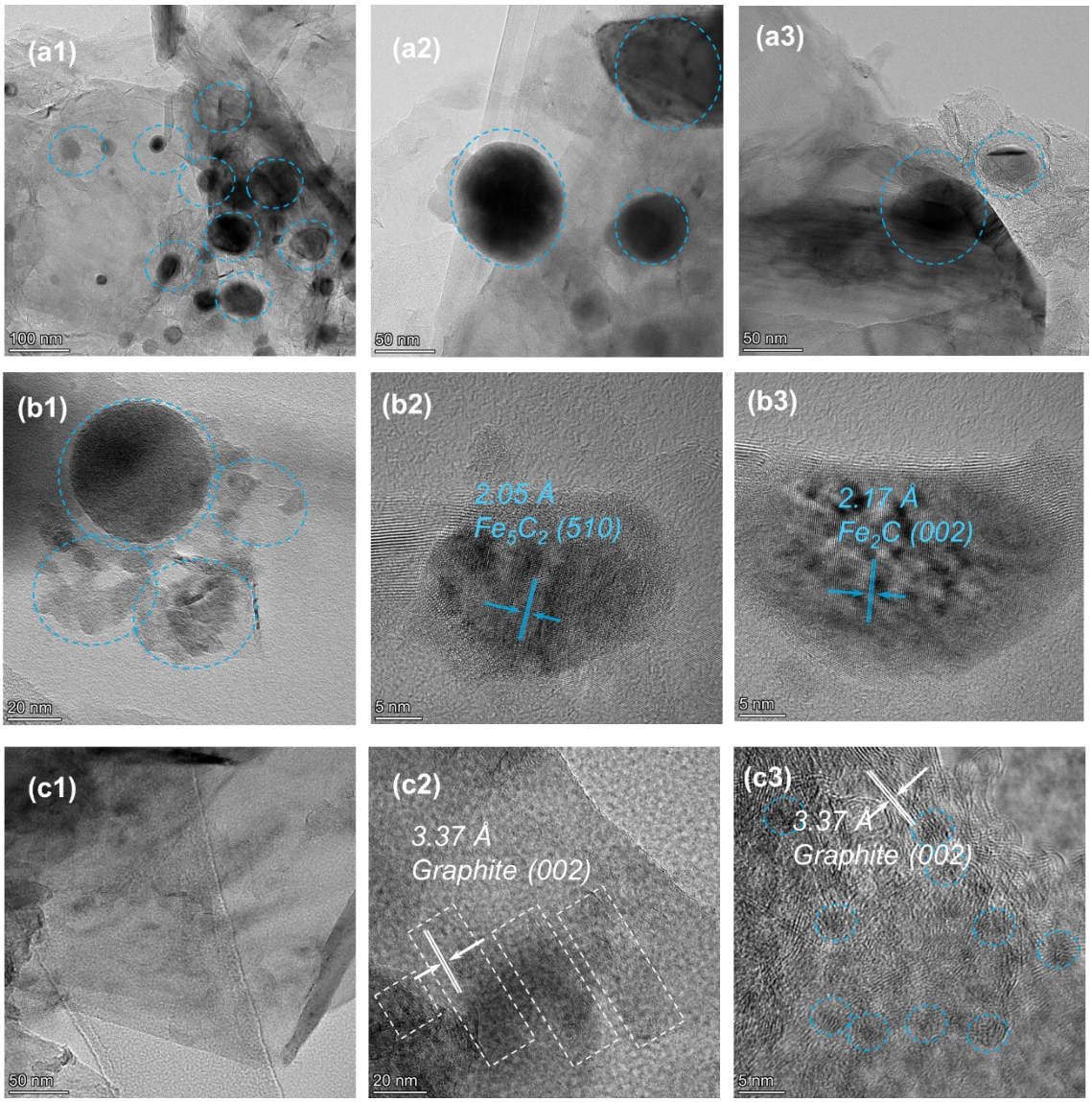

Fig. S13 TEM images of as-prepared K-Fe/GA-W-x samples (x=0, 5, 15).

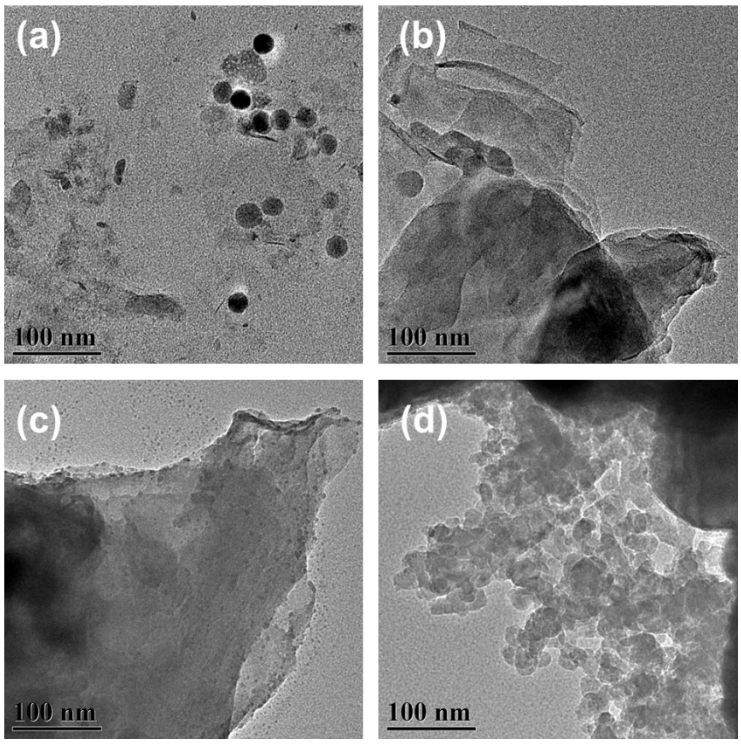

Fig. S14 TEM images of spent catalysts, (a) K-Fe/AC-W-0, (b) K-Fe/GA-W-5, (c) K-Fe/GA-W-10, and (d) K-Fe/GA-W-15 catalyst.

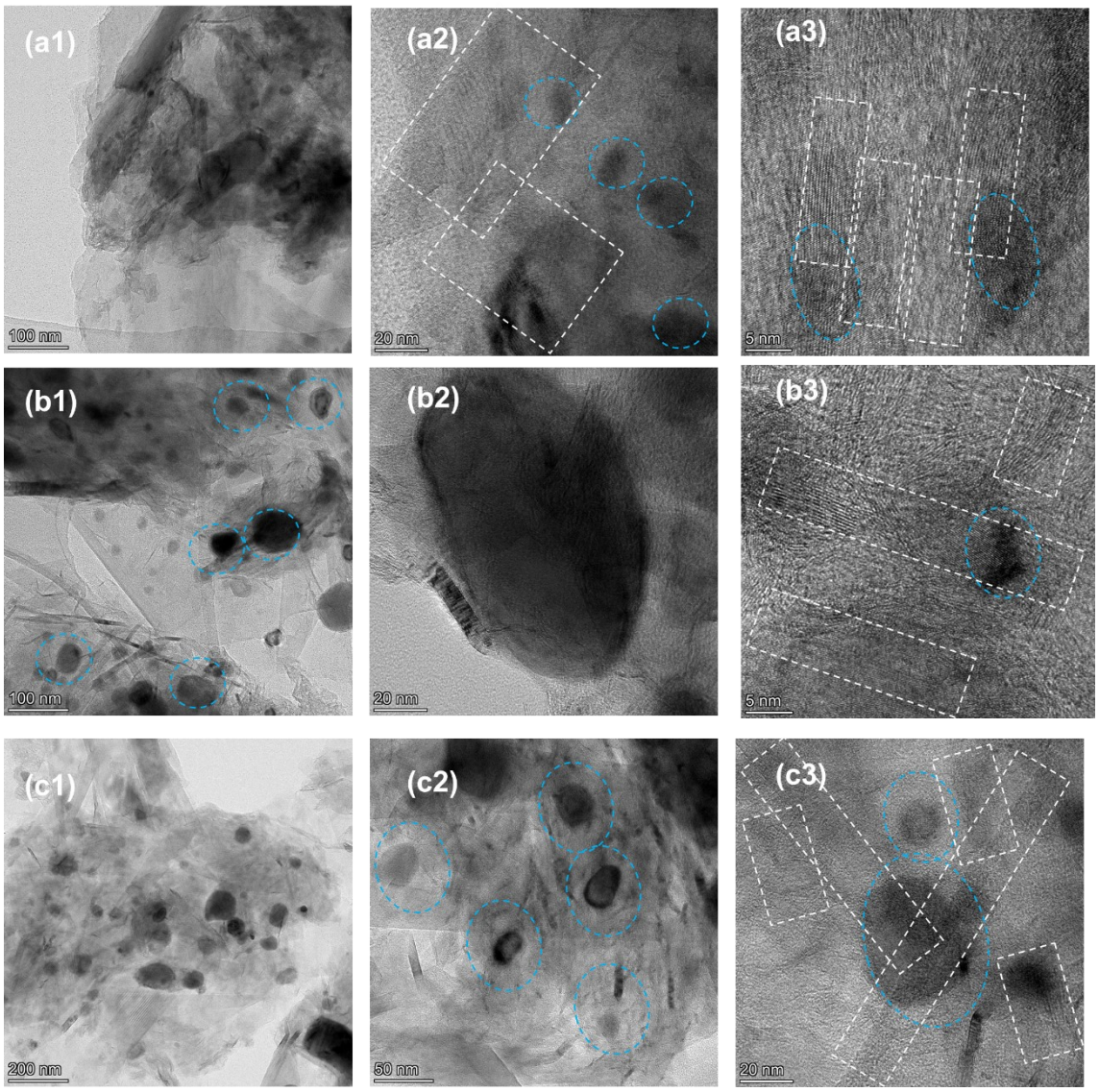

Fig. S15 TEM images of as-prepared K-Fe/GA-C-x samples (x=550, 700, and 850).

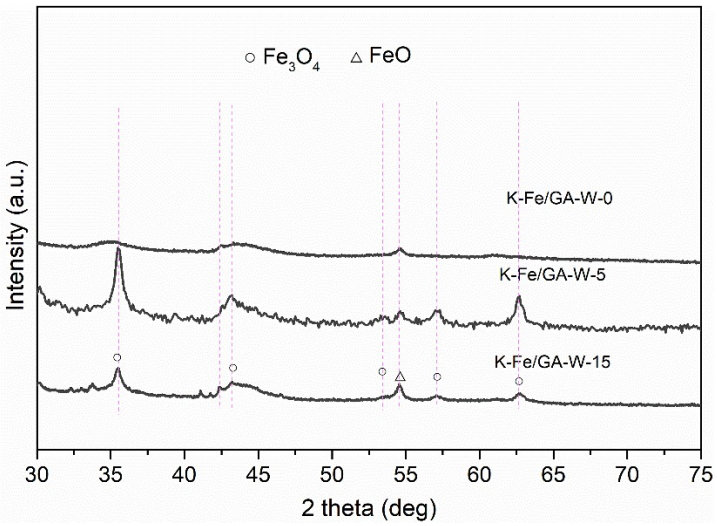

Fig. S16 XRD patterns of as-prepared K-Fe/GA-W-t samples (t=0, 5, and 15).

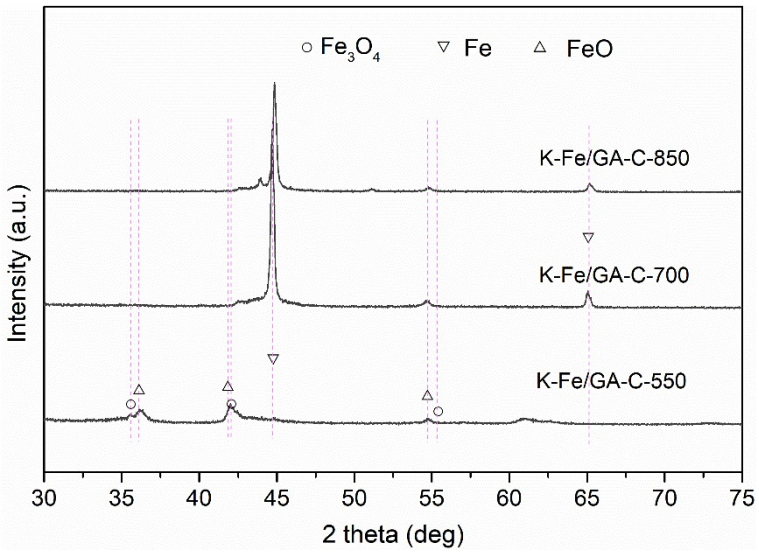

Fig. S17 XRD patterns of as-prepared K-Fe/GA-C-x samples (x=550, 700, and 850).

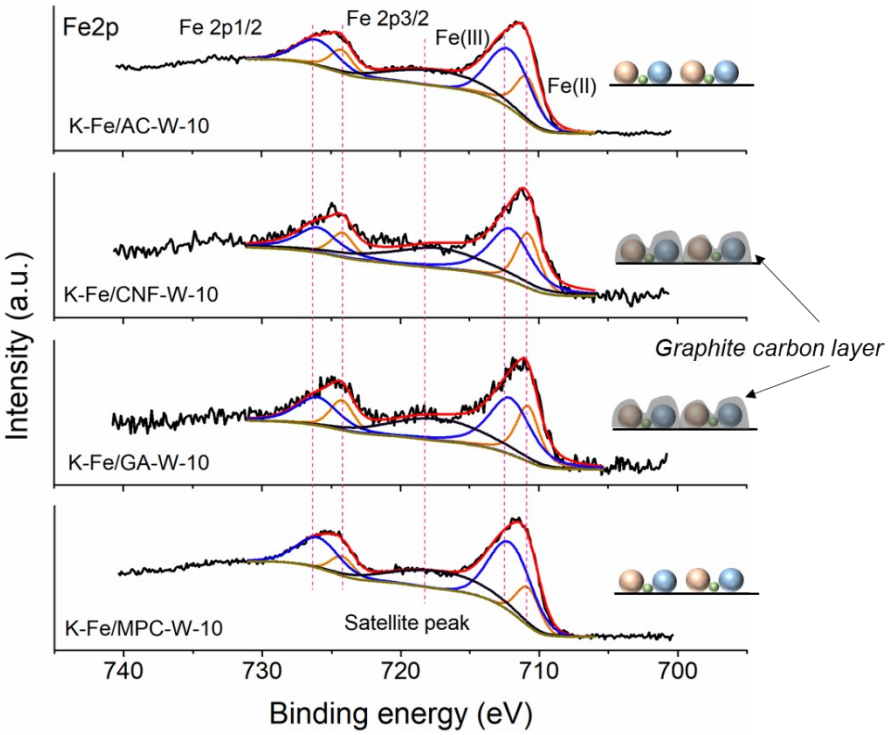

Fig. S18 Fe2p XPS spectra of as-prepared samples.

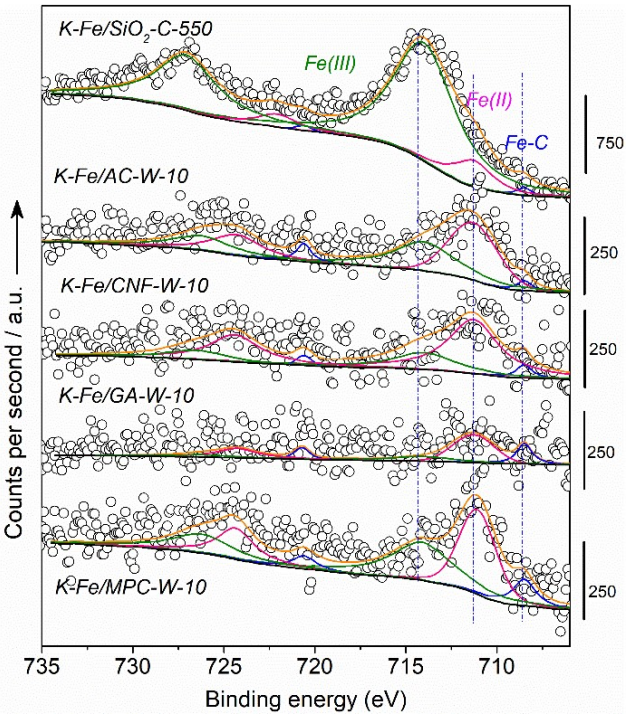

Fig. S19 Fe2p XPS spectra of spent samples.

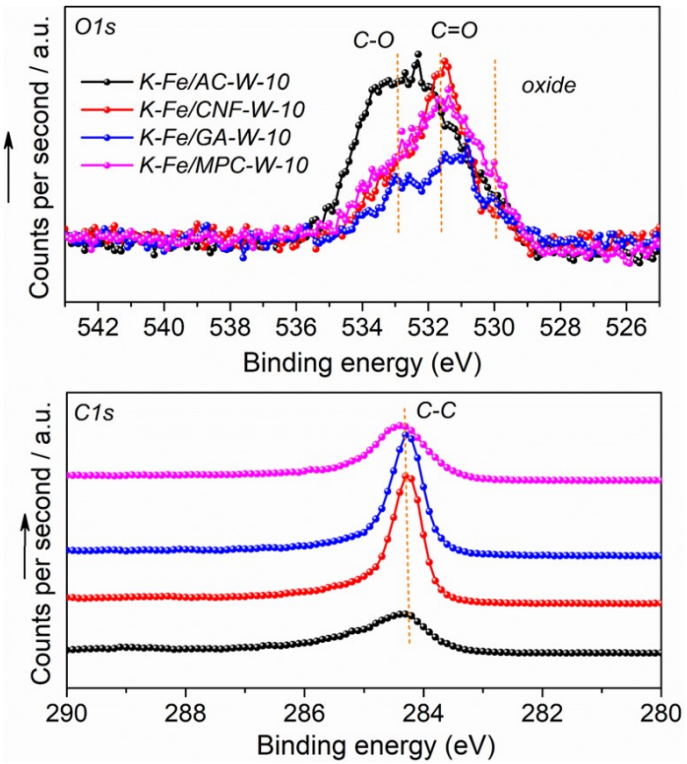

Fig. 20 O1s and C1s XPS spectra of different spent catalysts.

Table S5 Elemental compositions of carbon supported as-prepared catalysts.

Samples	XPS analysis (atom %)			
	K	Fe	O	C
K-Fe/AC-W-10	0.5	3.3	18.4	77.8
K-Fe/CNF-W-10	0.8	0.6	2.3	96.3
K-Fe/GA-W-10	1.1	0.6	7.4	90.9
K-Fe/MPC-W-10	0.6	3.5	21.7	74.2

Table S6 Elemental compositions of carbon supported as-prepared catalysts.

Samples	XPS analysis (atom %)			
	K	Fe	O	C
K-Fe/GA-W-0	0.8	2.8	12.7	83.7
K-Fe/GA-W-5	0.5	3.0	12.1	84.4
K-Fe/GA-W-10	1.1	0.6	7.4	90.9
K-Fe/GA-W-15	1.1	0.5	6.7	91.7

Table S7 Elemental compositions of carbon supported as-prepared catalysts.

Samples	XPS analysis (atom %)			
	K	Fe	O	C
K-Fe/GA-W-0	0.8	2.8	12.7	83.7
K-Fe/GA-C-550	1.1	0.3	5.0	93.6
K-Fe/GA-C-700	1.7	0.2	6.0	92.1
K-Fe/GA-C-850	0.6	0.3	3.8	95.3

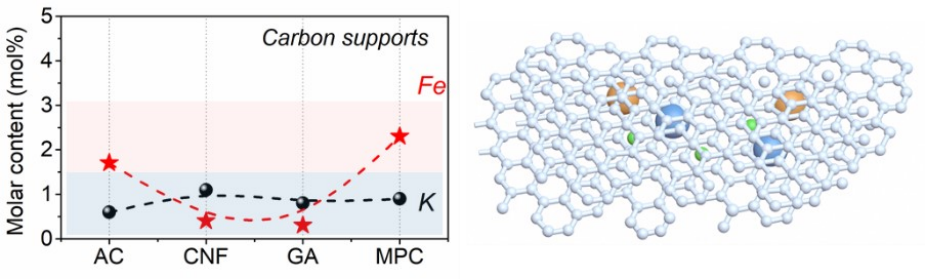

Fig. S21 Surface element compositions of used catalysts.

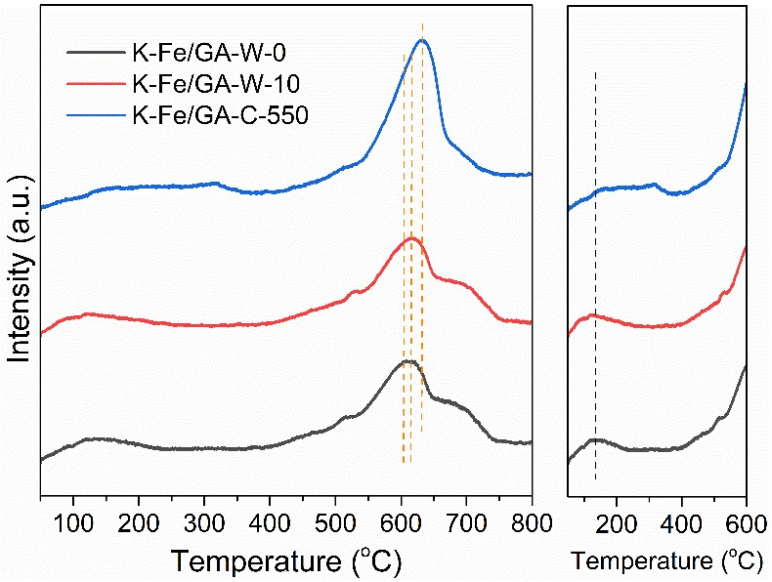

Fig. S22 CO-TPD curves of different as-prepared catalysts.

Table S8 Elemental compositions of spent catalysts.

Samples	XPS analysis (atom %)			
	K	Fe	O	C
K-Fe/AC-W-10	0.7	1.5	18.0	79.8
K-Fe/CNF-W-10	0.6	0.6	5.9	92.9
K-Fe/GA-W-10	0.7	0.2	5.9	93.2
K-Fe/MPC-W-10	0.8	0.7	12.9	85.6

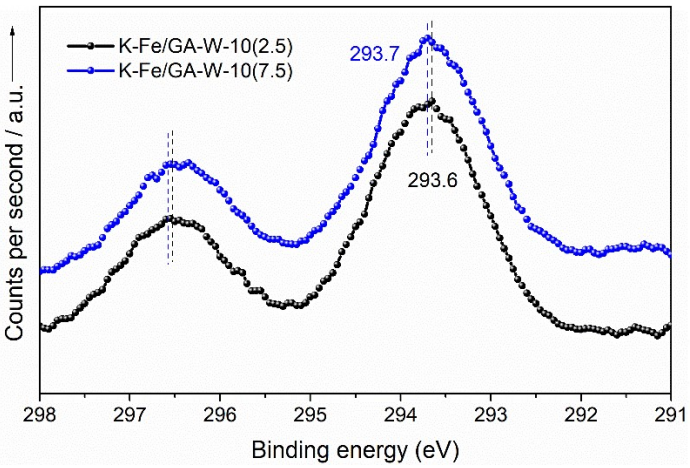

Fig. 23 K2p XPS spectra of used samples.

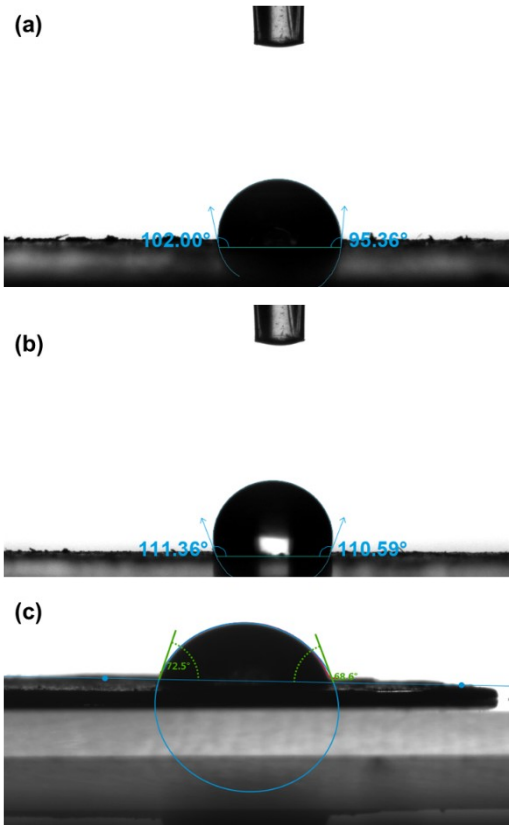

Fig. S24 Water contact angles of (a) as-prepared K-Fe/GA-W-0, (b) as-prepared K-Fe/GA-W-10, and (c) used K-Fe/GA-W-10.

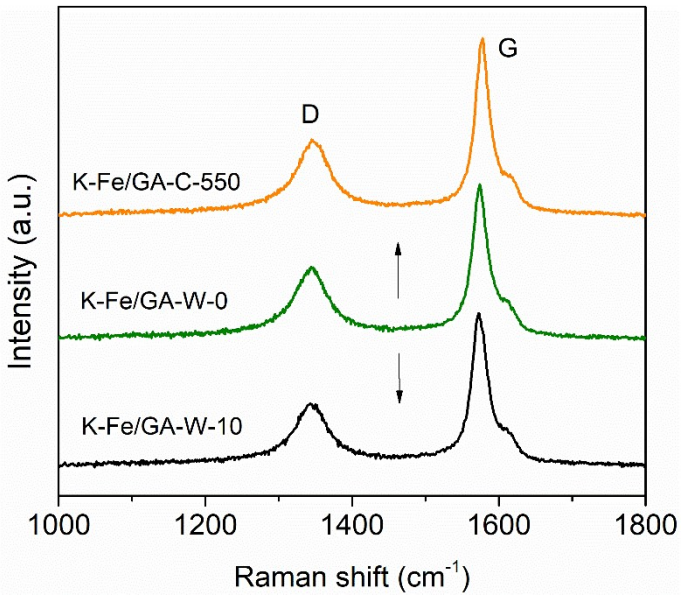

Fig. S25 Raman spectra of different samples.

Table S9 I_D/I_G of different catalysts.

Samples	K-Fe/GA-W-0	K-Fe/GA-C-550	K-Fe/GA-W-10
I_D/I_G	0.83	0.85	0.83

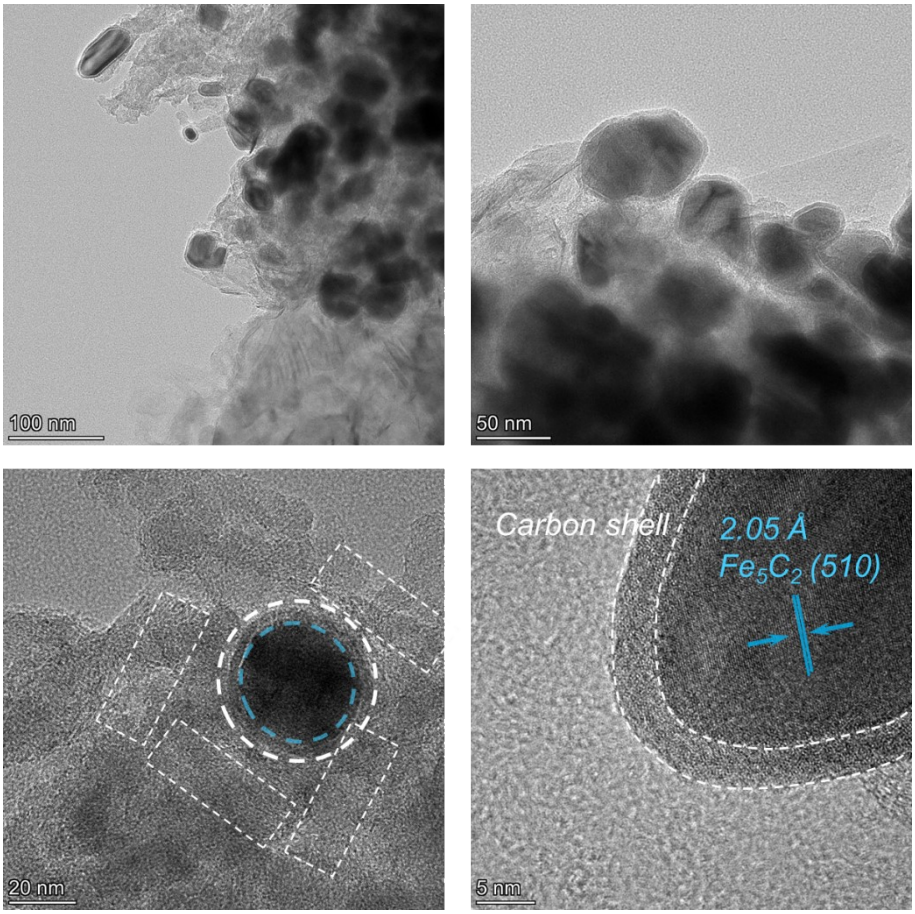

Fig. S26 TEM images of K-Fe/GA-W-10 catalyst after 200h reaction.