Supporting Information

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1. Experimental

1.1 Catalyst Characterization

Boehm titrations were carried out by placing 1 g of an AC sample in 50 mL of each of the following solutions: NaOH, Na₂CO₃ and NaHCO₃.^{1, 2} After being dispersed by sonicating for 20 min, the samples were heated at 373 K for 1.5 h and then filtered. Finally, the filtrates were pipetted into three flasks separately, and the excess base was titrated with HCl. The number of acid sites was determined under the assumption that NaOH neutralizes lactonic, carboxylic and phenolic groups, Na₂CO₃ neutralizes lactonic and carboxylic groups, and NaHCO₃ neutralizes only carboxylic groups. All the values obtained were the averages of three tests.

ICP-OES (Prodigy XP) was conducted to measure the concentration of Fe in the samples. Before the measurements, the samples were digested in an aqueous solution of HCl and HNO₃ assisted by microwave irradiation (CEM-Discover).

1.2 Catalytic Measurements (calculation method for the conversion, selectivity, turnover frequency and the concentrations of all products)

Under an atmosphere of 1-butene and CO_2 , there existed two pathways for BD synthesis over the iron-based catalysts, i.e., a one-step pathway (Eq. 1) and a two-step pathway (Eqs. 2–3).^{3, 4} In this study, the BD formed through both the one-step pathway and two-step pathway was calculated as the contribution of the ODH reaction. While, the BD formed through only Eq. 2 was calculated as the contribution of the dehydrogenation (DH) reaction. The ratio of BD produced through ODH or that

produced through DH was determined using Eqs. 4-5. The ratio_(ODH) calculated was in the 84.8–90.8% range, illustrating that the BD was produced mainly via ODH.

$$CH_2 = CH - CH_2 CH_3 + CO_2 \rightarrow CH_2 = CH - CH = CH_2 + CO + H_2O$$
(1)

$$CH_2 = CH - CH_2 CH_3 \rightarrow CH_2 = CH - CH = CH_2 + H_2$$
(2)

$$H_2 + CO_2 \rightarrow H_2O + CO \tag{3}$$

$$Ratio_{(DH)} = \frac{Moles_{H_2}^{outlet}}{Moles_{BD}^{outlet}} \times 100\%$$
(4)

$$Ratio_{(ODH)} = (1 - Ratio_{(DH)}) \times 100\%$$
(5)

Conversion, selectivity, turnover frequency (TOF) and turnover number (TON, the number of moles of active sites was calculated using the number of moles of Fe) were determined using Eqs. 6-10.

$$Conversion_{(1-butene)} = \frac{Moles_{1-butene}^{inlet} - Moles_{1-butene}^{outlet}}{Moles_{1-butene}^{inlet}} \times 100\%$$
(6)

$$Conversion_{(CO_2)} = \frac{Moles_{CO_2}^{inlet} - Moles_{CO_2}^{outlet}}{Moles_{CO_2}^{inlet}} \times 100\%$$
(7)

$$Selectivity_{(i)} = \frac{Moles \ of \ Component_{(i)}}{Moles_{1-butene}^{inlet} - Moles_{1-butene}^{outlet}} \times 100\%$$
(8)

$$TON = \frac{n_{BD}}{n_{Fe}} \tag{9}$$

$$TOF = \frac{TON}{t} \tag{10}$$

The concentrations of all products and the reactants in the exit gas were measured by GC. When the outlet flow was measured, a neutral calibration gas argon was added since pressure differences in the experiments. In that case one recalculates the concentrations of all hydrocarbon products in the outlet by multiplying by argon (inlet)/argon (outlet). And the product concentrations reported were normalized to 100%.

2. Surface Modification

The changes in the defect density of the AC before and after HNO₃ oxidation were determined using Raman spectroscopy (Figure S7). The peak at approximately 1337 cm⁻¹ (D band) corresponds to the vibrations of carbon atoms with dangling bonds in the disordered graphite structure.^{5, 6} The peak near 1600 cm⁻¹ (G band) is associated with the E_{2g} graphite mode and reflects the structural intensity of sp²-hybridized carbon atoms.^{5, 6} Usually, a higher ratio of the intensity of the D-band to the G-band (I_D/I_G) suggests a higher defect density in the material.⁷ Here, I_D/I_G is denoted as "R". As shown in Figure S1, the change trend of defect density was also consistent with the change in OCG amount, and AC-5M with an R of 1.21 possessed the highest defect density.

sv MFC I Mixer Vaporizer sv Pressure Indicator MFC II P мес ш Tuber Heater SV A Catalyst Reactor Temperature Controller **1-Butene** CO2 N2 Online GC 8-1 (SV) Pressure Reducing Valve Pressure Maintaining Valve Vent

3. Supporting Figures and Tables

Fig. S1. A schematic of the overall experimental configuration.



Fig. S2. Carbon balance for the evaluation experiment of Fe₇C₃@FeO/AC catalyst.



Fig. S3. A long run stability test for Fe₇C₃@FeO/AC catalyst: (a) BD rate, (b) BD

selectivity, (c) 1-butene conversion and (d) CO₂ conversion.



Fig. S4. XRD patterns of the spent Fe₇C₃@FeO/AC catalyst and the AC-5M support.



Fig. S5. TEM image of Fe/AC-1M.



Fig. S6. TEM image of Fe/AC-7M.



Fig. S7. Raman spectra of the AC supports modified by different concentration of HNO₃.

 Table S1. The concentrations (in mol%) of all products and the reactants in the exit

 gas over AC-supported Fe-based catalysts.

Sample	CO ₂	1-Butene	H_{2}	<i>Trans</i> -2- butene	Cis-2-butene	Methane	Ethane	Ethylene	Propylene	Butane
Fe ₇ C ₃ @FeO/AC	83.5	2.1	0.6	1.5	1.2	0.5	0.1	0.3	0.4	0.2
Fe/AC-0M	83.5	2.7	1.0	1.8	1.4	0.6	0.1	0.2	0.4	0.2
Fe/AC-1M	81.4	2.3	0.5	1.8	1.4	0.5	0.1	0.3	0.4	0.2
Fe/AC-3M	83.2	2.2	0.6	1.8	1.3	0.6	0.1	0.3	0.4	0.2
Fe/AC-7M	82.9	2.1	0.6	1.7	1.4	0.5	0.1	0.3	0.4	0.2
Fe/AC-9M	81.4	2.3	0.5	1.8	1.4	0.5	0.1	0.3	0.4	0.2

Loading of Fe (wt%)				
13.4				
12.5				
14.3				
14.7				
16.4				
15.9				

Table S2. The actural loading of Fe in the AC-supported Fe-based catalysts.

Table S3. The repeatability tests for the $Fe_7C_3@FeO/AC$ and Fe/AC-nM (n=0, 1, 3, 7

and	9)	catalysts.
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Sample	1-Butene conversion (%)		CO ₂ conversion (%)		BD selectivity (%)	
	1 ^[b]	2 ^[c]	1 ^[b]	2 ^[c]	1 ^[b]	2 ^[c]
Fe ₇ C ₃ @FeO/AC ^[a]	80	79	7	6	55	53
Fe/AC-0M ^[a]	72	73	6	6	46	44
Fe/AC-1M ^[a]	77	76	7	7	48	47
Fe/AC-3M ^[a]	78	79	6	6	53	52
Fe/AC-7M ^[a]	79	77	6	6	51	51
Fe/AC-9M ^[a]	76	76	7	8	47	46

^[a] Two batches of repeatedly prepared catalysts with the same name. ^[b] The first batch of the repeated catalysts. ^[c] The second batch of the repeated catalysts.

BD rate Sample Conversion (%) Selectivity from 1-butene (%) $(g_{BD}/kg_{cat}/h)$ CO_2 1-Butene BD 2-Butene Butane $C_1 \sim C_3$ AC 0 66 58 13 11 509 18 FeO_X^[a] 0 0 0 0 0 0 0

Table S4. The Performance of AC and FeO_X for the reaction of CO_2 reduction with 1butene.

^[a] Prepared using the coprecipitation method according to the reference.⁸

4. References

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