

## Supporting Information

### Carbon defects promoting syngas into liquid fuels over $\text{Fe}_3\text{C}@C$ catalysts

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## 1. Experimental section

### 1.1. Materials

Ferric nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), Terephthalic acid ( $\text{H}_2\text{BTC}$ ), and N, N-dimethylformamide (DMF) were bought from Aladdin Chemical industry (China). All chemicals were of commercially available analytical grade and used without further purification. The  $\text{H}_2$  (99.999%),  $\text{C}_2\text{H}_4$  (99.999%) and syngas (48.1% $\text{H}_2$ /48.1% $\text{CO}$ /3.8% $\text{Ar}$ ) was supplied by Nanjing Shangyuan Gas Co., Ltd.

### 1.2. MIL-101(Fe) Preparation.

4.04 g  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 1.6613 g  $\text{H}_2\text{BTC}$ , 47 mL DMF were mixed under stirring for 60 min, which were later transferred into a Teflon-lined autoclave at 110 °C for 24 h. After washed 3 times with ethanol, the obtained products were filtered and dried at 120 °C for 12 h, which named as MIL-101(Fe).

### 1.3. Catalyst Preparation

As-prepared MIL-101(Fe) was calcined in a tube furnace at 550 °C for 2 h with a heating rate of 5 °C·min<sup>-1</sup> under  $\text{H}_2$  flow (50 mL·min<sup>-1</sup>). After cooling to room temperature, the catalyst was extracted and stored with anhydrous ethanol, named  $\text{Fe}_3\text{C}@C\text{-H}$ . The same method was used to prepare  $\text{Fe}_3\text{C}@C\text{-C}$  and  $\text{Fe}_3\text{C}@C\text{-S}$  in  $\text{C}_2\text{H}_4$  and syngas, respectively.

### 1.4. Catalyst characterization

Bruker D8 diffractometer was applied to collect X-ray diffraction (XRD) patterns of catalysts at 40 kV and 100 mA. Raman studies employed a Bruker-RFS27. TEM was performed on FEI F200A operating at 300 kV. Auto Chem II 2920 with a thermal conductivity detector (TCD) was utilized to obtain CO-TPD and  $\text{H}_2$ -TPD profiles. The thermally stimulated luminescence (TSL) was measured using a thermoluminescence dosimeter (Beijing Nuclear Instrument Factory, FJ427A1). Thermogravimetric analysis (TGA) was performed with a METTLER TOLEDO TGA/DSC 1 thermogravimetric analyzer from 50 to 900 °C at a heating rate of 5 °C·min<sup>-1</sup> in  $\text{H}_2$ ,  $\text{C}_2\text{H}_4$  and syngas respectively.

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The concentration of surface carbon defects in the catalysts can be estimated by the integrated peak areas in XPS using the following equation:

$$C[C_D]\% = \frac{A_{sp^3 C}}{A_{sp^2 C} + A_{sp^3 C}}$$

$A_{sp^2 C}$ : peak area of  $sp^2 C$ ;  $A_{sp^3 C}$ : peak area of  $sp^3 C$ .

The defect depth calculated with Urbach's approximation<sup>1</sup>:

$$E = \frac{T_m}{500}$$

$T_m$  stands for measured emission band.

## 1.5. FTS test

FTS reactions were carried out in a tubular fixed-bed reactor (inner diameter 7 mm and length 400 mm) with syngas (48.1% $H_2$ /48.1% $CO$ /3.8% $Ar$ ,  $Ar$  as an internal standard), at 20 bar and 300 °C. Typically, 0.2 g of catalyst pellets (20-40 mesh) and 0.6 g of quartz were homogeneously mixed and loaded into the reaction tube. The reactor pressure increased to 20 bar via a backpressure valve, followed by reaction temperature ramped slowly to 300 °C. The gases ( $Ar$ ,  $CO$ ,  $CH_4$ ,  $CO_2$ ) in the effluent of the reactor were monitored by an online GC-5190 gas chromatograph (GC) equipped with a TDX-01 capillary columns and a thermal conductivity detector (TCD). Hydrocarbons were analyzed by an online GC-5190 with a flame ionization detector (FID) detector and an AT·SE-30 capillary column (50 m  $\times$  0.2 mm  $\times$  0.50  $\mu m$ ). The oil products were dissolved in octane and collected using a cold trap (around 0 °C), then analyzed by an offline GC-5190 with a flame ionization detector (FID) detector and an AT·SE-30 capillary column (50 m  $\times$  0.2 mm  $\times$  0.50  $\mu m$ ).

## 1.6. DFT calculations

**Methods.** All density functional theory (DFT) calculations were performed using the Vienna Ab Initio simulation package (VASP).<sup>2, 3</sup> The electron-ion interaction was described with the projector augmented wave (PAW) method.<sup>4, 5</sup> The electron exchange and correlation energies were treated within the generalized gradient approximation in

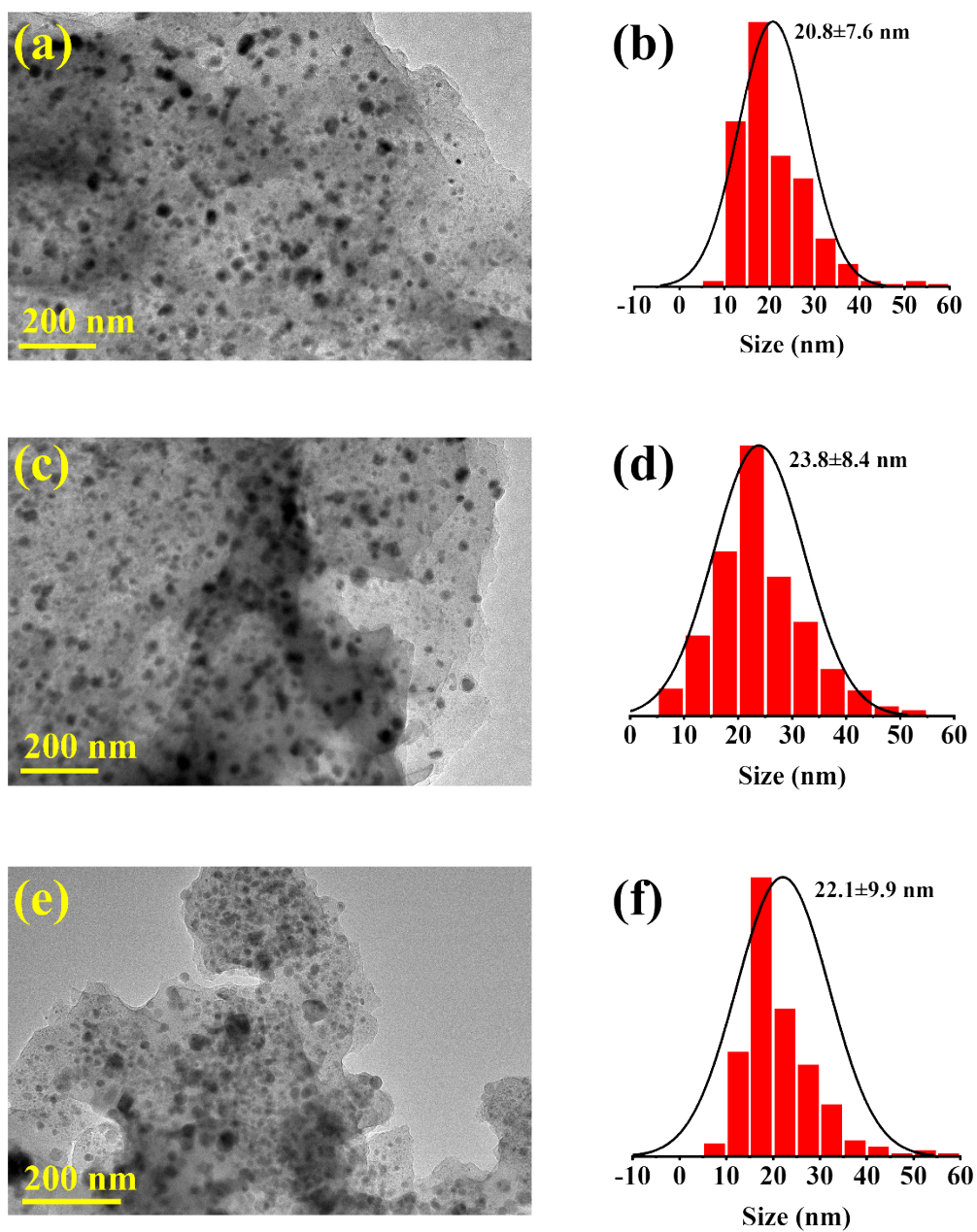
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the Perdew-Burke-Ernzerhof formalism (GGA-PBE).<sup>6</sup> The plane wave basis was set up to 500 eV, and the Monkhorst-Pack k-point sampling was used. The k-point meshes used were determined by the size of the model, and provided in the following section. The convergence criteria for structure optimization and energy calculation were set to accurate quality with the tolerance for SCF and energy of  $1.0 \times 10^{-4}$  eV/atom.

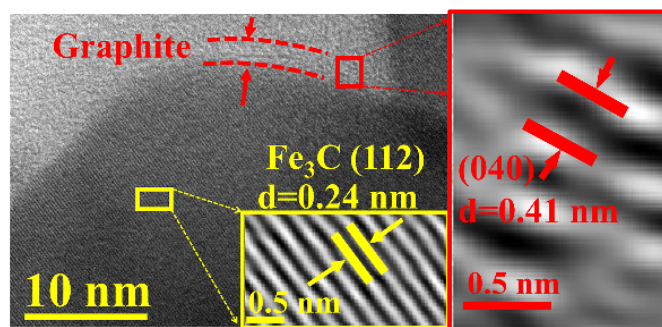
The adsorption energy of CO on graphite-carbon shell an defect was calculated by  $E_{ad} = E_{total} - E_{CO} - E_{plane}$ , where  $E_{total}$ ,  $E_{CO}$  and  $E_{plane}$  are the total energies of the CO adsorbed system, CO, and graphite-carbon shell/defect, respectively.

**Models:** The model of adsorption have been showed at the manuscript. The vacuum region between slabs was around 30 Å to prevent interactions between layers, and Monkhorst Pack meshes of  $3 \times 3 \times 1$  k-point sampling in the Brillouin zone was used.

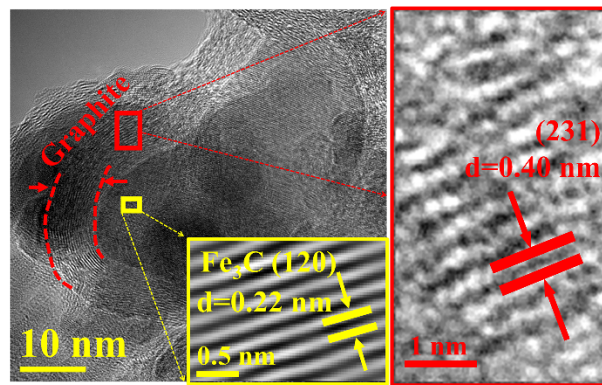
## 2. Catalyst Characterizations



**Fig. S1.** TEM images and particle size distributions of (a, b)  $\text{Fe}_3\text{C}@C\text{-H}$ , (c, d)  $\text{Fe}_3\text{C}@C\text{-C}$  and (e, f)  $\text{Fe}_3\text{C}@C\text{-S}$ .

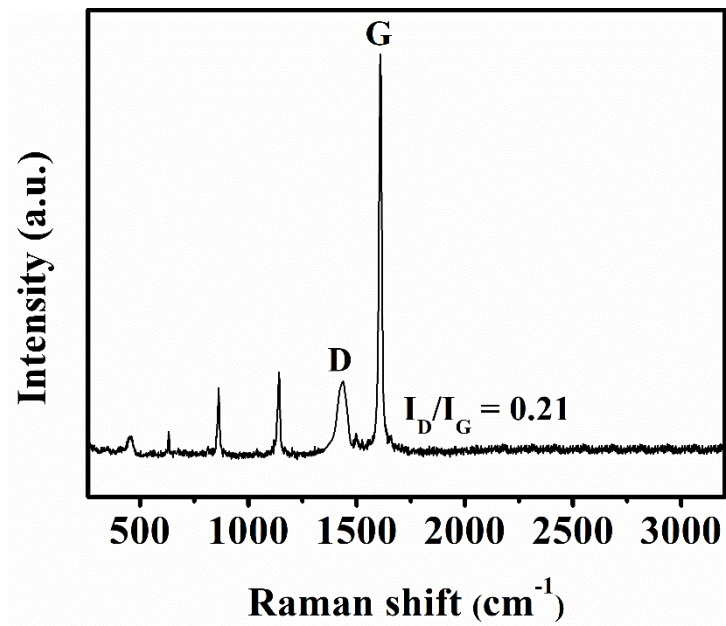


**Fig. S2.** HRTEM images of the Fe<sub>3</sub>C@C-H.



**Fig. S3.** HRTEM images of the Fe<sub>3</sub>C@C-C.





**Fig. S4.** Raman spectra of the MIL-101(Fe).

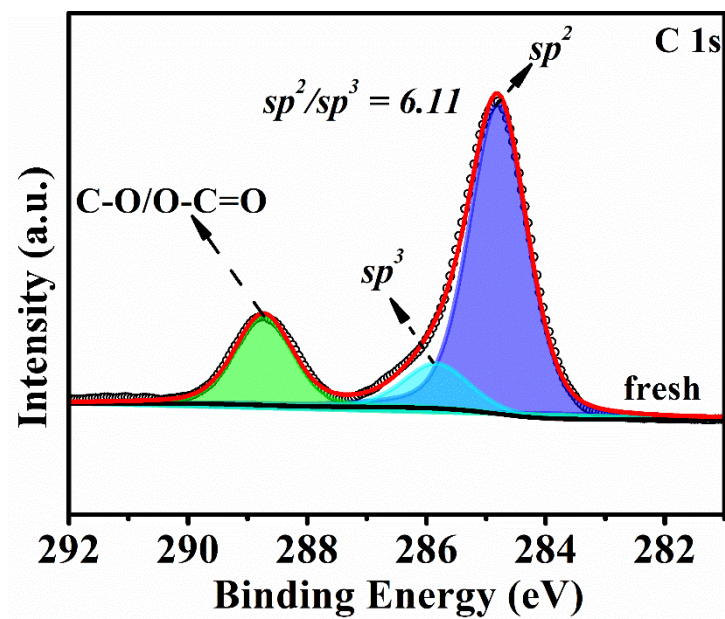


Fig. S5. Raman spectra of the MIL-101(Fe).

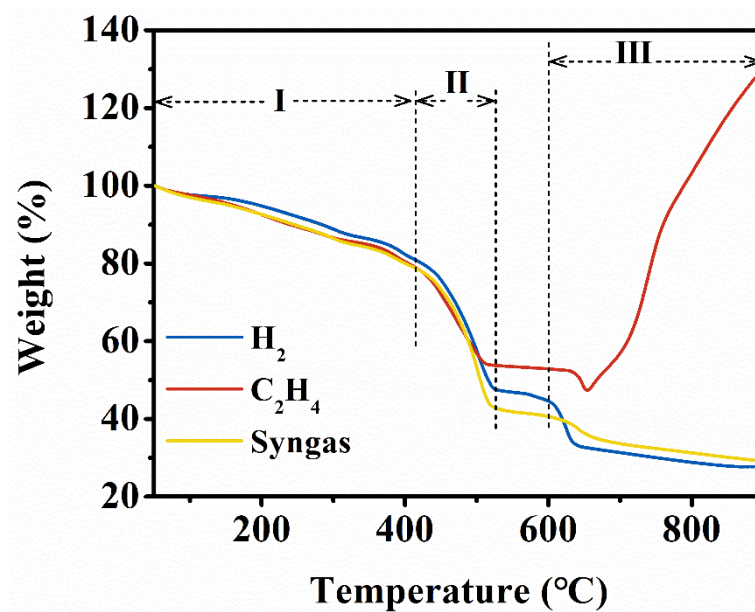


Fig. S6. TGA curves of the MIL-101(Fe) in different gases.

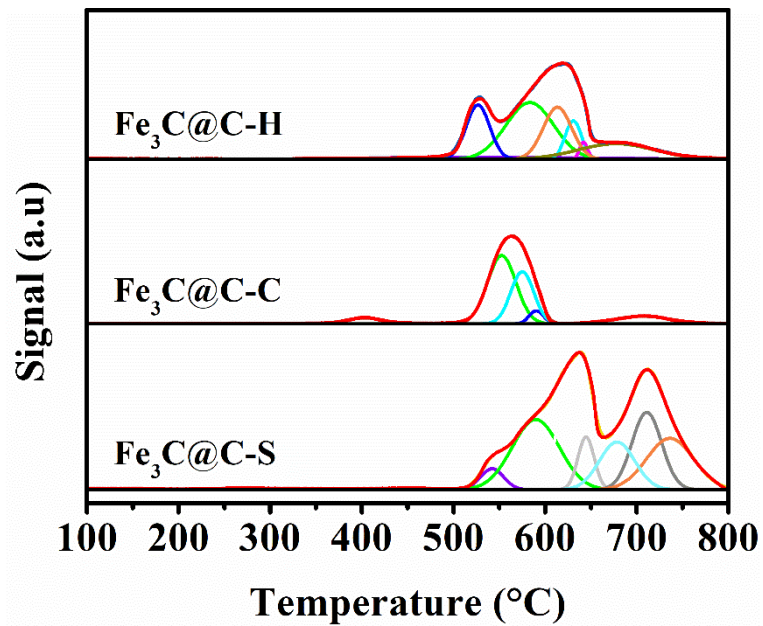
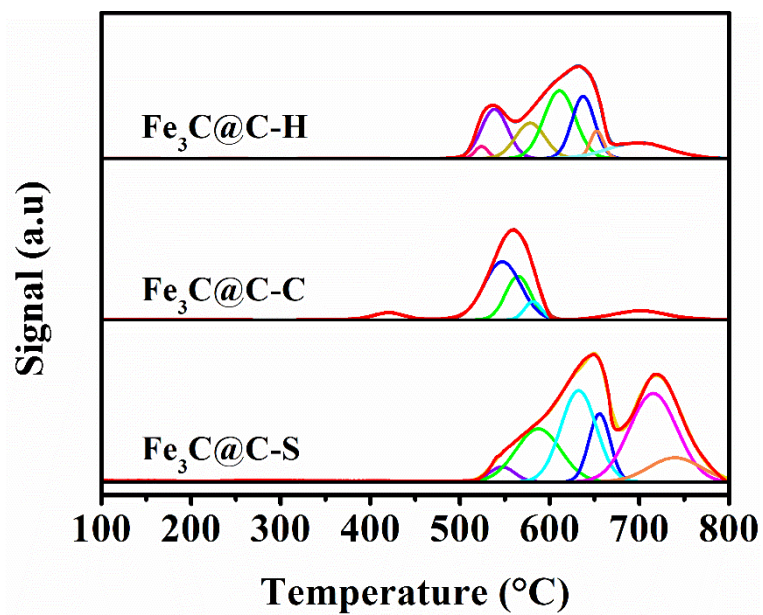
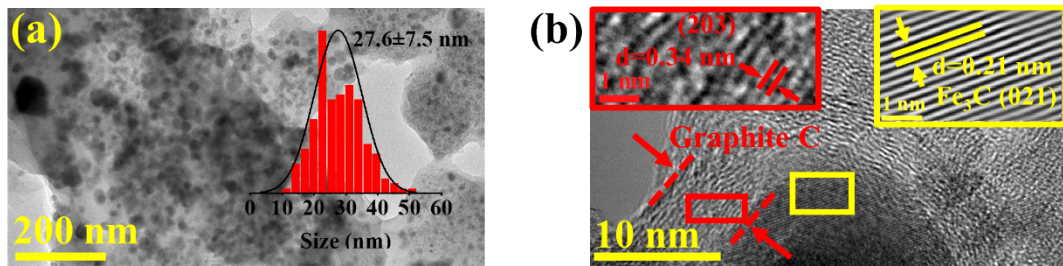


Fig. S7. CO-TPD spectra of the as-prepared catalysts.



**Fig. S8.** H<sub>2</sub>-TPD spectra of the as-prepared catalysts.



**Fig. S9.** (a) TEM image, particle size distribution, and (b) HRTEM of the used

Fe<sub>3</sub>C@C-S.

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**Table S1** Summary of the calculated results.

Entry	$E_{total}$	$E_{CO}$	$E_{plane}$	$E_{ad}$
pristine	-309.872	-14.793	-295.08	0.0017
one-defect	-294.418	-14.793	-278.084	-1.5404
two-defect	-280.186	-14.793	-263.06	-2.3321

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