

## Appendix - Supporting information

### Na modified Fe@C core-shell catalyst for excellent producing gasoline-range hydrocarbons via

#### Fischer-Tropsch synthesis

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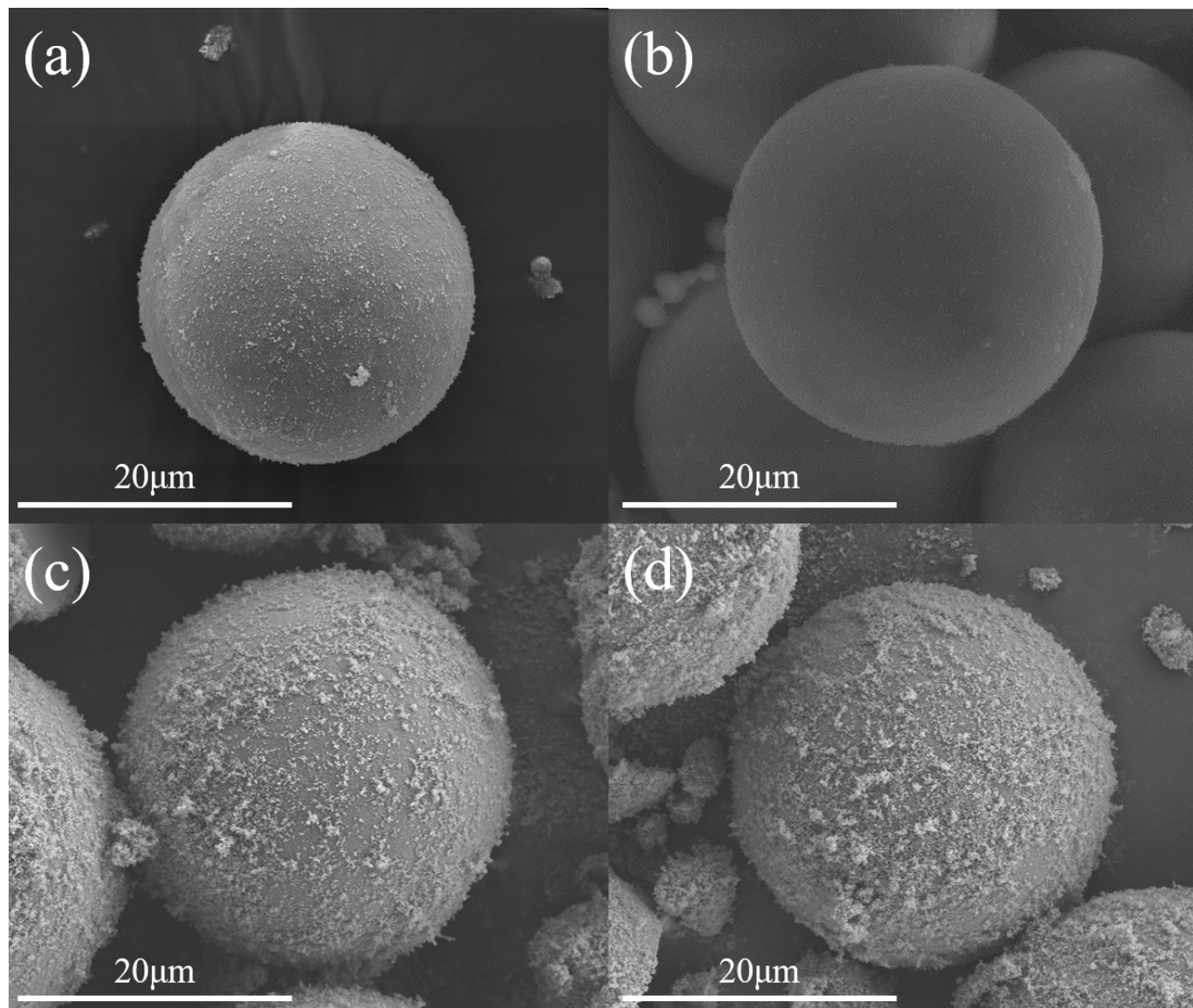
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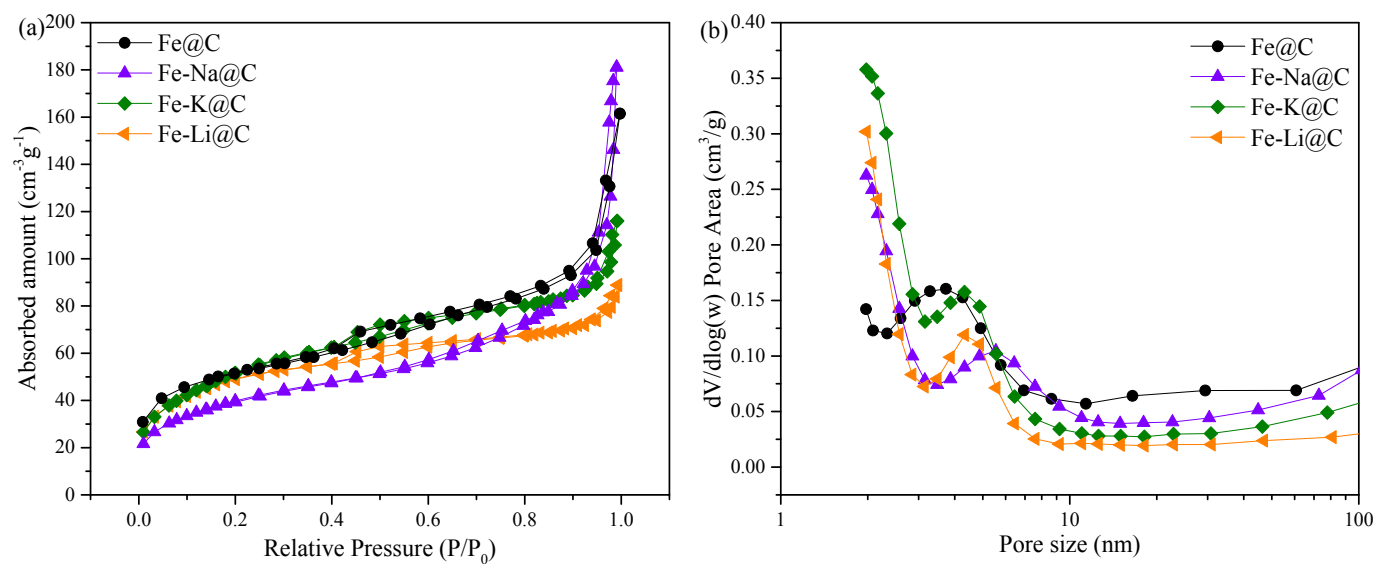
E-mail address: [dingmy@whu.edu.cn](mailto:dingmy@whu.edu.cn) (Mingyue Ding);



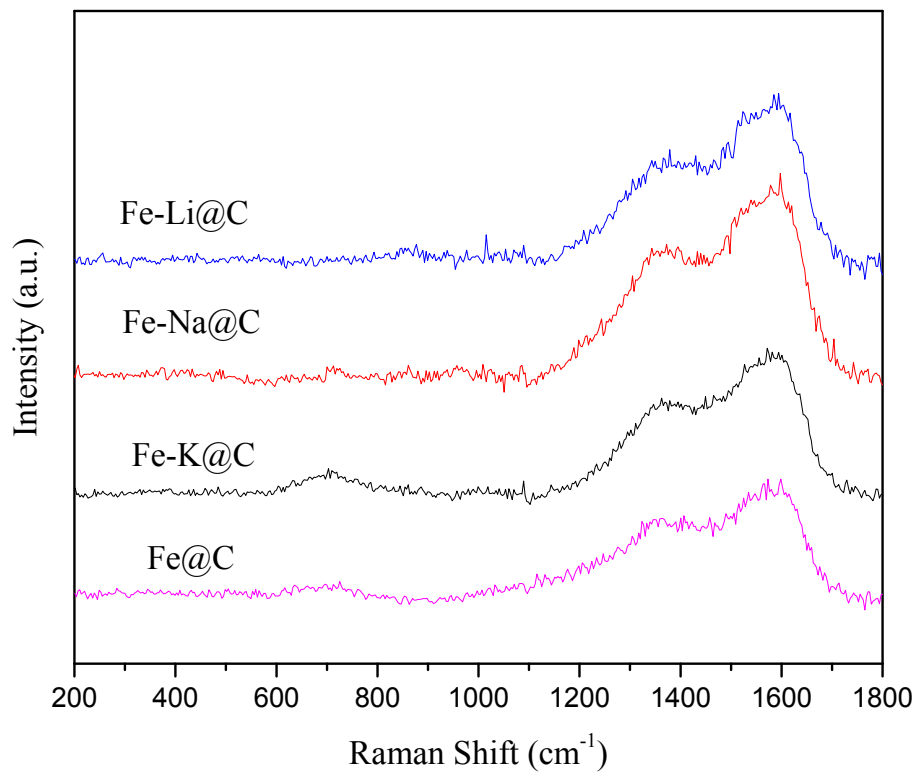
**Figure S1.** SEM image of Fe@C (a), FeNa@C (b), FeK@C (c) and FeLi@C (d) catalysts

**Table S1.** ICP data of the Fe-M@C catalysts

<b>Catalysts</b>	<b>Fe (wt. %)</b>	<b>Na (wt. %)</b>	<b>K (wt. %)</b>	<b>Li (wt. %)</b>
<b>Fe-Na@C</b>	45.89	0.63		
<b>Fe-K@C</b>	52.62		0.47	
<b>Fe-Li@C</b>	49.21			0.59



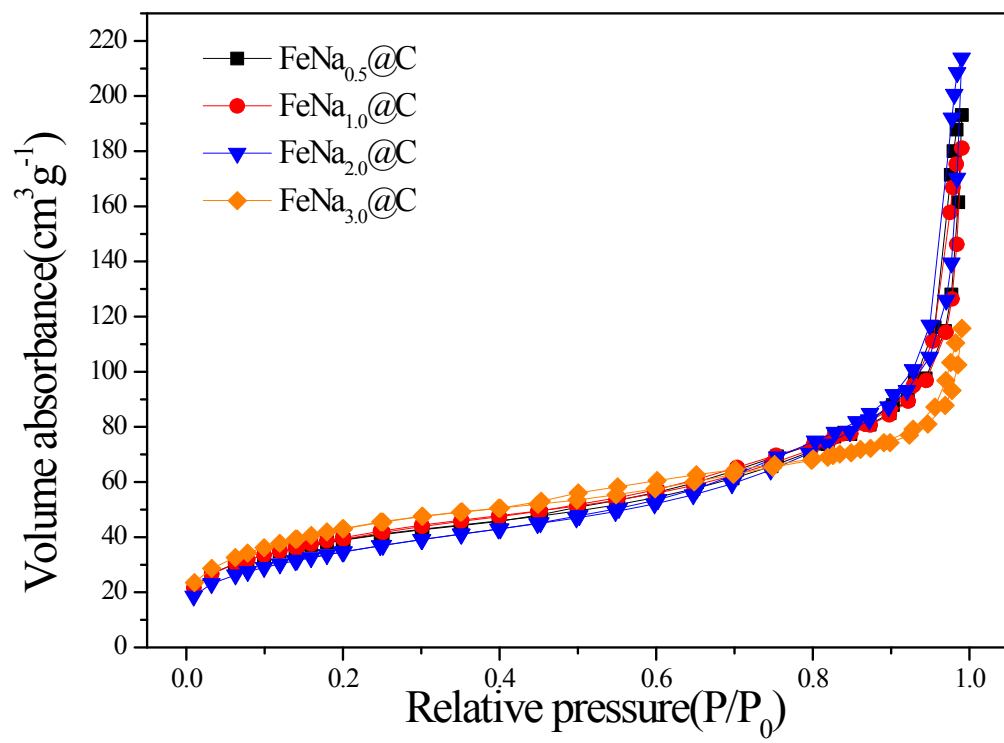
**Figure S2.** N<sub>2</sub> adsorption/desorption isotherms (a) and pore distributions of the catalysts (b).



**Figure S3.** Raman spectra profile of the catalysts.

**Table S2** Catalytic Performance of FeM@C catalysts (20 bar, 340°C, TOS=30h and H<sub>2</sub>/CO =1)

Catalyst	Fe@C	FeNa@C	FeK@C	FeLi@C
CO Conversion (mol %)	70.57	95.58	89.35	80.13
CO converted to CO <sub>2</sub> (mol %)	44.34	45.52	44.33	45.92
FTY( $\mu\text{mol}_{\text{CO}}\text{Fe}^{-1}\text{s}^{-1}$ )	35.16	55.27	53.58	48.25
Hydrocarbon selectivity (mol %, CO <sub>2</sub> -free)				
CH <sub>4</sub>	20.86	17.01	18.24	19.23
C <sub>2-4</sub>	40.10	32.05	34.40	38.20
C <sub>5+</sub>	39.04	50.94	47.36	42.57
C <sub>5-12</sub>	37.72	49.82	46.73	41.92
Olefin/paraffin				
C <sub>2-4</sub>	1.81	1.80	1.99	2.64
C <sub>5-12</sub>	2.35	1.89	2.04	3.14



**Fig. S4** N<sub>2</sub> adsorption/desorption isotherms of the catalysts.

**Table S3.** Textural properties of the catalysts.

<b>Samples</b>	<b>BET surface area (m<sup>2</sup>/g)</b>	<b>Pore volume (cm<sup>3</sup>/g)</b>	<b>Pore size (nm)</b>
<b>FeNa<sub>0.5</sub>@C</b>	139.1	0.28	4.50
<b>FeNa<sub>1.0</sub>@C</b>	143.2	0.27	5.96
<b>FeNa<sub>2.0</sub>@C</b>	126.6	0.33	7.12
<b>FeNa<sub>3.0</sub>@C</b>	155.0	0.16	3.81



**Table S4** Catalytic Performance of FeNa<sub>x</sub>@C catalysts (20 bar, 340°C, TOS=30h and H<sub>2</sub>/CO =1)

<b>Na loading (wt. %)</b>	<b>0</b>	<b>0.5</b>	<b>1.0</b>	<b>2.0</b>	<b>3.0</b>
<b>CO Conversion (mol %)</b>	70.57	90.31	95.58	94.91	92.65
<b>CO converted to CO<sub>2</sub> (mol %)</b>	44.34	47.84	45.52	42.19	45.45
<b>FTY(<math>\mu\text{mol}_{\text{CO}}\text{g}_{\text{Fe}}^{-1}\text{s}^{-1}</math>)</b>	35.16	47.81	55.57	57.40	57.43
<b>Hydrocarbon selectivity (mol %, CO<sub>2</sub>-free)</b>					
<b>CH<sub>4</sub></b>	20.86	18.00	17.01	14.65	17.05
<b>C<sub>2-4</sub></b>	40.10	35.95	32.05	27.87	32.60
<b>C<sub>5</sub><sup>+</sup></b>	39.04	46.05	50.94	57.48	50.35
<b>C<sub>5-12</sub></b>	37.72	45.14	49.82	56.06	49.41
<b>Olefin/paraffin</b>					
<b>C<sub>2-4</sub></b>	1.81	1.96	1.80	1.91	1.88
<b>C<sub>5-12</sub></b>	2.35	1.87	1.89	1.93	1.75

## Experimental Section

### Catalysts preparation

The Fe-M@C catalysts were prepared by a hydrothermal process, where M is the alkali metal. Typically,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and a desired amount of alkali metal promoters (NaCl, KCl, and LiCl) were dissolved in 80 mL ethylene glycol. 6.0 g urea and 0.4 g glucose were added into the solution under vigorous stirring. The solution was vigorously stirred for 30 min to form a clear solution, and then transferred into a 100 mL Teflon-lined stainless-steel autoclave which was heated at 200 °C for 12 h. The black samples were collected by centrifuge method, and then washed three times with deionized water and ethanol. The samples were finally dried overnight at 60 °C. The actual loadings of alkali metal promoters determined by inductively coupled plasma (ICP) were around 1.0 wt.%. In addition, the  $\text{FeNa}_x\text{@C}$  catalyst with different sodium loadings were prepared by the same method mentioned above. The weight percentage of sodium loading was 0.0, 0.5, 1.0, 2.0, and 3.0 wt.%, respectively.

### Catalyst characterization

The loadings of Fe and alkali elements in the prepared catalysts were determined by inductively coupled plasma optical emission spectroscopy (ICPOES; Atom-scan 16 spectrometer (TJA, USA)). The multipoint Brunauer-Emmett-Teller surface area, pore volume, and average pore diameter of the samples were measured by  $\text{N}_2$  physisorption on Micromeritics ASAP 2420 instrument at -196 °C. The samples were degassed under vacuum at 200 °C for 8 h prior to measurement.

The surface morphology of the catalysts was investigated with scanning electron microscopy (SEM) (QUANTA 400) with Energy dispersive X-ray spectroscopy detector (EDX) (GENESIS EDX). Powder X-ray diffraction (XRD) patterns were performed by using PANalytical X'Pert Pro diffractometer with Cu  $K\alpha$  radiation operated at 40 kV and 100 mA. XPS spectra of the catalysts were conducted by Thermo Scientific K-alpha XPS system with Al  $K\alpha$  X-ray source (1486.6 eV). Raman spectra were measured using a single monochromator renishaw system 1000 equipped with a thermoelectrically cooled charge coupled device

(CCD) detector and holographic super-notch filter. Infrared Fourier transform spectroscopy were collected using an infrared spectrometer (Thermo NICOLET 5700 FTIR Spectrometer), in the wavenumber range 4000-400  $\text{cm}^{-1}$  with KBr pellets.  $\text{H}_2$ -TPR experiments were performed using a quartz tube equipped with a thermal conductivity detector (TCD). The samples were pretreated in high purity  $\text{N}_2$  at 350  $^\circ\text{C}$  for 1.5 h to remove water and other contaminants. 5%  $\text{H}_2/\text{N}_2$  used as the carrier gas, was introduced into the system at a flow rate of 30 mL/min. The TCD signal and sample temperature were recorded during the programmed heating process from room temperature to 800  $^\circ\text{C}$  with a heating rate of 10  $^\circ\text{C}/\text{min}$ , and then held at 800  $^\circ\text{C}$  for 30 min.

### **Catalytic evaluation**

The Fischer-Tropsch synthesis performance of as-prepared catalysts were conducted in a fixed-bed reactor. Typically, 0.5 g catalyst diluted with 0.5g quartz powders with the same size (40-60 mesh) were loaded in the reactor. The catalyst was reduced firstly in flowing  $\text{H}_2$  (0.1 MPa and 2000  $\text{h}^{-1}$ ) at 350  $^\circ\text{C}$  for 10 h. The FTS test was performed in syngas ( $\text{H}_2$  (47.5 %)/  $\text{CO}$  (47.5 %)/  $\text{N}_2$  (5%), vol) under the reaction conditions as follows: temperature of 340  $^\circ\text{C}$ , gas hourly space velocity (GHSV) of 6000  $\text{h}^{-1}$ , and pressure of 2.0 MPa.

The FTS products were separated to liquid products and gaseous products by a hot trap (kept at 80  $^\circ\text{C}$ ) and a cold trap (kept at 5  $^\circ\text{C}$ ). Liquid products were detected using FULI GC 97 gas chromatograph equipped with RB-5 capillary column connected to flame ionization detector (FID). Gaseous products were detected online by a gas chromatograph (FULI GC 97) equipped with both thermal conductivity detector (TCD) and FID. Porapak Q and 5A MolSieve packed column were connected to TCD, while RB-PLOT  $\text{Al}_2\text{O}_3$  capillary column was connected to FID. CO conversion and product selectivity were calculated on carbon basis with carbon balances within 90-100 %.