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## **Supporting Information**

## Phase Transformation of Iron oxide to Carbide and Fe<sub>3</sub>C being Active Centers for RWGS Reaction

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Figure S1 SEM image of as-prepared spindle-like Mil-88A.





Figure S2 SEM images of Mil-88A derived spindle-like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.



Figure S3 CO<sub>2</sub> conversion and CO selectivity of as-prepared spindle-like iron oxide in RWGS. Reaction conditions: 600 °C, ambient pressure,  $CO_2/H_2$  (v/v)=1/2, WHSV=300,000 mL/g/h.



Figure S4 XRD patterns of the spent samples after 15h at 400 °C, 500 °C, 550 °C and 600 °C.



Figure S5 XRD patterns of the spent samples after 15h at 600 °C after different pretreatments. Reaction conditions: 0.1 MPa,  $CO_2/H_2$  (v/v)=1/2, WHSV=300,000 mL/g/h.

Catalyst	Reaction	Space volocity	CO <sub>2</sub> Conv.	CO Sel.	Producing CO rate	Ref.
	temp.(°C)	(mL/g/h)	(%)	(%)	(mmol/g/h)	
In-situ formed Fe <sub>3</sub> C	600	300,000	38	ca. 100	1695	Our work
	550	300,000	33	ca. 100	1471	
	500	300,000	28	ca. 100	1249	
Mo <sub>2</sub> C@N-C	600	24,000	58	98	152	1
Fe-Ce-Al	600	30,000	55	99	146	2
NiCu- Saponite	500	15,000	53	89	63	3
MnO	850	200,000	50	100	893	4
$Mo_2C$	550	12,000	60	100	64	-
Cs-Mo <sub>2</sub> C	550	12,000	66	100	70	2
Fe oxide	600	6,000	35	100	47	6
CsFe/Al <sub>2</sub> O <sub>3</sub>	600	12,000	63	98	66	7
BaZrYZn	600	2,400	37.5	97	19	8
Co-CeO <sub>2</sub>	600	600,000	35	98.5	4617	9
Ru/CeO <sub>2</sub>	600	120,000	38	ca. 100	1017	10
$\beta$ -Mo <sub>2</sub> C	600	300,000	42.5	99	1878	11

Table S1 Comparison of catalytic performance for the in-situ formed Fe<sub>3</sub>C and Literature Reported Catalysts

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