Supplementary Information

Mn decorated Na/Fe catalysts for CO_2 hydrogenation to light olefins

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Table S1 Catalytic performance of 5Mn-Na/Fe catalyst for CO_2 hydrogenation at different reaction pressure.

P(MPa)	X-CO_2	S-CO	S-CH_4	S-$C_2^{=}$-$C_4^{=}$	S-C_2^{0}-C_4^{0}	S-C_{5+}	O/P
3	38.6	11.7	11.8	30.2	4.0	42.1	7.5
2	34.5	17.1	9.9	29.5	3.0	40.0	9.8
1	32.0	22.5	6.8	27.2	2.3	40.7	12.1
0.5	28.8	32.2	6.4	25.6	2.2	33.0	11.7
0.1	23.4	70.7	4.4	13.0	1.2	9.3	11.3

Reaction conditions: $H_2/CO_2 = 3$; 320 ^{o}C; 2040 mL h^{-1} g_{cat}^{-1}; TOS = 10 h. O/P: The ratio of olefin to paraffin in the C_2–C_4 range hydrocarbons.

Table S2 Catalytic performance of $1Na/Fe_5C_2$ catalyst for CO_2 hydrogenation.

catalyst	X-CO_2	S-CO	S-CH_4	S-$C_2^=$-$C_4^=$	S-C_2^0-C_4^0	S-C_{5+}	O/P[a]
$1Na/Fe_5C_2$	34.7	11.9	8.3	24.7	2.5	52.1	9.8

[a] The ratio of olefin to paraffin in the C_2–C_4 range hydrocarbons. The catalyst was without H_2 pre-reduction and direct applied in CO_2 hydrogenation. Reaction conditions: $H_2/CO_2 = 3$; 320 °C; 3.0 MPa; 2040 mL h^{-1} g_{cat}^{-1}.

Table S3 Mössbauer parameters of the fresh and used $1Na/Fe_5C_2$ catalysts.

Catalyst	Assignment	IS (mm s^{-1})	QS (mm s^{-1})	Line Width	Hhf (kOe)	Relative Abundance (%)
Fresh $1Na/Fe_5C_2$	Fe_5C_2(I)	0.16	0.14	0.48	177	37.8
	Fe_5C_2(II)	0.22	0.09	0.48	215	46.5
	Fe_5C_2(III)	0.15	0.14	0.39	110	15.6
Used $1Na/Fe_5C_2$	Fe_3O_4(A)	0.3	0	0.29	493	26.8
	Fe_3O_4(B)	0.66	0	0.35	461	50.0
	Fe_5C_2(I)	0.22	0.09	0.22	183	9.2
	Fe_5C_2(II)	0.15	0.14	0.58	214	9.3
	Fe_5C_2(III)	0.14	0.11	0.58	107	4.7

Reaction conditions: $H_2/CO_2 = 3$; 320 °C; 3.0 MPa; 2040 mL h^{-1} g_{cat}^{-1}; TOS = 10 h.

Table S4 Catalytic performance of 1Na/Fe and 5Mn-Na/Fe catalyst for C_2H_4 hydrogenation

Catalyst	X C_2H_4	Y CH_4	Y C_2H_6	Y C_3H_6	Y C_3H_8
1Na/Fe	17.6	1.3	15.1	1.1	0.1
5Mn-Na/Fe	17.4	0.5	15.8	1.1	0.1

Reaction conditions: 320 ^{o}C; $H_2/C_2H_4 = 5$; 0.1 MPa; 3600 mL h^{-1} g_{cat}^{-1}; X C_2H_4 is the conversion of C_2H_4; Y is the yield of product.

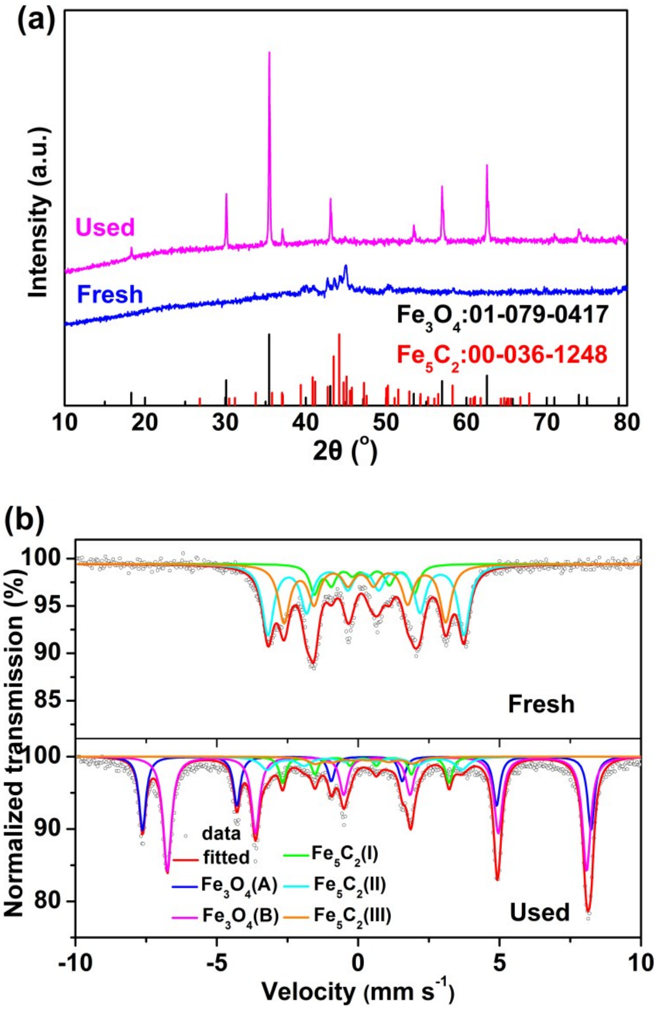

Fig. S1 XRD patterns (a) and Mössbauer spectra (b) of the fresh and used 1Na/Fe_5C_2 catalysts.

The 1Na/Fe_5C_2 catalyst was synthesized by carbonizing the iron oxide in CO/N_2 atmosphere as reported (J. Mater. Sci. 1990, 25, 4457-4461). XRD patterns (Fig. S1a) show the formation of Fe_5C_2 species (PDF: 00-36-1248), confirmed by the Mössbauer spectra (Fig. S1b and Table S3). Table S2 shows the catalytic performance of 1Na/Fe_5C_2 catalyst. The CO_2 conversion and $C_2^{=}$-$C_4^{=}$ selectivity of 1Na/Fe_5C_2 catalyst was basically equal to 1Na/Fe catalyst, confirming the role of Fe_5C_2. Mössbauer spectroscopy characterization of the used Fe_5C_2 catalyst indicated the Fe_3O_4 and Fe_5C_2 contents were 76.8% and 23.2%, respectively (Table S3). The majority of Fe_5C_2 species were converted to Fe_3O_4 under the CO_2 hydrogenation reaction conditions, possibly due to the oxidizing atmosphere of CO_2 and H_2O. Besides, this result also indicates that both the Fe_3O_4 and Fe_5C_2 species are important for CO_2 hydrogenation to olefins. Fe_3O_4 acted as active species for CO_2 converting to CO and Fe_5C_2 species are active for hydrocarbon formation from C-C coupling reaction. Therefore, it can be inferred that Fe_5C_2 species plays a critical role in the formation of olefins in CO_2 hydrogenation.