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Supplementary Information

New insights into the effect of sodium on Fe_3O_4-based nanocatalysts for CO_2 hydrogenation to light olefins

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Catalyst Preparation

The sodium-free Fe_3O_4 nanocatalyst was synthesized by a one-pot synthesis method. In a typical synthesis, 31.62 g of $FeCl_3 \cdot 6H_2O$ and 12.54 g of $FeCl_2 \cdot 4H_2O$ were dissolved in 150 ml deionized water containing 5.1 ml of 12.1 mol/l HCl. Next, 5 wt.% of $NH_3 \cdot H_2O$ was added dropwise into the above solution under stirring at 60 ^oC until the pH of the final solution was maintained at ~9. After continuously stirring for 1 h, the black-brown product was separated by a magnet, washed completely with deionized water, dried overnight at 60 ^oC and hereafter denoted as Fe_3O_4. The sodium promoter was added in a calculated amount to the Fe_3O_4 precursor by impregnation with aqueous solution of $NaNO_3$ to give the desired Na/Fe weight ratios of 1.2/100. This catalyst is denoted as Na/Fe_3O_4.

Finally, the catalyst samples were calcined in air at 400 ^oC for 3 h, pressed into pellets (30 MPa), crushed and sieved to 20-40 meshes for characterization and activity test.

Table S1 Reaction performance of Fe_3O_4-based catalysts for CO_2 hydrogenation. [a]

Catalyst	CO_2 conv. (%)	CO sel. (%)	Hydrocarbon distribution (wt.%)				O/P [b]	Yield (%)	
			CH_4	$C_2^=$–$C_4^=$	C_2^0–C_4^0	C_{5+}		$C_2^=$–$C_4^=$	C_{5+}
Fe_3O_4	29.3	16.6	60.3	0.1	36.4	3.1	0.0	0.0	1.2
Na/Fe_3O_4	39.5	14.8	15.7	45.8	8.1	30.3	5.6	14.8	9.8
FeNa(1.18)	40.5	13.5	15.8	46.6	7.5	30.1	6.2	15.7	10.1

[a] Reaction conditions: H_2/CO_2 = 3.0, 320 °C, 3.0 MPa, 2000 ml/(h·g_{cat}), TOS = 60 h. [b] The ratio of olefin to paraffin in the C_2–C_4 range hydrocarbons.

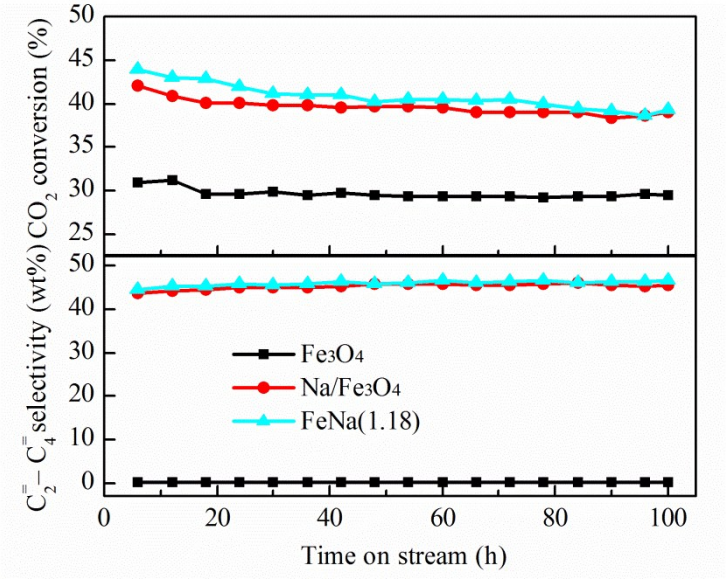

Fig. S1 CO_2 conversion and $C_2^=$–$C_4^=$ selectivity of Fe_3O_4-based catalysts as a function of time on stream. Reaction conditions: H_2/CO_2 = 3.0, 320 °C, 3.0 MPa, 2000 ml/(h·g_{cat}).

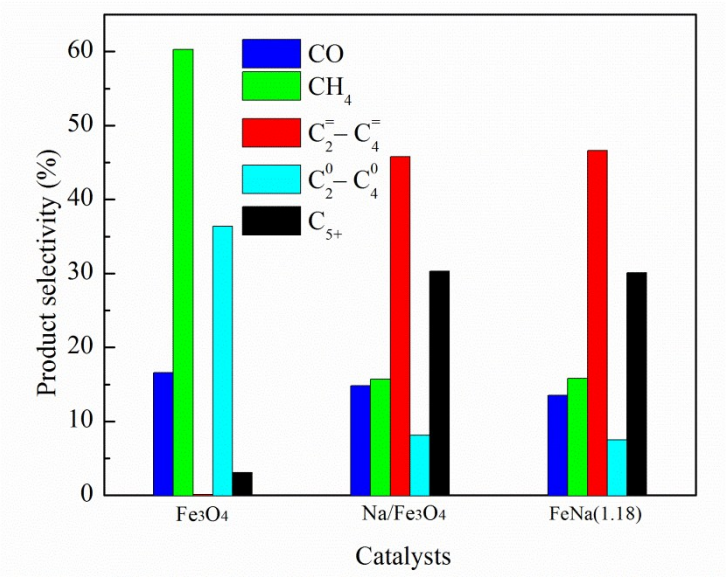

Fig. S2 CO and hydrocarbon selectivity for Fe_3O_4-based catalysts. Reaction conditions: H_2/CO_2 = 3.0, 320 °C, 3.0 MPa, 2000 ml/(h·g_{cat}), TOS = 60 h.