SUPPORTING INFORMATION

Selective olefin production on silica based iron catalysts in Fischer-Tropsch synthesis

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Table S1. Catalytic performance of 5Fe-SiO_2 catalyst reduced at 550 °C for 4 h in the FTS reaction.[a]

Catalyst	CO conversion (%)	CO_2 selectivity (%)	Hydrocarbon distribution (%)				Oxygenate selectivity (%)	α [b]	O/(O+P) [c] (%)	FTY [d] (10^{-5} mol_{CO} g_{Fe}^{-1} s^{-1})
			CH_4	$C_2^=$-$C_4^=$	C_2^0-C_4^0	C5+				
5Fe/SiO_2	9.4	28.9	68.0	17.5	9.7	4.8	4.9	0.4	64.3	0.96

[a] Reaction conditions: feedstock composition = 64% H_2, 24% CO, 8% CO_2 and 4% Ar; WHSV = 1800 mL g_{cat}^{-1} h^{-1}; P_{total} = 2.0 MPa, T = 340 °C. The data were obtained at 50 h.

[b] Chain growth probability (α) was calculated by obtaining a slope based on the Anderson-Schultz-Flory model.

[c] O/(O + P) was calculated as a percentage by dividing the amount of C2-C4 olefins produced by that of all C2-C4 hydrocarbons (olefin + paraffin).

[d] The iron time yield (FTY) was calculated as the moles of CO converted to products divided by moles of surface iron oxides on the SiO_2 surface per second.

	Si-O (Å)	O-O (Å)	Si-Si (Å)	O-Si-O (Å)	Si-O-Si (Å)
This work	1.645	2.631	3.031	106.000	133.900
Ref.[1]	1.650	2.650	3.020	107.120	132.850

Table S2. Angles and bond lengths between Si and O in the cluster ring.

Table S3. Binding energies of surface adsorbates.

Surface species	Binding energy (eV) [a]	
	χ-Fe_5C_2(001)	SiO_2/χ-Fe_5C_2(001)
H*	-3.08	-3.24
C*	-7.70	-7.75
O*	-6.50	-6.81
CO*	-2.63	-2.89
C_2H_4*	-1.21	-1.42
C_2H_5*	-2.00	-2.20
C_2H_6*	-0.26	-0.55

[a] The binding energies of individual surface adsorbates were defined with respect to their gas-phase energies using the following equation: $BE = E_{tot} - E_{slab} - E_{gas}$, where BE is the binding energy of the adsorbate, E_{tot} the total DFT energy of the adsorbed species and the slab, E_{slab} the total DFT energy of the clean slab, and E_{gas} the total energy of the adsorbate in the gas phase.

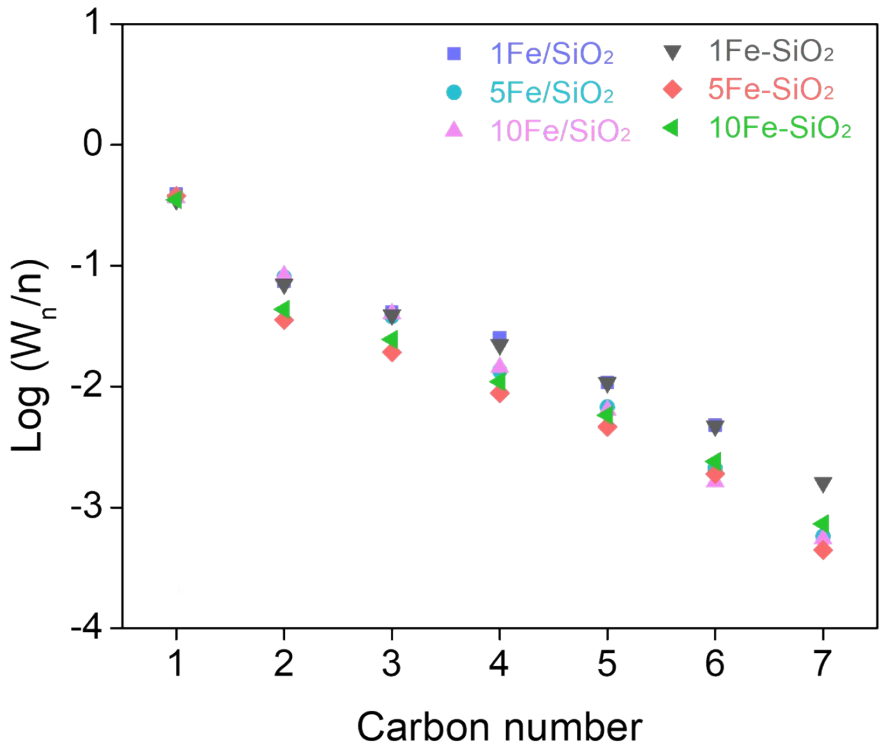

Figure S1. Hydrocarbon molecular weight distributions of Fe/SiO_2 and $Fe\text{-}SiO_2$ catalysts. (Reaction conditions: H_2:CO:CO_2:Ar = 64:24:8:4. WHSV = 1800 mL g_{cat}^{-1} h^{-1}, P_{total} = 2.0 MPa, and T = 340 °C.)

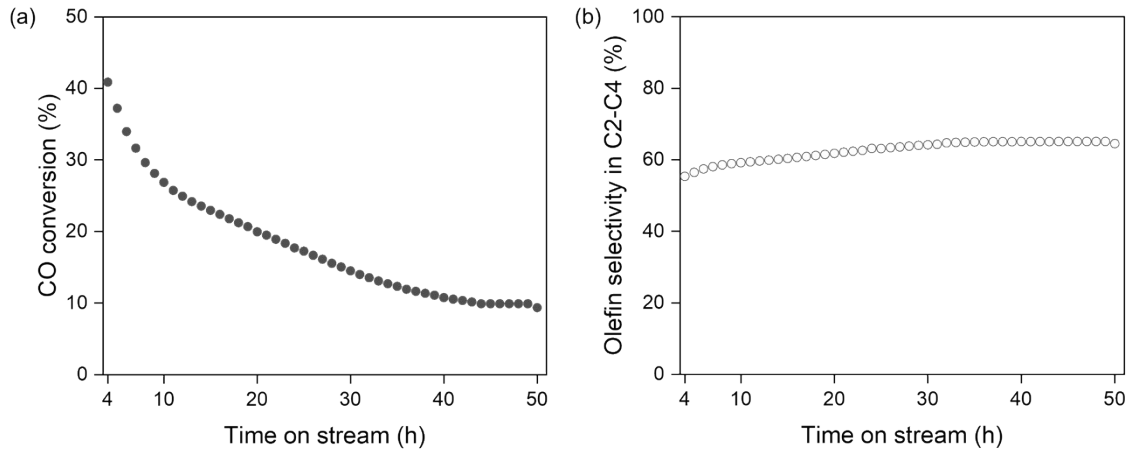

Figure S2. The catalytic performance of the 5Fe-SiO_2 catalyst reduced at 550 °C for 4 h. (a) CO conversion and (b) olefin selectivity at C2-C4. (Reaction conditions: H_2:CO:CO_2:Ar = 64:24:8:4. WHSV = 1800 mL g_{cat}^{-1} h^{-1}, P_{total} = 2.0 MPa, and T = 340 °C.)

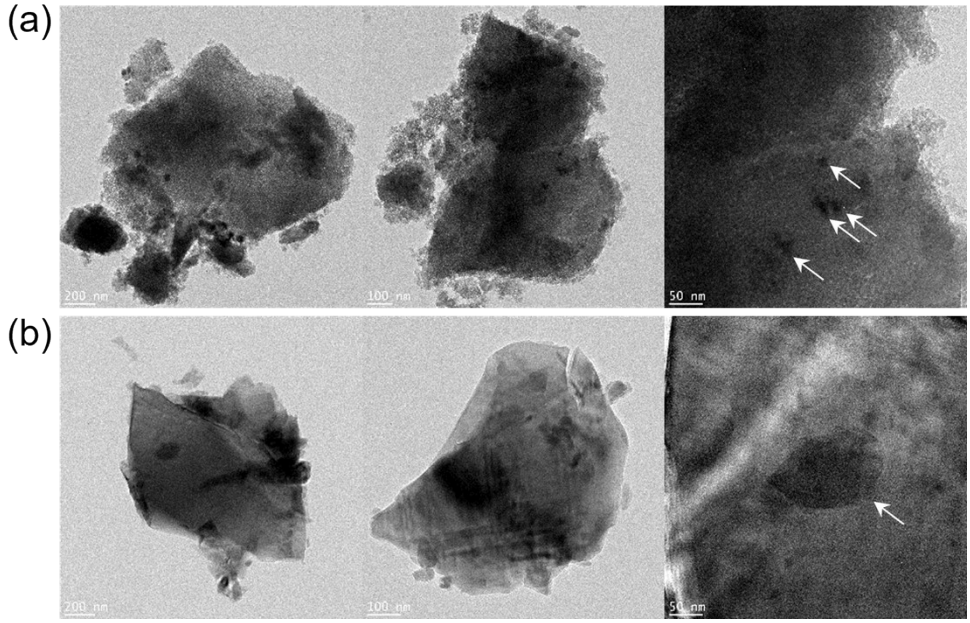

Figure S3. TEM images of the spent (a) 1Fe/SiO_2 and (b) 1Fe-SiO_2 catalysts. White arrows indicate particles that are expected to be Fe species.

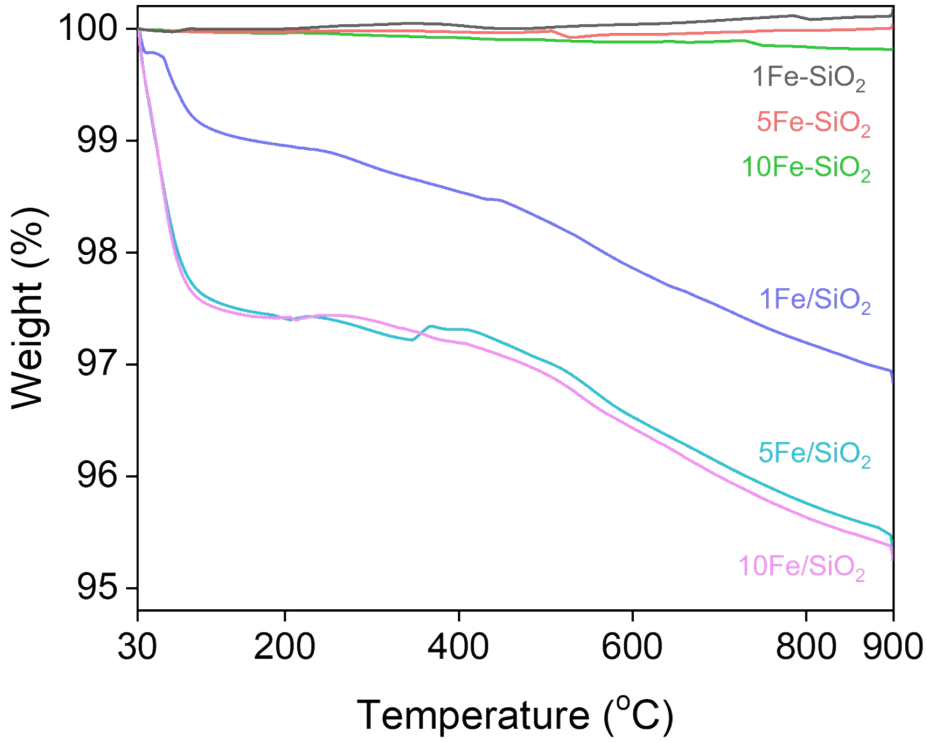

Figure S4. TGA results for spent Fe/SiO_2 and $Fe\text{-}SiO_2$ catalysts after 50 h of reaction.

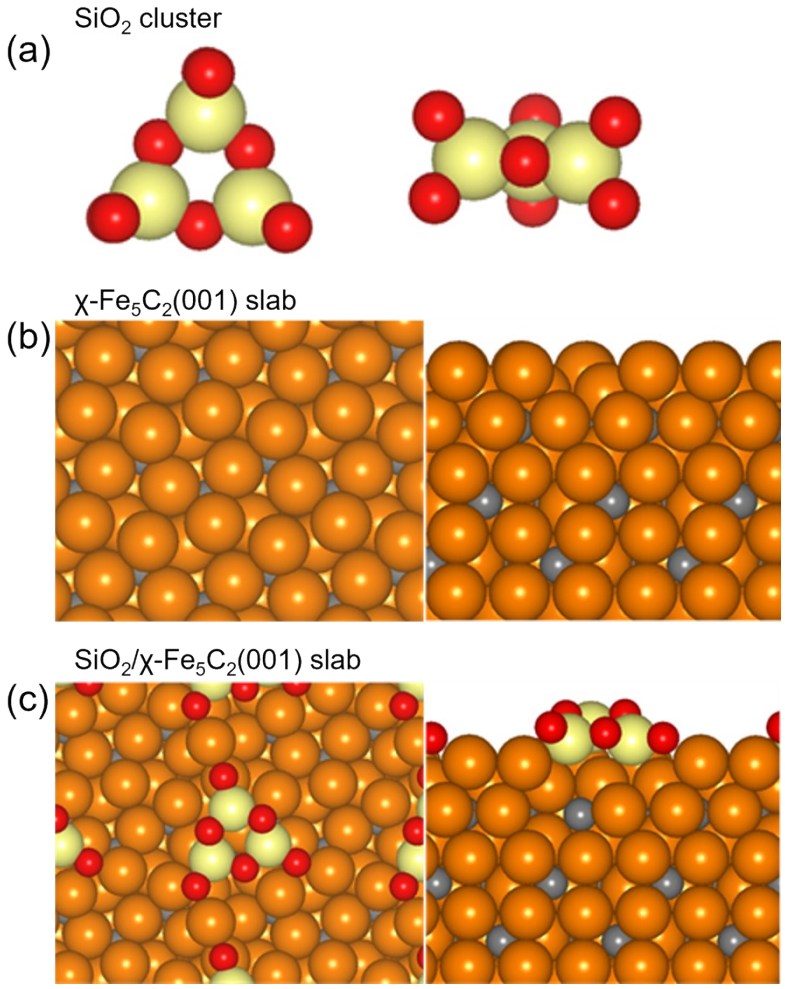

Figure S5. Top and side views of (a) SiO_2 cluster, (b) χ-$Fe_5C_2(001)$ slab, and (c) SiO_2/χ-$Fe_5C_2(001)$ slab. The spheres represent the following elements: orange, Fe; gray, C; light yellow, Si; and red, O.

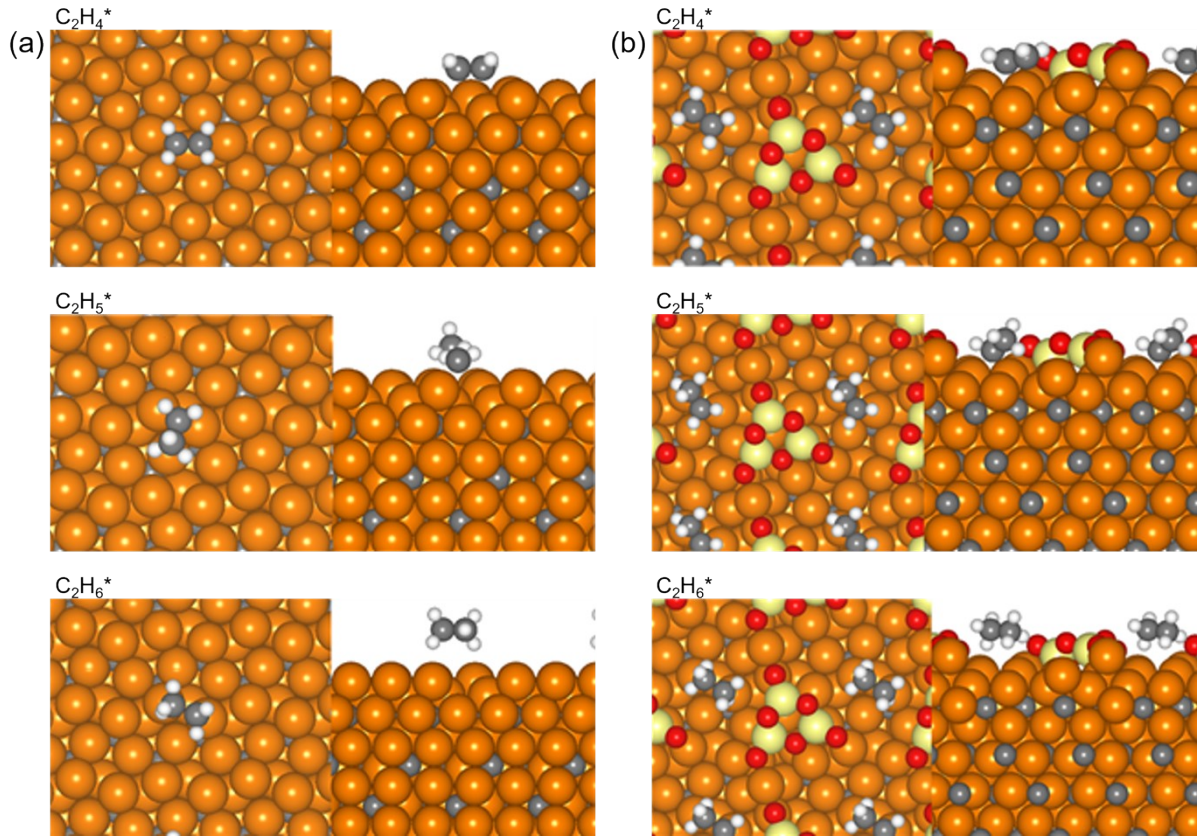

Figure S6. Top and side views of the C_2H_4*, C_2H_5*, and C_2H_6* on the (a) χ-Fe_5C_2(001) and (b) SiO_2/χ-Fe_5C_2(001) surfaces. The spheres represent the following elements: orange, Fe; gray, C; light yellow, Si; and red, O.

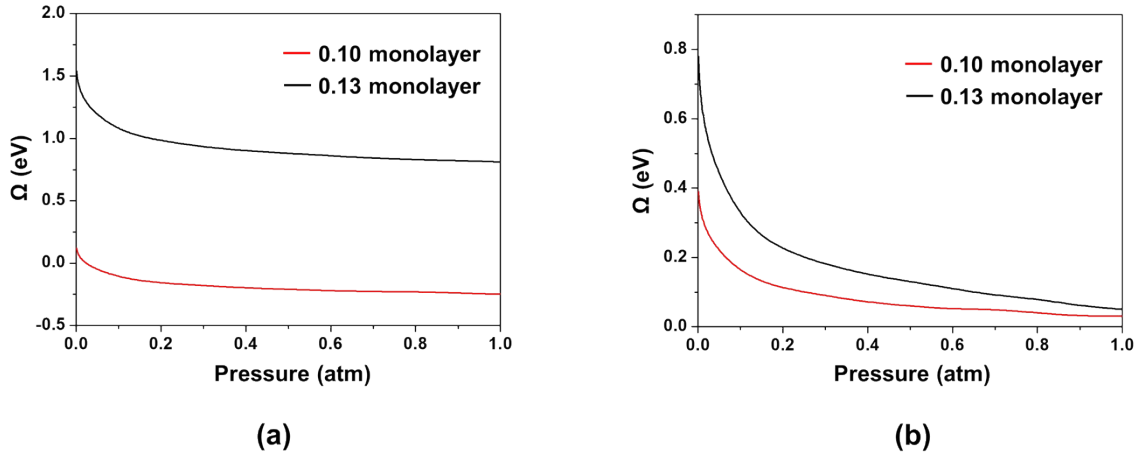

Figure S7. The grand potentials (Ω) of C_2H_4* on the (a) SiO_x/χ-Fe_5C_2(001) and (b) χ-Fe_5C_2(001) surfaces with different coverages. The most stable state (the most negative value for the grand potential) corresponds to the C_2H_4* coverage.

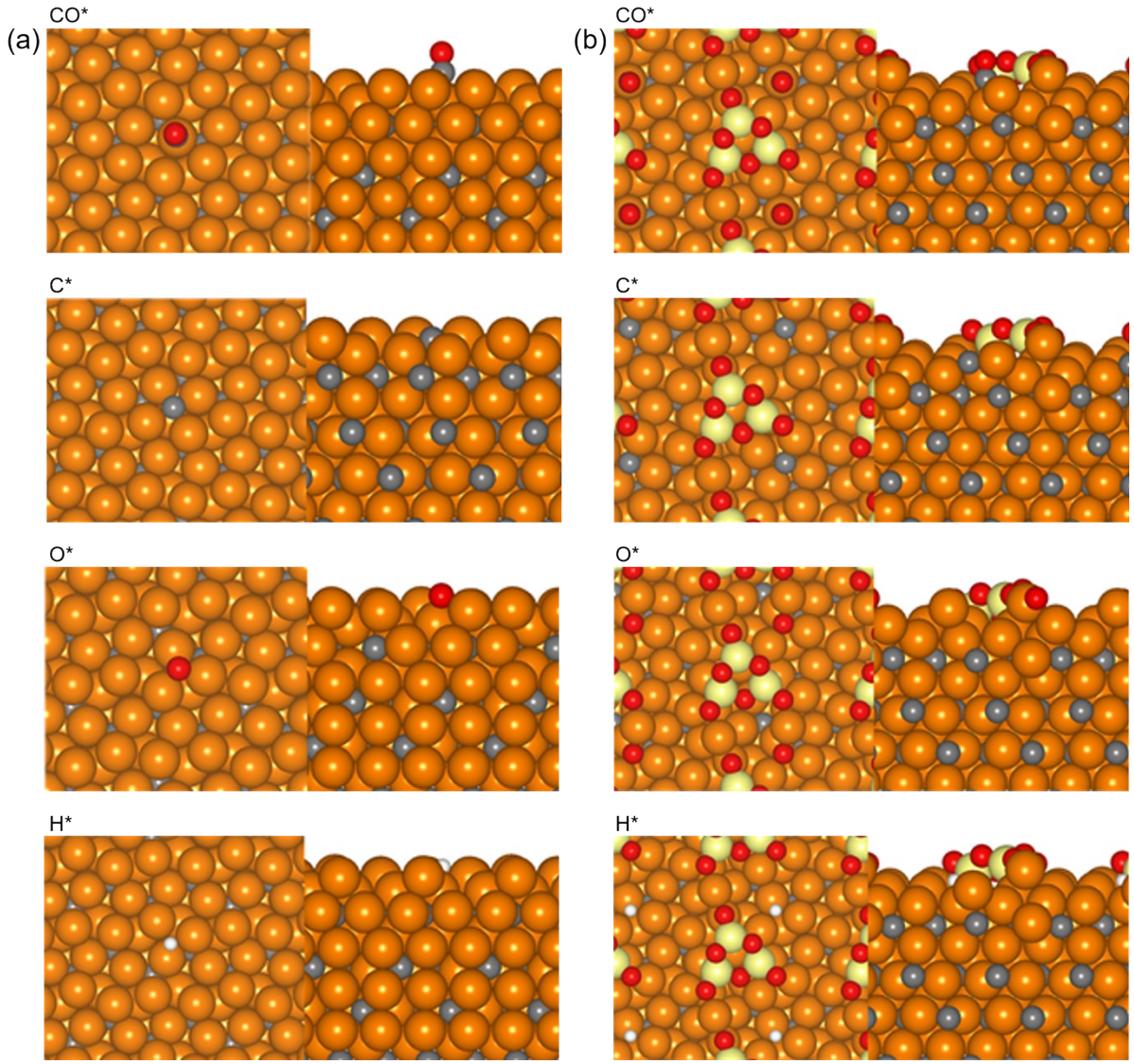

Figure S8. Top and side views of CO*, C*, O*, and H* on (a) χ-Fe_5C_2(001) and (b) SiO_2/χ-Fe_5C_2(001) surfaces. The spheres represent the following elements: orange, Fe; gray, C; light yellow, Si; and red, O.

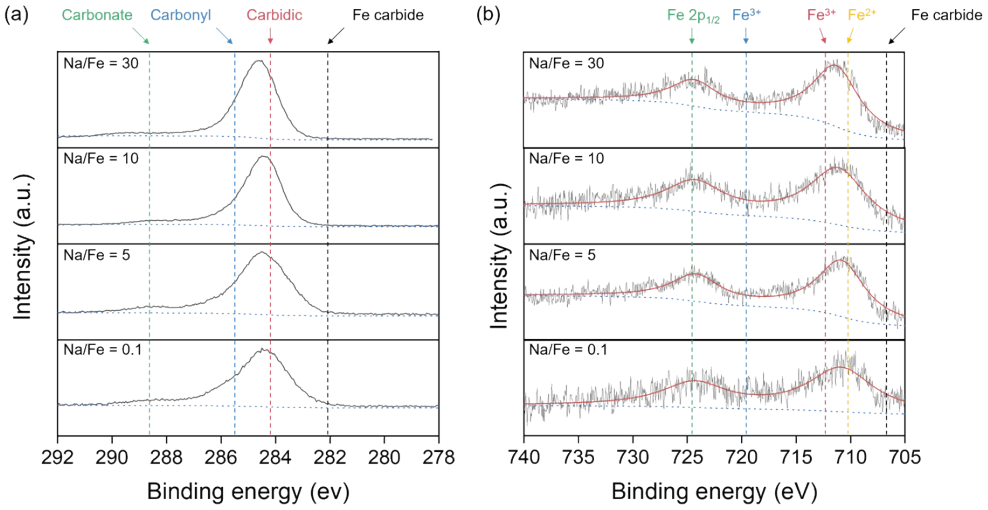

Figure S9. XPS spectra of the spent Na-promoted 5Fe-SiO_2 catalysts for (a) C 1s and (b) Fe 2p.

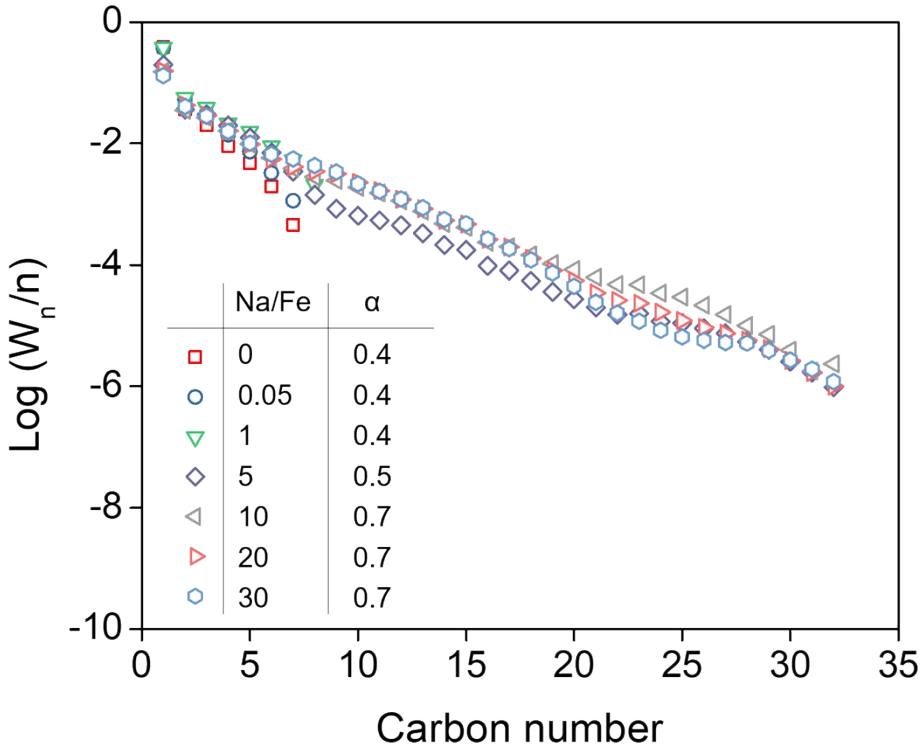

Figure S10. Hydrocarbon molecular weight distribution of Na-promoted 5Fe-SiO_2 catalysts.

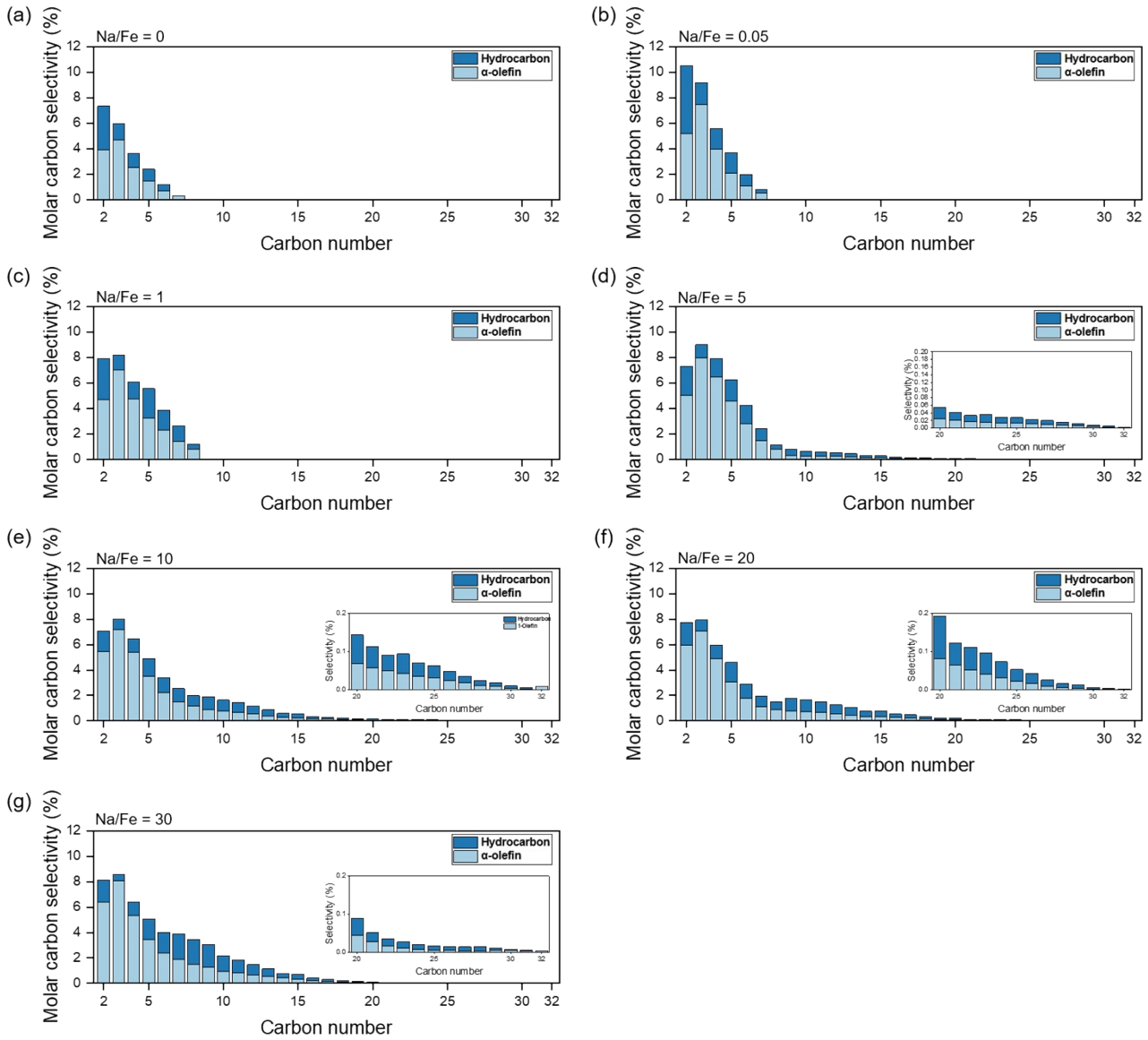

Figure S11. Molar carbon selectivity for hydrocarbons and α-olefins with respect to carbon number for the products of Na-promoted 5Fe-SiO_2 catalysts. (a) Na/Fe = 0, (b) 0.05, (c) 1, (d) 5, (e) 10, (f) 20, and (g) 30.

Reference

1. S.F. Zaman and K.J. Smith, *Mol. Simul.*, 2010, **36**, 118-126.