Electronic Supplementary Information

Effects of calcination and activation conditions on ordered mesoporous carbon supported iron catalysts for production of lower olefins from synthesis gas

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Supplementary Figures

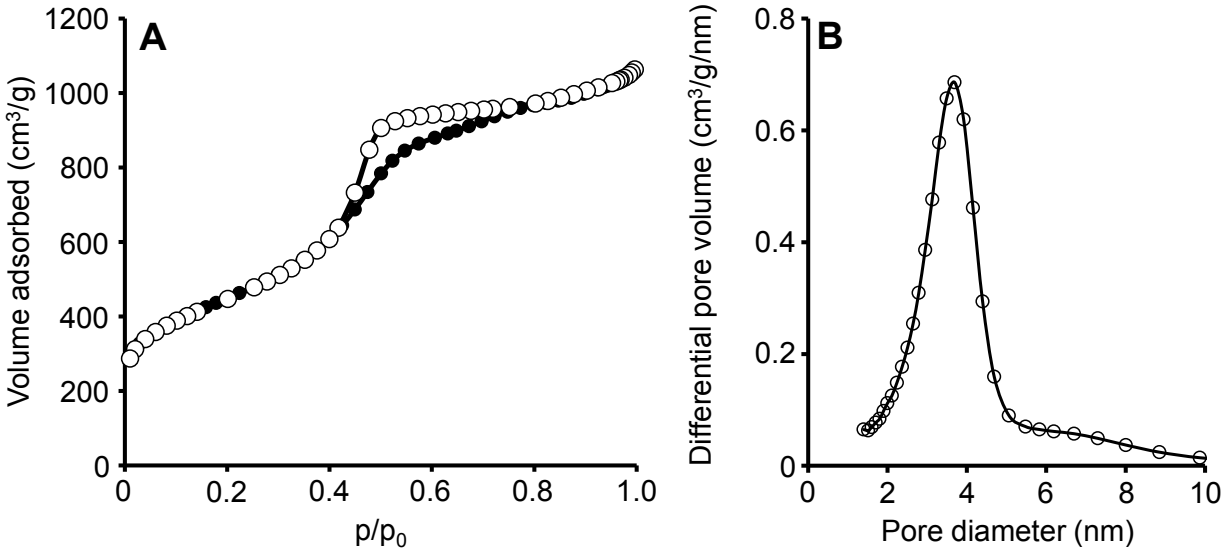

Fig. S1. (A) Nitrogen adsorption/desorption (filled symbols/empty symbols) isotherm (-196°C) as well as (B) BJH pore size distribution calculated from the adsorption branch of the pristine CMK-3 support.

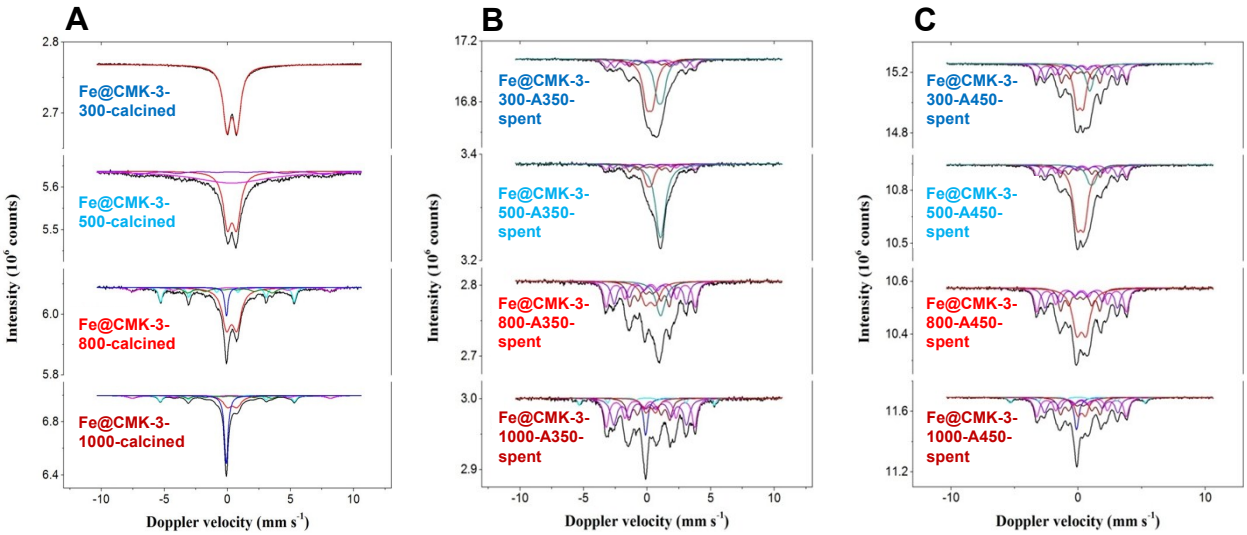

Fig. S2. Mössbauer spectra of (A) the catalysts after calcination and the spent catalysts (FTO at 1 bar for 18 h of TOS) after (B) activation at 350°C and (C) activation at 450°C. The assignment of the fitting curves to different iron species can be found in Table S1.

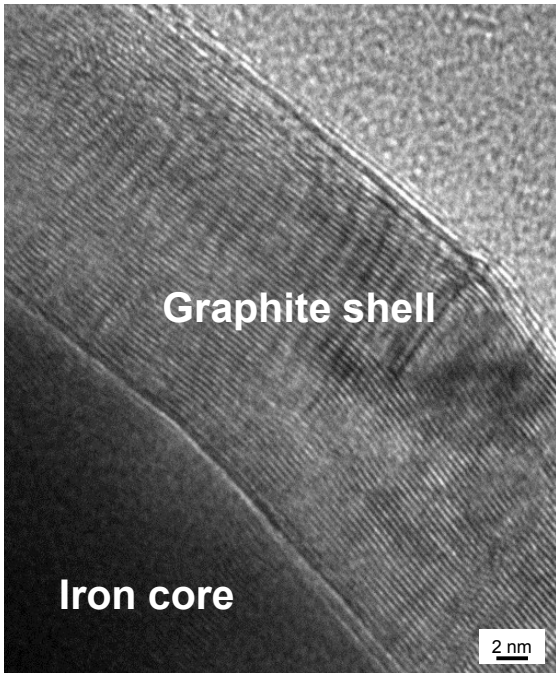

Fig. S3. TEM image of Fe@CMK-3-1000 after calcination.

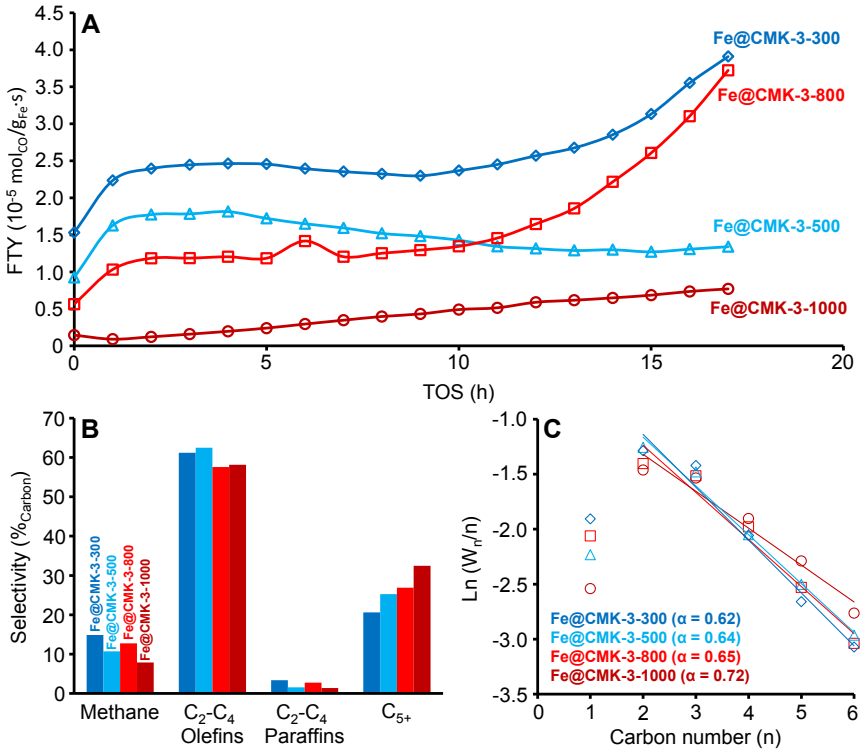

Fig. S4. (A) Iron-weight based activity (FTY) over time on stream (TOS) for sodium/sulfur promoted Fe@CMK-3 catalysts under FTO conditions after calcination at different temperatures and activation at 450°C, (B) product selectivity after TOS = 17 h based on hydrocarbons produced, and (C) corresponding ASF plots of the C_1-C_6 product fractions as well as chain growth probability (α) based on the C_2-C_6 products. Data obtained at GHSV = 3600 h^{-1}, H_2/CO = 1, T = 350°C, p = 1 bar.

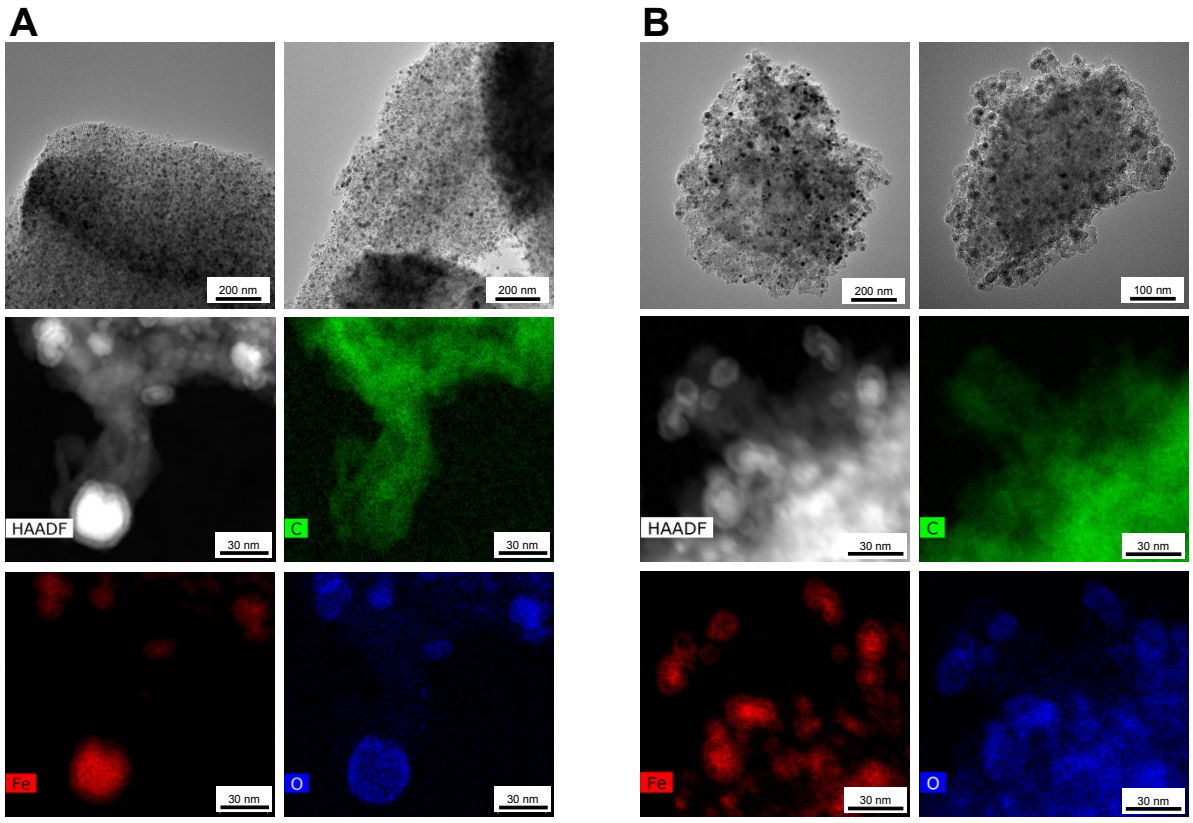

Fig. S5. TEM images and EDX elemental mapping TEM images of the spent Fe@CMK-3-500 catalyst (FTO at 1 bar) after (A) activation at 350°C (after 20 h TOS) and (B) activation at 450°C (after 17 h TOS). (Iron-red; Oxygen-blue; Carbon-green).

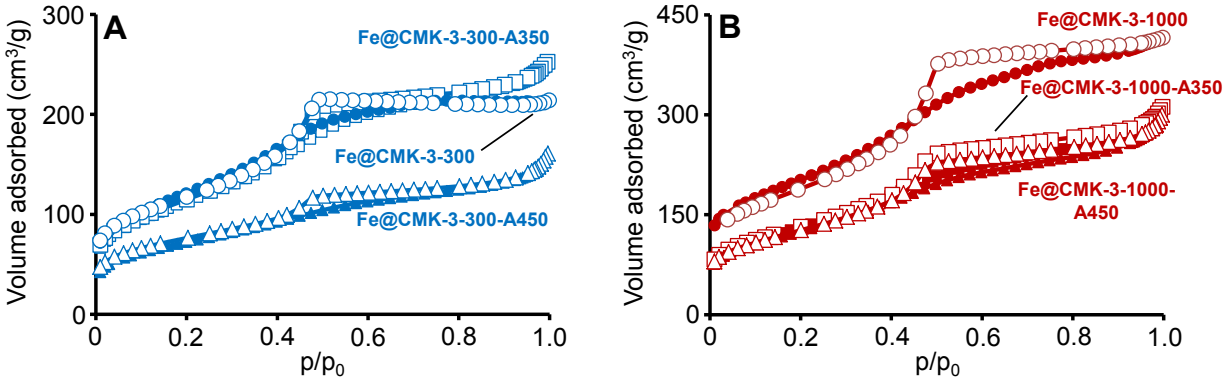

Fig. S6. Nitrogen adsorption/desorption (filled symbols/empty symbols) isotherms (-196°C) of (A) the Fe@CMK-3-300 catalyst and (B) the Fe@CMK-3-1000 catalyst after calcination (circles), after FTO (at 1 bar) with activation at 350°C (squares, TOS = 20 h) or 450°C (triangles, TOS = 17 h).

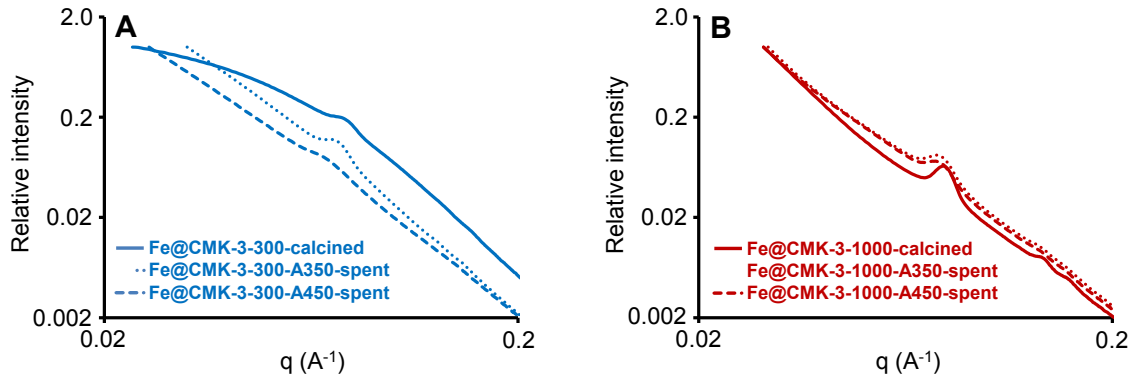

Fig. S7. Logarithmic plots of the small-angle X-ray scattering curves of (A) the Fe@CMK-3-300 catalyst and (B) the Fe@CMK-3-1000 catalyst after calcination (straight lines), after FTO (at 1 bar) with activation at 350°C (dotted lines, TOS = 20 h), or 450°C (dashed lines, TOS = 17 h).

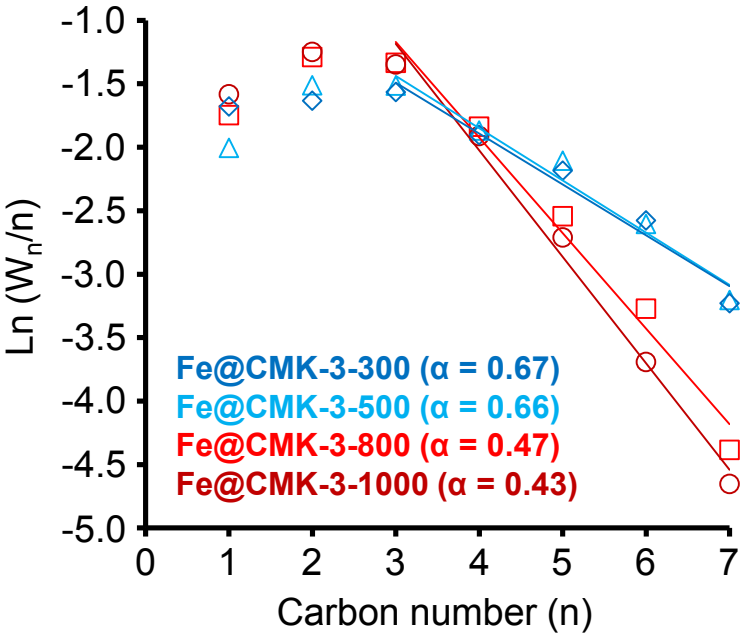

Fig. S8. ASF plots of the C_1-C_7 product fractions as well as chain growth probability (α) based on the C_3-C_7 products of the sodium/sulfur promoted Fe@CMK-3 catalysts calcined at different temperatures after 100 h TOS under industrially relevant FTO conditions. Data obtained at GHSV = 9600 h^{-1}, $H_2/CO = 2$, T = 340°C, p = 10 bar.

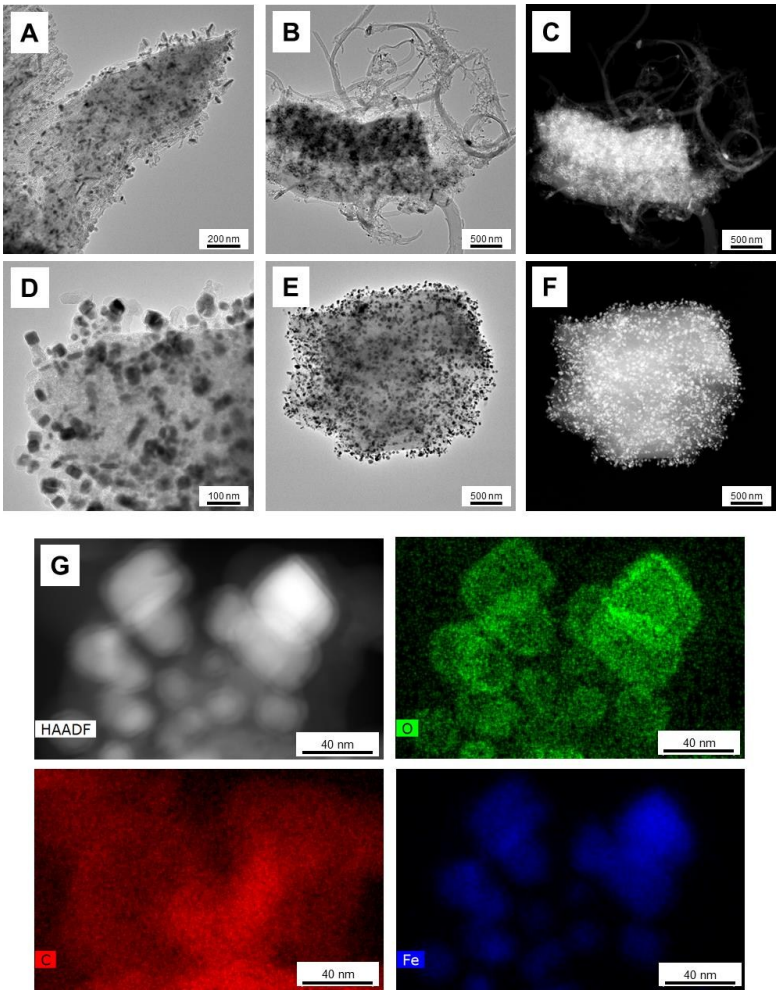

Fig. S9. TEM images of the (A-C) Fe@CMK-3-300 and (D-F) Fe@CMK-3-500 catalyst as well as (G) EDX elemental mapping TEM images of Fe@CMK-3-500 after 140 h TOS at GHSV = 9600 h^{-1}, $H_2/CO = 2$, T = 340°C, p = 10 bar. (Iron-blue; Oxygen-green; Carbon-red).

Supplementary Tables

Table S1. Fitted parameters of the Mössbauer spectra (27°C) of the FTO catalysts after calcination and after 18 h of TOS under FTO conditions (350°C, 1 bar,$H_2/CO = 1$) after activation at 350 or 450°C. For the Fe@CMK-3-300 and Fe@CMK-3-1000 catalysts, spectra were also acquired after activation without exposure to synthesis gas.

Material	IS (mm/s)	QS (mm/s)	Hyperfine field (T)	Γ (mm/s)	Phase	Spectral contribution (%)
Fe@CMK-3-300 Calcined	0.35	0.81	-	0.72	Fe^{3+} (red)	100
Fe@CMK-3-300 activated 350°C	0.22	0.30	-	0.42	Fe_xC (SPM[a])	15
	1.07	0.38	-	0.82	Fe^{2+}	85
Fe@CMK-3-300 activated 450°C	0.21	-	20.2	0.44	Fe_xC	8
	0.22	-	-	0.74	Fe_xC (SPM)	17
	0.00	-	32.9	0.37	Fe^0	34
	1.08	0.72	-	0.63	Fe^{2+}	41
Fe@CMK-3-300 activated 350°C after 18 h TOS	0.20	0.47	-	0.75	Fe_xC (SPM) (red)	37
	0.27	-	21.4	0.56	χ-Fe_5C_2 (I) (magenta)	13
	0.23	-	17.4	0.55	χ-Fe_5C_2 (II) (violet)	12
	0.21	-	9.9	0.56	χ-Fe_5C_2 (III) (wine)	10
	1.02	0.38	-	0.70	Fe^{2+} (dark cyan)	28

Fe@CMK-3-300 activated 450°C after 18 h TOS	0.17	0.50	-	0.64	Fe_xC (SPM) (red)	29
	0.27	-	21.9	0.48	χ-Fe_5C_2 (I) (magenta)	20
	0.22	-	17.7	0.44	χ-Fe_5C_2 (II) (violet)	18
	0.21	-	9.4	0.48	χ-Fe_5C_2 (III) (wine)	21
	0.91	-	-	0.71	Fe^{2+} (dark cyan)	12
Fe@CMK-3-500 Calcined	0.36	0.73	-	0.76	Fe^{3+} (red)	42
	0.35	-	-	7.10	Fe^{3+} (magenta)	48
	0.35	0.05	45.6	1.40	Fe^{3+} (violet)	10
Fe@CMK-3-500 activated 350°C after 18 h TOS	0.17	0.35	-	0.59	Fe_xC (SPM) (red)	16
	0.27	-	21.8	0.45	χ-Fe_5C_2 (I) (magenta)	9
	0.21	-	18.0	0.45	χ-Fe_5C_2 (II) (violet)	7
	0.22	-	10.0	0.45	χ-Fe_5C_2 (III) (wine)	12
	1.05	0.20	-	0.84	Fe^{2+} (dark cyan)	56
Fe@CMK-3-500 activated 450°C after 18 h TOS	0.20	0.56	-	0.77	Fe_xC (SPM) (red)	49
	0.28	-	21.9	0.43	χ-Fe_5C_2 (I) (magenta)	13
	0.27	-	17.7	0.49	χ-Fe_5C_2 (II) (violet)	15
	0.16	-	9.8	0.43	χ-Fe_5C_2 (III) (wine)	12
	1.06	0.35	-	0.71	Fe^{2+} (dark cyan)	11
Fe@CMK-3-800 Calcined	0.34	0.82	-	0.83	Fe^{3+} (red)	52
	0.28	0.02	48.5	0.85	Fe^{3+} (magenta)	11
	0.00	-	32.9	0.34	Fe^0 (cyan)	17
	-0.08	-	-	0.30	Fe^0 (SPM) (blue)	7
	0.20	-	20.8	0.84	Fe_xC (olive)	14
Fe@CMK-3-800 activated 350°C after 18 h TOS	0.27	0.79	-	0.84	Fe_xC (SPM) (red)	16
	0.28	-	21.8	0.49	χ-Fe_5C_2 (I) (magenta)	24
	0.23	-	17.7	0.52	χ-Fe_5C_2 (II) (violet)	23
	0.18	-	9.7	0.49	χ-Fe_5C_2 (III) (wine)	22
	1.06	-	-	0.89	Fe^{2+} (dark cyan)	15
Fe@CMK-3-800 activated 450°C after 18 h TOS	0.26	0.73	-	0.84	Fe_xC (SPM) (red)	35
	0.28	-	21.9	0.46	χ-Fe_5C_2 (I) (magenta)	23
	0.25	-	17.7	0.52	χ-Fe_5C_2 (II) (violet)	21
	0.17	-	9.6	0.46	χ-Fe_5C_2 (III) (wine)	21
Fe@CMK-3-1000 Calcined	0.38	0.76	-	0.83	Fe^{3+} (red)	25
	0.31	0.00	48.8	0.78	Fe^{3+} (magenta)	13
	0.00	-	33.1	0.39	Fe^0 (cyan)	15
	-0.09	-	-	0.34	Fe^0 (blue) (SPM)	35
	0.18	-	20.6	0.69	Fe_xC (olive)	12
Fe@CMK-3-1000 activated 350°C	0.00	-	33.0	0.36	Fe^0	71
	-0.08	-	-	0.38	Fe^0 (SPM)	29
Fe@CMK-3-1000 activated 450°C	0.00	-	32.9	0.40	Fe^0	70
	-0.08	-	-	0.40	Fe^0 (SPM)	30
Fe@CMK-3-1000 activated 350°C after 18 h TOS	0.28	0.76	-	0.61	Fe_xC (SPM) (red)	8
	0.26	-	21.6	0.47	χ-Fe_5C_2 (I) (magenta)	29
	0.23	-	17.8	0.58	χ-Fe_5C_2 (II) (violet)	31
	0.18	-	10.0	0.47	χ-Fe_5C_2 (III) (wine)	20
	0.00	-	33.0	0.29	Fe^0(cyan)	4
	-0.10	-	-	0.44	Fe^0 (SPM) (blue)	8
Fe@CMK-3-1000 activated 450°C after 18 h TOS	0.28	0.59	-	0.60	Fe_xC (SPM) (red)	14
	0.27	-	21.9	0.48	χ-Fe_5C_2 (I) (magenta)	26
	0.24	-	17.9	0.54	χ-Fe_5C_2 (II) (violet)	23
	0.17	-	9.7	0.48	χ-Fe_5C_2 (III) (wine)	22
	0.00	-	33.0	0.31	Fe^0 (cyan)	5
	-0.11	-	-	0.43	Fe^0 (SPM) (blue)	10

[a] SPM: superparamagnetic (in very small nanoparticles).

Experimental uncertainties: Isomer shift: I.S. ± 0.01 mm/s; Quadrupole splitting: Q.S. ± 0.01 mm/s; Line width: Γ ± 0.01 mm/s; Hyperfine field: ± 0.1 T; Spectral contribution: ± 3%.

Table S2. CO conversion, catalytic activity, and product selectivity of the CMK-3-supported FTO catalysts calcined and activated at different temperatures. Data obtained at 350°C, 1 bar, H_2/CO ratio = 1, GHSV = 3600 h^{-1}, TOS = 17 h). The differences to 100%$_C$ in hydrocarbons were detected as oxygenates.

Catalyst	CO conversion (%)	FTY (10^{-5} mol_{CO}/g_{Fe}·s)	Product Selectivity (%$_C$)			
			CH_4	C_2-C_4 Olefins	C_2-C_4 Paraffins	C_{5+}
Fe@CMK-3-300-A350	0.40	0.29	12.5	59.0	2.6	25.6
Fe@CMK-3-500-A350	1.04	0.69	8.2	61.6	1.5	28.7
Fe@CMK-3-800-A350	1.82	1.03	7.8	58.9	1.6	31.7
Fe@CMK-3-1000-A350	1.17	0.60	7.8	58.7	1.5	31.9
Fe@CMK-3-300-A450	5.00	3.91	14.9	61.2	3.4	20.6
Fe@CMK-3-500-A450	2.18	1.34	10.7	62.5	1.6	25.5
Fe@CMK-3-800-A450	7.28	3.72	12.7	57.6	2.7	26.9
Fe@CMK-3-1000-A450	1.39	0.77	7.9	58.2	1.4	32.5