



Supporting Online Material for

Supported Iron Nanoparticles as Catalysts for Sustainable Production of Lower Olefins

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This PDF file includes:

Materials and Methods

SOM Text

Figs. S1 to S6

Tables S1 to S6

Equations S1 and S2

Materials and Methods

Catalyst preparation

Preparation of supported Fe catalysts. Fe supported catalysts with a nominal loading of 10 wt% Fe were prepared by multi-step incipient wetness impregnation of the selected support (2 g) with 2.7 ml of a 1.4M aqueous solution of ammonium iron citrate (90-100%, J. T. Baker). The ammonium iron citrate as purchased contained low amounts of sulphur and sodium. Different support materials were used: α -Al₂O₃ (10 m² g⁻¹; BASF), β -SiC (25 m² g⁻¹; SICAT), γ -Al₂O₃ (250 m² g⁻¹; BASF), SiO₂ (495 m² g⁻¹; Grace Davison) and CNF (150 m² g⁻¹). Before impregnation, the β -SiC support was calcined at 700°C under static air for 3 hours. The carbon nanofibers support was prepared and surface-oxidized as described before (27). The solution was added to the support until the pore volume was completely filled. After each impregnation step, the catalysts were dried at room temperature and 60 mbar for 2 hours. 6 wt% and 25 wt% Fe/ α -Al₂O₃ catalysts were prepared by impregnation of 4 g of support with 2.8 ml (1.3M) and 12.8 ml (1.4M) of aqueous solutions of ammonium iron citrate. Impregnation and drying steps were repeated until incorporation of the total volume of the solution was achieved. The dried impregnates, except for the CNF supported sample, were heated at 500°C for 2 h, at a heating rate of 10 K min⁻¹ under air flow. Impregnated CNF was heated at 355°C for 2 h, at a heating rate of 10 K min⁻¹ under nitrogen flow.

Preparation of bulk Fe catalysts. A bulk promoted iron oxide catalyst (Fe-Ti-ZnO-K₂O with a weight composition 100:25:10:4) was synthesized according to the procedure reported by Büssemeier *et al.* (10). Additionally, two bulk (unpromoted Fe₂O₃ and Fe₂O₃/CuO/K₂O/SiO₂) catalysts were prepared by precipitation of an aqueous solution of ferric nitrate and adding a basic sodium carbonate solution as precipitating agent. 25 g of Fe(NO₃)₃·9H₂O (98% A.C.S. reagent, Acros) were dissolved in 100 ml of distilled water. For the promoted catalyst, 2.9 g of Cu(NO₃)₂·3H₂O (p.a. 99.5%, Merck) was added to the solution. The solution was heated to its boiling point and after that, a near boiling solution of 25 g of Na₂CO₃ (99%, Acros) in 100 ml of distilled water was slowly added while stirring vigorously. The precipitate was filtered and re-slurried in boiling water to remove residual sodium. The washing process was repeated until neutral pH was reached. The unpromoted catalyst was dried at 60°C for 6 h and then at 120°C for 24 h. Subsequently, the catalyst was calcined under air flow at 300°C for 5 h with a heating ramp of 5 K min⁻¹. For addition of K, after precipitation the Cu-promoted catalyst was re-slurried in 200 ml of distilled water. 16 g of potassium water glass solution (K₂O: SiO₂ 1:2.15, Akzo-PQ) were added to the slurry under vigorous stirring. 3 ml of HNO₃ was added to precipitate SiO₂ and to lower the potassium content. After this, the catalyst was washed, dried and calcined following the same procedure as for the unpromoted catalyst.

Catalyst characterization

X-ray fluorescence measurements were carried out to determine the iron loading and the elemental composition of the catalysts on Goffin Meyvis spectro X-lab 2000. X-ray diffraction measurements were performed with a Bruker AXS D8 ADVANCE diffractometer equipped with a CoK α 1 source ($\lambda=0.1789$ nm) in a wide angle range (from 20 to 90° in 2 θ). TEM images were obtained on a Philips Tecnai-20FEG (200 kV) microscope equipped with an EDX and HAADF detector. Thermal gravimetric analysis

of the spent catalysts to determine carbon lay-down was performed in a Perkin Elmer Pyris 1 TGA under oxygen flow (10 ml min^{-1}). Temperature was increased from 30°C to 600°C with a heating ramp of 5°C min^{-1} . After reaching 600°C , the samples remained at that temperature for 1 hour. Transmission ^{57}Fe Mossbauer spectra were collected at room temperature with a conventional constant acceleration spectrometer using a ^{57}Co (Rh) source. Velocity calibration was carried out using an $\alpha\text{-Fe}$ foil. The Mössbauer parameters were determined by fitting the spectra with calculated subspectra consisting of Lorentzian-shaped lines, using the Mosswin 3.0i program.

Catalytic tests

Low pressure testing. Fischer-Tropsch synthesis was performed at 1 bar and 350°C in a plug flow reactor (H_2/CO ratio of 1). 20 mg of the catalyst (particle size = 0.2-0.4 mm) were diluted with 200 mg of SiC (particle size = 0.2 mm) to achieve isothermal plug-flow conditions and reduced *in situ* in H_2/Ar (33% v/v; 60 ml min^{-1}) at 350°C for 2 h (Heating ramp: 5°C min^{-1}). Gas chromatography was used to determine the selectivity for hydrocarbons up to C_{16} . Catalytic activities and product selectivities were determined uptill 15 h of reaction at low CO conversions (0.5-1%). CO_2 selectivity was not measured. Product selectivity has been calculated as equivalent amount of carbon atoms in a product with respect to the total carbon atoms present in the hydrocarbons produced. The selectivity to oxygenates was below 1% and has been excluded from the reported product selectivities.

Medium pressure testing. The Fischer-Tropsch reaction was carried out at 20 bar and 340°C in a plug flow reactor. 2 ml of catalyst (particle size = 0.2-0.4 mm) were diluted with 10 ml of SiC (particle size = 0.2-0.4 mm) and reduced *in situ* under H_2 flow (22 ml min^{-1}) at 350°C for 2 h. After reduction, temperature was lowered to 290°C and the feed flow was switched to a syngas/internal standard mixture ($\text{H}_2/\text{CO}/\text{He}$: 45/45/10%v/v, GHSV= 1500 h^{-1}). Temperature was raised to 340°C (Heating ramp: 10°C h^{-1}). Catalytic activities and product selectivities were determined up to 64 h of reaction. Product selectivity was determined by gas chromatography analysis of the products up to C_{10} . Analysis of the liquid product confirmed the production of hydrocarbons, mainly in the range of C_8 to C_{15} . Only trace amounts (<1%) of alcohols (ethanol) were observed.

SOM Text

Mössbauer Spectroscopy

The Mössbauer spectral contributions consisting of quadrupole-split center lines are assigned to high-spin Fe^{3+} in an octahedral environment and, most likely, correspond to superparamagnetic Fe_2O_3 in the fresh samples. In magnetic nanocrystals with dimensions lower than 13.5 nm (34,35) the thermal energy is high enough to induce the random fluctuation of the magnetic moments, cancelling out the magnetic ordering. At low temperatures or in larger particles, the coupling forces prevail over the thermal energy, causing the magnetic moments of neighbouring atoms to align and the Mössbauer spectra becomes magnetically split (hyperfine sextuplets are observed).

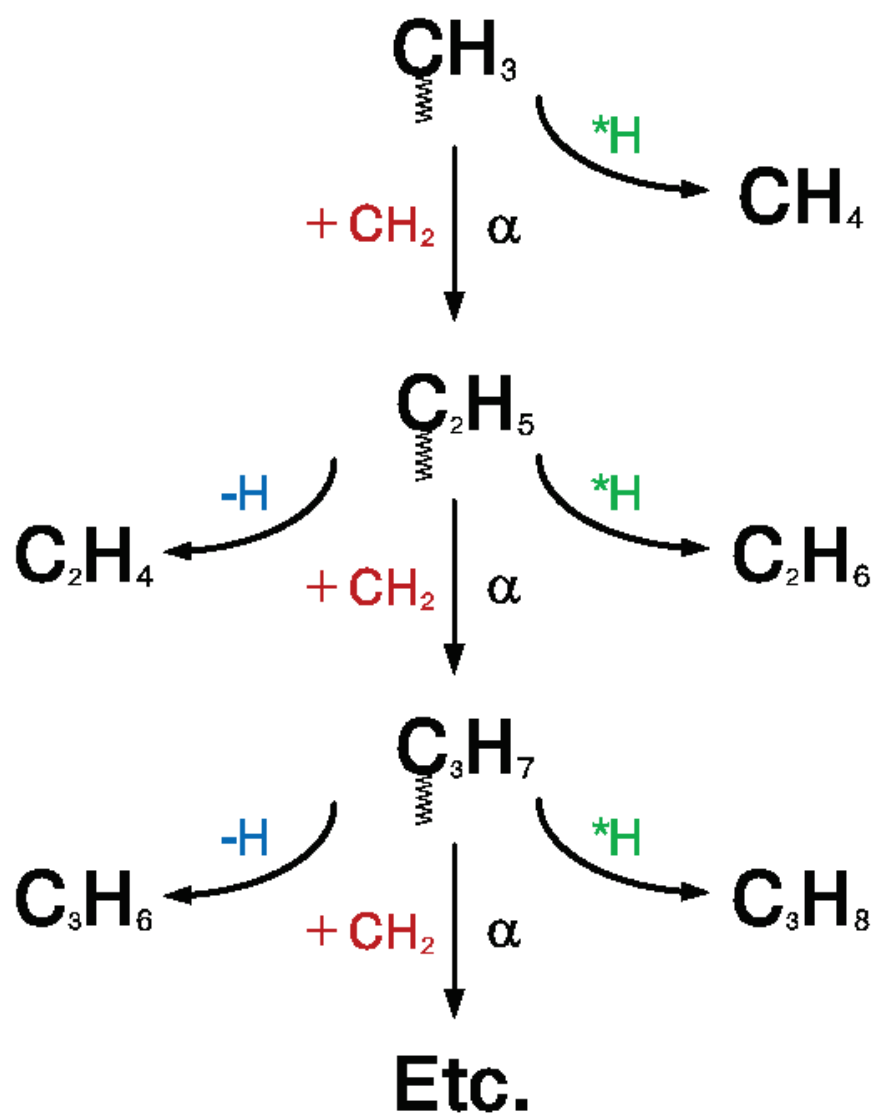


Fig. S1.

Fischer-Tropsch reaction mechanism (surface carbide mechanism). Methylene monomers (CH_2) are added to the adsorbed chain. The chain growth terminates by β -hydride elimination or by hydrogenation.

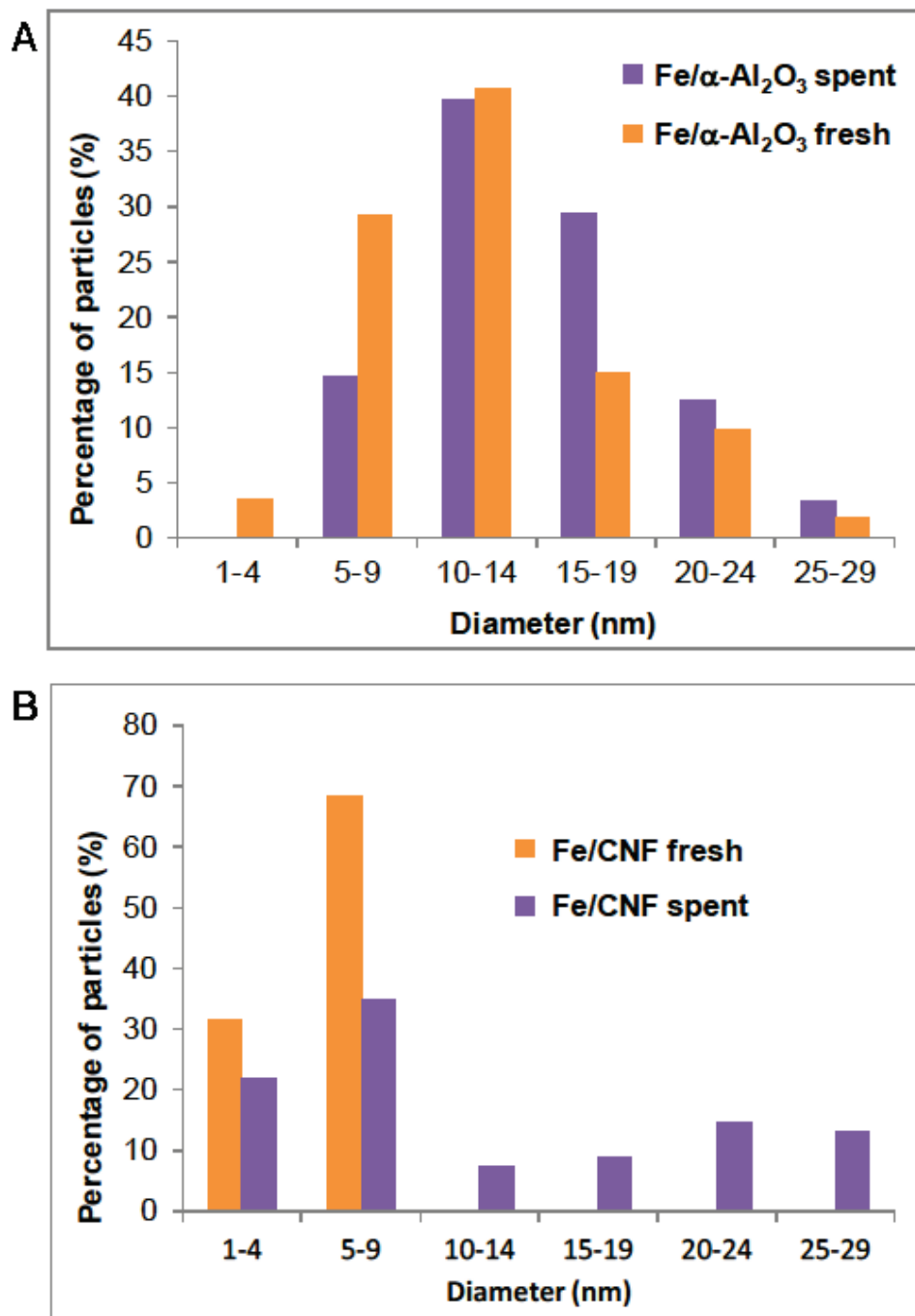


Fig. S2.
Particle size distribution of iron nanoparticles. (A) 12 wt% Fe/ α -Al₂O₃, **(B)** Fe/CNF. Fresh catalysts: dark-coloured bars. The spent catalysts (light-coloured bars) were analyzed after reaction at 340°C, 20 bar and H₂/CO ratio of 1 (TOS = 64 h).

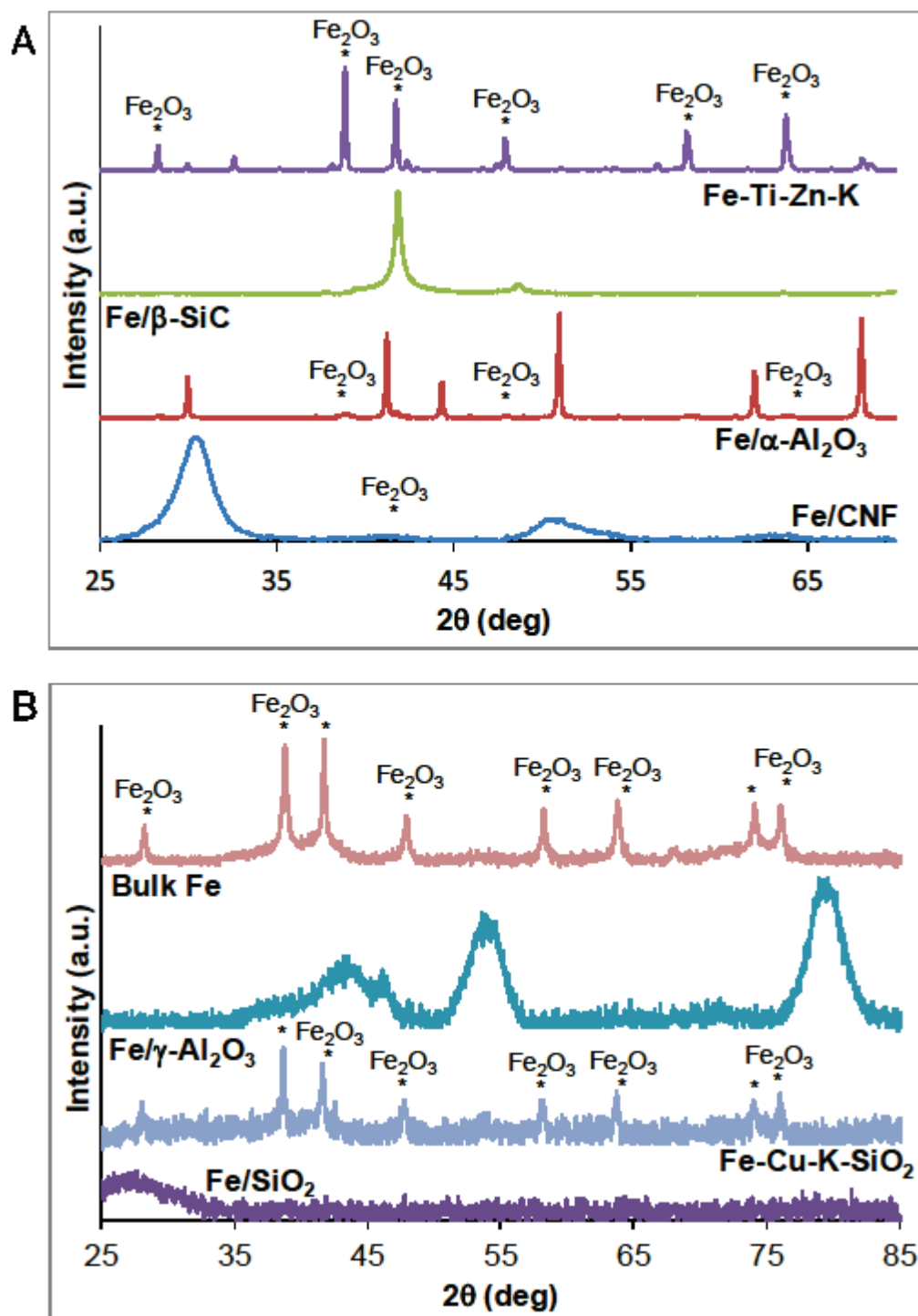


Fig. S3.
X-ray diffraction of supported and bulk Fe catalysts. Diffraction lines related to iron were not observed in catalysts supported on β -SiC (A), γ -Al₂O₃ and SiO₂ (B).

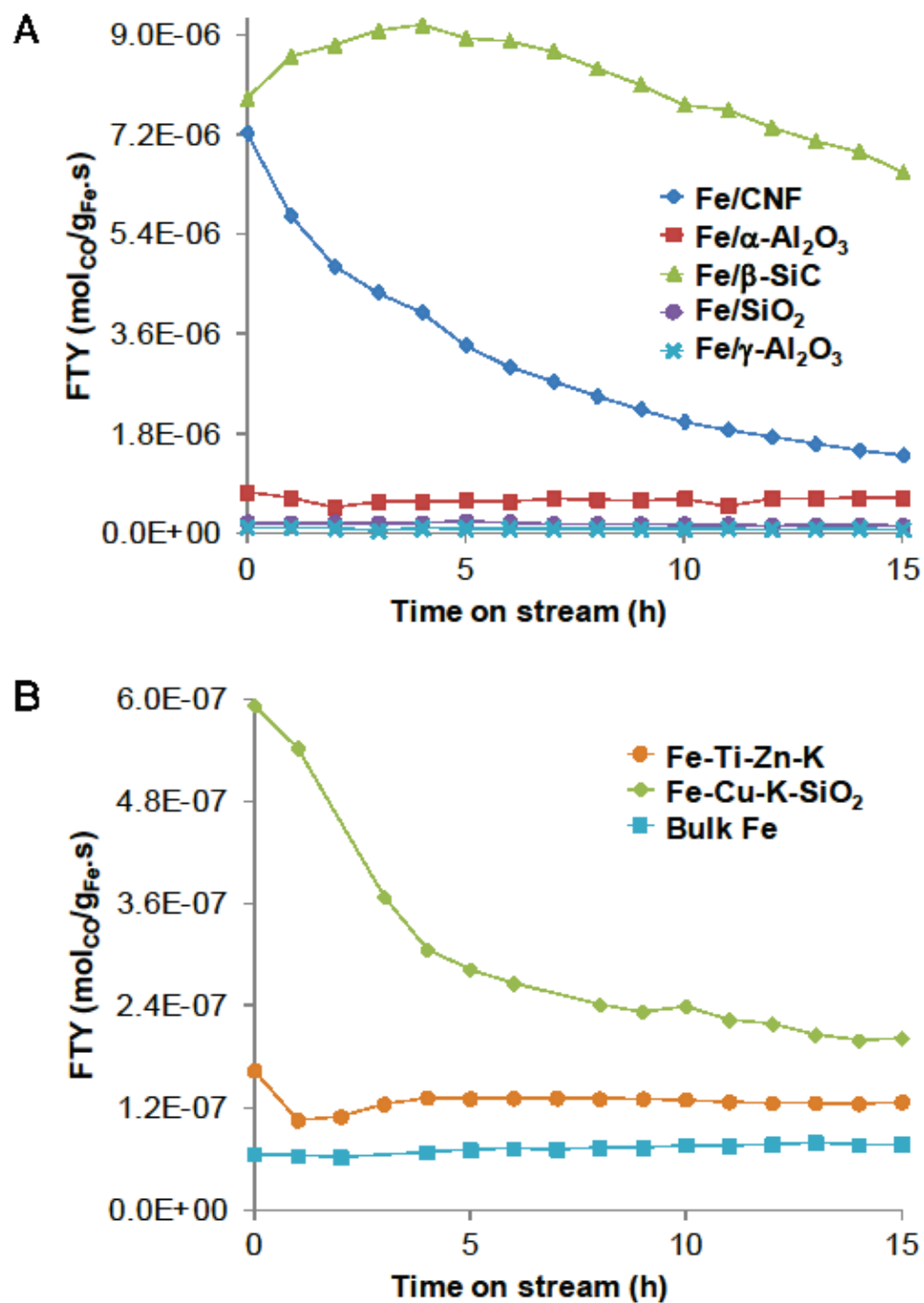


Fig. S4. Catalytic activity as a function of time of iron catalysts for the Fischer-Tropsch to Olefins process at 1 bar. Catalytic activity was measured at T=350°C, P=1 bar, H₂/CO ratio of 1, and low CO conversion levels (0.5-1%). (A), Iron time yield for supported Fe catalysts. (B), Iron time yield as a function of time on stream (TOS) for Fe bulk catalysts.

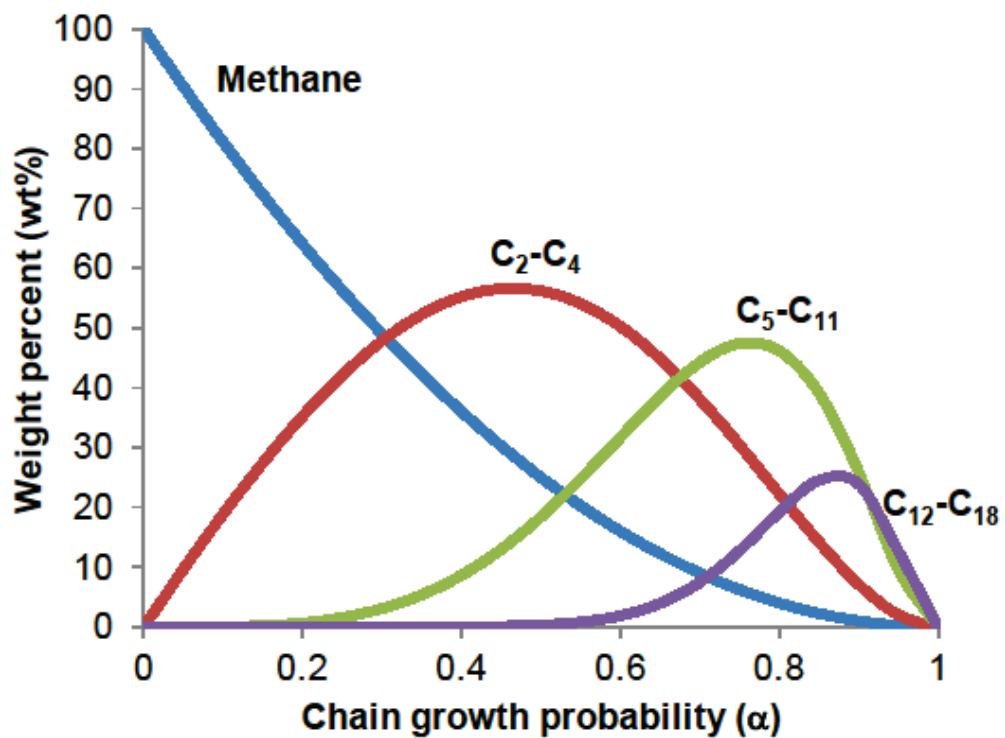


Fig. S5. Product distribution predicted by the Anderson-Schulz-Flory model. The maximum C₂-C₄ fraction is obtained at α -values between 0.4 and 0.5.

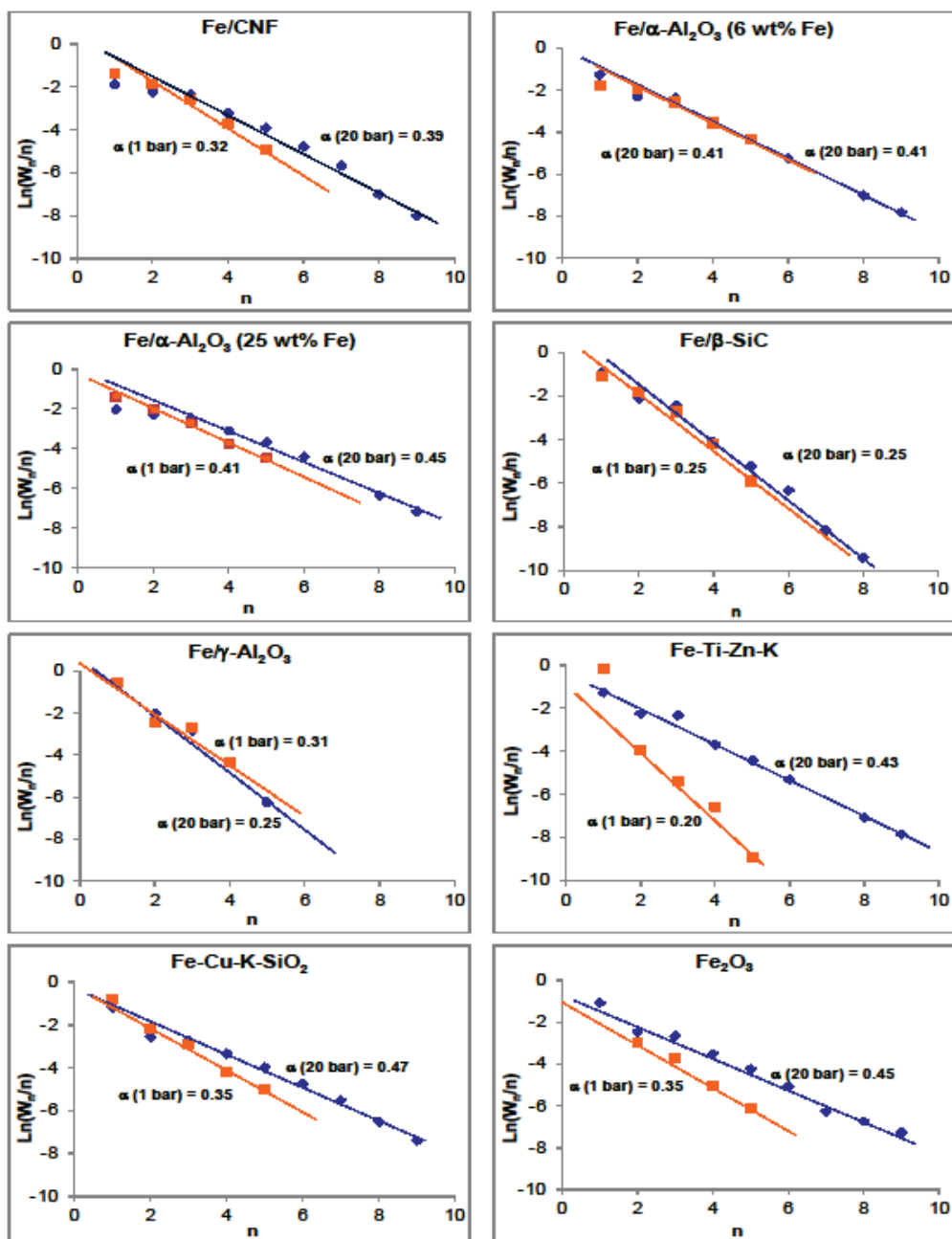


Fig. S6.

Anderson-Schulz-Flory plots. (■) Product distribution at 350°C, 1 bar and H₂/CO ratio of 1 (TOS = 15 h). (◆) Product distribution at 340°C, 20 bar and H₂/CO ratio of 1 (TOS = 64 h). W_n is the weight fraction of a product with n number of carbon atoms; α is the chain growth probability and 1- α is the probability of chain termination.

Table S1.

Catalytic results from the literature on supported iron catalysts tested under high temperature conditions.

Catalyst	Fe (wt%)	P (bar)	T (°C)	H ₂ /CO	CO conv. (%)	FTY (mol _{CO to HC} /g _{Fe} .s)	Selectivity (%C)		
							CH ₄	C ₂ -C ₄ olefins	C ₅₊
Fe/Al ₂ O ₃ (15)	20	15	280	1	22	N. A.	26	9	35
Fe-Pr/HT γ -Al ₂ O ₃ (28)	2	8	280	0.5	5.4*	1.95x10 ⁻⁵	5	51	42
Fe-Pr/HT γ -Al ₂ O ₃ (TOS = 64 h)	2	20	350	1	18	4.3x10 ⁻⁵	42	23	8
Fe/AC (29)	4	10	275	1	2.24*	1.7x10 ⁻⁵ ‡	35	38 [¶]	9
Fe/AC (21)	4.4	1	350	1	2.3	1.6x10 ⁻⁴ ‡ 4.6x10 ⁻⁵ §	18	60 [#]	5
Fe/CNT (30)	10.8	20	275	2	86	N. A.	9	13	70
Fe-Mn/C (31)	1.53	1	309	3	1.3*	N. A.	38	39	0
Fe-Ru-K/CNT (32)	9.8	8	275	2	25	1.0x10 ⁻⁴	15	N. A.	46
Fe-K/C spheres (33)	8.9	8	275	2	N.A.	1.8x10 ⁻⁵	3	4	92

* CO converted to hydrocarbons; † Selectivity towards C₂ and C₃ olefins; ‡ Initial activity; § Iron time yield after 20 h; N.A.= data not available.

|| This sample was prepared in our laboratory according to the procedure described by Baker *et al.*(28) and tested for comparison under our reaction conditions.

Please note that the activated carbon supported systems deactivated rapidly: ¶ the activity of this catalyst decreased 50% from its initial value after 17 h (H₂/CO ratio of 3) and # for this catalyst, activity decreased 71% after 20 h.

Table S2.Iron loading and average Fe₂O₃ crystallite size of fresh Fe catalysts.

Sample	Fe ₂ O ₃ crystallite size* (nm)	Fe loading [†] (wt%)
Fe/CNF	7	12
Fe/ α -Al ₂ O ₃	21	13
Fe/ β -SiC	N.A.	8
Fe/SiO ₂	N. A.	13
Fe/ γ -Al ₂ O ₃	N. A.	13
Fe-Ti-Zn-K	50	72
Fe-Cu-K-SiO ₂	40	32
Bulk Fe	30	63

N. A.: Not applicable

* Determined by X-ray diffraction (XRD).

† Determined by X-ray fluorescence (XRF).

Table S3.

Elemental analysis of the fresh catalysts determined with XRF (X-Ray Fluorescence).

Sample	Na (wt%)	Al (wt%)	Si (wt%)	Ca (wt%)	Sx (wt%)	Mn (wt%)	K (wt%)	Cr (wt%)
Fe/ α -Al ₂ O ₃ (12 wt%)	0.594	43.19	0.14	0.022	0.132	0.049	-	0.025
Fe/ β -SiC	0.245	0.091	41.42	0.028	0.045	0.036	-	0.015
Fe/SiO ₂	0.473	0.060	37.79	-	0.052	0.057	-	0.023
Fe/ γ -Al ₂ O ₃	0.496	42.28	0.137	-	0.062	0.057	-	0.020
Fe-Cu-K-SiO ₂	-	0.090	19.5	-	-	-	8.05	-
Bulk Fe	-	0.036	0.238	0.017	-	-	-	-

Table S4.

Mössbauer parameters of fresh Fe catalysts. Experimental uncertainties: Isomer shift: IS $\pm 0.01 \text{ mm.s}^{-1}$; Quadrupole splitting: QS $\pm 0.01 \text{ mm.s}^{-1}$; Line width: $\Gamma \pm 0.01 \text{ mm.s}^{-1}$; Hyperfine field: $\pm 0.1 \text{ T}$; Spectral contribution: $\pm 3\%$.

Sample	IS (mm.s^{-1})	QS (mm.s^{-1})	Γ (mm.s^{-1})	Hyperfine field (T)	Phase	Spectral Contribution (%)
Fe/CNF	0.36	0.81	0.58	-	$\alpha\text{-Fe}_2\text{O}_3$ (SPM)	100
Fe/ $\alpha\text{-Al}_2\text{O}_3$	0.34	0.81	0.83	-	$\alpha\text{-Fe}_2\text{O}_3$ (SPM)	24
	0.38	-0.21	0.46	50.8	$\alpha\text{-Fe}_2\text{O}_3$	76
Fe/ $\beta\text{-SiC}$	0.33	0.80	0.57	-	$\alpha\text{-Fe}_2\text{O}_3$ (SPM)	82
	0.39	-0.14	1.32	47.0*	$\alpha\text{-Fe}_2\text{O}_3$	18
Fe/SiO ₂	0.34	0.90	0.51	-	$\alpha\text{-Fe}_2\text{O}_3$ (SPM)	97
	0.39	-0.20	0.51	51.7	$\alpha\text{-Fe}_2\text{O}_3$	3
Fe/ $\gamma\text{-Al}_2\text{O}_3$	0.31	0.97	0.57	-	$\alpha\text{-Fe}_2\text{O}_3$ (SPM)	100
Fe-Ti-Zn-K	0.39	0.56	0.45	-	$\alpha\text{-Fe}_2\text{O}_3$ (SPM)	9
	0.38	-0.21	0.50	50.2	$\alpha\text{-Fe}_2\text{O}_3$	91
Fe-Cu-K-SiO ₂	0.33	0.73	0.49	-	$\alpha\text{-Fe}_2\text{O}_3$ (SPM)	87
	0.40	-0.21	0.47	51.8	$\alpha\text{-Fe}_2\text{O}_3$	13
Bulk Fe	0.33	0.72	0.51	-	$\alpha\text{-Fe}_2\text{O}_3$ (SPM)	67
	0.39	-0.23	0.48	51.6	$\alpha\text{-Fe}_2\text{O}_3$	33

* Mean magnetic hyperfine field.

Table S5.

Mössbauer parameters of spent Fe catalysts after 15 h of reaction at T=350°C, P=1 bar and H₂/CO ratio of 1. Experimental uncertainties: Isomer shift: IS \pm 0.01 mm.s⁻¹; Quadrupole splitting: QS \pm 0.01 mm.s⁻¹; Line width: Γ \pm 0.01 mm.s⁻¹; Hyperfine field: \pm 0.1 T; Spectral contribution: \pm 3%.

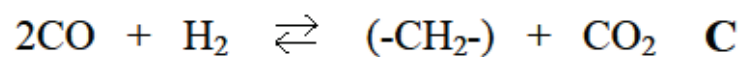
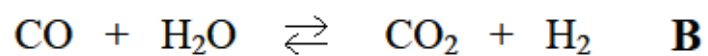
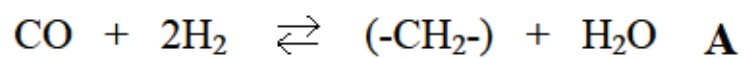
Sample	IS (mm.s ⁻¹)	QS (mm.s ⁻¹)	Γ (mm.s ⁻¹)	Hyperfine field (T)	Phase	Spectral Contribution (%)
Fe/CNF	0.21	-	0.71	16.4	χ -Fe ₅ C ₂ (I)	6
	0.28	-	0.71	20.3	χ -Fe ₅ C ₂ (II)	6
	0.23	-	0.71	10.1	χ -Fe ₅ C ₂ (III)	3
	0.31	0.74	0.71	-	Fe ³⁺	85
Fe/ α -Al ₂ O ₃	0.20	-	0.38	18.0	χ -Fe ₅ C ₂ (I)	31
	0.26	-	0.35	21.4	χ -Fe ₅ C ₂ (II)	28
	0.22	-	0.45	10.7	χ -Fe ₅ C ₂ (III)	20
	0.32	0.98	0.70	-	Fe ³⁺	21
Fe/ β -SiC	0.37	0.96	0.78	-	Fe ³⁺	66
	0.19	-	0.44	18.5	χ -Fe ₅ C ₂ (I)	14
	0.25	-	0.44	21.9	χ -Fe ₅ C ₂ (II)	13
	0.29	-	0.41	10.9	χ -Fe ₅ C ₂ (III)	7
Fe/SiO ₂	0.34	1.04	0.63	-	Fe ³⁺	100
Fe/ γ -Al ₂ O ₃	0.35	0.98	0.73	-	Fe ³⁺	90
	0.85	2.38	0.70	-	Fe ²⁺	10
Fe-Ti-Zn-K	0.23	-	0.77	18.1	χ -Fe ₅ C ₂ (I)	18
	0.28	-	0.72	21.7	χ -Fe ₅ C ₂ (II)	17
	0.24	-	0.41	11.5	χ -Fe ₅ C ₂ (III)	7
	0.44	0.50	0.55	-	Fe ³⁺	8
	0.70	2.00	0.53	-	Fe ²⁺	5
	0.30	-	0.58	46.9*	Fe ₃ O ₄ (I)	12
	0.68	-	0.54	44.1*	Fe ₃ O ₄ (II)	8
	0.57	-	2.01	36.6*	Fe ₃ O ₄ (II) [†]	25

* Mean magnetic hyperfine field; † Smear sextet.

Table S6.

Catalytic performance at 20 bar. Catalytic tests performed at 340°C and H₂/CO ratio of 1; results after 64 h on stream.

Sample	Total CO conversion (%)	CO ₂ (% of CO converted)	Chain growth probability α
Fe/CNF	88	42	0.39
Fe/ α -Al ₂ O ₃ (6 wt% Fe)	77	46	0.41
Fe/ α -Al ₂ O ₃ (12 wt% Fe)	81	41	0.39
Fe/ α -Al ₂ O ₃ (25 wt% Fe)	80	40	0.45
Fe/ β -SiC	77	42	0.25
Fe/ γ -Al ₂ O ₃	10	20	0.25
Fe-Ti-Zn-K	79	41	0.43
Fe-Cu-K-SiO ₂	79	37	0.47
Bulk Fe	97	34	0.45



Equation S1.

Reaction equations. **A**, General Fischer-Tropsch reaction. **B**, Water gas shift (WGS) reaction. **C**, Overall Fischer-Tropsch reaction valid on catalysts with WGS activity such as iron.

$$\ln \left(\frac{W_n}{n} \right) = n \ln \alpha + \ln \left[\frac{(1-\alpha)^2}{\alpha} \right]$$

Equation S2.

Anderson-Schulz-Flory model for the product distribution. n is the number of carbon atoms in a product; W_n is the weight fraction of a product with n number of carbon atoms; α is the chain growth probability and $1-\alpha$ is the probability of chain termination.