Electronic Supplementary Information (ESI)

Sintered precipitated iron catalysts with enhanced fragmentation-resistance ability for Fischer – Tropsch synthesis to lower olefins

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Table S1 The programmed temperatures for the calcination of catalysts.

Samples	T / ℃	t / min	T / ℃	t / min	T / ℃	t / min	T / ℃	t / min	T / ℃	t / min
500-calcin	20	30	120	30	120	190	500	300	500	
800-calcin	20	30	120	30	120	340	800	300	800	
1000-calcin	20	60	100	30	250	60	400	120	400	240
	1000	300	1000							
1200-calcin	20	60	100	30	250	60	400	120	400	240
	1000	200	1200	300	1200					
1400-calcin	20	60	100	30	250	60	400	120	400	240
	1000	200	1200	200	1400	300	1400			
1400-calcin-mix	20	60	100	30	250	60	400	120	400	240
	1000	200	1200	200	1400	300	1400			

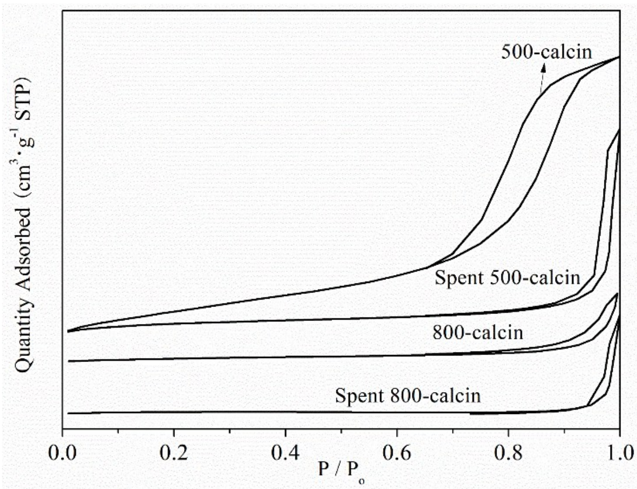

Fig. S1 N_2 adsorption–desorption isotherms of 500-calcin and 800-calcin, and spent 500-calcin and 800-calcin catalysts.

Table S2 Structural parameters of 500-calcin and 800-calcin, and spent 500-calcin and 800-calcin catalysts.

Sample	S_{BET} / $m^2 \cdot g^{-1}$	V_t / $cm^3 \cdot g^{-1}$	d_P / nm
500-calcin	59.84	0.15	9.91
800-calcin	6.77	0.02	--
Spent 500-calcin	16.70	0.03	--
Spent 800-calcin	5.23	0.01	--

Note: S_{BET} – surface area; V_t – total pore volume; d_P – average pore diameter.

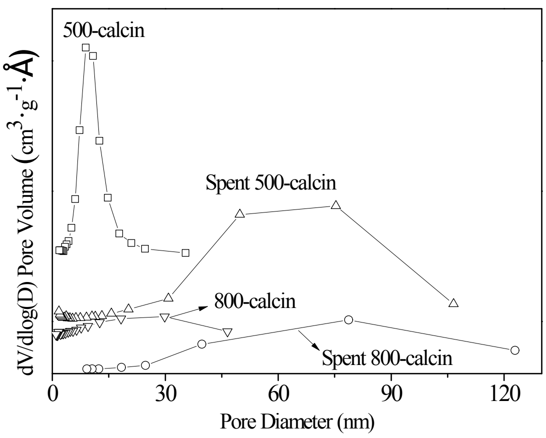

Fig. S2 Pore diameter distributions of 500-calcin and 800-calcin, and spent 500-calcin and 800-calcin catalysts.

Equations: (1) – (3).

$$\frac{1}{2}Fe_2O_3+\frac{1}{6}H_2 \rightleftharpoons \frac{1}{3}Fe_3O_4+\frac{1}{6}H_2O \qquad (1)$$

$$\frac{1}{3}Fe_3O_4+\frac{1}{3}H_2 \rightleftharpoons FeO+\frac{1}{3}H_2O \qquad (2)$$

$$FeO+H_2 \rightleftharpoons Fe+H_2O \qquad (3)$$

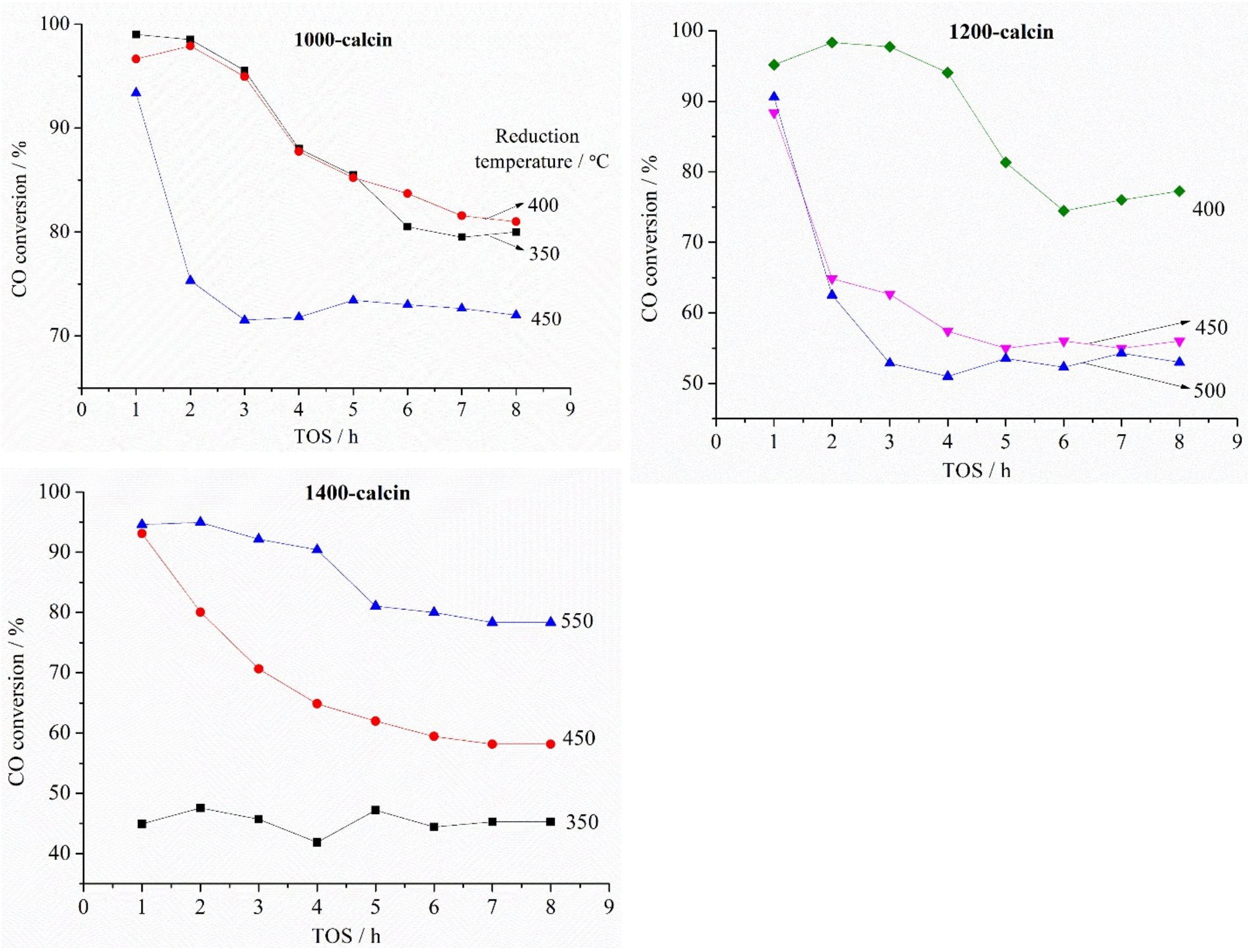

Fig. S3 CO conversion VS TOS of 1000-calcin, 1200-calcin, and 1400-calcin catalysts. (Reaction conditions: H_2 / CO = 1; 1.5 MPa; 310℃; GHSV = 4000 h^{-1}.).

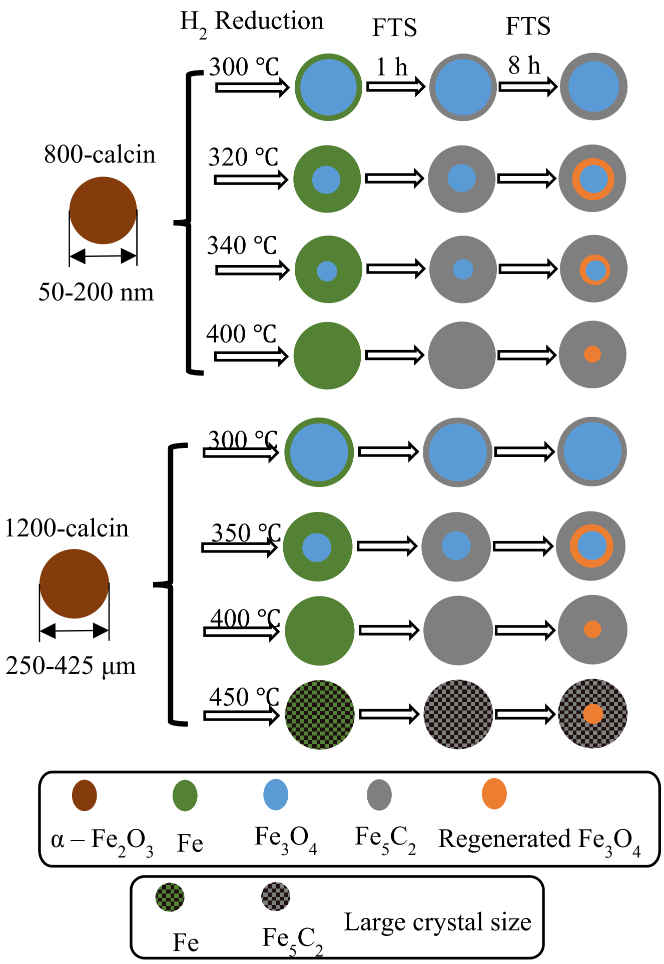

Fig. S4 Schematic evolution of various iron species of 800-calcin and 1200-calcin catalysts during reduction and Fischer Tropsch synthesis (FTS).

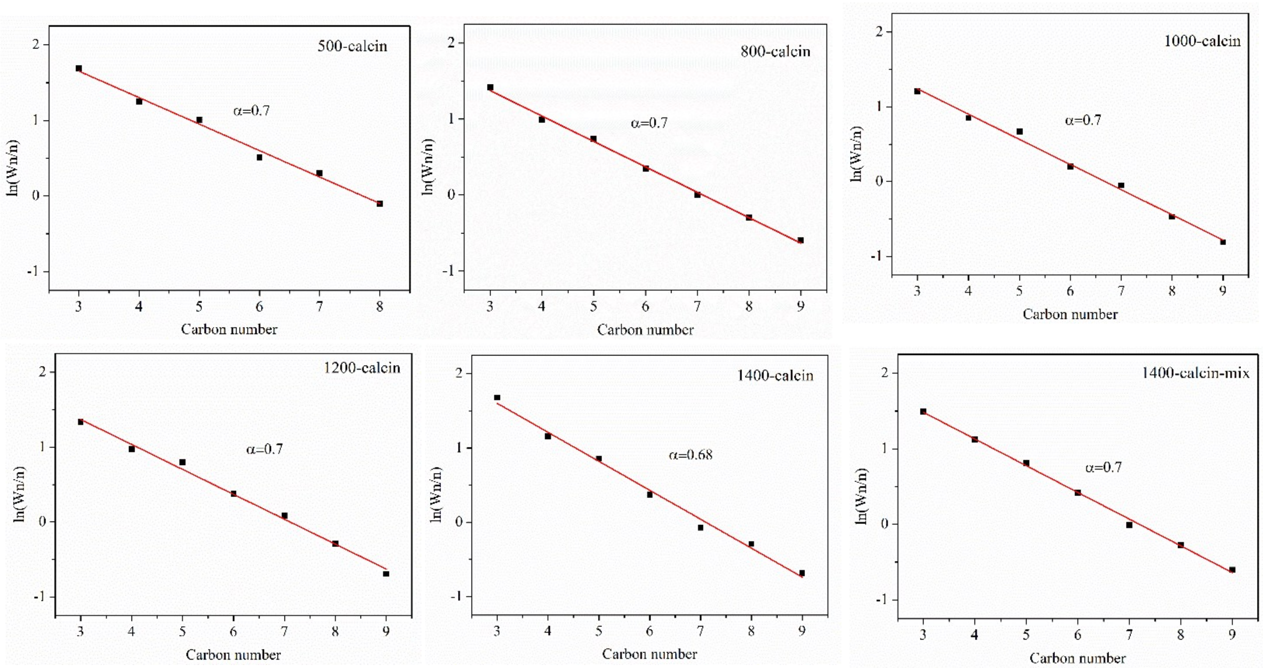

Fig. S5 Chain growth probability of catalysts. (Anderson-Schulz-Flory chain growth mechanism is described as: W_n / n = $(1-\alpha)^2\alpha^{n-1}$. Where n is the number of carbon atoms in the product, W_n is the weight fraction of a product with n number of carbon atoms; α is the overall chain growth probability. Reduction conditions: H_2; 12 h; GHSV = 4000 h^{-1}, 500-calcin: 300°C, 800-calcin, 1000-calcin, and 1200-calcin: 400°C, 1400-calcin and 1400-calcin-mix: 450°C. Reaction conditions: H_2 / CO = 1; 1.5 MPa; TOS = 8 h; 310°C; GHSV = 4000 h^{-1}.).

Table S3 Production distributions of traditional and sintered precipitated iron catalysts.

Catalysts	Reduction temperatures	X_{CO} / % [a]	S_{CO2} / % [b]	CH distribution / %				α [c]
				CH_4	$C_2^=–C_4^=$	$C_5–C_{11}$	$C_{12}+$	
500-calcin	300	97.7	29.3	15.0	23.9	43.9	9.6	0.70
800-calcin	400	92.1	26.5	11.7	29.8	46.5	7.6	0.70
1000-calcin	400	81.6	27.1	10.3	30.1	48.7	5.8	0.70
1200-calcin	400	77.3	27.9	10.3	29.4	49.0	6.1	0.70
1400-calcin	450	58.2	25.7	13.5	26.7	41.1	9.1	0.68
1400-calcin-mix	450	64.5	26.8	10.8	28.9	47.2	6.2	0.70

[a] X_{CO} denotes CO conversion. Reduction conditions: H_2; 12 h; GHSV = 4000 h^{-1}, 500-calcin and 500-calcin-1: 300°C, 800-calcin, 1000-calcin, and 1200-calcin: 400°C, 1400-calcin and 1400-calcin-mix: 450°C. Reaction conditions: H_2 / CO = 1; 1.5 MPa; TOS = 8 h; 310°C; GHSV = 4000 h^{-1}. [b] S_{CO2} denotes CO_2 selectivity. [c] α was calculated from Schulz-Flory equation between C_3 and C_9.

Table S4 Catalytic results from literatures on bulk iron-based catalysts.

<table>
<tr><td colspan="3">REF.</td><td>[1]</td><td>[2]</td><td colspan="2">[3]</td></tr>
<tr><td colspan="3" rowspan="2">Catalyst</td><td rowspan="2">100Fe33Mn4K[a]</td><td rowspan="2">bulk Fe[b]</td><td>LTFT</td><td>HTFT</td></tr>
<tr><td>Precipitated Fe[c]</td><td>Fused Fe[c]</td></tr>
<tr><td colspan="3">Reaction temperature / °C</td><td>320</td><td>340</td><td>240</td><td>340</td></tr>
<tr><td colspan="3">X_{CO} / %</td><td>98</td><td>97</td><td>--</td><td>--</td></tr>
<tr><td colspan="3">S_{CO2} / %</td><td>30</td><td>34</td><td>--</td><td>--</td></tr>
<tr><td rowspan="4">CH / %</td><td colspan="2">CH_4</td><td>15</td><td>30</td><td>4</td><td>7</td></tr>
<tr><td colspan="2">$C_2^= - C_4^=$</td><td>26</td><td>32</td><td>6</td><td>24</td></tr>
<tr><td rowspan="2">C_5+</td><td>$C_5 - C_{11}$</td><td rowspan="2">54</td><td rowspan="2">14</td><td rowspan="2">76.5</td><td>36</td></tr>
<tr><td>C_{12}+</td><td>21</td></tr>
<tr><td colspan="3">O / P ($C_2 - C_4$)</td><td>5</td><td>1.8</td><td>2.4</td><td>4</td></tr>
<tr><td colspan="3">α</td><td>--</td><td>0.45</td><td>0.95</td><td>0.7</td></tr>
</table>

[a] Reaction conditions: $H_2/CO = 2$, P = 1.5 MPa, GHSV = 1000 h^{-1}.

[b] Reaction conditions: $H_2/CO = 1$, P = 2 MPa, GHSV = 1500 h^{-1}.

[c] Industrial catalysts in SASOL.

Table S5 Combustion temperatures and weight losses of TG degradation.

Samples	Combustion temperatures / °C			Weight losses / %			
	First stage	Second stage	Third stage	First stage	Second stage	Third stage	Total
500-calcin	260 - 314	314 - 370	370 - 409	4.5	19.5	17.8	41.8
800-calcin	275 - 341	341 - 400	400 - 452	12.8	8.7	9.5	31.0
1200-calcin	250 - 340	340 - 440	440 - 473	2.8	6.0	3.7	12.5

References

[1] J. L. Zhang, L. H. Ma, S. B. Fan, T. S. Zhao and Y. H. Sun, *Fuel*, 2013, **109**, 116-123.

[2] H. M. T. Galvis and K. P. D. Jong, *Science*, 2012, **4**, 835-838.

[3] M. E. Dry, *Journal of Chemical Technology & Biotechnology*, 2002, **77**, 43–50.