catalysts

Supplementary Materials

Iron Based Core-shell Structures as Versatile Materials: Magnetic Support & Solid Catalyst

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Table S1. Average core size of as-made Fe@SiO_2 core-shell particles and the respective SiO_2 shell thickness measured from TEM micrographs; iron content and specific surface area calculated from measured values.

Material	Fe-oxide core size	shell thickness	iron content	specific Fe surface area
	$\bar{d}_{core}$ / nm	$\bar{d}_{shell}$ / nm	w_{Fe} / wt%	a_{Fe} / m² g⁻¹
6Fe(4)@SiO_2	4.2 ± 1.1	4.8 ± 0.4	6	352
a-13Fe(4)@SiO_2	4.3 ± 1.1	3.3 ± 0.6	13	344
b-13Fe(4)@SiO_2	4.3 ± 1.1	3.4 ± 0.6	13	344
15Fe(4)@SiO_2	4.2 ± 1.0	3.1 ± 0.7	15	352
20Fe(4)@SiO_2	4.3 ± 1.2	2.7 ± 0.9	20	343
15Fe(6)@SiO_2	5.8 ± 0.9	3.8 ± 0.4	15	254
a-34Fe(6)@SiO_2	5.7 ± 0.9	2.2 ± 0.6	34	259
b-34Fe(6)@SiO_2	5.8 ± 0.9	2.1 ± 0.7	34	255
42Fe(6)@SiO_2	5.7 ± 0.9	1.8 ± 0.8	42	259
13Fe(8)@SiO_2	7.8 ± 1.1	6.1 ± 0.6	13	189
20Fe(8)@SiO_2	7.7 ± 1.5	5.1 ± 0.3	20	192
37Fe(8)@SiO_2	8.0 ± 1.2	3.2 ± 0.9	37	185
46Fe(8)@SiO_2	7.8 ± 1.1	2.2 ± 1.0	46	188

Table S2. Mass of surfactants, concentration of $FeCl_3$ solution and volume of TEOS for defined synthesis of Fe based core-shell particles.

Material	Fe core size	Mass Brij C10	Mass Brij 58	Mass $FeCl_3$	Concentration $FeCl_{3,\,aq}$	Volume TEOS	hydrolyzation time	metal loading
	$\bar{d}_{\mathrm{Fe}}$ / nm	m_{C10} / g	m_{58} / g	m_{FeCl3} / g	c / mol L^{-1}	V_{TEOS} / mL	t / h	w_{grav} / wt%
6Fe(4)@SiO_2	4	34.2	--	0.6755	0.5	21.4	2	6.5
a-13Fe(4)@SiO_2	4	34.2	--	0.6755	0.5	10.7	2	13
b-13Fe(4)@SiO_2	4	34.2	--	0.6755	0.5	21.4	1	13
15Fe(4)@SiO_2	4	34.2	--	0.6755	0.5	17.8	1	15
20Fe(4)@SiO_2	4	34.2	--	0.6755	0.5	14.3	1	18
15Fe(6)@SiO_2	6	34.2	--	1.351	1	21.4	2	16
a-34Fe(6)@SiO_2	6	34.2	--	1.351	1	10.7	2	34
b-34Fe(6)@SiO_2	6	34.2	--	1.351	1	21.4	1	34
42Fe(6)@SiO_2	6	34.2	--	1.351	1	14.3	1	42
13Fe(8)@SiO_2	8	--	56.3	1.351	1	21.4	2	13
20Fe(8)@SiO_2	8	--	28.1	1.351	1	21.4	2	20
37Fe(8)@SiO_2	8	--	28.1	2.702	2	21.4	2	37
46Fe(8)@SiO_2	8	--	28.1	2.702	2	32.1	2	46

Table S3. Derivation Equation (3): specific surface area of Fe cores a_{Fe} derived from Fe_2O_3 core diameter d_{c} (measured via TEM).

Molar amount of spherical Fe cores	$n_{\mathrm{Fe}}=\frac{m_{\mathrm{Fe}}}{M_{\mathrm{Fe}}}=\frac{V_{\mathrm{Fe}}\rho_{\mathrm{Fe}}}{M_{\mathrm{Fe}}}=\frac{\pi}{6}d_{\mathrm{Fe}}^{3}\frac{\rho_{\mathrm{Fe}}}{M_{\mathrm{Fe}}}$
Molar amount of spherical Fe_2O_3 cores	$n_{\mathrm{Fe_2O_3}}=\frac{\pi}{6}d_{\mathrm{c}}^{3}\frac{\rho_{\mathrm{Fe_2O_3}}}{M_{\mathrm{Fe_2O_3}}}$
Material balance (molar basis) before and after reduction	$n_{\mathrm{Fe}}=2\,n_{\mathrm{Fe_2O_3}}$
Fe core diameter d_{Fe} as a function of Fe_2O_3 core diameter d_{c} from material balance	$d_{\mathrm{Fe}}=d_{\mathrm{c}}\left(2\frac{M_{\mathrm{Fe}}}{M_{\mathrm{Fe_2O_3}}}\frac{\rho_{\mathrm{Fe_2O_3}}}{\rho_{\mathrm{Fe}}}\right)^{-\frac{1}{3}}$
Specific surface area of reduced Fe cores	$a_{\mathrm{Fe}}=\frac{A_{\mathrm{Fe}}}{m_{\mathrm{Fe}}}=\frac{6}{d_{\mathrm{Fe}}}\frac{1}{\rho_{\mathrm{Fe}}}=\left(2\frac{M_{\mathrm{Fe}}}{M_{\mathrm{Fe_2O_3}}}\frac{\rho_{\mathrm{Fe_2O_3}}}{\rho_{\mathrm{Fe}}}\right)^{-\frac{1}{3}}\frac{6}{d_{\mathrm{c}}\,\rho_{\mathrm{Fe}}}$
Density of Fe_2O_3 core	ρ_{c} = 5240 kg m^{-3}
Density of Fe core	ρ_{Fe} = 7870 kg m^{-3}
Molar mass of Fe_2O_3 core	$M_{\mathrm{Fe_2O_3}}$ = 159.7 g mol^{-1}
Molar mass of Fe core	M_{Fe} = 55.8 g mol^{-1}
Main assumptions	– cores consist of one single spherical particle – as made core consists of Fe_2O_3 only – bulk density applies for nanoparticles

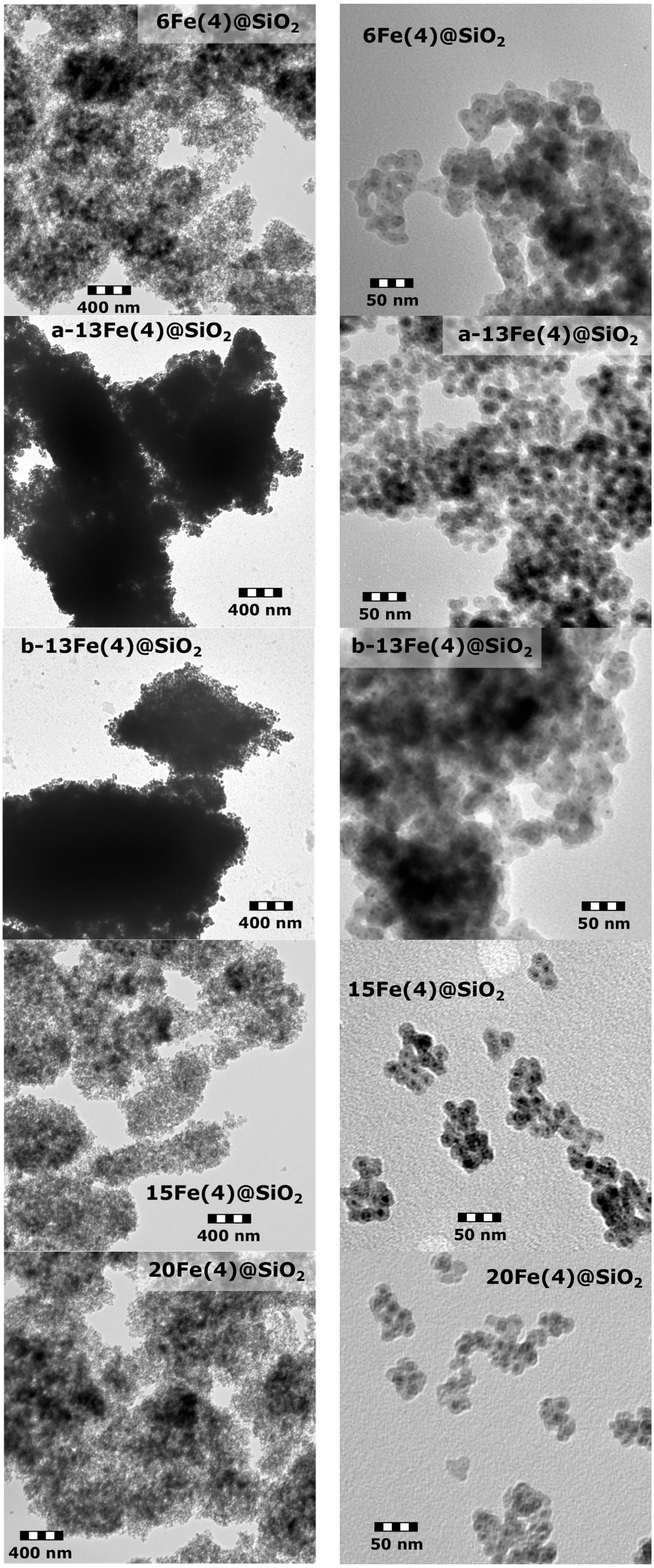

Figure S1. TEM micrographs of as-made core-shell particles with an average core diameter of 4 nm; left: overview micrographs; right: detail micrographs.

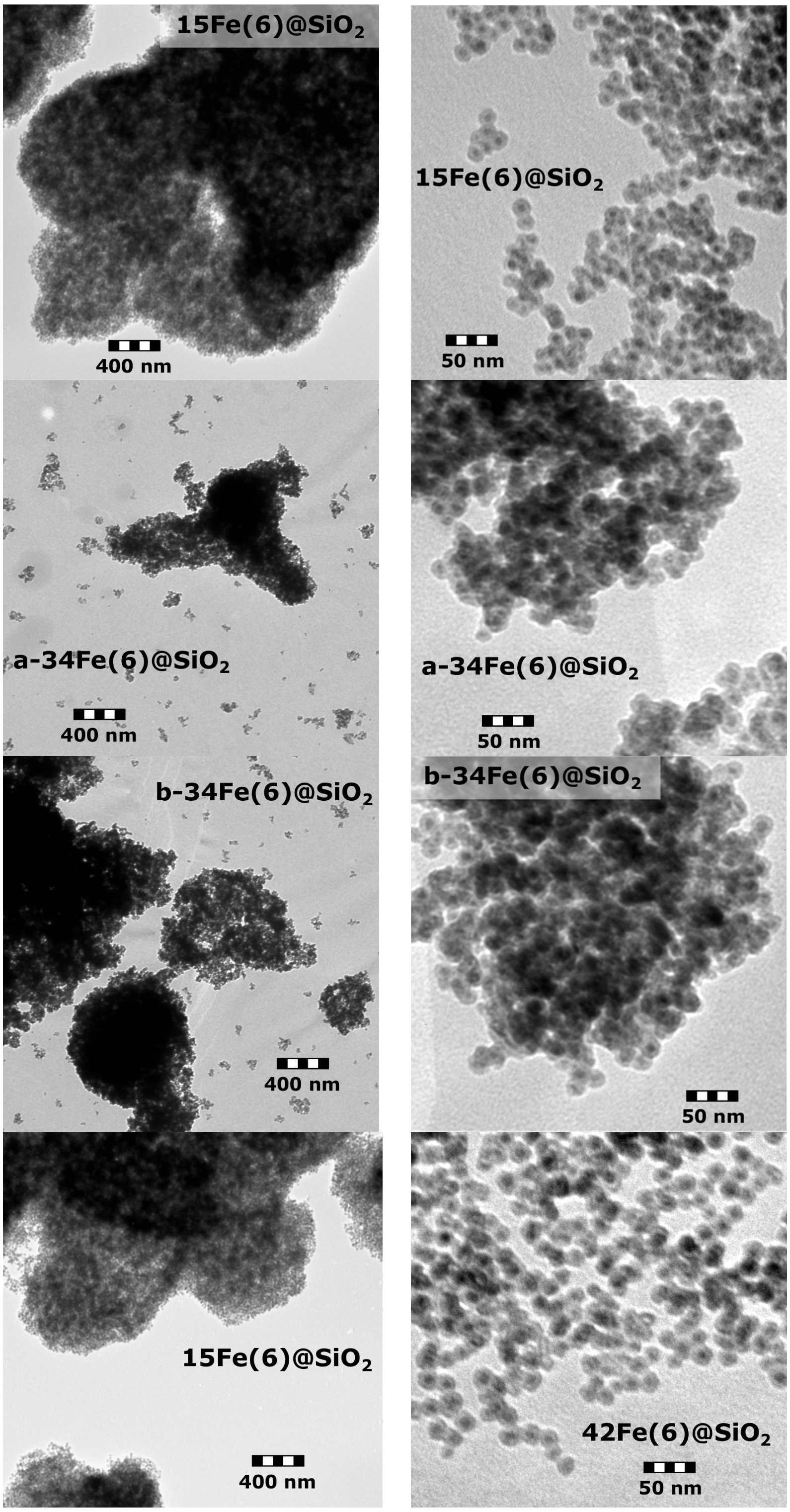

Figure S2. TEM micrographs of as-made core-shell particles with an average core diameter of 6 nm; left: overview micrographs; right: detail micrographs.

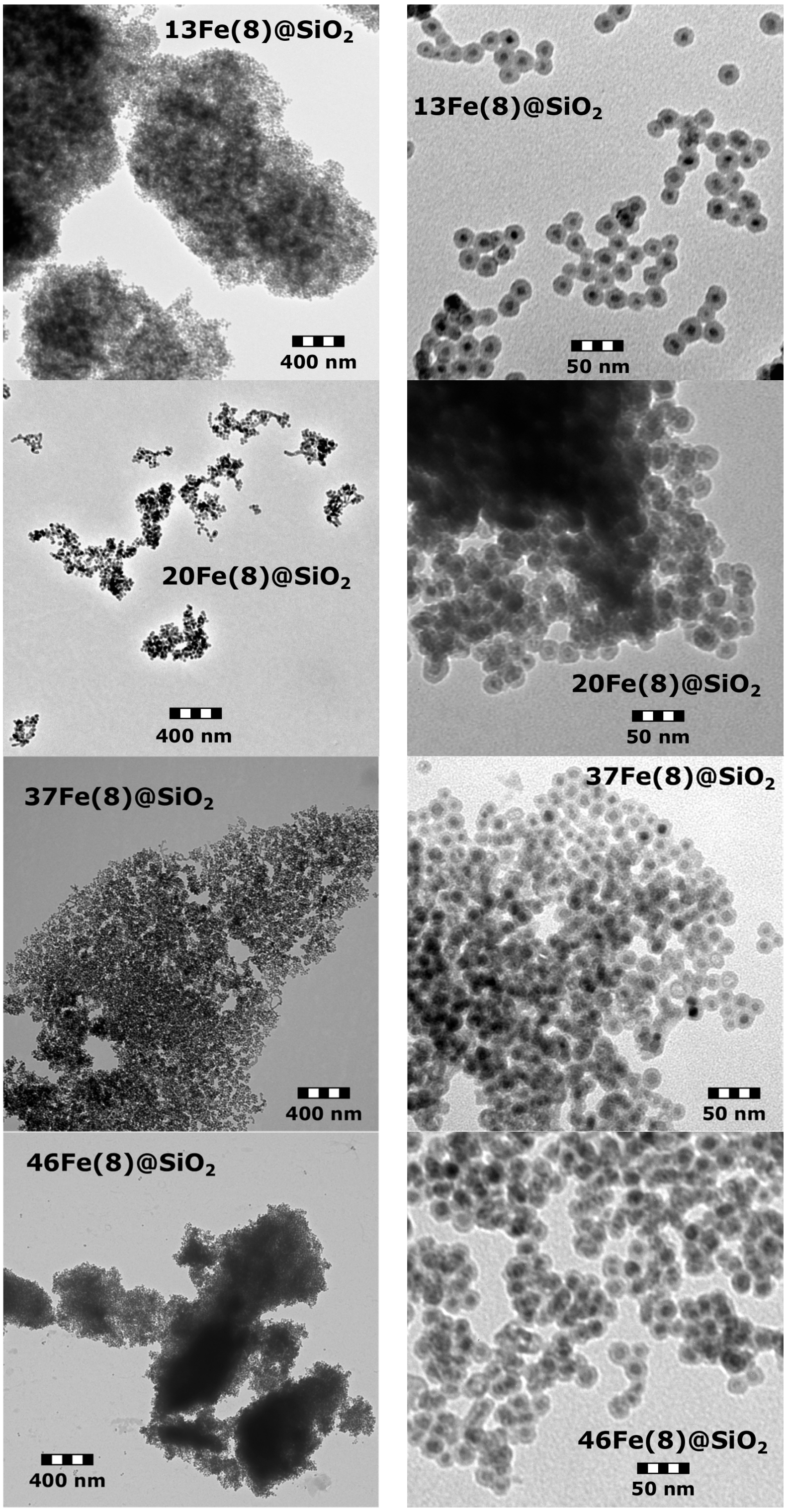

Figure S3. TEM micrographs of as-made core-shell particles with an average core diameter of 8 nm; left: overview micrographs; right: detail micrographs.

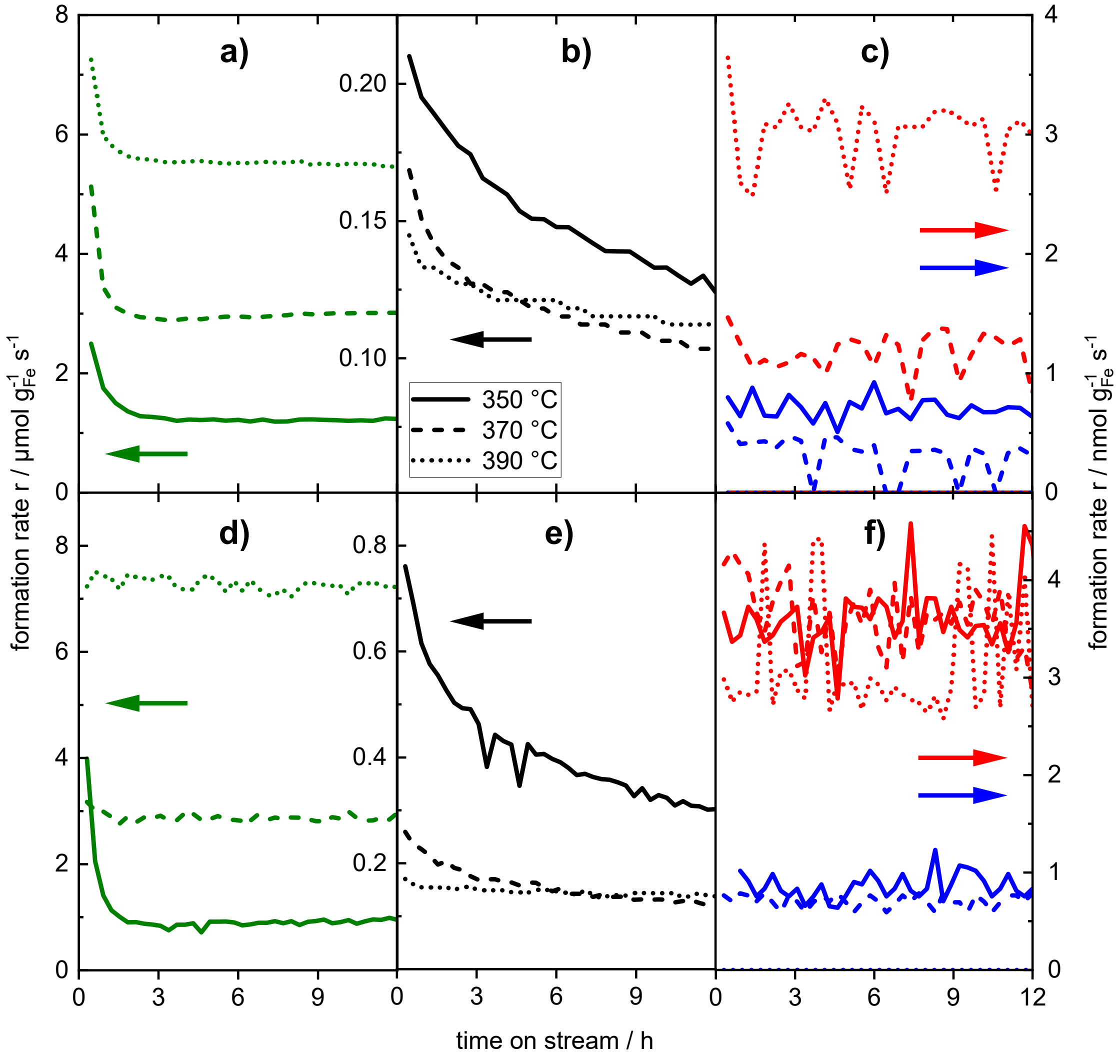

Figure S4. Time resolved product formation rates during CO_2 hydrogenation on 13Fe(8)@SiO_2 (top) with CO (**a**), CH_4 (**b**), C_2H_4 (**c**, red), and C_{3+} (**c**, blue) and 15Fe(4)@SiO_2 (bottom) with CO (**d**), CH_4 (**e**), C_2H_4 (f, red) and C_{3+} (**f**, blue).

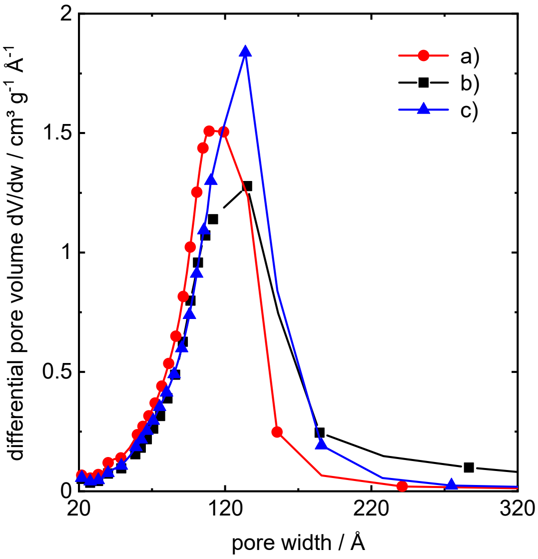

Figure S5. Pore size distribution for corresponding mesopore regime ($p/p^0 > 0.5$) calculated from desorption isotherm using Barrett-Joyner-Halenda (BJH) method.

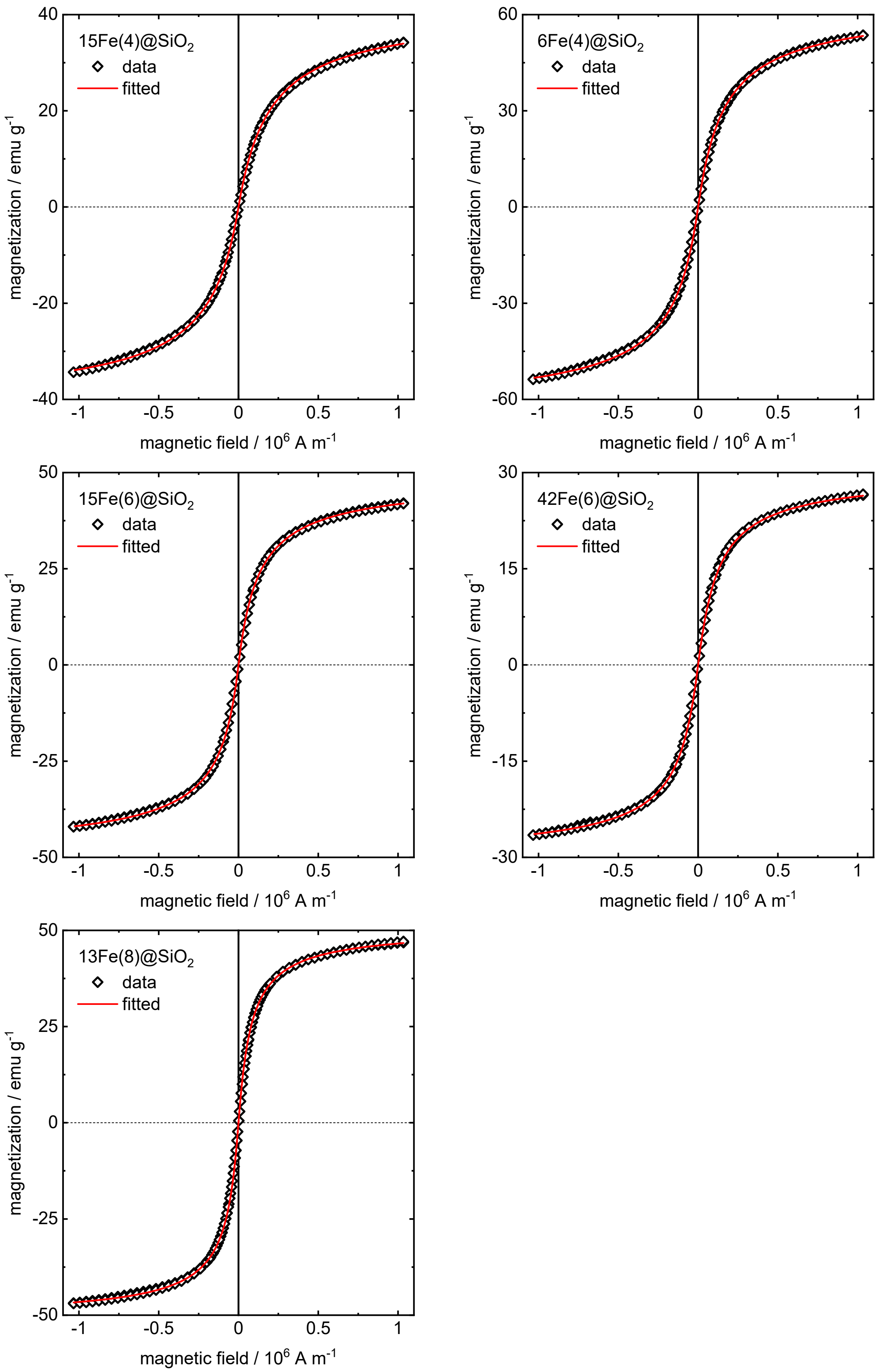

Figure S6. *M*-*H* curves of as-made Fe@SiO_2 core-shell particles measured by vibrating sample magnetometer (VSM) together with fitted curves with a superposition of Langevin functions.

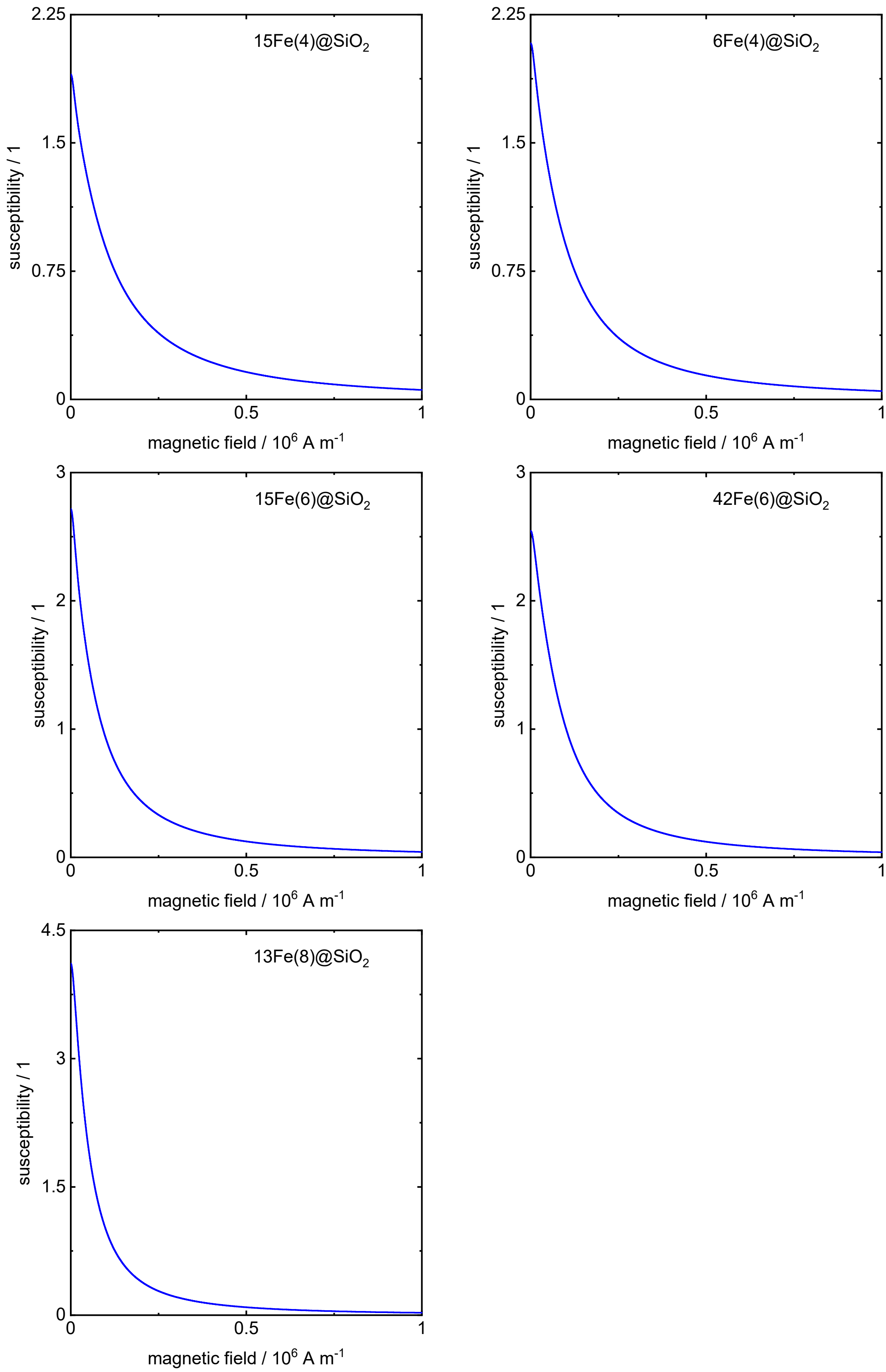

Figure S7. Core magnetic susceptibility vs external magnetic fields of as-made Fe@SiO_2 core-shell particles fitted from the corresponding M-H curve with a superposition of Langevin functions.