Electronic Supplementary Information

Influence of Copper and Potassium on the Structure and Carbidisation of Supported Iron Catalysts for Fischer-Tropsch Synthesis

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Table S1. Mössbauer parameters

Catalyst	Iron forms	δ, mm/s	Δ, mm/s	Γ, mm/s	H, kOe	A, %	χ^2
15% Fe	Fe 1	0.34(4)	0.90(14)	0.73(18)		6	1.5
	Fe 2	0.29(10)	0.48(18)	0.62		4	
	Fe 3	0.59(4)		0.37(8)		2	
	Fe 4				501.1(3)	88	1.5
15% Fe	Fe 1	0.30(1)	0.93(7)	0.54(8)		13	1.0
1% K	Fe 2	0.35(1)	0.46(4)	0.39(5)		9	
	Fe 3						
	Fe 4				502.0(4)	78	1.2
15% Fe	Fe 1	0.296(8)	0.90(2)	0.51(3)		16	
1% K	Fe 2	0.340(5)	0.56(1)	0.45(2)		25	
1% Cu	Fe 3		0.1(9)			4	
	Fe 4				493.7(2)	55	4.3
15% Fe	Fe 1	0.336(7)	0.91(1)	0.58(3)		22	1.4
1% Cu	Fe 2	0.367(6)	0.47(2)	0.39(3)		13	
	Fe 3						
	Fe 4				504.7(5)	65	2.3

The errors in the last digits are given in parentheses. δ is the isomer shift. Δ is the quadrupole splitting. H is the magnetic hyperfine field. Γ is the full line width at half maximum. A is relative area of spectral component, representing the relative content of the corresponding Fe species assuming a common recoilless fraction for all iron species in a sample and χ^2 is the deviation.

Table S2. Effective activation energies, pre-exponential factors and calculated rate constants for Fe_2O_3 reduction to Fe_3O_4 in CO and syngas

Catalyst	Reduction by CO						Reduction by H_2/CO					
	α=0.1			α=0.8			α=0.1			α=0.8		
	E, kJ/mol	k_0, s^{-1}	K, $gm^{-2}s^{-1}$ *	E, kJ/mol	k_0, s^{-1}	K, $gm^{-2}s^{-1}$ *	E, kJ/mol	k_0, s^{-1}	K, $gm^{-2}s^{-1}$ *	E, kJ/mol	k_0, s^{-1}	K, $gm^{-2}s^{-1}$ *
Fe	118.9	$6.19\ 10^8$	$9.3\ 10^{-3}$	197.0	$2.55\ 10^{15}$	$2.9\ 10^{-3}$	74.4	$1.13\ 10^5$	$1.9\ 10^{-2}$	55.3	$7.68\ 10^2$	$7.0\ 10^{-3}$
FeCu	83.6	$4.81\ 10^5$	$1.0\ 10^{-2}$	104.9	$1.69\ 10^7$	$4.1\ 10^{-3}$	73.8	$1.63\ 10^5$	$2.8\ 10^{-2}$	80.4	$3.26\ 10^5$	$1.5\ 10^{-2}$
FeK	104.0	$4.84\ 10^6$	$1.3\ 10^{-3}$	186.6	$4.59\ 10^{13}$	$3.6\ 10^{-4}$	95.9	$1.50\ 10^6$	$2.3\ 10^{-3}$	107.4	$1.03\ 10^7$	$1.4\ 10^{-3}$
FeCuK	97.9	$1.00\ 10^7$	$0.9\ 10^{-2}$	143.4	$5.87\ 10^{10}$	$3.6\ 10^{-3}$	96.2	$1.75\ 10^7$	$2.2\ 10^{-2}$	125.0	$2.72\ 10^9$	$8.0\ 10^{-3}$

* the rate constants are calculated for the temperature of 288°C (in CO) and at 312 °C (in syngas)

Table S3. Effective activation energies, pre-exponential factors and calculated rate constants for carbidisation ($Fe_3O_4 \rightarrow$ x-Fe_5C_2) in CO and syngas

Catalyst	In the presence of CO						In the presence of H_2/CO					
	α=0.1			α=0.6			α=0.1			α=0.6		
	E, kJ/mol	k_0, s^{-1}	K, $gm^{-2}s^{-1}$ *	E, kJ/mol	k_0, s^{-1}	K, $gm^{-2}s^{-1}$ *	E, kJ/mol	k_0, s^{-1}	K, $gm^{-2}s^{-1}$ *	E, kJ/mol	k_0, s^{-1}	K, $gm^{-2}s^{-1}$ *
Fe	69.8	$2.47\ 10^{2}$	$1.1\ 10^{-4}$	96.9	$5.99\ 10^{3}$	$8.7\ 10^{-6}$	99.0	$2.52\ 10^{5}$	$2.3\ 10^{-4}$	103.0	$2.83\ 10^{5}$	$1.1\ 10^{-4}$
FeCu	86.0	$2.19\ 10^{4}$	$2.8\ 10^{-4}$	110.9	$7.68\ 10^{5}$	$5.3\ 10^{-5}$	49.6	$3.13\ 10^{1}$	$1.4\ 10^{-3}$	48.2	$1.42\ 10^{1}$	$5.2\ 10^{-4}$
FeK	105.8	$8.77\ 10^{5}$	$1.7\ 10^{-4}$	165.9	$1.98\ 10^{10}$	$1.2\ 10^{-5}$	68.3	$6.13\ 10^{2}$	$3.1\ 10^{-4}$	85.2	$6.37\ 10^{3}$	$9.0\ 10^{-5}$
FeCuK	117.6	$2.17\ 10^{7}$	$4.3\ 10^{-4}$	148.9	$4.27\ 10^{9}$	$8.3\ 10^{-5}$	93.8	$3.24\ 10^{5}$	$6.8\ 10^{-4}$	131.0	$1.74\ 10^{8}$	$1.7\ 10^{-4}$

* the rate constants are calculated for the temperature of 410 °C