Supplementary Information

Highly Activated K-Doped Iron Carbide Nanocatalysts Designed by Computational Simulation for Fischer-Tropsch Synthesis

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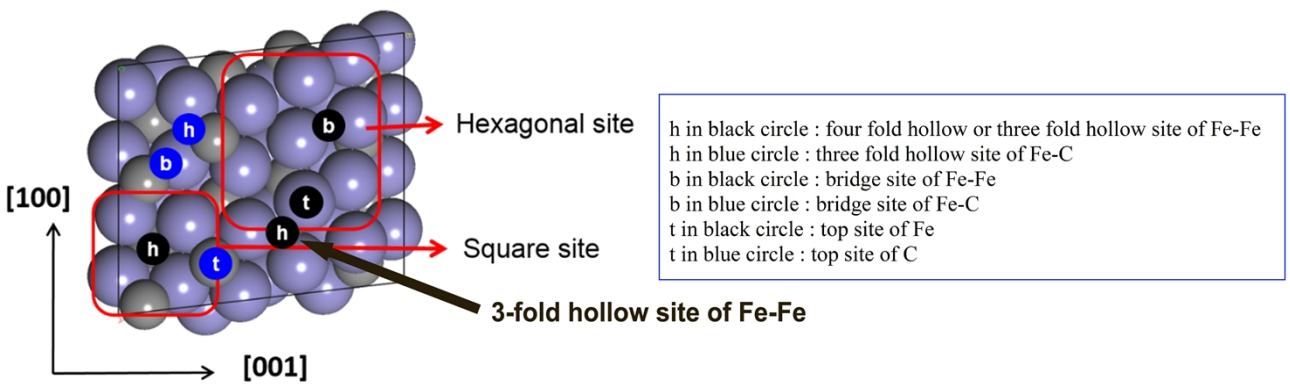

Fig. S1 K-free Hägg-carbide (χ-Fe_5C_2) model of a 1x2 super-cell in top view.

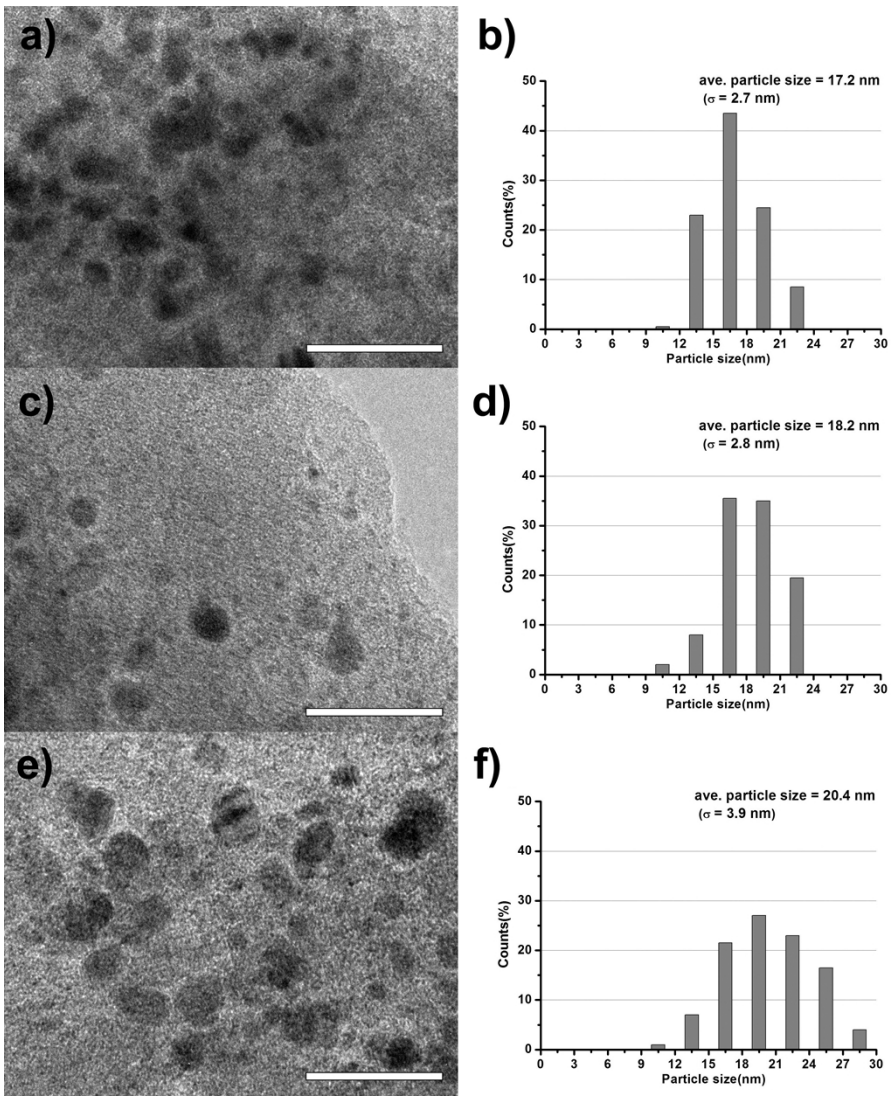

Fig. S2 TEM images and particle size distribution histograms of K-doped χ-Fe_5C_2 nanoparticles on activated charcoal: (a-b) K/Fe = 0.025, (c-d) K/Fe = 0.050, (e-f) K/Fe = 0.100. More than 200 particles were counted for each sample. All bars represent 50 nm.

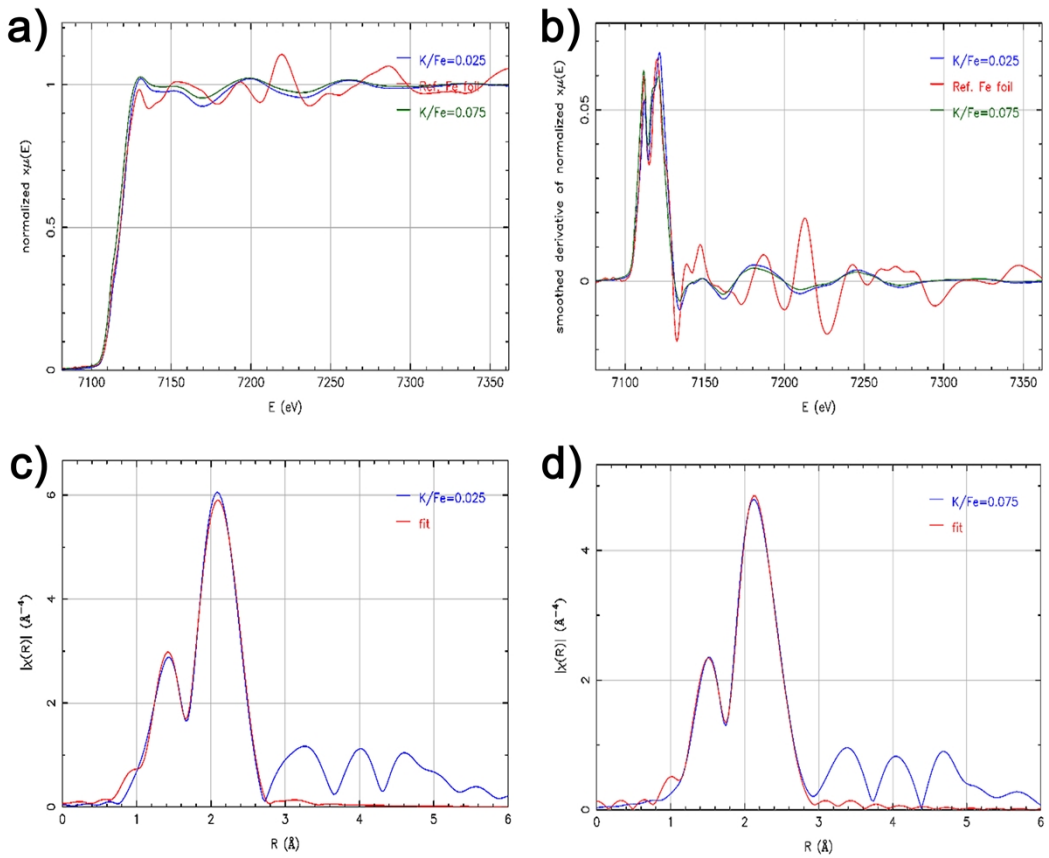

Fig. S3 (a) Normalized Fe K-edge X-ray absorption spectra, (b) derivative of normalized absorption coefficient, and (c-d) Fe K-edge EXAFS spectra for K-doped χ-Fe_5C_2 on activated charcoal at K/Fe = 0.025 and K/Fe = 0.075.

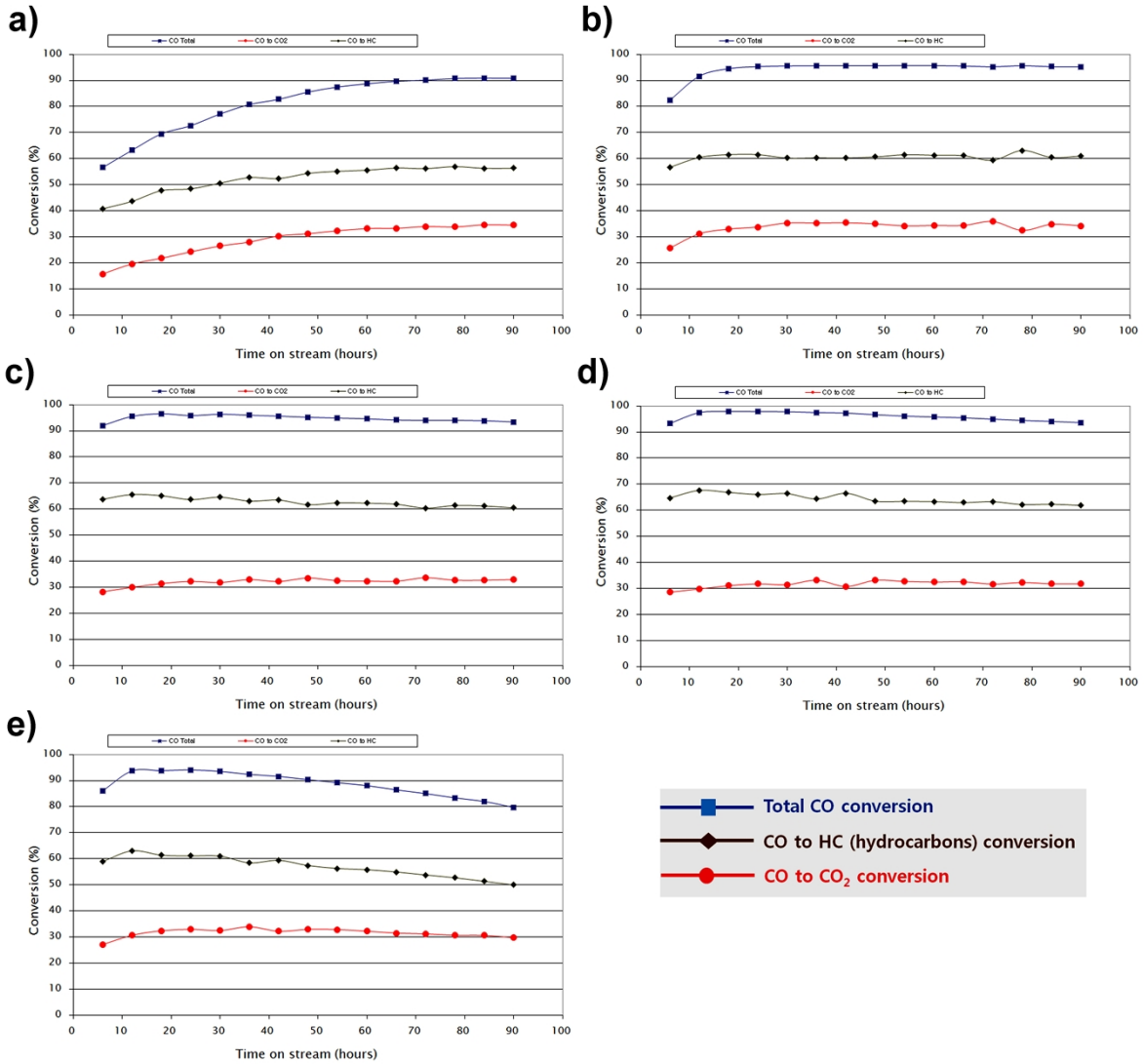

Fig. S4 CO conversion data for K-free and K-doped χ-Fe_5C_2/charcoal catalysts. (a) K-free Fe_5C_2, (b) K/Fe = 0.025, (c) K/Fe = 0.050, (d) K/Fe = 0.075, (e) K/Fe = 0.100.

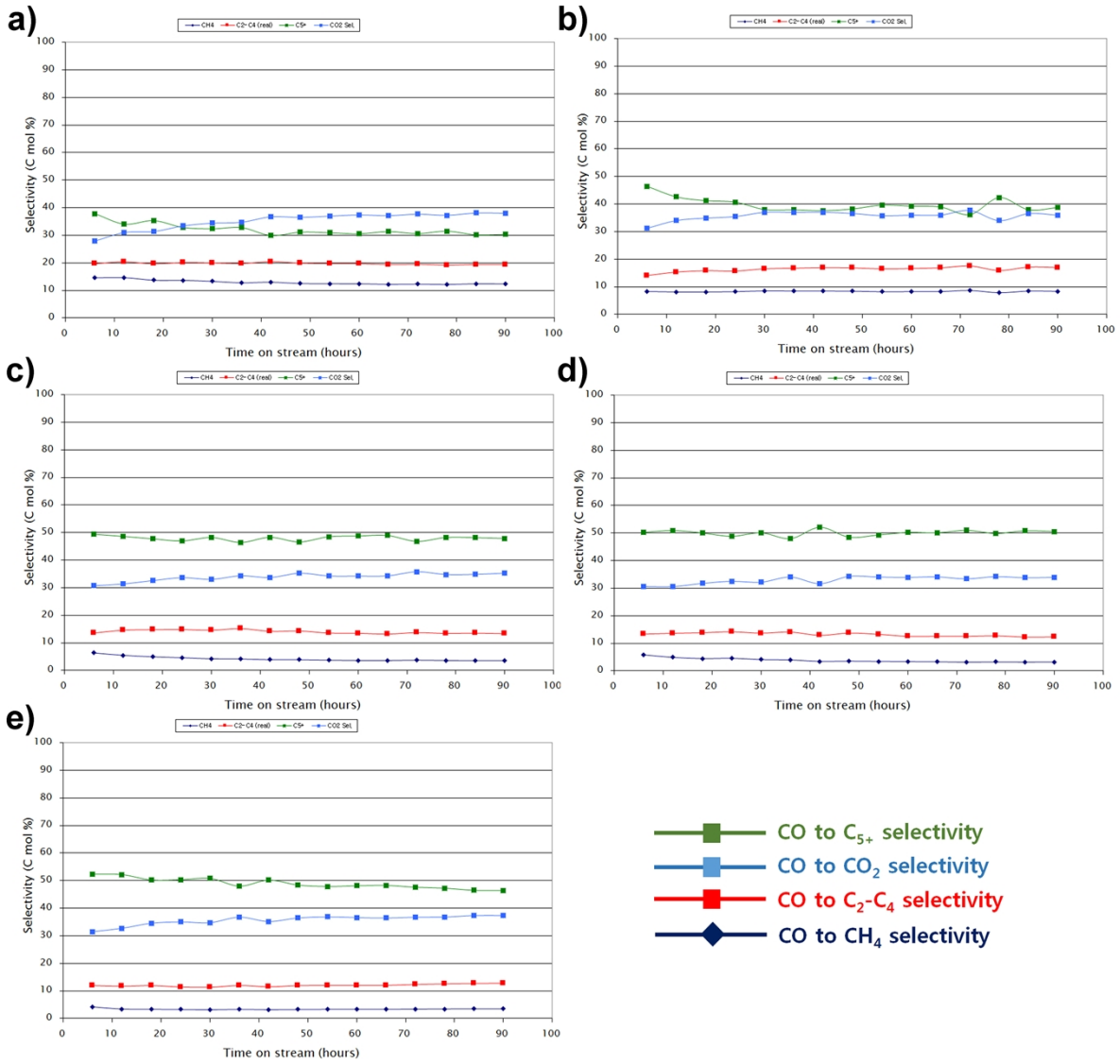

Fig. S5 CO_2 and hydrocarbon product selectivity data for K-free and K-doped χ-Fe_5C_2/charcoal catalysts. (a) K-free Fe_5C_2, (b) K/Fe = 0.025, (c) K/Fe = 0.050, (d) K/Fe = 0.075, (e) K/Fe = 0.100.

Table S1 Calculated adsorption energies (E_{ad}) and Bader charges (q) for the potassium atom located on the various adsorption sites of Hägg-carbide model.

Site		E_{ad} [eV]	$q_K(\Delta e)$
Fe-terminated	4-fold hollow	-2.45	0.82
	3-fold hollow	-2.48	0.86
	Fe-Fe bridge	-2.45	0.82
	Fe top	-2.21	0.78
C-terminated	3-fold hollow	-2.37	0.80
	Fe-C bridge	-2.45	0.82
	C top	-2.46	0.81

Table S2 Mössbauer parameters of K-free χ-Fe_5C_2/charcoal catalyst.

Temperature (K)		site			
		χ-Fe_5C_2			Fe_2O_3
		I (8f)	II (8f)	III (4e)	
4.2	H_{hf} (kO$_e$)	255.45	216.03	126.63	530.35
	δ (mm/s)	0.26	0.16	0.21	0.41
	E_Q (mm/s)	0.02	0.02	0.01	0.11
	Area (%)	35.38	34.32	17.92	12.38
295	H_{hf} (kO$_e$)	218.39	183.23	109.59	-
	δ (mm/s)	0.14	0.04	0.06	0.19
	E_Q (mm/s)	0.02	0.01	0.04	0.79
	Area (%)	33.17	36.65	17.74	12.44

H_{hf}: hyperfine magnetic field; δ: isomer shift (all the isomer shifts are referred to α-Fe at 295K); E_Q: quadrupole shift.

Table S3. Hydrocarbon product distributions (wt%) for each sample.

Catalyst / Product	K-free	K/Fe = 0.025	K/Fe = 0.050	K/Fe = 0.075	K/Fe = 0.100
CH_4	38.5	23.8	11.5	10.6	9.1
lower (C_2-C_4) olefins	10.2	15.7	24.7	23.8	23.1
lower (C_2-C_4) paraffins	43.8	26.7	8.9	7.8	5.0
C_5-C_{12} (gasoline)	5.3	27.8	34.5	34.4	33.9
C_{13}-C_{18} (diesel)	1.4	4.1	10.4	11.6	13.0
C_{19+} (wax)	0.8	2.0	10.0	11.8	15.9