Supporting Information

Iron–Potassium on Single-Walled Carbon Nanotubes as Efficient Catalyst for CO_2 Hydrogenation to Heavy Olefins

Shunwu Wang,[†] Tijun Wu,[†] Jun Lin,[‡] Yushan Ji,[†] Shirun Yan,[†] Yan Pei,[†] Songhai Xie,*[,†] Baoning Zong,[§] Minghua Qiao*[,†]

[†]Collaborative Innovation Center of Chemistry for Energy Materials, Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200438, P. R. China

[‡]Key Laboratory of Nuclear Analysis Techniques, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, P. R. China

[§]State Key Laboratory of Catalytic Materials and Chemical Engineering, Research Institute of Petroleum Processing, SINOPEC, Beijing 100083, P. R. China

Table S1. Comparison of the Results in Literature Works for CO_2 Hydrogenation to Olefins with the Selectivity to Heavy Olefins being Available

catalyst	T (K)	P (MPa)	H_2/CO_2 (v/v)	CO_2 conv. (%)	FTY_{HCs} (μmol_{CO2} g_{Fe}^{-1} s^{-1})	CO sel. (%)	hydrocarbon distribution (%)					$FTY_{C2-C4=}$ (μmol_{CO2} g_{Fe}^{-1} s^{-1})	$FTY_{C5+=}$ (μmol_{CO2} g_{Fe}^{-1} s^{-1})
							CH_4	C_2–$C_4^=$	C_2–C_4^0	$C_{5+}^=$	C_{5+}^0		
Fe/C-Bio[1]	593	1.0	3	31	11.6	23.2	11.8	21.7[a]	2.7[b]	50.3[c]	13.5[d]	2.5[a]	5.9[c]
Fe/C-K[1]	593	1.0	3	28	9.2	22.6	24	29.9[a]	8.2[b]	30.5[c]	7.4[d]	2.7[a]	2.8[c]
Fe/Co-Y_K[2]	573	1.0	3	25.9	2.0	21.1	13.9	25.0[a]	5.2[b]	45.9[c]	10[d]	0.5[a]	0.9[c]
CAT A[3]	533	13.7	2	27.2	26.7	21.5	28.2	36.4[a]	4.9[b]	29.5[c]	1.1[d]	9.7[a]	7.9[c]
K-Fe/ZrO_2[4]	613	2.0	3	43.0	13.6	15.0	18	44	9.2	19	9.8	6.0	2.6
K-Fe/CNT[4]	613	2.0	3	35.0	11.5	12.0	26	34	10	19	11	3.9	2.2
FeK+3Ca-ZSM-5[5]	648	3.0	3	45.9	24.3	17.3	19.6	43.2	10.1[e]	27.1	N.A.	10.5	6.6

FeK/SWNTs (This work)	613	2.0	3	52.7	66.5	9.6	13.5	22.5	8.6	39.8 (47.5[c])	15.6	15.0	26.5

[a]C_2–$C_3^=$ products. [b]C_2–C_3^0 products. [c]$C_{4+}^=$ products. [d]C_{4+}^0 products. [e]C_2–C_{10}^0 and aromatics products.

Table S2. Product Distribution over the FeK/SWNTs Catalyst in CO Hydrogenation[a]

catalyst	CO conv. (%)	CO_2 sel. (%)	hydrocarbon selectivity (wt%)				
			CH_4	$C_2–C_4^{=}$	$C_2–C_4^{0}$	$C_{5+}^{=}$	C_{5+}^{0}
FeK/SWNTs	69.5	44.7	16.2	21.6	8.9	35.9	17.4

[a]Reaction conditions: 200 mg of catalyst, T = 613 K, P = 2.0 MPa, H_2/CO = 1, GHSV = 9000 mL g_{cat}^{-1} h^{-1}, and TOS = 24 h.

Table S3. Product Distribution over the FeK/rGO Catalyst in CO_2 Hydrogenation[a]

catalyst	CO_2 conv. (%)	CO sel. (%)	hydrocarbon selectivity (wt%)				
			CH_4	C_2–$C_4^=$	C_2–C_4^0	$C_{5+}^=$	C_{5+}^0
FeK/rGO	39.4	34.2	24.8	50.3	12.1	8.5	4.3

[a]Reaction conditions: 200 mg of catalyst, T = 613 K, P = 2.0 MPa, H_2/CO_2 = 3, GHSV = 9000 mL g_{cat}^{-1} h^{-1}, and TOS = 24 h.

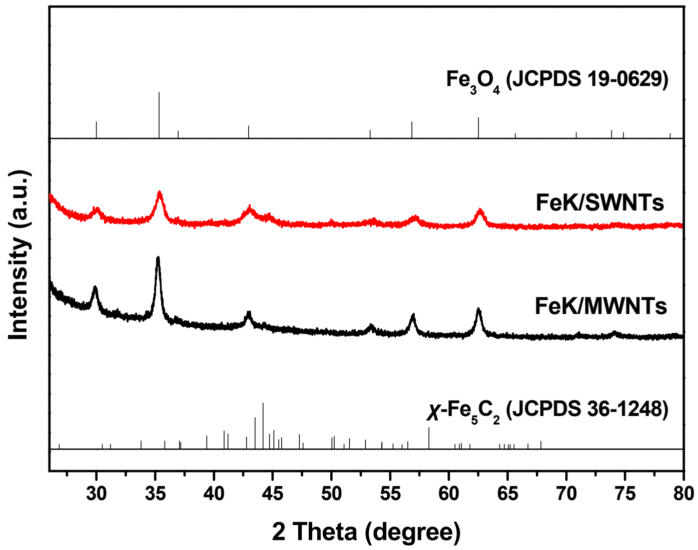

Figure S1. XRD patterns of the FeK/SWNTs and FeK/MWNTs catalysts after CO activation.

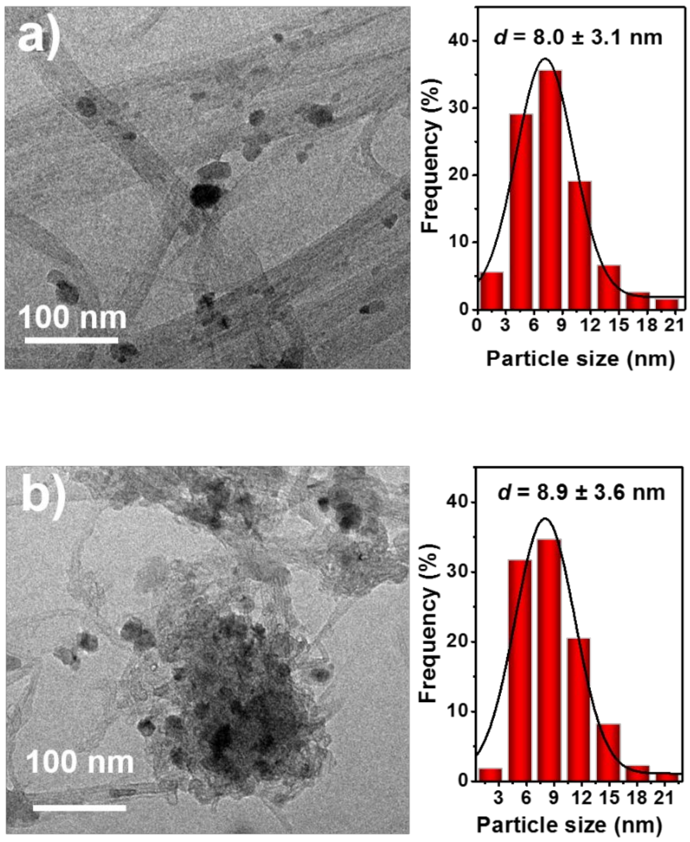

Figure S2. TEM images and PSD histograms with Gaussian analysis fittings of the (a) FeK/SWNTs and (b) FeK/MWNTs catalysts after CO activation.

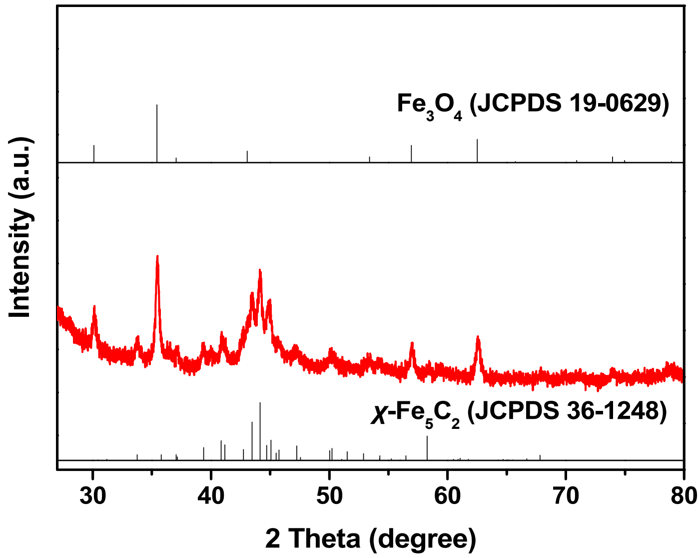

Figure S3. XRD pattern of the FeK/SWNTs catalyst after 120 h on stream in CO_2 hydrogenation.

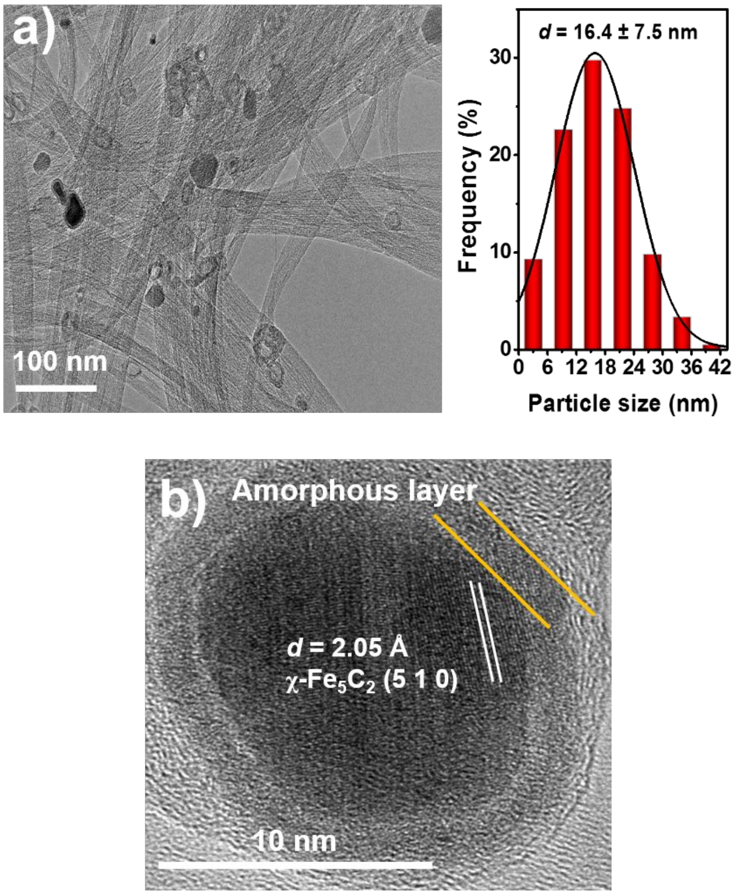

Figure S4. (a) TEM image and particle size distribution histograms with Gaussian analysis fitting and (b) HRTEM image of the FeK/SWNTs catalyst after 120 h on stream in CO_2 hydrogenation.

References

[1] Guo, L. S.; Sun, J.; Ji, X. W.; Wei, J.; Wen, Z. Y.; Yao, R. W.; Xu, H.Y.; Ge, Q. J. Directly Converting Carbon Dioxide to Linear α-Olefins on Bio-Promoted Catalysts. *Commun. Chem.* **2018**, *1*, 11.

[2] Guo, L. S.; Cui, Y.; Li, H. J.; Fang, Y.; Prasert, R.; Wu, J. H.; Yang, G. H.; Yoneyama, Y.; Tsubaki, N. Selective Formation of Linear-Alpha Olefins (LAOs) by CO_2 Hydrogenation over Bimetallic Fe/Co-Y Catalyst. *Catal. Commun.* **2019**, *130*, 105759.

[3] Hu, B. X.; Frueh, S.; Garces, H. F.; Zhang, L. C.; Aindow, M.; Brooks, C.; Kreidler, E.; Suib, S. L. Selective Hydrogenation of CO_2 and CO to Useful Light Olefins over Octahedral Molecular Sieve Manganese Oxide Supported Iron Catalysts. *Appl. Catal. B* **2013**, *132–133*, 54–61.

[4] Wang, J. J.; You, Z. Y.; Zhang, Q. H.; Deng, W. P.; Wang, Y. Synthesis of Lower Olefins by Hydrogenation of Carbon Dioxide over Supported Iron Catalysts. *Catal. Today* **2013**, *215*, 186–193.

[5] Dokania, A.; Chowdhury, A. D.; Ramirez, A.; Telalovic, S.; Abou-Hamad, E.; Gevers, L.; Ruiz-Martinez, J.; Gascon, J. Acidity Modification of ZSM-5 for Enhanced Production of Light Olefins from CO_2. *J. Catal.* **2020**, *381*, 347–354.