Electronic Supplementary Information

Iron doping boosts reactivity and stability of γ-Al_2O_3 nanosheet supported cobalt catalyst for propane dehydrogenation

Chang-Wu Zhang, Jing Wen, Lei Wang, Xin-Ge Wang, and Lei Shi*

School of Chemical Engineering, Dalian University of Technology, Dalian 116024, PR China

*Corresponding authors.

E-mail address: dlutshilei@dlut.edu.cn (L. Shi).

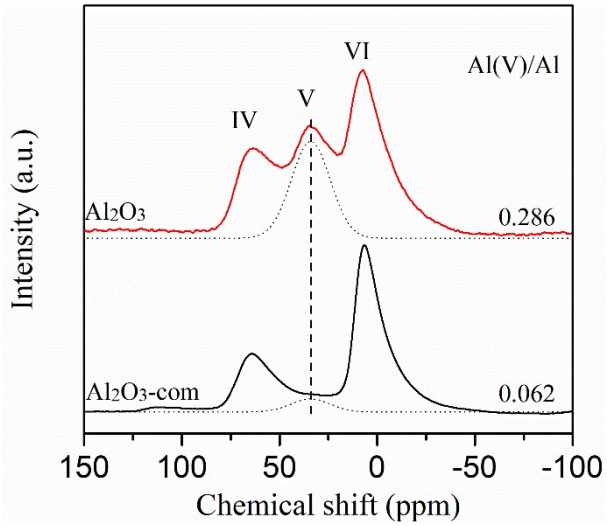

Fig. S1 ^{27}Al MAS NMR spectra and their deconvolution results of the 5Co1.6Fe/Al_2O_3 and 5Co1.6Fe/Al_2O_3-com catalysts.

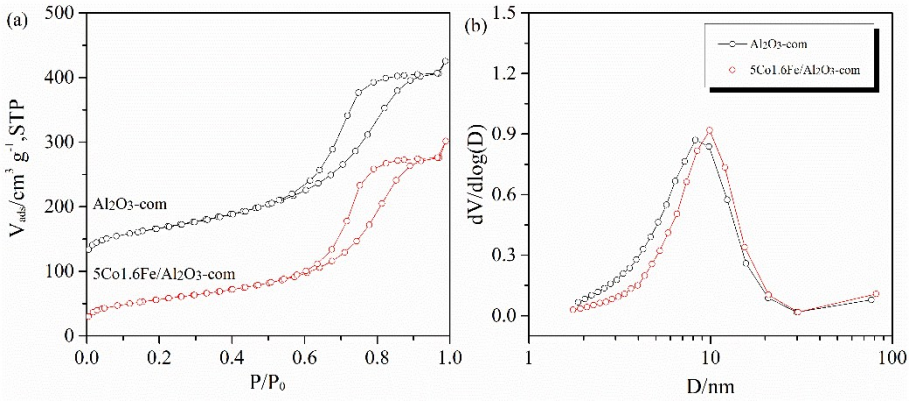

Fig. S2 (a) Nitrogen sorption isotherms of the Al_2O_3-com and 5Co1.6Fe/Al_2O_3-com catalysts. The isotherm of the Al_2O_3-com is offset vertically by 100 cm^3 g^{-1}, STP. (b) The pore size distribution of the Al_2O_3-com and 5Co1.6Fe/Al_2O_3-com catalysts.

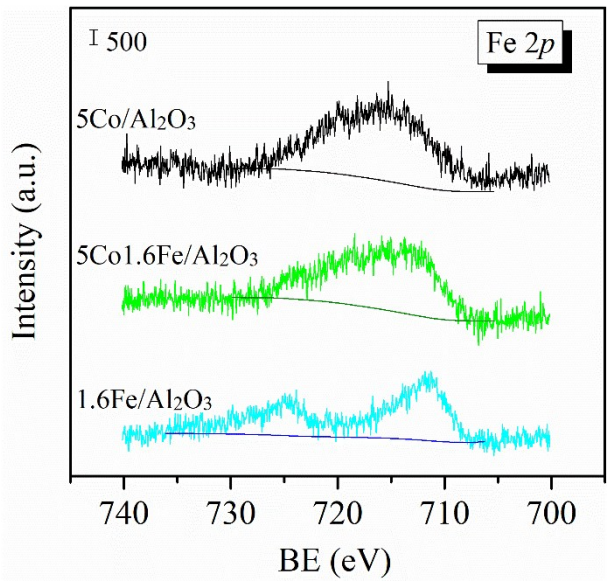

Fig. S3 XPS spectra in the Fe 2p region of the $5Co/Al_2O_3$, $5Co1.6Fe/Al_2O_3$ and $1.6Fe/Al_2O_3$ catalysts.

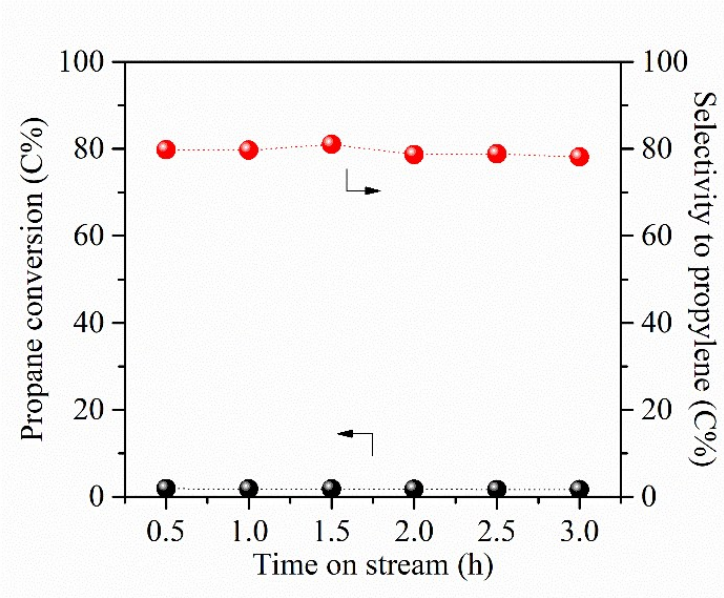

Fig. S4 Propane conversion and propylene selectivity over the $5Fe/Al_2O_3$ catalyst as a function of reaction time. Reaction conditions: temperature, 590°C; catalyst weight, 0.1 g; gas feed, 16.2 kPa C_3H_8, and N_2 balance; flow rate, 25 mL min^{-1}.

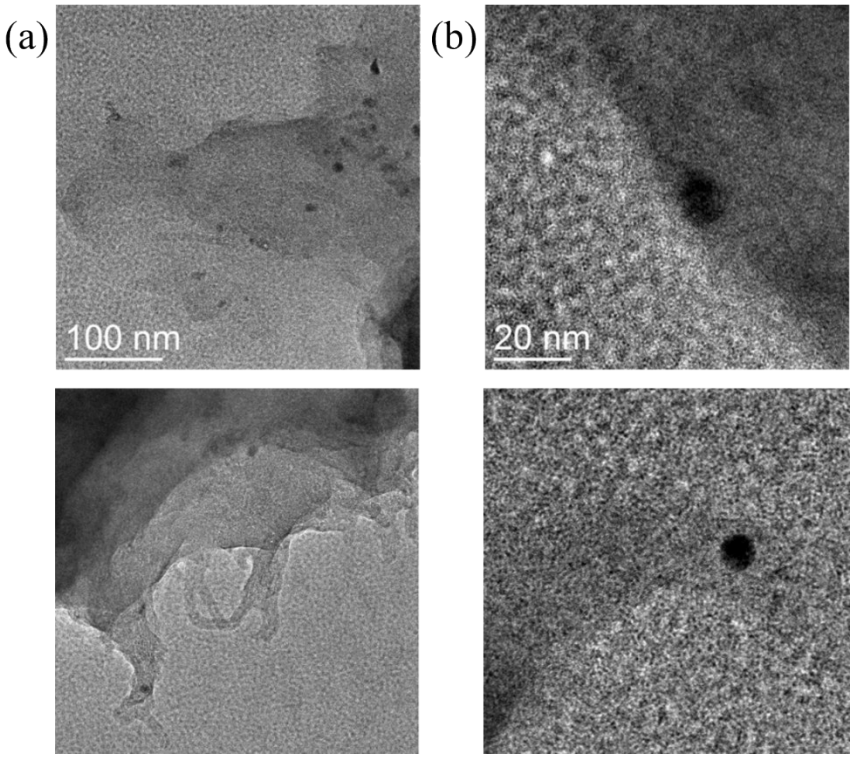

Fig. S5 (a,b) HR-TEM images of the 5Co1.6Fe/Al_2O_3 catalyst after 14-hour test in propane dehydrogenation reaction.

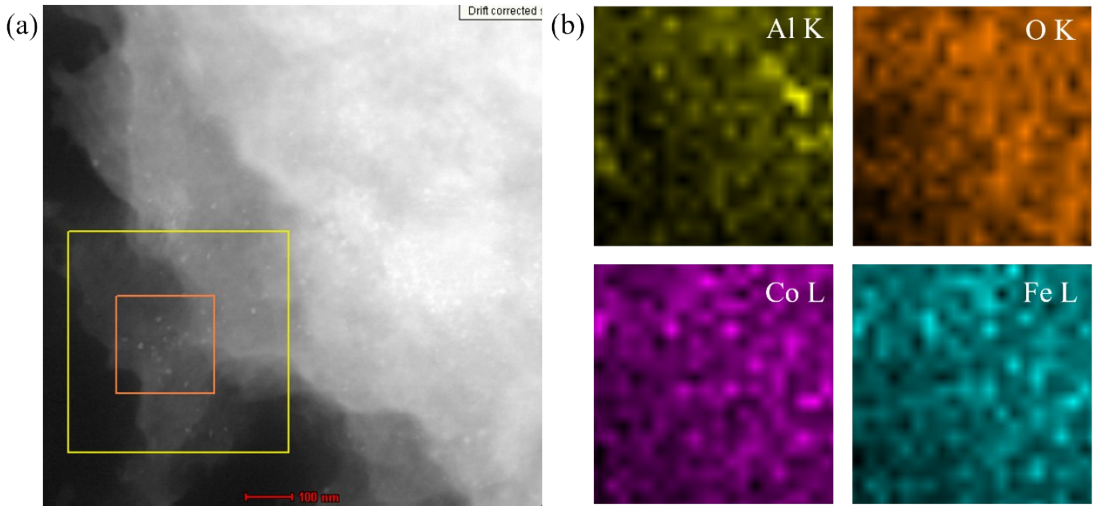

Fig. S6 (a) HAADF-STEM image of the 5Co1.6Fe/Al_2O_3 catalyst after 14-hour test in propane dehydrogenation, and (b) EDX elemental mapping analysis of Al-K, O-K, Co-L, and Fe-L edges.

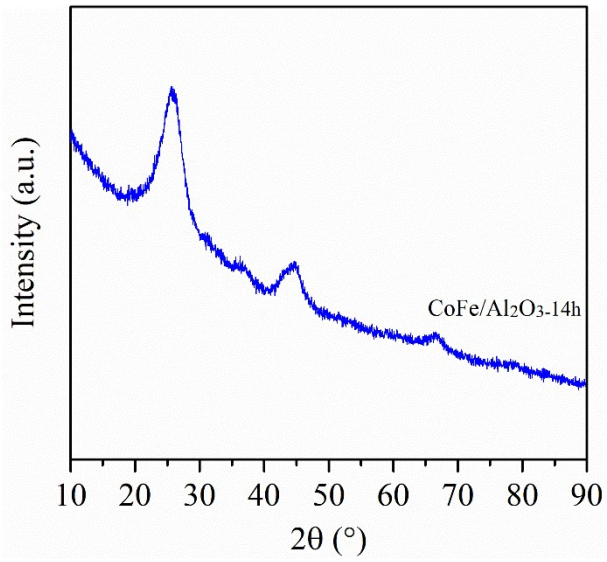

Fig. S7 XRD patterns of series of cobalt-based catalysts after the propane dehydrogenation test.

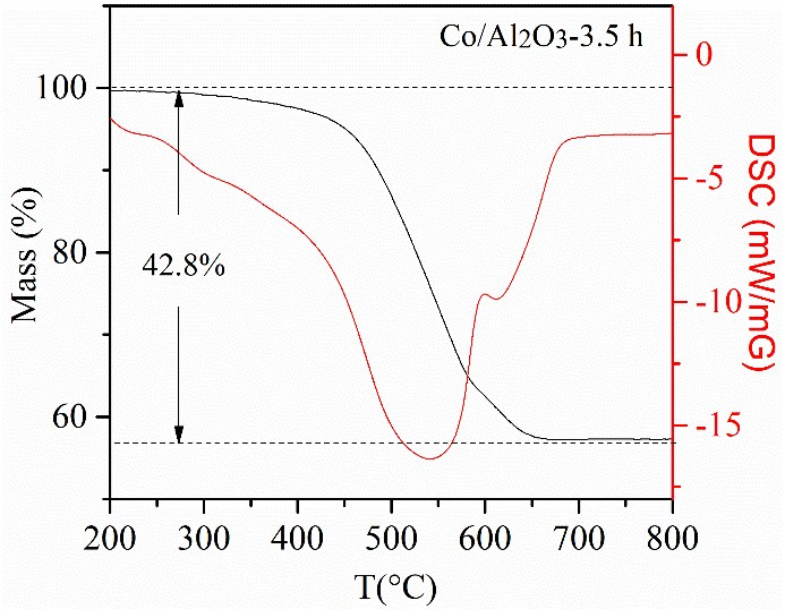

Fig. S8 TGA and DSC curves of the $5Co/Al_2O_3$ catalyst after 3.5-hour test in propane dehydrogenation.

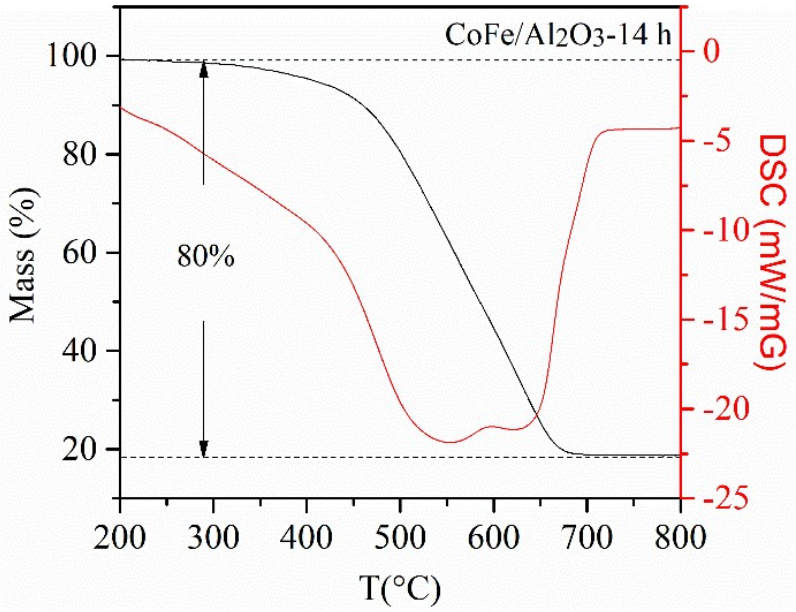

Fig. S9 TGA and DSC curves of the 5Co1.6Fe/Al_2O_3 catalyst after 14-hour test in propane dehydrogenation.

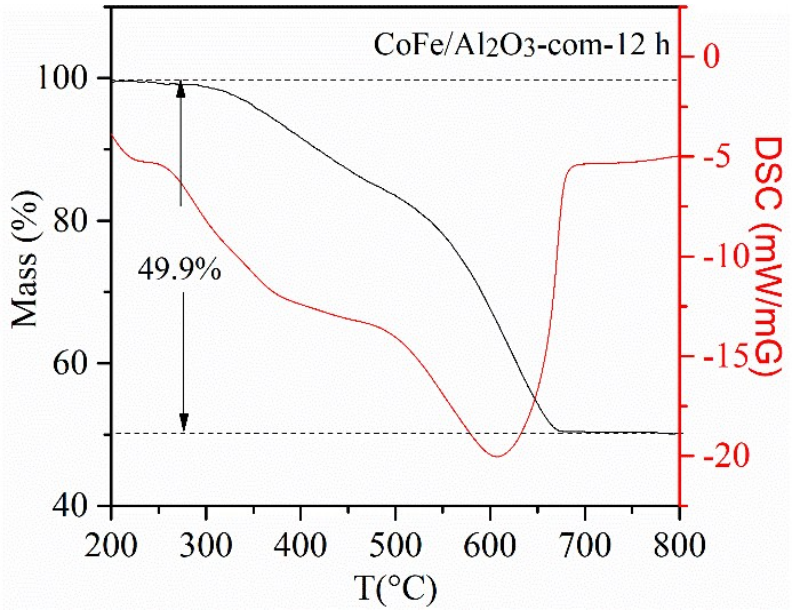

Fig. S10 TGA and DSC curves of the 5Co1.6Fe/Al_2O_3–com catalyst after 12-hour test in propane dehydrogenation.

Table S1. The catalytic properties of γ-Al_2O_3 nanosheet supported cobalt catalysts in propane dehydrogenation.[a]

Catalysts	Conversion (%)	Selectivity (%)			
		C_3H_6	C_2H_6	C_2H_4	CH_4
Al_2O_3	0.8	72.8	18.1	0.2	8.9
1Co/Al_2O_3	5.7	93.6	0.1	3.9	2.4
3Co/Al_2O_3	14.5	96.8	0.1	1.7	1.4
5Co/Al_2O_3	15.8	97.0	0.2	1.5	1.3
10Co/Al_2O_3	11.6	94	0.4	2.2	3.4

[a] Reaction condition: temperature, 590°C; catalyst weight, 0.1 g; gas feed, 16.2 kPa C_3H_8 and N_2 balance; flow rate, 25 mL min^{-1}; reaction time, 2h.

Table S2. The catalytic properties of series of cobalt-based catalysts in propane dehydrogenation.[a]

Catalysts	Conversion (%)	Selectivity (%)			
		C_3H_6	C_2H_6	C_2H_4	CH_4
5Co/Al_2O_3	15.8	97.0	0.2	1.5	1.3
5Co1.6Fe/Al_2O_3	22.4	97.3	0.2	1.2	1.3
5Co1.6Cu/Al_2O_3	10.4	95.4	0.1	2.8	1.7
5Co1.6Mn/Al_2O_3	13.4	96.9	0.1	1.6	1.4
5Co/Al_2O_3-com	16.2	96.9	0.1	1.7	1.3
5Co1.6Fe/Al_2O_3-com	16.5	96.2	0.4	1.7	1.7

[a] Reaction condition: temperature, 590°C; catalyst weight, 0.1 g; gas feed, 16.2 kPa C_3H_8, and N_2 balance; flow rate, 25 mL min^{-1}; reaction time, 2h.

Table S3. The summary of catalytic performances in propane dehydrogenation over some typical catalysts reported in literatures.

Catalysts	Temp (°C)	Gas feed (in volume ratio)	GHSV ($mL \cdot g_{cat}^{-1} \cdot h^{-1}$)	WHSV ($g \cdot g_{cat}^{-1} \cdot h^{-1}$)	Time (h)	Conversion (%)	Selectivity (%)	Specific activity [a] ($\times 10^{-3}$ $mol_{C3H6} \cdot mol^{-1} \cdot s^{-1}$)	Ref.
5 wt%Co1.6 wt%Fe/Al_2O_3	590	C_3H_8/N_2=4/21	2400	4.7	2	22.4	97.3	7.7	This work
5.7wt%Co/Al_2O_3-re-oxidizd	600	C_3H_8/N_2=15.4/30.8	465	0.9	2	26.0	93.0	2.5	[1]
20wt%Co5wt%S/Al_2O_3	560	C_3H_8=12	360	0.7	6	21.0	76.0	0.2	[2]
11.1wt%CoAl_2O_3	600	C_3H_8/N_2=1/19	300	0.6	5	15.0	80.0	0.6	[3]
5wt%Co/Al_2O_3	560	C_3H_8=12	240	0.5	6	28.0	90.0	0.9	[4]
5wt%Co/Al_2O_3-NS	600	C_3H_8/He=2.7/27.3	550	1.1	5	17.6	81.0	2.0	[5]
7wt%Co-Al_2O_3-HT	590	$C_3H_8/H_2/N_2$= 4/3.6/12.8	1600	2.9	5	21.1	97.1	3.7	[6]
20wt%Fe-P/Al_2O_3	600	C_3H_8/N_2= 1/20	150	0.29	5.5	15.0	80	0.06	[7]
5wt%Fe^{II}/SiO_2	650	C_3H_8/Ar= 3/97	100	0.2	18	6.3	99	0.1	[8]
12wt%VO_x/Al_2O_3	600	C_3H_8/H_2= 1/1	1530	3.0	--	33.0	94.0	2.5	[9]
1wt%Sn-Cr_2O_3/Al_2O_3	610	C_3H_8/N_2= 1/4	260	0.5	--	50.0	90.0	7.3	[10]
7wt%Cr_2O_3/Al_2O_3	580	$C_3H_8/H_2/N_2$= 7/7/11	2800	5.5	1	15.5	98.0	4.0	[11]

[a] Specific activity is defined as the moles of C_3H_6 formation per mole of metal atom per second.

References

[1] X. Li, P. Wang, H. Wang and C. Li, *Appl. Surf. Sci*., 2018, **441**, 688–693.

[2] Y. Sun, Y. Gao, Y. Wu, H. Shan, G. Wang and C. Li, *Catal. Commun*.,2015, **60**, 42–45.

[3] T. Mesoporous, C. S. Catalyst, N. Propane, A. B. Hu, W. Kim, T. P. Sulmonetti, L. Michele, S. Tan, J. So, Y. Liu, R. Dixit, S. Nair, C. W. Jones, B. Hu, W. Kim, T. P. Sulmonetti, M. L. Sarazen, S. Tan and J. So, *ChemCatChem*., 2017, **17**, 3330-3337. doi:10.1002/cctc.201700647.

[4] Y. Sun, Y. Wu, H. Shan and C. Li, *Catal. Letters*, 2015, **145**, 1413–1419.

[5] N. Dewangan, J. Ashok, M. Sethia, S. Das, S. Pati, H. Kus and S. Kawi, *ChemCatChem.*, 2019, **11**, 4923–4934.

[6] Y. Dai, J. Gu, S. Tian, Y. Wu, J. Chen, F. Li, Y. Du, L. Peng, W. Ding and Y. Yang, *J. Catal*., 2020, **381**, 482–492.

[7] S. Tan, B. Hu, W-G. Kim, S. H. Pang, J. S. Moore, Y. Liu, R.a S. Dixit, J. G. Pendergast, D. S. Sholl, S. Nair and C. W. Jones, *ACS Catal*. 2016, **6**, 5673−5683.

[8] B. Hu, N. M. Schweitzer, G. Zhang, S. J. Kraft, D. J. Childers, M. P. Lanci, J. T. Miller, and A. S. Hock, *ACS Catal*. 2015, **5**, 3494−3503.

[9] G. Liu, Z.-J. Zhao, T. Wu, L. Zeng and J. Gong, *ACS Catal*. 2016, **6**, 5207-5214.

[10] F. Cabrera, D. Ardissone and O. F. Gorriz, *Catal. Today*., 2008, **133**, 800-804.

[11] D. Shee and A. Sayari, *Appl. Catal. A-Gen*., 2010, **389**, 155-164.