Supporting Information

Solvent-free Aerobic Selective Oxidation of Hydrocarbons Catalyzed by Porous Graphitic Carbon Encapsulate Cobalt Composites

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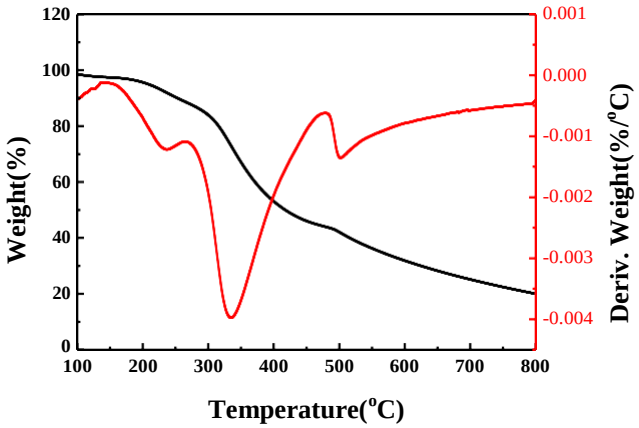


Figure S1. TGA curves of $Co@C_{800}$.

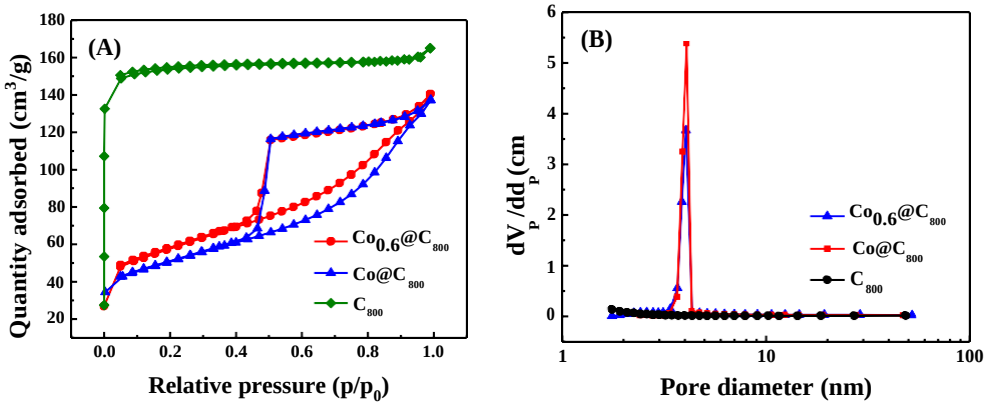


Figure S2. (A) Nitrogen adsorption-desorption isotherms of $Co_{0.6}@C_{800}$, $Co@C_{800}$ and C_{800}. (B) Pore size distribution of a) $Co_{0.6}@C_{800}$, b) $Co@C_{800}$ and C_{800}.

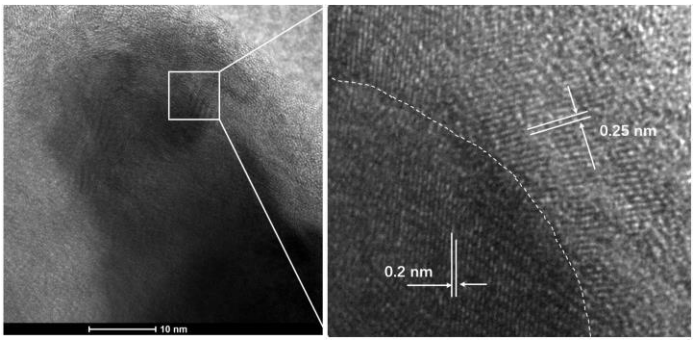


Figure S3. HTEM images of Co@C_{800}.

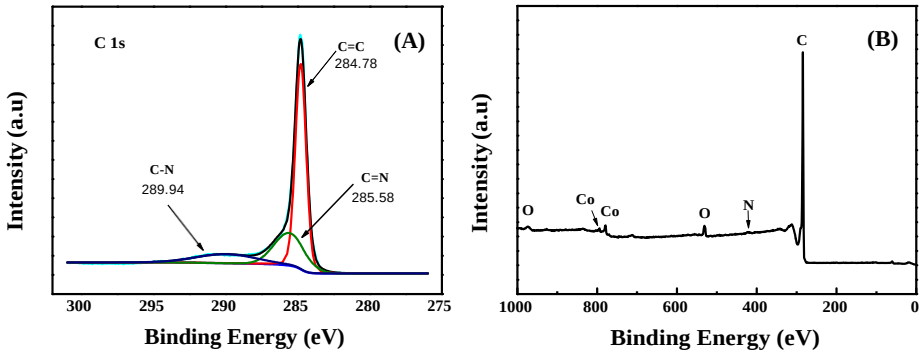


Figure S4. (A) C 1s spectra, and (B) XPS survey spectrum of Co@C_{800}.

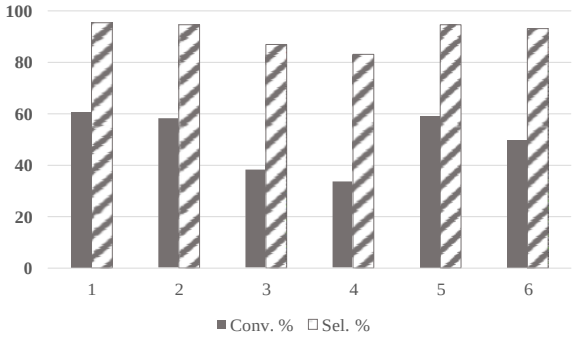


Figure S5. Catalyst recycling in oxidation of ethylbenzene with O_2 over Co@C_{800}. At the fifth run, the recovered catalyst was retreated through calcination at 600 ^{o}C in Ar.

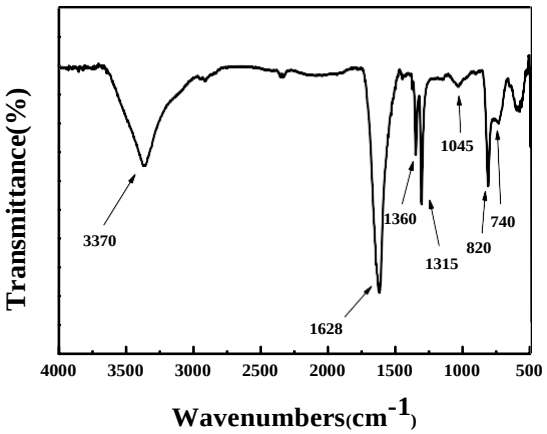
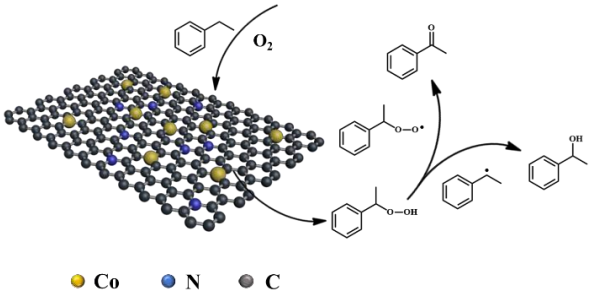


Figure S6. FTIR spectra of reused Co@C_{800} after the first four reactions before calcination.



Scheme S1. Proposed mechanism for the ethylbenzene oxidation over the Co@C_{800} using O_2 as an oxidant.

Table S1. The effect of the lazy glycine amount on the hybrid yield.

Resorcinol (g)	Formaldehyde (37 wt%) (g)	Cobalt acetate (g)	Lazy glycine	Yield [%]
3.0	4.42	1.5	0.5	22.0%
3.0	4.42	1.5	1.0	46.42%
3.0	4.42	1.5	1.5	45.21%

Table S2. The ratio analysis of the peaks in XPS spectra of the catalysts

	Content[a] (at%)			
Catalysts	C	N	O	Co
Co@C_{800}	94.743	1.302	3.048	0.907

[a]The contents of various elements were measured by X-ray photoelectron spectroscopy.

Table S3. Catalytic performance of Co@C_{800} and various reported catalytic system in literature for selective oxidation of ethylbenzene.

Entry	**Catalyst**	**T (K)**	**n_{FA}/n_{metal}**	**TOF (h^{-1})**	**Reference**
noble metal catalysts (entry 1-4)					
1	[(pymox-Me_2)$RuCl_2$]$^+$ BF_4^-	293	100	5[a]	Org. Lett., 2009, 11, 1567-1569.[S1]
2	Pd@C-Glu_A-550	393	200	245[a]	Nat. commun., 2013, 4, 1593.[S2]
3	AuNPs@3D-(N)GFs	273	666	128 [a]	Appl. Organomet. Chem., 2015, 29, 456-461.[S3]
4	nano Ag/ZnO (2)	413	5417	130 [a]	J. Mol. Catal. A: Chem., 2010, 331, 40-49.[S4]
Traditional small-scale test use Solvent (entry 5-10)					
5	Co/phen@CB-800-L	353	1000	124 [a]	Catal. Commun., 2017, 97, 130-133.[S5]
6	complex 1	353	100	4.4 [a]	Appl. Catal., A, 2017,531, 45-51.[S6]
7	CuTSPc@3D-(N)GFs	273	250	20 [a]	Chem. Commun., 2014, 50, 7855-7857.[S7]
8	Fe−N−C-700	273	175	33 [a]	J. Am. Chem. Soc. 2017, 139, 10790−10798.[S8]
9	Co/AC-salen-400	353	132	13 [a]	Phys. Chem. Chem. Phys. 2017, 19, 4967-4974.[S9]
10	Mn-PPOP-1	273	20	1.6 [a]	Dalton Trans., 2017, 46, 11372-11379.[S10]
11	Mn-MOF-74	408	1333	33 [a]	Dalton Trans., 2017, 46, 8415-8421.[S11]

Solvent-free largescale test used O_2 as oxidant (entry 12-21)					
12	Mn(OH)x//γ-Al_2O_3	408	1333	35 [a]	Catal. Sci. Technol., 2016, 6, 442-448.[S12]
13	CoNCB-2	393	20000	2064[b]	ChemCatChem, 2016, 8, 1782-1787.[S13]
14	Co–N–C/ CeO_2	393	2826	140 [a]	Phys. Chem. Chem. Phys., 2015, 17, 14012-14020.[S14]
15	Mn-MOF-74	408	1333	33 [a]	Dalton Trans., 2017,46, 8415-8421.[S15]
16	Mn–N–C@SiO_2	393	12177	3229 [b]	Chem. Commun., 2016, 52, 5577-5580.[S16]
17	FP-Co-SiO_2	393	7744	480 [a]	Chem. Commun., 2011, 47, 1336-1338.[S17]
18	Co-N-C-0.3/SiO_2	393	15543	1150 [b]	Phys. Chem. Chem. Phys., 2016, 18, 4635-4642.[S18]
19	MnS-1	383	2215	106 [a]	Microporous Mesoporous Mater., 2011, 146, 166-171.[S19]
20	Co–N–C-800	393	1016	20[a]	J. Mol. Catal. A: Chem., 2015, 408, 91-97.[S20]
21	Co@C_{800}	393	38857	4514[b]	This work

$$^{a}\text{TOF } (h^{-1}) = \frac{\text{the amount of ethylbenzene converted [mol]}}{\text{Total mol metal atoms [mol]} \cdot \text{ time [h]}}$$

$$^{b}\text{TOF } (h^{-1}) = \frac{\text{the amount of ethylbenzene converted [mol]}}{\text{metal atoms on the surface [mol]} \cdot \text{ time [h]}}$$

Supplementary References

S1 C. S. Yi, K. H. Kwon and D. W. Lee, *Org. Lett.*, 2009, **11**, 1567-1569.

S2 P. Zhang, Y. Gong, H. Li, Z. Chen and Y. Wang, *Nat. Commun.*, 2013, **4**, 1593.

S3 M. Mahyari, M. S. Laeini, A. Shaabani and H. Kazerooni, *Appl. Organomet. Chem.*, 2015, **29**, 456-461.

S4 M. J. Beier, B. Schimmoeller, T. W. Hansen, J. E. Andersen, S. E. Pratsinis and J. D. Grunwaldt, *J. Mol. Catal. A: Chem.*, 2010, **331**, 40-49.

S5 D. H. Tu, Y. Li, J. Li, Y. J. Gu, B. Wang, Z. T. Liu and J. Lu, *Catal. Commun.*, 2017, **97**, 130-133.

S6 S. B. Khomane, D. S. Doke, M. K. Dongare, S. B. Halligudi and S. B. Umbarkar, *Appl. Catal., A* 2017, **531**, 45-

51.S7 M. Mahyari, M. S. Laeini and A. Shaabani, *Chem. Commun.* 2014, **50**, 7855-7857.

S8 W. Liu, L. Zhang, X. Liu, X. Liu, X. Yang, S. Miao and T. Zhang, *J. Am. Chem. Soc.*, 2017, **139**, 10790-10798.
S9 K. Nakatsuka, T. Yoshii, Y. Kuwahara, K. Mori and H. Yamashita, *Phys. Chem. Chem. Phys.*, 2017, **19**, 4967-4974.
S10 Z. D. Ding, W. Zhu, T. Li, R. Shen, Y. Li, Z. Li and Z. G. Gu, *Dalton Trans.*, 2017, **46**, 11372-11379.
S11 Y. Kuwahara, Y. Yoshimura and Yamashita, H. *Dalton Trans.*, 2017, **46**, 8415-8421.
S12 Y. Kuwahara, Y. Yoshimura and Yamashita, H. *Catal. Sci. Technol.*, 2016, **6**, 442-448.
S13 Y. Chen, L. Fu, Z. Liu and Y. Wang, *ChemCatChem*, 2016, **8**, 1782-1787.
S14 Y. Chen, S. Zhao and Z. Liu, *Phys. Chem. Chem. Phys.*, 2015, **17**, 14012-14020.
S15 Y. Kuwahara, Y. Yoshimura and H. Yamashita, *Dalton Trans.*, 2017, **46**, 8415-8421.
S16 L. Fu, S. Zhao, Y. Chen and Z. Liu, *Chem. Commun.*, 2016, **52**, 5577-5580.
S17 C. Chen, J. Xu, Q. Zhang, Y. Ma, L. Zhou and M. Wang, *Chem. Commun.*, 2011, **47**, 1336-1338.
S18 C. Yang, L. Fu, R. Zhu and Z. Liu, *Phys. Chem. Chem. Phys.*, 2016, **18**, 4635-4642.
S19 N. N. Tušar, S. C. Laha, S. Cecowski, I. Arčon, V. Kaučič and R. Gläser, *Microporous Mesoporous Mater.*, 2011, **146**, 166-171.
S20 L. Fu, Y. Chen and Z. Liu, *J. Mol. Catal. A: Chem.*, 2015, **408**, 91-97.