Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Multistep protection strategy for preparation of atomically dispersed Fe-N catalyst for selective oxidation of ethylbenzene to acetophenone

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Detailed procedure for the O_2-TPD measurement.

Typically, 50 mg of Fe-N@HCS-900 catalyst was treated under 25 mL min^{-1} Ar flow at 120 ^oC for 30 min. After the catalyst sample was cooled to room temperature, the Ar flow switched to a 5% O_2/He flow with 25ml/min. Then, the sample was heated to 800 ^oC with the heating rate of 10 ^oC min^{-1}. The signal was recorded on a Micromeritics ChemiSorb 2720 instrument.

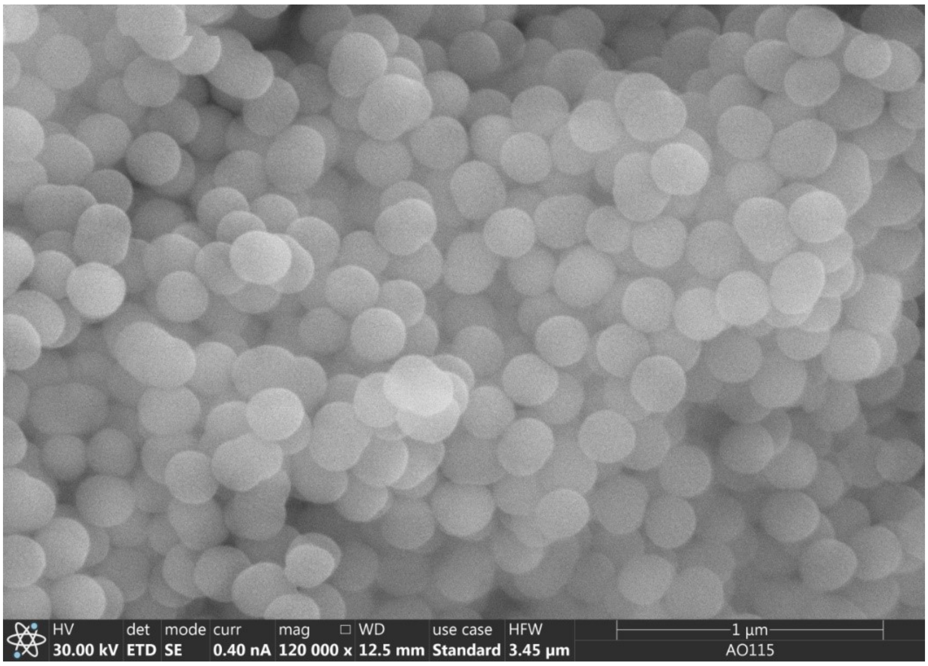

Figure S1. SEM image of SiO_2.

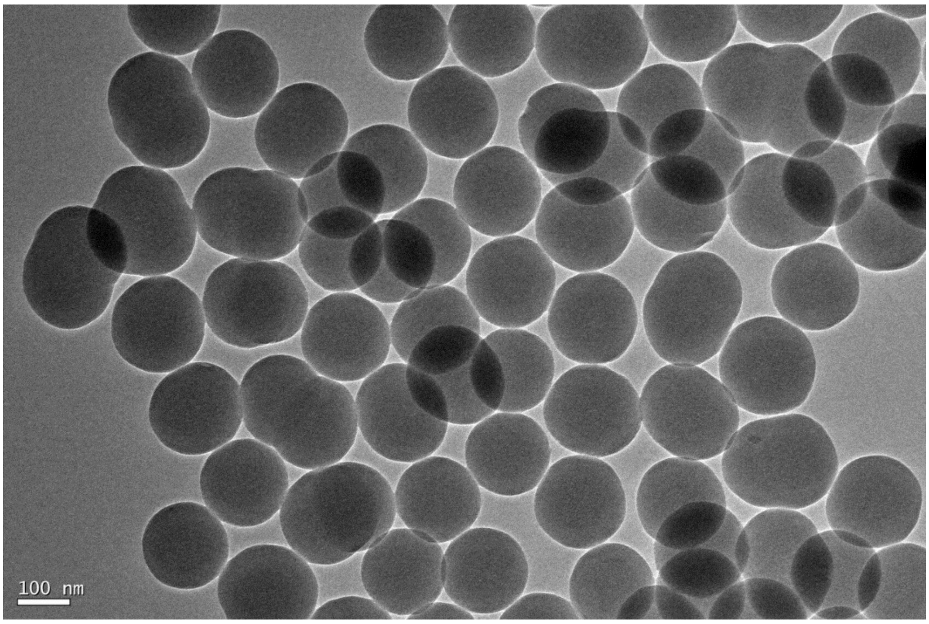

Figure S2. TEM image of SiO_2.

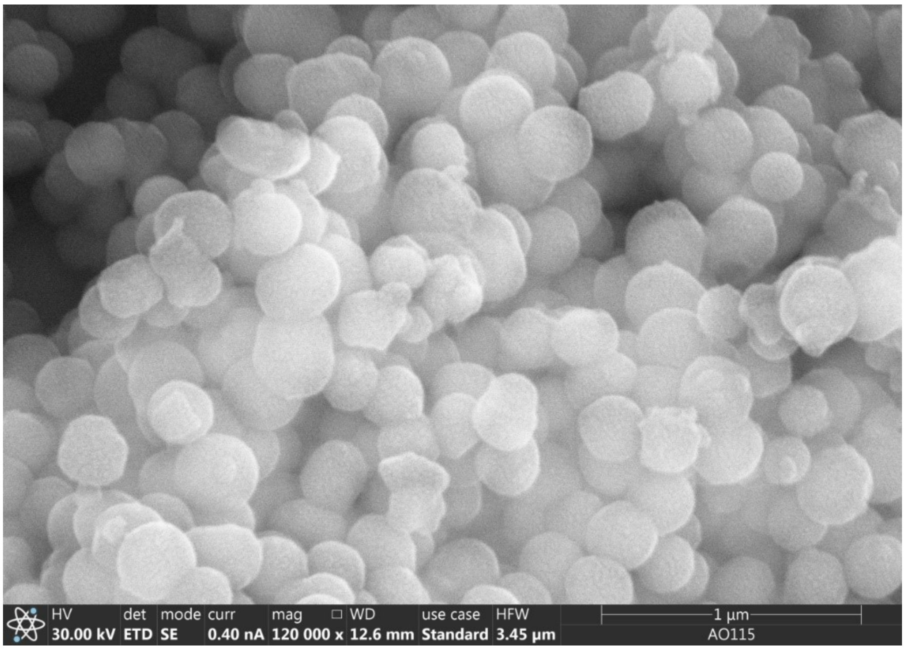

Figure S3. SEM image of Fe-N@SiO_2-900.

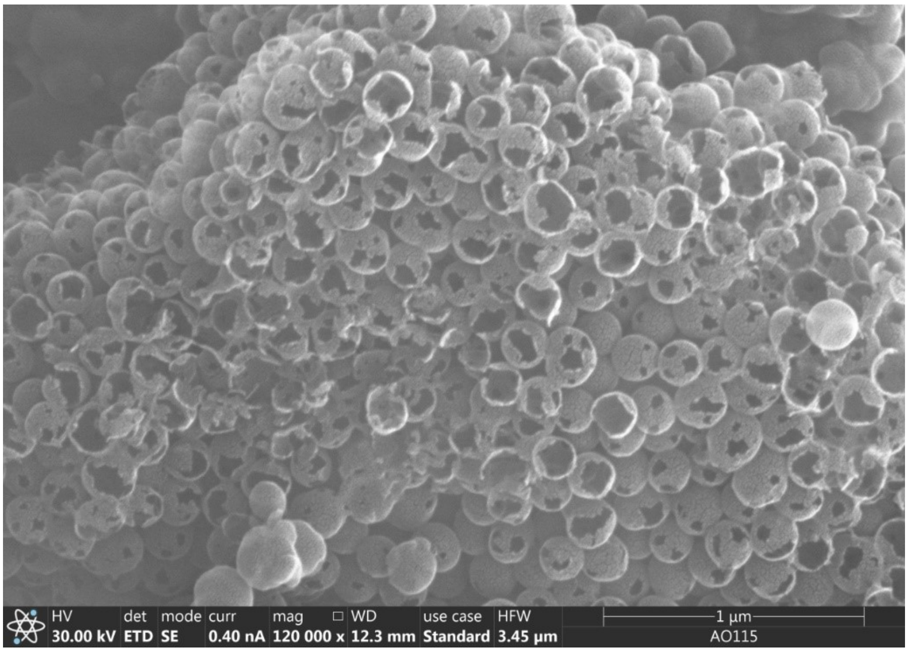

Figure S4. SEM image of Fe-N@HCS-900.

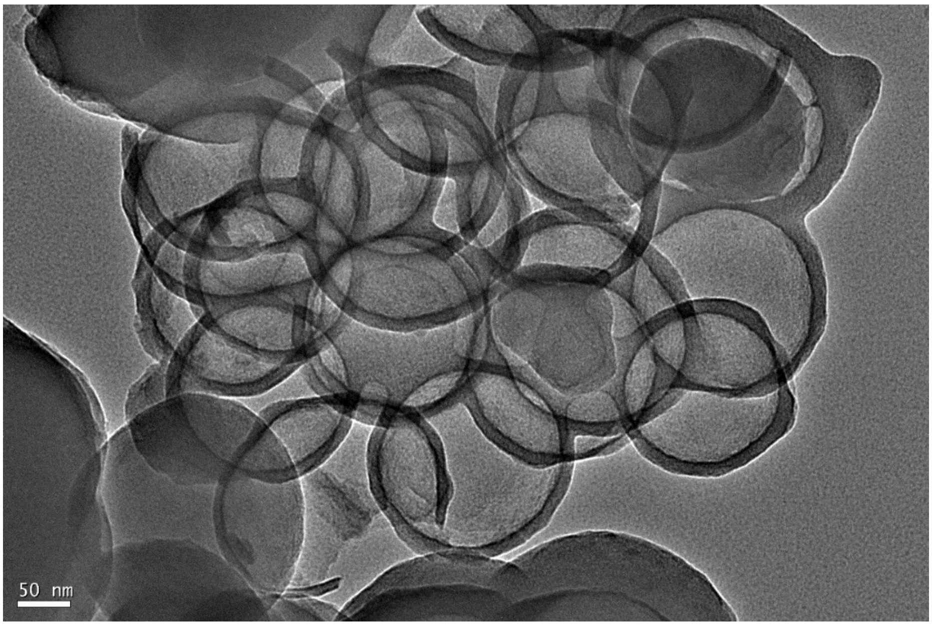

Figure S5. TEM image of Fe-N@HCS-700.

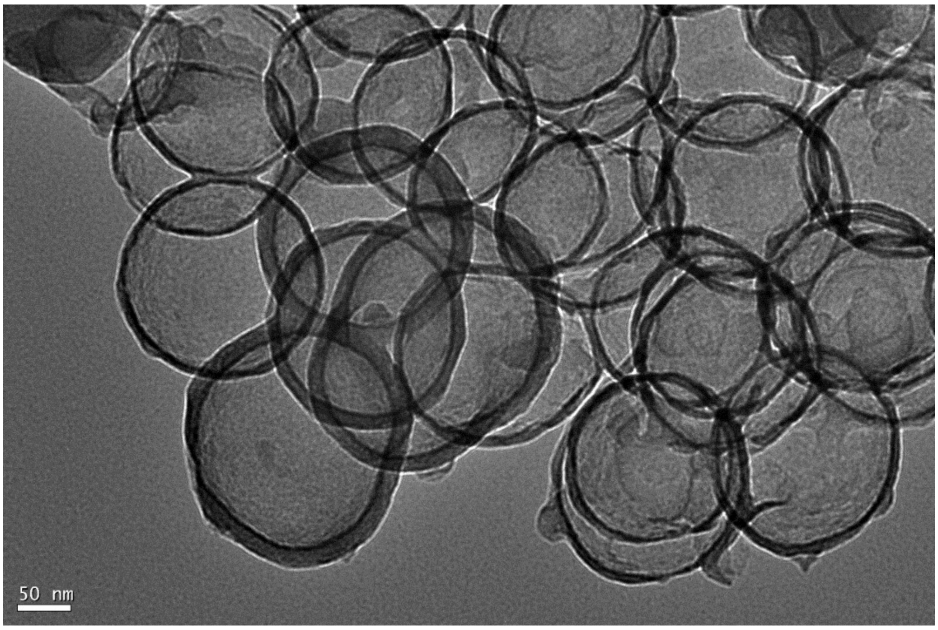

Figure S6. TEM image of Fe-N@HCS-800.

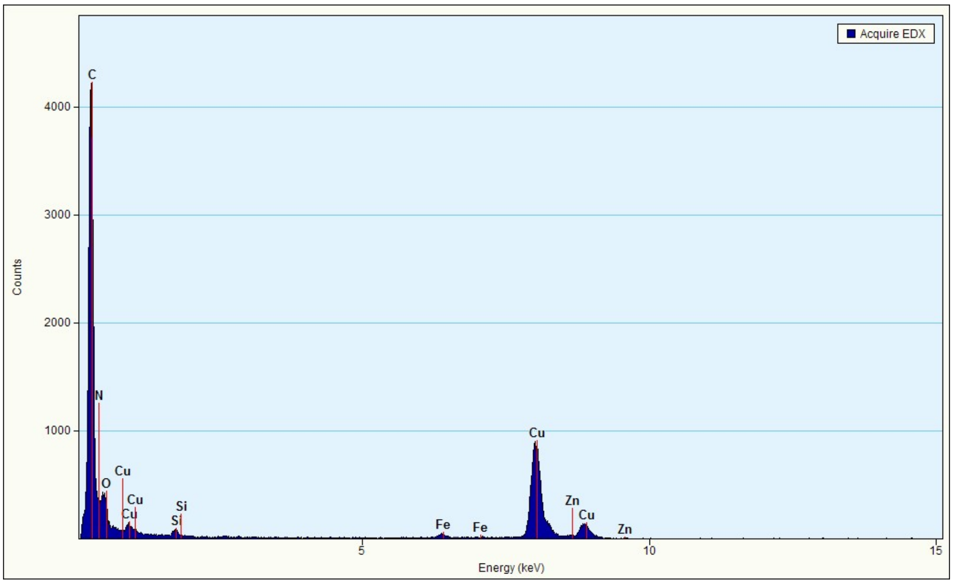

Figure S7. The EDX spectrum of Fe-N@HCS-900 catalysts.

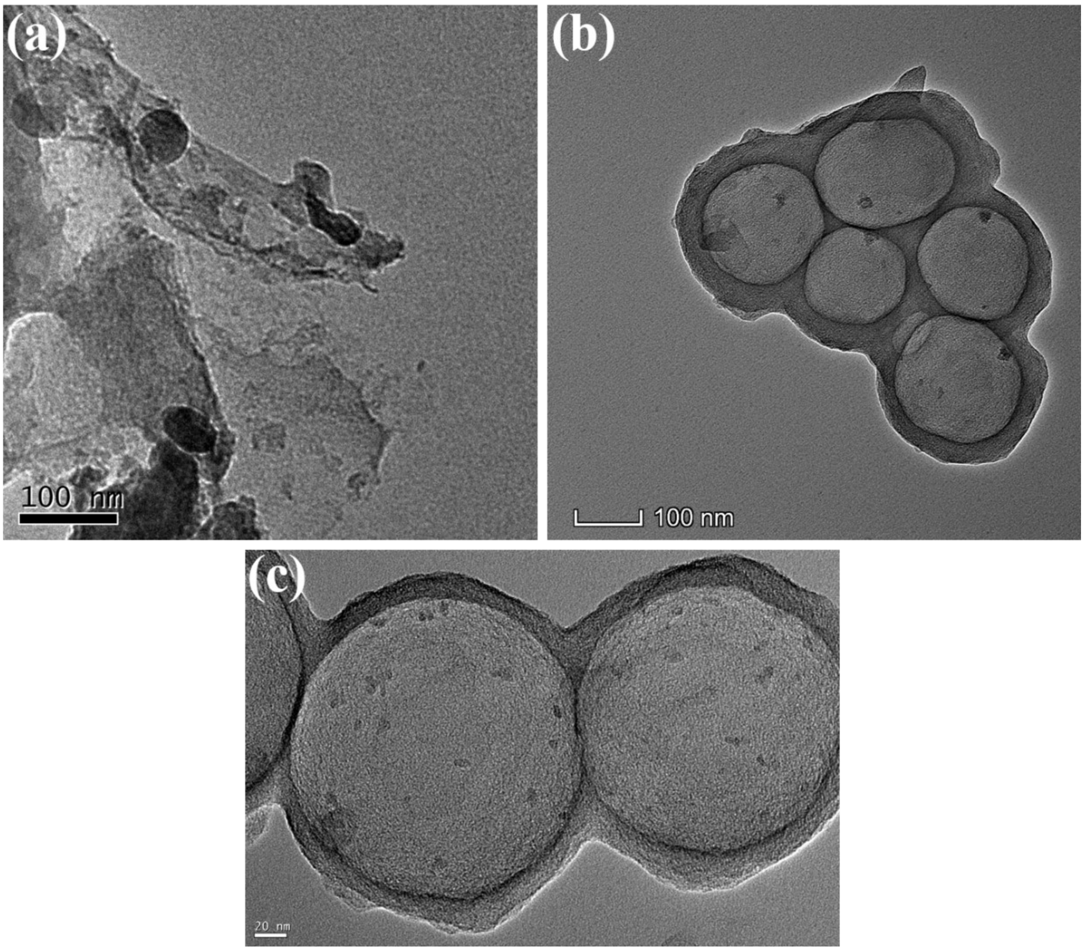

Figure S8. The corresponding TEM images of (a) Fe NPs@AC, (b) Fe NPs@HCS (without addition of Zn^{2+}), (c) Fe NPs@HCS (without addition of 1,10-phenanthroline).

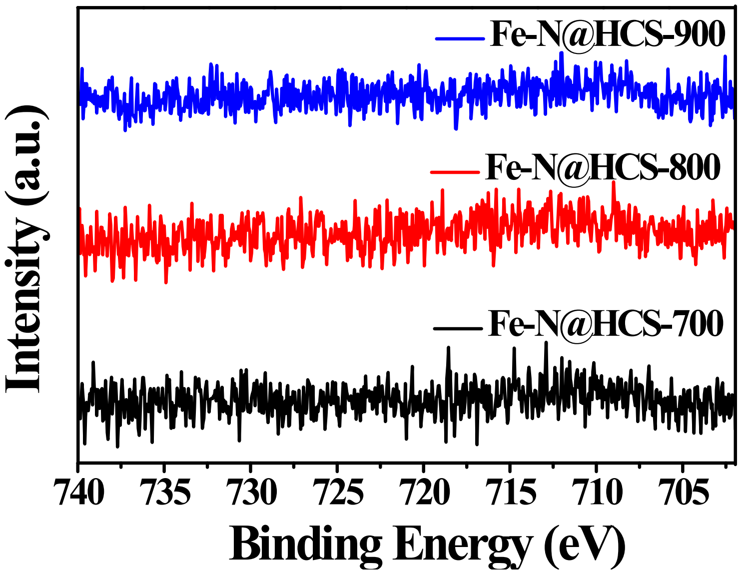

Figure S9. XPS Fe 2p spectra of Fe−N@HCS-T samples.

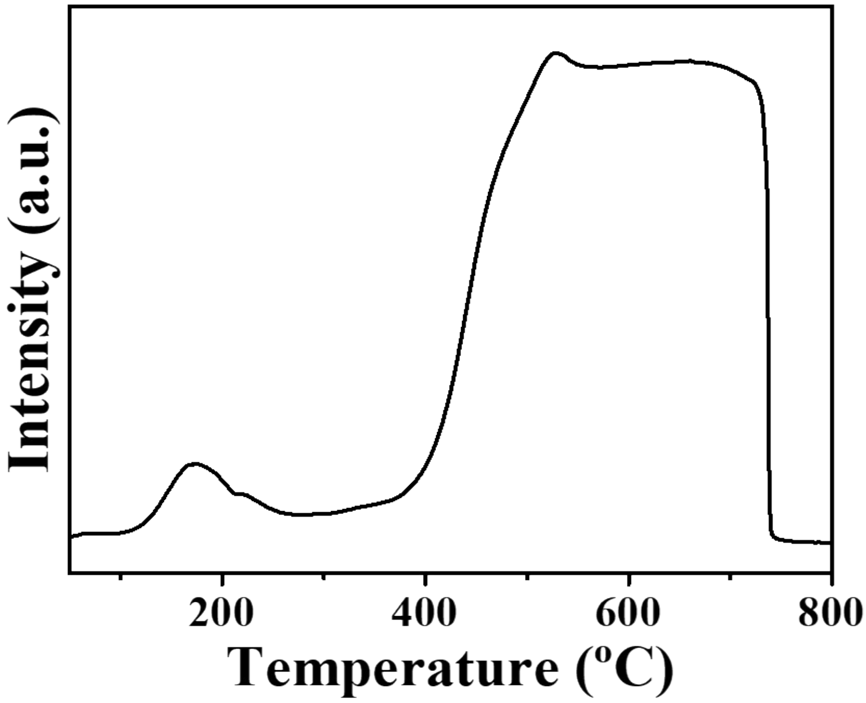

Figure S10. O_2-TPD results of Fe-N@HCS-900.

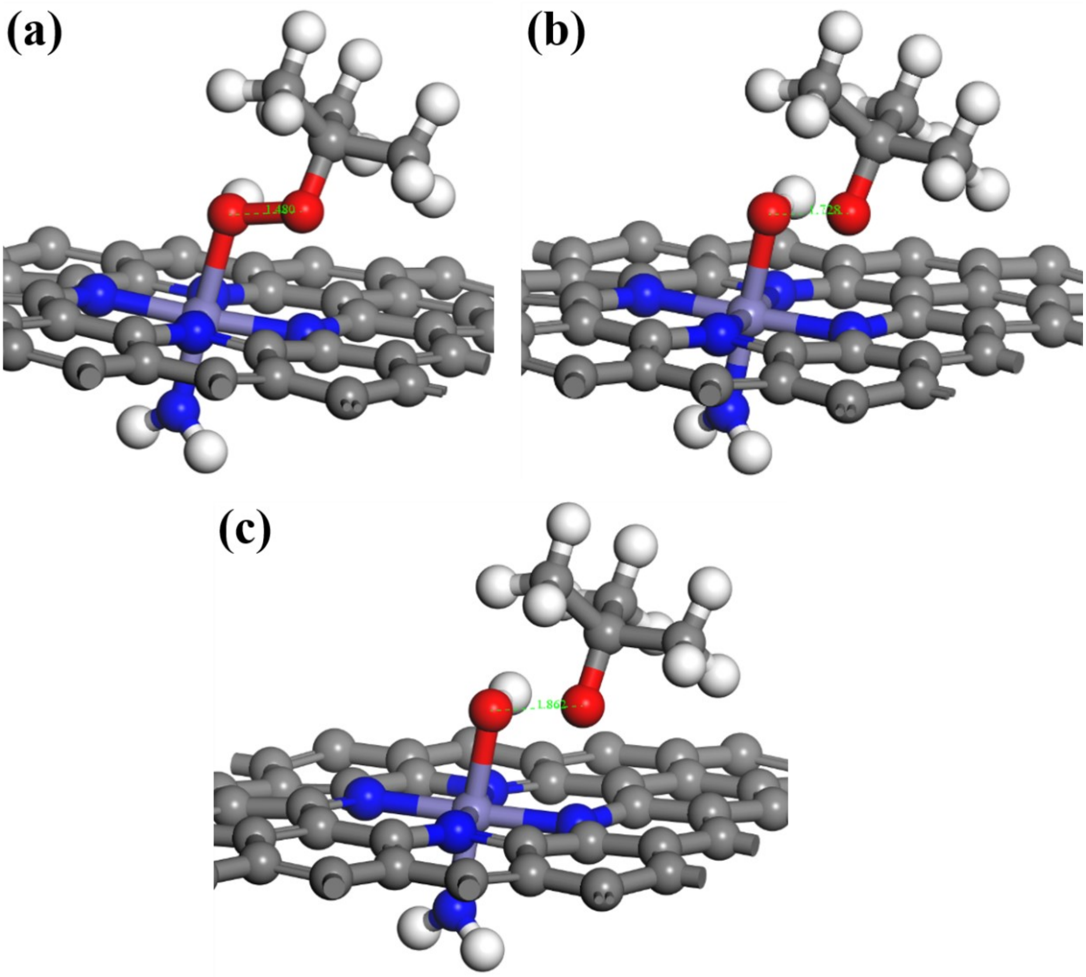

Figure S11. The optimized DFT model for the O-O bond length change in TBHP activated by Fe-N_5 sites.

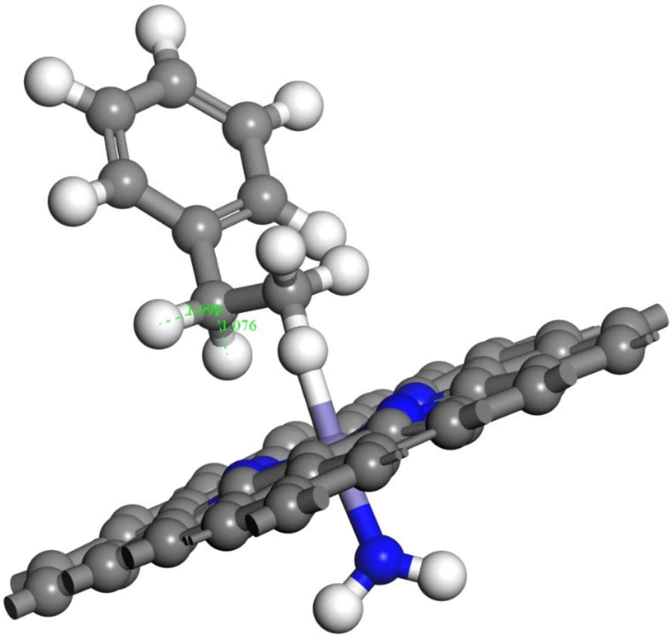

Figure S12. The DFT calculation model for polarized α-H in ethylbenzene.

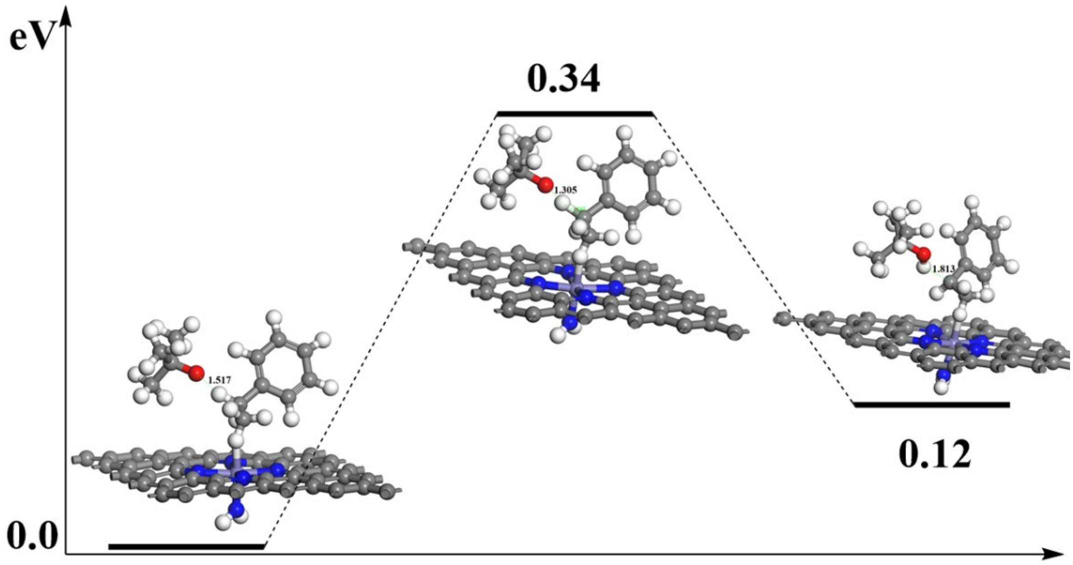

Figure S13. The reaction pathway and corresponding activation energy for ethylbenzene oxidation.

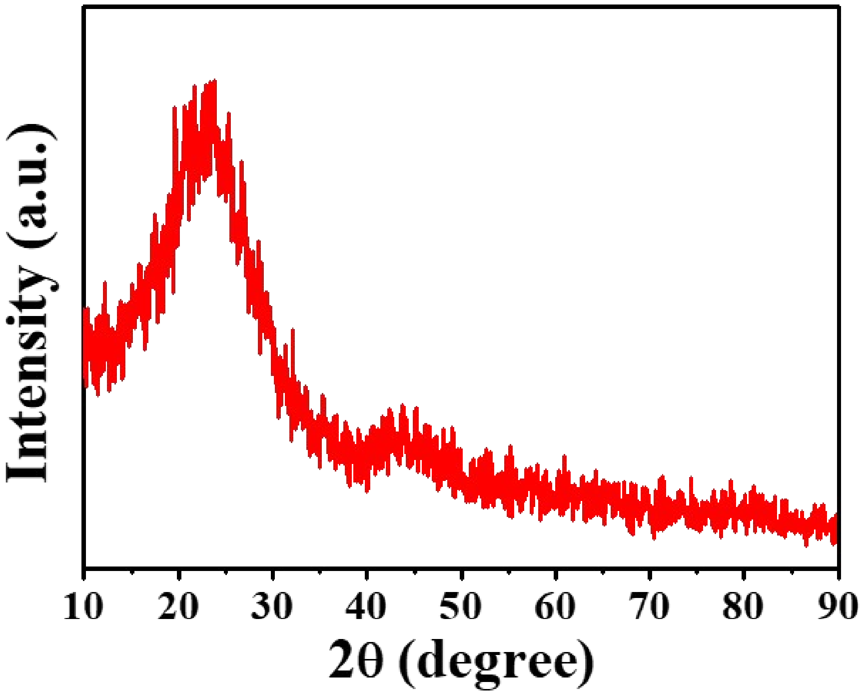

Figure S14. XRD pattern of Fe-N@HCS-900 after six cycles of reaction.

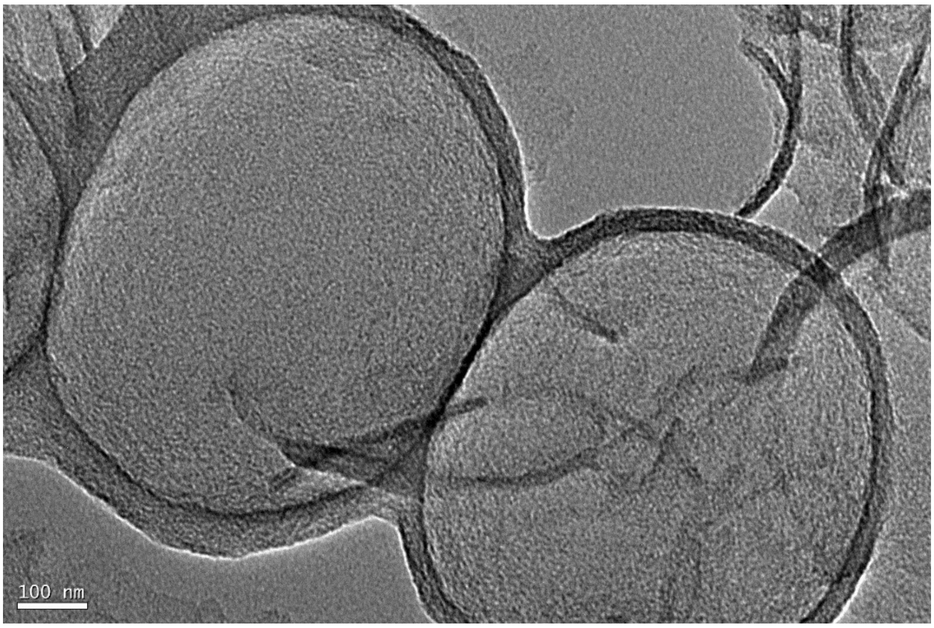

Figure S15. TEM image of the Fe−N@HCS-900 catalyst after six cycles of reaction.

Table S1. EXAFS fitting parameters at the Fe K-edge for Fe-N@HCS-900.

Sample	Shell	CN [a]	R (Å) [b]	σ^2 (Å^2·10^{-3}) [c]	ΔE0 (eV) [d]	*R* factor
Fe-N@HCS-900	Fe-N	5.2	1.97±0.03	10.5	-4.6	0.007

[a] C*N*: coordination number; [b] *R*: bond distance; [c] σ^2: Debye-Waller factors; [d] ΔE_0: the inner potential correction. *R* factor: goodness of fit. S_0^2 was set as 0.89 for Fe-N, which was obtained from the experimental EXAFS fit of reference FePc by fixing CN as the known crystallographic value and was fixed to all the samples.
Fitting parameters: k-range: [2.423:9.977], dk=1.00; R-range: [1.000 :1.994], dR=0.00; kweight=2,3; k-window=hanning, R-window=hanning, fit space=R, fit background: no.

Table S2. Structure parameters and the element content of the prepared catalysts.

Catalyst	Surface Area (m^2/g)	Pore volume (cm^3/g)	Fe (wt%)	Zn (wt%)	C (%)	N (%)	H (%)
Fe-N@HCS-700	81.2	0.15	0.69	3.02	60.43	6.64	1.71
Fe-N@HCS -800	75.0	0.16	0.61	2.67	67.78	6.22	1.40
Fe-N@HCS -900	460.8	0.39	0.66	0.08	75.15	4.89	1.58

Table S3. The comparison of the catalytic activity of Fe-N@HCS-900 with other reported catalysts.

Entry	Catalyst	Reaction conditions	Conv. (%)	Sel. (%)	Ref.
1	Fe-N-C	10.0 mg of catalyst, 0.5 mmol of ethylbenzene, 500 μL TBHP, 6.5 mL H_2O, 25 °C, 7 h.	99	99	[1]
2	Co/AC-salen-400	25.0 mg of catalyst, 1.0 mmol of ethylbenzene, 0.45mmol TBHP, 5.0 mL CH_3CN, 80 °C, 4 h.	47.9	83.5	[2]
3	Co-N-C-900/PCMK	15.0 mg of catalyst, 1.0 mmol of ethylbenzene, 490 μL TBHP, 3.0 mL H_2O, 80 °C, 12 h.	96	99	[3]
4	CoZnAl-MMO/Al_2O_3	100.0 mg of catalyst, 10 mmol of ethylbenzene, 30 mmol TBHP, 120 °C, 12 h.	69.5	80.4	[4]
5	$Co_2Ni_1Al_1O_x$	200.0 mg of catalyst, 5.0 mLof ethylbenzene, 15.0 mL TBHP, 10.0 mL CH_3COOH, 120 °C, 8 h	80.0	88.9	[5]
6	Co–N–C-20	15.0 mg of catalyst, 1.0 mmol of ethylbenzene, 3.5 mmol TBHP, 3 mL H_2O, 80 °C, 12 h.	90.9	99.3	[6]
7	Fe-N@HCS-900	20.0 mg of catalyst, 0.25 mmol of ethylbenzene, 0.35mL TBHP, 3 mL H_2O, room temperature, 6 h.	66.5	94.2	This work
8	Fe-N@HCS-900	20.0 mg of catalyst, 0.25 mmol of ethylbenzene, 0.35mL TBHP, 3 mL H_2O, room temperature, 18 h.	99	99.5	This work

References

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