

Biomass-derived Fe-NC hybrid for hydrogenation with formic acid: Control of Fe-based nanoparticles distribution

Lu Liu ^{a†}, Bowei Wang ^{abc†}, Ruixiao Gao ^a, Dan Zhang ^a, Wensheng Xu ^a, Ligong Chen ^{abc*}, Xilong Yan ^{abc}, Yang Li ^{abc*}

^a School of Chemical Engineering and Technology, Tianjin University, Tianjin 300350, P. R. China.

^b Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, P. R. China.

^c Tianjin Engineering Research Center of Functional Fine Chemicals, Tianjin, P. R. China.

* Corresponding authors. E-mail: lgchen@tju.edu.cn; liyang777@tju.edu.cn

† These authors contributed equally to this work.

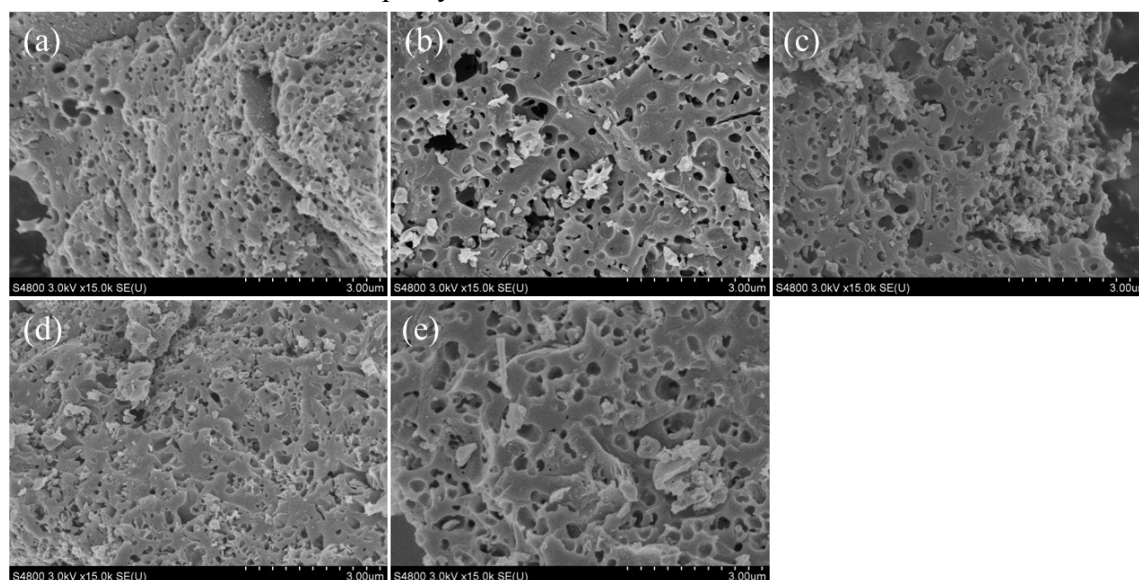


Fig. S1. SEM images of (a) Fe-NC-FeSO₄, (b) Fe-NC-FeCl₂, (c) Fe-NC-FeCl₃, (d) Fe-NC-Fe(acac)₃ and (e) Fe-NC-Fe(NO₃)₃.

Table S1 Texture properties of Co-NSPC-X samples.

Samples	S _{BET} (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
Fe-NC-FeSO ₄	337.9	0.284	17.06
Fe-NC-FeCl ₂	291.4	0.276	17.02
Fe-NC-FeCl ₃	336.5	0.319	15.13
Fe-NC-Fe(acac) ₃	298.8	0.270	16.99
Fe-NC-Fe(NO ₃) ₃	273.9	0.249	16.99

Table S2 The contents of four types of N in Fe-NC-X.

Samples	pyridinic N	pyrrolic N	Fe-N	graphitic N
Fe-NC-FeSO₄	69.89%	18.86%	5.92%	5.33%
Fe-NC-FeCl₂	60.46%	22.16%	11.58%	5.80%
Fe-NC-FeCl₃	67.12%	15.82%	12.06%	4.99%
Fe-NC-Fe(acac)₃	66.13%	16.31%	9.78%	7.77%
Fe-NC-Fe(NO₃)₃	58.49%	21.98%	11.89%	7.64%

Table S3 Catalytic hydrogenation results of nitrobenzene over different catalysts. ^a

Entry	Catalyst	Conversion(%)	Selectivity(%)
1	Fe-NC-FeSO ₄	52.2	87.4
2	Fe-NC-FeCl ₂	100	94.5
3	Fe-NC-FeCl ₃	95.1	92.8
4	Fe-NC-Fe(acac) ₃	100	97.7
5	Fe-NC-Fe(NO ₃) ₃	78.3	98.6

^a Reaction conditions: nitrobenzene (0.25 mmol), H₂ (3MPa), 21 mg of catalyst, solvent: 1 mL THF + 1 mL H₂O, 130 °C and 14 h.

Gas chromatograph is EWAI GC-4000A with an OV-101 capillary column. Analysis condition: initial temperature of 80 °C, hold for 2 min, and then increase the temperature at 20 °C/min for 10 min to 280 °C, hold for 5 min.

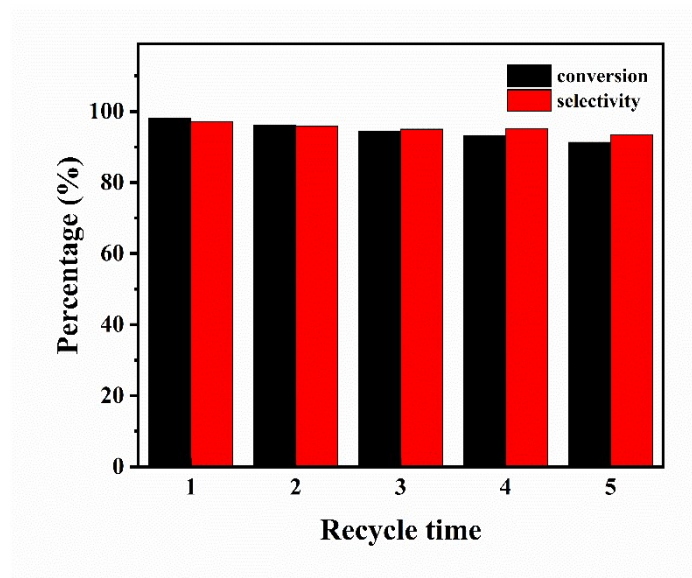


Fig. S4. Recycling performance of Fe-NC-FeCl₂ for CTH of nitrobenzene.

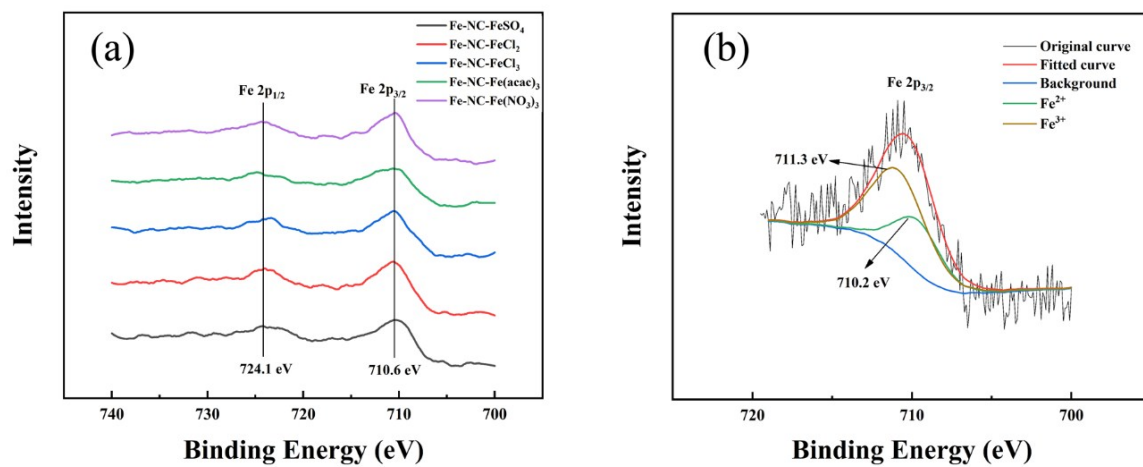


Fig. S5. (a) Fe 2p XPS spectra of Fe-NC-X, (b) Fe 2p_{3/2} spectra of Fe-NC-FeCl₂.

Table S4 The results of transfer hydrogenation of nitrobenzene compared with reported catalysts.

Catalyst	Hydrogen donors	Additive	T (°C)	t (h)	Yield (%)	Ref.
Co ₃ O ₄ -NGr@C	FA	Et ₃ N	100	15	96	[1]
Fe ₂ O ₃ -NGr@C	FA	Et ₃ N	120	24	94	[2]
Co-N _x /C-800-AT	FA	-	110	12	>99	[3]
CoHMA	<i>i</i> -PrOH	KOH	83	2	91	[4]
Fe ₃ O ₄ /Au	HCOONH ₄ (8 eq)	-	70	4	94	[5]
γ-Fe ₂ O ₃ /h-MCM	N ₂ H ₄ ·H ₂ O	-	80	2	100	[6]
[Mo ₃ S ₄ X ₃ (dmpe) ₃]BPh ₄	FA	Et ₃ N	70	10	>99	[7]
Fe(BF ₄) ₂	FA(4.5 eq)	PP ₃	40	1	95	[8]
Fe-NC-FeCl ₂	FA(3 eq)	-	120	6	95	This Work

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