Supporting Information

Highly efficient non-noble metallic NiCu nanoalloy catalysts for hydrogenation of nitroarenes

State Key Laboratory of Advanced Special Steel, School of Materials Science and Engineering，Shanghai University, 99 Shangda Road, BaoShan District, Shanghai 20444, China

Total number of Pages: 5

Total number of Table: 3

Total number of Figures: 3

Table S1 Textural properties of the prepared catalysts

Sample	Ni (wt%)	Ni dispersion[a] (%)	Cu (wt%)	C (wt%)	S_{BET} (m^2g^{-1})	V_p (cm^3g^{-1})	D_a (nm)	d_x[b] (nm)	d_t[c] (nm)
SiO_2	/	/	/	/	324	1.03	13.0	/	/
C@SiO_2-800	/	/	/	/	246	0.69	11.6	/	/
NiOCuO@SiO_2-800	13.9	/	4.2	/	211	0.69	12.8	12.7	11.8
NiCu@SiO_2-H_2-800	14.9	5.0	4.6	/	223	0.69	12.4	21.4	20.2
Ni/C@SiO_2-800	14.3	5.9	/	11.4	275	0.75	10.9	14.0	13.9
Cu/C@SiO_2-800	/	/	4.0	13.3	213	0.62	11.7	19.9	20.0
NiCu/C@SiO_2-750	13.8	8.2	3.7	8.1	243	0.68	10.7	4.0	3.9
NiCu/C@SiO_2-800	13.7	7.8	3.6	9.7	241	0.67	11.2	4.4	4.6
NiCu/C@SiO_2-850	13.8	7.5	3.7	10.3	226	0.65	11.7	5.0	5.1
NiCu/C@SiO_2-900	13.9	6.7	3.6	9.1	200	0.65	12.8	6.5	6.4

[a] Ni dispersion was calculated by the CO chemisorption method.

[b] Average crystal size from XRD.

[c] Average particle size from TEM.

Table S2 Total Ni contents and Ni compositions in individual Ni species on the catalyst surface by XPS

Catalyst	Total surface Ni (wt%)	Metallic Ni (wt%)	NiO (wt%)
Ni/C@SiO_2-800	4.7	1.3	3.4
NiCu/C@SiO_2-750	4.3	1.5	2.8
NiCu/C@SiO_2-800	4.0	2.4	1.6
NiCu/C@SiO_2-850	4.0	2.5	1.5
NiCu/C@SiO_2-900	4.1	2.7	1.4

Table S3 Activity comparison between NiCu/C@SiO_2-800 and metal catalysts ever reported for selective reduction of nitrobenzene

Catalyst	Nitrobenzene (mmol)	Hydrogen source	Temperature (°C)	Time	Con. (%)	TOF	Ref.
NiCu/C@SiO_2-800	50	H_2	120	0.5 h	91	46.5 s^{-1}	This work
Ni-Co/CeO_2-CEC	0.81	H_2	150	1 h	88	563 h^{-1}	1
NiFe@NC-3	0.64	H_2	80	2.5 h	98	65 h^{-1}	2
Ni/CeO_2-CAS	2.4	H_2	210	7 h	84	2 h^{-1}	3
Co/mCN-900	1	H_2	120	4 h	100	12 h^{-1}	4
CoN_x-OMC	1	H_2	110	1.5 h	>99	56 h^{-1}	5
Co@mesoNC	1	H_2	110	2 h	55	42 h^{-1}	6
acid MOF@C-800	0.5	H_2	120	20 h	98	1 h^{-1}	7
CoO_x@NC-800	0.5	H_2	110	5 h	100	2 h^{-1}	8
Co@NC-800	0.5	H_2	100	14 h	>99	12 h^{-1}	9
0.09%Pt/γ-Al_2O_3	1.27	H_2	40	50 min	2	216 h^{-1}	10
0.2%Pt/Fe_2O_3	1	H_2	30	2 h	>99	3170 h^{-1}	11
Ni-N-C-700	0.25	$NaBH_4$	r.t.	15 min	2	668 h^{-1}	12
Fe-CN@550	1	$NaBH_4$	50	10 h	98	1968 h^{-1}	13
PdCo/CCF	1	$NaBH_4$	r.t.	0.5 h	91	142 h^{-1}	14
Co@NC-800	1	$N_2H_4 \cdot H_2O$	80	30 min	100	33 h^{-1}	15

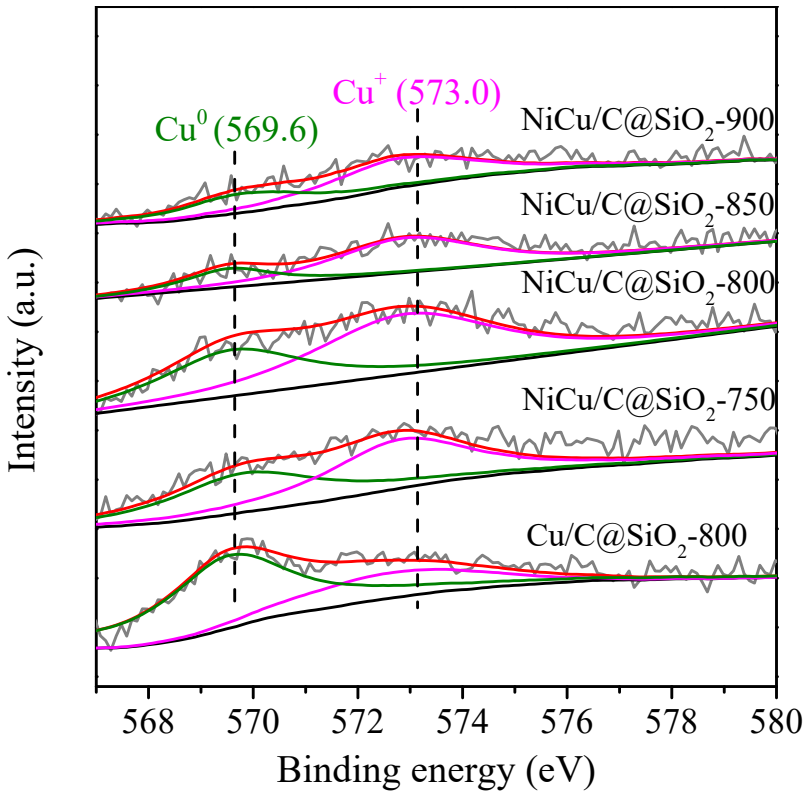

Fig. S1 Cu LMM Auger spectra of Cu/C@SiO_2 and NiCu/C@SiO_2-*T* catalysts.

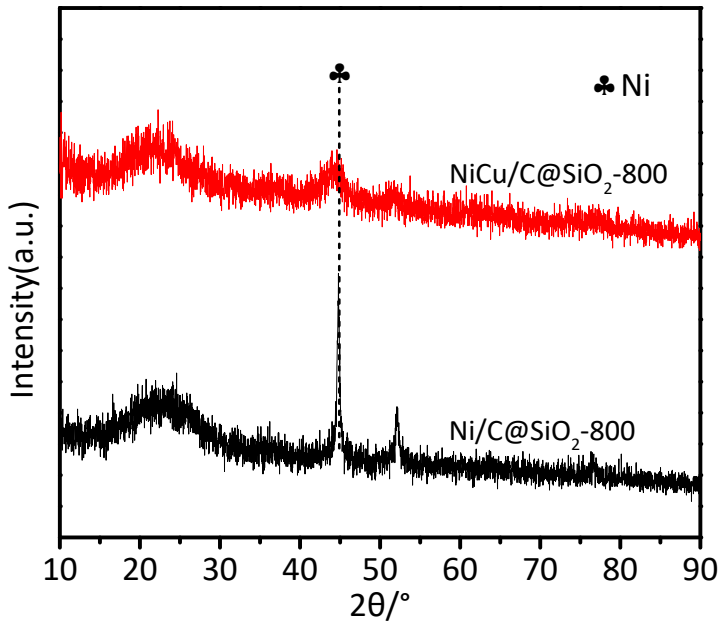

Fig. S2 XRD patterns of spent Ni/C@SiO_2-800 and NiCu/C@SiO_2-800 catalysts for the hydrogenation of nitrobenzene after the 10th run.

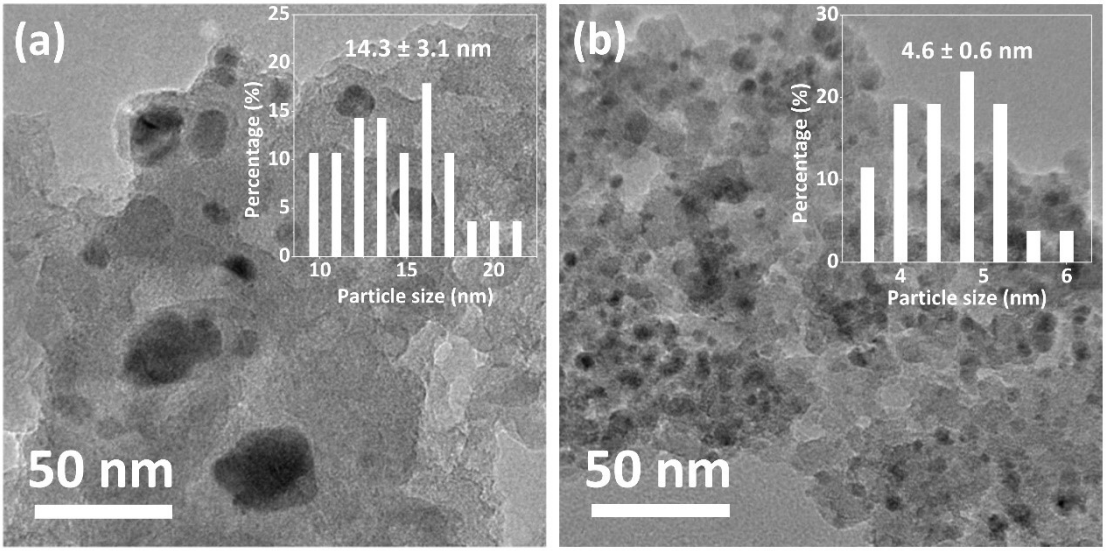

Fig. S3 TEM images of spent catalysts after the 10th run, (a) Ni/C@SiO_2-800 and (b) NiCu/C@SiO_2-800.

References

1 W. Li, W. She, J. Wang, X. Li, J. Li, J. Shi and G. Li, *ACS Appl. Nano Mater.*, 2020, **3**, 10796–10804.

2 Y. Zhang, C. Liu, G. Fan, L. Yang and F. Li, *Dalton Trans*., 2018, **47**, 13668–13679.

3 W. She, T. Qi, M. Cui, P. Yan, S. W. Ng, W. Li and G. Li, *ACS Appl. Mater. Interfaces*, 2018, **10**, 14698–14707.

4 X. Cui, K. Liang, M. Tian, Y. Zhu, J. Ma and Z. Dong, *J. Colloid Interface Sci*., 2017, **501**, 231–240.

5 X. Wei, Z. Zhang, M. Zhou, A. Zhang, W. D. Wu and Z. Wu, *Nanoscale*, 2018, **10**, 16839–16847.

6 Z. Zhang, X. Wei, Y. Yao, Z. Chen, A. Zhang, W. Li, W. D. Wu, Z. Wu, X. D. Chen and D. Zhao, *Small*, 2017. **13**, 1702243.

7 K. Murugesan, T. Senthamarai, M. Sohail, A. S. Alshammari, M.-M. Pohl, M. Beller and R. V. Jagadeesh, *Chem. Sci.*, 2018, **9**, 8553–8560.

8 T. Song, P. Ren, Y. Duan, Z. Wang, X. Chen and Y. Yang, *Green Chem*., 2018, **20**, 4629–4637.

9 S. Gutiérrez-Tarriño, S. Rojas, C. W. Lopes, G. Agostini, J. J. Calvino, A. Corma amd P. Oña-Burgos, *Green Chem.,* 2021, Advance Article.

10 Y Zhang and J Zhou, *J. Catal*., 2021, **395**, 445–456.

11 P. Jing, T. Gan, H. Qi, B. Zheng, X. Chu, G. Yu, W. Yan, Y. Zou, W. Zhang and G. Liu, *Chinese J. Catal*., 2019, **40**, 214–222.

12 F. Yang, M. Wang, W. Liu, B. Yang, Y. Wang, J. Luo, Y. Tang, L. Hou, Y. Li, Z. Li, B. Zhang, W. Yang and Y. Li, *Green Chem*., 2019, **21**, 704–711.

13 M. S. Mirhosseyni and F. Nemati, *Int. J. Biol. Macromol.*, 2021, **175**, 432–442.

14 J. Yang, W. D. Wang and Z. Dong, *J. Colloid Interface Sci*., 2018, **524**, 84–92.

15 Y. Cao, K. Liu and C. Wu, H. Zhang and Q. Zhang, *Appl. Catal., A*, 2020, **592**, 117434.