

Supporting Information

MOFs-derived Ni@NC catalyst: synthesis, characterization, and application in one-pot hydrogenation and reductive amination

Jiayi Li,^{a#} Bowei Wang,^{abc#} Yutian Qin,^a Qin Tao and Ligong Chen^{*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 author. E-mail: lgchen@tju.edu.cn (Ligong Chen)

These authors contributed equally to this work.

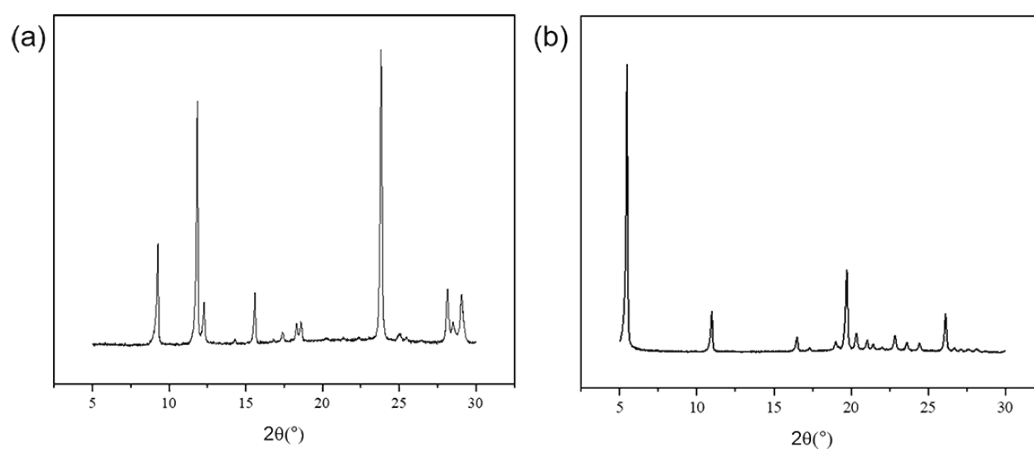


Figure S1. XRD partterns of (a) Ni-MOF-NH₂ and (b) Ni-MOF.

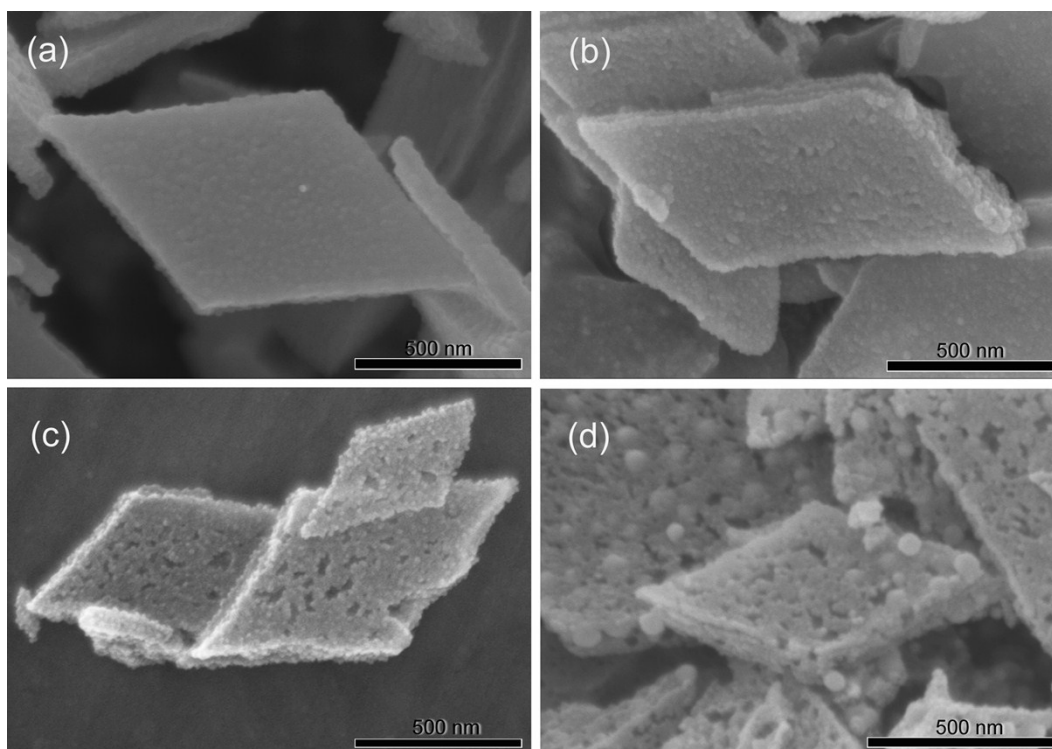


Figure S2. SEM images of (a) Ni@NC-400-1.5, (b) Ni@NC-500-1.5, (c) Ni@NC-600-1.5,(d) Ni@NC-700-1.5.

Table S1. Particle sizes of Ni@C-T-t and Ni@NC-T-t series materials caculated by Debye-Scherrer Equation and measured from TEM images

Sample	Ni@NC-400-1.5	Ni@NC-500-1.5	Ni@NC-600-1.5	Ni@NC-700-1.5	Ni@C-600-1.5	Ni@NC-600-1	Ni@NC-600-2
Size XRD/nm	5.5	5.7	6.3	11.0	66.7	5.9	30.9
Size TEM/nm	-	5.2-6.4	6.0-7.0	9.6-10.8	-	-	-

Table S2. Physicochemical properties of different Ni hybrids

complex	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Content(wt%)				
			C	N	H	O	Ni

Ni@NC-400-1.5	240.136	0.441	20.97	3.31	0.892	27.00	47.82
Ni@NC-500-1.5	257.972	0.298	19.95	2.65	0.64	25.78	51.47
Ni@NC-600-1.5	213.413	0.276	18.09	1.87	0.42	25.56	53.28
Ni@NC-700-1.5	184.431	0.233	18.65	1.15	0.28	20.65	59.36
Ni@C-600-1.5	36.605	0.041	1.15	0	0.06	37.71	61.08

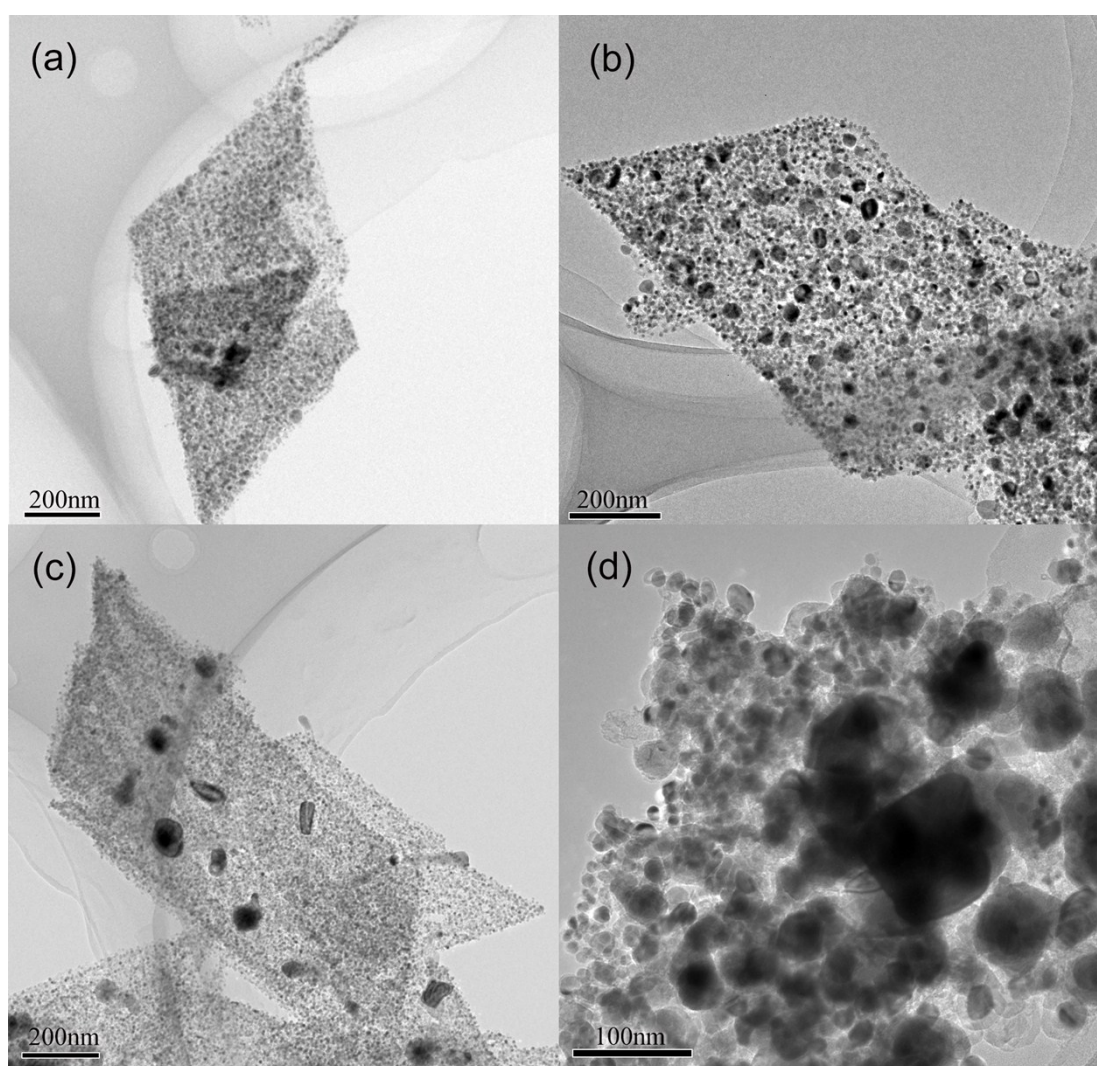


Figure S3. TEM images of (a)Ni@NC-500-1.5; (b) Ni@NC-600-1.5; (c) Ni@NC-700-1.5 and (d)Ni@C-600-1.5 hybrids.

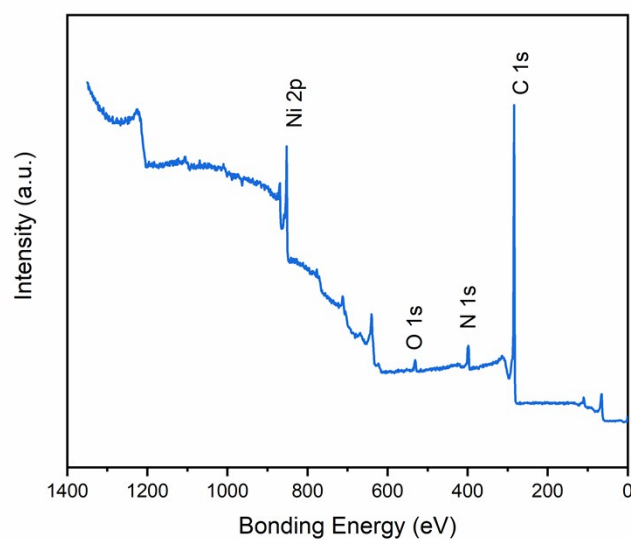


Figure S4. XPS global spectrum of Ni@NC-600-1.5.

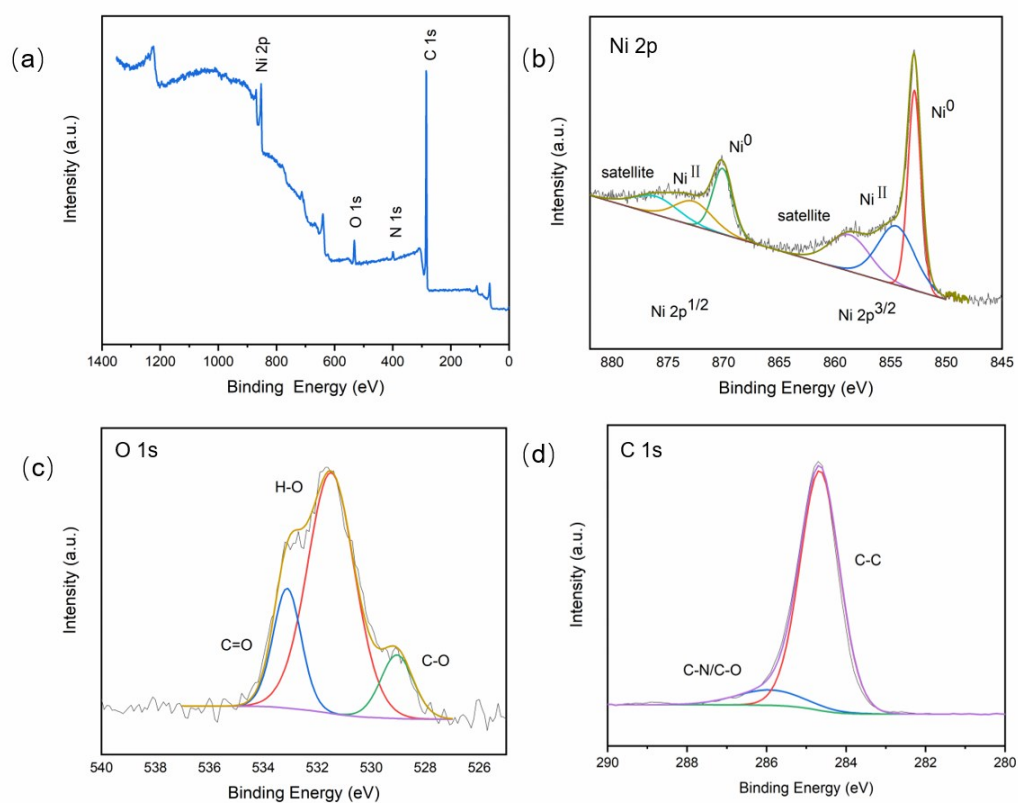


Figure S5. XPS spectra of Ni@NC-500-1.5. (a) Global spectrum, (b) Ni 2p, (c) O 1s and (d) C1s regions.

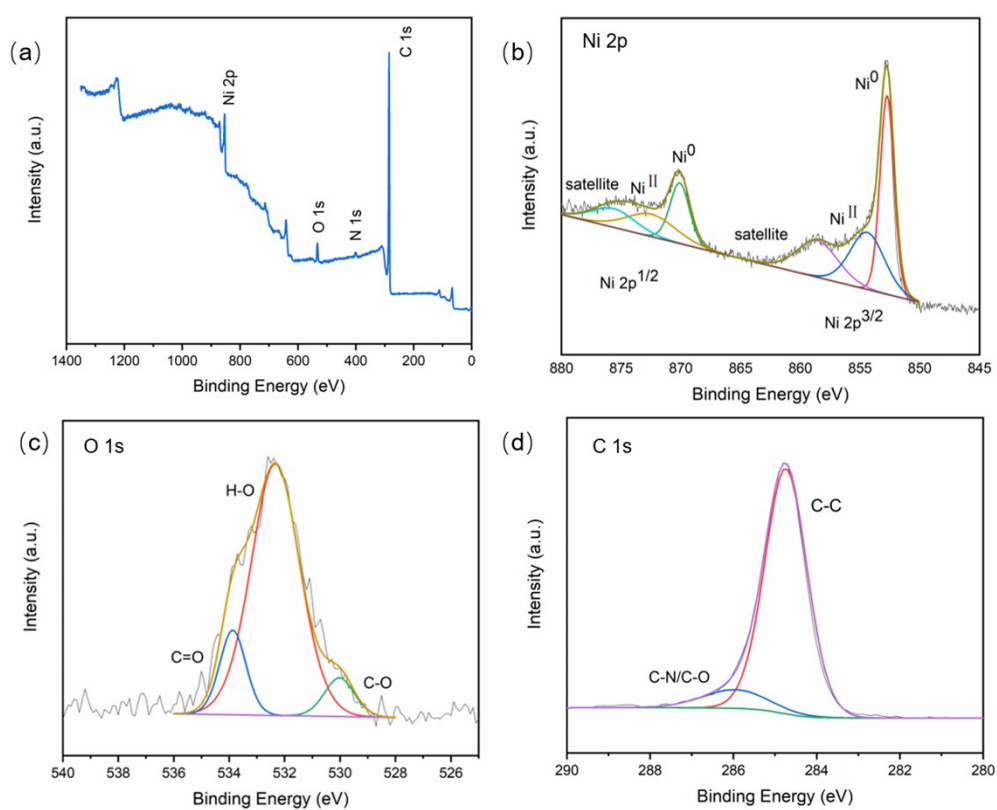


Figure S6. XPS spectra of Ni@NC-700-1.5. (a) Global spectrum, (b) Ni 2p, (c) O 1s and (d) C1s regions.

Table S3. Atomic ratios of different nitrogen species

	Ni-N	Pyridinic N	Pyrrolic N	Graphitic N	Ni-O
Ni@NC-500-1.5	0	50.14	13.40	33.22	3.23
Ni@NC-600-1.5	5.79	37.68	8.98	44.04	3.51
Ni@NC-700-1.5	2.86	34.65	8.45	50.28	3.76

Table S4. Surface element content of materials

	Atomic %			
	C	N	O	Ni
Ni@NC-500-1.5	88.20	3.03	5.17	3.58

Ni@NC-600-1.5	85.95	7.77	2.38	3.91
Ni@NC-700-1.5	90.49	2.67	3.88	2.96

Table S5. Comparison between the catalytic performance for one-pot reductive amination over various catalysts reported

catalyst	T/°C	P/Mp a	t/h	solvent	Yield (%)	Ref
Ni@NC-600-1.5	100	2	4	THF/H ₂ O (1:1)	98	this work
Co ₃ O ₄ /NGr@C	110	5	24	THF/H ₂ O (10:1)	95	¹
Co-N _x /C-800-AT	110	1	10	MeOH	70.9	²
Co-DABCO-TPA@C-800	120	4	24	t-BuOH	92	³
Co/mCN-900	150	1		EtOH	99.8	⁴
MoS ₄ -catalyst	70	2	18	THF	99	⁵
CuO/Al ₂ O ₃	125	5	0.75	toluene	67	⁶
Pd/Fe ₃ O ₄	RT	1	6	EtOH	92	⁷
Pd/Fe ₃ O ₄	RT	0.1	6	EtOH	94	⁸
Fe@Pd/C	80	3	8	H ₂ O	96	⁹
Pd/Fe ₃ O ₄ @C	60	0.1	8	H ₂ O	92	¹⁰
Co ₂ Rh ₂ /C	RT	1	24	MeOH	93	¹¹
AuPd-Fe ₃ O ₄	RT	0.1	3	MeOH	93	¹²

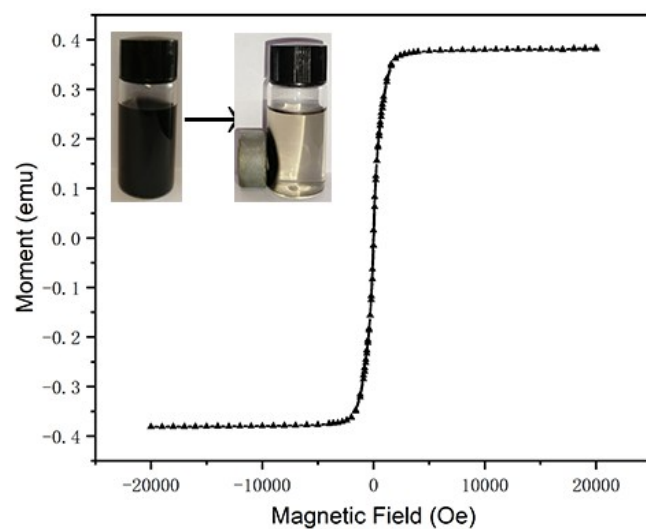


Figure S7. Magnetic hysteresis loop of the as-prepared Ni@NC-600-1.5 composite. Insert: Photograph showing the facile separation of the catalyst via an external magnet.

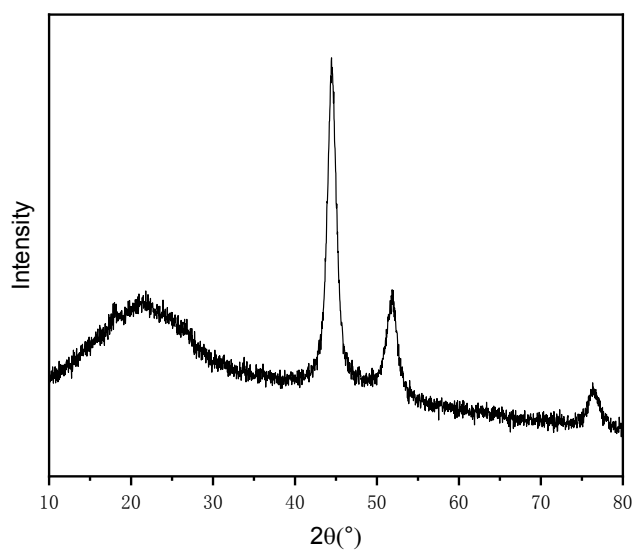


Figure S8. XRD patterns of recycled Ni@NC-600-1.5.

Reference

1. T. Stemmler, F. A. Westerhaus, A.-E. Surkus, M.-M. Pohl, K. Junge and M. Beller, *Green Chem.*, 2014, **16**, 4535-4540.
2. L. Jiang, P. Zhou, Z. Zhang, Q. Chi and S. Jin, *New J. Chem.*, 2017, **41**, 11991-11997.

3. R. V. Jagadeesh, K. Murugesan, A. S. Alshammari, H. Neumann, M. M. Pohl, J. Radnik and M. Beller, *Science*, 2017, **358**, 326-332.
4. X. Cui, K. Liang, M. Tian, Y. Zhu, J. Ma and Z. Dong, *J. Colloid Interface Sci.*, 2017, **501**, 231-240.
5. E. Pedrajas, I. Sorribes, K. Junge, M. Beller and R. Llusar, *Green Chem.*, 2017, **19**, 3764-3768.
6. A. L. Nuzhdin, E. A. Artiukha, G. A. Bukhtiyarova, E. A. Derevyannikova and V. I. Bukhtiyarov, *Catal. Commun.*, 2017, **102**, 108-113.
7. S. Wei, Z. Dong, Z. Ma, J. Sun and J. Ma, *Catal. Commun.*, 2013, **30**, 40-44.
8. M. Nasrollahzadeh and S. M. Sajadi, *J. Colloid Interface Sci.*, 2016, **464**, 147-152.
9. N. M. Patil and B. M. Bhanage, *Catal. Today*, 2015, **247**, 182-189.
10. X. Zhou, X. Li, L. Jiao, H. Huo and R. Li, *Catal. Lett.*, 2015, **145**, 1591-1599.
11. I. Choi, S. Chun and Y. K. Chung, *J. Org. Chem.*, 2017, **82**, 12771-12777.
12. A. Cho, S. Byun and B. M. Kim, *Adv. Synth. Catal.*, 2018, **360**, 1253-1261.