Electronic Supplementary Information

Carbon-embedded Ni nanocatalyst derived from Ni-MOFs by sacrificial template method for efficient hydrogenation of furfural to tetrahydrofurfuryl alcohol

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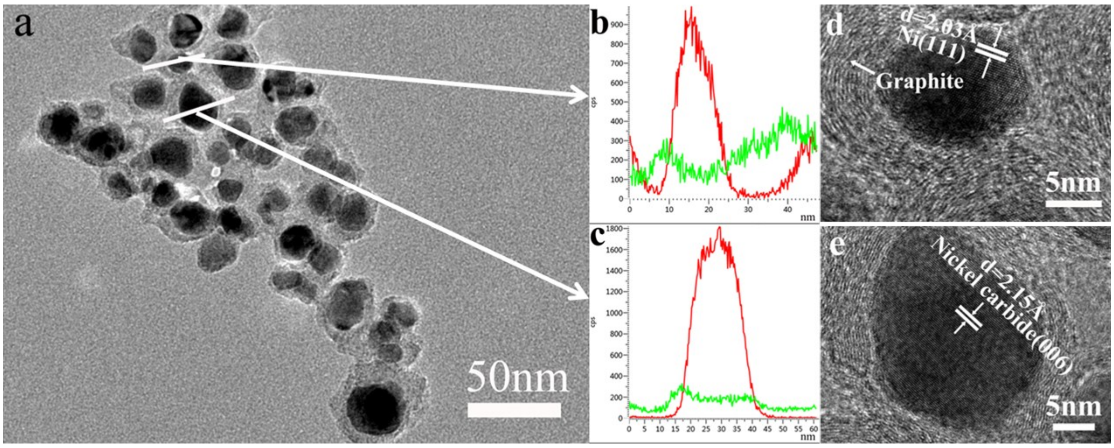

Fig. S1 TEM analysis of Ni/C-500 catalyst (a)TEM image, (b-c) Elemental line-scanning profiles along the direction marked by white lines in (a), (d-e)HRTEM images of Ni and Nickel carbide nanoparticles.

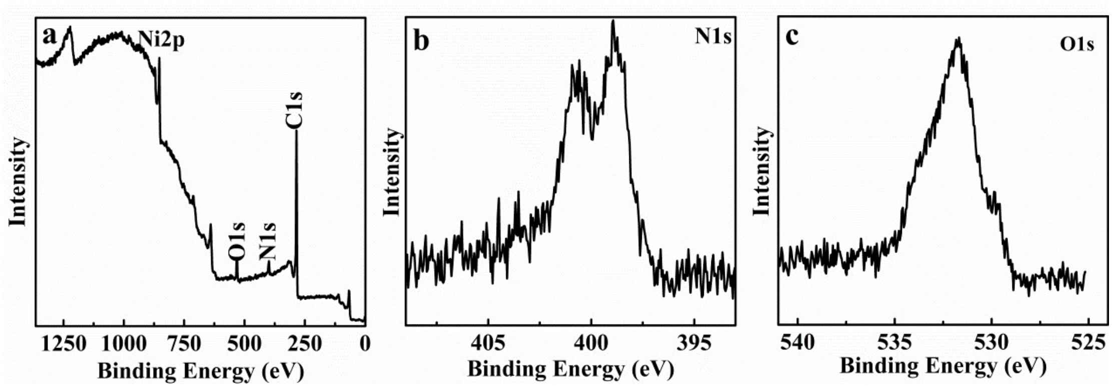

Fig. S2 XPS of Ni/C-500 nanocatalyst (a) full spectrum, (b) N1s and (c) O1s spectra.

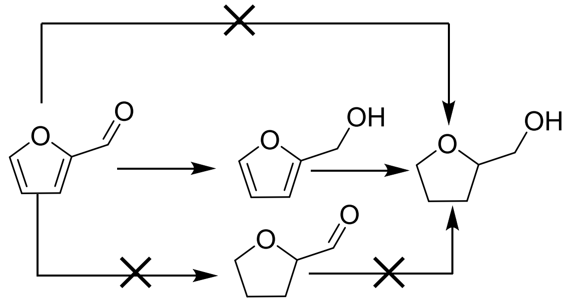

Fig. S3 Reaction network for FAL hydrogenation.

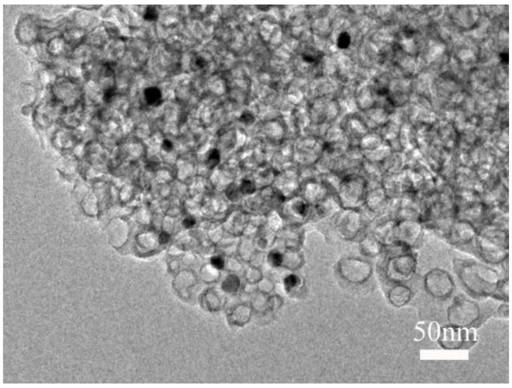

Fig. S4 TEM image of acid treated Ni/C-500 nanocatalyst.

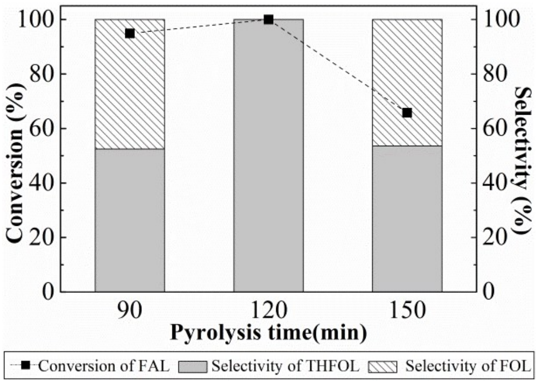

Fig. S5 Effect of pyrolysis time on the hydrogenation of FAL over Ni/C-500. Reaction conditions: catalyst to FAL mass ratio =1:1, FAL = 0.2 mmol, 120 °C, 1MPa H_2 pressure, 120 min, 500 rpm stirring, 5 mL 2-propanol.

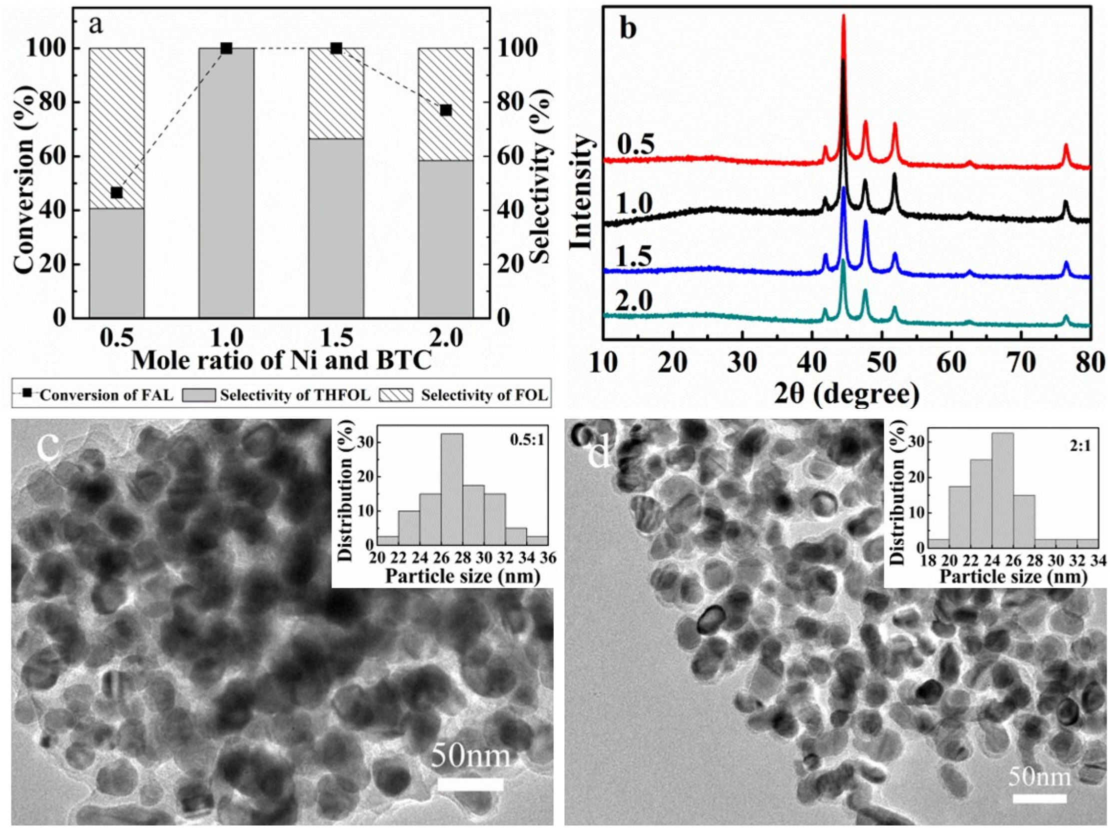

Fig. S6 The Ni/C nanocatalysts derived from the MOFs with different mole ratio of Ni and BTC (0.5-2.0) at 500 ºC for 2 h. (a) the catalytic performance of FAL hydrogenation (Reaction conditions: catalyst to FAL mass ratio =1:1, FAL = 0.2 mmol, 120 °C, 1MPa H_2 pressure, 120 min, 500 rpm stirring, 5 mL 2-propanol), (b) XRD patterns, (c-d) TEM images of the samples with mole ratio of Ni and BTC at 0.5(c) and 2.0(d).

Table S1 Comparison with selected synthesis routes.

Ni-MOFs	Synthesis route	Temperature (ºC)	Time (h)	Yields (%)	Reference
Ni-BTC[1]	Solvothermal	150	12	Not mentioned	1
$C_{82}H_{102}N_{12}O_{32}Ni_3$[2]	Hydrothermal	180	72	~50%	2
Ni- BTC[3, 4]	Solvothermal	150	24	Not mentioned	4
$C_9H_{10}NiO_9$[5]	Hydrothermal	130	72	63	5
$C_{15}H_{19}NO_{16}Ni_3$[6]	Hydrothermal	120	120	71	6
$C_{39}H_{44}N_4Ni_{14}O_{21}$[7]	Hydrothermal	160	48	Not mentioned	7
Ni-BTC[This work]	Oil-bath	150	2.5	88	This work

Table S2 The summary of the content of Ni and nickel carbide in Ni/C-500 nanocatalyst.

Type of Ni	Content in Ni/C-500 (%)
Metal Ni	51.10
Nickel carbide	2.53

Table. S3 Hydrogenation of FAL over Ni-based heterogeneous catalysts in recent published works.

Catalyst	Reaction conditions			Conversion (%)	Selectivity (%)		Cycle test
	T(ºC)	P_{H_2}(MPa)	T(min)		FOL	THFOL	
15%Ni/CNT [8]	100	3	600	94.6	<3	90.5	---
5 wt% Ni/CN[9]	200	1	240	96	95	2	1st to 5th little changed
Cu_1 Ni_3 /MgAlO [10]	150	4	180	>99	0	93	1st to 5th stability decrease regenerated
Fe(NiFe)O_4– SiO_2 [11]	90	2	240	94.3	100	---	---
Ni –Fe (2-1) HT-673 [12]	150	3	120	74	94	---	1st to 5th little loss in activity
Ni–Pd (5:1)/TiO_2 –ZrO_2[13]	130	5	400	>99	2.1	93.4	---
3% Pd/MFI[14]	220	3.4	300	84	---	99	1st to 5th slight decrease in conversion
Pt/MWNT-4[15]	150	2	300	94.4	79	---	1st to 3rd slight deactivation
This work	120	1	120	100	0	100	---
This work	120	1	60	99.4	24.8	75.2	1st to 5th slight decrease in conversion

As summarized in Table S1, our Ni/C-500 catalyst performed higher activity for hydrogenation of FAL to THFOL than other supported Ni catalysts, even better than some supported noble metal catalysts. In addition, there are little changes in the conversion of FAL and selectivity of THFOL, indicating the stability of Ni/C-500 catalyst.

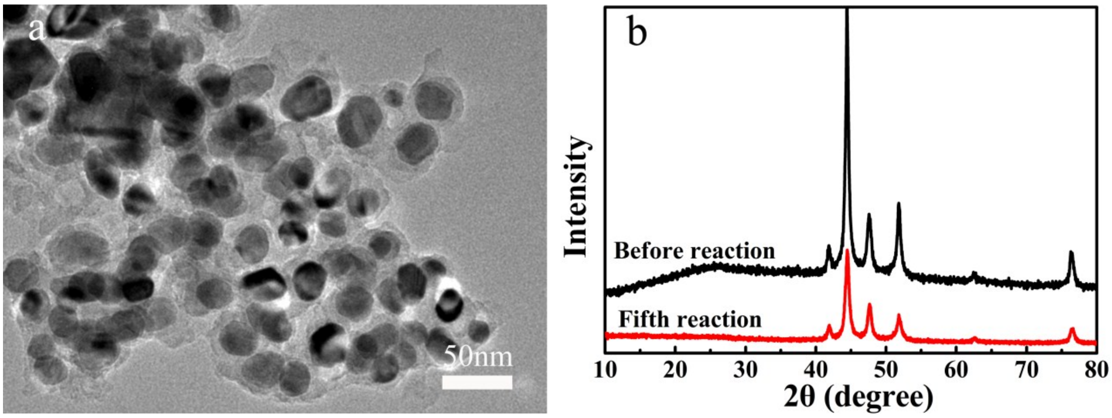

Fig. S7 (a) TEM of the Ni/C-500 nanocatalyst after reaction and (b) the comparison of the Ni/C-500 nanocatalysts before and after reaction.

Reference

1. T. Liu, C. Dai, M. Jia, D. Liu, S. Bao, J. Jiang, M. Xu and C. M. Li, *ACS Appl. Mater. Interfaces.*, 2016, 8, 16063-16070.
2. R. A. Agarwal and S. Mukherjee, *Polyhedron*, 2016, 105, 228-237.
3. T. Tian, L. A. Ai and J. Jiang, *RSC Adv.*, 2015, 5, 10290–10295.
4. T. Q. N. Tran, G. Das and H. H. Yoon, *Sensors and Actuators B: Chemical*, 2017, 243, 78-83.
5. S. Saheli and A. Rezvani, *Journal of Molecular Structure*, 2017, 1127, 583-589.
6. Y. Fu, J. Su, S. Yang, G. Li, F. Liao, M. Xiong and J. Lin, *Inorganica Chimica Acta*, 2010, 363, 645-652.
7. F. Israr, D. K. Kim, Y. Kim and W. Chun, *Quim Nova*, 2016, 39, 669-675.
8. L. Liu, H. Lou and M. Chen, *Int. J. Hydrogen Energy*, 2016, 41, 14721-14731.
9. T. V. Kotbagi, H. R. Gurav, A. S. Nagpure, S. V. Chilukuri and M. G. Bakker, *RSC Adv.*, 2016, 6, 67662-67668.
10. J. Wu, G. Gao, J. Li, P. Sun, X. Long and F. Li, *Appl. Catal., B Environ.*, 2017, 203, 227-236.
11. A. Halilu, T. H. Ali, A. Y. Atta, P. Sudarsanam, S. K. Bhargava and S. B. Abd Hamid, *Energ Fuel*, 2016, 30, 2216-2226.
12. W. S. Putro, T. Hara, N. Ichikuni and S. Shimazu, *Chem. Lett.*, 2017, 46, 149-151.
13. B. Chen, F. Li, Z. Huang and G. Yuan, *Appl. Catal., A Gen.*, 2015, 500, 23-29.
14. N. S. Biradar, A. M. Hengne, S. N. Birajdar, P. S. Niphadkar, P. N. Joshi and C. V. Rode, *ACS Sustain. Chem. Eng.*, 2014, 2, 272-281.
15. C. Wang, Z. Guo, Y. Yang, J. Chang and A. Borgna, *Ind Eng Chem Res*, 2014, 53, 11284-11291.