Supporting Information

Efficient single-atom Ni for catalytic transfer hydrogenation of furfural to furfuryl alcohol

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Chemical and reagents

$Ni(acac)_2 \cdot 2H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ were purchased from Adamas Reagent Co., Ltd. Dimethylimidazole was obtained from TCI (Shanghai) Development Co., Ltd. Furfural, furfuryl alcohol, methyl alcohol, ethyl alcohol, n-Propanol, 2-Propanol, n-Butanol, 2-Butanol and substrate extension chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. In addition, the commercial noble metals catalysts were purchased from Aladdin Reagent. All chemicals were used without further treatments.

Please note that Figure S12 has been corrected due to a previously unforeseen administrative error.

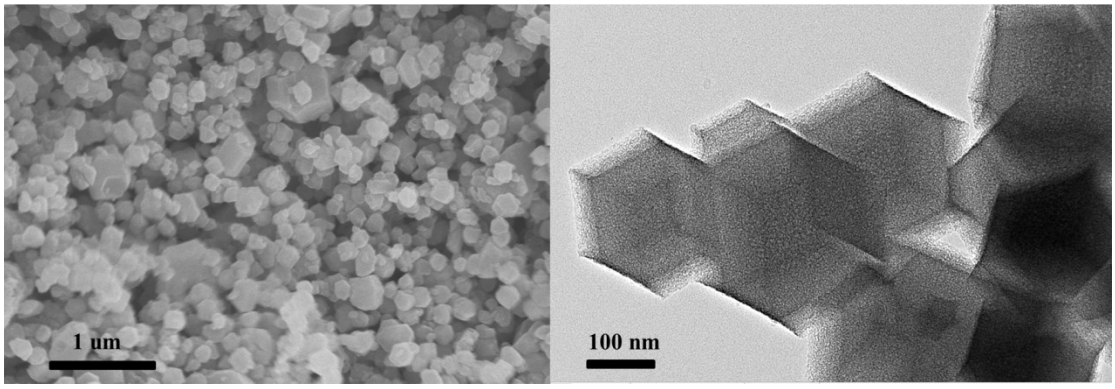

Figure S1. SEM and TEM of Ni@ZIF-8.

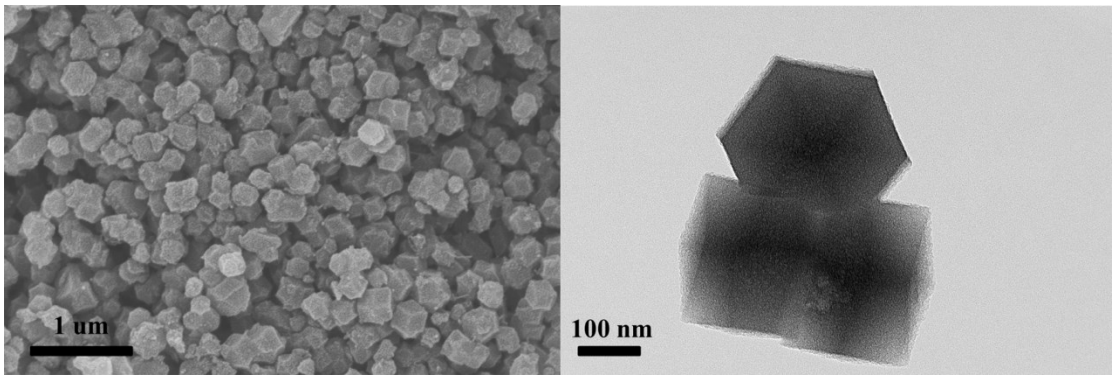

Figure S2. SEM and TEM of Ni-SAs/NC.

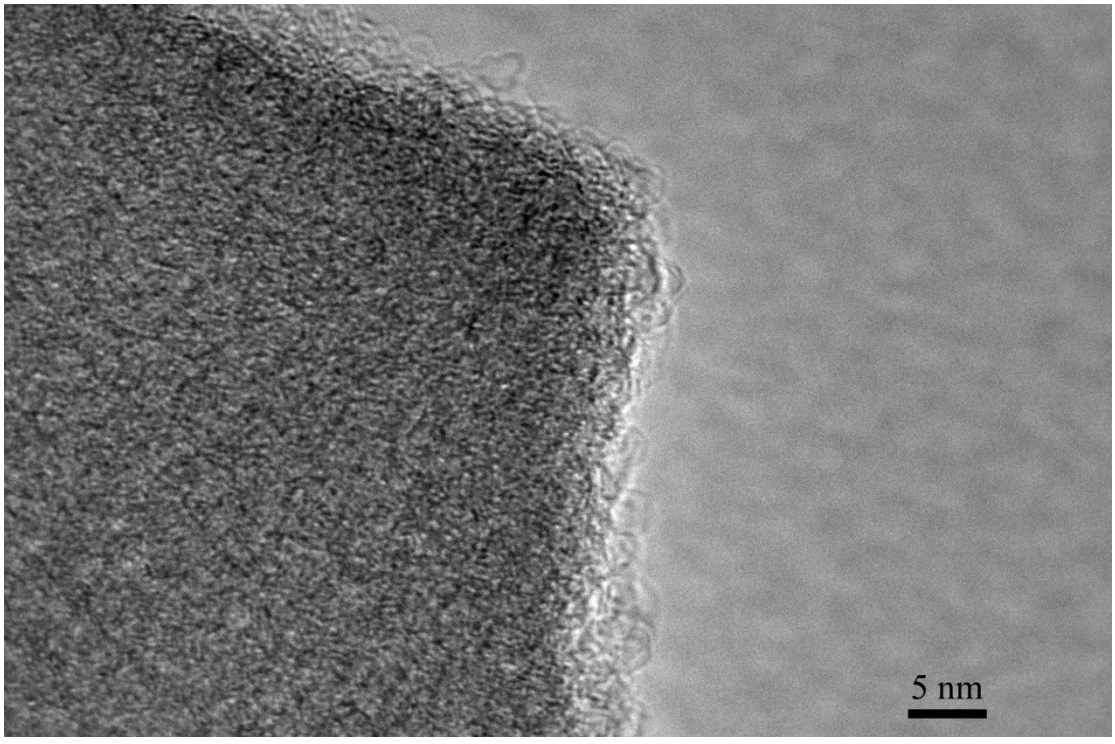

Figure S3. HR-TEM of Ni-SAs/NC.

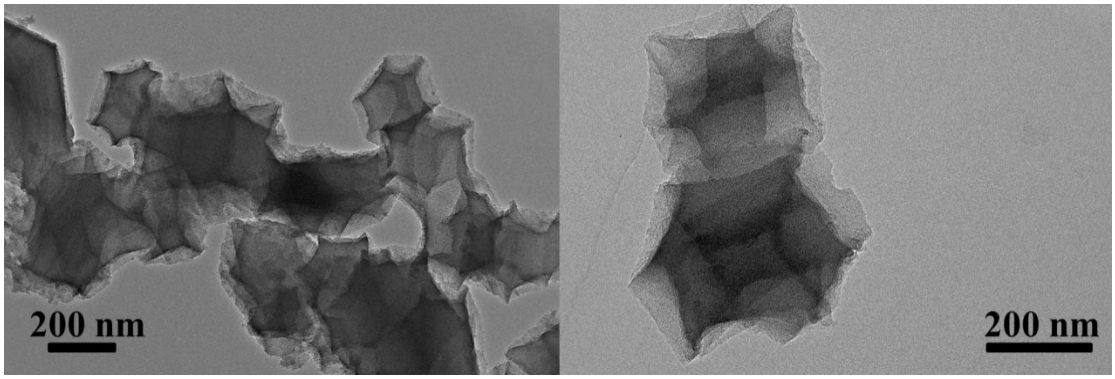

Figure S4. TEM of Ni-NPs/NC.

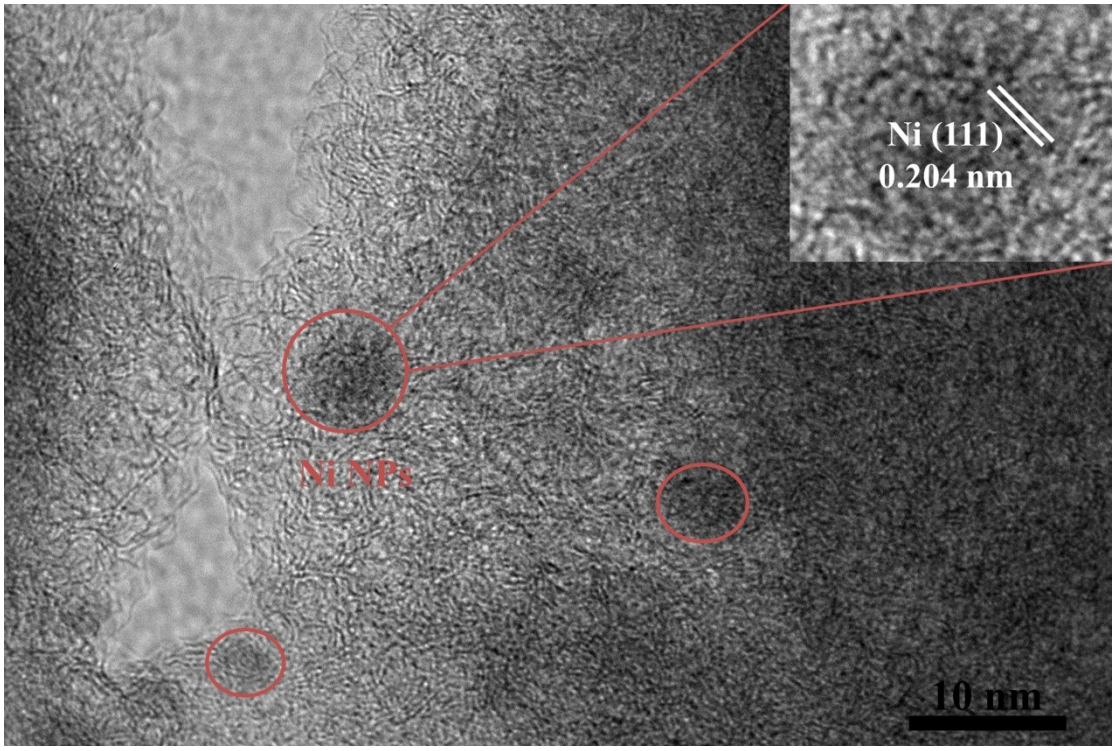

Figure S5. HR-TEM of Ni-NPs/NC.

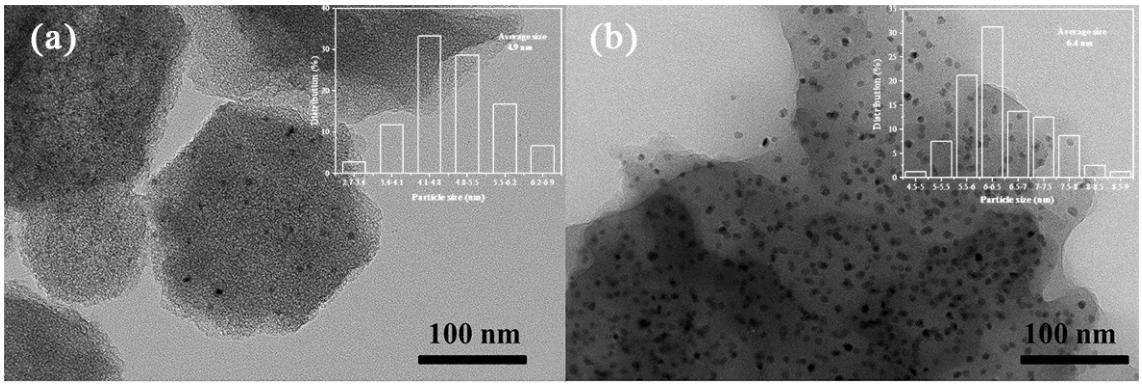

Figure S6. (a) TEM of Ni/NC, (b) TEM of Ni/AC.

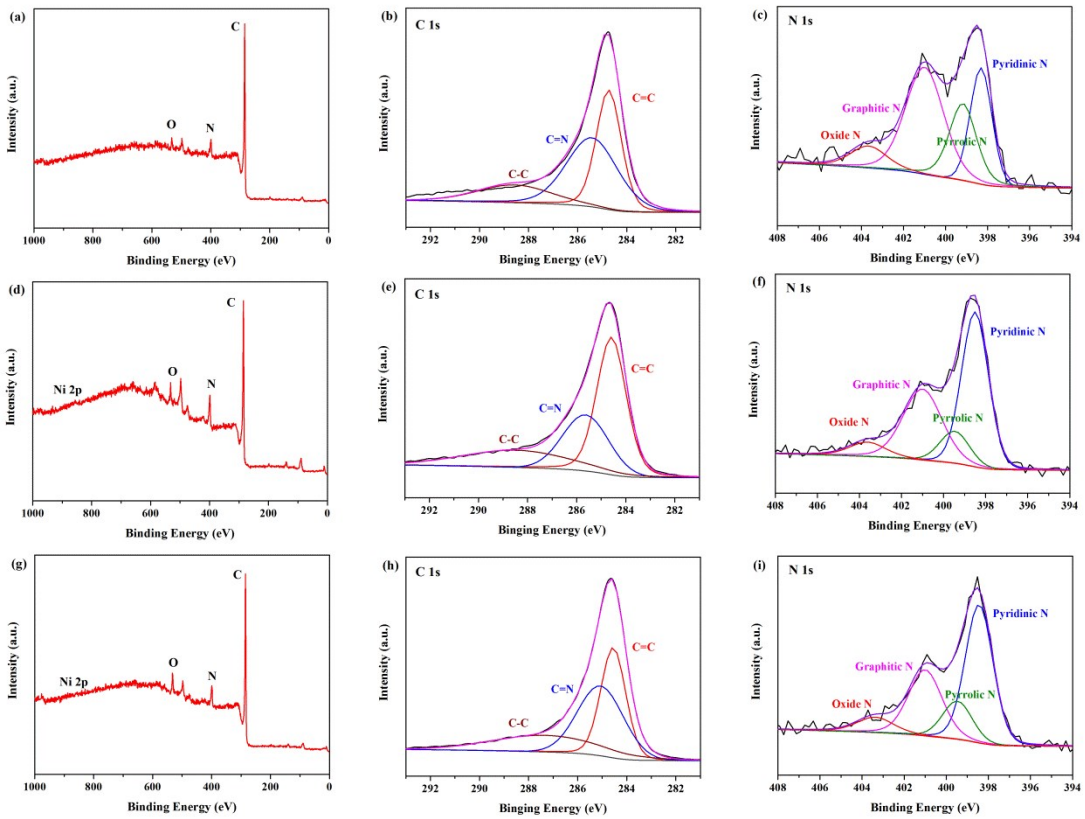

Figure S7. (a), (b) and (c) XPS spectra of NC; (d), (e) and (f) XPS spectra of Ni-SAs/NC; (g), (h) and (i) XPS spectra of Ni-NPs/NC;

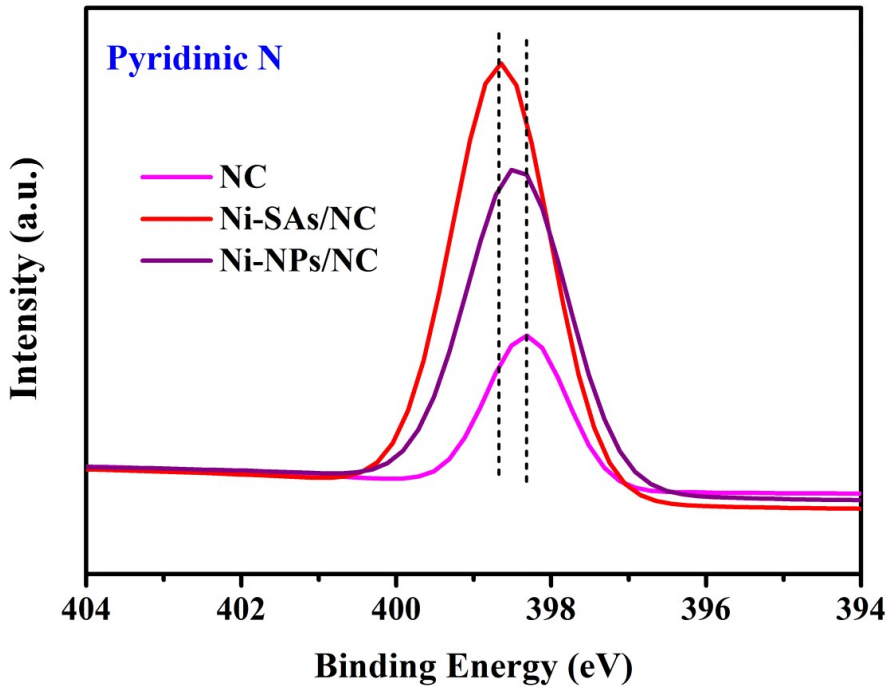

Figure S8. Pyridinic-N of NC; Ni-SAs/NC and Ni-NPs/NC.

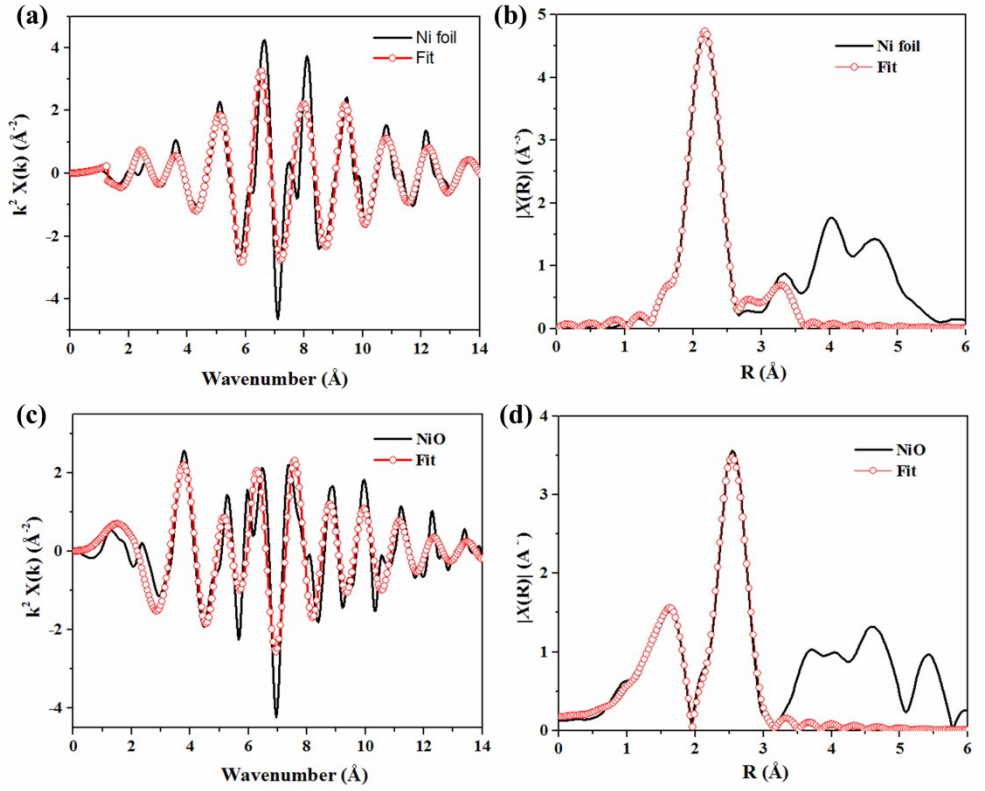

Figure S9. (a) and (b) the corresponding EXAFS fitting curves of Ni foil. (c) and (d) the corresponding EXAFS fitting curves of NiO.

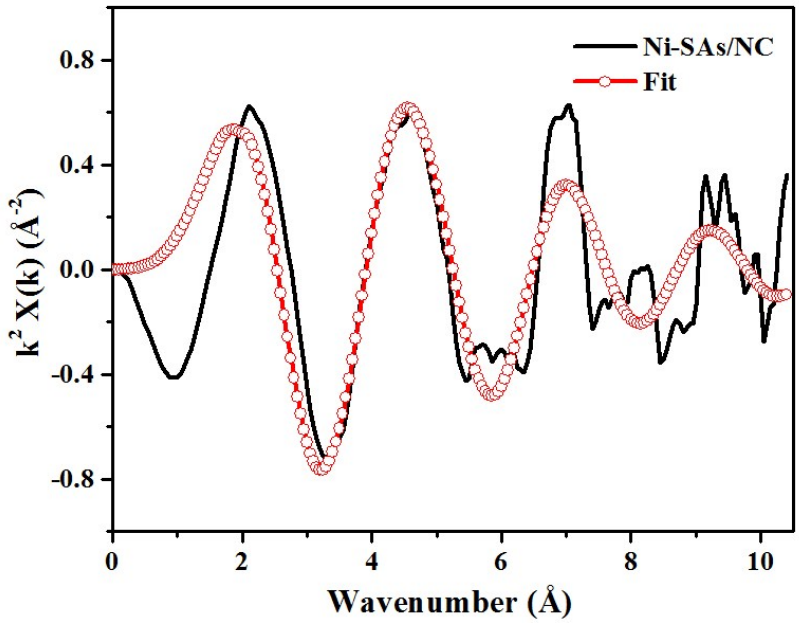

Figure S10. The corresponding EXAFS k space fitting curves of Ni-SAs/NC.

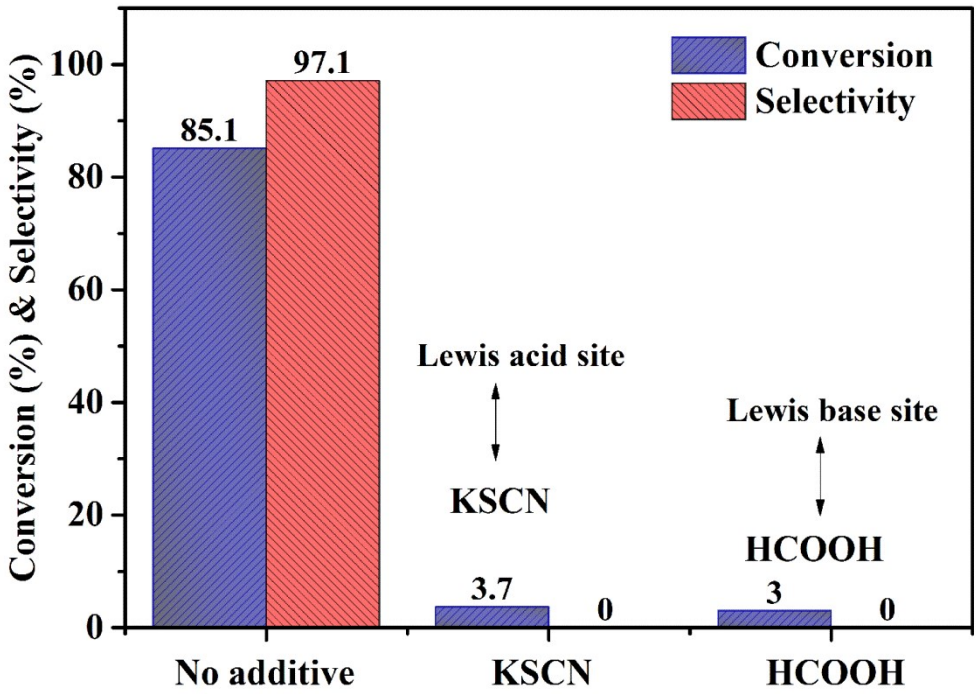

Figure S11. Control experiments in CTH of FF to FAL. Before the reaction, a specified amount of KSCN or HCOOH were injected into the reaction system. Reaction conditions: 1 mmol FF, 8 mL 2-propanol, 25 mg catalyst, 120 °C, 3 h, 2 MPa N_2

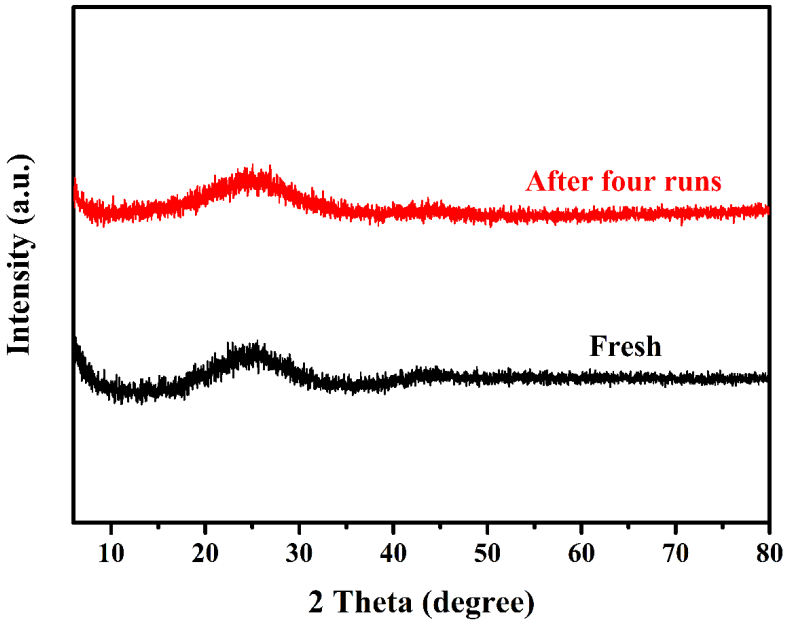

Figure S12. XRD patterns of the fresh and reused Ni-SAs/NC catalyst.

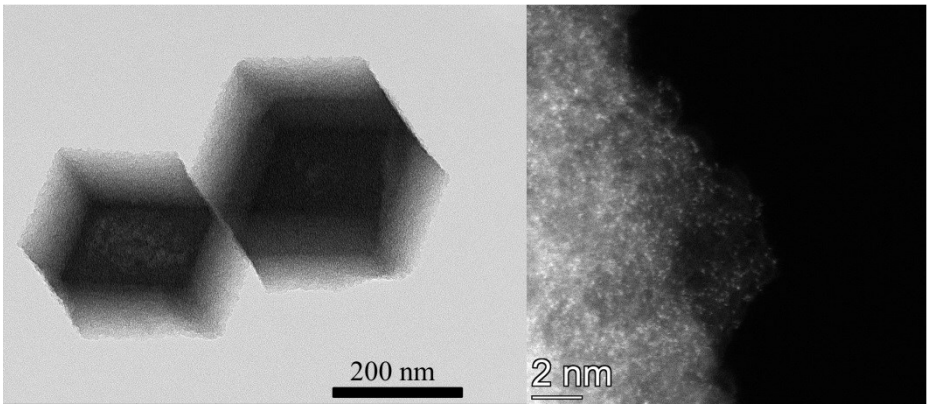

Figure S13. TEM and HAADF-STEM images of the reused Ni-SAs/NC catalyst.

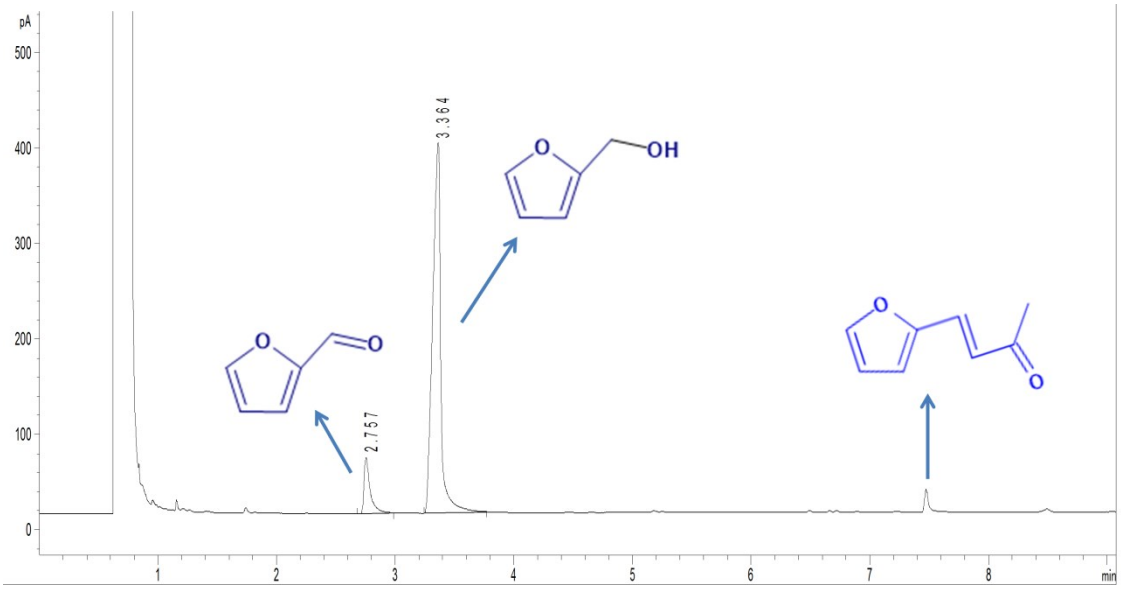

Figure S14. GC spectra with the main retention times (from GC-MS) of the reaction mixtures catalyzed by Ni-SAs/NC catalyst

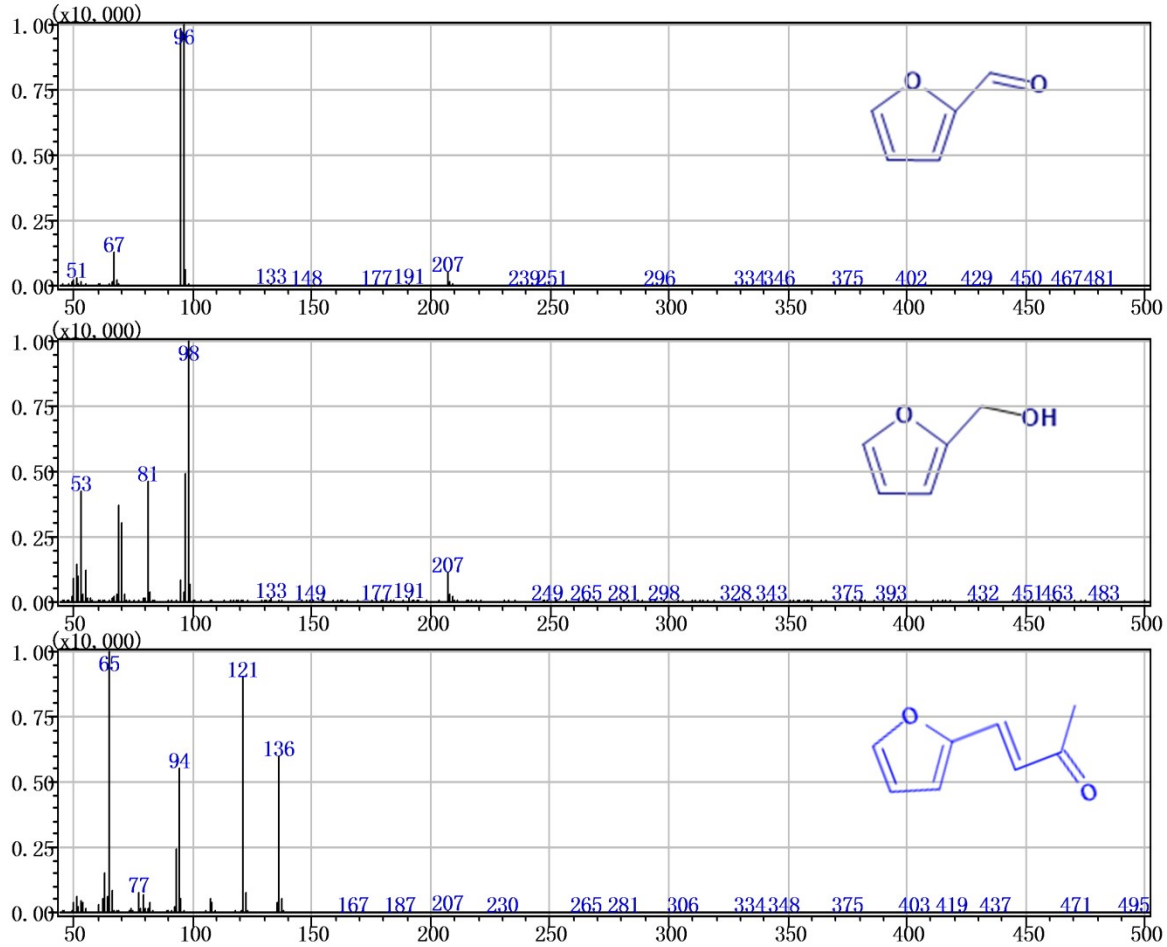

Figure S15. Representative MS spectra of the reaction mixture in FF hydrogenation.

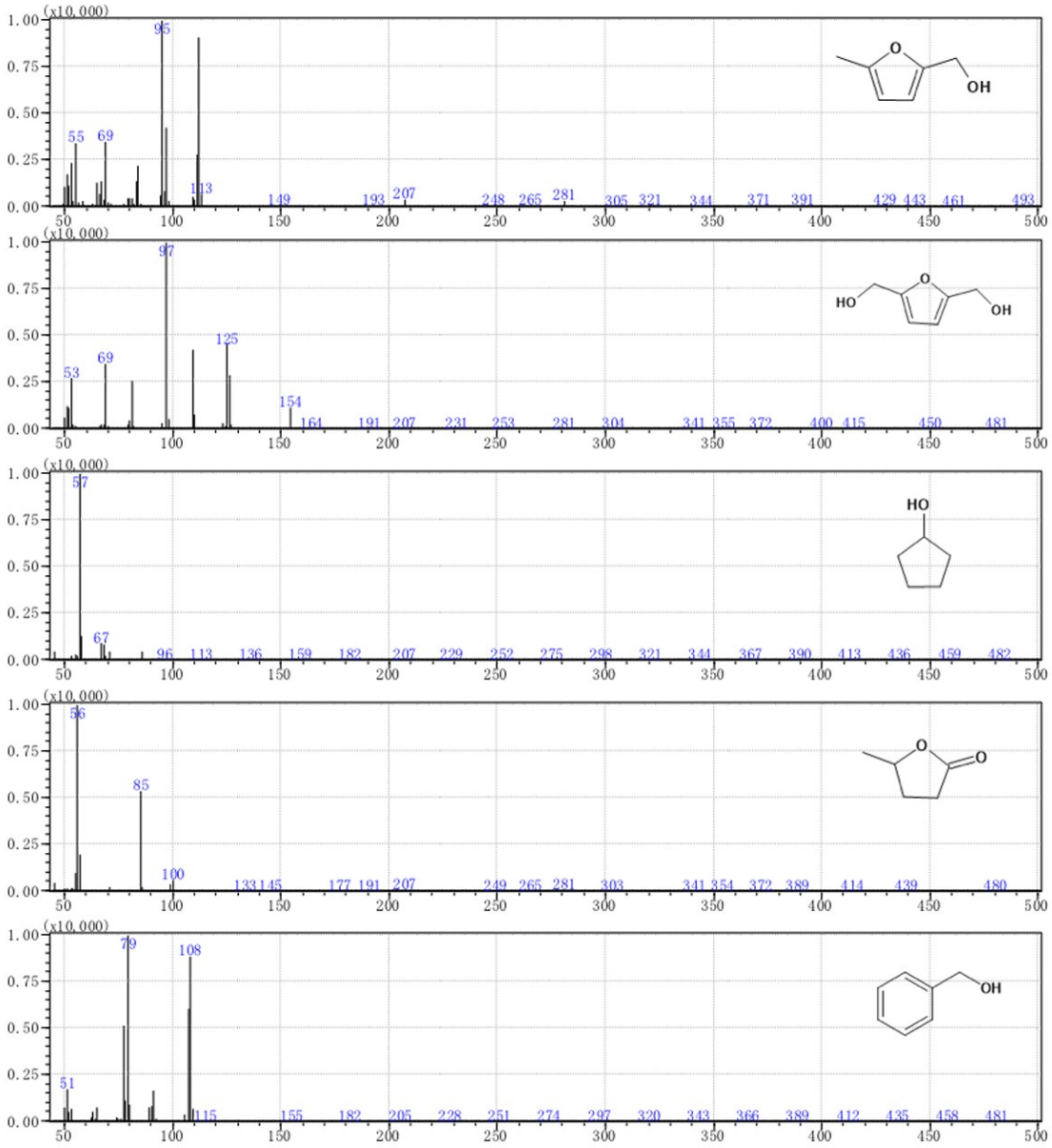

Figure S16. Representative MS spectra (from GC-MS) of the reaction products in Table 2.

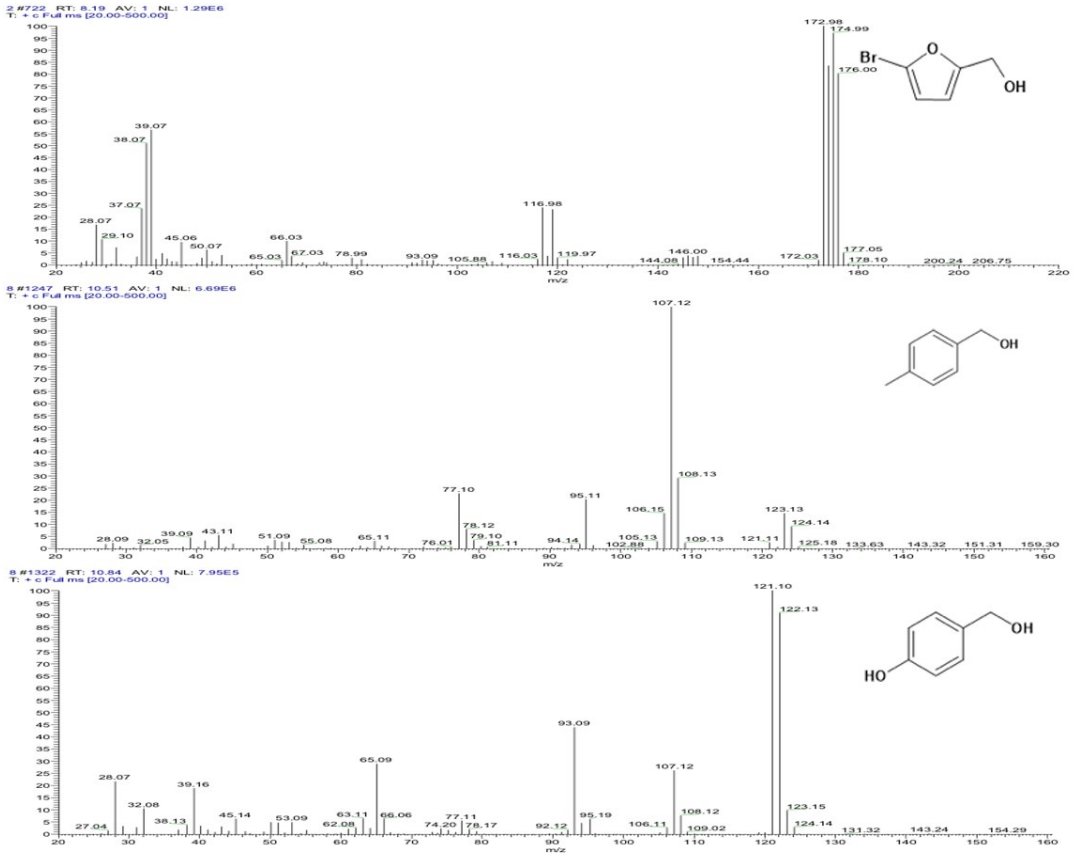

Figure S17. Representative MS spectra (from GC-MS) of the reaction products in Table 2.

Table S1. The specific surface area, average pore volume, pore size and Ni content.[a]

Sample	S_{BET} (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Average pore size (nm)	Ni [b] (wt %)
Ni@ZIF-8	1910	0.64	1.45	0.05
NC	1183	0.37	1.79	-
Ni-SAs/NC	1037	0.32	2.07	0.12
Ni-NPs/NC	954	0.31	1.87	0.65
Ni/NC	1114	0.27	2.35	4.39
Ni/AC	1275	0.21	2.67	5.16

[a]: by ASAP 2020 Plus, [b]: by ICP-OES.

Table S2. The XPS element analysis of different sampales.

Sample	C	N	O	Ni
Ni@ZIF-8	75.01	19.49	4.69	0.23
NC	91.29	6.32	2.39	-
Ni-SAs/NC	84.18	12.35	3.33	0.15
Ni-NPs/NC	86.43	8.66	4.63	0.89
Ni/NC	82.11	8.97	6.67	1.52
Ni/AC	88.52	-	10.31	1.18

Table S3. Ni K-edge EXAFS curves fitting paramerers.[a]

Sample	Path	N	ΔE (eV)	R (Å)	σ^2 ($Å^2$)	R-factor
Ni foil [b]	Ni-Ni1	12	0.67	0.38	0.47	0.006
	Ni-Ni2	6	0.67	1.35	1.63	
NiO [c]	Ni-O	6	1.34	1.24	1.17	0.004
	Ni-Ni	12	0.81	0.54	0.51	
Ni-SAs/NC [d]	Ni-N(O)	4.46	3.91	1.98	3.14	0.017

[a] N, coordination number; R, distance between absorber and backscatter atoms; σ^2, Debye-Waller factor to account for both thermal and structural disorders; Δ E, inner potential correction; R-factor indicates the goodness of the fit. [b] Fitting range: $3.0 \leq k$ (/Å) ≤ 12.4 and $1.0 \leq R$ (Å) ≤ 3.6. [c] Fitting range: $3.0 \leq k$ (/Å) ≤ 11.5 and $1.0 \leq R$ (Å) ≤ 3.0. [d] Fitting range: $3.0 \leq k$ (/Å) ≤ 10.4 and $1.0 \leq R$ (Å) ≤ 2.2.

Table S4. Summary of different catalysts for selective hydrogenation of FF to FAL.

	Catalyst	Reaction temperature (°C)	Reaction time (h)	Conv. (%)	Selec. (%)	Activation energy (kJ/mol)	Ref.
1	Fe_2O_3@HAP	180	10	96.2	95.3	47.69	[1]
2	Co_3O_4/MC	160	1	99.0	99.0	-	[2]
3	$NiFe_2O_4$	180	6	99.0	95.0	48.2	[3]
4	Cu/MgO-Al_2O_3	210	1	100	89.0	-	[4]
5	Cu-Mg-Al	150	6	100	100	-	[5]
6	$DyCl_3$-Ru/C	180	3	98.0	97.0	-	[6]
7	Mn-NCA-700	160	1	98.0	85.0	83.0	[7]
8	Zr-SBA-15	90	6	65.0	45.0	-	[8]
9	ZJU-199-350	130	3	97.1	99	-	[9]
10	ZrPN	100	15	93.0	96.8	70.5	[10]
11	Zr-LS	80	3	97.0	97.0	52.25	[11]
12	Ni-SAs/NC	130	2	95.6	96.8	36.86	This work

Reference

[1] F. Wang, Z. Zhang, *ACS Sustainable Chem. Eng.,* 2016**, 5**, 942-947.

[2] G.-H. Wang, X. Deng, D. Gu, K. Chen, H. Tüysuz, B. Spliethoff, H. J. Bongard, C. Weidenthaler, W. Schmidt, F. Schüth, *Angew. Chem., Int. Ed.* 2016, **55**, 11101−11105.

[3] J. He, S. Yang, A. Riisager, *Catal. Sci. Technol,* 2018**, 8**, 790-797.
[4] H. Chen, H. Ruan, X. Lu, J. Fu, T. Langrish, X. Lu, *Mol Catal.,* 2018**, 445**, 94-101.
[5] M.M. Villaverde, T.F. Garetto, A.J. Marchi, *Catal. Commun,* 2015, **58**, 6-10.
[6] P. Panagiotopoulou, N. Martin, D.G. Vlachos, *ChemSusChem,* 2015**, 8**, 2046-2054.
[7] S. Zhou, G. Chen, X. Feng, M. Wang, T. Song, D. Liu, F. Lu, H. Qi, *Green Chem.*, 2018, **20**, 3593-3603.
[8] Y. Sha, Z. Xiao, H. Zhou, K. Yang, Y. Song, N. Li, R. He, K. Zhi, Q. Liu, *Green Chem.,* 2017, **19**, 4829-4837.
[9] K. Chen, J.-L.L, C-D Wu, *Angew. Chem., Int. Ed,* 2020, **132**, 1941 – 1947.
[10] J. Song, B. Zhou, H. Zhou, L. Wu, Q. Meng, Z. Liu, B. Han, *Angew. Chem., Int. Ed.* 2015, **54**, 9399-403.
[11] S. Zhou, F. Dai, Z. Xiang, T. Song, D. Liu, F. Lu, H. Qi, *Appl. Catal., B,* 2019, **248**, 31-43.