Electronic Supplementary Information

Highly dispersed Co, Ni nanoparticles encapsulated in N-doped carbon nanotubes as efficient catalysts for reduction of unsaturated oxygen compounds in aqueous-phase

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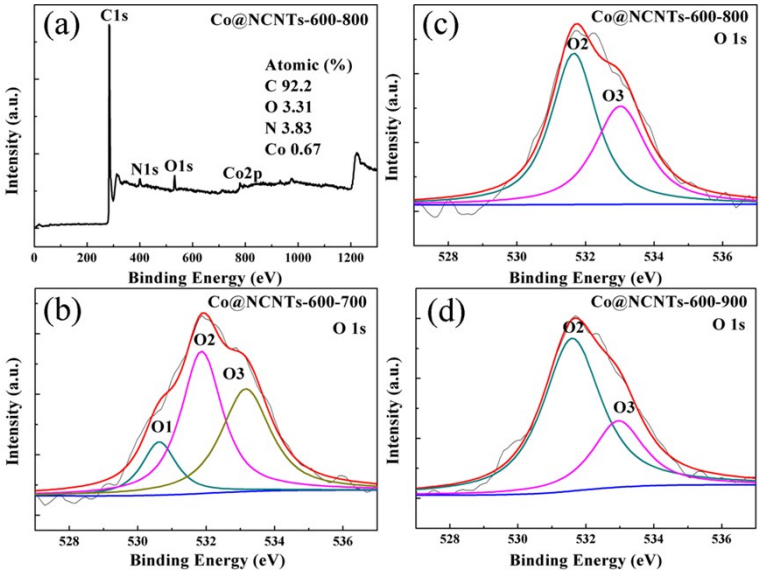

Fig. S1 XPS survey spectrum of Co@NCNTs-600-800 (a) and O 1s spectrum (b-d) of Co@NCNTs-600-700, Co@NCNTs-600-800 and Co@NCNTs-600-900 catalysts.

Table S1 Physicochemical characteristics of Co catalysts.

Samples	Content[a] (wt.%)	S_{BET}[b] (m^2/g)	V_{pore}[b] (cm^3/g)	Particle size[c] (nm)	Co Species[d] (%)		N Content[d]	Content of N types[d] (at.%)		
					Co	CoO_x		N1	N2	N3
Co@NCNTs-600-700	39.4	117.4	0.348	21.4	24.5	75.5	3.99	59.2	19.9	20.9
Co@NCNTs-600-800	40.3	200.7	0.588	28.6	26.2	73.8	3.83	67.5	0	32.5
Co@NCNTs-600-900	40.8	158.2	0.454	52.1	38.5	61.5	3.17	43.4	0	56.6

[a] Determined by ICP.

[b] Calculated by N_2 physisorption.

[c] Calculated by Scherrer equation.

[d] Determined by XPS.

N1: pyridinic-N

N2: pyrrolic-N

N3: graphitic-N

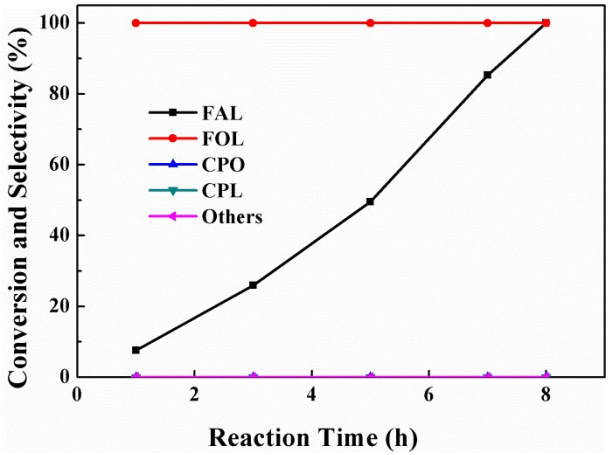

Fig. S2 Effect of reaction time on the hydrogenation of FAL over Co@NCNTs-600-800. Reaction conditions: Catalyst = 30 mg, FAL = 1 mmol, Water =10 mL, Reaction temperature = 80 ^{o}C, H_2 pressure = 4 MPa.

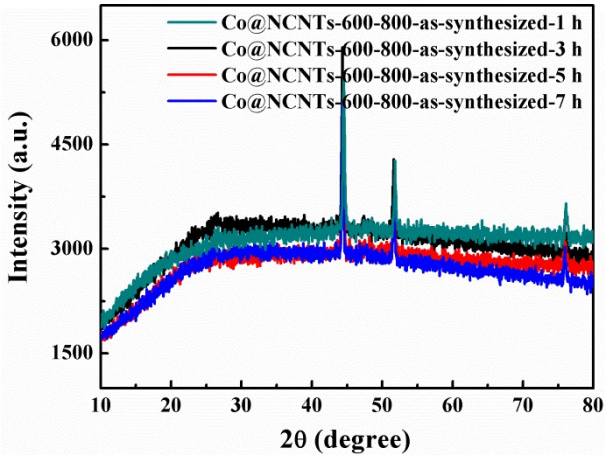

Fig. S3 The XRD patterns of the catalyst with different reaction time. Reaction conditions: Catalyst = 30 mg, FAL = 1 mmol, Water =10 mL, Reaction temperature = 140 ^{o}C, H_2 pressure = 4 MPa.

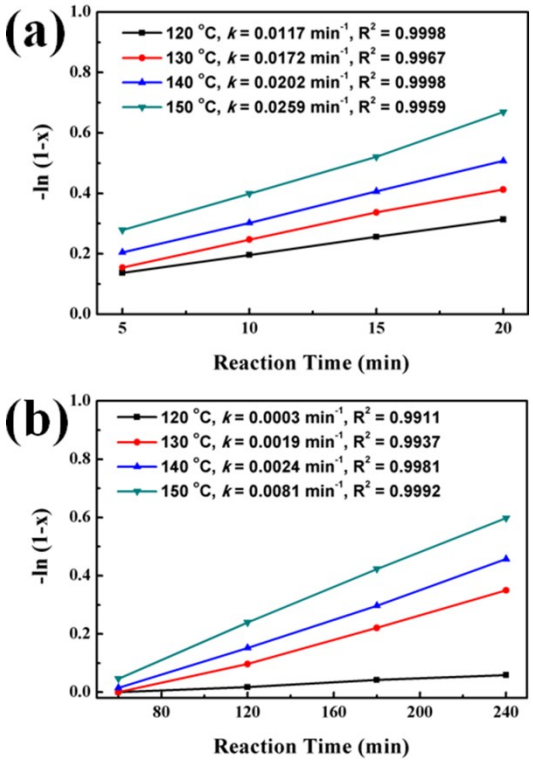

Fig. S4 First order kinetic fit for the hydrogenation of FAL to FOL (a) and CPO (b) over Co@NCNTs-600-800 catalyst at various temperatures: Plots of -ln(1-x) vs. time (min) to calculate rate constant *k*. Reaction conditions: Catalyst = 20 mg, FAL = 1 mmol, Water =10 mL, H_2 pressure = 4 MPa.

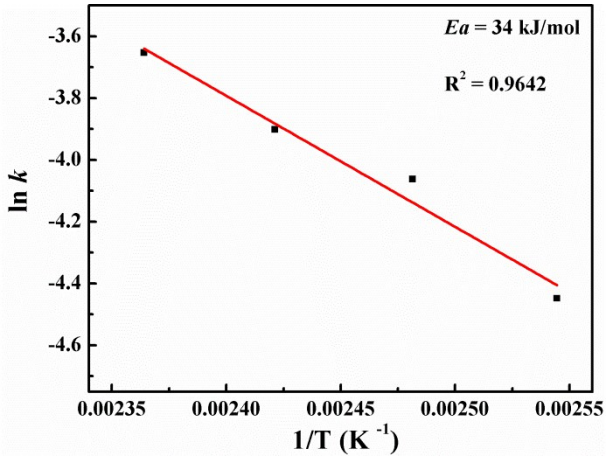

Fig. S5 Arrhenius type plots of catalytic activity for the FAL hydrogenation over the Co@NCNTs-600-800 catalyst.

Table S2 Catalytic performance of Co@NCNTs-600-800 in FAL hydrogenation[a]

Run. no.	Temperature (°C)	FAL conversion (%)	TOF[b] (h^{-1})
1	120	17.8	231
2	130	21.9	285
3	140	26.1	339
4	150	32.9	428

[a] Catalyst = 20 mg, FAL = 1 mmol, Water =10 mL, H_2 pressure = 4 MPa, Reaction time = 0.16 h.

[b] Turnover frequency (TOF) = mol $_{converted\ FAL}$/(mol$_{exposed\ surface\ Co}$·h).

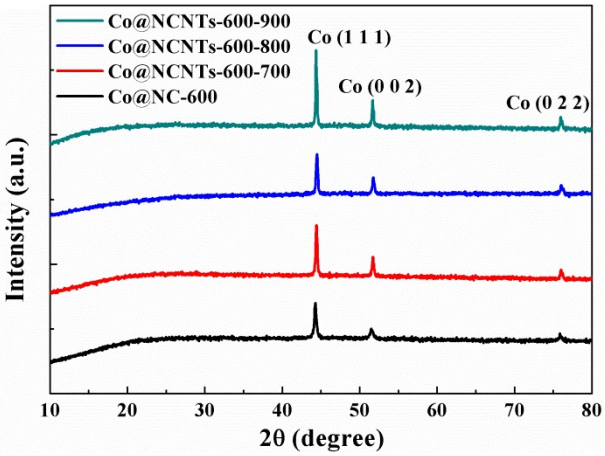

Fig. S6 XRD patterns of Co@NC-600, Co@NCNTs-600-700, Co@NCNTs-600-800 and Co@NCNTs-600-900 catalysts.

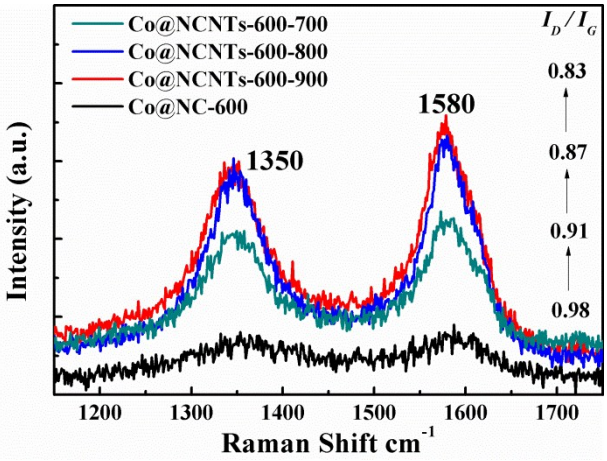

Fig. S7 Raman spectrums of Co@NC-600, Co@NCNTs-600-700, Co@NCNTs-600-800 and Co@NCNTs-600-900 catalysts.

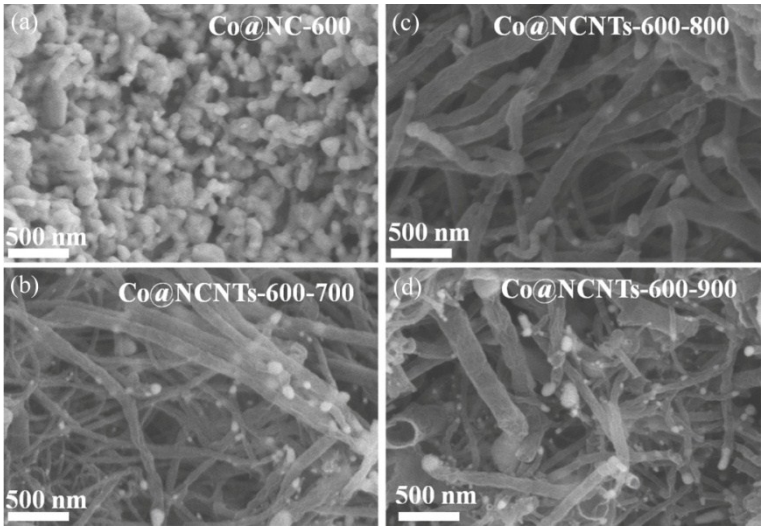

Fig. S8 The SEM images of (a) Co@NC-600, (b) Co@NCNTs-600-700, (c) Co@NCNTs-600-800 and (d) Co@NCNTs-600-900 catalysts.

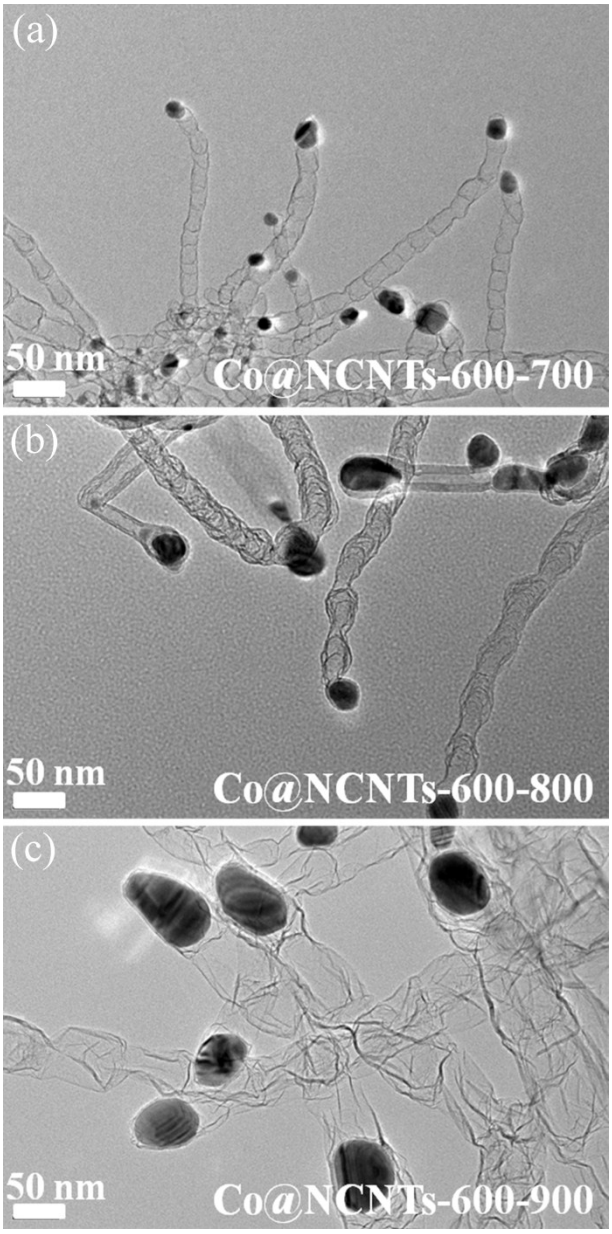

Fig. S9 The TEM images of Co@NCNTs-600-700, Co@NCNTs-600-800 and Co@NCNTs-600-900 catalysts.

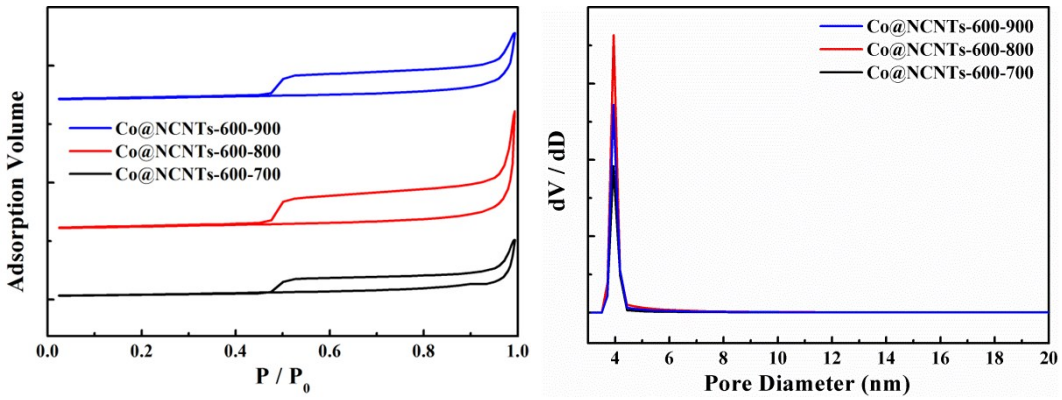

Fig. S10 N_2 adsorption–desorption isotherms (left) and BJH pore size distribution plots (right) of Co catalysts.

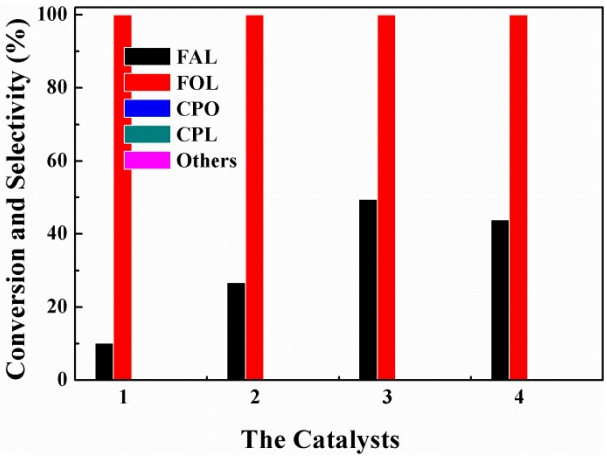

Fig. S11 Hydrogenation of FAL over different Co catalysts. 1, Co@NC-600; 2, Co@NCNTs-600-700; 3, Co@NCNTs-600-800; 4, Co@NCNTs-600-900. Reaction conditions: Catalyst = 30 mg, FAL = 1 mmol, Water =10 mL, Reaction temperature = 80 ^{o}C, H_2 pressure = 4 MPa, Reaction time = 5 h.

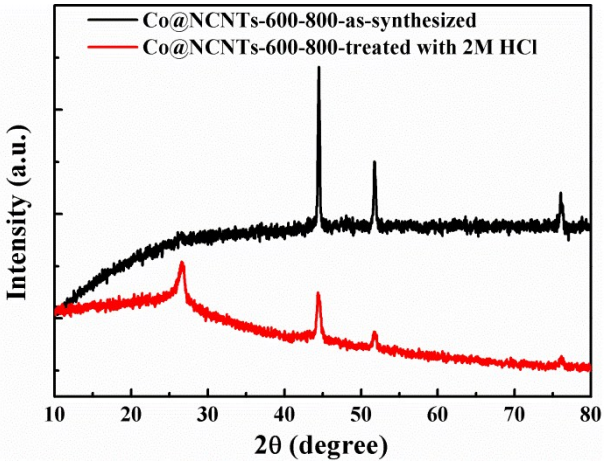

Fig. S12 The XRD patterns of the as-synthesized and treated Co@NCNTs-600-800 catalysts.

Table S3 Catalytic performance over the as-synthesized and treated Co@NCNTs-600-800 catalysts[a]

Catalysts	FAL Conv. (%)	FOL Sel. (%)	CPO Sel. (%)
As-synthesized Co@NCNTs-600-800	100	18.1	75.3
Treated Co@NCNTs-600-800	45.6	81.9	15.6

[a] Reaction conditions: Catalyst = 30 mg, FAL = 1 mmol, Water =10 mL, Reaction temperature = 140 ^{o}C, Reaction time = 5 h, H_2 pressure = 4 MPa.

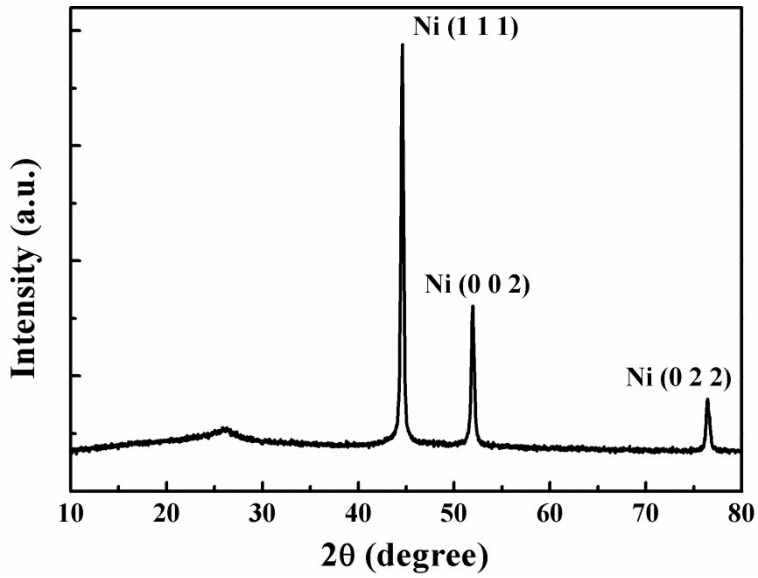

Fig. S13 The XRD pattern of Ni@NCNTs-600-800 catalyst.

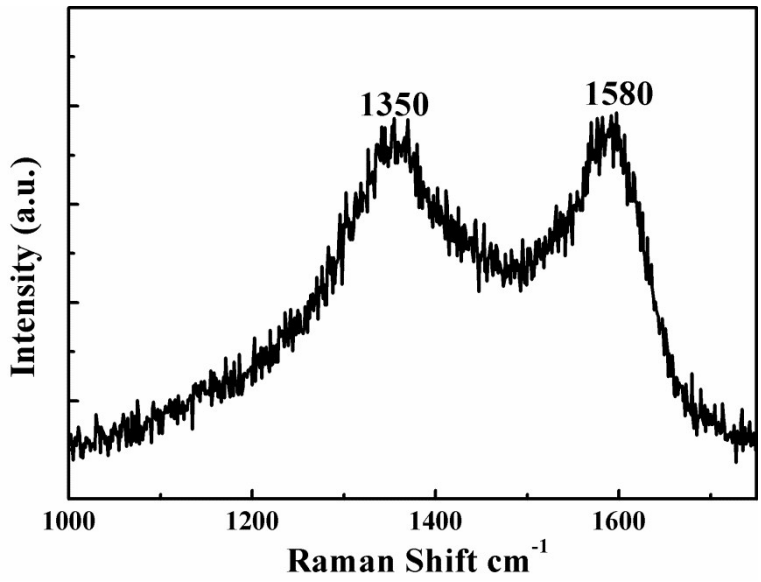

Fig. S14 The Raman spectrum of Ni@NCNTs-600-800 catalyst.

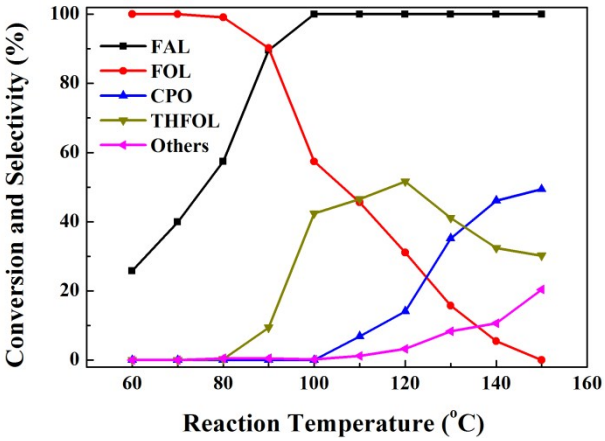

Fig. S15 Effect of reaction temperature on the hydrogenation of FAL over Ni@NCNTs-600-800. Reaction conditions: Catalyst = 30 mg, FAL = 1 mmol, Water =10 mL, H_2 pressure = 4 MPa, Reaction time = 5 h.

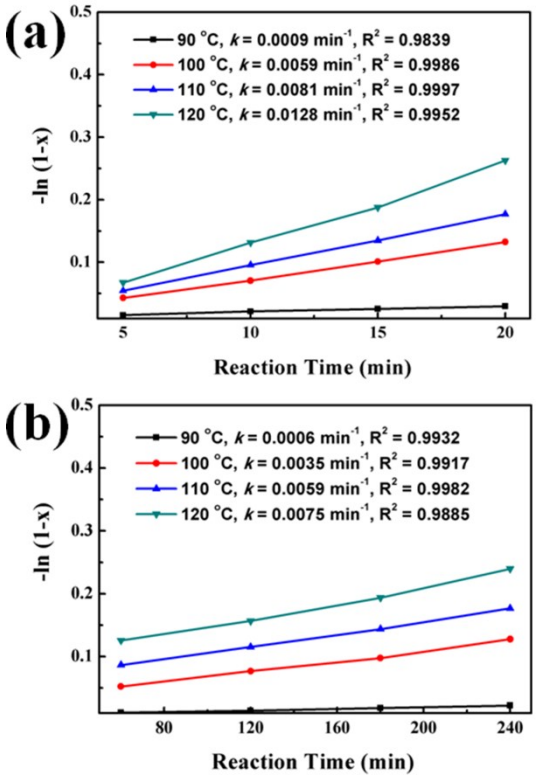

Fig. S16 First order kinetic fit for the hydrogenation of FAL to FOL (a) and THFOL (b) over Ni@NCNTs-600-800 catalyst at various temperatures: Plots of -ln(1-x) vs. time (min) to calculate rate constant *k*. Reaction conditions: Catalyst = 20 mg, FAL = 1 mmol, Water =10 mL, H_2 pressure = 4 MPa.

Table S4 Catalytic performance of Ni@NCNTs-600-800 in FAL hydrogenation[a]

Run. no.	Temperature (°C)	FAL conversion (%)	TOF[b] (h^{-1})
1	90	2.1	27
2	100	6.8	88
3	110	9.1	118
4	120	12.3	160

[a] Catalyst = 20 mg, FAL = 1 mmol, Water =10 mL, H_2 pressure = 4 MPa, Reaction time = 0.16 h.

[b] Turnover frequency (TOF) = $mol_{converted\ FAL}/(mol_{exposed\ surface\ Ni}\cdot h)$.