Rationally constructing hollow N-doped carbon supported Ru catalyst for enhanced hydrogenation catalysis

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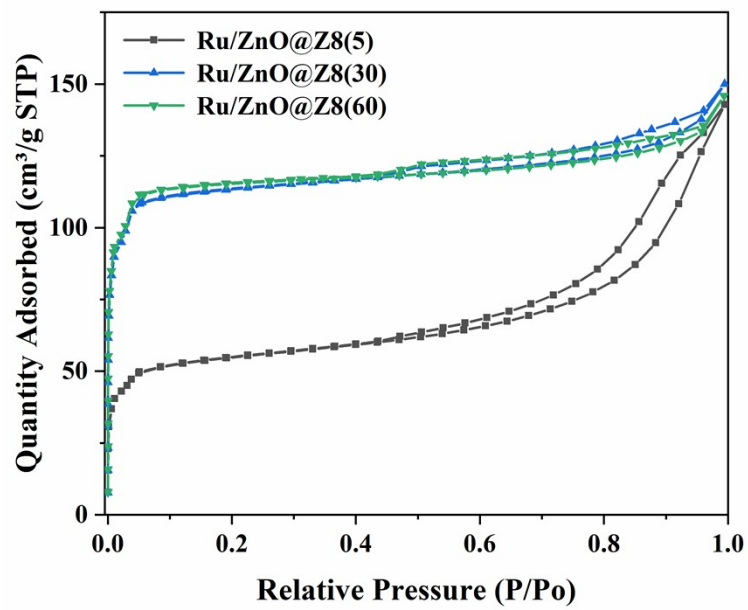[†] These authors contributed equally to this work.

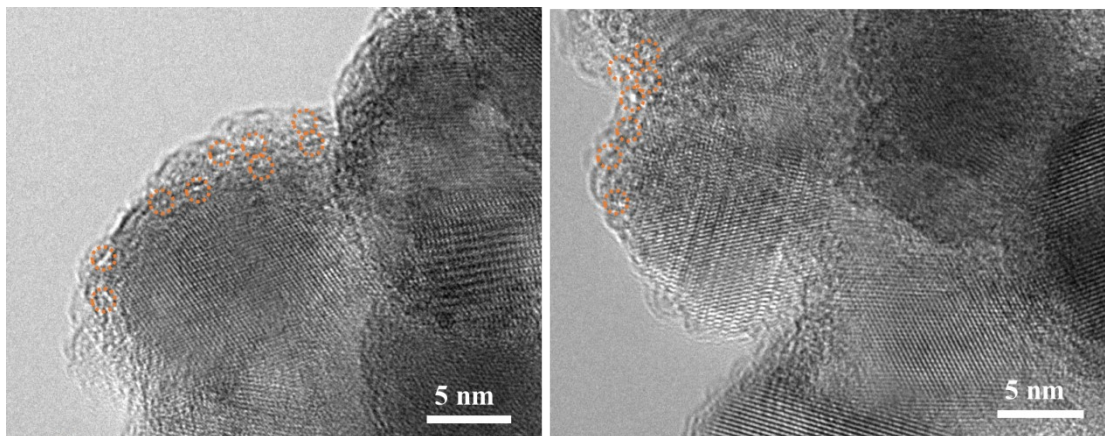Figure S1 N$_2$ adsorption-desorption isotherms of Ru/ZnO@Z8(x) catalysts.

Figure S2 Representative HRTEM images of Ru/ZnO@Z8(5)-C catalyst. The circles indicate there are many white spots or even belts in the overlayer, suggesting the presence of porous structure.
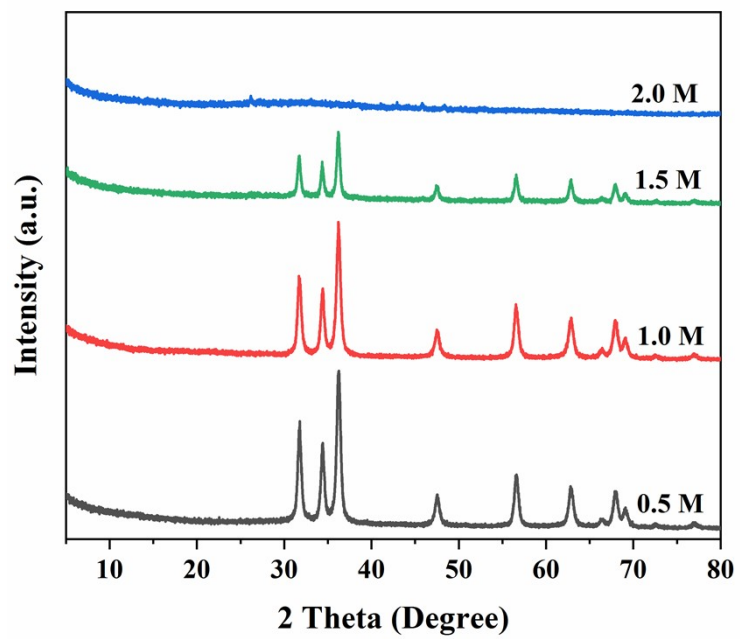
Figure S3 XRD patterns of Ru/ZnO@Z8(5)-C catalyst treated by NaOH solution with different concentration.
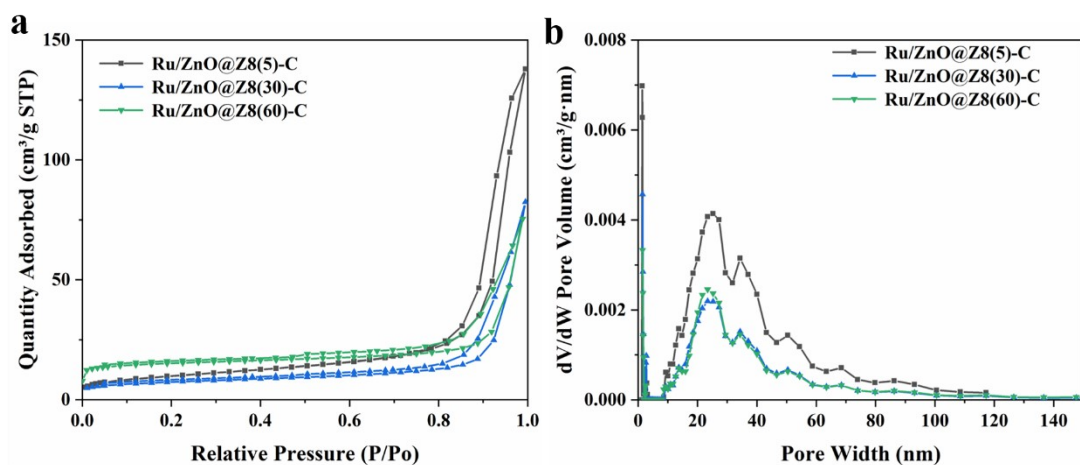
Figure S4 N$_2$ adsorption-desorption isotherms of Ru/ZnO@Z8(x)-C catalysts (a), the corresponding pore size distribution (b).
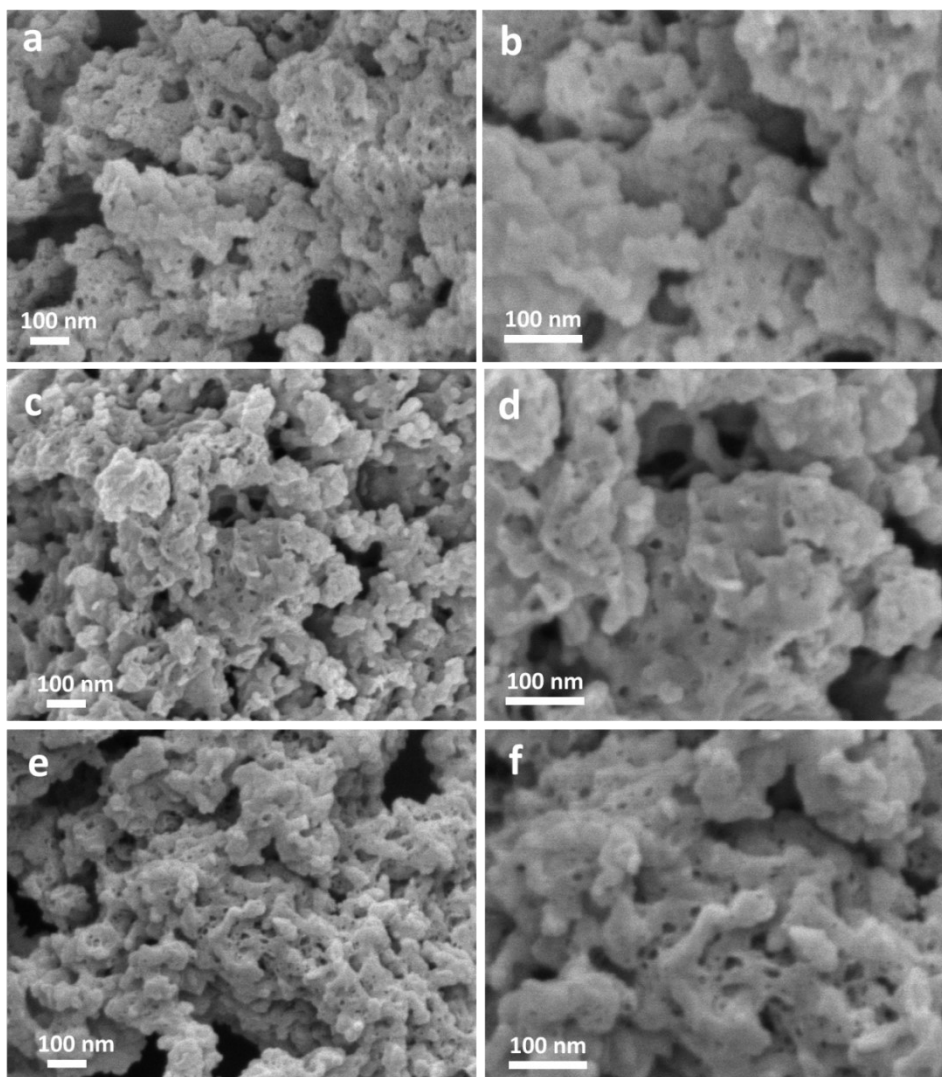
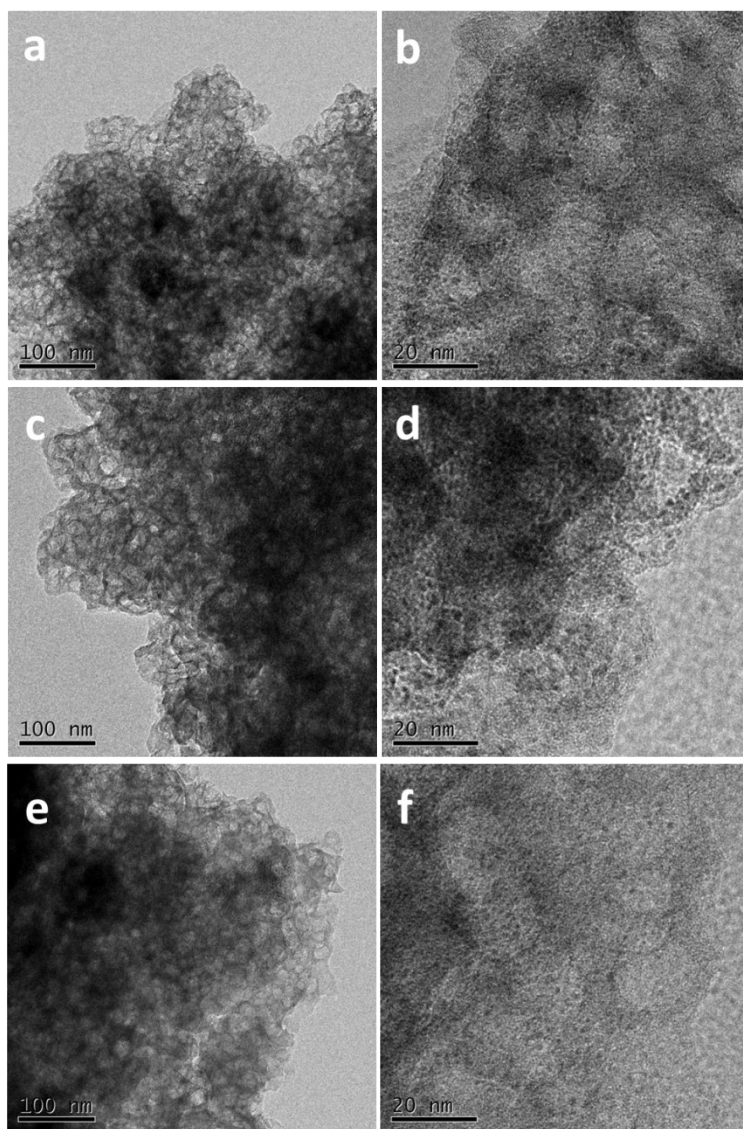Figure S5 SEM images of Ru/H(5)-NC (a, b), Ru/H(30)-NC (c, d), Ru/H(60)-NC (e, f) catalysts.

Figure S6 HRTEM images of Ru/H(5)-NC (a, b), Ru/H(30)-NC (c, d) and Ru/H(60)-NC (e, f) catalysts.
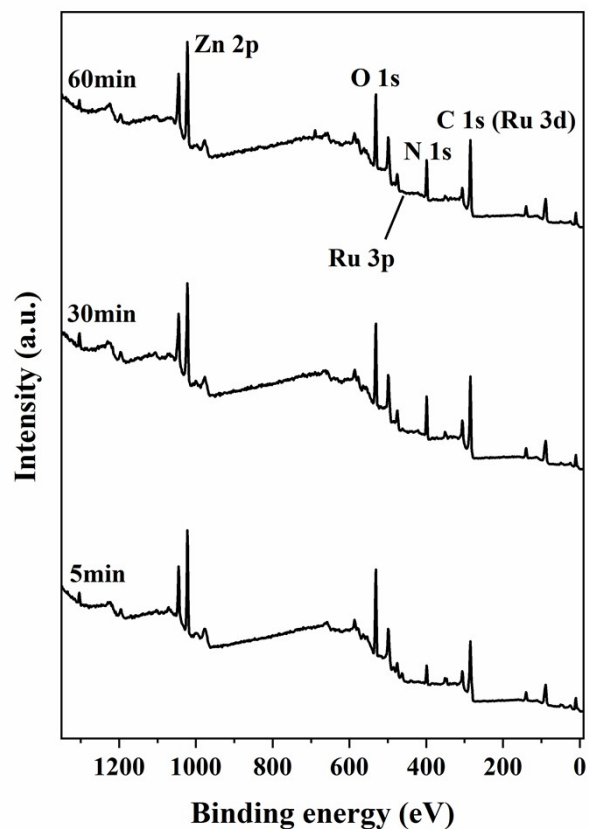
Figure S7 The full spectra of Ru/H(x)-NC catalysts by XPS analysis.
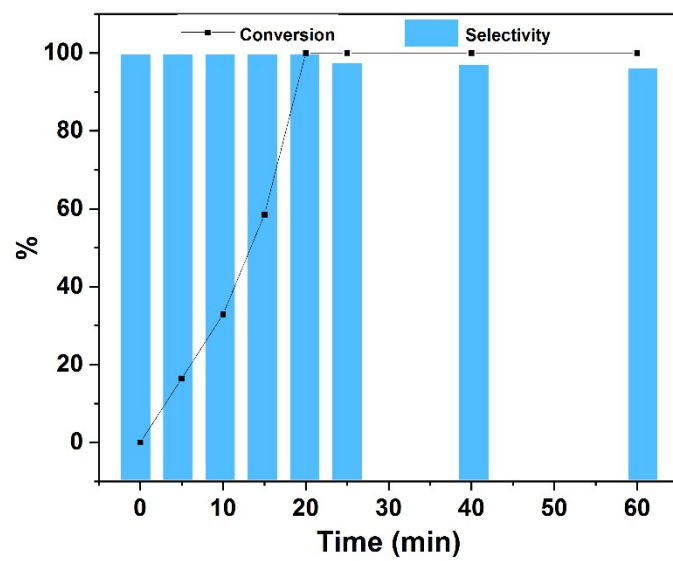
Figure S8 Conversion (Selectivity)-time diagram of Ru/H(5)-NC catalyst.
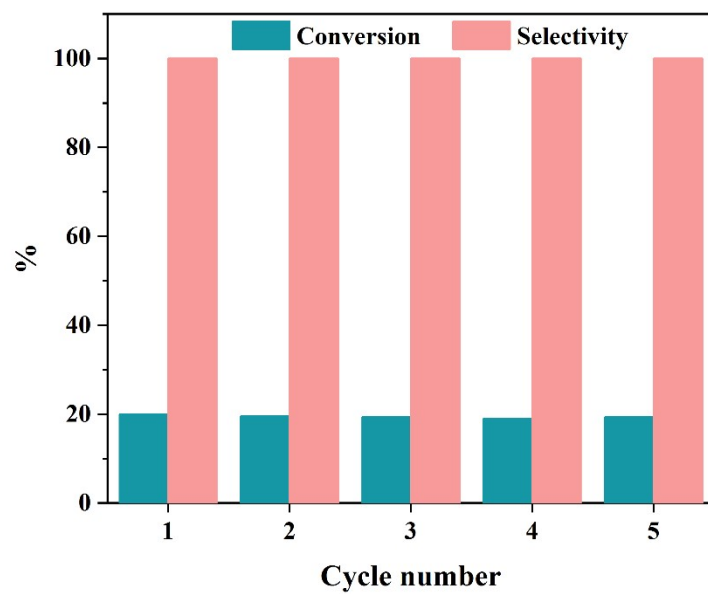
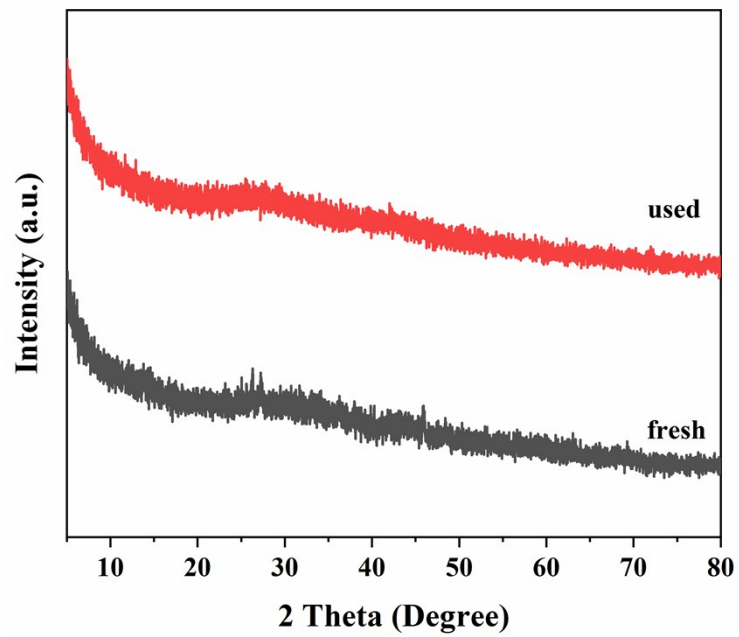Figure S9 Stability test with Ru/H(5)-NC catalyst under low conversion.

Figure S10 XRD patterns of Ru/H(5)-NC catalyst before and after hydrogenation reaction.
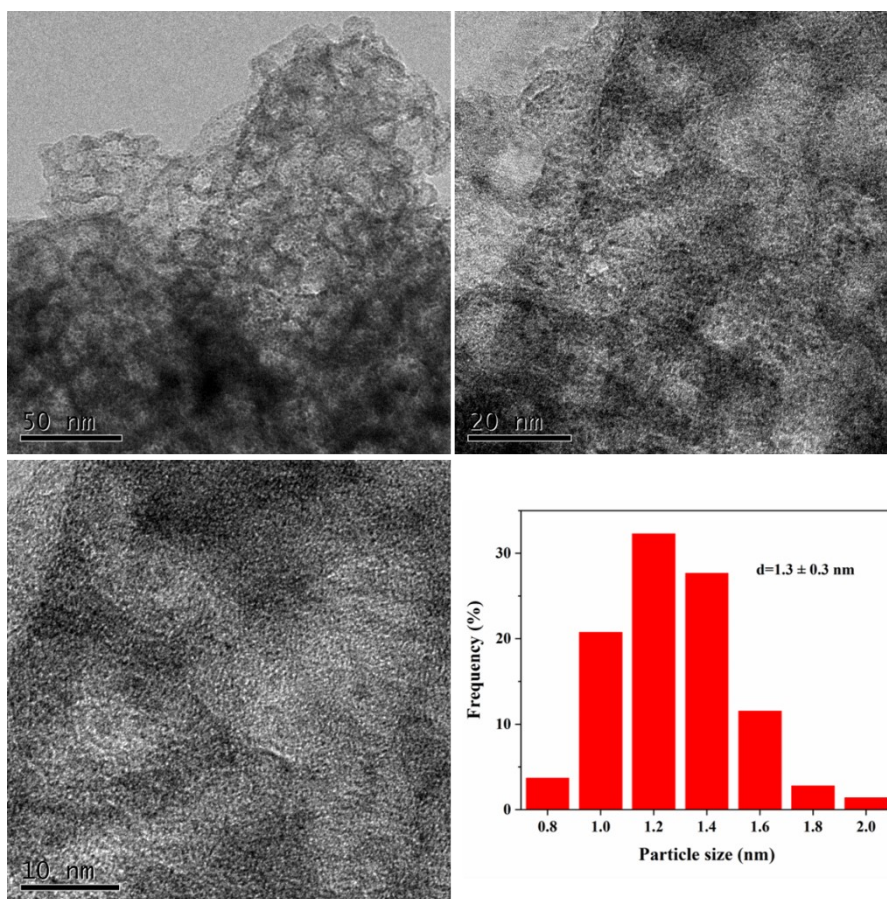
Figure S11 HRTEM images of Ru/H(5)-NC catalyst after cyclic experiments.
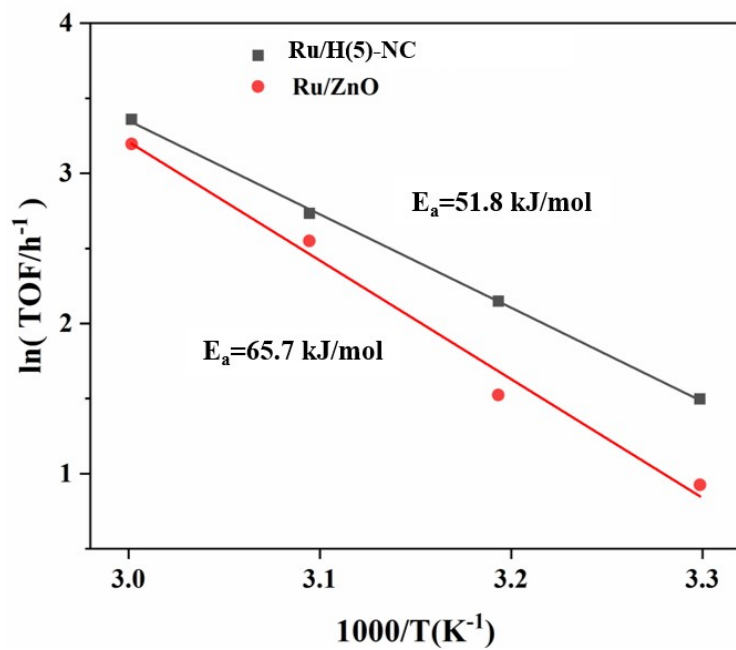
Figure S12 Activation energy tests for Ru/H(5)-NC and Ru/ZnO catalysts.

Table S1 The BET surface area and pore volume results for different catalysts.

Catalyst	BET Surface Area(m²/g)	Pore Volume (cm³/g)
Ru/ZnO@Z8(5)	173	0.19
Ru/ZnO@Z8(30)	347	0.21
Ru/ZnO@Z8(60)	349	0.20
Ru/ZnO@Z8(5)-C	30	0.082
Ru/ZnO@Z8(30)-C	17	0.043
Ru/ZnO@Z8(60)-C	14	0.039
Ru/H(5)-NC	271	0.60
Ru/H(30)-NC	216	0.51
Ru/H(60)-NC	197	0.45

Table S2 TEM and XRD analyses of the cavity size in Ru/H(x)-NC catalyst

Catalyst	$d_1{}^a$(nm)	$d_2{}^b$(nm)
Ru/H(5)-NC	17.4 ± 2.0	17.8
Ru/H(30)-NC	16.1 ± 2.0	16.3
Ru/H(60)-NC	15.4 ± 1.9	15.7

[a] The cavity size of the catalyst obtained by TEM characterization was calculated by measuring 200 hollow structure, [b] the particle size of the etched residual ZnO was obtained from XRD data by Scherrer's formula.

Table S3 The effect of solvent for the hydrogenation reaction with Ru/H(5)-NC catalyst.
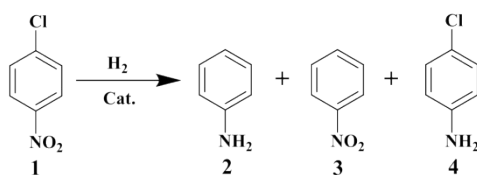
Solvent	Conv. (%)	Sel. (%)		
		2	3	4
toluene	98.7	0	0	>99
ethanol	97.2	8.7	0	91.3
methanol	98.2	6.3	0	93.7
tetrahydrofuran	31.3	0	0	>99
isopropanol	40.6	0	0	>99

Reaction condition: 50 °C, 0.5 MPa H_2, 0.5 mmol p-chloronitrobenzene, 0.25 mmol 1,3,5-trimethylbenzene (internal standard), 5 mL solvent, 19 min.

Table S4 The effect of temperature for the hydrogenation reaction with Ru/H(5)-NC catalyst.
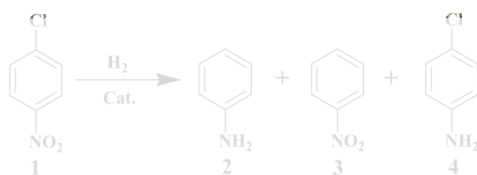
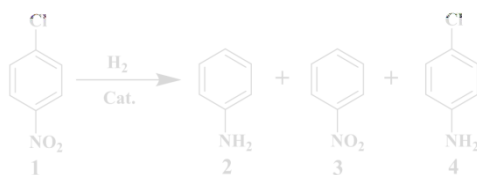| T	Conv.	Sel. (%)		
(°C)	(%)	2	3	4
30	72.8	0	0	>99
40	85.2	0	0	>99
50	98.2	0	0	>99
60 [a]	98.5	5.3	0	94.7

Reaction condition: 0.5 MPa H$_2$, 0.5 mmol p-chloronitrobenzene, 0.25 mmol 1,3,5-trimethylbenzene (internal standard), 5 mL toluene, 19 min. [a] 15 min.

Table S5 The effect of pressure for the hydrogenation reaction with Ru/H(5)-NC catalyst.

P	Conv.	Sel. (%)		
(MPa)	(%)	2	3	4
0.3	83.8	0	0	>99
0.5	98.2	0	0	>99
0.7	100	0	0	>99
1 [a]	100	0	0	>99

Reaction condition: 50 °C, 0.5 mmol p-chloronitrobenzene, 0.25 mmol 1,3,5-trimethylbenzene (internal standard), 5 mL toluene, 19 min. [a] 15 min.