Supporting Information

Highly dispersed Ru clusters embedded nitrogen-doped hollow carbon spheres with tunable electronic property for catalytic reductive amination of biomass-derived furfural

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1. Materials and Methods

1.1. Synthesis of Schiff base

Typically, 4 mmol of furfural and 4 mmol of furfurylamine were added to 10 mL of anhydrous methanol in a reactor. Replacement of air in the reactor by N_2 and then filling with 1 MPa N_2, rapidly stirred at 90 °C for 6 h. After the reaction, the solution was purified via spin distillation to isolate the intermediate Schiff base, and its purity was analyzed by gas chromatography.

1.2. Synthesis of other catalysts

NHCS-700 catalyst. 0.1 g of PS nanospheres was dispersed in 50 mL of deionized water under ultrasonication for 30 min. The mixture was then stirred in an oil bath for 5 min at room temperature, followed by the slow addition of 0.1 g of $C_8H_{12}ClNO_2$. After stirring for an additional 30 min, 0.30285 g of Tris and 62 μL of HCl were added to adjust the pH to 8.5. The resulting mixture was subsequently stirred for 22 h at room temperature. Finally, after centrifugal washing, drying, and sintering, the catalyst was obtained.

Ru@AC-700 catalyst. Adding 0.1 g of AC, 625 μL of Cl_3H_6ORu solution (10.859 mg mL^{-1}), and 15 mL of deionized water to a round-bottom flask, the mixture was sonicated for 30 min and then stirred at 85 °C for 6 h. Subsequently, the samples were oven-dried at 60 °C overnight to obtain the catalyst precursor.

Ru@NC-700 catalyst. 0.1 g of $C_8H_{12}ClNO_2$ and 625 μL of $Cl_3H_6O_2Ru$ solution (10.859 mg mL^{-1}) was dispersed in 50 mL of deionized water, stirring for 30 minutes. Then, 0.30285 g of Tris and 62 μL of HCl were added to adjust the pH to 8.5. The resulting mixture was subsequently stirred for 22 h at room temperature. Finally, after centrifugal washing, drying, and sintering, the catalyst was obtained.

Ru@HCS-700 catalyst. Adding 0.1 g of PS nanospheres, 0.1 mL of ammonia solution, 15 mL of deionized water and 35 mL of ethanol to a round-bottom flask, stirring for 10 minutes. Then, 0.1 g resorcinol, 0.2 mL formaldehyde solution (AR, 37%-40%) and 625 μL of $Cl_3H_6O_2Ru$ solution (10.859 mg mL^{-1}) were added sequentially. The resulting mixture was subsequently stirred for 22 h at room temperature. Finally, after centrifugal washing, drying, and sintering, the catalyst was obtained.

Pd@NHCS-700 and Pt@NHCS-700 catalysts. 0.1 g of PS nanospheres was dispersed in 50 mL of deionized water under ultrasonication for 30 min. The mixture was then stirred in an oil bath for 5 min at

room temperature, followed by the slow addition of 0.1 g of $C_8H_{12}ClNO_2$ and different metal precursors that maintaining identical theoretical metal loadings. After stirring for an additional 30 min, 0.30285 g of Tris and 62 μL of HCl were added to adjust the pH to 8.5. The resulting mixture was subsequently stirred for 22 h at room temperature. Finally, after centrifugal washing, drying, and sintering, the catalyst was obtained.

2. Figures and Tables

Fig. S1. TEM images and the corresponding particle size distribution histogram of Ru@NHCS-600 catalyst.

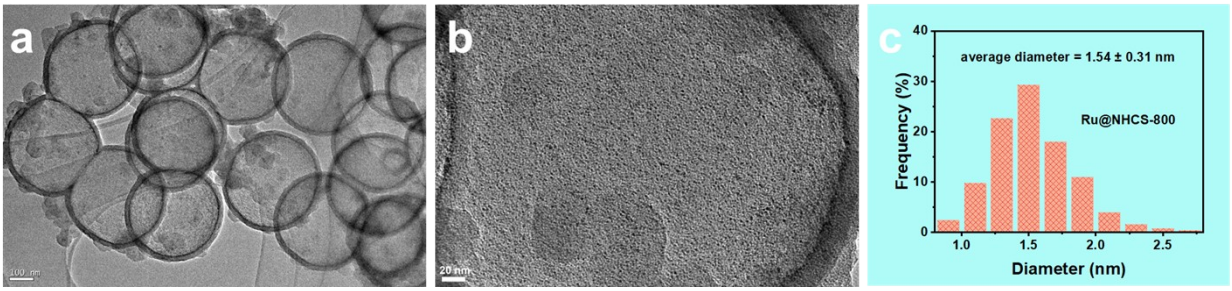

Fig. S2. TEM images and the corresponding particle size distribution histogram of Ru@NHCS-800 catalyst.

Fig. S3. TEM images and the corresponding particle size distribution histogram of Ru@NHCS-900 catalyst.

Table S1. Fitting results of high-resolution N 1s spectra of various Ru@NHCS and NHCS-700 catalysts.

Catalyst	Ru-N		pyridinic N	
	peak (eV)	relative content (%)	peak (eV)	relative content (%)
Ru@NHCS-600	399.44	12.5	398.04	33.6
Ru@NHCS-700	399.66	16.3	398.21	29.7
Ru@NHCS-800	399.58	14.6	398.06	19.5
Ru@NHCS-900	399.31	11.9	397.86	13.2
NHCS-700	-	-	397.98	33.4

Table S2. Fitting results of high-resolution Ru 3p spectra of various Ru@NHCS catalysts.

Catalyst	Ru^0	
	Peak (eV)	Relative content (%)
Ru@NHCS-600	462.17	64.1
Ru@NHCS-700	461.73	69.4
Ru@NHCS-800	462.04	66.7
Ru@NHCS-900	462.30	57.8

Table S3. Ru@NHCS-700 catalyzed the reductive amination of furfural and Schiff base under different reaction conditions.

Entry	Substrate (0.5 mmol)	$NH_3 \cdot H_2O$ (mL)	Atmosphere (0.5 MPa)	Conversion (%)	Selectivity (%)			
					FUA	FDA	FUI	Other
1	Furfural	1.5	N_2	86	-	-	24	76 [b]
2	Furfural	0	H_2	6	-	-	-	100 [c]
3	Schiff base	1.5	N_2	0	-	/	-	-
4	Schiff base	0	H_2	41	-	/	-	100 [d]

[a] Reaction conditions: methanol (5 mL), $NH_3 \cdot H_2O$ (25-28%), Ru@NHCS-700 catalyst (10 mg), 80 °C, 3 h. [b] hydrofuramide, [c] furfuryl alcohol, [d] secondary amine.

Table S4. Experimental data for calculating turnover frequency (TOF) and initial reaction rate (IRR) of various Ru@NHCS catalysts.

Catalyst	Time (h)	Conversion (%)	TOF (h^{-1})	IRR (mmol g_{Ru}^{-1} h^{-1})
Ru@NHCS-600	1	24.4	164.6	1628.8
Ru@NHCS-700	0.33	24.5	378.6	3745.8
Ru@NHCS-800	1	28.0	215.6	2132.8
Ru@NHCS-900	1	19.7	133.8	1323.4

Reaction conditions: catalyst (10 mg), Schiff bases (0.25 mmol), ethanol (5 mL), $NH_3 \cdot H_2O$ (1.5 mL, 25-28%), H_2 (0.5 MPa), 80 °C.

Table S5. The superior performance of Ru@NHCS-700 compared to the reported catalysts.

Entry	Catalyst	Metal/Substrate (mole ratio)	H_2 (MPa)	Nitrogen source/Substrate (mole ratio)	Tem. (°C)	Time (h)	Yield (%)	Production rate (mol_{FUA} mol_{metal}^{-1} h^{-1})	Ref.
1	Ru@NHCS-700	1:903	0.5	$NH_3 \cdot H_2O$ (42:1)	80	3	100	199	This work
2	Ru/SiO_2	1:670	5.2	$NH_3 \cdot H_2O$ (5:1)	130	4	90	151	1
3	Ru/MMT	1:84	1	$NH_3 \cdot H_2O$ (107:1)	90	3	89	25	2
4	Ru/BN-e	1:11	1.5	$NH_3 \cdot H_2O$ (28:1)	90	5	99	33	3
5	4Ru1Co/AC	1:39	2	$NH_3 \cdot H_2O$ (51:1)	80	1	92	37	4
6	Ru/BNC	1:91	2	$N_2H_4 \cdot H_2O$ (4:1)	80	16	99	6	5
7	Ru-NPs	1:253	2	NH_3 (16:1)	90	2	99	125	6
8	Ru1/NC	1:400	2	NH_3 (0.5 MPa)	100	10	97	178	7
9	Ru/TiO_2	1:167	1	NH_3 (35:1)	80	1	83	153	8
10	Ru/Nb_2O_5	1:250	2	NH_3 (0.1 MPa)	90	4	99	129	9
11	Ru/HZSM-5(46)	1:27	3	NH_3 (21:1)	100	0.25	76	82	10
12	Ru/TiP-100	1:500	1.7	NH_3 (0.3 MPa)	30	24	91	19	11
13	$Ru/T\text{-}ZrO_2$	1:126	2	NH_3 (44:1)	80	2.5	99	23	12
14	Ru/Ni_1MgAlO_x	1:600	2	NH_3 (3:1)	90	5	91.3	192	13
15	$Ru/\alpha\text{-}Al_2O_3$	1:35	2	NH_3 (0.2 MPa)	70	24	73.5	3	14
16	Ru/SBA-15	1:253	4	NH_3 (0.2 MPa)	90	2	99	126	15
17	$Ru@NC\text{-}Al_2O_3$	1:404	2	NH_3 (42:1)	100	3	90	133	16
18	Ru/NCB-600	1:202	2	NH_3 (35:1)	50	2	99	100	17
19	$Ru/Nb_2O_5 \cdot H_2O$	1:253	4	NH_3 (16:1)	70	4	89	56	18
20	Rh/TiO_2	1:497	2	$NH_3 \cdot H_2O$ (144:1)	100	2	93	196	19
21	Pd/MoO_{3-x}	1:39	2	NH_3 (37:1)	80	4	84	8	20
22	Pd NPs	1:2.7	0.1	NH_3 (4:1)	30	3	97	2	21
23	$Ni\text{-}Al_2O_3$	1:12	2	NH_3 (21:1)	100	2	92	9	22
24	$Ni/SiO_2\text{-}I\text{-}DP$	1:19	4	NH_3 (0.8 MPa)	90	1.5	95	12	23

Continued **Table S5**. The superior performance of Ru@NHCS-700 compared to the reported catalysts.

Entry	Catalyst	Metal/Substrate (mole ratio)	H_2 (MPa)	Nitrogen source/Substrate	Tem. (°C)	Time (h)	Yield (%)	Production rate (mol_{FUA} mol_{metal}^{-1} h^{-1})	Ref.
25	Raney Co	1:13	1	NH_3 (0.1 MPa)	120	2	98	11	24
26	$Co@CoO_x$	1.6:1	3	$N_2H_4 \cdot H_2O$	60	4	96	3	25

Table S6. The H_2 desorption characteristics of various Ru@NHCS catalysts.

Catalyst	Peak temperature (°C)	Amount (μmol g^{-1})
Ru@NHCS-600	336	54.2
Ru@NHCS-700	329	97.9
Ru@NHCS-800	366	70.0
Ru@NHCS-900	374	31.5

All data determined by H_2-TPD.

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