Supporting Information

3D-interconnected Hierarchical Porous N-doped Carbon

supported Ruthenium Nanoparticles as an efficient catalyst for

Selective Hydrogenation of Toluene and Quinoline

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Experimental section

Synthesis of the HPC-900

The HPC-900 was prepared through the same method as the HPC, the only difference was the calcination temperature set as 900 °C.

Synthesis of the NHPC-ball

A certain amount of NHPC was put in a ball-mill (ND 8-swing planetary ball mill, Nanjing south Tianzun electronics co., LTD) to destroy the 3D-interconnection macroporous framework. Operation was done at 50 Hz and room temperature, run for 120 min.

Synthesis of the NHPC-ball

Ru/NHPC-ball was prepared using the same method as Ru/NHPC.

Synthesis of the Ru/AC-H₂ catalyst

The Ru/AC-H₂ catalyst was systhesized through a hydrothermal method with hydrogen.¹ Typically, 0.2 g AC was dispersed into 20 mL deionized water and ultrasonicated at 50 kHz for 3 h. Then desired amount RuCl₃ aqueous solution (0.01 g/mL) was added, followed by ultrasonication for 3 h. The mixture was then stirred at room temperature overnight. Afterward, the mixture was transferred into a Teflon-lined steel autoclave and maintained at 150 °C and 4 MPa of H₂ for 2 h to reduce the Ru³⁺, followed by cooling to reaction temperature.

Synthesis of the Ru/AC-HCOOH catalyst

The Ru/AC-HCOOH was prepared by deposition-precipitation (DP) method using HCOOH as the reducing agent. Briefly, the AC was added to an aqueous solution of RuCl₃ (0.01 g/mL) and of Na₂CO₃ (0.05 M). The pH was adjust to ~10.

The suspension thermostated at 60 °C was vigorously stirred for 2 h and washed to pH \sim 7. Then the soild was dispersed in deionized water, added HCOOH (0.05 M) to reduce the Ru³⁺. After the reduce procedure, the Na₂CO₃ solution was added into the suspension to adjust the pH to 9~10.After the DP prodecure, the sample was washed with water and then centrifuged, vacuum-dried overnight.

ICP-AES

Firstly, 8 mg Ru catalysts were dispersed in 12 mL aqua regia for 48 h at 130 °C to dissolve it completely. Then, the resulting solutions were analyzed using ICP-AES (PerkinElmer Optima OES 8000) to get the results of Ru content.



Figure S1. The comparison of NHPC, HPC and AC with the same mass (0.2 g)



Figure S2. (A) N_2 adsorption/desorption isotherms and (B) pore size distributions for NHPC, HPC and AC using the DFT model; (C) pore size distribution and (D) cumulative pore area of NHPC, HPC and AC measured by mercury porosimetry



Figure S3. N 1s XPS spectra of the NHPC



Figure S4. Raman spectra of NHPC, HPC, AC and NHPC-bm



Figure S5. HRTEM images of Ru NPs on Ru/HPC and Ru/AC



Figure S6. HRTEM images and particle size distribution of Ru/AC-H $_2$



Figure S7. HRTEM images and particle size distribution of Ru/AC-HCCOH



Figure S8. The comparison of NHPC and NHPC-bm with the same mass (0.1 g)



Figure S9. SEM images of NHPC-bm



Figure S10. FTIR spectra of the NHPC and NHPC-bm

The FTIR spectra of the NHPC and the NHPC-bm showed no obvious difference. The peaks at 1632 cm⁻¹ is assigned to C=C stretching vibrations, the strong and broad peak at 3454 cm⁻¹ is attributed to the stretching vibration of the hydroxyl group.^{2, 3} This results indicate that no functional group was generated during the ball-mill treatment.



Figure S11. HRTEM images and particle size distribution of Ru/NHPC-bm



Figure S12. Effect of H₂ pressure on (A) toluene and (B) quinoline hydrogenation over Ru/NHPC

^a Reaction conditions of toluene hydrogenation: cat 10 mg, Toluene 188.8 mmol, 100
^oC, 1 h;

b Reaction conditions of quinoline hydrogenation: cat 10 mg, quinoline 8.5 mmol, ethonal 10 mL, 100 °C, 1 h

As expected, the H_2 pressure plays crucial role on the catalytic activity. Hydrogenation of aromatics typically involves hydrogen spillover mechanisms, which that the hydrogen molecules may be dissociative adsorbed on the surface of Ru NPs and spilled over from Ru NPs onto the support and that the aromatic compounds are often found to absorbed on the surface of the support.⁴ Thus, the increase of H_2 pressure has a significant impact on the H_2 molecules absorbed on the Ru NPs surface, thus facilitate the transport of hydrogen spillover species from the Ru NPs to the support for hydrogen spillover and hydrogenation reactions. In addition, it is noteworthy that the Ru/NHPC displayed as an excellent catalyst with a TOF of about 39001 h⁻¹ and 2858 h⁻¹ for toluene and quinoline, respectively, higher than that of most other supported Ru catalysts under similar moderate conditions (Table S1, S2).

Fasters	Dresstalvat	Conditions	TOF(h-	Ref	
Entry	Precataryst	T(°C)/PH ₂ (MPa)/solvent	¹)		
1	Ru(0)/HAp	25 °C/0.3 MPa/-	519	5 ⁵	
2	Ru(0)@nanozeolite	25 °C/0.3 MPa/-	600	6 ⁶	
3	Ru/NHPC	35°C/0.4 MPa/Ethanol	1154	This study	
4	Ru(0) nanoparticles	75 °C/0.4 MPa/-	1635	7 7	
5	Ru(0) aqueous	20.0C/2 MD-/W-4	150	8 8	
5	suspension	20°C/3 MPa/water	150		
6	Ru-MWCNT	50 °C/4 MPa/ Ethanol	100	9 ⁹	
8	Ru/NHPC	100 °C/1 MPa/ -	15792	This study	
9	$Ru(0)/SiO_2$ 100 °C/3 MPa/n-octa		360	10^{-10}	
10	Ru/CNF-P	100 °C/3 MPa/-	14200	11 11	
11	Ru/C-Silica	110 °C/4 MPa/-	9800	4 4	
12	Ru-OMC	110 °C/4 MPa/-	16884	12 12	
13	Ru/silica-PVP	110 °C/4 MPa/-	266000	13 13	
14	Ru/PVPy	120 °C/1 MPa/ THF	69	14 ¹⁴	
15	Ru/MgO	O 120 °C/1 MPa/ THF		15 ¹⁵	
16	Ru/rGO	130 °C/4 MPa/-	26000	16 ¹⁶	

Table S1. Comparison of the reaction conditions and catalytic activities for the Ru/NHPC system with the prior Ru-based catalysts system

^{*a*} TOF= mol of toluene consumed/mol catalyst•h

Entry	Duesetslast	Conditions	TOF(h ⁻¹)	Reference	
	Precatalyst	T(°C)/P _{H2} (MPa)/solvent	а		
1	Ru-SiO ₂ @mSiO ₂	90 °C/3MPa/ Water	30	17 ¹⁷	
2	nanoRu@hetorite	90 °C/3MPa/Water	96	18 18	
3	Ru/NHPC	100 °C/1MPa/ Ethanol	1127	This study	
4	Ru(0)/SiO ₂	100 °C/3 MPa/n-octane	49	10 10	
5	Ru/CSP	110 °C/2MPa/ Ethanol	74	3 3	
6	Ru/PVPy	120 °C/1MPa/THF	19	14 ¹⁴	
7	Ru/P4VPy	120 °C/3MPa/ Methanol	66	19 ¹⁹	
8	Ru/HAP	150 °C/5MPa/ Ethanol	50	20 ²⁰	
9	Ru/MgO	150 °C/5MPa/THF	3400	15 ¹⁵	

Table S2. Comparison of the reaction conditions and catalytic activities for the Ru/NHPC system with the prior Ru-based catalysts system

^{*a*} TOF= mol of quinoline consumed/mol catalyst•h

Samples	True density (g/cm ³)		
NHPC	0.17		
HPC	0.52		
AC	1.74		
NHPC-bm	0.85		

Table S3. The true density of different carbon samples ^{*a*}

^{*a*} The true density of carbon materials were measured by the method of pycnometer.

Material	S _{BET} (m ² g ⁻¹)	Micropore Area(m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	micropore volume	Micropore volume%	Pore size (nm)
NHPC	870	789	0.55	0.40	73	5.4
Ru/NHPC	867	791	0.54	0.40	74	5.1
HPC	279	250	0.19	0.13	65	7.1
Ru/HPC	259	232	0.14	0.14	61	6.9
AC	948	654	0.79	0.33	42	4.7
Ru/AC	862	582	0.74	0.30	39	4.8
NHPC-bm	615	588	0.37	0.27	73	5.7
HPC-900	616	-	0.48	0.14	30	4.6

Table S4. Specifications of the various carbon samples ^a

^{*a*} Derived from nitrogen adsorption-desorption isotherm.

Matarial	Content (wt. %)			
Material	С	Н	N	O(calculated)
NHPC	86.5	0.6	2.1	10.8
HPC	82.8	0.8	0	16.4

Table S5. Element analysis of the prepared carbon samples

Table S6. Specifications of the prepared catalyst samples

Material	Ru% ^a	Crystallic size(nm) ^b	Ru dispersion% c
Ru/NHPC	3.0	2.6	58
Ru/HPC	3.1	3.3	40
Ru/AC	3.3	5.1	12

^{*a*} Determined by ICP-AES.

^b Observed from the HRTEM images in Figure 2.

^{*c*} Determined by H₂-O₂ titration.

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