Supporting Information

Ruthenium(0) Nanoclusters Stabilized by Nanozeolite Framework; Isolable, Reusable, and Green Catalyst for the Hydrogenation of Neat Aromatics under Mild Conditions with the Unprecedented Catalytic Activity and Lifetime

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(References cited in here are independent from the main text)

Table S-1. The top seventeen catalysts in benzene hydrogenation at room temperature^(a).

entry	precatalyst	conditions [t (°C) / P _{H2} / solvent]	TTO ^(b)	TOF ^(c)	Reference
1	[RhCl(1,5-hexadiene)] ₂	20 °C / 1 atm / water	-	-	1
2	[Rh(COD)Cl] ₂	25 °C / 1 atm / neat	-	16	2
3	[Rh(COD)H] ₄	25 °C / bubbling / neat	-	-	3
4	RhCl ₃ ·3H ₂ O	20 °C / 1 atm / water	-	57	4
5	RhCl ₃ ·3H ₂ O	20 °C / 1 atm / water	-	90	5
6	RhCl ₃ ·3H ₂ O	20 °C / 1 atm / water	300	84	6
7	[(Cp*)Zr(CH ₃) ₃]@Al ₂ O ₃	25 °C / 1 atm / neat	-	960	7
8	IrCl ₃	25 °C / 2.7 atm / neat	-	375	8
9	RhCl ₃ ·3H ₂ O	22 °C / 1 atm / hexane	-	600	9
10	RuCl ₃ ·3H ₂ O	20 °C / 30 atm / neat	-	268	10
11	RhCl ₃ ·3H ₂ O	20 °C / 1 atm / water	-	114	11
12	RuCl ₃	20 °C / 1 atm / water	-	24	12
13	RuCl ₃	20 °C / 2.1 atm / water	-	600	13
14	Rh/AlO(OH)	25 °C / 1 atm / hexane	-	690	14
15	Intrazeolite Ru(0) NC's	22 °C / 2.7 atm / neat	2420	1040	15
16	RhCl ₃ ·3H ₂ O	25 °C / 1 atm / water	-	300	16
17	Rh(0) NC's@CNT	25 °C / 10 atm / neat	-	1038	17
18	NFS-Ru(0)	25 °C / 2.8 atm / neat	177200	5430	this study

(a) Selected from >1900 reports obtained by a SciFinder literature search for “benzene hydrogenation” and arranged chronologically. (b) The TTO values refer to number of mol H₂ per mol of catalyst. (c) The TOF values are in the units of (mol H₂)(mol catalyst)⁻¹h⁻¹.

Figure S-1. X-ray diffraction patterns of nanozeolite (NF, with FAU framework) and nanozeolite framework stabilized ruthenium(0) nanoclusters (NFS-Ru(0), with a ruthenium content of 0.27 %wt). All the samples are dehydrated in vacuum.

Figure S-2. Particle size distribution bar (and its sigmoidal fit) obtained from the dynamic light scattering analysis of the nanozeolite framework stabilized ruthenium(0) nanoclusters (NFS-Ru(0), with a Ru content of 0.27 %wt).

Figure S-3. (a) XPS survey scan spectrum, (b) high resolution Ru 3d XPS spectrum and its simulated peak fitting in the region of 279-292 eV, (c) high resolution Ru 3p XPS spectrum and its simulated peak fitting in the region of 470-450 eV of the nanozeolite framework stabilized ruthenium(0) nanoclusters (NFS-Ru(0), with a Ru content of 0.27 %wt).

Figure S-4. X-ray diffraction pattern of nanozeolite framework stabilized ruthenium(0) nanoclusters recovered after the hydrogenation of 1.0 mL benzene starting with 100 mg NFS-Ru(0) (with a Ru loading of 0.27 % wt corresponding to 2.7 μmol Ru) at 25 ± 0.1 $^{\circ}\text{C}$ with an initial H_2 pressure of 42 ± 1 psig.

Figure S-5. TEM images of the nanozeolite framework stabilized ruthenium(0) nanoclusters with a Ru content of 0.27 %wt dispersed in neat benzene at room temperature.

Figure S-6. Graph of benzene consumption versus time for the hydrogenation of neat benzene catalyzed by the nanozeolite framework stabilized ruthenium(0) nanoclusters with a Ru content of 0.27 %wt. (50 mg, 1.35 μmol Ru) at 25 ± 0.1 $^{\circ}\text{C}$ and an initial H_2 pressure of 42 ± 1 psig.

Figure S-7. The percentage of catalytic activity and conversion versus the number of catalytic runs for the hydrogenation of 1.0 mL benzene (11.2 mmol), catalyzed by NFS-Ru(0) (0.27 % wt.Ru, 100 mg, 2.7 μ mol Ru) at 25 ± 0.1 °C with an initial H₂ pressure of 42 ± 1 psig.

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