

## Supporting Information

**Ruthenium(0) nanoclusters supported on hydroxyapatite: highly active, reusable and green catalyst in the hydrogenation of aromatics under mild conditions with a record catalytic lifetime**

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

## Experimental section

**Materials.** Ruthenium(III) chloride trihydrate ( $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ ), sodium borohydride ( $\text{NaBH}_4$ , 98%), hydroxyapatite ( $[\text{Ca}_5(\text{OH})(\text{PO}_4)_3]_x$ ), benzene (99%), toluene (99%) and d-Chloroform ( $\text{CDCl}_3$ ) were purchased from Aldrich. Mesitylene (98%), and *o*-xylene (98%) were purchased from Fluka. All catalyst reaction solutions were prepared in oxygen free atmosphere (Labconco, drybox,  $\text{O}_2 < 5$  ppm,  $\text{H}_2\text{O} < 1$  ppm). Benzene, toluene, mesitylene and *o*-xylene were distilled over sodium under argon and stored in the drybox. Ruthenium(III) chloride was recrystallized from water and the water content of  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  was determined by TGA and found to be  $x = 3$ . Hydroxyapatite was calcinated under dry oxygen at 400 °C for 5h before use. Deionized water was distilled by water purification system (Milli-Q System). All glassware and Teflon coated magnetic stir bars were cleaned with acetone, followed by copious rinsing with doubly deionized water under ultrasonication before drying in an oven at 150 °C.

**Preparation of ruthenium(0) nanoclusters supported on hydroxyapatite (Ru(0)/HAp).** Ruthenium(0) nanoclusters supported on hydroxyapatite were synthesized by following a two-step procedure; (i) In the first step, ruthenium(III) cations were introduced into the Ca-HAp by ion-exchange<sup>1</sup> of 1000 mg Ca-HAp in 100 mL aqueous solution of 26 mg  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  (0.1 mmol) for 40 h at room temperature. The sample was then filtered by centrifugation (5200 rpm for 15 min) and the remnant was dried in vacuum. (ii) In the second step, the solid remnant was added into 100 mL  $\text{NaBH}_4$  solution (568 mg, 150 mM) at room temperature. Ruthenium(III) ion was reduced and the ruthenium(0) nanoclusters were formed; the reduction was considered to be complete when no more hydrogen evolution was observed. The Ru(0)/HAp sample was isolated by centrifugation (5200 rpm for 15 min) and filtered by suction filtration using Whatman-1 filter, washed three times with 100 mL of deionized water, and dried under vacuum ( $10^{-3}$  Torr) at 80 °C, then transferred into the drybox.

**Characterization of ruthenium(0) nanoclusters supported on hydroxyapatite (Ru(0)/HAp).** The ruthenium content of Ru(0)/HAp was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES; Varian-Vista) after the powdered sample was completely dissolved in the mixture of  $\text{HNO}_3$ :HCl with a 1:3 ratio. Powder X-ray diffraction (XRD) patterns were acquired on a MAC Science MXP 3TZ diffractometer using Cu-K $\alpha$  radiation (wavelength 1.5406 Å, 40 kV, 55 mA). Transmission electron microscopy (TEM) and high resolution-TEM (HRTEM) analyses were performed on a JEM-2010F microscope (JEOL). A small amount of powder sample was placed on the copper grid of the transmission electron microscope. Samples were examined at magnification between 100 and 400 K. XPS analysis was performed on a Physical Electronics 5800 spectrometer equipped with a hemispherical analyzer and using monochromatic Al K $\alpha$  radiation (1486.6 eV, the X-ray tube working at 15 kV, 350 W and pass energy of 23.5 keV). The nitrogen adsorption/desorption experiments were carried out at 77 K using a NOVA 3000 series (Quantachrome Instruments) instrument, which is applicable in the microporous size range of 0.35 nm – 300 nm. The sample was outgassed under vacuum at 573 K for 3 h before the adsorption of nitrogen. NMR spectra were recorded on a Bruker Avance DPX 400 (400.1 MHz for  $^1\text{H}$ ).

**General procedure for the Ru(0)/HAp catalyzed hydrogenation of arenes.** All reaction mixtures were prepared in a nitrogen-filled oxygen free drybox ( $\text{O}_2 < 5$  ppm,  $\text{H}_2\text{O} < 1$  ppm) following the procedure described elsewhere.<sup>2</sup> In a drybox 150 mg Ru(0)/HAp catalyst (150 mg, with a ruthenium content of 0.42 %wt corresponding to 6.23  $\mu\text{mol}$  Ru) was weighed into 40x20 mm borosilicate culture tube containing 5/16 in. x 5/8 in. Teflon coated magnetic stir bar, then the substrate (0.5 mL) in cyclohexane (1.5 mL) was added into this tube via gastight syringe. The culture tube was then placed inside the Fischer-Porter (F-P) pressure bottle. The F-P bottle was sealed, brought outside the drybox, placed inside a constant temperature circulating water bath at  $25 \pm 0.1$  °C, and connected via Swagelock TFE-sealed quick-connects to the hydrogenation line which had already been evacuated for at least 30 min to remove any trace oxygen and water present, then refilled with purified  $\text{H}_2$  at  $42 \pm 1$  psig. Then, the F-P bottle was the purged 10 times (15 s per purge, with stirring at  $>600$  rpm). The pressure in the F-P bottle was then set to a constant  $42 \pm 1$  psig of  $\text{H}_2$  and the reaction was started. The reaction was followed by monitoring the pressure change in the F-P bottle via RS-232 module and using Lab View 8.0 program on a PC. The pressure vs time data was processed using Microsoft Office Excel 2003 and Origin 7.0. Reaction rates were determined from the slope of the linear portion of the

H<sub>2</sub> uptake curve. The complete hydrogenation of each substrate was also confirmed by <sup>1</sup>H-NMR spectrum of reaction solution taken at the end of the reaction.

**Control experiment: testing the catalytic activity of hydroxyapatite in the hydrogenation of benzene.** The catalytic activity of ruthenium free hydroxyapatite (Ca-HAp, 150 mg) was checked in the hydrogenation of 0.5 mL benzene (in 1.5 mL cyclohexane), which was performed in the same way as described in the section of “General procedure for the Ru(0)/HAp catalyzed hydrogenation of arenes”. It was found that in the Ca-HAp catalyzed hydrogenation of benzene even after six hours later there is no hydrogen uptake. This result shows that the ruthenium free hydroxyapatite (Ca-HAp) is catalytically inactive in the hydrogenation of benzene.

**Isolability, bottleability and reusability of Ru(0)/HAp in the hydrogenation of benzene.** After the first run of the hydrogenation of 0.5 mL benzene (in 1.5 mL cyclohexane), catalyzed by 150 mg Ru(0)/HAp (150 mg, with a ruthenium content of 0.42 %wt corresponding to 6.23 μmol Ru), the FP bottle was removed from the line, taken into the drybox, opened and the suspension in the culture tube was transferred into a Schlenk tube, resealed and connected to vacuum line. After the evaporation of volatiles, the solid residue was weighed (132 and 115 mg for the second and third runs, respectively) and used again in the hydrogenation of 0.5 mL benzene (in 1.5 mL cyclohexane) under the same conditions (25 ± 0.1 °C and 42 ± 1 psig H<sub>2</sub> initial pressure). Ru(0)/HAp provide complete conversion of benzene into cyclohexane with an initial TOF values of **695** and **675** in the second and third runs, respectively. These result indicate that Ru(0)/HAP retains ~ 96 % of their initial catalytic activity in the hydrogenation of benzene with the complete conversion even at third run.

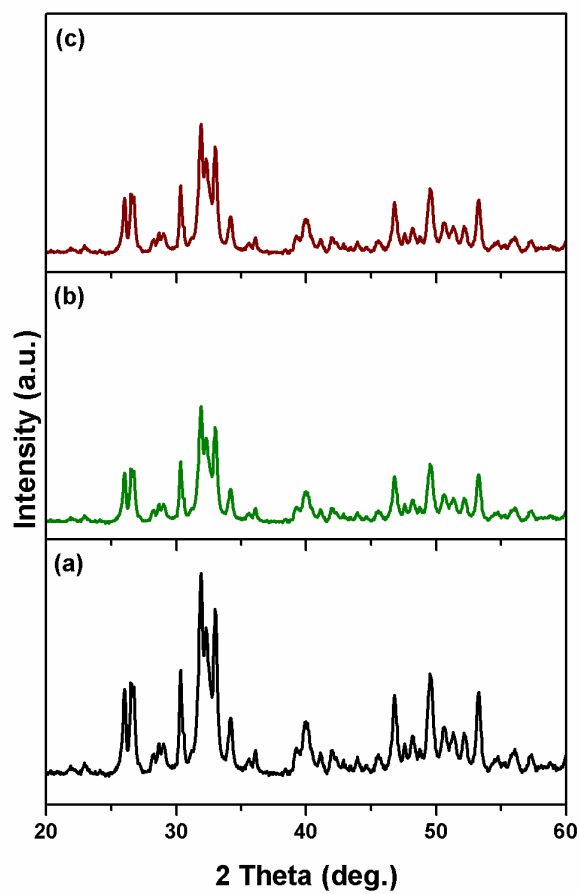
**The determination of the catalytic lifetime of Ru(0)/HAp in the hydrogenation of neat benzene.** The catalytic lifetime of nanozeolite framework stabilized ruthenium(0) nanoclusters was determined by measuring their total turnover number (TTO) in the hydrogenation of neat benzene. This experiment was started with a 150 mg nanozeolite framework stabilized ruthenium(0) nanoclusters (with a ruthenium loading of 0.42 %wt corresponding to 6.23 μmol Ru) and 3 mL benzene, and performed in the same way as described in the section of “General procedure for the Ru(0)/HAp catalyzed hydrogenation of arenes”. When the complete hydrogenation of benzene had been achieved the FP bottle was removed from the line, taken into the drybox, opened and more benzene was added into the reaction solution and the reaction was continued in this way until no hydrogen uptake was observed.

**The leaching test of Ru(0)/HAp in the hydrogenation of benzene.** After the first run of the hydrogenation of 0.5 mL benzene (in 1.5 mL cyclohexane), catalyzed by 150 mg Ru(0)/HAp (150 mg, with a ruthenium content of 0.42 %wt corresponding to 6.23 μmol Ru), the FP bottle was removed from the line, taken into the drybox, opened and the suspension in the culture tube was filtered, filtrate and 0.5 mL benzene was taken into the new culture tube and transferred into the FP bottle. The hydrogenation of benzene was performed in the same way as described in the section of “General procedure for the Ru(0)/HAp catalyzed hydrogenation of arenes”. No hydrogenation of benzene was observed after 8 hours. Additionally, no ruthenium metal was detected in the hot filtrate (~80 °C) by ICP which had a detection limit of 24 ppb for Ru.

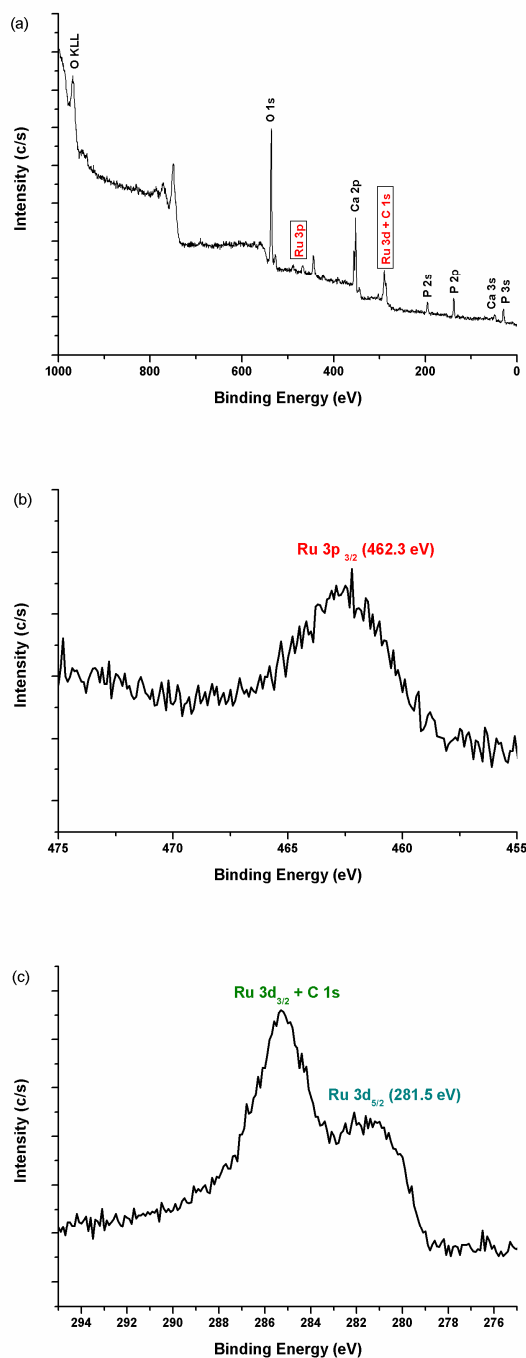
**Table S-1.** The eight catalyst systems achieve the complete hydrogenation of neat benzene shown in the table tabulated from a SciFinder literature search of “benzene hydrogenation” (>1900 citations) refined by “benzene hydrogenation at room temperature” (~95 hits), with those eight studies arranged chronologically.

entry	precatalyst	conditions		TTO <sup>(a)</sup>	TOF <sup>(b)</sup>	reference
		[t (°C) / P <sub>H2</sub> / solvent]				
1	[Rh(COD)Cl] <sub>2</sub>	25 °C / 1 atm / neat		ND	48	3
2	[Rh(COD)H] <sub>4</sub>	25 °C / bubbling / neat		ND	ND	4
3	[(Cp*)Zr(CH <sub>3</sub> ) <sub>3</sub> ]@Al <sub>2</sub> O <sub>3</sub>	25 °C / 1 atm / neat		ND	2880	5
4	RuCl <sub>3</sub> ·3H <sub>2</sub> O	20 °C / 30 atm / neat		ND	804	6
5	Intrazeolite Ru(0) NC's	22 °C / 2.7 atm / neat		2420	3120	7
6	Rh(0) NC's@CNT	25 °C / 10 atm / neat		ND	1038	8
7	Ru(0)/HAp	25 °C / 2.8 atm / neat		<b>192600</b>	<b>610</b>	this study

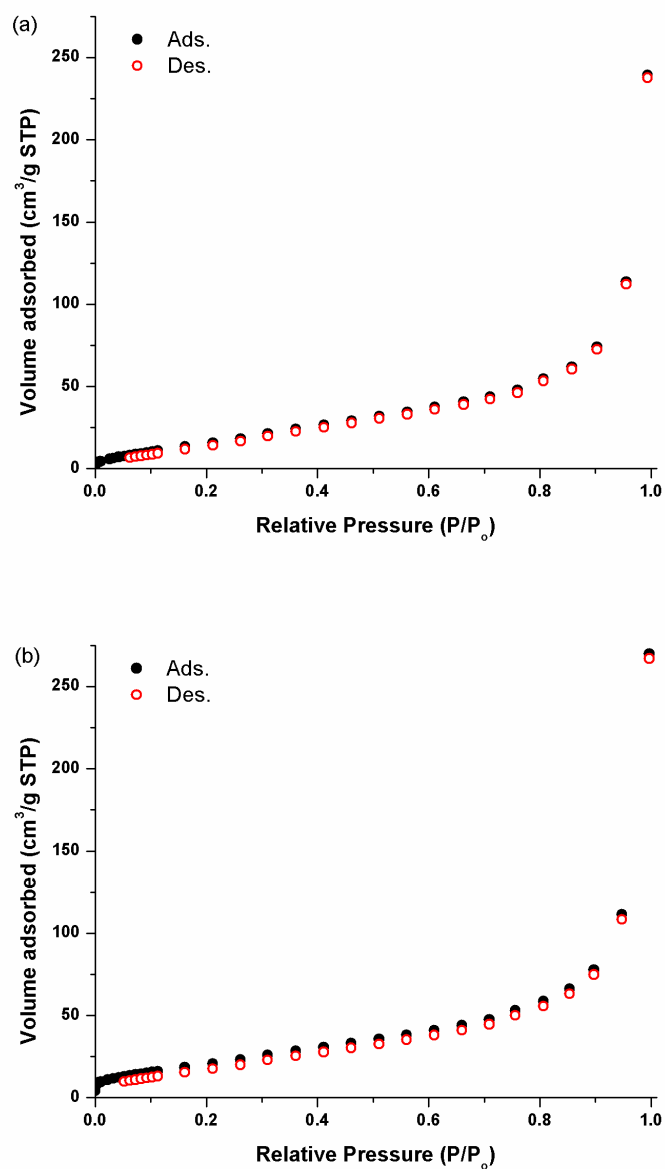
(a) (b) The TOF's and TTO's reported herein are those typically reported [TOF = (mol of H<sub>2</sub> consumed / mol of total catalyst loading)time]; [TTO = (TOF) (time)]. That is, the reported TOF's and TTO's are not corrected for the amount of metal that is on the surface of the catalyst and/or the actual number of active sites but only in Marks' study (entry 7) the actual number of active sites known with some certainty (virtually 100% active sites).(c) ND = not demonstrated.



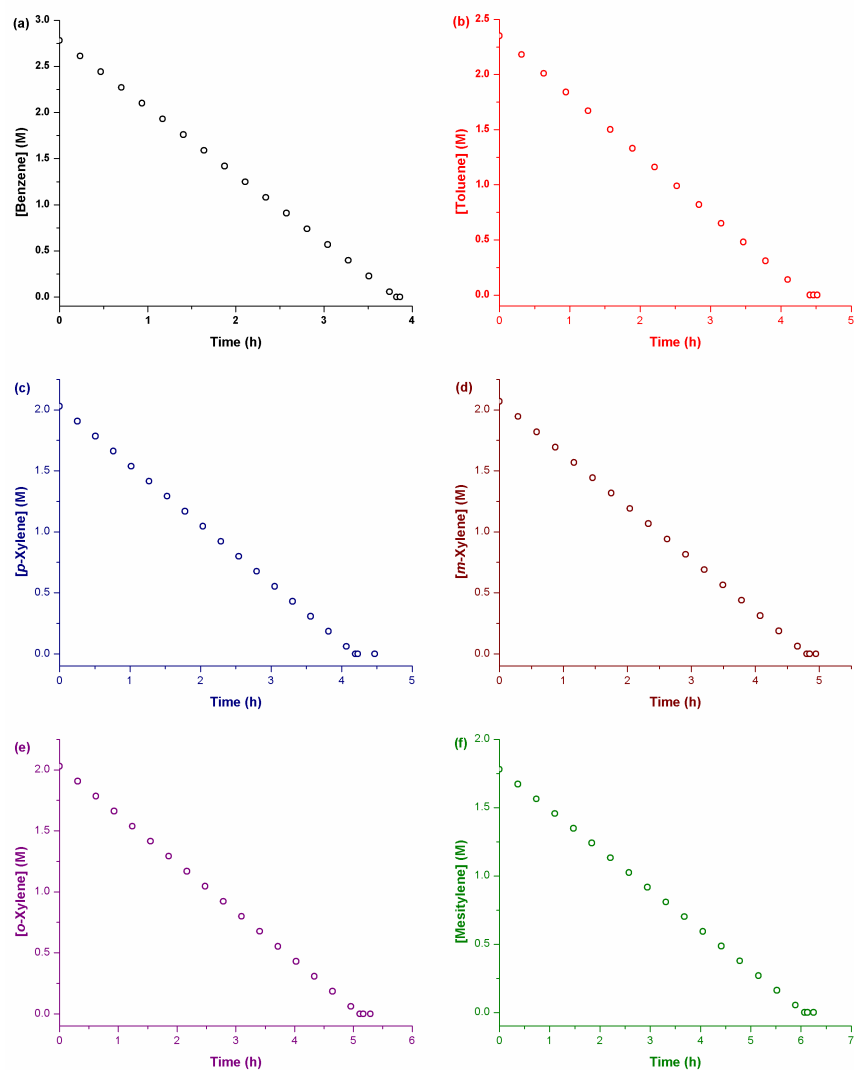
**Fig. ESI-1.** XRD patterns of (a) HAp, (b) Ru(0)/Hap, (c) Ru(0)/HAp recovered at the end of the third reuse from the hydrogenation of benzene



**Fig. ESI-2.** (a) XPS survey scan spectrum, (b) high resolution Ru 3p XPS spectrum, (c) high resolution Ru 3d XPS spectrum of the Ru(0)/HAp (with a ruthenium content of 0.42 %wt).

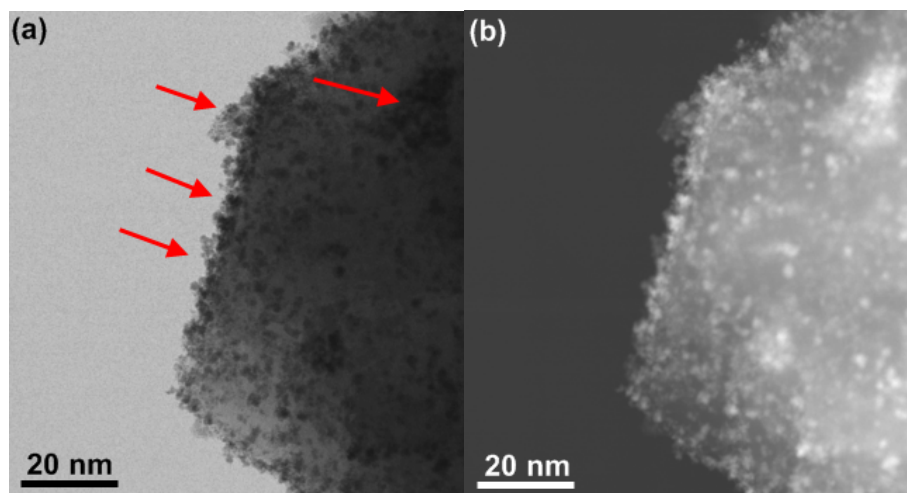


**Fig. ESI-3.** Nitrogen adsorption-desorption isotherms of (a) HAp, (b) Ru(0)/HAp (with a ruthenium content of 0.42 % wt).



**Fig. ESI-4.** Graphs of (a) [benzene], (b) [toluene], (c) [p-xylene], (d) [m-xylene], (e) [o-xylene] and (f) [mesitylene] consumption versus time for Ru(0)/HAp (150 mg, 6.23  $\mu$ mol Ru) catalyzed hydrogenation of 0.5 mL of substrate in 1.5 mL cyclohexane at 25  $\pm$  0.1 °C with an initial H<sub>2</sub> pressure of 42  $\pm$  1 psig.





**Fig. ESI-5.** (a) TEM image, (b) ZC-TEM image of Ru(0)/Hap (with a ruthenium content of 0.42 %wt) harvested at the end of the hydrogenation of benzene. Red arrows in image (a) indicate surface agglomerated ruthenium(0) nanoclusters.

## References

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