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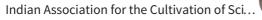
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## Fabrication of Ruthenium Nanoparticles in Porous Organic Polymers: Towards Advanced Heterogeneous Catalytic Nanoreactors

John Mondal,\*<sup>[a, b]</sup> Sudipta K. Kundu,<sup>[c]</sup> Wilson Kwok Hung Ng,<sup>[a]</sup> Ramana Singuru,<sup>[b]</sup> Parijat Borah,<sup>[a]</sup> Hajime Hirao,\*<sup>[a]</sup> Yanli Zhao,\*<sup>[a]</sup> and Asim Bhaumik\*<sup>[c]</sup>

**Abstract:** A novel strategy has been adopted for the construction of a copolymer of benzene–benzylamine-1 (BBA-1), which is a porous organic polymer (POP) with a high BET surface area, through Friedel–Crafts alkylation of benzylamine and benzene by using formaldehyde dimethyl acetal as a cross-linker and anhydrous FeCl<sub>3</sub> as a promoter. Ruthenium nanoparticles (Ru NPs) were successfully distributed in the interior cavities of polymers through NaBH<sub>4</sub>, ethylene glycol, and hydrothermal reduction routes, which delivered Ru-A, Ru-B, and Ru-C materials, respectively, and avoided aggregation of metal NPs. Homogeneous dispersion, the nanoconfinement effect of the polymer, and the oxidation state of Ru NPs were verified by employing TEM, energy-dispersive X-ray spectroscopy mapping, cross polarization magicangle spinning <sup>13</sup>C NMR spectroscopy, and X-ray photoelec-

tron spectroscopy analytical tools. These three new Rubased POP materials exhibited excellent catalytic performance in the hydrogenation of nitroarenes at RT (with a reaction time of only  $\approx\!30$  min), with high conversion, selectivity, stability, and recyclability for several catalytic cycles, compared with other traditional materials, such as Ru@C, Ru@SiO\_2, and Ru@TiO\_2, but no clear agglomeration or loss of catalytic activity was observed. The high catalytic performance of the ruthenium-based POP materials is due to the synergetic effect of nanoconfinement and electron donation offered by the 3D POP network. DFT calculations showed that hydrogenation of nitrobenzene over the Ru (0001) catalyst surface through a direct reaction pathway is more favorable than that through an indirect reaction pathway.

### Introduction

Porous organic polymers (POPs) have recently received a staggering degree of attention owing to their huge surface area, tunable pore size distribution, high hydrothermal and mechanical stability, flexible synthetic strategy, and readily modifiable functionality.<sup>[1]</sup> The assembly of nanoporous materials and

metal or metal oxide nanoparticles (NPs) has opened up an interdisciplinary research area for the development of new heterogeneous catalysts with limited agglomeration and leaching of NPs, as well as favorable mass transport in confined cavities; these features are desirable for catalysis. [2]

Although the porous channels and interior cavities can be easily tuned in the case of metal-organic frameworks (MOFs), which is an important property of platforms that encapsulate NPs, the versatile application of MOF-encapsulated NPs in heterogeneous catalysis has been a difficult challenge because of their unstable physicochemical nature towards moisture, acids, and bases and the labile nature of metal-ligand coordination bonds.[3] In contrast to MOFs, POPs are considered to have the most promising molecular architecture for the encapsulation of NPs because they possess relatively stable covalent bonds, low skeleton density, and hydrophobic components in their structures. Moreover, the structural integrity of POPs can be easily tuned by varying the synthetic strategy and selection of monomers.[4] The interaction between organic linkers in POPs and metal NPs can be readily enhanced by introducing coordination groups into metal precursors, which provide an extra advantage for the stabilization and improvement of the activity of metal NPs compared with other catalytic supports. Recent reports in the literature demonstrate that heterogeneous catalysts for morphology-tuned aerobic oxidation, [5] hydro-

[b] Dr. J. Mondal,\* R. Singuru Inorganic and Physical Chemistry Division CSIR-Indian Institute of Chemical Technology (IICT) Uppal Road, Hyderabad-500007 (India) E-mail: johncuchem@gmail.com

[c] S. K. Kundu,<sup>+</sup> Prof. Dr. A. Bhaumik Department of Materials Science Indian Association for the Cultivation of Science 2A & 2B Raja S. C. Mullick Road, Jadavpur, Kolkata 700 032 (India) E-mail: msab@iacs.res.in

- [+] These authors contributed equally to this work.
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<sup>[</sup>a] Dr. J. Mondal,<sup>+</sup> Dr. W. K. Hung Ng, Dr. P. Borah, Prof. Dr. H. Hirao, Prof. Dr. Y. Zhao Division of Chemistry and Biological Chemistry School of Physical and Mathematical Sciences Nanyang Technological University, 21 Nanyang Link, 637371 (Singapore) E-mail: hirao@ntu.edu.sg zhaoyanli@ntu.edu.sq

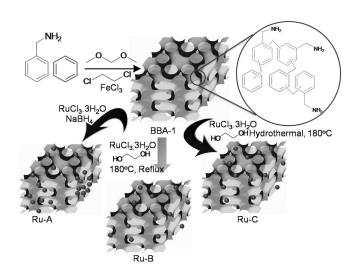




genation,<sup>[6]</sup> coupling,<sup>[7]</sup> cycloaddition reactions,<sup>[8]</sup> and so forth can be developed through the facile fabrication and encapsulation of metal NPs inside the nanoporous channel of POPs.

The hydrogenation of nitroarenes to produce aniline derivatives has attracted much attention in the field of heterogeneous catalysis because these compounds are the most important intermediates for the synthesis of dyes, agrochemicals, pharmaceuticals, polymers, and many other fine chemicals. A number of research groups have developed various types of heterogeneous catalysts with high efficiency and recyclability to produce anilines through the hydrogenation of nitroarenes. Beller and co-workers developed Co<sub>3</sub>O<sub>4</sub>@C- and Fe<sub>2</sub>O<sub>3</sub>@Cbased heterogeneous catalysts for the hydrogenation of nitroarenes under 50 bar of H<sub>2</sub> at 110 °C. [9] Xia et al. designed new functionalized carbon nanotube based Co<sub>3</sub>O<sub>4</sub> NPs as a heterogeneous catalyst for the hydrogenation of nitroarene at 250 °C. [10] Pd@POP has been employed as a heterogeneous catalyst by Wang et al. for nitroarene hydrogenation with H<sub>2</sub> (1 atm).[11] However, compared with traditional hydrogenation, catalytic transfer hydrogenation (CTH) with hydrogen-donor reagents is more advantageous because no special experimental setup or the use of high-pressure equipment is required, and hydrogen-donor reagents are abundant, inexpensive, and easy to handle. Recently, Beller et al. employed the Co<sub>3</sub>O<sub>4</sub>-NGr/C (NGr = modified nitrogen doped graphene layer) catalyst for the CTH reaction of nitroarenes with HCOOH-NEt<sub>3</sub> at 100 °C for 15 h. [12] Zeolite-supported copper NPs have been utilized as a catalyst for the selective hydrogenation of nitroarenes in 2-propanol at 80 °C. [13] Compared with low-cost iron and cobalt catalysts, ruthenium catalysts have some distinctive features (low melting and boiling points, and binding enthalpies, of Ru<sup>0</sup> organometallics indicates that the  $Ru^0$  (n-1) d electrons provide less polar carbon-metal bonds than those previously reported, with a high turnover frequency (TOF) for dehydrogenation of a metal hydride), which promotes the ability to carry out several hydrogenation reactions under high partial pressure and an oxygen-containing atmosphere to gain insights for designing new ruthenium-based catalysts, despite its high cost and low availability.[13b,c]

Herein, we have synthesized a benzene-benzylamine-1 (BBA-1) POP through Friedel–Crafts alkylation of benzylamine and benzene by using formaldehyde dimethyl acetal as a cross-linker with anhydrous FeCl<sub>3</sub> as a promoter.<sup>[14]</sup> Ruthenium NPs were successfully embedded in BBA-1 to form Ru-A, Ru-B, and Ru-C materials (Scheme 1). The BBA-1, Ru-A, Ru-B, and Ru-C materials were characterized by employing wideangle powder XRD, N<sub>2</sub> adsorption/desorption isotherms, X-ray photoelectron spectroscopy (XPS), solid-state cross polarization magic-angle spinning (CP MAS) <sup>13</sup>C NMR spectroscopy, TEM, energy-dispersive X-ray spectroscopy (EDX), field-emission (FE) SEM, and FTIR spectroscopy. Ru@POP exhibited excellent catalytic performance in the CTH of nitroarenes to produce anilines, compared with traditional Ru@C, Ru@SiO2, and Ru@TiO2 catalysts, with high reusability and recyclability at RT. To the best of our knowledge, herein, for the first time, we show that Ru@POP-based materials act as excellent heterogeneous nanocatalysts with high conversion and selectivity for the CTH of nitroarenes at RT, in which a shorter reaction time is required. DFT computational studies have been performed to predict whether the hydrogenation reaction occurs through a direct reduction pathway or an indirect reduction pathway; these calculations show that the hydrogenation of nitrobenzene over the Ru (0001) catalyst surface through a direct reaction pathway is more favorable than that through an indirect reaction pathway.



**Scheme 1.** Synthesis of nanoporous organic polymer BBA-1 and Ru@POP materials.

### **Results and Discussion**

### Synthesis and characterization of POP materials

A nanoporous organic polymer, BBA-1, with a brown color was synthesized (Scheme 1) by Friedel-Crafts alkylation of benzylamine and benzene by using formaldehyde dimethyl acetal as a cross-linker and anhydrous FeCl<sub>3</sub> promoter. This brown-colored polymer BBA-1 is insoluble in water and common organic solvents. Three different materials with Ru NPs embedded in the BBA-1 polymer were developed through the reduction of RuCl<sub>3</sub>·3 H<sub>2</sub>O by following three different reduction strategies. Coordination bonds were formed between Ru<sup>3+</sup> ions and the -NH<sub>2</sub> groups present in the BBA-1 polymer, when BBA-1 and RuCl<sub>3</sub>·3 H<sub>2</sub>O were stirred in methanol for 24 h at RT. The Ru-A material was prepared from the isolated solid Ru-polymer composite by employing the strong reducing agent NaBH<sub>4</sub>, which caused some agglomeration of Ru NPs. The Ru-B material was developed by heating the Ru-polymer composite at reflux in ethylene glycol; ethylene glycol itself acted as a reducing agent. The hydrothermal synthesis procedure with ethylene glycol as a solvent was applied to obtain the Ru-C material, in which Ru NPs were homogenously dispersed in the inner porous channels and on the external surface of BBA-1. The thermal stabilities of BBA-1, Ru-A, Ru-B, and Ru-C were determined from thermogravimetric analysis (TGA) data (Figure S1 in the Supporting Information). All materials were thoroughly characterized by XRD, TEM, SEM, EDX, XPS, N2 adsorption/de-





sorption analysis, FTIR spectroscopy, and CP MAS <sup>13</sup>C NMR spectroscopy. The Ru contents in the Ru-A, Ru-B, and Ru-C materials were 0.1739, 0.0897, and 0.0548 mmol g<sup>-1</sup>, respectively, as determined by inductively coupled plasma mass spectrometry (ICP-MS) analysis. The wide-angle powder XRD patterns of the pure microporous polymer BBA-1 and Ru NPs encapsulated in BBA-1 are shown in Figure 1 A. The presence of only a single broad diffraction peak for the BBA-1 polymer indicates its amorphous nature. Ru-B shows three broad peaks at  $2\theta = 38.2$ , 43.3, and 68.9 due to diffractions of the (100), (101), and (110) planes, respectively, which correspond to the hexagonal phase of metallic Ru NPs. Ru-C exhibits peaks at  $2\theta = 38.2$ , 42.2, 43.6, and  $68.5^{\circ}$  for the (100), (002), (101), and (110) diffraction planes, respectively. [15] The Ru-A polymer shows peaks at  $2\theta$  = 38.3 and 42.2° for the diffraction of the (100) and (002) planes, respectively. Broad peaks indicate the nanosized nature of ruthenium particles. BET surface areas and pore size distributions of the pure polymer and ruthenium-loaded polymers were measured by analyzing nitrogen adsorption and desorption isotherms at 77 K (Figure 1B and C). The y values for BBA-1, Ru-A, and Ru-B have been shifted upwards by 80, 40, and 10 ccg<sup>-1</sup>, respectively, and the values for Ru-C have been shifted downwards by 25 ccg<sup>-1</sup> for clarity (Figure 1B). The BET surface areas were measured over the relative pressure  $(P/P_0)$ range from 0.01 to 0.1. All polymers showed an initial high uptake, followed by a gradual increase in nitrogen adsorption with a mild hysteresis, and the steep rise in the high  $P/P_{\rm o}$  region indicates that the material consists of micro- and mesopores.<sup>[16]</sup>

The BET surface areas for BBA-1, Ru-A, Ru-B, and Ru-C are 607.8, 551.6, 523.2, and 543.3 m² g⁻¹, respectively. Pore size distributions were derived from the adsorption branches of the isotherms by using the nonlocal (NL) DFT (NLDFT) pore model, assuming a cylindrical pore geometry (Figure 1 C). The calculated pore volumes for the respective polymer and Ru NP incorporated materials are 0.416, 0.420, 0.387, and 0.431 ccg⁻¹, respectively. The solid-state CP MAS  $^{13}$ C NMR spectra of pure BBA-1 and the Ru NP-loaded polymers (Figure 1 D) confirmed the structural integrity of the polymers. Each spectrum exhibits three signals at  $\delta\!=\!37.0$ , 129.1, and 137.0 ppm. The signal at  $\delta\!=\!37.0$  ppm could be attributed to the benzylic carbon, whereas the signals at  $\delta\!=\!129.1$  and 137.0 ppm could be assigned to the carbon atoms of aromatic rings and the carbon attached to the benzylic carbon, respectively.  $^{[17]}$ 

XPS measurements were employed to elucidate the oxidation state of Ru NPs and to show that the NPs were coordinated by the amine groups of the polymer. The XPS survey spectra (Figure 2 A) for all materials demonstrate that, in addition to binding energy peaks corresponding to C 1s and N 1s (Figure 2 B), a new peak is generated that is attributable to the Ru 3 p binding energy. The binding energy peak of N1s (shown in Figure 2 B) centered at 397.9 eV signifies the presence of free

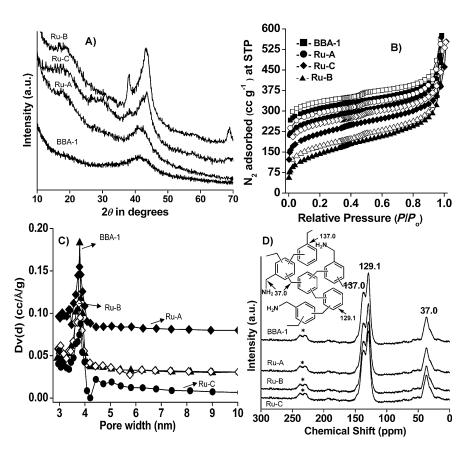


Figure 1. A) Wide-angle powder XRD patterns, B)  $N_2$  adsorption/desorption isotherms with some arbitrary shifts, C) pore size distributions, and D) solid-state CP MAS  $^{13}$ C NMR spectra; the asterisks indicate spinning side bands.





amine groups in the pure BBA-1 polymer. However, the positive shift in the binding energy for N 1s to higher energy (399.0 eV) in the Ru NPs indicates that the metals are coordinated strongly by the nitrogen atoms of the amino groups of the polymers. In Figure 2C, the binding energy for Ru 3p<sub>1/2</sub> in the Ru-A, Ru-B, and Ru-C materials shows peaks at 485.96, 484.54, and 484.03 eV, respectively, and the binding energy for  $3p_{3/2}$  gives peaks at 463.45, 462.2, and 462.03 eV, respectively. These XPS spectra for Ru-A, Ru-B, and Ru-C show that Ru NPs are in the zero oxidation state in these materials. The positive shift in the binding energy of Ru 3 p for Ru-A can be attributed to the strong interaction between the polymer network and Ru NPs, which suggests electron transfer from the metal to organic linkers, resulting in a partially positively charged metal phase (Ru $^{\delta+}$ ). The binding energy shift of the Ru 3 p core level ( $\approx$ 1.2 eV) in Ru-B and Ru-C, compared with Ru-A, can be explained by the interaction of surface -OH groups of ethylene glycol causing changes to the electron density over Ru NPs in these materials. Each of the XPS spectra in Figure 2D–F exhibits two prominent bands; the peaks are centered at binding energies of 284.0 and 281.1 eV, 283.96 and 280.7 eV, and 284.0 and 281.2 eV for Ru-A, Ru-B, and Ru-C, respectively, and the two peaks can be readily assigned to  $3\,\mathrm{d}_{3/2}$  and  $3\,\mathrm{d}_{5/2}$  of Ru<sup>0</sup>, respectively. It is notable that the Ru<sup>0</sup>  $3\,\mathrm{d}_{3/2}$  binding energy peak overlaps with the C 1s peak at around 283.9 eV. [18]

Elemental mapping and EDX patterns of carbon, nitrogen, and ruthenium for the Ru-A, Ru-B, and Ru-C materials are given in Figure 3. The elemental mapping images reveal that the homogeneous distribution of all elements in the materials and Ru NPs are homogenously dispersed in the nanoporous polymer BBA-1. The FTIR spectra (Figure S2 in the Supporting Information) signify characteristic absorption bands of organic

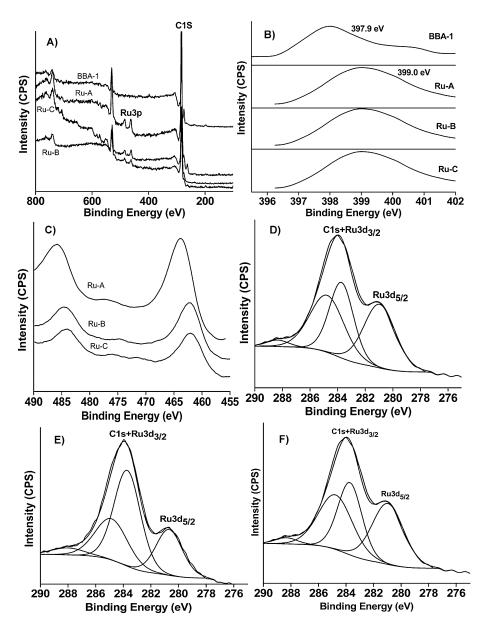


Figure 2. A) XPS survey spectra; B) N 1s spectra; C) Ru 3p spectra; and Ru 3d spectra of: D) Ru-A, E) Ru-B, and F) Ru-C.



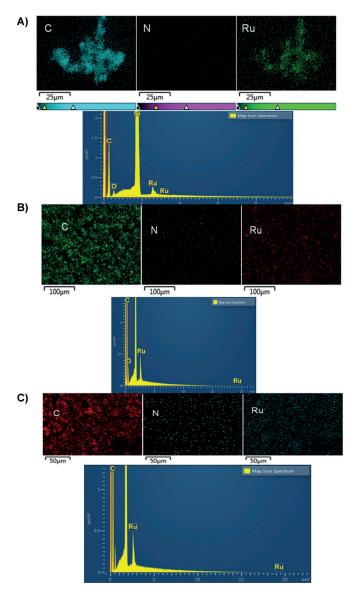


Figure 3. EDX analysis and corresponding elemental mapping of: A) C, N, and Ru for Ru-A, B) Ru-B, and C) Ru-C.

functional groups of the polymer. A TEM image of nanoporous polymer BBA-1 is provided in Figure S3 in the Supporting Information.<sup>[19]</sup>

TEM images of Ru-A (Figure 4A–C) clearly indicate that Ru NPs (black spots), varying in size from 3.5 to 7.0 nm with a certain degree of agglomeration, are uniformly distributed on the external outer surface of the porous polymer. This suggests that the nitrogen-rich polymer cannot entirely inhibit aggregation on the external surface of the NPs through Oswald ripening. The images in Figure 4D–F also reveal uniform dispersion of Ru NPs with sizes of 1.5 to 4.0 nm in Ru-B. The Ru NPs of Ru-C, with spherical morphology and dimensions of 2–4 nm (Figure 4G–I), are well dispersed in the nanoporous polymer BBA-1. In this case, the particle size is small enough, so that they can be easily encapsulated in the interior cavities of nanoporous polymer BBA-1. During the course of the synthesis of

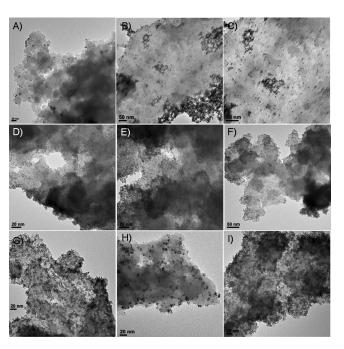


Figure 4. TEM images of: A-C) Ru-A, D-F) Ru-B, and G-I) Ru-C.

Ru-B and Ru-C, ethylene glycol has been used, which acts as a stabilizer to control particle growth and prevent aggregation.

### Catalytic performance of Ru<sup>0</sup>-POP-based nanocatalysts

The catalytic performance of all POP-encapsulated Ru NPs was evaluated by performing the CTH of nitroarenes at RT (25 °C). Initially, our study of this catalytic hydrogenation reaction began by stirring nitrobenzene (0.5 mmol) with Ru-A (5 mg) in EtOH (5 mL) at RT for 12 h (Table 1, entry 1); however, no conversion was observed. We then utilized formic acid (2.5 equiv) as a hydrogen source in EtOH and stirred the reaction mixture at RT. After 8 h, 52% conversion was achieved (Table 1, entry 2). We slowly increased the temperature of the reaction mixture to 80°C, and the progress of the reaction was observed to deliver 68% conversion after 6 h (Table 1, entry 3). iPrOH was also used as a hydrogen-donor source for this catalytic hydrogenation of nitrobenzene by stirring the reaction mixture in DMF for 6 h with 43% conversion (Table 1, entry 4). We also heated the reaction mixture at 75 °C and observed that 70% conversion was reached after 4 h (Table 1, entry 5). Glycerol was also utilized as a hydrogen source for this catalytic hydrogenation of nitrobenzene in diglyme by heating the reaction mixture at 125 °C. After 4 h, 82% conversion could be observed (Table 1, entry 6). We also carried out this catalytic reaction with 1 bar of  $\mathrm{H}_2$  gas at RT in the presence of Ru-A. After 4 h, 85% conversion was attained (Table 1, entry 7). We then examined the CTH of nitrobenzene (0.5 mmol) with NaBH<sub>4</sub> (1 mmol) in the presence of a mixture of THF/H<sub>2</sub>O (1:3 v/v) and Ru-A (5 mg) at RT (25  $^{\circ}$ C).

The catalytic reaction finished in 2.5 h with 92% conversion (Table 1, entry 8). We increased the ratio of NaBH<sub>4</sub> from 1 to 1.5 mmol (Table 1, entry 9) and observed 98% conversion after



**Table 1.** Optimization of the reaction conditions for the catalytic hydrogenation of nitrobenzene by the Ru nanocatalyst. [a]

Entry	H donor	Catalyst	Solvent	t [h]	Conv. [%]
1	no additive	Ru-A	EtOH	12	0
2	НСООН	Ru-A	EtOH	8	52
3 <sup>[b]</sup>	НСООН	Ru-A	EtOH	6	68
4	<b>&gt;</b> —ОН	Ru-A	DMF	6	43
5 <sup>[c]</sup>	<b>&gt;</b> —он	Ru-A	DMF	4	70
6 <sup>[d]</sup>	но он	Ru-A	diglyme	4	82
7	H <sub>2</sub> gas (1 bar)	Ru-A	EtOH	4	85
8	NaBH <sub>4</sub> (1 mmol)	Ru-A	THF/H₂O	2.5	92
9	NaBH <sub>4</sub> (1.5 mmol)	Ru-A	THF/H₂O	2	98
10	NaBH <sub>4</sub> (2.5 mmol)	Ru-A	THF/H₂O	0.5	98
11 <sup>[e]</sup>	NaBH <sub>4</sub> (2.5 mmol)	Ru-A	THF/H <sub>2</sub> O	0.5	45
12 <sup>[f]</sup>	NaBH <sub>4</sub> (2.5 mmol)	Ru-A	THF/H <sub>2</sub> O	0.5	25
13 <sup>[g]</sup>	NaBH <sub>4</sub> (2.5 mmol)	Ru-A	THF/H <sub>2</sub> O	0.5	98
14 <sup>[h]</sup>	NaBH <sub>4</sub> (2.5 mmol)	Ru-BBA-1	THF/H <sub>2</sub> O	6	32
15 <sup>[i]</sup>	HCOONa	Ru-A	H <sub>2</sub> O	6	73

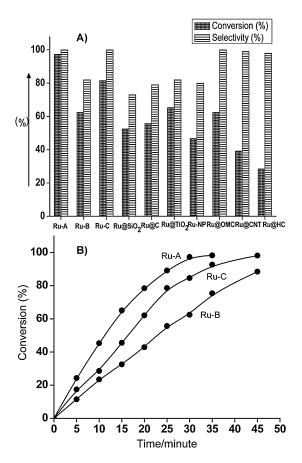
[a] Reaction conditions: nitroarene (0.5 mmol), Ru-A (5 mg,  $8.695\times10^{-7}$  mol Ru), solvent (5 mL), RT (25 °C). [b] Reaction temperature 80 °C. [c] Reaction temperature 75 °C. [d] Reaction temperature 125 °C. [e] Ru-A (2 mg,  $3.478\times10^{-7}$  mol Ru). [f] Ru-A (1 mg,  $1.739\times10^{-7}$  mol of Ru). [g] Ru-A (10 mg,  $1.739\times10^{-6}$  mol of Ru). [h] Ru-BBA-1 catalyst was prepared by physical mixing. [i] Reaction temperature 100 °C; conversion [%] determined by GC analysis with hexadecane as an internal standard.

2 h. When 2.5 mmol of NaBH<sub>4</sub> was employed for this reaction, surprisingly the reaction was complete within 30 min (Table 1, entry 10), affording 98% conversion of nitrobenzene into aniline (conversion was measured by GC analysis in the presence of hexadecane as an internal standard). The catalytic performance appeared to be dependent on the amount of catalyst (mol % loading of Ru), as proven by carrying out the reaction with different catalyst loadings. The reaction with catalyst loadings of 2  $(3.478\times10^{-7} \text{ mol of Ru})$  and 1 mg  $(1.739\times10^{-7} \text{ mol of Ru})$ 10<sup>-7</sup> mol of Ru) afforded conversions of 45 and 25%, respectively (Table 1, entries 11 and 12). However, no substantial change in product conversion was observed with a drastic increase in the amount of catalyst (Table 1, entry 13). Hence, we can conclude that 5 mg is the optimum amount of catalyst required to conduct this catalytic hydrogenation reaction. The physical mixture (Ru-BBA-1) exhibited a much lower catalytic activity (32% conversion after 6 h) than that with the Ru-A catalyst under identical conditions (Table 1, entry 14). This result established a clear synergistic effect for the Ru NPs inside the nanoporous channel of POP. We also examined the catalytic hydrogenation reaction with HCOONa in the presence of Ru-A, which afforded the corresponding amine with 73% conversion after 6 h (Table 1, entry 15). All Ru-POP-based catalysts (Ru-B and Ru-C) were subsequently screened for this catalytic hydrogenation of nitrobenzene to aniline under our optimized reaction conditions. All catalytic reactions were carried out in the presence of a 0.17 mol% loading of Ru in Ru@POP catalysts. We also employed Ru-B and Ru-C (0.17 mol% loading of Ru) for the CTH of nitrobenzene under identical reaction condi-

tions. However, conversions of only 62.5 and 81.5% were achieved with 82 and 100% product selectivity for the Ru-B and Ru-C catalysts, respectively (Figure 5 A). For comparison, the catalytic activities of some conventional Ru NP-based catalysts were also assessed by performing the same hydrogenation reaction of nitrobenzene under identical reaction conditions. Conventional catalysts, such as Ru@SiO<sub>2</sub>, Ru@C, and Ru@TiO2, were prepared by applying the same preparation method as that used for the synthesis of the Ru-A catalyst (the detailed reaction procedure is given in the Supporting Information). The amounts of all conventional Ru catalysts were employed for catalytic purposes in such a way that the Ru loading was 0.17 mol%. Figure 5 A shows that 52.5, 55.7, and 65.3% product conversions were attained for similar CTH reactions of nitrobenzene with Ru@SiO<sub>2</sub>, Ru@C, and Ru@TiO<sub>2</sub>, respectively. The nanoporous support matrix allows easy diffusion of organic substrates that can therefore interact with the catalytically active Ru NPs present in the nanoporous channel, as well as in the external surface area, which leads to improvement of the catalytic activity of the bare Ru NPs (Figure 5 A). The catalytic performance of the Ru@POP nanocatalysts is superior to that of the Ru@C and Ru@SiO2 catalysts, although the Ru@C catalyst demonstrates better catalytic performance than the Ru@SiO2 catalyst. This result implies that the hy-

drophobicity of the support matrix is the most important factor that controls this CTH reaction. The hydrophobic nature of the support matrix surface decreases in the order of porous polymer > porous carbon > porous SiO<sub>2</sub>. This trend was established by performing contact-angle measurements (Figure S4 in the Supporting Information). The organic substrate is adsorbed onto the nanoporous matrix for the catalytic reaction because the super-hydrophobic nature of the as-synthesized BBA-1 POP results in strong hydrophobic and  $\pi$ - $\pi$  stacking interactions between the hydrophobic organic substrate and support matrix. This also facilitates desorption of the hydrophilic product into the reaction mixture. To determine the advantage of nitrogen-rich highly cross-linked porous organic polymeric compounds as supports, a variety of non-nitrogenbased organic supports, including organic mesoporous carbon (OMC), commercial multiwalled carbon nanotubes (CNT), and hydrothermal carbon (HC), were used to fabricate Ru NPs on the supports and were examined for the catalytic efficiency of those catalysts in the hydrogenation of nitrobenzene to aniline under identical reaction conditions.

Among them, Ru@OMC, Ru@CNT, and Ru@HC catalysts resulted in nitrobenzene conversions to aniline of 62.5, 39.1, and 28.5%, respectively (Figure 5 A). These results demonstrate that nitrogen-rich highly cross-linked POP plays an important role when it is utilized as a support for the development of Rubased catalysts; thus, the Ru@POP-based materials have a high performance and show great promise as heterogeneous catalysts in hydrogenation. We also performed a comparative study on the catalytic conversion of nitrobenzene under opti-



**Figure 5.** A) A comparison of the catalytic performance of all Ru-based nanocatalysts for the CTH of nitrobenzene to aniline. Reaction conditions: nitrobenzene (0.5 mmol), NaBH<sub>4</sub> (2.5 mmol), THF/H<sub>2</sub>O (1:3 v/v), Ru catalyst (8.695  $\times$  10<sup>-7</sup> mol), for 30 min at RT (25 °C). B) Conversion of nitrobenzene to aniline as a function of time for the hydrogenation reaction. Ru loadings in all Ru catalysts were 0.17 mol%.

mized reaction conditions against time by employing different Ru–POP-based nanocatalysts with different Ru particle sizes (Figure 5 B). To investigate the reaction performance with different Ru–POP-based catalysts, product evolution for the hydrogenation reaction was observed by continuous sampling by GC at 10 min intervals. Ru NPs with large particle sizes ( $\approx 7~\rm nm$ ) and highly crystalline features embedded on the POP support for the Ru-A nanocatalyst are more beneficial for CTH

compared with the other catalysts with smaller particle sizes. Larger Ru NPs interact favorably with organic reactant molecules through their more exposed, highly crystalline facets, leading to an improvement in catalytic conversion over other Ru-POP-based nanocatalysts (Figure 5B). We believe that, during the course of the catalytic reaction, the first of the two oxygen atoms of the -NO<sub>2</sub> group of nitrobenzene coordinates to the exposed Ru (001) surface. This interaction is highly favored when the positive charge density on the Ru surface is increased, resulting in an enhancement of the catalytic performance of the Ru-A catalyst compared with the other catalysts, and this distinct catalytic performance is affected by the electronic environment, as revealed in the XPS spectra. We compared the catalytic performance of our newly developed cocatalyst with other previously reported heterogeneous catalysts for the catalytic hydrogenation of nitroarene (Table 2). All catalysts required a high catalyst loading (5 wt% or 10 mol%), high hydrogen pressure, excess use of hydrogen-donating agent (10 mmol), and had low recyclability. The results in Table 2 demonstrate that the Ru@POP catalyst is superior to previously reported catalysts because we have carried out our catalytic reactions with a very low loading of catalyst under very mild conditions, and our catalyst could be recycled in several catalytic runs without significant loss of catalytic activity. The superior catalytic efficiency of the Ru@POP materials compared with those of other conventional catalysts may be due to the synergetic effect of nanoconfinement and electron donation of BBA-1 POP. The amine organic backbone unit of 3D BBA-1 POP could coordinate to  $Ru^0$  through  $\pi$ -electron donation, so Ru surfaces could acquire enhanced activity for the dehydrogenation of NaBH<sub>4</sub>, and thus, efficient H<sub>2</sub> generation, thereby facilitating the transfer hydrogenation of nitroarenes. The high surface area of POP allows easy diffusion of organic substrates, thereby involving interactions with catalytic active centers to enhance catalytic rates, and the rigidity of the polymer increases recyclability by diminishing the leaching of Ru from backbone unit. By using the Ru-A catalyst and employing various substituted nitroarenes with different steric and electronic characters in a mixture of THF and H<sub>2</sub>O (1:3 v/v) at RT (25 °C), we examined the substrate scope of this CTH reaction.

Full conversions (100%) to the corresponding products with high selectivities were provided by nitroarenes with electron-

Catalyst <sup>[a]</sup>	Amount of catalyst	H <sub>2</sub> source	Reaction conditions	Ref.
Ru-BBA-1	0.17 mol % Ru	NaBH <sub>4</sub> (2.5 mmol)	THF/H₂O 25 °C	our work
Fe <sub>2</sub> O <sub>3</sub> @C	4.5 mol % Fe	50 bar H <sub>2</sub>	THF/H <sub>2</sub> O 120 °C	[9a]
Pd@POP	0.5 mol % Pd	1 atm H <sub>2</sub>	25 °C, 1 h	[11]
Ni-PVAm/SBA-15	0.12 g catalyst	NaBH <sub>4</sub>	25 °C	[26]
Fe-Ni bimetallic NPs	10 mol %	NaBH <sub>4</sub>	25 °C	[27]
Pd-pol	5 wt % Pd	10 mmol NaBH₄	H₂O, 2 h	[28]
Co <sub>3</sub> O <sub>4</sub> @C	1 mol%	50 bar H <sub>2</sub>	THF/H₂O 110°C	[9b]
Rh NPs/SBA <sup>[b]</sup>	10 mg catalyst	2 mmol N <sub>2</sub> H₄	RT	[29a]
Au/TiO₂-VS	1 mol% Au	CO/H₃O	25°C, 3 h	[29b]

[a] Ni-PVAm = nickel polyvinylamine, Pd-pol = polymer-supported Pd-nanoparticles,  $Au/TiO_2$ -VS = very small Au Nanoparticles. [b] Catalyst can be recycled up to six times.



donating groups (Table 3, entries 2 and 3). The -OH, -F, and -NH<sub>2</sub> functional groups were well tolerated for this CTH reaction (Table 3, entries 4, 8, and 10, respectively). 4-Chloronitrobenzene (Table 3, entry 6) gave 100% product conversion to 4-chloroaniline in 30 min and no dechlorinated product of aniline was observed. 4-Nitroacetophenone underwent 98% conversion with 92% selectivity for the corresponding aniline derivative, but, surprisingly, some carbonyl reduced product was obtained with 8% selectivity (Table 3, entry 5). Our catalyst was so active that the hydrogenation of 2,4-dinitrochlorobenzene (Table 3, entry 7) was achieved with 100% selectivity for the corresponding dianiline product. 1-Nitronaphthalene and 5-nitroindole (Table 3, entries 9 and 13) exhibited significant conversions in the CTH reaction. Successful CTH reactions were carried out for 4-nitrobenzyl alcohol and 1-iodo-4-nitrobenzene (Table 3, entries 11 and 12). Our newly developed Ru-A catalyst was also effective for carrying out the large-scale CTH reaction of 4-nitrotoluene with consistent product conversion (Table 3, entry 14). We carried out two additional catalytic processes to illustrate the versatility and potential of our newly designed POP-based catalytic system. We conducted the CTH reaction of an internal alkyne (diphenyl acetylene) to provide the alkene with E/Z selectivity and very high conversion with our Ru@POP nanocatalyst in the presence of formic acid as a hydrogen source. The reaction methodology is provided in Table S1 in the Supporting Information. We also performed the hydrogenation of lignocellulosic biomass-derived levulinic acid to give value-added γ-valerolactone (GVL) with 85% conversion and 95% selectivity by employing Ru@POP catalyst. The reaction methodology is provided in Table S2 in the Supporting Information.

## Experimental and computational DFT investigation into the reaction mechanism

Adsorption of an aromatic molecule on a metal surface depends on the type of molecule, the orientation, and nature of the metal surface. Among the three possible binding configurations of nitrobenzene on the Ru (0001) surface, the parallel orientation has the highest adsorption energy (44.59 kcal mol<sup>-1</sup>; Figure S6 in the Supporting Information), with a C–Ru distance of 2.2 Å, as supported by previously reported benzene adsorption on Ru (0001). [21]

The two oxygen atoms coordinate to ruthenium atoms, while the nitrogen atom bulges upwards, as in the cases of nitrobenzene adsorption on Ni (111) and Pt (111).<sup>[22]</sup> The most stable parallel adsorption configuration was used as a starting geometry for subsequent reaction pathway calculations. To investigate the catalytic hydrogenation pathway (Figure S7 in the Supporting Information), the progress of the reaction was monitored by UV/Vis (Figure S8 in the Supporting Information) and <sup>1</sup>H NMR spectroscopy (Figure S9 A in the Supporting Information)

Table 3. The CTH reaction of different nitroarenes catalyzed by the Ru-A nanocatalyst.[a Substrate Conv.[b] Entry Selectivity TOF  $[min^{-1}]$ [min] [%] [%] 30 100 100 19.1 2 45 100 100 12.7 3 45 12.7 100 100 60 100 9.5 100 90 98 92 6.26 100 100 19.1 120 100 100 4.79 60 100 100 9.5  $NO_2$ 60 99 98 9.4 12.6 11 45 98 100 12.5

[a] Reaction conditions: nitroarene (0.5 mmol), Ru-A catalyst (5 mg,  $8.695\times10^{-7}$  mol), THF/H<sub>2</sub>O (1:3 v/v), NaBH<sub>4</sub> (2.5 mmol), RT (25 °C); selectivity refers to the corresponding amine derivative. [b] Determined by GC analysis with hexadecane as an internal standard. [c] The reaction was carried out on a 10 mmol scale.

100

80

60

45

NO<sub>2</sub>

88

99

99

7.1

9.4

2.5

mation) to observe the formation of phenylhydroxylamine, nitrosobenzene (PhNO), and azoxybenzene intermediates.[23] According to the mechanism proposed by Pathak et al. for a nickel catalyst, [22a] there are two possible pathways for the formation of aniline, namely, direct and indirect pathways (Figure S7 in the Supporting Information). To determine the most plausible pathway, we performed DFT calculations. Because a full exploration of the potential energy surface through determination of transition-state structures is computationally prohibitive for this system, we optimized the geometries of key intermediates in the direct and indirect pathways (Figure S7 in the Supporting Information) to compare the stability of the intermediates by following the scheme provided by Pathak et al. [22a] To further reduce the computational cost, hydride transfer from NaBH<sub>4</sub>, which may yield a chemisorbed hydrogen atom, was not considered; rather, we assumed that the hydrogen source on the Ru (0001) surface was responsible for reduction. In addition, since the diffusion of a hydrogen atom on the Ru (0001) surface should be fast, we focused on the

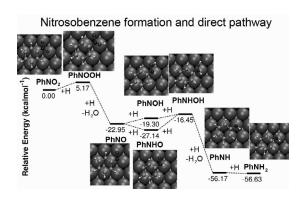




thermodynamic profile of the reacting nitrobenzene molecule. [24]

Nitrobenzene is first reduced to PhNO by the addition of two hydrogen atoms to release one water molecule with a large amount of energy  $(-22.95 \text{ kcal mol}^{-1}; \text{ Figure 6})$ . The PhNO thus formed would follow either the direct or indirect pathways to be followed. In the direct pathway, there are two possibilities for the hydrogen atom to bind to the substrate molecule, through either the nitrogen or oxygen atoms, to form PhNHO or PhNOH, respectively (Figure 6). In contrast to the exothermic reaction for the formation of PhNHO, the formation of PhNOH is slightly endothermic. The difference originates from a change in bonding after the addition of one hydrogen atom. When PhNHO is formed, the hydrogen atom increases the valency of the nitrogen atom, and the N-Ru  $(2.25\rightarrow 2.22 \text{ Å})$  and O-Ru  $(2.08\rightarrow 2.11 \text{ Å})$  distances are barely affected. By contrast, in the formation of PhNOH, the O-Ru distance is increased significantly by 0.27 Å. These two intermediate states are then converted into N-phenylhydroxylamine (PhNHOH), after the uptake of another hydrogen atom. The endothermic process ( $E_{\text{reaction}} = 10.69 \text{ kcal mol}^{-1}$ ), when considering the formation of PhNHOH from PhNHO, should be restricted; however, this endothermocity is not considered to be as critical as that for the indirect pathway. Subsequent sequential uptake of two hydrogen atoms generates aniline, which is seen to be thermodynamically very stable.

In the indirect pathway, PhNO and PhNHO molecules formed in the direct pathway are involved. The reference energy of the system is assumed to be the sum of the two intermediates ( $-22.95 + (-16.45) = -39.40 \text{ kcal mol}^{-1}$ ), at which these two molecules are placed far apart on the surface. The energy of the system is decreased by 2.52 kcal mol $^{-1}$  when the two molecules come close to each other. The subsequent release of one water molecule and the formation of the N-N covalent bond lead to a considerable energy decrease from -41.92 to -56.98 kcal mol $^{-1}$ , which suggests the formation of azoxybenzene, as supported by  $^{1}$ H NMR spectroscopy and GC-MS analyses (Figure S9 A and B in the Supporting Information). The coupled molecule then takes up two hydrogen atoms and forms Ph-NH-NOH-Ph, with a stepwise energy increase to -27.26 kcal mol $^{-1}$ . An increase in energy by 29.72 kcal mol $^{-1}$  in-



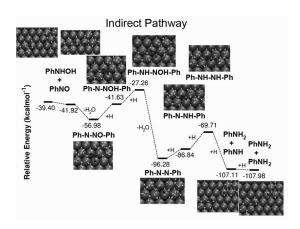
**Figure 6.** Energy profile for PhNO formation and the direct reduction pathway. The energy of the system with one nitrobenzene molecule adsorbed on the surface is taken as 0.00 kcal mol<sup>-1</sup>.

dicates that the indirect pathway, especially the process after the formation of azoxybenzene, is not energetically feasible. Ph-NH-NOH-Ph will then release one water molecule to form azobenzene (Ph-N-N-Ph) on the surface. A subsequent twohydrogen uptake process leads to the formation of 1,2-diphenylhydrazine (Ph-NH-NH-Ph), which is again a steeply uphill process with a large energy increase ( $\pm$  26.57 kcal mol<sup>-1</sup>). This energy increase also suggests that the indirect pathway is not involved in the reduction of nitrobenzene on the ruthenium surface. Aniline is produced after accepting two hydrogen atoms from Ph-NH-NH-Ph. Surprisingly, GC-MS analysis of the reaction mixture (Figure S9B in the Supporting Information) also shows the signal for Ph-N-N-Ph. However, the <sup>1</sup>H NMR spectrum of the reaction mixture does not display any significant signals for Ph-N-N-Ph (Figure S9 A in the Supporting Information), which implies that Ph-N-N-Ph is not generated in a significant or quantitative amount as a reaction intermediate. An insignificant amount of Ph-N-N-Ph could presumably be formed from azoxybenzene in the presence of excess NaBH<sub>4</sub>. It may also be possible that Ph-N-N-Ph is produced from phenylhydroxylamine through dehydration.[25] We examined the conversion of pure phenylhydroxylamine and Ph-N-N-Ph to aniline under the same optimized reaction conditions. A high selectivity for aniline production (92.5%) was achieved with 63.8% aniline conversion when pure phenylhydroxylamine was used as a hydrogenation substrate. Moreover, in the case of the direct reduction of pure Ph-N-N-Ph to give aniline, no aniline formation could be observed, even after a prolonged reaction time. Thus, together with the experimental data, our calculations suggest that the direct pathway is more favorable. In the indirect pathway, there are two thermodynamically difficult uphill processes (Figure 7). Even if azoxybenzene is formed on the surface (Figure 7), this species is likely to be decomposed because the energy of Ph-NH-N-OH-Ph is much higher than that of PhNO+PhNHOH. Importantly, the reaction of PhNHOH with a hydrogen atom to release one water molecule is a highly exothermic process (Figure 6).

## Recyclability and heterogeneous nature of the Ru-A nanocatalyst

The efficacy of the Ru<sup>0</sup> nanocatalyst was evaluated in terms of recyclability and reusability by carrying out the CTH reaction of nitrobenzene with the Ru-A nanocatalyst under optimized reaction conditions. After completion of the reaction, the nanocatalyst was recovered by centrifugation of the reaction mixture, subsequently washed with ethanol followed by acetone, and dried at 60 °C before being used in the next catalytic run. No special technique, such as the addition of acid or base or calcinations at higher temperature, was needed for the reactivation of our catalyst. Recycling tests for the Ru-A nanocatalyst suggested that the nanocatalyst could be effectively reused for 10 consecutive catalytic cycles (Figure 8). A drop in conversion between the 10th and 11th cycles from 87 to 80% was recorded; this may be due to the clogging of some catalytic active sites with organic reagents during the course of the reaction, although the selectivity is maintained in each catalytic run. To

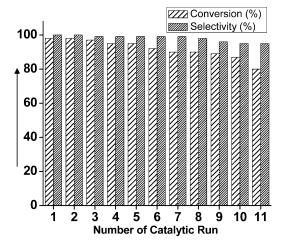




**Figure 7.** Energy profile for the indirect pathway. In the first step, there is an energy drop as PhNHOH and PhNO come closer to each other.

explain these results, we performed N<sub>2</sub> adsorption–desorption isotherm studies of the reused Ru-A catalyst after 11 cycles (Figure S10 in the Supporting Information). A decrease in BET surface area (from 551.6 to 482.6  $\rm m^2 g^{-1}$ ) led us to conclude that the accumulation of external materials hindered N<sub>2</sub> adsorption in the pore space (reduction of pore volume from 0.416 to 0.325 cc g $^{-1}$ ) and slight degradation of the supported catalyst into less active forms (extraneous loss in catalyst recovery in the 11th cycle) might also be an important contributor to successive decreases in catalytic conversion, although we were not aware of possible degradation products.

To check the mechanical stability of the Ru-A nanocatalyst after the 11th catalytic cycle, we characterized the reused Ru-A nanocatalyst. TEM analysis of the Ru-A nanocatalyst after the 11th cycle indicates no clear aggregation of Ru NPs during the course of the catalytic run (Figure 9 A). Solid-state CP MAS <sup>13</sup>C NMR spectroscopic analysis reveals that the structural integrity of organic functional groups on the nanoporous polymer backbone was retained (Figure 9 B). The XPS spectrum of the Ru 3 d region of the reused Ru-A nanocatalyst signifies that the oxidation state of Ru<sup>0</sup> NPs remains unchanged after the



**Figure 8.** Recyclability and reusability of the Ru-A nanocatalyst for the hydrogenation of nitrobenzene. Reaction conditions: nitrobenzene (0.5 mmol, 61 mg), Ru-A catalyst (5 mg, 0.17 mol%), THF/ $H_2O$  (1:3 v/v), NaBH<sub>4</sub> (2.5 mmol, 94 mg), RT (25 °C), 30 min.

catalytic reaction (Figure 9C). The wide-angle powder XRD pattern of reused Ru-A nanocatalyst demonstrates that the hexagonal phase of metallic Ru NPs in the porous polymeric framework remains unchanged (Figure 9D). All of these results signify that our newly developed nanocatalyst is stable and the structural integrity of organic functional groups on the nanoporous polymer backbone is preserved under the proposed methodology for the hydrogenation reaction.

To determine whether the CTH reaction of nitrobenzene with POP-encapsulated Ru<sup>0</sup> NPs is indeed heterogeneous in nature, we performed leaching tests (see the Experimental Section) by considering nitrobenzene as a model substrate under the optimized reaction conditions: after 15 min, 65% conversion was attained. The catalytic hydrogenation reaction was then continued for an additional 30 min with the filtrate only after removing the ruthenium nanocatalyst by centrifugation. However, no change in conversion was observed. Atomic absorption spectroscopy (AAS) was employed to verify whether any leaching of ruthenium took place during the course of the catalytic reaction. The results indicate that the ruthenium content in the filtrate was below the detection limit of the instrument and the filtrate was completely colorless. The Ru content in the Ru-A nanocatalyst after the 11th catalytic run was 0.169 mmol g<sup>-1</sup>, as determined by ICP-MS analysis, which was analogous to that of the fresh sample  $(0.173 \text{ mmol g}^{-1})$ . This study clearly established that no ruthenium leaching occurred during the course of the reaction and our catalyst is truly heterogeneous in nature.

### Conclusion

We successfully developed a new POP (BBA-1) by Friedel-Crafts alkylation of benzylamine and benzene with formaldehyde dimethyl acetal as a cross-linker and anhydrous FeCl<sub>3</sub> as a promoter. The Ru<sup>0</sup> NPs embedded in the nanoporous channels of this POP behave as a new efficient heterogeneous nanocatalyst for carrying out the CTH of nitroarenes with high reusability and recyclability at RT, compared with traditional Ru@C, Ru@SiO2 and Ru@TiO2 catalysts. This enhancement of the catalytic performance and recyclability of the Ru-POP nanocatalysts was observed due to the synergetic effect of nanoconfinement and electron donation offered by the 3D POP network. No metal leaching and the robust integrity of POP make the present materials attractive nanocatalysts for the CTH of nitroarenes. Results from DFT calculations suggest that hydrogenation of nitrobenzene over the Ru (0001) catalyst surface occurs through the direct reaction pathway rather than the indirect reaction pathway.

### **Experimental Section**

### Synthesis of BBA-1

Benzylamine (0.214 g, 2 mmol) and benzene (0.156 g, 2 mmol) were added to anhydrous 1,2-dichloroethane (10 mL), followed by the addition of formaldehyde dimethyl acetal (0.608 g, 8 mmol). Then iron(III) chloride (1.298 g, 8 mmol) was added and the reac-



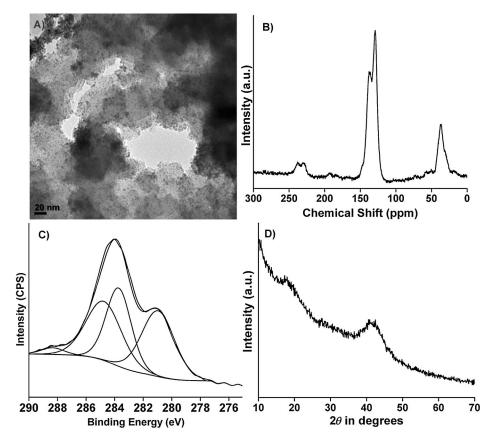


Figure 9. A) TEM image, B) CP MAS <sup>13</sup>C NMR spectrum, C) Ru 3 d XPS spectrum, and D) wide-angle powder XRD pattern of the reused Ru-A nanocatalyst after the 11th catalytic run.

tion mixture was heated to 80 °C for 20 h under a nitrogen atmosphere. The reaction mixture was cooled to RT, filtered, washed thoroughly with methanol until the filtrate became colorless, and then dried in a vacuum oven at 80 °C for another 24 h. The material was again washed with methanol by Soxhlet extraction for 48 h to give a brown material, which was designated as BBA-1.

### Synthesis of Ru-A

BBA-1 (50 mg) was dispersed in MeOH (60 mL) by stirring at RT for 2 h. Then  $RuCl_3\cdot 3\,H_2O$  (15 mg) was dissolved in MeOH (5 mL) and added to the previous polymer reaction mixture. The resulting reaction mixture was stirred at RT for 24 h. Methanol was then evaporated to dryness to deliver brown-colored solid Ru–polymer composite material. This material was dispersed in deionized  $H_2O$  (100 mL) by sonication and stirred at RT for 4 h. Then a solution of  $NaBH_4$  (5 mL, 1 m; cooled in ice) was added to the above reaction mixture and allowed to stir for 15 min at RT under a  $N_2$  atmosphere. This material was separated by centrifugation and washed repeatedly with MeOH followed by drying at RT. This isolated material was designated as Ru-A.

### Synthesis of Ru-B

BBA-1 (50 mg) was dispersed in MeOH (60 mL) by stirring at RT for 2 h. Then RuCl<sub>3</sub>·3 H<sub>2</sub>O (15 mg) was dissolved in MeOH (5 mL) and added to the previous polymer reaction mixture. The resulting reaction mixture was stirred at RT for 24 h. Methanol was then evaporated to dryness to obtain a brown-colored solid Ru–polymer

composite material. This material was dispersed in ethylene glycol (50 mL) and heated at 180 °C for 3 h. After cooling to RT, the material was separated by centrifugation and washed repeatedly with MeOH to remove ethylene glycol. This black material was designated as the Ru-B catalyst.

#### Synthesis of Ru-C

BBA-1 (50 mg) was dispersed in MeOH (60 mL) by stirring at RT for 2 h. Then  $RuCl_3\cdot 3\,H_2O$  (15 mg) was dissolved in MeOH (5 mL) and added to the previous polymer reaction mixture. The resulting reaction mixture was stirred at RT for 24 h. Methanol was evaporated to dryness to deliver a brown-colored solid material. This material was dispersed in ethylene glycol (50 mL) and hydrothermally treated in an autoclave at 180 °C for 4 h. After cooling to RT, the material was separated by centrifugation and washed repeatedly with MeOH to remove ethylene glycol. This black-colored material was designated as the Ru-C catalyst.

### CTH of nitroarenes with Ru-based catalysts at RT

In a typical CTH procedure, a mixture of nitrobenzene (0.0615 g, 0.5 mmol) with supported Ru@POP nanocatalyst (5 mg) mixed with THF (1 mL) was placed in a dry 25 mL sealed tube. Then the Ru catalyst was dispersed in the mixture by sonication. Then NaBH<sub>4</sub> (0.094 g, 2.5 mmol) in water (3 mL) was added to the previous reaction mixture. The tube was capped tightly and the reaction mixture was allowed to stir at RT (25 °C) for the time reported. The reaction was monitored periodically by analyzing the reaction mix-





ture by GC-MS until full conversion of the substrate. The products were confirmed by GC-MS analysis. The conversions of the corresponding aniline products were determined by using hexadecane as an internal standard.

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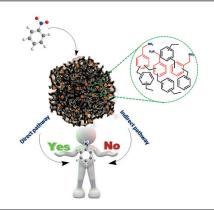
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### **FULL PAPER**

This way or that? A strategy has been adopted to develop a benzene–benzylamine-1 (BBA-1) porous organic polymer (POP) by Friedel–Crafts alkylation. Ru@POP behaves as a heterogeneous catalytic nanoreactor for the catalytic transfer hydrogenation of nitroarenes at RT through a direct reaction pathway, as supported by DFT computational calculations (see figure).



### Hydrogenation

J. Mondal,\* S. K. Kundu, W. K. Hung Ng, R. Singuru, P. Borah, H. Hirao,\* Y. Zhao,\* A. Bhaumik\*



Fabrication of Ruthenium Nanoparticles in Porous Organic Polymers: Towards Advanced Heterogeneous Catalytic Nanoreactors

