

# Recoverable rhodium nanoparticles: Synthesis, characterization and catalytic performance in hydrogenation reactions

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## Abstract

We here report the first magnetically recoverable Rh(0) nanoparticle-supported catalyst with extraordinary recovery and recycling properties. Magnetic separation has been suggested as a very promising technique to improve recovery of metal-based catalysts in liquid-phase batch reactions. The separation method is significantly simple, as it does not require filtration, decantation, centrifugation, or any other separation technique thereby, overcoming traditional time- and solvent-consuming procedures. Our new magnetically separable catalytic system, comprised of Rh nanoparticles immobilized on silica-coated magnetite nanoparticles, is highly active and could be reused for up to 20 times for hydrogenation of cyclohexene (180,000 mol/mol<sub>Rh</sub>) and benzene (11,550 mol/mol<sub>Rh</sub>) under mild conditions.

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## 1. Introduction

The development of new strategies for recovery and recycling of catalysts to enhance their lifetime and minimize the consumption of auxiliary substances used in achieving separations can result in significant economical and environmental benefits. Ongoing research activities in this area include the use of metal nanoparticles (MNPs) in catalysis [1–3]. It is widely accepted that MNPs are very active catalysts because of their large surface area and a great ratio of atoms remaining at the surface, and so available to the chemical transformation of substrates. However, the MNPs must be stabilized by protective agents to prevent agglomeration to the thermodynamically favored bulk metal. Although it results in very active soluble MNP catalysts, the separation of the catalyst from the reaction products can be problematic [4]. Attempts to improve separation

include the use of biphasic aqueous/organic systems [5–7], ionic-liquid biphasic conditions [8–11] and MNPs supported on large surface area solids [1,12–14]. From a practical point of view, catalysts that are not soluble in the same phase as organic reactants have the inherent advantage of easy separation. However, supported catalysts may also exhibit severe problems with respect to catalyst recovery in liquid-phase batch reactions. In this scenario, immobilization of catalysts on magnetically separable solid supports appears as an attractive way to give better handling properties to homogeneous [15–20] and MNP catalysts [21,22]. Solid supports containing magnetic nanoparticles can be easily separated from the product of interest due to the magnetic interaction between the magnetic nanoparticles and an external applied magnetic field. Furthermore, magnetic separation constitutes an alternative approach to traditional time- and solvent-consuming steps during the purification process since it is fast, it can be easily scaled-up, and it does not make use of other chemical reagents and solvents that present considerable environmental hazards.

Here we report a general methodology for the preparation of a magnetically recoverable rhodium metal nanocatalyst. The approach is based on the uptake of Rh<sup>3+</sup> by amino-functionalized

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silica-coated magnetic nanoparticles followed by metal reduction under controlled H<sub>2</sub> conditions, leading to the MNPs formation. We have presented the first example of a Rh(0) magnetically separable catalyst with enhanced recovery and recycling properties in hydrogenation reactions.

## 2. Experimental

### 2.1. Synthesis of oleic acid-coated magnetic nanoparticles

Fe<sub>3</sub>O<sub>4</sub> nanoparticles were prepared by the coprecipitation method and coated with oleic acid as reported elsewhere [23].

### 2.2. Synthesis of the silica-coated magnetic nanoparticles

In a typical experiment, 44.6 g of polyoxyethylene(5) isooctylphenyl ether was dispersed in 700 mL of cyclohexane. Then, 200 mg of Fe<sub>3</sub>O<sub>4</sub> dispersed in cyclohexane was added. The mixture was stirred until it became transparent. After this step, 9.44 mL of ammonium hydroxide (29% aqueous solution) was added to form a reverse microemulsion. Finally, 7.70 mL of tetraethylorthosilicate (TEOS) was added. The solution was gently stirred for 16 h. The nanocomposite Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> was precipitated with methanol and collected by centrifugation at 7000 rpm. After being washed with ethanol, the material was dried in vacuum.

### 2.3. Synthesis of the amino-modified silica-coated magnetic nanoparticles

Amino-modified silica particles were prepared as follows: 900 μL of 3-(aminopropyl)-triethoxysilane (APTES), dissolved in 100 mL of dried toluene, was added to 600 mg of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>. The solution was stirred for 2 h at room temperature. The amino-functionalized solid (Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-NH<sub>2</sub>) was washed with toluene, separated by centrifugation, and dried at 100 °C for 20 h.

### 2.4. Synthesis of the catalyst precursor

The catalyst precursor was prepared as follows: 50 mg of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-NH<sub>2</sub> were added to 10 mL of an aqueous rhodium chloride solution (2.1 mg). The mixture was stirred for 2 h at 25 °C. The solid was then magnetically collected from the solution and washed twice with acetone followed by drying at 100 °C for 3 h.

### 2.5. Hydrogenation experiments

The catalytic reactions were carried out in a modified Fischer–Porter glass reactor connected to a pressurized hydrogen tank at 20–50 atm. The Fischer–Porter bottle was set at a constant pressure for the entire course of the reaction by leaving it open to the hydrogen supply. In a typical experiment, catalytic quantities of rhodium (50 mg of magnetic solid) and the desired quantity of substrate were added to the reactor under inert atmosphere. The reactor was evacuated and attached to the

hydrogenation apparatus. The reaction was conducted under magnetic stirring (700 rpm) at the desired pressure and temperature. The temperature was maintained by a hot-stirring plate connected to a digital controller (ETS-D4 IKA). The fall in the hydrogen pressure in the hydrogen tank was monitored with a pressure transducer interfaced through a Novus Field Logger converter to a computer. The pressure versus time data were collected by the FieldChart Novus Software, stored as a data file and exported to MicroCal Origin 7.0 for the calculation of hydrogenation rates. The catalyst was recovered magnetically by placing a magnet in the reactor wall and the products were collected and analyzed by gas chromatography (GC) and GC–MS. The isolated catalyst could be reused when a new amount of substrate was added.

### 2.6. Catalyst characterization

The catalyst was analyzed by different techniques, which ensured a complete composition, morphology, and size characterization.

Transmission electron microscopy (TEM) was performed at the Instituto de Física (IFUSP) on a Philips CM200 microscope operating at 200 kV. Samples for TEM observations were prepared by placing a drop containing the nanoparticles in a coated carbon grid.

High-resolution transmission electron microscopy (HRTEM) and X-ray energy dispersive spectroscopy (EDS) were performed at the Laboratório Nacional de Luz Síncrotron (LNLS) using a Jeol-3010 ARP microscope.

Magnetization measurements  $M(T, H)$  were performed by using a superconducting quantum interference device magnetometer from Quantum Design. Applied magnetic fields  $H$  between  $-70$  and  $70$  kOe and temperatures ranging from  $5$  to  $300$  K were used in these experiments. In the zero-field cooled (ZFC) experiments, the sample was first cooled down to  $5$  K under zero applied magnetic field, the magnetic field was set, and the magnetization data were collected upon warming up to  $300$  K. In the field cooled (FC) process, the data were collected upon cooling the sample from  $300$  K down to  $5$  K under an applied magnetic field. In the hysteresis loops  $M(H)$  measurements, the sample was ZFC down to a desired temperature and the magnetic field sweep ( $-70$  kOe  $\leq H \leq 70$  kOe) was performed. These steps were repeated for several different measuring temperatures.

## 3. Results and discussion

The magnetic nanoparticles cores (Fe<sub>3</sub>O<sub>4</sub>  $\sim 10$  nm) were synthesized by the coprecipitation method and stabilized in cyclohexane with oleic acid [23]. Then, the Fe<sub>3</sub>O<sub>4</sub> nanoparticles were spherically coated with silica by means of a microemulsion technique, resulting in  $\sim 60$  nm silica spheres (Fig. 1a). The silica spheres were functionalized with 3-aminopropyl-triethoxysilane to improve the uptake of Rh<sup>3+</sup> ions from RhCl<sub>3</sub> solution. The metal-loaded solid was then subjected to reduction in 6 atm and 75 °C of H<sub>2</sub>, a process that resulted in Rh(0) nanoparticles stabilized on the surface of the magnetic

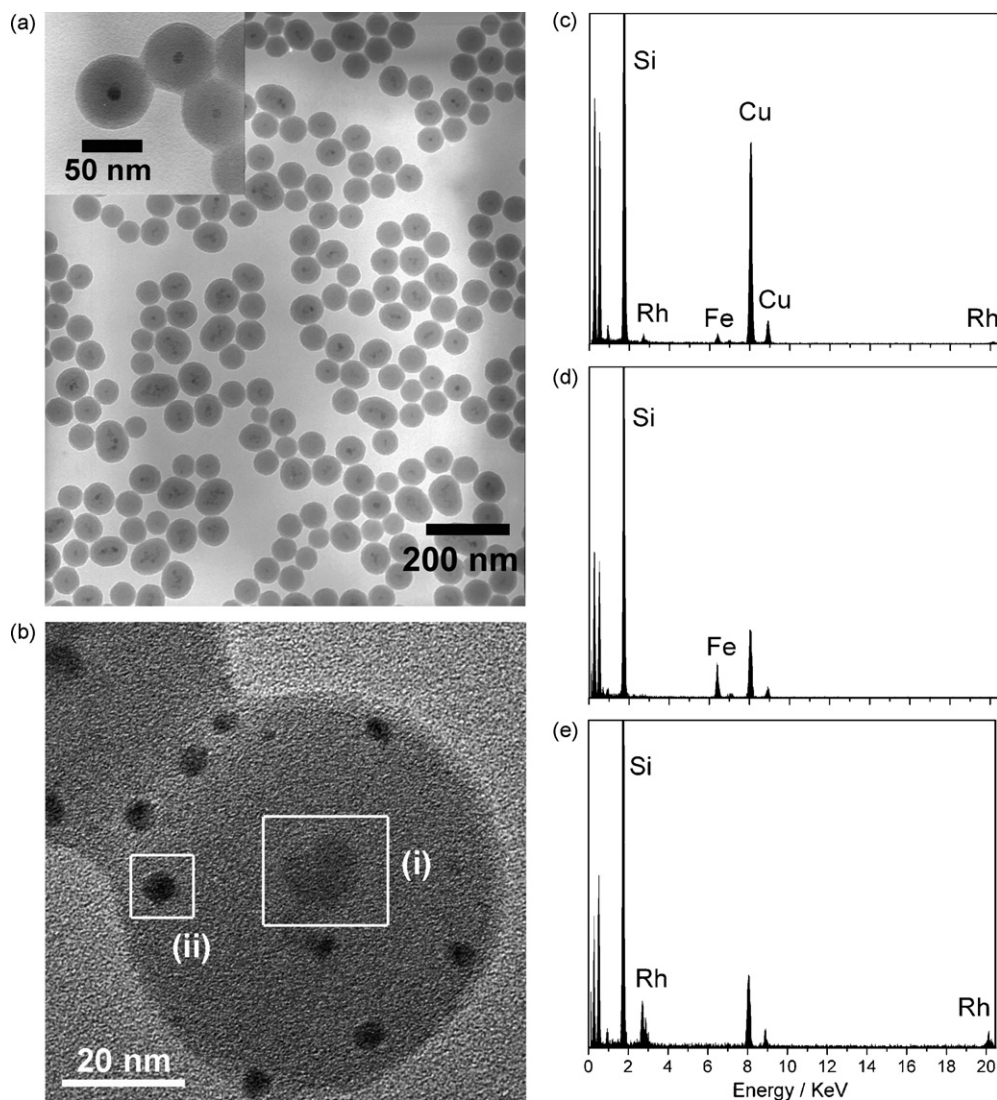


Fig. 1. (a) TEM image of silica-coated magnetic particles (inset: enlarged image); (b) HRTEM image of the spent catalyst, (c) EDS analysis of the area shown in image (b); (d) EDS analysis of the particle shown in box (i); (e) EDS analysis of the particle shown in box (ii).

support. The catalyst contains 1.55 wt% of Rh, as determined by atomic absorption analysis (ICP-AES). We have also found that when the support was not previously functionalized with amino groups only 0.14% of Rh was immobilized.

The catalyst exhibits a morphology comprised of silica spheres that contains magnetic cores and Rh(0) nanoparticles of about 3–5 nm decorating the silica shell (Fig. 1b). EDS analysis revealed the presence of Fe atoms in the core nanoparticles (box i, Fig. 1b) and Rh atoms in the nanoparticles with more contrast in the image (box ii, Fig. 1b), respectively, as displayed in Fig. 1c–e. The HRTEM image shown in Fig. 2 corroborates the presence of Rh(0) nanoparticles since an interplanar distance of 2.26 Å, corresponding to the (1 1 1) Bragg plane of cubic Rh(0), was obtained.

The magnetic properties of the catalyst sustained that the material is comprised of nanoparticles, with blocking temperature  $T_B \sim 70$  K, and negligible magnetic interaction between them, as inferred from the ZFC and FC curves displayed in Fig. 3a [24]. Indeed, the absence of magnetic

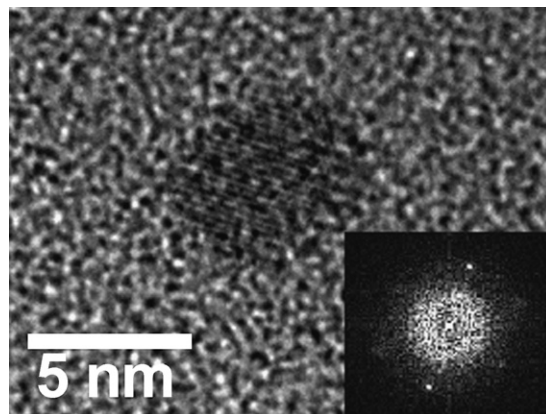


Fig. 2. HRTEM image of a Rh nanoparticle showing interplanar distances indicated by the Fourier transform obtained using Gatan software (inset).

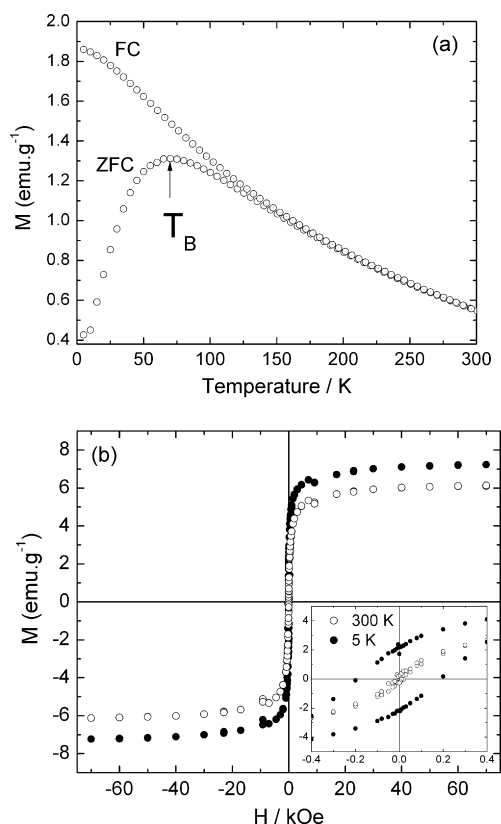


Fig. 3. (a) Temperature dependence of the magnetization (FC and ZFC curves) under magnetic field ( $H = 30$  Oe) and (b) hysteresis loops at 5 K (●) and 300 K (○) for the spent catalyst.

hysteresis at 300 K (Fig. 3b) further suggests the superparamagnetic behavior of the magnetic nanoparticles at room temperature. In spite of the  $\sim 10$  times lower magnetization when compared with the bare magnetite particles ( $\sim 62$   $\text{emu}/\text{g}$  at  $T = 300$  K and  $H = 2$  kOe) [23], the solid has been readily separated from the liquid media by using a small permanent magnet.

The catalytic activity of the magnetically separable Rh catalyst was investigated in the hydrogenation of cyclohexene and benzene in solventless conditions as shown in Table 1. The reactor loaded with the catalyst and the substrate was subjected to the desired hydrogen pressure and temperature, and the

Table 1  
Hydrogenation of cyclohexene<sup>a</sup> and benzene<sup>b</sup> by the magnetically recoverable Rh(0) catalyst under different reaction conditions

Entry	Substrate	$P$ (atm)	$T$ ( $^{\circ}\text{C}$ )	Time (min) <sup>c</sup>	TOF ( $\text{h}^{-1}$ ) <sup>d</sup>
1	Cyclohexene	6	75	15	7600
2	Cyclohexene	6	25	19	5937
3	Cyclohexene	1	75	40	2835
4	Cyclohexene	1	25	43	2638
5	Benzene	6	75	40	825
6	Benzene	6	25	168	196

<sup>a</sup> Catalyst/substrate molar ratio: 1/1900.

<sup>b</sup> Catalyst/substrate molar ratio: 1/550.

<sup>c</sup> Time required for conversion  $>99\%$  measured by GC.

<sup>d</sup> Catalytic turnover frequency: mole of substrate transformed per mole of catalyst per hour.

reaction was followed by the consumption of hydrogen in a tank connected to the main reactor. Curves of hydrogen pressure versus time were obtained for each experiment. An induction period without a detectable consumption of hydrogen was usually observed in the first use of the catalyst (first run), which is attributed to the in situ nanoparticle formation. When performing recycling studies we did not observe this induction period for the second cycle on. At the desired time, the reactor was cooled to room temperature and depressurized. The catalyst was recovered magnetically by placing a magnet in the reactor wall and the liquid contents were analyzed by GC. The conversion was usually complete after less than 1 h under mild conditions and gives the corresponding cyclohexane. Similar experiments performed under the same conditions but with  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  particles not loaded with metal did not show consumption of hydrogen even with an extended reaction time of 24 h.

A series of experiments were performed to verify the catalyst stability and recyclability. Turnover frequencies (TOFs) as high as 40,000 and  $1100$   $\text{h}^{-1}$  were obtained in the hydrogenation of cyclohexene and benzene at  $75$   $^{\circ}\text{C}$  and 6 atm  $\text{H}_2$  (Fig. 4a and b), respectively. Such values of TOF are remarkable when compared to those found for Rh nanoparticle-based catalysts [25,26]. For example, in solventless conditions (without stabilizing agents) and in ionic-liquid biphasic conditions, the TOF for hydrogenation of benzene, under similar conditions, were 21 and  $11$   $\text{h}^{-1}$ , respectively, and none of the recovered Rh nanoparticles could be recycled [25]. In aqueous biphasic conditions, Rh–PVP (polyvinylpyrrolidone) stabilized nanoparticles could be reused at least once, corresponding to a total turnover number (TON) of 3600 [26]. High turnovers and reusability were achieved in biphasic ionic liquid only under forced conditions (40 bar  $\text{H}_2$ ), reaching a total TON of 20,000 in five recycles [27]. We also mention that Rh nanoparticles supported on nanofibers were reused up to 10 times (TON of 10,000), although the separation was not straightforward as for most solid supports [28]. The new Rh magnetically separable catalyst could be reused for up to 20 successive batches without significant loss in catalytic activity, which resulted in a total TON of 180,000 and 11,550 for cyclohexene and benzene hydrogenation, respectively. All reaction batches achieved  $>99\%$  conversion in different time intervals, which explained the variation on TOF values observed in the series of experiments. The rates of the first and the last batches in cyclohexene hydrogenation were similar (close to  $20,000$   $\text{h}^{-1}$ ), which means that the active metal sites were maintained. Moreover, the catalyst activity did not change significantly, but peaks with higher activities were observed for batches 2–5, 9, 10, 12 and 13 (Fig. 4a). Similar behavior was observed for catalyst recycling in hydrogenation of benzene.

After each run the catalyst was easily separated magnetically, the product could be removed with a syringe, and new portions of the substrate were added to the reactor (Fig. 4c). The time interval for the catalyst separation and product removal ( $<1$  min) was negligible when compared to the time consumed during the reaction ( $\sim 40$  min for benzene 550 turnovers). This is a consequence of the magnetic separation that spares

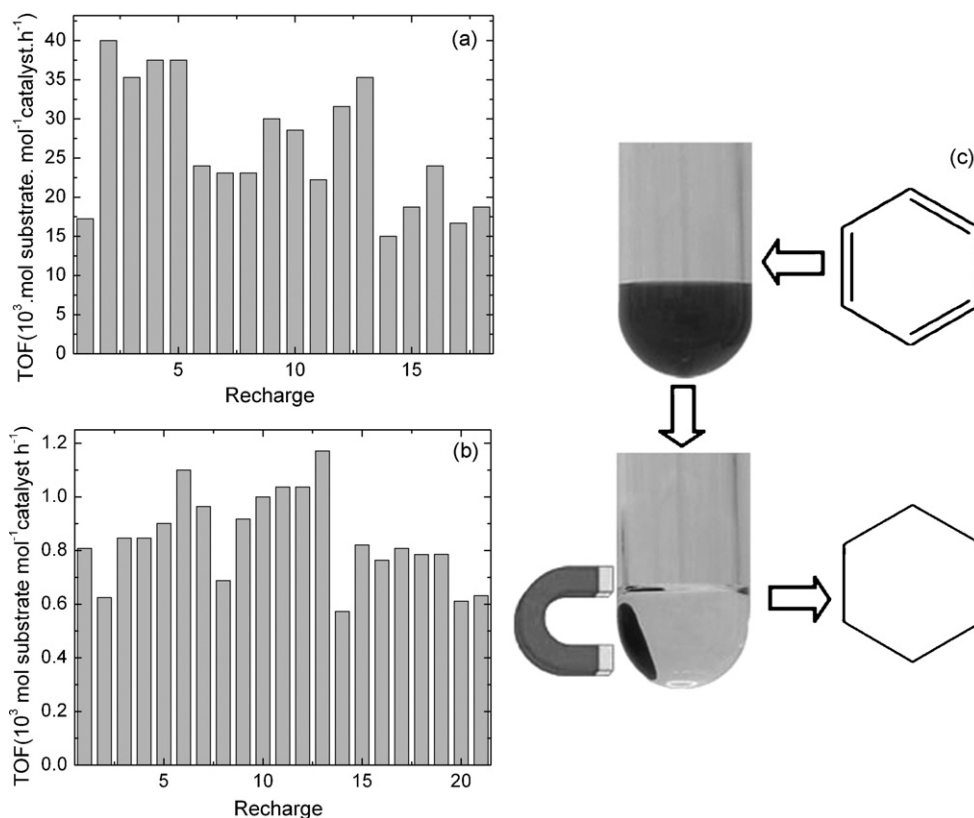


Fig. 4. Catalyst recycling in successive hydrogenation reactions: (a) cyclohexene (10,000 TON each batch), and (b) benzene (550 TON each batch). Data collected at 75 °C and under H<sub>2</sub> pressure of 6 atm. (c) Illustration of magnetic separation of the catalyst between each reaction batch.

filtration, decantation, centrifugation, or any other workup procedure. ICP-AES analysis indicated that Rh leaching was negligible after 20 successive batches (Rh content <0.67 ppm in the products). Changes in the size distribution of Rh nanoparticles after catalyst reuses were not appreciable and confirm the high stability of the system, also evidenced by high reusability and low metal leaching.

#### 4. Conclusions

In summary, we have successfully prepared a magnetically recoverable Rh nanocatalyst by a new method. The material is comprised of Rh nanoparticles immobilized on silica-coated magnetite supports. The catalyst showed considerably reproducible hydrogenation activity up to 20 cycles for the hydrogenation of benzene and cyclohexene, besides product separation was immediate due to the magnetic property of the material. These features provide a new appealing catalytic process. We also argue that the method employed here seems to be suitable for obtaining other transition-metal (Pt, Ru, Ir and Au) nanoparticle-based catalysts with increasing interest in liquid-phase reactions such as C–C couplings, hydrogenations, and oxidations.

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