



Iridium(0) nanoparticles dispersed in zeolite framework: A highly active and long-lived green nanocatalyst for the hydrogenation of neat aromatics at room temperature



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ABSTRACT

The complete hydrogenation of aromatic molecules is one of the key transformation employed in the synthetic and petroleum chemistry. Described herein is a new catalytic nanomaterial for the hydrogenation of neat aromatics under mild conditions. A novel nanocatalyst, consisting of iridium(0) nanoparticles stabilized by zeolite with FAU framework could reproducibly be prepared from the reduction of iridium(III)-exchanged zeolite in an aqueous sodium borohydride solution at room temperature and characterized by ICP-MS, P-XRD, HRTEM, XPS, N₂-Ads.-Des., and P(C₆H₁₁)₃ poisoning. The results reveal the formation of iridium(0) nanoparticles of 5.8 ± 2.1 nm size dispersed on the external surface along with iridium(0) nanoclusters in cavities of zeolite-Y whereby the host matrix remains intact. The resulting iridium(0) nanoparticles were employed as heterogeneous catalyst in the hydrogenation of various aromatic substrates (benzene, toluene, *o*-xylene and mesitylene) in the solvent-free systems at room temperature and 3 bar initial H₂ pressure. They are highly active catalyst in the hydrogenation of neat aromatics, such as they can completely hydrogenate benzene to cyclohexane with an initial turnover frequency value of TOF = 3215 h⁻¹. Moreover, they show high durability against to leaching and sintering throughout the catalytic runs, which make them reusable catalyst. More importantly, testing the catalytic lifetime of our iridium(0) nanoparticles showed that they provide previously unprecedented total turnover number of TTON = 197,000 over 92 h before deactivation in the hydrogenation of benzene at room temperature and 3 bar initial H₂ pressure.

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1. Introduction

The complete hydrogenation of aromatic molecules is one of the central reactions for the fine chemicals and intermediates in the petroleum, chemical and pharmaceutical industries [1,2]. For instance, in the petrochemical industry, many of the compounds found in crude oil are of little use since they contain C=C unsaturated bonds; they must be first transformed to their saturated counterparts before commercial use such as gasoline [3]. In the fine chemical and active pharmaceutical ingredient industries, the hydrogenation reaction is often an important step in producing the target products [4]. Most studies regarding the hydrogenation of aromatic compounds have used benzene as the model molecule, and various homogeneous and heterogeneous catalysts have been thoroughly employed in this catalytic transformation [5]. Indeed,

benzene is difficult to hydrogenate when compared to olefins because of the resonance stabilization resulting from the strong π -conjugation in the aromatic ring [6]. Thus, hydrogenation reaction conditions often require high temperatures >373 K, initial H₂ pressures >30 atm, and proper organic solvent-systems, leading to generation of by products and requiring product separation procedures. In the literature only a few reports exist on catalyst systems that can perform the complete hydrogenation of benzene under mild conditions (i.e., <373 K and initial H₂ pressures <30 atm) and under solvent-free conditions with notable hydrogenation rates (see Table 1 *vide supra*) [7–19].

As seen from the inspection of reports cited in Table 1 (*vide supra*) the majority of these catalysts are suffering from low activity. Therefore, the development of simply prepared, highly active and durable catalytic materials that can hydrogenate neat aromatics under mild conditions still remains a thorny challenge in this research field. Recent reports have already shown that Ru [13–15], Ir [8,17,20] and Rh [18] nanoparticles confined in solid materials can act as highly active hydrogenation catalyst. These

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Table 1
Catalyst systems that can hydrogenate neat benzene to cyclohexane under mild conditions.

| Entry | Catalyst | T (K) | P H ₂ (bar) | TOF [33] (h ⁻¹) | Reference |
|-------|---|-------|------------------------|-----------------------------|------------|
| 1 | Rh NPs | 298 | 1.0 | 48 | [7] |
| 2 | [(Cp [*])Zr(CH ₃) ₃] ₂ @Al ₂ O ₃ | 298 | 1.0 | 2880 | [10] |
| 3 | Ir NPs | 298 | 1.0 | 91 | [11] |
| 4 | Ru NPs@SBA-15 | 293 | 3.0 | 804 | [12] |
| 5 | Ru NPs@zeolite | 295 | 3.0 | 1040 | [13] |
| 6 | Rh@CNT ^a | 298 | 10.0 | 1038 | [14] |
| 7 | Ru@nanozeolite | 298 | 3.0 | 5430 | [15] |
| 8 | Ru@HAp ^a | 298 | 3.0 | 610 | [16] |
| 9 | Ir NPs/[Ir(COD)Cl] ₂ @zeolite | 295 | 3.0 | 1250/47 | [17] |
| 10 | Rh@HAp | 298 | 3.0 | 1770 | [18] |
| 11 | Ru–Ni/C | 293 | 3.0 | 7905 | [19] |
| 12 | Ir NPs@zeolite | 298 | 3.0 | 3190 | This study |

^aCNT and HAp stand for carbon nanotube and hydroxyapatite, respectively.

results encouraged us to focus on the development of new supported metal nanoparticles catalyst for this important catalytic transformation. Herein, we report the preparation and characterization of new iridium nanocatalyst, iridium(0) nanoparticles stabilized by zeolite of FAU framework, hereafter referred to as IrNPs@FAU, plus their notable catalytic performance in terms of the activity, selectivity, reusability and lifetime in the hydrogenation of neat aromatics at 298 K with a 3 bar initial H₂ pressure. IrNPs@FAU can be reproducibly prepared from our previously established simple two steps procedure [21,22] comprising of the ion-exchange of Ir³⁺ ions with extra framework Na⁺ ions of zeolite followed by their reduction within the zeolite framework by sodium borohydride (NaBH₄) in aqueous solution at room temperature. The resultant IrNPs@FAU were characterized by using a combination of advanced analytical techniques including inductively coupled plasma mass spectroscopy (ICP-MS), powder-X-ray diffraction (P-XRD), transmission electron microscopy (TEM), high-resolution-TEM (HRTEM), X-ray photoelectron spectroscopy (XPS), nitrogen-adsorption-desorption (N₂-Ads.-Des.) analyses and P(C₆H₁₁)₃ poisoning experiments, which reveal that the formation of highly crystalline well-dispersed iridium(0) nanoparticles of 5.8 ± 2.1 nm on the external surface as well as iridium(0) nanoclusters in the cavities of zeolite by keeping the host framework intact.

The resulting IrNPs@FAU were found to be highly active and selective catalyst in the hydrogenation of aromatics in the solvent free systems at room temperature. They provide an *initial* turnover frequency value of TOF = 3215 h⁻¹ in the hydrogenation of neat benzene as a model reaction at 298 K and under 3 bar initial H₂ pressure with the complete reduction of benzene to cyclohexane. Moreover, they exhibit high durability throughout their catalytic use in the hydrogenation reaction against agglomeration and leaching. This significant property makes them a reusable catalyst in the hydrogenation of aromatics such that they retain >50% of their *initial* activity even at the fifth catalytic run in the hydrogenation of neat benzene. More importantly, they have a previously unprecedented catalytic lifetime in the hydrogenation of neat benzene by providing a total turnover number of TTON = 197,000 over 92 h before deactivation under the identical conditions given above. Additionally, IrNPs@FAU catalyst system fulfills the majority of the “Green Chemistry” [23] requirements which impose neat/solventless systems whenever possible.

2. Experimental

2.1. Materials

Iridium(III) chloride trihydrate (IrCl₃·3H₂O), sodium borohydride (NaBH₄, 98%), benzene (99%), toluene (99%), *d*-chloroform

(CDCl₃) and cyclohexane (99%) were purchased from Aldrich. Cyclohexene (99%), mesitylene (98%), and *o*-xylene (98%) were purchased from Fluka. Sodium zeolite-Y (Si/Al = 2.5) was purchased from Zeolyst and slurried with 0.1 M NaCl to remove sodium defect sites, washed until free of chloride and calcined in dry oxygen at 773 K for 12 h before to use. All catalyst reaction solutions were prepared in oxygen free atmosphere (Labconco, drybox). Benzene, toluene, *o*-xylene and mesitylene were distilled over sodium under argon and stored in the drybox. 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 distilled water before drying in an oven at 423 K.

2.2. Characterization

The chemical composition of IrNPs@FAU was determined by inductively coupled plasma mass spectroscopy (ICP-MS; Varian-Vista). Powder X-ray diffraction (P-XRD) patterns were acquired on a MAC Science MXP 3TZ diffractometer using Cu-Kα radiation (wavelength 1.5406 Å, 40 kV, 55 mA). Transmission electron microscopy (TEM) was performed on a JEM-2010F microscope (JEOL) operating at 200 kV. XPS analysis performed on a Physical Electronics 5800 spectrometer equipped with a hemispherical analyzer and using monochromatic Al-Kα radiation (1486.6 eV, the X-ray tube working at 15 kV, 350 W and pass energy of 23.5 keV). NMR spectra were recorded on a Bruker Avance DPX 400 (400.1 MHz for ¹H) spectra were obtained in CDCl₃ in 5 mm o.d. Optima NMR tubes at room temperature and were referenced to the residual solvent impurity. The nitrogen adsorption-desorption experiments were carried out at 77 K using a NOVA 3000 series instrument (Quantachrome Instruments). The sample was out-gassed under vacuum at 573 K for 3 h before the adsorption of nitrogen.

2.3. Preparation of iridium(0) nanoparticles stabilized by zeolite framework (IrNPs@FAU)

IrNPs@FAU were synthesized by following a two-step procedure; (i) in the first step, Ir³⁺ ions were introduced into the zeolite by ion-exchange of 1000 mg zeolite in 100 mL aqueous solution of 100 mg IrCl₃·3H₂O (0.29 mmol) for 72 h at room temperature. The sample was then filtered by suction filtration using Whatman-1 filter paper and the remnant was dried in vacuum, (ii) next, the solid remnant was added into NaBH₄ solution (100 mL, 264 mM) at room temperature. Ir³⁺ ions were reduced and the iridium(0) nanoparticles were formed; the reduction was considered to be complete when no more hydrogen evolution was observed. The resulting IrNPs@FAU sample was isolated by suction filtration followed by

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