

Sustainable Synthesis of Magnetic Ruthenium-Coated Iron Nanoparticles and Application in the Catalytic Transfer Hydrogenation of Ketones

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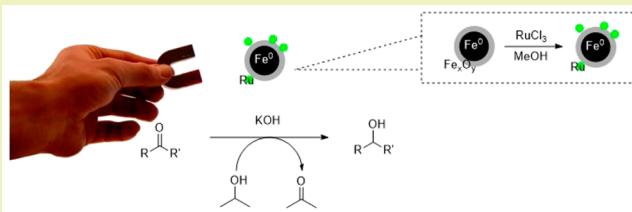
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Supporting Information

ABSTRACT: The galvanic reduction of catalytically active metals onto iron/iron oxide core/shell nanoparticles is a rapid, efficient and sustainable method to access new catalysts, already explored with copper and palladium. Herein, we present novel bimetallic ruthenium–iron nanoparticles synthesized by this method. This material constitutes a magnetically recoverable heterogeneous catalyst for transfer hydrogenation with a pronounced selectivity for ketones over aldehydes and nitro groups. The nanoparticles are recyclable up to five times without a significant decrease in activity or leaching, and characterized by transmission electron microscopy, X-ray photoelectron spectroscopy and inductively coupled plasma.

KEYWORDS: Magnetic nanoparticles, Zero-valent iron, Iron, Ruthenium, Transfer hydrogenation, Ketone



INTRODUCTION

Metal nanoparticles (NPs) are a class of materials intensely researched for their powerful properties applicable in the broad fields of medicine, electronics, optics and catalysis. Because metal NPs are kinetically stabilized materials, their synthesis often relies on the use of excess solvents, additives and strong reducing agents. In recent years, efforts have been made to develop more sustainable synthetic methods to access these high-value materials,^{1–3} including solvent-free methods,^{4,5} biomass-based approaches⁶ and efforts to use greener reducers.^{7–10} All these approaches attempt to promote atom economy,^{11–13} a central concept and one of the 12 principles of green chemistry,^{14–16} and expand it from organic chemistry, where it has been extensively researched, to nanoscience. One interesting avenue to promote atom-economical NPs synthesis relies on the use of iron/iron oxide core/shell NPs (FeCSNPs) as support, seed and reducer for other catalytically active metals. FeCSNPs, also referred to as nanoscale zero-valent iron, have been used as a remediation agent for wastewater and groundwater contaminated with organic and inorganic pollutants.^{17,18} This technique, first developed by the group of Veinot with palladium, consists of simply adding metal salts into a water dispersion of FeCSNPs, to allow galvanic reduction of the salt and formation of secondary particles attached to the surface.¹⁹ With palladium, Sonogashira coupling catalysts were accessed.¹⁹ The copper version was developed by our group^{20,21} and others²² and the resulting catalysts were active

for the azide–alkyne “click” reaction and the cyclopropanation of diazoesters.²³

In the context of catalysis, metal NPs are interesting, as they combine the catalytic activity of homogeneous catalysts with the ease of recovery of their bulk heterogeneous counterparts.^{24–26} Iron-containing NPs, such as metal-coated FeCSNPs, are also appealing because they feature magnetic properties, offering one of the easiest means of catalyst recovery and recycling, by simple application of an external magnet.^{27–31} Catalytically active magnetic NPs (MNPs) are divided in two main categories. In the first, the MNPs are coated with a polymer^{32,33} or silica,^{34,35} to which a metal binding ligand is then anchored. Further simplification includes the direct anchorage of the metal binding ligand^{36–38} or organocatalyst^{39,40} onto the nanoparticle surface. In the second, the surface of the MNPs itself is responsible for catalysis, rather than any anchored species. This bare magnetic NP approach was recently reviewed⁴¹ and relies on one of the following types of particles: iron oxide (Fe_3O_4 ^{42–44} or Fe_2O_3 ⁴⁵), metal ferrite^{46–53} ($[\text{M}]\text{Fe}_2\text{O}_4$), zero-valent iron,^{54,55} core–shell iron–iron oxide,⁵⁶ or core–shell iron–iron oxide decorated with another metal ($\text{M}@\text{FeCSNP}$).^{19,20} The various reported systems allow chemists to tackle a large number of synthetic challenges, including the oxidation of olefins⁵⁷ and alcohols,⁴⁵

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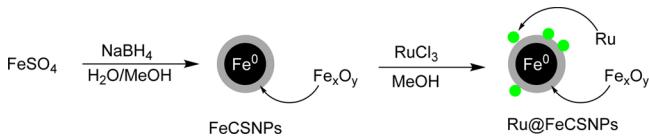
and cross dehydrogenative coupling,⁴³ three-component coupling of aldehyde, amine and alkyne,⁴⁴ as well as related reactions.⁴²

In the last 5 years, important research effort was dedicated to the development of catalysts based on Fe(0) NPs^{54,55,58–64} and FeCSNPs.⁵⁶ These catalysts are active and selective for the hydrogenation of olefins and alkynes with H₂,^{54–56} for the transfer hydrogenation of carbonyl compounds with isopropyl alcohol,⁶³ for the dehydrogenation of ammonia borane for release of stored hydrogen fuel^{65–68} and Grignard type reactions.⁶⁹ For industrial applications, however, Fe(0) NPs remain limited by their propensity to readily oxidize in the presence of air or water, despite recent progress.^{56,61}

Hydrogenation is a ubiquitous reaction industrially important at all scales, from petrochemicals to pharma.^{70,71} Transfer hydrogenation is an attractive alternative to hydrogenation with H₂ if the use of pressurized gases is a concern in the experimental setup, and it may offer complementary selectivity to the traditional H₂ approach.^{72–74} Ruthenium,⁷⁵ both in the form of organometallic complexes and nanoparticles,^{76–78} has demonstrated high efficiency to reduce carbonyls, often selectively over alkenes and alkynes. Adapting transfer hydrogenation catalysts, both pseudohomogeneous and purely heterogeneous, to magnetic particles is a rapidly progressing field. Two prominent demonstrations exemplify this strategy. One uses a ligand bound directly to a magnetic particle,⁷⁹ and the second uses a silica⁸⁰ or selenated silica⁸¹ coated magnetic particle as an effective ruthenium support. The resulting recyclable catalysts are active for appealing reactions, including the one-pot synthesis of primary amides.⁸¹ Our contribution represents further simplification of the system by forgoing the need for a metal binding ligand or silica coating. Instead, the catalytic ruthenium particles are bound directly to the surface of the as synthesized magnetic FeCSNPs, thereby shortening the synthetic route to the catalyst, eschewing the use of organic ligands, and avoiding the need for pH adjustments. After Pd and Cu, it constitutes the third example of a metal galvanically deposited onto FeCSNPs. The resulting NPs were characterized by transmission electron spectroscopy (TEM), X-ray photoelectron spectroscopy (XPS), inductively coupled plasma (ICP) and shown to be active for the transfer hydrogenation of ketones using isopropyl alcohol as a reducing solvent.

Synthesis of Ru@FeCSNPs Nanoparticles. FeCSNPs were synthesized according to a previously reported⁵⁶ NaBH₄ reduction of FeSO₄ in H₂O/MeOH. Subsequent addition of a methanol RuCl₃ solution (Scheme 1) dropwise to the

Scheme 1. Synthesis of FeCSNPs and Ru@FeCSNPs by Galvanic Reduction



sonicating FeCSNP solution afforded ruthenium-coated FeCSNPs (Ru@FeCSNPs), in a similar approach to the synthesis of copper-coated FeCSNPs.²⁰ The particles were then magnetically recovered, rinsed three times with MeOH and used directly in catalysis.

Characterization of Ru@FeCSNPs Nanoparticles. Unreacted FeCSNPs and the resulting Ru@FeCSNPs were characterized by TEM. As shown in Figure 1, unreacted

FeCSNPs are 100–200 nm NPs, mostly composed of a dense core of Fe(0) and they assemble as chains on the grid as reported before.^{82,83} A thin shell of iron oxide is clearly visible at the FeCSNPs surface.^{82,83} After Ru plating, these particles become decorated with smaller NPs of 8.3 ± 2.4 nm in diameter. The surface of the FeCSNPs is no longer visible, while the smaller particles form clusters that entirely cover the surface of iron oxide. The overall chain-like structure of the original particles remains. This morphology is comparable to what has been observed with both Pd¹⁹ and Cu^{20,21} exposure. To quantify the loading of Ru, an inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis was performed. A careful sample digestion methodology was applied to avoid issues linked to Ru volatilization in the form of RuO₄.^{84–86} Detailed experimental procedures are available in the Supporting Information. It was established that the Ru content in these species is 2.63 wt %. We also verified that FeCSNPs did not contain detectable quantities of Ru (Method Quantification Limit of 25 ppb). An XPS analysis was also performed to determine the surface content as well as the chemical speciation. In XPS, unfortunately, the carbon 1s and the Ru 3d orbitals have similar binding energies and their signals overlap, preventing a proper integration. Deconvolution allowed us to extract two Ru 3d_{5/2} peaks at 281.7 and 284.1 eV, which are very consistent with the reference spectrum of hydrated RuO₂ (Figure S1 of the Supporting Information).⁸⁷ The O 1s portion was also instructive and pointing toward the spectrum of hydrated RuO₂. The two main peaks are at 529.8 and 531.3 eV and are consistent with O²⁻ and OH, respectively.⁸⁷ This formula is in good agreement with the following material synthesis: (1) adsorption of Ru(III) salts at the surface of FeCSNPs, (2) a reduction of Ru(III) to Ru(0) by galvanic reduction, and formation of the small particle clusters at the FeCSNPs surface and (3) oxidation of the Ru(0) to Ru(IV) in air to yield hydrated RuO₂, one of the most stable forms of Ru. Supported Ru(OH)₃ were shown to be active transfer hydrogenation substrates and we thus tested our catalyst for this reaction.^{76,77}

Ru@FeCSNPs Nanoparticles for Transfer Hydrogenation. To test the activity of Ru@FeCSNPs for transfer hydrogenation, 10 mL reaction vessels were sealed after being charged with 5 mL of 2-propanol (which served both as the solvent and hydrogen transfer agent) and 1 mmol hydrogenation substrate with 1.3 mol % Ru@FeCSNPs (with respect to Ru content).

Reaction conditions were optimized for transfer hydrogenation, using acetophenone as a model substrate (Table 1). In the presence of KOH as a base, temperature was an important parameter, with yield improving from 30 to 95% when temperature was varied from 85 to 100 °C (entries 1 and 2). The base was essential to activity, as yield dropped to 12% in its absence (entry 3). Further blanks were performed and demonstrated that ruthenium was essential to activity as FeCSNPs with base alone afforded poor yields at 100 °C (entries 4 and 5). FeCSNPs without base, or the absence of any catalyst or base, afforded no yield (entries 6 and 7). We also checked that KOH alone could not act as a catalyst for this reaction (entry 8). With optimized reaction conditions (entry 2), the study probed the reactivity of other substrates (Table 2). Acetophenone derivatives displayed reactivity proportional to the steric bulk near the carbonyl. For example, 2'-bromoacetophenone reacted slower than acetophenone and the even bulkier 2'-iodoacetophenone reacted slower still

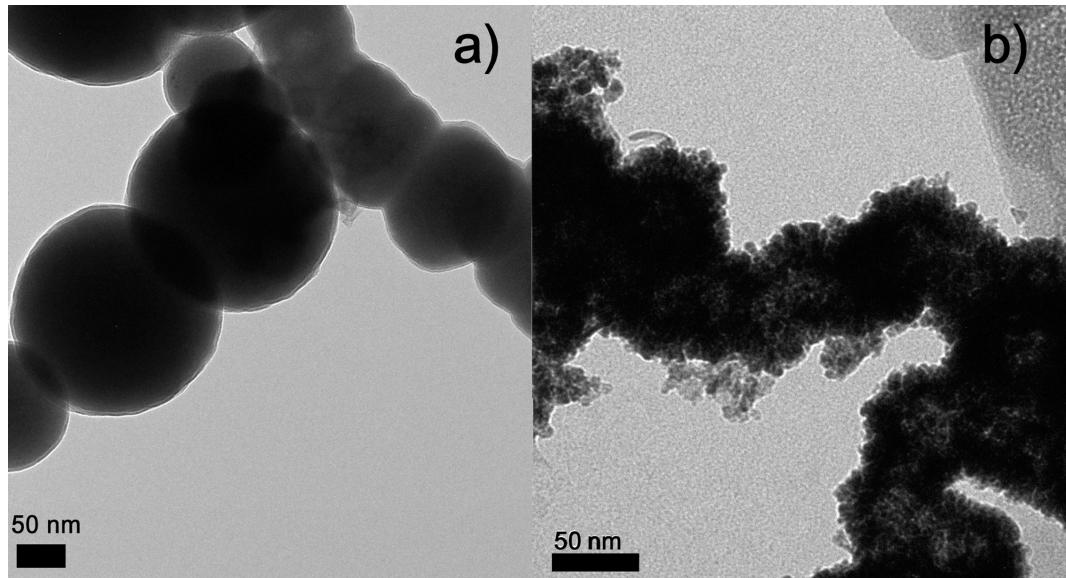


Figure 1. TEM images of (a) FeCSNPs and (b) Ru@FeCSNPs.

Table 1. Transfer Hydrogenation Condition Screening^a

entry	catalyst	base	temperature (°C)	yield (%) ^b
1	Ru@FeCSNPs	KOH (15 mol %)	85	30
2	Ru@FeCSNPs	KOH (15 mol %)	100	95
3	Ru@FeCSNPs	none	100	12
4	FeCSNPs	KOH (15 mol %)	85	11
5	FeCSNPs	KOH (15 mol %)	100	12
6	FeCSNPs	none	100	0
7	none	none	100	0
8	none	KOH	100	0

^aReaction conditions: 1 mmol acetophenone, 50 mg (1.3 mol %) catalyst, 5 mL 2-propanol, 24 h. ^bYield determined by GC-FID with decane as internal standard.

(entries 1–3). Likewise, 2'-methoxyacetophenone (entry 13) and 2'-aminoacetophenone (entry 11) were also slower to react. Moving the substituent to the 3'-position (3'-bromoacetphenone) brought the yield more in line with acetophenone (entry 4). Comparison of substrates brominated at the 2'- (entry 2), 3'- (entry 4) and 4'- (entry 14) positions suggests that sterics effect the yield more than electronics; the 2'- substituted substrate reacts the slowest (74%), whereas moving the substituent away from the reactive center to the 3'- and 4'- positions (altering the electronics but not particularly the sterics) does not as greatly affect the yield (84% and 81%, respectively). Bulky and rigid substrates, such as 3,4-dihydro-2H-naphthalen-1-one and 2,6-dimethoxyphenylacetophenone did not perform as well (entries 5 and 6). Trifluoroacetophenone displayed excellent reactivity (entry 7). The system was not efficient for nitro (entry 8), nitrile (entry 16) or aldehyde (entry 4) reduction, and thus displays an interesting selectivity for ketones (entries 8 and 9).

To demonstrate its durability and reusability, the catalyst was magnetically recovered and recycled for the transfer hydrogenation of acetophenone. The catalyst could be used up to five times with no appreciable decrease in yield (Table 3). The overall turnover number (TON) for this recycling sequence is 374, with an average overall turnover frequency (TOF) of 3

h^{-1} , this performance been comparable to those of similar systems in the literature.⁷⁹

To provide evidence for a heterogeneous mechanism, the study probed the reactivity of species in the reaction supernatant. First, Ru@FeCSNPs were subjected to the regular catalytic conditions, then, while still hot, the supernatant was filtered through Celite and subsequently used for catalysis, which only resulted in trace amounts of product. Second, the standard reaction of acetophenone was allowed to run for 1 h, then similarly hot filtered through Celite to remove any heterogeneous material and then allowed to complete the 24 h reaction time. The yield did not appreciably increase from the prefILTERING value (18%) to the value after reacting for another 23 h in the absence of heterogeneous material (20%), a second result suggestive of a heterogeneous mechanism. The leaching of metal species in the product was also carefully analyzed on this system. After reaction, the product solution was separated from the catalysts by magnetic seclusion and the Ru and Fe were quantified by ICP-OES using the digestion method described in the Supporting Information. Ru and Fe were found to be present at 12 and 4 ppm, respectively.

On the basis of these results, we propose the mechanism depicted in Scheme 2. In the literature,⁷³ ruthenium catalysts for transfer hydrogenation are considered to proceed through a ruthenium hydride mechanism. From the ruthenium hydroxide species^{76,77} covering the Ru@FeCSNPs, as shown by XPS (vide supra), we propose a displacement by isopropanolate. β -Elimination then affords the required hydride species. 1,2 insertion of the ketone reagent, followed by exchange with isopropyl alcohol, affords the alcohol product. The base favors the formation of isopropanolate, a key species to enter the catalytic cycle, which explains why the reaction cannot proceed in its absence.

CONCLUSIONS

This study demonstrated the synthesis of a novel Ru@FeCSNPs catalyst generated by simple addition of RuCl₃ to a solution of core–shell iron–iron oxide nanoparticles. These magnetically recyclable particles could be used directly for transfer hydrogenation reactions, providing good yields on

Table 2. Transfer Hydrogenation Substrate Scope^a

Entry	Substrate	Product	Yield(%) ^b	Entry	Substrate	Product	Yield(%) ^b
1			95	9			4
2			74	10			51
3			13	11			59
4			84	12			71
5			14	13			68
6			26	14			81
7			91	15			43
8			0	16			0

^aReaction conditions: 1 mmol substrate, 1.3 mol % Ru@FeCSNP, 15 mol % KOH, 2-propanol (5 mL). ^bYield determined by GC-FID with decane as internal standard.

Table 3. Catalyst Recycling for Acetophenone Transfer Hydrogenation^a

run	1	2	3	4	5
yield (%) ^b	95	99	99	99	94

^aReaction conditions: 1 mmol acetophenone, 1.3 mol % Ru@FeCSNP, 15 mol % KOH, 2-propanol (5 mL), 24 h. ^bYield determined by GC-FID with decane as internal standard.

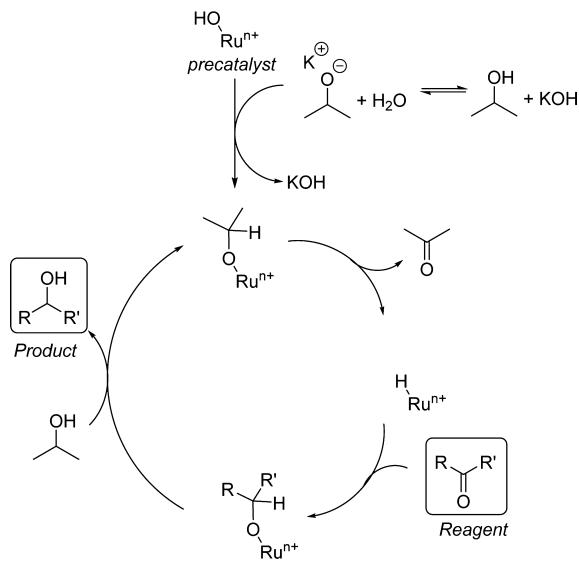
many acetophenone derivatives and demonstrated an interesting selectivity for ketones over aldehydes and nitro groups. The catalyst could be recycled and evidence of heterogeneous mechanism is provided. These particles are based on an atom economical synthesis, are easy to use and recycle and afford a low-leaching system, making them a potentially attractive option for practical industrial applications.

EXPERIMENTAL SECTION

Materials. All reactions were carried out in an oxygen-free glovebox, unless otherwise indicated, and all solvents were degassed prior to use. All reagents were purchased from major suppliers and used as received, unless specified otherwise.

Equipment. TEM analysis was performed on a Tecnai F20 operated at 200 kV. Reaction yields were obtained on a GC-FID (Agilent Technologies, 7890A). XPS analysis was performed on a VG Escalab 3 MKII at 300 W (15 kV, 20 mA) and analyzed at a depth of

Scheme 2. Proposed Mechanism for the Transfer Hydrogenation of Ketones by Ru@FeCSNPs in Isopropyl Alcohol



50–100 Å. ICP-OES measurements were performed using a Thermo Fisher Scientific ICP-OES ICAP 6500.

Synthesis of FeCSNPs. The synthesis of the nanoparticles was based on previous procedures.²⁰ In MeOH-H₂O (60 mL/140 mL), a solution of iron(II) sulfateheptahydrate (99%) (4.5 g in 200 mL H₂O) was reduced with aqueous NaBH₄ (0.8 g in 20 mL H₂O added at a rate of approximately 2 mL per minute). The resulting FeCSNPs were then washed three times with 10 mL of methanol, using a magnet to immobilize the particles.

Synthesis of Ru@FeCSNPs. Afterward, a RuCl₃ solution was prepared (10 mg of RuCl₃ in 10 mL of methanol) and added dropwise to the sonicating solution of iron nanoparticles (100 mg in 10 mL). The resulting mixture was left to sonicate for 30 min. The supernatant was magnetically decanted, and the resulting Ru@FeCSNPs were rinsed three times with methanol (~10 mL) and dried prior to use.

Transfer Hydrogenation Catalytic Tests. To a 50 mL round-bottom flask were added internal standard (decane, 1 mmol), substrate (1 mmol), 15 mol % KOH in isopropyl alcohol (5 mL) and the catalyst (50 mg, 1.3 mol % with respect to ruthenium), and the mixture was stirred and heated (100 °C) under reflux for 24 h. After cooling, the magnetic particles were magnetically separated from solution and recovered (if they were to be used for recycling tests, they were rinsed three times with isopropyl alcohol before fresh reagents were added) the supernatant was subsequently filtered to remove any remaining solid material prior to injection into the GC-FID (in order to protect the instrument) for quantification of reaction yields. TON and TOF were calculated based on the total quantity of Ru present in the sample.

Digestion of Ru@FeCSNPs, FeNPs and Reaction Supernatant for ICP-OES Measurements. The Ru@FeCSNPs, FeCSNPs and the catalytic tests supernatants were digested in 7 mL of a 6:1 HCl/HNO₃ acid mixture (Fisher trace metal grade) in semiclosed HDPE vessels at 90 °C for 3 h following a similar procedure outlined by Perämäki and co-workers.⁸⁴ Samples were topped up to 50 mL using Milli-Q water and analyzed by ICP-OES. An average of two lines for Ru (269.2, 267.8 nm) was taken to correct for matrix effects. No matrix effects were seen for Fe, and one line was used (259.9 nm). An external calibration curve was used, with standard solutions of 0.5, 5 and 50 ppm of Ru and Fe with an average *r*² of 0.9995 for the two Ru lines.

Spike Recovery Study Using ICP-OES (Method Validation). A spike recovery study was conducted to validate the sample digestion procedure. It is known that in boiling solutions of HNO₃, Ru can oxidize into RuO₄, which has a boiling point of 40 °C. This leads to volatilization of Ru and potential loss during the digestion process.^{85,86} To ensure our digestion method did not have significant Ru loss, we prepared three blank spikes and three matrix spikes with 25 ppm of Ru. These samples were prepared, digested and analyzed using the method established for above. An average of the three blank spike and matrix spike solutions were taken. Based on the 25 ppm Ru added to each, the blank spike recoveries were 100% and the matrix spike recoveries were 94%. This indicates our digestion method is suitable for this type of matrix and no Ru volatilization is observed.

ASSOCIATED CONTENT

Supporting Information

XPS spectra of Ru@FeCSNPs. This material is available free of charge via the Internet at <http://pubs.acs.org/>

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Author Contributions

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Notes

The authors declare no competing financial interest.

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