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Magnetic Silica-Supported Ruthenium Nanoparticles: An Efficient Catalyst for Transfer Hydrogenation of Carbonyl Compounds

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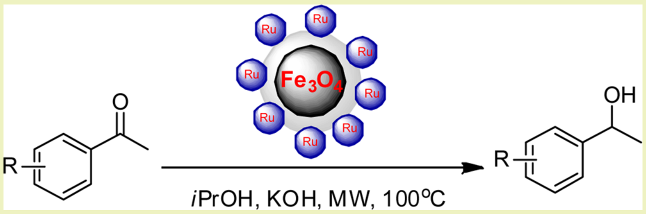
ABSTRACT: A one-pot synthesis of ruthenium nanoparticles on magnetic silica is described, which involves in situ generation of magnetic silica ($Fe_3O_4@\ SiO_2$) and ruthenium nanoparticle immobilization. The transfer hydrogenation of carbonyl compounds occurs in high yield along with excellent selectivity using this catalyst under microwave irradiation conditions.



KEYWORDS: *Green synthesis, Magnetic silica, Ruthenium nanoparticles, Transfer hydrogenation, Microwave irradiation*

INTRODUCTION

The conversion of carbonyl compounds to alcohols is a very important transformation in organic synthesis. Most of the methods reported in the literature require the use of a stoichiometric amount of sensitive reagents or the use of dangerous hydrogen gas under high pressure.[1−3] Transfer hydrogenation has become the center of attraction because the hydrogen donors, such as 2-propanol, etc., are readily available, inexpensive, easy to handle, and do not require elaborate experimental setups, such as high pressure reactors. Homogeneous metal catalysts (Ru and Ir complexes) are often used as effective catalysts for these reactions.[4−9] However, they have difficulties in the recovery and reuse of expensive metals. Most of the reactions do not proceed without the use of expensive ligands. Heterogeneous catalysts (noble metals such as Pt, Pd, and Au) have been reported as effective and reusable catalysts for these reactions.[10−15] However, in addition to their high cost, they require additives for the efficacy of the reactions. There have been other methods developed using solid-supported Ni, Cu, Sn, Zr, etc., catalysts.[16−22] Invariably, most of these catalysts require high temperature, longer reaction times, high catalytic loading, excess base, and a tedious procedure, such as centrifuge or filtration, for the recovery of the catalyst.

Magnetic nanoparticles have emerged as a robust, high-surface-area heterogeneous catalyst support;[23−26] they are good alternatives to filtration or centrifugation. This strategy reduces the loss of catalyst and enhances reusability, rendering the catalyst cost-effective and promising for industrial applications. Recently, we have reported on a nanoferrite-dopamine-Ru catalyst for the transfer hydrogenation of carbonyl compounds.[27] Although the catalyst works well, it suffers from the requirement of an elaborate and tedious procedure for its synthesis, which involves three steps: (a) synthesis of nanoferrite, (b) post-synthetic modification via anchoring of toxic organic ligands, and (c) immobilization of ruthenium metal. To overcome these drawbacks and avoid the use of toxic ligands and reagents, a one-step procedure for the synthesis of magnetic silica-supported ruthenium as a magnetically retrievable catalyst has been developed, and its application in the transfer hydrogenation has been demonstrated.

RESULTS AND DISCUSSION

The first step in the accomplishment of this goal was the convenient synthesis of magnetic silica-supported ruthenium catalyst by sequential addition of reagents in one-pot. The magnetic nanoferrite (Fe_3O_4) was generated in situ via a hydrolysis method by stirring a solution of $FeSO_4{\cdot}7H_2O$ and $Fe_2(SO_4)_3$ (1:1) in water at pH 10 (adjusted using 25% ammonium hydroxide solution) followed by heating in a water bath at 50 °C for 1 h. The reaction mixture was cooled to room temperature. To this solution, tetraethyl orthosilicate (TEOS) was added and vigorous stirring was continued for 18 h at ambient conditions. To this solution, $RuCl_3$ was added, and the pH of the solution was adjusted to ~10 using an ammonium hydroxide solution (25%) and stirring continued for another 24 h (Scheme 1). Magnetic silica-supported Ru nanoparticles were separated using an external magnet, washed with water followed by acetone, and dried under vacuum at 50 °C for 8 h. Catalyst characterization by X-ray diffraction (XRD) (Figure 1b,c) and transmission electron microscopy (TEM) (Figure 1a) confirmed the formation of single-phase silica-coated Fe_3O_4 nanoparticles, nano-Fe@SiO_2Ru, with spherical morphology and a size range of 15−30 nm. The signals pertaining to Ru metal and Si were not detected in XRD (Figure 1c), indicating that the Ru and Si species is highly dispersed on ferrites. The weight percentage of Ru was found to be 3.96% and Si 6.85%,

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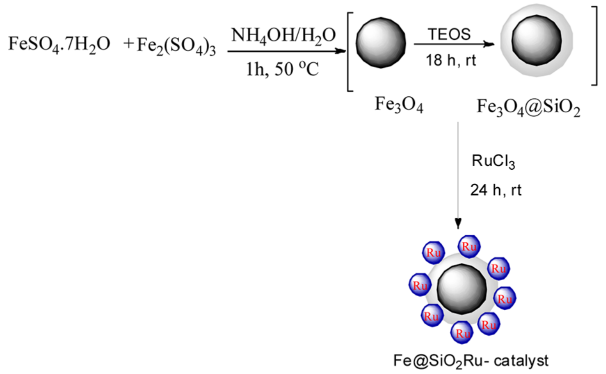
Scheme 1. One pot Synthesis of Nano-Fe@SiO$_2$Ru Catalyst



Scheme 2. Hydration of Nitriles Using Fe@SiO$_2$Ru/H$_2$O

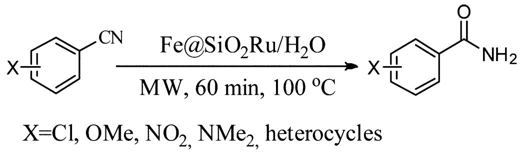
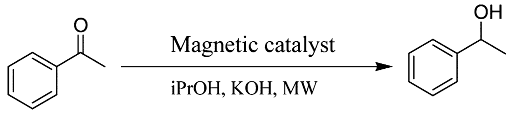


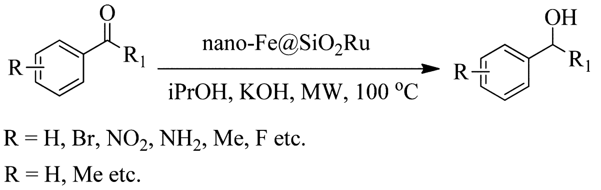
Table 1. Optimization of Reaction Condition



entry	catalyst	time	temperature (°C)	yield^{a,b}
1	none	30 min	100	–
2	Fe$_3$O$_4$	30 min	100	–
3	Fe$_3$O$_4$	30 min	150	–
4	Fe$_3$O$_4$@SiO$_2$	30 min	100	–
5	Fe$_3$O$_4$@SiO$_2$	30 min	150	–
6	Fe@SiO$_2$Ru	30 min	100	>99%^{c}

[a] Reactions were carried out with 1 mmol of acetophenone, 100 mg nanocatalyst, and KOH (0.2 mmol), in isopropanol under MW irradiation. [b] Monitored by GC-MS. [c] GC yield.

Scheme 3. Nano-Fe@SiO$_2$Ru-Catalysed Transfer Hydrogenation of Carbonyl Compounds



respectively, by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis.

Earlier, we successfully demonstrated the hydration of nitrile under aqueous media using Fe$_3$O$_4$@SiO$_2$Ru catalyst (Scheme 2).[28] In continuation of our work toward the development of sustainable organic transformations,[29−35] herein we report the application of heterogeneous magnetic silica-supported ruthenium nanocatalyst, Fe@SiO$_2$Ru, for transfer hydrogenation of carbonyl compounds.

The reaction conditions for the transfer hydrogenation of acetophenone were optimized using isopropanol as a solvent and KOH as base (Table 1). First, the reaction was conducted using KOH alone and then with KOH mixed with nano-Fe$_3$O$_4$ and Fe$_3$O$_4$@SiO$_2$, respectively; the transfer hydrogenation reaction with these control experiments did not proceed even at 150 °C and after prolonged exposure to microwaves (30 min) (Table 1, entries 1−5). The magnetic silica catalyst Fe$_3$O$_4$@SiO$_2$ was modified using RuCl$_3$ (particle size 15−30 nm), termed magnetic silica-supported ruthenium catalyst, nano-Fe@SiO$_2$Ru (Table 1), and tested for the transfer hydrogenation of acetophenone at 100 °C for 30 min under microwave (MW) irradiation conditions. The quantitative conversion of acetophenone to corresponding alcohol was observed (Table 1, entry 6).

The scope of the catalyst was then demonstrated for the transfer hydrogenation of a range of carbonyl compounds under MW conditions (Scheme 3). MW irradiation was used because it provides rapid and uniform heating, which reduces reaction time.[36,37] The use of MW has reduced the time period to 30−45 min instead of several hours in the case of conventional heating experiments. All the reactions were completed within a time period of 30−45 min, depending on the substrates, with high selectivity and conversion. Acetophenone and its derivatives (Table 2, entries 1−4) were converted to the corresponding alcohols within 30 min. Interestingly, in the case of nitro-substituted ketones, the nitro group was selectively reduced to amine, instead of the hydrogenation of the carbonyl group (Table 2, entry 5), whereas MW exposure for longer time leads to the formation of completely reduced amino alcohol (Table 2, entry 6). Bromo-substituted ketones (Table 2, entries 2, 3, 4, and 8) were also selectively converted to its alcohol in 30 min. However, in some cases, debromination (Table 2, entry 8) at extended reaction times was observed. The use of catalyst was further explored for the transfer reduction of aldehydes; interestingly, the catalyst system also hydrogenated the aldehydes to the corresponding alcohols successfully (Table 2, entries 9, 10 and 11).

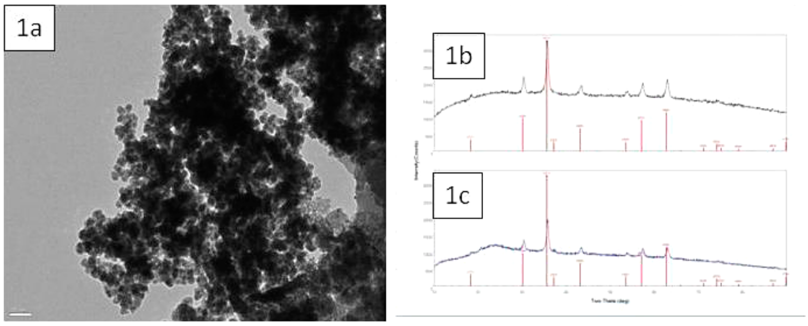
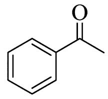
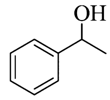
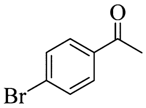
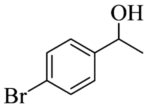
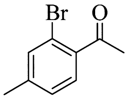
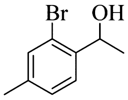
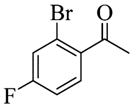
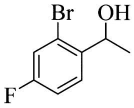
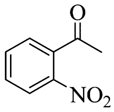
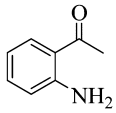
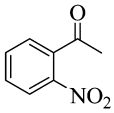
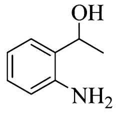
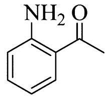
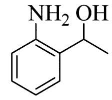
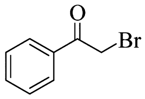
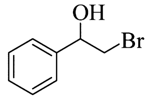
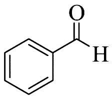
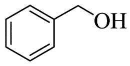
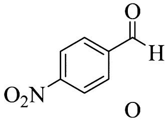
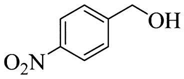
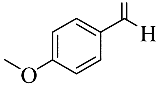
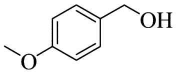
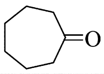


Figure 1. (a) TEM of Fe$_3$O$_4$@SiO$_2$Ru (Fe@SiO$_2$Ru). (b) XRD of Fe$_3$O$_4$. (c) XRD of Fe$_3$O$_4$@SiO$_2$Ru (Fe@SiO$_2$Ru).

Table 2. Transfer Hydrogenation of Carbonyl Compound with Nano-Fe@SiO_2Ru

Entry	Substrate	Product[a]	Yield[b,f]
1			86%
2			88%
3			85%
4			83%
5			80%
6			71%[c]
7			82%
8			69%[d]
9			85%[e]
10			88%[e]
11			81%[e]
12		NR	--

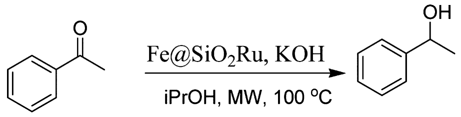
[a] Reaction conditions: substrate 1.0 mmol, catalyst 100 mg, KOH (0.2 mmol), iPrOH (5.0 mL), 100 °C, 30−45 min. [b] Isolated yields. [c] Reaction time 2 h. [d] 80 °C, 30 min. [e] K_2CO_3 used as a base. [f] Reactions were performed under microwave irriadiation.

Nevertheless, the catalyst was ineffective for the transfer hydrogenation of cycloheptanone (Table 2, entry 12)

The lifetime of the catalyst and its level of reusability are very important for practical application. To clarify this issue, a set of experiments for the transfer hydrogenation of acetophenone using the nano-Fe@SiO_2Ru catalyst were established. After the completion of the first reaction to afford the corresponding alcohol, the catalyst was recovered magnetically, washed with acetone, and dried at 50 °C. A new reaction was then performed with fresh acetophenone under the same conditions. The nanomagnetic silica-supported ruthenium catalyst nano-Fe@SiO_2Ru could be used at least three times without any change in the activity (Table 3).

Metal leaching was studied by ICP-AES analysis of the catalyst before and after the three reactions. The Ru concentration was found to be 3.96% before the reaction and 3.88% after the reaction. The TEM image of the catalyst taken after the third cycle of the reaction did not show significant change in the morphology or in the size of the catalyst nanoparticles (15−30 nm) (Figure 2), which indicates the retention of the catalytic activity after recycling. No Ru metal was detected in the reaction solvent after completion of the

Table 3. Recyclability Studies with the $Fe_3O_4@SiO_2Ru$ Catalyst



entry[a]	catalyst	time	temperature (°C)	yield[b,c,d]
1	$Fe@SiO_2Ru$	30 min	100	>99%
2	$Fe@SiO_2Ru$	30 min	100	>99%
3	$Fe@SiO_2Ru$	30 min	100	>99%

[a] Reactions were carried out with 1 mmol of acetophenon, 100 mg nanocatalyst, KOH (0.2 mmol), and in iPrOH under MW irradiation. [b] Reactions were monitored by GC-MS. [c] GC Yields. [d] Fresh KOH has been used in each cycle.

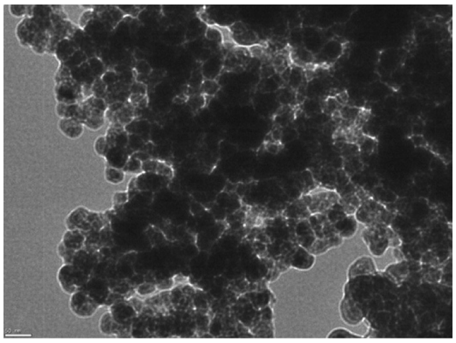


Figure 2. TEM image of the recycled catalyst.

reaction. This confirms the fact that nanomagnetic silica held the ruthenium metal very tightly, thus minimizing the deterioration of the catalyst, minimizing metal leaching, and facilitating efficient catalyst recycling.

CONCLUSION

A novel magnetic silica-supported ruthenium nanocatalyst has been developed, which can be readily prepared in gram quantities in one-step under ambient conditions in aqueous media. This nanomaterial catalyzed the transfer hydrogenation of carbonyl compounds, and the desired reactions proceeded smoothly to deliver the corresponding alcohols in very good yields. Because of the magnetic nature of the catalyst, it can be separated using an external magnet, which eliminates the requirement of catalyst filtration after completion of the reaction, which is an additional attribute of the catalyst.

EXPERIMENTAL SECTION

Synthesis of Magnetic Silica-Supported Ruthenium Nanoparticles. $FeSO_4{\cdot}7H_2O$ (2.78 g) and $Fe_2(SO_4)_3$ (4.0 g) were dissolved in 200 mL water in a 500 mL beaker. Ammonium hydroxide (25%) was added slowly to adjust the pH of the solution to 10. The reaction mixture was then continually stirred for 1 h at 50 °C and then cooled to room temperature. To this solution, tetraethyl orthosilicate (TEOS, 10 mL) was added and vigorous stirring was continued for 18 h at ambient conditions. To this solution, $RuCl_3$ (600 mg) was added, and the pH of the solution was adjusted to ~10 using ammonium hydroxide (25%) and stirring continued for another 24 h. Magnetic silica-supported Ru nanoparticles were separated using an external magnet, washed with water, followed by acetone, and dried under vacuum at 50 °C for 8 h. Catalyst was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The weight percentage of Ru was found to be 3.96% and Si 6.85%, respectively, by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis.

Transfer Hydrogenation of Carbonyl Compounds. In a typical reaction, 1 mmol of the substrate was added to 5.0 mL of isopropyl alcohol (reagent grade) in a 10 mL microwave tube. Catalyst (0.1 g) and 0.2 mmol (0.011 g) of potassium hydroxide were then added. The reaction mixture was subjected to MW irradiation in a CEM Discover MW system for 30−45 min at 100 °C. After the reaction was completed, the reaction vessel was kept undisturbed for 5 min, wherein the catalyst adhered to the magnetic bar. The reaction mixture was collected by decantation and washed with water; the product was extracted by dichloromethane and characterized. The catalyst was then washed with acetone, dried at 80 °C in an oven for 15 min, and reused up to three times without any loss in activity.

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Notes

The authors declare no competing financial interest.

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