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Magnetically recoverable supported ruthenium catalyst for hydrogenation of alkynes and transfer hydrogenation of carbonyl compounds

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ABSTRACT

A ruthenium (Ru) catalyst supported on magnetic nanoparticles ($NiFe_2O_4$) has been successfully synthesized and used for hydrogenation of alkynes at room temperature as well as transfer hydrogenation of a number of carbonyl compounds under microwave irradiation conditions. The catalyst shows excellent selectivity towards the desired products with very high yield even after 5 repeated uses.

1. Introduction

Hydrogenation and transfer hydrogenation of carbonyl compounds and alkynes to their respective saturated compounds is in high demand in the petrochemical, pharmaceutical, and food industries. Since the discovery of ruthenium as a catalyst, it has been widely used for hydrogenation[1–3] and transfer hydrogenation protocols.[4–6] Although the scope of homogeneous catalysis has been well demonstrated,[7] heterogeneous catalysis is preferred from both economical and environmental points of view when high cost and toxic species are involved. The salient advantages of heterogeneous catalysts are efficient recycling, minimization of metal traces in the product, and an improved handling and process control; these result in overall lower costs. Recently, Miao et al. described a method for preparing Ru catalyst by immobilizing Ru nanoparticles on montmorillonite (MMT) clay with the assistance of ionic liquids.[8] While the Ru/MMT catalyst exhibited excellent activity for the hydrogenation of benzene, the Ru nanoparticles were found to aggregate to form larger particles after a few reaction runs. Highly dispersed Ru nanoparticles on the pores of mesoporous silica, have also been described.[9] Similarly, Ru nanoparticles supported on alkali-exchanged zeolite Beta,[10] activated carbons,[11] and titanium oxides have also been reported.[12] However, these methods suffer from a number of problems, such as particle aggregation and catalyst leaching. In addition, the process of filtration or centrifugation for catalyst separation is tedious.

Magnetic separation is an attractive alternative to filtration or centrifugation as it prevents loss of catalyst and enhances reusability, rendering the catalyst cost-effective and promising for industrial applications. Recently Hu et al reported Fe_3O_4 immobilized chiral Ru catalyst for the asymmetric hydrogenation of aromatic alcohols.[13] Yi et al reported synthesis of nano-Pd on SiO_2-coated Fe_2O_3 and its application in hydrogenation of nitrobenzene.[14] Baruwati et al. have demonstrated the application of Pd nanoparticles immobilized on dopamine-modified nickel ferrite nanoparticles for the hydrogenation of a number of unsaturated compounds, as well as for the Heck and Suzuki C-C coupling reactions.[15,16]

In our ongoing program on eco-friendly applications of magnetic nanomaterials as catalyst,[17] herein, we report the synthesis of a highly active magnetic nanoparticle ($NiFe_2O_4$) supported Ru catalyst and its application for chemo-selective hydrogenation of alkynes to their respective alkanes at room temperature, as well as transfer hydrogenation of carbonyl compounds under microwave (MW) irradiation conditions.

2. Results and discussions

The magnetic nanoparticles used as the support for Ru nanoparticles have been synthesized via a hydrothermal route. The as-synthesized magnetic nanoparticles were surface-modified with dopamine hydrochloride and Ru was then deposited on the surface-modified magnetic nanoparticles to obtain the final catalyst. The catalyst henceforth is referred to as nano ferrite-Ru.

The X-ray diffraction pattern confirms the formation of single phase $NiFe_2O_4$ nanoparticles. [JCPDS-10 (325)]. Figure 1c shows

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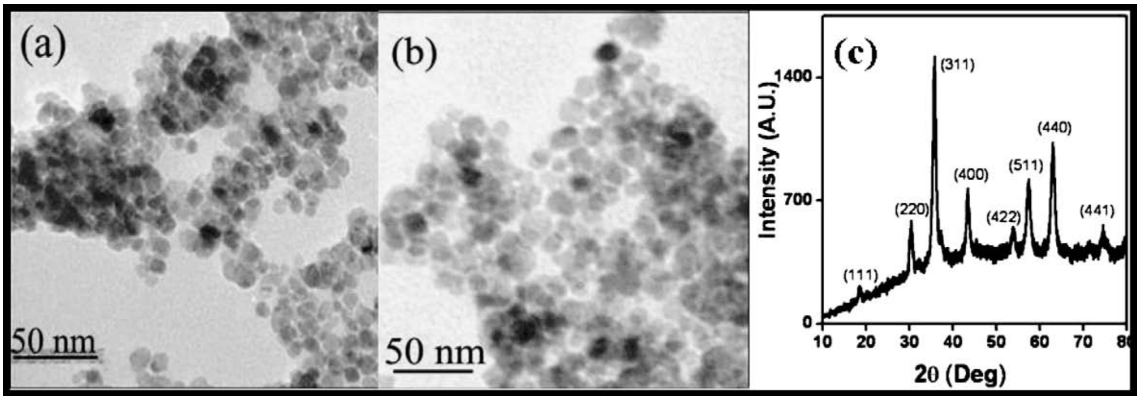


Figure 1. TEM micrographs of the catalyst (a) before reaction and (b) after 3 reaction cycles; (c) X-ray diffraction pattern for the $NiFe_2O_4$ nanoparticles with dopamine and Ru.

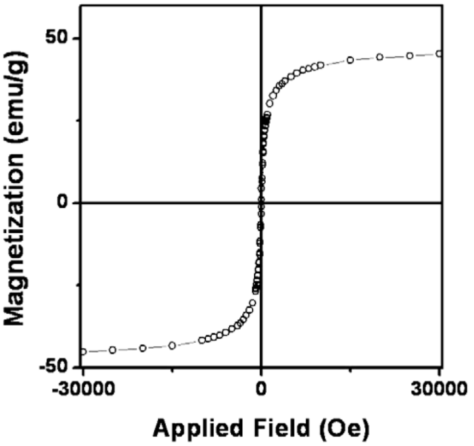
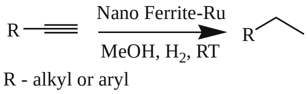


Figure 2. Magnetization versus applied field plot for the as-synthesized $NiFe_2O_4$ nanoparticles showing the superparamagnetic behavior at room temperature.

the X-ray diffraction pattern for the $NiFe_2O_4$ nanoparticles after Ru incorporation. All the diffraction planes correspond to the single phase spinel $NiFe_2O_4$. No peaks corresponding to Ru can be seen in the X-ray pattern. This might be because of the low percentage (less than 4%) of Ru in the sample. The crystallite size, calculated from Scherer formula, was found to be 8.3 nm.

TEM micrographs show the particles to be highly dispersed with spherical morphology and a size range of 10–12 nm, which is comparable with the crystallite size calculated from X-ray spectrum. This confirms the particles to be single domain up to a near approximation. The morphology of the particles remains unchanged even after three repeated reactions. Figure 1(a, b) shows the TEM micrographs of the catalyst system before and after three repeated reactions. The weight percentage of Ru in the catalyst has been confirmed to be 3.89% before reaction and 3.82% after three times reaction with ICP-AES studies. This confirms the minimal loss of metal during the reaction and explains its high efficiency for the repeated applications, which is highly desirable from economic point of view.

The magnetization versus applied field studies show that the as-synthesized nanoparticles are superparamagnetic at room temperature, which is the main criterion for magnetic separation. The saturation magnetization and coercivity of the sample was found to be 42.24 emu/g and 12 Oe respectively. Fig. 2 shows the magnetization versus applied field plot for the as-synthesized $NiFe_2O_4$ nanoparticles.



Scheme 1. Hydrogenations of various alkynes.

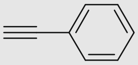
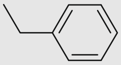
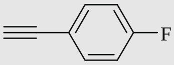
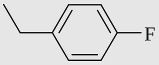
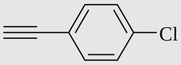
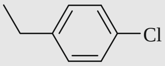
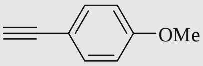
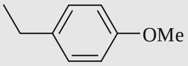
Hydrogenations of various alkynes were studied using the nano ferrite-Ru catalyst in methanol (Scheme 1). The reactions proceeded smoothly at room temperature to give the desired products with greater than 90% of product yield and the results are summarized in Table 1.

The scope of the as prepared catalyst was then tested for the transfer hydrogenation of a range of carbonyl compounds under MW conditions (Scheme 2).

MW irradiation provides rapid and uniform heating of reagents, solvents, and intermediates which provides the advantage of short reaction time.[18,19] In our case, the use of MW has reduced the time period to 30-45 minutes compared to several hours in the case of conventional heating.[10] We observed that all the reactions were completed within a time period of 30-45 minutes depending on the substrates, with high selectivity and conversion. Substrates like acetophenone, bromoacetophenone, etc. (Table 2, entries 1, 2, 5, 8) were converted to the corresponding alcohols within 30 minutes with more than 98% selectivity even after 5 times of reaction. Interestingly, in case of nitro-substituted ketones, we observed that the nitro group was converted selectively to its amine form instead of the hydrogenation of carbonyl group. (Table 2, entries 3, 4), which is a highly important reaction in organic transformations. Bromo-substituted ketones (Table 2, entries 2, 8) were also selectively converted to its alcohol in 30 minutes. However, we observed debromination at extended reaction times. We further tested the catalyst for the transfer reduction of aldehydes and, interestingly, the catalyst system also hydrogenated the aldehydes to the corresponding alcohols with yields of 90% (Table 2, entries 9, 10).

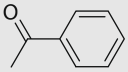
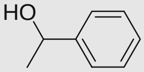
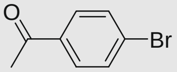
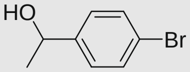
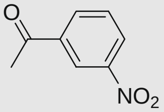
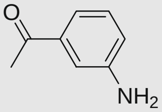
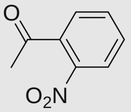
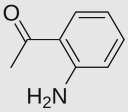
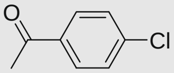
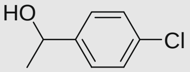
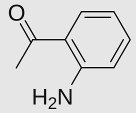
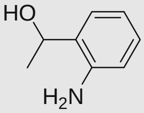
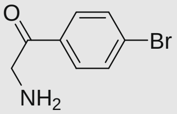
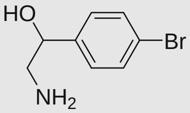
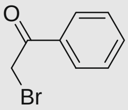
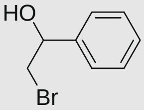
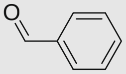
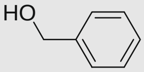
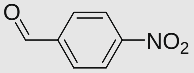
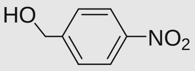
The results obtained using MW-assisted method were compared with conventional heating for the transfer hydrogenation reaction of acetophenone, 4’-bromoacetophenone and 2’-nitroacetophenone in an oil bath at the same temperature. The experiments afforded comparable yield of the products, but in an extended period of time (4-8 hrs). Specifically, acetophenone was converted to the corresponding alcohol in 4 h under conventional conditions as compared to less than 30 minutes under MW conditions. 2’-Nitroacetophenone also required more than 6 h for complete conversion. In the case of bromoacetophenone, however, even after 6 h of conventional heating, only 50% conversion to the corresponding alcohol was attained because of the debromination of the substrate.

Table 1
Hydrogenation of alkynes with nano ferrite-Ru catalyst

Entry	Substrate	Product	Yield (%)
1			95
2			96
3			96
4			95
5	$H_3C(H_2C)_7-\equiv$	$CH_3(CH_2)_7CH_2CH_3$	98

Reactions performed at room temperature, catalyst 0.05 g, MeOH 2.0 mL, substrate 1 mmol, time 18 h.

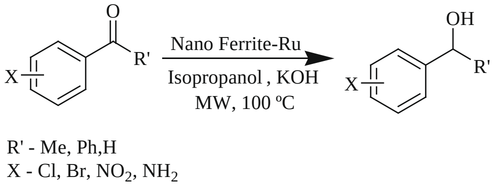
Table 2
Transfer hydrogenation of carbonyl compounds with nano ferrite-Ru catalyst

Entry	Substrate	Product	Yield (%)
1			98[a]
2			98
3			98
4			98
5			98
6			95
7			95
8			95
9			90[b]
10			90[b]

Reaction performed at 100 °C, isopropyl alcohol 5.0 mL, KOH 0.1 mmol, substrate 1 mmol, catalyst 0.1 g.

[a] Yield after 5th cycle.

[b] Reaction carried out at 120 °C and K_2CO_3 was used as a base. All the reactions are carried out under MW conditions.



Scheme 2. Transfer hydrogenation of carbonyl compounds.

3. Conclusions

A Ru catalyst supported on dopamine-modified magnetic nanoparticles has been synthesized and shown to be exceedingly efficient for the selective hydrogenation of alkynes to their respective alkanes at room temperature, as well as the transfer hydrogenation of a variety of carbonyl compounds under MW conditions. The use of MW decreased the reaction time to a few minutes (30-45 min) from several hours (12-48 h) in case of conventional heating. The catalyst was recoverable with the simple use of an external magnetic field and remained highly active even after 5 repeated uses.

4. Experimental Section

All the chemicals were purchased from Aldrich and used without further purification. The phase of the as-synthesized nanoparticles was determined by X-ray diffraction in a MMS X-ray diffractometer with a Cu Kα source in the 2θ range 10 to 70. The data were collected with a step of 0.5 deg/min. TEM micrographs were recorded on a JEOL JSM-1200 II microscope at an operating voltage of 120 kV. The particles were dispersed in ethanol by ultrasonication, loaded on a carbon-coated copper grid, and then allowed to dry at room temperature before recording the micrographs. Elemental analyses of the catalyst before and after reactions were performed on a Perkin Elmer Optima 3300 DV inductively coupled atomic emission spectroscope (ICP-AES). 5 mg of each sample was dissolved in 2.5 mL of concentrated aqua regia and the volume was adjusted to 50 mL in a volumetric flask. This solution was then used for the elemental analysis. Gas chromatographic mass spectroscopy (GCMS) spectra were collected on a HP 6890 series GC system coupled with a 5973 Mass Selective Detector. Magnetic characterization of the as-synthesized $NiFe_2O_4$ nanoparticles was done using a Quantum Design MPMS-XL SQUID magnetometer under field cooled and zero field conditions as well as at room temperature.

4.1. Synthesis of the catalyst

$NiFe_2O_4$ nanoparticles were synthesized via hydrothermal route at 250 °C using $Fe(NO_3)_3 \cdot 9H_2O$ and, $Ni(NO_3)_2 \cdot 6H_2O$ as the precursors. The pH of the reaction mixture was maintained at 9 by addition of ammonium hydroxide solution. The as-synthesized particles were highly magnetic in nature. Two grams of the as-synthesized particles were then dispersed in 100 mL of deionized water by sonication for 15 min. Three grams of dopamine hydrochloride were then added refluxed overnight under magnetic stirring. The particles were then separated by applying a magnetic bar at the bottom of the reaction vessel, washed several times with ethanol, and dried under vacuum at 45 °C. The dopamine-modified particles were then dispersed in 100 mL of water. The particles were observed to be highly dispersed in water after modification with dopamine. 0.095 g of ruthenium(III)chloride was then added to the solution, and pH was maintained at 9 by addition of sodium borohydride. The reaction mixture was kept under magnetic stirring overnight. The final particles were separated from the solution by applying a magnetic field, washed three times with water to remove any chloride ions present, and dried under vacuum.

4.2. Hydrogenation of alkynes

To a solution of alkynes (1 mmol) in 2.0 mL methanol, 0.05 g of catalyst was added. The reaction vessel was purged three times with hydrogen and charged to 100 psi, and then closed off to the source of hydrogen. The reaction was stirred at room temperature for 18 h; after completion of the reaction, product was isolated by removing the catalyst magnetically from reaction mixture.

4.3. Transfer hydrogenation of carbonyl compounds

In a typical reaction, 1 mmol of the substrate was added to 5.0 mL of isopropyl alcohol in a 10 mL microwave tube. Catalyst (0.1 g) and 0.1 mmol (0.056 g) of potassium hydroxide were added. The reaction mixture was then 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 before characterizing with GCMS. The catalyst was then washed with acetone, dried at 80 °C in an oven for 15 minutes, and reused.

Acknowledgments

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