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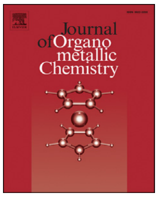

Polymer anchored ruthenium complex: A highly active and recyclable catalyst for one-pot azide–alkyne cycloaddition and transfer-hydrogenation of ketones under mild conditions

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A new polymer supported Ru(III) complex has been synthesized and characterized. The catalytic performance of the complex has been tested for the first time azide–alkyne cycloaddition reaction in water and transfer-hydrogenation reaction of ketones in open air. 1,4-disubstituted-1,2,3-triazoles were obtained in excellent yields from azides and terminal alkynes in aqueous medium in the presence of the above catalyst. Aromatic ketones have been converted to their corresponding alcohols using the polymer supported Ru(III) catalyst. The effects of solvents, reaction time, catalyst amount for the azide–alkyne cycloaddition reaction and transfer-hydrogenation reaction were studied. This catalyst showed excellent catalytic activity and recyclability. The polymer supported Ru(III) catalyst could be easily recovered by filtration and reused more than five times without appreciable loss of its initial activity. There was no evidence of leached Ru from the catalyst during the course of reaction has been observed, suggesting true heterogeneity in the catalytic process.

Introduction

The copper-catalyzed azide–alkyne cycloaddition (CuAAC) yielding 1,2,3-triazoles is a powerful one pot click reaction [1]. 1,2,3-triazoles are five-membered nitrogen heterocyclic compounds that are widely used in various research fields including synthetic organic, medicinal, materials, and biological chemistry [2–5]. Most azide–alkyne cycloaddition (AAC) have been carried by homogeneous copper catalysts [6–10]. Homogeneous catalysts have some disadvantages, such as they may easily be destroyed during the course of the reaction and they cannot be easily recovered after the reaction for reuse and the use of copper salt is restricted as it often leads to the formation of undesired homocoupled product of alkyne [11–13].

To get rid from these serious issues various solid-supported copper catalysts were also reported. The supports employed to date are activated carbon, inorganic materials, such as zeolites, amine-bound silica, superparamagnetic mesoporous silica, AlO(OH), metal oxide, hydrotalcite, an ionic liquid, a ligand-bound organic polymer, and polysaccharide [14–23]. Most of these reported CuAAC studies are on two component reaction systems using organic azides which are synthesized in advance. These organic azides are potential hazards especially in the isolation or the purification process and thus can be problematic. To overcome these drawbacks some copper catalysts were reported where organic azides were synthesised in situ to avoid the handling of such hazardous materials [24–27]. But these methodologies suffer from several drawbacks like use of long reaction time and elevated temperature.

It is thus desirable to develop an efficient one-pot methodology to avoid all these difficulties. More recently, it has been disclosed that (pentamethylcyclopentadienyl) ruthenium chloride complexes can effectively catalyze the facile cycloaddition of a wide range of azides and terminal alkynes (RuAAC) to afford regioselectively the complementary 1, 5-disubstituted 1,2,3-triazoles

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[28,29]. But Pei et al. reported that ruthenium complexes lacking cyclopentadienyl ligands, can catalyze the cycloaddition of terminal acetylenes and azides to give selectively 1, 4-substituted triazole regioisomers rather than 1, 5-disubstituted 1,2,3-triazoles [30,31].

In our present work, we have synthesized a polymer anchored ruthenium(III) complex and utilized it to catalyze the azide–alkyne cycloaddition reaction. During the course of our effort to develop ruthenium mediated cycloaddition of azides and alkynes, we have found that polymer anchored ruthenium(III) complex not only catalyze the three component cycloaddition of terminal acetylenes, sodium azide and alkyl halides to give selectively 1,4-substituted triazole regioisomers but also catalyze the transfer-hydrogenation reaction under mild conditions.

Amongst the many catalytic applications of Ru(III) in organic synthesis transfer-hydrogenation has become very popular in the last decade. It is indeed a very powerful tool for the reduction of ketones to their corresponding alcohols. The catalytic transfer-hydrogenation of ketones represents a viable method, not only in the laboratory but also on a commercial scale, because of its ease of handling, lower cost and safety compared with the typically used expensive, hazardous and dangerous reagents such as borane reagents, high-pressure hydrogen gas [32–37]. Among the different metal catalyzed transfer-hydrogenation reactions, ruthenium-based catalytic systems are found to be effective in the transfer-hydrogenation of ketones [38].

Herein we report the synthesis and characterization of a polymer supported ruthenium catalyst and illustrate its application for the synthesis of 1,4-disubstituted triazoles via three-component coupling of alkynes, azides and alkyl halides in water medium and transfer-hydrogenation reaction of various ketones in open air.

Experimental section

Materials

Analytical grade reagents and freshly distilled solvents were used throughout the experiments. All reagents and substrates were purchased from Merck. Liquid substrates were predistilled and dried by molecular sieve and solid substrates were recrystallized before use. Distillation, purification of the solvents and substrate were done by standard procedures. 5.5% crosslinked chloromethylated polystyrene and ruthenium trichloride were purchased from Sigma Aldrich and used as without further purification.

Physical measurements

The FT-IR spectra of the samples were recorded from 400 to 4000 cm^{-1} on a Perkins Elmer FT-IR 783 spectrophotometer using KBr pellets. UV–vis spectra were taken using a Shimadzu UV-2401PC doubled beam spectrophotometer having an integrating sphere attachment for solid samples. Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/DTA 851e. Surface morphology of the samples was measured using a scanning electron microscope (SEM) (ZEISS EVO40, England) equipped with EDX facility. Ruthenium content in the catalyst was determined using a Varian AA240 atomic absorption spectrophotometer (AAS). NMR spectra were recorded on a Varian Mercury plus NMR spectrometer (^{1}H NMR at 300 and 500 MHz and ^{13}C NMR at 75 MHz and 125 MHz) in pure deuterated solvents.

Synthesis of the metal complex

The synthesis of the immobilized polymer supported ruthenium(III) catalyst is illustrated in Scheme 1. It was readily prepared through a two-step procedure. First, 0.2 g of chloromethylated polystyrene (5.5 mmol Cl/g of resin) was treated with 0.979 g of β-alanine in DMF to produce the corresponding polymer supported ligand (PS-L). Then, the polymer was washed thoroughly with DMF to remove excess β-alanine. Finally, it was washed with double distilled water, dried and stored at room temperature for further use.

In the second step, the polymer supported β-alanine ligand (1 g) in DMF (20 mL) was treated with 5 mL 1% (w/v) DMF solution of $RuCl_3.3H_2O$ over a period of nearly 30 min under constant stirring. The reaction mixture was refluxed for 24 h. The deep grey coloured ruthenium complex thus formed was filtered and washed thoroughly with ethanol and dried in room temperature under vacuum.

General procedure for the formation of triazoles

Polymer supported metal catalyst (25 mg, 21×10^{-3} mmol) in water (5 mL) was taken in a 50 mL round bottom flask. Then phenylacetylene (1 mmol), sodium azide (1.2 mmol) and benzyl bromide (1 mmol) were added and stirred at room temperature for 180 min. After the completion of the reaction, the catalyst was filtered off and washed with water followed by acetone and dried in oven. The filtrate was extracted with ethyl acetate (3 × 20 ml) and the combined organic layers were dried with anhydrous Na_2SO_4 by vacuum. All the prepared compounds were confirmed by ^{1}H and ^{13}C NMR.

General procedure for the catalytic transfer hydrogenation reaction

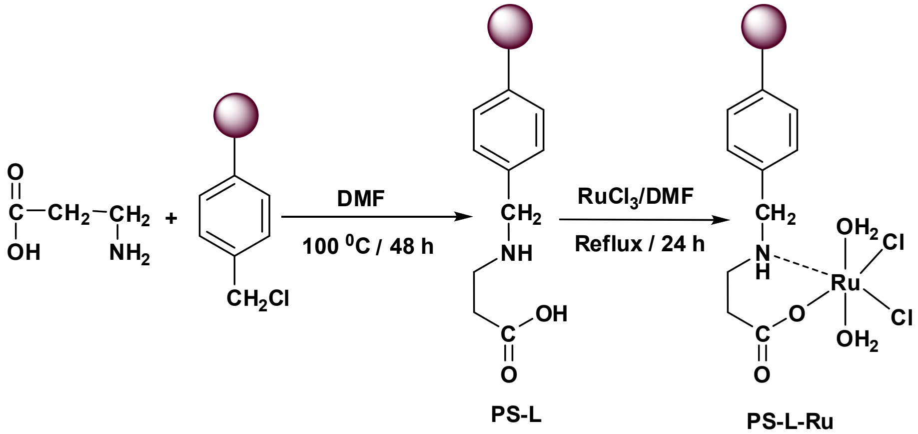
The substrate (ketone) (2.4 mmol), ruthenium catalyst (2.5 μmol), and propan-2-ol (5 mL) were introduced into a two necked round-bottomed flask fitted with a condenser and heated at 80 °C for 15–20 min in an open air atmosphere. Then, a solution of KOH (0.05 mmol) in 2-propanol (5 mL) was introduced to initiate the reaction and it was heated at 80 °C. The progress of the reaction was monitored by GC analysis of the samples.

Results and discussion

Characterization of the polymer supported catalyst

Due to insolubilities of the polymer supported ruthenium catalyst in all common organic solvents, its structural investigation was limited to its physicochemical properties, chemical analysis, SEM, TGA, IR and UV–vis spectroscopic data. Table 1 provides the data of elemental analysis of polymer supported ligand and the polymer supported ruthenium catalyst. Ruthenium content in the catalyst determined by AAS suggests 8.50 wt% Ru in the catalyst.

Various frameworks bonding present in the polymer supported metal catalyst were obtained from the FT-IR spectrum (Fig. 1). The sharp C–Cl peak due to $-CH_2Cl$ group in polymer (Fig. S1, supporting information) at 1264 cm^{-1} had disappeared in the polymer anchored ligand. A new strong band appeared at 3426 cm^{-1} showed the presence of a secondary (–NH–) amine group in the ligand. The (C=O), ν_{asym} (COO) and ν_{sym} (COO) stretching vibrations are observed at 1733, 1667 and 1513 cm^{-1} for polymer anchored bidente ligand [39] bound to the central metal ion through the carboxylic OH and the secondary amino group; (–NH–). The bands at 1667 and 1513 cm^{-1}, due to ν_{asym} (COO) and ν_{sym} (COO) of the amino acids, appear at 1663 and 1510 cm^{-1} in the complex. The shifting of these two bands suggests the involvement of the carboxylic group of the polymer supported ligand in the complex formation [40,41]. The participation of OH group in bonding was confirmed from the shift in the position of the C–O stretching vibration of the free ligand (1424 cm^{-1}) in the spectra of the complex. The decrease in the intensity of N–H stretching frequency of the



Scheme 1. Synthesis of the polymer supported Ru(III) catalyst.

Table 1
Chemical composition of polymer anchored ligand and polymer supported catalyst.

Compound	C%	H%	Cl %	N%	Metal%
PS-L	71.34	6.80	8.45	4.10	–
PS-L-Ru	58.66	5.36	5.90	2.95	8.50

secondary amine group in the complex indicates that the ‘N’ of amino group may be coordinated to the metal [42]. Weak bands in the far IR region at ~300–310 cm^{-1} and ~440–460 cm^{-1} have been assigned to $\nu_{\text{Ru–Cl}}$ and $\nu_{\text{Ru–N/O}}$ vibrations [43,44]. Thus, making precise assignments to distinguish Ru–O from Ru–N bands in the far IR region is rather difficult.

The scanning electron micrographs (Fig. 2) of the polymer supported ligand and ruthenium catalyst clearly show the morphological change which occurred on the surface of polystyrene after loading of metal on it. Energy dispersive spectroscopy analysis of X-rays (EDAX) data for the polymer anchored ligand and ruthenium catalyst are given in (Fig. 3). The EDAX data also inform that the attachment of metal on the surface of the polymer matrix.

The electronic spectrum (Fig. 4) of the polymer supported ruthenium catalyst has been recorded in the diffuse reflectance spectrum mode as $MgCO_3/BaSO_4$ disc. The polymer supported ruthenium(III) complex is in the +3 oxidation state. The electronic spectra of ligand and the complex showed three to four bands in the region 680–217 nm. The bands around 619–506 nm range have been assigned to the spin allowed d–d transition. The absorption around 260–275 nm may be attributed to π–π* transition in phenyl moiety. The other high intensity bands around 379–494 nm have been assigned to charge transfer transitions (LMCT) [45].

Thermal stability of the complexes was investigated using TGA at a heating rate of 10 °C/min in air over a temperature range of 30–600 °C. TGA–DTA curves of the polymer supported ligand and supported ruthenium catalyst are shown in Fig. 5. The ligand and ruthenium complexe were stable up to 350–370 °C and above this temperature they decomposed. Thermogravimetric study suggests that the polymer supported ruthenium complexe degrade at considerably higher temperature.

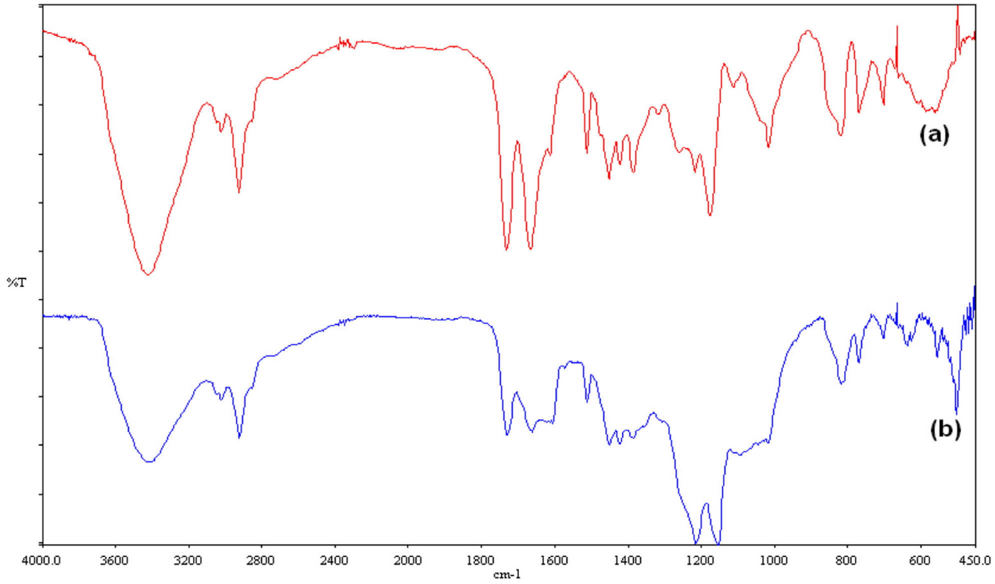


Fig. 1. FT-IR Spectra of polymer anchored ligand (a) PS-L and (b) PS-L-Ru complex.

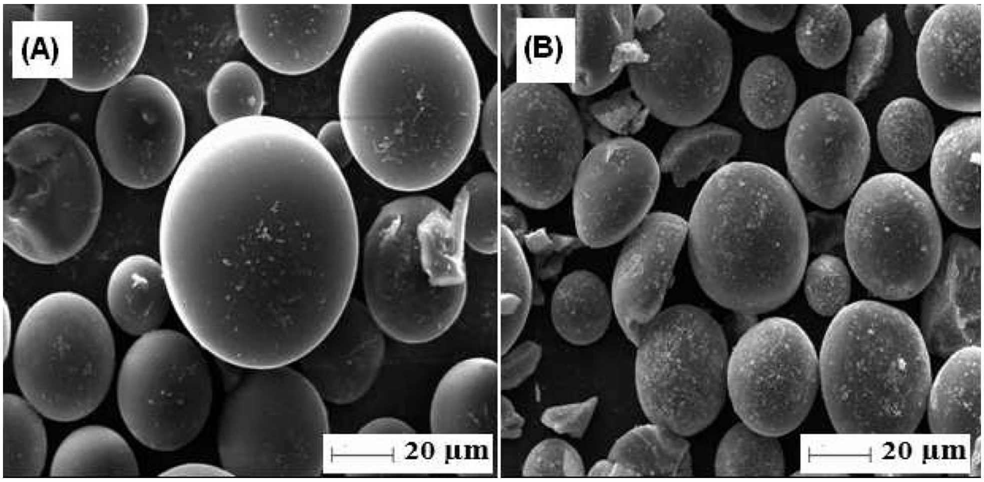


Fig. 2. FE-SEM of polymer anchored ligand (PS-L) (A) and PS-L-Ru complex (B).

Catalytic activities

Azide–alkyne cycloaddition reaction

Three component coupling reaction of alkyne, azide and alkyl halide represents a powerful method for the 1,2,3-triazole formation. Construction of 1,2,3-triazole compounds via the polymer supported ruthenium catalyzed azide–alkyne cycloaddition reaction is an interesting area in organic synthesis. We started our investigation for azide–alkyne cycloaddition reaction (Scheme 2) of phenylacetylene and benzyl bromide with sodium azide as model reaction. The performance of ruthenium-catalyzed azide–alkyne cycloaddition reaction is known to be governed by the number of factors such as the solvent, reaction time and catalyst amount etc. The influences of catalyst amount, solvent and reaction time were tested for cycloaddition reaction and found that trace amount of 1,2,3-triazole was obtained in the absence of polymer supported catalyst. To optimize the reaction conditions various solvents were screened. The influence of solvents on the yield are summarised in Table 2. From Table 2, it was found that water was the most effective solvent, while the use of other solvents such as toluene, ethanol, CH_3CN, CH_2Cl_2, dioxane resulted in lower yields.

The reaction was carried out for different time also (Fig. 6), ranging from 60 min to 180 min and it was found that at 180 min the yield of the reaction was 100% at room temperature.

The influence of amount of catalyst on the yield was also investigated (Fig. 7). An increase in the catalyst amount from 10 mg to 25 mg resulted in an increase in the yield up to 100%. Further increase in catalyst amount had no profound effect on the yield of the desired product.

With these optimized reaction conditions, a wide range of diversely substituted phenylacetylenes were reacted with various substituted and non-substituted benzyl halides and sodium azide to produce the corresponding 1,4-disubstituted-1,2,3-triazoles. The results are summarized in Table 3.

The substitution of electron withdrawing and electron donating groups on the phenyl ring of phenylacetylenes did not have any appreciable influence on the outcome of the reaction (Table 3, entries 4 and 11). The reaction went uniformly for all *o*-, *m*-, and

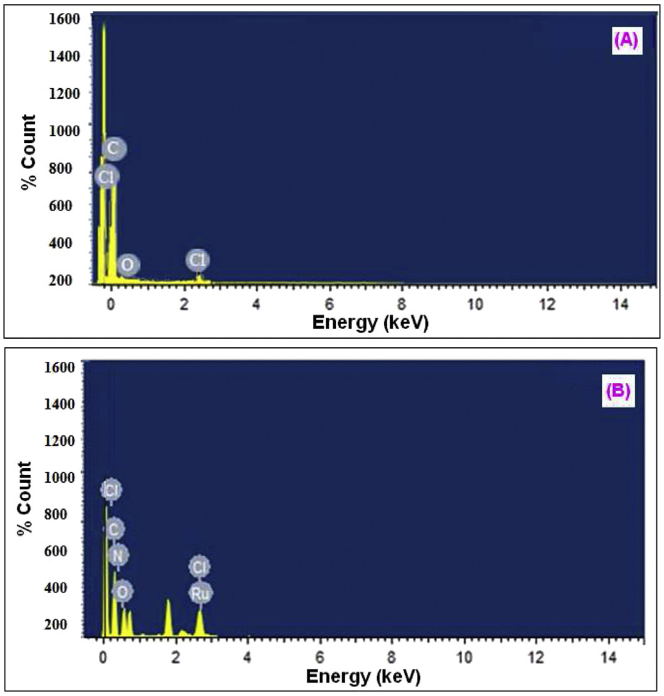


Fig. 3. EDAX spectra of polymer supported ligand (PS-L) (A) and PS-L-Ru complex (B).

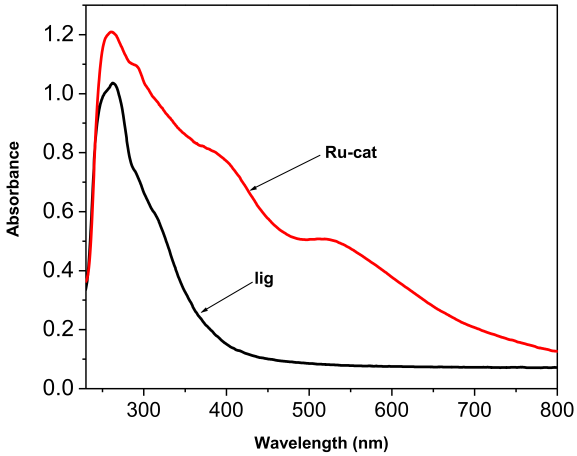


Fig. 4. DRS-UV–visible absorption spectra of the polymer supported ligand and ruthenium catalyst.

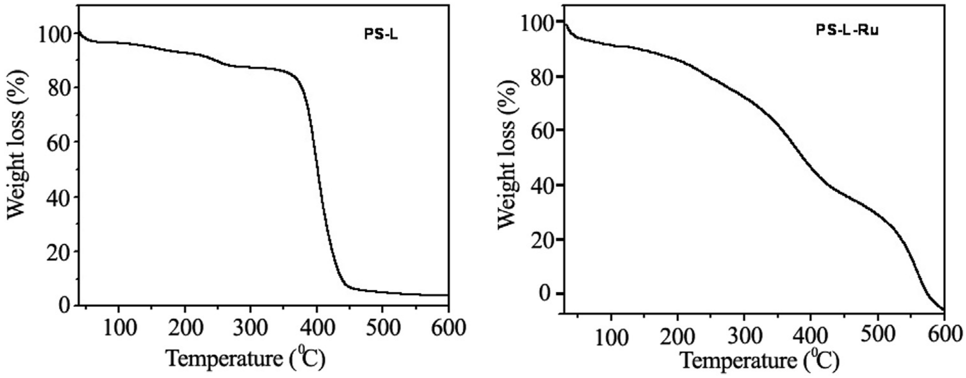
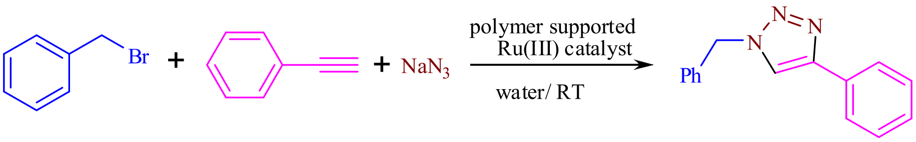


Fig. 5. Thermogravimetric weight loss plots for the polymer supported ligand (PS-L) and PS-L-Ru complex.



Scheme 2. Azide–alkyne cycloaddition reaction.

Table 2
Effect of solvents on 1,4-disubstituted 1,2,3- triazoles synthesis catalyzed by polymer supported Ru(III) catalyst.

Entry	Solvent	Isolated yield (%)
1	Toluene	40
2	Ethanol	76
3	CH_3CN	58
4	CH_2Cl_2	52
5	Dioxane	37
6	DMSO	82
7	H_2O	100

Reaction condition: phenylacetylene (1 mmol), benzyl bromide (1 mmol) and sodium azide (1.2 mmol), catalyst (25 mg, 21×10^{-3} mmol) in 5 mL water, time 180 min at room temperature (40 °C).

p-substituted phenylacetylenes (Table 3, entries 4, 3, and 2). The 1,4-diethynylbenzene produced the corresponding bis-triazole derivatives (Table 3, entry 5). The hetero-aryl substituted acetylene 3- ethynylthiophene underwent a clean reaction to produce 1-benzyl-4(thiophen-3-yl)-1,2,3-triazole (Table 3, entry 6). Alkyl acetylene such as propargyl alcohol also participated in this reaction to provide the corresponding product (Table 3, entry 7). No rigorous extraction of product by solvent and work-up were necessary. A simple washing of the reaction residue by ethanol followed by evaporation of the solvent furnished the pure product. Chromatographic separation was not a necessary requirement. Thus this procedure avoids use of a hazardous organic solvent in the whole process.

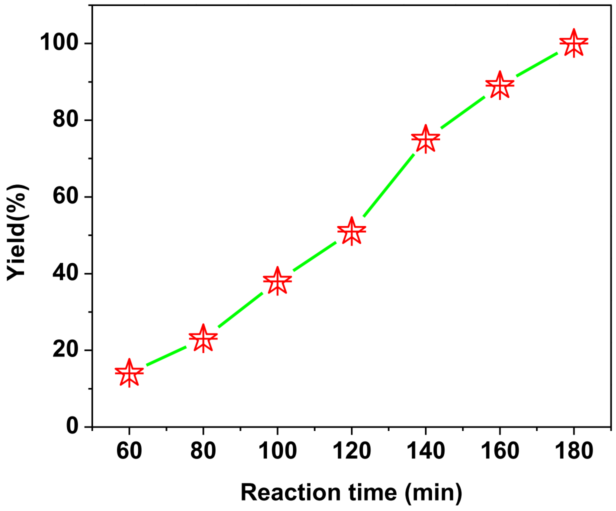


Fig. 6. Effect of reaction time on azide–alkyne cycloaddition reaction.

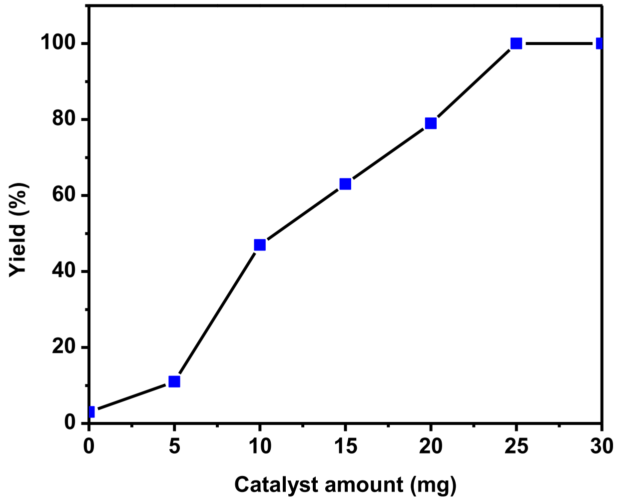
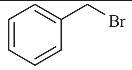
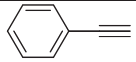
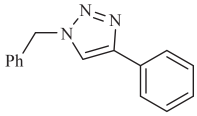
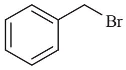
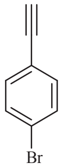
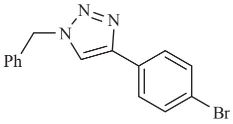
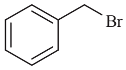
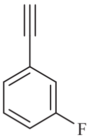
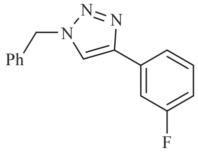
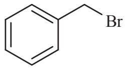
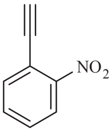
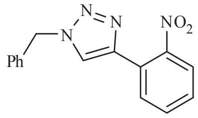
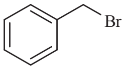
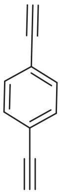
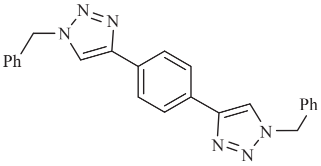
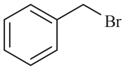
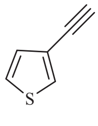
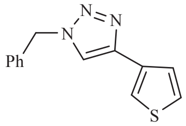
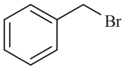
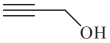
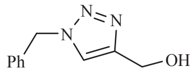
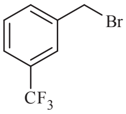
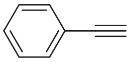
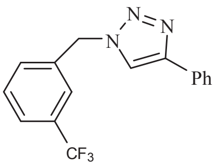
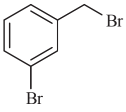
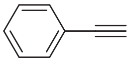
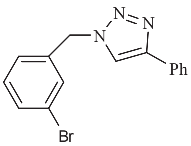


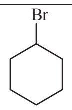
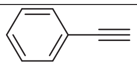
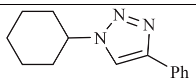
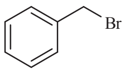
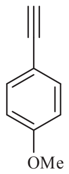
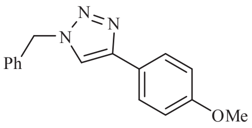
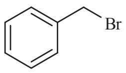
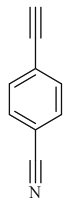
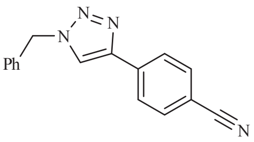
Fig. 7. Effect of catalyst amount on azide–alkyne cycloaddition reaction.

Table 3
Polymer supported ruthenium(III) catalyzed azides–alkyes cycloaddition reactions.

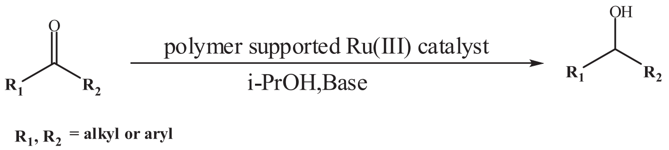
Entry	Halides	Alkynes	Triazoles	Isolated Yield (%)
1				100
2				93
3				89
4				94
5				89
6				83
7				83
8				89
9				90

(*continued on next page*)

Table 3 *(continued)*

10				76
11				85
12				87

Reaction conditions: alkynes (1 mmol), benzyl halides (1 mmol) and sodium azide (1.2 mmol), time (180 min), catalyst (25 mg, 21 × 10^{-3} mmol) in 5 mL water, at room temperature (40 °C) and all the prepared compounds were confirmed by ^{1}H NMR, ^{13}C NMR.



Scheme 3. Ruthenium catalyzed transfer-hydrogenation of ketones.

Transfer-hydrogenation reaction

Transfer hydrogenation reaction, in which hydrogen is transfered from one organic molecule to another, is of great importance and has become an efficient method in organic synthesis. The use of ruthenium complex, as an effective catalyst for transfer hydrogenation reaction, encouraged us to carry out this type of reaction using polymer supported ruthenium catalyst (Scheme 3).

Table 4
Effect of base and temperature on the transfer hydrogenation of cyclohexanone.

Entry	Base	Temperature (°C)	Yield (%)[a]
1	–	80	0
2	NaOH	30	<10
3	NaOH	80	84
4	NaOH	90	84
5	$NaHCO_3$	80	22
6	Na_2CO_3	80	20
7	KOH	60	60
8	KOH	80	98
9	KOH	90	98
10	Et_3N	80	<10
11	CH_3COONa	80	12
12	*i*-PrOK	40	50
13	*i*-PrOK	80	95
14	*i*-PrOK	90	95
15	Pyridine	80	<10

Reaction conditions: cyclohexanone (2.4 mmol), catalyst (2.5 μmol), base (0.05 mmol) in *i*-PrOH (5 mL) in air.

[a] Yield was determined by GC analysis, internal standard (m-xylene, 30 μL, 0.24 mmol).

In order to optimize the reaction conditions such as base and reaction temperature, the transfer hydrogenation reaction of cyclohexanone to cyclohexanol was chosen as model reaction in the presence of polymer supported ruthenium catalyst in *i*-PrOH (Table 4). The reaction rates were found to be strongly dependent on the base employed and variety of bases were screened. A remarkable increase in the product formation was observed in presence of strong inorganic bases like NaOH or KOH. When weak inorganic bases such as $NaHCO_3$, Na_2CO_3 and CH_3COONa or organic bases such as triethylamine, pyridine were employed, the conversion of the product was drastically reduced. Temperature was found to have a strong influence on the performance of the catalyst and a decrease in the conversion was observed at lower temperature. The formation of cyclohexanol proceeded slowly at 40 °C. The results obtained from the optimization of reaction conditions indicate that relatively high conversion can be achieved in the transfer hydrogenation of cyclohexanone to cyclohexanol with polymer supported catalyst using i-PrOH/KOH at 80 °C. Next, to optimize the effect of catalyst amount,

Table 5
Effect of catalyst amount and reaction time on the transfer hydrogenation of cyclohexanone.

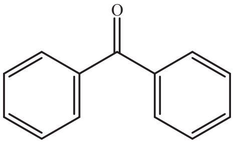
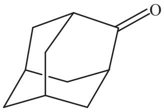
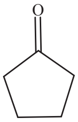
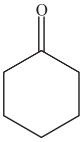
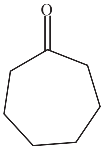
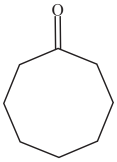
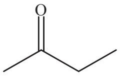
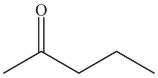
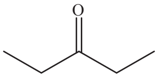
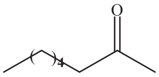
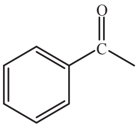
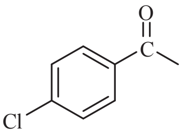
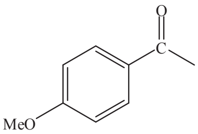
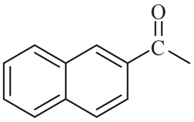
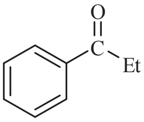
Entry	Catalyst (μmol)	Time (min)	Yield (%)[a]
1	–	90	0
2	1.0	90	45
3	1.5	90	60
4	2.0	90	81
5	**2.5**	**90**	**98**
6	3.0	90	98
7	2.5	70	85
8	2.5	80	90
9	2.5	100	98

Reaction conditions: cyclohexanone (2.4 mmol), 0.05 mmol KOH in *i*-PrOH (5 mL) at 80 °C in air.

Bold values represent optimized condition.

[a] Yield was determined by GC analysis, internal standard (m-xylene, 30 μL, 0.24 mmol).

Table 6
Transfer hydrogenation of various ketones catalyzed by polymer supported Ru(III) catalyst.

Entry	Ketone	Isolated yield (%)[a]	TON
1		97.5	936
2		97	931
3		87	835
4		98	941
5		94	902
6		88	849
7		99	950
8		95	912
9		90	864
10		91	874
11		89	854
12		93	893
13		85	816
14		86	826
15		84	804

Reaction conditions: ketone (2.4 mmol), KOH (0.05 mmol) in *i*-PrOH (5 mL), catalyst (2.5 μmol) at 80 °C in air for 90 min.

[a] Yield was determined by GC analysis, internal standard (m-xylene, 30 μL, 0.24 mmol).

different amount of catalyst was tested in the transfer hydrogenation reaction of cyclohexanone in i-PrOH/KOH and the results are summarized in Table 5. It was found that 2.5 μmol of ruthenium catalyst was the most effective catalytic system. This transfer-hydrogenation reaction was also found to be highly sensitive to the reaction time. From the results (Table 5, entries 6–9), it can be shown that the formation of cyclohexanol initially increased with the progress of the reaction, reached a maximum and then remained unchanged. Reasonably good conversion (98%) for the formation of cyclohexanol was observed at the optimum reaction time of 90 min. Longer reaction time of 90 min–120 min doesn't produce a considerable improvement in the conversion of cyclohexanone to cyclohexanol. From the above discussion, it is shown that the best yield was obtained by using the base KOH in *i*-PrOH solvent at 80 °C for 90 min under open air with the polymer supported ruthenium(III) catalyst (2.5 μmol).

Under the optimized conditions, the transfer hydrogenation reaction of a range of ketones was investigated to know about the scope of our method. The transfer hydrogenation reaction of several aromatic and aliphatic ketones was carried out with the ruthenium catalyst using *i*-PrOH and KOH at 80 °C and the results are summarized in Table 6. The products were identified by GC after doing the required workup. The polymer supported ruthenium complex catalyzed the transfer hydrogenation of ketones to their corresponding alcohols with good to excellent yields in all the cases. Excellent yields are obtained for both aliphatic and aromatic ketones. The complex efficiently catalyzed the reduction of aliphatic ketones such as methyl ethyl ketone, methyl propyl ketone and diethyl ketone (Table 6, entries 7–9) to their corresponding alcohols. Moreover, this catalyst efficiently catalyzed the reduction of benzophenone, 2-adamantanone, cyclopentanone and cycloheptanone to their corresponding alcohols (Table 6, entries 1–3 and 5). The complex also showed good activity for eight membered cyclic ketone cyclooctanone with 88% isolated yield (Table 6, entry 6). The isolated yield of alcohol in case of acetophenone is 89%. The presence of electron withdrawing (Cl) and electron donating ($-OCH_3$) substituents on the substrates plays a significant role in the conversion of ketones to alcohols. 4-chloro acetophenone and 4-methoxy acetophenone were converted to their corresponding alcohols with 93% and 85%, respectively (Table 6, entries 12 and 13). Electron-withdrawing substituent (Cl) on the aryl ring gave higher conversions compared to that of acetophenone whereas electron-donating substituents (–OCH_3) on the ring gave lower conversions than that of acetophenone.

Heterogeneity test

An important point concerning the use of heterogeneous catalyst is its lifetime, particularly for industrial and pharmaceutical applications. Heterogeneity of the catalyst was examined by the "hot filtration test" for the transfer hydrogenation reaction.

Hot-filtration test

Hot-filtration test was performed in the transfer hydrogenation reaction to investigate whether the reaction proceeded in a heterogeneous or a homogeneous fashion. After continuing the reaction for 1 h, the catalyst was removed by filtration and the determined conversion was 76%. The resulting filtrate was subjected to heating for further 2 h it has been found that after separation of the catalyst no conversion takes place in the filtrate part. This confirms that the reaction did not proceed upon the removal of the solid catalyst. Further, no evidence for leaching of ruthenium or decomposition of the complex catalyst was observed during the catalytic reaction and no metal could be detected by atomic absorption spectroscopic measurement of the filtrate after removal of catalyst. These studies clearly demonstrated that metal was intact to a considerable extent with the heterogeneous support, and there is no significant amount of leaching occurred during reaction.

Catalyst reusability

Recovery and reuse of catalyst are important issues in heterogeneous catalysis. Easy catalyst separation and recycling in successive batch operations can greatly increase the efficiency of the reaction. We studied the reusability of the present heterogeneous ruthenium catalyst in the azide–alkyne cycloaddition reaction, taking the reaction of benzyl bromide and phenylacetylene (Fig. 8). After completion of the reaction, the catalyst was recovered by simple filtration and washed with ethyl acetate followed by acetone then dried in reduced pressure. The recovered catalyst was employed in the next run with further addition of substrates in appropriate amount under optimum reaction conditions. Reusability test was also performed for transfer hydrogenation of cyclohexanone and the results are given in Fig. 8. The catalysts show almost same activity up to six reaction cycles. No catalysts deterioration was observed, confirming the high stability of the heterogeneous catalyst under the reaction conditions.

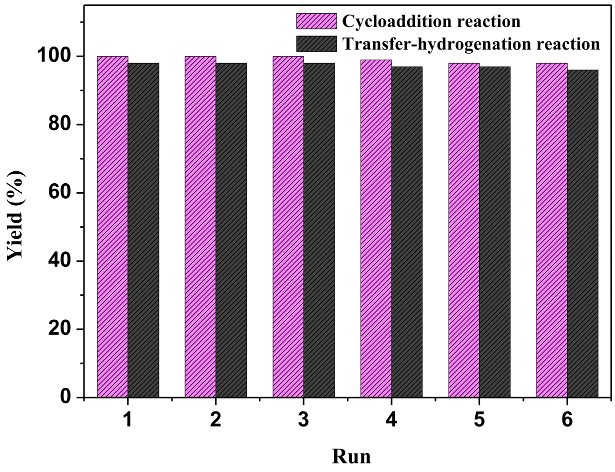


Fig. 8. Catalyst reusability test of the polymer supported Ru catalyst.

Conclusion

In conclusion, we have reported the preparation and characterisation of polystyrene supported Ru(III) complex and its successful applications for the azide–alkyne cycloaddition reaction in aqueous medium at room temperature and transfer hydrogenation reaction in open air. The Ru(III) catalyzed one-pot azide–alkyne cycloaddition reaction is a efficient method for rapid and green synthesis of 1,2,3 triazoles with excellent yield via multicomponent coupling in aqueous medium at room temperature. To the best of our knowledge, we are not aware of synthesis of 1,4-disubstituted 1,2,3-triazoles in water using polymer supported ruthenium catalyst and thus we believe that this protocol will find an useful application in green organic synthesis. This polymer supported Ru(III) catalyst is found to be an efficient catalyst in transfer hydrogenation of both aliphatic as well as aromatic ketones in the presence of isopropanol/KOH. This catalyst was effective for transfer hydrogenation of ketones to their alcohols. The present system is highly air and moisture stable and the catalyst can be synthesized readily from inexpensive and commercially available starting materials. Moreover, the catalyst can be reused for six consecutive cycles with consistent catalytic activity. Further work is in progress to broaden the scope of this catalytic system for other organic transformation.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2014.11.007.

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