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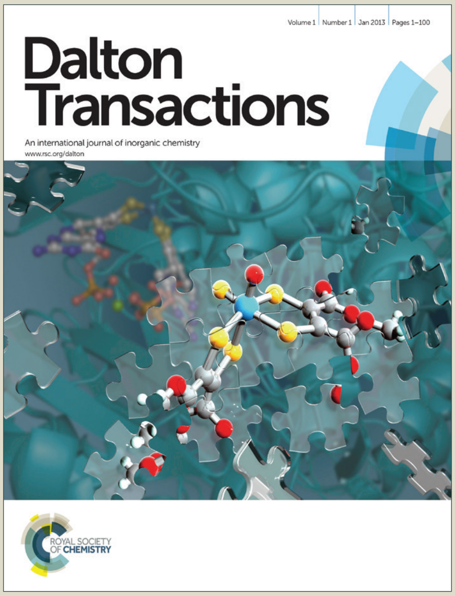

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Ruthenium-grafted triazine functionalized mesoporous polymer: A highly efficient and multifunctional catalyst for transfer hydrogenation and Suzuki–Miyaura cross-coupling reactions

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Abstract

A new ruthenium-grafted mesoporous organic polymer Ru-MPTAT-1 has been synthesized via the simple and facile in situ radical polymerization of 2,4,6-triallyloxy-1,3,5-triazine (TAT) in aqueous medium in the presence of an anionic surfactant (sodium dodecyl sulfate) as template, followed by grafting of Ru(II) at its surface. Ru-MPTAT-1 has been characterized by elemental analysis, powder XRD, HR TEM, FT-IR, UV-vis DRS, TG-DTA, FE-SEM and XPS characterization tools. The Ru-MPTAT-1 material showed very good catalytic activity in Suzuki–Miyaura cross-coupling reaction for aryl halides and transfer hydrogenation reaction for a series of carbonyl compounds. The catalyst is easily recoverable from the reaction mixture and can be reused for several times without appreciable loss of catalytic activity in the above reactions. Highly dispersed and strongly bound Ru(II) sites at the mesoporous polymer surface could be responsible for the observed high activities of the Ru-MPTAT-1 catalyst in these reactions.

Keywords: Mesoporous polymer, 2,4,6-triallyloxy-1,3,5-triazine, Ru-grafting, transfer hydrogenation, Suzuki–Miyaura cross-coupling.

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Introduction

The selective reduction of carbonyl compounds to the corresponding alcohols is a very important and demanding transformation in organic synthesis. Most of the methods reported in the literature for catalytic reduction require the use of a stoichiometric amount of sensitive reagents or the use of dangerous hydrogen gas under high pressure conditions.[1–3] Transfer hydrogenation has become the centre 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. Similarly, the Ru-catalyzed olefination of aryl halides (Heck-Mizoroki reaction)[4] and closely relevant Pd-catalyzed cross-couplings (e.g. Sonogashira, Suzuki-Miyaura reactions, etc.)[4-5] have been developed as one of the most efficient tools for the carbon-carbon and carbon-heteroatom bond formation reactions in the synthetic organic chemistry. The catalytic pathway is very simple, attractive and versatile for a wide range of organic transformations because they usually offer high product yields, good regio- and stereoselectivity, and excellent compatibility with many functional groups. Efficiency of the reactions has been successfully demonstrated in the synthesis of natural products, organic building blocks, pharmaceuticals, and agricultural derivatives. Homogeneous metal catalysts are often used as effective catalysts for these reactions.[6-12] However, there are serious difficulties in the recovery and reuse of expensive metal-catalysts and most of the reactions do not proceed without the use of expensive ligands.

Heterogeneous catalysis, which can be prepared by heterogenisation of homogeneous counterpart (metal complex, metal salt, metal or metal oxide nanoparticles) into insoluble solid porous matrices, has emerged an increasing attention due to their easy separation technique, recovery and reusability of the catalyst.[13] Numerous heterogeneous catalysts (noble metals such as Ru, Pt, Pd, and Au) have been reported as effective and reusable catalysts for these reactions.[14-18]

In this context functionalized mesoporous materials have gained increasing interests and successfully utilized as drug-delivery vehicle,[19] adsorption,[20] metal ion sensing,[21] catalysis,[22] selective separation [23] and gas storage[24] due to their exceptionally high surface area, thermal and mechanical stability. To date, mesoporous materials composed of inorganic oxides[25] and inorganic–organic hybrid silicas[26] have been studied extensively, but only limited research works have been carried out on purely organic mesoporous materials, which could bear strong donor sites for binding active metal ions at its surface.[27-29] Thus, to design an efficient heterogeneous catalyst, which could support a reactive ruthenium complex via oxygen and nitrogen donor atoms of the mesoporous framework is of great significance. This is particularly important due to their multi-electron transfer properties, its ability to have a wide range of oxidation states and thus potential catalytic efficiency.[30-32]

Thus, we designed a new functionalized mesoporous material based on an organic polymer framework, grafting it with an active metal centre and to explore its potential application in C–C coupling reactions and transfer hydrogenation reaction. Very recently, a new functionalized mesoporous polymer (MPTAT-1) has been synthesized by using sodium dodecyl sulfate as template, which could bind active Pd(II) sites strongly at its surface.[33] Inspired by the above observations, in the present work we have designed a mesoporous organic polymer catalyst through the polymerization of 2,4,6-triallyloxy-1,3,5-triazine monomer unit, grafted it with ruthenium at its surface, and explored its potential in transfer hydrogenation and Suzuki-Miyaura C–C cross-coupling reactions reaction maintaining eco-friendly reaction conditions.

Experimental Section

Materials and reagents

2,4,6-Triallyloxy-1,3,5-triazine (TAT, monomer), $RuCl_3$ and other reactants for the catalytic reactions were obtained from Sigma Aldrich. N, N, N', N'-tetramethylethylenediamine (TMED, promoter), ammonium persulfate (APS, radical initiator), sodium dodecyl sulfate (SDS, template) were purchased from Loba Chemie, India. All other chemicals used for this investigation purposes were of analytical grade produced by Merck, India unless mentioned otherwise.

Instrumentation

Powder X-ray diffraction (XRD) patterns of different samples were analyzed with a Bruker D8 Advance X-ray diffractometer using Ni–filtered Cu Kα (λ=0.15406 nm) radiation. Transmission electron microscopy (TEM) images of the mesoporous polymer were obtained using a JEOL JEM 2010 transmission electron microscope operated at 200 kV. Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/DTA 851e. Scanning electron microscopic measurements were performed with a JEOL JEM 6700F field-emission scanning electron microscope (FE SEM). Carbon, hydrogen and nitrogen contents of both the mesoporous MPTAT-1 and Ru-grafted polymer were analyzed using a Perkin Elmer 2400 Series II CHN analyzer. UV-Vis spectra of the samples were taken using a Shimadzu UV-2401PC doubled beam spectrophotometer having an integrating sphere attachment for solid samples. The reaction products were quantified (GC data) by Varian 3400 gas chromatograph equipped with a 30 m CP-SIL8CB capillary column and a flame ionization detector and identified by Trace DSQ II GC-MS equipped with a 60 m TR-50MS capillary column.

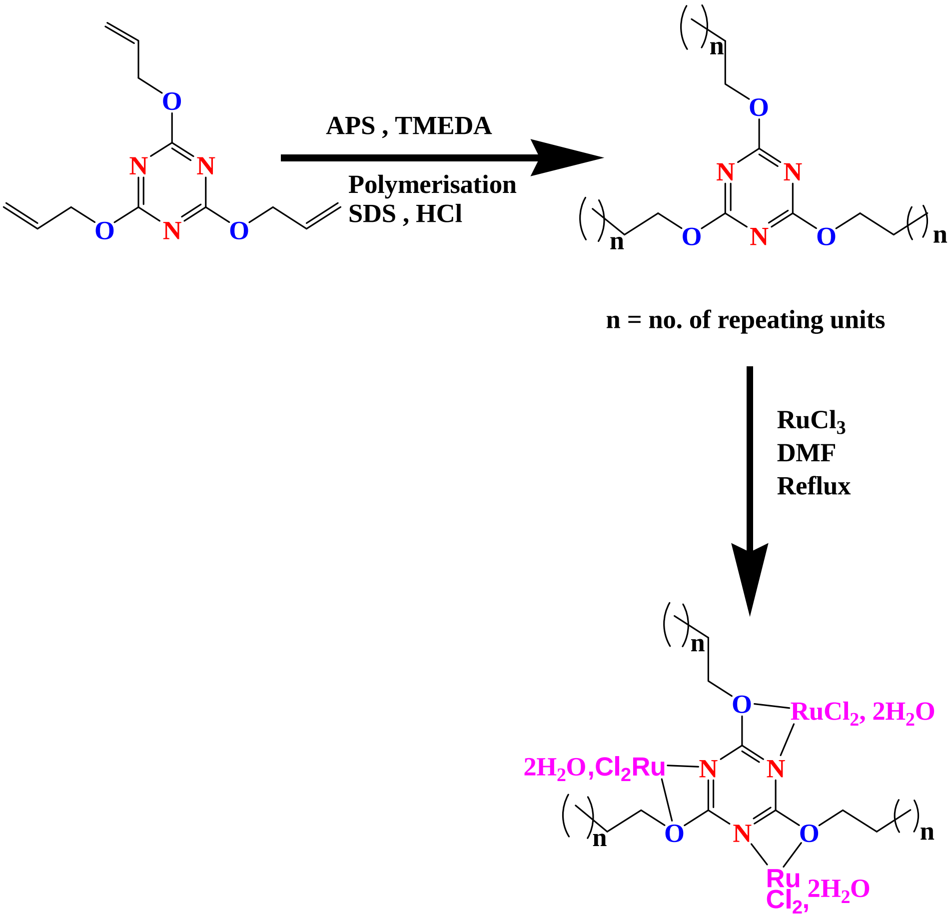
Preparation of the catalyst

Synthesis of mesoporous poly-2,4,6-triallyloxy-1,3,5-triazine (MPTAT-1)

MPTAT-1 has been synthesized through the aqueous-phase polymerization of 2,4,6-triallyloxy-1,3,5-triazine (TAT) under hydrothermal condition by using ammonium persulfate (APS) as an initiator. In a typical synthesis, 2.35 g (0.00814 mol) of SDS was dissolved in 40 ml of water with constant stirring followed by the addition of 2 g (0.008 mol) of 2,4,6-triallyloxy-1,3,5-triazine. After the addition of 0.94 g (0.00814 mol) of TMED to this mixture, concentrated HCl (12 N) was added dropwise to obtain a clear solution. This helps the protonation of the N-atoms of the TAT molecules, which facilitates the ionic interaction of the organic monomers with the negative charge of $C_{12}H_{23}SO_3^-$ of the SDS molecules. The pH of the gel was maintained at *ca.* 7.0. Finally, 5.2 g (0.016 mol) of APS dissolved in 10 ml of distilled water was added quickly into the solution with vigorous stirring. A white precipitate appeared immediately after the addition of APS. The resultant slurry was stirred for another 3 h at room temperature and then autoclaved at 348 K for 3 days without stirring. The final pH of the synthesis gel was *ca.* 4.0–5.0. After aging, the resultant precipitate was filtered, washed thoroughly with de-ionized water, yielding mesoporous polymer MPTAT-1. The surfactant was removed from the as-synthesized mesoporous polymer material by extraction of 1.0 g of the MPTAT-1 material with 0.5 g acetic acid taken in 50 ml water under 4 h stirring at room temperature. This template extraction procedure was repeated three times to obtain template-free MPTAT-1.

Synthesis of ruthenium grafted mesoporous poly-2,4,6-triallyloxy-1,3,5-triazine (Ru-MPTAT-1)

Synthetic procedure for grafting of ruthenium onto the mesoporous poly-2,4,6-triallyloxy-1,3,5-triazine (MPTAT-1) has been illustrated in Scheme 1. For Ru loading, 1.0 g of the template-free mesoporous polymer was dispersed in 20 ml of DMF taken in a round bottom flask. To this 0.5 g ruthenium chloride was added and the suspension was refluxed for about 12 h under vigorous stirring. At the end, the resulting solid was filtered and washed thoroughly with methanol and finally dried under vacuum for 24 h to obtain Ru-MPTAT-1.



Scheme 1. Organic–organic in situ radical polymerization of 2,4,6-triallyloxy-1,3,5 triazine by APS by using a SDS template and grafting of Ru(II) at its surface to obtain Ru-MPTAT-1.

General experimental procedure for Transfer Hydrogenation of Carbonyl Compounds

In a typical reaction an oven dried 100 ml RB flask, Ru-MPTAT-1 catalyst (0.05 g), isopropyl alcohol (10 ml), substrate (1 mmol) and NaOH (0.4 mmol) were stirred under nitrogen atmosphere at 60 ^{0}C. The reaction mixtures were collected at different time interval and identified by GC-MS and quantified by GC analysis. 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 three times with ethyl acetate (3 x 20 ml) and the combined organic layers were dried with anhydrous Na_2SO_4 under high vacuum. The filtrate was concentrated and the resulting residue was purified by column chromatography on silica gel to obtain the desired product.

General experimental procedure for Suzuki–Miyaura coupling reaction

In a typical reaction a mixture of aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), DMF (5 ml) and Ru-MPTAT-1 catalyst (0.05 g) was stirred at 80 ^{0}C in a closed round-bottom flask. To study the progress of the reaction the reaction mixtures were collected at different time interval and quantified by GC analysis. At the end of the reaction, the catalyst was separated by simple filtration. Filtrate was extracted with CH_2Cl_2 and passed through a pad of silica gel. The organic phase thus collected was dried over Na_2SO_4, filtered, concentrated and the residue was purified through the flash chromatography on silica gel. The product was analyzed by ^{1}H NMR. All prepared compounds are known and their respective NMR spectra were compared with authentic samples.

Results and discussion

Formation of mesophase

In the presence of the anionic structure directing agent SDS, organic-organic supramolecular templating interaction takes place in aqueous medium. In the acidic pH conditions the positively charged protonated N-atoms of the triazine moiety preferentially interact with the negatively charged polar head groups of the dodecyl sulfonate moiety *i.e.* $C_{12}H_{23}SO_3^-$ and condensed around the micelle to form a continuous mesophase. The resulting array of organic mesophases upon removal of the surfactant via acid extraction has retained its mesoporous structure. In Scheme 1, we have described the polymerisation of TAT monomer in the presence of ammonium persulfate, which is a good radical initiator for aqueous phase polymerization of olefins under mildly acidic conditions.[34] Since one monomer contains three olefinic double bonds in each of its branches, this polymerization gives random cross-linking, leading to a highly stable and robust cross-linked porous organic framework. Immobilization of ruthenium and its strong binding at the MPTAT-1 surface has been facilitated due to the presence of strong donor N- and O- sites in the triazine moiety.[27c]

Characterization of Ru-MPTAT-1 material

In Figure 1 we have shown the proposed polymeric network in the as-synthesized MPTAT-1, template-free MPTAT-1 and Ru-MPTAT-1. As-synthesized mesoporous polymer synthesized through the radical polymerization of 2,4,6-triallyloxy-1,3,5-triazine in the presence of SDS template upon acid extraction yielded template free MPTAT-1. This template free mesoporous polymer upon impregnation by $RuCl_3$ in air resulted Ru-MPTAT-1. AAS analysis revealed that ruthenium content in the Ru(II)-grafted mesoporous polymer was 4.56 wt%.

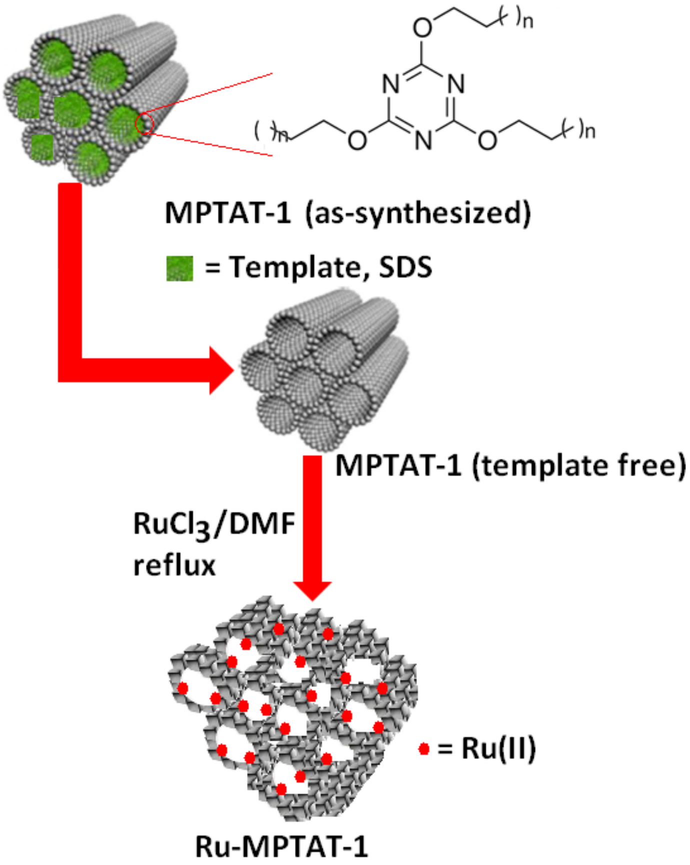


Figure 1. Schematic synthetic pathway for MPTAT-1 (as-synthesized), MPTAT-1 (template free) and Ru-MPTAT-1.

X-ray diffraction

In Figure 2 small angle powder X-ray diffraction pattern of ruthenium loaded mesoporous organic polymer Ru-MPTAT-1 is shown. It shows one distinct diffraction peak cantered at 2θ = 2.30 degree, corresponding to the mesophase with interplanar distance 3.85 nm. In the XRD pattern of the template-free MPTAT-1 shows the 100 diffraction peak at 2θ = 2.08 degree, whereas after Ru-grafting 2θ value increases considerably, suggesting that the contraction of pore walls occurred during the anchoring of ruthenium at the mesopore surface.[33]

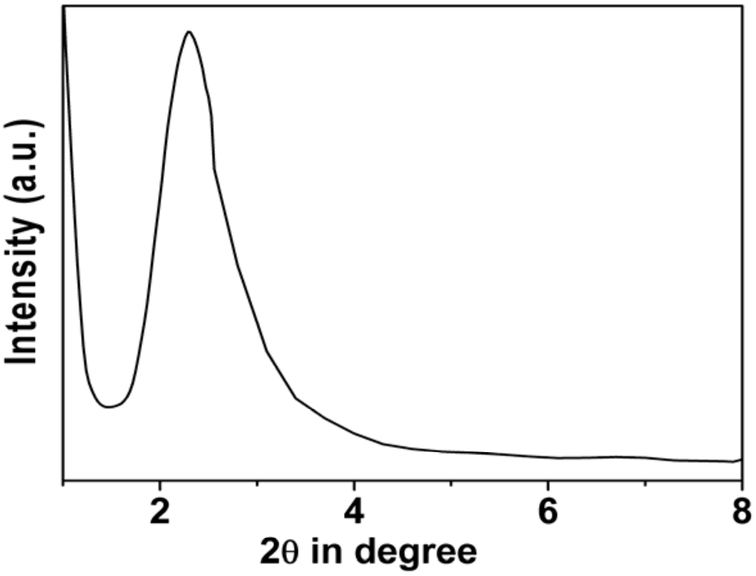


Figure 2. Small angle powder XRD pattern of Ru-MPTAT-1 material.

N_2 adsorption-desorption

In Figure 3 nitrogen adsorption-desorption isotherm of Ru-MPTAT-1 material is shown. This isotherm is closely related to type IV isotherm, which is the characteristic of mesoporous materials. However, no sharp capillary condensation was observed. The BET surface areas for the template-free MPTAT-1 and Ru-MPTAT-1 material are 135 m^2g^{-1} [33] and 30 m^2g^{-1}. The considerable decrease in the BET surface area of Ru-MPTAT-1 suggests considerable amount of Ru-centers have been anchored in the polymer. Pore size distribution (PSD) of this sample employing non-local density functional theory (NLDFT) is shown in the inset of the Figure 3. The pore size distribution peaks are centered at 1.5 nm, 2.8 nm and 4.73 nm suggesting the material contain wide range of pores in the supermicropore to mesopore region. The pore volume of the material is 0.0364 ccg^{-1}.

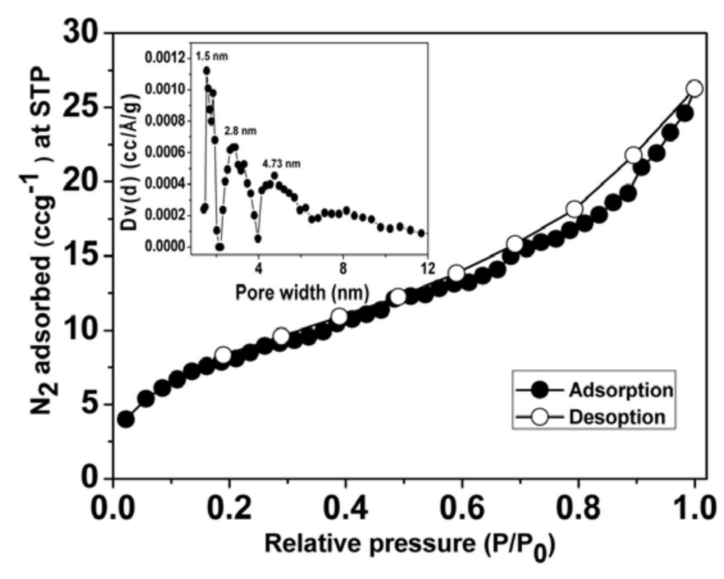


Figure 3. N_2 adsorption-desorption isotherm of Ru-MPTAT-1. Adsorption points are marked by filled circles and those for desorption are by open circles. NLDFT pore size distribution is shown in the inset

Electron microscopic analysis (SEM and TEM)

Field emission scanning electron microscopic (FE SEM) image of Ru-MPTAT-1 is shown in Figure 4. This FE SEM image indicates uniform spherical morphology of the Ru-MPTAT-1 material with the average dimension of *ca*. 64 nm. Here the spherical particles get aggregated among themselves to form large assembly of particles.

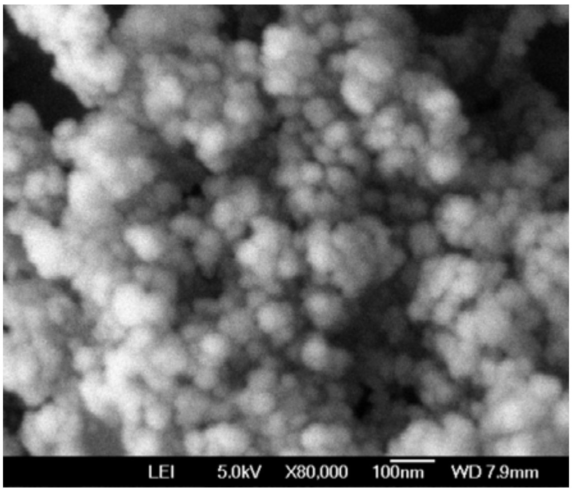


Figure 4. FESEM image of Ru-MPTAT-1 materials.

HR TEM images of Ru-MPTAT-1 are shown in Figure 5. These images showed the presence of ruthenium species (dark spots) and hollow sphere nanostructure.[35,36] This Ru-grafted mesoporous organic polymer consisting of almost all spherical shaped nanoparticles together with smooth shell wall. These hollow spheres are uniformly distributed throughout the specimen grid and ruthenium species are anchored to a considerable extent at the surface of these hollow spheres. The size of these nanospheres showed wide size distribution of *ca.* 50-180 nm.

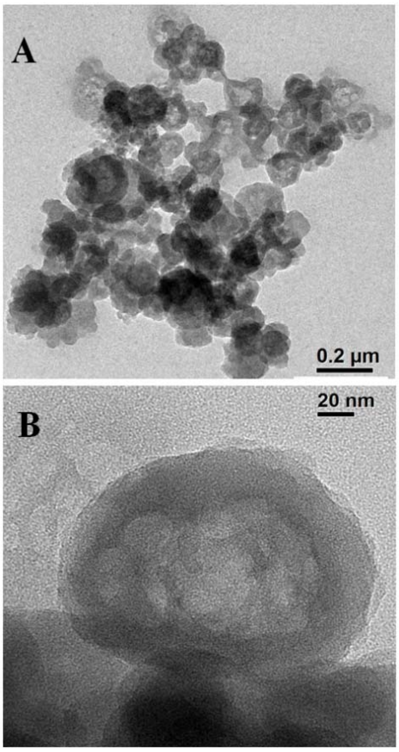
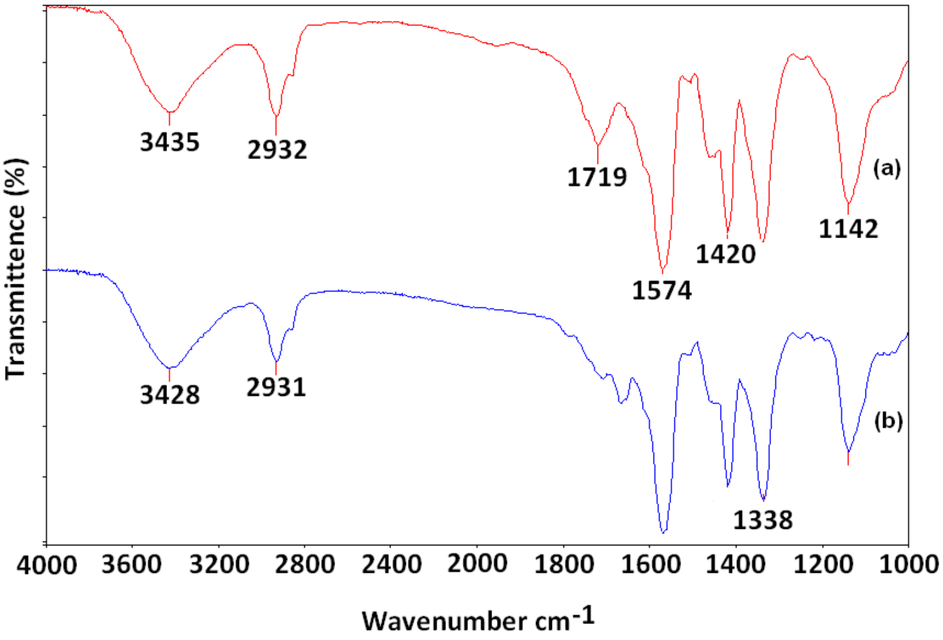
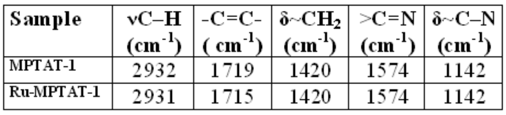


Figure 5. HR TEM images of Ru-MPTAT-1.

Bonding and framework structure

FT IR spectra of both mesoporous polymers MPTAT-1 and Ru-MPTAT-1 are shown in Figure 6. Both the samples showed two distinct C–H vibrations in the region 2932–2950 cm^{-1}, corresponding to non-identical C–H bonds in the triazine framework. Both samples exhibited very strong band at 1574 cm^{-1} due to ring >C=N stretching vibration together with two additional sharp peaks at 1142 cm^{-1} (δ~C–N) and 1420 cm^{-1}(δ~CH_2). Further, the allylic double bond (-C=C-) stretching of 2,4,6-triallyloxy-1,3,5-triazine moiety at 1840 cm^{-1}, has disappeared and the intensity of another at 1719 cm^{-1} has diminished considerably, suggesting near completion of polymerization reaction. All the framework vibrations are assigned in tabular form at the bottom of the FT IR spectra and this result suggested the presence of 2,4,6-triallyloxy-1,3,5-triazine moiety in MPTAT-1 and Ru-MPTAT-1 materials.





Sample	νC–H (cm^{-1})	-C=C- (cm^{-1})	δ~CH_2 (cm^{-1})	>C=N (cm^{-1})	δ~C–N (cm^{-1})
MPTAT-1	2932	1719	1420	1574	1142
Ru-MPTAT-1	2931	1715	1420	1574	1142

Figure 6. FT IR spectra of MPTAT-1 (a) and Ru-MPTAT-1 (b). Vibrations bands are tabulated at the bottom of the spectra.

Thermal analysis:

The quantitative estimation of the organic content and the framework stability of the Ru-MPTAT-1 sample is obtained from the thermogravimetric (TG) and differential thermal analysis (DTA). TGA-DTA plots of Ru-MPTAT-1 are shown in Figure 7. The TGA of this material showed the first weight loss below 100 ^{0}C due to desorption of physisorbed water. This was followed by a gradual decrease in the weight after 250 ^{0}C. Thus this thermal analysis data suggested that Ru-MPTAT-1 sample is stable up to 250 ^{0}C. Above 250 ^{0}C Ru-MPTAT-1 structure collapse involving two major steps corresponding to the collapse of the mesostructure and the polymeric framework.

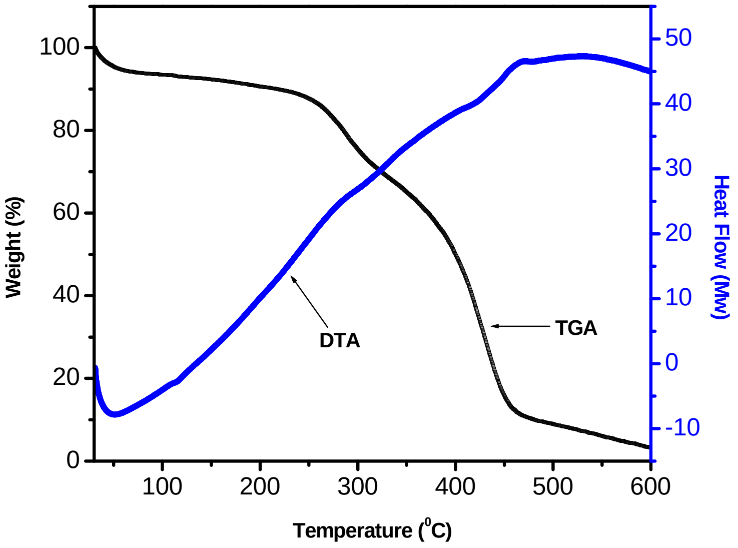


Figure 7. TGA (a) and DTA (b) profiles of Ru-MPTAT-1 material.

XPS analysis

In Figure 8, XPS data of Ru-MPTAT-1 material is shown. XPS spectrum of Ru-MPTAT-1 shows two major peaks with binding energies 286.4 eV and 532.2 eV. Mild peak at *ca*. 400 eV is attributed to the N 1s of triazine nitrogen atoms. The binding energies of 284.1 and 280.0 eV are usually observed for the Ru $3d_{3/2}$ and Ru $3d_{5/2}$ photoelectron lines for metallic ruthenium.[37] Observed main peak at 286.4 eV could be assigned due to the combination of C 1s of the carbon atoms of the organic polymeric network and Ru $3d_{3/2}$ in Ru-MPTAT-1. On the other hand in the Ru 3d region (Figure 8A) weak peak at 277.8 eV could be assigned due to Ru $3d_{5/2}$ of Ru(II) species present at the surface of the polymeric network.[38] Thus, this X-ray photoelectron spectroscopic result suggested that the +2 oxidation state of ruthenium is present in our Ru-grafted mesoporous polymer Ru-MPTAT-1.

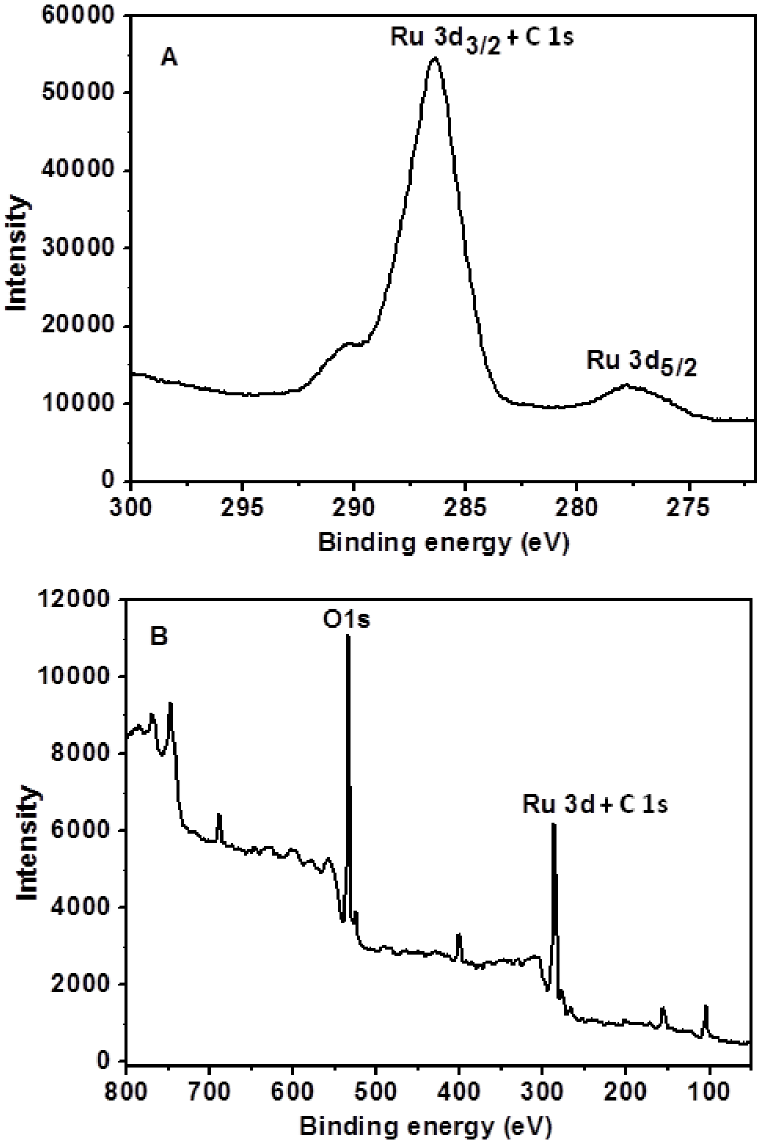


Figure 8. XPS spectra of Ru 3d region (A) and full scale (B) pattern of Ru-MPTAT-1.

UV-vis spectroscopy study

UV-vis absorbance spectrum of MPTAT-1 exhibits no strong characteristic absorbance, except two very weak peaks at 207 and 266 nm due to very weak π→π* transitions. But a distinguishable change in absorbance is observed in case of Ru-MPTAT-1 material (Figure 9). This material displays two intense absorptions in the region 250-650 nm which can be assigned due to the metal to ligand charge transfer along with intra-ligand transitions. The high intensity bands with peaks at around 340 and 256 nm has been designated as n→π* and π→π* transitions, respectively. This phenomenon could be due to the relative destabilization of the ruthenium t_{2g} orbital possibly due to the electron donation from the two anionic chloride ligands to ruthenium center.[39,40]

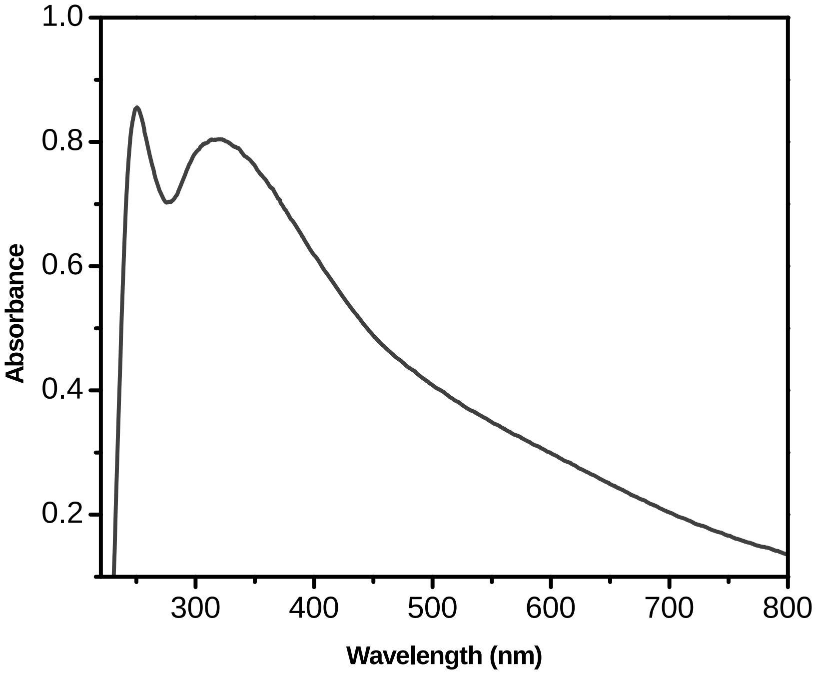


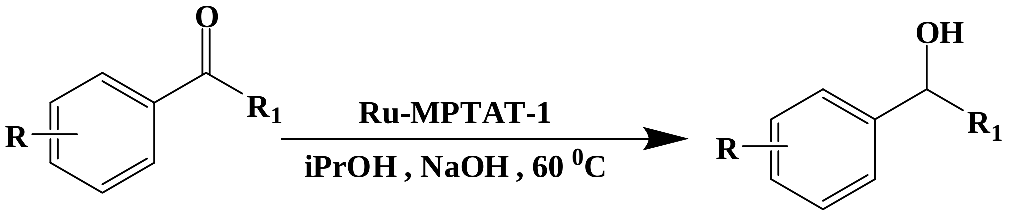
Figure 9. UV-Visible absorbance of Ru-MPTAT-1.

Catalytic Activity

Since mesoporous materials supported with active Pd metal sites exhibit high catalytic activity in a wide range of important reactions,[33] we have explored the catalytic activity of Ru-MPTAT-1 in the C–C cross-coupling reactions of different aryl halides and transfer hydrogenation of ketons in the presence of NaOH as base.

Catalytic transfer hydrogenation of ketones

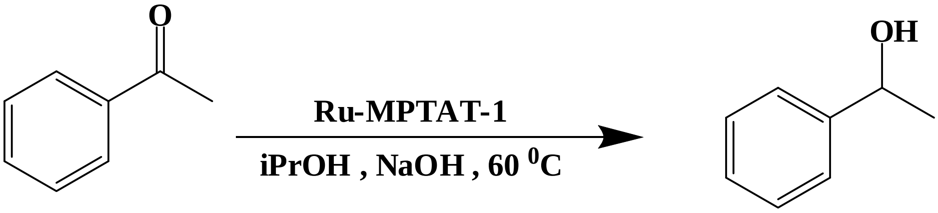
Ruthenium mediated transfer hydrogenation reactions are found to be effective catalytic systems in which hydrogen is transferred from one organic molecule to another under liquid phase reaction conditions and this made us to carry out this reaction over Ru-MPTAT-1. The catalytic activity of Ru-MPTAT-1 in the transfer hydrogenation of various aliphatic and aromatic ketones in the presence of isopropanol and base as promoter has been explored (Scheme 2). The reaction conditions for the transfer hydrogenation of acetophenone have been optimized. In order to optimize the reaction conditions, different solvents and bases were studied.



Scheme 2. Ru-MPTAT-1 catalyzed transfer hydrogenation of carbonyl compounds.

We have carried out the transfer hydrogenation over Ru-MPTAT-1 in the presence of various solvents and NaOH as a base, and the results are summarized in Table 1. Methanol, ethanol, and isopropanol were taken for investigations and isopropanol is found to be a suitable reducing agent for the maximum conversion of acetophenone. As seen in Table 1, the use of methanol resulted in poor conversion of the substrate (entry 1) when compared to ethanol and isopropanol. Interestingly, the reaction performed using isopropanol (iPrOH) as the hydride donor gave the overall the highest yield. The effect of the bases on the catalytic performance of this system has been investigated in details. In transfer hydrogenation, the base facilitates the formation of ruthenium alkoxide by abstracting proton from the alcohol and subsequently alkoxide undergoes β-elimination to give ruthenium hydride, which is an active species in this reaction. This mechanism has been proposed by several workers for the ruthenium catalyzed transfer hydrogenation reaction by metal hydride intermediates.[41] The substrate was allowed to react with a catalytic amount of complex in the presence of different bases like NaOH, KOH, LiOH, K_2CO_3 and Et_3N, with isopropanol (Table 1). It was found that the use of NaOH and KOH leads to 81-93% of conversion (entries 3 and 4). In the absence of a base, no conversion of ketones into alcohol was observed (entry 8). Similarly, the use of triethylamine as base also leads to trace conversion (entry 6). As a result NaOH was selected as the optimum base. We observed the best yield in the transfer hydrogenation reaction of acetophenone by using NaOH as base iPrOH as solvent at 60 ^{0}C for 5 h.

Table 1. Optimization of Reaction Conditions[a]

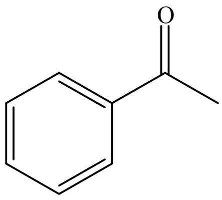
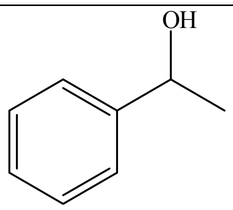


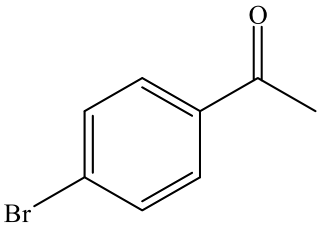
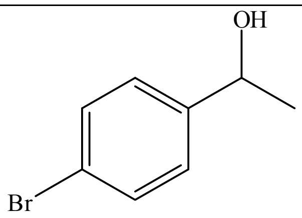
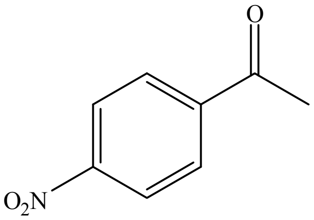
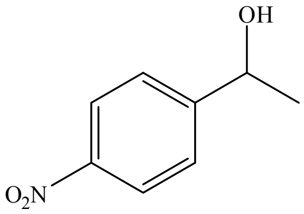
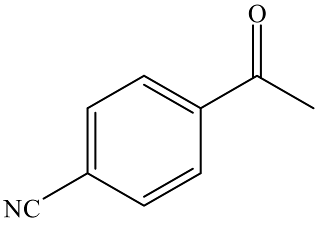
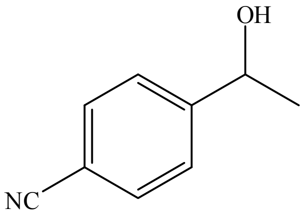
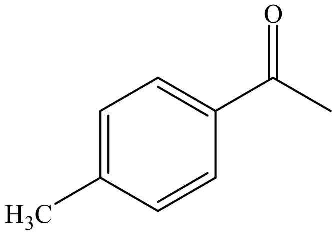
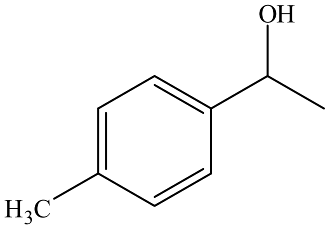
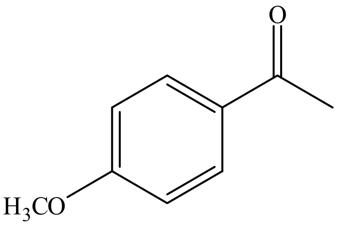
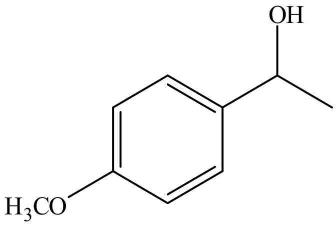
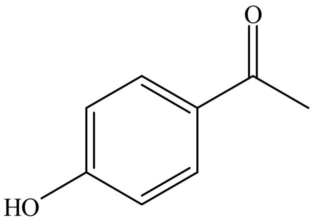
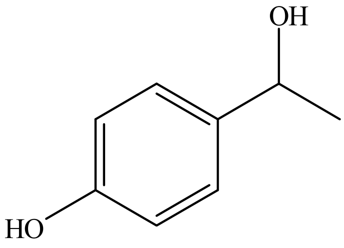
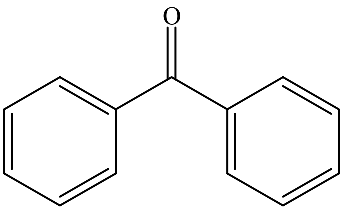
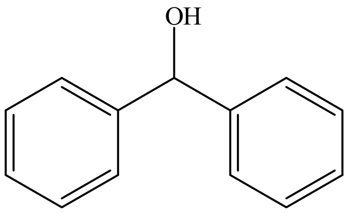
Entry	Alcohol	Base	Yield (%)[a]
1	MeOH	NaOH	30
2	EtOH	NaOH	48
3	iPrOH	NaOH	93
4	iPrOH	KOH	81
5	iPrOH	LiOH	43
6	iPrOH	Et_3N	Trace
7	iPrOH	K_2CO_3	38
8	iPrOH	-	-

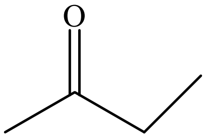
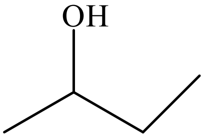
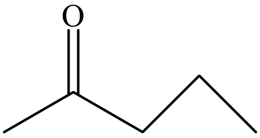
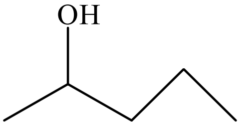
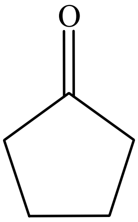
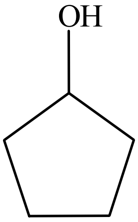
[a]Reactions condition: acetophenone (1 mmol), Ru-MPTAT-1 (0.05g), and base (0.4 mmol), solvent (8 ml), temperature (60 ^{0}C), time 5h, N_2 atom . [b]Yield determined by GC and GCMS analysis.

The transfer hydrogenation reaction of a series of carbonyl compounds have been carried out over Ru-MPTAT-1 using i-PrOH and NaOH at 60 ^{0}C and the results are summarized in Table 2. All the reactions are carried out under identical conditions to allow reasonably good comparison of results. The products are identified by GC and GC-MS after doing the required workup. The complex catalyzes the transfer hydrogenation of ketones to their corresponding alcohols with good to excellent conversions in all the cases. Acetophenone with different substituent of varying electronic properties are efficiently reduced to the corresponding secondary alcohols in excellent conversions. The presence of electron-withdrawing or electron-donating substituent on the aromatic ring has significant effect in the conversion. In general, electron-withdrawing substituent (4'-bromo, 4'-chloro, 4'-nitro and 4'-cyano) on the aryl ring gave higher conversions (entries 2-4) when compared to that of acetophenone whereas electron-donating substituent (4'-methyl, 4'-methoxy and 4'-hydroxy) on the ring gave lower conversions (entries 5-7) than that of acetophenone. On the other hand, benzophenone is quantitatively reduced to 1,1-diphenylmethanol and shows the conversion of 82% (entry 8). Further, ruthenium complex has been demonstrated to be a very active catalyst toward a variety of alkyl ketones. 2-Butanone and 2-pentanone underwent transfer hydrogenation to afford the corresponding alcohol in 65% and 69% respectively (entry 9-10). Similarly, the Ru-MPTAT-1 shows good catalytic activity for the transfer hydrogenation of cyclic ketones. Particularly, 1-cyclopentanone has been reduced to 1-cyclopentanol almost quantitatively over Ru-MPTAT-1 (entry 11).

Table 2. Catalytic Transfer Hydrogenation of carbonyls over Ru-MPTAT-1[a]

Entry	Substrate	Product	Conversion (%)[b]
1			93

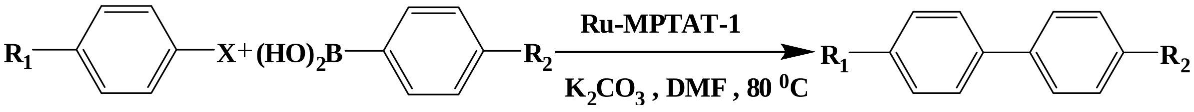
2			94
3			97
4			95
5			89
6			85
7			84
8			82

9			65
10			69
11			90

[a] Reactions condition: acetophenone (1 mmol), Ru-MPTAT-1 (0.05g), and NaOH (0.4 mmol), iPrOH (8ml), temperature (60 ^{0}C), time 5h, N_2 atom.
[c] Yield determined by GC and GCMS analysis.

Suzuki–Miyaura cross-coupling reaction

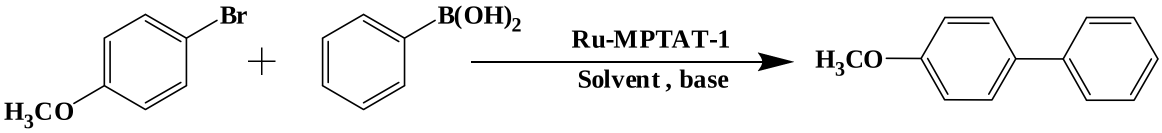
Suzuki–Miyaura cross-coupling reaction represents a very powerful method for the C-C bond formation reaction in the organic synthesis. Construction of biaryl compounds via the Suzuki–Miyaura reaction is an interesting area in organic synthesis. The importance of biaryl units as molecular components in pharmaceuticals, herbicides and natural products, as well as in engineering materials such as conducting polymers, molecular wires and liquid crystals, has attracted enormous interest. We started our investigation for Suzuki–Miyaura reaction (Scheme 3) with the coupling of aryl halides and phenylboronic acid as model reaction in presence of ruthenium catalyst. In order to optimize the reaction condition, the performance of a ruthenium-catalyzed Suzuki–Miyaura reaction is known to be governed by the number of factors such as the bases, solvents, reaction temperatures etc.



Scheme 3. Ru-MPTAT-1 catalyzed Suzuki–Miyaura cross-coupling reactions

To verify the solvent effect in Suzuki–Miyaura cross-coupling reactions, a series of reactions were investigated by taking this model reaction over Ru-MPTAT-1 in different solvents. Quantitative yields were observed with polar solvents such as DMF and methanol (Table 3). On the contrary, unsatisfactory yields were obtained with nonpolar solvents like toluene, THF or *p*-xylene. The catalytic activity was also observed in water and the desired product was obtained in 42% yield (Table 1, entry 7). Since the starting 4- bromoanisole and the biphenyl product had poor solubility in water, but high solubility in DMF, presence of DMF could accelerate the reaction rate. Consequently, DMF was chosen as the medium of choice for this coupling. The effect of the added base on the catalytic performance of this system was investigated by employing various bases. Comparison of inorganic bases utilized showed that carbonate bases were more stable than the other ones. Within a short time the reaction proceeded in high yield in presence of Na_2CO_3 or K_2CO_3. We found that using K_2CO_3 as base in DMF at 80 ^{0}C gave the coupled product in 96% yields. The other inorganic bases such as NaOH, K_3PO_4, NaOAc and organic bases like Et_3N were not as effective as K_2CO_3, only affords moderate to low yields of coupling products (entries 8-11). As a result, K_2CO_3 was selected as the optimum base. In the absence of base, no coupling reaction was observed (entry 12). Thus, the optimized conditions for the Suzuki cross-coupling reactions reaction are K_2CO_3 as base and DMF as solvent at 80 ^{0}C.

Table 3. Optimization of Reaction Conditions for C-C coupling reactions[a]

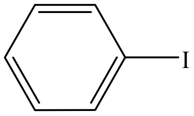
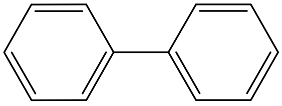
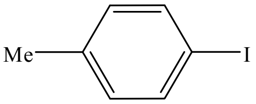
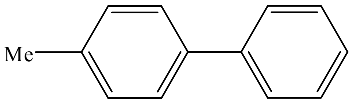
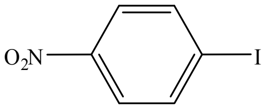
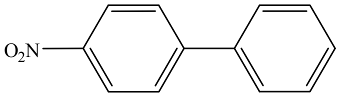
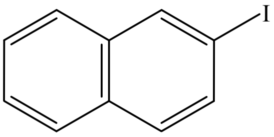
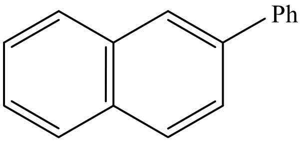
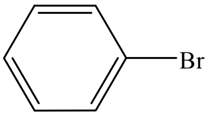
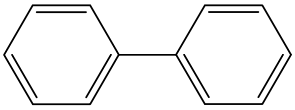
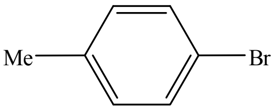
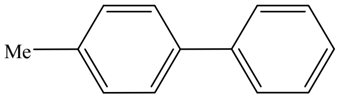
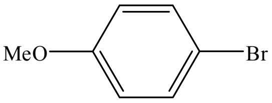
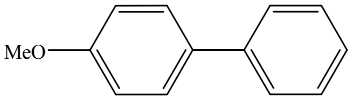
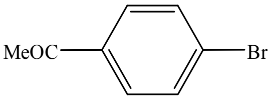
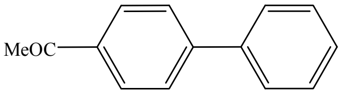


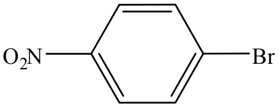
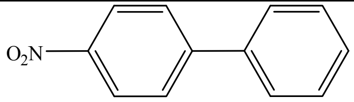
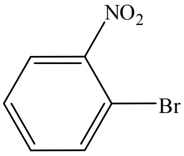
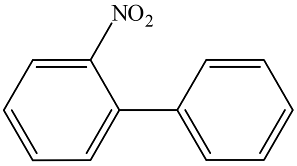
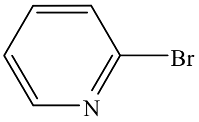
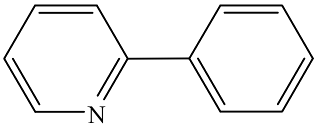
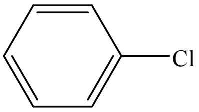
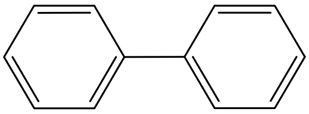
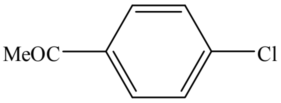
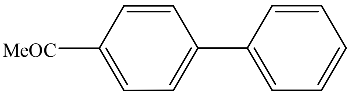
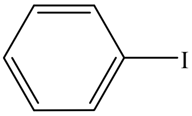
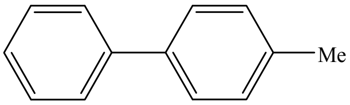
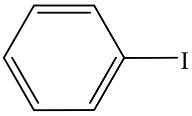
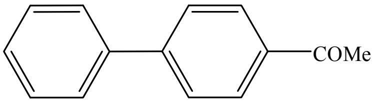
Entry	Solvent	Base	Yields (%)[b]
1	DMF	K_2CO_3	96
2	Toluene	K_2CO_3	12
3	Methanol	K_2CO_3	54
4	Acetonitrile	K_2CO_3	25
5	ρ-xylene	K_2CO_3	10
6	THF	K_2CO_3	12
7	H_2O	K_2CO_3	59
8	DMF	Na_2CO_3	80
9	DMF	NaOH	27
10	DMF	NaOAc	36
11	DMF	Et_3N	13
12	DMF	-	no reaction

[a] Reaction conditions: 4-bromoanisole (1.0 mmol), phenylboronic acid (1.5 mmol), Ru-MPTAT-1 (0.05g), base (2.0 mmol), solvent (5ml). Yields were determined by GC and GCMS analysis.

To examine the scope of this coupling reaction, a variety of aryl halides were coupled with different phenylboronic acids in DMF in the presence of Ru-MPTAT-1 using K_2CO_3 as base. The experimental results are summarized in Table 4 (^{1}H NMR: Supporting information). A control experiment indicated that the coupling reaction did not proceed in the absence of catalyst. Aryl halides bearing either electron-donating or electron-withdrawing substituents in the *para* positions, afforded the corresponding biphenyls in good to excellent yields. Heteroarylbromide, 2-bromopyridine, was coupled efficiently with phenylboronic acid to give the desired product in excellent yield (Table 4, entry 11). The cross-coupling of sterically hindered arylhalides, 2-iodonaphhalene and 2-nitro bromobenzene also proceed quite well (Table 4, entries 4, 10).

Table 4. Suzuki–Miyaura cross-coupling reaction of aryl halides and arylboronic acids using Ru-MPTAT-1[a]

Entry	ArX	Product[b]	Time (h)	Yield (%)[c]
1			5	96
2			5	89
3			5	95
4			6	65
5			6	89
6			8	70
7			8	83
8			6	86

9			6	88
10			8	78
11			6	79
12			12	47
13			12	39
14			8	81
15			8	86

[a]Reaction conditions: Aryl halides (1.0 mmol), phenylboronic acid (1.5 mmol), Ru-MPTAT-1 (0.05g), K_2CO_3 (2.0 mmol), DMF (5ml).; All the reactions were carried out in air. [b]Products were identified by comparison of their IR, GC-MS and ^{1}HNMR spectral data those reported in the literature. [c]Yield of product was determined by GC and GC-MS analysis using dodecane as internal standard.

Although there are some efficient Ru-based heterogeneous catalysts like inorganic SiO_2 supported Ru(II) complex for efficient transfer hydrogenation of ketones[42] and Suzuki-Miyaura cross-coupling reactions,[43] the use of Ru-grafted mesoporous organic polymer in both these reactions for the synthesis of value added fine chemicals are rarely found in literature. O and N donor sites of the 2,4,6-triallyloxy-1,3,5 triazine moiety of the polymeric framework could chelate the reactive Ru(II) sites strongly at the mesopore surface (Scheme 1), leading to high catalytic activity.

Recycling of Catalyst

For a heterogeneous catalyst, it is important to examine its ease of separation, recoverability and reusability. The reusability of the mesoporous Ru-MPTAT-1 catalyst was investigated in transfer hydrogenation and Suzuki–Miyaura cross coupling reactions. After each run the filtrate was concentrated and the resulting residue was purified. After a simple wash using ethyl acetate and dried, the catalyst was reused for the next run and almost consistent activity was observed for next six consecutive cycles (Figure 10, reaction conditions are given in the footnote). The strong interaction between ruthenium and the highly functionalized polymeric surface due to the presence of the three N-atoms in the triazine moiety and the three allylic O-atoms, facilitates strong coordination with the Ru centres. This prevents the leaching of Ru(II) species during the catalytic reactions, rendering highly activity and selectivity of the catalyst. As seen from the figure that the catalyst can be efficiently recycled and reused for repeating cycles without appreciable decrease in product yield.

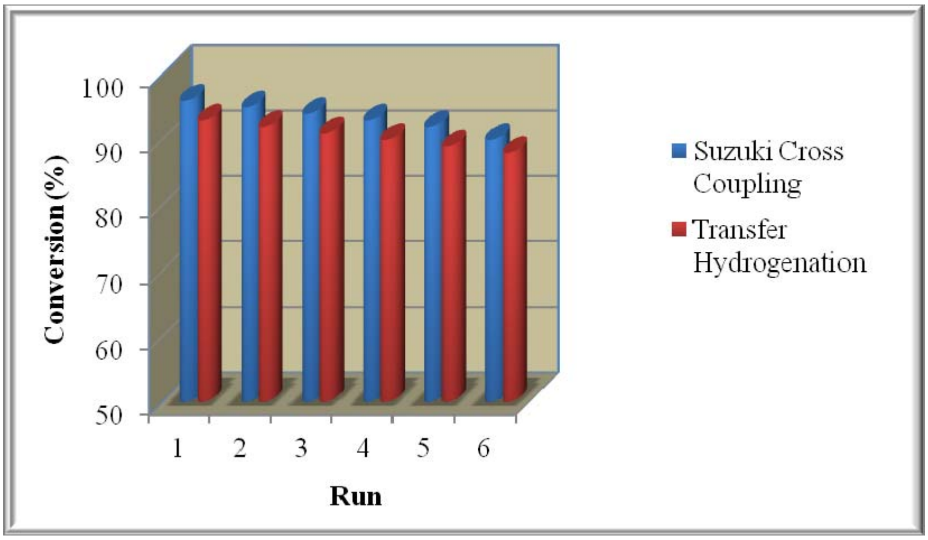


Figure 10. Recycle efficiency of Ru-MPTAT-1 for Suzuki–Miyaura cross-coupling and transfer hydrogenation reactions. Reactions condition for the transfer hydrogenation reactions: acetophenone (1 mmol), Ru-MPTAT-1 (0.05 g), and NaOH (0.4 mmol), iPrOH (8ml), temperature (60 ^{0}C), time 5h, N_2 atom; for Suzuki–Miyaura cross-coupling: iodobenzene (1.0 mmol), phenylboronic acid (1.5 mmol), Ru-MPTAT-1 (0.05 g), K_2CO_3 (2.0 mmol), DMF (5 ml), temperature (80 ^{0}C).

Proof of heterogeneity of the catalyst

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

To examine whether ruthenium was being leached out from the solid support to the reaction medium during the course of the catalytic reaction, a controlled experiment has been carried out in the transfer hydrogenation reaction over Ru-MPTAT-1 mesoporous catalyst to know whether the reaction proceeded in a heterogeneous or a homogeneous fashion.[44] For the rigorous proof of heterogeneity, a test was carried out by filtering catalyst from the reaction mixture at 60 ^{0}C after 3 h and the filtrate was allowed to react up to the completion of the transfer hydrogenation reaction (6 h). It was noticed that after filtration of the catalyst from the reactor at the reaction temperature, transfer hydrogenation reactions do not proceed further. Atomic absorption spectrometric analysis of the supernatant solution of the reaction mixture collected by filtration also confirmed the absence of ruthenium ions in the liquid phase. All these results clearly demonstrate that surface bound Ru remained intact within the mesoporous solid framework and even a trace amount of Ru could not be leached out from the solid catalyst to the solution. Thus our novel polymeric Ru-MPTAT-1 is an outstanding heterogeneous catalyst for the transfer hydrogenation in the presence of isopropyl alcohol.

Conclusions

In summary, we have successfully synthesized a novel Ru-grafted mesoporous organic polymer through facile and simple polymerization of 2,4,6-triallyloxy-1,3,5-triazine using APS as radical initiator and SDS as the template under acidic pH conditions followed by the impregnation of ruthenium at the polymer surface. This Ru-grafted mesoporous material has been successfully used as a heterogeneous catalyst for the transfer hydrogenation reaction of carbonyl compounds and Suzuki-Miyaura cross-coupling reaction of aryl halides with excellent yields. The catalytic system reported herein offers a number of advantages, such as excellent stability, easy separation from the reaction mixture by filtration, reusability for several times with very minimum loss of activity. Further work is in progress to broaden the scope of the ruthenium grafted mesoporous polymer as catalytic system for other organic transformations.

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Ruthenium-grafted triazine functionalized mesoporous polymers: A highly efficient and multifunctional catalyst for transfer hydrogenation and Suzuki–Miyaura cross-coupling reactions

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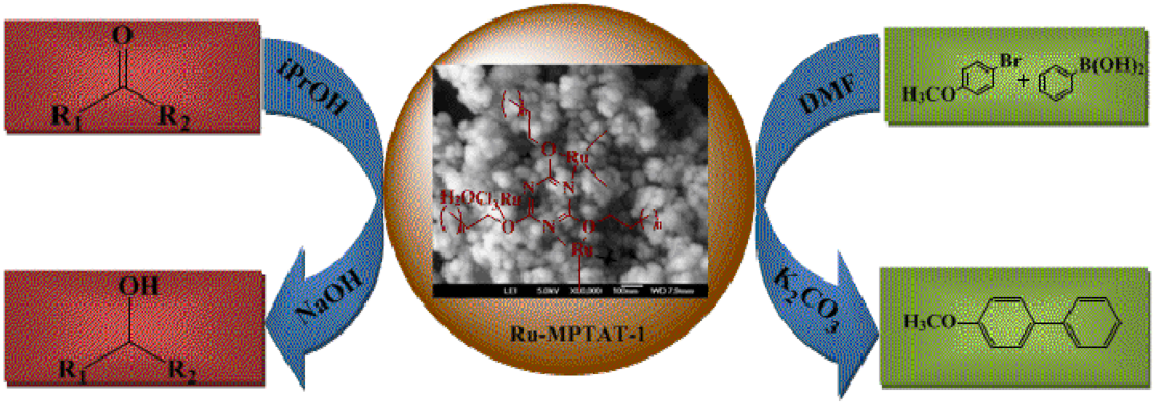

A new ruthenium grafted mesoporous organic polymer catalyst Ru-MPTAT-1 has been synthesized via the simple and facile pathways and it showed excellent catalytic activity in transfer hydrogenation and Suzuki–Miyaura cross-coupling reactions.