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Silver nanoparticles embedded over mesoporous organic polymer as highly efficient and reusable nanocatalyst for the reduction of nitroarenes and aerobic oxidative esterification of alcohols

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ABSTRACT

Silver nanoparticles (Ag-NPs) have been finely dispersed at the mesoporous organic polymer via post-synthetic chemical grafting over mesoporous poly-triallylamine (MPTA-1). The resulting Ag-MPTA-1 nanomaterial has been characterized by elemental analysis, powder x-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), UV–vis diffuse reflectance spectroscopy (DRS), thermogravimetric analysis (TGA), EPR spectroscopy and AAS elemental analysis. The Ag-MPTA-1 acts as an efficient heterogeneous nanocatalyst in the reduction of substituted nitrobenzenes via transfer hydrogenation. The material also showed excellent catalytic activity in one-step catalytic oxidative esterification of primary alcohols using molecular oxygen as a green oxidant. The catalyst is air-stable, inexpensive, easy to prepare and reused several times without significant decrease in activity and selectivity.

1. Introduction

Chemical grafting of a homogeneous metal complex on a porous solid surface is a versatile strategy to create a site-isolated metal complex with a regulated metal-coordination structure having unique catalytic properties [1–5]. The advantage of a supported metal-complex catalyst is not only in making the separation of the catalyst from the reaction medium easy but also improves of the activity and stability of the catalyst due to the site isolation of the active metal site. Further, this leads to the formation of reusable new metal coordination structure on a support surface or supported metal nanoparticles with more or less uniform particle size distribution [6–10].

There are several methods to chemically coordinate metal complexes on solid surfaces and the grafting over mesoporous polymers bearing the donor atoms is one of the typical ways to obtain the immobilized metallic nanoparticles [11]. These supported metallic nanoparticles have drawn intense attention in recent years as catalysts in many organic transformation reactions because of their high surface area-to-volume ratio, low coordination number, and easy access to a large number of active sites [12–16]. Among the different noble metal nanoparticles, stabilized silver nanoparticles (Ag-NPs) have been widely employed as catalysts for a wide range of organic reactions. They show good catalytic activity towards coupling, cycloaddition, sigmatropic rearrangement, cycloisomerization and nitrene transfer reactions [17]. Various approaches have been attempted in the last few years for the synthesis and fabrication of Ag-NPs stabilized over a wide variety of mesoporous materials, such as alumina, titania, silica, carbon, etc. due to their easy separation and recovery from the reaction medium [18–20].

The catalytic hydrogenation of nitro compounds is one of the most important chemical reactions as the product amines are potent intermediates for the synthesis of various industrial products like agrochemicals, pharmaceuticals, dyes, polymers, rubbers, photographic developers, corrosion inhibitors, anticorrosion lubricants, hair-dye products and many more [21–23]. The traditional synthesis routes for reduction of nitrobenzenes proceeds through catalytic hydrogenation, electrolytic reduction, metal mediated reductions etc [24]. But many of these processes utilize potentially explosive H_2 gas, high pressure reactors, hazardous and harmful materials like mineral acids etc. are carried out at a moderately high pressure [25,26] and temperature [26,27], which lead

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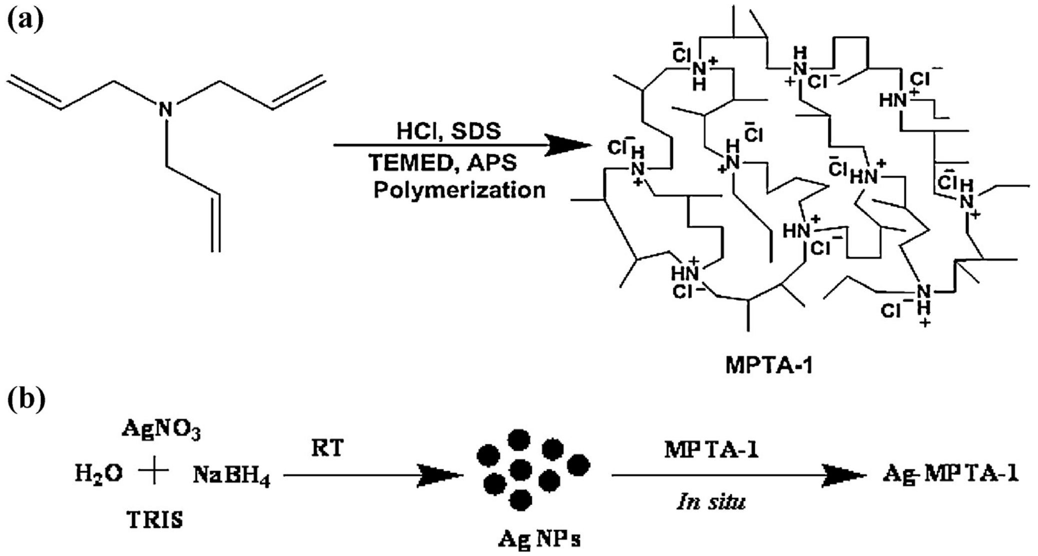


Scheme 1. Schematic diagram for the synthesis of mesoporous polymer MPTA-1 (a) and loading of Ag-NP on it at room temperature to obtain Ag-MPTA-1 nanocatalyst (b).

to low selectivity for the desired product due to nonselective hydrogenation of other functional groups. In this context, transfer hydrogenation is advantageous over the traditional hydrogenation reaction in respect of selectivity, where an alcohol like isopropanol, considered as one of the green solvents, acts as solvent as well as the source of hydrogen and the reaction takes place at atmospheric pressure and relatively low temperature [24,28,29]. Similarly, aromatic esters have always attracted a great deal of interest in organic synthesis as intermediates such as liquid crystal polymers, cosmetics, pharmaceuticals, agrochemicals, and food additives because of their versatility [30]. Methyl esters in particular are very useful from the viewpoints of atom economy, versatility for further transformations and chemical industry specially, in odoriferous components in flowers and fruits [31] and biodiesel intermediates [32]. The present ecological standards increase the pressure to the development of environmentally benign methods. The use of molecular oxygen or hydrogen peroxide in catalytic oxidation reactions has attracted considerable attention in this context [33–35]. In this scenario, a more elegant and environmentally benign method for the preparation of methyl esters based on the one-step direct oxidative esterification of primary alcohols is very demanding [36–38].

Herein, we wish to report the synthesis of a robust and non air sensitive silver nanoparticles embedded mesoporous polytriallylamine nanocatalyst Ag-MPTA-1 and its excellent catalytic activity in the reduction of substituted nitrobenzenes via transfer hydrogenation and aerobic oxidative esterification of alcohols in presence of molecular oxygen.

2. Experimental

2.1. Materials

Triallylamine (TAA) and tris(hydroxymethyl) aminomethane (TRIS) were obtained from Sigma–Aldrich. *N,N,N',N'*-tetramethylenediamine (TEMED) and ammonium persulfate (APS) were obtained from Loba Chemie, India and used as received. Sodium lauryl sulfate (SDS) was purchased from Loba Chemie and used as structure-directing agent. Silver nitrate ($AgNO_3$) was purchased from Universal Chemicals, India. Sodium borohydride ($NaBH_4$) was obtained from Spectrochem, India and used as received. All other reagents and substrates were also purchased from Merck, India.

2.2. Synthesis of mesoporous polytriallylamine MPTA-1

Mesoporous polymer MPTA-1 was synthesized through the polymerization of triallylamine under hydrothermal conditions by using APS as radical initiator (Scheme 1) [39]. In a typical synthesis 1.17 g of SDS was dissolved in 25 ml of water with constant stirring followed by the addition of 1.12 g of TAA. Then 0.47 g TEMED was added in this mixture and conc. HCl (12 N) was also added dropwise until a clear solution is obtained. Addition of acid helps the protonation of the N-atoms of the triallylamine molecules, which facilitates the ionic interaction with the sulfonate group of the SDS molecules. The pH of the gel was maintained nearly around 7.0. Then 3.71 g of APS dissolved in 8 ml of water was added quickly into the solution under vigorous stirring. A white precipitate was appeared immediately. The resultant mixture was stirred for another 1 h and then autoclaved at 348 K for 3 days without stirring. The observed final pH of the synthesis gel was ca 4.0–5.0. After the hydrothermal treatment the product was filtered and washed with deionized water for several times. Resultant solid was dried under vacuum to obtain mesoporous polymer MPTA-1.

We have chosen TAA as a precursor for the synthesis of MPTA-1 because one TAA molecule contains three olefin double bonds in each of its branches; this polymerization process gives random cross-linking, leading to a high stability of the organic polymer framework of MPTA-1. MPTA-1 has mesoporosity, thus Ag-NPs can be immobilized at the surface of mesopores and can get stabilized through the interaction between surface of the NPs and N-atoms of MPTA-1 framework.

2.3. Synthesis of colloidal Ag nanoparticles

In a typical synthesis, 0.1 ml of an aqueous solution of 1% $AgNO_3$ was taken in 10 ml of water containing 0.5 mg TRIS and was stirred for 2 min. Then, 0.25 ml of an aqueous solution of $NaBH_4$ (0.08%) was added drop-wise under stirring. The stirring was continued for another 10 min, and the resulting nanocolloid was stored at 4 °C.

2.4. Synthesis of Ag-MPTA-1 nanocatalyst

In a typical synthesis of Ag-MPTA-1, 50 mg of template-free MPTA-1 was dispersed in a 10 ml of TRIS-stabilized Ag-NPs and stirred for 1 h at room temperature. The colour of the colloidal nanoparticles gradually disappeared while stirring. The supernatant solution was colourless after 1 h of stirring at room temperature, whereas the colour of MPTA-1 changed to black, indicating the loading of Ag-NPs onto the surface of MPTA-1. After centrifugation, black coloured Ag-NP loaded mesoporous polymer Ag-MPTA-1 was obtained. This mesoporous material was washed several times with distilled water and dried at room temperature. The loading of Ag-NPs onto MPTA-1 was further confirmed by AAS analysis (0.2 wt%).

2.5. General procedure for the transfer hydrogenation reduction of nitrobenzenes

0.2 mmol of the reactant was dissolved in 20 ml isopropanol followed by the addition of 50 mg of Ag-MPTA-1 and 20 mg NaOH (0.5 mmol) in a 100 ml round bottom flask. The reaction mixture was refluxed at 80 °C for the desired time period under a nitrogen atmosphere. To study the progress of the reaction, the reaction mixtures were collected at different time intervals. The products were quantified by a GC and identified by a GC-MS.

2.6. General procedure for the aerobic oxidative esterification of benzylic alcohols with methanol

In a typical aerobic oxidation, a mixture of benzylic alcohol (0.145 ml, 2.5 mmol), K_2CO_3 (87 mg, 0.4 mmol), methanol (6.0 ml) and Ag-MPTA-1 catalyst (50 mg) were taken in a 50 ml RB flask. The reaction was carried out for 12 h under O_2 atmosphere at 45 °C. 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 four times with ethyl acetate (4 × 15 ml) and the combined organic layers were dried with anhydrous Na_2SO_4 by vacuum. The filtrate was concentrated and the resulting residue was purified by column chromatography on silica gel to obtain the final product.

2.7. Characterization techniques

Powder x-ray diffraction (XRD) patterns of the mesoporous polymer and Ag-MPTA-1 samples were analyzed with a Bruker D8 Advance x-ray diffractometer using Ni-filtered Cu Kα ($\lambda = 0.15406$ nm) radiation. Transmission electron microscopy (TEM) images of the mesoporous polymer were obtained using a JEOL JEM 2010 transmission electron microscope operating at 200 kV. Ag content in Ag-MPTA-1 was estimated by using a Shimadzu AA-6300 atomic absorption spectrometer (AAS) fitted with a double beam monochromator. EPR measurements were performed on a Bruker EMX EPR spectrometer at x-band frequency (9.46 GHz) at room temperature (298 K). Thermogravimetric analysis (TGA) of Ag-MPTA-1 was carried out using a Mettler Toledo TGA/DTA 851e. UV–Vis spectrum of Ag-MPTA-1 was obtained from a Shimadzu UV-2401PC doubled beam spectrophotometer having an integrating sphere attachment for solid samples. The reaction products of the liquid phase reactions were quantified by using a 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.

3. Results and discussion

3.1. Characterization of catalyst

Small angle powder XRD pattern of the sample Ag-MPTA-1 is shown in Fig. 1a. A single and broad diffraction peak is obtained in the small angle XRD having a 2θ value of 2.241°, indicating the presence of the mesophase in the material. The interparticle distance corresponding to this broad diffraction is ca 3.88 nm. Absence of higher order diffraction peak suggested the disorder mesostructure of the sample, same as that of parent MPTA-1. The wide angle x-ray powder diffraction pattern for the Ag-MPTA-1 material is shown in Fig. 1b. The formation of silver nanoparticles was confirmed from this wide angle powder XRD pattern of Ag–MPTA-1. The sharp diffraction peaks at 2θ values 38.84°, 45.04°, 65.43°, 78.08° can be indexed to the diffraction planes (1 1 1), (2 0 0), (2 2 0), (3 1 1) of pure face-centred cubic (fcc) silver [40]. This indicates the presence of face-centred cubic Ag nanoparticles bound at the surface of the polymer matrix. In Fig. 2 HR-TEM images of the Ag-MPTA-1 materials at different magnifications are shown. In this figure silver nanoparticles with diameter 15–20 nm are clearly observed (dark spots) and these are uniformly distributed throughout the specimen grid. The FFT diffractogram of a selected area of the grid is shown in image. Diffraction spots in this FFT pattern suggested crystalline feature of the Ag-nanoparticles bound at the surface of Ag-MPTA-1 and the planes are indexed. Debye–Scherrer equation for average crystallite size calculation is $D = 0.9\lambda/\beta\cos\theta$, where D is the average crystallite size (Å), λ is the x-ray wavelength (CuKα = 1.5406 Å), β is the full width at half maximum (FWHM) in radians and θ is the Bragg diffraction angle of the most intense peak (1 1 1). Using this equation average crystallite size has been estimated to be 15.0 nm which matches well with the HR-TEM data [41].

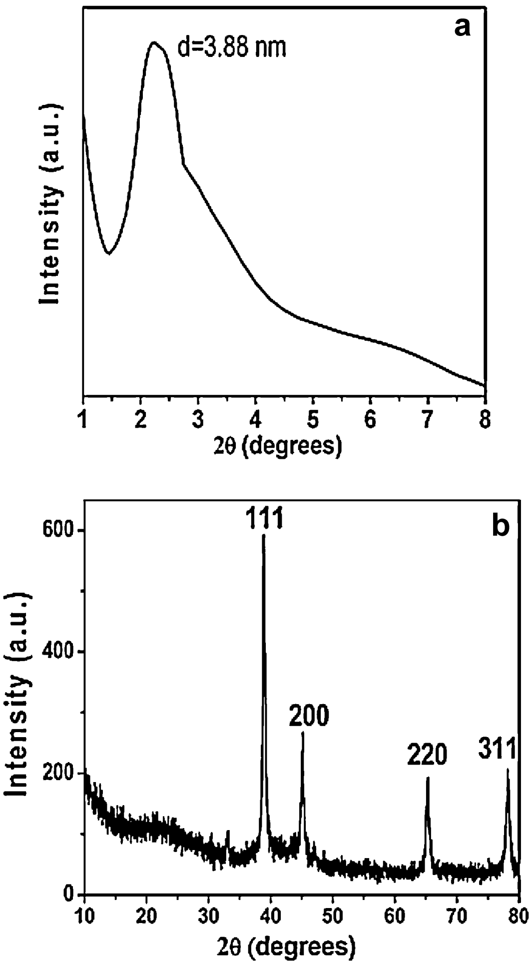


Fig. 1. Small (a) and wide angle (b) powder XRD pattern of Ag -MPTA-1.

In Fig. 3 the EPR spectrum of the Ag-MPTA-1 in solid state at room temperature (298 K) is shown. It provides information on the nature of the metal ion environment in the Ag-grafted mesoporous

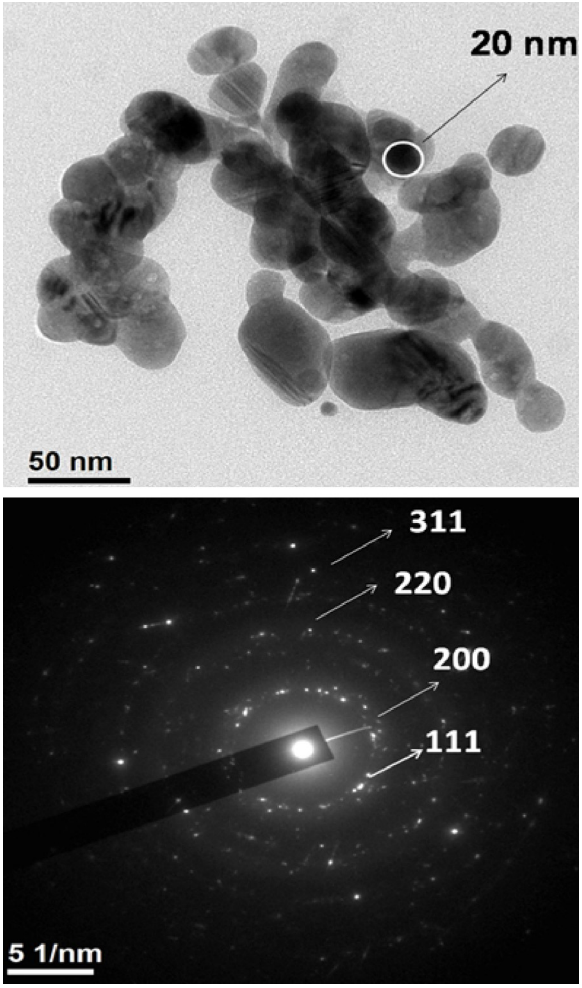


Fig. 2. HR-TEM images of the Ag-MPTA-1 at different magnifications.

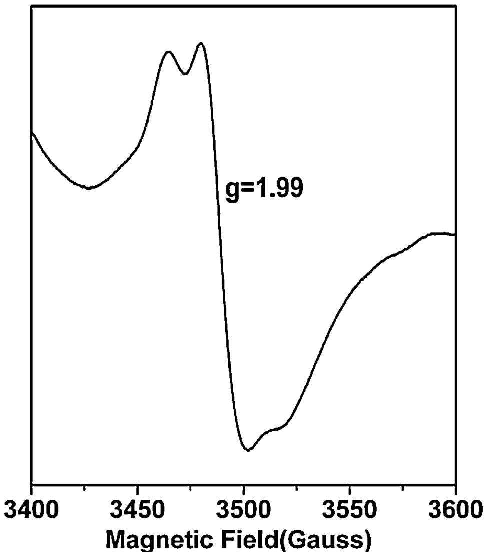


Fig. 3. EPR spectrum of Ag -MPTA-1.

polymer. It shows a symmetric signal and *g* value corresponding to this signal is calculated to be 1.99, which could be attributed to the presence of Ag-nanoparticles embedded into the polymer matrix [42]. UV–vis spectrum (Fig. 4) of the as-prepared Ag-MPTA-1 showed that the colloidal silver thus formed exhibits a strong absorption between 400 and 420 nm, corresponding to the surface plasmon resonance (SPR) of Ag NPs [43] suggesting the formation of Ag NPs on the MPTA-1 surface. Additional absorption bands at 240 and 300 nm could be attributed to the chromophoric organic functionality of the polymer matrix.

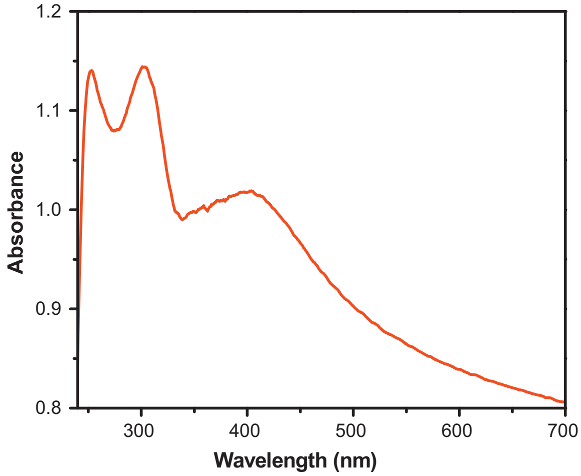


Fig. 4. UV–vis absorbance spectra of Ag-MPTA-1.

The quantitative determination of the organic content and the framework stability of the Ag-MPTA-1 samples are obtained from the thermogravimetric (TGA) and differential thermal analysis (DTA) under N_2 flow (not shown). The TGA of this material showed the first weight loss below 100 °C due to desorption of physisorbed water. This was followed by a gradual decrease in the weight up to 200 °C. Further weight loss above 200 °C corresponds to the collapse of the nanostructure and the polymer together with broad DTA signal. Thus, this thermal analysis result suggested that Ag-MPTA-1 sample is stable up to 200 °C.

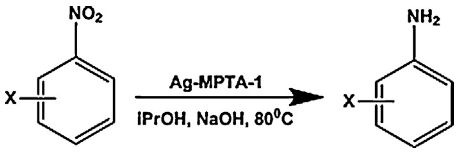
3.2. *Catalytic activity*

Supported metals are useful as heterogeneous catalysts in a wide variety of organic transformation. Specially stabilized nanoparticles, in comparison to bulk solids, have a significantly high catalytic activity and demand for clean technology and sustainability. Thus, we have investigated the catalytic activity of the mesoporous polymer Ag-MPTA-1 in the transfer hydrogenation reduction of substituted nitrobenzenes and one-step catalytic oxidative esterification of primary alcohols using molecular oxygen as a green oxidant.

3.3. *Catalytic transfer hydrogenation reduction of nitrobenzenes*

Among the hydrogenation reactions catalyzed by silver nanoparticles, catalytic hydrogenation of aromatic nitro compounds is very exciting. The use of silver nano-complex as effective catalyst for transfer hydrogenation encouraged us to carry out this type of reaction using mesoporous polymer supported silver nanocatalyst. The effect of mesoporous Ag-MPTA-1 nanocatalyst on their catalytic activity for the hydrogenation of nitrobenzene was investigated as a model reaction (Scheme 2).

For the optimization of the product yield, nitrobenzene was taken as test substrate for different conditions. We have carried out the hydrogenation of nitrobenzene in the presence of various solvents and base and the results are summarized in Table 1. Firstly, we have carried out the transfer hydrogenation 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 was found to be a



Scheme 2. Hydrogenation of nitrobenzenes to amines in the presence of AgNPs-MPTA-1 as nanocatalyst.

Table 1
Optimization of reaction conditions.[a]

Entry	Alcohol	Base	Yield (%)[b]
1	MeOH	NaOH	14
2	EtOH	NaOH	67
3	iPrOH	NaOH	97
4	iPrOH	KOH	78
5	iPrOH	Et_3N	Trace
6	iPrOH	LiOH	32
7	iPrOH	K_2CO_3	28
8	iPrOH	–	–

[a] Reaction conditions: nitrobenzene (0.2 mmol), Ag-MPTA-1 (0.05 g), and base (0.5 mmol), solvent (20 ml), temperature (80 °C), time 10 h, N_2 atmosphere.
[b] Yield determined by GC and GCMS analysis.

suitable reducing agent for the maximum conversion of nitrobenzene. As seen in Table 1, the use of methanol resulted in poor conversion of the substrate (entry 1) when compared to ethanol and isopropanol. Most gratifyingly, the reaction performed using isopropanol (iPrOH) as the hydride donor gave in overall the highest yield. The effect of the bases on the catalytic performance of this system has also been investigated. The substrate was allowed to react with a catalytic amount of complex in the presence of different bases like NaOH, KOH, K_2CO_3, LiOH and Et_3N, with isopropanol (Table 1). It was found that the use of NaOH and KOH leads to 78–91% of conversion (entries 3, 4). In the absence of base, no conversion of nitrobenzene into aniline was observed (entry 8). Similarly, the use of triethylamine as base also leads to trace conversion (entry 5). As a result NaOH was selected as the optimum base. From the above discussions, it can be seen that the best yield was obtained in the reduction of nitrobenzene by using NaOH as base in iPrOH as solvent at 80 °C for 10 h.

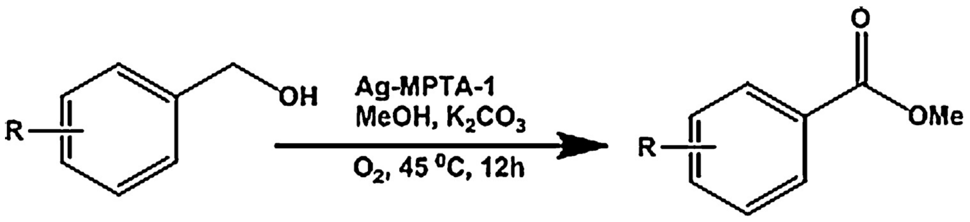
To examine the scope of the Ag-MPTA-1 catalytic system for the reduction of the nitro group, a series of nitroarenes with structurally divergent functional groups were examined. The catalytic system was found to be very efficient regardless of the presence of electron-withdrawing or electron-donating substituents in the aromatic ring. The results are presented in Table 2. Simple unsubstituted nitrobenzene yielded the desired aniline product in 97% yield (Table 2, entry 1). *o*-, *m*- and *p*-nitrophenols gave excellent yields of the corresponding anilines (Table 2, entries 2–4). *m*-Nitrophenol was found to be the most reactive among all the three nitrophenols. Halogenated nitroarenes were selectively reduced to their corresponding halo anilines in good to excellent yields and no dehalogenation of the product was observed which was often encountered with several procedures such as hydrogenation (Table 2, entries 5–11). It was seen that *ortho*-substituted halo nitroarenes displayed somewhat poor reactivity compared to their *para*-substituted counterparts (Table 2, entries 5–7 and 9–11). This proves that our catalytic system is sensitive to steric effects. Further, the Ag-MPTA-1 showed high chemoselectivity in the reduction of the $-NO_2$ group without affecting the –CN and $-COCH_3$ groups (Table 2 entries 14 and 15). Nitroarenes possessing electron-donating groups also afforded excellent yields of the corresponding product (Table 2, entries 12 and 13).

3.4. Aerobic oxidative esterification of benzylic alcohols catalyzed by Ag-MPTA-1

Aromatic esters have always attracted a great deal of interest in organic synthesis as intermediates such as liquid crystal polymers, cosmetics, pharmaceuticals, agrochemicals, and food additives because of their versatility. We started our investigation for aerobic oxidative esterification of benzylic alcohols in methanol as solvent (Scheme 3) as model reaction in presence of silver nano catalyst.

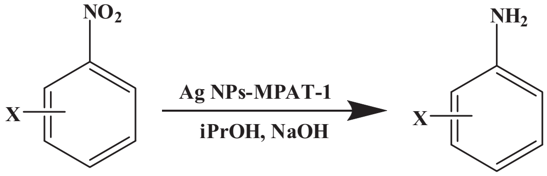
In order to optimize the reaction condition, the performance of a silver-catalyzed aerobic oxidative esterification is known to be governed by the number of factors such as the bases, solvents etc. Benzylic alcohol and methanol were used in the model reaction and molecular oxygen was employed as the oxidant (Table 3). In presence of Na_2CO_3 as base it showed the good result with 71% yield of the desired product 2a and 42% yield of the aldehyde 2b (entry 5) as determined by GC but no selectivity desired product obtained. In absence of base no esterification reaction in MeOH was observed (entry 8). While a stronger base (K_2CO_3) gave the best reactivity with a 95% yield of the ester, as determined by GC and the aldehyde could not be observed (entry 1). To verify the solvent effect in this reaction, a series of reactions were investigated by taking the model reaction in different solvents. Using MeOH as solvent gave the best result with 95% ester and no aldehyde. However, solvents such as EtOH, H_2O, THF and DMSO were not suitable for the reaction and no satisfactory yields were obtained (entries 2–4).

To further test the catalytic performances of the Ag-MPTA-1, the oxidative esterification of other benzylic alcohols over Ag NPs-MPTA-1 catalyst were carried out under O_2 at 45 °C for 12 h. The results are presented in Table 4. Aromatic alcohols containing both electron-donating and -withdrawing groups were converted to the corresponding methyl esters in good to high yields. The conversion of benzyl alcohol was as high as 95% (Table 4, entry 1). For the $-CH_3$ and $-OCH_3$ substituted benzylic alcohols, 89% and 91% conversions were achieved, respectively. For benzylic alcohols containing electron-withdrawing groups, such as $-NO_2$, –Cl, and –Br, the moderate conversions (69%, 34%, and 75%) were still obtained (Table 4, entries 4, 6, and 5). The oxidative esterification of 4-bromobenzyl alcohol resulted in relatively low selectivity (60.0%). The differences in conversion reflect the influences of substituent on the reactivity of substrates. However, an aliphatic alcohol was not oxidized smoothly. In order to examine the limitations of our catalyst, we conducted the oxidative esterification of the less reactive straight-chain alcohols over Ag-MPTA-1 (Table 4,



Scheme 3. Ag-MPTA-1 catalyzed aerobic oxidative esterification reactions.

Table 2
Catalytic reduction of substituted nitrobenzene over Ag -MPTA-1 nanocatalyst[a]



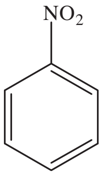
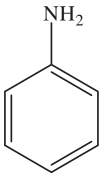
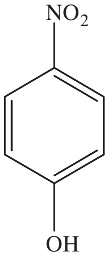
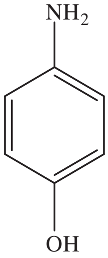
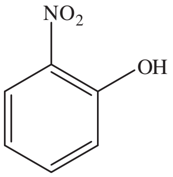
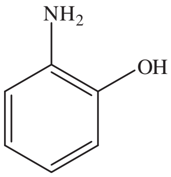
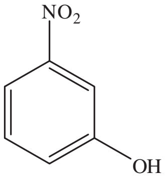
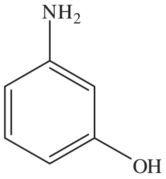
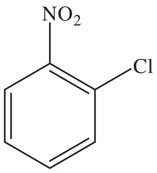
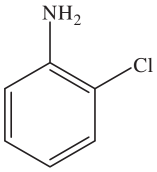
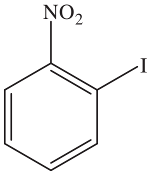
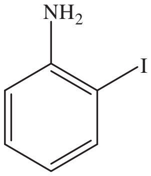
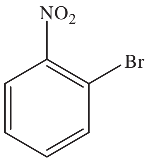
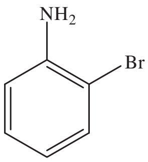
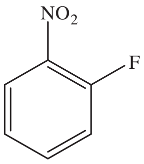
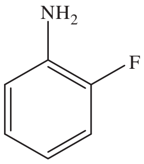
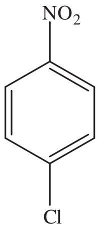
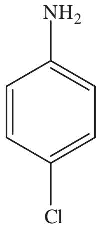
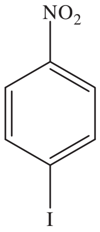
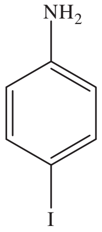
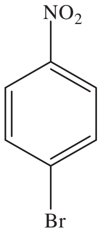
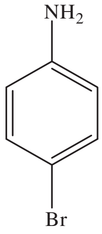
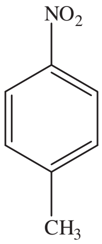
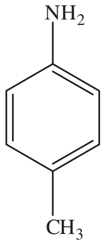
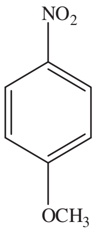
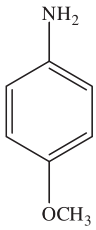
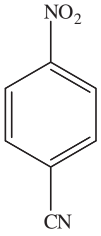
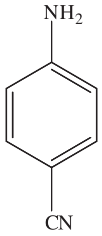
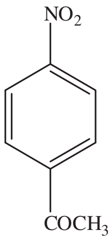
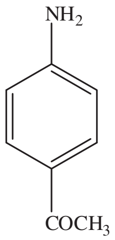
Entry	Substrate	Product	Time (h)	Yield (%)[b]
1			10	97
2			10	96
3			8	97
4			8	98
5			12	81
6			12	85
7			12	86
8			12	83

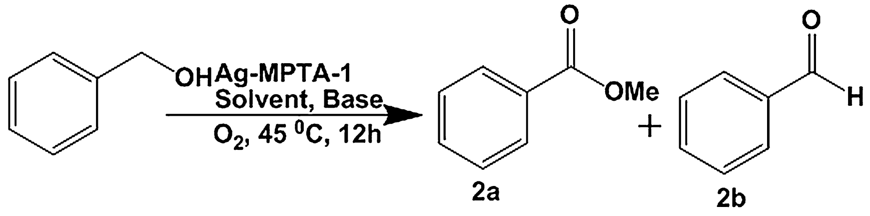
Table 2 (*Continued*)

Entry	Substrate	Product	Time (h)	Yield (%)[b]
9			10	84
10			10	87
11			10	88
12			5	85
13			8	86
14			12	87
15			12	89

[a] Reaction conditions: substrate (0.2 mmol), Ag-MPTA-1 (0.05 g), and NaOH (0.5 mmol), iPrOH (20 ml), temperature (80 °C), N_2 atmosphere.

[b] Yield determined by GC and GCMS analysis.

Table 3
Impact of reaction parameters on the oxidative esterification of benzylic alcohols with methanol.[a]



Entry	Solvent	Base	Yields (%)[b] Ester (%) 2a	 Aldehyde (%) 2b
1	MeOH	K_2CO_3	95	–
2	DMSO	K_2CO_3	–	–
3	THF	K_2CO_3	–	–
4	H_2O	K_2CO_3	24	37
4	EtOH	K_2CO_3	25	13
5	MeOH	Na_2CO_3	71	42
6	MeOH	Cs_2CO_3	54	21
7	MeOH	K_2PO_4	23	37
8	MeOH	–	–	–

[a] Reaction conditions: benzylic alcohol (0.145 ml, 2.5 mmol), base (0.4 mmol), solvent (6 ml), 45 °C, oxygen balloon, time (12 h), Ag-catalyst (50 mg).
[b] Yield of product was determined by GC and GC-MS analysis.

entry 7–9). For n-butanol, a 41% conversion was obtained. The conversions of n-pentanol and n-hexanol could reach 53% and 57%, respectively.

3.5. *Recyclability of Ag-MPTA-1 nanocatalyst*

For a heterogeneous catalyst, it is important to examine its ease of separation, recoverability and reusability. The reusability of the mesoporous Ag-MPTA-1 nanocatalyst was investigated in transfer hydrogenation reduction of nitrobenzenes and oxidative esterification of benzyl alcohol. After each run the filtrate was concentrated and the resulting residue was purified. After the completion of the reaction, the contents were centrifuged to separate the solid catalyst from the reaction mixture. The catalyst was then thoroughly washed with distilled water followed by acetone and then dried in air before using in the next run and almost consistent activity was observed for next five consecutive cycles (Fig. 5). As seen from the figure the catalyst can be efficiently recycled and reused for repeating cycles without appreciable decrease in product yield. Little decrease in the product yields during the recycling could be attributed to the loss of the catalyst amount in the separation process from the reaction mixture.

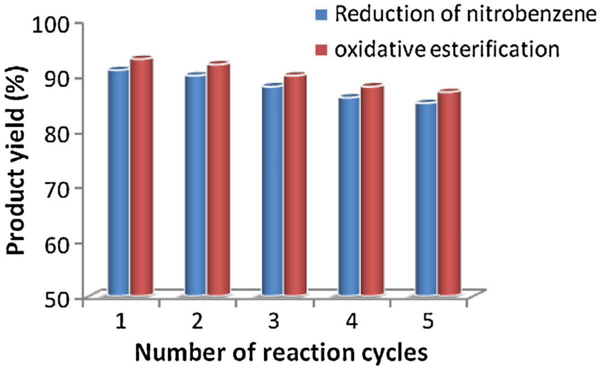


Fig. 5. Recycling efficiency of Ag-MPTA-1 nanomaterial in transfer hydrogenation reduction of nitrobenzenes and oxidative esterification of benzyl alcohol.

3.6. *Heterogeneity test*

3.6.1. *Hot filtration test*

To examine whether silver was being leached out from the solid support to the solution, experiment has been carried out in the transfer hydrogenation reduction of nitrobenzene with our supported Ag-MPTA-1 nano-catalyst. A typical hot filtration test was performed in the transfer hydrogenation reduction to investigate whether the reaction proceeded in a heterogeneous or a homogeneous fashion. For the rigorous proof of heterogeneity, a test was carried out by filtering catalyst from the reaction mixture at 80 °C after 4 h and the filtrate was allowed to react up to the completion of the reaction (6 h). In this case no change in conversion was observed, which suggests that the catalyst is heterogeneous in nature. No evidence for leaching of silver or decomposition of the complex catalyst was observed during the catalytic reaction. It was noticed that after filtration of the catalyst from the reactor at the reaction temperature, hydrogenation reactions do not proceed further. Atomic absorption spectrometric analysis of the supernatant solution of the reaction mixture thus collected by filtration also confirmed the absence of silver ions in the liquid phase. Thus, results of the hot filtration test suggested that Ag-nanoparticle/ions are not being leached out from the solid catalyst during the transfer hydrogenation reactions.

3.7. *Comparison with other reported catalytic system*

Transfer hydrogenation reduction of nitrobenzenes and oxidative esterification of benzyl alcohol under heterogeneous conditions over a variety of catalysts has been studied (Table 5). Table 5 provides a comparison of the results obtained for our present catalytic system with those reported in the literature [44–47]. From Table 5, it is seen that Ag-MPTA-1 showed higher catalytic activity over these catalysts (higher TOFs than most of the related catalytic systems). Although core–shell Ag@Ni magnetic nanocatalyst showed high catalytic activity in transfer hydrogenation using isopropyl alcohol as hydrogen donor [45] it remained unexplored in oxidative esterification of alcohols. Similarly Au nanoparticles dispersed on mesoporous silica material in Au-HMS-M showed high catalytic activity in oxidative esterification of alcohols only [46]. Ag-NPs dispersed in the mesoporous polymeric framework of

Table 4
Oxidative esterification of benzylic alcohols over Ag-MPTA-1 nanocatalyst[a]

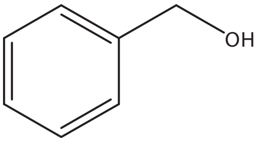
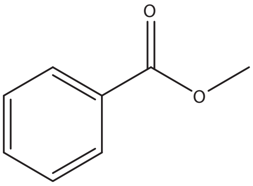
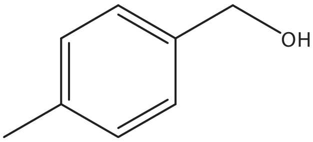
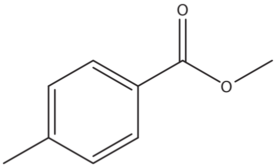
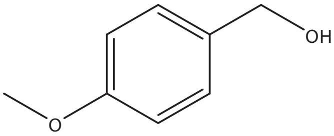
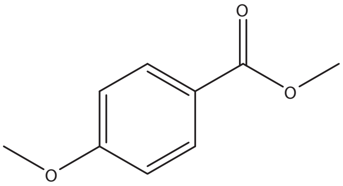
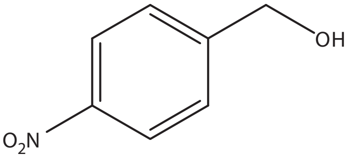
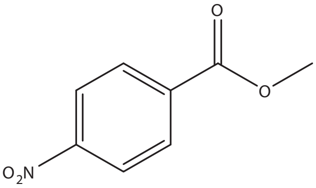
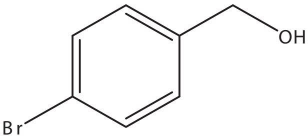
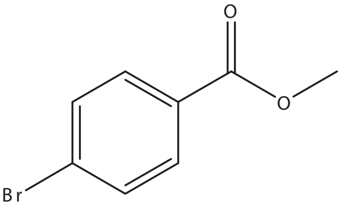
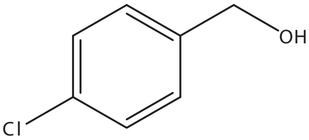
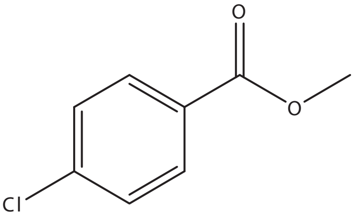
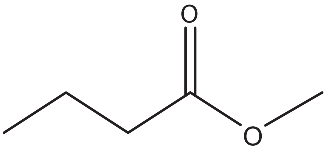
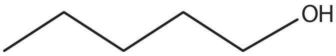
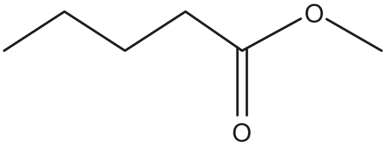
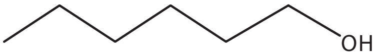
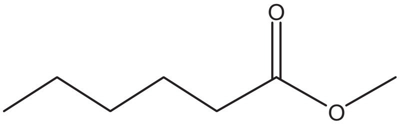
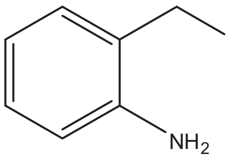
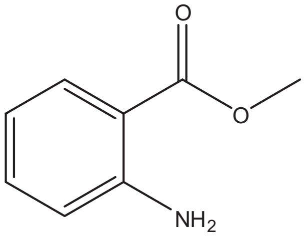
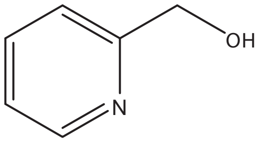
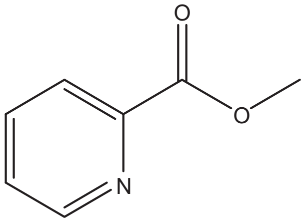
Entry	Substrates	Product	Yield (%)[b]
1			95
2			89
3			91
4			69
5			75
6			34
7			41
8			53
9			57

Table 4 (*Continued*)

Entry	Substrates	Product	Yield (%)[b]
10			42
11			39

[a] Reaction conditions: alcohol (2.5 mmol), K_2CO_3 (0.4 mmol), MeOH (6 ml), 45 °C, oxygen balloon, time (12 h), Ag-catalyst (50 mg).

[b] Yield of product was determined by GC and GCMS analysis.

Table 5

Comparison of catalytic activity of the Ag-MPTA-1 in transfer hydrogenation reduction of nitrobenzene and oxidative esterification of benzyl alcohol with other reported systems.

Entry	Catalyst	Reaction conditions	Transfer hydrogenation reduction reaction Yield (%) (TOF/h^{-1})	Oxidative esterification reaction Yield (%) (TOF/h^{-1})	Ref.
1	Cu nanoparticles/$HCOONH_4$	Ethylene glycol, 120 °C, 12 h	86 (0.03)	–	[43]
2	Ag@Ni magnetic nanocatalyst	Isopropyl alcohol, KOH, 80 °C, 2 h	96 (4.8)	–	[44]
3	Pd/Char, $Bi(NO_3)_3$	KOMe, 60 °C, oxygen (1 atm), 2 h	–	92 (11.5)	[45]
	Au-HMS-M	K_2CO_3, 130 °C, oxygen (10 atm), 4 h	–	94 (410)	[46]
4	Ag-MPTA-1 nanocatalyst	NaOH, iPrOH, 80 °C, 10 h (Transfer hydrogenation) K_2CO_3, 45 °C, oxygen balloon, 12 h (Oxidative esterification)	97 (19.4)	95 (198)	This study

Ag-MPTA-1 found highly reactive for both class of reactions and thus have future potential for multifunctional catalytic activities.

4. Conclusions

From our experimental observations we can conclude that a new Ag-nanocatalyst has been developed by embedding of Ag-nanoparticles at the surface of mesoporous polymer MPTA-1 and it has been successfully employed as a recyclable heterogeneous catalyst for the hydrogenation of aromatic nitroarenes and oxidative esterification of alcohols for a wide range of substrates. Both these catalytic processes are green and offer a number of advantages, such as easy work-up and separation of the catalyst from the reaction mixture by filtration, reusability for several times with minimal loss of catalytic activity. These key findings make the nanotechnology based recyclable heterogeneous catalysis platform inherently advanced, economical, green and environmentally sustainable.

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