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A novel silver nanoparticle embedded mesoporous polyaniline (mPANI/Ag) nanocomposite as recyclable catalyst in the acylation of amines and alcohols under solvent free condition

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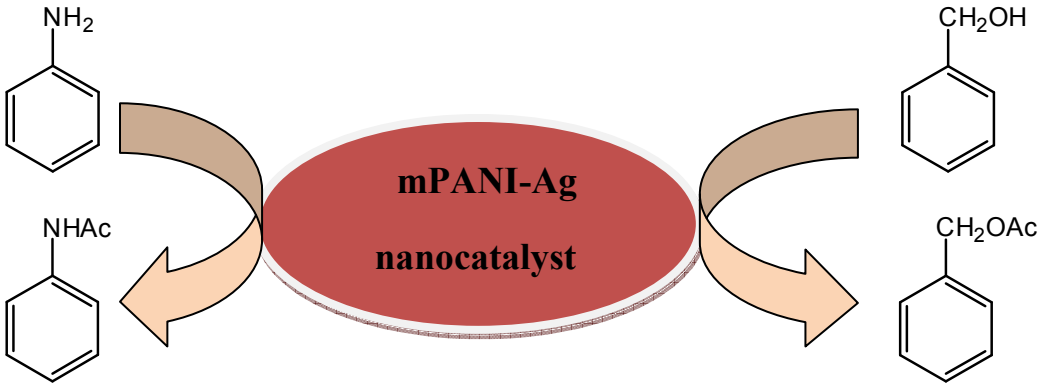
Highly dispersed silver nanoparticles (Ag NPs) have been embedded into mesoporous organic polymer through the reaction of silver nitrate with mesoporous polyaniline (mPANI) and the material showed high catalytic activity in the acylation of substituted amines and alcohols using acetic acid.



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A novel silver nanoparticle embedded mesoporous polyaniline (mPANI/Ag) nanocomposite as recyclable catalyst in the acylation of amines and alcohols under solvent free condition

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Abstract

Mesoporous polyaniline/silver (mPANI/Ag) nanocomposite has been prepared by mesoporous organic polymer polyaniline with silver nitrate via radical polymerization of aniline monomer in the presence of hydrochloric acid. The mPANI/Ag nanocomposite has been characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), energy-dispersive X-ray spectra (EDX), Fourier transform infrared spectroscopy (FT-IR), ultraviolet-visible absorption spectra (UV-vis). The XRD patterns indicated that the crystalline phase of Ag is cubic. TEM image shows that the Ag nanoparticles are well dispersed in the mesoporous polyaniline matrix. The mPANI/Ag acts as an efficient heterogeneous nanocatalyst in the acylation of substituted amines and alcohols using acetic acid. The catalyst is air-stable, inexpensive, easy to prepare and reused several times without significant decrease in activity and selectivity.

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Keywords: Mesoporous material, Polyaniline, Silver nanoparticles, Acylation, Amines, Alcohols.

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Introduction

Nanocomposites formed by metal nanoparticles (NPs) dispersed in electrically conducting polymers, such as polyaniline or polypyrrole, have received much attention in the past few years.[1-5] These hybrid nanomaterials are expected to display several synergistic properties between the polymer and the metal nanoparticles, making them potential candidates for application in several fields such as catalysis,[1] biosensors,[2] memory devices,[3] sensors,[4] and others.[5] Polyaniline (PANI) is a conducting polymer of particular interest, due to its ease of preparation, high conductivity,[6] good environmental stability under ambient conditions, promising chemical, electrical and optical properties, as well as its unique redox tenability.[7] Polyaniline has been extensively studied as a novel material for potential use in batteries,[8] chemical sensors, antistatic coating,[9] electromagnetic shielding,[10] and corrosion protective coating.[11]

The choice of Ag in our work is mainly guided by its highest electrical conductivity among all the metals[12] as well as its enhanced catalytic activity, antibacterial properties and good biocompatibility.[13-17] On the other hand silver nanoparticles have applications in conductive inks, catalysis photonics, thick film pastes and adhesives for various electronic components due to

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their unique optical, electrical, electrochemical and catalytic properties.[18,19] Hence it is achievable to develop specific properties with the selection of the organic and inorganic phases and produce novel materials which exhibit both organic and inorganic characteristics. This nanocomposite can be used as conductive components, active electrode materials, catalytic materials, batteries, and sensors.[20,21]

In the recent years, a lot of methods have been employed for the preparation of PANI/silver composites either chemically or electrochemically and their different properties studied. The most dominant methods are ‘‘in situ’’ chemical polymerization in an aqueous solution, the electrochemical route, photolysis,[22] and using sono-chemical and ionizing radiation techniques.[23] The structural and electrical properties of a PANI/silver nanocomposite were studied by Afzal et al.,[18] and Gupta et al. reported the optical and electrical transport properties of a PANI/silver nanocomposite.[24] The effect of concentration variation of silver in a PANI/silver nanocomposite on gas sensing properties was investigated by Choudury et al.[12b] PANI/silver nanocomposite films in a water-in-ionic liquid microemulsion and an ionic liquid-in-water were prepared by chronopotentiometry and their electrochemical properties studied by Zhou et al.[25] To the best of our knowledge, there is no report on mPANI/Ag as a catalyst. So in our study, we attempt to use mPANI/Ag as a potential catalyst for various organic reactions like acylation of amines and alcohols using acetic acid as acylating agent.

The acylation process of amines and alcohols to corresponding acetamides and acetates using acetic acid is both economically and environmentally advantageous. A variety of procedures are routinely performed for the preparation of acetyl derivatives, including homogeneous or heterogeneous catalysts, such as p-toluenesulfonic acid,[26] alumina,[27] montmorillonite K-10 and KSF,[28] $Cu(OTf)_2$,[29a] $Mg(NTf_2)_2$,[29b] $In(OTf)_3$,[29c] $Ce(OTf)_3$,[29d] silver

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triflate,[29e] magnesium bromide,[30] bismuth(III) salts,[31] $Mg(ClO_4)_2$,[32a] $HClO_4$–SiO_2,[32b] HBF_4–SiO_2,[32c] zinc chloride,[33] $ZrCl_4$,[34] $TaCl_5$.[35] However, some of the reported methods for the acylation suffer from one or more of the disadvantages, such as drastic reaction conditions, expensive catalysts, hygroscopicity and thermal instability of the catalysts, use of halogen-containing solvents and catalysts, long reaction times and low yields. Therefore, there is a need to develop a reusable and inexpensive heterogeneous catalyst for the acylation, using acetic acid as acylating agent to achieve high atom economy.

In this paper, we are describing our work on the successful use of non-toxic, environmentally benign and inexpensive mPANI/Ag as a solid catalyst for the acylation of amines and alcohols with acetic acid. This catalyst can be easily separated by using a simple filtration technique and can be reused five times without significant loss of catalytic activity.

Experimental

Materials

Aniline, ammonium persulfate [$(NH_4)_2S_2O_8$], silver nitrate ($AgNO_3$) and conc. HCl were obtained from E-Merck. $(NH_4)_2S_2O_8$ was used as initiator for the polymerization of aniline in aqueous medium. Sodium dodecylsulfate (SDS) was purchased from Loba Chemie and used as a structure-directing agent (SDA). Tris(hydroxymethyl) aminomethane (TRIS) was obtained from Sigma Aldrich. Sodium borohydride ($NaBH_4$) was purchased from Spectrochem, India. All other reagents and substrates were also purchased from Merck, India.

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Characterization techniques

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 operating at 200 kV. UV-Vis spectra were taken using a Shimadzu UV-2401PC doubled beam spectrophotometer having an integrating sphere attachment for solid samples. FT-IR spectra of these samples were recorded on KBr pellets by using a Perkin-Elmer FT-IR 783 spectrophotometer. The reaction products were quantified through a Varian 3400 gas chromatograph equipped with a 30m 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 Mesoporous Polyaniline (mPANI)

The template polymerization of aniline for the synthesis of mesoporous PANI has been carried out following the previous report.[6] In a typical synthesis, aniline (0.02 mol) was first dissolved into 5 mL aqueous solution of HCl (0.02 mol, ~ 1.0 mL). This solution was added to 20 mL aqueous solution of SDS (0.01 mol, 2.88 g) under stirring condition. The mixture was then placed in an ice-salt bath, so that the temperature was maintained at 4-5 ^{0}C. Finally, 20 mL aqueous solution of the oxidizing agent, $(NH_4)_2S_2O_8$ (0.04 mol, 9.12 g), in ice-cold water was added slowly to the above mixture and the whole mass was allowed to become homogeneous. Then stirring was stopped and the mixture was allowed to age under static condition for 2 days at 4-5 ^{0}C. The resultant precipitate was filtered, washed with deionized water and dried under vacuum at ambient temperature. Finally, the template-free or SDA free mesoporous polymer mPANI was obtained after extraction in an aqueous solution containing ammonium acetate.

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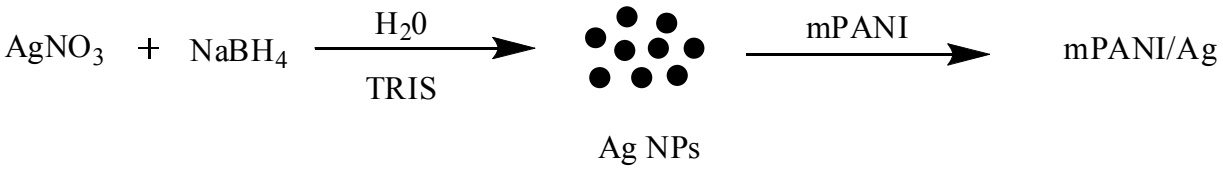
Synthesis of Colloidal Ag Nanoparticles

In a typical synthesis, 0.1 mL of an aqueous solution of 1% $AgNO_3$ was added to 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.

Synthesis of mPANI/Ag nanocatalyst

A total of 50 mg of mPANI was dispersed in 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 mPANI changed to black, indicating the loading of Ag-NPs onto the surface of mPANI. After centrifugation, black coloured Ag-NPs containing mesoporous polymer mPANI/Ag (Scheme 1) was obtained. This mesoporous material was washed further with copious amounts of water and dried at room temperature. The loading of Ag-NPs onto PANI was further confirmed by spectral measurements.



Scheme 1 Schematic diagram showing the formation of mPANI/Ag nanocatalyst at room temperature

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General procedure for acylation of amines using mPANI/Ag nanocatalyst

In a typical acylation procedure, aniline (0.9 mL, 10 mmol), acetic acid (0.6 mL, 10 mmol) and mPANI/Ag nanocatalyst (25 mg) were heated to 140 °C in a 50 mL round bottomed flask. After 3 hours the hot reaction mixture was diluted with ethyl acetate and the catalyst was removed from the reaction mixture by filtration, regenerated, and used for five consecutive cycles to study the recycling efficiency. The filtrates were washed with saturated sodium bicarbonate solution and then dried over anhydrous sodium sulfate. To study the progress of the reaction, the reaction mixtures were collected at different time intervals and identified by GC-MS and quantified by GC.

General procedure for acylation of benzyl alcohol using mPANI/Ag nanocatalyst

Benzyl alcohol (0.2 mL, 2 mmol), and acetic acid (2 mL, 34 mmol) were taken in a 50 mL round bottomed flask. Then 25 mg of the catalyst was added to the mixture and heated to 100 ^{o}C. It took approximately 3 h to complete the acylation reaction and the catalyst was collected by filtration. To study the progress of the reaction, the reaction mixtures were collected at different time intervals and identified by GC-MS and quantified by GC. After the completion of the reaction, the catalyst was filtered off and washed with saturated sodium bicarbonate solution 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 by vacuum. The filtrate was concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

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Results and Discussion

Characterization of catalyst

XRD studies

XRD pattern of mPANI/Ag nanoparticle is shown in Figure 1. The sharp intense peaks of the XRD pattern indicate that the synthesized nanocomposite is well crystalline and confirms the formation of single crystalline Ag nanoparticles in polyaniline material. Bragg's reflections at 2θ = 38.16, 44.54, 64.53, and 77.54 degree corresponds to (111), (200), (220) and (311) lattice planes, respectively, for the face-centered cubic (fcc) structure of silver nanoparticles embedded in mPANI.[36] The broad peak at 2θ value at 15–30 is due to amorphous nature of polyaniline. The wide-angle PXRD pattern of the material (mPANI/Ag) proves that silver nanoparticle successfully embedded inside the polyaniline matrix. The small angle XRD pattern of the mPANI/Ag material is shown in Figure S1 (Supporting information). The material showed one peak at 2θ = ~2.4, corresponding to the mesophase.

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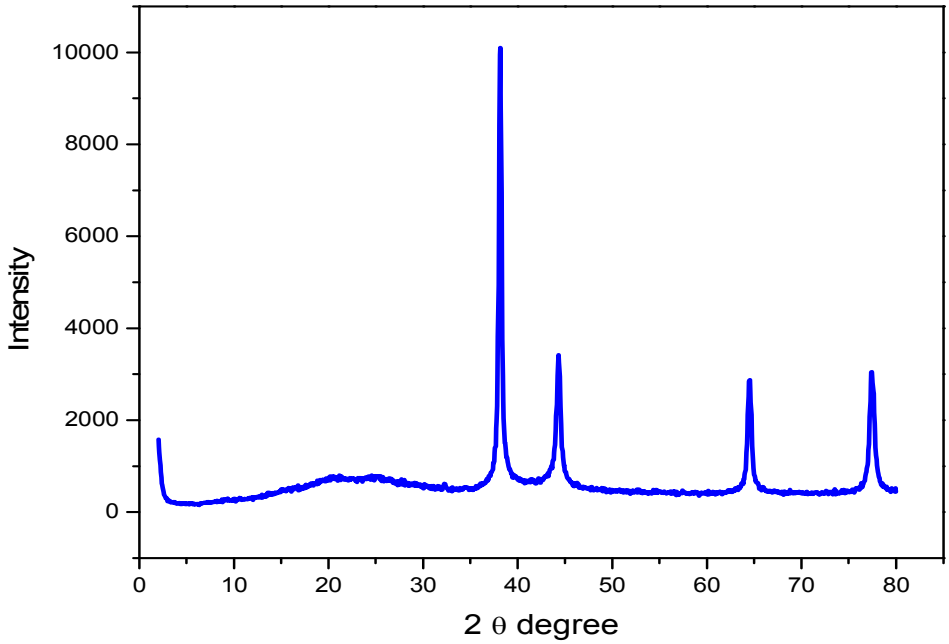

Figure 1 XRD of mPANI/Ag nanocomposite

TEM Analysis

The morphological diversity of mPANI/Ag material was examined by TEM analysis as shown in Fig. 2. This micrograph indicates that the Ag particles produced are in the nanoscopic domain. It is possible to observe in the micrograph that the silver nanoparticles of dimension ca.~ 5-6.5 nm are well dispersed in the polymeric matrix. This kind of arrangement of Ag nanoparticles will have high impact on the catalytic activity of the materials. Fig. 3 shows an EDX spectrum of the mPANI/Ag nanocomposite which shows the presence of Ag particles. These results also indicate the successful preparation of mPANI/Ag nanocomposite.

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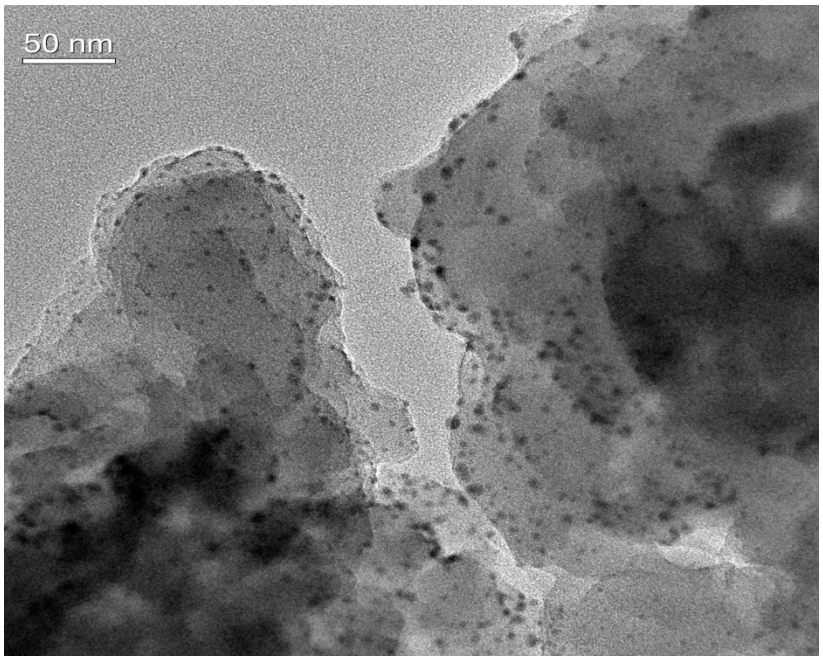

Figure 2 TEM image of mPANI/Ag nanocomposite

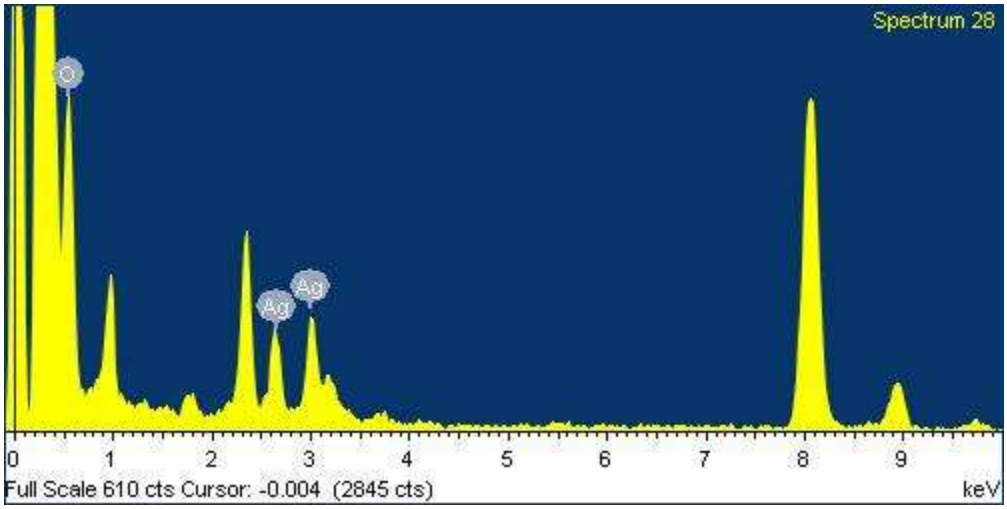

Figure 3 EDX spectra of mPANI/Ag nanocomposite.

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UV-Vis spectra

UV-vis absorption spectra of the pure mPANI and mPANI/Ag nanocomposite are shown in Figure 4. The characteristic bands of pure mPANI appear at 340, 400, and 700 nm which are attributed to π-π* transition of benzenoid rings, polaron- π* transition, and π-polaron transition, respectively[37a] (Figure 4a). However, for the mPANI/Ag nanocomposite, the characteristic bands at 340 and 400 nm are shifted to lower region but at 405 nm the band is observed because the absorption of Ag nanoparticles overlaps those of PANI (Figure 4b). The absorption band of the Ag nanoparticles usually appears at around 400 nm, which is caused by surface plasmon resonance.[37b] It is difficult to differentiate these bands due to the overlap.[38] The UV-vis absorption spectra further support the formation of mPANI/Ag nanocomposite.

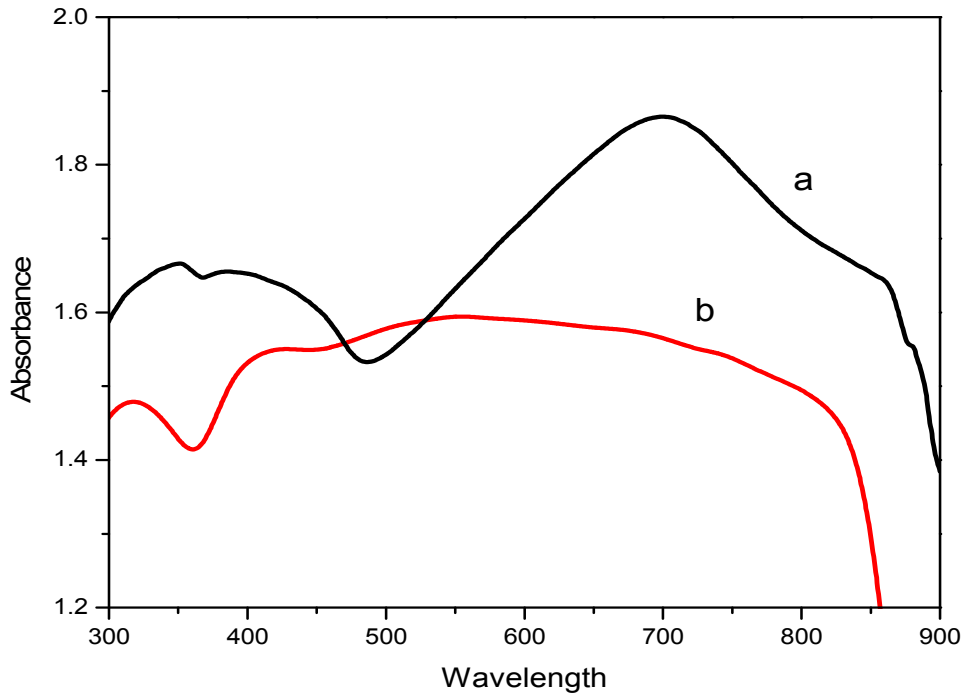

Figure 4 UV-Vis spectra of (a) pure mPANI and (b) mPANI/Ag nanoparticle.

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FTIR spectra

FTIR spectra of pure mPANI and mPANI/Ag nanocomposite are shown in Figure 5. For the pure mPANI (Figure 5a), the peaks in the frequency range of 2900-3500 cm^{-1} are due to the N-H stretching vibrations of the aromatic amine. The peak at 1145 cm^{-1} assigned to the characteristic Q=NH+-B (where Q and B denote quinoid ring and benzene ring, respectively) is also observed.[39] The peak at 1299 cm^{-1} relates to the C-N stretching vibration with aromatic conjugation. The well-resolved peaks at 1564 and 1489 cm^{-1} correspond to the C=C stretching vibration of benzeniod and quinoid rings, respectively. Another characteristic band in the infrared spectra refers to quinoic unit at about 1234 cm^{-1} arises due to protonation of PANI.[39c] The FT-IR spectrum of the PANI-Ag nanocomposite is very similar and also shows all the bands of PANI, confirming polymer formation (Figure 5b). However, it can be found that the integrated peak intensity of benzeniod rings against quinoid rings of the composite is higher than that of pure PANI, showing that PANI in the mPANI/Ag nanocomposite has a higher conjugation length than that of pure PANI.[39d]

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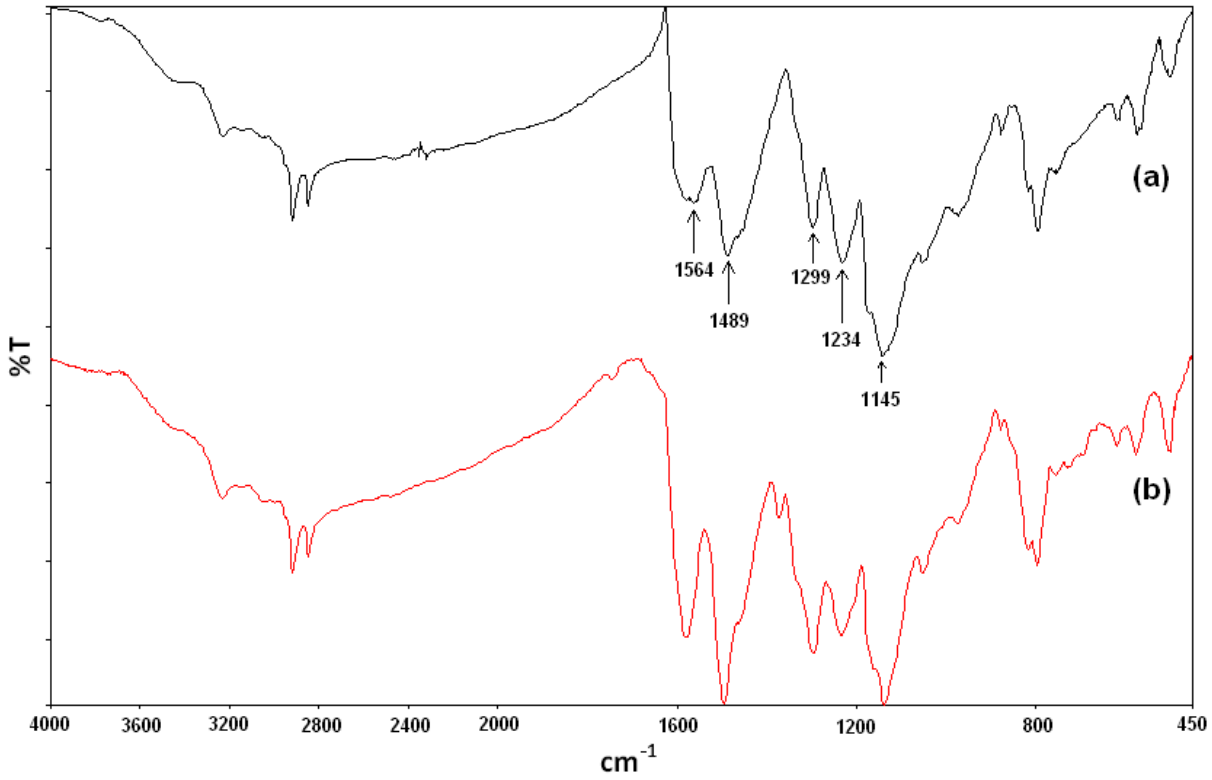

Figure 5 FTIR spectra of (a) pure PANI and (b) mPANI/Ag nanocomposite.

N_2 sorption and BET surface area analysis

The N_2 adsorption–desorption isotherm for mPANI/Ag material has been shown in Figure 6. The BET surface area calculated from this isotherm of the material is 3.55 m^2g^{-1}. This decrease in surface area from parent mPANI material (surface area 47 m^2g^{-1}) can be attributed to be the incorporation of Ag nano particles in the porous framework of polyaniline. The pore size of the material has been determined by NLDFT method (shown in the inset of Figure 6). The pore diameter of the material is 2.10 nm which proves that the resulting mPANI/Ag material after the successful incorporation of Ag nano particles over mPANI material is also mesoporous in nature.

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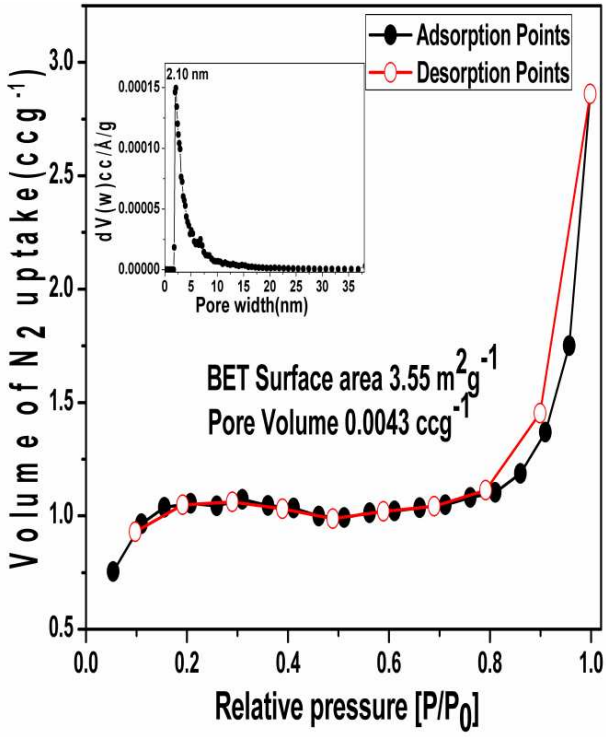

Figure 6. N_2 adsorption and desorption isotherms for Ag/mPANI. Adsorption points are marked by filled circles and the desorption points by empty circles. NLDFT pore size distribution is shown in the inset.

Catalytic activity

Supported metals are useful as heterogeneous catalysts in a wide variety of organic transformation. Nanoparticles, in comparison to bulk solids, have a significantly high catalytic activity and exhibit novel characteristics of quantum size effects. Heterogeneous catalysts are also in great demand for clean technology and sustainable development and these are extensively studied, we decided to investigate the catalytic activity of the mesoporous polymer mPANI/Ag in the acylation of substituted amines and alcohols using acetic acid.

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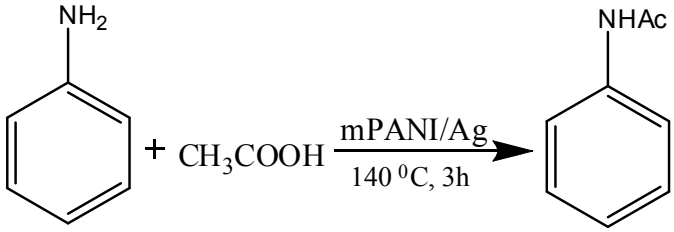
Acylation of amines using acetic acid catalyzed by mPANI/Ag nanocomposite

The acylation of amines is one of the most frequently used transformations in organic synthesis as it provides an efficient and inexpensive means for protecting amino groups in a multistep synthetic process. To examine the catalytic activity of mPANI/Ag nanocomposite, acylation of aniline with acetic acid as acylating agent was chosen initially as a model reaction (Scheme 2).



Scheme 2 Acylation of aniline using acetic acid

In order to optimize the reaction condition, the performance of a silver-catalyzed acylation is known to be governed by the number of factors such as solvent, reaction temperature, amount of catalyst and reaction time. Firstly, we have carried out the acylation of aniline in the presence of various solvents such as acetonitrile, dichloromethane and the results are summarized in Table 1. Without using any solvent (Table 1, entry 2) maximum conversion of aniline to acetanilide is obtained. As seen in Table 1, the use of acetonitrile resulted in poor conversion of the substrate (entries 4, 8). Similarly the use of dichloromethane gave 62% yield. It was observed that, 25 mg of catalyst afforded acylated product in high yield (Table 1, entry 2). The effect of the temperature on the catalytic performance of this system has also been investigated. The substrate was allowed to react with a catalytic amount of complex at different temperature. It was found that at 140 ^{o}C the yield was maximum (Table 1, entries 2 and 5). At 100 ^{o}C the yield is moderate but the reaction took prolonged time for completion (Table 1, entry

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5). As a result 140 ^{o}C was selected as the optimum temperature. In the absence of catalyst, low conversion (less than 5 %) of aniline into acetanilide was observed (Table 1, entry 9). From the above discussions, it can be seen that the best yield was obtained in the acylation of aniline using acetic acid at 140 ^{o}C for 3 h. The comparative studies of acylation of aniline using Ag(0), mPANI and mPANI/Ag as a catalyst are also studied (Table 1, entries 2, 10 and 11) to see the effectiveness of mPANI/Ag catalyst under identical experimental reaction conditions. The yield of the acylated product is higher with mPANI/Ag. This might be due to high content of Ag exposed on the surface of mPANI and thus enhance the acidic property.

Table 1 Optimization of reaction conditions for the acylation of aniline with acetic acid using mPANI/Ag nanocomposite.[a]

Entry	mPANI/Ag (mg)	Temperature (^{o}C)	Solvent	Time (h)	Yield (%)[b]
1	50	140	-	3	98
2	**25**	**140**	**-**	**3**	**98**
3	75	140	-	3	98
4	25	140	CH_3CN	10	60
5	25	100	-	16	68
6	25	140	CH_2Cl_2	10	62
7	50	100	-	14	53
8	50	140	CH_3CN	10	64
9	-	140	-	24	Less than 5
10[c]	25	140	-	3	69

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11[d]	25	140	-	3	82

[a] Aniline (10 mmol), acetic acid (10 mmol). [b]Yield were determined by GC analysis. [c]Ag nano used as catalyst. [d]mPANI used as catalyst.

After having optimized the reaction conditions for aniline, acylations of various amines with AcOH have been carried out in the presence of 25 mg of mPANI/Ag as a catalyst at 140 ^{0}C (Table 2). The reaction proceeds very smoothly at 140 ^{0}C in 3 h. In mPANI/Ag nanocatalyst the yields are good to excellent. The electron donating groups facilitate the reaction whereas electron withdrawing groups slow down the reaction. The reaction of aniline and substituted anilines with acetic acid gave the corresponding amides in excellent yields in shorter reaction time under solvent-free conditions (Table 2, entries 1-7). The presence of nitro group at *para* position of aniline and at *ortho* position of aniline affects the nucleophilicity and steric hindrance, respectively and thus, the corresponding products are obtained in low yields (Table 2, entries 4 and 5). Benzyl amine and substituted benzyl amines underwent reaction with acetic acid and the corresponding acetamides were obtained in good yields (Table 2, entries 8-10). 1-Naphthylamine, N-Methyl aniline and cyclohexyl amine with acetic acid also gave the corresponding product in high yields (Table 2, entries 11, 12 and 13). In case of 2-aminophenol and 4-aminophenol, only amine group was selectively acylated to form 2- acetamidophenol and 4-acetamidophenol, respectively (Table 2, entries 14 and 15). This is in contrast to the results obtained in the acylation of 2-aminophenol using acetic anhydride as acylating agent wherein both hydroxyl and amine groups were acylated when acylating agent was used in excess.[40] In the acylation of 2-aminothiophenol using acetic acid, both amine and thiol groups were acylated (Table 2, entry 16) but the yield of the product was low after long reaction time 10 h.

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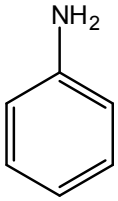
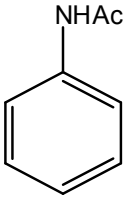
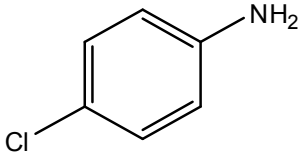
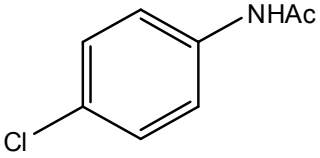
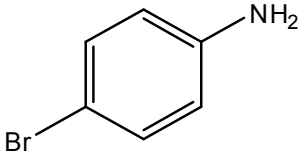
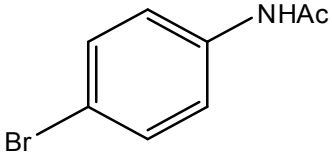
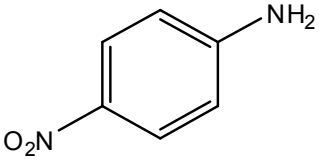
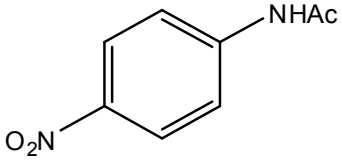
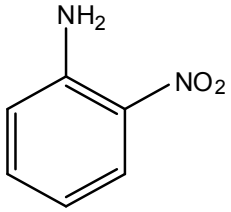
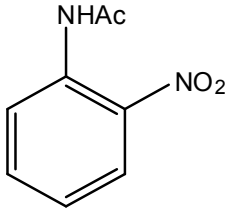
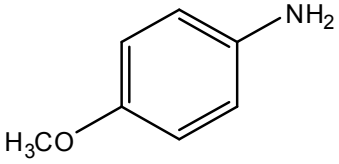
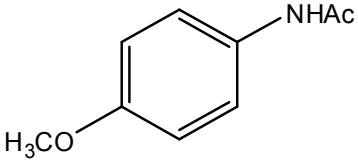
Table 2 Acylation of amines with acetic acid over mPANI/Ag nanocatalyst.[a]

Entry	Amine	Product	Yield (%)[b]
1			98
2			97
3			90
4			74
5			70
6			94

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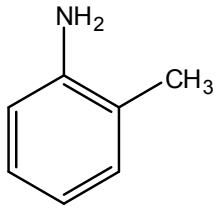
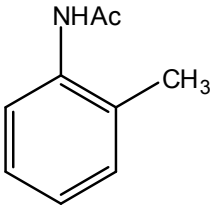
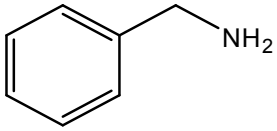
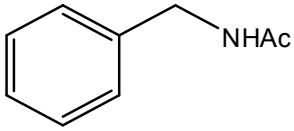
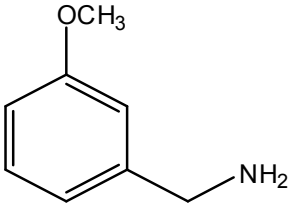
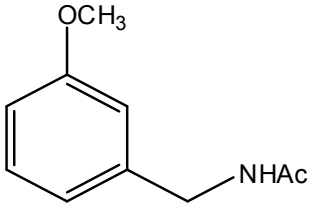
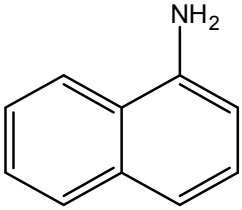
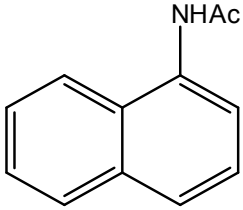
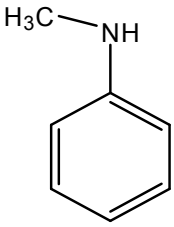
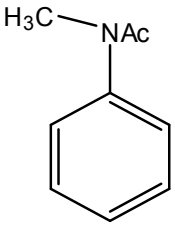
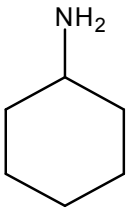
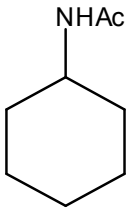
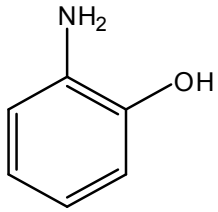
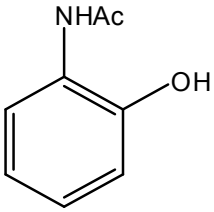
7			93
8			99
10			92
11			92
12			90
13			97
14			75

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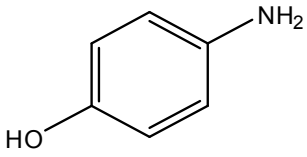
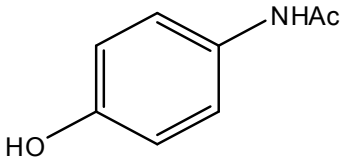
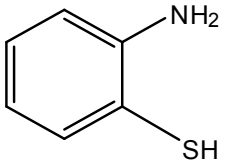
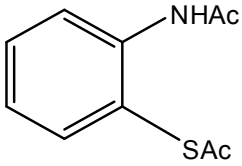
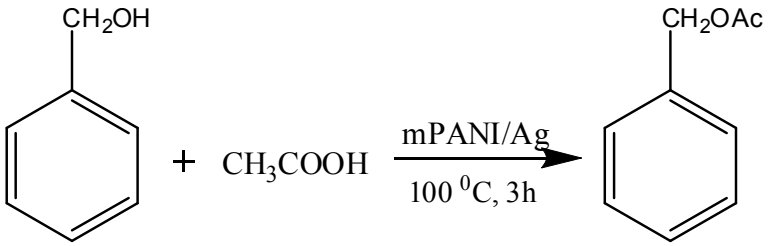
15			88
16[c]			48

[a]Reaction conditions: amine (10 mmol), acetic acid (10 mmol), and mPANI/Ag (25 mg), temperature (140 ^{0}C), time 3 h. [b]Yield determined by GC analysis. [c]reaction time 10 h.

Acylation of benzyl alcohol using acetic acid catalysed by mPANI/Ag nanocomposite

Acylation of alcohols, one of the most fundamental transformations in organic synthesis, is widely used in laboratories and pharmaceutical industries. Acylation of alcohols produce the corresponding esters which are used in the production of valuable compounds such as polymers, fragrances, or fatty acids. We started our investigation for acylation of benzyl alcohol using acetic acid (Scheme 3) as a model reaction in presence of silver nanocatalyst.



Scheme 3 Acetylation of benzyl alcohol using acetic acid.

The acylation of benzyl alcohol almost failed to proceed in the absence of catalyst (Table 3, entry 1). The effect of solvents (acetonitrile, acetone, dichloromethane, carbon tetrachloride and n-hexane) in the acylation of benzyl alcohol with acetic acid using mPANI/Ag as catalyst is

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studied. The best yield was obtained only when acetic acid was used as a solvent (Table 3, entries 2 and 3). The present reaction was also conducted using different amount of the catalyst and it was found that the reaction conducted with 25 mg of catalyst is optimum requirement for the better conversion (Table 3, entry 2). The temperature effect was also verified in this reaction and it was found that at 100 ^{o}C the yield is maximum but at 80 ^{o}C the yield is very low only 50% (Table 3, entry 4). From the above discussions, it can be seen that the best yield was obtained in the acylation of benzyl alcohol using acetic acid at 100 ^{o}C for 3 h. The comparative studies of acylation of benzyl alcohol using Ag(0), mPANI and mPANI/Ag as a catalyst are also studied (Table 3, entries 2, 9 and 10) to see the effectiveness of mPANI/Ag catalyst under identical experimental reaction conditions. The yield of the acylated product is higher with mPANI/Ag due to high content of Ag exposed on the surface of mPANI and higher acidic property. In homogeneous Ag(0) catalysed reactions, though the catalytic activity was moderate compared to mPANI/Ag catalyst, it is difficult to recover and reused.

Table 3 Optimization of reaction conditions for the acylation of benzyl alcohol with acetic acid using mPANI/Ag nanocatalyst.[a]

Entry	mPANI/Ag (mg)	Temperature (^{o}C)	Solvent	Time (h)	Yield[b] (%)
1	-	100	-	20	<3
2	**25**	**100**	**-**	**3**	**97**
3	50	100	-	3	97
4	75	80	CH_3CN	8	50
5	25	100	CH_2Cl_2	8	64
6	50	80	Acetone	18	60

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7	25	80	CCl_4	20	50
8	25	100	n-hexane	20	55
9[c]	25	100	-	3	63
10[d]	25	100	-	3	78

[a]benzyl alcohol (2 mmol), acetic acid (2 mL, 34 mmol). [b]Yield were determined by GC analysis. [c]Ag nano used as catalyst. [d]mPANI used as catalyst.

To explore the generality and scope of this reaction a wide range of structurally varied alcohols were subjected to react with acetic acid using 25 mg of mPANI/Ag at 100 ^{o}C to afford corresponding acetates in good to excellent yields. The results are reported in Table 4. Various electron-rich, sterically hindered benzyl alcohols underwent reaction with acetic acid at 100 ^{0}C for 3 h to afford the corresponding acylated products in high yields (Table 4, entries 1–6). The excellent 'electrophilic activation' was observed for alcohols having electron withdrawing groups that decrease the nucleophilic property of the hydroxyl group (Table 4, entries 7–10). Acylation of phenolic hydroxy group could not be facilitated under similar conditions whereas selective acylation was observed with alcoholic hydroxy group (Table 4, entry 11). Similarly in presence of donating group, the alcoholic hydroxy group was acylated selectively to their corresponding esters (Table 4, entry 12). It is important to note that in acylation of both primary and secondary alcohols, there was no by-product formation observed. Secondary alcohols when subjected to reaction with acetic acid the corresponding O-acylated products were obtained in high yields (Table 4, entry 13). In addition, allylic alcohols can be acylated in high yields (Table 4, entry 14). In addition, we also checked the selectivity of this catalyst in the acylation of 4-aminobenzyl alcohol (Table 4, entry 15). The results showed that alcohol end was acylated

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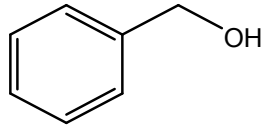
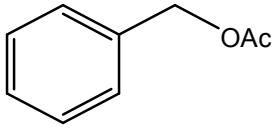
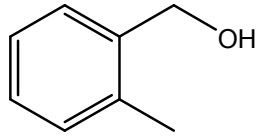
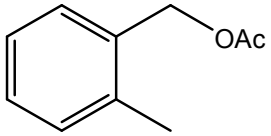
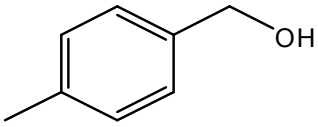
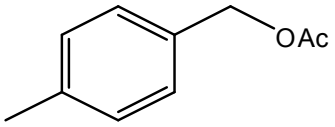
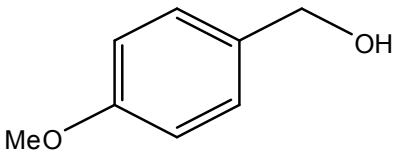
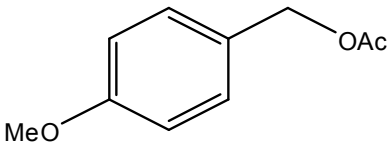
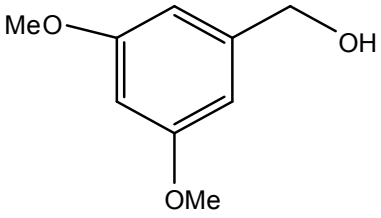
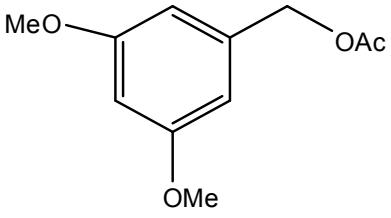
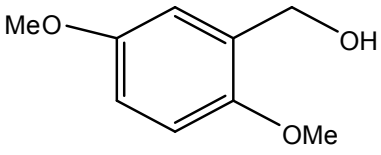
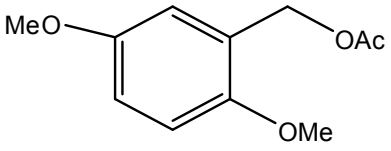
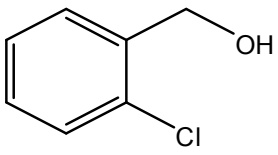
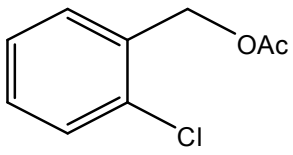
selectively upto 1 h but with progress of the reaction both the ends acylared and did not give any selective products at 3 h. Alkylthio substituted benzyl alcohol also afforded the corresponding O-acylated derivatives in moderate yield when treated with acetic acid (Table 4, entry 16).

Table 4 Acylation of alcohols with acetic acid over mPANI/Ag nanocatalyst.[a]

Entry	Alcohol	Product	Yield (%)[b]
1			97
2			96
3			90
4			97
5			90
6			95
7			97

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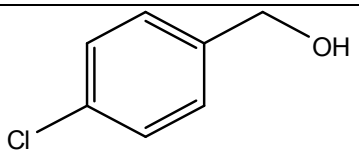
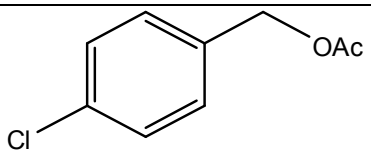
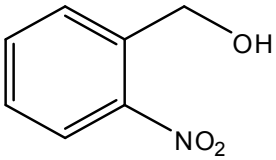
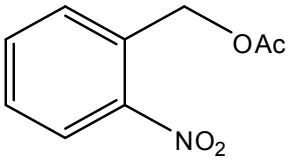
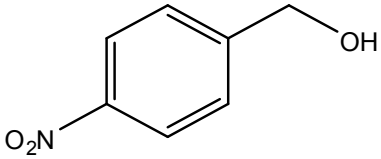
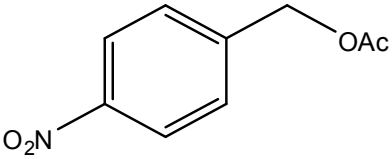
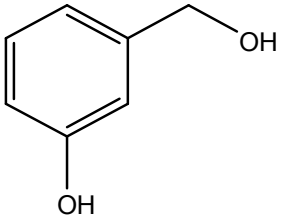
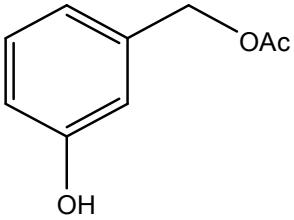
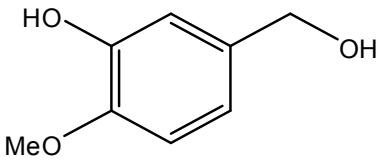
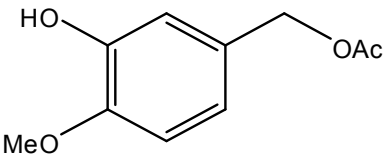
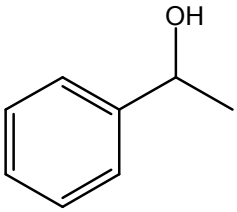
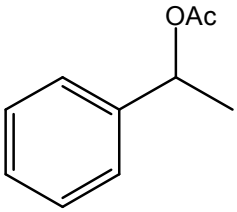
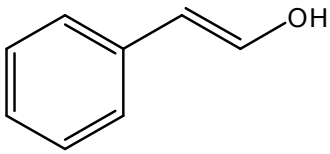
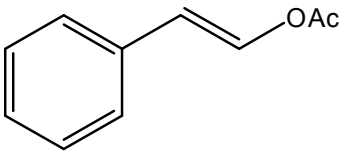
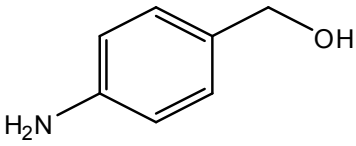
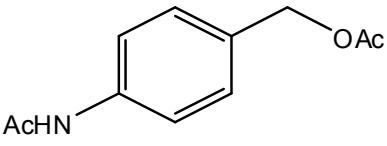
8			96
9			91
10			98
11			89
12			80
13			96
14			97
15			96 (34[c])

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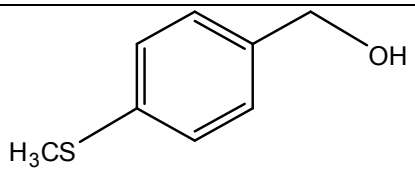
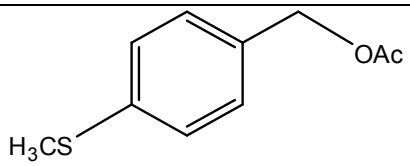
16[d]			62

[a]Reaction conditions: benzyl alcohol (2 mmol), acetic acid (2 mL, 34 mmol), and mPANI/Ag (25 mg), temperature (100 ^{0}C), time 3 h. [b]Yield determined by GC analysis. [c]Selective acylated product at the alcohol end after 1 h. [d]reaction time 10 h.

Recyclability of mPANI/Ag nanocatalyst

For a heterogeneous catalyst, it is important to examine its ease of separation, recoverability and reusability. The reusability of the mesoporous mPANI/Ag nanocatalyst was investigated in acylation of amines and alcohols. 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 (Figure 7). As seen from the figure that the catalyst can be efficiently recycled and reused for repeating cycles without appreciable decrease in product yield.

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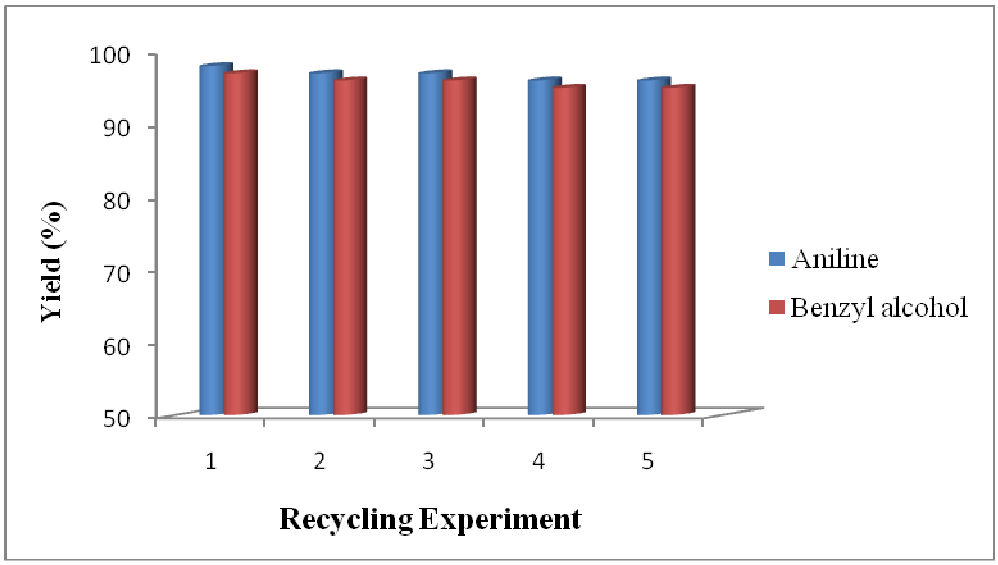

Figure 7 Recycling efficiency of mPANI/Ag in acylation of aniline and benzyl alcohol.

Heterogeneity Test

Hot Filtration Test

To examine whether silver was being leached out from the solid support to the solution, an experiment has been carried out in the acylation of amines with our mPANI/Ag nanocatalyst. A typical hot filtration test was performed in the acylation of amines 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 140 ^{0}C after 2 h and the filtrate was allowed to react up to the completion of the reaction (1 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, acylation 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

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the liquid phase. Thus, results of the hot filtration test suggested that Ag was not being leached out from the solid catalyst during the acylation reactions.

Comparison with other reported system

Acylation of various substituted amines and alcohols with acetic acid 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 [41-44]. From Table 5, it is seen that present catalyst exhibited higher yields compared to the other reported system [41-44].

Table 5 Comparison of catalytic activity of the present catalyst in acylation of aniline and benzyl alcohol with other reported systems.

Catalyst	Acylation of aniline		Acylation of benzyl alcohol		Ref.
	Reaction Condition	Yield (%)	Reaction Condition	Yield (%)	
Montmorillonite KSF	-	-	Benzyl alcohol (1 mol), Ac_2O (2 mol), RT	90	41
$Gd(OTf)_3$	Aniline (18.5 mmol), Ac_2O (27.5 mmol), solvent ([bmim][BF_4]), catalyst (0.2 mol%), RT	96	Benzyl alcohol (18.5 mmol), Ac_2O (27.5 mmol), solvent ([bmim][BF_4]), catalyst (0.5 mol%), RT	92	42
poly(N-vinylimidazole)	Aniline (1 mmol),	90	Benzyl alcohol (1	98	43

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(PVIm)	Ac_2O (1 mmol), catalyst (20 mg), RT		mmol), Ac_2O (1 mmol), catalyst (20 mg), RT		
Zeolite Hβ	Aniline (2 mmol), acetic acid (2 mmol), catalyst (200 mg), temperature (117^oC), under microwave irradiation	73	Benzyl alcohol (2 mmol), acetic acid (2 mmol), catalyst (200 mg), temperature (117^oC), under microwave irradiation	98	44
mPANI/Ag	Aniline (10 mmol), acetic acid (10 mmol), catalyst (25 mg), temperature (140 ^oC)	98	Benzyl alcohol (2 mmol), acetic acid (2 mL), catalyst (25 mg), temperature (100 ^oC)	97	This study

Conclusions

From our experimental observations we can conclude that a new Ag-nanocatalyst has been developed by embedded of Ag nanoparticles on the surface of mesoporous polymer PANI and has been successfully performed efficiently as a recyclable heterogeneous catalytic system for acylation of amines and alcohols. Thus the catalytic process is green and it offers 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 often minimal loss of activity. These key findings make the nanotechnology based recyclable heterogeneous catalysis platform provided herein inherently advanced, economical, green and environmentally sustainable.

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