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Introduction

Direct oxidative esterification of alcohols and hydration of nitriles catalyzed by a reusable silver nanoparticle grafted onto mesoporous polymelamine formaldehyde (AgNPs@mPMF)†

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A nitrogen-rich mesoporous organic polymer was synthesized as a novel support. A silver nanoparticle was synthesized and grafted onto it. The prepared catalyst (AgNPs@mPMF) was characterized by powder X-ray diffraction (XRD), scanning electron microscopy(SEM) and energy dispersive X-ray spectrometry (EDS), thermogravimetric analysis (TGA), high-resolution transmission electron microscopy (HRTEM), UV-vis diffuse reflectance spectroscopy (DRS), N₂ adsorption, Raman spectroscopy and EPR study. The catalytic activity was evaluated for the oxidative esterification reaction of alcohols and hydration of nitriles. The oxidative esterification was carried out for various activated alcohols giving excellent yields of the corresponding ester products. The catalyst was also efficient in the hydration of nitriles. Both reactions were optimized by varying the bases, temperatures and solvents. The catalyst can be facilely recovered and reused six times without a significant decrease in its activity and selectivity.

Ester and amide groups are among the highly important and abundant functional groups in chemistry and can be found in bulk chemicals, fine chemicals, natural products, polymers, detergents, lubricants and drug stabilizers.¹ Traditional methods for the synthesis of esters had several drawbacks; they involved strong acidic and basic conditions, produced a large amount of unwanted by-products and suffered from low regioselectivity.² With the development of transition metal

regioselectivity.² With the development of transition metal catalysed cross coupling reactions, esters can be synthesized by carbonylation of aryl halides. But high temperature, high CO pressure as well as the presence of halide anions make this reaction environmentally unfavorable.³ As an economical alternative to traditional methods, direct ester synthesis *via* oxidative esterification of aldehydes with alcohols has been developed. However, these protocols usually require

stoichiometric amounts of reagents such as oxone, MnO₂, sodium dichromate and peroxides and the required aldehydes are usually obtained from alcohols by selective oxidation. A large amount of unwanted waste is produced and multiple reaction steps are involved.⁴ Some ruthenium pincer complexes were developed for the oxidative esterification of primary alcohols. [Ru-(PPh₃)₃(CO)H₂]/xantphos was utilized for the catalytic synthesis of methyl esters from primary alcohols in the presence of crotonitrile as a hydrogen acceptor. A cationic rhodium catalyst in the presence of a hydrogen acceptor could also catalyze esterification. But, in most cases, stoichiometric amounts of organic by-products are formed.⁵ Thus, from the viewpoint of green and sustainable chemistry, a single-step direct catalytic oxidative esterification of alcohols with alcohols is highly desirable, as alcohols are more readily available as bulk chemicals, more stable than the carbonyl compounds, cheaper, less toxic, and easier to handle.⁶ Very recently, some palladium and gold catalyzed direct oxidative esterification of alcohol with alcohol has been reported.⁷ Although they gave very good yields of ester products, most of them are homogeneous in nature. Also both palladium and gold are very costly metals.7a-c Our group developed a heterogeneous silver nanoparticle embedded over a mesoporous organic polymer as an efficient catalyst for this type of esterification.8 As a continuation to our work, we have now developed a new silver nanoparticle grafted onto mesoporous

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polymelamine formaldehyde which catalyzes direct oxidative esterification with extended substrate scope.

Again, amides are typically prepared from the union of carboxylic acids and its derivatives (halides, anhydrides or esters) with amines.9 However, these methods present several drawbacks such as the use of toxic, corrosive and/or expensive materials, highly exothermic reactions, low tolerance to sensitive functional groups, complex reaction conditions and wasteful procedures. With the development of synthetic methods, metal-catalyzed transformations have emerged as the most promising alternatives for the atom-economical and cost effective synthesis of amides. In view of this growing technology, the hydration of nitriles to amides has become an important transformation in the pharmaceutical industry.¹⁰ There are several reports on homogeneous metal catalyzed hydration of nitriles under neutral conditions. But they suffer from several disadvantages including difficulty in the separation of product and catalyst from the reaction mixture, use of organic solvent, high price, low activity for hydration of hetero-aromatic nitriles, as well as the use of an inert atmosphere for handling air-sensitive metal catalysts.¹¹ Thus the use of recyclable heterogeneous catalysts came into being.^{1e} The use of water as solvent for the hydration of nitriles is an ideal condition from the environmental and practical viewpoints and few heterogeneous silver nanoparticles that catalyze hydration of nitriles have been reported.¹³ The growing interest in this field led us to develop a silver nanoparticle embedded in a mesoporous polymelamine formaldehyde system for hydration of nitriles.

Metal nanoparticles have attracted a great deal of attention due to their chemical and physical characteristics that distinguish them from the bulk metal.¹⁴ Metal nanoparticles (NPs) reside in the size range between bulk and monomeric metal species and are applied in a wide range of technologies from electronic, optic and magnetic devices, photo and DNA assays, quantum dots (QDT) to advanced catalytic materials. Currently, metal NP catalysts are receiving much attention for use in organic synthesis under liquid-phase conditions.¹⁵ Among them, a good number of studies on catalytic applications of silver nanoparticles (AgNPs) have been conducted.¹⁶

A smaller size of metal nanoparticles leads to a high surface to volume ratio, and consequently, a large number of potential active sites would be available to the substrates, resulting in the enhancement of their catalytic activity. However, metal nanoparticles, due to high surface energy, are not stable as such. During a reaction, the highly active surface atoms destabilize the NPs. Hence immobilization of metal nanoparticles into a suitable rigid matrix has come into practice to increase the stability of the catalysts.¹⁷

Heterogeneous catalysts present a high surface area of the catalytically active phase to the reactants and have separation and recycling advantages compared to homogeneous catalysts. A high surface area of the active catalyst is achieved by dispersing it on a high surface area support preferably in the form of very small crystallites, maybe of nanometer size.¹⁸

Various supports such as SiO_2 , carbon, CeO_2 , alumina, hydroxyapatite, graphene and Fe_3O_4 have been used for the immobilization of silver nanoparticles.^{1e,13b,18b,19} These supports, although advantageous in some cases, retain some of the common drawbacks that pertain to the traditional and cumbersome isolation procedure after completion of reactions and most importantly are deficient in the reusability aspect.

Mesoporous polymeric materials have gained much attention in recent years due to their high specific surface area, uniform pore diameter and chemical stability for recyclability.²⁰ However, ordinary mesoporous materials are poor in functional groups and the impregnation of metal nanoparticles often results in polydisperse nanoparticles on the supportive materials. The organic mesoporous polymers are a class of advanced materials, which possess the textural porosities of mesoporous materials and also the advantages of organic polymers with high hydrophobicity, containing aromatic sections and higher stability in acid or base media in comparison to silica-based materials.^{21,22} Recently, our group has reported several mesoporous organic polymersupported metal catalysts with the view of benign and sustainable chemistry.^{8,23}

In this context, a mesoporous poly-melamine-formaldehyde polymer with a high surface area, good porosity and a high density of amine and triazine functional groups was synthesized and characterized.²⁴ It proved to be an efficient heterogeneous catalyst for oxidative esterification reaction and hydration of nitriles.

Experimental section

Chemicals

Melamine, paraformaldehyde and tris(hydroxymethyl)aminomethane (TRIS) were purchased from Sigma-Aldrich. AgNO₃ was purchased from Universal Chemicals, India. Sodium borohydride (NaBH₄) was obtained from Spectrochem, India and used as received. All other reagents and substrates were also purchased from Merck, India and were used without further purification. Solvents were dried and distilled through a standard procedure.

Physical measurements

The FT-IR spectra of the samples were recorded from 400 to 4000 cm⁻¹ on a Perkin Elmer FT-IR 783 spectrophotometer using KBr pellets. UV-Vis spectra were taken using a Shimadzu UV-2401PC doubled beam spectrophotometer having an integrating sphere attachment for solid samples. Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/DTA 851e. The silver content was determined by using a Varian (USA) AA240 atomic absorption spectrophotometer (AAS). The surface morphology of the samples was measured using a scanning electron microscope (SEM) (ZEISS EVO40, England) equipped with an EDX facility. The specific surface area of the sample was measured by adsorption of nitrogen gas at 77 K and applying the Brunauer-Emmett-Teller (BET) calculation. Prior to

adsorption, the samples were degassed at 250 °C for 3 h. Powder X-ray diffraction (XRD) patterns of different samples were analyzed using a Bruker D8 Advance X-ray diffractometer with Ni-filtered Cu K α (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. NMR spectra were recorded on a Varian Mercury plus NMR spectrometer (¹H NMR at 300 and 400 MHz and ¹³C NMR at 75 MHz and 100 MHz) in pure deuterated solvents.

Synthesis of the mesoporous poly-melamine-formaldehyde polymer (mPMF)

Melamine (0.378 g, 3 mmol) and paraformaldehyde (1.8 eq., 0.162 g, 5.4 mmol) were mixed with 3.36 ml (overall concentration of 2.5 M) of dimethyl sulfoxide (DMSO) in a 15 ml Teflon container secured in a steel reactor. The reaction mixture was heated to 120 °C in an oven for 1 h. The reactor was then carefully removed from the oven for stirring on a magnetic stirrer plate to obtain a homogeneous solution. It was then heated to 170 °C in the oven for 72 h. The reaction was allowed to cool to room temperature, and the obtained solid was crushed, filtered, and washed with DMSO, acetone, tetrahydrofuran (THF) and CH₂Cl₂. The resulting white solid was dried under vacuum at 80 °C for 24 h (Scheme 1).

Synthesis of colloidal Ag nanoparticles

In a typical synthesis, 100 mg of AgNO₃ was added to 10 ml of water containing 0.5 mmol of TRIS and was stirred for

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2 min. Then, 0.25 ml of an aqueous solution of NaBH₄ (0.08%) was added dropwise under stirring. The stirring was continued for another 10 min, and the resulting nanocolloid was stored at 4 °C.

Synthesis of the mPMF-Ag⁰ nanocatalyst

A total of 600 mg of mPMF 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 mPMF changed to black, indicating the loading of Ag-NPs onto the surface of mPMF. After centrifugation, black coloured Ag-NPs containing mesoporous polymer mPMF-Ag⁰ were obtained (Scheme 2). This mesoporous material was washed further with copious amounts of water and dried at room temperature. The loading of Ag-NPs onto mPMF was further confirmed by spectral measurements. Ag⁰ loading to the mPMF was determined to be 14.40 wt% by AAS.

General procedure for the oxidative esterification reaction

A mixture of mPMF-Ag⁰ nanocatalyst (20 mg) and K₂CO₃ (13.8 mg, 0.1 mmol) in methanol (4 mL) was stirred for 1 min at room temperature in a 25 mL flask. Then 1 mmol of benzylic alcohol was added to the mixture. After stirring for 2 min, the resulting mixture was transferred to an autoclave. After the autoclave was closed, dioxygen was charged to 0.1 MPa. The temperature was set to 70 °C. After the reaction

mPMF-Ag

Scheme 1 Schematic diagram showing the formation of the mesoporous polymer.

NH₂

+ Paraformaldehyde

NH

Scheme 2 Schematic diagram showing the formation of the mPMF-Ag⁰ nanocatalyst.



= Ag nano

170 °C. 72 hrs

Paper

was complete, the reactor was quickly cooled to room temperature. The excess oxygen was depressurized slowly. The progress of the reaction was verified by GC analysis of the reaction mixtures. The solvent was removed under reduced pressure and the product was isolated by column chromatography. All the prepared compounds were confirmed by ¹H and ¹³C NMR spectra.

General procedure for the hydration of nitrile to amide

Under air, 1 mmol of nitrile, 3 mL of water and 20 mg of the mPMF-Ag⁰ nanocatalyst were added to a Teflon-sealed screwcap round bottomed flask and stirred at 90 °C for 7 h. The GC yields were obtained by taking a small aliquot (\approx 50 µL from the hot solution and extracted with CH₂Cl₂) (2 mL × 3). Isolated yields were obtained by either decanting the aqueous layer from the product crystals or by evaporation of the solvent followed by column chromatography over silica gel (eluent:ethyl acetate).

Results and discussion

Characterization of the mPMF-Ag⁰ material

X-ray diffraction. In Fig. 1, the powder X-ray diffraction pattern of mPMF- Ag^0 is shown. The mesoporous polymer,



Fig. 1 Powder XRD pattern of the mPMF-Ag⁰ material.

mPMF, shows one broad diffraction peak centred at 2θ = 21.70, which corresponds to a characteristic peak of the mPMF (Fig. S1†). In the XRD pattern of the mPMF-Ag⁰, the additional prominent diffraction peaks at the respective 2θ values are for zero valent FCC silver, representing (111), (200), (220) and (311) crystal planes due to Braggs reflection at 2θ = 38.06, 44.24, 64.66 and 77.43 degrees. All these indicate that the mPMF-Ag⁰ nanocatalyst existed in the crystalline state.²⁵

TEM analysis. Fig. 2 shows HR-TEM images of Ag-NPs supported on mesoporous poly-melamine-formaldehyde. HR-TEM images (Fig. 2) suggested a foam-like interconnected mesoporous network structure containing high electron density dark spots throughout the specimen, which are spherical in nature. These spherical particles are assigned to Ag-nanoparticles in mPMF-Ag⁰. The particle size of the silver nanoparticles ranges from 7.8 \pm 0.2 nm (obtained from Fig. 3b). Particles are well dispersed inside the pores and have uniform size distribution over the surface.²⁶ TEM-EDX from the obtained nanomaterials (Fig. 3c) indicated the presence of the expected elements in the structure of the catalyst, namely silver, nitrogen and carbon. The SAED image is provided in Fig. 3a.

SEM analysis. The scanning electron micrograph of the mPMF-Ag⁰ is shown in Fig. 4. The FE-SEM image indicates uniform submicron-sized spherical morphology of the polymer mPMF-Ag⁰ material. Spherical particles are aggregated among themselves to form a large assembly of particles and they are interconnected with each other.

UV-vis spectroscopy study. Optical absorption of the mPMF-Ag⁰ was investigated in Fig. 5. UV-vis absorbance spectra (Fig. 5) of mPMF exhibit two peaks at 266 and 306–316 nm due to $n-\pi^*$ and $\pi \rightarrow \pi^*$ transitions, respectively. But a distinguishable change in absorbance is observed in the case of the mPMF-Ag⁰ material. This material displays intense absorption in the region 250–550 nm which can be assigned to the metal to ligand charge transfer followed by intraligand transitions, respectively. A new band in the region 400–550 nm was also observed with the characteristic absorption band of Ag nanoparticles at around 400 nm and smooth shoulder near 500 nm.^{18b,24,27}

FT-IR analysis. The loading of the silver nanoparticle onto the mesoporous polymelamine (mPMF) support was



Fig. 2 HR-TEM images of the mPMF-Ag⁰ material.



Fig. 3 (A) SAED image. (B) Size distribution plot. (C) TEM-EDX image of the mPMF-Ag⁰ material.

confirmed by comparison of the FT-IR spectra (Fig. 6) of the support before and after loading with the metal, in the mid-IR (4000–400 cm⁻¹) region. IR spectra show a stretching vibration for $-CH_2$ at 2916 cm⁻¹ for the mPMF support and mPMF-Ag⁰ nanocomplex. FT-IR spectrum of mPMF shows peaks associated with -NH-stretching at 3409 cm⁻¹ which is lowered to 3405 cm⁻¹ in mPMF-Ag⁰. The imine stretching at 1651 cm⁻¹ is observed. Other characteristic peaks of melamine are observed around 1438 cm⁻¹, 1020 cm⁻¹ and



Fig. 4 FE-SEM images of the mPMF-Ag⁰ material (A) 10 μ m and (B) 2 μ m.

813 cm⁻¹ in mPMF. These peaks are also observed in mPMF-Ag⁰ around 1053 cm⁻¹ and 814 cm⁻¹. The triazine stretching at 1547 cm⁻¹ and 1474 cm⁻¹ in mPMF is shifted to



Fig. 5 UV-vis spectra of mesoporous mPMF and mPMF-Ag⁰.



Fig. 6 FT-IR spectra of mPMF and mPMF-Ag⁰.

1552 $\rm cm^{-1}$ and 1478 $\rm cm^{-1},$ respectively, in the mPMF-Ag^0 nanocomplex. 24,28

EPR study. We further extended our investigations to the characterization of mPMF-Ag⁰. We carried out careful EPR measurement of mPMF-Ag⁰ at room temperature (298 K) in solid state and the corresponding spectrum is shown in Fig. 7. It provides information on the nature of the metal ion environment in the Ag-grafted mesoporous polymelamine formaldehyde framework. It shows a symmetric signal and the *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 mesoporous polymelamine formaldehyde matrix.²⁹

Raman spectral study. In addition to the above discussed spectroscopy studies, Raman spectroscopy also provided useful information regarding the interaction of Ag nanoparticles and mesoporous mPMF. Raman spectra of mPMF and mPMF-Ag⁰ (Fig. 8a and b), the same sample of mPMF-Ag⁰, are provided. Raman spectra of mPMF-Ag⁰ show two well documented D and G bands at 1341 cm⁻¹ and 1532 cm⁻¹, respectively (Fig. 8a). The D band at 1341 cm⁻¹ is attributed



Fig. 7 EPR spectrum of mPMF-Ag⁰.

to the defect or disorder in carbon atom and the G band at 1532 cm^{-1} is attributed to sp^2 in plane vibration of the carbon atom. Raman spectroscopy of mesoporous mPMF-Ag⁰



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Fig. 8 Raman spectra of mPMF and mPMF-Ag $^{\rm 0}$ (a) and Raman spectra of Ag nano in mPMF (b).

Paper

showed different intensity peaks from each component. The peak at 524 cm^{-1} corresponded to Ag nano³⁰ which is shown in Fig. 8b.

Thermal analysis. The quantitative determination of the organic content and the framework stability of the mPMF and mPMF-Ag⁰ samples are obtained from the thermogravimetric (TG) analysis under N₂ flow. TGA of the mPMF-Ag⁰ material is shown in Fig. 9. The TGA of this material showed the first weight loss around 150 °C due to desorption of physisorbed water. This was followed by a gradual decrease in weight after 400 °C. Thus this thermal analysis data suggested that the mPMF-Ag⁰ sample is completely decomposed after 550 °C.

Specific surface area. The surface area of the mPMF-Ag⁰ determined by the N₂-adsorption study reveals that mPMF-Ag⁰ exhibits a specific surface area of about 118.751 m² g⁻¹. The BET surface area of mPMF is 930.000 m² g⁻¹ with an average pore size of 15.7 nm.²⁴ A considerable decrease in the surface area to 118.751 m² g⁻¹ in mPMF-Ag⁰ suggests that silver nanoparticles are anchored in the inner surface of the pores (Fig. 10).

Catalytic activities

Oxidative esterification reaction. The catalytic activity of the newly synthesized mPMF-Ag⁰ was investigated for the direct oxidative esterification reaction of activated alcohols with alcohols. Benzyl alcohol and methanol were used in the model reaction with K_2CO_3 as base and mPMF-Ag⁰ as the catalyst. Molecular oxygen was employed as the oxidant. Methyl benzoate was obtained as the product (Scheme 3). The effect of base, temperature, time, oxidant and amount of catalyst were studied for the reaction.

Initially, the reaction of benzyl alcohol with methanol in the presence of 30 mg of mPMF-Ag⁰ and 3 mol% K_2CO_3 at 70 °C under 1 atm of oxygen atmosphere for 3 h afforded methyl benzoate in 35% yield (Table 1, entry 1). When the amount of K_2CO_3 was increased to 5 mol%, a yield of 72% for methyl benzoate was obtained (Table 1, entry 2). The amount of base was further adjusted (Table 1, entries 3 and 4). To our great delight, a very good yield of methyl benzoate



Fig. 9 TGA curves of mPMF and mPMF-Ag⁰.



was obtained with the amount of K_2CO_3 increasing to 10 mol%. An excellent yield of methyl benzoate (98%) could be achieved by prolonging the reaction time from 3 h to 5 h (Table 1, entry 4). The oxidative esterification reaction was tremendously influenced by the base used (Table 1, entries 5–12). No desired product was obtained in the absence of a base (Table 1, entry 5) and thus the addition of a base was essential for achieving the reaction. Among the screened bases, K_2CO_3 and Na_2CO_3 were found to be effective bases (Table 1, entries 4 and 6). Li_2CO_3 , Cs_2CO_3 and KHCO₃ had moderate activities, giving the desired product in 70%, 52% and 60% yields, respectively (Table 1, entries 7–9). Other employed bases including K_3PO_4 , NaOAc, and KOAc were less effective, giving methyl benzoate in only 7%, 4%, and



Scheme 3 Oxidative esterification of benzyl alcohol.

Table 1 Effect of base on the oxidative esterification of benzyl alcohol with MeOH catalyzed by mPMF-Ag^{0a}

Entry	Base (mol%)	Time (h)	Conversion (%)	Selectivity (%)
1	$K_2CO_3(3)$	3	35	82
2	$K_2CO_3(5)$	3	72	94
3	$K_2 CO_3 (10)$	3	85	92
4	K_2CO_3 (10)	5	98	99
5	_	5	No reaction	_
6	Na_2CO_3 (10)	5	96	97
7	Li_2CO_3 (10)	5	70	92
8	$Cs_2CO_3(10)$	5	52	80
9	KHCO ₃ (10)	5	60	86
10	$K_{3}PO_{4}(10)$	5	7	68
11	NaOAc (10)	5	4	12
12	KOAc (10)	5	2	5

^{*a*} Reaction conditions: benzyl alcohol (1 mmol), mPMF-Ag⁰ (20 mg), 4 mL of MeOH, 70 °C, 1 atm O₂. Reaction progress was determined by GC and isolated products were characterized by ¹H and ¹³C NMR.

2% yields, respectively (Table 1, entries 10-12). The reaction gave methyl benzoate as the major product, with a selectivity of 99% at nearly complete conversions. Only trace amounts of benzaldehyde were detected as a by-product in the reaction. In the oxidative esterification reaction, the 1st step is the oxidation of alcohol to aldehyde, for which a base is essential. The aldehyde further reacts with MeOH to give the desired ester. In our study, we have found that, up to a certain limit of basicity of the medium, the desired ester product was maximum. Beyond this limit, the selectivity of ester decreases with the basicity of the medium. This observation is well supported by literature evidences.7d,e The reason behind this phenomenon is that, in a strong basic medium, either homocoupling reaction occurs or the desired ester product is further hydrolyzed to give the corresponding acids. Thus 10 mol% K₂CO₃ in 4 ml of methanol was found to give the maximum ester product. The distribution of the products depended strongly on the nature of the doping metal in the mPMF support and, for a given catalyst, on the reaction time. However, in most of the runs, methyl ester was a predominant product at the end of the reaction. The reactions occurred in highly concentrated solutions of the substrate in methanol, which allowed us to achieve high concentrations of the product in the final mixtures. Turnover numbers (TONs) also reached high values (1680) reflecting the high stability of the catalyst. TONs rarely exceed a few hundred units.33 These features represent the important technological advantages of the process. It is also important that the catalysts are solid materials which are insoluble in the reaction mixture and can be separated from the products by simple centrifugation or filtration and re-used.

The reaction temperature was also investigated. A very poor yield was obtained at room temperature (25 °C). Then the temperature was increased to 50 °C giving 40% yield of methyl benzoate. The temperature was gradually increased to 60 °C and finally to 70 °C when the best result was obtained. No noticeable change in yield was observed at temperatures higher than 70 °C and thus 70 °C was chosen as the optimized reaction temperature (Fig. 11).

The effect amount of catalyst was also verified for the esterification reaction. The reaction was not fruitful without the presence of the catalyst. The catalyst amount was varied from 10 mg to 30 mg. It was found that 20 mg of catalyst served best for the reaction (Fig. S2†). An important advantage of this catalytic system is that an air atmosphere in place of pure dioxygen also affords good yields (Table 2, entries 1–3). The blank experiment shows that only an 8% yield of methyl benzoate was obtained under N₂ atmosphere (Table 2, entry 5). In the direct oxidative ester synthesis process, one of the key steps is the formation of aldehyde from alcohol which slows down in N₂ medium, so the yield is highly decreased.

With these optimized reaction conditions, we explored our substrate scope of various activated alcohols. Delightfully, a high degree of functional group tolerance for the alcohols was observed and the results are demonstrated in Table 3. A



Fig. 11 Effect of temperature on the oxidative esterification of benzyl alcohol.

Table 2 Effect of reaction atmosphere on the oxidative esterification of benzyl $alcohol^{\alpha}$

Entry	Atmosphere	Time (h)	Yield (%)	Selectivity (%)
1	Air	5	86	92
2	Air	6	87	94
3	Air	10	90	94
4	O_2	5	98	99
5	N_2	12	8	30

 a Reaction conditions: benzyl alcohol (1 mmol), mPMF-Ag^0 (20 mg), K₂CO₃ (10 mol%), time (5 h), 4 mL of MeOH, 70 °C. Reaction progress was determined by GC and isolated products were characterized by $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR.

series of esters were obtained in good to excellent yields. It was also identified that in order to get a high yield of the product, the reaction time was not an important consideration. Benzylic alcohols with electron-donating and electronwithdrawing groups gave excellent yields of products (Table 3, entries 1–20). Like *para-* and *meta-*substituted substrates, the sterically more hindered *ortho-*substituted alcohols also gave excellent results under the same reaction conditions (Table 3, entries 4 and 15). It was worth noting that lignin model compounds could be successfully oxidized into the desired products in excellent yields (Table 3, entries 19 and 20). 1-Methyl naphthoate was also produced in descent yield from the corresponding alcohol (Table 3, entry 21). Standard yields of the respective esters were also obtained from heteroatom alcohols (Table 3, entries 22 and 23).

Hydration of nitriles in aqueous medium. The catalytic activity of mPMF- Ag^0 was also verified for the hydration of nitriles in aqueous medium to produce the respective primary amides (Scheme 4). Aqueous hydration of benzonitrile to benzamide in air was taken as the model reaction (Scheme 5). The temperature of the reaction was varied. No reaction occurred at room temperature. Very little conversion was observed at 50 °C. The temperature was gradually raised to 75 °C and finally 92% product yield was obtained at 90 °C. The

Paper

Table 3 mPMF-Ag⁰ catalyzed oxidative esterification of activated alcohols with methanol under O2^a



Paper



^{*a*} Reaction conditions: alcohol (1 mmol), mPMF-Ag⁰ (20 mg), K_2CO_3 (10 mol%), time (5 h), 4 mL of MeOH, 70 °C, 1 atm O_2 . Reaction progress was determined by GC and isolated products were characterized by ¹H and ¹³C NMR.





Scheme 5 Hydration of benzonitrile under optimized conditions.

reaction temperature was further raised but no major change in conversion was noticed (Fig. 12).

With the optimized reaction conditions, the scope of the reaction was explored by the hydration of a range of nitriles to the corresponding amides in air. The results are summarized in Table 2. All nitriles were efficiently converted to amides with 90-99% conversion in 7 h and at 90 °C. After completion, the reactions were cooled to 0 °C, and in most cases, the product amides crystallized as white needles and were easily isolated. The identity of the isolated amides was confirmed by GC and NMR spectroscopy. Yet, so far, the studies of the influence of the silver particle size on the catalytic activity have been mostly confined to particles that are larger than 20 nm in diameter. The properties of small nanoclusters, especially below 10 nm, could be dramatically different from larger ones due to the quantum size effects. It is still scarce due to the difficulty in the synthesis of small Ag clusters. Recently, silver nanoclusters with a controlled core size have been successfully synthesized by different methods, which make it possible to study the catalytic activity of Ag nanoclusters toward hydration of nitriles.³⁴ Here, we synthesized 7.8 \pm 0.2 nm silver nanoparticles. On the other hand, we have used mPMF as the support, which is highly porous with a large number of nitrogen atoms. So, very small sized silver nanoparticles can easily be incorporated into it and Ag⁰ NPs at the surface of the mPMF strongly bind with a nitrogen



Fig. 12 Variation of % yield of amide with temperature.

atom present in mPMF. The mPMF-Ag nanocatalyst is highly stable and effective for the hydration of nitriles. The mesoporous and nitrogen-enriched surface of mPMF increased the catalyst novelty. It is an effective catalyst, affording benzamides as the major product in 90–98% yield (Table 4). A trace amount of benzoic acid was formed as a side product *via* over-hydrolysis of benzamide.

The substituted benzonitriles bearing electron-withdrawing groups (Table 4, entries 2-10) exhibited slightly more efficient conversions to amides than those with electron-donating groups (entries 11-16). Presumably, the presence of the electron withdrawing group makes the nitrile carbon more susceptible to nucleophilic attack by an activated water molecule. This is in agreement with other catalyst systems³¹ although there have been exceptions reported.¹²¹ As previously reported, 32 ortho-substituted benzonitriles exhibited lower conversion relative to meta and para-substituted benzonitriles (Table 4, entries 2-4, 6-9, 14-16), which is attributed to steric hindrance of the ortho-substituted benzonitriles. The conversion proceeded smoothly even in the presence of heteroatoms such as N, O and S in the substrates (entries 17-23) and a range of heterocyclic aromatic amides was obtained in excellent isolated yields. Even indole-3-carbonitrile (entry 23) and 2-naphthonitrile (entry 24) were converted to indole-3carboxamide (98%) and 2-naphthamide (92%), respectively, in admirable yields. It was interesting to note that in all these reactions no other by-products such as carboxylic acids were present. Thus, the catalytic conditions described here are compatible with halides (entries 2-7), nitro (entries 8 and 9), trifluoromethyl (entry 10), methoxy (entries 11 and 12), thiomethyl (entries 13), methyl (entries 14-16), pyridyl (entries 17-19), furyl (entry 20), thiophenyl (entries 21-22), indoyl (entry 23) and naphthyl (entry 24) functional groups, which establish wide synthetic scope. The catalytic conditions described here are compatible with alkyl (entries 25 and 26) functional groups, which establish wide synthetic scope.

Possible reaction pathway

We have not studied the mechanism for the oxidative esterification reaction and hydration of nitriles. In the literature study, we have found that in case of oxidative esterification reaction, benzylic alcohol is oxidized to aldehyde which further oxidizes to hemiacetal in the presence of methanol. Silver nanoparticles present at the surface of the mPMF support play an important role in the oxidative dehydrogenation of hemiacetal to give the desired ester (Scheme 6).^{7a,d,40}

In case of hydration of nitriles, the rate of hydration depends on two factors: (a) electrophilic nature of "C" of the nitrile group and (b) nucleophilic nature of the water molecule. Thus, our aim was to develop a catalytic system, which can co-ordinate with the nitrile group, to make "C" more electrophilic as well as enhance the attacking power of the nucleophile (H_2O) to the electrophilic carbon centre. Several groups showed that the rate of hydration increases significantly when a "H" from a secondary coordination sphere interacts with water (Scheme 7).

 Table 4
 Hydration of various nitriles catalysed by mPMF-Ag^{0a}

Entry	Nitrile	Amide product	Amide yield (%)
1	CN		92
2	CI	NH ₂	97
3	CI		95
4	CN		94
5	Br		95
6	F CN	Br O NH ₂	99
7	F CN	F C NH2	97
8	O ₂ N CN		98
9	CN NO ₂		96
10	F ₃ C CN		96
11	MeO	F ₃ C NH ₂	94
12	MeO		90
	ОМе	MeO	

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Entry	Nitrile	Amide product	Amide yield (%)
13	MeS	O C NH ₂	91
14	CN		93
15	CN		90
16	CN		92
17	CN CN		97
18	CN CN		98
19	CN		96
20	CN CN		94
21	S CN	S C NH ₂	95
22	S CN		94
23	CN	NH ₂	98
24	H CN		92

Table 4 (continued)



^{*a*} Reaction conditions: nitrile (1 mmol), mPMF-Ag⁰ (20 mg), H₂O (3 mL), 90 °C, 7 h, in air. The products were isolated either by decantation or by column chromatography. They were identified by ¹H and ¹³C NMR.



Scheme 6 Possible mechanism of mPMF-Ag⁰ catalyzed esterification.



• Ag nano

 $\label{eq:scheme 7} \begin{array}{l} \mbox{Scheme 7} & \mbox{Possible mechanism of mPMF-} Ag^0 \mbox{ catalyzed hydration of nitrile.} \end{array}$

In our mPMF-Ag⁰ catalyst, Ag co-ordinates with the nitrile group to increase the electrophilicity of "C" of nitrile. Our mPMF support contains a large number of electron deficient aminal groups which can form a hydrogen bond with H_2O to increase the rate of attack of H_2O to electrophilic "C" of nitrile.^{1e,41}

Recyclability of mPMF-Ag⁰

For a heterogeneous catalyst, it is important to examine its ease of separation, recoverability and reusability. The reusability of the meso nanocatalyst was investigated in aerobic oxidative esterification of benzyl alcohol and hydration of benzonitrile. 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. As seen in Fig. 13, the catalyst can be efficiently recycled and reused six times without an appreciable decrease in product yield as compared to other reported systems (Table 5).

Heterogeneity test

A hot filtration test was performed with the mPMF-Ag⁰ catalyst to examine whether silver is being leached out from the mPMF support. The experiment was performed for the oxidative aerobic esterification reaction of benzyl alcohol. For the rigorous proof of heterogeneity, a test was carried out by filtering the catalyst from the reaction mixture at 70 °C after 3 h and the filtrate was allowed to react up to the completion of the reaction (5 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, the esterification reaction did not

Table 5 Comparison of catalytic activity of the present catalyst in the synthesis of ester and hydration of nitrile with other reported systems

Reaction	Catalyst	Reaction conditions	Conversion (%)/yield (%)	TON/reusable	Ref.
A ^a	Pd/Char	MeOH, 60 °C, O ₂ (1 atm), KOMe, 8 h	—/70	824/—	35
	Au/HMS	K ₂ CO ₃ , methanol, 130 °C, 10 atm O ₂ , 4 h	95/78	1960/6	36
	Ag-MPTA	K ₂ CO ₃ , MeOH, 45 °C, oxygen balloon, time 12 h	95/95	198/5	8
	mPMF-Ag	K ₂ CO ₃ , time 5 h, MeOH, 70 °C, 1 atm O ₂	99/>99	1960/6	This work
B^b	AgHAP	Water, 140 °C, 3 h	94/99	313/4	37
	Ag-CIN-1 nanocatalyst	Water, 100 °C, 3 h	96/96	—/5	38
	PVP-Ag	Water, 150 °C, 6 h	82/82	8200/5	39
	mPMF-Ag	Water, 90 °C, air, 7 h	>99/97	1960/6	This work

^{*a*} A = esterification of 4-chlorobenzyl alcohol. ^{*b*} B = hydration of 4-chlorobenzonitrile.



Fig. 13 Recyclability test of mPMF-Ag⁰.

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 silver was not being leached out from the solid catalyst during the oxidative aerobic esterification reaction of benzyl alcohol.

Conclusions

From our experimental observations, we conclude that a new silver nanoparticle grafted onto polymelamine formaldehyde has been developed as an efficient recyclable heterogeneous catalytic system for the direct oxidative esterification of alcohols and also for hydration of nitriles under neutral conditions. The catalyst is highly air and moisture stable and the catalytic process is advanced, green, economical and environmentally sustainable. The catalytic system offers a number of advantages, such as easy work-up, separation of the catalyst from the reaction mixture by filtration and reusability for several times with minimal loss of activity. All these taken together make the catalyst especially useful for practical applications in organic synthesis. Further work on other applications of the present catalytic system is in progress.

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