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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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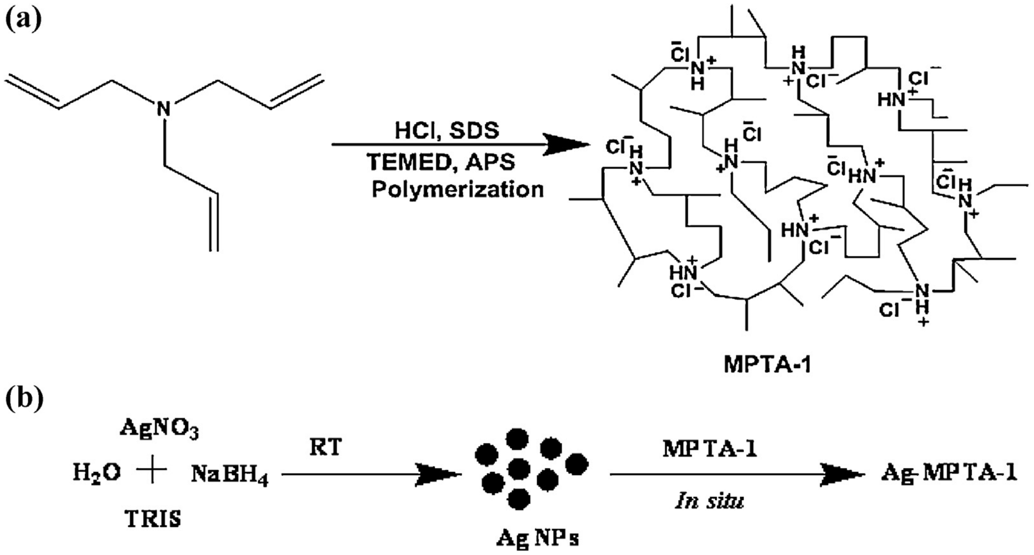

Scheme 1. Schematic diagram for the synthesis of mesoporous polymer MPTA-1 (a) and loading of Ag-NP on it at room temperature to obtain Ag-MPTA-1 nanocatalyst (b).

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