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Synthesis of silver nanoshell-coated cationic polystyrene beads: A solid phase catalyst for the reduction of 4-nitrophenol

Subhra Jana, Sujit Kumar Ghosh, Sudip Nath, Surojit Pande, Snigdhamayee Praharaj, Sudipa Panigrahi, Soumen Basu, Takeshi Endo, Tarasankar Pal *

Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, India

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Abstract

Silver nanoshell-coated cationic polystyrene beads have been synthesized at room temperature through immobilization of specific silver precursor ions, followed by wet chemical reduction. The electrostatic field force has been taken into consideration for the immobilization of precursor ions onto the resin beads. The as-synthesized particles were characterized by XRD, XPS, SEM, TEM, EDX, and FTIR studies and have been exploited as a solid phase catalyst for the reduction of 4-nitrophenol in the presence of sodium borohydride. The detailed kinetics of the reduction process was monitored under varied experimental conditions. At the end of the reaction, the catalyst particles remain active. They can thus be separated from the product, 4-aminophenol, and can be recycled a number of times after the quantitative reduction of 4-nitrophenol. The activity of the solid catalyst particles has also been examined to promote the reduction of other nitrophenols, e.g., 2-, 3-nitrophenol. The synthesis of the solid catalyst particles, their applications and detailed kinetic aspects of the reduction of 4-nitrophenol have been reported.

Keywords: Silver nanocomposites; Resin; Nitrophenols; Catalysis; Kinetics

1. Introduction

In recent years, fabrication of composite materials has received enormous attention due to their potential applications in the field of electronics, photonics, magnetics and catalysis [1–9]. The advent of composite materials is playing a pivotal role in the field of materials research. Thus, the scope of the research activity on advanced materials will centre on such composite materials and will include their peripheral fields such as nanotechnology. These composite materials may find a wide range of applications in the areas of microelectronic devices, non-linear optics, electrochemical sensors, bioanalysis [10–12], chemical sensors [13] and capsules for controlled release of therapeutic agents [14].

Among the metallic nanoparticles, silver has drawn great scientific interest because of its wide range of applications such as in catalysis [15–17], surface-enhanced Raman scattering studies [18,19], and photographic processes [20,21], etc. In particular, fabrication of silver-coated polystyrene beads is of special interest. Several routes have been developed to fabricate them, including micro cutting, nanolithography [22], electron beam lithography [23], photolithography [24], *in situ* chemical reduction [9,25,26] and self-assembly [27,28]. The employment of template synthesis techniques has also been demonstrated for the preparation of such nanocomposites [29,30]. Again, immobilization of metal nanoparticles on the surfaces of the polystyrene beads is one of the most popular routes for their synthesis [31]. However, in most cases, the degree of surface coating of the polystyrene bead is low and the metal coating is non-uniform, owing to the interparticle Coulomb repulsion, leaving a large number of uncovered polystyrene beads [27]. Thus, how to achieve complete coverage of polystyrene beads by ultra-thin uniform layers of silver nanoparticles is at present a challenge to the researchers.

The solid phase synthesis technique was first reported by Merrifield in 1963 [32]. Since 1963, such a novel technique has become an extremely powerful tool for the scientists in combinatorial chemistry research [8,9,33] and has also accelerated the drug discoveries [34–36]. The important advantage of solid phase over solution phase synthesis is the

* Corresponding author. Tel.: +91 3222 283 320; fax: +91 3222 282 252.
E-mail address: tpal@chem.iitkgp.ernet.in (T. Pal).

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simplified purification procedure and the easy handling of multiple reaction vessels. Again, the unreacted reagents and impurities can be easily filtered off from the reaction mixture, leaving the pure product attached to the solid support [37].

This article reports a facile approach for the synthesis of silver nanoshell-coated resin beads, based on the three-dimensional entrapment of the silver nanoparticles by electrostatic attraction between polystyrene beads and the oppositely charged complex precursor ions, followed by wet chemical reduction. The as-synthesized particles were characterized by XRD, XPS, SEM, TEM, EDX and FTIR studies. Finally, the resin-bound silver nanocomposites have been successfully exploited as a solid phase catalyst for the reduction of 4-nitrophenol in presence of $NaBH_4$. The detailed kinetic aspects of the reduction were studied under varied experimental conditions. Thus, the present work is related to a simple and straightforward technique for the synthesis of resin-bound silver nanocomposites, a novel and fruitful solid phase catalyst, which at the end of the reaction remain active and can be separated from the reaction mixture. To the best of our knowledge, there exists no other report about a solid phase catalyst for the reduction of 4-nitrophenol while taking resin-bound silver nanocomposites into consideration.

2. Experimental

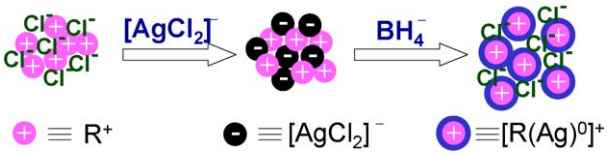
2.1. Reagents and instruments

All the reagents were of AR grade. Double distilled water was used throughout the experiment. Anion exchange resin SERALITE-SRA-400 was purchased from Sisco Research Laboratory, India. Silver nitrate ($AgNO_3$) and HCl were obtained from Merck. Nitroaromatics, viz. 4-nitrophenol (4-NP), 3-nitrophenol (3-NP) and 2-nitrophenol (2-NP) (all from Aldrich), were used as received. Sodium borohydride ($NaBH_4$, Sigma) solution was prepared freshly in ice-cold distilled water each time just before use. Hydrazine hydrate and ascorbic acid were purchased from BDH, India, and were used as received.

All UV–vis absorption spectra were recorded in a SPECTRASCAN UV 2600 digital spectrophotometer (Chemito, India) with the solution in a 1 cm quartz cuvette. TEM analysis was performed with an instrument H-9000 NAR, Hitachi, using an accelerating voltage of 300 kV. XRD was done in a PW1710 diffractometer, a Philips, Holland, instrument. The XRD data were analyzed using JCPDS software. XPS and FTIR studies were performed with an ESCALAB-MK-II, UK, and a Thermo-Nicolet continuum FTIR microscope, respectively. SEM analysis was performed with a JEOL, JSM 5800 instrument and an EDX machine (Oxford, Link, ISIS 300) is attached to the instrument to obtain the particle morphology.

2.2. Preparation of resin-bound silver nanocomposites

Resin-bound silver nanocomposites were synthesized by a two-step procedure. At first, a few drops of dilute HCl (1 M) solution were added to the stirred freshly prepared aqueous solution of silver nitrate. A white curdy precipitate of silver chloride thus obtained was washed thoroughly by distilled water to remove HNO_3, then dried on a water bath and kept under nitrogen atmosphere. The silver precursor $[AgCl_2]^-$ complex was prepared by dissolving 0.3 g of solid AgCl in concentrated HCl solution and placing the mixture in an ultrasonic bath for dissolution. Next, the silver precursor ions were allowed to exchange with Cl^- ions of the neat chloride form of anion-exchange resin beads (R^+Cl^-) and the mixture was kept overnight. The resin beads, on which silver precursor ions were immobilized, were washed several times with water to drain out the liberated HCl and un-exchanged $[AgCl_2]^-$ and then reduced with a freshly prepared ice-cold aqueous solution of sodium borohydride. The reduction of the attached silver precursor ions leads to silver nuclei and nanoparticles deposition onto the polystyrene beads (Scheme 1). The as-prepared shining reddish-black-silver-coated beads $[R(Ag)^0]^+Cl^-$, were washed thoroughly with distilled water and dried at room temperature (25 °C) under vacuum. These beads were employed as solid phase catalysts for the reduction of nitro compounds. The catalytic activity of the solid matrices remains unaltered over six months. The mechanism of the above synthetic procedure is represented below:



Scheme 1. Schematic representation of synthesis of silver nanoshell-coated polystyrene beads.

$$AgNO_3 + HCl \rightarrow AgCl\downarrow + HNO_3$$

$$AgCl + HCl \rightarrow H^+[AgCl_2]^-$$

$$R^+Cl^- + H^+[AgCl_2]^- \rightarrow R^+[AgCl_2]^- \xrightarrow{[H]} [R(Ag)^0]^+Cl^-.$$

2.3. Catalytic reaction

In a typical reaction, 0.0015 g solid catalyst was taken along with an aqueous solution of 4-nitrophenol (0.1 mM) in a 1 cm quartz cuvette and the volume of the solution was made up to 3 mL. Next, 0.3 mL of 0.1 M aqueous $NaBH_4$ solution was added to the reaction mixture and time-dependent absorption spectra were recorded in the UV–vis spectrophotometer at 30 ± 2 °C.

3. Results and discussion

Anion exchange resin is a polymer that contains quaternary ammonium groups or amines as an integral part of the polymer lattice with an equivalent number of anions such as chloride, hydroxyl, or sulfate ions [38]. SERALITE-SRA-400, a cross-linked polystyrene containing quaternary ammonium groups as an integral part, was supplied in the chloride form with ion