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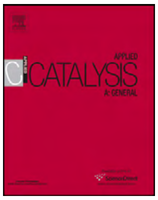

New catalytic route: Hydrogels as templates and reactors for *in situ* Ni nanoparticle synthesis and usage in the reduction of 2- and 4-nitrophenols

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ABSTRACT

Nickel nanoparticles inside poly(2-acrylamido-2-methyl-1-propansulfonic acid) (p(AMPS)) hydrogel were prepared by reduction of Ni(II) ions absorbed within hydrogel network. TEM images confirmed that *in situ* formed nickel particle in p(AMPS) hydrogel networks are about 100 nm. These nickel metal nanoparticles containing hydrogel-composites were utilized as catalysts and reaction media for the reduction reactions of aromatic nitro compounds, 2- and 4-nitrophenols with aqueous $NaBH_4$. The reduction rate constants at four different temperatures (30, 40, 50 and 60 °C) and activation parameters were calculated. The activation energies (E_a) for 4- and 2-nitrophenols are 25.70 and 38.69 kJ mol^{-1}, respectively. It was found that these types of hydrogel-composite catalyst systems can be used repetitively up to five times with 100% conversion and only with 25% reduction in the initial reduction rate.

1. Introduction

Recently, metal nanoparticles with various supports have been utilized for a number of applications as sensors, electronic devices, catalysts in many related fields such chemistry, physics, biotechnology and material science due to their nanoscale optical, electrical and catalytic properties [1–3]. The surface area of nanoparticles is fairly important in heterogeneous catalysts. The main issue that hinders pervasive use of metal nanoparticles as catalyst is their high tendency to aggregate. Thus, to prevent aggregation, metallic nanoparticles are usually situated on supports such as polymers, metal oxides, silicates, dendrimers, colloids and latex particles [1,4]. Previously, hydrogel networks were reported as suitable support materials for the design and fabrications of metallic nanoparticles [5,6], however, never been used as reaction vessel. As known, hydrogels are three-dimensional crosslinked hydrophilic polymer networks imbibing large amounts of water due to the hydrophilic and/or ionizable functional groups such as $-SO_3H$, $-OH$, $-NH_2$, $-COOH$, $-CONH_2$ in their network structures [7–9]. Due to their versatility, hydrogels found various applications ranging from drug delivery and tissue engineering to environmental applications [10–13].

Aromatic amines are important organic pollutants and are intermediates or side products of many industrial products such as dyes, pharmaceuticals, agro-chemicals, cosmetics, photographic chemicals, additives, chelating agents, and so on [14–17]. For instance, p-aminophenol is an important reagent in the production of paraceatamol, which is used as an analgesic and antipyretic drugs [18,19]. Conventionally, p-aminophenol is produced by iron–acid reduction of p-nitrophenol. The major disadvantage of the iron–acid reduction process is the generation of large amount of Fe–FeO sludge that causes a serious pollutions problem [19]. Therefore, a great number of studies for reduction of p-nitrophenol to p-aminophenol have been performed over the past few decades [20–22]. Some of these methods are reduction with $NaBH_4$ in the presence of palladium nanoparticles [1], silver nanoparticles [3], gold nanoparticles [4], and reduction with H_2 in the presence of Ni–B alloy catalysts [23], reduction with hydrazine hydrate in the presence of Ni particles [2], and reduction with iron powder or stannous chloride under ultrasonic irradiation [24]. In addition to reduction of p-nitrophenol to p-aminophenol by hydrogen with Ni particles synthesized by different surfactants [25], many different catalysts based on precious metals such as Au and pt have also been used [26–28]. There are also reports in the literature for Pt and Pd and/or Au nanocluster preparation in organic reaction conditions with a series of microgels based on N,N-dimethyl acrylamide (DMAA)

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and N,N-dimethylaminoethylmethacrylate (DMAEMA) with varying crosslinking degree using ethylene dimethacrylate (EDMA) as crosslinking agent [29].

In this study, for the first time, we demonstrated that hydrogel network can be utilized for *in situ* nickel nanoparticles preparation by reduction of nickel ions absorbed into p(AMPS) hydrogel networks with a suitable reducing agent such as $NaBH_4$ and can be used as catalyst. Furthermore, these hydrogel-composites (*in situ* prepared nickel nanoparticle and p(AMPS) hydrogel network) were exploited as reaction vessel in the reduction of nitroaromatic compounds such as 4-nitrophenol and 2-nitrophenol to their corresponding aminophenols. The progress of the reduction reactions was followed by UV–vis spectrophotometer. The reactions were carried out at four different temperatures to calculate the activation parameters. The effects of catalyst and reduction agent amounts on the reduction of 4-nitrophenol were investigated at 30 °C. In order to determine the shelf-life of the catalyst various experiments were also performed on hydrogel-composite systems that were stored at different time periods after their syntheses.

2. Materials and methods

2-Nitrophenol (2-NP), 4-nitrophenol (4-NP), and $NaBH_4$ were purchased from Merck and used without further purification. Hydrogel was prepared using 2-acrylamido-2-methyl-1-propansulfonic acid (AMPS) as monomer, N,N′-methylenebisacrylamide as crosslinker (X-er), 2,2′-azobis(2-methylpropionamidine) dihydrochloride as an UV initiator. $NiCl_2{\cdot}6H_2O$ was used as metal ion source. All products were of analytical grade and purchased from Sigma–Aldrich, Acros and Fluka Chemical Companies. The 18.2 MΩ cm (Millipore Direct-Q3 UV) distilled water was used throughout the studies.

2.1. Characterization

Absorbed amount of nickel by p(AMPS) hydrogel was determined using Varian Liberty II AX Sequential ICP-AES (Inductive Coupled Plasma-Atomic) Spectrometry. The amount of catalyst was determined with TG measurements using a thermal Analyzer (SII TG/DTA 6300) by heating up to 1200 °C with a heating rate of 10 °C/min under 100 mL/min nitrogen flow. TEM images were acquired using JEOL 2010 (Japan) under vacuum operating at 200 kV. The sample was prepared for TEM imaging by suspending grinded hydrogel-composites in ethyl alcohol and a drop of this suspension placed on formwar-coated TEM grid. To monitor the conversion of nitro compounds (2-NP and 4-NP) to the corresponding reduced forms, a UV–vis spectrophotometer was employed (PG Instruments Ltd., T80+ model).

2.2. Hydrogel synthesis

P(AMPS) hydrogels were prepared via free radical polymerization in the presence of UV initiator by photo-polymerization technique. In a typical hydrogel synthesis procedure, 4.5 g (0.0217 mol) AMPS and 0.0167 g X-er (0.5 mol.% with respect to monomer) and the photo-initiator (∼10 mg) were dissolved in 3.5 mL of water. After mixing thoroughly, the precursor solution was injected into plastic straws (4 mm in diameter) and irradiated for 2 h to complete polymerization and crosslinking reaction simultaneously in photoreactor equipped with 8 lambs at 420 nm. The formed bulk hydrogels were removed from the plastic straws and cut into 4–5 mm length in cylindrical shapes, and cleaned by placing in distilled water for 3 days. The wash water replenished every 12 h to remove unreacted species (monomer, polymer, crosslinker, and initiator). After the cleaning procedure, hydrogels were dried in an oven to a constant weight at 50 °C and kept in sealed containers for further use.

2.3. In situ nickel nanoparticle synthesis in hydrogel network

Nickel particles inside hydrogel matrices were prepared according to the previously reported method [5]. Briefly, cleaned and known amount of dried hydrogel were placed in 0.1 M $NiCl_2{\cdot}6H_2O$ (100 mL) solution to load the hydrogels with nickel ions. The absorption studies were performed in water shaker bath at room temperature for 2 days. At the end of nickel ion absorption period, nickel ion loaded hydrogels were kept in distilled water for another 24 h remove unbound nickel ions. To form nickel particles *in situ*, cleaned nickel ion loaded hydrogels were transferred into 0.5 M $NaBH_4$ aqueous solution (100 mL), and the reduction reaction was proceeded for 12 h in a water shaker bath at ambient temperature. Again, nickel particles containing hydrogel-composites were washed in DI further and utilized for reduction reactions of nitro compounds as catalysis media. In order to determine the storage ability of the catalyst system, the composite hydrogels in water was purged with nitrogen for 10 min and stored in DI at room temperature in dark.

2.4. Catalytic reduction of nitro compounds

$NaBH_4$ (1.44×10^{-2} mol) was added to solution of nitro compounds (7.19×10^{-4} mol) in 50 mL of distilled water. 50 mg dried hydrogel-composites containing 5.92 mg nickel particles were placed in this solution. After the addition catalysts (hydrogel-composite), samples were directly withdrawn from the reaction medium at certain time intervals and diluted with DI followed by measuring UV–vis spectra of these solutions to monitor the decrease in intensity of the absorption peak at 400 nm for 4-NP, and 414 nm for 2-NP. The rate constant of the reaction was determined by measuring the change in intensity of these peaks with time. The progress of the reactions was followed at four different temperatures (30, 40, 50 and 60 °C), and the activation parameters for the reduction reactions of 4-NP and 2-NP to their corresponding amine forms, 4-aminephenol and 2-aminophenol, respectively, were calculated. For the recycling experiment, catalyst systems were collected by decantation after the reactions and washed three times with DI water and reused in the next reaction.

3. Results and discussion

A schematic representation of nickel particle synthesis in p(AMPS) hydrogel network is shown in Fig. 1. As shown in the figure, due to the electrostatic interactions between nickel ions and $-SO_3H$ groups of p(AMPS) network, the nickel ions can be loaded into the hydrogel network. With the suitable reducing agent such as $NaBH_4$, nickel ions are then reduced to its metallic nanoparticle forms as demonstrated in digital camera images of the figure (dark hydrogel picture). This procedure is facile and economically feasible not requiring heat or any other tools for metal nanoparticle synthesis in comparison to other methods that are tedious and have many experimental restrictions. The Ni metal nanoparticles in the presence of some other stabilizing agents such as linear polymer (i.e., linear p(vinyl alcohol) and p(N-vinyl-2-pyrrolidone)) and some surface active agents such as sodium dodecyl sulfate and a capping agents oleic acid [30,31]. The amount of nickel ions loaded to hydrogels was determined with ICP-AES in two ways. In the first method, the amounts of absorbed nickel ions were determined from the solution during metal ion loading studies. It was found that 122.6 mg nickel ion was absorbed by 1 g dry gels. In the second method, after loading the hydrogel network with nickel