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Silver nanoparticles immobilized on fibrous nano-silica as highly efficient and recyclable heterogeneous catalyst for reduction of 4-nitrophenol and 2-nitroaniline

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ABSTRACT

In this study, a novel fibrous nano-silica (KCC-1) based nanocatalyst (Ag/KCC-1) with high surface area and easy accessibility of active sites was successfully developed by a facile approach. KCC-1 with high surface area was functionalized with amino groups acting as the robust anchors so that the silver nanoparticles (Ag NPs) with average diameter of about 4 nm were well-dispersed on the fibers of the KCC-1 microspheres, without aggregation. The synthesized Ag/KCC-1 nanocatalyst exhibited excellent catalytic activity for the reduction of 4-nitrophenol and 2-nitroaniline using sodium borohydride ($NaBH_4$) in water at room temperature owing to the easy accessibility of the active sites. Importantly, the Ag/KCC-1 nanocatalyst was easily recovered and reused for at least ten cycles in both the reduction reactions; thus, confirming its good stability. The enhanced stability was attributed to the modification of the fibrous nature of KCC-1 by the amino groups; thus, restricting Ostwald ripening and leaching of Ag NPs. Therefore, the abovementioned approach based on fibrous KCC-1 provided a useful platform for the fabrication of noble metal nanocatalysts with easy accessibility, which would be highly efficient in various catalytic reductions.

1. Introduction

Recently, green chemistry has attracted considerable attention to overcome the problem pertaining to the environmental pollution being encountered by the global population. The processes avoiding the use of organic solvents for the transformation of harmful organic wastes into reusable compounds with low toxicity in aqueous solutions under mild condition are extremely significant for the chemists. In this aspect, the disposal of nitroaromatic compounds is an area of intensive research, recently [1–6]. Nitrophenols (NP) are among the most common organic pollutants in industrial and agricultural wastewaters. In particular, 4-NP is a notorious industrial pollutant exhibiting high solubility and stability in water [7,8]. Moreover, even low concentration of 2-nitroaniline (2-NA) in water is harmful to aquatic life and human health in terms of its toxicity, and potential carcinogenic and mutagenic effects [9,10]. Therefore, the Unites States Environmental Protection Agency has listed 4-NP and 2-NA as hazardous wastes and priority toxic pollutants. It is therefore important to develop effective methods for their removal. Till date, various processes have been developed for the disposal of these nitro-compounds including microbial degradation, photocatalytic degradation, microwave-assisted catalytic oxidation, electro-Fenton method, electrocoagulation, and electrochemical treatment [11–13]. However, the reduction of nitro group to amino group is considered to be the most efficient, green, and economical approach to dispose nitro-compounds [14–18], and the reduction products namely, 4-aminophenol (4-AP) and *o*-phenylenediamine (*o*-PDA) can be reused because they are important intermediates for the synthesis of drugs and dyes [9,19]. Therefore, development of low-cost, stable, and highly effective catalyst for the reduction of nitro-compounds in aqueous solutions under mild condition is highly desirable.

Noble metal nanoparticles (NPs) have attracted significant attention in catalysis science due to their high efficiency as heterogeneous catalysts in numerous liquid-phase catalytic processes [20–26]. The catalytic activity of NPs is strongly dependent on the active atoms on the surface that are usually related to the specific surface area, surface structure, and edges of the catalysts [27–29]. Smaller NPs exhibit superior catalytic activities because of their higher surface-to-volume ratio. However, stability of metallic NPs

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is another crucial issue for their further application. The surface energy of NPs increases with decrease in the particle size; thus, making them unstable leading to high tendency for inter-particle aggregation [30]. This eventually reduces catalytic efficiency of the catalysts. In order to control their catalytic properties, the catalytically active metal NPs are usually immobilized on the solid supports with mesopores such as SBA-15 [31,32], Al_2O_3 [33–35] and MCM-41[36–38] regarded as ideal supports for heterogeneous catalyst due to their excellent stability, high surface area, tunable pore size, and robust surface chemistry. The effectiveness of these materials as catalyst supports is attributed to the dispersion of the active catalytic sites on the large specific surface areas and pores, which in turn prevent the aggregation of NPs and improve the activity of the catalyst system. However, poor accessibility to these active sites inside the pores limits their applications for which significant mass transport is essential. Therefore, silica supports with easily accessible high surface areas, not due to the pores, are needed. Vivek Polshettiwar reported the fabrication of fibrous silica nanospheres (KCC-1) with easily accessible high surface area attributed to its fibers and not pores [39,40]. Therefore, the unique property of KCC-1 is extremely useful for the design of silica-supported catalysts, for which the accessibility of active sites can be increased significantly.

Inspired by the abovementioned considerations, this study aimed to develop novel catalysts with well-dispersed noble metal NPs and high accessibility, for the catalytic reduction of 4-NP and 2-NA by an eco-friendly approach. Silver (Ag) is relatively cheap compared to other noble metals such as gold (Au), palladium (Pd), and platinum (Pt). Moreover, Ag is non-toxic and eco-friendly. Thus, in this study, KCC-1 was used as the supporting material to stabilize Ag nanoparticles (Ag NPs) to obtain Ag/KCC-1 nanocatalyst with enhanced accessibility for active sites and high surface area. This novel catalyst displayed not only suitable catalytic reaction rate, but also excellent reusability in the catalytic reaction of 4-NP and 2-NA. The robust activity of this catalyst is attributed to its high accessibility and low likelihood of the aggregation of the Ag NPs on the KCC-1 nano-silica support system. Thus, Ag NPs immobilized on KCC-1 exhibited highly effective catalytic property, showing promising potential for the catalytic reduction of nitroaromatic compounds leading to their safe and eco-friendly disposal.

2. Experimental

2.1. Materials

Tetraethyl orthosilicate (TEOS), 3-aminopropyltriethoxysilane (3-APTES), 4-NP, and 2-NA were purchased from Sigma Aldrich and used as received. Reagent-grade cyclohexane, pentanol, cetylpyridinium bromide (CPB), and sodium borohydride ($NaBH_4$) were purchased from Tianjing Guangfu Chemical Company and used as supplied. All other reagents and solvents were used without further purification.

2.2. Preparation of KCC-1

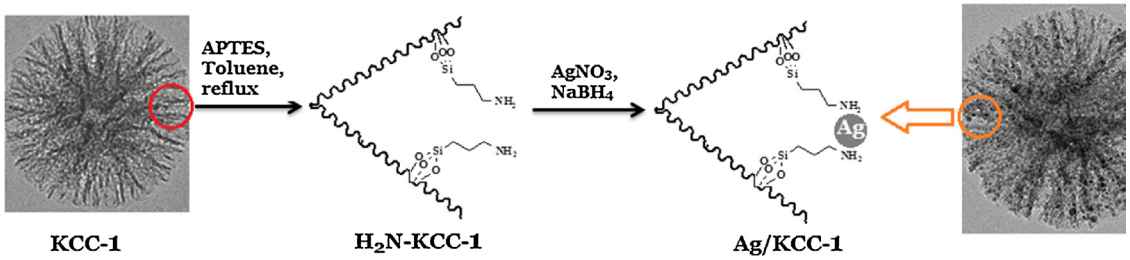
Vivek Polshettiwar reported the synthesis of KCC-1 by the microwave assisted hydrothermal technique [39]. However, in this study, KCC-1 was successfully synthesized by hydrothermal method instead of microwave assisted technique. The detailed experimental procedure was similar to the microwave assisted hydrothermal method. TEOS (2.5 g, 0.012 mol) was dissolved in a solution of cyclohexane (30 mL) and pentanol (1.5 mL) followed by the addition of a stirred solution of CPB (1 g, 0.0026 mol) and urea (0.6 g, 0.01 mol) in water (30 mL). The mixture so obtained was stirred for 30 min at room temperature, and the resulting solution was placed in a teflon-sealed hydrothermal reactor and heated at 120 °C for 5 h. After completion of the reaction, the mixture was cooled to room temperature and the silica so obtained was isolated by centrifugation, washed with distilled water and acetone, and finally dried overnight in a vacuum drying oven. The as-synthesized material was then calcined at 550 °C for 6 h in air to obtain KCC-1.

2.3. Preparation of Ag/KCC-1 nanocatalyst

The synthetic procedure for Ag/KCC-1 nanocatalyst is outlined in Scheme 1. KCC-1 was modified using 3-APTES by the following method: KCC-1 (1 g) and 3-APTES (0.3 g) were mixed in toluene (100 mL) and refluxed with stirring for 12 h under nitrogen atmosphere. White solid of aminopropylfunctionalized KCC-1 (H_2N-KCC-1) thus obtained was centrifuged, washed successively with chloroform, dichloromethane, and ethanol; and finally dried in vacuum. H_2N-KCC-1 (0.5 g) was ultrasonically dispersed in H_2O (50 mL), and subsequently $AgNO_3$ (0.1 g) was added. After being stirred for about 30 min, excess amount of $NaBH_4$ solution was added dropwise. Then the Ag NPs were formed and anchored on the aminopropylfunctionalized fibrous silica. Thus, the Ag/KCC-1 nanocatalyst was obtained by centrifugation and finally dried in vacuum.

2.4. General procedure for the reduction of 4-NP and 2-NA

4-NP was reduced by the following procedure: aqueous 4-NP solution (2.5 mL, 0.12 mM) was mixed with freshly prepared aqueous $NaBH_4$ solution (0.5 mL, 0.5 M) resulting in the formation of deep yellow solution. Subsquently, Ag/KCC-1 catalyst (20 μL, 10 mg mL^{-1}) was added to the yellow solution. The solution became colorless upon the completion of the reaction. For catalytic reduction of 2-NA, aqueous suspension of Ag/KCC-1 catalyst (30 μL, 10 mg mL^{-1}) was added in H_2O (2.8 mL), and then mixed with 2-NA aqueous solution (40 μL, 1.26×10^{-2} mol L^{-1}) and $NaBH_4$ (0.13 mL, 0.5 M) solution was injected rapidly with stirring. The color of the mixture vanished gradually, indicating the reduction of 2-NA. For both the abovementioned reduction reactions, the ambient temperature was maintained at 20 °C. Progress of the reaction was monitored by measuring the UV–Vis absorption spectra of the reaction mixture.



Scheme 1. Synthesis of Ag/KCC-1 nanocatalyst.