



Research paper

Silver nanoparticles assembled on modified sepiolite nanofibers for enhanced catalytic reduction of 4-nitrophenol



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ABSTRACT

Acid-activated sepiolite nanofibers (ASep) were organically modified with (3-aminopropyl) triethoxysilane (APTES) to produce the amino-functionalized nanofibers (NH₂-ASep). Due to the amino groups, highly dispersed silver nanoparticles (AgNPs) were assembled on the surface of NH₂-ASep by a simple chemical reduction approach, and the AgNPs were smaller than those directly deposited onto ASep surface. The as-synthesized Ag/NH₂-ASep nanofiber catalysts exhibited an excellent catalytic activity in the reduction process of 4-nitrophenol to 4-aminophenol with full conversion within 150 s in the presence of NaBH₄ as the reductant. The results indicated that Ag/NH₂-ASep nanofiber catalysts exhibited excellent catalytic activities because the highly dispersed of small-sized AgNPs were exposed on the surface of highly dispersed nanofibers with amino functional groups, allowing effective contact with the reactants and catalysis of the reaction. Moreover, the Ag/NH₂-ASep nanofiber catalysts are stable and easy to use for the catalytic reaction due to their one-dimensional nanofiber structure with functional amino groups.

1. Introduction

Green chemistry has been attracting considerable attention to overcome the problem pertaining to the environmental pollution. Nitrophenols (NP) are one kind of hazardous and toxic pollutants in industrial and agricultural wastewaters (Zhang et al., 2013a, 2013b; Yan et al., 2018). In particular, 4-nitrophenol (4-NP) is a notorious industrial pollutant exhibiting high solubility and stability in water, and is genotoxic and carcinogenic to human and animals (Zhang et al., 2012a, 2012b; Li et al., 2017). Therefore, the United States Environmental Protection Agency has listed 4-NP as hazardous wastes and priority toxic pollutants. It is therefore important to develop eco-friendly, stable and effective methods for the removal of 4-NP. Till date, the reduction of 4-NP over noble metal nanoparticles in the presence of NaBH₄ is an efficient and eco-friendly route to dispose 4-NP, and the reduction products namely, 4-aminophenol (4-AP) can be reused because they are important intermediates for the synthesis of drugs and dye (Saha et al., 2010; Tang et al., 2010).

As cost-effective and eco-friendly noble metal, silver nanoparticles (AgNPs) have been applied in various catalytic reactions (Chen et al.,

2007; Shimizu et al., 2011; Shi et al., 2012; Zhang et al., 2012a, 2012b; Dubey et al., 2014). It is well-known that the size of AgNPs is a critical factor in catalysis, and smaller-sized AgNPs tend to show a higher catalytic activity owing to they have a much greater surface-to-volume ratio. However, smaller AgNPs tend to easily aggregate due to their higher surface energy resulting from the high surface-to-volume ratio, which could remarkably reduce their catalytic activities (Dong et al., 2014; Yan et al., 2018). Also, the small sized AgNPs are difficult to recover from the solution after the catalytic reaction, so their recycling is not satisfactory for large-scale applications. Thus, AgNPs are usually assembled on the surface of solid substrates (e.g., clays, carbons, metal oxides and polymeric substance) to avoid the aggregation of small sized AgNPs and to improve the catalytic activity, recovery and flexibility (Wunder et al., 2010; Mu et al., 2013; Zhao et al., 2015).

Actually, the natural clay mineral sepiolite nanofiber has been used to prepare emerging catalysts for environmental application (Uğurlu and Karaoğlu, 2011; Ma and Zhang, 2016), due to its low cost, material availability and environmental friendliness (Lescano et al., 2014; Alcantara et al., 2015; Shen et al., 2016). However, pristine sepiolite nanofibers contain the serious fiber aggregation, small surface areas

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and a little hydroxyl groups, which are unfavorable to the fabrication of substrate-supported Ag nanofiber catalysts with a highly dispersed distribution of small sized AgNPs. Meanwhile, pristine sepiolite nanofibers have a very low adhesion to bond metal nanoparticles due to the absence of chemical conjunction, leading to the catalyst particles easily leaching from the substrate surface during the reactions (Zhang et al., 2013a, b). Thus, it is very necessary and important to disaggregate sepiolite fibers prior to loading of AgNPs and improve the adhesion between the metal nanoparticles and the substrates. However, to our best of knowledge, few studies have been reported concerning the above issues, which seriously restricts the application of sepiolite nanofibers in catalysis. In our previous work, the pristine sepiolite was pre-activated by acid treatment, and then we specially designed the method of (3-aminopropyl) triethoxysilane (APTES) grafting to obtain the highly dispersed sepiolite-based nanofibers with highly dispersed functional amino groups at low temperature for a short time (Zhang et al., 2018). The metal affinity amino group (-NH₂) grafted onto the sepiolite-based nanofibers surface can stabilize and disperse metal nanoparticles, which is also conducive to increase the amounts of the metal particles loaded (Dong et al., 2012; Zhang et al., 2013a, b; Dong et al., 2014). Therefore, the prepared highly dispersed sepiolite-based nanofibers with the high surface area and highly dispersed functional amino groups could be used as excellent catalyst substrates for the efficient fabrication of metal nanoparticles, which would be highly efficient in various catalytic reductions.

In this work, the synthesized highly dispersed sepiolite-based organic modified nanofibers are used as excellent catalyst substrates for the efficient fabrication of AgNPs. The sepiolite-based organic modified nanofiber catalysts with the high dispersion of small-sized AgNPs possessed the higher activities in catalyzing the reduction of 4-NP by NaBH₄ in the aqueous phase, compared to those sepiolite nanofibers without organic modification. Moreover, due to the one-dimensional nanofiber structure with functional amino groups, the catalysts are stable and easy to use for the catalytic reaction compared to the conventional powdery catalysts.

2. Experimental procedure

2.1. Materials

Pristine sepiolite was obtained from Hebei province, China. The major composition (wt%) is: SiO₂ 44.8%, MgO 21.3%, CaO 16.5%, Al₂O₃ 0.60%, K₂O 0.09%, and Na₂O 0.07%. Pristine sepiolite was washed with 2 M HCl then deionized water in order to remove impurities and the surface dust, and designated as Sep. The acid-activated sepiolite (ASep) and organically modified sepiolite (NH₂-ASep) were produced according to the literature (Zhang et al., 2018). 3-aminopropyltriethoxysilane (APTES), silver nitrate (AgNO₃) and sodium borohydride (NaBH₄) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China), and analytical reagents and deionized water were used in all experiments.

2.2. Catalyst preparation

0.2 g of the as-prepared samples (Sep, ASep and NH₂-ASep) were dispersed in 30 mL deionized water under ultrasonication for 30 min, followed by adding 20 mL of 1 mM AgNO₃ solution, and then 10 mL deionized water containing 3 mg NaBH₄ was added dropwise under stirring for 30 min at 25 °C. The resultant precipitate was filtered, repeatedly washed with deionized water, dried under vacuum, ground into fine powder, and denoted as Ag/Sep, Ag/ASep and Ag/NH₂-ASep, respectively.

2.3. Characterization

The chemical composition of sepiolite was determined by means of

PANalytical Axios mAX wavelength dispersive X-ray Fluorescence (XRF) spectrometer. X-ray diffraction (XRD) analysis was performed on a Bruker-AXS D8 Advance diffractometer using Cu K α radiation (0.15406 nm), operated at 40 kV and 40 mA in a scanning range of 3–80° (2 θ). Fourier transform infrared (FTIR) spectra were recorded in a Perkin-Elmer Spectrum One spectrometer, using the KBr pellet technique. Spectra were recorded between 400 and 4000 cm⁻¹, with a nominal resolution of 4 cm⁻¹. X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo Scientific Escalab 250Xi spectrometer equipped with an Al K α monochromator X-ray source. The binding energy (BE) was referenced to the C 1s peak at 284.6 eV. N₂ adsorption measurements were performed at 77 K using a Micromeritics ASAP 2020 gas sorption instrument. Before measurement, the samples were degassed at 120 °C for > 6 h. The specific surface areas were calculated using the multi-point BET (Brunauer-Emmett-Teller) method and the total pore volumes (V_{tot}) were estimated from the adsorbed volume at a relative pressure (P/P₀) of 0.995. The pore size distributions were determined by the adsorption branch of isotherms using the BJH (Barett–Joyner–Halenda) method. The micropores area (S_{micro}) and the micropore volume (V_{micro}) were obtained via t-plot analysis. Scanning electron microscopy (SEM) combined with EDS analysis was conducted on a Tescan Mira3 LMU. Scanning transmission electron microscopy (STEM) observations combined with EDS analysis were performed using a Titan G2 60–300 microscope operated at an accelerating voltage of 300 kV. UV–Vis absorption spectra were measured at room temperature with a Shimadzu UV-2600 UV–vis spectrophotometer.

2.4. Catalytic property evaluation

2.7 mL of 4-nitrophenol (4-NP, 0.12 mM) and fresh NaBH₄ solution (7.2 mM) mixed solution was transferred into a quartz cuvette. 50 mg of the as-prepared samples (Ag/Sep, Ag/ASep and Ag/NH₂-ASep) were fully dispersed in 25 mL of deionized water. Subsequently, 0.3 mL of the above solution was added into the quartz cuvette. The reaction was carried out at room temperature without stirring. Progress of the reaction was monitored at λ_{\max} = 400 nm using a UV–vis spectrophotometer. To investigate the reusability of the Ag/NH₂-ASep catalyst, 10 mg of the sample and the corresponding amounts of 4-NP and fresh NaBH₄ solutions noted previously were used. The reaction was performed at room temperature for 6 min with continuous stirring, and then 3 mL of the mixture was filtered through a 0.22 μ m membrane filter, and measured by UV–vis spectrophotometer. The catalyst was separated and reused for 5 cycles under the same reaction procedure.

3. Results and discussion

3.1. Characterization of Ag/NH₂-ASep

Schematic illustration for the synthetic route of Ag/NH₂-ASep is shown in Fig. 1. Acid washed sepiolite (Sep) fibers have flat or straight shapes agglomerated in dense bundles. After acid activation, ASep showed a disaggregated fiber morphology and the nanofibers were broken into smaller fibers. To acquire highly dispersed nanofibers with amino functional groups, APTES was introduced on the ASep surface by grafting method. Finally, AgNPs were successfully fabricated by a simple chemical reduction approach to produce Ag/NH₂-ASep nanofiber catalysts. To investigate the influence of the modification processes on the surface performance of APTES and the crystalline natures of the Ag/NH₂-ASep, wide-angle XRD patterns of Sep, ASep, NH₂-ASep and Ag/NH₂-ASep were analyzed (Fig. 2). All of the X-ray reflections of Sep can be indexed to the sepiolite structure (JCPDS 75-1597), associated with a little of talc impurities. After acid activation, the XRD pattern of ASep formed a new broad reflection at 2 θ \approx 23°, which is a typical characteristic of amorphous silica based materials. It indicates that the most sepiolite was converted to amorphous silica after acid

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