Facile synthesis of silver-deposited silanized magnetite nanoparticles and their application for catalytic reduction of nitrophenols

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** Abstract **

We have demonstrated a facile fabrication of silver-deposited silanized magnetite (Fe\textsubscript{3}O\textsubscript{4}/SiO\textsubscript{2}@Ag) beads, along with their catalytic performance in the reduction of nitrophenols. Initially, 283 ± 40 nm sized spherical magnetite (Fe\textsubscript{3}O\textsubscript{4}) particles composed of ~13 nm superparamagnetic nanoparticles were synthesized, and then they were silanized following the modified Stöber method. Silica-coated magnetic (Fe\textsubscript{3}O\textsubscript{4}/SiO\textsubscript{2}) nanoparticles are then resistant to oxidation and coagulation. In order to deposit silver onto them, Fe\textsubscript{3}O\textsubscript{4}/SiO\textsubscript{2} nanoparticles were dispersed in a reaction mixture consisting of ethanolic AgNO\textsubscript{3} and butylamine. With this simple and surfactant-free fabrication method, we can avoid any contamination that might make the Fe\textsubscript{3}O\textsubscript{4}/SiO\textsubscript{2}@Ag particles unsuitable for catalytic applications. The as-prepared Fe\textsubscript{3}O\textsubscript{4}/SiO\textsubscript{2}@Ag particles were accordingly used as solid phase catalysts for the reduction of 4-nitrophenol (4-NP) in the presence of sodium borohydride. The reduction of other nitrophenols such as 2-nitrophenol (2-NP) and 3-nitrophenol (3-NP) were also tested using the Fe\textsubscript{3}O\textsubscript{4}/SiO\textsubscript{2}@Ag nanoparticles as catalysts, and their rate of reduction has been found to follow the sequence, 4-NP > 2-NP > 3-NP. The Fe\textsubscript{3}O\textsubscript{4}/SiO\textsubscript{2}@Ag particles could be separated from the product using an external magnet and be recycled a number of times after the quantitative reduction of nitrophenols.

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1. Introduction

Magnetic nanoparticles are a class of nanoparticle which can be manipulated using magnetic fields [1–3]. Such particles commonly consist of magnetic elements such as iron, nickel or cobalt and their chemical compounds [4–7]. These particles have been the focus of much research recently because they possess attractive properties which could see potential use in catalysis, biomedicine, magnetic resonance imaging, data storage, and environmental remediation [8–15]. Nonmagnetic metal nanoparticles have also attracted a great deal of interest today [16–20]. Among others, gold and silver nanoparticles are receiving great attention due to their unique optical properties associated with surface plasmon resonance [21–25]. Metallic nanoshells composed of a magnetic core and a concentric noble metal shell find many applications in trace analysis and in heterogeneous catalysis [26–28]. Unfortunately, these colloids are generally unstable, owing to aggregation of the metal nanoparticles. In order to improve the stability of metal nanoparticles, various procedures have been employed to obtain silica–metal composites. This is because colloidal silica, which is thermostable and resistant to coagulation, avoids the aggregation of the metal particles. Guo et al. [29] reported a general route to construct multifunctional Fe\textsubscript{3}O\textsubscript{4}/metal hybrid nanostuctures using 3-aminopropyltrimethoxysilane (APTMS) as a linker. Recently, we have shown that Ag can be deposited onto the silica beads, without using a linker like APTMS, by soaking them in ethanolic solutions of AgNO\textsubscript{3} and butylamine [30,31]. The extent of silvering could be adjusted by varying the relative concentrations of butylamine and AgNO\textsubscript{3}. The Ag-deposited silica (SiO\textsubscript{2}@Ag) beads were then used as efficient surface-enhanced Raman scattering (SERS) substrates that could be used as core materials of SERS–based biosensors [31]. We have also demonstrated the facile synthesis of Ag-deposited Fe\textsubscript{3}O\textsubscript{4} (Fe\textsubscript{3}O\textsubscript{4}@Ag) particles and their application as solid phase catalysts for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) in the presence of NaBH\textsubscript{4} [8]. The Fe\textsubscript{3}O\textsubscript{4} (hematite) particles used earlier were commercial products with very irregular shape and size distribution. Accordingly, it was difficult to enjoy fully the properties of superparamagnetism, as would be expected from nanometer sized magnetite (Fe\textsubscript{3}O\textsubscript{4}) particles. Bare Fe\textsubscript{3}O\textsubscript{4} nanoparticles are, however, likely to form a large