Chinese Journal of Catalysis 36 (2015) 705–711

available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/chnjc

Article

A Fe_3O_4@Nico@Ag nanocatalyst for the hydrogenation of nitroaromatics

U. Kurtan, Md. Amir, A. Baykal *

Department of Chemistry, Fatih University, 34500 B.Çekmece-İstanbul, Turkey

A R T I C L E I N F O

Article history:
Received 19 January 2015
Accepted 6 February 2015
Published 20 May 2015

Keywords:
Magnetic recycable nanocatalyst
Nitro compound
Catalytic reduction
Magnetic nanomaterial
Hydrogenation

A B S T R A C T

We report the fabrication and characterization of a magnetically recyclable Fe_3O_4@Nico@Ag catalyst for reduction reactions in the liquid phase. Fe_3O_4 is a magnetic core and nicotinic acid was used as the linker for Ag. The characterization was done with X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, thermogravimetric analysis, vibrating sample magnetometry (VSM), and ultraviolet-visible spectroscopy. VSM measurements proved the superparamagnetic property of the catalyst.

1. Introduction

Nitroaromatic compounds are dangerous and poisonous to the environment (humans, fishes, and invertebrates) due to the presence of the nitro group. They are widespread environmental contaminants in the soil and groundwater as a result of their wide use for manufacturing dyes, drugs (several analgesic and antipyretic drugs), pesticides, herbicides, fungicides, paints, and explosives [1–6]. In the dye industry, 4-nitroaniline is also an important nitroaromatic compound and a major component of hazardous wastewater. These refractory organics are hard to decompose with conventional ways such as the active sludge method. They are used as the precursor in several chemical synthesis of various azo dyes, poultry medicine, antioxidants, antiseptic agents, pesticides, fuel additives as well as an important corrosion inhibitors [7]. Their disposal in wastewater results in high toxicity, carcinogenicity, and mutagenicity to several organisms [8–12]. However, aminophenol compounds are important for the preparation of several analgesic and antipyretic grugs such as parcetamol, acetanilide, and phenacetin.

A nicotinic acid complex with a metal, Mn, Co, Ni, Zn, or Cu, has been synthesized and reported in several research works [13]. Due to the electron donor behavior of the N atom of nicotinic acid, it has the ability to attract the metal through the N atom of the pyridine [14,15]. Fe_3O_4 nanoparticles (NPs) have been extensively researched for many years for their supermagnetic behavior and catalytic properties, including their use in many applications such as microwave absorption, medical diagnostics, and catalytic degradation [16–19]. Ag NPs have been studied and found to be an effective catalytic material [20–25]. The chemical grafting of a homogeneous metal complex onto a solid magnetic surface is a versatile method to synthesize a metal complex with a regulated metal-coordination structure having special catalytic properties [26–30].

In recent years, due to their high surface-to-volume ratio and unique electronic and surface properties, nanoparticles

---

* Corresponding author. Tel: +90-212-8663300-2060; Fax: +90-212-8663402; E-mail: hbaykal@fatih.edu.tr

DOI: 10.1016/S1872-2067(14)60316-8 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 36, No. 5, May 2015

have gained much attention for catalysis [31,32]. There are many reports in the literature on the application of metal nanoparticles (Au, Ag, Pd, and Pt NPs are the most common) as catalyst for the reduction of nitrophenols to aminophenols in the presence of $NaBH_4$ [33,34]. Due to the easy separation of magnetic nanoparticles from the reaction medium (due to the superparamagnetic nature of the material), nanocomposites which combine a noble metal with a magnetic material have been extensively studied. Ag and Fe_3O_4 both have catalytic activity and several nanocatalysts have been synthesized and reported, e.g., magnetic photocatalyst Fe_3O_4@C@Ag [35], Fe_3O_4@C@Ag, and Ag-coated Fe_3O_4@TiO_2 [36,37], and Au-Fe_3O_4 heterostructures for nitrophenol reduction [38]. The use of a Fe_3O_4@Nico@Ag magnetic nanocatalyst for the reduction of 4-nitrophenol and 4-nitroaniline and their mixture has not been reported so far.

2. Experimental

2.1. Chemicals and instruments

$FeCl_3$·$6H_2O$, $FeCl_2$·$4H_2O$, nicotinic acid, $AgNO_3$, $NaBH_4$, 4-nitroaniline, 4-nitrophenol, and NH_3 were obtained from Merck and used without further purification. Fourier transform infrared (FT-IR) spectra were recorded in the transmission mode with a PerkinElmer BX FT-IR spectrometer. The powder samples were ground with KBr and pressed into a pellet. FT-IR spectra in the range 4000–400 cm^{-1} were recorded to investigate the nature of the chemical bonds formed.

The crystalline structure of the nanoparticles was determined with X-ray diffraction (XRD) measurements using a Rigaku D/Max-IIIC instrument with Cu-K_α radiation in the 2θ range of 20°–70°. The surface morphology of the composite was analyzed with a JEOL JSM 7001F scanning electron microscope (SEM).

The ultraviolet-visible (UV-Vis) spectrometer used was a Model Shimadzu UV-Vis 2600 in the range of 300–800 nm. The thermal stability was determined by thermogravimetric analysis (TGA, PerkinElmer Instruments model, STA 6000). The TGA thermograms were recorded with 6 mg of powder sample at a heating rate of 10 °C/min in the temperature range of 30–800 °C under a N_2 atmosphere. Vibrating sample magnetometry (VSM) measurements were performed using a vibrating sample magnetometer (LDJ Electronics Inc., Model 9600). The magnetization measurements were carried out in an external field up to 15 kOe at room temperature.

2.2. Preparation of the Fe_3O_4@Nico@Ag nanocomposite

The Fe_3O_4@Nicotinic acid nanocomposite was synthesized by the reflux method. Stoichiometric amounts of metal salts, Fe (III) and Fe (II) chlorides with the mole ratio of Fe^{3+}/Fe^{2+} equal to 2, were dissolved in 40 mL of distilled water in a three neck round-bottom flask and their homogeneous solution was prepared using magnetic stirring. A stoichiometric amount of nicotinic acid was added to this mixture under vigorous stirring and then concentrated NH_3 solution was added dropwise under constant stirring to adjust the pH to 10 at which the precipitation of the ferrites takes place. After transferring the flask to the heating mantle, it was refluxed under a N_2 atmosphere at 80 °C for 5 h. Finally, the synthesized Fe_3O_4@Nicotinic acid nanocomposite was separated by a permanent magnet and washed with distilled water and ethanol solution several times to remove impurities. A black powder product was obtained and dried at 80 °C for 4 h.

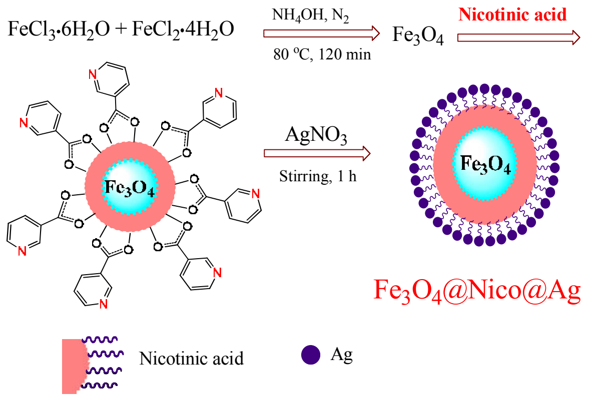
The synthesized Fe_3O_4@Nico nanocomposite (150 mg) was dispersed in 50 mL of deionized water and sonicated for 30 min. This was followed by the addition of 30 mL of $AgNO_3$ solution (0.2 mmol/L). The solution was vigorously stirred for 30 min and then 0.6 g of $NaBH_4$ was quickly added and the mixture was allowed to react for 3 h under rapid stirring. The product was separated magnetically and washed several times with deionized water and ethanol to eliminate impurities. The synthesis of the Fe_3O_4@Nico@Ag nanocomposite is outlined in the Scheme 1.

3. Results and discussion

3.1. Characterizations

The XRD powder pattern of the Fe_3O_4@Nico@Ag nanocatalyst is given in Fig. 1(a). It indicated the presence of both Fe_3O_4 ((220), (311), (400), (422), (511), (440)) [39] and Ag ((111) and (200)) [40]. All the diffraction peaks matched well with Ag (JCPDS 87-0720) NPs and Fe_3O_4 NPs (JCPDS 75-0033). Using Scherer's formula and the FWHM of the strongest peak of the Fe_3O_4 NPs, the average crystallite size was estimated as 10.1 nm.

The FT-IR spectra of the Fe_3O_4@Nicotinic acid@Ag magnetic nanocatalyst, Fe_3O_4@Nicotinic acid, and nicotinic acid are presented in Fig. 1(b). The surface molecules in the adsorbed state were subjected to the field of the solid surface. It is worth noting that the C=O stretching band of the carboxyl group, which was present at 1696 cm^{-1} in the pure nicotinic acid, was absent in the nanocomposite. Tao et al. [41] and Ahn et al. [42] suggested two binding modes for the surface carboxylate bonding. When the carboxylate is bonded symmetrically to the surface, only the symmetric C=O stretching band appears at 1404 cm^{-1} [41,43]. In our case, only one peak at 1403 cm^{-1}



Scheme 1. Illustration for the fabrication of the Fe_3O_4@Nico@Ag magnetic nanocatalyst.