Silver nanoparticles supported on ionic-tagged magnetic hydroxyapatite as a highly efficient and reusable nanocatalyst for hydrogenation of nitroarenes in water

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A novel chemically modified magnetic hydroxyapatite (MHAp) was prepared and used as support and stabilizer for the synthesis of silver nanoparticles. First, 1,4-diazabicyclo[2.2.2]octane (DABCO) was successfully grafted onto the surface of MHAp, and then silver nanoparticles were homogeneously loaded on mesoporous MHAp-DABCO (ionic-tagged MHAp) nanocomposite by in situ chemical reduction of silver nitrate using sodium borohydride. The structure and properties of the resulting MHAp-DABCO-Ag nanocomposite were confirmed using various techniques. The catalytic activity of ionic-tagged MHAp-Ag nanocatalyst was investigated for the hydrogenation reaction of nitroarenes in aqueous media. The results reveal that the Ag-containing inorganic–organic nanocomposite is highly efficient for the reduction of a wide range of aromatic nitro compounds under green conditions. The superparamagnetic nature of the nanocatalyst leads to its being readily removed from solution via application of a magnetic field, and it can be easily stored and reused.

KEYWORDS
aqueous media, hydrogenation of nitroarenes, ionic-tagged magnetic hydroxyapatite, organometallic nanocatalyst, silver nanoparticle

1 | INTRODUCTION

Metal nanoparticles (NPs) as an important class of catalysts are versatile substrates in organic synthesis. Silver nanoparticles (Ag NPs) because of their attractive physical and chemical characteristics have been extensively used in the fields of biology, electronics and catalysis. Ag NPs as an inexpensive, non-toxic, chemically stable and high surface-to-volume ratio metal have been applied in a variety of catalytic reactions, such as reductions, epoxidations and oxidations.

The use of Ag NPs has some disadvantages, such as their agglomeration, due to high surface energy, and their inseparability in a reaction mixture due to the homogeneous character. Therefore, there have been many efforts to fabricate heterogeneous catalysts in which metal NPs are immobilized on various kinds of solid support such as organic polymers, silica, zeolite, alumina, graphite oxide and magnetic NPs. Moreover, the relatively high surface area and appropriate pore size of inorganic supports maintain their competitive advantages over others. Hydroxyapatite is a potentially useful material for designing new functionalized heterogeneous catalysts, because of its properties such as thermal and chemical stability, biocompatibility, adsorption capacity, high surface area and ionic substitution ability. Magnetic NPs, as nanotemplate and support for the synthesis of nanometric heterogeneous hosts for Ag NPs, provide quasi-homogeneous reaction conditions. Among these magnetic NPs, iron oxides magnetite (Fe3O4) and maghemite (γ-Fe2O3) have been identified as the ideal and most widely used supports in catalysis because of
their low toxicity, superparamagnetic behaviour, eco-friendliness, cost efficiency and easy preparation.[29–38] 1,4-Diazabicyclo[2.2.2]octane (DABCO) has received considerable attention as a catalyst for some organic transformations such as N-methylation of indoles,[39] Knoevenagel condensation,[40] allylic trifluoromethylthiolation reaction of Morita–Baylis–Hillman carbones,[41] nucleophilic substitution reaction of benzyl halides,[42] and Suzuki–Miyaura and Mizoroki–Heck couplings.[43] DABCO can be chemically bonded to a magnetic hydroxyapatite (MHAp) surface to create ionic sites as hydrophilic domain and an organophilic environment via unhindered amines. For Ag NPs immobilized on the ionic-tagged MHAp (IT-MHAp) surface, the amines act as NP stabilizer against aggregation and also increase the catalytic activity of the NPs. The dual role of IT-MHAp, with organophilic and hydrophilic characteristics, can also allow nitroarene compounds and hydrogenation agent in a solid support to physically come together.[44–49]

Nitroarene compounds are relatively rare in nature and have been introduced into the environment by human activities such as plastics and dyeing industries, agriculture, etc. These compounds are usually present in agricultural waste water and industrial effluents. The catalytic hydrogenation of nitroarene compounds is one of the most important methods for the production of their corresponding amines and as well as for the decontamination of nitroarene compound-containing media.[50–52] Reactions in aqueous media are of paramount importance for organic synthesis and, given their lower cost and environmental pollution and higher safety, they have recently attracted attention and constitute the basis of some environment-friendly research.[53,54]

By considering all the issues mentioned above for the development of novel magnetic heterogeneous nanocatalysts for organic transformations, herein we report the hydrogenation reaction of nitroarenes catalysed by IT-MHAp-Ag nanocatalyst. This magnetic heterogeneous nanocatalyst can be used safely and efficiently in aqueous medium, as a green solvent, and can easily be recovered using an external magnet.

2 | EXPERIMENTAL

2.1 | General

All reagents were purchased from Fluka and Merck and were used as received without further purification. Fourier transform infrared (FT-IR) spectra were obtained using potassium bromide pellets in the range 400–4000 cm⁻¹ with a BOMEM MB-Series 1998 FT-IR spectrometer. Field emission scanning electron microscopy (FE-SEM) and energy-dispersive X-ray (EDX) mapping analysis were conducted using a MIRA3 TESCAN-XMU SEM instrument. Transmission electron microscopy (TEM) images were obtained using a Zeiss EM10C 80 kV TEM instrument. X-ray diffraction (XRD) patterns, at Bragg angle ranging between 10° and 80°, were recorded with a Philips model PW 1840. Magnetic measurements were carried out using a vibrating sample magnetometer (Megnetic Daghigh, Daneshpajouh Co., Iran) at room temperature. Thermogravimetric analysis (TGA) was carried out using a Netzsch STA 409 PC (TG/DSC) instrument at a heating rate of 10 °C min⁻¹ in air. Zeta potential was obtained using a Brookhaven ZetaPALS instrument. The surface properties of samples were determined using nitrogen adsorption/desorption isotherms at −197 °C using a Micrometeritics ASAP 2000 instrument, and the surface area and the pore size distribution were investigated using Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) analyses, respectively. The Ag concentration of samples was determined using an atomic absorption spectrophotometer (Analytik Jena). Reaction monitoring and purity determination of products were accomplished using TLC on gel F254 plates. Products were characterized by comparing their physical data and FT-IR, ¹H NMR and ¹³C NMR spectra with those of known samples (Figures S5–S9, supporting information). ¹H NMR and ¹³C NMR spectra were recorded with a Bruker Advance DPX 400 NMR instrument, using tetramethylsilane as an internal standard.

2.2 | Synthesis of Ag NPs Incorporated on Mesoporous MHAp–DABCO (IT-MHAp-Ag)

2.2.1 | Synthesis of MHAp (γ-Fe₂O₃@HAp)

MHAp was synthesized according to a previously reported method.[55] FeCl₂⋅4H₂O (1.85 mmol) and FeCl₃⋅6H₂O (3.7 mmol) were dissolved in deoxygenated water (30 ml) under nitrogen atmosphere at room temperature and the resulting solution was added to a 25 wt% NH₄OH solution (10 ml) with vigorous mechanical stirring. A black precipitate of Fe₃O₄ was produced instantly. After 15 min, 100 ml of Ca(NO₃)₂⋅4H₂O (33.7 mmol) and (NH₄)₂HPO₄ (20 mmol) solutions, adjusted to pH = 11, were added dropwise to the obtained precipitate during 30 min with mechanical stirring. The resulting milky solution was heated to 90 °C for 2 h. After cooling the mixture, it was aged for 12 h without stirring. The formed dark brown precipitate was filtered, washed repeatedly with deionized water until neutrality and then dried at room temperature. The synthesized sample was calcined at 300 °C for 3 h, giving a reddish-brown powder.