



Original Research Article

Synthesis of a new Ag supported on hydroxyapatite-core-shell- γ -Fe₂O₃ nanoparticles (γ -Fe₂O₃@HAp-Ag NPs) and its application as a Lewis acid catalyst in the preparation of β -azidoalcohols and β -thiocyanohydrins from epoxides

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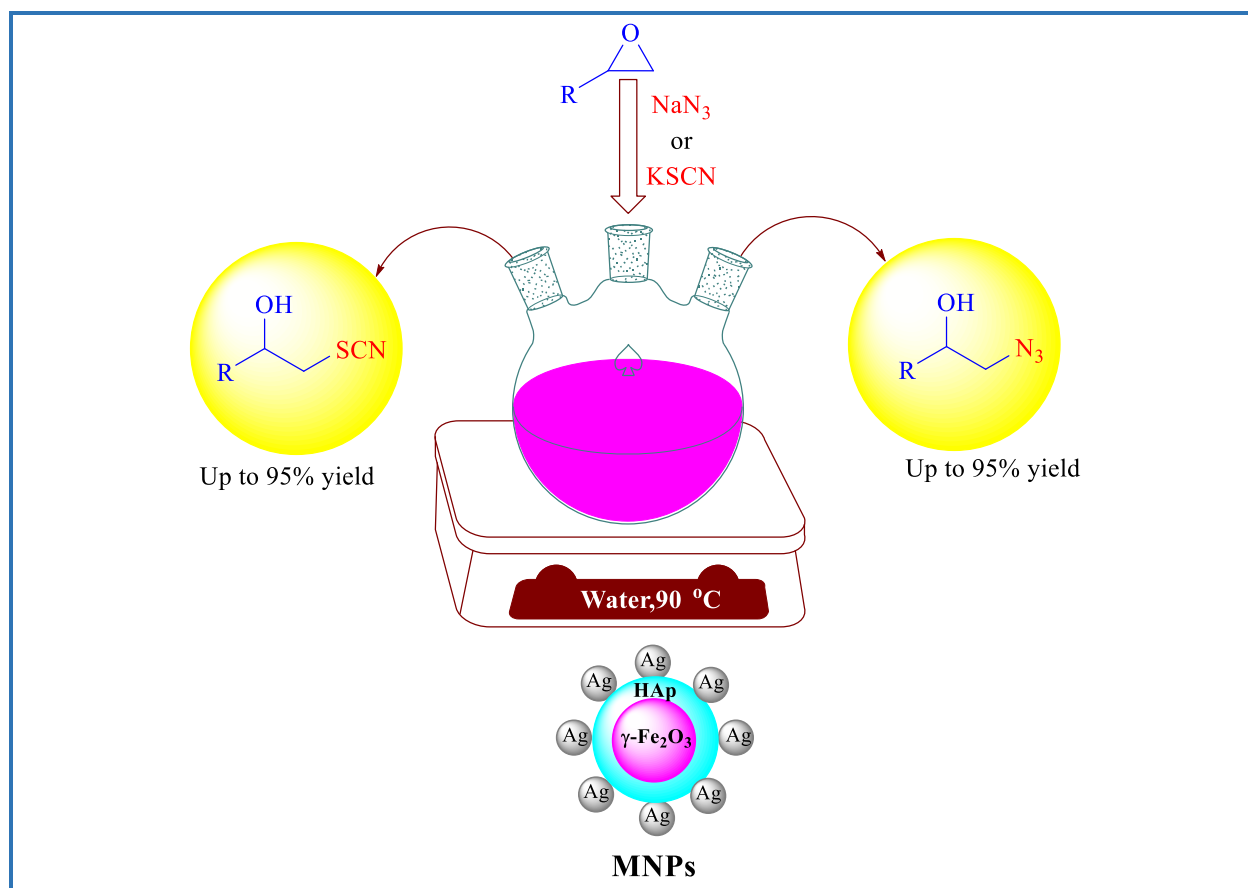
Ag supported
 β -azido alcohols
Ring opening
Regioselective
Lewis acid

ABSTRACT

In this study, we synthesized Ag supported on hydroxyapatite-core-shell- γ -Fe₂O₃ nanoparticles (γ -Fe₂O₃@HAp-Ag NPs) as a new, lewis acid, and reusable heterogeneous nancatalyst. Then, it was successfully used for the synthesis of β -azido alcohols and β -thiocyanohydrins from the regioselective conversation of some epoxides by azide and thiocyanate anions in water. The reaction afforded the corresponding products with high regioselectivity under mild reaction conditions.

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Graphical Abstract



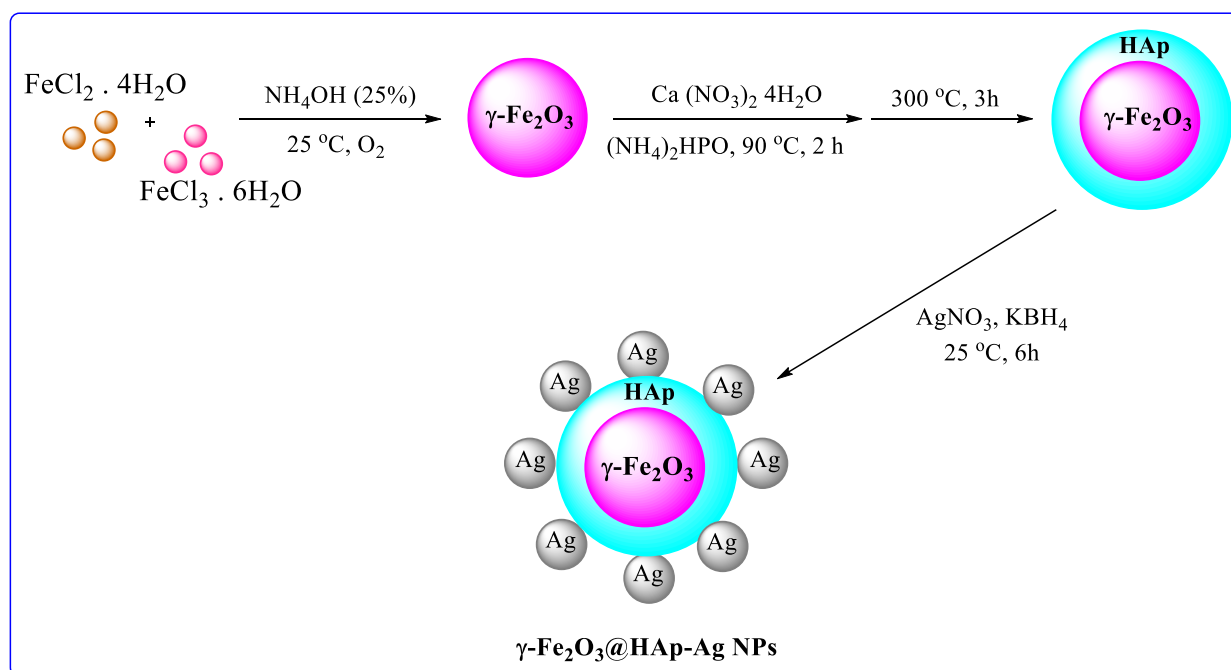
Introduction

Recently, the application of nanoparticles (NPs) as attractive and interesting materials has been more and more increased, because of their high surface area and unique magnetic properties. Moreover, they have a wide range of usage in various fields; such as magnetic fluids [1], biology and medical applications [2], magnetic resonance imaging [3], data storage [4], environmental remediation [5], and their application as catalysts in organic transformations [6, 7]. Magnetic nanoparticles owing to their attractive properties, have been used as excellent candidates as support materials for the preparation of MNP-supported heterogeneous catalysts which have been applied in traditional metal catalysis [8], organocatalysis [9], and enzyme catalysis [10]. Among the most arguable magnetic nanoparticles as the core magnetic supports, Fe_2O_3 and Fe_3O_4 nanoparticles are the most extensively studied [11], because of their high surface-area resulting in high catalyst loading capacity, conductivity, magnetic susceptibility, catalytic activity and striking stability [12].

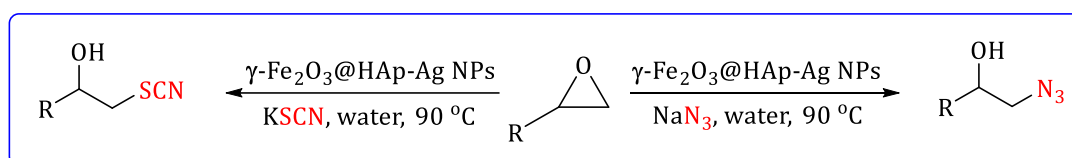
β -azido alcohols are compounds of interest in organicsynthesis as either precursors of vicinal amino alcohols or in the chemistry of carbohydrates, nucleosides, lactames, and oxazocines [13].

Several catalysts have been used to the synthesis of β -azido alcohols and β -thiocyanohydrins [14–18]. However, many of these methods which involve the use of expensive and stoichiometric amounts of reagents or catalysts suffer from poor regioselectivity, strongly acidic conditions and also require extended reaction times. Therefore, the development of a new and efficient protocol for this transformation under mild and more convenient conditions is still needed. Ag supported on hydroxyapatite-core-shell- γ - Fe_2O_3 nanoparticles (γ - Fe_2O_3 @HAp-Ag NPs) as an attractive and reusable Lewis acid magnetic nanocatalyst was designed to the synthesis of coumarin derivatives for the first time by Rezayati et al. (Scheme 1).

In this work, we prepared γ - Fe_2O_3 @HAp-Ag NPs for the one-pot synthesis of β -azido alcohols and β -thiocyanohydrins from the regioselective conversation of some epoxides by sodium azide (NaN_3) and thiocyanate (KSCN) anion (Scheme 2).



Scheme 1. Synthesis of catalyst



Scheme 2. One-pot preparation of β -azido alcohols and β -thiocyanohydrins using γ - Fe_2O_3 @HAp-Ag NPs

Experimental

Materials and methods

Products were separated and purified by different chromatographic techniques and were identified by the comparison of their IR, NMR, and melting point with those reported for the authentic samples. Melting points were taken on an electrothermal capillary melting point apparatus and are uncorrected. The progress of reaction was followed with thin-layer chromatography (TLC) using silica gel SILG/UV 254 and 365 plate. All the solvents and reagents were purchased from Aldrich and Merck with high-grade quality and used without any purification.

Preparation of γ -Fe₂O₃@HAp-Ag NPs

γ -Fe₂O₃@HAp-Ag NPs were prepared according to the literature procedure, and then the mean size and the surface morphology of the γ -Fe₂O₃@HAp-Ag NPs were characterized by TEM, SEM, VSM, XRD and FT-IR techniques [19].

General procedure for the preparation of β -azido alcohols in the presence of γ -Fe₂O₃@HAp-Ag NPs

A mixture of epoxide (1 mmol), NaN₃ (1.1 mmol), and γ -Fe₂O₃@HAp-Ag NPs (15 mg), and 5 mL of water (5 mL) in an oil bath for a specific time was presented. After complete consumption of epoxide as judged by TLC (using *n*-hexane/ethylacetate, 5:1) as eluent, the catalyst was separated utilizing an external magnet. The product was extracted with diethyl ether (3×5 mL), the organic phase was concentrated and dried using Na₂SO₄. After evaporation of the solvent under reduced pressure with a rotary evaporator, the *b*-cyanohydrins were obtained with 88–96% yield.

General procedure for the preparation of β -thiocyanohydrins in the presence of γ -Fe₂O₃@HAp-Ag NPs

A mixture of epoxide (1 mmol), KSCN (1.1 mmol), and γ -Fe₂O₃@HAp-Ag NPs (15 mg), and 5 mL of water (5 mL) in an oil bath for a specific time was also presented. After complete consumption of epoxide as judged by TLC (using *n*-hexane/ethylacetate, 5:1) as eluent, the catalyst was separated utilizing an external magnet. The product was extracted with diethyl ether (3×5 mL), the organic phase was concentrated and dried using Na₂SO₄. After evaporation of the solvent under reduced pressure with a rotary evaporator, the β -cyanohydrins were obtained with 87–95% yield.

Results and Discussion

Herein, we wish to report an extremely convenient and efficient method for regioselective ring opening of epoxides using γ -Fe₂O₃@HAp-Ag NPs as a new, efficient and recyclable catalyst in water

at 90 °C. In this study, the γ -Fe₂O₃@HAp-Ag NPs was prepared according to the literature procedure and was characterized by TEM, SEM, VSM, XRD and FT-IR techniques [19].


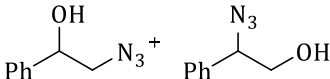
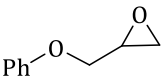
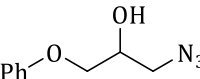
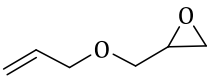
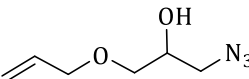
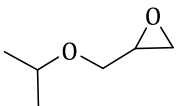
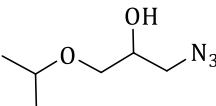
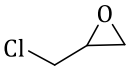
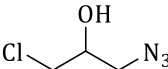
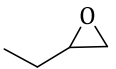
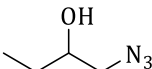
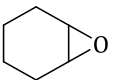
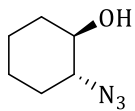
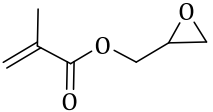
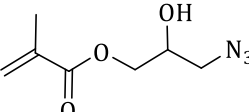
As a model reaction, the reaction of phenyl glycidyl ether (1 mmol) with NaN₃ (1.1 mmol) was tested using different amounts of γ -Fe₂O₃@HAp-Ag NPs at range of 60–100 °C in the various of solvent. The results are summarised in Table 1, where it can be seen that this reaction was strongly influenced by the amount of catalyst. No product was obtained in the absence of the catalyst even after 24 h (Table 1, entry 1) indicating that the catalyst is necessary for the reaction. The best results were obtained when amount of the catalyst was 15 mg at 90 °C in water, and give the product in excellent yield and in short reaction time (Table 1, entry 9).

After optimisation of the reaction conditions, various aromatic and aliphatic epoxides (1 mmol) reacted smoothly with sodium azide (1.1 mmol) in the presence of γ -Fe₂O₃@HAp-Ag NPs at 90 °C in water under similar reaction conditions to produce the corresponding β -azido alcohols in excellent yields and short reaction time (Table 2). In general, Table 2 shows the results that clarify the fact that the reaction proceeds very efficiently in all cases. Various epoxides underwent ring opening easily in the presence of γ -Fe₂O₃@HAp-Ag NPs at 90 °C. A glimpse to Table 2 makes clearly evident the generality of this methodology. Different functional groups, including ether, ester and double bond, are easily tolerated in the reaction conditions. The results clearly indicate the high regioselectivity of epoxide ring-opening by the azide anion.

Table 1. Effect of the catalyst amount, solvent and temperature on the reaction between phenyl glycidyl ether (1 mmol) with NaN₃ (1.1 mmol)

Entry	Catalyst amount (mol%)	Temperature (°C)	Solvent	Time (min)	Yield (%) ^a
1	None	25	-	24 h	Trace
2	1	25	-	130	38
3	5	25	-	90	55
4	10	25	-	65	78
5	15	25	-	40	82
6	20	25	-	40	85
7	15	60	water	25	91
8	15	80	water	25	93
9	15	90	water	25	95
10	20	60	water	25	89
11	20	80	water	25	90
12	20	90	water	25	90

Table 2. Preparation of β -azido alcohols from various epoxides with sodium azide anion in the presence γ -Fe₂O₃@HAp-Ag NPs in water

Entry	Epoxide	product	Time (min)	Yield (%) ^a
1			25	95
2			30	95
3			20	94
4			15	92
5			30	94
6 ^b			20	95
7			10	94
8			10	90

^a Isolated yield

The good reusability of a catalyst is an important aspect of green chemistry and environmental points of view. The recovery and reusability of the catalyst was studied using 2,3-epoxypropyl phenyl ether with sodium azide as model reaction. Since the catalyst can be separated from the reaction mixture using an external magnetic field, it was recovered with a simple magnet after the dilution of the reaction mixture with water. The catalyst was consecutively reused seven times without any noticeable loss of its catalytic activity ([Figure 1](#)).

In another study, after the success of γ -Fe₂O₃@HAp-Ag NP for the synthesis of β -azido alcohols, we decided to explore the catalytic activity of γ -Fe₂O₃@HAp-Ag NP for the synthesis of β -thiocyanohydrins. For this purpose, the condensation reaction between epoxide (1 mmol), SCN (1.1 mmol) in the presence of γ -Fe₂O₃@HAp-Ag NP (15 mg) in water at 90 °C was chosen as a model reaction. All the β -thiocyanohydrins were obtained in excellent yields and short reaction time ([Table 3](#)).

Figure 1. The catalytic activity of γ - Fe_2O_3 @HAp-Ag NP in seven cycles

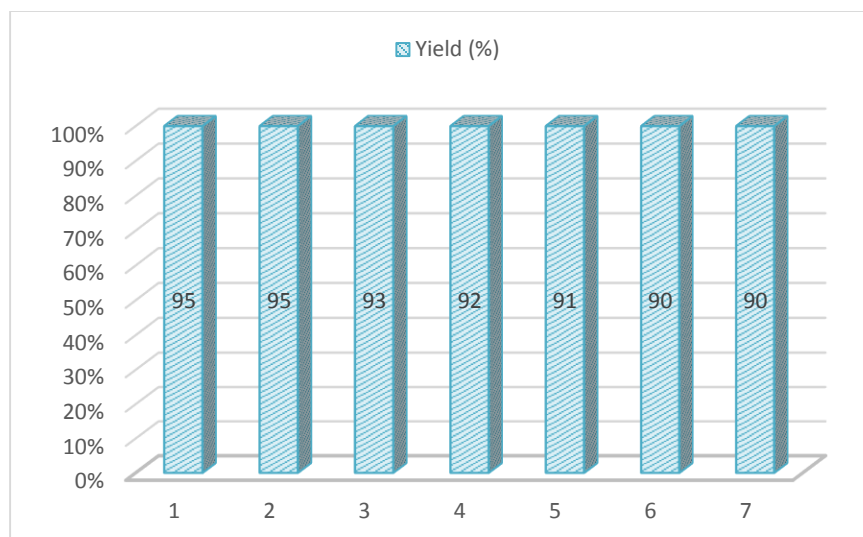


Table 3. Preparation of β -thiocyanohydrins from various epoxides with thiocyanate anion in the presence γ - Fe_2O_3 @HAp-Ag NPs in water

Entry	Epoxide	product	Time (min)	Yield (%) ^a
1			25	94
2			30	94
3			15	92
4			10	94
5			25	93
6 ^b			15	95
7			12	95
8			15	92

^a Isolated yield

Conclusion

In conclusion, a new Ag supported on hydroxyapatite-core-shell- γ - Fe_2O_3 nanoparticles (γ - Fe_2O_3 @HAp-Ag NPs) was synthesized and its application as an efficient, green, and reusable catalyst for regioselective ring opening of epoxides to β -azido alcohols and β -thiocyanohydrins in water at 90 °C was presented. The advantages of the present protocol include being an environmentally friendly alternative, the short reaction times, high yield of products, simple work-up procedure and excellent regioselectivity. Moreover, the catalyst was recyclable and has been reused for seven successive runs with little loss of the catalytic activities.

Disclosure Statement

No potential conflict of interest was reported by the authors.

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