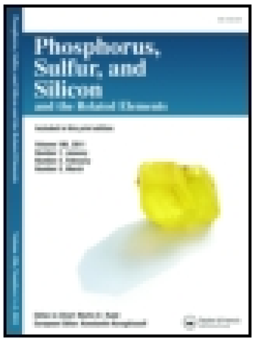

Phosphorus, Sulfur, and Silicon and the Related Elements

ISSN: 1042-6507 (Print) 1563-5325 (Online) Journal homepage: http://www.tandfonline.com/loi/gpss20

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To cite this article: Ronak Eisavi & Somayieh Alifam (2017): $ZnFe_2O_4$ nanoparticles: A green and recyclable magnetic catalyst for fast and regioselective conversion of epoxides to vicinal hydroxythiocyanates using NH_4SCN under solvent-free conditions, Phosphorus, Sulfur, and Silicon and the Related Elements, DOI: 10.1080/10426507.2017.1390460

To link to this article: http://dx.doi.org/10.1080/10426507.2017.1390460

$ZnFe_2O_4$ nanoparticles: A green and recyclable magnetic catalyst for fast and regioselective conversion of epoxides to vicinal hydroxythiocyanates using NH_4SCN under solvent-free conditions

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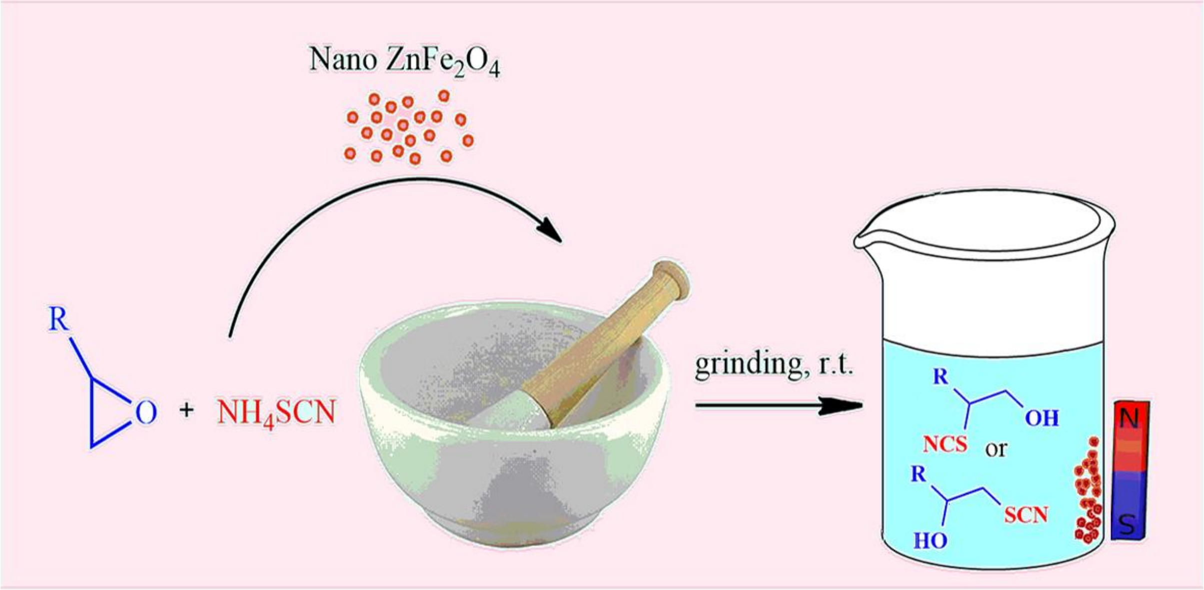
Abstract

$ZnFe_2O_4$ nanoparticles were synthesized and used as recyclable magnetic catalyst in the solvent-free conversion of different epoxides to vicinal hydroxythiocyanates with NH_4SCN at room temperature. The reactions were carried out by grinding in a mortar with perfect regioselectivity within short times (2-25 min) and with high to excellent yields (75-95%). The nanocatalyst was separated easily using an external magnet and reused for four consecutive cycles without any noticeable loss of efficiency or magnetic property.

Graphical Abstract

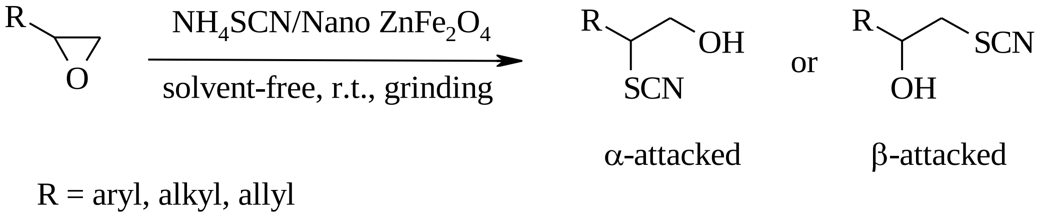


Keywords: epoxide, nano $ZnFe_2O_4$, NH_4SCN, solvent-free, vicinal hydroxythiocyanate

1. Introduction

Nowadays, removal of toxic and volatile solvents from chemical reactions in order to realize the aims of green chemistry is one of the main challenges facing organic chemists. Using solvent-free conditions is one of the best ways to achieve this goal.[1] The use of grinding technique under solvent-free conditions has unique advantages such as low cost, simplified workups, eliminating of pollution, reduced explosion risk, and benign conditions.[2] In recent years, although magnetic nano-ferrites due to biological utilizations such as drug delivery properties have received remarkable attention,[3] their catalytic potentials have not been much considered in organic transformations.[4,5] Recently, magnetic nanocatalysts have been successfully used for accomplishing several organic reactions.[6-10] Among these nanoparticles, $ZnFe_2O_4$ is an effective heterogeneous nanocatalyst. It has a high surface area and amazing properties such as economical price, recoverability, eco-friendliness and effortless separation that shows perfect regioselectivity to generate high yields of products within short reaction times under mild circumstances.[11-13]

Thiocyanates are valuable intermediates that play a key role in biochemistry, agriculture and pharmaceuticals.[14-16] Preparation of thiiranes from epoxides with thiocyanate ions is carried out through intermediacy of the corresponding vicinal hydroxythiocyanates, but these compounds are not isolated due to quick conversion to thiiranes.[17] Hence, the synthesis of these precious intermediates is of paramount importance. Although few methods for the synthesis of vicinal hydroxythiocyanates bearing aryl or alkyl groups have been reported in the literature, some of them suffer from limitations such as expensive and non-recyclable catalysts, the use of toxic solvents, difficult and tedious workup procedures, low regioselectivity and product yields, long reaction times and harsh reaction conditions.[18-31] Therefore, inspired by the remarkable effects of zinc nano-ferrites, and in connection with our works on nanoparticles[32,33] and synthesis of 1,2-difunctional derivatives from epoxides,[34-38] herein, we want to introduce nano $ZnFe_2O_4$ as a green recyclable catalyst for the rapid and regioselective conversion of different epoxides to aryl or alkyl substituted vicinal hydroxythiocyanates through attack of thiocyanate ions to the α- or β-position respectively, under solvent-free conditions at room temperature (Scheme 1).



Scheme 1. Preparation of vicinal hydroxythiocyanates bearing different groups in the presence of catalytic amounts of nano $ZnFe_2O_4$.

2. Results and Discussion

2.1. Characterization of the catalyst

The synthesized $ZnFe_2O_4$ nanoparticles[39] were characterized by X-ray diffraction (XRD), scanning electron micrograph (SEM) and FT-IR techniques. Figure 1 shows an XRD pattern of the $ZnFe_2O_4$ nanoparticles. The X-ray pattern displays sharp peaks coinciding with the standard data of the spinel $ZnFe_2O_4$ (Franklinite) phase (JCPDS card No. 74-2397). The average crystallite size of these nanoparticles was calculated to be about 43 nm using Scherrer's equation.[40] The morphology of the synthesized nanocatalyst was confirmed by scanning electron microscopy (Figure 2). The SEM image shows that the size of spherical zinc ferrite nanoparticles is between 43 to 46 nm. These results are in perfect harmony with the XRD data. Figure 3 represents the FT-IR spectrum of the nano $ZnFe_2O_4$. A broad band at 3421 cm^{-1} is due to stretching mode of H_2O molecules indicating the presence of OH groups on the surface of nanoparticles. The band at 1637 cm^{-1} corresponds to the bending mode of H_2O molecules. The absorption bands in the range of 1000-400 cm^{-1} are assigned to metal-oxygen stretching vibrations of the ferrite spinel structure. A strong band at 548 cm^{-1} is related to the Fe-O stretching vibration at the tetrahedral site.[41] Magnetic characterization of $ZnFe_2O_4$ nanoparticles was carried out using a Vibration Sample Magnetometer (VSM) at room temperature (Figure 4). The variation of magnetization as a function of applied field shows a narrow cycle, and the hysteresis loop of the sample presents the behavior of soft ferromagnetic materials.

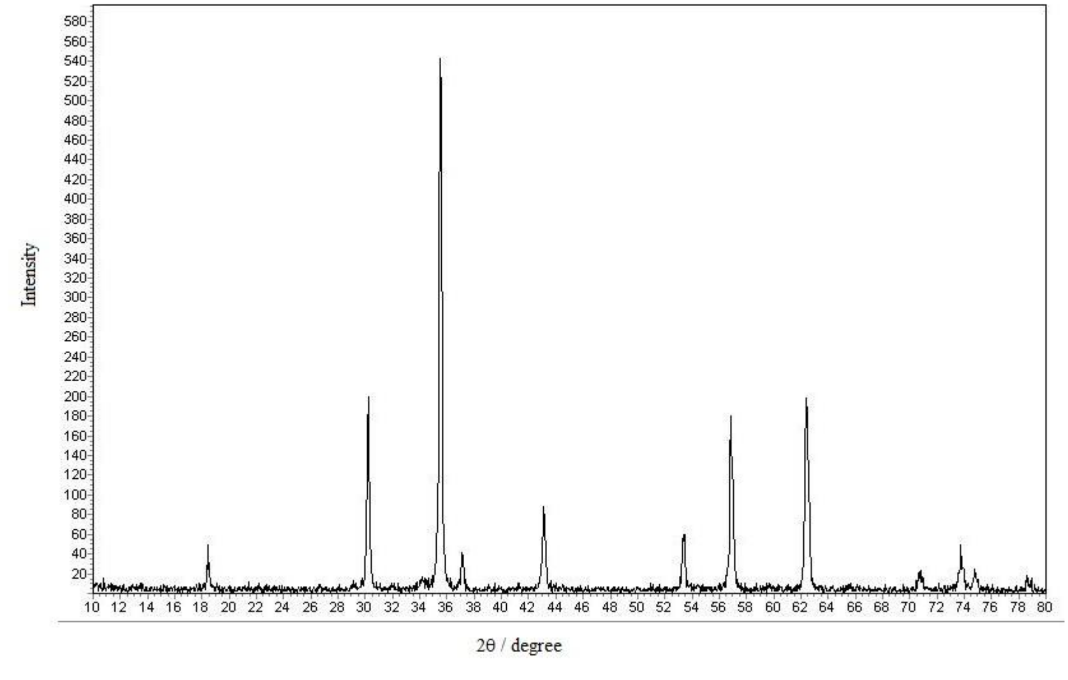


Figure 1. The X-ray diffraction pattern of calcinated nano $ZnFe_2O_4$

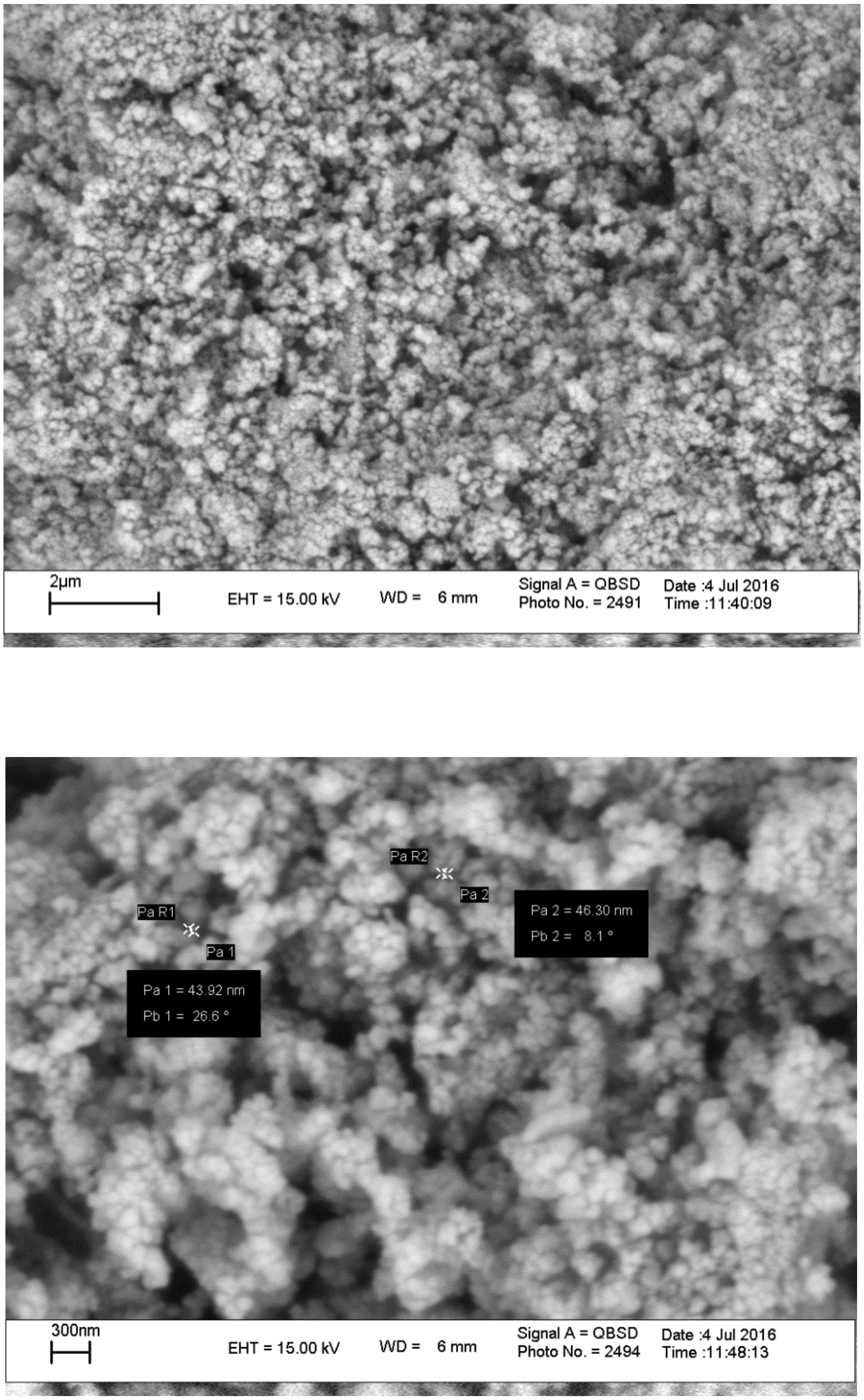


Figure 2. The SEM images of nano $ZnFe_2O_4$

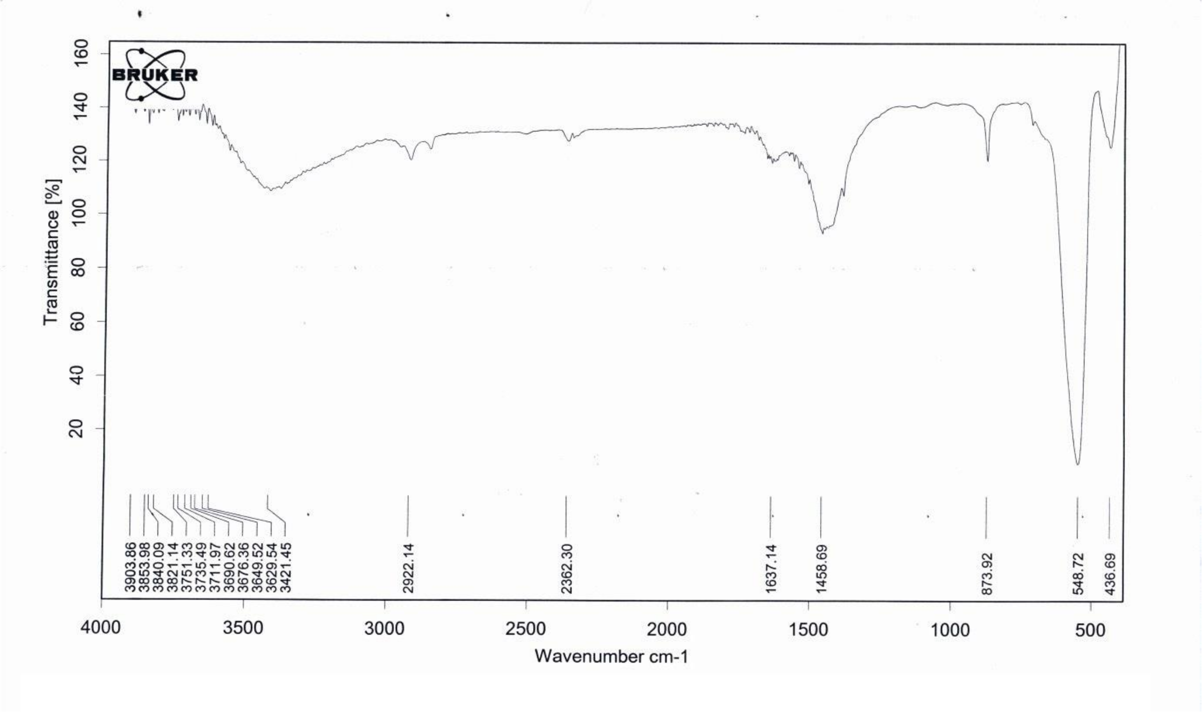


Figure 3. FT-IR (KBr) spectrum of nano $ZnFe_2O_4$

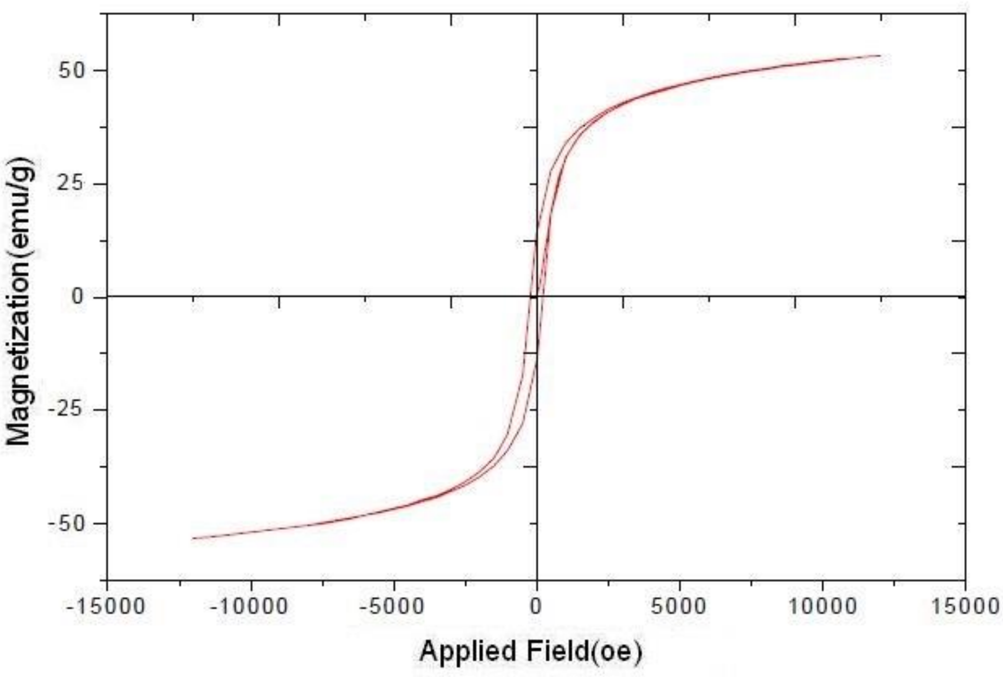
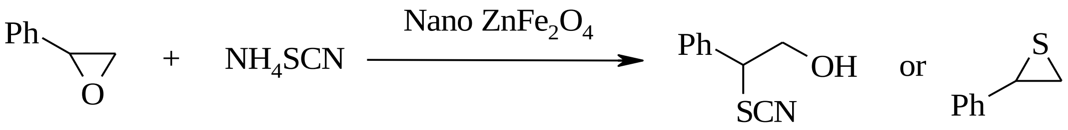


Figure 4. Magnetic hysteresis loop of nano $ZnFe_2O_4$ at room temperature

2.2. Conversion of epoxides to vicinal hydroxythiocyanates with NH_4SCN catalyzed by nano $ZnFe_2O_4$

Table 1 shows optimization experiments for the reaction of styrene oxide, NH_4SCN and $ZnFe_2O_4$ nanoparticles under different conditions. The best result in terms of molar ratio, selectivity, reaction time and mild conditions was obtained using 1 mmol styrene oxide, 1 mmol NH_4SCN and 5 mol% of nano $ZnFe_2O_4$ at room temperature by grinding in the mortar under solvent-free conditions. The method was regioselective. Thiocyanate attack at the phenyl substituted carbon (α-position) led to 2-hydroxy-1-phenylethyl thiocyanate as the only product in excellent yield (Table 1, entry 3). In order to optimize the quantity of catalyst, the reaction was carried out using different amounts of nano $ZnFe_2O_4$ (3, 5 and 10 mol%). It is noteworthy that in the absence of catalyst, the reaction was not accomplished. To evaluate the effect of solvent, the reaction was performed in the presence of various solvents such as acetonitrile, chloroform, *n*-hexane, ethanol and ethyl acetate. The results showed that the phenyl substituted vicinal hydroxythiocyanate could not be obtained in the presence of solvent and the only generated product was styrene episulfide in acetonitrile after 15 min. The reaction did not occur in the presence of chloroform and *n*-hexane after 50 min. By the use of ethanol and ethyl acetate, the reaction was not complete and led to the production of thiirane.

Table 1. Nano $ZnFe_2O_4$ catalyzed reaction of styrene oxide with NH_4SCN under different conditions[a]

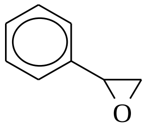
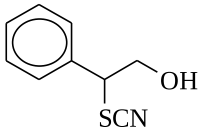
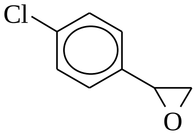
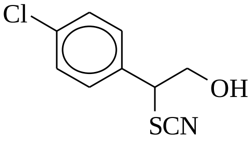
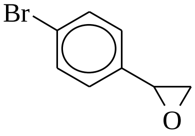
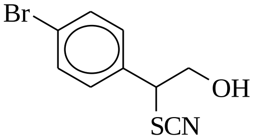
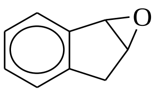
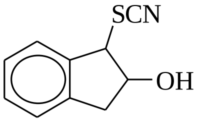
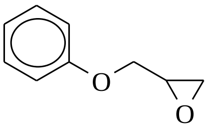
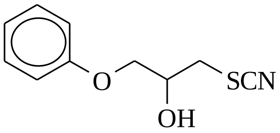


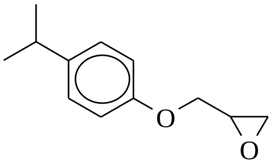
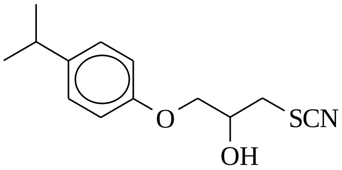
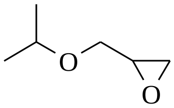
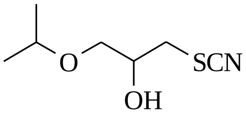
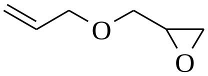
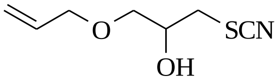
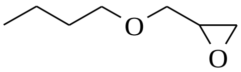
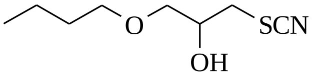
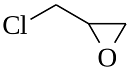
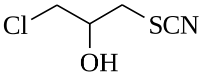
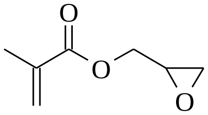
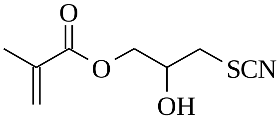
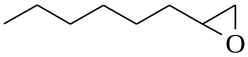
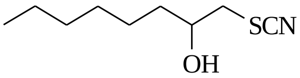
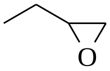
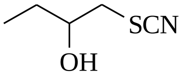
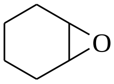
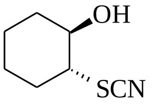
Entry	Nano $ZnFe_2O_4$ (mol%)	NH_4SCN (mmol)	Conditions	Time (min)	β-Hydroxy-thiocyanate (%)	Thiirane (%)	Epoxide[b] (%)
1	-	2	Solvent-free/r.t./grinding	40	0	0	100
2	3	1	Solvent-free/r.t./grinding	20	80	0	20
3	5	1	Solvent-free/r.t. /grinding	10	100	0	0
4	5	2	Solvent-free/r.t. /grinding	10	100	0	0
5	10	1	Solvent-free/r.t. /grinding	8	100	0	0
6	10	2	Solvent-free/r.t. /grinding	8	100	0	0
7	5	1	CH_3CN/r.t.	15	0	100	0
8	5	1	$CHCl_3$ / r.t.	50	0	0	100
9	5	1	*n*-Hexane / r.t.	50	0	0	100
10	5	1	C_2H_5OH/r.t.	40	50	0	50
11	5	1	Ethyl Acetate/r.t.	45	30	0	70

[a] All reactions were carried out with 1 mmol of styrene oxide. [b] Yield of recovered styrene oxide.

The capability and generality of this procedure was further studied by solvent-free reactions of various epoxides carrying electron-withdrawing and -donating groups under the optimum conditions. All epoxides were simply converted to aryl or alkyl substituted vicinal hydroxythiocyanates in high yields and with perfect regioselectivity. A notable advantage of this synthetic method is that the formation of thiirane as a side-product was not observed and vicinal hydroxythiocyanates were produced as the only products in all reactions (Table 2).

Table 2. Conversion of epoxides to vicinal hydroxythiocyanates bearing different groups with NH_4SCN in the presence of nano $ZnFe_2O_4$^{a}

Entry	Epoxide (a)	vicinal hydroxythiocyanate (b)	Time (min)	Yield (%)^b	Ref.
1			10	90	42,43
2			12	89	23
3			12	89	23
4			15	90	26
5			25	90	42,43

6			25	91	18
7			7	90	42,43
8			10	92	42,43
9			7	91	43
10			2	75	42
11			4	90	43
12			9	89	23,42
13			3	90	22
14			4	95	42,43

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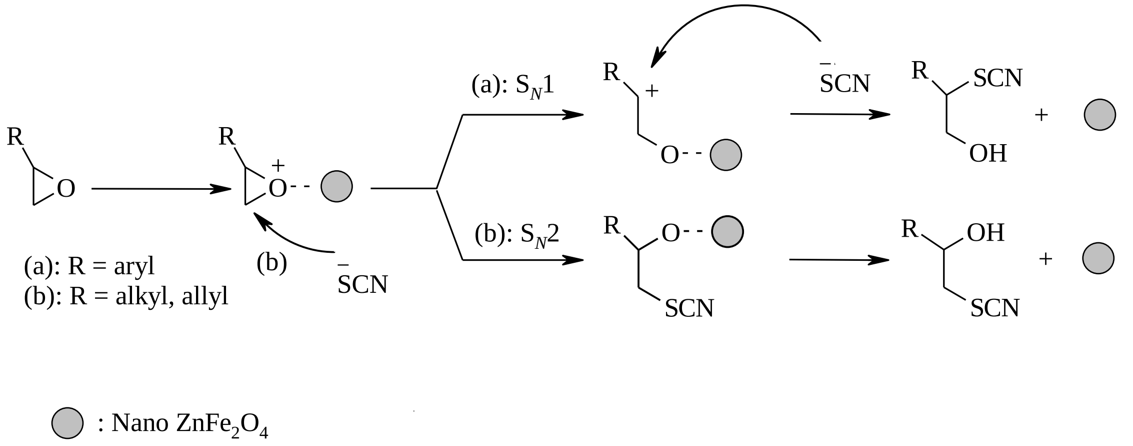
[a] All reactions were carried out with 1 mmol of epoxide in the presence of ammonium thiocyanate (1mmol) under solvent-free conditions at room temperature. [b] Yields refer to isolated pure products.

Although the exact mechanism of this reaction is still unclear the following pathways seems however reasonable (Scheme 2). As shown in Scheme 2, the regioselectivity of the ring opening of epoxides depends on the reaction mechanism, and it is especially influenced by steric and electronic factors. For epoxides bearing alkyl groups, the steric factor is prevailing and the nucleophilic attack of thiocyanate anion at the less hindered carbon atom of epoxides is significantly preferred (S_N2 type mechanism). On the opposite side, for epoxides bearing aryl groups, the electronic factor is dominant and the nucleophilic attack of the thiocyanate anion is favored at the more stabilized benzylic carbocation (S_N1 type mechanism).



Scheme 2. A proposed mechanism for the conversion of epoxides to vicinal hydroxythiocyanates bearing different groups with the NH_4SCN/nano $ZnFe_2O_4$ system.

Performing the reaction under solvent-free conditions, recyclability and reusability of the $ZnFe_2O_4$ nanoparticles are the green aspects of this methodology. After completion of the reaction, the nano-ferrite particles are conveniently collected by an external magnet, washed with double distilled water three times, dried at 80°C for 2 h and applied for the next run. The nanocatalyst can be reused four times without loss of magnetic property or catalytic activity (Figure 5).

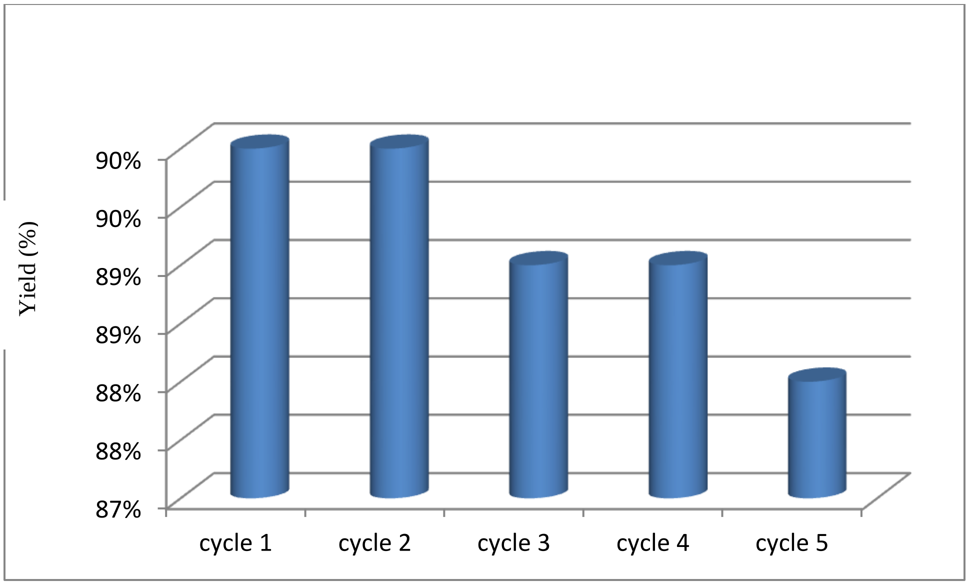
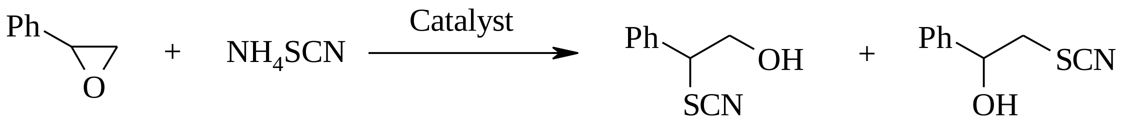


Figure 5. Recycling of nano $ZnFe_2O_4$ in the conversion of styrene oxide to 2-hydroxy-1-phenylethyl thiocyanate.

The advantages of the present synthetic method were revealed by comparison of conversion of styrene oxide to 2-hydroxy-1-phenylethyl thiocyanate with the methods reported in the literature (Table 3). In viewpoints of recoverability, easy preparation and separation of magnetic nanocatalyst, perfect regioselectivity, short reaction times, mild and eco-friendly conditions and high efficiency, our procedure is more preferable.

Table 3. Comparison of the reaction of styrene oxide with NH_4SCN in the presence of various catalysts [a].



(I) (II)

Entry	Catalyst	NH_4SCN (mmol)	Conditions	Product	Time (min)	Yield (%)	Ref.
1	Nano $ZnFe_2O_4$ (5 mol%)	1	solvent-free/ r.t./ grinding	I	10	90	b
2	Selectfluor (10 mol%)	1	CH_3CN/r.t.	I+II	50	95 (16:84)	18
3	MPTC (20 mol%)	2	H_2O/reflux	I+II	15	88 (5:95)	31
4	DDQ (10 mol%)	3	CH_3CN/reflux	I+II	50	91 (89:11)	14
5	$GaCl_3$ (10 mol%)	1.5	H_2O/r.t.	I	18	92	23
6	PEG-SO_3H (10 mol%)	3	H_2O/r.t.	I+II	60	84 (5:95)	27
7	PEG-SO_3H (10 mol%)	3	CH_2Cl_2/r.t.	I+II	60	83 (96:4)	25
8	T(4-OHP)P (10 mol%)	1	CH_3CN/reflux	I+II	20	96	20
9	PPI (20 mol%)	1	CH_3CN/reflux	I+II	45	95 (17:83)	26
10	PTC (0.1 g)	3	CH_3CN/reflux	I+II	90	90 (90:10)	21
11	TABCO (150 mol%)	3	CH_3CN/82 °C	I+II	25	94 (93:7)	30

[a] All reactions were carried out with 1 mmol of styrene oxide. [b] The present method.

3. Conclusion

In summary, we have demonstrated that nano $ZnFe_2O_4$ is an efficient catalyst for the conversion of different epoxides to the corresponding aryl and alkyl substituted vicinal hydroxythiocyanates at room temperature under solvent-free conditions. This novel method exhibits several remarkable advantages including perfect regioselectivity, short reaction times, high yields, eco-friendly and benign conditions, simple work-up, and the use of recyclable and reusable magnetic nanocatalysts which recommend the described protocol as a preferable method for the preparation of vicinal hydroxythiocyanates bearing aryl and alkyl groups from epoxides.

4. Experimental

4.1. General

All reagents and substrates were purchased from commercial sources with the best quality and they were used without further purification. The synthesized nano $ZnFe_2O_4$ was characterized by XRD on a Bruker D8-Advanced diffractometer with graphite-monochromatized Cu Kα radiation (λ = 1.54056 Å) at room temperature. SEM images were determined on a LEO 1430 VP scanning electron microscopy. The magnetic property of the nano $ZnFe_2O_4$ was measured using a VSM (Meghnatis Daghigh Kavir Co., Kashan Kavir, Iran) at room temperature. IR and $^1H/^{13}C$ NMR spectra were recorded on Thermo Nicolet Nexus 670 FT-IR and 300 MHz Bruker Avance spectrometers, respectively. The products were characterized by their spectroscopic data and comparison with the reported data in the literature. All yields refer to isolated pure products.

TLC was applied for the purity determination of substrates, products and reaction monitoring over silica gel 60 F_{254} aluminum sheet.

4.2. Preparation of $ZnFe_2O_4$ nanoparticles

$ZnFe_2O_4$ nanoparticles were synthesized using the reported method by Sun et al.[39] In an agate mortar, $Zn(CH_3COO)_2 \cdot H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, NaOH, and NaCl were mixed in a molar ratio of 1:2:8:2 and ground together for 50 min. The exothermic reaction started easily after 3 min. The mixture became pasty and during the reaction its color changed from green to dark orange. In order to remove the additional salts, this mixture was washed with double-distilled water for several times. After washing, the obtained combination was dried at 80°C for 2 h. Then the powders were calcined at 300 °C, 500 °C, 700 °C and 900 °C for 2 h to obtain final nanoparticles.

4.3. Solvent-free conversion of epoxides to vicinal hydroxythiocyanates with the NH_4SCN/nano $ZnFe_2O_4$ system: a general procedure

A mixture of epoxide (1 mmol), NH_4SCN (0.076 g, 1 mmol) and nano $ZnFe_2O_4$ (0.012 g, 0.05 mmol) was thoroughly ground in a mortar for an appropriate time at room temperature. The progress of the reaction was monitored by TLC using *n*-hexane/EtOAc (5:2) as eluent. After completion of the reaction, the mixture was washed with EtOAc (3 × 5 mL) and the catalyst nanoparticles were separated by an external magnet. Then the washing solvent was evaporated under reduced pressure to give the corresponding vicinal hydroxythiocyanate for further purification by a short-column chromatography over silica gel (75-95%) (Table 2). The accumulated nano $ZnFe_2O_4$ was washed with ethanol and then with distilled water. The nanocatalyst was dried and kept for the next run. All products are known compounds and were identified by comparison of their spectroscopic and physical data with the literature. The ^{1}H and ^{13}C NMR and FT-IR data of the products were in good agreement with those of authentic samples.[18,26,22,23,42,43] These data are presented in the Supplemental Materials.

Spectral data for a selected product:

2-Hydroxy-1-phenylethyl thiocyanate (1b): ^{1}HNMR ($CDCl_3$, 300 MHz) δ 7.46-7.33 (m, 5H, Ar-H), 4.52 (t, J = 6.6 Hz, 1H, CH-S), 4.19 (d, J = 6.6 Hz, 2H, CH_2-OH), 2.16 (bs, 1H, OH); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 135.35 (ArC), 129.44, 129.34, 127.90 (5 × ArCH), 111.11 (SCN), 64.95 (CH_2OH), 54.75 (CH-S); IR (ν_{max}/cm^{-1}, neat) 3428, 3031, 2918, 2849, 2153, 1658, 1454, 1063, 760, 699.

Acknowledgements

Financial support of this work by the Research Councils of Payame Noor University is gratefully acknowledged.

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