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Green synthesis of thiiranes from epoxides catalyzed by magnetically separable $CuFe_2O_4/Mg(OH)_2$ nanocomposite in water under benign conditions

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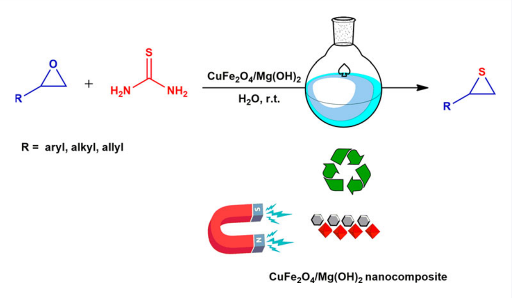
ABSTRACT

The magnetically separable $CuFe_2O_4/Mg(OH)_2$ nanocomposite was prepared and characterized by FT-IR, XRD, SEM, EDS, and VSM techniques. The synthesized nanoparticles were used as a new and efficient heterogeneous catalyst for the conversion of various epoxides to the corresponding thiiranes with thiourea in water solvent at room temperature. The reactions were completed within 1–3.7 h to give thiiranes in 70–99% yields. The applied $CuFe_2O_4/Mg(OH)_2$ nanocomposite was separated easily using an external magnet and reused for several times without any considerable loss of activity.



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Epoxide; $CuFe_2O_4/Mg(OH)_2$; nanocomposite; thiirane; thiourea

1. Introduction

Thiiranes, the simplest sulfur heterocycles, are used in polymer, pharmaceutical, pesticide and herbicide industries [1] They are also the essential heterocyclic building blocks of valuable biologically active compounds [2–5]. Transformation of epoxides to thiiranes by an oxygen-sulfur replacement reaction is the most straightforward synthetic method for the formation of thiiranes. The sulfur-transfer agents such as thiourea [6], inorganic

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thiocyanates [7], dimethylthioforamide [8], phosphine sulfide [9] silica-gel supported KSCN [10] Dowx-50WX8- supported thiourea [11] have been employed for this purpose.

Although there are numerous protocols for the preparation of thiiranes in the literature, most of them suffer from disadvantages such as high temperatures, long reaction times, low yield of products, the use of unsafe reagents and solvents, the formation of by-products, tedious work-up procedures, and the use of irrecoverable catalysts.

The combination systems of different protic or Lewis acids such as $TiO(TFA)_2$ [12], $TiCl_3(OTf)$ [12], $Mg(HSO_4)_2$ [13], $RuCl_3$ [14], $InBr_3$ [15], $BiCl_3$ [16], 2,4,6-trichloro-1,3,5-triazine [17], $Bi(TFA)_3$ [18], $Bi(OTf)_3$ [18], TiO_2 [19], $Al(DS)_3{\cdot}3H_2O$ [20], $Sn(TTP)(OTf)_2$ [21], $Sn(TTP)(BF_4)_2$ [22], SiO_2-HBF_4 [23], $SbCl_3$ [24], polymeric cosolvents [25], etidronic acid [26], montmorillonite K-10 [27], $(NH_4)_8[CeW_{10}O_{36}]{\cdot}20H_2O$ [28], $LiBF_4$ [29], $LiClO_4$ [30], I_2 [31], oxalic acid [32], CAN [33], $[bmim]PF_6$ [34], β-cyclodextrin [35], poly(4-vinylpyridine)-supported $Ce(OTf)_4$ [36], polystyrene supported $AlCl_3$ [37], (*R*)-TRIP [38], graphite oxide [39], and microwave irradiation [40] with thiourea or NH_4SCN have also been reported for transformation of epoxides to thiiranes.

In organic synthesis, the use of eco-friendly solvents and recyclable magnetic nanocatalysts under mild conditions facilitates the achievement of green chemistry goals. In recent years, magnetic nano-ferrites due to their amazing properties such as chemical stability [41], the large surface area to volume ratio and high catalytic activity [42], easy separation using a simple magnet without need for filtration [43], and recyclability have received great consideration in organic transformations. Nevertheless, these nano-ferrites often suffer from adsorption difficulties, because of their high tendency of self-aggregation and lack of sufficient functional groups on the surface [44,45]. Nanocomposites containing cores of magnetic ferrites with a functionalized shell provide a helpful solution for efficiency improvement of nano-ferrites [46].

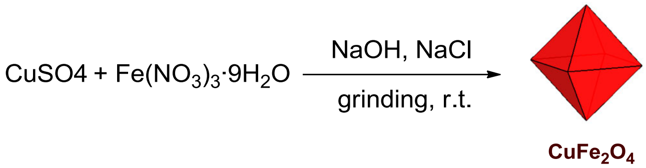
As a part of our research program on the synthesis of thiiranes [47–49] and in connection with our work on nano-ferrites [50–53], we wish to introduce an efficient and eco-friendly method for the conversion of various epoxides to the corresponding thiiranes using thiourea in the presence of $CuFe_2O_4/Mg(OH)_2$ nanocomposite as an active and recyclable catalyst in water solvent at room temperature in high to excellent yields.

2. Results and discussions

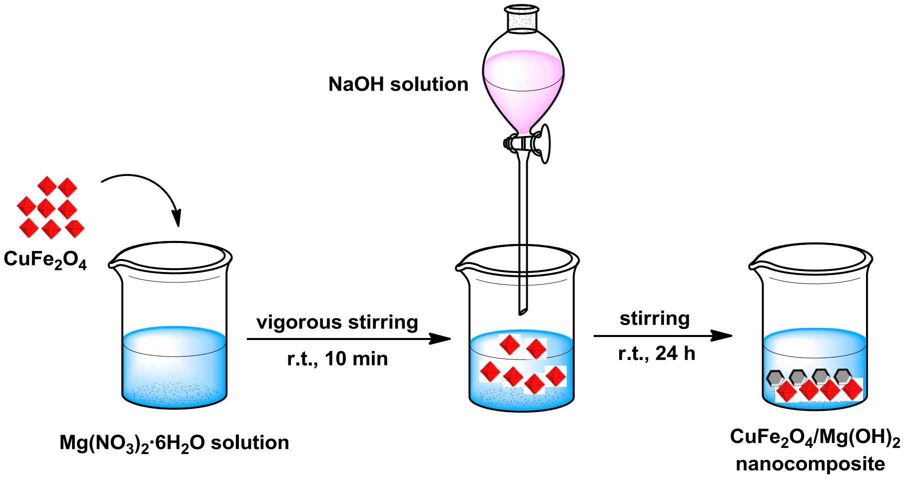
2.1. Synthesis and characterization of $CuFe_2O_4/Mg(OH)_2$ nanocomposite

Recently, we have used $CuFe_2O_4$ as a magnetic nanocatalyst for the preparation of thiiranes from epoxides with thiourea in refluxing ethanol [50]. However, conversion of epoxides to thiiranes catalyzed by $CuFe_2O_4/Mg(OH)_2$ nanocomposite in water at room temperature, compared to the use of bare copper nanoferrite under reflux in ethanol, is preferred. The presence of hydroxyl functional groups on the surface of nano-ferrite not only increases the catalytic activity, but can also reduce the self-aggregation of nanoparticles. Avoiding the use of high temperatures and organic solvents are the other advantages of the present method.

$CuFe_2O_4/Mg(OH)_2$ nanocomposite was synthesized in a two steps procedure. In the first step, nano-$CuFe_2O_4$ was prepared by a solid-state reaction of inorganic salts of $CuSO_4$, $Fe(NO_3)_3{\cdot}9H_2O$, NaCl and NaOH (Scheme 1) [54]. Then, the obtained $CuFe_2O_4$ was



Scheme 1. Synthesis of $CuFe_2O_4$ nanoparticles.



Scheme 2. Synthesis of $CuFe_2O_4/Mg(OH)_2$ nanocomposite.

added to the aqueous solution of $Mg(NO_3)_2{\cdot}6H_2O$ followed by dropwise addition of NaOH solution with stirring (Scheme 2). The $CuFe_2O_4/Mg(OH)_2$ nanocomposite was collected as a dark brown powder and characterized by FT-IR, X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectrometer (EDS), and vibration sample magnetometer (VSM) analyses.

2.1.1. X-ray diffraction (XRD)

The XRD patterns of nano-$Mg(OH)_2$, $CuFe_2O_4$ nanoparticles and $CuFe_2O_4/Mg(OH)_2$ nanocomposite are shown in Figure 1. The lines (220), (311), (222), (400), (422), (511), and (440) related to $2\Theta = 30.04$, 34.96, 37.26, 43.92, 55.81, 58.01, and 63.84 respectively, are assigned to the diffraction of $CuFe_2O_4$ crystals and indicate that the synthesized $CuFe_2O_4$ nanoparticles are pure and highly crystalline. This pattern is in agreement with the pure spinel $CuFe_2O_4$ in the standard data ((JCPDS card No. 34-0425) [54]. In the XRD pattern of $CuFe_2O_4/Mg(OH)_2$, all the peaks of $CuFe_2O_4$ and $Mg(OH)_2$ are observed. The lines (001), (101), (102), (110), (103), and (201) related to the sharp peaks at $2\Theta = 18.49$, 38.21, 50.99, 58.85, 68.37, and 75.08 respectively, are corresponded to hexagonal phase of magnesium hydroxide crystal, which are very close to standard card of (JCPDS No. 84-2164) [53]. The peak at 62.47 for magnesium hydroxide overlaps with the 63.84 peak of $CuFe_2O_4$. The average crystallite size of the sample was calculated using the Scherrer equation (24 nm).

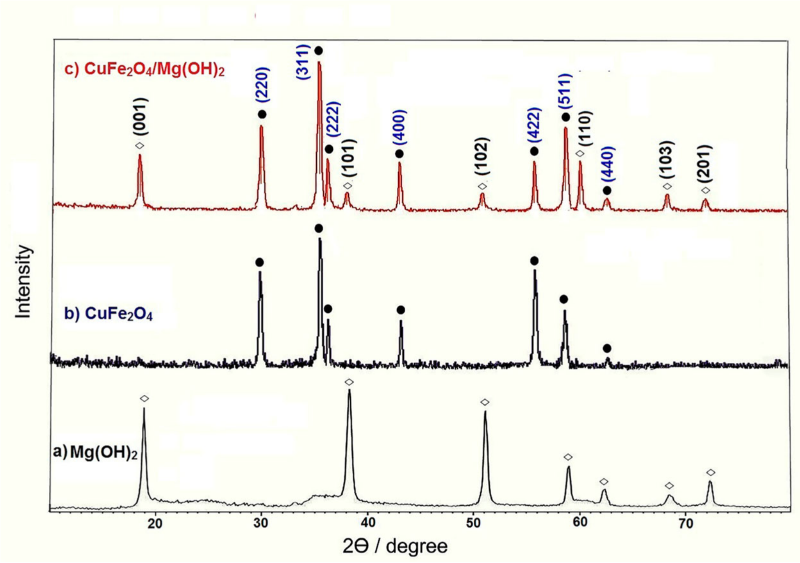


Figure 1. The X-ray diffraction patterns of (a) nano-$Mg(OH)_2$, (b) nano-$CuFe_2O_4$ and (c) $CuFe_2O_4/Mg(OH)_2$ nanocomposite.

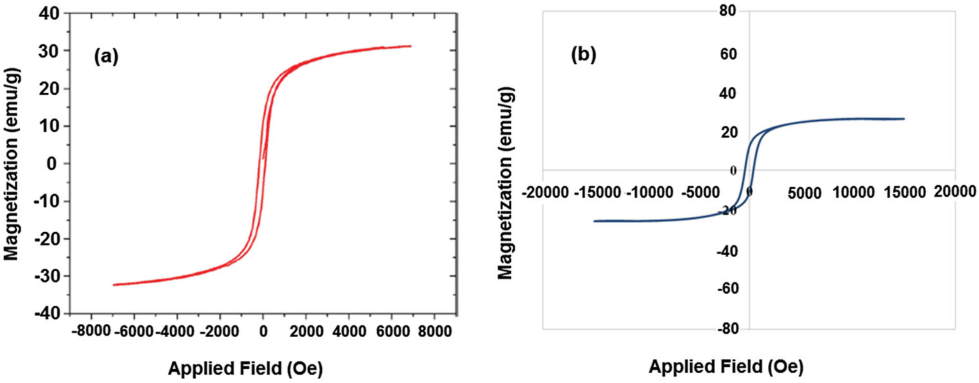


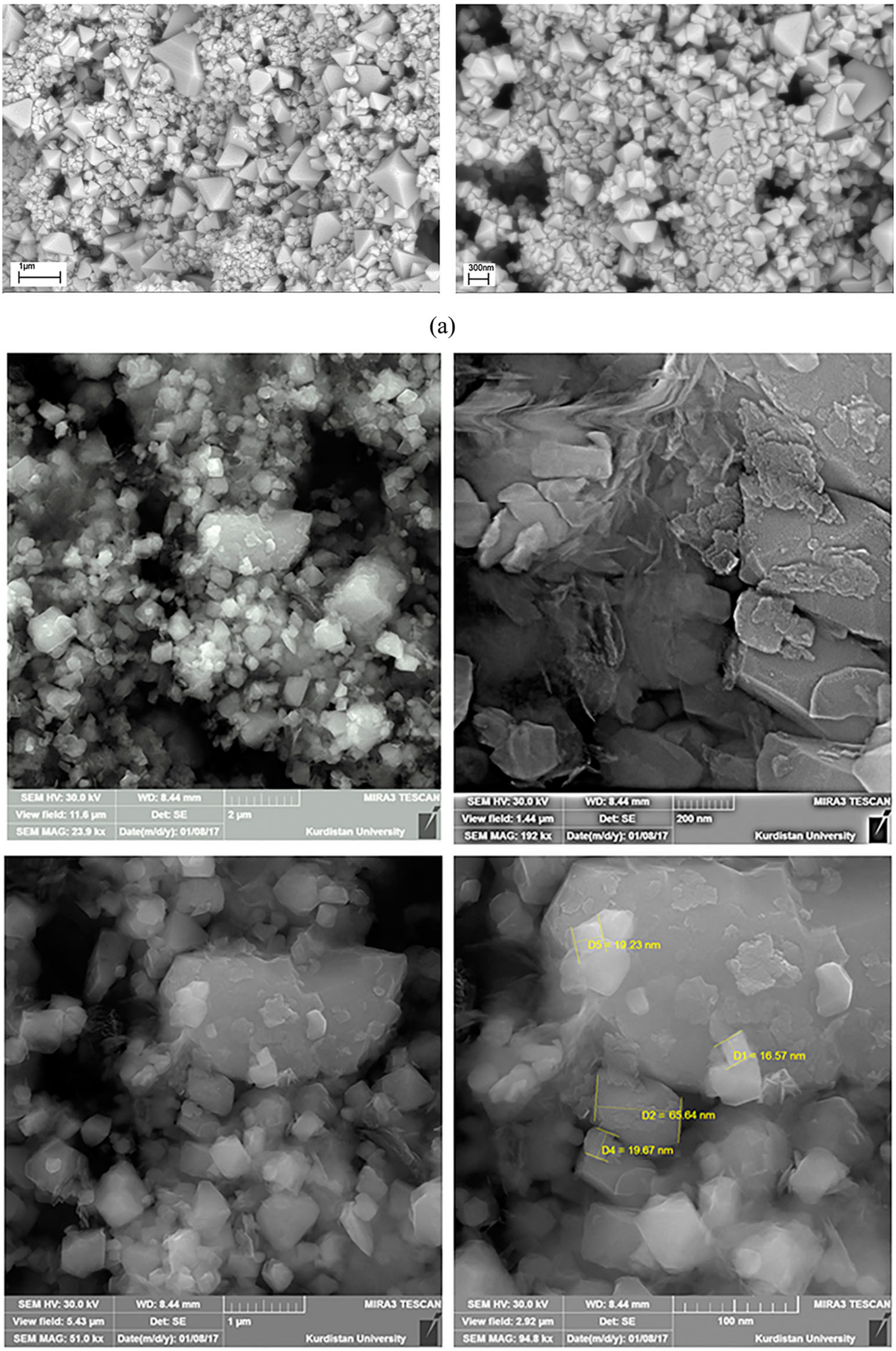
Figure 2. Magnetization curves of $CuFe_2O_4$ (a) and (b) $CuFe_2O_4/Mg(OH)_2$.

2.1.2. Vibration sample magnetometer (VSM)

Figure 2 shows magnetization curves of $CuFe_2O_4$ nanoparticles and $CuFe_2O_4/Mg(OH)_2$ nanocomposite at room temperature. The $CuFe_2O_4/Mg(OH)_2$ nanocomposite showed the same ferromagnetic behavior, but the incorporation of $Mg(OH)_2$ with copper ferrite led to decrease the saturation magnetization and coercivity. The decrease in saturation magnetization can be explained by the presence of nonmagnetic $Mg(OH)_2$ in the sample.

2.1.3. Scanning electron microscopy (SEM)

The morphology of as-prepared $CuFe_2O_4$ and $CuFe_2O_4/Mg(OH)_2$ nanoparticles has been analyzed by the SEM technique (Figure 3). $CuFe_2O_4$ nanoparticles are in tetragonal crystalline shapes with uniform distribution in the sample. The nanoparticles of $Mg(OH)_2$ with



(a)

(b)

Figure 3. SEM images of (a) $CuFe_2O_4$ and (b) $CuFe_2O_4/Mg(OH)_2$ nanoparticles.

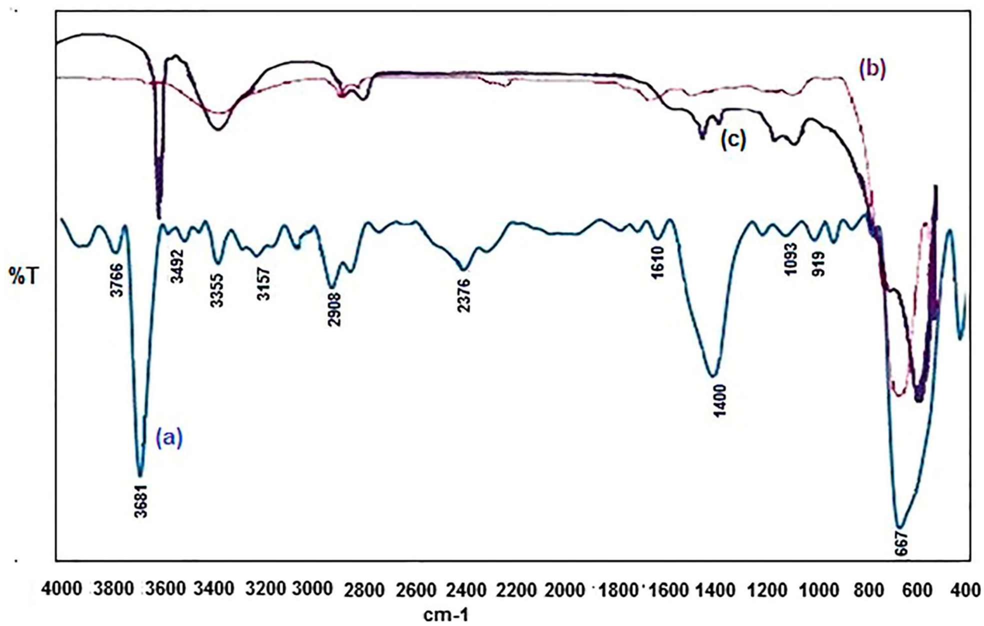


Figure 4. FT-IR (KBr) spectrum of (a) $CuFe_2O_4/Mg(OH)_2$, (b) $CuFe_2O_4$ and (c) $Mg(OH)_2$.

hexagonal shape are regularly immobilized on the whole surfaces of $CuFe_2O_4$ nanoparticles. These images show that particle lies in the range of 16–65 nm. The obtained results are in good agreement with XRD data.

2.1.4. Fourier transform infra-red (FT-IR) spectrum

Figure 4 shows the FT-IR spectrum of $CuFe_2O_4$, $Mg(OH)_2$ and $CuFe_2O_4/Mg(OH)_2$. The sharp and strong absorption band at 3681 cm^{-1} is related to the O–H stretching vibrations in the crystal structure of $Mg(OH)_2$ [53]. The broad absorption peaks at 3492 and 1610 cm^{-1} correspond to the stretching and bending modes of hydroxyl group in surface absorbed water, respectively. A broad peak at 1400 cm^{-1} is assigned to the O-H bent vibrations in $Mg(OH)_2$. The formation of tetrahedral-octahedral structures of the metal oxide (Fe-O and Cu-O) is confirmed by the absorption bands at around 400–600 cm^{-1} [50].

2.1.5. Electron dispersive spectroscopy (EDS)

The chemical combination of nano-$CuFe_2O_4/Mg(OH)_2$ was determined with EDS analysis. In the EDS spectrum, Fe, O, Cu, and Mg signals are observed (Figure 5).

2.2. Conversion of epoxides to thiiranes catalyzed by $CuFe_2O_4/Mg(OH)_2$ nanocomposite

In order to optimize the reaction conditions, the conversion of styrene oxide to styrene episulfide using thiourea in the presence of catalytic amount of $CuFe_2O_4/Mg(OH)_2$ nanocomposite was studied (Scheme 3). According to a literature survey, the catalyst and reactant quantities, reaction temperature, time, and solvents were investigated as optimization factors. The optimization experiments are summarized in Table 1. The best result

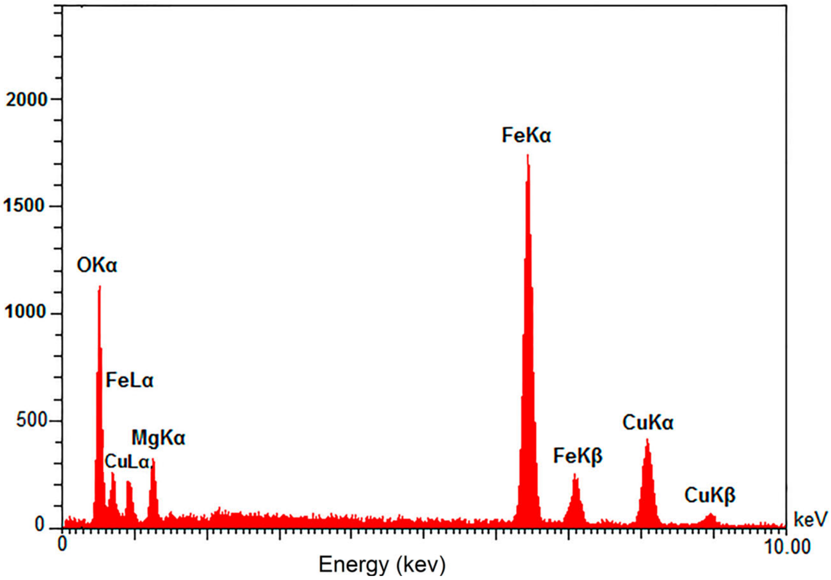
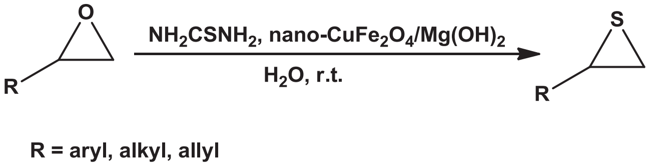


Figure 5. EDS of $CuFe_2O_4/Mg(OH)_2$ nanocomposite.

was obtained using styrene oxide (1 mmol) and thiourea (1 mmol) in the presence of $CuFe_2O_4/Mg(OH)_2$ (0.05 g, 0.17 mmol) in water at room temperature (Table 1, entry 4). The use of catalytic amount of nanocomposite was necessary to perform the reaction, and epoxide transformation did not proceed without catalyst even after 3 h (Table 1, entry 1). Various amounts of $CuFe_2O_4/Mg(OH)_2$ (0.03, 0.04 and 0.05 g) were applied, and the most satisfying outcome was achieved using 0.05 g of catalyst (Table 1, entry 4). The enhancement of catalyst quantity from 0.03 to 0.05 g not only accelerated the reaction rate, but also increased the product yield effectively (Table 1, entries 2–4). More amounts of nano-$CuFe_2O_4/Mg(OH)_2$ did not improve the yield of product (Table 1, entry 5). The more amounts of thiourea (2 and 3 mmol) were also examined in the conversion of styrene oxide to styrene episulfide. The reaction time and product yield were similar to results obtained using 1 mmol of thiourea (entries 6 and 7). The effect of solvent, was considered by comparing results from reactions carried out in water and other solvents such as acetonitrile, chloroform, ethyl acetate and ethanol (Table 1, entries 8–11). Water as a green and eco-friendly solvent was chosen as the best option for this transformation. Furthermore, H_2O with hydrogen bonding capability facilitates the ring opening of epoxides by nucleophilic reagents in the presence of catalyst. In comparison with water, the reaction times were longer and the product yields were lower in all other solvents. In addition, the model reaction was also considered under solvent-free conditions. The reaction was not accomplished in the absence of solvent even under grinding condition (Table 1, entries 12 and 13).

In order to study the influence of temperature on the reaction, the conversion of styrene oxide to corresponding thiirane was carried out at different temperatures (Table 1, entries 14 and 15). Increasing the temperature and performing the reaction in refluxing water raised the reaction rate but it did not significantly affect the product yield. In order to apply mild conditions, room temperature was selected as the best option.



Scheme 3. Conversion of epoxides to thiiranes with thiourea catalyzed by $CuFe_2O_4/Mg(OH)_2$ nanocomposite.

Table 1. Optimization experiments for conversion of styrene oxide to styrene episulfide with thiourea catalyzed by nano-$CuFe_2O_4/Mg(OH)_2$[a].

Entry	NH_2CSNH_2 (mmol)	$CuFe_2O_4/Mg(OH)_2$ (g)	Conditions	Time (h)	Conversion (%)[b]	Yield (%)[c]
1	1	–	H_2O/r.t.	3	0	0
2	1	0.03	H_2O/r.t.	3.5	100	80
3	1	0.04	H_2O/r.t.	2.7	100	85
4	1	0.05	H_2O/r.t.	2.3	100	90
5	1	0.06	H_2O/r.t.	2.3	100	90
6	2	0.05	H_2O/r.t	2.3	100	90
7	3	0.05	H_2O/r.t	2.3	100	90
8	1	0.05	CH_3CN /r.t.	6	60	50
9	1	0.05	$CHCl_3$ /r.t.	4.7	50	45
10	1	0.05	EtOAc /r.t.	6	20	Trace
11	1	0.05	EtOH /r.t.	4	90	70
12	1	0.05	Solvent-free /r.t.	4	60	50
13	1	0.05	Solvent-free/r.t./grinding	0.5	60	50
14	1	0.05	Solvent-free/oil bath (75°C)	4	70	65
15	1	0.05	H_2O/reflux	1	100	91
16[d]	1	0.05	H_2O/r.t.	2.3	50	40
17[e]	1	0.05	H_2O/r.t.	2.3	50	42

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

[b] Conversion of less than 100% was determined on the basis of the recovered epoxide.

[c] Isolated yields.

[d] Catalysed by $CuFe_2O_4$.

[e] Catalysed by $Mg(OH)_2$.

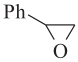
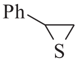
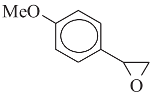
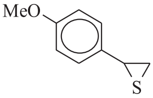
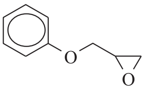
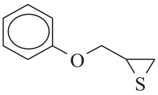
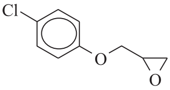
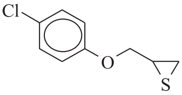
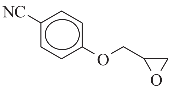
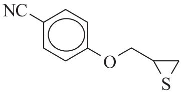
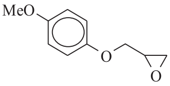
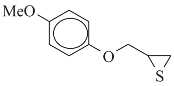
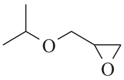
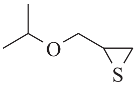
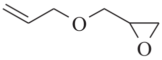
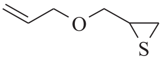
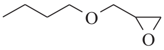
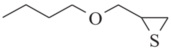
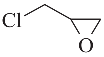
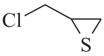
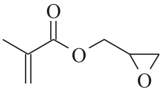
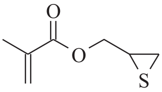
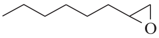
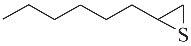
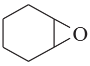
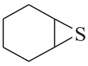
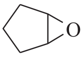
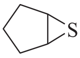
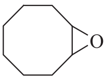
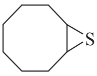
Conversion of styrene oxide to styrene episulfide was also investigated using bare $CuFe_2O_4$ and $Mg(OH)_2$ nanoparticles under the same reaction condition (entries 16 and 17). The reactions were not complete and results showed that the interactions between the $Mg(OH)_2$ and $CuFe_2O_4$ nanoparticles may increase the catalytic activity of $CuFe_2O_4/Mg(OH)_2$ composite.

The generality of the presented procedure in the preparation of thiiranes from epoxides was established by reaction of various epoxides bearing either electron-donating or -withdrawing substituents, and cyclic epoxides with thiourea in the presence of $CuFe_2O_4/Mg(OH)_2$ nanocomposite under the optimized conditions. The results are summarized in Table 2. All reactions were carried out successfully within 1–3.7 h to give thiiranes in 70–99% yields.

2.3. Recycling of $CuFe_2O_4/Mg(OH)_2$ nanocomposite

The recycling of the nanocatalyst was investigated under optimized reaction conditions (Table 2, entry 1). The nanoparticles were easily collected using a simple magnet, washed

Table 2. Conversion of epoxides to thiiranes with thiourea catalyzed by nano-$CuFe_2O_4/Mg(OH)_2$[a].

Entry	Epoxide (a)	thiiranes (b)	Time (h)	Yield (%)[b]	Ref.
1			2.3	90	[51]
2			2.2	88	[51]
3			3.7	99	[51]
4			3.5	95	[34]
5			3.2	90	[51]
6			3.7	98	[34]
7			1	80	[51]
8			1.5	75	[51]
9			2.1	91	[34]
10			2	75	[34]
11			3	82	[51]
12			2.5	90	[34]
13			2	75	[51]
14			2	70	[51]
15			2.1	79	[51]

[a] All reactions were carried out with 1 mmol of epoxide in the presence of thiourea (1 mmol) and nano-$CuFe_2O_4/Mg(OH)_2$ (0.05 g) in water at room temperature.
[b] Yields refer to isolated pure products.

with distilled water and after drying reused under the same reaction conditions. In order to have a logical comparison, the reaction time was kept constant in all cycles. The obtained results showed that the nanocatalyst could be recycled four times without significant

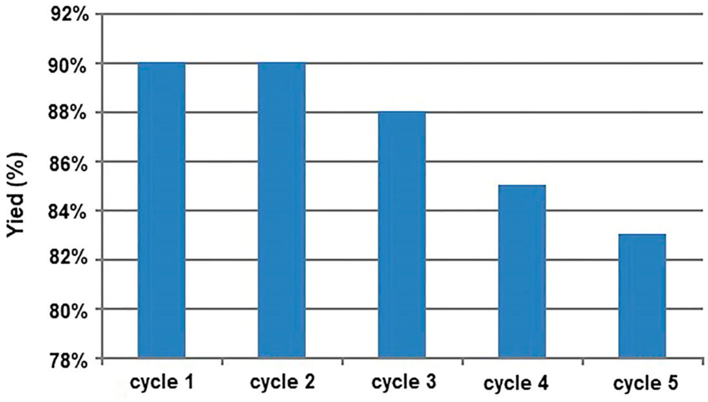


Figure 6. Recycling of $CuFe_2O_4/Mg(OH)_2$ nanocatalyst in the conversion of styrene oxide to styrene episulfide.

activity loss, and even after five runs the yields remained still high (Figure 6). The slowly decreasing activity in five consecutive cycles, might be attributed to the slight loss of catalyst during the reaction and recovery processes.

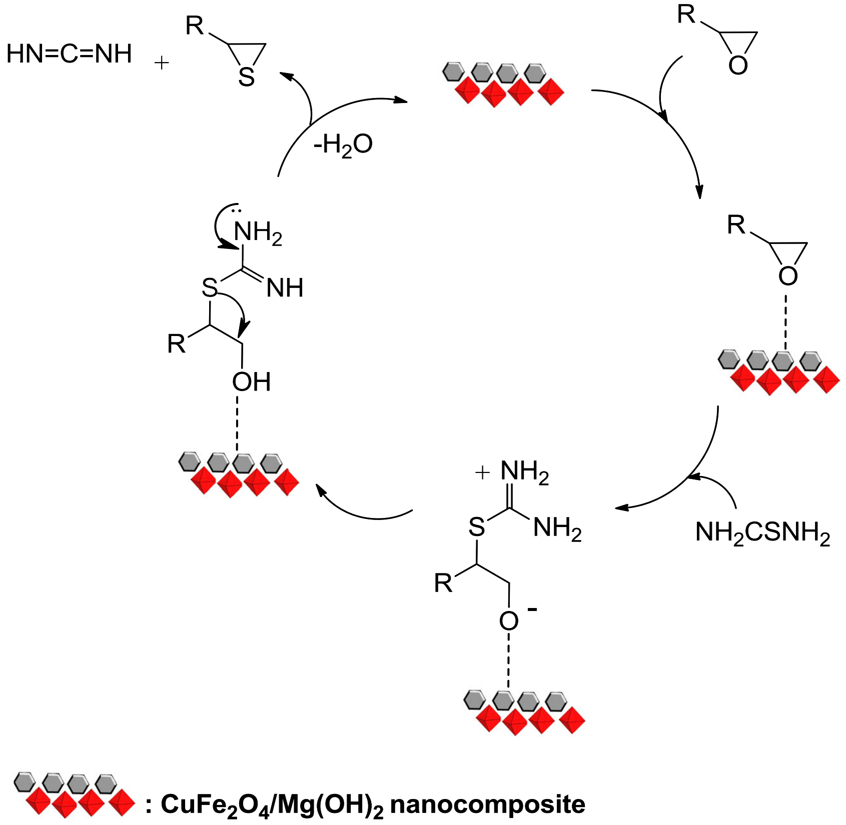
The hot filtration test was used for confirming the heterogeneity of as-prepared catalyst. Accordingly, the filtration of the catalyst was carried out after 30 min at 100°C and the filtrate was allowed to react for additional 2 hours, but the reaction due to the absence of catalyst did not take place, and no transformation was observed. Further, the extent of Cu, Fe and Mg leaching during the catalytic reaction was studied by ICP-OES analysis of the supernatant liquid after removal of catalyst and the result showed no presence of Cu, Fe or Mg in supernatant liquid.

2.4. Proposed mechanism for conversion of epoxides to thiiranes with thiourea catalyzed by $CuFe_2O_4@Mg(OH)_2$ nanocomposite

The exact mechanism of this transformation is not clear at present. However, a possible mechanism is shown in Scheme 4. The immobilized $Mg(OH)_2$ shell on the surface of $CuFe_2O_4$ reduced the self-aggregation tendency of copper ferrite nanoparticles and also increased the quantity of hydroxyl functional groups on the catalyst surface which led to an enhancement of its activity. The hydroxyl groups facilitate the ring opening of oxirane through the formation of hydrogen bonds with oxygen. On the other hand, the coordination of oxygen in epoxide with copper and magnesium also catalyzes the opening of the oxirane ring especially in water as a protic and polar solvent.

2.5. Comparison of catalytic activities of $CuFe_2O_4/Mg(OH)_2$ and other catalysts

The advantages of the presented method were demonstrated by comparison of styrene oxide transformation to styrene episulfide with other methods reported in the literature (Table 3). Our procedure due to the mild and eco-friendly conditions such as recoverability and reusability, easy preparation and separation of magnetic nanocatalyst, performing the reaction at low temperature, and the use of water as a green solvent is preferred. The



Scheme 4. Proposed mechanism for conversion of epoxides to thiiranes with thiourea catalyzed by nano-$CuFe_2O_4/Mg(OH)_2$

proposed procedure was also compared to other literature methods in terms of reaction time and yield of products, and it showed a more or comparable efficiency towards the other protocols.

Comparison of the catalytic effects of bare $CuFe_2O_4$ and $CuFe_2O_4/Mg(OH)_2$ nanocomposite indicated that the properties of the coated copper nanoferrite were amazingly different from the $CuFe_2O_4$ particles (Table 3, entries 1 and 7). The new synthesized $CuFe_2O_4/Mg(OH)_2$ nanocomposite takes advantage of both magnetic core and functionalized surface, which make the present procedure more efficient than the other methods that use the bare nanoferrites. Conversion of styrene oxide to styrene episulfide was not accomplished using $CuFe_2O_4$ catalyst in water at room temperature even after long times [50], while $CuFe_2O_4/Mg(OH)_2$ nanocomposite easily catalyzed this reaction in water under mild conditions. The eco-friendly solvent and low temperature are very important factors in organic synthesis. On the other hand, the bare $CuFe_2O_4$ particles often suffer from agglomeration problem. So, minimizing the aggregation of nanoparticles was the other remarkable advantage of $CuFe_2O_4/Mg(OH)_2$ nanocomposite, which increased the dispersibility of nanoparticles and facilitated the recovering and recycling of catalyst. In addition, the presence of large amounts of hydroxyl groups on the surface of

Table 3. Comparison of the conversion of styrene oxide to styrene episulfide catalyzed by $CuFe_2O_4/Mg(OH)_2$ and other reported methods[a].

Entry	Reagent	Catalyst	Condition	Time (min)	Yield (%)[b]	Ref.
1	NH_2CSNH_2	$CuFe_2O_4/Mg(OH)_2$	H_2O/r.t.	138	90	This work
2	NH_2CSNH_2	Ps-$AlCl_3$	CH_3CN/reflux	90	85	[37]
3	NH_2CSNH_2	$Mg(HSO_4)_2$	CH_3CN/reflux	150	80	[13]
4	NH_2CSNH_2	$Sn^{IV}(tpp)(OTf)_2$	CH_3CN/reflux	60	98	[21]
5	NH_2CSNH_2	$Sn^{IV}(tpp)(BF_4)_2$	CH_3CN/reflux	50	98	[22]
6	NH_2CSNH_2	SiO_2-$AlCl_3$	CH_3CN/45°C	84	85	[55]
7	NH_2CSNH_2	Nano $CuFe_2O_4$	EtOH/reflux	40	92	[50]
8	NH_4SCN	Nano $NiFe_2O_4$	Solvent-free/oil bath 60°C	20	94	[51]
9	NH_4SCN	Nano $MgFe_2O_4$	Solvent-free/oil bath 60°C	25	92	[51]
10	KSCN	$InCl_3$	CH_3CN/reflux	270	89	[15]
11	KSCN	$[bmim]BF_4 \cdot H_2O$	H_2O/r.t.	300	89	[34]
12	KSCN	BTPBDC	H_2O/r.t.	150	87	[56]
13	NH_2CSNH_2	–	Solvent-free/120°C	15	65	[6]

[a] All reactions were carried out using 1 mmol of styrene oxide.

[b] Yields refer to isolated pure products.

nanocomposite increased the catalytic activity through hydrogen bond formation with oxygen atom of oxirane which helps to the ring opening of epoxide.

3. Conclusions

In summary, in this research, we have reported the synthesis and characterization of $CuFe_2O_4/Mg(OH)_2$ nanocomposite and evaluated its potential as a novel and green magnetic nanocatalyst in the conversion of structurally different epoxides to corresponding thiiranes with thiourea in water at room temperature. The recoverability, reusability and simple separation of magnetic catalyst from the reaction mixture, low temperature, short reaction times, high to excellent product yields, the use of green solvent, and easy work-up are among the remarkable advantageous of the presented method.

4. Experimental

4.1. Instruments and materials

All materials were purchased from the Merck and Aldrich Chemical Companies with the best quality and they were used without further purification. The synthesized nanocomposite was characterized by XRD on a Bruker D8-Advanced diffractometer with graphite-monochromatized Cu Kα radiation ($\lambda = 1.54056$ Å) at room temperature. Magnetic property of synthesized nanocatalyst was measured using a VSM (Meghnatis Daghigh Kavir Co., Kashan Kavir, Iran) at room temperature. The energy dispersive X-ray spectrometer (EDS) analysis was taken on a MIRA3 FE-SEM microscope (TESCAN, Czech Republic) equipped with an EDS detector (Oxford Instruments, UK). SEM images were determined using FESEM-TESCAN. 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 spectra and comparison with the authentic data in the literature. All yields refer to isolated pure products.

4.2. Preparation of $CuFe_2O_4$ nanoparticles

$CuFe_2O_4$ nanoparticles were synthesized through a solid-state method. Briefly, in an agate mortar, $CuSO_4$, $Fe(NO_3)_3 \cdot 9H_2O$, NaOH, and NaCl were mixed in a molar ratio (1:2:8:2) and ground together for 50 min. The exothermic reaction started and was accompanied by changing the color of pasty mixture from blue to brown after 4 min. The obtained mixture was washed with distilled water for several times and then was dried at 80°C for 2 h. In order to remove the additional salts completely, the generated powder was calcined at 900°C for 2 h to give the final $CuFe_2O_4$ nano-ferrite.

4.3. Synthesis of $CuFe_2O_4/Mg(OH)_2$ nanocomposite

To a solution of $Mg(NO_3)_2 \cdot 6H_2O$ (1.28 g, 5 mmol) in distilled water (30 mL), $CuFe_2O_4$ (1.03 g, 4.3 mmol) was added. The mixture was stirred vigorously for 15 min at room temperature. Next, the resulting mixture was slowly basified by dropping of NaOH solution (2 M) up to pH ~ 12. The stirring of the mixture was continued at room temperature for 24 h. The dark brown $CuFe_2O_4/Mg(OH)_2$ nanoparticles were separated using a magnet, washed with distilled water and then dried under air atmosphere during 2 days.

4.4. Conversion of epoxides to thiiranes using thiourea catalyzed by $CuFe_2O_4/Mg(OH)_2$ nanocomposite: a general procedure

In a round-bottomed flask equipped with a magnetic stirrer, a mixture of epoxide (1 mmol), thiourea (0.47 g, 3 mmol) and $CuFe_2O_4/Mg(OH)_2$ nanoparticles (0.05 g, 0.17 mmol) in H_2O (2 mL) was prepared and stirred at room temperature for 1—3.5 h. The progress of the reaction was monitored by TLC using *n*-hexane: EtOAc (10:4) as an eluent. After completion of the reaction, $CuFe_2O_4/Mg(OH)_2$ nanoparticles were recovered with an external magnet, washed with ethyl acetate, and used for subsequent cycles after drying under vacuum. The reaction mixture was extracted by CH_2Cl_2 (3 × 5 mL) and then dried over anhydrous Na_2SO_4. The organic solvent was evaporated to give crude thiirane for further purification by a short-column chromatography over silica gel (70–99% yield) (Table 2). All products are known compounds and were characterized by comparison of their spectra ((FT-IR, ^1H NMR and ^{13}C NMR)) with those of valid samples; [34,51] these data are presented in the supplementary information (http://dx.doi.org/10.1080/17415993.2019.1567728).

Disclosure statement

No potential conflict of interest was reported by the authors.

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