

Fe₃O₄@SiO₂/DABCO(OH) Core-Shell Hybrid Nanocomposite: Efficient Nanomagnetic and Basic Reusable Catalyst in the One-pot Synthesis of Trithiocarbonate Derivatives

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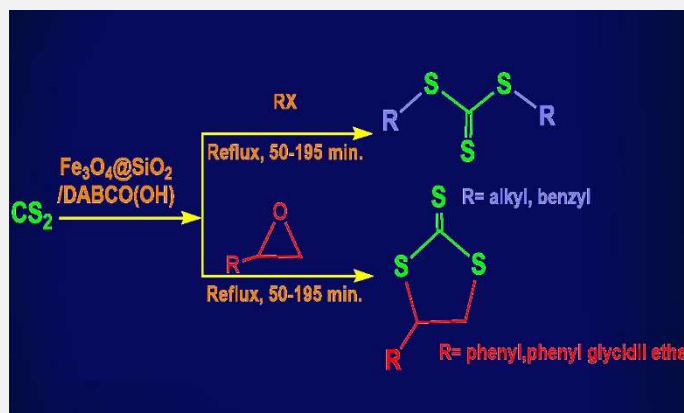


ABSTRACT

DABCO-based ionic liquid supported on magnetic core-shell nanoparticles, Fe₃O₄@SiO₂/DABCO(OH), as a novel magnetic nanocomposite was prepared and characterized by Fourier Transform Infrared spectroscopy (FTIR), Scanning Electron Microscopy (SEM), X-ray powder Diffraction (XRD), Transmission Electron Microscopy (TEM) and Vibrating Sample Magnetometer (VSM) analysis. The hybrid nanocomposite was successfully used as an efficient heterogeneous basic catalyst for the facile synthesis of symmetrical dialkyl trithiocarbonates and cyclic trithiocarbonates from alkyl halides and epoxides respectively under mild reaction conditions.

The results showed that aryl halides bearing electron-donating groups as well as electron-withdrawing groups converted to the corresponding symmetrical dialkyl trithiocarbonates in good to high isolated yields (80-95%). In addition, styrene oxide and phenyl glycidyl ether epoxide were converted to the corresponding cyclic trithiocarbonates in good yields in CS₂ and the presence of nanocomposite without the formation of any by-product. Recycling experiments confirmed that Fe₃O₄@SiO₂/DABCO(OH) was recyclable and could be used for several consecutive reaction runs.

Keywords: Cyclic trithiocarbonate, double-charged hybrid silica, hybrid nanocomposite, silica-coated magnetic nanoparticles, symmetrical dialkyl trithiocarbonates



1. Introduction

In the last few decades, magnetic core-shell-structured nanocomposite materials have received much attention due to their widespread application in various fields including catalysis, biomedicine, biotechnology, environmental remediation, magnetic resonance imaging, and magnetic fluids [1, 2]. Magnetic nanoparticles (MNPs) indicate unique and substantial properties, such as rigidity, chemical stability, good biocompatibility, high surface areas, less toxicity, large pore volumes, resistance to microbial attack, and uniform and tunable pore sizes [3-6].

On the other hand, because of the high solvation ability of ionic liquids (ILs) for a wide range of organic, inorganic, and organometallic compounds [7, 8], their effective application as catalysts and solvents in organic syntheses has attracted researchers. However, ILs encompass problems such as the limit of their practical applications in chemical processes, high viscosity, and some troubles with inhomogeneity and recovery [9]. Immobilization of Ionic liquids on magnetic nanoparticles to achieve heterogeneous magnetic catalysts was suggested as an alternative way to overcome these problems [10, 11].

Organic trithiocarbonates demonstrate an important class of organic compounds containing C-S bonds that have been used especially as intermediates in organic synthesis [12-15], lubricating additives [12], pharmaceuticals [16, 17], agrochemicals [18, 19], pesticides [20, 21] and reversible addition-fragmentation chain-transfer agent in the free radical polymerization reactions [14, 22]. The most common protocol for the synthesis of symmetrical trithiocarbonates is the reaction of trithiocarbonate anion (CS₃²⁻) with alkyl halides. The trithiocarbonate anion [13,



23] is usually prepared by in situ one-pot reaction of carbon disulfide with an alkali metal or ammonium sulfide [12, 24, 25], hydroxide [26], carbonate [27], and the phosphate [24] of the alkali metal group, KF/alumina or alumina [28-30], Imidazole [18], anion-exchange resin [31], aluminum(salen) complex $[Al(salen)]_2O$ and tetrabutylammonium bromide [32].

In this study, we present the design, preparation, and characterization of novel magnetic double-charged diazoniabicyclo[2.2.2]octane hydroxide silica hybrid ($Fe_3O_4@SiO_2/DABCO(OH)$) as a magnetic basic ionic liquid for the in situ one-pot preparation of trithiocarbonate anion from CS_2 and its reaction by alkyl halides and epoxides to produce symmetrical trithiocarbonate and cyclic derivatives respectively.

2. Experimental

2.1. General

All chemical reagents in high purity were purchased from Fluka and Merck companies and used with no additional purification. All the compounds were characterized by comparison of their physical data, with reported samples in the literature. The FT-IR spectrum of the samples was recorded on a BOMEM MB-Series 1998 FT-IR spectrometer in the region 400–4000 cm^{-1} using pressed KBr discs. Reactions were monitored by thin-layer chromatography (TLC) on silica gel PolyGram SILG/UV 254 plates. X-ray diffraction (XRD) patterns were obtained on a Philips X-ray diffraction model PW 1840. The particle size and external morphology of the particle were studied with SEM (Philips XL30 scanning electron microscope) and TEM (Zeiss; EM10C; 80 kV). The magnetic property of the catalyst was measured on VSM (Meghnatis Daghigh Kavir Co. Iran).

2.2. Preparation of Fe_3O_4 magnetic nanoparticles

Fe_3O_4 magnetic nanoparticles synthesis process was adapted from our previous reports [3]. According to this procedure, $FeCl_2 \cdot 4H_2O$ (6.4 g, 32 mmol) and $FeCl_3 \cdot 6H_2O$ (15 g, 56 mmol) were dissolved in 640 mL of deionized water. The blended solution was stirred under the nitrogen atmosphere to remove oxygen and heated at 80 °C for 1 h. Then 80 mL of $NH_3 \cdot H_2O$ (25%) was added to the reaction mixture rapidly. The solution was stirred under N_2 for another 1 h and then cooled to room temperature. The precipitated particles were washed five times with hot water and collected with magnetic decantation. Lastly, Magnetic iron oxide nanoparticles were dried under a vacuum at 60 °C.

2.3. Preparation of bis(n-propyltrimethoxysilane)-1,4-diazoniabicyclo [2.2.2] octane chloride (BPTDABCOCI)

BPTDABCOCI was obtained according to the procedure reported by Arenas et al. [33]. At first, to 0.9 g of a solution of DABCO (8.0 mmol) in 5 mL of DMF, 3.18 g of 3-chloropropyltrimethoxysilane (CPTMS) (16 mmol) was added. The reaction mixture was stirred at 90 °C for 72 h under argon. The white solid was obtained by filtration, washed with methanol, and dried for 2 h under a vacuum at 90 °C.

2.4. Synthesis of nanomagnetic double-charged diazoniabicyclo[2.2.2]octane hydroxide silica hybrid ($Fe_3O_4@SiO_2/DABCO(OH)$)

$Fe_3O_4@SiO_2/DABCO$ was synthesized according to our previous reports [34]. The prepared magnetic iron oxide nanoparticles (3.0 g) were initially suspended in a mixture of water (60 mL), absolute ethanol (180 mL), and 5.0 mL ammonia aqueous (25%). The suspension was ultrasonically dispersed for 15 min and BPTDABCOCI (7 g) previously dissolved in DMF (15 mL), was added to it. Next, 2.2 mL of TEOS diluted in ethanol (60 mL) was gradually added to this dispersion, and after stirring for 48 h, the $Fe_3O_4@SiO_2/DABCO$ was magnetically separated, washed with ethanol, and dried under vacuum. Then, the obtained nanocomposite was immersed for 10 minutes in 80 mL NaOH 0.5% (w/v). The synthesized basic magnetic nanocomposite, $Fe_3O_4@SiO_2/DABCO(OH)$, was collected by magnetic separation and washed several times with deionized water, and dried under vacuum at 60-70 °C overnight.

2.5. General procedure for the synthesis of symmetrical dialkyl trithiocarbonates

A round-bottomed flask (50 mL) was charged with $Fe_3O_4@SiO_2/DABCO(OH)$ (1.5 g) in carbon disulfide (5 mL) as a solvent and sulfur source and the mixture was stirred vigorously for 30 min. Then, alkyl halide (1 mmol) was added and the suspension was stirred under reflux conditions for the time as shown in **Table 2**. Upon completion of

the reaction monitored by TLC analysis (*n*-hexane), the reaction mixture was cooled to room temperature and the catalyst was magnetically separated. Next, the solution was dried over CaCl₂ and concentrated under reduced pressure to give the desired trithiocarbonates.

2.6. General procedure for the synthesis of cyclic trithiocarbonates

A round-bottomed flask (50 mL) was charged with Fe₃O₄@SiO₂/DABCO(OH) (1.5 g) in carbon disulfide (5 mL) and the mixture was stirred vigorously for 30 min. Then, epoxide (1 mmol) was added and the suspension was stirred under reflux conditions for the time as shown in **Table 2**. Upon completion of the reaction monitored by TLC analysis (*n*-hexane), the reaction mixture was cooled to room temperature and the catalyst was magnetically separated. Next, the solution was dried over CaCl₂ and concentrated under reduced pressure to give the desired cyclic trithiocarbonates.

2.7. Selected spectral data

Bis(phenylmethyl) Trithiocarbonate (**Table 2**, entry 1, 2). IR: 1063 cm⁻¹ (C=S). ¹H-NMR (400 MHz, CDCl₃): δ = 4.68 (4H, s), 7.32-7.41 (10H, m). ¹³C-NMR (100 MHz, CDCl₃): δ = 41.62, 128.34, 128.58, 128.80, 134.99, 222.26.

Bis(2-chlorophenyl methyl) Trithiocarbonate (**Table 2**, entry 3). IR: 1058 cm⁻¹ (C=S). ¹H-NMR (400 MHz, CDCl₃): δ = 4.77 (4H, s), 7.21-7.47 (8H, m). ¹³C-NMR (100 MHz, CDCl₃): δ = 38.02, 127.44, 128.27, 128.98, 129.75, 130.04, 138.11, 223.58.

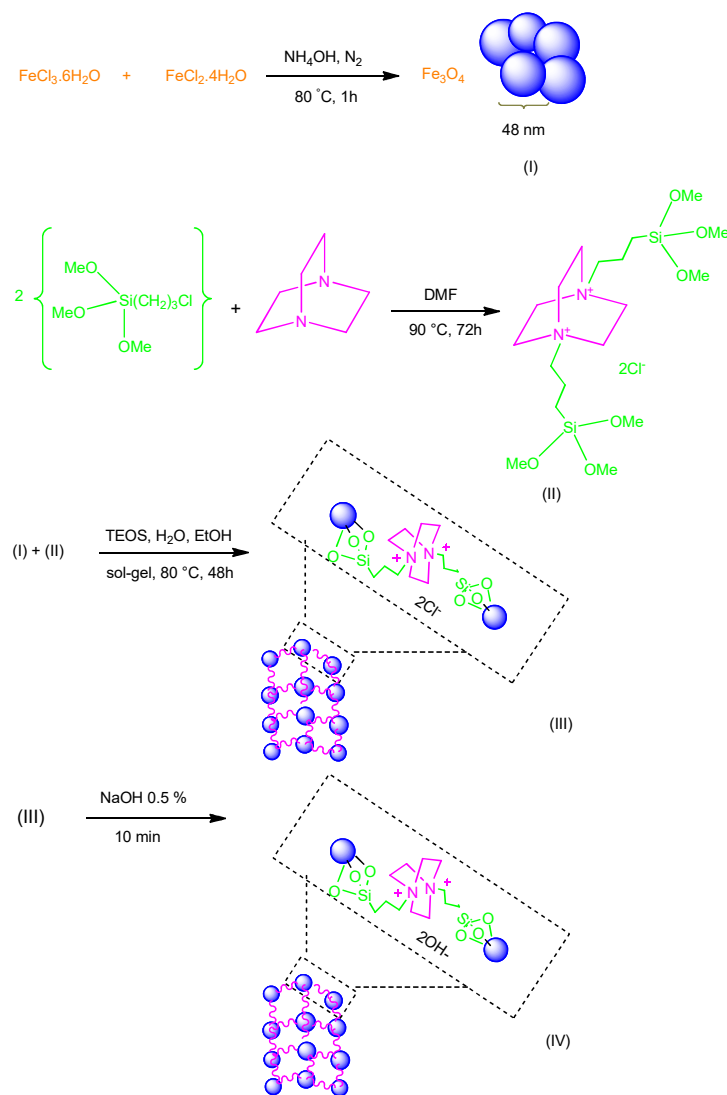
Bis(2,4-dichloro phenylmethyl) Trithiocarbonate (**Table 2**, entry 4). IR: 1067 cm⁻¹ (C=S). ¹H-NMR (400 MHz, CDCl₃): δ = 4.83 (4H, s), 7.22-7.51 (6H, m). ¹³C-NMR (100 MHz, CDCl₃): δ = 37.70, 128.38, 131.11, 132.43, 132.81, 134.02, 134.65, 225.13.

Bis(phenylmethyl) Trithiocarbonate (**Table 2**, entry 5). IR: 1075 cm⁻¹ (C=S). ¹H-NMR (400 MHz, CDCl₃): δ = 3.24 (4H, m), 3.71 (4H, t), 7.21-7.43 (10H, m). ¹³C-NMR (100 MHz, CDCl₃): δ = 35.21, 36.37, 127.25, 127.68, 130.11, 143.22, 214.19.

Bis allyl Trithiocarbonate (**Table 2**, entry 7). IR: 1061 cm⁻¹ (C=S). ¹H-NMR (400 MHz, CDCl₃): δ = 4.15 (4H, d), 5.20 (2H, d), 5.32 (2H, d), 5.77-5.85 (2H, m). ¹³C-NMR (100 MHz, CDCl₃): δ = 39.48, 119.83, 131.11, 222.48.

3. Results and discussion

A schematic illustration of the synthetic strategy for the preparation of nanomagnetic double-charged diazoniabicyclo[2.2.2]octane hydroxide silica hybrid, Fe₃O₄@SiO₂/DABCO(OH), is shown in **Scheme 1**. The Fe₃O₄ magnetic nanoparticles spheres as the core was synthesized initially via the simple co-precipitation method of FeCl₃ and FeCl₂ under basic conditions and coated by the positively double-charged organic-inorganic hybrid silica as the shell by simple sol-gel method. Finally, the counter ion, Cl⁻ was easily exchanged by OH⁻ in 0.5% (w/v) of NaOH.



Scheme 1. Synthesis of $\text{Fe}_3\text{O}_4@/\text{SiO}_2/\text{DABCO}(\text{OH})$

$\text{Fe}_3\text{O}_4@/\text{SiO}_2/\text{DABCO}(\text{OH})$ was comprehensively characterized by Scanning Electron Microscopy (SEM), Fourier Transform Infrared spectroscopy (FTIR), Transmission Electron Microscopy (TEM), Vibrating Sample Magnetometer (VSM) and X-ray Diffraction (XRD) analysis. The FT-IR spectra of (a) Fe_3O_4 , (b) $\text{Fe}_3\text{O}_4@/\text{SiO}_2/\text{DABCO}(\text{OH})$ and (c) BPTDABCOCl are shown in **Figure 1**. The FT-IR analysis of the Fe_3O_4 and $\text{Fe}_3\text{O}_4@/\text{SiO}_2/\text{DABCO}(\text{OH})$ depicts a basic characteristic peak in the region of 580 cm^{-1} , which corresponds to the presence of Fe-O stretching vibration. In BPTDABCOCl and $\text{Fe}_3\text{O}_4@/\text{SiO}_2/\text{DABCO}(\text{OH})$ spectra, the presence of peaks in the region of 440 and $990\text{--}1200\text{ cm}^{-1}$ referred to Si-O-Si symmetric and asymmetric stretching vibrations. The C-H stretching peaks in the spectral regions $2870\text{--}3000\text{ cm}^{-1}$ in the $\text{Fe}_3\text{O}_4@/\text{SiO}_2/\text{DABCO}(\text{OH})$ spectra demonstrated that the magnetic particles were successfully coated by double-charged diazoniabicyclo[2.2.2]octane hydroxide silica hybrid. BPTDABCOCl and $\text{Fe}_3\text{O}_4@/\text{SiO}_2/\text{DABCO}(\text{OH})$ indicated a peak at 1635 cm^{-1} , which indicates the OH bending of absorbed water.

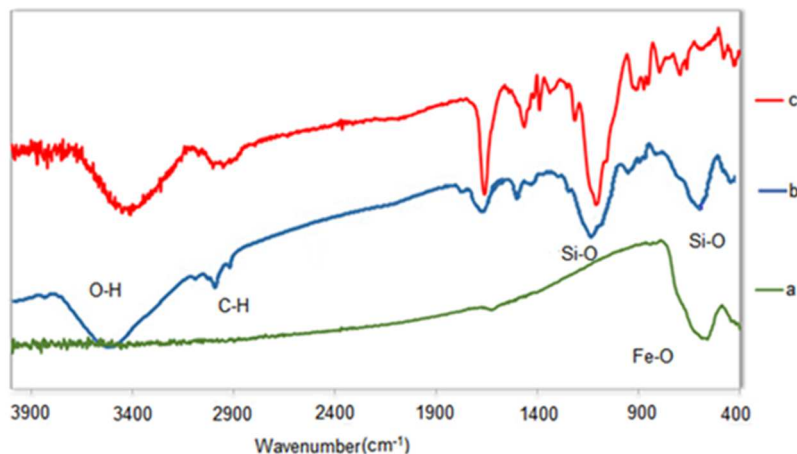


Figure 1. The FT-IR spectra of (a) Fe_3O_4 , (b) $\text{Fe}_3\text{O}_4@/\text{SiO}_2/\text{DABCO}(\text{OH})$ and (c) BPTDABCOCl.

The presence and degree of crystallinity of magnetic iron oxide (Fe_3O_4) in the synthesized $\text{Fe}_3\text{O}_4@/\text{SiO}_2/\text{DABCO}(\text{OH})$ were acquired from XRD patterns (**Figure 2**). The pattern of $\text{Fe}_3\text{O}_4@/\text{SiO}_2/\text{DABCO}(\text{OH})$ demonstrates a most intense at $2\theta = 35.83$. This line, which is completely matched with the pure Fe_3O_4 [35], confirms the presence of Fe_3O_4 and indicates that all modifications do not alter the Fe_3O_4 phase [36].

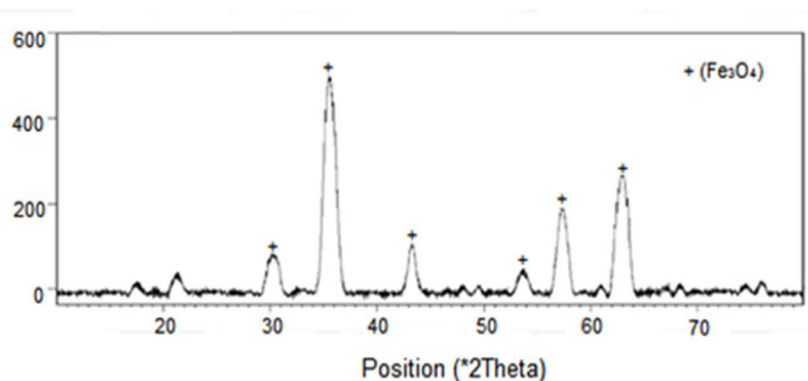


Figure 2. XRD pattern of $\text{Fe}_3\text{O}_4@/\text{SiO}_2/\text{DABCO}(\text{OH})$

The accurate information about particle morphology and size of the immobilization silica parts on the magnetic core were also investigated by TEM. The TEM image of $\text{Fe}_3\text{O}_4@/\text{SiO}_2/\text{DABCO}(\text{OH})$ confirms its nanometer size and displays that dark MNP cores are surrounded by an amorphous silica layer (**Figure 3**).

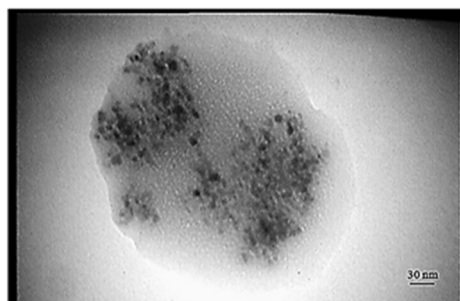


Figure 3. TEM image of $\text{Fe}_3\text{O}_4@/\text{SiO}_2/\text{DABCO}(\text{OH})$

Figure 4 shows the SEM images of magnetic iron oxide (Fe_3O_4) and $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{DABCO}(\text{OH})$ nanoparticles are similar in shape and size and have nano-dimensions around 48 and 74 nm, respectively. The particles are rather monotonous in their morphology.

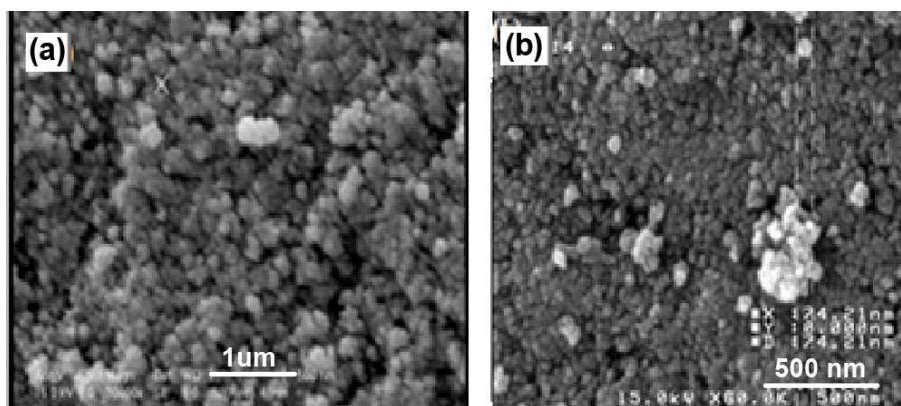


Figure 4. The SEM images of (a) Fe_3O_4 and (b) $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{DABCO}(\text{OH})$ microspheres

The magnetization curves of the uncoated Fe_3O_4 nanoparticles and $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{DABCO}(\text{OH})$ composite are shown in **Figure 5**. As shown in **Figure 5**, the saturated magnetization values for (a) Fe_3O_4 and (b) $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{DABCO}(\text{OH})$ nanoparticles are 68 and 49 emu g^{-1} respectively. The diminution of saturation magnetization was ascribable to the presence of a nonmagnetic shell around the magnetic core.

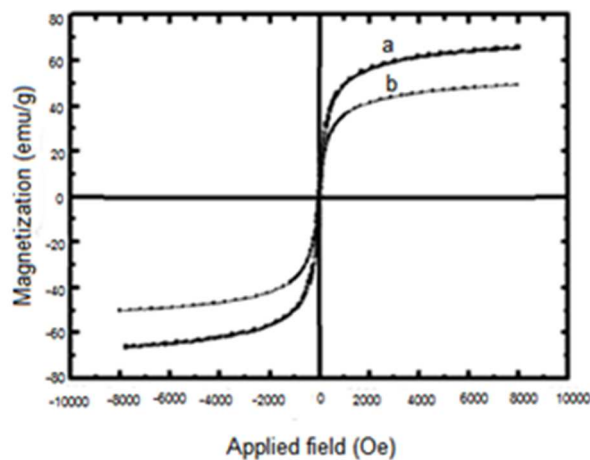


Figure 5. VSM magnetization curves of the (a) Fe_3O_4 , (b) $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{DABCO}(\text{OH})$ nanoparticles

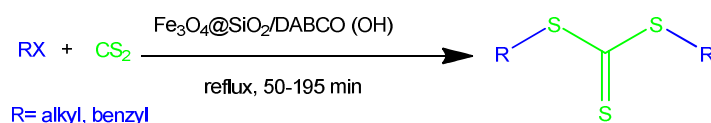
The basic capacity of the nanocomposite was characterized using potentiometry and was confirmed by acid–base titration. Therefore, 0.1 g of $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{DABCO}(\text{OH})$ was added to 25 mL of 1 M aqueous solution of NaCl (initial $\text{pH} = 5.8$) and follow through, stirring the resulting mixture for 24 h, the pH of the solution changed to 8.5. Thus, the basic capacity of the nanocomposite is 4×10^{-4} mmol OH^- per gram of catalyst.

After verifying the structure of the nanocomposite, the study of its catalytic basic activity was undertaken. In this line, the utility of $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{DABCO}(\text{OH})$ nanocomposite in the facile conversion of CS_2 to CS_3^{2-} and the promotion of its nucleophilic substitution with alkyl halide was investigated. First, the reaction of the benzyl bromide as a model with carbon disulfide in the presence of $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{DABCO}(\text{OH})$ nanocomposite was studied to optimize the reaction conditions for the synthesis of symmetrical dialkyl trithiocarbonates. As shown in **Table 1**, the best result was achieved when 1.0 mmol benzyl bromide reacted with 5 mL carbon disulfide in the presence of 1.5 g of basic nanocomposite and under reflux conditions.

Table 1. Optimization of reaction conditions for conversion of benzyl bromide (1 mmol) to the corresponding trithiocarbonate in CS₂ (5 mL) as a solvent and a sulfur source under reflux conditions.

Entry	Catalyst (g)	Time (min)	Yield (%)
1	0.5	90	Trace
2	1.0	90	Trace
3	1.5	50	93

With optimum reaction conditions in hand, various derivatives of symmetrical dialkyl trithiocarbonates were synthesized using various alkyl and benzyl halides (**Table 2**) to investigate the generality of the protocol. According to these results, aryl halides bearing electron-donating groups as well as electron-withdrawing groups converted to the corresponding product in high to excellent yields (**Scheme 2** and **Table 2**). It should be pointed out that due to the S_N2 nature of the reaction, an increase in the reaction time was obtained in the case of secondary alkyl halide. In addition, the nature of the halide ion has a more important effect on the reaction rates.

**Scheme 2.** Synthesis of symmetric trithiocarbonates.

Next, to study the efficiency of the presented basic nanocomposite, its ability to promote the facile conversion of epoxides to cyclic trithiocarbonates was also investigated. As shown in **Table 2**, styrene oxide and phenyl glycidyl ether epoxide in CS₂ and the presence of nanocomposite were successfully converted to the corresponding cyclic trithiocarbonates in good yields without the formation of any by-product (**Entry 9** and **10**).

Table 2. Synthesis of trithiocarbonate derivatives catalyzed by Fe₃O₄@SiO₂/DABCO(OH).

Entry	Reagent	Product	Time (min)	Yield (%) ^a	Ref.
1			50	93	[37]
2			60	89	[27]
3			70	89	[27]
4			95	95	[27]
5			135	80	[18]
6			180	80	[38]

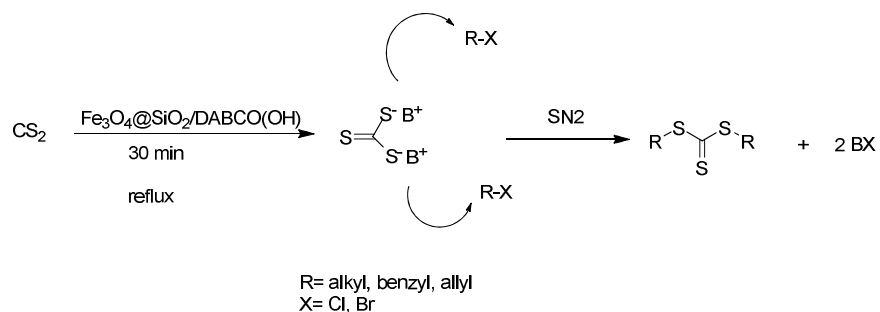
7			70	80	[24]
8			195	80	[18]
9			120	95	[39]
10			150	90	[40]

^a Isolated yields

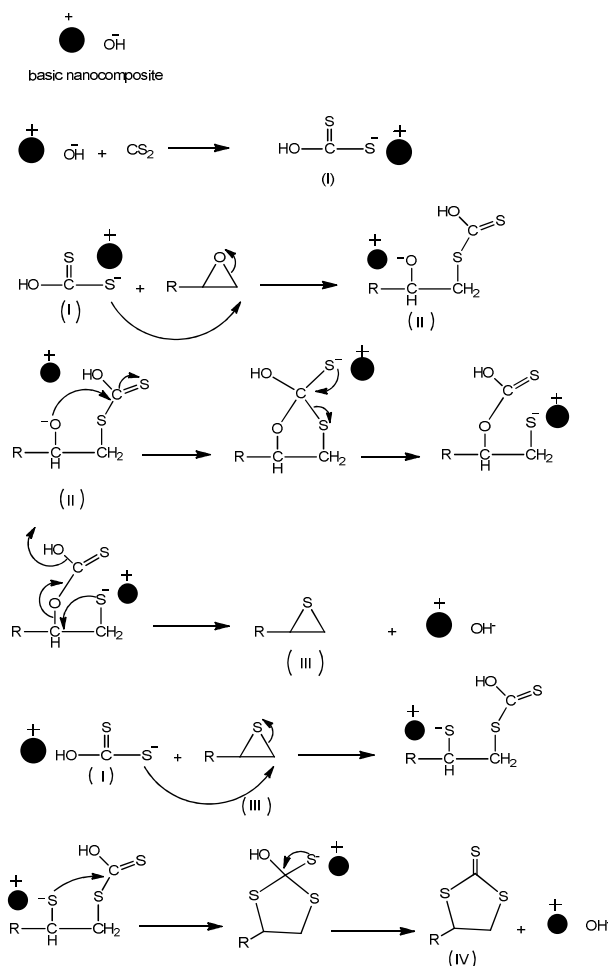
The trithiocarbonate anion (CS_3^{2-}) was formed according to the equation below:



The proposed mechanisms for the formation of dialkyl and cyclic trithiocarbonates from carbon disulfide, alkyl halides, or epoxides and in the presence of $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{DABCO}(\text{OH})$ nanocatalyst are shown in (Schemes 3-4) [27, 40].



Scheme 3. A plausible mechanism for the synthesis of symmetric trithiocarbonates in the presence of $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{DABCO}(\text{OH})$.



Scheme 4. A plausible mechanism for the synthesis of cyclic trithiocarbonates in the presence of $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{DABCO}(\text{OH})$.

To evaluate, the simplification and efficiency of this approach, the yield of product and the reaction conditions for the conversion of benzyl bromide to symmetrical trithiocarbonate and styrene oxide to cyclic trithiocarbonate have been compared with those of the previously reported methods using inorganic or organic catalysts. As shown in **Tables 3-4**, $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{DABCO}(\text{OH})$ is a good promoter for this reaction for the yield of product, reaction time, and conditions.

Table 3. The comparison efficiency of $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{DABCO}(\text{OH})$ with other reported catalysts for the synthesis of dibenzyl trithiocarbonate (**Table 2**, Entry 1)

Entry	Catalyst	Conditions	Time (min)	Yield (%) ^a	Ref.
1	$\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{DABCO}(\text{OH})$	CS_2 / reflux	50	93	This method
2	basic IL	CS_2 / 50 °C	30	90	[41]
3	basic IL	CS_2 / KOH/ reflux	25	94	[27]
4	TBAB/ Al_2O_3	DMF/ CS_2 / 50 °C	600	92	[24]
5	K_3PO_4 K_2CO_3	DMF/ air/ 40 °C	360	95	[37]

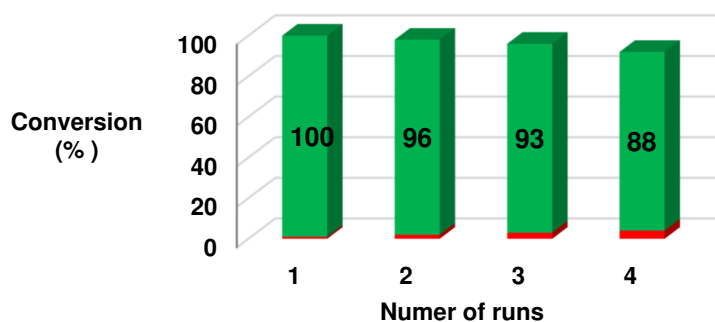
^aIsolated yields

Table 4. The comparison efficiency of $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{DABCO}(\text{OH})$ with other reported catalysts for synthesis of 4-phenyl-1,3-dithiolane-2-thione (**Table 2, Entry 9**).

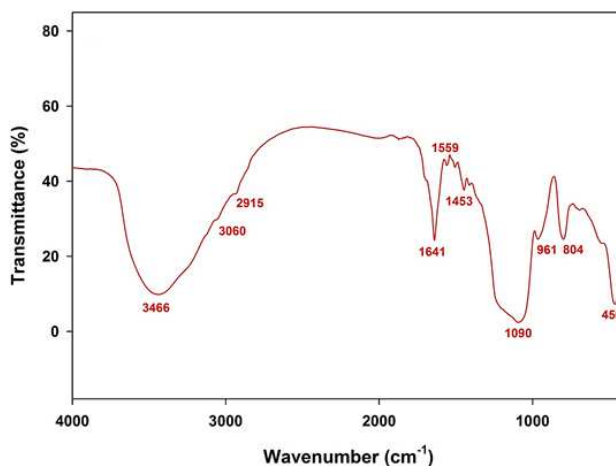
Entry	Catalyst	Conditions	Time (h)	Yield (%) ^a	Ref.
1	$\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{DABCO}(\text{OH})$	$\text{CS}_2/\text{reflux}$	2	95	This method
2	Imidazole(in)ium chlorides/ K_2CO_3	$\text{DMSO}/80\text{ }^\circ\text{C}$	48	95	[39]
3	$\text{LiBr}/\text{KOH}/[\text{Bmim}]\text{Br}$	$70\text{ }^\circ\text{C}$	24	95	[40]

^a Isolated yields

The reusability of $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{DABCO}(\text{OH})$ was also examined in the reaction of benzyl bromide with CS_2 . At the end of the reaction, the catalyst was fixed on the sidewall of the reaction vessel with a magnet, and the recovered catalyst was washed with NaOH (5%), H_2O , and ethanol and then dried and reused for at least four runs. It should be noted that in all runs, to make a more accurate comparison of the catalyst activity, the reaction time is 50 min and the conversion of benzyl bromide to the corresponding trithiocarbonate was followed by GC. As shown in **Figure 6**, after 4 runs and at 50 min, the conversion decreased to 88%, and the product is contaminated by unreacted starting material (12%). It should be noted that by increasing the time from 50 to 65 min, all benzyl bromide was converted into the product.

**Figure 6.** Recyclability of $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{DABCO}(\text{OH})$ for conversion of benzyl bromide (1 mmol) to the corresponding trithiocarbonate in CS_2 (5 mL) under reflux conditions

The FT-IR spectrum of the reused nanocomposite after four runs are shown in **Figure 7**. The comparison of these spectra with the spectra of the fresh nanocomposite (**Figure 1b**) confirms that during the reaction and recycling of the nanocomposite, there is no specific change in its structure.

**Figure 7.** The FT-IR spectrum of reused $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{DABCO}(\text{OH})$ after four runs

4. Conclusion

In this paper, nanomagnetic double-charged diazoniabicyclo[2.2.2]octane hydroxide silica hybrid, $\text{Fe}_3\text{O}_4@ \text{SiO}_2/\text{DABCO}(\text{OH})$, as a novel basic catalyst was synthesized. The catalytic activity of the nanocomposite for the preparation of trithiocarbonates from the reaction of carbon disulfide, alkyl halides, and epoxides was studied. According to the results, the $\text{Fe}_3\text{O}_4@ \text{SiO}_2/\text{DABCO}(\text{OH})$ showed desirable strong basicity to render a high catalytic activity during the reaction, easy-to-handle procedure, short reaction time, recycle exploitation, and excellent isolated yields.

Acknowledgments

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Conflict of interest

The author declares any conflict of interest.

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