

Design, Synthesis, and Catalytic Performance of $\text{CoFe}_2\text{O}_4/\text{SiO}_2/\text{PB@M}$ (M = Ni or Cu) Nanocatalysts for Efficient Sulfide Oxidation: Statistical Optimization Using Response Surface Methodology

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Design, Synthesis, and Catalytic Performance of $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{M}$ (M = Ni or Cu) Nanocatalysts for Efficient Sulfide Oxidation: Statistical Optimization Using Response Surface Methodology

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Abstract

In this study, magnetic mesoporous silica nanoparticles with the general formula of $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{M}$ (M=Cu or Ni) were synthesized and investigated for the oxidation reaction of sulfides. First, the magnetic cores were coated with a mesoporous silica coating and then functionalized with nickel and copper complexes. Evaluation of the catalytic performance of this nanocomposite in the oxidation of sulfides showed that the system has high activity under mild reaction conditions (ambient temperature, short time), such that samples containing copper showed better performance than nickel. In order to optimize the effective parameters in the oxidation of sulfides, the response surface engineering (RSM) method with the Box-Behnken approach was used, which led to the determination of the optimal reaction conditions with acceptable accuracy. The unique features of this nanocatalyst, including strong magnetic properties (for easy recovery), structural stability and reusability in multiple reaction cycles without significant loss of activity, make it an ideal choice for advanced applications in green syntheses and selective removal of sulfur compounds.

Keywords: Magnetic Nanocatalyst, Response Surface Methodology (RSM), Copper, Nickel, Oxidation of Sulfides

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1. Introduction

Catalysts are categorized into homogeneous and heterogeneous types based on the phase they share with the reactants [1]. Heterogeneous catalysts are typically solid materials introduced to a liquid or gas reaction mixture. Their ability to enhance reaction rates stems from collision theory, which posits that reacting molecules must collide correctly to react [2]. As such, a catalyst can be recovered unchanged after its use. Catalysts generally speed up reactions by reducing activation energy or altering the reaction mechanism [3]. While catalysts are a part of the reaction process, they are eventually regenerated and remain intact. Because they are not consumed, many molecules can interact with these catalysts, which are crucial for executing certain industrial processes [4]. Homogeneous catalysts are those that create a single phase with the reactants during reactions and are often difficult, if not impossible, to retrieve post-reaction [5]. Due to their ability to accelerate reaction rates without raising temperatures, homogeneous catalysts find varied applications in industry. Conversely, heterogeneous catalysts can be easily separated from the reaction mixture through straightforward methods such as filtration, enabling efficient recovery of costly catalysts [3, 4]. However, a challenge with heterogeneous catalysts is their limited active surface area.

Nanocatalyst research remains a captivating topic within nanochemistry and green chemistry [1, 4]. This area of study emphasizes developing safe chemical reactions and products with optimal efficiency (minimized resource use), where nanocatalysts can help us achieve this standard [1]. They merge the advantages of both homogeneous (large surface area) and heterogeneous (ease of separation) catalysts, enhancing reaction speed and efficiency through their high active surface and selectivity [4, 6].

Specifically, iron oxide magnetic nanoparticles like Fe_3O_4 have garnered significant interest due to their distinctive characteristics and possible applications in diverse scientific and industrial areas [3, 7, 8]. A key benefit of these magnetic nanoparticles is their straightforward separation from reaction mixtures with the aid of an external magnetic field [3, 9]. The extensive use of nano ferrites in various applications, such as permanent magnets, smart drug delivery systems, data storage, and ferrofluids, has elevated interest in this magnetic material [9, 10]. Cobalt ferrite (CoFe_2O_4) is one of the most utilized nanoparticles in fields such as engineering, medicine, and environmental science [11, 12]. Cobalt ferrite possesses a hard magnetic nature and an inverse spinel structure, making it particularly attractive due to its distinct attributes, which include magnetic anisotropy, mechanical hardness, and excellent chemical resilience. The applications of this ceramic magnetic material encompass permanent magnets, targeted drug delivery, data storage devices, ferrofluids, photocatalysis, and bioengineering [3, 11-13].

A mesoporous membrane is an advanced filtration medium characterized by its well-ordered arrangement of uniform nanoscale pores, generally ranging from 2–50 nm in diameter [4, 12].

This meticulously designed configuration allows for size-selective separation of molecules and ions, rendering these membranes adaptable for tasks ranging from water purification and gas separation to acting as catalysts' support structures [1, 4]. The performance of membranes is critically dependent on the meticulous control of three primary factors: pore size distribution, surface chemistry, and porosity [12].

These qualities make mesoporous membranes particularly effective for sulfide oxidation processes, which are vital for environmental remediation and chemical engineering applications [9, 14]. The complex oxidation of hydrogen sulfide (H_2S) or metal sulfides typically requires a precisely defined reaction interface and catalytic assistance to convert reactants selectively into elemental sulfur or sulfate. Mesoporous membranes provide an exceptional platform for these reactions. Their high surface area enables dense catalytic site incorporation, while adjustable pore geometry optimizes reactant diffusion and retention time [15, 16]. This confined yet accessible nanoenvironment mitigates unwanted reactions, such as excessive oxidation to sulfate, and minimizes catalyst fouling, thereby improving selectivity and the lifespan of desulfurization systems [14, 15].

In this investigation, a new magnetic nanocatalyst with a hierarchical mesoporous structure was created. This design features cobalt ferrite (CoFe_2O_4) nanoparticles as a magnetically active core, encased in a mesoporous silica shell that offers a high-surface-area base, and is functionalized with nickel and copper complexes to serve as dual catalytic sites. The synthesis occurred through three steps: (i) the production of cobalt ferrite nanoparticles using co-precipitation, (ii) applying a mesoporous silica layer via sol-gel templating, and (iii) attaching nickel and copper complexes to the silica surface. The resulting nanostructures were thoroughly analyzed through various spectroscopic and microscopic methods. The catalytic capabilities were tested in the selective oxidation of sulfides to sulfoxides using hydrogen peroxide (H_2O_2) as an eco-friendly oxidant. Reaction parameters were systematically refined using response surface methodology (RSM) to clarify the impact of critical variables on conversion rates and selectivity. Additionally, the magnetic recovery and reusability of the nanocatalyst were evaluated across multiple cycles, demonstrating its potential for sustainable catalytic applications.

2. Experimental

2.1. Materials and methods

Cobalt(II)chloride hexahydrate, Ferric chloride hexahydrate, sodium hydroxide, DodecyltrimethylammoniumBromide (DOTAB), ethanol, ammonia, tetramethyl orthosilicate (TMOS), 3-chloropropyltrimethoxysilane, benzocaine, triethylamine, nHeptane, Copper(II)chloride dehydrate, Nickel(II)nitrate hexahydrate, H_2O_2 , Ethyl acetate, n-hexane, Toluene, Methyl phenyl sulfide, TLC Silica gel, Solvents and materials were obtained from Merck and other similar companies. To confirm the success of the synthesis, several

instrumental analytical methods were used to investigate the synthesized nanocatalysts ($\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@M$ ($M = \text{Cu}$ or Ni)). The particle size and morphology were examined by field-emission scanning electron microscopy (FE-SEM) using a TESCAN MIRA3 instrument. Fourier-transform infrared (FT-IR) spectroscopy was conducted on KBr pellets with a BRUKER VERTEX 70 spectrometer. Powder X-ray diffraction (XRD) patterns were recorded using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54060 \text{ \AA}$). Magnetic properties were evaluated with a vibrating sample magnetometer (VSM, MDKFD model). Elemental composition was determined by energy-dispersive X-ray spectroscopy (EDX) coupled with the FE-SEM system.

2.1.1. Preparation of $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}$ nanoparticles

To create these catalysts, it was essential to first synthesize CoFe_2O_4 nanoparticles, which were then modified to yield the catalyst. The process of synthesizing CoFe_2O_4 involved the following steps: Initially, 50 ml of double-distilled water was added to a flask, followed by the addition and dissolution of 2.63 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 1.19 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. A magnet was placed in the solution, which was then stirred. Subsequently, 3 g of NaOH was dissolved in 20 ml of water and gradually added dropwise to the salt solution in the flask. This mixture was refluxed for one hour. Afterward, the final product was repeatedly washed with distilled water and ethanol to eliminate impurities and unreacted materials and separated by filtration using filter paper, and was then dried in an oven at 60°C . The CoFe_2O_4 nanoparticles were obtained in a pure, dry state. To synthesize $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}$, 50 ml of distilled water was mixed with 110 ml of ethanol in a beaker, 0.5 g of CoFe_2O_4 was weighed out, added to the mixture, and then sonicated for 30 min. The ultrasonication ensured even dispersion of the nanoparticles in the solvent. Next, The reaction vessel was removed from the ultrasonic bath and placed on a magnetic stirrer. A magnet was then placed inside the vessel and 1.78 g of white DOTAB powder and 10 mL of 25% ammonia solution were added to it, respectively. The resulting mixture was stirred continuously at 40°C for several minutes. Next step 0.62 ml of TMOS solution was introduced and the mixture was stirred for 30 min, while making sure to cover the beaker to prevent solvent loss. After this duration, the resulting dark solution was transferred to an autoclave and placed in an oven at 100°C for 48 h. Once the autoclave was cooled to room temperature, the resultant solution was placed in a centrifuge tube and centrifuged in order to discard the liquid above the solid. The final black mixture was washed multiple times with water until the solvent was removed and was then left to dry in the open air. After drying, the mixture was weighed, and for each gram of this substance, 1.5 ml of 3-chlorotrimethoxysilane was added. Both components were mixed into 50 cc of toluene in a flask with a stirring magnet and heated to reflux for 24 h. The resulting precipitate was washed with toluene or n-hexane and allowed to dry in the open air. For every 0.7 g of the obtained powder, 1.5 mmol of benzocaine and 3 ml of triethylamine were extracted and mixed in 70 ml of toluene for a 24 h

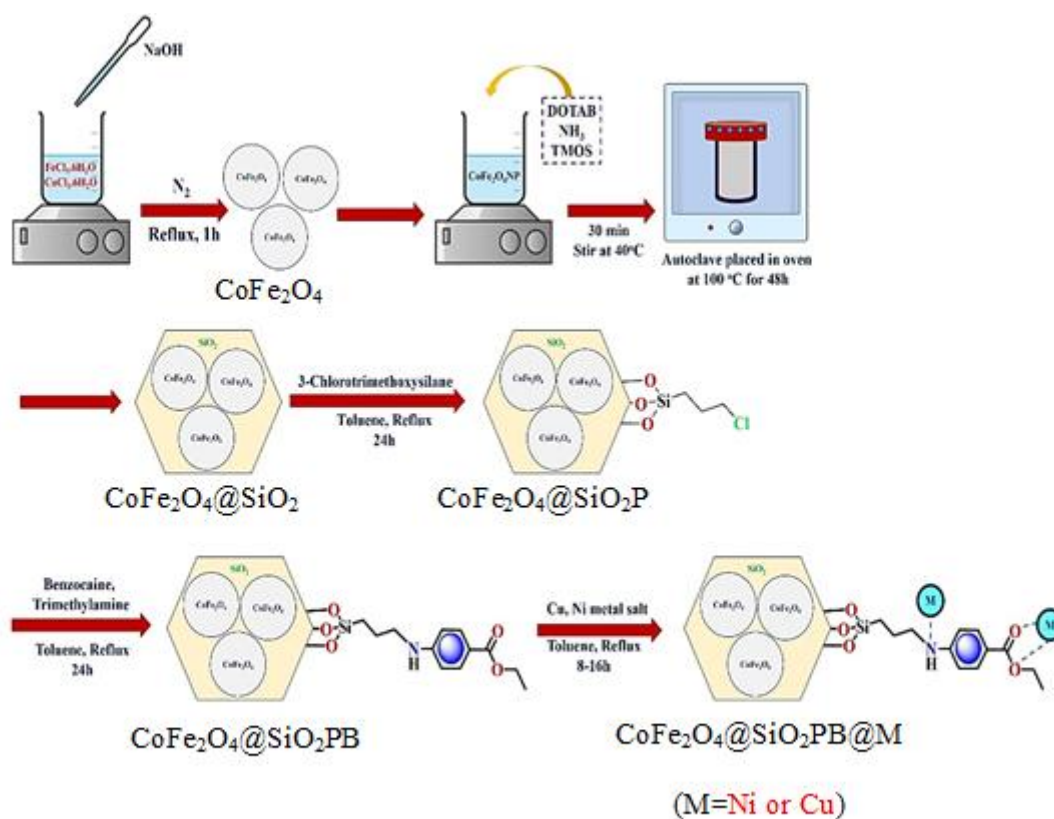
reflux. The final mixture was subsequently washed with n-heptane and allowed to dry in the open air. [11-13, 17].

2.1.2. Preparation of $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Cu}$ nanocatalyst

To create the copper nanocatalyst, 1 g of $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}$ was combined with 1.5 mmol of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in 30 ml of ethanol and stirred while refluxing for 16 h. Afterwards, the solution was rinsed with ethanol, and the solid was collected using filter paper and left to dry in the open air. At this point, the copper nanocatalyst was fully synthesized [18].

2.1.3. Preparation of $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Ni}$ nanocatalyst

To synthesize a nickel nanocatalyst akin to the method used for the copper catalyst, 1.5 mmol of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was mixed with 1 g of $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}$ nanoparticles in 30 ml of ethanol. After refluxing for 16 h, the mixture was washed with ethanol and then air-dried (Scheme 1) [18].



Scheme 1. Synthesis of $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{M}$ (M= Ni or Cu)

2.1.4. Oxidation of sulfides using $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@M$ ($M = \text{Ni}$ or Cu) catalysts

To utilize the synthesized nanocatalysts $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Cu}$ and $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Ni}$ for converting sulfides into sulfoxides, the following steps were taken: The specified ranges for catalyst values, H_2O_2 , and anticipated duration for the experiment were entered into the Design Express software in order to generate optimized parameters for the reaction. Methyl phenyl sulfide served as the substrate in this experiment. For the oxidation of sulfides using the nanocatalysts, a consistent sulfide amount, precisely 0.124 g, was maintained. Upon entering these parameters into the software, a table containing 17 rows was produced, with 5 rows repeated for trial-and-error assessments to verify the reproducibility of results with identical inputs. The table generated by the software allowed to first pinpoint the maximum values for the catalyst, H_2O_2 , and reaction time, after which a preliminary test with these maximum values was conducted [17, 18].

3. Results and Discussion

In order to clarify the structural integrity and validate the successful surface functionalization of the synthesized catalyst, an extensive characterization was conducted utilizing X-ray diffraction (XRD), Fourier-transform infrared (FT-IR) spectroscopy, and thermogravimetric analysis (TGA). The XRD pattern confirmed that the cobalt ferrite spinel crystal structure was maintained after modification and indicated the presence of included metal species. FT-IR spectroscopy confirmed the existence of specific functional groups related to the grafted nickel and copper complexes, thus validating the surface modification. The TGA analysis demonstrated the thermal stability of the composite material and allowed for the determination of the ratio of organic to inorganic content.

The FT-IR spectra for CoFe_2O_4 (a), $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}$ (b), $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Ni}$ (c), and $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Cu}$ (d) are presented in Figure 1. In this analysis, the spectral range of $400\text{--}700\text{ cm}^{-1}$ corresponded to the Fe-O and M-O ($M = \text{Cu}$ and Ni) bonds. An increase in the intensity of the bands associated with the Si-O-Si bond was observed between $1000\text{--}1100\text{ cm}^{-1}$, suggesting effective surface modification using chlorotrimethoxy silane. The peak located in the $1250\text{--}1300\text{ cm}^{-1}$ region signifies the presence of Si-O-C bonds. Additionally, C-H stretching vibrations and C-N bending vibrations can be found within the $1300\text{--}500\text{ cm}^{-1}$ range. A rise in intensity of the C=O band is noted in the $1600\text{--}1700\text{ cm}^{-1}$ range, highlighting the stabilization of benzocaine on the surface. Alterations in OH- and NH- bands from $2800\text{--}3600\text{ cm}^{-1}$ demonstrate the introduction of new functional groups from silane and benzocaine [9, 11-13, 16-18]. The reduced intensity of OH bonds in the $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Ni}$ and $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Cu}$ catalysts compared to the baseline sample indicates the formation of new surface bonds between the metals and nanoparticles. Finally, the peak observed in the 600--

700 cm^{-1} range for $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Cu}$ and $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Ni}$ compared to $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}$ shows the incorporation of Cu and Ni ions into the catalyst framework.

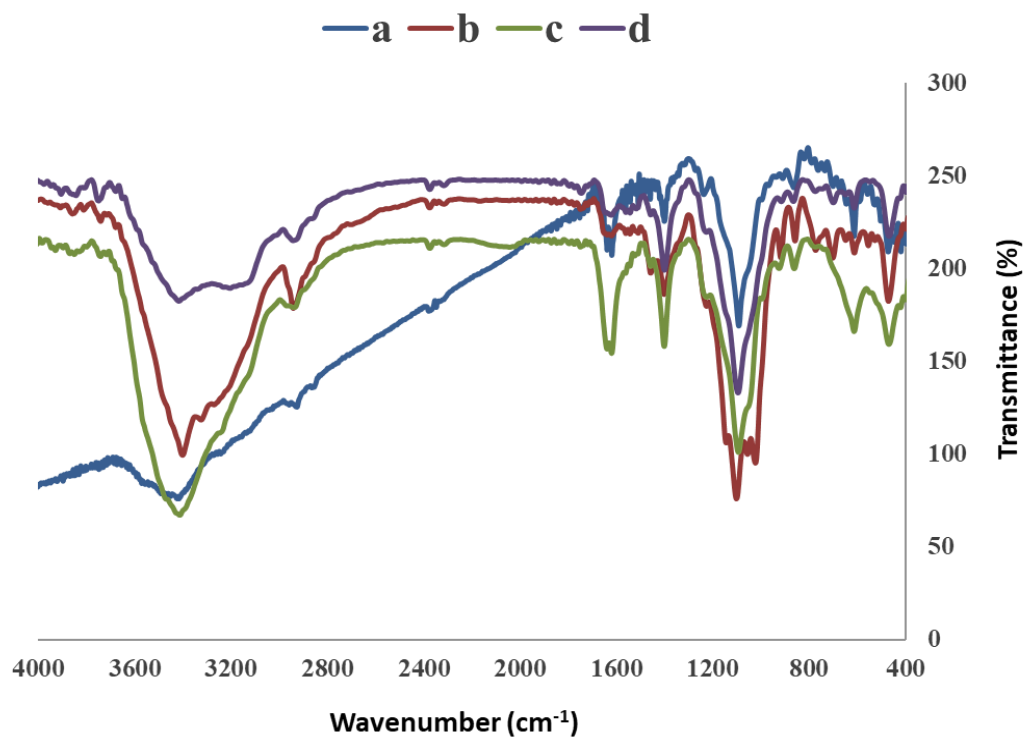


Fig. 1. FTIR spectrum of CoFe_2O_4 (a), $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}$ (b), $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Ni}$ (c) and $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Cu}$ (d)

The VSM spectra for CoFe_2O_4 (a), $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Ni}$ (b) and $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Cu}$ (c) are shown in Figure 2. The saturation magnetization values were recorded as 29, 20 and 14 emu g^{-1} for CoFe_2O_4 , $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Ni}$ and $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Cu}$, respectively. The observed decrease in CoFe_2O_4 after functionalization is attributed to the presence of nonmagnetic silica and copper and nickel complexes [8, 13, 17, 19].

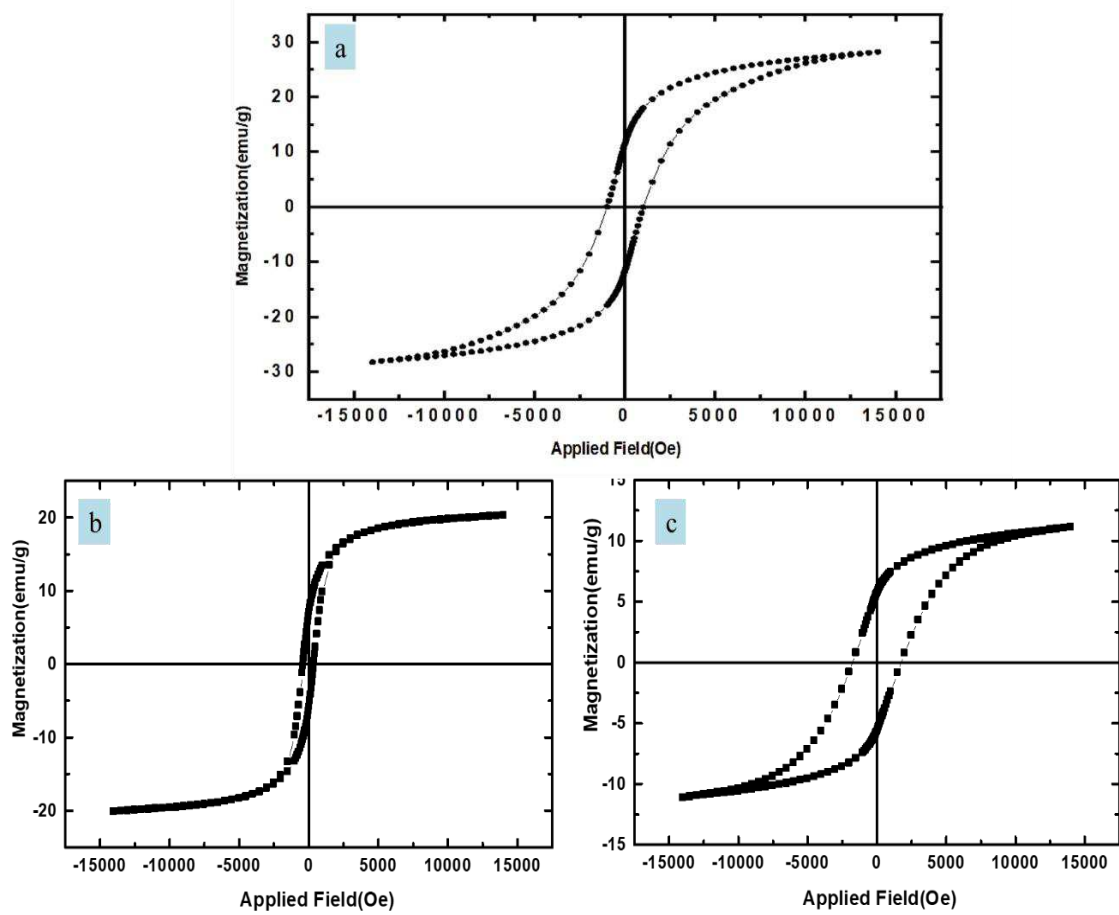


Fig. 2. VSM curves of CoFe₂O₄ (a) CoFe₂O₄@SiO₂PB@Ni (b) and CoFe₂O₄@SiO₂PB@Cu (c)

The EDX spectrum for CoFe₂O₄@SiO₂PB@Ni and CoFe₂O₄@SiO₂PB@Cu verifies the successful incorporation of Ni and Cu metals into the catalyst framework (Figure 3). Both spectra exhibited peaks associated with Si, O, C, and N, which are indicative of the surface modification and catalyst preparation processes.

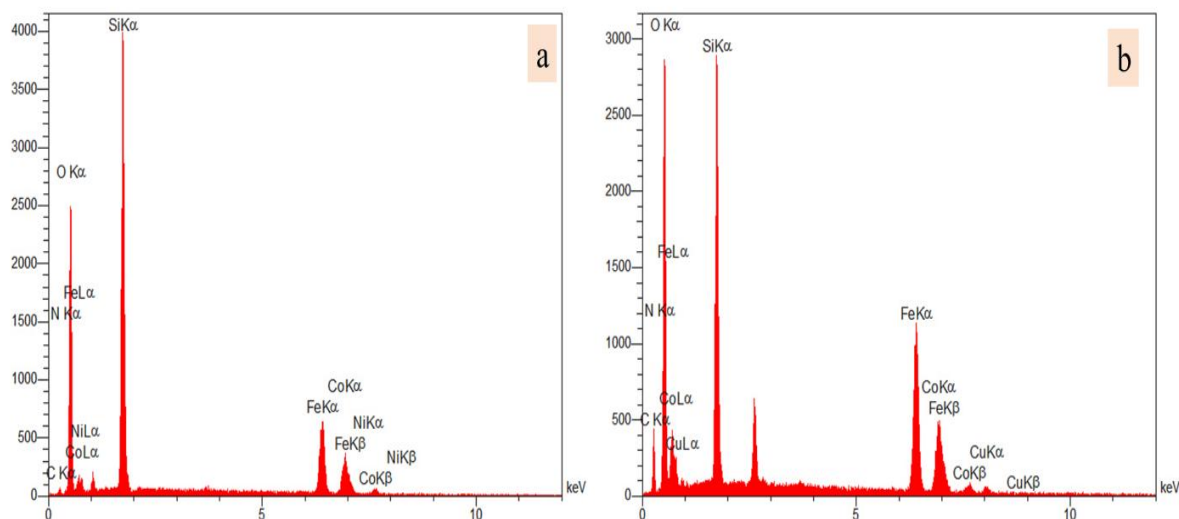


Fig. 3. EDX spectrum of (a) $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Ni}$ and (b) $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Cu}$

XRD analysis was used to examine the crystalline nature and phase structure of the nanocomposite (a) CoFe_2O_4 , (b) $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Ni}$, and (c) $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Cu}$ (Figure 4). The catalysts single-phase XRD examination unequivocally demonstrates that the substrate is a distinct entity that is securely bonded to each of the nanocomposites constituent parts. The spinel nanoparticles of CoFe_2O_4 are identified by the diffraction peaks that correspond to the (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) diffraction planes. It is evident that the substrate magnetic nanoparticle phase's crystal structure did not significantly alter following the composite's incorporation of SiO_2PB complexes. The inclusion of Ni and Cu metals in the composite did not alter the distinctive peaks of $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}$ [13, 17-19].

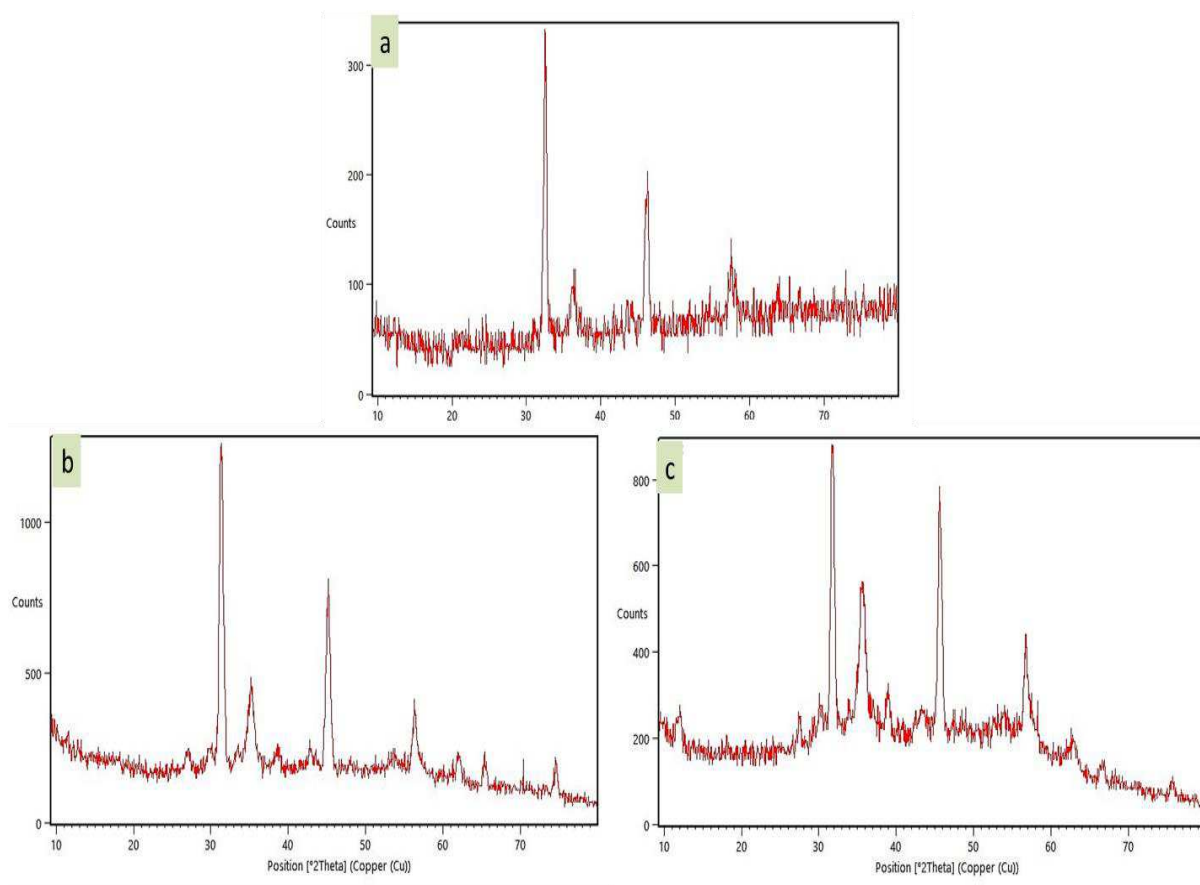


Fig. 4. XRD patterns of (a) CoFe₂O₄, (b) CoFe₂O₄@SiO₂PB@Ni and (c) CoFe₂O₄@SiO₂PB@Cu

SEM images of CoFe₂O₄@SiO₂PB@Ni (Figures 5a-d) and CoFe₂O₄@SiO₂PB@Cu (Figures 5e-h) display consistently spherical nanoparticles with a tight size distribution, validating the successful synthesis.

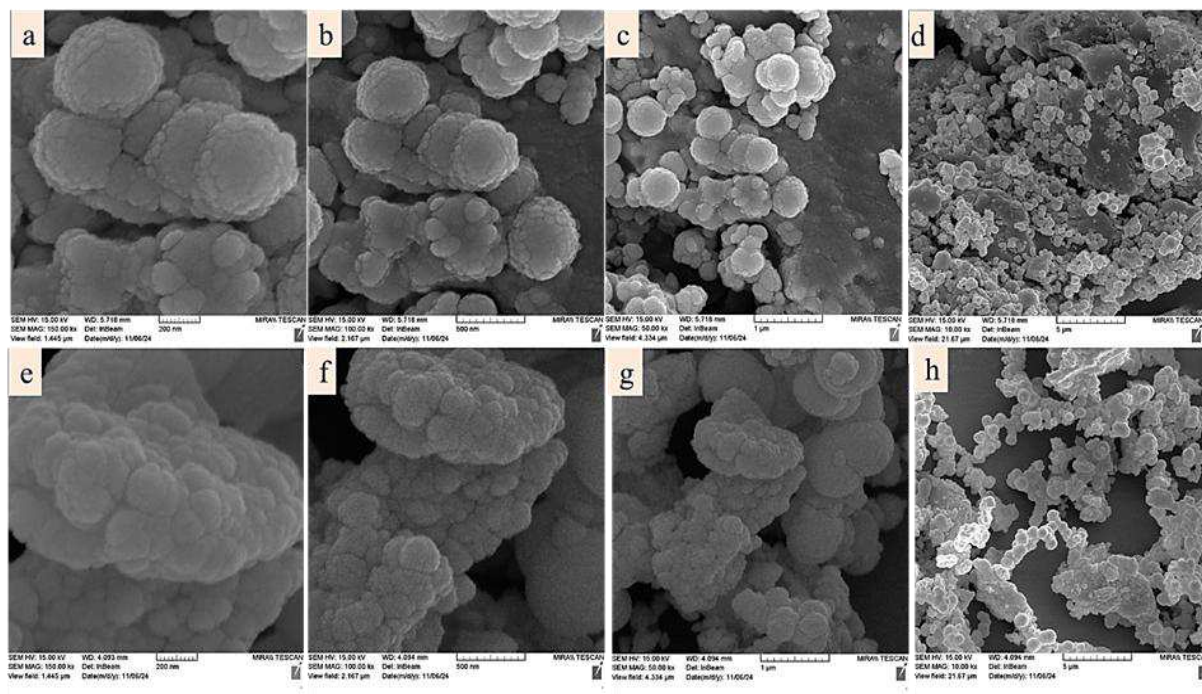


Fig. 5. SEM image CoFe₂O₄@SiO₂PB@Ni (a, b, c and d) and CoFe₂O₄@SiO₂PB@Cu (e, f, g and h) at different magnification

EDX elemental mapping (Figures 6a and 6b) confirms the effective functionalization of CoFe₂O₄@SiO₂PB with nickel and copper complexes. The even distribution of Cu and Ni within the nanostructure validates the successful immobilization of the catalytic components. Additionally, the consistent presence of nitrogen and carbon, which originates from the organic ligands of the metal complexes, illustrates the stable attachment of functional groups to the mesoporous silica surface. This strong organic-inorganic integration improves both the structural stability and catalytic performance of the nanocomposite materials [13, 17-19].

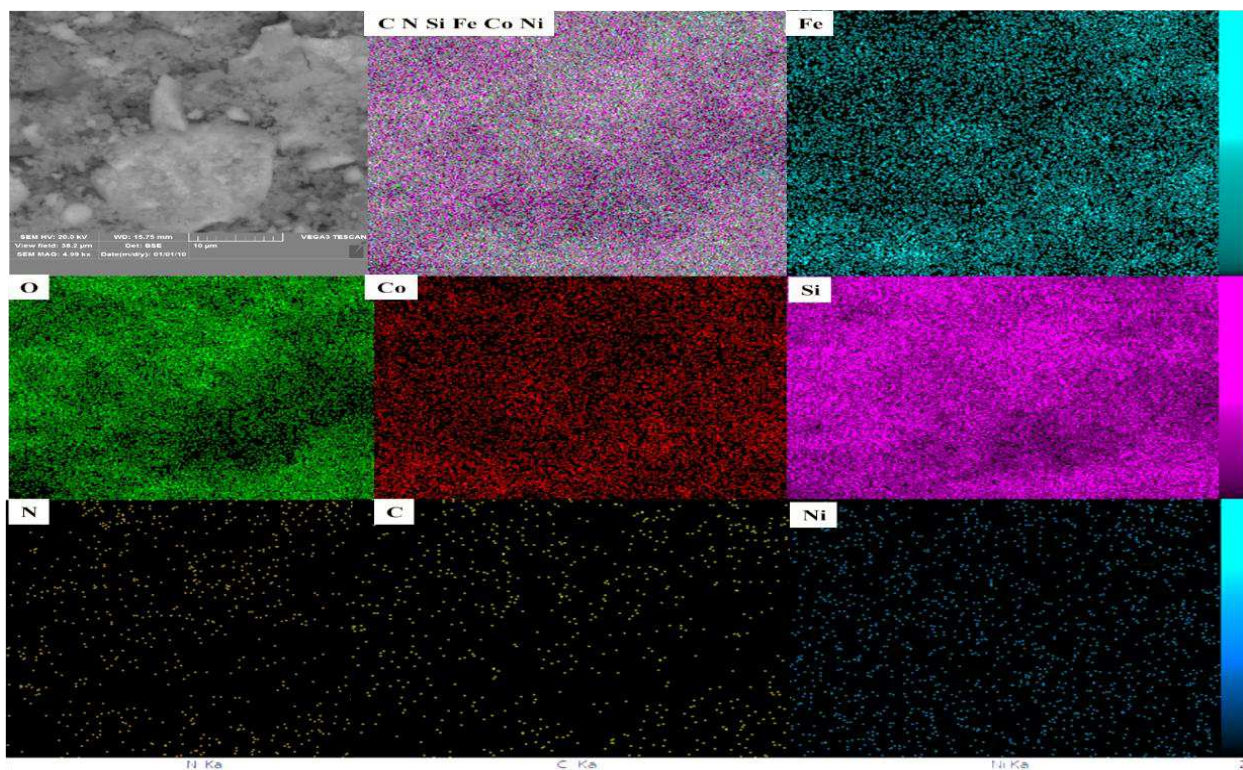


Fig. 6a. EDX elemental mapping of $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Ni}$

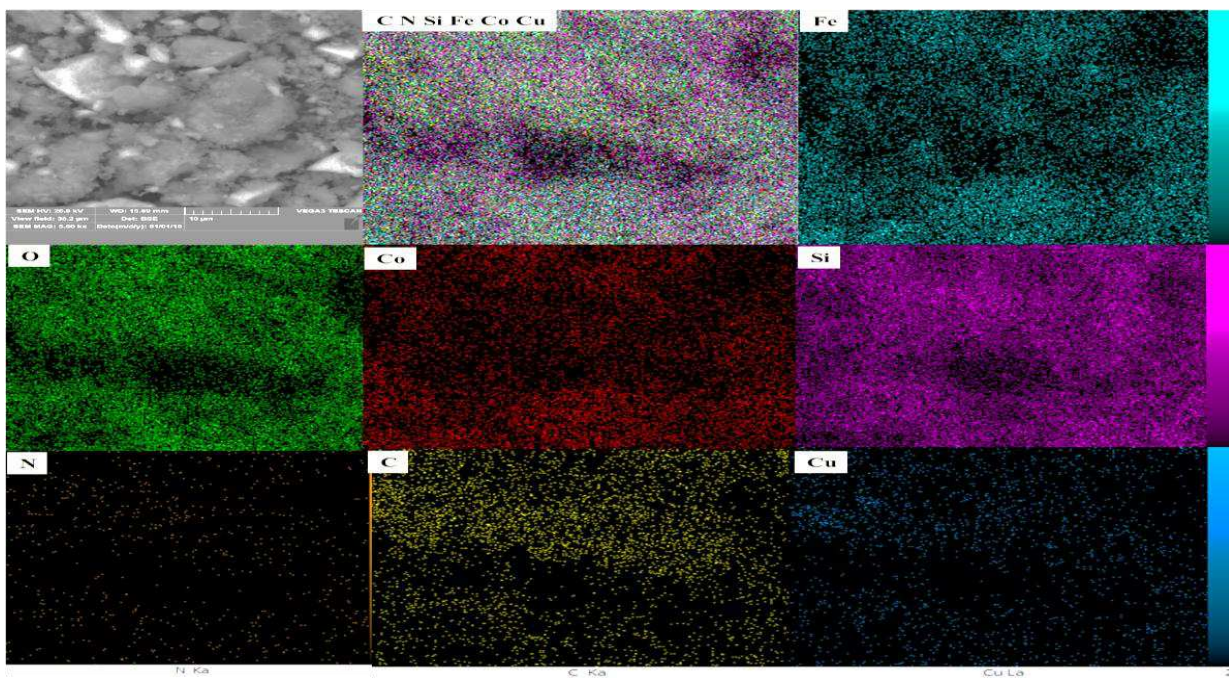


Fig. 6b. EDX elemental mapping of $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Cu}$

Thermogravimetric analysis (TGA) was performed to assess the thermal stability of the synthesized materials. The curves for (a) $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}$ (b) $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Ni}$, and (c) $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Cu}$. are shown in Figure 7. The mass loss in the region below 200 °C in the curves is related to the removal of OH groups and solvents that are physically bound to the surface. The weight loss observed in the region 200-650°C for $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}$, $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Ni}$ and $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Cu}$, is due to the significant decomposition of stable organic species. The results of thermogravimetric analysis (TGA) show that nickel and copper complexes are successfully immobilized on the substrate. The difference in the thermal behavior and weight loss pattern of the modified samples compared to the original substrate indicates the presence and effective stabilization of these metal complexes on the surface of the substrate. [17, 19].

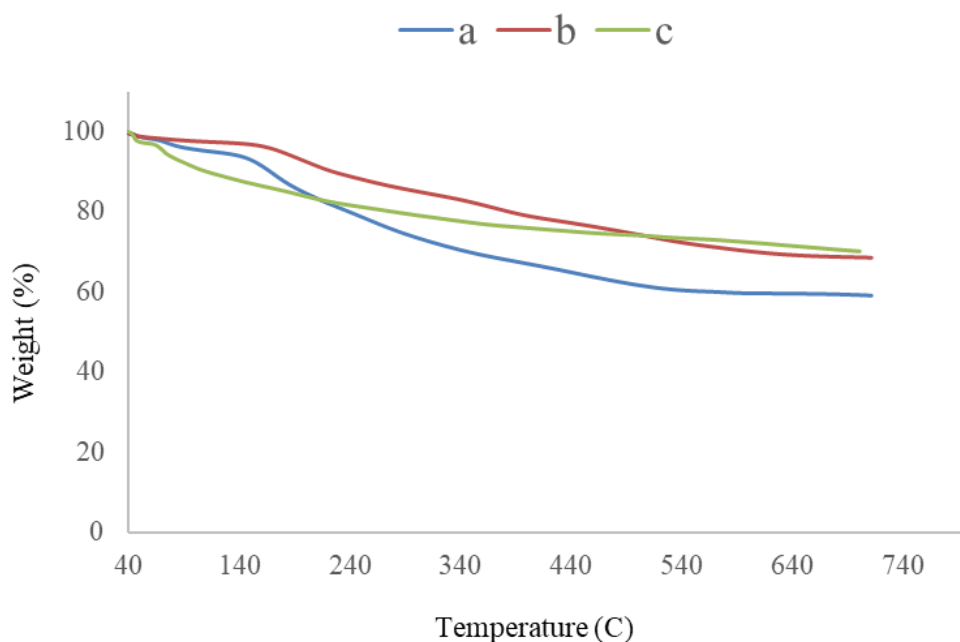
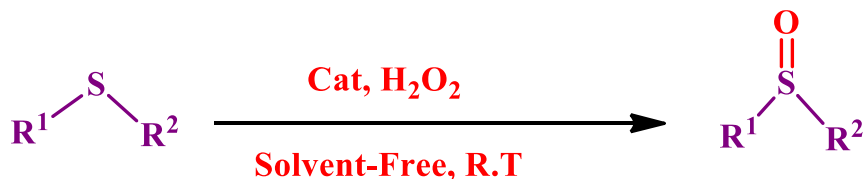


Fig. 7. TGA curves of $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}$ (a), $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Ni}$ (b) and $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Cu}$ (c)

3.1. Catalyst Performance Analysis

The effectiveness of the synthesized $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Ni}$ and $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Cu}$ nanocatalysts was assessed in the selective oxidation of methyl phenyl sulfide to sulfoxide using H_2O_2 as an environmentally friendly oxidant. The amount of catalyst, the volume of H_2O_2 consumed, and time are the parameters which were examined. Experimental data for the optimized yield of oxidation of methylphenyl sulfide in various conditions over

CoFe₂O₄@SiO₂PB@Ni (a) and CoFe₂O₄@SiO₂PB@Cu (b) nanocatalysts are shown in the Table 1.



Scheme 2. CoFe₂O₄@SiO₂PB@M (M=Ni or Cu) catalyzed the oxidation of sulfides to sulfoxides.

Table 1. Experimental data for the optimized yield of oxidation of methylphenyl sulfide in various conditions over CoFe₂O₄@SiO₂PB@Ni and CoFe₂O₄@SiO₂PB@Cu nanocatalysts.

Entry	A: Catalyst (mg)	B: H ₂ O ₂ (mL)	C: Time (min)	Yield (%) ^a	
				CoFe ₂ O ₄ @SiO ₂ PB @Ni	CoFe ₂ O ₄ @SiO ₂ PB @Cu
1	1	0.3	45	61	65
2	1	0.45	20	65	67
3	5.5	0.45	45	78	85
4	5.5	0.3	20	70	78
5	5.5	0.6	20	83	85
6	5.5	0.45	45	76	85
7	10	0.45	20	92	95
8	5.5	0.45	45	76	86
9	5.5	0.45	45	76	86
10	1	0.6	45	68	73
11	10	0.3	45	90	94
12	5.5	0.3	70	74	81
13	5.5	0.6	70	88	90
14	10	0.6	45	100	100
15	1	0.45	70	64	70
16	10	0.45	70	98	98
17	5.5	0.45	45	78	85

^aIsolated yield.

A systematic optimization of crucial reaction parameters such as catalyst amount, H₂O₂ volume, temperature, and time showed that increasing the catalyst dosage enhanced catalytic efficiency,

emphasizing the necessity for accessible active sites. Full conversion (100% yield) was reached under optimized conditions: 10 mg of catalyst, 0.6 mL of H₂O₂, and a 45 min reaction time at room temperature (Table 2). Reducing the oxidant volume to 0.3 mL or shortening the duration to 20 min led to incomplete conversion, confirming that both adequate oxidant supply and sufficient reaction time are vital for total substrate transformation. Under similar conditions, CoFe₂O₄@SiO₂PB@Cu displayed slightly better activity than the Ni counterpart, likely due to the advantageous redox properties of Cu²⁺ that facilitate effective oxygen transfer during the catalytic process.

Both catalysts exhibited statistically significant models in which amount of catalyst and time factors showed notable effects on the oxidation process, while factor H₂O₂ was negligible. R² values (~97%) and adequate precision (>39) indicate acceptable model reliability and predictive capability. As shown in Tables 2 and 3, both Ni- and Cu-based catalysts demonstrated similar performance trends influenced primarily by the amount of catalyst factor.

Table 2. Analysis of variance (ANOVA) for the of oxidation of methylphenyl sulfide over CoFe₂O₄@SiO₂PB@Ni

Source	Sum of square	df	Mean Square	F-Value	P-Value	Remarks
Model	2127.00	3	709.00	151.39	< 0.0001	significant
A-A	1860.50	1	1860.50	397.27	< 0.0001	
B-B	242.00	1	242.00	51.67	< 0.0001	
C-C	24.50	1	24.50	5.23	0.0396	
Residual	60.88	13	4.68			not significant
Lack of Fit	56.08	9	6.23	5.19	0.0638	
Pure Error	4.80	4	1.20			
Cor Total	2187.88	16				

- R-Squared 0.97.
- Adj R-Squared 0.97.
- Pred R-Squared 0.95.
- Adeq Precision 39.53.

Table 3. Analysis of variance (ANOVA) for the of oxidation of methylphenyl sulfide over CoFe₂O₄@SiO₂PB@Cu

Source	Sum of square	df	Mean Square	F-Value	P-Value	Remarks
Model	1705.00	3	568.33	278.50	< 0.0001	significant
A-A	1568.00	1	1568.00	768.35	< 0.0001	
B-B	112.50	1	112.50	55.13	< 0.0001	
C-C	24.50	1	24.50	12.01	0.0042	
Residual	26.53	13	2.04			not significant
Lack of Fit	25.33	9	2.81	9.38	0.0228	
Pure Error	1.20	4	0.3000			
Cor Total	1731.53	16				

- R-Squared 0.98.
- Adj R-Squared 0.98.
- Pred R-Squared 0.98.
- Adeq Precision 51.23.

The plots in Figure 8. illustrate the correlation between predicted and actual values for the oxidation of methylphenyl sulfide using CoFe₂O₄@SiO₂PB@Ni(a) and CoFe₂O₄@SiO₂PB@Cu (b) catalysts based on the RSM model. In both cases, the data points are reasonably clustered around the diagonal line ($y = x$), indicating good agreement between experimental and predicted values. The distribution shows that the RSM models can reliably estimate the response across the studied range. Slight deviations from the diagonal suggest minor prediction errors, consistent with the moderate R² values obtained from ANOVA [18, 19].

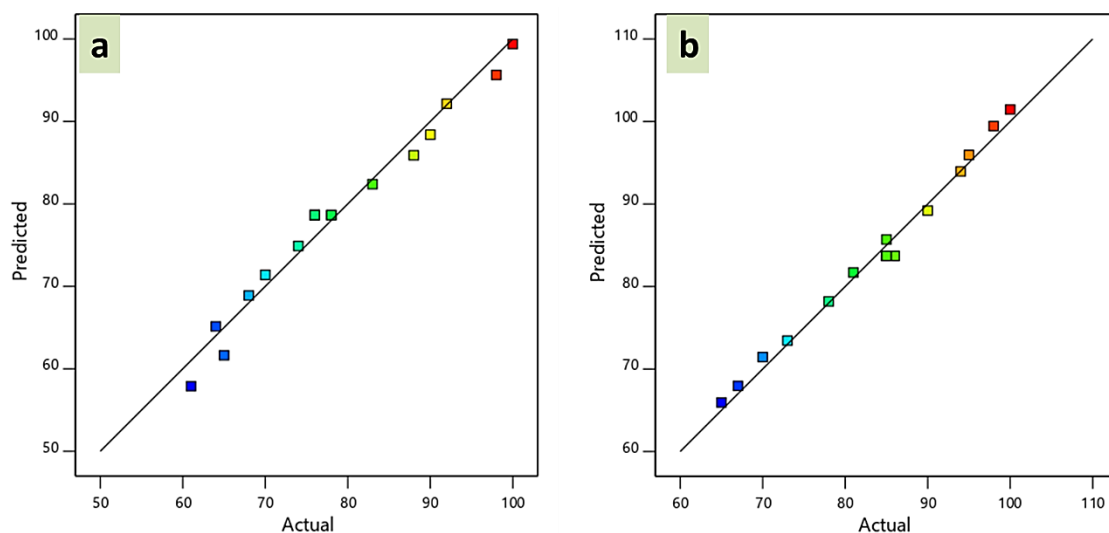


Fig. 8. The evaluation of predicted value against the actual value by the RSM in $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Ni}$ (a) and $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Cu}$ (b)

RSM is employed to create 3D response surface contour plots that illustrate the influence of independent variables or parameters on efficient sulfide oxidation. Figure 9. displays a contour plot demonstrating the influence of catalyst and hydrogen peroxide quantities, during a specified duration, on the sulfide oxidation yield (%) for $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Ni}$ (a) and $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Cu}$ (c), respectively. In both plots, productivity rises with the catalyst load from 1 to 10 mg and concurrently with the increase of hydrogen peroxide from 0.3 to 0.6 mL. Figure 9. illustrates the efficiency (%) in relation to differing quantities of catalyst and reaction time for $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Ni}$ (b). The same is demonstrated for $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Cu}$ (d), respectively. Efficiency increases in these plots as the catalyst dose is elevated from 1 to 10 mg and the time is prolonged from 20 to 70 min.

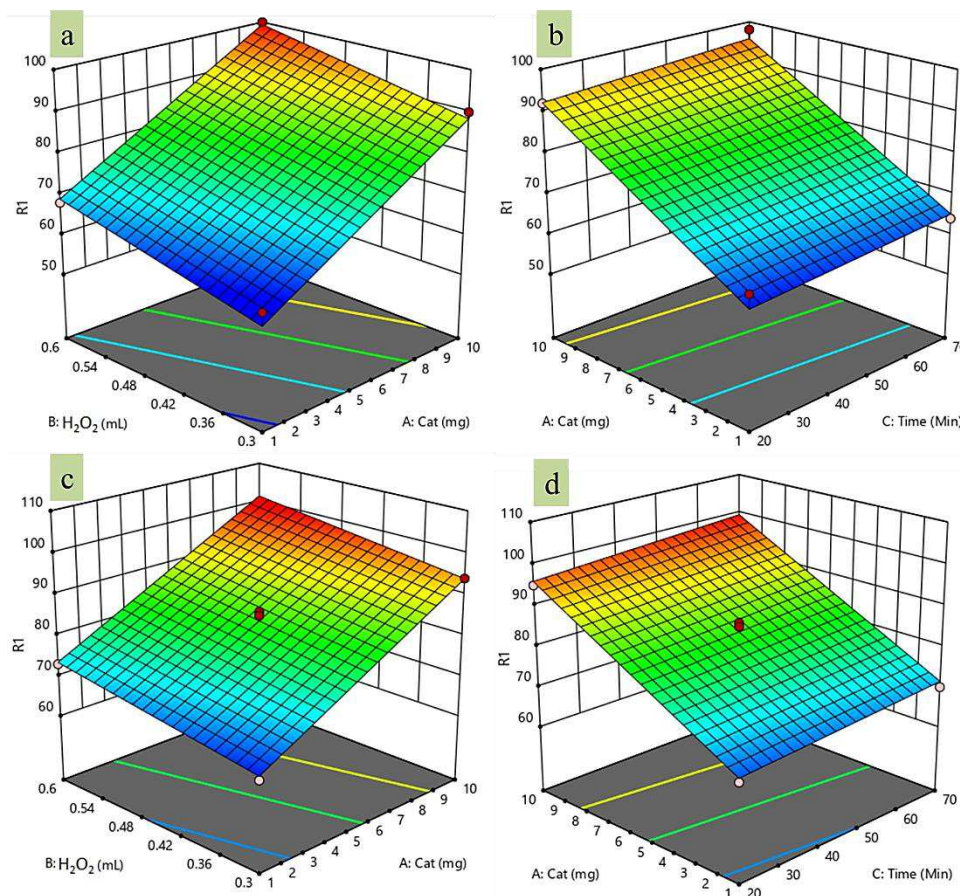
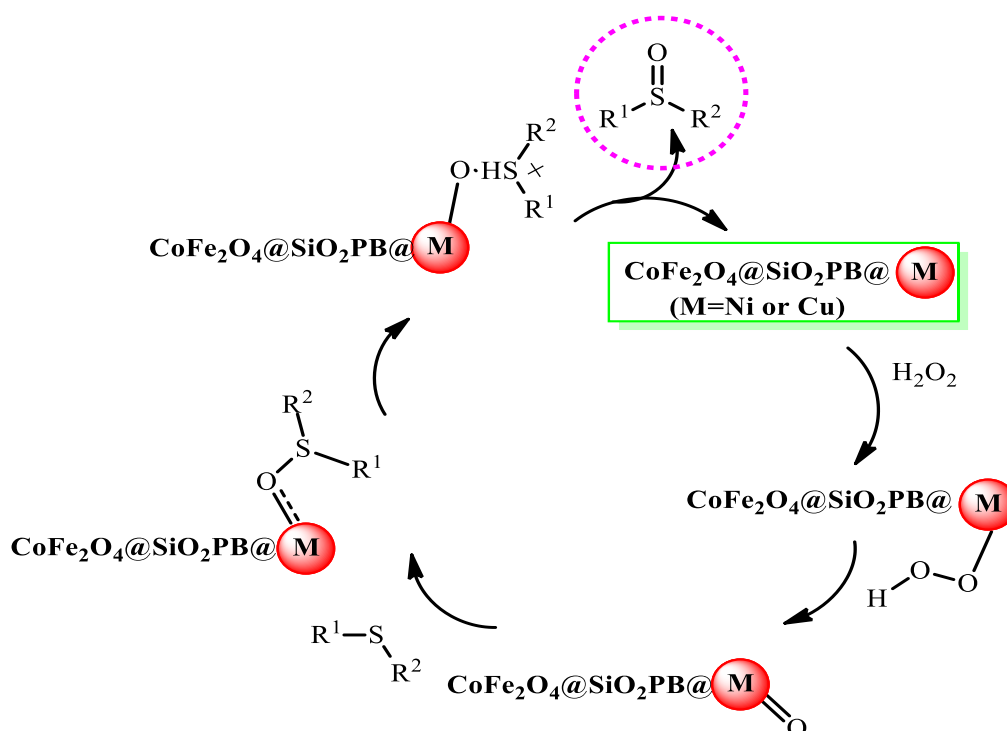


Fig. 9. 3D response surface plots of A: amount of catalyst, B: H_2O_2 and C: Time for $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Ni}$ (a and b) and $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Cu}$ (c and d)

4. Reusability of the catalyst

One of the essential advantages of heterogeneous catalysts is their potential for recovery and reuse, which directly impacts the sustainability and cost-effectiveness of the process. In this work, the recyclability of $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{M}$ ($\text{M} = \text{Ni}$ or Cu) was investigated through repeated oxidation cycles of methylphenyl sulfide. As shown in Scheme 3, $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{M}$ ($\text{M} = \text{Ni}$ or Cu) catalyzed the oxidation of sulfides to sulfoxides. To evaluate practical usability, the nanocatalysts were magnetically separated after each reaction cycle, rinsed with ethanol and distilled water, dried at 60°C , and reused.



Scheme 3. Proposed mechanism for the oxidation of sulfide.

A comparative evaluation with unmodified materials demonstrated significantly lower activity and swift deactivation. This difference underscores the essential role of the mesoporous silica framework and the covalent immobilization method in improving both catalytic effectiveness and stability. The uniform distribution of metal complexes within the high-surface-area structure enhances active site availability while reducing aggregation and leaching. In conclusion, the engineered $CoFe_2O_4@SiO_2PB@M$ ($M = Ni$ or Cu) nanocatalysts exhibited remarkable activity, outstanding selectivity towards sulfoxide, magnetic recoverability, and robust operational stability. Both catalysts maintained over 95% activity across three consecutive cycles without any measurable leaching.

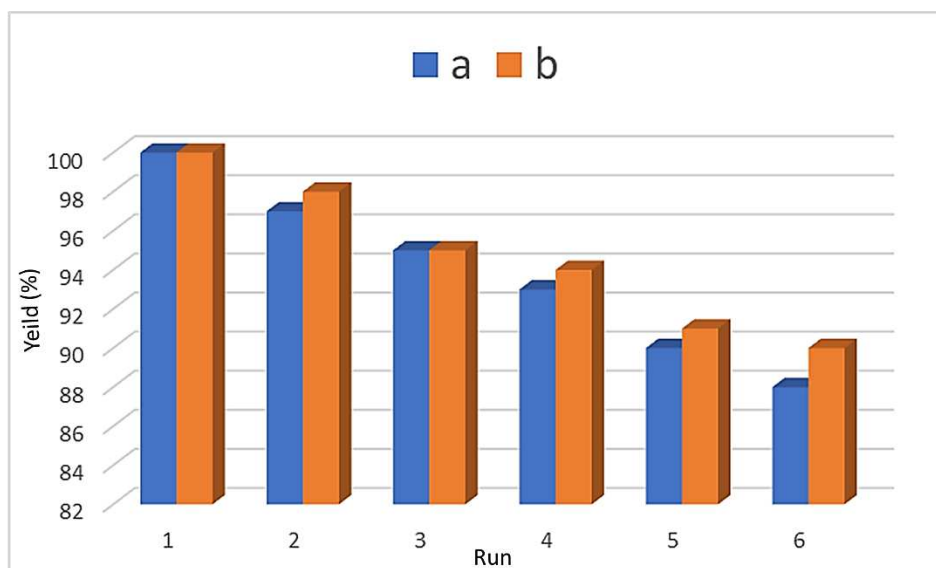


Fig. 10. Recyclability $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Cu}$ and $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{Ni}$ in the oxidation of methylphenyl sulfide over three cycles.

4.1. Comparison of the catalyst

To evaluate the efficiency of the synthesized $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{PB}@\text{M}$ ($\text{M} = \text{Ni}$ or Cu) catalysts, their performance was compared with several reported systems used in the selective oxidation of sulfides. In terms of conversion efficiency, both catalysts exhibited high activity under mild conditions, often achieving near-complete conversion within relatively short reaction times. This is particularly notable when compared to conventional systems requiring either harsher reaction conditions, higher catalyst loading, or the use of toxic or non-recoverable oxidants. Furthermore, the magnetic recoverability of these catalysts offers a significant operational advantage over many traditional homogeneous or non-magnetic heterogeneous systems, which typically require filtration or centrifugation for recovery. This feature not only simplifies the post-reaction workup but also enhances the sustainability and cost-effectiveness of the process. Another key point of distinction is the structural stability observed across multiple catalytic cycles. While some previously reported catalysts show notable deactivation after a few runs, the current catalysts maintained their activity with minimal loss, emphasizing their robustness and practical utility. Taken together, the combination of high catalytic performance, ease of recovery, and excellent recyclability positions these catalysts as competitive alternatives to existing systems, particularly for green and scalable oxidation protocols (Table 4).

Table 4. Comparison of CoFe₂O₄@SiO₂PB@M (M= Ni or Cu) for the oxidation of methylphenylsulfide with previously reported procedure

Entry	Catalyst	Oxidant	solvent	Time (min)	Yield (%) ^a	Selectivity (Sulfoxide %)	Ref.
1	Fe ₃ O ₄ -SA-PPCA-Ni	H ₂ O ₂	CH ₃ CN	60	98	100	[20]
2	Fe ₃ O ₄ @SiO ₂ -Ag	H ₂ O ₂	H ₂ O	120	92	96	[21]
3	CoFe ₂ O ₄ /MCM-41/Cu	H ₂ O ₂	EtOH	45	96	100	[12]
4	Magnetic-Core@Shell-Ti	H ₂ O ₂	CH ₃ CN	90	94	98	[22]
5	CoFe ₂ O ₄ /SBA-15/CuPc@Gd	H ₂ O ₂	EtOH	45	91	99	[14]
6	SBA-15@Creatinine@Y(III)	H ₂ O ₂	EtOH	60	96	98	[15]
7	CoFe ₂ O ₄ @SiO ₂ PB@Cu	H ₂ O ₂	EtOH/H ₂ O	30	98	>99	In this work
8	CoFe ₂ O ₄ @SiO ₂ PB@Ni	H ₂ O ₂	EtOH/H ₂ O	40	97	>99	In this work

5. Conclusion

In this study, CoFe₂O₄@SiO₂PB@M (M= Ni or Cu) magnetic catalysts were successfully synthesized and used in the oxidation reaction of methyl phenyl sulfide. The results showed that these catalysts exhibited high efficiency under mild reaction conditions and maintained the ability to be recycled and reused for up to five cycles without a noticeable decrease in activity. The magnetic property of these catalysts allows for their rapid and efficient separation from the reaction medium, which is a significant advantage from an operational and environmental perspective. Compared with previously reported catalysts, such as non-magnetic heterogeneous catalysts, shows that the present catalysts offer a combination of high efficiency, structural stability, and ease of recycling. These properties make them a suitable option for green and scalable oxidation processes. Overall, the favorable catalytic behavior, durability, and recyclability of these catalysts indicate that they can be used as effective and sustainable replacements for existing catalysts in selective sulfide oxidation reactions.

Funding Declaration

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