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Oxidative desulfurization catalyzed by magnetically recoverable CoFe₂O₄ nano-particles



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ABSTRACT

In this study, the magnetic CoFe₂O₄ was fabricated and utilized as catalysts to activate peroxymonosulfate (PMS) for removal of dibenzothiophene (DBT) in model oil with the extraction-coupled catalytic combined with oxidation desulfurization system (ECODS). The prepared magnetic CoFe₂O₄ was characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), Vibrating Sample Magnetometer VSM etc. The results showed that the prepared magnetic CoFe₂O₄ with a large specific surface area and exhibited excellent magnetism, phase composition, crystallinity and uniform distribution of the elements. The sulfur removal of DBT in n-octane was 95 % in 60 min at 40 °C under the conditions: 6 mL of model oil (600 ppm), O/S = 3:1 and 125 mg of CoFe₂O₄ magnetic nanoparticles function well in both desulfurization and catalysis for PMS.

1. Introduction

In recent times, the escalating occurrence of air pollution has become a global concern. The emission of sulfur oxides (SOx gases) stands as the primary culprit behind respiratory problems, air pollution, acid rain, soil fertility degradation, and various other forms of environmental contamination (Daglar et al., 2022). Consequently, the removal of sulfur compounds such as sulfides, disulfides, and thiophene present in petroleum products has become an imperative, garnering substantial attention on an international scale (Haruna et al., 2022). In pursuit of controlling pollution issues and mitigating the impact of toxic gases, many nations have taken decisive steps by imposing restrictions and enacting stringent regulations regarding the allowable sulfur content in fossil fuels (Chen et al., 2022). In light of environmental and health considerations, the production of low-sulfur fuel plays a pivotal role in preserving a clean and sustainable environment.

To advance cutting-edge breakthroughs and enhance the efficiency of fuel production, all while maintaining cost-effectiveness and expediency, scientists and engineers have been actively involved in the development of diverse desulfurization technologies. These technologies aim to reduce the sulfur content in crude oil to comply with stringent regulations. As a result, a multitude of desulfurization methods have been proposed, including hydrodesulfurization (HDS) (Yue et al., 2022), biodesulfurization (BDS), adsorptive desulfurization (ADS) (Omar et al., 2022, Saeed et al., 2022a), extractive desulfurization (EDS) (Abro et al., 2022), oxidative desulfurization (ODS) (Cao et al., 2020, Jabar et al., 2022, Saeed et al., 2022b, Armandsefat et al., 2024), as well as processes based on alkylation, chlorinolysis, and supercritical water (Nasyrova et al., 2022).

Oxidative desulfurization (ODS), considered one of the most advanced and promising desulfurization methods, exhibits the capability to reduce refractory organosulfur compounds to less than 10 ppm under mild operating conditions and at a low cost. Utilizing molecular oxygen as the oxidant, Wei et al. (Jiang et al., 2022) have achieved high removal efficiency for stubborn sulfur compounds such as DBT, 4-methyldibenzothiophene (4-MDBT), and 4,6-DMDBT. They harnessed the combined strengths of robust single-atom catalysts derived from metalsupport interactions. Ahmadian et al. (Ahmadian and Anbia 2022), on the other hand, explored the catalytic activity of mesoporous silica supports like SBA-15 and MOR-SBA-15 for the oxidative desulfurization

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of model fuel containing BT, dibenzothiophene (DBT), and 4,6-DMDBT. Mohammad Ali Rezvani reported on the synthesis and characterization of a new heterogeneous nanocatalyst comprised of the sandwich-type polyoxotungstate [(FeW₉O₃₄)₂Fe₄(H₂O)₂]⁻¹⁰ (Fe₆W₁₈O₇₀) clusters and copper ferrite (CuFe₂O₄) nanoparticles (Rezvani and Imani 2021). Mohammad Ali Rezvani et al designed a series of organic-inorganic catalysts for the oxidative desulfurization and obtained ideal effects (Rezvani and Zonoz 2015, Rezvani et al., 2016, Rezvani et al., 2018, Rezvani and Fereyduni 2019, Rezvani et al., 2020a, Rezvani et al., 2020b, Rezvani et al., 2022a). Saeed et al reported that a Ni-WO₃@g-C₃N₄ composite as an efficient and recoverable nanocatalyst for oxidative desulfurization of both and real oil. They obtained findings revealed that 97 for DBT, 89.5 for diesel and 91.2 % for kerosene (Jabar et al., 2022, Saeed et al., 2022). Typically, the ODS process comprises two stages: oxidation and sulfone generation, followed by separation. Notably, an extraction-coupled catalytic oxidative desulfurization (ECODS) approach has been adopted to enhance the conventional ODS process, achieving deep desulfurization at a relatively lower cost compared to other existing desulfurization technologies.

Traditionally, efficient catalytic oxidative reactions relied on the use of hydrogen peroxide (H₂O₂) (Harutyunyan et al., 2011, Rezvani et al., 2019, Rezvani et al., 2021, Rezvani and Imani 2021, Rezvani et al., 2022a, Rezvani et al., 2022b, Khalafi et al., 2023, Rezvani et al., 2023a) or aerobic oxidants like O₂ or air (Jiang et al., 2019, Guo et al., 2022). However, these oxidants are prone to decomposition, resulting in reduced efficiency, and often come with drawbacks related to transportation, storage, and usage. In comparison, solid oxidants like peroxymonosulfate (PMS) (Li et al., 2021, Liu et al., 2021) have gained prominence for their stability and practical advantages. Recently, considerable attention has been drawn to sulfate radicals (SO $- 4 \cdot$) due to their numerous merits, including a high redox potential (2.5–3.1 V) and a prolonged half-life (30-40 ms). Significantly, SO - 4. can be readily generated from PMS through the activation of transition metal ions, such as Fe^{2+} , Mn^{2+} , Ni^{2+} , and Co^{2+} . Among these, Co^{2+} has emerged as the most efficient homogeneous catalyst for PMS activation (Tan et al., 2017). Consequently, sulfate radicals hold great promise for achieving outstanding performance in oxidative desulfurization (ODS).

For an oxidant to effectively function in an oxidative desulfurization (ODS) system, a catalyst is crucial to expedite the activation process of the oxidant. Nano-sized cobalt ferrite (CoFe₂O₄), a typical bimetallic spinel ferrite, is widely recognized as a highly effective catalyst in oxidation reactions. This recognition is due to its exceptional catalytic activity, stability, magnetic separation capabilities, low cost, abundant resources, electrical properties, magnetic anisotropy, and ecofriendliness (Zhao et al., 2017). Furthermore, the synergistic interaction between its iron (Fe) and cobalt (Co) components leads to a substantial enhancement in catalytic activity compared to the individual oxides. CoFe_2O_4 exhibits rich redox properties (both Co^{2+} and Fe^{3+} are active species), high electronic conductivity, superior catalytic activity, cost-effectiveness, and, most importantly, environmental friendliness (Zhu et al., 2022). These advantages position CoFe₂O₄ as a highly promising candidate for catalytic applications. Notably, recent research has extensively reported the activation of peroxymonosulfate (PMS) by CoFe₂O₄. Du et al. (Du et al., 2016) investigated CoFe₂O₄ and MnFe₂O₄ as heterogeneous catalysts for peroxymonosulfate (PMS) in the degradation of paracetamol (APAP) in water. The results demonstrated that both CoFe₂O₄ and MnFe₂O₄ magnetic nanoparticles activated PMS, representing promising technologies for addressing water pollution. Additionally, Peng et al. (Peng et al., 2022) successfully prepared a series of Fenton-like catalysts by loading CoFe₂O₄ nanoparticles onto the surface of MoS₂ to activate PMS. Their findings revealed that these $CoFe_2O_4@MoS_2$ catalysts, with varying mass ratios of $CoFe_2O_4$ and MoS₂, exhibited superior catalytic performance in tetracycline (TC) degradation. To date, limited efforts have been dedicated to exploring the potential of CoFe₂O₄ nanoparticles as a heterogeneous catalyst for PMS activation in the removal of sulfur compounds from oil.

In this study, we synthesized magnetic $CoFe_2O_4$ nanoparticles using the hydrothermal method and employed them as catalysts to activate peroxymonosulfate (PMS) for the removal of sulfur-containing compounds, including dibenzothiophene (DBT), benzothiophene (BT), and 4,6-Dimethyldibenzothiophene (4,6-DMDBT) from n-octane. We conducted a comprehensive microstructural analysis of the $CoFe_2O_4$ catalyst using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) surface area analysis, and vibrating sample magnetometry (VSM). Subsequently, we analyzed the products obtained after the desulfurization process using gas chromatography-mass spectrometry (GC–MS) and delved into the desulfurization mechanism.

2. Experimental

2.1. Materials

CoCl₂·6H₂O (>99.99 % purity, Aladdin), Fe(NO₃)₃·9H₂O (>99.99 % purity, Aladdin), Ascorbic acid (AA, >99.99 % purity, Aladdin), Urea (CH₄N₂O, >99.99 % purity, Aladdin), Ethanol absolute (Kaitong), Dibenzothiophene (DBT, Aladdin), 1-Benzothiophene (BT, Aladdin), 4,6-Dimethyldibenzothiophene (4,6-DMDBT, Aladdin), Peroxymonosulfate (PMS, 2KHSO₅·KHSO₄·K₂SO₄, KHSO₅ 47 %, Meryer), Acetonitrile (C₂H₃N, DaMao), *n*-octane (DaMao) and deionized water (DI water, no lower than 18.3 MΩ·cm) were purchased from Sigma-Aldrich.

2.2. Preparation of CoFe₂O₄ powders

Cobalt salt (CoC1₂·6H₂O) and ferric salt (Fe(NO₃)₃·9H₂O), in a specific ratio, were dissolved in deionized water along with 0.5 g of ascorbic acid and urea (CH₄N₂O). This solution was then stirred with a magnetic force in a mixer for 20 min. Subsequently, the clear solution was transferred to a Teflon-lined autoclave. The hydrothermal process was carried out at various temperatures and durations. The resulting products were collected through magnetic separation, thoroughly washed with deionized water and ethanol, and finally, dried in a vacuum oven at 70 °C for 6 h. Ultimately, the dried precipitates underwent calcination in ambient air at specific temperatures and for specific durations to yield magnetic CoFe₂O₄ nanoparticles. The preparation process for CoFe₂O₄ powders is illustrated in Fig. 1.

2.3. Desulfurization process

Dissolved thiophene sulfur in *n*-octane to prepare 300–1200 ppm DBT simulated oil. The model fuel oil is sealed and stored to prevent volatilization. Added a certain amount of CoFe₂O₄ and 1 mL acetonitrile to 6 mL prepared model oil, for 30 min to achieve adsorption and extraction equilibrium. After a specific amount of the catalyst and PMS (wt. 20 %) solution were added, the mixture was vigorously stirred, and the time was recorded as "0". In the reaction process, the liquid in the upper oil phase was regularly extracted and diluted. The thiophene sulfur in the model fuel oil was detected by UV–visible spectrophotometer (DBT and 4,6-DMDBT at 312 nm; BT at 297 nm, the UV–visible spectra in Fig S1. The desulfurization rate in model oil is calculated by the following formula (1).

$$R = 100\% (C_0 - C_t) / C_0 \tag{1}$$

where R is the desulfurization rate, C_0 is the initial concentration of sulfur-containing substances, and C_t is the concentration of sulfur-containing substances at time *t*.

All other conditions are tested with the default values below when exploring the effect of one of these factors on desulfurization seen in Fig. S2. The hydrothermal reaction temperature is 160 $^{\circ}$ C, the



Fig. 1. Schematic illustration of CoFe₂O₄ through the Hydrothermal-Calcination process.

hydrothermal reaction time is 7 h, the calcination reaction temperature is 550 °C, the calcination reaction time is 5 h, Co:Fe = 2:4, the catalyst dose is 125 mg, the temperature of desulfurization is 40 °C, initial sulfur content is 600 ppm, O/S = 3:1, sulfur-containing compounds is DBT.

-30,000 to +30,000 Oe. A Brunauer – Emmett – Teller (BET) method was employed to evaluate the surface area and pore size distribution by nitrogen gas absorption–desorption using a Micromeritics APSP 2460 system at 300 °C.

2.4. General information & characterization

The crystallographic information of the as-prepared samples was checked by the powered X-ray Diffractometer Technique (XRD) patterns obtained by Bruker D2 Phaser powder diffractometer having Cu Ka radiation at a step size of 20 range of 10-80°. The particle size, crystallinity, and composition of the as-prepared samples were examined by Scanning Electron Microscope (SEM) using Gemini SEM 300, Transmission Electron Microscope (TEM) using FEI Tecnai G2 F20, Energy Dispersive X-ray spectroscopy (EDS) using SDD super-X instrument. Xray Photoelectron Spectroscopy (XPS) measurements were performed by a photoelectron spectrometer with Al Ka source, a concentric hemispherical analyzer operating in a fixed-analyzer transmission mode, and a multichannel detector. Fourier transform infrared (FT-IR) spectra of the nanofibers were carried out by Shimadzu Trace-100 spectrometer in the region of 4000–400 cm^{-1} with the 4 cm^{-1} resolution and 32 times scanning. Magnetic hysteresis loops were obtained through the VSM system at room temperature in an applied magnetic field sweeping from

3. Results and discussion

3.1. Characterizations of CoFe₂O₄

Fourier transform infrared spectroscopy (FT-IR) was conducted on $CoFe_2O_4$ within the range of 4000 to 400 cm⁻¹, as shown in Fig. 2(a). Specifically, the peak observed at approximately 400 cm⁻¹ corresponds to the stretching vibrations of $Fe^{3+}-O^{2-}$ bonds in $CoFe_2O_4$, while the peak centered at 600 cm⁻¹ indicates the stretching vibration of $Co^{2+}-O^{2-}$ bonds within $CoFe_2O_4$ (Kumbhar et al., 2012). The peak at 1628 cm⁻¹ corresponds to the bending vibration pattern of H_2O molecules, and the broad peak at 3379 cm⁻¹ represents the H-OH vibrations of adsorbed water molecules (Hosseini et al., 2018). The test results indicate the absence of significant impurity peaks, except for the water peak. This suggests that the Co-Fe precursors have undergone complete oxidation, resulting in the formation of pure CoFe₂O₄ nanoparticles.

Magnetic measurements were performed to understand the magnetic behavior of CoFe₂O₄. We observed typical magnetic hysteresis loops of



Fig. 2. FT-IR (a); VSM (b); XRD (c); N₂ adsorption/desorption isotherm and pore size distribution (inset) (d) of as-prepared CoFe₂O₄.

 $CoFe_2O_4$ powder under a magnetic field of ± 3000 Oe (Fig. 2(b)). The magnetic saturation (MS) value of the $CoFe_2O_4$ powder was determined to be 59 emu·g⁻¹. VSM measurements also confirmed the typical magnetic behavior of $CoFe_2O_4$. The presence of magnetic properties indicates that $CoFe_2O_4$ can be efficiently and conveniently separated from the model oil using an external magnet.

As-synthesized CoFe₂O₄ was characterized using several spectroscopic and microscopic studies. The powder XRD of the as-synthesized CoFe₂O₄ powder showed the characteristic peaks of 2 θ which are located at 18.29°, 30.08°, 35.43°, 37.06°, 43.06°, 53.42°, 56.94°, 62.53° and 73.97°. corresponded to (111), (220), (311), (222), (400), (422), (511), (440) and (533) plane of cubic CoFe₂O₄, respectively (Fig. 2(c)) (Li et al., 2017). The XRD pattern is consistent with the JCPDS 22-1086 standard card. No distinct impurity peak was detected, indicating that the pure CoFe₂O₄ powders were obtained by hydrothermal method.

Subsequently, the porous nature of $CoFe_2O_4$ was determined through N₂ adsorption studies. The N₂ adsorption–desorption curves, as shown in Fig. 2(d), closely approach the X-axis in the low-pressure range (0–0.1) and the medium-pressure range (0.3–0.8), implying modest N₂ adsorption forces on the material's surface. However, in the high-pressure range (0.8–1.0), the curves exhibit a significant increase in N₂ self-adsorption–desorption curves display a typical hysteresis loop characteristic of type IV isotherms, according to the IUPAC classification. This hysteresis loop categorization aligns with H3 type features, underscoring the mesoporous structure of $CoFe_2O_4$ generated between the interstitial spaces of flake-like particles.

We employed various techniques to characterize the morphology of the CoFe₂O₄ film obtained. The scanning electron microscopy (SEM) characterization, as depicted in Fig. 3(a-b), reveals some degree of aggregation within the CoFe₂O₄ nanoparticles. This aggregation can be attributed to their magnetic properties and weak surface interactions between the primary particles, which are held together by van der Waals forces(Sagadevan et al., 2016). However, the surface morphology of the CoFe₂O₄ nanoparticles shows the presence of numerous pores. These pores can increase the specific surface area of the nanomaterials and enhance the number of catalytic active sites, ultimately resulting in increased catalytic activity. Transmission electron microscopy (TEM) characterization further confirms that the majority of the CoFe₂O₄ nanoparticles exhibit an approximately cubic shape, although there are also a few particles that appear elongated (Fig. 3(c-d)). The average particle size of the measured particles falls within the range of approximately 10 to 15 nm. Furthermore, high-resolution TEM (HRTEM) (Fig. 3(e)) reveals well-defined lattice spacing within the CoFe₂O₄, indicating that the prepared CoFe₂O₄ nanoparticles possess good crystallinity, with d-spacing values of 0.219 nm and 0.300 nm, corresponding to the (4 0 0) and (2 2 0) planes of CoFe₂O₄ (JCPDS 22-1086), respectively. The selected area electron diffraction (SAED) pattern in (Fig. 3(f)) displays distinct concentric circles, indicating that the CoFe₂O₄ sample is polycrystalline in nature. Moreover, the diffuse rings in the SAED pattern can be attributed to the lattice planes of (511), (400), (311), and (220) of CoFe₂O₄ (JCPDS 22-1086). The CoFe₂O₄ material, featuring a porous architecture and polycrystalline structure, is expected to exhibit robust catalytic activity. Notably, both SAED and XRD analyses reveal that the (311) lattice planes exhibit the most intense reflections. These results collectively affirmed the successful preparation of CoFe₂O₄ nanoparticles.

Fig. 4 displays the EDS data for the $CoFe_2O_4$ samples. The EDS spectra reveals the presence of all elements corresponding to $CoFe_2O_4$, indicating the chemical purity of the samples. In Fig. 4(a), a table presents the weight and atomic percentages of the sample elements obtained from the EDS spectrum. The atomic ratio of Co:Fe:O, which is approximately 1.00:2.23:3.85, closely resembles the elemental atomic number ratio of Co:Fe:O, which is 1.00:2.00:4.00 in CoFe₂O₄. To gain insight into the distribution of various ions within the CoFe₂O₄ samples, we conducted elemental mapping of the materials in the selected sample region. The results, depicted in Fig. 4(b-f), show that all components of the sample are distributed relatively evenly throughout, without any noticeable segregation. This uniform distribution further supports the successful synthesis of $CoFe_2O_4$ nanoparticles.

The metallic state and surface composition of the synthesized spinel $CoFe_2O_4$ was investigated using X-ray photoelectron spectroscopy (XPS). The XPS spectrum of the synthesized nanoparticles in Fig. 5(a) confirms the presence of Co, Fe, and O elements. In Fig. 5(b), the XPS spectra of Co 2p for both $CoFe_2O_4$ and Co_3O_4 show peaks at 779.6 eV and 779.8, while peaks at 781.9 eV and 782.1 eV correspond to Co^{3+} [23]. These results indicate the coexistence of Co^{3+} and Co^{2+} in the samples. It's worth noting that only Co^{2+} (from $CoC1_2 \cdot 6H_2O$) was employed in the sample preparation, and the presence of Co^{3+} may be due to the precursor oxidizing Co^{2+} during the calcination process. In



Fig. 3. SEM at lower resolution (a); SEM at higher resolution (b); TEM at lower resolution (c); TEM at higher resolution(d); HR-TEM (e); SAED (f) of CoFe₂O₄.



Fig. 4. EDS (a); and EDS mapping of CoFe₂O₄ (Co, Fe, O) (b-f).



Fig. 5. XPS survey spectra of the CoFe₂O₄ (a); The XPS spectra for Co 2p of both CoFe₂O₄ and Co₃O₄ (b); The XPS spectra for Fe 2p of both CoFe₂O₄ and Fe₂O₃ (c); The XPS spectra for O 1s of both CoFe₂O₄, co₃O₄, and Fe₂O₃ (d).

 Co_3O_4 , the peak area of Co^{3+} and Co^{2+} was 48.8 % and 51.2 %, respectively, while in CoFe₂O₄, it was 46.9 % and 53.1 %, respectively. Besides, the XPS spectra of Fe 2p for both CoFe₂O₄ and Fe₂O₃ show peaks at 779.6 eV and 779.8 eV; while peaks at 781.9 eV and 782.1 eV correspond to Fe $^{3+}$. These results indicate the coexistence of Fe $^{3+}$ and Fe $^{2+}$ in the samples. In Fe2O3, the peak area of ${\rm Fe}^{3+}$ and ${\rm Fe}^{2+}$ was 63.8 % and 36.2 %, respectively, while in CoFe₂O₄, it was 28.8 % and 71.2 %, respectively. This suggests that in CoFe₂O₄, Co and Fe atoms interact to varying degrees, leading to electron rearrangements and a certain degree of electronic synergistic effect between the metals. The O 1 s spectra (Fig. 5(d)) can be deconvoluted into three oxygen contributions peaks. Hydroxyl oxygen (531.4 eV) and adsorbed oxygen (533.2 eV) in CoFe₂O₄, Co₃O₄, and Fe₂O₃ have similar binding energies, around 533.2 eV and 531.4 eV, respectively. However, the binding energies of lattice oxygen in CoFe₂O₄, Co₃O₄, and Fe₂O₃ materials show slight variations. with values of 529.8 eV, 530.0 eV, and 529.5 eV, respectively. This suggests that lattice oxygen plays a significant role in the synthesis of CoFe₂O₄. The coexistence of Co and Fe results in a shift in the electron binding energy on the O 1 s orbital in CoFe₂O₄, indicating an interaction between Co and Fe. The content of Co^{2+} and Fe^{2+} in prepared $CoFe_2O_4$ is higher than that in Co₃O₄ and Fe₃O₄ monometallic oxides. This higher content enhances the reducibility of the material, making it more catalytically active toward oxidants. Consequently, compared with Co₃O₄ and Fe₂O₃, CoFe₂O₄ is expected to exhibit superior catalytic performance in future catalytic oxidation desulfurization applications.

3.2. Optimization of desulfurization conditions

Acetonitrile, characterized by its low surface tension, facilitates efficient mass transfer at the biphasic solvent interface. Additionally, it exhibits superior extraction properties for dibenzothiophene, making it an ideal choice as a solvent, resulting in higher desulfurization rates. The CoFe₂O₄ catalyst enhances the oxidative desulfurization (ODS) efficiency, and the resultant DBTO₂ can be efficiently extracted from model oil using acetonitrile, further enhancing the overall desulfurization

efficiency(Muhammad et al., 2018). Therefore, the use of acetonitrile as an extractant is pivotal in investigating the catalytic performance of $CoFe_2O_4$ in Extractive Catalytic Oxidative Desulfurization (ECODS) experiments.

The catalyst dosage significantly influences the oxidation of DBT. We evaluated the impact of $CoFe_2O_4$ powder dosage on sulfur removal, as shown in Fig. 6(a). Desulfurization efficiencies increased as the $CoFe_2O_4$ powder dosage ranged from 50 mg to 125 mg within a 20 min time-frame. This result suggests that higher catalyst loadings generate more active sites for the activation of PMS. A remarkable sulfur removal efficienc was up to 95 % was achieved within just 60 min when a catalyst loading of 125 mg was used. However, desulfurization rates declined when the catalyst amount exceeded 125 mg. The mesoporous structure of $CoFe_2O_4$ facilitated substrate diffusion, with its relatively large channels proving more suitable for adsorption and desorption of large sulfur-containing compounds compared to narrower materials. Furthermore, this outcome underscores the exceptional desulfurization performance of the $CoFe_2O_4$ and PMS combined system.

Fig. 6(b) illustrates the desulfurization rates at different desulfurization temperatures. During the extraction stage, DBT diffused from the oil phase into the extraction phase. Following the addition of PMS to the system, the desulfurization rate improved as temperatures increased. Sulfur removal efficiencies notably increased between 30 °C and 40 °C within 80 min. However, desulfurization rates decreased at temperatures of 50 °C and 60 °C, as excessively high temperatures are unfavorable for catalytic oxidation(Li et al., 2009). Additionally, PMS is unstable and readily decomposes at 65 °C(Kermani et al., 2018). Taking into consideration both heat source utilization efficiency and catalytic performance, catalytic ODS is most effective at 40 °C.

Achieving an appropriate oxygen-to-sulfur ratio (O/S), using the correct amount of PMS (20 wt%), is crucial for an efficient ODS process. If the O/S ratio is too low, the system's ability to oxidize DBT in the model oil will be compromised(Zhang et al., 2012). Conversely, excessive PMS is detrimental to the catalytic oxidation ability of cobalt ions. Therefore, determining the right PMS dosage is crucial. As depicted in



Fig. 6. The S removal efficiency of different factors on oxidative desulfurization: the effect of catalyst dosage (a), the effect of reaction temperature (b), the effect of O/S molar ratio (c), the effect of initial sulfur content (d-e), the effect of substrates (f).

Fig. 6(c), the desulfurization rate increased from 71.49 % to 95.10 % as the O/S ratio increased from 1:1 to 3:1. However, when the O/S ratios further increased from 3:1 to 7:1, the desulfurization rate decreased noticeably. This observation can be attributed to the PMS content exceeding the optimal value, as the strong acidity of hydrogen persulfate is unfavorable for the catalytic oxidation of cobalt ions. Furthermore, hydrogen persulfate also acts as a scavenger of sulfate radicals (Madhavan et al., 2008), which is detrimental to the reaction. Consequently, the optimal O/S ratio for the desulfurization system is found to be 3:1.

In Fig. 6(d), the effect of the initial DBT concentration on the desulfurization process is shown. Increasing the initial sulfur content from 300 to 1200 ppm resulted in decreased removal efficiencies, dropping from 20.05 % to 16.60 % in the initial extraction phase. However, in the second extraction-oxidation catalytic desulfurization (EOCDS) phase, sulfur removal efficiencies significantly increased within the first 20 min for all initial sulfur content concentrations. $CoFe_2O_4$ catalyzes PMS to produce a large number of HSO_5^- ions due to its excellent catalytic activity, leading to a rapid and significant improvement in desulfurization efficiency. At a constant initial $CoFe_2O_4$ dosage and PMS dosage, sulfur removal efficiency decreased as the initial sulfur content increased (Fig. 6(e)).

Desulfurization tests were conducted on BT, DBT, and 4,6-DMDBT under identical conditions to investigate the effects of $CoFe_2O_4$ nanoparticles on various sulfur-containing compounds. The results revealed that the catalytic oxidation reaction of sulfur-containing compounds had a more pronounced removal effect on DBT compared to 4,6-DMDBT and BT, as depicted in Fig. 6(f). This variation in reactivity can be attributed to the electron density of the sulfur atom in each compound, with BT having the lowest electron density (5.696), which is lower than that of DBT (5.758) and 4,6-DMDBT (5.760) (Shujiro Otsuki et al., 2000). Consequently, BT exhibited lower reactivity. While the electron concentrations of the sulfur atoms in DBT and 4,6-DMDBT are similar, the presence of two methyl groups in 4,6-DMDBT may introduce steric hindrance, reducing the interaction between the $CoFe_2O_4$ nanoparticle catalyst and the oxide. As a result, the removal of 4,6-DMDBT is more challenging than that of DBT.

Table 1 presents a comparison with other cobalt-containing or ironcontaining catalysts, highlighting the advantages of the $CoFe_2O_4$ catalyst. It exhibits the shortest reaction time, requires the lowest temperature, and uses the least amount of oxidant while achieving the same level of efficiency as other catalysts.

3.3. Recycling of CoFe₂O₄ powder

After the ODS tests, the $CoFe_2O_4$ catalyst was separated from the solution using a magnet due to its strong magnetic properties. It was subsequently cleaned, dried, and subjected to a cycle of testing. Remarkably, the $CoFe_2O_4$ catalyst maintained a consistent sulfur removal efficiency of approximately 90 % even after three usage cycles, as illustrated in Fig. 7(a). However, following the fourth cycle of desulfurization testing, the desulfurization rate dropped to 82 %, indicating a decrease in the catalyst's activity by approximately 13 %. Fig. 7 (b) shows the XRD spectra of $CoFe_2O_4$ before and after the recycling tests, revealing no significant differences. This suggests that the decline in the catalyst's reuse performance was not due to damage to its crystalline structure. The diminished performance may be attributed to several factors: (1) Contamination of the catalyst's active sites; (2) A minor leaching of metal ions from the catalyst during the catalytic process, recovery, and washing stage.

3.4. Desulfurization mechanism

Therefore, possible desulfurization mechanism was constructed as seen in Fig. 8. According to similarity-intermiscibility theory (Wang et al., 2017a), nonpolar DBT is readily soluble in nonpolar octane. Part of the DBT dissolved into the acetonitrile phase when acetonitrile was added to the simulated oil, which is actually an extraction process. Added PMS to the reaction system, DBT was oxidized to polar DBTO/DBTO₂ and extracted by acetonitrile and separated from oil phase. DBTO/DBTO₂ can be detected by gas chromatography-mass spectrometry (GC–MS). In acetonitrile phase, the possible specific oxidation reaction mechanism as follow.

In acetonitrile phase, the CoO can catalyze the cleavage of the peroxide bridge of HSO₅⁻ to produce sulfate radicals (SO₄⁻) and hydroxyl radicals. Meanwhile, CoO can give one of its electrons to the hydroxyl radical and form an unstable Co–O covalent bond. The sulfate radical can attack lone pair electrons of sulfur atom in DBT molecule. The electron cloud density of sulfur is relatively high, which is conducive to the formation of covalent double bonds with an oxygen atom. Therefore, DBT can be oxidized to form DBTO. The unstable Co–O covalent bond can obtain an electron from the S–O bond in HSO₅⁻ to form a stable CoO. Briefly, the HSO₅⁻ can release the active oxygen to form S=O bond under CoFe₂O₄ as a catalyst. DBTO₂ can also be produced in a similar mechanism.

Table 1

Catalyst	Oxidant	Dosage (g/L)	Concentration (ppm)	O/S Ratio	Temperature (℃)	Time (min)	S Removal Efficiency (%)	Ref.
CoFe ₂ O ₄	PMS	20	600	3	40	60	95	Current study
[Co ₃ (oba) ₃ (O) (Py) 0.5] _n ·4DMF·Py	TBHP	4	500	3	60	480	75.2	(Guo et al., 2022)
Fe–Ni–Mo/Al ₂ O ₃	H_2O_2	40	800	15.8	60	150	99	(Muhammad et al., 2018)
CoPcTcCl ₈	O2	20	800	_	20	180	94.42	(Gao et al., 2019)
Co ₃ O ₄ /Al ₂ O ₃	Air	_	1000	-	200	180	81	(Nawaf et al., 2015)
H3PW12O40/nano-Fe3O4/SiO2	H_2O_2	32	500	20	60	180	91.40	(Liu et al., 2017)
PTA@MIL-100(Fe)	H_2O_2	15	500	4	70	120	92	(Wang et al., 2017b)
PMo ₁₁ Cd@MnFe ₂ O ₄ ,	H ₂ O ₂ / CH ₃ COOH	2	500	-	35	60	96	(Rezvani et al., 2020c)
(Gly) ₃ PMo ₁₂ O ₄₀ @MnFe ₂ O ₄	H ₂ O ₂ / CH ₃ COOH	2	500		35	60	95	(Rezvani et al., 2022a)
((n-C ₄ H ₉) ₄ N) ₄ H[PW ₁₁ FeO ₃₉] @NiO)	CH ₃ COOH/ H ₂ O ₂	2	500	-	60	120	95	(Rezvani et al., 2023b)
t-B.PWFe/NiO	CH ₃ COOH/ H ₂ O ₂	2	500	_	35	60	97	(Rezvani and Aghmasheh 2021)
[C ₁₆ H ₃₃ N (CH ₃) ₃] ₇ H ₃ SiV ₃ W ₉ O ₄₀ -TiO ₂	H ₂ O ₂	20	200	_	30-80	60	984	(Rezvani and Zonoz 2015)
CoFe ₂ O ₄	H_2O_2	5	272.8	20	25	8	99.82	(Rezvani et al., 2023c)
CoFe ₂ O ₄	H_2O_2	5	272.8	20	25	8		(Zhang et al., 2021)



Fig. 7. Recycle test of cofe₂O₄ (a); XRD of CoFe₂O₄ before and after use (b).



Fig. 8. Catalytic oxidative desulfurization of CoFe₂O₄ possible desulfurization mechanism.

After the reaction, the interaction of $CoFe_2O_4$ with DBTO₂ is reduced because the electron-bonding ability of S atoms in DBTO₂ is severely decreased. Therefore, the oxidation product (DBTO₂) can be desorbed and released from the surface of the catalyst. In addition, the DBTO₂ can thoroughly dissolve in acetonitrile because the polarity of its S=O bonds is considerably stronger than the polarity of the S–C bonds in DBT using electronegativity analysis(Yuan et al., 2022).

Gas chromatography-mass spectrometry (GC–MS) was employed to identify and assess the compounds present in the acetonitrile phase at various time intervals(Armandsefat et al., 2024), as depicted in Fig. 9. At the point of extraction equilibrium (0 min), the DBT peak was clearly discernible in the acetonitrile phase, indicating that oxidative desulfurization (ODS) had not yet commenced. After the addition of PMS at 1 min, the intensity of the DBT peak slightly diminished. Importantly, small peaks corresponding to DBTO and DBTO₂ emerged, signifying the initiation of ODS and the continuous conversion of DBT into DBTO and DBTO₂. As the oxidation reaction progressed, the distinctive DBT peak in the simulated oil gradually decreased, while the characteristic peak intensity of DBTO initially increased and then declined, and the characteristic peak intensity of DBTO₂ continued to rise. This observation implies that the remaining DBT in the simulated oil was being continuously oxidized. After 20 min of reaction time, the distinctive DBT peak was nearly completely oxidized. The insets in Fig. 9 display the Mass Spectra of DBT, DBTO, and DBTO₂, respectively. These experimental results elucidate that DBT undergoes initial oxidation to the intermediate transition product DBTO, followed by further oxidation of DBTO to yield the final product DBTO₂ during the catalytic oxidation process of DBT.".

4. Conclusion

Under favourable reaction conditions, involving 6 mL of simulated oil with a dibenzothiophene concentration of 600 ppm, 1 mL of acetonitrile, 125 mg of $CoFe_2O_4$ nanoparticles (hydrothermal reaction temperature of 160 °C, hydrothermal reaction time of 5 h, calcination temperature of 550 °C, calcination time of 7 h, cobalt-iron molar ratio of 2:4) at a desulfurization system temperature of 40 °C and an O/S ratio of 3, the S removal efficiency exceeded 95 % after 60 min of reaction time. It is noteworthy that compared to other cobalt or iron-containing catalysts reported in the literature, $CoFe_2O_4$ exhibited shorter ODS reaction times and required lower temperatures and oxidant amounts to achieve the same level of desulfurization efficiency. The GC–MS analysis of the products in the acetonitrile phase unveiled the mechanism by which DBT is first oxidized to dibenzothiophene sulfoxide (DBTO) as a



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Fig. 9. GC–MS diagrams of DBT and its oxidation products the acetonitrile phase at different oxidation reaction times.

transitional intermediate, ultimately culminating in the formation of dibenzothiophene sulfone (DBTO₂). This insightful mechanism showcases the tremendous potential of CoFe₂O₄ catalysts for application in oxidative desulfurization processes, owing to their high activity and recyclability.

CRediT authorship contribution statement

Fengmin Wu: Writing – review & editing, Project administration, Investigation, Funding acquisition, Conceptualization. Qinlin Yuan: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. Jinlong Wang: Investigation, Data curation. Xiaowei Wang: Writing – review & editing, Investigation. Jie Luo: Writing – review & editing, Methodology, Funding acquisition. Yafei Guo: Writing – review & editing. Hang Xu: Writing – review & editing, Funding acquisition. Xuefeng Wei: Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

The UV–visible spectra of BT, DBT and 4,6-DMDBT, the optimization of $CoFe_2O_4$ preparation conditions and blank experiments. Supplementary data to this article can be found online at https://doi.org/10.1016/j.arabjc.2024.106076.

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