Development of graphitic carbon nitride supported novel nanocomposites for green and efficient oxidative desulfurization of fuel oil

Ghulam Jabar¹, Muhammad Saeed², Sadaf Khoso¹, Anham Zafar¹, Javed Iqbal Saggu³ and Amir Waseem¹

Abstract
The catalysts utilized for oxidative desulfurization have acquired significant attention and ability to improve the quality of the fuel oil by removing sulfur. In this work, the catalysts used for oxidative desulfurization include CoWO₄ and Bi₂WO₆ with graphitic carbon nitride (g-C₃N₄) as support were synthesized by the one-pot hydrothermal method. Graphitic carbon nitride was obtained by thermal polycondensation of melamine at 550°C for 5 h. These catalysts were homogeneously dispersed on the surface of the support and their structure, morphology, and properties were determined by different characterization techniques (Powder X-Ray Diffractometer, Fourier Transform Infrared Spectroscopy, Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy, Specific Surface Area (Brunauer, Emmett and Teller (SBET))). The parameters that affect the efficiency of the desulfurization process such as catalyst amount, amount of oxidizing agent, and reaction temperature have been optimized thoroughly. The oxidative desulfurization reaction was studied in terms of kinetics which shows that reaction is pseudo first order. The thermodynamic studies revealed that the reaction is endothermic and spontaneous in nature. The results determined that the catalytic efficiency for the removal of sulfur (as dibenzothiophene) is more than 90% in the presence of support (g-C₃N₄) to obtain sulfur free fuel.

Keywords
Graphitic carbon nitride, oxidative desulfurization, dibenzothiophene, kinetics, thermodynamics

Date received: 10 March 2022; accepted: 24 May 2022

Introduction
Raw oil is the world’s largest source of energy that accounts for nearly half of the globe’s total energy resource and its requirements have risen worldwide day by day. Crude oil is mostly made up of straight-chain hydrocarbons, aromatics, and compounds with a heteroatom. The combustion of Sulphur containing compounds that include, benzothiophenes (BT), dibenzothiophenes (DBT) thiophenes (T), and mercaptans produces sulfur oxides and other harmful gases...
which cause air pollution (such as smog and photochemical haze), soil pollution in form of acid rain and disturb the ecosystem.1,2 The elimination of sulfides is essential for the manufacturing of pollution-free fuel and to meet the requirement of the United States Environmental Protection Agency which has standard criteria of sulfur content (<10 mg/L).3,4 The sulfides are classified into two main categories in fuel: Sulfur, hydrogen sulfide, and mercaptan are categorized as active sulfides whereas thioketones, disulfides, benzothiophenes, and dibenzothiophenes are examples of inactive sulfides. Due to their least complicated structures, thiol, sulfides, and disulfides could be easily removed during the desulfurization process. However, it is hard to eliminate thiophene, benzothiophenes, dibenzothiophene, and its derivatives as they have aromatic and sterically hindered structures. So, the removal of thiophene derivative molecules is considered to be the key goal in desulfurization.5

Recently, several methods for eradicating sulfur from fossil fuels have been investigated which include oxidative desulfurization (ODS),6 adsorptive desulfurization,7 extractive desulfurization8 and hydrodesulfurization techniques.9 Hydrodesulfurization (HDS) in combination with carbon rejection technologies, such as coking and fluid catalytic cracking, are the main technologies industrially employed for the desulfurization of heavy oil.10 HDS is expensive method for the removal of sulfur-containing compounds due to the requirements of high temperature (>600 K) and pressure (>3 MPa). This technique is also not effective for the removal of alkylated organic sulfur compounds and polyaromatic sulfur compounds such as BT and DBT due to steric hindrance and low reactivity of these compounds in hydrogenation treatments.11,12 Comparison with other techniques, ODS has attained more consideration and is supposed to be the most promising owing to cost effective and no high temperature and pressure requirements. Sulfides and other sulfur-containing compounds are oxidized to sulfones and sulfoxides by using a catalyst in ODS and then extracted from the fuel.13,14 In ODS, the choice of oxidant and catalyst is critical. The most promising oxidizing agent include hydrogen peroxide owing to amount of active oxygen increase by 47% by mass unit and also no harmful side product formation. The heterogeneous catalyst is used along with hydrogen peroxide to increase the mass transfer which makes this reaction fast and commercial.

In order to achieve deep desulfurization, the catalyst is essential in the ODS. Organic acids, heteropoly acids, ionic liquids (ILs) and tungstate-based catalysts have been reported for oxidation desulfurization process.15–18 Although homogeneous catalysts work well for the desulfurization of model fuel oil, a portion of the catalyst is lost during the reaction as separation and recovering after the reaction is challenging that results in a greater cost.19 Heterogeneous catalysts, on the other hand, have a number of benefits that help them overcome these constraints, including the ease with which they can be separated, recovered, and circulated, as well as the fact that they are environmentally beneficial.20 As a result, heterogeneous catalysts are commonly utilized in ODS. Tungsten oxides-based metal catalysts have significant importance due to easy synthesis, low toxicity, cheap cost, and consistent multifunctional performance.21 The active components are frequently put on supports to improve the activity and separation of the catalysts. Silica, alumina, activated carbon, zeolite, carbon nitride (g-C3N4), and other supports have all been studied.22–25 Boron nitride was also used as a metal-free catalyst in oxidative desulfurization of fuel with H2O2 as the oxidant. It was postulated that the boron radicals activate the H2O2 which results in ultra-deep desulfurization.26 As a carrier, g-C3N4 is usually modified with metals inorganic carbon materials, resulting the formation of heterojunctions which increase its electron conduction and catalytic activity.27 The use of g-C3N4 as support gets significant importance because of the larger surface area provided by this support.28

Regarding the above remarks, the present study comprises the synthesis of two novel nanocomposites (Bi2WO6@g-C3N4 and CoWO4@g-C3N4) via hydrothermal method and study its performance for the first time in oxidative desulfurization of model fuel oil. The prepared materials were characterized via Fourier Transform Infrared Spectroscopy (FT-IR), Powder X-Ray Diffractometer (P-XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX). Optimization, kinetics and thermodynamics parameters were discussed in detail.

Materials and method

Materials

All the chemicals were used of analytical grade; melamine (C3H6N6, 99%, MW= 126.12 g/mol) and sodium tungstate dihydrate (Na2WO4·2H2O; 98% MW = 329.85 g/mol) were purchased from DAEJUNG, Korea, Cobalt (II) Chloride hexahydrate (Cl2CoH12O6, 99%, MW = 237.93 g/mol) and Bismuth (III) nitrate pentahydrate (Bi (NO3)3·5H2O, 99% MW = 485.07 g/mol) were purchased from Sigma -Aldrich. Synthesis of g-C3N4, CoWO4@g-C3N4 and Bi2WO6@g-C3N4

Graphitic carbon nitride was synthesized by thermal polycondensation of melamine at 550°C for 5 h. The resultant yellow product was collected and milled into powder for further use as support as well as a catalyst in our reaction.29 The synthesis of CoWO4@g-C3N4 was conducted by mixing sodium tungstate dihydrate (Na2WO4·2H2O, 1.0 g) with cobalt (II) chloride hexahydrate (C3H2CoH12O6, 1.5 g) in 100 mL distilled water. Similarly, for the preparation of
Bi$_2$WO$_6@g$-C$_3$N$_4$; sodium tungstate dihydrate (Na$_2$WO$_4$·2H$_2$O, 1.0 g) was mixed with bismuth (III) nitrate pentahydrate (Bi(NO$_3$)$_3$·5H$_2$O, 2.91 g), in 100 mL of distilled water. Then stirred for 15 min for complete mixing followed by sonication for 20 min to obtain the uniform size particles. Afterward, a few drops of hydrazine were added for reduction. This solution was kept in the autoclave at 150°C for 6 h. The product (CoWO$_4$ and Bi$_2$WO$_6$) was then cooled, filtered, and ground. Consequently, CoWO$_4$ or Bi$_2$WO$_6$ (1 g each) and g-C$_3$N$_4$ (4 g) were taken in 100 mL of distilled water, stirred for 5 min and sonicated for 20 min for uniformly dispersion of particles. It was kept in the autoclave at 150°C for 12 h, filtered and ground via pestle mortar.

**Catalytic activity tests and product analysis**

25 mL of DBT solution (50–500 mg/L in n-hexane) with acetonitrile (25 mL) was taken in two necks round bottom flask. The ODS procedure was performed by adding catalyst along with oxidizing agent (H$_2$O$_2$) and stirring it at different time intervals. After the equilibrium was reached, the lower layer containing n-hexane with DBT was analyzed by using a UV spectrophotometer and calculated sulfur concentration in fuel oil as DBT shows an absorption ($\lambda_{\text{max}}$) at 284 nm. The formation of sulfones in acetonitrile was checked by thin-layer chromatography. The formation of sulfones was also confirmed by the melting point of the product obtained (229–232°C).

**Results and discussion**

**Characterization**

**Fourier transform infrared spectroscopy.** The Infrared spectroscopic analysis was performed to confirm the presence of specific functional groups via IR-TRACER-100 in the range of 4000–400 cm$^{-1}$ with scan rate of 15 cm$^{-1}$. The g-C$_3$N$_4$ has strong absorption peaks in the range of 1200–1650 cm$^{-1}$, which could be attributed to the C=N vibration at (1637 cm$^{-1}$) in the aromatic ring and, the stretching vibration of C–N at (1237,1317, and 1406 cm$^{-1}$). Moreover, the bending vibration of C–N in the heterocyclic triazine ring system at (810 cm$^{-1}$) is also noticed. The broad absorption band at 3156 cm$^{-1}$, can be attributed to the stretching mode of the N–H bond as shown in Figure 1(a). The pure Bi$_2$WO$_6$ sample demonstrates main absorption peaks at 400–800 cm$^{-1}$, which are ascribed to Bi–O, W–O stretching and W–O–W bridging stretching modes (Figure 1(b)). These peaks are still present in Bi$_2$WO$_6@g$-C$_3$N$_4$, also suggesting that no structure change of Bi$_2$WO$_6$ appears during the process, which is consistent with the XRD result. Furthermore, all characteristic absorption bands of C$_3$N$_4$ and Bi$_2$WO$_6$ appeared in the spectra of Bi$_2$WO$_6@g$-C$_3$N$_4$, showing the coexistence of catalyst with support as shown in Figure 1(c). The peaks at 800 and 626 cm$^{-1}$ are the characteristic peaks of CoWO$_4$. The CoWO$_4$ with g-C$_3$N$_4$ support contains all the vibration peaks of both pristine g-C$_3$N$_4$ and pure CoWO$_4$. Hence, we concluded that there were no structural changes in the g-C$_3$N$_4$ during the introduction of the CoWO$_4$. The FT-IR spectra contain the characteristic peaks of CoWO$_4$ (810 and 626 cm$^{-1}$) and g-C$_3$N$_4$ (1240, 1320, 1403, and 1637 cm$^{-1}$) in CoWO$_4@g$-C$_3$N$_4$ (Figure 1(d) and (e)).

**X-ray diffraction.** Powder X-ray diffraction (P-XRD) using Cu-K$_\alpha$ radiation detector having wavelength 0.154 nm with a scanning rate of 2°/min in the range of 20 from 20–70° by a powder diffractometer and was confirmed by Joint Committee on Powder Diffraction Standards (JCPDS) cards. The crystallite sizes were measured with the help of Sherrer’s equation (equation (1)) using the full-width half maximum (FWHM) of the sharpest peak.

$$D = k\lambda/(\beta\cos\theta)$$

Where D is the average crystalline size in nm, K is the shape factor (0.9), $\lambda$ is the wavelength of X-ray used (0.154 nm), and $\beta$ is FWHM (full-width half maximum) of respective diffraction peaks. The average crystallite size (D) was found <60 nm in both nanocomposites. The P-XRD data indicates that Bi$_2$WO$_6$ shows a series of sharp and narrow diffraction
peaks, which represents the orthorhombic phase of Bi$_2$WO$_6$ (JCPDS 73–1126). The more intense peak positioned at 28.54° attributed to the (113) plane of Bi$_2$WO$_6$, while the peaks at 33.10°, 47.38°, 56.19°, and 58.69° belong to (200), (311), and (313) crystallographic planes of orthorhombic crystal for Bi$_2$WO$_6$ and the peak at 27.4° corresponds to the (002) plane of g-C$_3$N$_4$, which represents to interlayer stacking of aromatic parts as shown in Figure 2. The g-C$_3$N$_4$ layer was too thin and used as supporting material, so there is the invisibility of diffraction of C$_3$N$_4$ in Bi$_2$WO$_6@g$-C$_3$N$_4$. According to the powder-XRD data of CoWO$_4@g$-C$_3$N$_4$, the characteristic peaks appeared at position 30.8°, 31.4°, 36.4° and 54.3° ascribed to (111), (020), (120), and (131) crystal planes of monoclinic crystal with wolframite structure for CoWO$_4$, while the peak at position 27.4° attributed to (002) plane of g-C$_3$N$_4$, which illustrates the successful synthesis of CoWO$_4@g$-C$_3$N$_4$ as shown in Figure 2. The prepared CoWO$_4$ samples are consistent with the standard structure (JCPDS card no. 15–0867) of CoWO$_4$.33

**Scanning electron microscopy.** Scanning microscope scans a centered beam of the electron over a surface to form an image in which the electrons within the beam act with the sample, manufacturing numerous signals that may be used to acquire data regarding the surface topography and composition. The signals which were derived from electron-sample interactions revealed information relating to the sample along with external morphology (texture), chemical composition, crystalline structure, and orientation of materials making up the sample. SEM (NOVA Nano) images show the uniform distribution of the Bi$_2$WO$_6$ in the form of nanoflakes over the g-C$_3$N$_4$ support. The nanoflakes have a very large surface area and are densely interconnected with each other without any small gap as shown in Figure 3(b). These nanoflakes have shown rough morphology with agglomerates of small particles.34,35 SEM images at different resolutions show that CoWO$_4$ nanoparticles were uniformly distributed on the g-C$_3$N$_4$ support.36 In less resolution, the particles have given the rock-like structure. While in the case of high resolution the particles have shown cauliflower-like morphology with high surface area and more porosity as shown in Figure 3(c). This gives the sites for catalytic activity with good results. Additionally, SEM images of g-C$_3$N$_4$ show the coral-reef type morphology with high surface area to provide the site for catalytic activity as shown in Figure 3(a).

**Energy-dispersive X-ray spectroscopy.** The elemental composition of the prepared catalyst is being justified by performing EDX analysis, where a beam of X-ray is being interacted with the sample surface. As a result, a unique set of peaks is generated depending upon the characteristic composition of each element. The prepared catalysts have a combination of various elements that gave their characteristic peak. According to the EDX micrograph of Bi$_2$WO$_6@g$-C$_3$N$_4$, the successful preparation of nanocatalyst is confirmed by the existence of Bi, W, C, and N elements with an approximated percentage quantity of 15.03, 6.72, 37.01, 41.24 wt. %, respectively as is evident from Figure 4. Additionally, the EDX micrograph of CoWO$_4@g$-C$_3$N$_4$ shows the existence of Co, W, C, and N elements with an approximated quantity of 3.39, 12.07, 52.59, 31.95 wt. %, respectively as illustrated in Figure 4. Comparatively, the EDX of g-C3N4 only shows two peaks of C and N with 34.85 and 65.15 wt. % respectively.

**Specific surface area analysis.** The surface area analysis (Brunauer, Emmett and Teller) was performed from the nitrogen adsorption isotherms at 77 K with a Micromeritics Gemini VII instrument. The nitrogen adsorption-desorption curves of the catalysts are displayed in Figure 5. The Brunauer, Emmett and Teller (BET) surface areas of synthesized g-C$_3$N$_4$, Bi$_2$WO$_6@g$-C$_3$N$_4$, and CoWO$_4@g$-C$_3$N$_4$ catalysts were found to be 19.8, 31.5, 35.8 m$^2$/g respectively. The specific surface areas of the g-C$_3$N$_4$ increased after composites formation with Bi$_2$WO$_6$ and CoWO$_4$. This finding may be related to the catalyst being well dispersed on the g-C$_3$N$_4$ nanosheets, entering the interlayer, and interacting with triazine units of the nanosheets, resulting in expansion of the interlayer, which further leads to an increase of the surface areas of the composites. These finding are in similar to the previously reported studies.37,38

![Figure 2. Powder X-ray diffractometer pattern of g-C$_3$N$_4$ and composites.](image-url)
Catalytic oxidative desulfurization studies. The graph (Figure 6(a) and (b)) exhibited the catalytic activity of catalysts with and without support and it was observed that the catalytic activity enhanced prominently when support was added because of increased surface area and by using support catalyst is well dispersed on the support and provides more active sites for the reaction. Bi$_2$WO$_6$ and CoWO$_4$ oxidized the sulfur-containing compounds up to 41.17% and 48.22% respectively without support, while using the support of g-C$_3$N$_4$ the percentage oxidation of sulfur compounds increased up to more than 90% and 80% respectively.

The conversion of sulfur-containing compounds from sulfides to sulfoxides and sulfones increased with the passage of time. All sulfur-containing compounds are oxidized within 2 h of time duration. The CoWO$_4@g$-$\text{C}_3\text{N}_4$ removes the sulfur up to 84.7% and Bi$_2$WO$_6@g$-$\text{C}_3\text{N}_4$ removes the sulfur-containing compound up to 91.3% as shown by Figure 6(c) and (d). The same trend was observed for Fe$_2$W$_{18}$Fe$_4$@NiO@CTS hybrid nanocatalyst and polysilicotungstate supported β-cyclodextrin composite reported previously.$^{1,39}$

The catalyst loading has a crucial impact on the removal of sulfur-containing compounds from the fuel oil. With the increase of catalyst amount from 0.02 g to 0.06 g, the percentage oxidation of sulfur also increased. The optimum amount of catalyst was taken as 0.06 g for better catalytic results as with the increase of catalyst amount, more active sites are available for the catalytic activity to convert sulfur-containing compounds into sulfones as shown in Figure 6(e) and (f). The same trend is observed in the case of Fe$_2$W$_{18}$Fe$_4$@NiO@CTS hybrid nano catalyst and polysilicotungstate supported β-cyclodextrin composite.$^{1,39}$

The oxidation of sulfur compounds in fuel oil has been increased by the increase of temperature (up to 60°C). The optimum temperature for the best ODS result was taken as 60°C and by increasing temperature to a certain limit catalytic activity has increased. At high temperatures, the ODS process decreases because at high temperatures decomposition of H$_2$O$_2$ starts and this will reduce the oxidative conversion of sulfides into sulfoxides as displayed in Figure 6(g) and (h).

Effect of temperature on percentage oxidation was evaluated for WO$_3$/mesoporous ZrO$_2$, Fe$_2$W$_{18}$Fe$_4$@NiO@CTS hybrid Nano catalyst show the comparable result with CoWO$_4@g$-$\text{C}_3\text{N}_4$ and Bi$_2$WO$_6@g$-$\text{C}_3\text{N}_4$. The same trend was observed as in the case of CoWO$_4@g$-$\text{C}_3\text{N}_4$ and Bi$_2$WO$_6@g$-$\text{C}_3\text{N}_4$ which shows that the percentage oxidation of sulfur increases when we increase temperature up to 60°C.

Many types of oxidants have been used and for ODS process. The oxidants such as peroxyacids (performic acid, per trifluoroacetic acid, mixture of formic acid or trifluoroacetic acid, tert-butyl hydroperoxide, and hydrogen peroxide) reported to be the most efficient oxidants.$^{38,41}$ In the current study, H$_2$O$_2$ is used due to its strong oxidizing potential, cheap and easy availability. The increase of oxidizing agents enhanced the ODS process itself. Although by increasing H$_2$O$_2$ (as an oxidizing agent), the ODS increases as represented by Figure 6(i) and (j) but H$_2$O$_2$ can be used up to a specific limit. The optimum amount of hydrogen peroxide used for ODS in presence of given catalysts is 0.6 mL, as higher amount of H$_2$O$_2$ can cause self-decomposition that would not be effective for the oxidation process. These results are comparable with some other catalysts such as $[P_2W_{18}O_{62}]^{6-}$ and $[P_5W_{30}O_{110}]^{14,1}$.

Oxidative desulfurization mechanism. In the presence of metal-based nanocomposites and hydrogen peroxide as an efficient oxidizing agent, ODS process has been done by oxidizing a sulfur atom in DBT to DBT-sulfone, which was
aided by Bi$_2$WO$_6$ and CoWO$_4$ catalysts over g-$C_3$N$_4$ as support (Figure 7). A simplified chemical process implies that oxygen radicals from hydrogen peroxide ($H_2O_2$) attack the electron-rich sulfur atom of DBT in succession, resulting in the formation of a DBTO$_2$ molecule. According to the literature and our experimental data, the oxidation of DBT to the corresponding sulfone may be explained by the process. The following is the suggested ODS process for sulfur-containing compounds catalyzed by the heterogeneous catalysts Bi$_2$WO$_6$@g-$C_3$N$_4$ and CoWO$_4$@g-$C_3$N$_4$. The active peroxo intermediate species are generated when the oxidizing agent reacts with the metal oxide catalyst in a reversible process. The nucleophilic attack of peroxo species on a sulfur atom changes the aromatic sulfur compound (DBT) in the form of sulfides into the corresponding sulfoxide (DBTO). In the next step, another active peroxo species oxidizes the sulfoxide (DBTO) to the correspondent sulfone (DBTO$_2$). The inclusion of the tungsten aids in the donation of electron density to peroxo species and provides the metal atoms

Figure 4. Energy dispersive X-ray spectroscopy spectrums of g-$C_3$N$_4$, Bi$_2$WO$_6$@g-$C_3$N$_4$ and CoWO$_4$@g-$C_3$N$_4$.

Figure 5. The nitrogen adsorption-desorption curve of the synthesized g-$C_3$N$_4$, Bi$_2$WO$_6$@g-$C_3$N$_4$ and CoWO$_4$@g-$C_3$N$_4$ catalysts.
Figure 6. Comparative studies with or without support via Bi$_2$WO$_6$@g-C$_3$N$_4$ (a) and CoWO$_4$@g-C$_3$N$_4$ (b). Optimization for oxidative desulfurization process: Effect of time (Bi$_2$WO$_6$@g-C$_3$N$_4$ (c) and CoWO$_4$@g-C$_3$N$_4$ (d)), Effect of catalyst loading (Bi$_2$WO$_6$@g-C$_3$N$_4$ (e) and CoWO$_4$@g-C$_3$N$_4$ (f)), Effect of temperature (Bi$_2$WO$_6$@g-C$_3$N$_4$ (g) and CoWO$_4$@g-C$_3$N$_4$ (h)) and Effect of oxidant (Bi$_2$WO$_6$@g-C$_3$N$_4$ (i) and CoWO$_4$@g-C$_3$N$_4$ (j)).
bismuth and cobalt a more nucleophilic nature. The reaction is carried out in a two-phase system in this study. The oxidation and extraction phases are carried out simultaneously in this desulfurization process. The extraction process is quick, and the oxidation process is the rate-determining slow step, according to the findings. Both the oxidation of DBT to its sulfone (DBTO₂) and the extraction of the oxidized DBT take place at the same time. The oxidation of dibenzothiophene takes place at the interface between the oil phase and the extraction phase (acetonitrile). Because of their polarity, the reaction products aggregate in the polar phase, which is advantageous for extraction using an acetonitrile solvent.3,4,39,42,43

The kinetic studies for oxidative desulfurization. The rate of reaction can be determined by the reaction kinetics. The following equation (equation (2)) is used to calculate the rate constant of the reaction.

\[
\ln\left(\frac{C_0}{C}\right) = kt \tag{2}
\]

The reaction mixture has two layers; the upper oily layer contains DBT along with n-hexane and the lower layer consists of the catalyst with an oxidant. The results revealed that the oxidative desulfurization follows first-order kinetics, and a straight line is obtained between \( \ln C_0/C \) versus time of reaction \( (t) \) at 60°C as shown in Figure 8(a) and (b) and Table 1. The trend shows a better result as compared to other metal-based catalysts such as PMoCu@MgCu₂O₄-PVA and Fe₂W₁₈Fe₄@NiO@CTS composites.30,39

Thermodynamics studies. The Eyring equation used to calculate the basic thermodynamic of the reaction system44

\[
\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{3}
\]

This equation is obtained by comparing the following equations45

\[
\Delta G = \Delta H - T\Delta S \tag{4}
\]

\[
\Delta G = -RT\ln K_c \tag{5}
\]

The reaction aspects can be determined by thermodynamic parameters that give information about Gibbs free energy (\( \Delta G \)), entropy (\( \Delta S \)), and enthalpy (\( \Delta H \)) of reaction. The negative value of Gibbs free energy shows that the reaction is spontaneous and thermodynamically feasible, and it can proceed quickly with good desulfurization results.

Figure 6. Continued.
as it is evident from Table 1 and Figure 7(c) and (d). The positive value of enthalpy represents that the reaction is endothermic. The positive value of entropy shows that the thermodynamic feasibility of reaction is due to the increase of entropy, which represents the increase of disorder of the system.

**Comparative study.** Bi$_2$WO$_6$@g-C$_3$N$_4$ and CoWO$_4$@g-C$_3$N$_4$ have shown excellent results with the efficiency of about 91.3% and 84.1% respectively for removal of sulfur molecule (DBT in n-hexane as model fuel) at 60°C in 2 h. As a carrier, g-C$_3$N$_4$ is usually modified with metals inorganic carbon materials, resulting the formation of heterojunctions which increase its electron conduction and catalytic activity. A phosphotungstic acid IL [C$_{12}$mim]$_3$PW$_{12}$O$_{40}$ (C$_{12}$PW) immobilized on the graphitic carbon nitride was reported to exhibit ODS efficiency of 100% for DBT removal.\textsuperscript{27} Rezvani et al. studied the catalytic oxidative desulfurization of model oil by using Fe$_6$W$_{18}$O$_{70}$ clusters and copper ferrite (CuFe$_2$O$_4$) as a catalyst along with H$_2$O$_2$ as an oxidant with 64% efficiency.\textsuperscript{2} Rezvani et al. also used IMID@PMA@CS nanocomposite as catalyst for desulfurization of DBT with optimal conditions and using 3 mL of H$_2$O$_2$ as an oxidizing agent. The catalyst removed the sulfur up to 71% from the model oil.\textsuperscript{46} Nano organic-inorganic hybrid (TBA) 4PW11Fe@TiO$_2$@PVA used as the

**Figure 7.** Oxidative desulfurization mechanism for model fuel oil.

**Table 1.** Kinetics and thermodynamic parameters for desulfurization of dibenzothiophenes at (333 K).

| Catalytic system                  | Pseudo first order kinetics | Thermodynamic parameters |
|-----------------------------------|-----------------------------|--------------------------|
|                                   | $k \times 10^{-3}$ (min$^{-1}$) | $R^2$ | $\Delta G$ (kJ/mole) | $\Delta H$ (kJ/mole) | $\Delta S \times 10^{-2}$ (kJ/mole) |
| Bi$_2$WO$_6$@g-C$_3$N$_4$         | 3.45                        | 0.9926                   | -5.20                   | 1.74                   | 3.002                                |
| CoWO$_4$@g-C$_3$N$_4$             | 6.21                        | 0.9717                   | -8.313                  | 1.849                  | 3.3                                  |
Figure 8. Pseudo first order kinetics of Bi$_2$WO$_6$@g-C$_3$N$_4$ (a) and CoWO$_4$@g-C$_3$N$_4$ (b) and Thermodynamics of Bi$_2$WO$_6$@g-C$_3$N$_4$ (c) and CoWO$_4$@g-C$_3$N$_4$ (d).

Table 2. Comparative study of different metal-based catalysts.

| Materials                          | DBT conc. (mg/L) | Oxidant used (mL) | Kinetics order | Reaction temp. (°C) | Rate of reaction (min$^{-1}$) | DBT removal (%) | Ref   |
|------------------------------------|-------------------|-------------------|----------------|--------------------|-----------------------------|----------------|-------|
| MoO$_2$/g-C$_3$N$_4$ – 550         | 500               | TBHP (0.114 g)    | —              | 80                 | —                           | 100            | 38    |
| WO$_3$/g-C$_3$N$_4$                | 500               | H$_2$O$_2$ (0.3 mL) | —              | 60                 | —                           | 91.2           | 37    |
| V/P-CN                             | 500               | TBHP (0.031 g)    | —              | 40                 | —                           | 100            | 49    |
| PMoV/Fe$_3$O$_4$/g-C$_3$N$_4$      | 500               | H$_2$O$_2$        | —              | 80                 | —                           | >90            | 50    |
| PMoCu@MgCu$_2$O$_4$-PVA            | 500               | H$_2$O$_2$/HOAc (3 mL) | Pseudo first | 35                 | 0.051                       | 99             | 30    |
| (TBA) 4PW11Fe@TiO$_2$@PVA          | 500               | H$_2$O$_2$/HOAc (6 mL) | Pseudo first | 60                 | 0.029                       | 99             | 47    |
| IMID @ PMA @ CS (C$_3$N$_2$H$_5$)$_3$ PMo$_{12}$O$_{14}$/CS | 0.498 (5 wt %) | H$_2$O$_2$/HOAc (3 mL) | Pseudo first | 35                 | 0.049                       | 97             | 46    |
| MoO$_3$/TCN                        | 320               | H$_2$O$_2$, n(O)/n(S) = 4 | —              | 60                 | —                           | 96             | 51    |
| HPW-NH$_2$-CPRNSs                  | 300               | H$_2$O$_2$, n(O)/n(S) = 6 | —              | 60                 | —                           | 98.9           | 48    |
| h-BN                               | 500               | H$_2$O$_2$, n(O)/n(S) = 5 | —              | 80                 | —                           | 99.4           | 26    |
| C$_{12}$PW@g-C$_3$N$_4$            | 500               | H$_2$O$_2$, n(O)/n(S) = 4 | Pseudo first | 60                 | 0.08554                     | 100            | 27    |
| CoWO$_4$@g-C$_3$N$_4$              | 100               | H$_2$O$_2$ (0.6 mL) | Pseudo first | 60                 | 0.00621                     | 84.7           | Present work |
| Bi$_2$WO$_6$@g-C$_3$N$_4$          | 100               | H$_2$O$_2$ (0.6 mL) | Pseudo first | 60                 | 0.00345                     | 91.3           | Present work |

DBT: dibenzothiophenes.
catalyst for the oxidative desulfurization of model oil at optimized conditions with H2O2/HOAc as oxidant (v/v ratio 1:1) with 99% removal efficiency. Recently, heterogeneous catalyst (HPW-NH2-CPRNSs) was reported, the catalyst was prepared by immobilizing phosphotungstic acid on amino grafted phenolic resin nanospheres. The removal rate of DBT removal of 98.9% in 90 min was reported. The comparative study of the metal-based catalysts has revealed that Bi2WO6@g-C3N4 and CoWO4@g-C3N4 have shown good performance in catalytic oxidative desulfurization of sulfur-containing compounds from the model oil using very small amount of H2O2 oxidant. The comparison of current study with reported literature is shown in Table 2.

Conclusions

CoWO4@g-C3N4 and Bi2WO6@g-C3N4 were successfully synthesized by hydrothermal method and first time used for the oxidation of sulfur containing compounds in fuel oil. The catalysts exhibited the outstanding performance for the oxidation of DBT under moderate reaction conditions. The excellent results of catalysts for catalytic activity were attributed to g-C3N4 as support which enhanced porosity, surface area, crystallinity, and active sites. The removal rate of DBT from oil enhanced up to 90% by optimization of reaction parameters which include 0.06 g catalyst dose, 0.6 mL hydrogen peroxide as oxidant, reaction temperature 60°C and 2 h of reaction time. The kinetics studies revealed that the reaction was pseudo-first order with apparent rate constant of 0.00345 min⁻¹ (R² = 0.9926) and 0.00621 min⁻¹ (R² = 0.9717) for Bi2WO6@g-C3N4 and CoWO4@g-C3N4 respectively, while the thermodynamics studies determined that the reaction is endothermic with apparent enthalpy values of 1.74 kJ/mole and 1.849 kJ/mole for Bi2WO6@g-C3N4 and CoWO4@g-C3N4 respectively. This work demonstrated a very good catalytic activity in ODS system for improving the quality of liquid fuel.

Acknowledgements

The authors are grateful to Pakistan Science Foundation for financial assistance under project no. (PSF-NSFC-IV/Chem/C-QAU (27)).

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

The author(s) disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: This study is supported by Pakistan Science Foundation (PSF-NSFC-IV/Chem/C-QAU (27)).

ORCID iD

Amir Waseem https://orcid.org/0000-0001-8414-0374

References

1. Rezvani MA, Khandan S, Sabahi N, et al. Deep oxidative desulfurization of gas oil based on sandwich-type poly-silicotungstate supported β-cyclodextrin composite as an efficient heterogeneous catalyst. Chin J Chem Eng 2019; 27: 2418–2426.

2. Rezvani MA and Imani A. Ultra-deep oxidative desulfurization of real fuels by sandwich-type polyoxometalate immobilized on copper ferrite nanoparticles, Fe6W18O70CuFe2O4, as an efficient heterogeneous nanocatalyst. J Environ Chem Eng 2021; 9: 105009.

3. Bakar WAWA, Ali R, Kadir AAA, et al. Effect of transition metal oxides catalysts on oxidative desulfurization of model diesel. Fuel Process Technol 2012; 101: 78–84.

4. Subhan S, Rahman AU, Yaseen M, et al. Ultra-fast and highly efficient catalytic oxidative desulfurization of dibenzothiophene at ambient temperature over low Mn loaded Co-Mo/Al2O3 and Ni-Mo/Al2O3 catalysts using NaClO as oxidant. Fuel 2019; 237: 793–805.

5. Yu F and Wang R. Deep oxidative desulfurization of dibenzothiophene in simulated oil and real diesel using heteropolyanion-substituted hydrotalcite-like compounds as catalysts. Molecules 2013; 18: 13691–13704.

6. Liu X-Y, Li X-P, and Zhao R-X. Ce2(MoO4)3 as an efficient heterogeneous catalyst. Fuel Process Technol 2012; 101: 78–84.

7. Saeed M, Riaz A, Intisar A, et al. Synthesis, characterization and application of organoclay for adsorptive desulfurization: isothermal, kinetic and thermodynamics studies. Sci Rep 2022; 12: 7362. DOI: 10.21203/rs.3.rs-1208540/v1

8. Wang Q, Zhang T, Zhang S, et al. Extractive desulfurization of fuels using trialkylamine-based protic ionic liquids. Sep Purif Technol 2020; 231: 115923.

9. Shafiq I, Shafiaque S, Akhter P, et al. Recent developments in alumina supported hydrodesulfurization catalysts for the production of sulfur-free refinery products: a technical review. Catal Rev 2020; 64: 1–86.

10. Javadil R and de Klerk A. Desulfurization of heavy oil. Appl Petrochem Res 2012; 1: 3–19. DOI: 10.1007/s13203-012-0006-6

11. Mohd Nazmi NAS, Rosid SJM, Mohd Shukri N, et al. Catalytic oxidative desulfurization of model diesel using TBHP-DMF system. Key Eng Mater 2022; 908: 355–360.
12. Desai K, Dharaskar S, Khalid M, et al. Effectiveness of ionic liquids in extractive–oxidative desulfurization of liquid fuels: a review. Chem Pap 2022; 76: 1–40.

13. Fedorova E, Zhirkov N, Tarakanova A, et al. Oxidative desulfurization of diesel fuel with hydrogen peroxide in the presence of vanadium peroxide complexes. Pet Chem 2002; 42: 253–256.

14. de Angelis A, Pollesel P, Molinari D, et al. Heteropolyacids as effective catalysts to obtain zero sulfur diesel. Pure Appl Chem 2007; 79: 1887–1894.

15. Yang G-C, Pan Q-Y, Yang P, et al. Heteropolyacids supported on hierarchically macro/mesoporous TiO2: efficient catalyst for deep oxidative desulfurization of fuel. Tungsten 2022; 4: 28–37.

16. Mohammadi P. Ionic liquids for desulfurization. In: Ionic liquid-based technologies for environmental sustainability. Amsterdam, Netherlands: Elsevier, 2022, pp. 61–74.

17. Zhou L, Du Y, Jin Y, et al. Grinding-induced solvent-free synthesis of mesoporous zirconia-supported tungsten oxide composite and its superior oxidative desulfurization performance. Fuel 2022; 315: 123181.

18. Saeed M, Munir M, Intisar A, et al. Facile synthesis of a novel Ni-WO3@g-C3N4 nanocomposite for efficient oxidative desulfurization of both model and real fuel. ACS Omega 2022; 7: 15809–15820. DOI: 10.1021/acsomega.2c00886

19. Su T, Chi M, Chang H, et al. Enhanced oxidative desulfurization in fuel liquid in TiO2 quantum dots catalysts modified with anderson-type polyoxometalate. Colloids Surf A 2022; 632: 127821.

20. Zhang Y, Yang W, Yang X, et al. Rational design of efficient polar heterogeneous catalysts for catalytic oxidative-adsorptive desulfurization in fuel oil. Appl Catal A: Gen 2022; 632: 118498.

21. Lukiyanchuk I, Vasilyeva M, Ustinov AY, et al. Ti/TiO2/SiO2 nanospheres as an efficient oxidative desulfurization catalyst. Chem Eng Sci 2022; 248: 117225.

22. Wu P, Lu L, He J, et al. Hexagonal boron nitride: a metal-free catalyst for deep oxidative desulfurization of fuel oils. Green Energy Environ 2020; 5: 166–172, DOI: 10.1016/j.gee.2020.03.004

23. Yu Z, Huang X, Xun S, et al. Synthesis of carbon nitride supported amphiphilic phosphotungstic acid based ionic liquid for deep oxidative desulfurization of fuels. J Mol Liq 2020; 308: 113059, DOI: 10.1016/j.molliq.2020.113059

24. Gonçalves DA, Pinheiro MV, Kramb Brock K, et al. Oxidative desulfurization of dibenzothiophene over highly dispersed Mo-doped graphitic carbon nitride. Chem Pap 2022; 76: 1–12.

25. Liang Q, Shao B, Tong S, et al. Recent advances of melamine self-assembled graphitic carbon nitride-based materials: design, synthesis and application in energy and environment. Chem Eng J 2021; 405: 126951.

26. Rezvani MA, Shaterian M, Akbarzadeh F, et al. Deep oxidative desulfurization of gasoline induced by PMoCu@MgCu2O4-PVA composite as a high-performance heterogeneous nanocatalyst. Chem Eng J 2018; 333: 537–544.

27. Zhou L, Du Y, Zhao Z, et al. Hydrothermal synthesis of mpg-C 3 N 4 and Bi 2 WO 6 nest-like structure nanohybrids with enhanced visible light photocatalytic activities. RSC Adv 2017; 7: 38682–38690.

28. Tian Y, Chang B, Lu J, et al. Hydrothermal synthesis of graphitic carbon nitride–Bi2WO6 heterojunctions with enhanced visible light photocatalytic activities. ACS Appl Mater Interfaces 2013; 5: 7079–7085.

29. Sagadevan S, Podder J, and Das I. Synthesis and characterization of CoWO4 nanoparticles via chemical precipitation technique. J Mater Sci Mater Electron 2016; 27: 9885–9890.

30. Chaves MdJS, de Oliveira Lima G, de Assis M, et al. Environmental remediation properties of Bi2WO6 hierarchical nanostructure: a joint experimental and theoretical investigation. J Solid State Chem 2019; 274: 270–279.

31. Yi H, Qin L, Huang D, et al. Nano-structured bismuth tungstate with controlled morphology: fabrication, modification, environmental application and mechanism insight. Chem Eng J 2019; 358: 480–496.

32. Sahoo S, Behera A, Mansingh S, et al. Facile construction of CoWO4 modified g-C3N4 nanocomposites with enhanced photocatalytic activity under visible light irradiation. Mater Today Proc 2021; 35: 193–197.

33. Zhao R, Li X, Su J, et al. Preparation of WO3@g-C3N4 composites and their application in oxidative desulfurization. Appl Surf Sci 2017; 392: 810–816.

34. Chen K, Zhang X-M, Yang X-F, et al. Electronic structure of heterojunction MoO2/g-C3N4 catalyst for oxidative desulfurization. Appl Catal B: Environ 2018; 238: 263–273.

35. Rezvani MA and Maleki Z. Facile synthesis of inorganic–organic Fe2W18Fe4@NiO@CTS hybrid nanocatalyst induced efficient performance in oxidative desulfurization of real fuel. Appl Organomet Chem 2019; 33: e4895.
oxidation of dibenzothiophene in diesel. J Mater Sci 2018; 53: 15927–15938.

41. Wang D, Qian EW, Amano H, et al. Oxidative desulfurization of fuel oil: part I. oxidation of dibenzothiophenes using tert-butyl hydroperoxide. Appl Catal A: Gen 2003; 253: 91–99, DOI: 10.1016/S0926-860X(03)00528-3

42. Haghighi M and Gooneh-Farahani S. Insights to the oxidative desulfurization process of fossil fuels over organic and inorganic heterogeneous catalysts: advantages and issues. Environ Sci Pollut Res 2020; 27: 39923–39945.

43. Kermani AM, Mahmoodi V, Ghahramaninezhad M, et al. Highly efficient and green catalyst of {Mo132} nanoballs supported on ionic liquid-functionalized magnetic silica nanoparticles for oxidative desulfurization of dibenzothiophene. Sep Purif Technol 2021; 258: 117960.

44. Saeed M, Munir M, Nafees M, et al. Synthesis, characterization and applications of silylation based grafted bentonites for the removal of Sudan dyes: isothermal, kinetic and thermodynamic studies. Microporous Mesoporous Mater 2020; 291: 109697, DOI: 10.1016/j.micromeso.2019.109697

45. Saeed M, Farooq K, Nafees M, et al. Green and eco-friendly removal of mycotoxins with organo-bentonites: isothermal, kinetic, and thermodynamic studies. Clean–soil, Air, Water 2020; 48: 1900427.

46. Rezvani MA, Shaterian M, Shokri Aghbolagh Z, et al. Oxidative desulfurization of gasoline catalyzed by IMID@PMA@ CS nanocomposite as a high-performance amphiphilic nanocatalyst. Environ Prog Sustain Energy 2018; 37: 1891–1900.

47. Rezvani MA, Ogroubeek ZN, Khandan S, et al. Synthesis and characterization of new nano organic-inorganic hybrid (TBA) 4PW11Fe@ TiO2@ PVA as a promising phase-transfer catalyst for oxidative desulfurization of real fuel. Polyhedron 2020; 177: 114291.

48. Zhang Y, Yang W, Yang X, et al. Rational design of efficient polar heterogeneous catalysts for catalytic oxidative-adsorptive desulfurization in fuel oil. Appl Catal A: Gen 2022; 632: 118498. DOI: 10.1016/j.apcata.2022.118498

49. Chen L, Ren J-T, and Yuan Z-Y. Atomic heterojunction-induced electron interaction in P-doped g-C3N4 nanosheets supported V-based nanocomposites for enhanced oxidative desulfurization. Chem Eng J 2020; 387: 124164.

50. Rafiee E and Khodayari M. Synthesis and characterization of PMoV/Fe3O4/g-C3N4 from melamine: An industrial green nanocatalyst for deep oxidative desulfurization. Chin J Catal 2017; 38: 458–468.

51. Wang C, Miao Q, Huang X, et al. Fabrication of various morphological forms of a gC3N4-supported MoO3 catalyst for the oxidative desulfurization of dibenzothiophene. New J Chem 2020; 44: 18745–18755.