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Designing polyoxometalate based hybrid catalysts for efficient removal of hazardous sulfur from fuel *via* heterogeneous oxidative desulfurization

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ABSTRACT

Hydrodesulfurization is a common but less effective technique to remove sulfur content of oils due to severe operating conditions of temperature, pressure and cost. Oxidative desulfurization(ODS) is preferable due to low cost and mild operating conditions. Coupling of the extractive catalytic desulfurization with the ODS give rise to extractive catalytic oxidative desulfurization(ECODS), a more promising for the elimination of sulfur contents of fuel oil. Herein we present by polyoxometalate based hybrids, $[H_2TPP][K_5BVW_{11}O_{40}]\bullet 2CH_3CN\bullet 2H_2O$ (1), $[H_2TPP]_2[K_3BVW_{11}O_{40}]\bullet CH_3CN\bullet 3H_2O$ (2), and $[H_2TPP]_3[KBVW_{11}O_{40}]\bullet 2CH_3CN$ (**3**) for efficient ECODS of hazardous model fuel. These were synthesized by facile method and characterized by elemental analysis, inductive couple plasma, powder X-ray diffraction analysis, thermo-gravimetric/differential thermal analysis, fourier transform infrared, and UV–visible analysis. These polyoxometalate based hybrids contain cations $[H_2TPP]^{2+}$(organic) and $[BVW_{11}O_{40}]^{7-}$(inorganic) with stoichiometric ratios(*i.e.*, 1:1, 2:1, 3:1). The stoichiometry of these hybrids was also established by Job's analysis which agreed well with the results of TG-DTA and elemental analyses. Interestingly, an increase in catalytic efficiency is observed with increase of organic cations. The maximum ~99.5 % conversion of dibenzothiophene at 60 °C after 2 h has been achieved with **hybrid 3** which could be employed up to ten cycles without a significant decrease in efficiency.

Introduction

Desulfurization is an important practice in oil refineries to remove hazardous sulfur compounds from transportation fuel because these compounds get converted into SO_x during combustion which contribute to air pollution, acid rain and also descends the combustion efficiency of transportation fuel [1,2]. It is an essential requirement to clean the fuel oils from sulfur to minimize the sulfur contents (S-contents) up to the international standards across the globe [3]. In order to minimize the S-contents in transportation fuel oils, different strategies have been employed [4,5]. Hydrodesulfurization (HDS) technique is widely active in oil refineries in which, the compounds containing sulfur are converted into hydrogen sulphide (H_2S) after reaction with hydrogen by using catalysts (*i.e.,* Ni-Mo/Al_2O_3 and Co-Mo/Al_2O_3) and resultant H_2S can easily be removed [6,7]. However, some limitations *i.e.*, requirement of hydrogen supply at start and severe operation conditions are associated with this technique which hindered to obtain the zero % S-contents in oil [8,9]. More importantly, this technique is not fruitful to remove heterocyclic S-compounds (benzothiophene, dibenzothiophene and thiophene and their derivatives) due to steric hindrance of surface-etched catalyst. Therefore, more intense reaction conditions (~400 °C, ~20 MPa and active catalyst) are required which causes economic burden as well as oil loss [10,11]. Consequently, alternative techniques *i.e.,* oxidation-/extraction-/adsorption- and bio-desulfurization

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[12–14], are studied among which the oxidative desulfurization (ODS) is more preferable because it operates at mild and simple conditions [4]. Recently, coupling of extractive desulfurization (EDS) with ODS, has gained much attention due to its advantages of operating protocol at low temperature and atmospheric pressure. This method can be used to defeat the limitations of ODS demanding multistep post treatment protocols such as extraction, adsorption, or distillation to get rid of sulfur containing compounds from oils and to avoid of EDS demanding numerous extractions leading to long duration process and expansive utilization of extractants [15]. ECODS is beneficial due to severance of sulfur containing components in a single unit and simultaneous reactions. Furthermore, in ECODS method, sulfur containing components are catalytically oxidized to sulfones under mild conditions and the sulfones are extracted *via* extraction, adsorption, and distillation [16]. Various catalytic systems, *i.e.,* polyoxometalate (POMs), organic acid, solvents, and metal organic frameworks (MOFs) such as Ti-based MOFs have been reported for ODS [17–20]. Among them, POMs as an individual or POMs based catalytic systems have attracted significant attention due to their high efficiency of sulfur removal and their structural stability [8].

POMs, a specific class of discrete metal–oxygen anionic inorganic clusters, can play a key function in various fields of science and technology such as medicine, electro/photo-chemistry and catalysis [17,21,22]. It is due to their structural versatility, greater negative charges and physio-chemical properties [23,24]. The catalytic applications of POM based materials are uprising incessantly because of their stronger acidity and thermal stability [17,21]. However, low surface area (1–10 m^2/g) confined their application in industry [22]. Therefore, different approaches have been adopted to increase the surface area such as immobilizing POMs onto different neutral or acidic materials for instance γ-Al_2O_3/TiO_2, encapsulation into zeolites, metallophthalocyanine, polymers, ionic liquids, polyanilines, graphene composites [12,25–30]. Moreover, the use of solvent-free system consisting of heterogeneous catalysts has also been found successful in oxidative diesel desulfurization [31]. Despite of multiple advantages, some hindrances (such as leaching of POMs from supports and suffering from structural rearrangements of POMs) have been noticed which may decrease the catalytic activity of POMs [22].

On the other hand, porphyrin is found to be the most promising candidate because of its highly conjugated system, stability, flexibility of excited state properties, and versatile structural modifications [32]. This chromophore has been extensively applied in photodynamic therapy, electro-catalysis, solar cells and nonlinear optics [11,33]. Recently, the catalytic application of porphyrin towards desulfurization has gained great interest in various aspects of social benefits and is found to be economic based on its attractive structural properties [34]. A lot of works have been made to design different combinations of porphyrin(s) to study the structure–property relationship between catalytic activity and porphyrin(s) components [24,33]. However, some limitations hindered their applications such as, solubility, structural stability and inert sites of porphyrin. Therefore, the properties of porphyrin can be modulated to achieve high efficiency in catalysis. In this context, such kind of POM(s)-porphyrin(s) fabrications are required which can resolve these issues: (1) solubility problems; (2) to increase their structural stability; (3) to enhance their surface area; (4) to create microenvironment to direct and enhance the reactivity/selectivity. Therefore, in this manuscript, porphyrin-POM hybrid system has been developed which is a first example to study the ODS of model oil to the best of our knowledge. In the current work, three new polyoxometalate (POM) based hybrid compounds, $[H_2TPP][K_5BVW_{11}O_{40}]\bullet 2CH_3CN\bullet 2H_2O$ (1), $[H_2TPP]_2[K_3BVW_{11}O_{40}]\bullet CH_3CN\bullet 3H_2O$ (2), $[H_2TPP]_3[KBVW_{11}O_{40}]\bullet 2CH_3CN$ (**3**) were synthesized by one pot reaction at room temperature. These compounds were composed of different ratios of cation and anion. Thorough investigation of catalytic performance in ODS of model fuel has been performed, involving a variety of factors such as amount of catalyst, reaction temperature, reaction time, amount of H_2O_2 and regeneration of the catalyst.

To date, the catalytic application in desulfurization of model fuel using ECODS method for such kind of porphyrin- POM (H_2TPP-POM) hybrids with special surroundings and bifunctional active sites is not reported.

Experimental

Materials

$[H_2TPP][ClO_4]_2$ (tetraphenylporphyrin perchlorate) and $K_7[BVW_{11}O_{40}]\bullet nH_2O$ (polyoxovanadotungstate denoted as BVW) were prepared according to the reported methods [35]. Dibenzothiophene (DBT) was purchased from Sigma Aldrich. Rest of the solvents and chemicals were also of analytical grade and purchased from Sigma Aldrich.

Synthesis of hybrids 1, 2 and 3

Three organic–inorganic hybrid compounds were prepared by using same method but different mole ratios. Therefore, general method is described here:

$[H_2TPP][ClO_4]_2$ in 10 mL CH_3CN (acetonitrile 99.8 %) and BVW in 10 mL $CHCl_3$ (chloroform 99.5 %) were dissolved separately. The both solutions were mixed with five minutes constant stirring which produced green precipitates. The green powder was filtered through vacuum filtration, washed thoroughly with $CHCl_3$ and CH_3CN to remove the impurities and air dried. Hybrid **1**: Molar ratio (1:1), $[H_2TPP][ClO_4]_2$ (0.0030 mmol, 23.3 mg); BVW (0.0030 mmol, 91.4 mg). Hybrid **2**: Molar ratio (2:1), $[H_2TPP][ClO_4]_2$ (0.0060 mmol, 46.6 mg); BVW (0.0030 mmol, 91.4 mg). Hyrbrid **3**: Molar ratio (3:1), $[H_2TPP][ClO_4]_2$ (0.0090 mmol, 69.9 mg); BVW (0.0030 mmol, 91.4 mg).

Characterization

Perkin-Elmer 240C was used for elemental analyses of H, C, N and ICPS-7500 model of inductively coupled plasma-emission spectrometer (ICP-ES) was used for to analyze the molar ratio of K/V. In this technique, all the samples were dissolved in dilute HCl prior to use. Thermo gravimetric analyses and differential thermal analysis were performed at room temperature and heating @ of 10 °C·min^{-1} on a NETZSCH STA 449C unit. FT-IR data were recorded through (Nicolet) MAGNA-IR 750 spectrophotometer. KBr was used along with sample to make pellet and spectra range 400–4000 cm^{-1} was used. Shimadzu UV-2550 spectrophotometer was used to measure UV–visible with the range of 200–800 nm. The stoichiometry of compounds **1**–**3** were measured through Job's plot analyses experiments. The different sample solutions were prepared by varying molar rations of BVW/porphyrin but keeping constant overall molarity of BVW and porphyrin (*i.e.,* 5×10^{-6} $mol.L^{-1}$). The S-contents were analyzed by Agilent 1100 Series HPLC.

Extraction and catalytic oxidative desulfurization system (ECODS)

Oxidative desulfurization reactions of DBT were performed using $[H_2TPP][K_5BVW_{11}O_{40}]\bullet 2CH_3CN\bullet 2H_2O$ (1), $[H_2TPP]_2[K_3BVW_{11}O_{40}]\bullet CH_3CN\bullet 3H_2O$ (2), and $[H_2TPP]_3[KBVW_{11}O_{40}]\bullet 2CH_3CN$ (**3**) as catalysts to investigate their catalytic performance. Model fuel was prepared by adding Dibenzothiophene (DBT) 0.00406 g

in n-octane (20 g). The resultant clear solution contained 200 ppmw (elemental S/oil) sulfur concentration. This experiment was conducted in 150 mL round-bottom flask with three-necks fitted out with refluxing condenser, and magnetic stirrer with thermometer. All the experiments were operated under controlled temperatures (25, 40, 60 and 80 °C) and with constant 500 rpm speed of vigorous stirring. The constant speed and temperature was controlled by magnetic agitator and thermostatically controlled heating jacket respectively. Then 20 mL acetonitrile was added as an extracting agent. Oxidative desulfurization was started on addition of a particular amount of 30 % H_2O_2 (4 mL, 6 mL, 8 mL, 10 mL, 12 mL and 14 mL respectively) with catalyst dose (20 mg, 40 mg, 60 mg and 80 mg, respectively). Agilent HPLC 1100 Series with C-18 column, length 250 mm, with diameter 4.6 mm was used to monitor the concentration of DBT in octane phase after fixed time intervals. The following formula is used to calculate the DBT removal;

$$\% X_{DBT} = [(C_i - C_t)/C_i \times 100\ ] \quad (1)$$

(C_i) = DBT initial concentration;(C_t) = DBT concentration after t minutes of reaction.

There was no considerable effect of mass and volume therefore these were considered as constants. The catalysts were collected after filtration at the end of the reaction and washed them with extensive water and ethanol. Then the catalysts were kept for drying in oven at 50 °C for 2 h and reused.

Results and discussion

Hybrids 1, 2 and 3

$[H_2tPP][K_5BVW_{11}O_{40}]\bullet 2CH_3CN\bullet 2H_2O$ (1)

Its yield was 73.37 mg, 73 % based on BVW. FT-IR (ν/cm^{-1}, KBr): 778 (s, W-O_c-W), 830 (m, W-O_b-W), 934 (s, W-O_t), 1185 (m, B-O_a), 1140 (sh, B-O_a), 1247 (w, $\delta(C_\beta\text{-H})^{asym}$), 1429 (w, Phenyl), 1464 (m, $\nu(C_a\text{-C})^{sym}$), 3121 (w, $\nu(C_\beta\text{-H})^{p-asym}$), 3154 (w, $\nu(C_\beta\text{-H})^{p-asym}$), 3491 (m, ν(N—H).) UV–vis (DMF): λ^{max} (ε, $mM^{-1}cm^{-1}$) = 415 (53.02), 510 (2.33), 546 (0.97), 590 (0.531), 648 nm (0.39). The molar ratio of K/V determined by ICP elemental analysis was 4.97. Combustion elemental analysis calculated for $C_{24}H_{24}BK_5N_6O_{42}VW_{11}$ (3348 gm): C, 8.61; H, 0.72; N, 2.51 %. Found: C, 8.69; H, 0.77; N, 2.58 %.

$[H_2tPP]_2[K_3BVW_{11}O_{40}]\bullet CH_3CN\bullet 3H_2O$ (2)

Its yield was 75.3 mg 79.8 % based on BVW. FT-IR (ν/cm^{-1}, KBr): 764 (s, W-Oc-W), 819 (m, W-O_b-W), 909 (s, W-Ot), 1076 (w, B-O_a), 1150 (w, B-O_a), 1250 (m, $\delta(C_\beta\text{-H})^{asym}$), 1239 (w, $\delta(C_\beta\text{-H})^{sym}$), 1433 (m, Phenyl), 1561 (m, $\nu(C_a\text{-C})^{p-asym}$), 3091 (w, $\nu(C_\beta\text{-H})^{p-asym}$), 2989 (w, $\nu(C_\beta\text{-H})$), 3444 (m, ν(N—H)). UV–vis (DMF): λ^{max} (ε, $mM^{-1}cm^{-1}$) = 415 (54.82), 510 (2.35), 546 (0.99), 590 (0.533), 648 nm (0.42). The molar ratio of K/V determined by ICP elemental analysis was 2.99. Anal. Calcd. for $C_{42}H_{37}BK_3N_9O_{43}VW_{11}$ (3557 gm): C, 14.18; H, 1.05; N, 3.54 %. Found: C, 14.23; H, 1.11; N, 3.58 %.

$[H_2tPP]_3[KBVW_{11}O_{40}]\bullet 2CH_3CN$ (3)

Its yield was 69.2 mg 80.2 % based on BVW. FT-IR (ν/cm^{-1}, KBr): 751 (s, W-O_c-W), 802 (s, W-O_b-W), 907 (s, W-O_t), 1072 (w, B-O_a), 1027 (m, B-O_a), 1339 (m, $\delta(C_\beta\text{-H})^{asym}$), 1290 (w, $\delta(C_\beta\text{-H})^{asym}$), 1430 (w, Phenyl), 1559 (m, $\nu(C_a\text{-C})^{sym}$), 3057 (w, $\nu(C_\beta\text{-H})^{p-asym}$), 2963(w, $\nu(C_\beta\text{-H})^{p-asym}$), 3428 (m, ν(N—H)). UV–vis (DMF): λ^{max} (ε, $mM^{-1}cm^{-1}$) = 415 (58.33), 510 (2.53), 546 (0.97), 590 (0.61), 648 nm (0.44). The molar ratio of K/V determined by ICP elemental analysis was 0.97. Anal. Calcd. for $C_{64}H_{48}BKN_{14}O_{40}VW_{11}$: C, 20.38; H, 1.53; N, 5.40 %. Found: C, 20.35; H, 1.47; N, 5.38 %.

FT-IR studies

The FT-IR spectra of $[H_2TPP][ClO_4]_2$, BVW, and resultant porphyrin–BVW hybrids (**1–3**) are represented in Fig. 1. The mode numbers and bond assignments are shown in Table 1. In the spectra of hybrids **1–3**, all the C=C, N—H and C—H stretching vibrations related to the benzene ring fall in the range of 1200–1400 cm^{-1} while W–O_b–W, W–O_c–W, W–O_t and B–O_a vibrations in the band region of 700–1200 cm^{-1} [36,37]. The results are indicated that the structures of [BVW] anions and $[H_2TPP]^{2+}$ remain intact in the resulting hybrids. The occurrence of $[H_2TPP]^{2+}$ in the resultant hybrids was further confirmed by the presence of bands intensities at 720–1650 cm^{-1} and near 3350, 3150 cm^{-1} (Fig. 1). By comparing the FT-IR spectra of the resulting hybrids with virgin BVW, the W–O_b–W, W–O_c–W, W–O_t and B–O_a vibrational bands show red-shift in hybrids and show drastic interaction between BVW anion and $[H_2TPP]^{2+}$ [36].

Annotation: symbols *ν* and *δ* denote stretching, in-plane bending modes, respectively. The subscripts *sym* and asym represent the symmetric and asymmetric modes, respectively. Superscript *p* denotes protonated pyrrole. The data in the parentheses are IR data of the corresponding parent BVW.

UV–Visible spectroscopic studies

The UV–vis spectroscopic analysis was used to examine the electronic behavior of the resulting hybrids **1–3**. All three hybrids showed the absorption peaks at 259, 415, 510, 546, 590 and 648 nm (Fig. 2). Two strong peaks at 259 nm, 415 nm and the four weak peaks appeared at 510, 549, 590 and 648 nm were attributed to tungsten-oxygen charge transfer, porphyrin Soret band and Q band respectively [37]. The overall spectral studies showed the presence of $[H_2TPP]^{2+}$ cation and BVW anions structures in the porphyrin-BVW (~H_2TPP-BVW) hybrids which is the indication of successful synthesis. In the spectra, the quenching of peaks intensities at 415 nm for all compounds compared to the precursors clearly showed the strong electronic interaction between the both individual reactants of resultant hybrids in the ground states [38].

Job's plot analysis

The Job's plot analysis method was used to investigate the stoichiometry of hybrids **1–3** by analyzing the absorption changes at 420 nm as shown in Supporting Information **Fig. S1**. In this perspective, the corrected value of absorbance, Y, is defined as [39]:

$$Y = A - C_b(\varepsilon_{Por}X_{Por} + \varepsilon_{POM}X_{POM}) \quad (2)$$

Where, A = absorbance (at 420 nm), C = total concentration [porphyrin + BVW], b = optical path length, X_{Por} = (porphyrin)/C, X_{BVW} = [BVW]/C, ε_{Por} (2.9×105 L mol^{-1} cm^{-1}), ε_{BVW} (5.42×102, 3.35×102 and 4.78×102 L mol^{-1} cm^{-1} for different ratio (*i.e.*, 1, 2, and 3 respectively of BVW) and Y = absorbance deviation of the solution for porphyrin and the different ratio of BVW (Fig. 3). Fig. 3 shows that the formation of the 1:1, 2:1, 3:1 complexes between $[H_2TPP]^{2+}$ and $[BVW_{11}O_{40}]^{7-}$ at three maximum mole fractions i.e., 0.5, 0.55, 0.6 respectively. These results are well matched with the TG-DTA results and elemental analysis results [36].

TGA –DTA studies

The TG-DTA curves showed that hybrids **1–3** has lost all water molecules, lattice solvent and organic part in a single step (Fig. 4). From 28 °C to 500 °C, the hybrid **1** losses 12.8 % weight with exothermal peaks at 357 °C and 436 °C in DTA curve respectively. It is related to two lattice water, two lattice CH_3CN and one

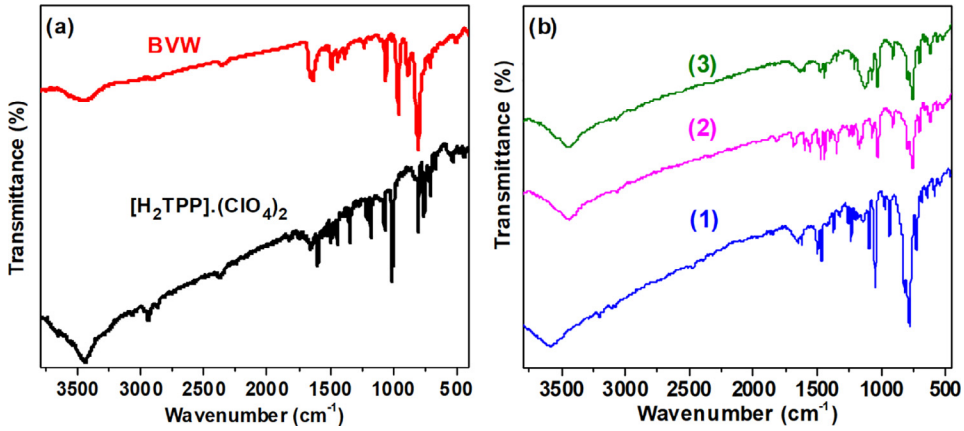


Fig. 1. FT-IR spectra (a) of BVW and $[H_2TPP][ClO_4]_2$ and (b) of compounds **1**, **2** and **3**.

Table 1
FT-IR data of $[H_2TPP][ClO_4]_2$, BVW, and compounds **1** – **3**.

$[H_2TPP][ClO_4]_2$	BVW	Compound **1**	Compound **2**	Compound **3**	Assignment
Wavenumber (cm^{-1})	Wavenumber (cm^{-1})	Wavenumber (cm^{-1})	Wavenumber (cm^{-1})	Wavenumber (cm^{-1})	Wavenumber (cm^{-1})
3449	3427	3491	3444	3428	ν(N—H)
3063, 2934, 2873	3130, 3057, 2917	3153, 3121, 3069	3091, 2989, 2923	3057, 2963, 2940	$\nu(C_\beta\text{-H})^{p}_{asym}$
1483	1485	1465	1561	1559	$\nu(C_a\text{-C})^{sym}$
1450	1446	1429	1433	1430	Phenyl
1237	1227	1247	1250. 1239	1339, 1290	$\delta(C_\beta\text{-H})^{asym}$
-	1077, 1166	1185, 1140	1076, 1150	1072, 1027	B-O_a
-	947	934	909	907	W-O_t
-	869	830	819	802	W-O_b-W
-	791	778	764	751	W-O_c-W

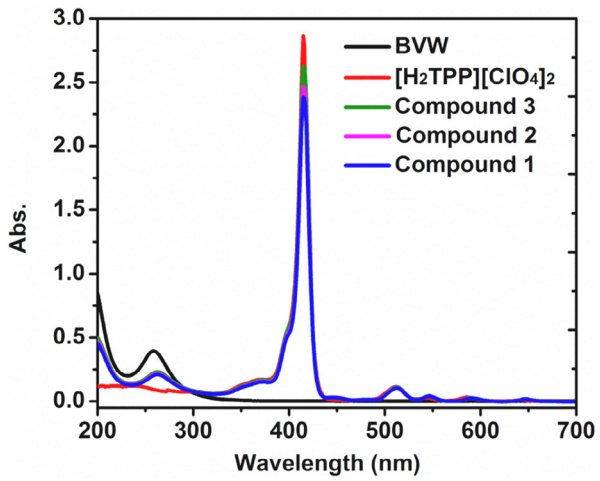


Fig. 2. UV-spectra of BWV, $[H_2TPP][ClO_4]_2$ and compounds **1**, **2** and **3** in DMF with concentration 4.5×10^{-5} $molL^{-1}$.

H_2TPP (calculated value: 12.78 %). Hybrid **2** loses 20.1 % weight in temperature range of 48 °C – 470 °C, related to loss of three CH_3CN, two H_2TPP and one water (calculated value: 20.17 %) with two exothermal peaks corresponding at 384 °C, 469 °C in DTA curve respectively. Hybrid **3** loses 26.83 % weight in the temperature range of 20 °C–480 °C, related to loss of two CH_3CN and three H_2TPP (calculated value: 26.79 %) with exothermal peaks at 386, 470 °C in DTA curve respectively. All the molecular formulas of hybrids **1–3** were matched with the results of element analysis. Fig. 4 clearly shows that $[H_2TPP]^{2+}$ of hybrids (**1–3**) begin to decompose at 265 °C, 287 °C and 322 °C respectively.

Hybrids **1–3** thermo-stability increase in the order: **1** < **2** < **3**, which belong to the strong interaction between BVW anions and the porphyrin cations. The more electrons the BVW anions of the hybrid compounds have the more drastic interaction resulting lower decomposed temperature of the organic part $[H_2TPP]^{2+}$ of H_2TPP-BVW hybrids.

ECOD activity of catalyst

Scheme 1 shows the comprehensive study had been carried out for the S-oxidation of DBT which were dissolved in acetonitrile and oxidizing agents H_2O_2 [40,41]. It is common phenomena previously reported that DBT converts to sulfones through sulfoxides after continuous oxidation in acetonitrile phase. The highly polar sulfones prefer to stay in polar phase. It causes an ease to remove DBT from the nonpolar phase towards the polar phase [42]. It is important to mention here that 55 % of the concentration of DBT remains in n-octane phase by establishment of extraction equilibrium which comes from the HPLC testing results in the non-catalyzed reaction (Fig. 5).

For the sake to get the optimal oxidative desulfurization effect of DBT with the H_2TPP-BVW hybrids (**1–3**) as catalysts, different reaction conditions such as reaction time, catalyst dosage, reaction temperature and H_2O_2/DBT molar ratio (represented as O/S) were investigated. The performances of three hybrids (as catalysts) were investigated to find out the best catalyst among them.

Mechanistic studies

The proposed mechanism is shown in the Fig. 6.

The oxidative desulfurization of model fuel was carried out in the presence of hybrids **1–3**. The hybrids are composed of organic cation part $[H_2TPP]^{2+}$ and inorganic anion part $[BVW_{11}O_{40}]^{7-}$. The inert surrounding of organic cationic linker is reduced by the intro-

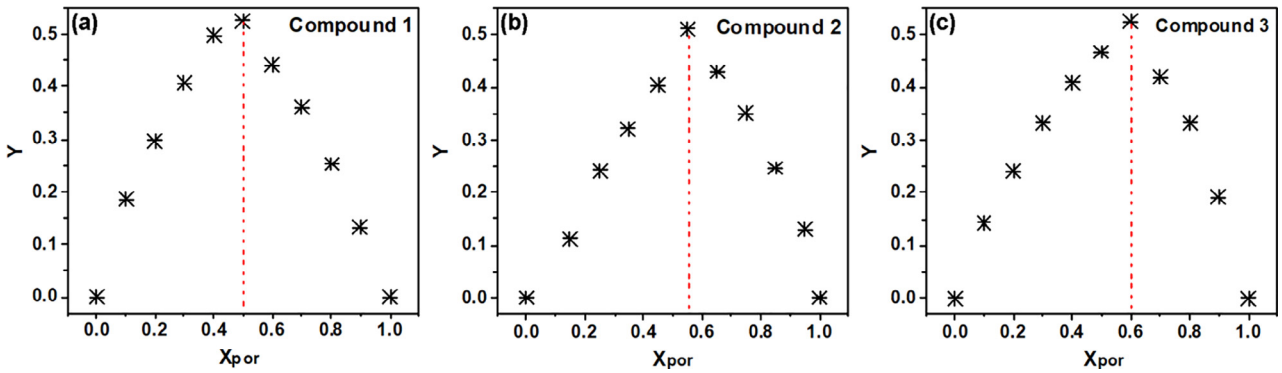


Fig. 3. The graphs for Job's plots analysis of $[H_2TPP]^{2+}[K_5BVW_{11}O_{40}]^{2-}$ (a), $\{[H_2TPP]^{2+}\}_2[K_3BVW_{11}O_{40}]^{4-}$ (b) and $\{[H_2TPP]^{2+}\}_3[KBVW_{11}O_{40}]^{6-}$ (c) at λ = 420 nm. The X_{Por} is shown by red colored dash lines.

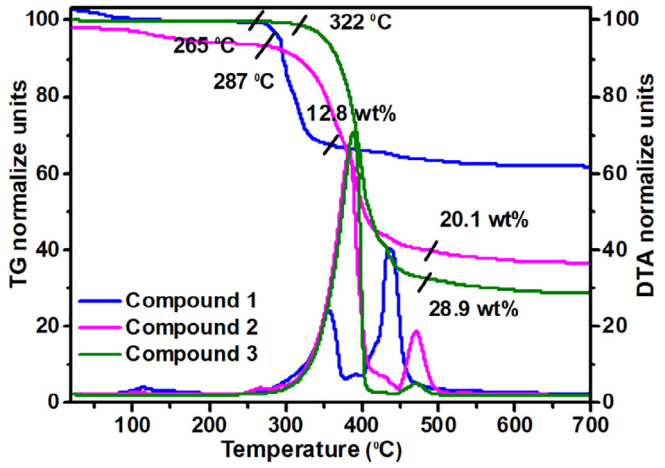


Fig. 4. TG-DTA curves of hybrids **1**–**3**.

duction of inorganic anions $[BVW_{11}O_{40}]^{7-}$. The resultant hybrids caused the enhancement in desulfurization efficiency.

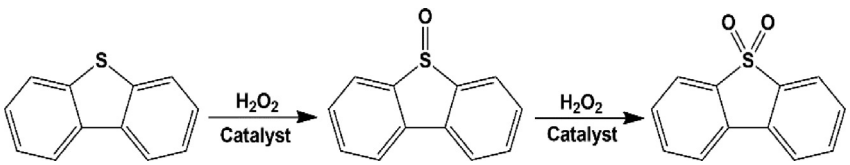
It infers that the $[BVW_{11}O_{40}]^{7-}$ actively takes part in the catalytic efficiency in the oxidation of DBT. The outer layer of $[BVW_{11}O_{40}]^{7-}$ consists of bridging oxygen (W-O_b) and terminal oxygen (W = O_t). In the presence of hydrogen peroxide, the W = O_t is converted into tungsten-peroxo group (W = O_2) Fig. 6. In the presence of excess oxygen, W = O_2 donates its oxygen moiety to DBT by first converting it into DBT oxide and then to DBT sulfone. The tungsten-peroxo groups regenerates in the presence of hydrogen peroxide again [44]. Thus, DBT present in model fuel was converted into DBT sulfone in the presence of prepared hybrid systems. By increasing the ratio of organic cationic linker enhancement of the catalytic efficiency was observed due to following factors, I) the band gaps of resulting compounds were decreased such as {$[BVW_{11}O_{40}]^{7-}$ = 4.27 eV, $[H_2TPP]^{2+}$ = 2.05 eV, (1) = 2.03 eV, (2) = 2.00 eV, and (**3**) = 1.85 eV (Fig. S2 in Supporting Information)}, II) the increase in the synergistic interaction between two moieties (confirmed by Job's plot) and III) due to the electron-transfer from the electron-rich anions towards electron deficient cations [43].

Effect of catalyst dosage

Desulfurization efficiency was examined by using varyious amounts of catalyst dosage. A direct relationship between catalyst dosage and desulfurization efficiency was observed that is; desulfurization increases progressively as catalyst dosage of all hybrids **1**–**3** increase as shown in **Fig. S3** in Supporting Information. The results showed that the desulfurization efficiency reached up to 70.3, 85.5 and 99.5 % for hynrids **1, 2** and **3,** respectively, after 120 minutes reaction proceeding. After 120 minutes, the desulfurization efficiency was not increased significantly. Fig. 7 shows the comparative catalytic efficiencies for H_2TPP- BVW hybrids which is increased in the following order; **1 < 2 < 3**. As the catalyst dosage increased, the available surface area also increased thus providing more active sites for the binding of sulfur components. The desulfurization reached up to maximum when the dosage was increased from 20 to 60 mg. However, on increasing catalyst's dosage beyond 60 mg, the desulfurization efficiency remained constant and no more sulfur is removed further even after increasing the dosage up to 140 mg [45,46]. This implied that there were enough active sites for oxidation of sulfur compounds in the case of 60 mg catalyst's dosage. It is also observed that as the number of porphyrin group is increased in the hybrid the efficiency is also increased which might be due to transformation of electron from porphyrin to BVW. Thus, the optimal supposed catalyst dose is 60 mg which is also beneficial economically and thus employed in rest of experiments of ECOD processes.

Influence of H_2O_2/DBT ratio on removal of DBT

In previous literature, high catalytic activity was shown by various catalysts in ECOD scheme. *e.g.*, Balula et al., [47] Liu Yunqi et al., [48] and Zhang et al., [49] utilized PW9@MIL-101(Cr), PTA@MIL-101 and Cobalt phthalocyanines ($CoPc(Cl)_n$) as catalysts with higher O/S ratios. Due to expensive price of hydrogen peroxide, the catalysts with high O/S were not suitable to use in industrial application. Therefore, it is very important to get the catalyst with low O/S (molar ratio, H_2O_2/DBT) and excellent desul-



Scheme 1. The catalytic reaction mechanism [42].

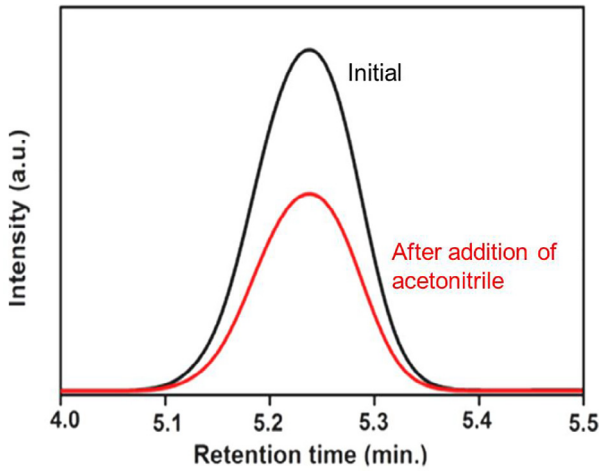


Fig. 5. Liquid chromatograms before addition of the catalyst; {[H_2TPP][$K_5BVW_{11}O_{40}$]•2CH_3CN •2H_2O (**1**), [H_2TPP]$_2$[$K_3BVW_{11}O_{40}$]•CH_3CN•3H_2O (**2**), and [H_2TPP]$_3$[$KBVW_{11}O_{40}$]•2CH_3CN (**3**).

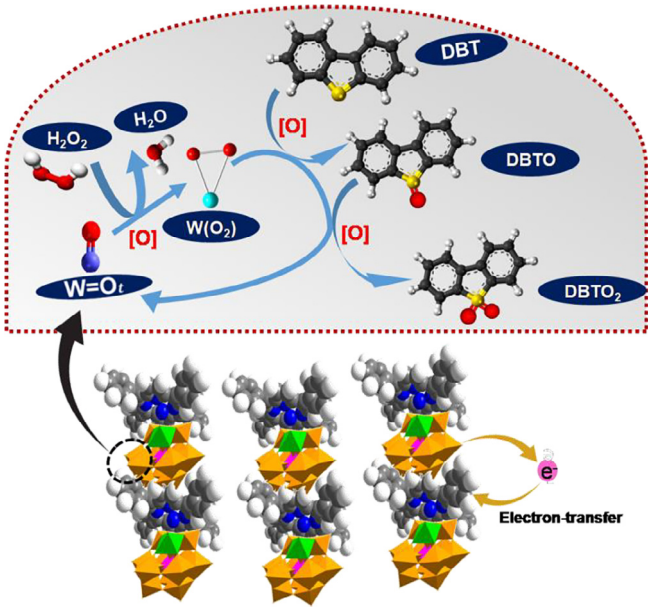


Fig. 6. Proposed mechanism of oxidative desulfurization process.

furization efficiency [47–50]. Therefore, different ratios of O/S are used to study their influence on the oxidative properties (Fig. 8 and **Fig. S4**). It was observed that as the O/S increased from 2 to 8, desulfurization also increased drastically from 65 % to 69.3 % for **1**, 70.3 % to 85.5 % for **2** and 85.5 % to 99.5 % for **3**, after 2 h and after that no further degradation was found. Thus, the most favorable O/S in this procedure is 6:1 and the correspondent efficiency of desulfurization is 70.2 %, 85.2 % and 99.5 % for hybrids **1, 2** and **3** respectively.

Effect of temperature

The effect of various temperatures for S-removal of DBT in n-octane is shown in Fig. 9 and **Fig. S5**. The results clearly showed that desulfurization continuously increases with the increment of reaction time. From temperature 25 to 80 °C, the DBT conversion was also increased from 64.5 % to 71.13 %, 78.5 % to 86.6 % and 87.2 to 99.45 % for hybrids **1, 2** and **3** respectively. However, with further increase in temperature, no considerable effect was

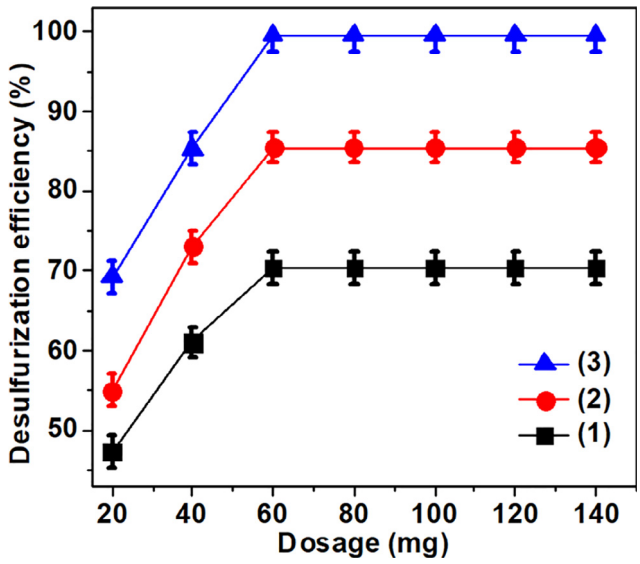


Fig. 7. Comparative studies of desulfurization efficiency with different amount of catalyst dosages (20, 40, 60 80,100, 120 and 140 mg) for hybrids **1–3** under experimental conditions: O/S = 6:1; temperature 60 °C; time 120 minutes.

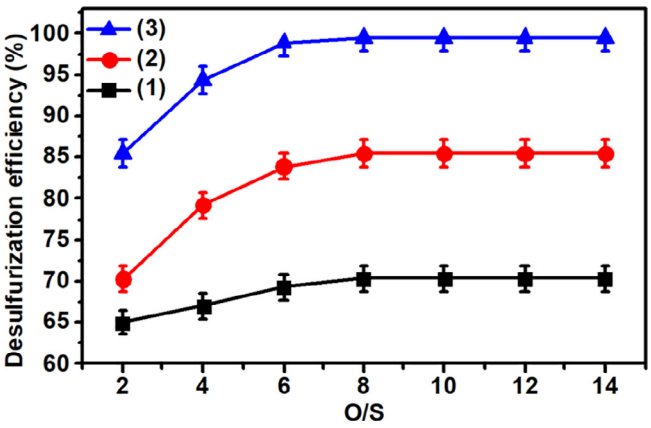


Fig. 8. Desulfurization efficiency of hybrids **1–3** by varying the O/S molar ratios (2:1, 4:1, 6:1 8:1, 10:1, 12:1 and 14:1) under experimental conditions: dosage, 60 mg; temperature 60 °C; time, 120 minutes.

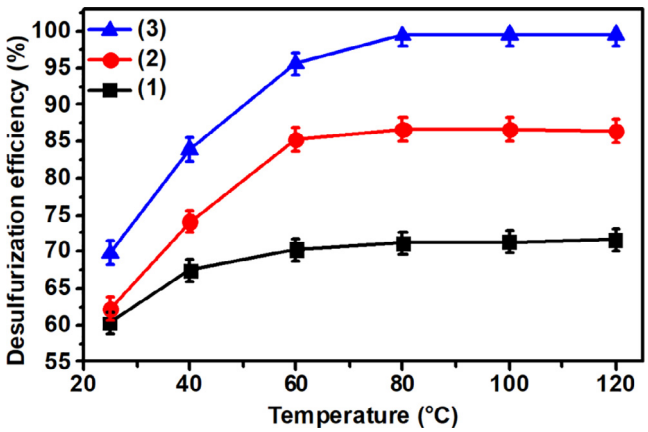


Fig. 9. Effect of temperature on desulfurization efficiency of catalysts **1–3** under experimental conditions: O/S = 6:1; dosage, 60 mg; time, 120 minutes.

observed. This can be assumed that when the temperature of the system was elevated above 80 °C, the self-decomposition of H_2O_2 turned to be more consequential thereby lowering desulfurization efficiency [51,52]. Thus the optimal conditions can be concluded as: (1) reaction time is 120 min, (2) reaction temperature is 80 °C, (3) O/S ration is 6:1 and (4) catalyst dosage is 60 mg. Under these conditions the desulfurization efficiencies were 71.13 %, 86.6 % and 99.45 % for **1, 2** and **3** respectively. The 200 ppmw model fuel decreased to 1.03 ppmw and came in between the range set by the EU standard that is less than 10 ppmw S-content. The catalytic behavior shown by the three catalysts is as follows: hybrid **3** > hybrid **2** > hybrid **1**.

Comparison of catalyst effect of reactant with hybrids 1 – 3

The extractive and catalytic oxidation desulfurization (ECODS) reaction of DBT in model fuel was carried out using $[H_2TPP][ClO_4]_2$, BVW and three hybrids **1–3** for comparison. ECODS reactions were performed at optimal conditions mentioned in previous section and results clearly showed that there is big difference between the desulfurization of virgin $[H_2TPP][ClO_4]_2$, BVW and hybrids **1–3** (Fig. 10). By comparing the hybrids, it is found that desulfurization rate of hybrid **3** (99.5 %) is higher than **2** (85.5 %) than that of hybrid **1** (70.3 %). As a matter of fact, the hybrid **3** exhibited maximum desulfurization *i.e.*, 99.5 % which is rational in comparison to recently reported modified POM novel systems [53–60]. Further Table 2 shows a brief comparison of hybrid 3 with different reported catalysts used in extractive oxidative desulfurization of DBT.

Recycling of used catalysts

Catalyst stability and reusability is another extremely important factor which makes catalyst distinguish and effective in term of industrial utilization. Fig. 11 represents the reusability of hybrid **3** after ten times under selected conditions in which desulfurization efficiencies decrease from 99.5 % to 98 % after ten recycles. This indicates the high stability of catalyst and capability after many cycles to sustain its catalytic activity towards ECODS. Surprisingly, hybrid **3** did not show any considerable change in the IR spectrum before and after 10 time's use of the catalyst (**Fig. S6**). Very small decrease in the catalytic activity can be ascribed to the small loss/dissolution of BVW entities in the ECODS process. The excellent reusability is due to electrovalent bond formed between $[H_2TPP]^{2+}$ cation and $[BVW_{11}O_{40}]^{7-}$ anion that stops the solubilization of resulting hybrids through the catalytic process. In addition besides the stability and better reusability, the catalytic recyclability through decantation method is connected to its millimeter size and elevated mechanical strength.

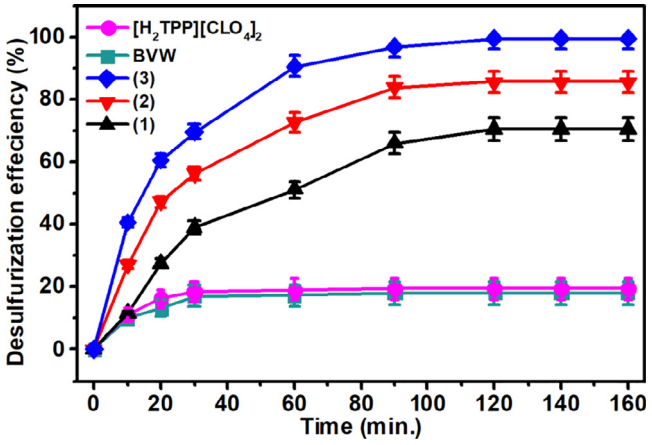


Fig. 10. Comparison of desulfurization efficiency (experimental conditions: dosage, 60 mg, temperature, 60 °C, O/S = 6:1) with loading of reactants and compounds **1–3**.

Table 2
Comparison of reported catalysts used in extractive oxidative desulfurization of DBT.

Catalyst	DBT removal	Reference
Ionic liquid $[C_4VIM]PMoV_2$	98.9 %	[53]
Cu-SPOM@PbO@PVA composite	98 %	[54]
Amine-functionalized PW_9V_3/APTES-CeM-50	99.26 %	[55]
Cobalt tetraphenylporphyrin (CoTPP)	91 %	[56]
N-methyl-pyrrolidone $C_5H_9NO{\cdot}SnCl_2$ coordinated ionic liquid	94.8 %	[57]
phosphonium-based ionic liquid (PIL) trihexyl tetradecyl phosphonium chloride ([THTDP]Cl)	74.98 %	[58]
POM-based 3DOM ZrO_2	88.7 %	[59]
Quaternary ammonium salt of copper II-monosubstituted phosphomolybdate $[(n\text{-}C_4H_9)_4N][PMo_{11}CuO_{39}]$ (TBAPMo$_{11}$Cu) and copper oxide (CuO)	98 %	[60]
Hybrid (POM@Porphyrin)	~99.5 %	This study

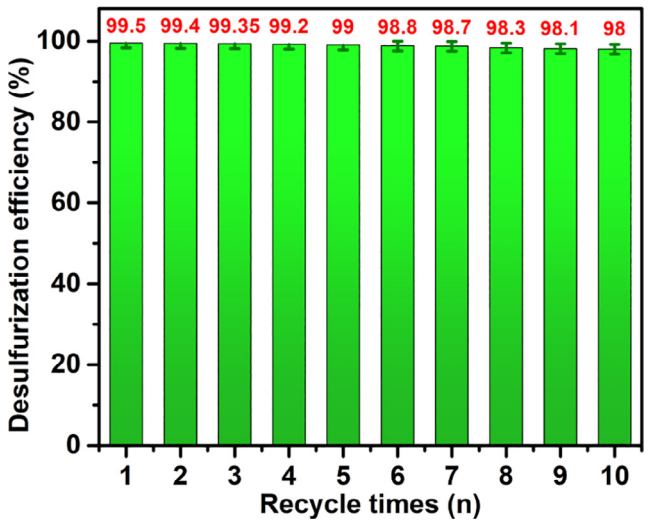


Fig. 11. The reusing ability of compound **3** under experimental condition 60 mg of compound 3, O/S molar ratio = 6:1, time = 120 min and temperature = 60 °C.

Conclusion

In this work, the essential requirement to clean the fuel by minimizing the S-contents within the international standard range has been successfully achieved *via* ECODS process. Firstly, three new polyoxometalate based hybrid compounds **1–3** were successfully synthesized by one pot reaction of $[H_2TPP]^{2+}$ cation (organic) and anion $[BVW_{11}O_{40}]^{7-}$ (inorganic) at room temperature and further used as catalysts in the ECODS process. Series of tests were performed to determine the influence of catalyst dosage, time and temperature. The most interesting feature was observed that as the number of organic cations was increased in the synthesized hybrid compounds, the catalytic efficiency was also increased accordingly. Furthermore, the reusability of randomly selected hybrid **3** displayed tremendous catalytic performance over the attained optimal conditions after many cycles. Consequently, the superior performance of simple system composed of H_2TPP-BVW, acetonitrile and H_2O_2 delineates great catalytic potential for oxidative desulfurization practices. Accordingly, a great mechanism for oxidative desulfurization that has the ability to produce less hazardous and eco-friendly fuels was proposed which may initiate

more insights that could be functional at ordinary conditions for catalytic oxidative desulfurization in order to resolve environmental issues.

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

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jiec.2022.09.034.

References

[1] P. Grange, Catalytic hydrodesulfurization, Catal. Rev. Sci. Eng. 21 (1980) 135–181.
[2] C. Song, An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel, Catal. Today 86 (2003) 211–263.
[3] P. Vasudevan, J.G. Fierro, A review of deep hydrodesulfurization catalysis, Catal. Rev. 38 (1996) 161–188.
[4] R. Abro, A.A. Abdeltawab, S.S. Al-Deyab, G. Yu, A.B. Qazi, S. Gao, et al., A review of extractive desulfurization of fuel oils using ionic liquids, RSC Adv. 4 (2014) 35302–35317.
[5] L. Shi, K. Tin, N. Wong, C. Li, Hydrodesulfur1zation of petroleum components, Pet. Sci. Technol. 17 (1999) 519–533.
[6] Y. Chen, S. Zhao, Y.F. Song, An efficient heterogeneous catalyst based on highly dispersed Na7H2LaW10O36·32H2O nanoparticles on mesoporous silica for deep desulfurization, Appl. Catal. A: Gen. 466 (2013) 307–314.
[7] J. Eßer, P. Wasserscheid, A. Jess, Deep desulfurization of oil refinery streams by extraction with ionic liquids, Green Chem. 6 (2004) 316–322.
[8] R.G. Finke, M.W. Droege, P.J. Domaille, Trivacant heteropolytungstate derivatives. 3. Rational syntheses, characterization, two-dimensional tungsten-183 NMR, and properties of tungstometallophosphates P2W18M4 (H2O) 2O6810-and P4W30M4 (H2O) 2O11216-(M= cobalt, copper, zinc), Inorg. Chem. 26 (1987) 3886–3896.
[9] B. Gates, H. Topsøe, Reactivities in deep catalytic hydrodesulfurization: challenges, opportunities, and the importance of 4-methyldibenzothiophene and 4, 6-dimethyldibenzothiophene, Polyhedron 16 (1997) 3213–3217.
[10] Q. Gu, G. Wen, Y. Ding, K.H. Wu, C. Chen, D. Su, Reduced graphene oxide: a metal-free catalyst for aerobic oxidative desulfurization, Green Chem. 19 (2017) 1175–1181.
[11] B.J. Hamstra, B. Cheng, M.K. Ellison, W.R. Scheidt, Molybdenum (V) on an Oxide String. Synthesis and Structure of the Novel Linear Trinuclear Complex [MoO (TPP)][O– Mo (TPP)– O][MoO (TPP)] ClO4, Inorg. Chem. 38 (1999) 3554–3561.
[12] Y. Gao, L. Cheng, R. Gao, G. Hu, J. Zhao, Deep desulfurization of fuels using supported ionic liquid-polyoxometalate hybrid as catalyst: a comparison of different types of ionic liquids, J. Hazard. Mater. 401 (2021) 123267.
[13] S.S. Shah, I. Ahmad, W. Ahmad, Adsorptive desulphurization study of liquid fuels using Tin (Sn) impregnated activated charcoal, J. Hazard. Mater. 304 (2016) 205–213.
[14] M. Stylianou, I. Vyrides, A. Agapiou, Oil biodesulfurization: a review of applied analytical techniques, J. Chromatogr. B 1171 (2021) 122602.
[15] H. Huang, Z. Zhou, J. Qin, Y. Li, G. Liu, W. Wu, A facile synthesis of mesoporous Mo–Al oxides for desulfurization of dibenzothiophene in the extractive catalytic oxidative desulfurization system, React. Kinet. Mech. Catal. 130 (2020) 363–379.
[16] A. Khodadadi Dizaji, H.R. Mortaheb, B. Mokhtarani, Extractive-catalytic oxidative desulfurization with graphene oxide-based heteropolyacid catalysts: investigation of affective parameters and kinetic modeling, Catal. Lett. 149 (2019) 259–271.
[17] D.E. Katsoulis, A survey of applications of polyoxometalates, Chem. Rev. 98 (1998) 359–388.
[18] K. Leng, Y. Sun, X. Zhang, M. Yu, W. Xu, Ti-modified hierarchical mordenite as highly active catalyst for oxidative desulfurization of dibenzothiophene, Fuel 174 (2016) 9–16.
[19] K. Leng, X. Li, G. Ye, Y. Du, Y. Sun, W. Xu, Ti-containing hierarchical Beta with highly active sites for deep desulfurization of fuels under mild conditions, Catal. Sci. Technol. 6 (2016) 7615–7622.
[20] G. Ye, Y. Gu, W. Zhou, W. Xu, Y. Sun, Synthesis of defect-rich titanium terephthalate with the assistance of acetic acid for room-temperature oxidative desulfurization of fuel oil, ACS Catal. 10 (2020) 2384–2394.
[21] A. Proust, R. Thouvenot, P. Gouzerh, Functionalization of polyoxometalates: towards advanced applications in catalysis and materials science, ChemComm. (2008) 1837–1852.
[22] J.T. Rhule, C.L. Hill, D.A. Judd, R.F. Schinazi, Polyoxometalates in medicine, Chem. Rev. 98 (1998) 327–358.
[23] A. Dolbecq, E. Dumas, C.R. Mayer, P. Mialane, Hybrid organic– inorganic polyoxometalate compounds: from structural diversity to applications, Chem. Rev. 110 (2010) 6009–6048.
[24] S.U. Hassan, H.M. Asif, Y. Zhou, L. Zhang, N. Qu, J. Li, et al., "Closer is better and two is superior to one": third-order optical nonlinearities of a family of porphyrin-Anderson type Polyoxometalate hybrid compounds, J. Phys. Chem. C 120 (2016) 27587–27599.
[25] I. Kozhevnikov, K. Matveev, Homogeneous catalysts based on heteropoly acids, Appl. Catal. 5 (1983) 135–150.
[26] H. Mei, B. Mei, T.F. Yen, A new method for obtaining ultra-low sulfur diesel fuel via ultrasound assisted oxidative desulfurization, Fuel 82 (2003) 405–414.
[27] Y. Nie, C.X. Li, Z.H. Wang, Extractive desulfurization of fuel oil using alkylimidazole and its mixture with dialkylphosphate ionic liquids, Ind. Eng. Chem. Res. 46 (2007) 5108–5112.
[28] E. Pedernera, R. Reimert, N.L. Nguyen, V. Van Buren, Deep desulfurization of middle distillates: process adaptation to oil fractions' compositions, Catal. Today 79 (2003) 371–381.
[29] L. Qin, Y. Zheng, D. Li, Y. Zhou, L. Zhang, Z. Zuhra, Phosphotungstic acid immobilized on amino functionalized spherical millimeter-sized mesoporous γ-Al2O3 bead and its superior performance in oxidative desulfurization of dibenzothiophene, Fuel 181 (2016) 827–835.
[30] J. Li, Z. Yang, S. Li, Q. Jin, J. Zhao, Review on oxidative desulfurization of fuel by supported heteropolyacid catalysts, J. Ind. Eng. Chem. 82 (2020) 1–16.
[31] S.O. Ribeiro, C.M. Granadeiro, P.L. Almeida, J. Pires, M.C. Capel Sanchez, J.M. Campos Martin, et al., Oxidative desulfurization strategies using Keggin-type polyoxometalate catalysts: biphasic versus solvent-free systems, Catal. Today 333 (2019) 226–236.
[32] M. Taniguchi, J.S. Lindsey, Synthetic chlorins, possible surrogates for chlorophylls, prepared by derivatization of porphyrins, Chem. Rev. 117 (2016) 344–535.
[33] S.U. Hassan, Y. Zhou, L. Zhang, Z. Shi, D. Yang, H.M. Asif, et al., Remarkable enhancement in the nonlinear optical responses of porphyrins realized by combination with polyoxometalates via covalent bonding: a case study, J. Phys. Chem. C 120 (2016) 7757–7766.
[34] R. Zhao, J. Wang, D. Zhang, Y. Sun, B. Han, N. Tang, et al., Deep catalytic oxidative desulfurization of model fuel based on modified iron porphyrins in ionic liquids: anionic ligand effect, ACS Sustain. Chem. Eng. 5 (2017) 2050–2055.
[35] Z. Shi, Y. Zhou, L. Zhang, C. Mu, H. Ren, D.U. Hassan, et al., New supramolecular compounds based on porphyrin and polyoxometalate: synthesis, characterization and nonlinear optical and optical limiting properties, RSC Adv. 4 (2014) 50277–50284.
[36] J.W. Blasecki, Of therapy, toxicity and tungstates: The anti-retroviral pharmacology of polyoxometalates, in: M.A. Pope M.T. (Ed.) Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity, Springer, Dordrecht, 1994, pp. 373-385.
[37] X.M. Yan, P. Mei, L. Xiong, L. Gao, Q. Yang, L. Gong, Mesoporous titania–silica–polyoxometalate nanocomposite materials for catalytic oxidation desulfurization of fuel oil, Catal. Sci. Technol. 3 (2013) 1985–1992.
[38] H. Zhang, G. Shan, H. Liu, J. Xing, Preparation of (Ni/W)-γ-Al_2O_3 microspheres and their application in adsorption desulfurization for model gasoline, Chem. Eng. Commun. 194 (2007) 938–945.
[39] Z.D. Hill, P. MacCarthy, Novel approach to Job's method: an undergraduate experiment, J. Chem. Educ. 63 (1986) 162.
[40] J. Li, B. Hu, J. Tan, J. Zhuang, Deep oxidative desulfurization of fuels catalyzed by molybdovanadophosphoric acid on amino-functionalized SBA-15 using hydrogen peroxide as oxidant, Transit. Met. Chem. 38 (2013) 495–501.
[41] B. Heimlich, T. Wallace, Kinetics and mechanism of the oxidation of dibenzothiophene in hydrocarbon solution: oxidation by aqueous hydrogen peroxide-acetic acid mixtures, Tetrahedron 22 (1966) 3571–3579.
[42] J. Campos Martin, M. Capel Sanchez, J. Fierro, Highly efficient deep desulfurization of fuels by chemical oxidation, Green Chem. 6 (2004) 557–562.
[43] L.X. Cai, S.C. Li, D.N. Yan, L.P. Zhou, F. Guo, Q.F. Sun, Water-soluble redox-active cage hosting polyoxometalates for selective desulfurization catalysis, J. Am. Chem. Soc. 140 (2018) 4869–4876.
[44] M.A. Rezvani, M. Shaterian, Z. Shokri Aghbolagh, R. Babaei, Oxidative desulfurization of gasoline catalyzed by IMID@PMA@CS nanocomposite as a high-performance amphiphilic nanocatalyst, Environ. Prog. Sustain. Energy 37 (2018) 1891–1900.
[45] S. Mohsen, Desulfurization of AL-Ahdab crude oil using oxidative processes, J. Eng. 21 (2015) 102–112.
[46] M. Zhang, W. Zhu, S. Xun, H. Li, Q. Gu, Z. Zhao, et al., Deep oxidative desulfurization of dibenzothiophene with POM-based hybrid materials in ionic liquids, Chem. Eng. J. 220 (2013) 328–336.
[47] C.M. Granadeiro, A.D. Barbosa, S. Ribeiro, I.C. Santos, B. de Castro, L. Cunha-Silva, et al., Oxidative catalytic versatility of a trivacant polyoxotungstate incorporated into MIL-101 (Cr), Catal. Sci. Technol. 4 (2014) 1416–1425.
[48] X. Hu, Y. Lu, F. Dai, C. Liu, Y. Liu, Host–guest synthesis and encapsulation of phosphotungstic acid in MIL-101 via "bottle around ship": an effective catalyst for oxidative desulfurization, Microporous Mesoporous Mater. 170 (2013) 36–44.

[49] J. Zhang, J. Li, T. Ren, Y. Hu, J. Ge, D. Zhao, Oxidative desulfurization of dibenzothiophene based on air and cobalt phthalocyanine in an ionic liquid, RSC Adv. 4 (2014) 3206–3210.
[50] M. José da Silva, L. Faria dos Santos, Novel oxidative desulfurization of a model fuel with H_2O_2 Catalyzed by AlPMo12O40 under phase transfer catalyst-free conditions, J. Appl. Chem. 2013 (2013) 1–7.
[51] J. Zhu, P. Wu, L. Chen, J. He, Y. Wu, C. Wang, et al., 3D-printing of integrated spheres as a superior support of phosphotungstic acid for deep oxidative desulfurization of fuel, J. Energy Chem. 45 (2020) 91–97.
[52] A. Akopyan, E. Eseva, P. Polikarpova, A. Kedalo, A. Vutolkina, A. Glotov, Deep oxidative desulfurization of fuels in the presence of brönsted acidic polyoxometalate-based ionic liquids, Molecules 25 (2020) 536.
[53] M. Zhang, J. Liu, H. Li, Y. Wei, Y. Fu, W. Liao, et al., Tuning the electrophilicity of vanadium-substituted polyoxometalate based ionic liquids for high-efficiency aerobic oxidative desulfurization, Appl. Catal. B 271 (2020) 118936.
[54] M.A. Rezvani, N. Khalafi, Deep oxidative desulfurization of real fuel and thiophenic model fuels using polyoxometalate-based catalytic nanohybrid material, Mater. Today Commun. 22 (2020) 100730.
[55] C. Wang, Z. Liu, R. Gao, J. Liu, S. An, R. Zhang, et al., Deep oxidative desulfurization of model fuels catalyzed by polyoxometalates anchored on amine-functionalized ceria doped MCM-41 with molecular oxygen, New J. Chem. 44 (2020) 6251–6260.
[56] D. Tripathi, I. Yadav, H. Negi, R.K. Singh, V.C. Srivastava, M. Sankar, Highly efficient Co(II) porphyrin catalysts for the extractive oxidative desulfurization of dibenzothiophene in fuel oils under mild conditions, J. Porphyr. Phthalocyanines 25 (2020) 24–30.
[57] F.-T. Li, C.-G. Kou, Z.-M. Sun, Y.-J. Hao, R.-H. Liu, D.-S. Zhao, Deep extractive and oxidative desulfurization of dibenzothiophene with $C_5H_9NO{\cdot}SnCl_2$ coordinated ionic liquid, J. Hazard. Mater. 205–206 (2012) 164–170.
[58] K. Desai, S. Dharaskar, J. Pandya, S. Shinde, Ultrasound-assisted extractive/oxidative desulfurization of oil using environmentally benign trihexyl tetradecyl phosphonium chloride, Environ. Technol. Innov. 24 (2021) 101965.
[59] Y. Du, L. Zhou, Z. Liu, L. Yang, Polyoxometalate-based 3DOM ZrO_2 material for deep oxidative desulfurization of DBT with ultrahigh stability, J. Porous Mater. 28 (2021) 109–116.
[60] Z. Shokri Aghbolagh, M.R. Khanmohammadi Khorrami, M.S. Rahmatyan, Oxidative desulfurization and denitrogenation of simulated fuels catalyzed by TBAPMo11Cu@CuO as a high-performance and recoverable heterogeneous phase-transfer catalyst, Energy Fuels 34 (2020) 16366–16380.