Original research article

Mixing-assisted oxidative desulfurization of model sulfur compounds using polyoxometalate/H_2O_2 catalytic system

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ABSTRACT

Desulfurization of fossil fuel derived oil is needed in order to comply with environmental regulations. Dibenzothiophene and benzothiophene are among the predominant sulfur compound present in raw diesel oil. In this study, mixing-assisted oxidative desulfurization of dibenzothiophene and benzothiophene were carried out using polyoxometalate/H_2O_2 systems and a phase transfer agent. The effects of reaction time (2—30 min) and temperature (30—70 °C) were examined in the oxidation of model sulfur compounds mixed in toluene. A pseudo first-order reaction kinetic model and the Arrhenius equation were utilized in order to evaluate the kinetic rate constant and activation energy of each catalyst tested in the desulfurization process. Results showed the order of catalytic activity and activation energy of the different polyoxometalate catalysts to be $H_3PW_{12}O_{40} > H_3PM_{12}O_{40} > H_4SiW_{12}O_{40}$ for both dibenzothiophene and benzothiophene.

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1. Introduction

In the last three decades, the consumption of fossil fuel derived-oil drastically increased in demand due to rapid technological advancements and increasing world population. Moreover, heat and power generation in various sectors currently uses fossil fuels that would result in risking the stability and sustainability of the environment [1—3]. The use of fossil fuels such as petroleum and its fraction contains organic sulfur compounds (OSCs) which possess an environmental concern. OSCs in untreated diesel oil composed mainly of dibenzothiophene (DBT), benzothiophene (BT) and its alkylated derivatives [4]. In transportation fuels, upon combustion OSCs contributes to corroding parts of internal combustion in engines and poisoning catalytic converters. The presence of OSCs also leads to the formation of sulfur oxides (SO_x) and sulfate particulate matters which is a major source of air pollution [4—6]. SO_x is also known as a major precursor to acid rain as well as secondary particulate matter which adds up to the importance of desulfurization. Therefore, stringent environmental regulations are implemented in recent years. The United States Environmental Protection Agency has set regulations to reduced sulfur content in gasoline and diesel oil to 30 [7] and 15 ppm [8], respectively. European Union issued sulfur concentrations regulation of 10 ppm in diesel oil [9].

The conventional technology, hydrodesulfurization (HDS), is used as a large-scale chemical process in industries to produce low-sulfur diesel fuel [10]. The process of HDS utilizes hydrogen with a catalyst such as Ni—Mo or Co—Mo in heated oil [11]. The C—S bond in HDS breaks which produces H_2S and a sulfur free hydrocarbon. However, there are several problems present in HDS. First, this process has low reactivity towards OSCs such as DBT and BT [4,12]. Second, severe reaction conditions such as high operating pressure (690—3450 kPa), reaction temperature (300—400 °C) and a long residence time are required to achieve low sulfur concentrations in HDS. Consequently, this implies that HDS requires high operating cost in order to comply with low-sulfur containing diesel fuel. Alternative desulfurization processes or techniques are of necessity in order to complement the conventional technology into achieving an efficient way upon compliance to environmental regulations.

Oxidative desulfurization (ODS) has drawn significant attention in recent years due to its capacity to operate at mild operating conditions as compared to HDS [2]. In the ODS process, OSCs can be selectively oxidized to form sulfones (1-oxides) and/or sulfoxides (1,1-dioxide) without breaking the C—C bond due to the strong

affinity of sulfur towards the electrophilic addition of oxygen [13,14]. Oxidized sulfur compounds are substantially more polar compared to the hydrocarbons which can easily be removed through adsorption, solvent extraction or distillation. To date, various oxidants and/ or oxidation systems such as Fenton's reagent [15], ferrate [16,17], hydrogen peroxide [4,10,18,19], ozone [20] and superoxides [21] have been investigated. Hydrogen peroxide (H_2O_2) is preferred over the other oxidation systems due to its oxidation capacity, low cost, and environment friendly water by-product formation. However, an important consideration upon using H_2O_2 in fuel oil is its formation of a biphasic system. This requires attention in order to further improve desulfurization performance.

The ultrasound-assisted oxidative desulfurization (UAOD) is a well-established technology in which the oxidation efficiency is enhanced through the use of an ultrasonicator as compared to conventional ODS process [2,4,10,15,16,18]. However, several disadvantages of UAOD such as the difficulty to up-scale in industries due to high energy utilization and high capital cost due to additional sono-reactor, amplifier and function generator remain its limitation [18]. Lu et al. [18] showed an alternative process to UAOD in which a high shear mixer is utilized and showed desulfurization efficiencies matching that of an ultrasonicator. This process is called mixing-assisted oxidative desulfurization (MAOD). The development of this innovative desulfurization technology improves the efficiency of the ODS process. MAOD has shown a promising and efficient oxidation reaction performance [18,22,23]. Using H_2O_2 requires good dispersion between the organic and aqueous phase in order to accelerate oxidation reaction. The MAOD process essentially provides an enhanced fluid/ fluid interfacial area through molecular diffusion due to the utilization of a high-shear mixer. The organic phase can easily breakdown to smaller droplets which improves the mass transfer to the oxidant or aqueous phase [24]. Rapid mixing provides an adequate contact between the biphasic system which improves the desulfurization in ODS.

In recent years, polyoxometalate (POM) catalysts have shown to attract wide attention due to being a well-known green catalyst and its effective combination with H_2O_2 in the ODS process [4,10,13,18,22,25,26]. POMs contain early transition metal-oxygen clusters anions. There are a wide variety of applications in POMs but catalysis is considerably the most important [26]. However, the application of different POM catalysts in the MAOD process has not yet been report. Furthermore, there is also limited information in the comparative assessment of the oxidation kinetics for DBT and BT in MAOD.

The main objective of this study is to determine and compare oxidation performance of DBT and BT compounds using different POM/H_2O_2 systems at different reaction time and temperature. Various POM catalysts to be investigated include phosphotungstic acid (PW), phosphomolybdic acid (PMo), and silicotungstic acid (SiW). Furthermore, the kinetic rate constant and activation energy of the different POM catalysts were determined through a kinetic model and Arrhenius equation, respectively.

2. Materials and methods

2.1. Chemicals and materials

Chemicals used were analytical grade without further purification treatment. The model sulfur compounds BT (97% purity) and DBT (99% purity) were procured from Acros Organics (Taiwan) and Alfa Aesar (Taiwan), respectively. Toluene (0.99 mass fractions) was purchased from Merck (USA). Tetraoctylammonium bromide (98% purity) was acquired from Hungyao (Taiwan). Hydrogen peroxide (50% concentration) and PW hydrate ($H_3PW_{12}O_{40}$, 98% purity) were obtained from G-Watt Co. (Taiwan). PMo ($H_3PM_{12}O_{40}$) was obtained from Ferak Berlin GmbH (Germany) while SiW ($H_4SiW_{12}O_{40}$, 99.9% purity) was procured from Sigma−Aldrich (Wisconsin, USA).

2.2. Experimental method

Synthetic oil containing model sulfur compounds of DBT and BT were dissolved separately in toluene in order to acquire a 500 ppm stock solution. The MAOD experiments were carried out using a glass reactor adding equal amounts of synthetic oil and hydrogen peroxide along with tetraoctylammonium bromide and 0.0694 mmol of POM catalyst. The catalyst loading was based on the study of Wan et al. [27]. The mixture was agitated at 10,000 rpm from 2 to 30 min using a high-shear mixer (IKA Ultra Turrax T25 digital). Reaction temperature was maintained by a water bath from 30 to 70 °C. This is to test the oxidation capacity of the MAOD process from ambient temperature of 30 °C up to a limit of 70 °C in order to avoid side reactions due to H_2O_2 thermal decomposition [28,29]. After cooling, the emulsified samples were subjected to centrifugation for 10 min in order to separate the emulsion. The organic phase containing the synthetic oil was drawn out for further analysis.

2.3. Instrumental analysis

A gas chromatography (Agilent GC, 7890A, California, USA) is coupled with a sulfur chemiluminescence detector was used to detect the presence of sulfur compounds in the sample before and after oxidation. The initial GC oven temperature was set at 150 °C for 1 min, heated at a rate of 20 °C min^{-1} to 220 °C and retained for 1 min for the analysis of BT. Concurrently, the column temperature setting for the analysis of DBT was set at 200 °C for 1 min and then heated at a rate of 20 °C min^{-1} to 280 °C for 1 min.

3. Results and discussion

3.1. Catalytic oxidation of sulfur compounds

POMs containing transition metals like Ti, Mo, V and W are effective catalysts used in conjunction with H_2O_2. The derivatives of the transition metals readily react with H_2O_2 that forms peroxocomplexes in the system [30]. The peroxocomplexes are stronger oxidants than the parent peroxides and result to be highly selective and effective oxidants of both substrates that are organic and inorganic [30]. The electron density for the oxidation of sulfur atom using H_2O_2 at mild conditions is from 5.716 to 5.739 [31]. This makes the oxidation of DBT and BT possible due to having an electron density of 5.739 and 5.758, respectively [31].

The oxidation of DBT and BT in the POM/H_2O_2 system of the MAOD process involves the following mechanism. In the aqueous phase, the presence of excess H_2O_2 reacts with the POM catalyst. This is peroxidized and disaggregated forming peroxocomplexes that are effective species for expoxidation [4,27]. The tetraoctylammonium bromide used as the phase transfer agent (PTA) brings the peroxocomplexes to the organic phase which activates the oxidation reaction of DBT and BT. The peroxocomplexes are reduced to its original form after oxidation and dissociates with PTA which are transferred back to the aqueous phase.

3.2. Comparison of POM catalysts

The MAOD process was applied in the oxidation of model sulfur compounds DBT and BT to compare different POM catalysts. The catalyst loading was based from a previous study where the

amount of PW catalyst was varied from 0 to 0.2 g [27]. Optimum results showed highest desulfurization efficiency at 0.2 g or 0.0694 mmol due to introducing more peroxometal complex to oxidize sulfur compounds [27]. The amount for each POM catalyst in this study was fixed at 0.0694 mmol in order to maintain consistent catalyst dosage and appropriately compare oxidation performances of various commercially available POM catalysts.

Results show that the PW catalyst has the highest oxidation performance for both DBT and BT (Figs. 1 and 2). The PMo and SiW catalysts conversely has a lower sulfur conversion for both DBT and BT in comparison to the PW catalyst. Phosphorus as the central atom has shown dominant oxidation capacity over the silicon based catalysts counterpart [32]. This is due to the formation of more stable peroxometal complex that favors oxidation reaction in sulfur compounds. For the comparison of PW and PMo, it is noted that PW has a lower oxidation potential than that of PMo [33]. This implies that PW is less sensitive to reduction than PMo catalyst which favors the occurrence of oxidation reactions in sulfur compounds.

3.3. Effect of reaction time and temperature

The reaction time for high-shear mixing concerns the contact time between the sulfur compound DBT or BT to the POM/H_2O_2 systems [18]. Increasing the mixing time would lead to higher oxidation performances as shown in Figs. 1 and 2. This is due to a longer emulsification reaction between the oxidizing agent (aqueous phase) and the sulfur compound (organic phase). Therefore, longer reaction time promotes more efficient sulfur to sulfone formation due to the electrophilic addition of oxygen to the sulfur compound.

Increasing the reaction temperatures for the three systems evaluated consistently promotes higher oxidation reactions for both DBT and BT. This is due to the formation of more peroxometal complexes that has a higher oxidation activity than that of the H_2O_2 alone [19]. At 70 °C, it is observed that DBT and BT can be easily oxidized using the PW/H_2O_2 system. While PMo/H_2O_2 and SiW/H_2O_2 systems can moderately and weakly oxidize sulfur compounds, respectively. This implies the dominance of PW as the catalyst of choice for oxidizing sulfur compounds.
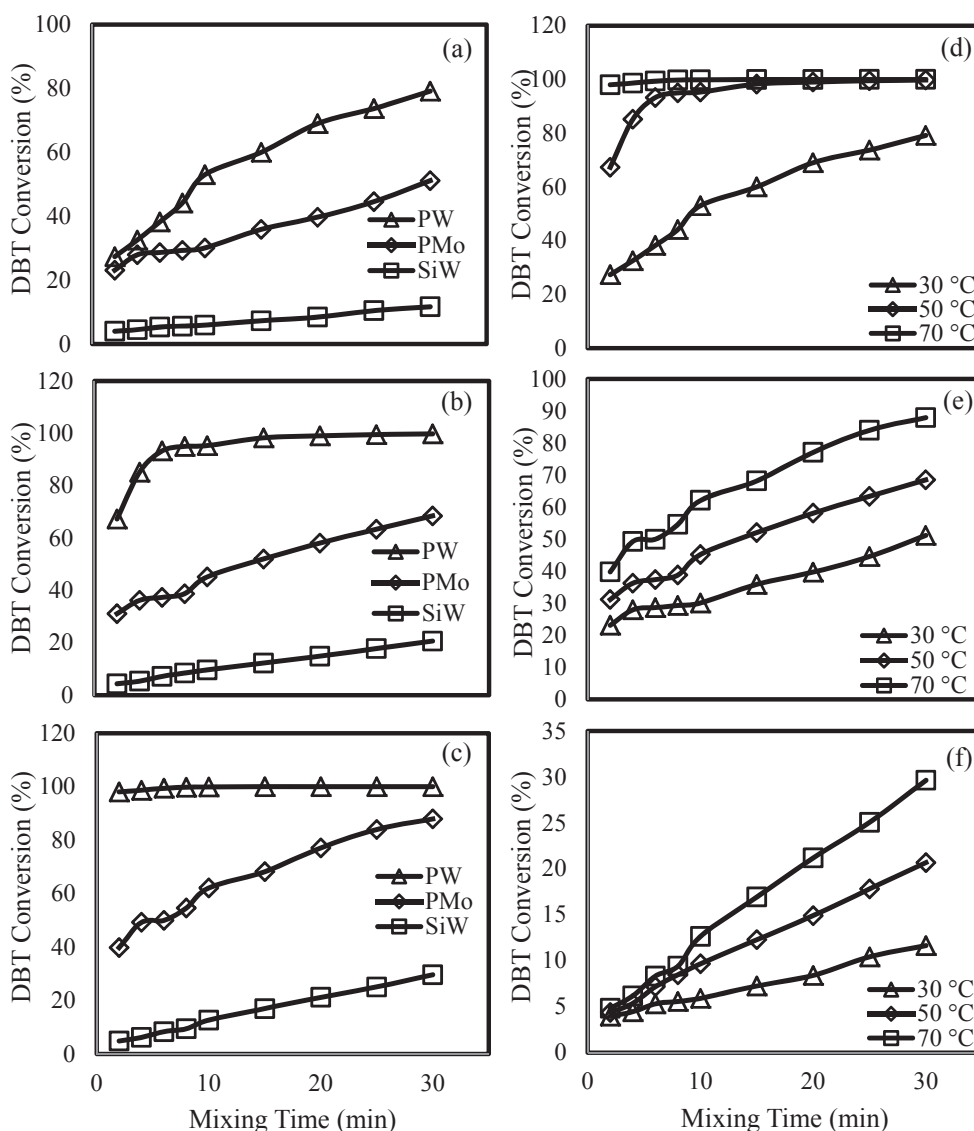

Fig. 1. Oxidation of dibenzothiophene based on different reaction temperatures: (a) 30 °C, (b) 50 °C and (c) 70 °C and polyoxometalate catalysts: (a) PW, (b) PMo and (c) SiW.
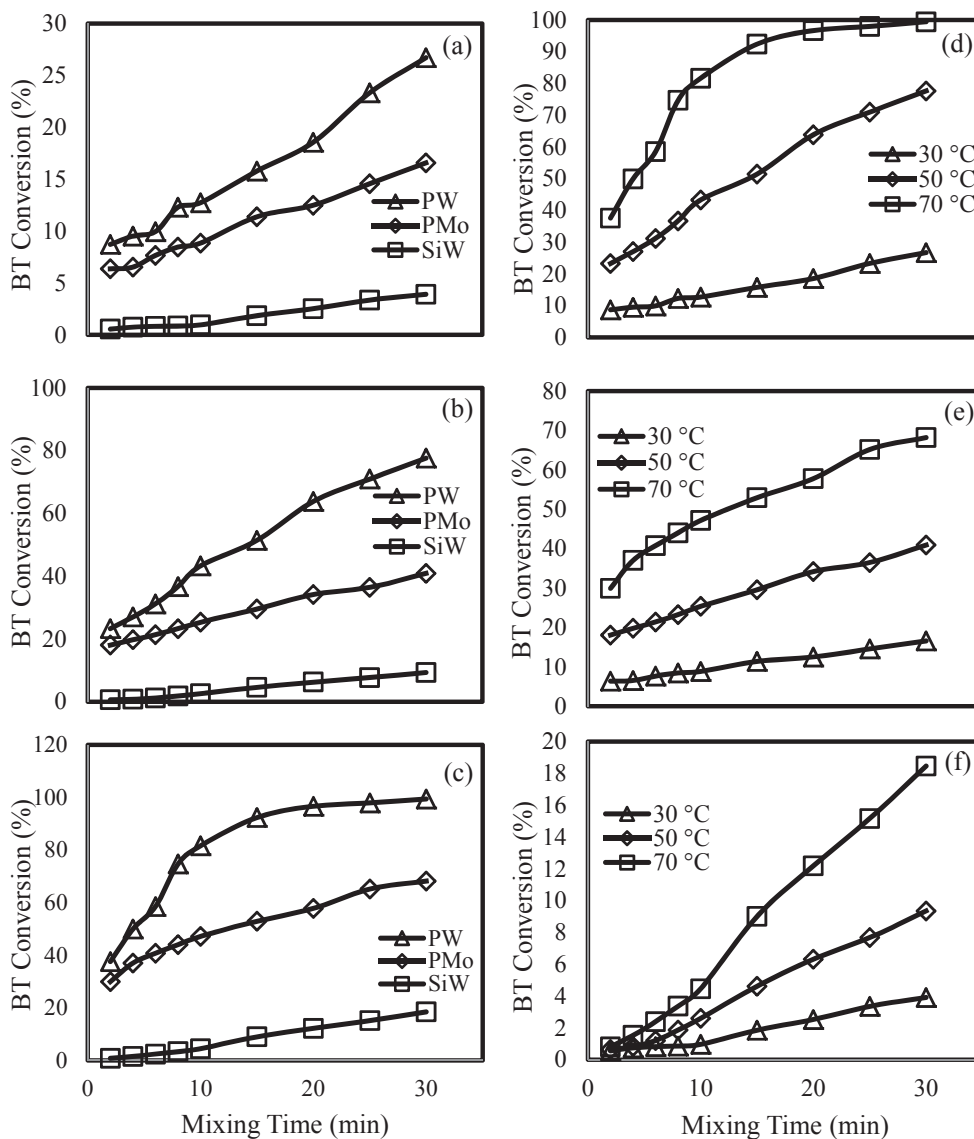
Fig. 2. Oxidation of benzothiophene based on different reaction temperatures: (a) 30 °C, (b) 50 °C and (c) 70 °C and polyoxometalate catalysts: (a) PW, (b) PMo and (c) SiW.
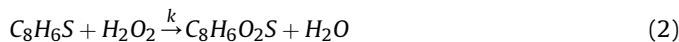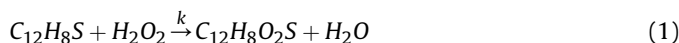
3.4. Kinetic study

The kinetics for the oxidation of DBT ($C_{12}H_8S$) and BT (C_8H_6S) were examined using the chemical reactions in Eqs. (1) and (2), respectively.

$$C_{12}H_8S + H_2O_2 \xrightarrow{k} C_{12}H_8O_2S + H_2O \quad (1)$$

$$C_8H_6S + H_2O_2 \xrightarrow{k} C_8H_6O_2S + H_2O \quad (2)$$

For the utilization of a solid catalyst, oxidation of aromatic sulfur compounds such as DBT and BT follows pseudo-first order kinetics [18,27,32]. Assuming that the amount of H_2O_2 was taken in excess and the change of H_2O_2 concentration compared to the change of the DBT or BT concentration was negligible. Hence, the term that is dependent on H_2O_2 concentration has been neglected. Therefore, the catalytic oxidation reaction of DBT or BT is considered to be as a pseudo-first-order which is shown in Eq. (3).

$$\ln \frac{[C]_o}{[C]_t} = kt \quad (3)$$

where $[C]_o$ and $[C]_t$ denotes the initial concentration and concentration at a given time for the model sulfur compound, respectively, and k is the apparent rate constant for the catalytic oxidation reaction of DBT or BT.

Results (Figs. 3 and 4) show high coefficient of correlation between 0.970 to 0.998 for DBT oxidation and 0.975 to 0.997 for BT oxidation. This suggests that the pseudo-first-order reaction kinetics is highly suitable to describe the oxidation activity of DBT and BT. Table 1 summarizes the kinetic constant of DBT and BT. It is consistently observed that using PW as the catalyst for oxidation exhibits the highest kinetic rate constant at different temperatures. The kinetic rate constant for the oxidation DBT is higher than that of BT. This is due to a lower electron density of BT that makes its electrons more compact which hinders the occurrence of oxidation reaction [34].
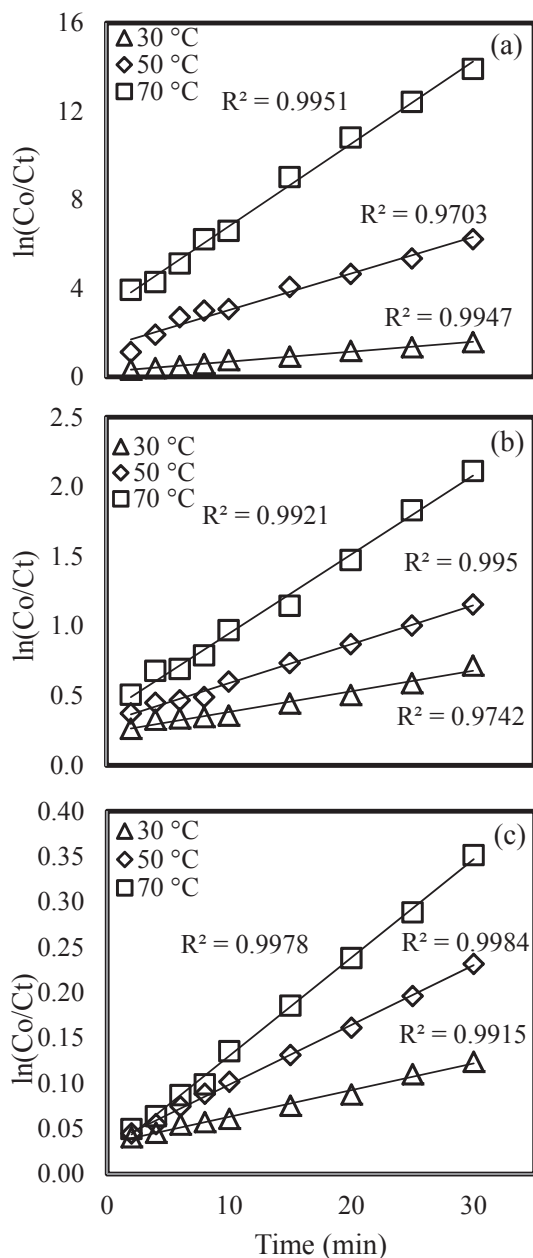
Fig. 3. Oxidation kinetics of dibenzothiophene using (a) PW, (b) PMo and (c) SiW catalysts.

Fig. 4. Oxidation kinetics of benzothiophene using (a) PW, (b) PMo and (c) SiW catalysts.

The activation energy is obtained through the use of the Arrhenius equation shown in Eq. (4).

$$\ln k = -\frac{E_a}{R}\frac{1}{T} + \ln A \tag{4}$$

where E_a, R, T and A are the activation energy, gas constant, reaction temperature and pre-exponential factor, respectively.

Fig. 5 illustrates the Arrhenius plot of -lnk vs $1/T$ for DBT and BT. High coefficient of correlation is observed ranging from 0.990 to 0.996 and 0.998 to 0.999 for DBT and BT, respectively. This strongly suggests that the Arrhenius plot is well suitable to predict the activation energy of DBT and BT using different POM catalysts.

Table 2 summarizes the activation energy of the different POM catalysts used to oxidize DBT and BT. Results showed lower activation energy in DBT than that of BT which reiterates the ease of
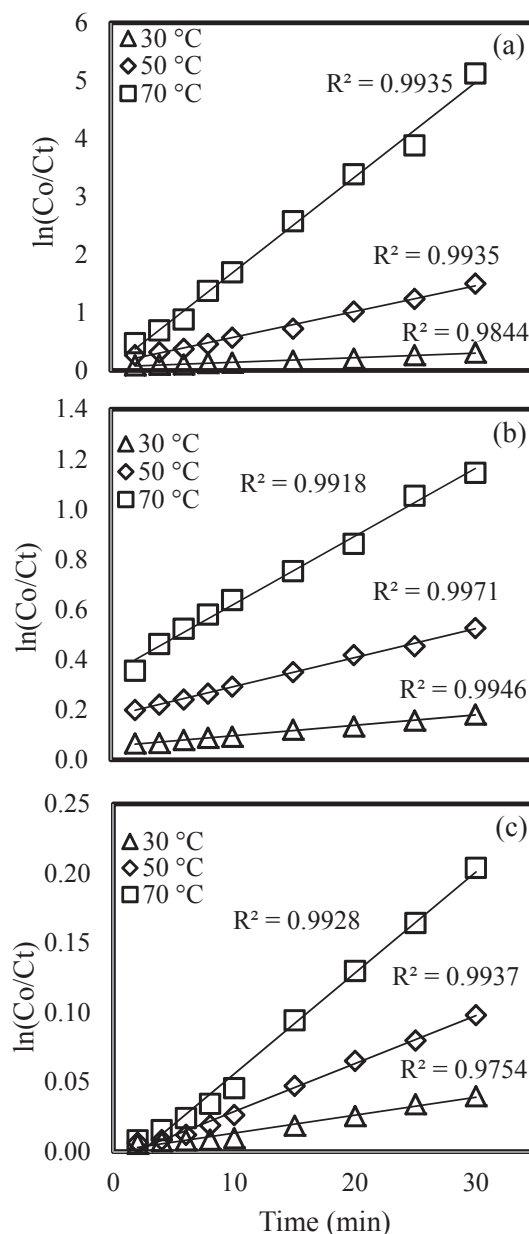
Table 1
Oxidation of DBT and BT rate constants for various polyoxometalate/H_2O_2 systems.

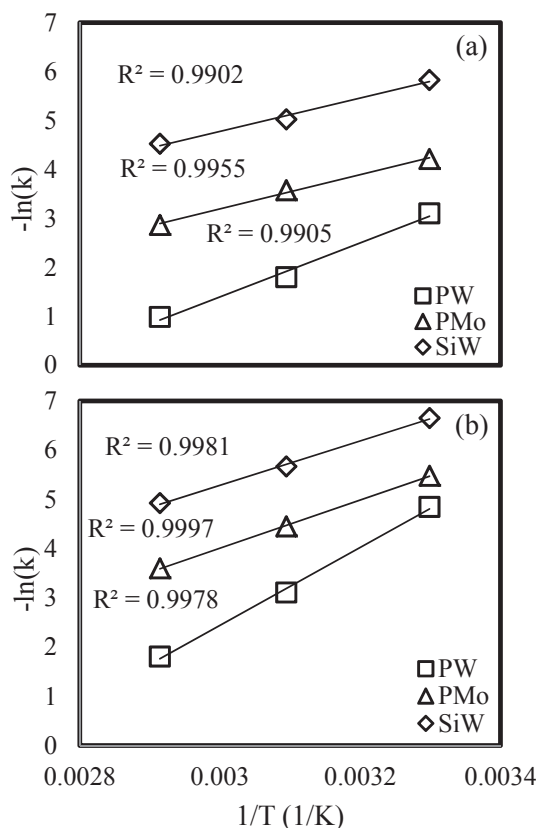| Polyoxometalate catalysts	Temperature (°C)	Rate constant (min^{-1})	
		DBT	BT
H$_3$PW$_{12}$O$_{40}$ (PW)	30	0.045	0.0078
	50	0.17	0.045
	70	0.37	0.16
H$_3$PMo$_{12}$O$_{40}$ (PMo)	30	0.015	0.0042
	50	0.028	0.012
	70	0.057	0.027
H$_4$SiW$_{12}$O$_{40}$ (SiW)	30	0.0029	0.0013
	50	0.0066	0.0034
	70	0.0108	0.0073

Fig. 5. Arrhenius plot for (a) dibenzothiophene and (b) benzothiophene.

Table 2
Activation energy of DBT and BT for various polyoxometalate/H_2O_2 systems.

Polyoxometalate catalysts	Activation energy (kJ mol^{-1})	
	DBT	BT
$H_3PW_{12}O_{40}$ (PW)	45.9	65.8
$H_3PMo_{12}O_{40}$ (PMo)	29.0	40.6
$H_4SiW_{12}O_{40}$ (SiW)	28.3	37.4

oxidation for DBT. Both PMo and SiW catalysts have lower activation energy which indicates that reaction temperature did not have a substantial change on the oxidation capacity of DBT and BT. This is because activation energy is sensitive to the reaction according to the change in temperature [35]. Lower activation energy means that the reaction is less sensitive to temperature change [35].

The study of Te et al. [32] showed the oxidation of DBT rate constants of 0.078 min^{-1} and 0.28 min^{-1} for 50 and 70 °C, respectively, and activation energy of 53.8 kJ mol^{-1}. In this study using a PW catalyst showed 0.17 and 0.37 min^{-1} for 50 and 70 °C, respectively, and activation energy of 45.9 kJ mol^{-1}. It is apparent that the utilization of PW catalyst in this study has an advantage of performing faster oxidation process at a lesser activation energy.

4. Conclusions

The desulfurization process of MAOD through the use of various POM/H_2O_2 systems has shown a promising technique to oxidize sulfur compounds. The PW catalyst showed to be the most efficient catalyst due to displaying the highest kinetic rate constant for the oxidation of DBT and BT. PMo and SiW were the other catalysts tested and showed an inferior oxidation performance in comparison

with the PW catalyst. The kinetic rate constant and activation energy for each POM catalyst upon the oxidation of DBT or BT exhibited a similar trend of $H_3PW_{12}O_{40} > HPM_{12}O_{40} > H_4SiW_{12}O_{40}$. Therefore, the utilization of MAOD with the PW/H_2O_2 system is favorable for the oxidation of actual oil. This is due to an effective oxidation performance towards major sulfur compounds such as DBT and BT present in fuel oils.

Acknowledgements

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