Efficient Catalytic Oxidative Desulfurization (CODS) of model fuel with H₂O₂ Catalyzed by HPA/SiO₂ under mild conditions

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Abstract - *Oxidative desulfurization (ODS) process was applied to model fuel oil (dibenzothiophene dissolved in iso-octane), catalyst and hydrogen peroxide as the oxidant were used for sulfur removal from model fuel oil. Dibenzothiophene (DBT) was oxidized by hydrogen peroxide (H₂O₂) in batch operation using heteropolyacid over silica supported catalyst (HPA/SiO₂). The catalyst was prepared and characterized by FTIR, XRD, and SEM analysis. The experimental results demonstrated that the SiO₂ supported catalyst with 30wt% of HPA exhibit high catalytic activity to achieving the DBT conversion of 97.2% at 60°C, atmospheric pressure, and H₂O₂/DBT molar ratio 5 in 80min. The kinetic study shows that the oxidative desulfurization of DBT was pseudo first order reaction. The activation energy of DBT is 13.069kJ/mol. Under mild operating conditions, HPA/ SiO₂ could be recycled four times without significant decrease in catalytic activity.*

***Key Words*:** *Oxidative desulfurization, dibenzothiophene, heteropolyacid, hydrogen peroxide, model oil.*

1.INTRODUCTION

The organo sulfur compounds present in transportation fuels causes environmental pollution after combustion and leads to significant impact upon the quality of petroleum fuel [1]. Currently many countries around the world introducing stringent regulation to decrease the sulfur content in fuels to an ultra-low. The United States (US) Environmental Protection Agency (EPA) provide a sulfur standard of 15 ppm in diesel fuel in June 2006 [2]. The China has regulated the sulfur content in diesel fuel less than 10 ppm according to Euro V standard at Beijing in recent years. Thus, the production of ultra clean fuels has become an enormous challenge for current desulfurization methods. So it is necessary to develop deep desulfurization processes such as hydrodesulfurization(HDS) and Non hydrodesulfurization process(Non-HDS) [3].

HDS process is commonly used process for removal of sulfur from aliphatic sulfur compounds such as thiols, sulfides and disulfides due to its activity. But it is not efficient to remove refractory sulfur compounds such as benzothiophene(BT), dibenzothiophene(DBT) and 4,6-dimethyldibenzothiophene-(4,6-DMDBT)[4]. Hydrodesulfurization (HDS) required high temperature and pressure to remove recalcitrant sulfur

species which brings different problems such as high operating cost, high investment and high hydrogen consumption [5]. To avoid these problems in HDS process, researchers have been developed various processes to remove sulfur content from liquid fuels such as, oxidative desulfurization process(ODS) [6], extractive desulfurization [7], adsorptive desulfurization [8] and Biodesulfurization process [9]. Among these processes Oxidative desulfurization (ODS) is very efficient process for desulfurization of liquid fuels which operates at mild reaction conditions such as at atmospheric pressure and temperature below 100⁰C and no need of Hydrogen. The phenomenon of this technology is that refractory sulfur compounds initially oxidized into sulfones or sulfoxides which is easily separated by adsorption or extraction [10]. Oxidizing agent plays vital role in ODS process. Different types of oxidizing agent have been used till now such as molecular oxygen [11] Hydrogen peroxide [12] and organic peroxide [13], NO₂ [14], and Ozone [15]. Among these oxidizing agent H₂O₂ has been widely used because it is inexpensive, environmental friendly and produces water as the byproduct after donating the oxygen atom in oxidative desulfurization process [16]. Up to now different types of ODS system have been reported in presence of H₂O₂ as oxidizing agent and various catalyst such as acetic acid [17], Phosphotungustic acid [18], Polyoxometalate acid [19], Hetropolyacid (HPA) [20]. Among them heteropolyacid widely employed for oxidative desulfurization because of high potential in oxidation reactions [21].

Supported heteropolyacid (HPA) catalysts are important for applications because bulk heteropolyacid (HPAs) have a low specific surface [22]. The acidity and catalytic activity of supported HPAs depends on the type of the carrier, the amount of HPA loading and conditions of pretreatment, etc. Acidic or neutral substances such as SiO₂ [23] active carbons [24] etc. are suitable as supports, the most often used being SiO₂. Silica is relatively inert toward HPAs, at least above a certain loading level, although some chemical interaction takes place between HPA and SiO₂ The thermal stability of HPA over SiO₂ seems to be comparable to or slightly lower than that of the parent HPA. On the other hand, a thermally decomposed Keggin structure on the SiO₂ surface may be reconstructed on exposure to water vapor [25]. Ammonium salt of heteropolyacid(HPA) over silica supported is most efficient catalyst for oxidative desulfurization of refractory sulfur compounds. Various studies have been performed on the catalytic activity of Keggin-type heteropoly acids(HPAs)

for refractory sulfur compounds under mild operating conditions [24].

2. EXPERIMENTAL

2.1 Materials

All the chemicals used in the study were of analytical reagent (AR) grade. Ammonium heptamolybdate($(NH4)_6Mo7O24.4H2O$, 99%), diammonium hydrogen orthophosphate ($(NH_4)_2HPO_4$, 98%) and Nitric acid (HNO_3, 69-71%) was purchased from Molychem Mumbai, India. hydrogen peroxide (H_2O_2, 30wt %,), Isooctane-($(CH_3)_3CCH_2CH(CH_3)_2$,99.5%, Loba chemie Pune India), dibenzothiophene (DBT, combi blocks.inc, 98%). Acetonitrile (CH_3CN, RFCL, Haryana, India, 99%).

2.2. Preparation of catalyst:

An ammonium salt of molybdenum heteropolyacid was prepared according to the procedure reported in literature [26] An aqueous solution of ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$ (4.24g, 0.0034moles) was prepared by dissolving it in 40 ml of water at 373 K. Similarly, an aqueous solution of diammonium hydrogen orthophosphate, $(NH_4)_2HPO_4$ (0.27g, 0.002moles) was prepared in 20 ml of water. Then they were mixed and its pH was adjusted to 1.0 by addition of nitric acid. The yellow precipitate obtained was the ammonium salt of molybdenum heteropoly acid, $(NH_4)_3PMo_{12}O_{40}$ and which was denoted by HPA). This suspension was directly used for the preparation of the heterogeneous catalyst. Instead of separating it by filtration and drying, this suspension is used to modify the acidity of the SiO_2 catalyst. In The certain amount of heteropolyacid (30wt% of the silica) dissolved in deionized water was added by dropping and stirred for 1 hr. after that mixer was kept on magnetic stirrer at 50^0C for 2hr and maintain the pH 1. After that it was separated by filtration and washed it by deionized water and dried it at 120^0C in oven. At the end dried sample calcined at 320^0C for 3hr in a furnace.
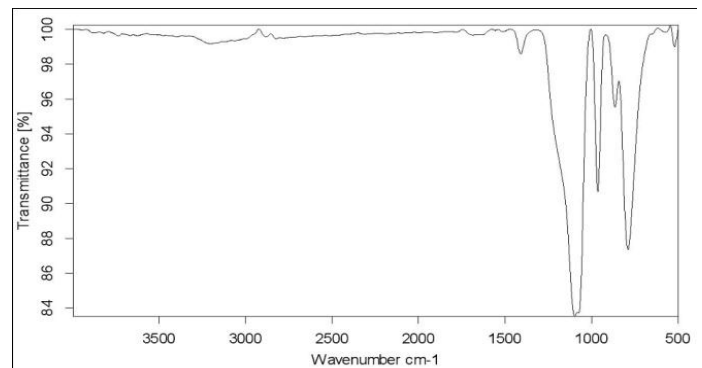
3. RESULTS AND DISCUSSION

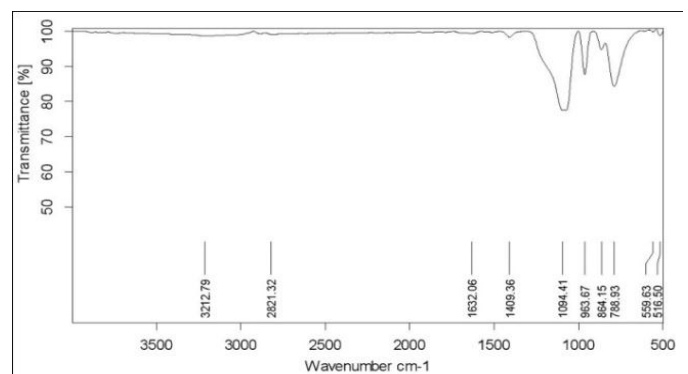## 3.1. Characterization of catalyst

3.1.1. FTIR Analysis of Catalyst

The FTIR spectrum of heteropolyacid (HPA) over silica supported, prepared at pH 1 (Fig. 1a), shows the characteristic bands of the Keggin type structure in the wave number region (1,100–500 cm^{-1}). According to Rocchiccioli-Deltcheff et al. [28], the vibration bands at 1094, 963, 864, 788 and 519 cm^{-1} correspond to ν_{as}(P–O_A), ν_{as}(Mo-O_D) ν_{as}(Mo–O_B–Mo), ν_{as} (Mo–O_C–Mo) and δ(P–O), respectively. In Keggin unit, O_A refers to O atom common to PO_4 tetrahedron and a trimetallic group: O_B refers to O atom that connects two trimetallic groups, O_C refers to O atom which connects

with two MoO_6 octahedrals inside a trimetallic group $Mo_3O_{13}$and O_D is the terminal oxygen atom. In addition, the deposition of molybdenum heteropolyacid on the surface of the silica support was shown by the bands at 1403, 1094, and 963 cm^{-1} which represent the stretching vibrations of NH_4^+ ion, P-O, and Mo-O respectively [29].

(a)

(b)

Fig. 1. FTIR spectra (a) Silica Support (b) 30 wt% HPA over Silica

3.1.2.XRD analysis of catalyst

X-ray diffraction measurements of the HPA/SiO_2 catalyst were carried out on a Sietronics XRD diffractometer equipped with Cu-Kα (λ = 1.54nm) radiation. The voltage and current applied to the X-ray tube were 40 kV and 20 mA respectively and the sampling step was set at 0.05^0 with scanning speed as 3^0/minute (2θ = 10 ^{0} to 80 ^{0}). The diffraction peaks in the range of 2θ = 10-20^0 and 25-30^0 correspond to the deposition of molybdenum heteropoly acid (HPA) [27-25] The XRD results of heteropolyacid acid pretreatment at 320°C as some lines of amorphous cubic phases and peaks corresponding to the α MoO3 oxides phase (2θ = 10.66, 21.5, 26.41, 30.6) resulting from the partial decomposition of this salt. The XRD analysis shows the formation of molybdenum trioxide in the monoclinic form(β MoO3) and in the orthorhombic form (α MoO3) whatever

the salt composition. These two species (α and βMoO3) were already observed by Rocchiccioli-Deltcheff [25].
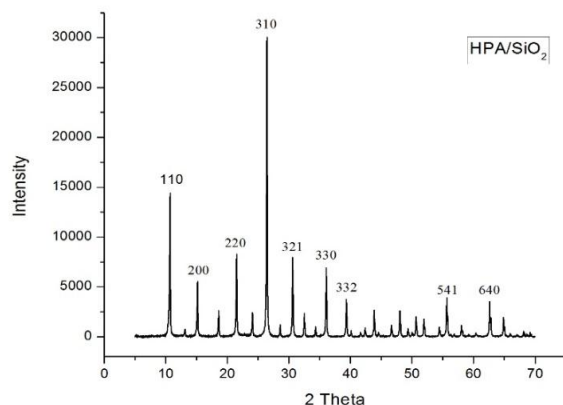

Fig: 2. XRD pattern of heteropolyacid (HPA) supported over silica.

3.1.3. Scanning Electron Microscope (SEM) analysis

The SEM micrographs (200 nm) of the HPA over silica catalyst at 15kV acceleration voltages has been used to analyze change in structural morphology of the HPA/SiO$_2$ the SEM picture of loaded catalyst is shown if fig 3 The deposition of molybdenum heteropolyacid (HPA) on Silica support is confirmed by the presence of extra material as shown in the fig the powdered sample was kept under vacuum in a gold coated form so that it can conduct electrons effectively.
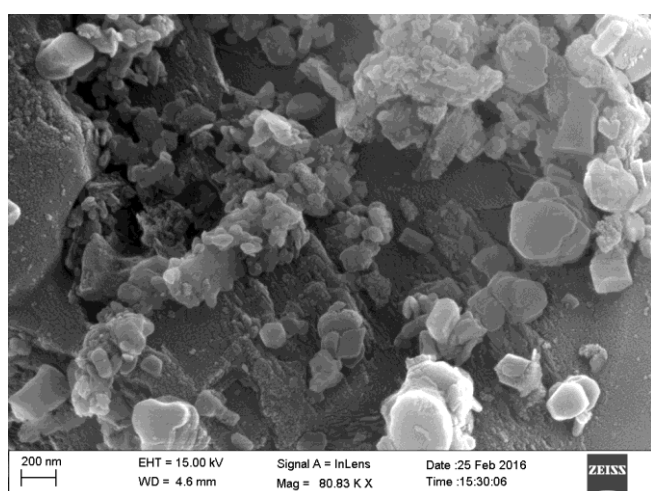

Fig: 3. SEM picture of HPA Loaded over silica catalyst

3.2. Catalytic oxidative desulfurization

The oxidative desulfurization process was carried out in a 25ml three necked round bottom glass reactor and equipped with a total reflux system. Three necked glass reactor was immersed in a thermostatically controlled oil bath to carry out the reactions at different temperature. The three necked round bottom glass reactor along with oil bath, which was kept on a magnetic stirrer with hot plate. The reaction system of model fuel oil with the sulfur content of is 500 ppm. The mixture of 25 ml of the model fuel oil (A certain amount of DBT was dissolved in isooctane to get model fuel oil) and a certain amount of HPA/SiO$_2$ solid catalyst and hydrogen peroxide (H$_2$O$_2$) was adding into the oil bath. In each run, the reactor was charged with 25 ml of model oil and appropriate amount of catalyst and oxidant. The oil bath was then heated up and stabilized to the desired reaction temperature which called as time zero (t = 0), (t= 0 stands for, the reaction was taken when final temperature was reached. this reaction temperature was maintained constant during on complete experiment run.

A certain amount of DBT was dissolved in isooctane to get model fuel oil with the sulfur content of 500 ppm. The reaction was performed in oil bath at mild operating conditions. After that a certain amount of H$_2$O$_2$ was added into the mixture, and the reaction was kept at 60^{0}C at 500rpm for 80 min and then the mixture was cooled down to room temperature and at the end mixture was separated by extraction process by using of Acetonitrile (extracting agent) with the model oil volume ratio of 1:4. The upper oil was analyzed by GC-FID equipped with a HP-5 capillary column of 30m x 0.32mm x 0.25µm film thickness.
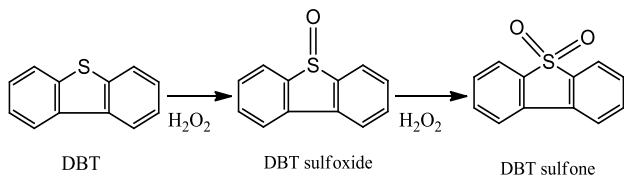Conversion of sulfur:
The Experimental data were used to calculate the percentage of sulfur conversion by using the given relationship:

Sulfur removal fraction (%) $= \dfrac{(C_A - C_{A0}) * 100}{C_A}$

Where C_A is the initial concentration of the sulfur and C_{A0} is the concentration of the sulfur after treatment for time (t).

2.4. Reaction Mechanism of ODS

During Typical oxidative desulfurization of DBT, the DBT reacts with H$_2$O$_2$ in the presence of 30wt% HPA/SiO$_2$ catalyst to form DBT sulfoxide, which reacts with another H$_2$O$_2$ molecule to form or sulfones (Scheme 1). In the previous studies organic phase transfer reagent like acetic acid or organic solvents has been used to assist the transfer of H$_2$O$_2$ from polar phase to non-polar oil phase during oxidative desulfurization process. To solve this type of problem we anchored quaternary ammonium cation into the catalyst frame work which can help in hydrophobic distribution of the catalyst in oil phase, which favors less mass transfer resistance and faster reaction rate.

Scheme 1: Catalytic oxidative desulfurization of DBT to DBT sulfone

4. Kinetic model of oxidative desulfurization (ODS)

The kinetic of ODS of dibenzothiophene (DBT) was studied under various temperature ranging $40, 50, 60°C$. The reaction is three phase heterogeneous kind, the organic phase contains the reactant DBT, the aqueous phase contains the hydrogen peroxide (H_2O_2) as oxidant and catalyst HPA/SiO_2 makes the solid phase. The interfacial mass transfer effect between two liquid phases and the liquid solid phase are eliminated by fixing the optimum stirrer speed has been discussed. The oxidative reaction of DBT considered as pseudo first order reaction, where the rate is apparently depending on the concentration of the limiting reactant. The reaction can be described as

$$-\frac{dC_{DBT}}{dt} = k'[H_2O_2]^m[C_{DBT}]^n \quad \text{..(1)}$$

The amount of H_2O_2 was taken in access and the change in concentration of H_2O_2 in comparison to change in dibenzothiophene concentration is negligible, so term dependent on H_2O_2 was negligible

Compared to the change DBT concentration [29], so equation (2) can be expressed as:

$$-\frac{dC_{DBT}}{dt} = k'[C_{DBT}]^n \quad \text{..(2)}$$

Where $k = k'[C_{DBT}]^n$, which may be expressed as apparent rate constant.

The oxidative desulfurization of model sulfur compound (DBT) in isooctane using H_2O_2 as oxidant was assumed to the pseudo first order reaction equation (3) has been integrated for n =1, with limit taken as t= 0, and $C_{DBT} = C_E$(removal of sulfur compound(DBT) at time zero), t=t, $C_{DBT} = C_t$ and initial concentration (C_0) = 500 ppm.

After integration equation (3) can be expressed as

$$\ln\left(\frac{C_0}{C_t}\right) = kt + \ln\left(\frac{C_0}{C_E}\right) \quad \text{..(3)}$$

The plot of $\ln\left(\frac{C_0}{C_t}\right)$ versus time(min) is linear, as shown in Fig.

5. The kinetic equation, rate constant k, and correlation coefficient R are listed in Table: 1.
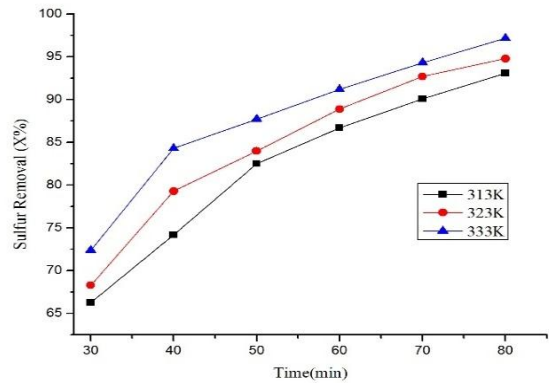

Fig: 4. Sulfur removal (X%) versus the reaction time at different reaction temperatures, Conditions: O/S = 5:1(molar ratio), DBT (S:500 ppm) in isooctane and 1g catalyst.
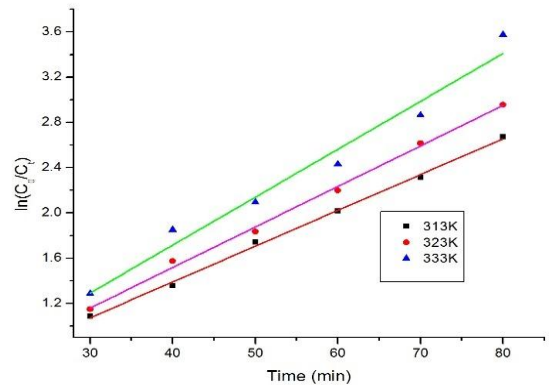

Fig: 5. The Plot of $\ln\left(\frac{C_0}{C_t}\right)$ vs time, under different reaction temperature conditions: model oil = 25 ml, catalyst amount 1 g, molar ratio = 5.

The oxidative desulfurization of DBT follows pseudo first order kinetics from the reaction rates determined at various temperatures, the apparent activation energy for the oxidation of dibenzothiophene (DBT) was derived from Arrhenius equation as shown in Fig: 5. The activation energy (E_a) of DBT is 13.069kJ/mol.Ibrahim and coworkers [30] have reported that in heteropolyacid over silica catalyst and hydrogen peroxide was used as oxidant and the apparent activation energy of dibenzothiophene (DBT) was 11.5 kJ/mol. The apparent activation energy value was similar with the reported reference because of the use of the stronger oxidant and heteropolyacid over silica supported catalyst.

Table 1
Kinetic equation, rate constant k^{-1}, and correlation coefficient (R) at different temperatures (K)

T(K)	Kinetic equation	Rate constant (k^{-1})	Correlation Coefficient R	$t_{1/2}$ (min)
313	$\ln(C_0/C_t) = 0.03163t + 0.04324$	0.03163	0.99719	21.90958
323	$\ln(C_0/C_t) = 0.08564t + 0.05851$	0.08564	0.99599	8.092013
343	$\ln(C_0/C_t) = 0.02272t + 0.04233$	0.02272	0.96885	30.50176

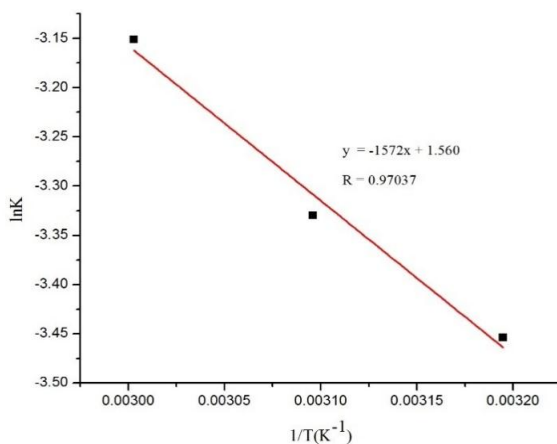$y = -1572x + 1.560$

$R = 0.97037$

Fig: 6. Pseudo first order kinetics for the oxidation of dibenzothiophene.

5. CONCLUSION

The HPA/SiO2 catalyst was very efficient for oxidative desulfurization of sulfur compounds in the model fuel oil using H_2O_2 as the oxidant. Under the reaction condition of catalyst dosage 1 g, H_2O_2 dosage 0.05 ml and the reaction temperature

70°C, the conversion rate of DBT reached 97.2% only in 80 min. the kinetic study shows that the oxidative desulfurization of DBT was pseudo first order reaction. The activation energy of DBT is 13.069kJ/mol.

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