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Preparation of Modified Monovacant Keggin Compound and Study of its Catalytic Performance in Removal of Sulfur compounds from Diesel Fuel

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Abstract

The surfactant cetyltrimethyl ammonium encapsulated monovacant Keggin units $(C_{19}H_{42}N)_4H_3(PW_{11}O_{39})$ designated as CTA-POM was prepared and characterized by Fourier Transform Infrared (FT-IR) and Thermogravimetric analysis (TGA). The prepared product was used as a catalyst in emulsion for oxidative desulfurization of diesel fuels with (30%) hydrogen peroxide as oxidizing agent and the oxidized organosulfur compounds was further removed from diesel fuel by extraction with methanol as polar solvent. The amphiphilic catalyst in the Water/Oil emulsion system exhibits very high activity for oxidative desulfurization, it reduced the sulfur of actual diesel oil 68.0 ppm S to level of 20.5 ppm S corresponding to 69.9% sulfur removal using 200 mg catalyst, 25 ml of diesel oil, 2 ml (30%) hydrogen peroxide for 3 hours at 70 °C and followed by extraction with 25 ml of methanol.

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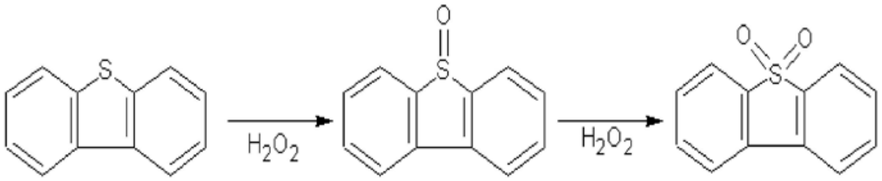
Also the catalyst was separated from oil after catalytic reaction, washed by methanol, dried and analyzed by FT-IR and the result indicate that the integrity of the catalyst was retained and can be reuse for further run.

Introduction

The development of high-performance catalysts is still very important for using an applicable industrial that is possessing unique structures, properties and eco-friendly has been under attention. Polyoxometalates (POMS) are the metal-oxygen clusters anions (P.souchay, 1969; Pope, 1983)These are diverse class of nanoscale metal-oxide structures with characteristics that make them remarkably attractive as potential components for self-assembled composite nanosystems (Okun, *et al* 2003) Systematic investigation of catalysis by polyoxometalates began in the early 1970s when the great potential of these compounds for catalytic applications became apparent (Eric, 2002) POMs are anions, and their counteractions may be exchanged by metathesis reactions. Typically tetra butyl ammonium (TBA) and acetyl tri methyl ammonium bromide (CTAB) are chosen as the countercation for organic phase reactions and the appropriate pH (~ 2—4.5) (Eric, 2002; , Kozhevnikov, 2002]. POMs can be helpful used as catalysts for oxidation in biphasic systems. Can li *et al* 2004 reported that a $[(C_{18}H_{37})_2N^+ (CH_3)_2]_3[PW_{12}O_{40}]$ catalyst, assembled in an emulsion in diesel, can selectively oxidize the sulfur-containing molecules present in diesel in to their corresponding sulfones by using H_2O_2 as the oxidant under mild conditions. Oxidative desulfurization process (ODS) is an attractive process and used as alternative or complementary to hydrodesulfurization (HDS) to remove the refractory organosulfur compounds that are the most difficult to eliminate by HDS and more reactive on ODS to obtain ultra low sulfur diesel (ULSD) (Shiraishi *et al* 2002; Otsuki, *et al* 2000). The oxidation of the organic sulfur compounds to sulfones possessing higher polarity and then separating them by different methods. During the oxidative desulfurization, sulfur compounds can be oxidized by the electrophilic addition of oxygen atoms to the sulfur to form sulfoxides (1-oxides) and sulfones (1,1-dioxides) (Scheme 1).



Scheme 1 Catalytic oxidation of Dibenzothiophine

The chemical and physical properties of sulfoxides and sulfones are significantly different from those of hydrocarbons in fuel oil, and consequently they can be removed by distillation, solvent extraction, or adsorption. Potential catalytic oxidative routes to produce low-S fuels include various types of oxidants, including nitrogen oxides (Tam *et al* 1984) nitric acid (Baxendale *et al*, 1946) hydrogen peroxide (Collinsand Lucy, 1997)., ozone (Paybarah *et al*, 1982), organic hydroperoxides (Drushel and Millar, 1958)., molecular oxygen (Shiraishi *et* al, 2001), acetic acid (Babich and Moulijn, 2003), and others. The oxidation of thiophene derivatives with H_2O_2 is known to occur over various catalytic system, such as HCOOH [CF_3COOH (Zannikos and Stournas,1995), methyltrioxorhenium(VII) (Treiber, 1997), phosphotungstenic acid and metal supported on alumina (Brown and Espenson, 1996) or molecular sieves. The use of transition-metal (Ti, Mo, Fe, V, W, Re, Ru) complexes as active catalysts for selective oxidation of sulfur compounds in homogeneous condition has also been reported. In the case of metal-containing molecular sieves, the pore dimensions of the material, as well as the metal coordination, oxidizing agent, and solvent, play critical roles in catalyst activity and life for the oxidative desulfurization (ODS) of industrial feeds.

In this work, we will prepare the catalyst monovacant lacunary Keggin-type POMs associated with quaternary ammonium salt. The prepared catalyst, $(C_{19}H_{42}N)_4H_3(PW_{11}O_{39})$, assembled in emulsion in commercial diesel, can selectively oxidize the sulfur-containing compounds to sulfoxide and sulfone with H_2O_2 under free solvent conditions. Then the sulfones can then be readily separated from the diesel using an extraction process. The purpose of incorporation of quaternary ammonium salt was to facilitate hydrophobic distribution of the catalyst in favor of less mass transfer resistance and faster reaction rate due to its lipophilic cationic character.

Experimental

Chemicals

All the chemicals were used as recieved without further purification and the hydrotread diesel fuel used in this work was commercially available.

Instrumentation*:*

The Fourier Transform Infrared spectrophotometer (FT-IR) was recorded on a nexus FT-IR 8400 source of light a laser spectrometer. The Thermal Gravimetric Analysis (TGA) was done on TGA PT/1000 with a heating rate of 10°C/min. The sulfur content in diesel oil was determined using Ultraviolet Fluorescence D 5453-04 equipped with an electric furnace held at a temperature (1075 ± 25 ˚C) sufficient to pyrolyze all of the sample and oxidize sulfur to SO_2.

Preparation of CTA-POM

Cetyltrimethylammonium encapsulated monovacant lacunary Keggin polyoxometalate $(C_{19}H_{42}N)_4H_3(PW_{11}O_{39})$ was perpared based on a previously reported procedure (Ali *et al*, 2009; Simoes *et al*, 1999]. By mixing Na_2HPO_4 (1.290 g) and $Na_2WO_4.2H_2O$ (29.382 g) in 200 ml of distilled water and adjusting the pH to 4.8 by adding acetic acid drop-wise. Then an aqueous solution of CTA bromide 8.200 g in water (20 ml) was added drop-wise, with contineous stirring at 85 °C to the mixture. The solid formed was filtered off and dried. The resultant $(C_{19}H_{42}N)_4H_3(PW_{11}O_{39})$ solid is designated as CTA-POM.

Catalytic test

The required amount of catalyst and 25ml of diesel with 68 ppm sulfur content were added to three neck flask equipped with a reflux condenser and a mechanical stirrer. Then the required volume of H_2O_2 was slowly added and the reaction mixture was stirred at constant temperature 70°C for 3 hours. At the end of the catalytic reaction, the oxidized oil was extracted with 25 ml methanol and the remaining sulfur was determined by Ultraviolet Fluorescence technique.

Result and Discussion

Characterization of CTA-POM

Figure-1 shows the FT-IR spectra of CTA-POM. The bands at 2852.52 and 2923.88 cm^{-1} are characteristic of $–CH_2$ symmetric and asymmetric stretching vibrations, while the peaks at 1469.66 and 1373.22 cm^{-1} are associated with the scissoring and in-phase twisting modes of the $– (CH_2)_n –$ group. Also in the FT-IR spectra, the band at 1080.06 cm^{-1} attributed to the asymmetric vibration of P-O of tetrahedral PO_4, while the bands at 975.91, 894.91 and 813.90 cm^{-1} are ascribed to the stretching modes of the terminal $W\text{-}O_d$, edge sharing $W\text{-}O_b\text{-}W$ and corner sharing $W\text{-}O_c\text{-}W$ units, respectively. These, peak 1080.06, 975.91, 894.91 and 813.90 cm^{-1} due to the monovacant keggin structure. The presence of all of these bands for monovacant lacunary Keggin unit, $(CH_3)_4N^+$ and $– (CH_2)_n–$ confirm the encapsulation of cetyl trimethyl ammonium salt to the lacunary Keggin unit (Massart *et al,* 1977). Figure-2 shows the thermogravimetric analysis (TGA) of CTA-POM, which as similar it's these reported in literatures. Three main peaks were observed, a peak in the temperature range of 190—290°C accounted for the loss of $6H_2O$ molecules per Keggin unit, a peak in the range of 330—380°C due to the decomposition of organic surfactant Cetyl trimethyl ammonium (CTA) and a peak at range of 410—570°C corresponding to the loss of 1.5 H_2O molecules corresponding to the loss of all acidic protons and the beginning of the decomposition of the Keggin structure in to WO_3 and P_2O_5. These peaks indicate that Cetyl trimethyl ammonium encapsulated Keggin unit $(C_{19}H_{42}N)_4 H_3(PW_{11}O_{39})$ catalyst has high thermal stability.

Catalytic ODS of diesel oil

The catalytic performance of the CTA-POM in the oxidation desulfurization of commercial diesel oil under free solvent condition was studied using different amount CTA-POM as catalyst and hydrogen peroxides as oxidant at 70 °C for 3 hours. After the catalytic reaction the oxidized sulfur compound was removed from oil phase using polar extracting solvent (methanol). Table-1 shows effect of sulfur removal by different amount of catalyst i.e. 0, 200 and 600 mg on ODS of diesel oil with 0.5 ml H_2O_2. The experimental result demonstrate that the sulfur compounds with initial concentration of 68 ppm S with 0 mg catalyst can be reduced to 49 ppm S corresponding to 27.9% S removal, while an increase the amount of the catalyst to 200 and 600 mg decreased the sulfur content to 24 and 23 ppm S corresponding to 64.7% and 66.2% sulfur removal respectively.

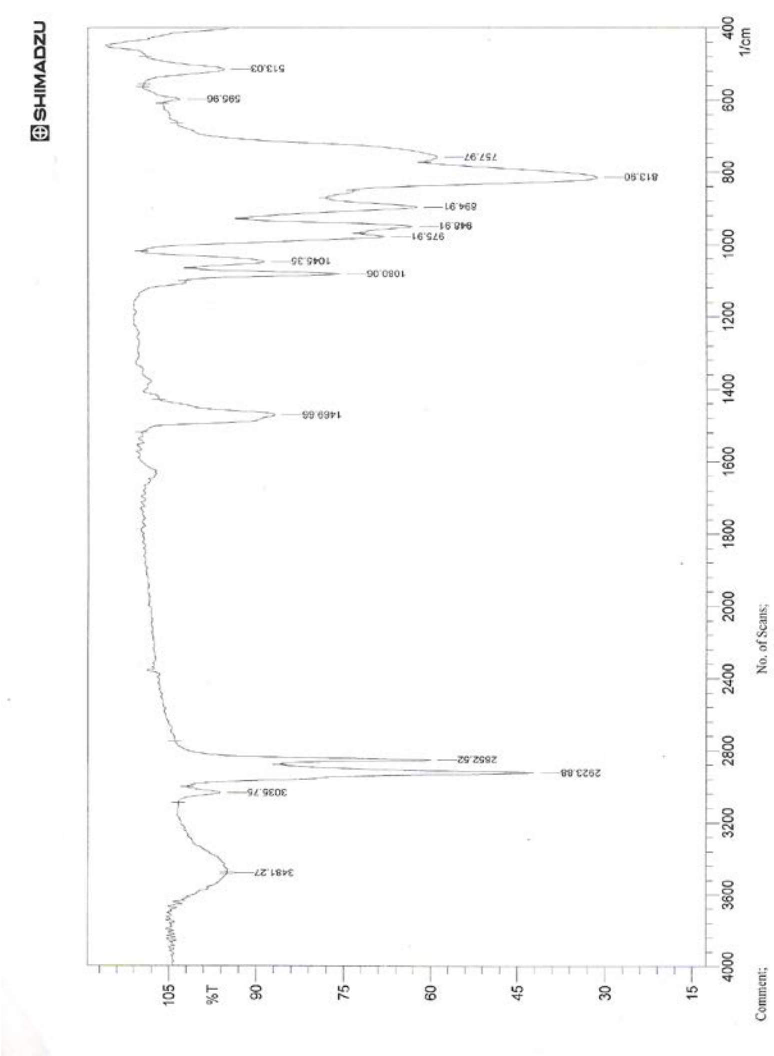


Figure 1 FT-IR spectra of CTA-POM

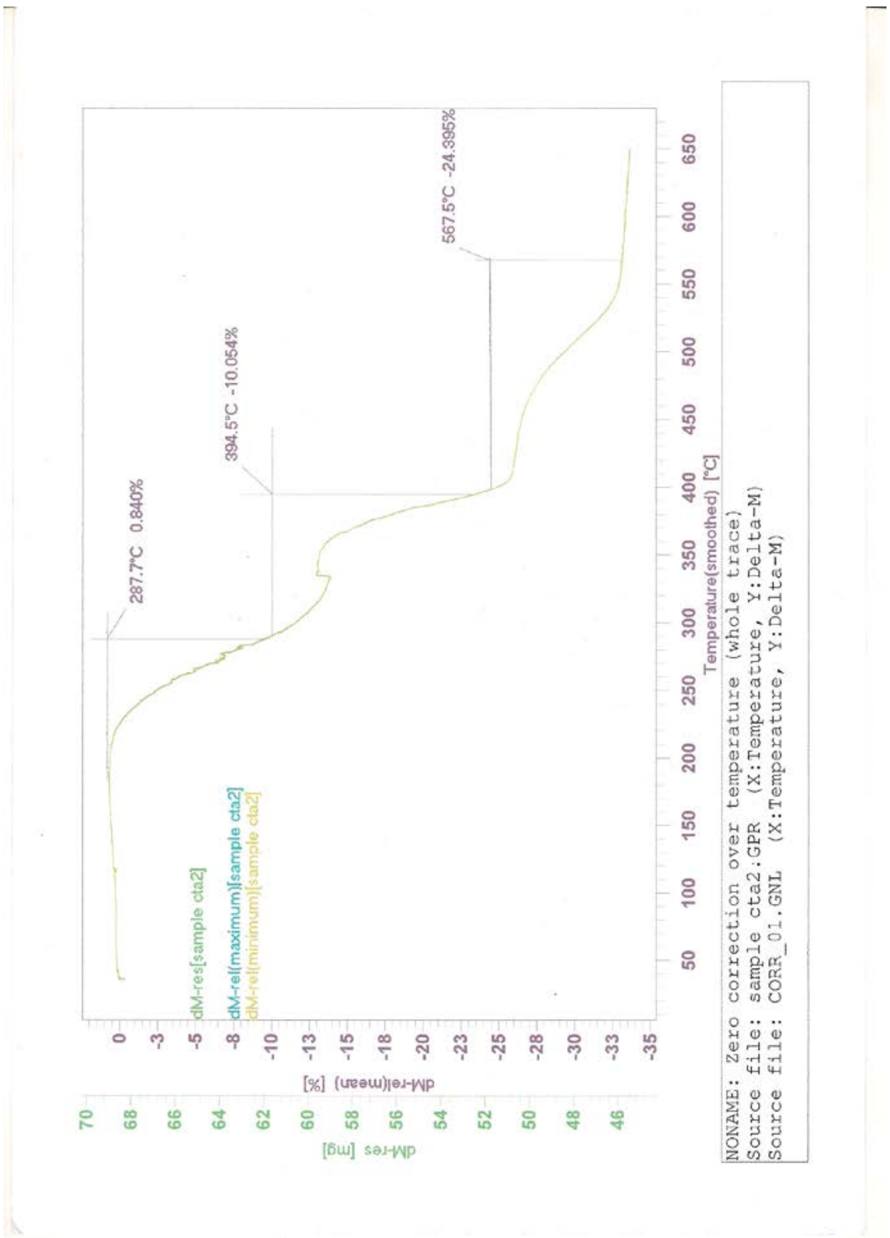


Figure 2 TGA of CTA-POM

Table-1 The effect of catalyst amount on sulfur compounds from diesel oil..

Weight of CTA-POM (mg)	Sulfur remain (ppm)	Sulfur removal (%)
0	49.0	27.9
200	24.0	64.7
600	23.0	66.2

Conditions: 25 ml of diesel oil (68ppm), 0.5ml of H_2O_2, 3h, 70°C, 25 ml methanol

Table -2 The effect of H_2O_2 amount on the catalytic removal of sulfur compounds from diesel oil.

Volume of H_2O_2 (ml)	Sulfur remain (ppm)	Sulfur removal (%)
0.75	23.0	66.2
1.00	21.0	69.1
2.00	20.5	69.9

Conditions : 25 ml of diesel oil (68ppm), 200mg of CTA-POM, 3h, 70°C, 25 ml methanol

Table-2 shows the effect of hydrogen peroxide as oxidant (0.75, 1.00 and 2.00 ml) on ODS of diesel oil with 200 mg CTA-POM. The experimental result reveal that the sulfur compounds with initial concentration of 68 ppm S can be reduced to 23 ppm S corresponding to 66.2% S removal with 0.75 ml H_2O_2, while an increase the volume of the oxidant to 1 and 2 ml decreased the sulfur content to 21.0 and 20.5 ppm S corresponding to 69.1% and 69.9% sulfur removal respectively.

Table-3. The extraction effect on sulfur removal from diesel oil (blank effect)

Diesel (ml)	Methanol (ml)	Sulfur remain (ppm)	Sulfur removal (%)
25	25	64	5.88

Conditions: 25 ml of diesel (68ppm), 0 g of catalyst, 0ml of H_2O_2, 25 ml methanol at room temperature.

The effect of solvent extraction in sulfur removal also was done (table 3) using untreated diesel oil by 25 ml of methanol and the total sulfur decreased from 68 ppm S to 64 ppm S corresponding to 5.88% , so we can say that our catalyst has a prominent role in ODS of real diesel oil. At the end of the reaction, the catalyst was recovered by simple filtration, washed with methanol several times to remove the adsorbed sulfur compounds (sulfones) and analyzed by FT-IR.

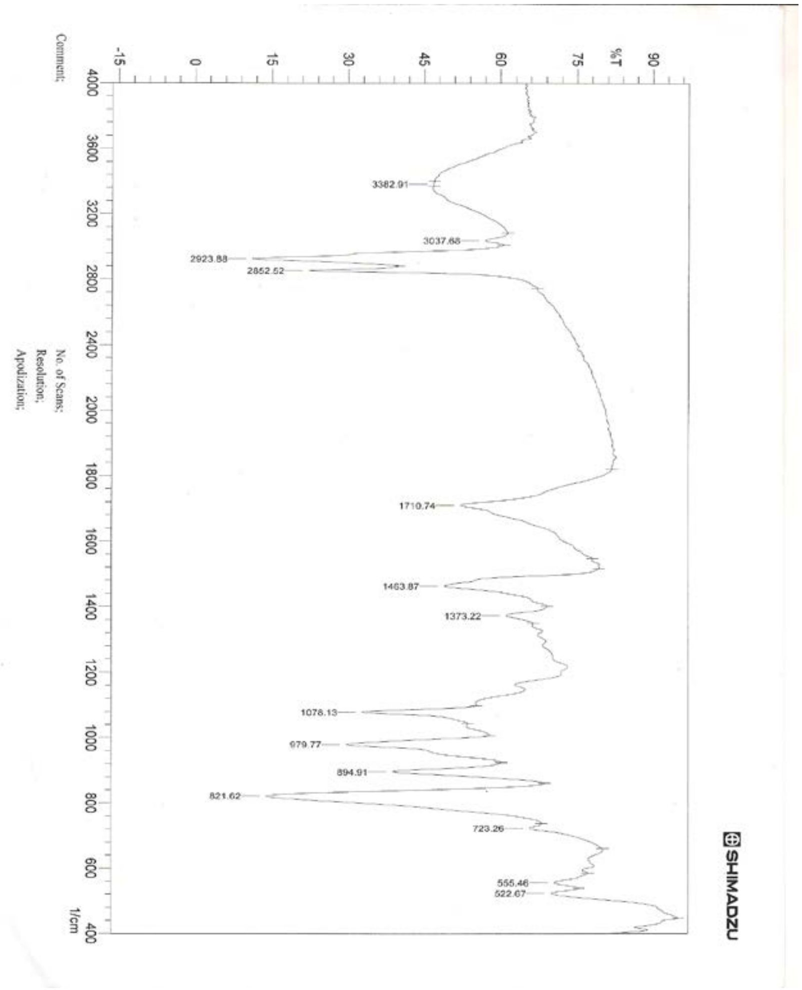


Figure-3 The FT-IR of Recycled CTA-POM

In figure-3 the FT-IR of recycled CTA-POM show the same of main peaks in the catalyst which may indicate that CTA-POM is an efficient and heterogeneous catalyst and can be considered as reusable, and promising catalyst for ultra-deep desulfurization of refractory organosulfur compounds in diesel oil.

Conclusions

In this study $(C_{19}H_{42}N)_4H_3(PW_{11}O_{39})$ catalyst was successfully prepared and characterized by FT-IR and thermo gravimetric analysis TGA, and its activity was performed in oxidative desulfurization of diesel fuel. In catalytic reactions of diesel oil under mild condition at 70° C for 3 hours three factors were studied; the effect of catalyst amount, volume of hydrogen peroxide and effect of extraction process. The catalyst was found to be highly efficient for selective oxidation of the sulfur-containing compounds in commercial diesel fuel using hydrogen peroxide as oxidant, followed by extraction. So we can say that CTA-POM catalyst efficient in ODS of real diesel oil. The catalyst was recovered and analyzed by FT-IR and the result show the catalyst was retained unchanged. Therefore, it is reasonable to conclude that the present catalysis is heterogeneous in nature.

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