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Oxidation Reactivities of Dibenzothiophene and its Derivative in Model Oil Using Polyoxometalates /H_2O_2 Systems

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ABSTRACT

In order to reduce the sulfur level in liquid hydrocarbon fuels for environmental protection and fuel cell applications, deep desulphurization of model sulfur compounds dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT) and 4,6-dmethyldibenzothiophene (4,6-DMDBT), which have the lowest reactivity in hydrodesulfurization process (HDS). The oxidation reaction was performed in biphasic mixtures of n-octane/acetonitrile using different polyoxometalates as catalysts and hydrogen peroxide (H_2O_2) as oxidant. $H_3PW_{12}O_{40}$ was identified as an effective catalyst for the oxidative removal of DBT under mild reaction conditions of atmospheric pressure and 60 °C. Ranking of catalyst efficiency is as follows: $H_3PW_{12}O_{40}$ (NPW)> $Na_3PW_{12}O_{40}$ (NAPW)>$H_3PMo_{12}O_{40}$ (HPMO)> $H_4SiW_{12}O_{40}$ (HSIW). The conversion of DBT was nearly 100%. As a result, because of the influence of the electron density and the space steric hindrance, the oxidation reactivity of the different sulfur compounds in simulated oil followed the order DBT > 4-MDBT >4,6-DMDBT.

Keywords: Desulfurization, Simulated Oil, hydrogen peroxide.

فعالية تفاعل أكسدة ثنائي بنزوثيوفين ومشتقاته في نموذج الزيت باستخدام بولي أوكسوميتالات/H_2O_2

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ملخص البحث

لهدف خفض مستوى الكبريت في وقود الهيدروكربونات السائلة لغرض حماية البيئة وتطبيقات خلايا الوقود، أُجريت عملية إزالة الكبريت العميقة لمركبات الكبريت النموذجية: ثنائي بنزوثيوفين(DBT) و4-ميثيل ثنائي بنزوثيوفين (4-MDBT)، و4,6-ثنائي ميثيل ثنائي بنزوثيوفين(4,6-DMDBT) ، والتي يصعب ازالتها في عملية إزالة الكبريت بالهيدروجين (HDS). أُجري تفاعل الأكسدة في خليط ثنائي الطور من نورمال -أوكتان/ أسيتونتريل باستخدام بولي أوكسوميتالات مختلفة والتي تستخدم كمحفزات، وبيروكسيد الهيدروجين (H_2O_2) كمؤكسد. وُجد أن $H_3PW_{12}O_{40}$ محفز فعال لإزالة DBT في ظروف تفاعل معتدلة من الضغط الجوي ودرجة حرارة 60 درجة مئوية. حيث كانت كفاءة المحفز كالتالي: $H_3PW_{12}O_{40}$ (NPW)> $Na_3PW_{12}O_{40}$ (NAPW)>$H_3PMo_{12}O_{40}$ (HPMO)> $H_4SiW_{12}O_{40}$ (HSIW) بلغت نسبة تحويل DBT ما يقارب 100%. ونتيجةً لتأثير كثافة الإلكترونات والعوائق الفراغية، اتبعت فعالية تفاعل أكسدة مركبات الكبريت المختلفة في الزيت بالترتيب التالي DBT > 4-MDBT > 4,6-DMDBT.

الكلمات الدالة: إزالة الكبريت، النفط المُحاكي، بيروكسيد الهيدروجين.

1. INTRODUCTION

Currently, the manufacturing of fuels for transportation free from harmful substances is necessary globally. The extraction of sulfur from crude oil or petroleum derivatives is essential for both manufacturing and ecological factors. Sulfur within Petroleum products contaminate catalytic converters, rusts components of internal combustion engines and refineries due to the creation of oxy-acids of sulphur. Air contamination from diesel emissions is a significant worry to the public too. To facilitate reduce pollution, fresh environmental regulations limits for sulfur in diesel have been set in numerous nations. The typical sulfur level in diesel has been limited to 10 ppm, including the zero level in the upcoming future [1]. The industrial method of Desulfurization refers to hydrodesulfurization (HDS), that can eliminate the majority of sulfur compounds, including sulfurs, mercaptans, polysulfides. However, a few resistant sulfur compounds like dibenzothiophene (DBT) through the HDS procedure continues remain in diesel and in quantities significantly below the standard of environmental laws. The traditional the technique for lowering sulfur is catalytic hydrodesulfurization, necessitating elevated partial pressure of hydrogen and elevated reaction temperature, rendering HDS an extremely expensive choice for intensive desulfurization. Additionally, HDS is not efficient for eliminating heterocyclic sulfur compounds like dibenzothiophene (DBT) and its derivatives, particularly in the case of the alkyl dibenzothiophenes (DBTs) featuring one and/or two alkyl substituents at the 4- and/or 6-positions [2]. Confronted due to ongoing fuel quality issues, refiners have started to examine the oxidative desulfurization process (ODS), in significantly less severe reaction conditions, as a substitute for the complementary process to HDS for thorough desulfurization. The ODS procedure is essentially a two-step procedure, oxidation, succeeded through liquid extraction. In the oxidation phase, the sulfur-containing compounds undergo oxidation through suitable oxidizers to transform these substances into their related sulphones. These are extracted preferentially from oil because of their elevated relative polarity [3; 1]. During the extraction stage, the oxidized substances can be removed from the petroleum utilizing a solvent that does not mix. Depending on the solvent utilized for the extraction, the solvent and oxidized compounds are separated from the oil through gravitational separation or centrifugation. The water washes the oil to retrieve any remnants of solvent for extraction dissolved and polished us another approaches like absorption utilizing silica gel and alumina. The solvent is separated from the mixture of solvent and oxidized compounds (sulphones) by a simple distillation for recycling and re-use. Various kinds of oxidizing agents have been employed, incorporating different reactant gases such as H_2, CO, CO_2, O_2, HNO_3/AcOH, NO/NO_2, NO_2, HNO_3, H_2O_2 /H_2SO_4, BuOOH and O_3 [4]. Aida and Yamamoto [5] indicated that peroxyacids like performic acid, perfluoro acetic acid, and a blend of formic acid or trifluoroacetic acid and H_2O_2 was among the most effective oxidants for targeted oxidation of sulfur compounds in fuel oil. In light of this context, the objective of this study was to perform a comparative analysis of the oxidation of dibenzothiophenes utilizing a sequence of polyoxometalates serving as precursors for catalysts. Hydrogen peroxide was selected as an oxidizing agent since it does not negatively impact the product or result in ecological issues.

EXPERIMANTAL

2.1 Chemical Reagents

Chemical reagents in this study were of analytical grade and used without further purification. Three types of model sulfur compounds are selected to evaluate the reactivity of sulfur in the oxidation reaction. The chosen sulfur compounds are dibenzothiophene ($C_{12}H_8S$, DBT, 98%), 4-methyldibenzothiophene ($C_{13}H_{10}S$, 4-MDBT, 98%) and 4,6-dmethyldibenzothiophene

($C_{14}H_{12}S$, 4,6-DMDBT, 97%) were purchased from Aldrich. Hydrogen peroxide (30 wt % H_2O_2, oxidant) was supplied from the Surechem products Ltd. Phosphotungstic acid hydrate ($H_3PW_{12}O_{40}$ 20 H_2O, 99%), sodium phosphotungstic hydrate ($Na_3PW_{12}O_{40}$ 14 H_2O, 99%), phosphomolybdic acid hydrate ($H_3PMo_{12}O_{40}$ 15 H_2O, 99%) and silicotungstic acid hydrate ($H_4SiW_{12}O_{40}$ 25 H_2O, 99.9%) were used as catalysts and supplied from Aldrich. Acetonitrile and normal octane were used as solvents and supplied from Aldrich.

2.2 Catalytic Activity test

Based on ASTM D4294 method, Energy-Dispersive X-Ray Fluorescence (EDXRF) was used to determine the total sulfur content in the model oil before and after reaction. The Sulfur-in-Oil Analyzer (SLF A-1100, Horiba Inc., California) was employed to determine any sample with total sulfur content range from 0 to 5 wt. % of sulfur. Catalytic desulfurization activity was recorded in terms of DBT conversion using Eq. (1).

$$\text{DBT Conversion }\% = \frac{Ci - Cf}{Ci} \times 100 \qquad (1)$$

where:

C_i is the initial concentration of DBT

C_f is the final concentration of DBT

2.3 Batch Reactor

A 500 ml four necked flask fitted with a mechanical stirrer, a thermocouple and a thermometer was used to carry out the oxidation reaction. The reaction flask was placed in a heating mantel equipped with a temperature controller (within ±2 ^{0}C).

2.4 Procedure of Oxidation Experiments

The model sulfur compound (DBT, 4-MDBT, 4,6-DMDBT) was dissolved in n-octane to a simulate the model oil with sulfur concentration of 455 ppm. In experiments, at first the $H_3PW_{12}O_{40}$ (catalyst) was mixed with 30% aqueous peroxide in a 5 mL test tube. A few minutes later, the mixture was added into the reactor in which the simulated oil (20 ml) and acetonitrile (20 ml) were added. The resulting mixture was heated to the required reaction temperature and stirred at 750 rpm. This procedure was carried at different reaction temperatures (40 ºC, 50 ºC, 60 ºC and 70 ºC). Samples from the reactor are taken at 10, 20, 30 and 40 minutes. The collected samples were left to settle for few minutes after which two layers were formed; the top layer (model oil) and bottom layer (solvent). The top layer is analyzed by XRF to measure sulfur content. The same procedure was done for other catalysts.

3. RESULTES AND DESSCUSIN

Sulfur compound existed in liquid petroleum fuel, accounting for 85% of overall sulfur, is mainly thiophenic sulfur. Benzothiophene and its derivative are above 70% of thiophenic sulfur [6]. Removal of them and their alkylated derivative from fuel is difficult. In this work, oxidative desulfurization of simulate fuel using polyoxometalates catalysts synthesized was systematically investigated.

Various polyoxometalates catalysts were compared their catalytic activity in the oxidation reaction of DBT under the reaction conditions: DBT 544 ppm, catalyst 0.0074 gm, H_2O_2 (30 wt.%) 5ml, reaction temperature 60 °C. Under the experimental conditions, the DBT is directly converted into the corresponding DBT sulfone [7]; [2]. The results are shown in Figure 1. From this Figure, it is shown that phosphotungstic compounds (NPW) are much better catalyst precursors compared to their molybdenum counterparts (HPMO), while polyoxometalate compounds with silicon (HSIW) as their central atoms show the lowest activity**.** The phosphotungstic acid seemed slightly higher in oxidation activity compared to its salt form (NaPW). Based on these preliminary results, as the NPW displayed better performance in ODS reaction, it was selected for the next steps of the study, similar results have been found with homogeneous systems [8].

3.1 Effect of Reaction Temperature on the Oxidation Reaction of Model Oil

The effect of reaction temperature on the oxidation reaction of DBT was investigated (40-70 ^{O}C). Acetonitrile was used as the extraction solvent in the oxidation reaction system. The maximum reaction temperature was 70 ^{O}C due to the 81.1 ^{O}C boiling point of acetonitrile. The conversion profiles of DBT in the oxidation reaction versus the reaction time at four different temperatures under the same conditions are shown in Figure 2.

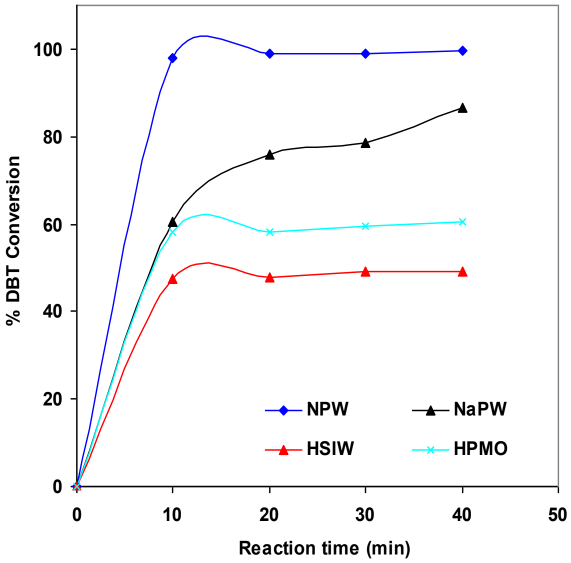

Fig. 1 Oxidation of DBT as a function of reaction time at various polyoxometalates compounds.

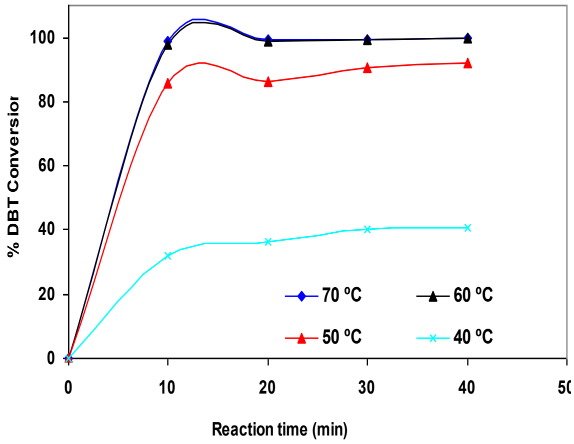

Fig. 2 Oxidation of DBT as a function of reaction time and reaction temperature using NPW as catalyst with 5 ml oxidant.

As shown in this Figure (Fig.2), at low temperature (40 ^{O}C), DBT conversion was only 40% in 40 min. However, 92 % sulfur removal efficiency was achieved in 40 min at 50 ^{O}C. When the reaction temperature was increased to 60 ^{O}C, a high DBT conversion (98%) was obtained in 10 min. However, the DBT conversion increased slightly by adding the reaction time. This may be due the decomposition of oxidant at high reaction temperature. When the reaction temperature went from 50 ^{O}C to 70 ^{O}C, the desulfurization efficiency was nearly 100% after 10 min of oxidation reaction. Consequently, the optimum oxidation reaction temperature of DBT can be determined as 60 ^{O}C.

3.2 Reactivity of Various Sulphur Compounds

To investigate the influence of the catalyst on the relative reactivity of different sulfur compounds (DBT, 4-MDBT and 4,6-DMDBT) was carried out at 60 °C. Under the same reaction conditions, the desulfurization efficiency of these compounds is shown in Figure 3. As shown in this Figure it was clearly that the conversion of DBT in simulated oil could reach nearly 100% after 10 min of reaction. Thus, the oxidative reactivity of the sulfur containing compounds decreased in the order DBT > 4-MDBT >4,6-DMDBT, which is in agrement with the reasults of HCOOH/H_2O_2 system [7] and oxometalytates /H_2O_2 in biphase catalytic system [8], [9]. This may be releated to electron densities of the sulfur atoms. The electron densities on the sulfur atoms of 4,6-DMDBT and DBT were 5.760 and 5.758, respectively [7],[8], [11]. When the electron density on sulfur atom was higher, the catalyst activity was higher [12] [13] [14]. Compared with DBT and 4,6-DMDBT, the difference in the electron density on the sulfur is very small, and it is the steric hindrance of the methyl groups (4-MDBT has one methyl group and 4,6-DMDBT has two methyl groups) that governs the reactivity, which become on obstacle for the approach of the sulphur atom to the catalytically active sites in a biphase system. The electron density for 4,6-DMDBT is the highest, but its oxidation reactivity was lower than DBT, this is due to the steric effect from the alkyl groups at the 4 and 6 positions.

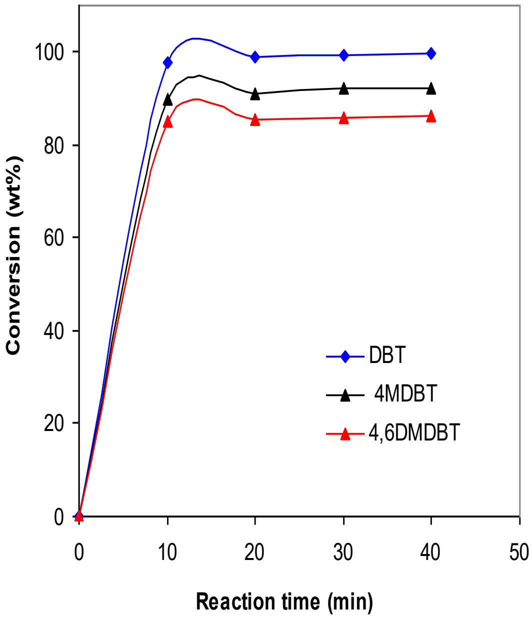

Fig. 3 Conversion variation with the reaction time in the reaction oxidation of DBT, 4-MDBT and 4,6-DMDBT using HPW as catalyst with 5 ml oxidant at 60 °C.

4. CONCLUSIONS

This work demonstrates that the removal of DBT, and also of 4-MDBT and 4,6-DMDBT, can be effectively accomplished by oxidation with hydrogen peroxide as oxidant and polyoxometalates as catalyst under mild reaction conditions; namely, reaction temperatures close to ambient (40-70 ^{0}C) and atmospheric pressure. The reaction activity of different sulfur-containing compounds decreased in the order DBT > 4-MDBT > 4,6-DMDBT. Under the optimum experimental conditions, the conversion of DBT was nearly 100%. In a word, this study clearly shows that NPW are an effective catalyst for ODS and they seem to be a promising alternative for sulfur removal in the petroleum industry.

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