Oxidative Desulfurization of Dibenzothiophene in a Micro-Structured Reactor

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It is known that the desulfurization process has great potential to be a complementary process to traditional hydrodesulfurizaion for producing deeply desulfurized diesel fuel. However, the traditional batch reactor system needs a long reaction time and high O/S molar ratio to achieve high conversion. In the present work, a micro-structured reactor system was used to investigate the oxidative desulfurization performance of dibenzothiophene. The results indicated that more than 90 % dibenzothiophene was oxidized within 3 min. The excellent mass transport capability of micro-structured reactor lead the dibenzothiophene oxidation carried out under stoichiometric ratio.

Key Words: Oxidative desulfurization, Dibenzothiophene, H_2O_2, Micro-structured reactor.

INTRODUCTION

Sulfur in transportation fuels remains a major source of SO_x which contributes to air pollution and acid rain[1]. Thus, the threshold limit for sulfur in gasoline and diesel is expected to be regulated on a global level to less than 50 ppm of weight (ppmw) over the next few years.

The current hydrodesulfurizaion (HDS) technology can desulfurize aliphatic and acyclic sulfur-containing organic compounds from liquid fuels on the industrial scale. However, aromatic dibenzothiophene (DBT) and especially 4,6-alkyl-substituted aromatic dibenzothiophenes are difficult to convert to H_2S due to the sterically hindered nature of these compounds on the catalyst surface[2]. For this reason, the removal of the aromatic dibenzothiophenes by hydrodesulfurizaion, to give the desired low levels of sulfur in diesel, requires high tempe-rature and H_2 pressure conditions and hence a bigger reactor size as well as an active catalyst. From an environmental and economic viewpoint, it is extremely desirable to develop alternative more energy-efficient desulfurizataion processes for the production of virtually sulfur-free fuel.

Recently, oxidative desulfurization (ODS) has attracted attention as one of the most effective methods to remove the remaining aromatic compounds in hydrotreated engine fuels. The aromatic sulfur-containing compounds show higher reactivity in oxidation than thiophenes and benzothiophene, in the reverse reactivity order of hydrodesulfurizaion[3]. Oxidative desulfurization takes place under mild conditions, converting sulfur-containing compounds to the corresponding polar sulfones which can be easily removed by solvent extraction[3]

or by adsorption[4]. In oxidative desulfurization, the oxidant and the corresponding catalytic system determine the performance and feasibility of the reaction system. The oxidants used in oxidative desulfurization include hydrogen peroxide[5,6], organic peroxides[7], nitric acid/NO_2[8], ozone[9], molecular oxygen[10] and potassium superoxide[11]. Of these oxidants, H_2O_2 has been extensively investigated because it is highly reactive and produces only water as the by-product after donating the active oxygen atom in oxidative desulfurization. The oxidation of sulfur-containing compounds takes place effectively in presence of formic acid[3] and acetic acid[12], because of the formation of peracids by H_2O_2 oxidation. However, in conventional batch reactor system, either the high reaction temperature or long reaction time causes the decomposition of H_2O_2. Therefore, a large excess of H_2O_2 is generally needed in the reaction system which increase the cost. In addition, because of the poor mass transport between oil and water phases, the reactant and the oxidant contact deficiently which cause the low reactant conversion. Therefore, increasing the mass transport between oil and water phases has been extensively pursured.

In the past decades, chemical reaction in flow micro-structured reactor systems has received significant research interests from both academia and industry[13-15]. Recent investigations revealed significant features of flow micro-structured reactor systems involving fast mixing from short diffusion path and fast heat transfer by virtue of high surface-to-volume ratio. In conventional batch reactor system, components are mixed through intensive stirring, while in micro-structures this process is mainly realized through diffusion. Despite laminar flows in micro-structures, molecules have short paths to over-

come so that a nearly complete mixture is achieved within a few seconds. Multilamination is one of the most useful principles which applied for the mixing of liquids. With the help of geometrical focusing, mixing times for liquid-phase reaction are possible in the millisecond time regime[16]. Therefore, in micro-structured reactors, the mass transport is considerably improved. Moreover, in liquid-phase reaction, the excellent mass transport capability leads to the reactants react near the stoichiometric ratio, which is significant important in practical application[17]. In this work, oxidative desulfurization of aromatic dibenzothiophene was investigated using H_2O_2 and acetic acid in vitreous interdigital micro-structured reactor system. The influence of reaction condition such as temperature, O/S molar ratio and reaction time were investigated.

EXPERIMENTAL

Toluene (AR grade), aromatic dibenzothiophene, acetic acid (AR grade) and H_2O_2 were purchased from Sinopharm Chemical Reagents Co., Ltd. (China) and used without purification. The setup of the micro-structured reactor system is shown in Fig. 1. It consists of two pumps, two preheating tube coils, one vitreous interdigital micro-structured reactor (IMM Mainz, Germany) with a standard mixing channel of 65 μm × 150 μm (Fig. 2) and a loop tubular reactor (1.80 mm in inner diameter and 3 m in length). The structure and mixing principle of this vitreous interdigital micro-structured reactor was shown in Fig. 3. The preheating tube coils and the micro-structured reactor were emerged in a circulating water bath (volume: 20 L). The temperature of the water bath was kept constant during the reaction. 1000 ppm aromatic dibenzothiophene solution in toluene and the mixer of H_2O_2 and acetic acid ($V_{H_2O_2}$:$V_{acetic\ acid}$ = 1:5) were injected by two syringe pumps, respectively. The advantage of our set-up lies in the fact that the reactants are preheated separately and thus the reaction is triggered at the desired temperature when they meet in the micro-structured reactor. Because the retention time in the reactor is in the milliseconds range, the reaction proceeds

Fig. 1. Schematic diagram of the micro-structured reactor system
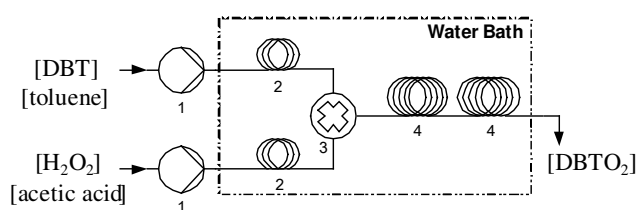
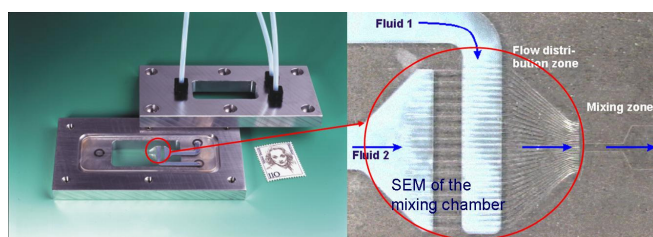1. Syringe pump ; 2. preheating coil ; 3. micro-structured reactor ; 4. delay pipe

Fig. 2. Photo (left) and the SEM of the mixing chamber (right) of vitreous interdigital micro-structured reactor (source IMM)
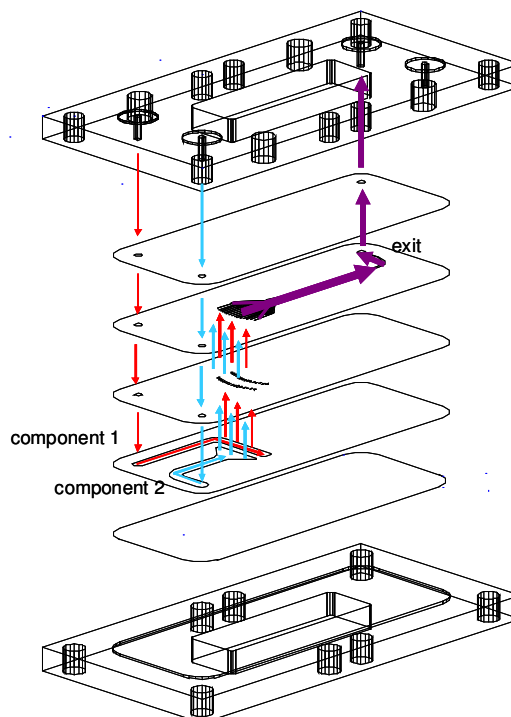

Fig. 3. Structure and mixing principle of vitreous interdigital micro-structured reactor (source IMM)

mainly in the tubular reactor. The flux was controlled to adjust the O/S molar ratio and residence time. We measured the temperatures at the outlet of the micro-mixer and in the middle of the tubular reactor. The measurement at nearly complete conversion indicated that only 0.8 ºC temperature difference was observed. It is therefore assumed that the reaction takes place at nearly isothermal conditions, which is in accordance with the prediction of the modeling from Waterkamp *et al.*[16]. The oxidation reaction equation is as follows:
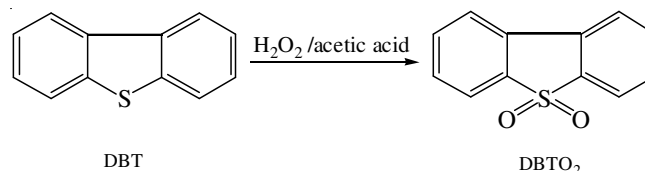
For comparison, oxidative desulfurization of benzothiophene and 4,6-dimethyl dibenzothiophene (4,6-DMDBT) were investigated in a similar way.

Detection method: The liquid sample was separated by centrifugation into two phases. The obtained oil phase was analyzed on an Agilent-6890 + gas chromatograph equipped with an FID using an HP-5 capillary column (5 % phenyl methyl polysiloxane, 30.0 m × 320 μm × 0.25 μm).

RESULTS AND DISCUSSION

Generally, the oxidation of aromatic dibenzothiophene is considered to be a consecutive reaction, *i.e.*, sulfur-containing compounds to sulfoxide to sulfone. In our study, no sulfoxide was detected by GC analysis under all reaction conditions. Therefore, the rate-determining step is the "sulfide to sulfoxide" and sulfoxide formation is considered to dominate the reaction rate[18]. Fig. 4 shows the variation of aromatic dibenzothiophene
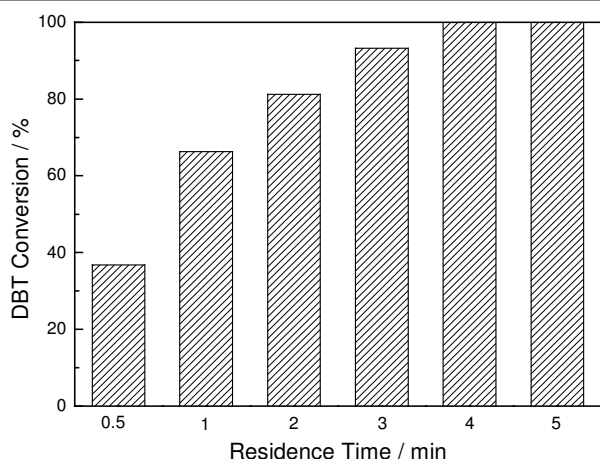
Fig. 4.　Variation of aromatic dibenzothiophene (DBT) conversion with residence time at O/S molar ratio of 3 and 70 ºC in micro-structured reactor
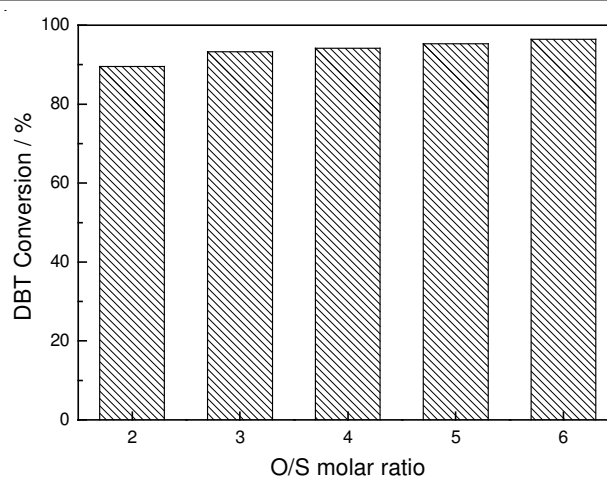

Fig. 5.　Variation of aromatic dibenzothiophene (DBT) conversion with O/S molar ratio at 70 ºC and residence time of 3 min in micro-structured reactor

conversion with residence time at O/S molar ratio of 3 and 70 ºC in micro-structured reactor. Over 60 % aromatic dibenzothiophene was oxidated to aromatic dibenzothiophene sulfone within 1 min which much faster than that reported in conventional batch reactor system. When the residence time increased to 4 min, complete conversion of aromatic dibenzothiophene was achieved. This indicated that the step "sulfide to sulfoxide" was accelerated in micro-structured reactor.

The O/S molar ratio is an important factor that affects the efficiency and economy of the reaction system. In the early studies on oxidative desulfurization, very high O/S molar ratios were used to enhance the kinetics. For example, an O/S molar ratio of 148 was used for the phosphotungstic acid-H_2O_2 oxidation system[19] and 162 for the polyoxometalate acid-H_2O_2 system[20]. Apparently, such a high O/S molar ratio is unfavourable, because a large excess of expensive H_2O_2 is wasted and the unreacted H_2O_2 poses a safety risk. Fig. 5 shows the variation of aromatic dibenzothiophene conversion with O/S molar ratio at residence time of 3 min and 70 ºC in micro-structured reactor. Almost 90 % aromatic dibenzothiophene conversion at O/S molar ratio of 2, the stoichiometric ratio, indicated that the excellent mass transport capability of micro-structured reactor cause the oxidative desulfurization reaction carried out under stoichiometric ratio. In the oxidation, there exist two parallel reactions, in which H_2O_2 is inolved. The undesirable thermal decomposition of H_2O_2, which is non-catalytic, takes place simultaneously with the catalytic oxidation. The competition of these two parallel reactions determines the utilization of H_2O_2 in the reaction and thus the conversion of aromatic dibenzothiophene. It is known that the decomposition rate of H_2O_2 mainly depends on temperature. Although the reaction temperature is 70 ºC, the excellent mass transport capability accelerated the aromatic dibenzothiophene catalytic oxidation which decreased the H_2O_2 decomposition. Moreover, the short residence time decreased the H_2O_2 decomposition effectively. The aromatic dibenzothiophene conversion increased to 93.2 % when the O/S molar ratio of 3. When the O/S molar ratio beyond 3, the aromatic dibenzothiophene conversion increased slightly, indicating the oxidant is amplitudinous when the O/S molar ratio of 3.

According to the Arrhenius formula, the reaction temperature shows a significant influence on the reaction rate constant. Increasing the reaction temperature always leads to the increased reaction rate constant. In conventional oxidative desulfurization of aromatic dibenzothiophene system, the reaction temperature is always below 60 ºC. This is because the H_2O_2 is instable and decompose rapidly at high temperature[3,6]. Fig. 6 shows the variation of aromatic dibenzothiophene conversion with reaction temperature at resi-dence time of 3 min and O/S molar ratio of 3 in micro-structured reactor. It is shown that aromatic dibenzothiophene conversion increased slowly at low temperature (30 and 40 ºC). It is likely that the oxidation reaction rate at low temperatures might be limited by kinetics. At higher temperature, aromatic dibenzothiophene conversion was markedly enhanced and the optimal temperature is 70 ºC. When the temperature is beyond 70 ºC, the aromatic dibenzothiophene conversion decreased slightly. In principle, increasing reaction temperature accelerates both aromatic dibenzothiophene oxidation and H_2O_2 thermal decomposition, which take place in parallel. Therefore, the decreased aromatic dibenzothiophene conversion may be due to the acceleration of H_2O_2 decomposition at such high temperature.
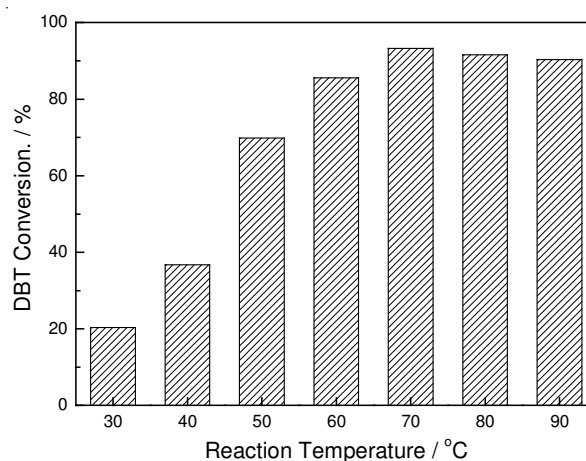

Fig. 6.　Variation of aromatic dibenzothiophene (DBT) conversion with reaction temperature at residence time of 3 min and O/S molar ratio of 3 in micro-structured reactor

Fig. 7 shows the variation of aromatic dibenzothiophene conversion with reaction time at O/S molar ratio of 3 and 70 ºC in conventional batch reactor. The aromatic dibenzothiophene conversion was less than 60 % after 2 h, much lower than the conversion in micro-structured reactor system with the same reaction condition. This indicated that the excellent mass transport capability of micro-structured reactor leads to the more molecular collision between aromatic dibenzothiophene and oxidant which greatly accelerate the oxidation reactivity.
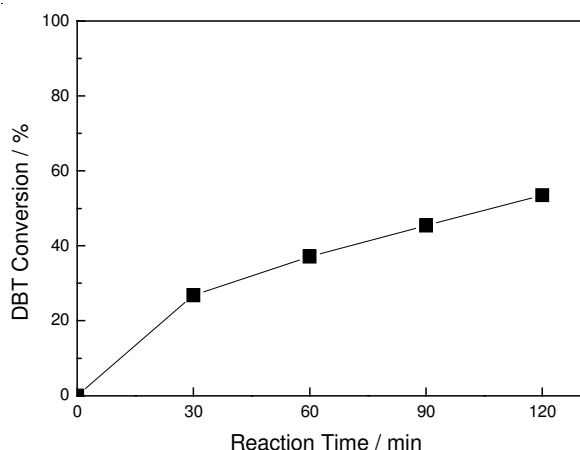

Fig. 7. Variation of aromatic dibenzothiophene (DBT) conversion with reaction time at O/S molar ratio of 3 and 70 ºC in conventional batch reactor

Fig. 8 compares the oxidative desulfurization performance of benzothiophene, aromatic dibenzothiophene and 4,6-dimethyl dibenzothiophene in micro-structured reactor. The oxidation reactivity decreased in the order: aromatic dibenzothiophene > 4,6-dimethyl dibenzothiophene > benzothiophene, the same order as observed in the polyoxometallates-H_2O_2 biphasic catalytic system which reported before[20]. Otsuki *et al.*[3] investigated the relationships between the rate constants of the oxidation of these model sulfur compounds to corresponding sulfones and the electron densities. The results indicated that rate constant increases with the increase of electron density. The divalent sulfur of aromatic dibenzothiophene can be oxidized by the electrophilic addition reaction of oxygen atoms to the hexavalent sulfur of aromatic dibenzothiophene sulfone. Hence,
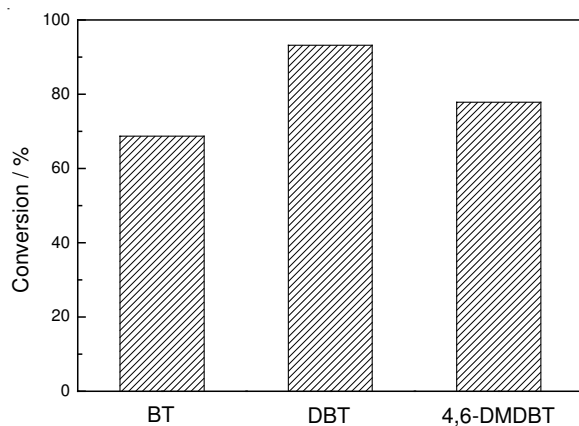

Fig. 8. Comparison of oxidative desulfurization performance of benzothiophene (BT), aromatic dibenzothiophene (DBT) and 4,6-dimethyl dibenzothiophene (4,6-DMDBT) in micro-structured reactor (reaction condition is 70 ºC, 3 min residence time and O/S molar ratio of 3)

the reactivity of oxidation becomes higher for a sulfur atom with high erelectron density. Therefore, the lowest reactivity of benzothiophene may be related to its lowest electron density. In addition, the low reactivity of 4,6-dimethyl dibenzothiophene may be attributed to the steric hindrance by methyl groups in the 4,6-dimethyl dibenzothiophene molecule which cause the decreased molecular collision between aromatic dibenzothiophene and oxidant.

Conclusion

Oxidative desulfurization of aromatic dibenzothiophene has been investigated using H_2O_2 and acetic acid in vitreous interdigital micro-structured reactor system. The results indicated that almost 90 % aromatic dibenzothiophene was oxidized within 3 min, whereas less than 60 % aromatic dibenzothiophene was oxidized after 2 h in traditional batch reactor system. Complete conversion of aromatic dibenzothiophene was achieved with 4 min at O/S molar ratio of 3 and 70 ºC. The excellent mass transport capability of micro-structured reactor leads to more molecular collision between aromatic dibenzothiophene and oxidant which greatly accelerate the aromatic dibenzothiophene oxidation.

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