



Oxidation kinetics of dibenzothiophenes using cumene hydroperoxide as an oxidant over MoO₃/Al₂O₃ catalyst



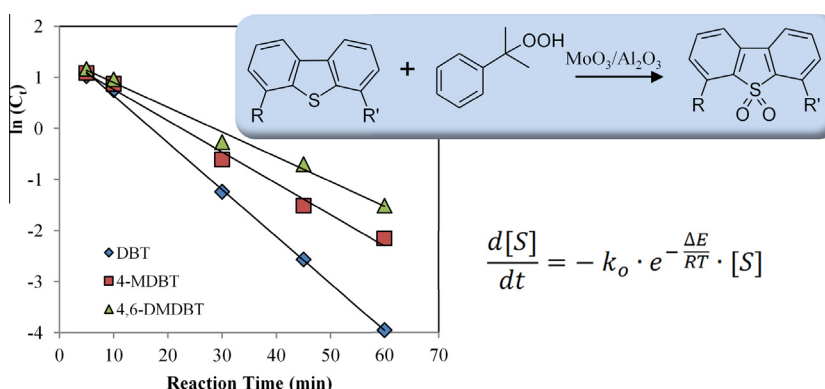
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HIGHLIGHTS

- Catalytic oxidation kinetics of the representative dibenzothiophenes in the presence of oil-soluble cumene hydroperoxide on a MoO₃/Al₂O₃ catalyst was firstly studied in detail.
- This oxidation system is promising for developing a cost-effective process to produce ultra-clean diesel.
- The presence of alkyl groups around the sulfur atom in dibenzothiophenes have significant effect on their oxidative reactivity, and more than 95% conversion of all dibenzothiophenes can be achieved at 75 °C.

GRAPHICAL ABSTRACT



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ABSTRACT

A study in oxidation kinetics of dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT) in a model fuel with cumene hydroperoxide as an oxidant over a MoO₃/γ-Al₂O₃ catalyst was carried out. Effects of the catalyst, hydroperoxide-to-sulfur molar ratio, reaction time, and reaction temperature on the oxidation were investigated in detail. The oxidation kinetics parameters for each sulfur compound were estimated. The oxidation rate constants decreased in the order of DBT > 4-MDBT > 4,6-DMDBT, indicating that the methyl groups around the sulfur atom in dibenzothiophenes have a significant effect on their oxidative reactivity. More than 95% conversion of all dibenzothiophenes was achieved at 75 °C with a hydroperoxide-to-sulfur molar ratio of 25 within 60 min.

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1. Introduction

In recent years, worldwide research interests in the production of ultra-low sulfur fuels have risen significantly [1,2]. The sulfur compounds in liquid hydrocarbon fuels are recognized as the substances of very high concern, as they produce sulfur oxides and other airborne particulate in combustion, resulting in the acid rain, and other environmental pollution [3]. These sulfur compounds in

liquid hydrocarbon streams also play a major role in the corrosion of combustion engines [4]. Moreover, the SO_x produced from the sulfur compounds in transportation fuels during combustion is known to poison the catalysts in catalytic converters that are for reducing CO and NO_x [4,5]. As a result, stringent environmental regulations on the specifications of sulfur in transportation fuels have been established in recent years. The petroleum refining industry is under massive pressure to produce ultra-low sulfur diesel to an upper limit of 15 ppmw in US and 10 ppmw in EU [6]. Given that a significant part of oil reserves consists of heavier fractions that contain higher content of sulfur levels, deep

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desulfurization for producing the clean transportation fuels with inexpensive ways has become a hot research topic and highly demanded in recent years [1,2,4,5,7].

In the petroleum refining industry, hydrodesulfurization (HDS) is a main technology currently for removal of the sulfur compounds from liquid hydrocarbon fuels. Typically, HDS process is conducted at high temperatures and high pressures with a huge consumption of hydrogen. This technology is fully efficient for the removal of thiols, sulfides, disulfides, and some thiophenic compounds, whereas it is difficult, or costly, for removing the refractory sulfur compounds, such as the alkyl dibenzothiophenes (DBTs) with their alkyl substituents at the 4- and/or 6-positions [4,7]. As a result, the HDS process is usually carried out at severe conditions to effectively remove the refractory sulfur compounds [8]. In order to achieve ultra-deep desulfurization of the fuels, low space velocities, higher hydrogen partial pressures, higher temperatures and higher hydrogen consumption are required, eventually resulting in a significant increase of the operating costs [2,5,8,9]. Therefore, it is urgently desired to develop some alternative ultra-deep desulfurization processes for producing ultra-clean fuels with inexpensive technology, low energy consumption and low environmental impact.

Oxidative desulfurization (ODS), combined with adsorption or extraction of the oxidized sulfur compounds, is considered to be a promising technology, because it is capable of removing the refractory sulfur compounds under mild conditions (e.g. atmospheric pressure and low reaction temperatures) without hydrogen consumption [1,2,4,5]. In a typical ODS process, non-polar organic sulfides are initially oxidized to their corresponding sulfones, followed by a second step of subsequent separation of the polar sulfones through extraction [10,11] or adsorption [12,13]. The formed sulfones may be used as low cost feedstock for synthesis of various engineering and conducting polymers [14,15]. In recent years, various oxidation systems with water soluble or oil soluble oxidants, such as acetic acid/H₂O₂ [11], molybdenum-based catalyst/H₂O₂ [16], polyoxometalate/H₂O₂ and formic acid/H₂O₂ [17], vanadium-oxide-based catalyst/H₂O₂ [18], molybdenum-based catalyst/*t*-butyl hydroperoxide (*t*-BuOOH) [12], titanium- and vanadium-based metal organic frameworks/*t*-BuOOH [19,20], isobutyl aldehyde/air/*t*-BuOOH [21], and Fe(III) salts/O₂ [13], have been studied for the oxidative desulfurization.

Otsuki et al. reported an exceptionally encouraging oxidation reactivity trend for the refractory sulfur compounds in a formic acid/H₂O₂ system, at an oxidation temperature of 50 °C and atmospheric pressure [22]. They found that the oxidation rate constants decreased in the order of 4,6-dimethyldibenzothiophene (4,6-DMDBT) > 4-methyldibenzothiophene (4-MDBT) > DBT. This oxidation reactivity trend is the inverse of the typical reactivity trend of dibenzothiophenes in hydrodesulfurization process. They explained that DBTs with more methyl groups at the 4- and/or 6-positions have higher electron density around the sulfur atom, resulting in their higher reactivity in oxidation with hydrogen peroxide. Unlike the HDS process, the oxidation of all the thiophenic compounds can be achieved at mild conditions.

Unfortunately, the ODS technology using oil-insoluble H₂O₂ as an oxidant, which forms biphasic liquid system, has not gained much recognition as an industrial application process. This is due to various obstacles that include low-oxidation rate due to mass transfer limitations caused by the formation of the interface between aqueous phase and oil phase, which decreases the diffusion rates of the oxidant and the oxidized sulfur compounds, resulting in excessive consumption of the oxidant or the need to add other agents (such as phase transfer agents) to improve the diffusion through the water–oil interface [4,11,16–18,22]. In addition, the biphasic ODS process, especially with some agent, leads to difficulty in separation of oil phase from aqueous solution due to formation of

emulsion, and thus reduce the oil yield. Moreover, the high volume ratio of aqueous-phase to oil phase in the oxidation system also reduces the efficiency of the reactor, and the aqueous phase with H₂O₂ also causes severe corrosion problem to the equipment. Therefore, researchers started using oil soluble oxidants such as tertiary butyl hydroperoxide (*t*-BuOOH), which forms a single phase ODS system [12,19–21]. The usage of oil soluble oxidants improves overall oxidation rate of the refractory sulfur compounds. Nonexistence of aqueous phase prevents from the formation of emulsion, and results in high-oxidation rate and less consumption of the oxidant in comparison with the biphasic ODS system.

Some researchers also explored other oil soluble oxidants, such as cumene hydroperoxide. Han et al. reported the oxidation of DBT with cumene hydroperoxide on a MoP_xO/SiO₂ catalyst in a fixed-bed reactor [23]. The total sulfur in the treated diesel fuel was reduced from 298 to 5 ppmw through oxidation with cumene hydroperoxide and ensuing dimethylformamide extraction step. As well, Chang et al. reported the oxidation of dibenzothiophenes in decalin using cumene hydroperoxide on alkaline earth metal modified MoO₃/SiO₂ catalysts [24]. The DBT conversion reached 95% at ambient conditions (60 °C), while 4,6-DMDBT showed lower oxidation reactivity than DBT due to steric hindrance. However, there is also a significant shortage for using oil soluble oxidants in ODS, as the oxidants are usually unstable and dangerous for mass storage and transportation. In order to solve these problems, some researchers have started to explore the direct usage of molecular oxygen as an oxidant in ODS [6,25–29].

Sundaraman et al. reported a novel ODS process, where cumene hydroperoxide is generated in-situ using air as an oxidant [6]. Cumene can usually be found in gas oil, so the generation of an oil soluble oxidant, such as cumene hydroperoxide, using molecular oxygen (such as O₂ in air) would decrease the operating costs, solve the safety issue, and result in an environmentally friendly process along the way. Zhang et al. reported the oxidative desulfurization using in-situ-generated peroxides in diesel by light irradiation [25]. All these studies indicate that using in-situ-generated cumene hydroperoxide as an oxidant for the ODS is a promising process for deep desulfurization of diesel.

As well known, kinetic studies in ODS of typical sulfur compounds with cumene hydroperoxide are crucial in deep understanding of the reaction mechanism and development of the ODS process for practical application. Selvavathi et al. has studied the oxidation kinetics of sulfur compounds in diesel with *t*-BuOOH [30]. Zhang et al. have examined the effect of the reaction time on conversion of DBT, 4-MDBT and 4,6-DMDBT in ODS with the in-situ-generated peroxides, although not given any kinetics parameters [25]. There are no any kinetic studies reported in available literature about the oxidation of the typical sulfur compounds with cumene hydroperoxide, although such kinetic study is significant, regardless using the in-situ-generated or non-in-situ-generated cumene hydroperoxide. The present paper reported our recent study in oxidation kinetics of DBT, 4-MDBT and 4,6-DMDBT with cumene hydroperoxide on a MoO₃/γ-Al₂O₃ catalyst. The effects of the reaction time, reaction temperature, O/S molar ratio as well as catalyst on the oxidation were examined in detail. The different reactivities of the sulfur compounds were also discussed according to the obtained results in comparison with those in other oxidation systems reported in literature.

2. Experimental

2.1. Materials

All chemicals, including *N*-hexadecane (99%), *n*-tetradecane (>99%), toluene (>99%), dibenzothiophene (DBT) (98%), 4,6-

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