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Research article

Oxidative removal of dibenzothiophene and related sulfur compounds from fuel oils under pressurized oxygen at room temperature with hydrogen peroxide and a phosphorus-free catalyst: sodium decatungstate

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ABSTRACT

We investigated the removal of dibenzothiophene (DBT) and related compounds, 4-methyldibenzothiophene (4-MeDBT), 4,6-dimethyldibenzothiophene (4,6-DMeDBT), 2,8-dimethyldibenzothiophene (2,8-DMeDBT), and 1-benzothiophene (1-BT) from several oil media at room temperature under pressurized O_2 (0.6 MPa) by means of a three-phase reaction system consisting of the oil phase, an aqueous phase containing the phosphorus-free polyoxotungstate catalyst $Na_4W_{10}O_{32}{\cdot}8H_2O$, H_2O_2, and tetraoctylammonium bromide, and the gas phase. Under conditions in which the initial DBT concentration in octane was 10.1 mM, the desulfurization ratio reached 87% after reaction for 6.5 h. The sulfur atoms in the initial DBT were well accounted for by the sulfur atoms in the residual DBT, the dibenzothiophene sulfone and dibenzothiophene 5-oxide in the octane phase, and the dibenzothiophene sulfone that precipitated. Prolonged reaction time to 18 h resulted in 92% desulfurization. The desulfurization of octane decreased in the order 2,8-DMeDBT ~ DBT > 4-MeDBT > 1-BT ~ 4,6-DMeDBT. Light oil and kerosene could also be desulfurized efficiently: after reaction for 6.5 h, the desulfurization ratios reached 77 and 78% for light oil and kerosene, respectively.

1. Introduction

Environmental regulations require desulfurization of fuel oils to minimize air pollution by SO_x species [1]. In addition, fuel oils used as hydrogen sources in fuel cell systems must be desulfurized to avoid poisoning of the reforming catalysts and the catalysts in fuel cell electrodes [2–5]. In refining industry, sulfur is commonly removed from fuel oils by means of catalytic hydrodesulfurization (HDS), which converts organosulfur compounds to hydrogen sulfide and nonsulfur compounds by reaction with H_2 in the presence of a catalyst [6–12]. However, HDS requires the use of high temperature (300–360 °C), high H_2 pressure (3.0–5.0 MPa), and expensive catalysts such as $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ [4, 6, 8, 10, 12]. Furthermore, this process does not effectively remove dibenzothiophene (DBT) and its alkyl-substituted derivatives, because steric bulk around the sulfur atoms hinders adsorption of these compounds on the catalyst surface [6, 8, 12]. Therefore, methods such as two-stage HDS are used to produce ultraclean fuel oils [8], but these methods are energy intensive.

Studies aimed at improving the HDS process and developing alternative desulfurization processes, such as alkylation, extraction, oxidation, and precipitation, have been carried out [9, 10]. Among the various alternatives, oxidative desulfurization (ODS) is attractive because it proceeds at temperatures and pressures lower than those required for HDS. As catalysts for ODS, polyoxotungstates have been widely investigated since Collins and coworkers first reported that DBT can be removed from toluene with a two-phase system consisting of the toluene solution of DBT and an aqueous solution containing phosphotungstic acid (tungstophosphoric acid, $H_3PW_{12}O_{40}$) as a catalyst and H_2O_2 as an oxidant [13]. Te and coworkers also examined the oxidation of DBT with polyoxotungstates (e.g., $H_3PW_{12}O_{40}$, $Na_3PW_{12}O_{40}$, and $H_4SiW_{12}O_{40}$) [14], and Yazu and coworkers reported that DBT can be removed from octane or light oil by means of a two-phase oil (octane or light oil)/acetonitrile (MeCN) system in the presence of $H_3PW_{12}O_{40}$ and H_2O_2 [15]. In these systems, DBT is transferred from the oil phase (toluene, octane, or light oil) to the extractant phase (containing the polyoxotungstate and H_2O_2), where the DBT is oxidized to highly polar dibenzothiophene sulfone (DBT-O_2, Fig. 1a).

Various modifications of ODS processes that use polyoxotungstate catalysts have been reported: such modifications include the use of ultrasound irradiation [16, 17], immobilized polyoxotungstate

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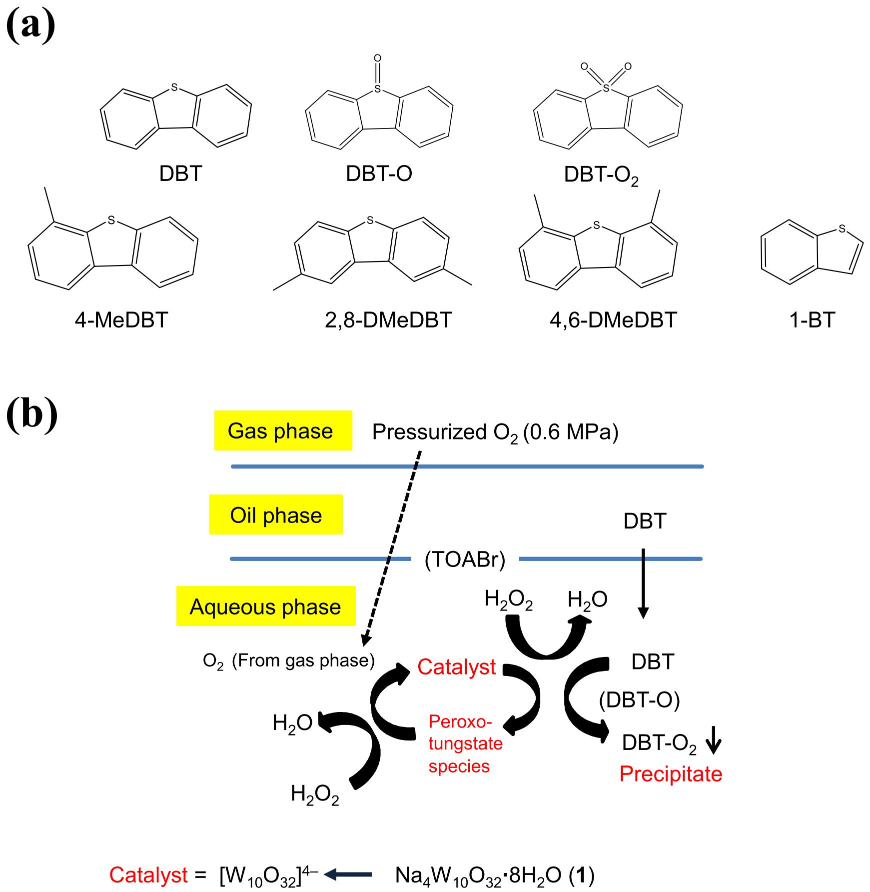

Fig. 1. (a) Structures of sulfur compounds used in this study and (b) proposed mechanism of desulfurization by means of the three-phase system.

[17–27], an amphiphilic polyoxotungstate [28–33], an ionic liquid as an extractant or catalyst component [21, 23, 34–38]. However, most of these systems use acid or salt forms of polyoxotungstates with a heteroatom—that is, heteropolyanion structures represented by the formula of $[XW_mO_n]^{z-}$, where X is a heteroatom (typically, pentavalent phosphorus). In addition, the effect of the gas phase above the oil phase has not been examined. Because the presence of heteroatoms such as phosphorus presents a major obstacle to recovery of the valuable tungsten from the catalyst waste [39], polyoxotungstates without a heteroatom—that is, isopolyanions consisting of only tungsten and oxygen atoms—would be highly desirable to facilitate the recycling of tungsten. However, only a few studies have focused on ODS involving isopolyanions [30, 35, 37]. Specifically, there have been two studies involving decatungstate ($[W_{10}O_{32}]^{4-}$), which is a representative isopolyanion: a study of DBT oxidation mediated by a surfactant-type catalyst consisting of $[W_{10}O_{32}]^{4-}$ and a hydrophobic cation [30] and a study involving a combination of the same catalyst and an ionic liquid [35]. Efficient desulfurization using a simple salt of decatungstate, such as $Na_4W_{10}O_{32}$, in the absence of a specialized extractant such as ionic liquid has not been reported.

In the present work, we investigated the removal of DBT, 4-methyldibenzothiophene (4-MeDBT), 4,6-dimethyldibenzothiophene (4,6-DMeDBT), 2,8-dimethyldibenzothiophene (2,8-DMeDBT), and 1-benzothiophene (1-BT) from several oil phases (octane, light oil, kerosene, and toluene) at room temperature under pressurized O_2 by means of a three-phase reaction system consisting of the oil phase and an aqueous phase containing $Na_4W_{10}O_{32}·8H_2O$ (**1**) as a catalyst, H_2O_2 as an oxidant, and tetraoctylammonium bromide (TOABr) as a phase-transfer agent, and the gas phase. We evaluated the effects of the gas phase, the structure of the sulfur compounds, and the nature of the oil phase not only on the removal of the individual organosulfur compounds but also on the total sulfur concentration in the oil phase. In addition, we compared the results with those obtained with $Na_3PW_{12}O_{40}$.

2. Experimental

2.1. Materials

DBT (> 98%) and 1-BT (> 95%) were purchased from Wako Pure Chemical Industries (Osaka, Japan). DBT-O_2 (97%), 4-MeDBT (96%), and 4,6-DMeDBT (97%) were obtained from Sigma-Aldrich (St. Louis, MO, USA). 2,8-DMeDBT (> 97.0%) and dibenzothiophene 5-oxide (DBT-O) were obtained from Tokyo Chemical Industry (Tokyo, Japan) and Santa Cruz Biotechnology (Santa Cruz, CA, USA), respectively. $Na_3PW_{12}O_{40}·13H_2O$ was a gift from Nippon Inorganic Colour & Chemical (Tokyo, Japan). Light oil (grade for petroleum products testing) and kerosene were purchased from Kanto Chemical (Tokyo, Japan). Combustion ion-chromatography revealed that total sulfur concentrations in the light oil and kerosene were 1.2 and 1.1 mM, respectively, although HPLC showed that these oils contained no DBT.

Catalyst **1** was prepared from $Na_2WO_4·2H_2O$ according to the literature method [40] with some modifications, as follows. $Na_2WO_4·2H_2O$ (0.10 mol) was dissolved in pure (Milli-Q) water (200 mL) and the solution was heated at 95 °C with stirring. To this solution was added 1.0 M HCl (200 mL), and the solution was stirred for 10 s and then divided into two equal portions. Each portion was rapidly cooled to 30 °C with ice bath, and then NaCl (0.51 mol) was added to each solution. The two solutions were stirred for an additional 10 min with cooling from an ice bath, and the precipitates that formed were collected. The two precipitates were combined, dried in vacuo, and dissolved in MeCN (100 mL) at 75 °C, and the mixture was passed through a glass filter. The filtrate was stored overnight in a refrigerator