

Desulfurization of diesel via the H₂O₂ oxidation of aromatic sulfides to sulfones using a tungstate catalyst

Farhan Al-Shahrani^{a,b}, Tiancun Xiao^a, Simon A. Llewellyn^a, Sami Barri^c, Zheng Jiang^a,
Huahong Shi^a, Gary Martinie^b, Malcolm L.H. Green^{a,*}

^a*Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, UK*

^b*R&DC, Dhahran 31311, Saudi Arabian Oil Company, Saudi Arabia*

^c*Chemical Engineering Department, Imperial College, London, UK*

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Abstract

A simplified oxidative desulfurization (ODS) catalytic system composed of Na₂WO₄, 30% H₂O₂ and CH₃CO₂H has been found suitable for the deep removal of sulfur in diesel. By combining ODS and methanol extraction, the sulfur level in a commercial diesel has been reduced from 1100 ppm to 40 ppm. Treatment of model solutions of octane containing dibenzothiophene and 4,6-dimethyl dibenzothiophene with our ODS system shows 100% conversion of the thiophenes to sulfones at 70 °C in less than 1 h.

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1. 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 [2].

The removal of sulfur-containing compounds from liquid fuels is currently achieved by hydrodesulfurization (HDS) using a Co–Mo/Al₂O₃ or a Ni–Mo/Al₂O₃ catalyst (360 °C and 3–5 MPa H₂ pressure) [3]. The current HDS technology can desulfurize aliphatic and acyclic sulfur-containing organic compounds on the industrial scale. However, aromatic dibenzothiophene (DBT) and especially 4,6-alkyl-substituted DBTs are difficult to convert to H₂S due to the sterically hindered nature of these compounds on the catalyst surface [4,5]. For this reason, the removal of the DBTs by HDS, to give the desired low levels of sulfur in diesel, requires high temperature and H₂ 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 desulfurization processes for the production of virtually sulfur-free fuel.

Reported deep desulfurization processes include, but are not limited to, selective adsorption [5], extraction with ionic liquids [6], oxidative desulfurization (ODS) [7–10], biodesulfurization [11], and other processes [12]. Due to a short reaction time at ambient conditions, high efficiency and selectivity, ODS combined with extraction is regarded to be the most promising of these processes. Various studies on the ODS process have employed different oxidizing agents such as NO₂ [13] *tert*-butyl-hydroperoxide [10] and H₂O₂ [7–10]. H₂O₂ is commonly used as an oxidizing reagent due its affordable cost, environmental compatibility, and commercial availability. H₂O₂ is effective in the presence a transition-metal based catalyst and in acid media [7–10].

Different transition metal catalysts have been used, such as tungstophosphoric acid [7], Na₂WO₄ + [(*n*-C₄H₉)₄N]Cl [14], K₁₂WZnMn₂(ZnW₉O₃₄)₂ and [CH₃(*n*-C₈H₁₇)₃N]Cl [15], 2-NO₂C₆H₄SeO₂H [16], hemoglobin [17] and others [12]. In previous papers, it has been reported that tungsten catalysts are very effective for the oxidation of thioethers to sulfoxides and consequently to sulfones using H₂O₂ as the oxidant in a two

* Corresponding author. Tel.: +44 186575917; fax: +44 1865272690.

E-mail address: malcolm.green@chemistry.oxford.ac.uk (M.L.H. Green).

phase liquid–liquid system with a phase transfer catalyst (PTC) [8,18,19].

Here we describe a simplified and highly effective tungsten based catalytic system for the oxidation of aromatic sulfur-containing compounds such as dibenzothiophene without the use of PTCs. The catalytic system was evaluated for the removal of sulfur-containing compounds in both a model solution and a commercial diesel sample.

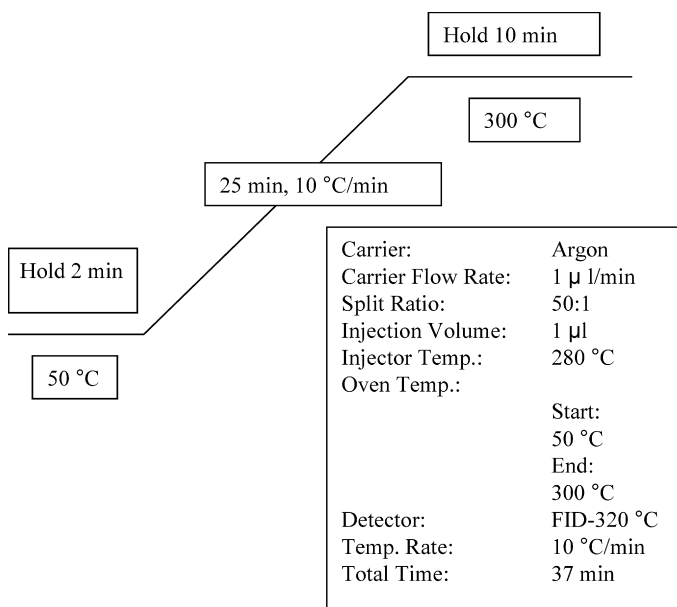
2. Experimental

2.1. Materials

n-Octane, glacial acetic acid, sodium tungstate, dibenzothiophene (DBT), 4,6-dimethyl dibenzothiophene (4,6-DMDBT) and hydrogen peroxide were all bought from Sigma–Aldrich, Europe and used without further purification. Hydrotreated (HT) diesel with a sulfur content of 1100 ppm was obtained from the Rabigh Refinery of Saudi Aramco in the Kingdom of Saudi Arabia. Model solutions containing DBT or 4,6-DMDBT were prepared by dissolving equimolar quantities of DBT and 4,6-DMDBT in *n*-octane to give solutions with a sulfur content of 500 ppm.

2.2. Analysis of organosulfur content in model systems

A Perkin-Elmer GC coupled with flame ionization detector (GC-FID) was used to identify the various sulfur compounds and their concentrations in the model solutions. The GC was equipped with a split/splitless injection port and operated in 50:1 split mode. A 30 m × 0.32 mm inner diameter × 1.0 μm film thickness HB-1 MS capillary column was used for separation. High purity argon and hydrogen gases were used as carrier and fuel for the FID, respectively. Sample volumes of 1 μl were injected without any solvent dilution. The temperature profile used is given below.



2.3. Analysis of organosulfur content in diesel

Diesel in general is known to contain many aliphatic and aromatic compounds, thus analysis by GC-FID is not sufficient. Instead, another specific sulfur detector should be utilized such as PFD or PFPD. An original hydrotreated (HT) Diesel (1100 ppmw S) obtained from the Rabigh Refinery in Saudi Arabia was analyzed by a Gas Chromatography hyphenated to a Pulsed Flame Photometric Detector (GC-PFPD). The analyses of the diesel samples were carried out on a Varian CP SIL 5CB column with 25 m length, 0.25 mm internal diameter and 1.2 μm coating. The gas chromatograph (Varian 3100) was equipped with Varian PFPD and the benzothiophene was used as internal standard. This technique was able to identify 79 sulfur-containing compounds with detection limit of up to $2 \times 10E-13$ g S/s, the highest abundance of which are shown in Fig. 1.

2.4. Catalytic ODS testing on model solutions

The catalyst system was prepared by combining 0.2 g of sodium tungstate (Na_2WO_4), 1 ml of 30% hydrogen peroxide (H_2O_2) with 5 ml of acetic acid ($\text{CH}_3\text{CO}_2\text{H}$) with the molar ratio 1:10:87, respectively. The catalyst system was separately mixed with 50 ml of the DBT and 50 ml of the 4,6-DMDBT model solutions (1:1 molar ratio). In separate runs, new mixtures were stirred and heated up to 30, 50, 70 and 90 °C with a reaction time of 30 min at each temperature. In each run, the Na_2WO_4 started to dissolve in the mixture forming first an emulsion and then an opaque lower layer which formed a white milky layer above 70 °C. The progress of each reaction was monitored periodically by withdrawing 0.1 ml aliquots of the upper hydrocarbon layer of the reaction mixture for GC-FID analysis.

2.5. Catalytic ODS testing on HT diesel

An analogous experimental procedure to that described in Section 2.4 was applied here but with HT diesel instead of

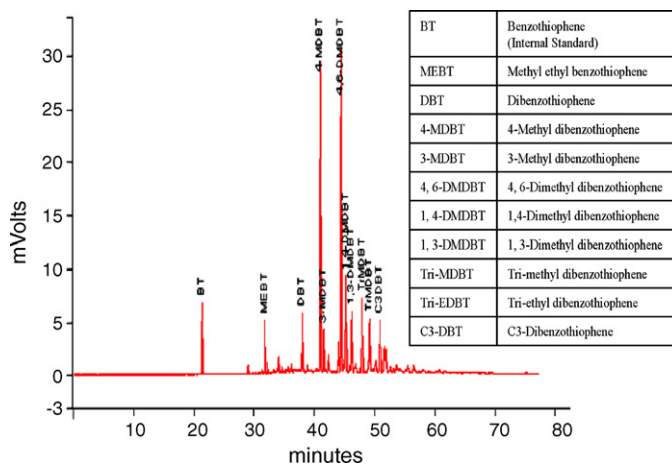


Fig. 1. GC-PFPD chromatograph of the sulfur-containing compounds in the HT diesel.

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