



Roles of surface chemistry and structural defects of activated carbons in the oxidative desulfurization of benzothiophenes



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HIGHLIGHTS

- Acid-treated, wood-based activated carbon promotes benzothiophene oxidation.
- Effective materials possess high surface area and high density of surface acids.
- In situ formation of surface-bound percarboxylic acids is hypothesized.

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ABSTRACT

A range of different activated carbons was characterized and evaluated for promotion of the oxidative desulfurization (ODS) of JP-8 fuel using H₂O₂ oxidant and acetic acid. Wood-based carbons activated by acid treatment showed much higher effectiveness than all other carbon types, regardless of source or activation method. Under identical test conditions designed to differentiate material performance, the most effective carbon material yielded 69% oxidation of 2,3-dimethylbenzothiophene (2,3-DMBT) whereas the ineffective materials scarcely out-performed the control (10% oxidation). To understand the characteristics most associated with reaction promotion, the textural, chemical, and defect features of the carbon materials were examined using a battery of techniques. The effective promoters all shared in common high surface areas and high pore volumes; however, surface area and pore volume alone could not explain the observed trends in performance. Investigating surface chemistry, presence of strong acid sites was strongly related to ODS performance. Overall, long-range order was not required for high activity, yet neither were edge defect sites. These results suggest that carbon promotes ODS by formation of percarboxylic acid species at defect sites within the carbon basal planes. Post-reaction analysis of the carbon materials provided evidence to support this explanation.

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1. Introduction

Because of increasingly stringent environment legislations, sulfur content in transportation fuels has been strictly limited to very low levels. For example, in the USA, the acceptable level of sulfur in diesel was reduced to 500 ppm in 1995 by the Clean Air Act amendments; it was then reduced to 350 ppm in 2000; 50 ppm in 2005; and finally 15 ppm since 2006 [1–9]. Similarly, in the European Union, maximum sulfur in the market diesel was reduced to 10 ppm since 2008 [10]. To address these strict

regulatory requirements, several technologies have been developed for deep desulfurization of oil refinery fuels, which can be generally classified [11] into hydrodesulfurization (HDS) [2,12–14], oxidative desulfurization (ODS) [15–23], biodesulfurization [24–28], adsorption desulfurization (ADS) [6,29–41], and extractive desulfurization using organic solvent, ionic liquids [42,43], or deep eutectic solvent mixtures [44]. Of these different technologies, ODS has proven effective at reducing sulfur concentrations in fuels to meet the new legislations [11]. Among a wide variety of materials that have been examined for ODS, carbon-based materials [18,45–47] have attracted great attention because of their abundance, low cost, large surface area (500–2500 m²/g),

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satisfactory porous structure (varying from micro- to mesoporosity), and high surface concentration of oxygen functional groups [31–33,36,48–51].

For activated carbon promoted ODS, the strategy is to oxidize fuel sulfur compounds to increase their polarity, and then remove them from the fuel by adsorption onto a polar sorbent [52,53]. Thus, oxidation and adsorption may be combined into one process with the carbon playing simultaneous adsorption and catalytic roles. Even without sulfur compound oxidation, some carbon materials have shown high capacity and selectivity in the removal of dibenzothiophenes (DBTs) from petroleum fuels [7,31–33,36–38,49,51]. For example, Triantafyllidis et al. [54] reported that the dibenzothiophene adsorption capacity of carbon materials could be correlated with their micro- and mesoporosity. In separate works, correlations [31,50,55,56] between adsorption capacity and the chemical properties of the carbon surface have been established.

Unfortunately, most of the published papers regarding desulfurization using carbon materials are confined to model fuels with only a limited number of papers on the studies of activated carbon as a catalyst for real fuel desulfurization [2,18,19]. Furthermore, although the surface chemistry of carbons has been shown important for thiophenic compound adsorption [31–33,36,50,57] and (separately) catalysis [31,58–60], the specific role of activated carbon in promoting the oxidation reaction is not yet clear. As a result, relationships between carbon characteristics and performance are unknown, making process optimization a trial-and-error process.

In previous work, we found that carbon-promoted ODS was capable of achieving <10 ppm sulfur levels in JP-8 jet fuel and that a wood-based carbon was more effective than a peat-based carbon [18]. Safe concentrations of the low-cost oxidant hydrogen peroxide were used in the process, along with low concentration of formic acid. The oxidant phase is fuel immiscible [52,61], permitting >90% fuel recovery post-treatment even at small scale [18].

The challenge in ODS is achieving cost competitiveness with HDS. To improve the economics of ODS, we therefore set out to understand the role of the activated carbon promoter so as to reduce its use, thereby improving process economics. In a second published work [19] we showed that, depending on the types of sulfur compounds present in the fuel, either oxidization of the benzothiophene (BT) content [62] or removal of oxidized sulfides/disulfides/thiophenes [63] could limit overall ODS performance. Given that BT oxidation can limit ODS performance, the motivation of our ongoing research was the selection of the best carbon material for oxidation of BT compounds [19]. Again, our previous work [18,19] indicated that all BT compounds responded similarly to the carbon-promoted ODS treatment and that 2,3-DMBT was the most recalcitrant of the jet fuel BT compounds. Hence, we focused our attention on ODS of this compound.

We have measured the BT oxidation performance of performic acid in the presence of a range of activated carbons, representing different raw materials (peat, wood, coal), different activation protocols (steam, acid), and different vendors. The carbons were then characterized using a battery of techniques including N₂ physisorption, solid state Boehm titration, Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), Raman microspectroscopy, and carbon k near edge X-ray absorption fine structure (C K-NEXAFS) spectroscopy to investigate the roles of textural, chemical, and defect features on ODS promotion effects. Based on the combined analysis results, we hypothesize a mechanism of ODS promotion by activated carbon that involves transient formation of highly active surface-bound percarboxylic acid sites.

2. Experimental methods

2.1. Carbon materials

In this work, 12 carbon materials were examined for ODS performance. The carbon materials were donated by Meadwestvaco, Pica, and Norit (since purchased by Cabot). Table 1 lists the carbon materials, the feedstock used as the carbon source, activation method, and vendor information. The carbon materials can be classified into 3 groups: 8 samples are wood-based carbons, 2 are peat based carbons, and 2 are coal-based carbons. Activation methods include phosphoric acid, steam, ammonia, and thermal treatment. We have also tested several carbon black materials and found them to be active for ODS promotion but these results are not presented here. All carbons were used after washing with copious amounts of DI water (10 × volume) and oven drying over night at 80–100 °C.

2.2. ODS promotion tests

All ODS promotion tests were performed in 40-mL disposable glass sample vials (obtained from Ace Glass with PTFE-lined caps) that were agitated at room temperature using a wrist-action shaker (Burrell). Up to 8 samples could be processed at a time, providing a rapid procedure to perform ODS performance tests. Table 2 provides typical conditions used for shaker tests. In previous work [18,19], we have already shown that the activated carbon promoted ODS technique can be effective; the ODS conditions used in the current study were selected to provide a maximum range in performance so that carbons could be differentiated more precisely. Accordingly, superior ODS performance and rates could have been achieved using similar materials simply by increasing the reaction temperature – as we have previously demonstrated [18].

JP-8 jet fuel, donated by the Air Force Research Laboratory and with a fuel sulfur content of 717 ppm_w, was used for all tests. JP-8 contains a complex mixture of benzothiophene and sulfide/disulfide/thiophene compounds [19,62,63]. Following on our earlier work [18], we tracked ODS performance by monitoring the disappearance of BT compounds. Here, we report data for disappearance of 2,3-dimethylbenzothiophene (2,3-DMBT) specifically. We select this compound for reporting purposes as we previously found that all BT compounds responded similarly to the ODS treatment, with 2,3-DMBT being the most recalcitrant [18]. Accordingly, oxidation data for 2,3-DMBT are representative of BT compounds as a class.

Treated fuels were analyzed for BT and specifically 2,3-DMBT content using a gas chromatograph (GC, Agilent 6890) coupled to a mass selective detector (MS, Agilent 5975) in select-ion mode using $m/z = 162$ and a retention time of 11 min. As shown in the Supporting Information, the BT content of JP-8 is easily identified using this technique. The details of the GC method are: HP-5MS

Table 1
Select data for activated carbon samples.

Sample ID	Manufacturer	Carbon source	Activation method
MW 2001-R-06	Meadwestvaco	Wood	Phosphoric acid
MW 252-R-07	Meadwestvaco	Wood	Phosphoric acid
MW 99-R-06	Meadwestvaco	Wood	Phosphoric acid
Aquaguard	Meadwestvaco	Wood	Ammonia
Darco KBG	Norit	Wood	Phosphoric acid
Darco KBM	Norit	Wood	Phosphoric acid
SX-1	Norit	Peat	Thermal
SX Ultra	Norit	Peat	Thermal
Darco S-51	Norit	Lignite coal	Steam
Pac 200	Norit	Coal	Not disclosed
HP120	Pica	Wood	Phosphoric acid
B9	Pica	Wood	Steam

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