



Effect of gasoline composition on oxidative desulfurization using a phosphotungstic acid/activated carbon catalyst with hydrogen peroxide



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HIGHLIGHTS

- Concerned with the question why ODS catalyst is not effective for real gasoline.
- Reported the strong inhibiting effect of gasoline composition on ODS for the 1st time.
- ODS reactivity is suggested to be determined by partial charge on S atom of thiophene.
- Proposed approaches to improve ODS selectivity for real gasoline desulfurization.

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ABSTRACT

This work is concerned with the question of why oxidative desulfurization (ODS) catalyst that show good catalytic performance for ODS of model gasoline thiophenic compounds is not effective for real gasoline. For the first time, the effects of gasoline composition on ODS using a phosphotungstic acid/activated carbon (HPW/AC) catalyst with H_2O_2 were investigated. ODS of thiophene, one of the most difficult thiophenic compounds to be oxidized, was studied in a model fuel system, where a high thiophene conversion rate of 90% could be reached in 2 h at 90 °C. However, when applying the ODS to a real gasoline, the ODS conversion rate decreased to only 32%, suggesting a strong inhibiting effect of gasoline composition on ODS. The ODS studies in different model fuels suggested that the inhibiting effect can be ascribed to the competitive adsorption and oxidation with the presence of the alkenes and alkylated aromatic hydrocarbons in real gasoline. The active pi-electrons in alkenes and alkyl groups in alkylated aromatic hydrocarbons may react with polyoxoperoxy species or peroxo-metallate complexes formed by phosphotungstic acid- H_2O_2 interaction. Additionally, it was indicated that the ODS selectivity followed the order of benzothiophene > trimethylthiophene > dimethylthiophene ~ methylthiophene > thiophene, suggesting the partial charge on the electron-rich sulfur atom may play a decisive role for its oxidation reactivity. To mitigate the inhibiting effect of gasoline composition on ODS, we propose (a) implementation of selective separation-oxidation processes; (b) choice of suitable selective oxidants; (c) optimization of selective ODS reaction temperature, etc. to improve ODS selectivity for real gasoline desulfurization applications.

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1. Introduction

Desulfurization has become an increasingly important research subject worldwide [1–3]. Hydrodesulfurization (HDS) is currently the major process for desulfurization from liquid fuels in petroleum refineries. This process operates at high temperature (300–400 °C) and high hydrogen pressure (3–6 MPa) to convert organosulfur compounds to hydrogen sulfide (H_2S) over sulfided CoMo or NiMo catalysts [4]. Even though deep desulfurization of gasoline can be achieved by catalytic HDS, the dominant issue is

the saturation of olefins (contributed to the enhancement of octane number) in gasoline during HDS, which resulted in a great loss in the octane number of gasoline [5]. As high content of olefins (i.e., 20%) are present in gasoline, the undesirable loss of octane number can be significant, and the octane number losses have to be recovered or restored after the HDS. Therefore, it is desirable to develop alternative or supplementary energy-efficient and cost-effective technologies for desulfurization.

Among the developed alternative desulfurization technologies proposed in the literature, oxidative desulfurization (ODS) shows great promises as it operates at mild conditions (<100 °C, ambient pressure) coupled with no hydrogen requirement [6] at low investment and operation cost. ODS of gasoline [7,8] has been studied in

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the presence of ODS catalyst and oxidant under mild conditions. As an economic and environment-friendly catalyst due to its acid–base and redox properties [9], heteropolyacid (HPA) has been proposed as an ODS catalyst [10,11]. Gall et al. [12] studied ODS of thioether using $H_5PV_2Mo_{10}O_4$, and reported that the oxidation reactivities of the representative thioethers may be governed by the steric effects. Yet, the applications of HPA have been limited by the small amount of available activity sites due to its low surface area ($<10\text{ m}^2/\text{g}$), and difficulty in handling on a large scale. Supporting HPA onto a solid porous substrate has been proposed as a potential solution. Li et al. [13] reported a mesoporous silicate incorporated with phosphotungstic acid for dibenzothiophene (DBT) oxidation, which yielded a 98–99% of DBT conversion rate from a model fuel. Li et al. [14] synthesized molybdovanadophosphoric acid on amino-functionalized SBA-15 for ODS, and reported 97.8% of DBT conversion rate from a model fuel. As low-cost materials with porous structures, activated carbons (ACs) have been studied as potential supporting materials for HPA for various redox reactions [15]. With the presence of oxygen functional groups on the carbon surface [16,17] ACs can be used to bind/support acidic HPA and result in an extraordinary stability/regenerability toward HPA leaching from the AC support [18]. However, limited studies have been carried out using AC supported HPA for ODS. Herein, AC supported HPA catalyst was chosen for gasoline desulfurization in this study.

It can be noted in the literature that high organosulfur conversion rates were reported for the ODS of thiophenic compounds from model fuels, e.g., 98–99% of DBT conversion rate using phosphotungstic acid/SBA-15 [13], and 98.7% of DBT conversion rate using molybdovanadophosphoric acid/amino-functionalized SBA-15 [14]. However, model fuels are generally prepared with a simple formula of thiophenic compounds and an aliphatic hydrocarbon solvent, e.g., hexane, which is far from the complicated composition of real fuels. Gasoline is a mixture of various types of hydrocarbons, including not only straight chain, branched and cyclic aliphatic compounds, but olefins, aromatics, etc. (A typical composition of commercial gasoline is listed in Table 1.) The nature of the fuel composition may have a critical impact on the selective oxidation of the thiophenic compounds at the part per million by weight (ppmw) level over ODS catalysts, where no systematic work has been carried out to address the fuel composition effects on ODS.

Typical sulfur compounds in gasoline include: mercaptanes, sulfides, disulfides, thiophene and its alkylated derivatives, benzo-thiophene, etc. [22]. Among them, thiophene was reported to be one of the most difficult sulfur compounds to be removed by ODS due to its low reactivity [23]. Therefore, in this work, thiophene was chosen as the model sulfur compound in gasoline to study ODS of model fuel using the HPW/AC catalyst with H_2O_2 . In comparison, ODS of commercial gasoline was also investigated. The ODS selectivity/reactivity of various model sulfur compounds in gasoline was studied based on the GC-SCD analyses and a density function theory (DFT) calculation of electron density and partial electron charge on the sulfur atom of the thiophenic compounds. The effects of gasoline composition, in particular

olefins and aromatics, on ODS conversion over a HPW/AC catalyst with hydrogen peroxide have been examined in a batch ODS system, which was further discussed on the basis of the calculated electronic properties and molecule size of these compounds. Additionally, to mitigate the inhibiting effect of gasoline composition on ODS, approaches to improve ODS selectivity for real gasoline desulfurization applications were proposed in this study.

2. Experimental

2.1. Materials

Thiophene (98%), xylene (AR grade), octadiene (AR grade), cyclohexene (AR grade), n-tetradecane (99%), n-hexane (AR grade), cetyltriethylammonium bromide (CTAB, $C_{16}H_{33}(CH_3)_3NBr$, AR grade) were purchased from Beijing J&K Chemicals, Ltd. Phosphotungstic acid (HPW, $H_3PO_{40}W_{12}\cdot xH_2O$, AR grade) was purchased from Tianjing Beilian Chemicals, Ltd. Hydrogen peroxide solution (30 wt%) was purchased from Guangzhou Chemicals, Ltd. All the reagents were used as such without further purification.

2.2. Catalyst preparation

The HPW/AC catalyst was prepared by the wet impregnation method. AC (SY-6, Liaoning Chaoyang Activated Carbon Company, Ltd.) was added into an excess amount of 0.1 mol/L of phosphotungstic acid (HPW, $S_{HPW} < 10\text{ m}^2\text{ g}^{-1}$) solution, and stirred for 24 h at room temperature. After that, the impregnated AC catalyst was filtered and dried at 110 °C for 12 h. Prior to its use, AC was washed with distilled water, and pretreated at 110 °C in an oven for 12 h. Table 2 listed the textural properties of the HPW/AC catalyst characterized by the N_2 adsorption test (ASAP 2010 surface area and porosimetry analyzer, Micrometrics).

2.3. Fuels

The initial model fuels were prepared by dissolving thiophene (T) into n-hexane with a sulfur concentration of 489 ppmw (10 mmol/L). To investigate the effects of gasoline composition, 1 wt%, 10 wt%, and 15 wt% of xylene, octadiene, and cyclohexene were added as the partial of the solvents (pure n-hexane initially) into the thiophene-containing model fuels, respectively, while the sulfur concentration still remained the same as 489 ppmw. The commercial gasoline with 280 ppmw-S was provided by Maoming refinery in Guangdong, China.

2.4. Batch ODS experiments

The ODS experiments were carried out in a 100 ml three-neck batch reactor. After heating 20 ml of model/real fuel to a desired temperature, the optimized amounts of H_2O_2 , emulsion agent, and the HPW/AC catalyst (The formula of the HPW/AC catalytic oxidation system used in this work was optimized as 4 ml of 30%

Table 1
Composition of a typical commercial gasoline [19–21].

	Hydrocarbon type	Concentration ^a (wt%)
Saturates	Straight-chain, branched and cyclic aliphatic hydrocarbons (C5–C12)	~50%
Aromatics	Alkylated monoaromatics	~30%
Olefins	Alkenes, cyclic alkenes	~20%
Heterocyclic aromatics	S/N compounds	ppm level
Additives	Ether oxygenates, alcohol oxygenates, etc.	1–3%
Others	Moisture	ppm level

^a The concentrations of different types of hydrocarbons vary from barrel to barrel from various sources and refining processes.

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