Deep desulfurization of liquid fuels with molecular oxygen through graphene photocatalytic oxidation

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ABSTRACT

A simple extraction and photocatalytic oxidative desulfurization (EPODS) system for model oil was successfully developed on the basis of as-prepared graphene oxide (GO), air, formic acid (MeA), and acetonitrile (MeCN). Under UV radiation, the main reaction conditions influencing sulfur removal were systematically investigated, including the amount of GO, the volume ratio of MeCN to model oil, the amount of MeA, the initial S-concentration, air/N_2 bubbling, different sulfur compounds, and fuel composition. The reactivities of different sulfur compounds decreased in the order of benzothiophene > dibenzothiophene (DBT) > 4,6-dimethyldibenzothiophene, and this was attributed to the influences of the electronic structure of the lowest-lying triplet state of each species and to steric hindrance. The photocatalytic oxidative desulfurization mechanism was investigated using radical scavenger experiments, gas chromatography-mass spectrometry, electron spin-resonance spectroscopy, and density functional theory. DBT was initially extracted into the MeCN phase and then oxidized to the mixed oxidation products including sulfone. This was accomplished by the produced $HO_2^\bullet$ and $HO^\bullet$, which mainly originated from the oxygen-containing functional groups with absorbed O_2, ambient H^+, and the additional electrons at the zigzag edge and at the defect sites of GO. This work presents a promising approach to the highly-efficient removal of heterocyclic aromatic sulfur compounds from liquid fuels with an ultra-low dosage of carbon catalyst under mild conditions. Additionally, it provides insights into the fundamental knowledge on the origin of GO activity and the nature of the active oxygen functional groups in the photocatalytic process.

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1. Introduction

Liquid fuels are widely used both in the generation of electricity and in various transportation systems (e.g. cars, buses, trucks, and marine vessels) [1]. Sulfur compounds in liquid fuels poison the catalysts in emission control systems in vehicles and convert to sulfur dioxide during combustion resulting in acid rain and serious haze [2]. To reduce air pollution, increasingly stringent regulations have been imposed worldwide to limit the sulfur content of fuels to a very low level [3]. For instance, according to the standard JIS K 2202, Japan has restricted the sulfur content of motor gasoline to be less than 10 ppm since 2007. In the U.S., the sulfur content limit of highway diesel was reduced from 15 ppm to less than 10 ppm at the beginning of 2017 [4,5]. At the same time, China has executed the V generation vehicle gasoline and diesel standards program, which limits the sulfur content of regular gasoline and diesel fuels from 50 ppm to less than 10 ppm.

To meet the quality demands of liquid fuels with ultra-low sulfur content (<10 ppm of S content), hydrodesulfurization (HDS) has been a classic technology used by refineries. HDS takes a series of measures for deep removal of sulfur compounds and has included expensive hydrotreating catalysts and harsh process parameters such as temperature >370 °C and pressure >40 atm [6]. As a result, these measures not only increase extra operating and investment costs, but also cause quality loss of liquid fuel under high temperature. However, HDS is still less efficient at removing heterocyclic aromatic sulfur compounds (HASCs) such as benzothiophene (BT), dibenzothiophene (DBT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT) because of their lower hydrogenation activity and steric hindrance [7]. Consequently, more attention has been paid to non-HDS methods and their combined forms, such as extractive desulfurization [8], biodesulfurization [9], oxidative desulfurization (ODS) [10–12], and adsorptive desulfurization (ADS) [13–15].

Among the aforementioned non-HDS methods, the ODS method has gained enormous interest from the scientific community worldwide because of its lower investment and operating costs, mild reaction conditions, and simpler process [16]. Generally, an effective ODS system consists of an oxidant, a catalyst, and either an extractant or an adsorbent. The sulfur compounds are oxidized to highly polarized sulfones, which can be easily removed by extraction or absorption [17]. Up to now, the ODS method has been developed in a variety of forms, including extraction coupled with thermocatalytic ODS, microbial ODS, photocatalytic ODS, and photochemical ODS [18].

Several oxidants, such as molecular oxygen (O_2) [19], hydrogen peroxide [20], ozone [21,22], and *tert*-butyl hydroperoxide [23,24] have been used in previous ODS studies. Although O_2 is undoubtedly the most cost-effective and most highly abundant oxidant, it is inactive because its ground state is a low-energy triplet ($^3O_2$). To activate O_2 for the desulfurization of liquid fuels, earlier thermocatalytic ODS studies focused on using metal-containing catalysts, such as V-Mo [19], Mn-Co [25,26], Fe [27], Pd [28], Co-Mo [29], and Mo [30,31]. However, these reactions have to be carried out with either pure O_2 and/or at high temperatures, or with a long reaction time. In response to these problems, photocatalytic ODS has been considered to be an effective alternative method. Some metal-based photocatalysts, such as CuW/TiO_2-graphene oxide (GO) [18], Pt–RuO_2/$BiVO_4$ [32], Pt–RuO_2/TiO_2 [33], and Cu-Fe/TiO_2 [34], have been used in photocatalytic ODS systems. However, their high-cost and complicated production processes seriously limit further practical applications. As a result, metal-free photocatalytic methods have attracted extra attention [35].

Recently, the emergence of carbon materials (e.g., graphene, GO, and carbon nanotubes) provides an excellent alternative to metal-containing catalysts in various catalysis fields [36,37]. As promising metal-free catalysts, graphene (GR) and GO have attracted more attention for fuel desulfurization because of their high specific surface areas and special layer structure. In particularly, GO contains both aromatic (sp^2) and aliphatic (sp^3) domains, which easily form π-complexes with aromatic sulfurs and supply active sites because of the oxygen-containing functional groups. Up to now, GR and GO have been widely used for ADS and ODS [38–41]. For instance, Gonçalves et al. found that three-dimensional GO foam was a promising catalyst for the oxidation of thioanisole with H_2O_2 as an oxidant at room temperature [41]. However, most of these studies focus on ADS, which suffers from a limited absorption capacity to process a large number of S-containing fuel oils. A few studies on ODS use explosive oxidants such as H_2O_2, which challenge the strict fire safety regulations at refineries. To the best of our knowledge, until now only limited studies have been done to activate O_2 with GO to remove sulfur compounds from fuels. Therefore, developing a deep ODS system using the unique characteristics of GO with environmentally friendly and inexpensive O_2 is a promising technology in terms of sustainability and the green chemical industry.

Although GO has been widely used in various catalysis fields [36], its structure, composition, and role in reaction have not been fully understood. According to the Account reported by Loh et al. [42], the well-accepted structural models of GO depict hydroxyl and epoxide groups as the primary functional groups present on the basal plane. A number of potential active sites allow GO to function as a solid acid or as a green oxidant. In some catalytic oxidation reactions, it is still difficult to determine exactly whether GO is a catalyst or an oxidant [43]. Additionally, the enhanced photocatalytic effect is also ambiguous in GO and dye systems, and this is attributed to the interaction between GO and the dye, or the inherent high surface area and excellent electron transfer capability of GO [44]. These issues are still difficult to eliminate, largely because of the lack of knowledge on the origin of GO activity and the nature of the active oxygen functional groups participating in the reaction

[45]. In general, monitoring the reaction intermediates formed on the surface of GO represents a possible platform for understanding the reaction pathway and mechanism. However, it is difficult to observe in situ these adsorbed species because of their extremely short lifetimes. Herein, computational quantum chemistry using on density functional theory (DFT) was employed to predict the possible intermediates formed during the desulfurization reaction process and to evaluate their stabilities.

In this work, a simple extraction and photocatalytic oxidative desulfurization (EPODS) system was investigated. The system was composed of GO, air, formic acid (MeA), and acetonitrile (MeCN) for the deep removal of sulfur compounds from model oil. Sulfur compounds in model oil were extracted in the MeCN phase and oxidized to high-polarity products by the reactive oxygen species (ROS) under UV radiation, achieving deep desulfurization. The main parameters influencing desulfurization performance were examined in detailed, such as the amount of GO, the amount of MeA, the volume ratio of MeCN to model oil ($r_{M/o}$), the initial S-concentration, air/N_2 bubbling, different sulfur compounds, and fuel composition. Moreover, radical scavenger experiments, electron spin-resonance spectroscopy (ESR), gas chromatography-mass spectrometry (GC–MS), and DFT calculations were employed to investigate the mechanism of the EPODS system to establish a base of detailed knowledge for the desulfurization of fuels through GO photocatalytic oxidation.

2. Experimental section

2.1. Materials

BT (98%), DBT (98%), and 4,6-DMDBT (98%) were purchased from Wuhan Greatwall chemical Sci-Tech development Co. Ltd (China). Other chemical reagents were purchased from Tianjin Kermel Chemical Reagent Co., Ltd (China). All chemicals were analytical reagent grade and used without further purification.

2.2. Preparation and characterization

GO was prepared from commercial graphite powder (Tianjin Kermel Fine Chemical Corporation, China) using the modified Hummers method. Graphite powder (2.0 g) and $NaNO_3$ (1.0 g) were dispersed in 60 mL of 98% H_2SO_4 in a flask held in an ice bath. After stirring for 1 h in the ice bath, $KMnO_4$ (6.5 g) was slowly added to the above mixture in a 7 °C water bath. After stirring for 24 h in the water bath, the flask was transferred to a 38 °C water bath for 0.5 h, and 10% H_2SO_4 (80 mL) was slowly added to the suspension. The temperature was increased to 95 °C, and deionized water (65 mL) was slowly added to the suspension, which was removed from the water bath after 0.5 h and 30% H_2O_2 (35 mL) and 10% HCl (40 mL) were added. The suspension was diluted with 420 mL of deionized water.

Transmission electron microscope (TEM) imaging was conducted on a FEI Tecnai G2 F20 TEM operating at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed using a multifunctional imaging electron spectrometer (Thermo ESCALAB 250XI) with Al Ka radiation. Attenuated total reflectance Fourier-transform infrared (ATR FT-IR) measurements were carried out using a Nicolet iN10. Raman spectra were recorded on a Laser confocal micro-Raman spectrometer (Horiba Jobin Yvon LabRAM HR800) with a 514.3 nm Ar laser. The X-band ESR spectra were recorded at ambient temperature on a Bruker E500 spectrometer.

2.3. Desulfurization testing

The model oil was prepared by dissolving BT, or DBT, or 4,6-DMDBT in *n*-decane with a corresponding S-content of 500 ppm.