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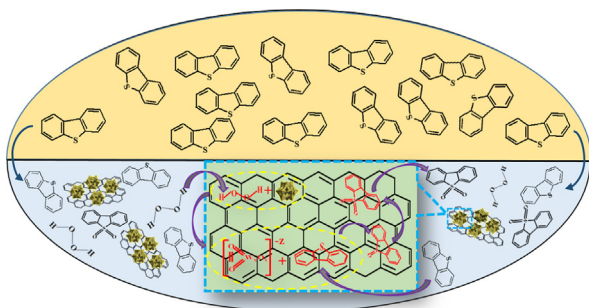
Deep and fast oxidative desulfurization of fuels using graphene oxide-based phosphotungstic acid catalysts

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GRAPHICAL ABSTRACT



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ABSTRACT

Extractive-catalytic oxidative desulfurization (ECOD) technology is a potential industrial application for attaining low-sulfur fuel oils. In this research, novel graphene oxide (GO)-based heterogeneous catalysts were synthesized by immobilization of different amounts of phosphotungstic acid $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (HPW) on GO. The obtained HPW-GO catalysts were characterized by FT-IR, SEM, EDX, TEM, AFM, and RAMAN analyses. The ECOD was applied for removal of dibenzothiophene (DBT) from a model fuel with H_2O_2 as the oxidant, acetonitrile as the extracting solvent, and HPW-GOs as the catalysts. Among the catalysts with different HPW contents (5, 10, 20, 25, 30, 40 wt%), the catalyst with 40 wt% HPW had the best performance. The optimum reaction time, temperature, H_2O_2 /sulfur molar ratio (O/S) as well as the kinetic parameters (kinetic constants and apparent activation energy) were evaluated. 100 percent desulfurization yield was achieved in a short time ($t = 30$ min) using the 40 wt% catalyst under moderate conditions (catalyst loading = 5 g/l, O/S = 6, $T = 333$ K). Aiding by synergism, the heterogeneous HPW-GO catalyst showed a higher desulfurization yield compared to that by the homogeneous HPW. The reactivity of 4,6-dimethyldibenzothiophene (4,6-DMDBT) in the ECOD process was found to be equal to that of DBT but much higher than the reactivity of benzothiophene (BT) within 60 min. The catalyst could be recycled for eight times without significant decrease in activity. A reasonable reaction pathway was proposed based on the GC-MS analysis. Almost all of the sulfur content of a real fuel could be completely oxidized and removed by the ECOD. Comparing to the results reported in literature, the features of proposed one-step fast ECOD process, which requires very low catalyst at moderate conditions for complete desulfurization without any phase transfer agent, makes it distinctive for practical applications.

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1. Introduction

Deep desulfurization of fuels to meet the strict regulations on the sulfur level in the fuels has gained wide interests [1]. Catalytic hydrodesulfurization (HDS) is the conventional method for removal of sulfur. However, the process is carried out under severe operating conditions and is less effective for aromatic thiophenes [2–8]. To overcome these drawbacks and to produce ultra-low sulfur fuels, new alternative or complementary desulfurization processes are necessary [9]. Oxidative desulfurization (ODS) is a promising method, which is not only carried out under mild conditions but also can remove all the aromatic sulfur compounds that are hardly eliminated by HDS [3,6,10]. On the other hand, the ODS units are desirable for small and medium size refineries because they have no need to the hydrogen utilities [1]. Among the ODS studies, the researches on extraction combined with catalytic oxidative desulfurization (ECOD) carried out in a biphasic system show very high efficiencies in removing of sulfur compounds [5,7,11–14]. The advantages of this process are simultaneous reaction and separation of sulfur compounds in a single unit, no sulfone adsorption on the catalyst, and no need to strong stirring or sonication to achieve good mixing between the oxidizing agent, the catalyst, and the oil [2,5,9]. Various types of extracting solvents and oxidants have been explored for the ODS process [9,15]. Although the solvent and oxidizing agent are important, the fundamental challenge for a successful ODS process is to use a prominent catalyst with high activity.

Heteropolyacids (HPAs), have attracted wide attentions as catalysts due to their nanosize dimensions, strong acidity, proper distribution of charges, and fast reversible electron transformation under mild conditions [3–7,16–22]. However, industrial applications of them are seriously limited due to their general high solubilities in the polar solvents and their problematic recovery processes [8,22]. One way to overcome these problems is to immobilize them on a solid support [22]. Many researchers have tried to design heterogeneous catalysts by incorporating HPAs into various solid supports such as SiO₂ [23], Al₂O₃ [13], MOFs [24,25], CNT [7], and activated carbon [26]. However, those catalysts frequently have deficiencies such as small surface area, pore blocking, long reaction time, and weak interaction of HPAs with the solid material and its consequent leaching. Therefore, developing ideal catalysts with large specific surface area, high activity, and good recyclability is still a challenging task.

Graphene with a planar structure consisting of sp² carbon atoms and its derivatives are appropriate nanostructures with unique thermal, mechanical and electronic properties as well as high specific surface area [15,27,28]. These features prompt researchers to explore the applications of graphene and graphene-based materials such as graphene oxide (GO) as a new kind of catalyst and support in the desulfurization processes. Hajjar and coworkers showed that the Co–Mo/graphene catalysts were more active than the industrial Co–Mo/ γ -Al₂O₃ catalyst [28]. Menzel et al. reported GO-containing inorganic hybrid materials for adsorption of sulfur from liquid hydrocarbons [27]. Zhang and Wang claimed that GO has a high compatibility with the oxidative-adsorptive desulfurization system [10]. Gu and coworkers found out that reduced GO can enhance the adsorption and activation of the oxidant in the process [15].

In present research, novel recyclable heterogeneous catalysts composed of phosphotungstic acid (HPW) supported on GO (HPW-GO) are synthesized, characterized, and used in ECOD process for the first time. By combining the GO advantages with HPW properties, the objectives of this research are to improve the ECOD performance and to surpass the challenges in the catalytic oxidative desulfurization process such as low yield, long reaction time, high catalyst consumption, leaching of the active species, and difficulty in catalyst separation.

Table 1

Purities and suppliers of applied chemicals.

Chemical name	Supplier	Purity (Mass percent)
Pristine graphite (PG) powder (325 mesh)	Timcal	99.9%
Sulfuric acid	Sigma-Aldrich	98%
Phosphoric acid	Sigma-Aldrich,	99%
Hydrochloric acid	Merck	37%
Potassium permanganate	Merck	99.5%
Sodium nitrate	Merck	99.5%
Hydrogen peroxide	Merck	30% in H ₂ O
n-hexane	Merck	99%
Hexadecane	Merck	99%
Ethyl acetate	Merck	99%
Acetonitrile	Merck	99.5%
Benzothiophene (BT)	Merck	98%
Dibenzothiophene (DBT)	Merck	99%
4,6-Dimethyldibenzothiophene (4,6-DMDBT)	Haohua Company	≥ 99%
Phosphotungstic acid hydrate	Sigma Aldrich	99%

2. Experimental

2.1. Materials

The suppliers and purities of the chemicals are introduced in the Table 1.

2.2. GO synthesis

Graphene oxide (GO) was synthesized according to the modified Hummer method [29–31]. Briefly, a mixture of 400 ml H₂SO₄ and H₃PO₄ (volume ratio = 9:1) was slowly added to a mixture of 21 g commercially available graphite flakes and KMnO₄ (weight ratio = 1:6) in a three-neck round bottom flask. The flask was stirred in an oil bath (50 °C) for 12 h. After cooling to room temperature, the reaction vessel was placed in an ice bath. 3 ml of 30% H₂O₂ and 400 ml of deionized water were added to the flask little by little. The supernatant was decanted away after the mixture was centrifuged (15,000 rpm, 10 min). The separated solids were washed with 600 ml mixture of water, 30% HCl, and ethanol with equal volume ratios. After vacuum drying overnight at 85 °C, the solids were crushed to a fine powder in an agate mortar.

2.3. Catalyst preparation

In order to find the best impregnation conditions for effective HPW immobilization, an study was performed in our previous research in terms of pH, solvent, and support type [30]. The results demonstrated that GO is the most effective support, in which electrostatic bonds are formed between the positive-charge surface functional groups of GO and HPWs anions. According to the results, GO showed the 427 mg/g equilibrium adsorption capacity (correspond to the 42.5% wt of POM). The catalysts in the current study were prepared considering the POM percentage below the maximum adsorption capacity (40, 30, 25, 20, 10, and 5 wt%), to be assure about the effective immobilization of the active species [30].

A colloidal suspension of the support in the solvent (water/methanol with volume ratio of 1:1) was prepared by sonication in a vial. The required amount of HPW was poured into the vial. It is noticeable that while the pH is slightly varied by adding different contents of HPW, it always remains below the isoelectric point of GO. The samples were kept under constant stirring (500 rpm) overnight at room temperature using a magnetic stirrer. The solvent was evaporated in a vacuum rotary evaporator (90 °C, 700 rpm) and then dried at 100 °C for 12 h. The solid product was crushed to a fine powder in an agate mortar. The solid catalysts were calcined at 300 °C for 3 h. According to Scheme 1,

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