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Nanocarbon materials for oxidative-adsorptive desulfurization using air oxygen under mild conditions

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ABSTRACT

A new oxidative-adsorptive desulfurization (OADS) process using graphene oxide (GO) and HNO_3 modified carbon black (mCB) as adsorbents, and octanal-air as oxidation system was investigated under mild conditions in model fuel. GO was prepared by modified Hummer's method and characterized by X-ray diffraction (XRD), transition electron microscopy (TEM), scanning electron microscopy (SEM) and fourier transform infrared spectroscopy (FT-IR). In the OADS/Nanocarbon system, molar ratio of S and octanal, mass ratio of model fuel and nanocarbon, OADS temperature was optimized to be 24:1, 200:1 and 60 °C respectively. High desulfurization uptakes of 45.1 and 45.4 mg-S/g-sorb were achieved under OADS system on GO and mCB, which are much higher than that under adsorptive desulfurization (ADS) system without *in situ* oxidation of dibenzothiophene (DBT). The desulfurization reactivity of various sulfur compounds in OADS system followed the order: Thiophene (TH)>DBT>4, 6-dimethyldibenzothiophene (4, 6-DMDBT)>Thianaphthene (BT) over GO, and 4, 6-DMDBT>TH-DBT>BT over mCB. Remarkably, 4, 6-DMDBT and TH could be effectively removed with the desulfurization efficiencies of 96.1% and 98.4%, respectively. The desulfurization capacity of GO could be completely regenerated in three recycles.

1. Introduction

Sulfur content of diesel fuel has attracted worldwide attention as the main source of many kinds of environmental pollutions [1]. Organic sulfur compounds exist in fuel will also poison the catalysts used for reducing the emission of CO and NO_x [2]. <15 and 10 ppmw S in diesel was regulated in United States and European Union which brought a major challenge for petroleum refining industry [3]. Therefore ultra-deep desulfurization has been regarded as an important subject around the world.

Hydrodesulfurization (HDS) has been widely used in refinery operation, but the process has disadvantages including high energy cost and low efficiency on dibenzothiophene (DBT) and its derivatives due to the steric hindrance [3–5]. Owing to the difficulties, many alternative methods have been investigated to meet the demand of ultra-clean fuel production. Among these methods, adsorptive desulfurization (ADS) is considered as a promising approach for deep desulfurization with the advantage of removing refractory sulfur compounds under ambient conditions. In ADS, absorbents play a key role, and the effect of ADS greatly depends on the properties of absorbents, such as the pore structure and surface functional groups [6]. Up to now, various adsorbents for ADS have been studied, including reduced metals [7], metal oxides [8], metal organic frameworks [9], zeolite-based materials [10], carbon or carbon-based composite materials [11–15]. Recently, significant attention has been paid to carbon materials because of its higher surface area, easily modified structure, wide source, cheaper cost and higher selectivity in desulfurization [16].

As two important members of nanocarbon family, the desulfurization properties of carbon black (CB) and grapheme oxide (GO) have been used for adsorbents in many other fields such as adsorption of rare earth elements and heavy metal ions including Hg [II] ion. [17–20]. Particularly, GO composited with molecularly imprinted polymers (MIPs) [21] and a series of mixed metal oxides [22] were used for desulfurization of fuels in recent years, and good results were achieved. However, in this paper, GO was used alone for desulfurization. According to literature, oxidation or polarization of carbon materials will increase the adsorptive capacity evidently [16]. So in this paper, the desulfurization ability of GO and HNO_3 modified CB (mCB) will be discussed.

Selectivity to refractory sulfur compounds is always a nonnegligible challenge in ADS process using carbon materials because besides sulfur compounds, other aromatic compounds are also adsorbed in significant quantities which will cause loss of fuel [23]. In order to solve this trouble, a coupling oxidation-adsorption process was developed where the refractory sulfur compounds were firstly oxidized to corresponding sulfones and then selectively adsorbed immediately [24]. After being oxidized, sulfur compounds such as DBT and 4, 6-DMDBT are strongly adsorbed on the surface of carbon materials due to the polar groups,

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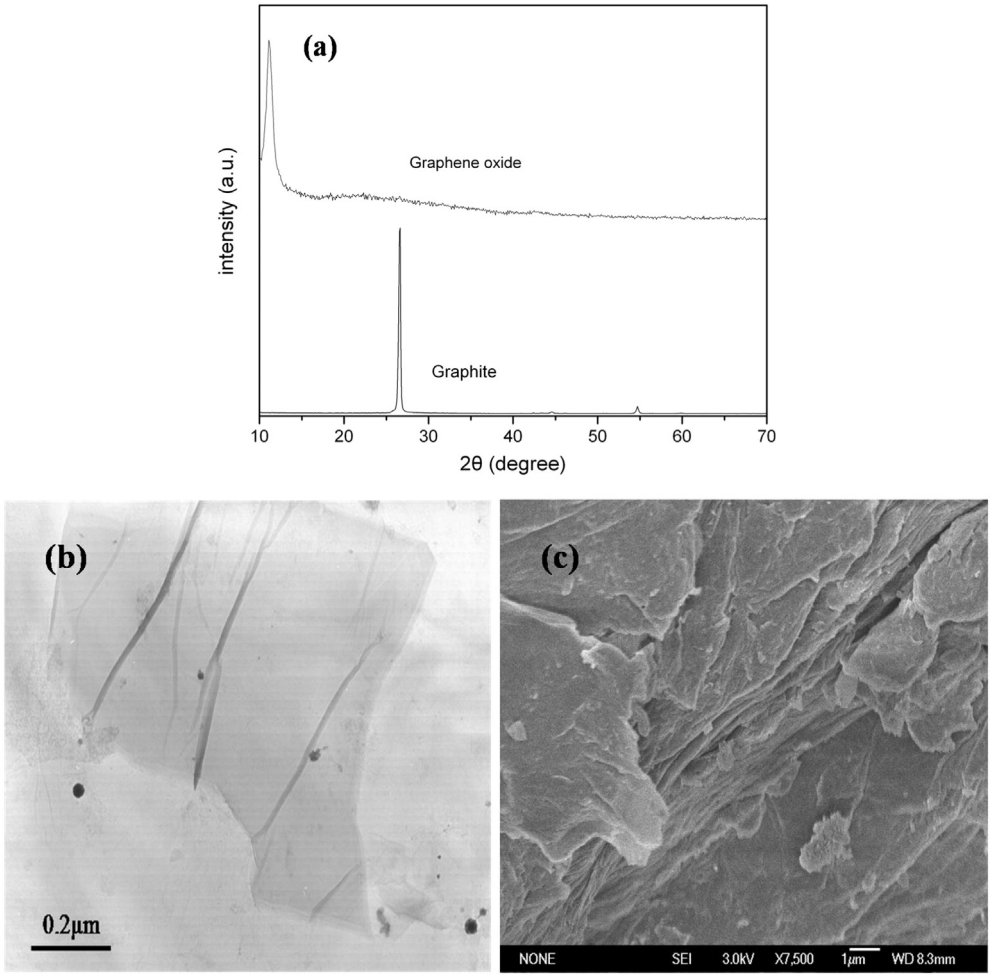

Fig. 1. (a) X-ray diffraction patterns of pristine graphite and synthesized GO. (b) TEM image of synthesized GO powders. (c) SEM image of synthesized GO powders.

whereas the adsorption of aromatic hydrocarbon decreases with an increase in the extent of oxidation [23,25]. Herein we adopt n-octanal-air system to achieve the oxidation of sulfur compounds without using any catalyst and the desulfurization capacity of several carbon materials was tested firstly in this system [26]. We found the combination of oxidation and adsorption has significant effect on increasing the efficiency of desulfurization compared with single ADS process. It is worth mentioning that this novel system is quite effective in the elimination of 4, 6-DMDBT and thiophene (TH) with the corresponding removal rates of 96.1% and 98.3%.

2. Experimental

2.1. Materials and apparatus

Dibenzothiophene (DBT) was purchased from Acros Organics; 4, 6-dimethyldibenzothiophene (4, 6-DMDBT) and thiophene (TH) was purchased from J&K Chemical Ltd.; Thianaphthene (BT) was supplied by Sigma-Aldrich Company. Carbon black (CB, 50 LB) was produced by Degussa Company. The natural graphite was purchased from Qingdao Huataitech Co., China. The multi walls carbon nanotubes were supplied

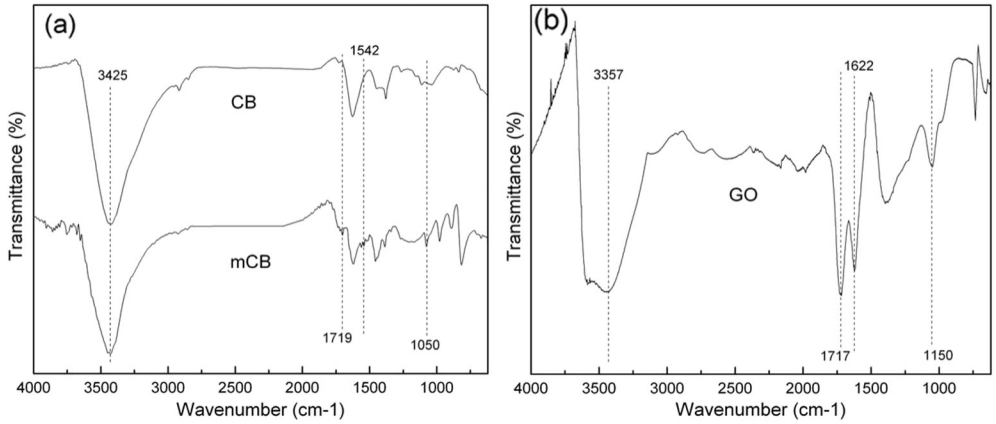

Fig. 2. FT-IR spectra of (a) pristine CB and modified CB and (b) synthesized GO.

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