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Understanding capacity loss of activated carbons in the adsorption and regeneration process for denitrogenation and desulfurization of diesel fuels

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ABSTRACT

Activated carbon (AC), after successive adsorption–regeneration processes, is found to lose its capacity in the adsorptive removal of nitrogen (N) and sulfur (S) containing compounds from diesel fuels. This work is the first attempt to identify the root causes of reduction in adsorption capacity of diesel spent AC due to solvent regeneration. The diffusion resistance from micropores prevents the adsorbed N- and S-containing compounds from being removed via solvent extraction. Meanwhile, coke is formed on the inner walls of the pores in AC during carbon re-activation. The residues and the coke result in a decrease in the specific surface area and porosity of the regenerated carbons, which thus lowers their performance. The loss of oxygen functional groups such as carboxylic acid groups, pyrone type groups, lactone groups, carbonyl groups, carboxylic anhydride groups and phenolic groups might also cause the reduction in the re-adsorption of N and S compounds.

1. Introduction

The heterocyclic nitrogen (N) and sulfur (S) compounds contained in the petroleum streams can cause environmental issues [1,2]. Many countries have established regulations to restrict the S content in petroleum products to be 15 ppm [2,3]. The sulfur content in the off-road fuels has been required to be less than 15 ppm and zero emission is even expected [4]. Using current hydrotreating technology to achieve this deep desulfurization will cause some problems such as large energy consumption, side reactions, low cetane number and catalyst deactivation [1,5,6]. Therefore, it is necessary to seek alternative technologies to remove the N- and S-containing compounds from diesel fractions.

Adsorptive desulfurization and denitrogenation is promising as it is an easy-to-conduct and environmentally friendly approach without the need of hydrogen gas [7]. The co-existing aromatic compounds in diesel have similar structures to N- and S-containing compounds. Therefore, a sorbent material, which can selectively remove N and S compounds, is vital to the adsorption process. Activated carbon (AC) has been studied as an adsorbent in the selective removal of N and S compounds from gasoline and diesel fractions, and excellent results were obtained due to the large surface area and appropriate surface chemistry of AC [6]. In addition to the great adsorption performance, a good sorbent material is expected to be reusable. Only a few studies on the regeneration of diesel spent AC have been reported – in which solvent extraction by toluene was a frequently used method. This method worked well when model diesels served as the feed – especially when the spent carbons were regenerated only once [6,8]. However, it was often reported that the regeneration performance for AC samples decreased – especially when using real diesel [9–12]. A mesoporous carbon CMK-5 with bimodal pore system has been reported to have an 86% regeneration efficiency for dibenzothiophene (DBT), and the recovery in the adsorption of DBT by its analog but with unimodal pore system, CMK-3, was 77% [9]. A ~21% decrease in adsorption capacity for total S was observed with regenerated AC with micropores dominant, compared to that with mesopores dominant [10]. Xiong et al. reported that the DBT adsorption capacity was reduced from 8.66 mg S/g for fresh AC to 8.00 mg S/g for the AC having been reused for three times [11]. The results of Han et al. also showed that 93% of the fresh adsorption capacity of AC for a model diesel containing indole was recovered by toluene extraction in the first cycle of adsorption–regeneration. The regeneration efficiency for indole dropped to 88% after five adsorption–regeneration cycles. When the model diesel was replaced by a real diesel, light cycled oil (LCO), the results became worse [12].

Although some experimental results have been obtained, little attention has been paid to identify the reasons that cause the

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decreased regeneration performance of carbons. From our previous results, the reduced regeneration efficiencies seemed to relate to the loss of porosity in regenerated AC samples [12]. Zhou et al., on the other hand, proposed that the micropores of AC reduced the diffusion rate of solvent and adsorbates, and thus lowered the regeneration performance [10]. Other authors have stated that the carbon with less oxygen functional groups was easier to capacity restoration [6]. As no conclusion has been achieved, further study is needed in order to fully understand the capacity loss during carbon adsorption–regeneration. In the present work, the AC samples spent by model diesel fuel or LCO were regenerated by toluene washing. The changes to the physical and chemical properties of carbon samples after regeneration were studied in detail using a variety of techniques including elemental analysis, N_2 adsorption–desorption, transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), temperature programmed desorption (TPD) and thermogravimetric analysis combined with Fourier transform infrared spectroscopy (TGA–FTIR). The factors that caused the decrease of regeneration efficiency were explored.

2. Experimental

2.1. Compositions of model diesel fuel and LCO

The model diesel fuel was composed of indole (Acros Organics), carbazole (Sigma–Aldrich), DBT (Acros Organics), naphthalene (Fisher Scientific), ethyl acetate (Caledon) and dodecane (Fisher Scientific). Indole and carbazole were used to represent nitrogen-containing compounds, DBT for sulfur-containing compounds and naphthalene for aromatic compounds in diesel fractions. Each N (indole and carbazole), S (DBT) and aromatic compound (naphthalene) had a concentration of 23.8 μmol/g. In order to dissolve carbazole, 26.5 wt% ethyl acetate was added. The LCO contained 520 ppmw N, 5268 ppmw S, 72.1 wt% aromatic compounds and the balance consisted of paraffins.

2.2. Adsorption and regeneration

A wood-based activated carbon WV-B 1500 (purchased from MeadWestvaco Corporation) was used as the adsorbent. The detailed procedure of batch adsorption was described in the previous work [12,13]. Briefly, 2 g AC was mixed with 56 g model diesel or LCO in a capped bottle at ambient conditions for 24 h to adsorption equilibrium [12–14]. Magnetic stirring was kept at 300 rpm. The sorbent-to-oil mass ratio was kept at 1:28 in all adsorption experiments. The spent AC samples were desorbed by toluene extraction for 22 h in a Soxhlet apparatus, followed by being purged with N_2 (180 ml/min) at 300 °C for 3 h to remove solvent residues. The resultant AC samples, which were considered as regenerated carbons, were examined in the next cycle of adsorption. This adsorption–regeneration process was repeated 10 times. The regenerated carbon samples in Cycle 10 were denoted as ‘‘AC-MO’’ and ‘‘AC-LCO’’ with model diesel fuel and LCO as feed, respectively. ‘‘AC-Fresh’’ stands for the fresh activated carbon.

Eq. (1) defines the regeneration efficiency of AC samples:

$$\text{Regeneration efficiency (\%)} = \frac{\text{Adsorption capacity of regenerated AC}}{\text{Adsorption capacity of AC} - \text{Fresh}} \times 100\% \tag{1}$$

The concentrations of N and S compounds in the adsorbed model diesel fuels were determined using a GC-450 gas chromatograph (Varian) with a flame ionization detector. The total contents of N and S in the adsorbed LCOs were analyzed using an NS-9000 analyzer (Antek Instruments Inc.) following ASTM D5762 and ASTM D5453. The N and S species in LCOs were quantified using a GC-950 gas chromatograph (Shanghai Haixin Chromatographic Instrument Co. Ltd.) with a nitrogen phosphorus detector and a GC-450 gas chromatograph with a pulsed flame photometric detector, respectively.

2.3. Characterization

2.3.1. Elemental analysis

A CHNS-932 elemental analyzer (Leco) was used to determine the C and H content of the adsorbents while an NS-9000 analyzer was used to monitor the variations of N and S. The O content was calculated by subtracting the weight fractions of C, H, N and S from unit. The ash content in AC samples was obtained using the procedure described in ASTM D2866-94.

2.3.2. Nitrogen adsorption–desorption

The nitrogen adsorption–desorption isotherms were obtained using an Autosorb-1 (Quantachrome Instruments) at −196 °C. The AC samples were pretreated at 200 °C under high vacuum for 3 h prior to the test. The total pore volume of sample, V_{Total}, was measured based on the amount of adsorbed N_2 at the relative pressure (P/P_0) of around 0.995. The specific surface area (S_{BET}), micropore volume (V_{Micro}) and pore size distribution of carbon were calculated using the multipoint Brunauer–Emmett–Teller (BET) method, the Dubinin–Radushkevich (DR) equations and the density functional theory (DFT) method, respectively. The mesopore volume (V_{Meso}) was determined by subtracting V_{Micro} from V_{Total}.

2.3.3. Transmission electron microscopy

The TEM of AC samples were done by a JEOL 2011 scanning transmission electron microscope (JEOL) at 200-kV accelerating voltage. The AC samples were ground to powder and then dispersed on a carbon grid by means of ultrasonication in ethanol. After being dried, the samples were subjected to analysis. The TEM images were processed to see the pore channels in carbon samples, based on the method Huang et al. used [15]. In brief, the original TEM images were converted to the power spectra by using fast Fourier transform (FFT). A ring-shape mask was applied to the power spectra to set the pore size range. Afterwards, the selected zone was transferred to a space image of the pore channels by applying inverse fast Fourier transform (IFFT). All the operations were conducted on the software that accompanied the instrument. In order to see the pores clearly, the space images were converted to the binary pictures which correspond to the cross section of the pores in any arbitrary direction.

2.3.4. Fourier transform infrared spectroscopy

The FTIR spectra were recorded using a Nicolet 6700 Fourier transform instrument (Thermal Scientific). The ground AC samples were diluted with KBr till the concentration of AC in the mixture was about 0.1 wt%. The sample spectra were collected in the wavenumber range of 4000–400 cm^{-1} at ambient temperature, with the resolution of 4 cm^{-1}.

2.3.5. Temperature programmed desorption

TPD examinations were performed on Autosorb-1-c (Quantachrome Instruments) using He as the carrier gas with a flow rate of 50 ml/min. Samples were pre-heated at 100 °C for 1 h, and then heated up to 1000 °C at 10 °C/min. The release of CO_2 and CO was recorded by an RGA 200 amu residual gas analyzer (Stanford Research Systems). PeakFit v4.12 software was utilized to fit the TPD plots into Gaussian peaks.