



The role of oxygen functional groups in the adsorption of heteroaromatic nitrogen compounds



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HIGHLIGHTS

- Oxygen groups improve the adsorption selectivity of nitrogen compounds.
- Different oxygen groups function differently on the selectivity.
- Proper oxidation can effectively increase the oxygen groups on carbon surface.
- Excessive oxidation can damage carbon pore structure.

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ABSTRACT

A wood-based activated carbon (AC) was oxidized using different oxidants. The resultant adsorbents were applied to adsorb nitrogen (N) containing compounds that appeared in light cycled oil. Appropriate oxidation treatment can increase oxygen functional groups on the surface of AC without much damage to its pore structure. Oxygen functional groups play a key role in enhancing adsorptive selectivity of carbons. Lactone groups can facilitate the selective removal of 1-ring N compounds. Phenolic groups, total CO₂-releasing groups and total O groups show an improvement in the adsorption of 2-ring N compounds. Aldehyde groups favor the adsorption of 3-ring and 4-ring N compounds. However, excessive oxidation can result in the collapse of pore structure and closure of pore channels. For instance, the carbon oxidized by a mixture of concentrated H₂SO₄ and HNO₃ has an extremely low adsorption performance.

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1. Introduction

Environment Canada limited the sulfur (S) content in the on-road diesel fuel to be lower than 15 ppm. Hydrodesulfurization (HDS) is a common practice in refineries to lower the S content in diesel. Co-existing nitrogen (N) compounds would compete for and poison the active sites of HDS catalysts [1,2]. The N-containing compounds in petroleum may also result in tank and pipe corrosion as well as oil degradation during storage [3]. Elimination of N compounds before diesel fraction being sent to hydrotreater for hydrodesulfurization may address the challenges.

Different approaches have been studied in terms of denitrogenation, which include hydrodenitrogenation (HDN) [2], adsorption [1,4], oxidation [5,6], extraction by ionic liquids [7] and sub- or supercritical water [8]. Using sorbent materials to selectively

remove N compounds is a promising approach. The commonly used adsorbents include zeolites [9–11], oxides such as silica and alumina [4,12,13] and activated carbon (AC) [1,2,14,15]. Due to superior textural and surface properties, activated carbon showed higher adsorptive capacity than activated alumina and Ni/SiO₂–Al₂O₃ in the removal of both basic and nonbasic N-containing compounds from a model diesel fuel [1,14]. The type of oxygen functional groups is a key factor of N selectivity. Sano et al., 2004 reported that the adsorption of N compounds in a straight run gas oil was promoted by the CO₂-releasing groups but inhibited by the CO₂-releasing groups [16]. Some researchers proposed that the N compounds were captured by oxygen functional groups by means of acid–base interaction and/or H bond interaction [14,15].

Oxidation is an effective way to introduce oxygen functional groups on the carbon surface. The selected oxidant determines the quantity and distribution of oxygen functional groups produced on AC. Ammonium persulfate ((NH₄)₂S₂O₈) solution, nitric acid (HNO₃) and sulfuric acid (H₂SO₄) are commonly used oxidants for AC oxidation. Pradhana and Sandle, 1999 reported that AC, which had undergone HNO₃ treatment, had the oxygen content more

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than doubled, and the oxygen content increment of a saturated $(\text{NH}_4)_2\text{S}_2\text{O}_8$ oxidized AC was even higher [17]. By controlling the oxidation conditions, the amount of oxygen can reach 18.7 mmol/g [18]. Research showed that oxidation processes increase acidic oxygen groups. Xue et al., 2008 reported that the concentration of acidic groups on AC was improved from 0.51 mmol/g on the original AC to 1.64 mmol/g and 0.88 mmol/g for HNO_3 and H_2SO_4 oxidized AC samples, respectively [19]. Aburub and Wurster, 2006 oxidized the activated carbon using a $\text{H}_2\text{SO}_4/\text{HNO}_3$ mixture [20]. Increase of oxygen functional groups was observed, especially for the carboxylic groups and lactone groups, up to 21.4 and 17.7 folds of increase, respectively.

A few efforts have been made to address the role that oxygen functional groups play in the denitrogenation, but limited to model diesel. Li et al., 2011 reported that phenolic groups, carbonyl groups and especially carboxylic acid groups promoted the adsorption of both indole and quinoline while lactone groups had the opposite effect [21]. No studies have been documented with regards to the influence of oxygen functional groups of AC samples on the adsorptive denitrogenation of a real diesel fuel. This study addresses the gap. Various distributions of oxygen groups on AC were obtained by oxidizing a commercial activated carbon using different oxidants such as tert-butyl hydroperoxide (TBHP) solution, sodium hypochlorite (NaClO) solution, saturated $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution, concentrated HNO_3 , and mixed acids of concentrated H_2SO_4 and HNO_3 . Temperature programmed desorption (TPD) technique was used to identify and quantify the oxygen functional groups on the resultant AC samples. The relationship between the oxygen functional groups on AC-based adsorbents and the adsorptive removal of N compounds in light cycled oil (LCO) was investigated.

2. Experimental

2.1. Materials

$(\text{NH}_4)_2\text{S}_2\text{O}_8$ (99.1%) and H_2SO_4 (95–98%) were purchased from Fisher Scientific. NaClO solution (available chlorine 10–13%), HNO_3 (68.0–70.0%) and TBHP solution (~80% in di-tert-butyl peroxide/water 3:2) were purchased from Sigma–Aldrich, Caledon and Fluka, respectively. The wood-based activated carbon WV-B 1500 (denoted as AC-Fresh) was purchased from MeadWestvaco Corporation.

2.2. Oxidation of carbon

Oxidation was performed at ambient conditions. The original adsorbent, denoted as AC-Fresh, was soaked in oxidant solutions (1 g AC-Fresh per 20 ml oxidant solution) while being stirred for 12 h. The samples were then filtrated, washed with distilled water (ethanol was used before distilled water for TBHP oxidized AC only) and dried at 120 °C for 12 h. The AC samples oxidized by TBHP solution, NaClO solution, saturated $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution, concentrated HNO_3 , and a mixture of concentrated H_2SO_4 and HNO_3 with the volume ratio of 3:1 are denoted as AC-TBHP, AC-NaClO, AC- $(\text{NH}_4)_2\text{S}_2\text{O}_8$, AC- HNO_3 and AC- $\text{H}_2\text{SO}_4/\text{HNO}_3$, respectively.

2.3. Composition of LCO

The LCO used in this study contained 520 ppmw N and 5268 ppmw S. The concentrations of mono-aromatics, di-aromatics, poly-aromatics in LCO were 13.8 wt%, 49.1 wt% and 9.2 wt%, respectively.

2.4. Adsorption

Batch-mode adsorption experiments were carried out at ambient temperature and pressure for 24 h with stirring. The mass ratio of adsorbent to LCO was 1:28. The adsorption capacity for N was estimated by Eq. (1):

$$\text{Adsorption capacity (mmol/g)} = \frac{\text{Amount of N in feed LCO} - \text{Amount of N in adsorbed LCO}}{\text{Weight of AC}} \quad (1)$$

The contents of total N and total S were determined using an NS-9000 analyzer (Antek Instruments Inc.) which meets ASTM D5453 and D5762, with the detection limit of ppb levels. The N compounds were analyzed using a GC 950 gas chromatograph (Shanghai Haixin Chromatographic Instrument Co. Ltd.) equipped with a nitrogen phosphorus detector (detection limit: 3.5×10^{-13} gN/s). The oven heating program used by Vassilaros et al., 1982 was adopted, which is isothermal at 40 °C for 2 min and then heating to 265 °C at 4 °C/min [22].

2.5. Characterization

The nitrogen adsorption–desorption isotherms of AC samples were measured at -196 °C using an Autosorb-1 (Quantachrome Instruments). The carbon sample in a quartz cell was first out-gassed at 200 °C under 10^{-5} mbar for 3 h. Afterwards, the cell was transferred to the analysis station. During analysis, the cell bottom where the AC sample stays was kept in a Dewar bath filled with liquid nitrogen. The specific surface area (S_{BET}) was estimated according to the multipoint Brunauer–Emmett–Teller method. The total pore volume (V_{Total}) was obtained by the adsorbed N_2 amount at $P/P_0 = 0.995$. The micropore volume (V_{Micro}) was calculated based on the Dubinin–Radushkevich equations. The mesopore volume (V_{Meso}) was expressed by the difference of V_{Total} and V_{Micro} . The pore size distributions of samples were analyzed by means of the density functional theory.

The Fourier transform infrared spectroscopy (FTIR) was conducted on a Nicolet 6700 Fourier transform instrument (Thermal Scientific) at room temperature. A wafer of 0.1 wt% AC was formed by mixing ground AC with KBr. The spectra were obtained by scanning the wafer in $4000\text{--}400$ cm^{-1} with a resolution of 4 cm^{-1} .

TPD analysis was performed on an Autosorb-1-c (Quantachrome Instruments) in flowing He (50 ml/min). AC samples were first heated to 100 °C at 3 °C/min and kept for 1 h, followed by being heated up to 1000 °C at a heating rate of 10 °C/min. An RGA 200 amu residual gas analyzer (Stanford Research Systems) was employed to monitor the evolution of CO_2 and CO. The TPD curves were fit with Gaussian peaks using PeakFit v4.12 software. The amount of oxygen functional groups per surface area of the resultant AC samples is denoted as the surface density of O groups.

3. Results and discussion

3.1. Selective removal of N compounds

The N compounds in LCO samples were analyzed by GC-NPD. The spectrum of feed LCO is illustrated in Fig. 1. Herein the N compounds can be classified into 4 categories based on their ring number. Indole and its alkylated derivatives represent 2-ring N compounds, carbazole and its alkylated derivatives stand for 3-ring N compounds, anilines and benzocarbazoles for 1-ring and 4-ring N compounds, respectively. The nitrogen compounds were quantified using the GC spectrum. The dominant N species in the LCO feedstock are 3-ring N compounds which account for 51% of the total N. The fraction of 2-ring N compounds is approximately 40%

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