Adsorptive Denitrogenation of Liquid Hydrocarbon Streams on Carbon-Based Adsorbents

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Introduction

In recent years, the removal of nitrogen compounds (NCs) has received great attention [1]. Due to the relative difficulties and costs of the catalytic removal of NCs through hydrodenitrogenation (HDN), researchers worldwide are seeking alternative approaches to achieve deep denitrogenation of liquid hydrocarbon streams [2]. A great attention has been paid to use of adsorbents for selective removal of NCs in recent years, which can be beneficial not only for nitrogen reduction, but also for achieving the desired sulfur level in the subsequent HDS process [3]. Several studies [2-4] have shown that activated carbon can have much higher adsorption capacity for NCs than activated alumina [2] and silica gel [3]. Nevertheless, the influence of the physical and chemical properties of activated carbons on adsorptive denitrogenation of liquid hydrocarbon fuels has not been delineated.

Adsorption capacity, selectivity, and regenerability of the adsorbent are the three critical factors for its practical application in industry. Adsorption selectivity and regenerability of the adsorbent are especially important in commercialization of a successful adsorption process. However, there is very limited information available in the literature for adsorption selectivity and regenerability of activated carbons for NCs, in comparison with their capacity. The adsorption capacity and selectivity of different adsorbents for different compounds in the model diesel fuel (MDF) were quantitatively measured and discussed. The regeneration method of the spent activated carbons was also explored. At a more fundamental level, we try to gain insight into the adsorptive denitrogenation mechanism by which selective adsorption of NCs takes place, to clarify the roles of oxygen functionalities in adsorption capacity and selectivity.

Materials and Methods

Different types of activated carbons (AC1-AC7) that were produced from a variety of carbon source materials by different activation methods were examined. The textural and chemical surface properties of activated carbons were characterized by the adsorption of N_2 and temperature-programmed desorption (TPD) respectively. In this study, a model diesel fuel (MDF), containing the same molar concentrations (10.0 µmol/g) of dibenzothiophene (DBT), 4,6-dimethyl-dibenzothiophene (4,6-DMDBT), indole, quinoline, naphthalene (NA), 1-methylnaphthalene (1-MNA), and fluorine (FLRN), was prepared using decane as a solvent. The total nitrogen and sulfur concentrations of the MDF were 280 and 641ppmw, respectively. The adsorption experiments were conducted in a fixed-bed flowing adsorption system. After packing and drying the column, the MDF was then fed into the adsorbent column at room temperature and a LHSV of 4.8 h^{-1}. The treated MDFs were periodically sampled. After saturation of adsorbents, they were subjected to a regeneration test. Toluene at 80 °C was used to wash out the adsorbates from the spent adsorbents. All treated MDF samples were analyzed by a gas chromatography equipped with a flame ionization detector (FID).

Results and Discussion

The adsorption capacity of the studied activated carbons is shown in **Figure 1**. AC3 showed the highest adsorption capacity for NCs, while AC4 showed exceptional performance for the removal of 4,6-DMDBT. One of reasons for high adsorption capacity of AC3 and AC4 may be contributed to the much high surface area (over 2000 m^2/g) as compared to others.

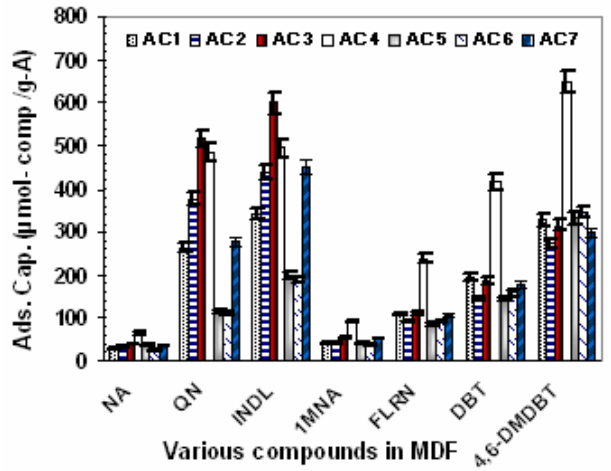

Figure 1. Adsorption capacity for various activated carbons at 25ºC, 4 h adsorption time, and MDF/adsorbent ratio of 100 g-MDF/g-A.

It is well known that the surface chemistry of activated carbon plays an important role in the selective adsorption process. Adsorption capacities Vs textural and chemical properties were correlated and discussed. The results of adsorption capacity and selectivity for various carbons indicate that the functional groups that contribute to the adsorption sites on the surface may be quite different. The current study indicates that an increase of surface oxygen functionalities increases the adsorption capacity of NCs, implying that oxygen functionalities on the carbon surface are a key parameter in controlling the adsorption capacity of NCs. As well-know that there are many types of oxygen functional groups on the activated carbon surface. Clarification of role of various oxygen functional groups on the surface in adsorptive denitrogenation is critical for building the structure-performance correlation. The role of acidic and basic oxygen functional groups for the adsorptive denitrogenation and desulfurization will also be discussed.

Significance

Characterization and correlation between the surface structure of various activated carbons and their adsorption performance indicate that the textural properties are important, but the oxygen functional groups on the surface are the key in determining their adsorption performance. Increasing surface oxygen functionalities increases the adsorption capacity of NCs. The spent activated carbon can be regenerated by toluene washing. The high capacity and selectivity of the activated carbon for NCs, along with their good regenerability, indicate that some activated carbon is a promising adsorbent to achieve deep denitrogenation of liquid hydrocarbon streams.

Acknowledgement. This work was supported by the U. S. Environmental Protection Agency through NSF/EPA TSE Grant No. EPA RD-83147101 and U.S. Department of Energy through DOE-CPCPC Grant No. DE-FC26-03NT41874. The Kuwait Institute for Scientific Research (KISR) is gratefully acknowledged for supporting M.A. at Penn State.

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