Denitrogenation of Fuels

Denitrogenation of Transportation Fuels by Zeolites at Ambient Temperature and Pressure**

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The oil industry is facing increasing pressure to remove organic nitrogen compounds from transportation fuels (gasoline, diesel, and jet fuels).[1–5] Denitrogenation and desulfurization are accomplished commercially by hydrotreating using catalysts in reactors under high temperature and pressure. Denitrogenation is considerably more difficult than desulfurization because the organonitrogen compounds are much less reactive than the organosulfur compounds.[1–5] In this work, we show that denitrogenation can be achieved effectively by using a zeolite sorbent that removes the nitrogen-containing molecules by selective adsorption at ambient temperature and pressure. The sorbent can remove nitrogen from a commercial diesel fuel that contains 83 parts per million by weight (ppmw) nitrogen to well below 0.1 ppmw nitrogen at a sorbent capacity of 43 cm^3 diesel per gram of sorbent. The sorbent can be regenerated for re-use.

There is an increasing need to remove organonitrogen compounds from liquid fuels for two reasons: 1) denitrogenation is essential to many different refinery processes, and 2) to lower emission of nitrogen oxides from combustion processes.[1–3] In addition, it becomes increasingly important to process heavy, low-quality stocks and the anticipated syncrudes, both are rich in highly refractory nitrogen compounds. Denitrogenation and desulfurization are coupled and are performed simultaneously in catalytic hydrotreating, which is an integral part of oil refining. Thus, hydrodenitrogenation (HDN) is accomplished by reacting with hydrogen at 20–100 atm pressure and 300–380 °C using $CoMo/Al_2O_3$ or $NiMo/Al_2O_3$ as the catalyst. Two types of organic nitrogen compounds are found in petroleum and syncrudes: heterocycles and non-heterocycles. The latter consist of anilines and aliphatic amines that are relatively easy to remove by HDN. The heterocycles include compounds containing the six-membered pyridine ring and those containing the five-membered pyrrole ring. The derivatives of pyridine and pyrrole include those with one or two benzene rings as well as alkyl-substituted benzene rings. The kinetics of HDN are not well understood; however, some basic facts are known. The reactivities of the organonitrogen compounds are significantly lower than that of the corresponding organosulfur compounds.[1–5] For example, the alkyl-substituted carbazoles (i.e., pyrrole sandwiched between two benzene rings, the most abundant nitrogen compounds) appear to react at rates about 1/10 as fast as those of alkyl-dibenzothiophenes of comparable structures.[2] Thus, it is considerably more difficult to remove organonitrogen compounds than organosulfur compounds.

The new challenge is to use adsorption to selectively remove these nitrogen compounds from transportation fuels. Because adsorption would be accomplished at ambient temperature and pressure, success in this development would lead to major advances in petroleum refining. However, the commercially available sorbents[6] cannot selectively adsorb the nitrogen compounds.

A class of highly nitrogen-selective and high-nitrogen-capacity sorbents have been discovered and are reported here. This class of sorbents bind the organonitrogen compounds selectively by π complexation. This class of sorbents has been reported recently for desulfurization of transportation fuels, also by π complexation.[7]

The new sorbent for denitrogenation is a zeolite containing cuprous cations and was prepared by ion exchange of zeolites using known ion-exchange procedures.[8] First, this candidate was identified in a screening study that used molecular orbital (MO) theory to search for sorbents that would bond the organonitrogen molecules more strongly than benzene. Here benzene was used as a model compound for aromatic compoundss in transportation fuel that would compete for adsorption sites (by π complexation) against the nitrogen compounds. The calculations were performed at the Hartree–Fock (HF) and density functional theory (DFT) level using effective core potentials (ECPs).[9] The restricted Hartree–Fock (RHF) theory at the LanL2DZ level basis set[10] was used to determine the geometries and the adsorption bonding energies.[11] Moreover, natural bond orbital (NBO) analysis at the B3LYP/LanL2DZ level was used for studying the electron density distribution of the adsorption system.[11] A cluster model was used to represent the zeolite framework structure to which Cu^+ ions were bonded. The results for the adsorption bond energies are shown in Figure 1. Thiophene, the basic molecule for organosulfur compounds in transportation fuels, was also included for comparison. These results indicate that the Cu^+–zeolite could adsorb organonitrogen compounds preferentially over benzene. Thiophene is also preferentially adsorbed by CuY, but the adsorption of the organonitrogen compounds is significantly stronger. The natural bond orbital analysis showed that the bonding followed the classical picture of π complexation, with some donation of electron charges from the π orbital of the pyrrole ring to the vacant s orbital of metals known as σ donation and, simultaneously, back donation of electron charges from the d orbitals of metals to the π* orbital (i.e., antibonding π orbital) of pyrrole, or π back donation. Since many of the d-block metals and their cations are capable of π complexation,[6–8] zeolites with other d-block cations are expected to preferentially adsorb the organonitrogen compounds as well. It should be mentioned that for molecules containing amine or other functional

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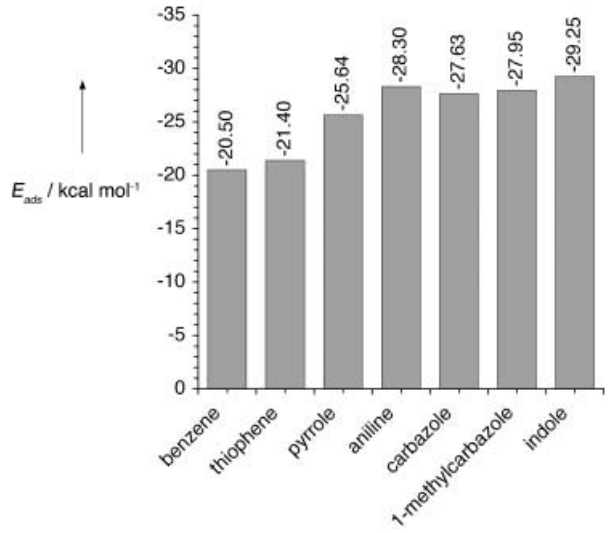

Figure 1. Energy of adsorption for different molecules on CuY zeolite.

groups, the adsorption energy is higher because of the electron-donating effect of the methyl group to the aromatic ring (Figure 1). A schematic representation of an aniline molecule interacting with a cuprous zeolite cluster is shown in Figure 2. Because of π complexation, all organonitrogen molecules adsorb on CuY in a flatwise, face-down manner, and hence are devoid of steric hindrance which inhibits their reaction in HDN.

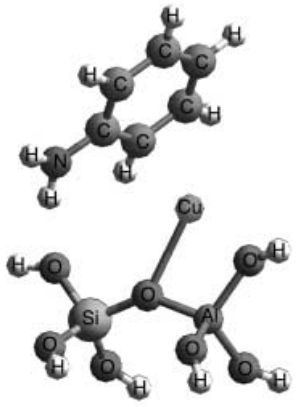

Figure 2. Optimized structure of aniline on Cu–Zeolite.

Then we proceeded to perform adsorption experiments for denitrogenation of a commercial diesel in a fixed-bed adsorber that contained particles of CuY zeolite, at ambient temperature and pressure. The zeolite was prepared by ion exchange of NaY zeolite (Si/Al = 2.43) with Cu^{2+}. The Cu^{2+} exchanged form was subsequently subjected to auto-reduction[12] to form $Cu^{I}Y$. The adsorber bed contained 1–2 g zeolite, while the feed flow rate was maintained at 0.5 $cm^3 min^{-1}$. Effluent (or eluent) samples were collected at regular intervals until saturation was reached, and the samples were subsequently analyzed for nitrogen-containing compounds with a gas chromatograph (GC) equipped with a chemiluminescent nitrogen detector (CLND, by Antek Instruments, Inc.). The CLND was operated at a sensitivity (or detection limit) of approximately 0.015 ppbw N.[2]

The results with the commercial diesel (containing 83 ppmw nitrogen) are summarized in Figure 3 for CuY as the sorbent in the main bed. A thin layer of activated carbon

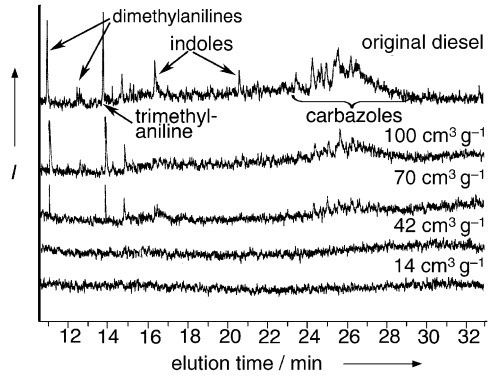

Figure 3. GC-CLND chromatograms of a commercial diesel for nitrogen analysis and progression of nitrogen breakthrough during diesel adsorption in the bed. The sampling time is expressed by cumulative effluent volume normalized by the sorbent weight ($cm^3 g^{-1}$). *I* = intensity in arbitrary units.

(15 % of the bed) was used as the guard bed that extended the sorbent capacity of the main bed by adsorbing the largest molecules from the fuels. For desulfurization, the sulfur capacity was increased by about 20 % by the guard bed.[7] However, the concentration of nitrogen in the effluent (before nitrogen breakthrough) remained the same without the guard bed. The nitrogen contents in the effluent product before the breakthrough point were below 0.1 ppmw nitrogen. The detailed nitrogen breakthrough behavior is shown in Figure 4. The detailed nitrogen analysis showed that the earliest nitrogen breakthrough appeared at a cumulative effluent volume of 43 $cm^3 g^{-1}$. This corresponds to a very high and practical sorbent capacity of 3 mg nitrogen per gram

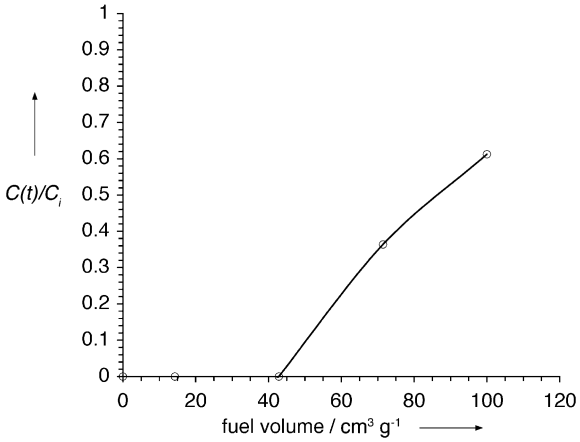

Figure 4. Breakthrough of total nitrogen heterocyclic compounds in a fixed-bed adsorber with AC/Cu^{I}-Y adsorbent, for diesel feed at room temperature. C_i is the total nitrogen concentration of the feed (83 ppmw).

sorbent.[6] It should be mentioned that the zeolite sorbent selectively and effectively remove all alkylcarbazoles (see Figure 3). It is well known that substituted carbazoles poison the hydrodesulfurization (HDS) of the refractory sulfur species in diesel.[13,14]

Experiments on sorbent regeneration were also performed, which showed that CuY can be effectively regenerated either thermally or with solvents. CuY was regenerated by first treating with air at 350 °C (to burn off sulfur) followed by auto-reduction (of Cu^{2+} to Cu^{+}). Afterwards, the original adsorption capacity was completely recovered. For thermal regeneration, activated carbon would not be suitable for the guard bed; activated alumina would be effective.[8]

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