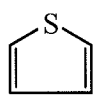
Desulfurization of Transportation Fuels with Zeolite Adsorbents

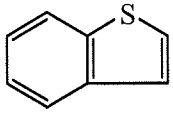
Michael D. Gustavson Inorganic Literature Seminar November 1, 2004

Crude petroleum contains sulfur complexes as impurities that must be removed during petroleum processing.[xi] The combustion of petroleum products containing sulfur produces SO_x, which is one of the leading causes of acid rain. Furthermore, the production of SO_x by automobiles leads to many problems including poisoning of the catalytic converter by binding to and deactivating the metal catalyst as well as corrosion of internal engine components.

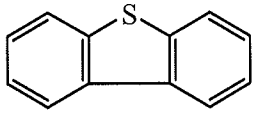
The hydrodesulfurization (HDS) process is currently used industrially to remove sulfur species from fuel.[xii] This process employs a Co-Mo/Al_2O_3 or Ni-Mo/Al_2O_3 catalyst, temperatures of 300 to 340 °C, and 20 to 100 atm of H_2. The products are H_2S and hydrocarbons. This process works quite well for removing sulfides, thiols, and disulfides, but is less effective for removing aromatic sulfur species such as thiophene, benzothiophene, and dibenzothiophene, which are the major sulfur species left in diesel fuel and gasoline after HDS.



Thiophene



Benzothiophene



Dibenzothiophene

In response to the environmental concerns with SO_x emission, the Environmental Protection Agency (EPA) recently passed regulations governing the acceptable sulfur levels in gasoline and diesel fuel. The sulfur content in gasoline must be lowered from 300 parts per million weight (ppmw) sulfur to 30 ppmw sulfur, and the sulfur content in diesel must be lowered from 500 ppmw sulfur to 15 ppmw sulfur, both by 2006.[xiii] The current HDS process is not adequate to reduce sulfur content to the required levels.[xiv]

Selective adsorption of the sulfur species is an attractive alternative desulfurization process due to the ambient, or near ambient, temperature and pressure required. Zeolites are ideal adsorbents because of the channels present in the structure and the ease in which the properties are tuned. Weitkamp *et al.* examined the removal of thiophene from benzene under dynamic conditions using zeolite ZSM-5 and observed adsorption capacities of 15-17 mg thiophene per gram of zeolite.[xv] Another study showed zeolite ZSM-5 removed thiophene, 2-methyl thiophene, and 2,5-dimethyl thiophene from toluene or *p*-xylene under static conditions.[xvi]

Studies using zeolite 13X produced similar results. Zeolite 13X reduced the sulfur level in a non-HDS treated naphtha solution from 36.26 mg of sulfur per liter (mg S/L), about 50 ppm, to 0.74 mg S/L, about 1 ppm and a non-HDS treated naphtha solution from 412.2 mg S/L, about 550 ppm, to 287.3 mg S/L, about 383 ppm.[xvii] This sulfur level does not meet the new environmental regulations.

Extensive work has been reported using metal exchanged zeolite Y for the desulfurization of fuels. Song *et al.* demonstrated that Pd(II)-Y zeolite adsorbed 3.0 mg of sulfur per gram of zeolite (mg S/g) from a 510 ppmw sulfur model jet fuel, giving a final sulfur content less than 5 ppmw, while a Ce(III)-Y zeolite adsorbed 2.8 mg S/g from the same model jet fuel, giving a final sulfur content of 41 ppmw.[xviii] The same two zeolite adsorbents adsorbed about 2.7 mg S/g from a HDS treated 750 ppmw sulfur real jet fuel, giving a final sulfur content of about 383 ppmw. The Ce(III)-Y zeolite adsorbs all sulfur species through direct metal-sulfur interactions while the Pd(II)-Y zeolite adsorbs aromatic sulfur species through π-complexation.

Cu(I)-Y zeolite and Ag(I)-Y zeolite also adsorb sulfur species through π-complexation.[xii,xix] Adsorption of thiophene with Cu(I)-Y zeolite via π-complexation occurs as shown in Figure 1. There is σ-donation from the π-electrons of the thiophene to the empty 4s orbital of Cu(I) along with d-π^* back-donation of electrons from the Cu(I) 3d orbitals to the π^* orbitals of thiophene.[xx]

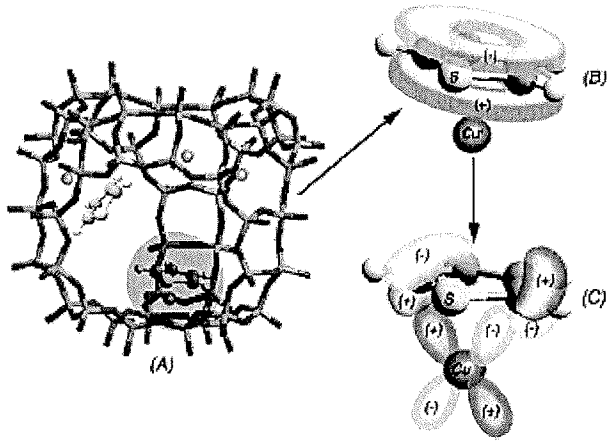


Figure 1: (A) Cu(I)-Y zeolite with adsorbed thiophene; (B) σ-donation from thiophene to Cu(I)-Y zeolite; (C) π back-bonding from Cu(I)-Y zeolite to thiophene.[xx]

Cu(I)-Y zeolite, prepared by solution phase ion-exchange of Na-Y zeolite, is superior to all the other zeolite adsorbents studied in the desulfurization of diesel and gasoline.[xii,xix,xx] Combined with a layer of activated carbon, Cu(I)-Y zeolite reduced the sulfur level of a commercial diesel fuel pretreated with HDS (430 ppmw sulfur) to less than 0.2 ppmw sulfur, yielding 34 cm^3 of fuel per gram of zeolite.[xii] Vapor phase ion exchange increased the amount of Cu(I) in the zeolite and lead to even greater sulfur adsorption.[xx] This Cu(I)-Y zeolite reduced the sulfur content in an HDS treated commercial diesel fuel (297.2 ppmw sulfur) to 0.032 ppmw sulfur, well below the environmental regulations, with a capacity of 0.29 mmol of sulfur per gram of zeolite. In addition, the adsorbents were regenerated to about 95% of the original capacity by heating in air and reducing the Cu(II) to Cu(I).[xixc]

Selective adsorption of sulfur species from fuels using zeolites offers the advantages of using relatively inexpensive materials and ambient temperature and pressure. The combination of HDS followed by treatment with a zeolite adsorption bed should allow deep desulfurization levels to be reached.

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