Removal of Sulfur Components from Low Sulfur Gasoline Using Copper Exchanged Zeolite Y at Ambient Temperature

David L. King*and Liyu Li
Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352
*david.king@pnl.gov

Introduction

The removal of sulfur components from hydrocarbon fuels is necessary for efficient operation of fuel reforming catalysts and to protect the anode of the fuel cell. Although sulfur content in gasoline and diesel fuel are moving to progressively lower levels, additional steps to remove the remaining sulfur are still required. Significant work by others has been expended in the development of regenerable adsorbents that can lower the sulfur concentration to sub-ppm levels. Among the materials reported, zeolites exchanged with metals such as copper, nickel, and cerium have been cited as showing promise, although total adsorbent capacities remain low [1,2]. Divalent copper exchanged in zeolite Y (Cu(II)Y) has been shown to be effective in removing odorant molecules such as dimethyl sulfide, t-butyl mercaptan, and tetrahydrothiophene from natural gas at ambient temperature [3]. However, it appears that Cu(II)Y is less successful in removing thiophenic species from gasoline at ambient temperature [1]. On the other hand, monovalent copper Cu(I)Y has been shown to be effective in removing thiophenic sulfur from a variety of liquid hydrocarbons fuels at ambient temperature, and a π-bonding mechanism has been invoked [2]. As a result of programmatic needs to prepare very low sulfur feedstocks to enable fuel reforming for fuel cell operation, we investigated Cu(I)Y zeolite with the intention to verify and quantify its performance. We have not been successful in removing thiophenic sulfur from gasoline and gasoline surrogate blends to the sub-ppm levels required. Moreover, we have found evidence that chemical reactions catalyzed by both Cu(I)Y and Cu(II)Y zeolite convert mercaptans present in gasoline to higher molecular weight species, and thus chemical reactivity needs to be considered in any sulfur removal scheme.

Materials and Methods

Cu(II)Y zeolite, (Cu/Al molar ratio 0.4) was prepared by ion exchange of NaY zeolite (Zeolyst) two times with a 0.5M solution of copper nitrate (cc/g), with 500°C calcination between exchanges. Cu(I)Y was prepared via autoreduction of Cu(II)Y in flowing He at 450°C for 6h. For the adsorption studies, 0.15g adsorbent was added to 15 ml of the sulfur-containing hydrocarbon sample, and the samples placed overnight in a shaker apparatus operating at ambient temperature. Samples were initially purged with nitrogen to remove any dissolved O_2. Analysis of the sulfur content in the samples was carried out with a HP6890 chromatograph equipped with a sulfur chemiluminescent detector (SCD). Three sulfur-containing samples were used: i) 30 ppmw thiophene in isooctane; ii) 30 ppmw thiophene in a gasoline surrogate (74 wt.% isooctane, 20 wt.% xylene, 5 wt.% cyclohexane, 1 wt.% 1-pentene); iii) premium grade low sulfur gasoline obtained from a local ARCO gas station containing ~5ppmw sulfur, predominantly ethanethiol and propanethiol, to which was added 3ppmw of the following compounds: ethanethiol, 2-propanethiol, 2-methyl-2-propanethiol, thiophene, 2-methyl-thiophene, 3-methylthiophene, 2,5-dimethylthiophene, benzothiophene, and dibenzothiophene.

Results and Discussion

Due to the promising published literature on Cu(I)Y zeolite for thiophenic sulfur removal, we investigated this adsorbent first. For the sample containing 30ppmw thiophene in isooctane, the adsorbent was able to remove 98% of the thiophene and the adsorbent color did not change significantly. For the thiophene-spiked benchmark fuel sample, Cu(I)Y was able to remove only 12% of the thiophene and the adsorbent turned black immediately after addition to the hydrocarbon. For the spiked commercial gasoline sample, we saw virtually complete disappearance of the thiols, but at the same time new sulfur compounds were observed in the GC trace, while the intensity the thiophenic components was unchanged, see Figure 1. Cu(II)Y zeolite showed similar performance with the spiked gasoline sample, i.e. formation of new compounds but no apparent removal of thiophenes. NaY zeolite removed approximately 70% of the thiols and none of the thiophenes, but did not produce any new compounds. However if the gasoline sample was not first purged with N_2, these new compounds were observed. We are further characterizing these new sulfur products, which are preliminarily assigned as disulfides formed via oxidative coupling. Since Cu(I) and Cu(II) are both reducible, oxygen would not be required for disulfide formation, whereas oxygen would be required with NaY. These results indicate that Cu(I)Y zeolite is not as effective as hoped for the removal of thiophenic sulfur molecules from real gasoline feeds, and moreover it can catalyze other undesired chemistries involving sulfur-containing hydrocarbons.

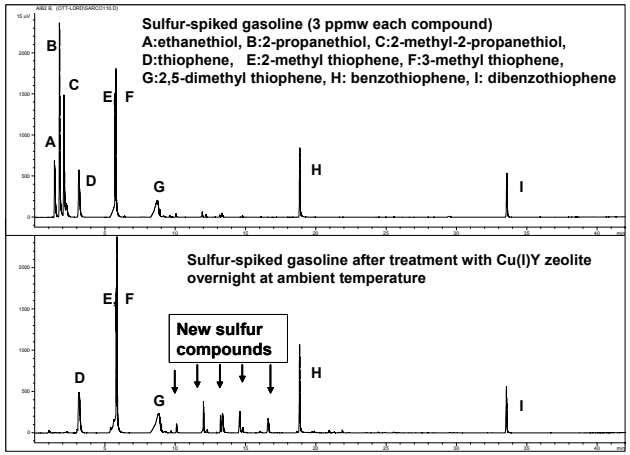

Figure 1. GC-SCD traces of sulfur-spiked gasoline before (above) and after (below) reaction with Cu(I)Y zeolite overnight at ambient temperature.

References

1. Velu, S., Ma, X., Song, C. *Ind. Eng. Chem. Res.* 42, 5293 (2003).
2. Hernandez-Maldonado, A.J., Yang, R.T. Ind. Eng. Chem. Res. 42, 123 (2003).
3. King, D.L., Birnbaum, J.C., and Singh, P. *Fuel Cell Seminar Abstracts*, 782 (2002).