

Sulfur Removal From HDS-Treated Light Cut JP-8 Fuel Using Small Crystal Cu(II)Y Zeolite Adsorbent

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Introduction

This study was initiated to support a project aimed at generating and desulfurizing a light fraction of JP-8 fuel, providing a product having sulfur concentration 1ppmw or less. This fuel would be subsequently reformed for PEM fuel cell use. A light fraction has a lower sulfur concentration, and the remaining species are easier to remove since no bulky alkyl-substituted benzothiophenes are present. A combined hydrodesulfurization (HDS) process [1] and adsorptive desulfurization process was used. The HDS process decreased the sulfur level from ~300 ppmw to ~15 ppmw, and adsorption process was charged with selectively adsorbing the remaining sulfur species to achieve the 1 ppmw sulfur target. Here we report results from adsorptive desulfurization of HDS-treated light cut JP-8 fuel.

After screening a number of potential adsorbents, we fixed on a zeolite adsorbent that contained divalent copper cations incorporated within the structure as exchangeable cations (copper-Y zeolite, CuY). This was the best material in our tests, which is consistent with our previous desulfurization work using CuY zeolites [2, 3]. However, we were unable to remove sulfur from the HDS product to the required 1 ppmw level without using excessive quantities of the adsorbent. We postulated that the larger sulfur molecules might be adsorbed near the external surface of the crystal, blocking access of additional sulfur molecules to the adsorption sites in the interior of the zeolite crystal and thereby limiting adsorption capacity. As a result, we investigated the effect of reducing the particle size of the CuY zeolite to increase the surface-to-volume ratio of the material. With that modification, we were successful in reducing sulfur levels of the HDS product to approximately 1 ppmw with reasonable quantities of adsorbent. Small crystal CuY zeolite showed better sulfur removal performance than standard CuY zeolite kinetically as well.

Materials and Methods

Standard Cu(II)Y zeolite was prepared by ion exchanging NaY zeolite (Zeolyst CBV100) two times with a 0.5 M solution of copper nitrate (16 ml/g), with 500°C calcination between exchanges. Small crystal size Cu(II)Y zeolite was prepared by ball-milling standard Cu(II)Y in an aqueous slurry at ambient temperature. The adsorption experiments were carried out with HDS-treated light cut JP-8 fuel, generated from a JP-8 fuel (from BP Tacoma refinery) having an initial content of 1225 ppmw sulfur. The feed used for the adsorption studies contained 15 ppm sulfur, comprising thiols, sulfides, thiophenes and benzothiophenes. Adsorption experiments were carried out in batch mode, using a heated shaker bath. Typically, 1g of the solid, pre-dried at 110°C, was added to the low sulfur fuel at a selected temperature (ambient to 87°C) for a given period. Analysis of the hydrocarbon liquid for sulfur content was carried out using an Agilent 6890 gas chromatograph equipped with a sulfur chemiluminescent detector and a DB-5 column.

Results and Discussion

Figure 1 shows the SEM images of standard and small crystal CuY zeolite, and Figure 2 displays the difference in sulfur removal performance between these two materials. The conditions for these tests were as follows: 1 g sorbent was added to 36 mL of HDS product, and the slurry was stirred at each temperature for 11 hr. The test was carried out using the same sorbent sample throughout the run, while the temperature was increased progressively from 17°C to 87°C. Figure 2 shows that the small crystal CuY zeolite adsorbent is superior to standard CuY zeolite, and also that more sulfur can be removed from the HDS product by both materials with increasing temperature.

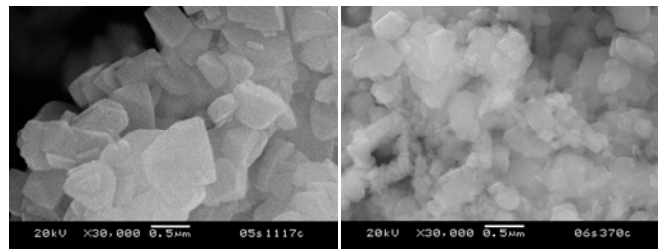


Figure 1. SEM images of regular size CuY zeolite (right) and small crystal CuY zeolite (left)

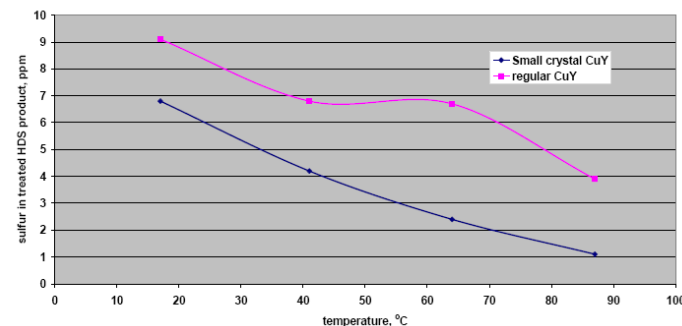


Figure 2. Comparison of sulfur removal performance at different temperatures from HDS-treated light cut JP-8 fuel using standard and small crystal size CuY adsorbents

Significance

Small crystal size CuY zeolite shows better sulfur removal performance from HDS-treated light cut JP-8 fuel than standard CuY zeolite. Use of the small crystal zeolite provides a method to significantly reduce the total amount of adsorbent required.

References

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