

Removal of sulfur components from low sulfur gasoline using copper exchanged zeolite Y at ambient temperature

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Abstract

Copper-exchanged zeolite Y has been shown to be an effective material for removal of a variety of sulfur species from hydrocarbon streams, and both monovalent (Cu(I)) and divalent (Cu(II)Y) materials have been claimed to be effective. In this work we discuss experiments aimed at providing a direct performance comparison between the two copper-containing materials. Cu(I)Y zeolite is somewhat more effective than Cu(II)Y in removing thiophene from various fuel blends. Capacity of both materials for thiophene diminishes markedly when aromatics and/or olefins are present, and Cu(I)Y immediately turns dark on exposure to such feeds. Both materials demonstrate ability to convert thiols to disulfides at ambient temperature.

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1. 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 concentrations 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 hydrocarbon fuels at ambient temperature, and a π -bonding

mechanism has been invoked [2,4,5]. As a result of programmatic needs to prepare very low sulfur feedstocks to enable fuel reforming for fuel cell operation, we investigated both Cu(II)Y and Cu(I)Y zeolite with the intention to verify and quantify their performance with several different hydrocarbon–sulfur mixtures, focusing on gasoline and gasoline surrogate compositions. The primary objective of this work is to compare and quantify the performance of Cu(I) and Cu(II)Y zeolite in removing different types of sulfur species from a low sulfur gasoline feedstock.

2. Experimental

Cu(II)Y zeolite was prepared by ion exchange of NaY zeolite (Zeolyst CBV100) two times with a 0.5 M solution of copper nitrate (16 ml/g), with 500 °C calcination between exchanges. Cu(I)Y was prepared via auto-reduction of Cu(II)Y in flowing He at 450 °C for 6 h following procedures described by Takahashi et al.[6]. For the adsorption studies, 0.15 g adsorbent pre-dried at 110 °C was added to 15 ml of the sulfur-containing hydrocarbon sample, and the samples placed overnight in a shaker apparatus operating at ambient temperature. Some samples were purged with nitrogen to remove any dissolved oxygen. Analysis of the sulfur content in the samples was carried out with a HP6890 chromatograph equipped with a sulfur chemiluminescent detector (SCD).

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3. Results

Elemental analysis of the Cu(II)Y zeolite, as obtained by SEM/EDS, is summarized in Table 1. Based on the Na/Al ratio, the degree of exchange by Cu is about 80% of theoretical. However, the Cu/Al ratio is measured at 0.48, indicating that there is some fraction of Cu that is not located at cation exchange positions within the zeolite, and is most likely present as extraframework CuO.

It is important to note that the adsorbent identified as Cu(I)Y actually contains both monovalent as well as divalent copper cations. The He-based auto-reduction was shown to provide only ~50% reduction of Cu²⁺ to Cu⁺, as measured by ESR [7]. We assume a similar level of reduction was achieved with our materials. Following the reduction procedure, the zeolite will also contain some H⁺ sites to maintain charge neutrality. Given limited resources, no detailed characterization of the cationic speciation was carried out in this work, as we were looking only for qualitative differences in performance between Cu(I)Y and Cu(II)Y.

In the first study, three simple fuel blends were prepared that varied in composition (alkane, cycloalkane, aromatic, olefin). These fuel blends, along with a 100% isooctane sample, were spiked with approximately 20–30 ppmw thiophene. The compositions of these fuel mixtures are summarized in Table 2. In moving progressively from isooctane through blends 1–3, the compositions were selected to place increasing demands on the adsorbent through the addition of components that could compete with thiophene for the copper cation sites.

To 15 ml of each of the fuel blends was added 0.15 g of either Cu(I) or Cu(II) Y zeolite. After overnight stirring, the residual thiophene was measured by chromatographic analysis using sulfur chemiluminescent detection (SCD). On a eight weight basis, complete adsorption of the thiophene from the liquid by the adsorber would require a capacity of approxi-

Table 3

Comparative performance of Cu(I)Y and Cu(II)Y zeolite with prepared fuel blends: amount of sulfur removed

	Iso-octane (%)	Fuel blend 1 (%)	Fuel blend 2 (%)	Fuel blend 3 (%)
Cu(I) Y	98	99	18	12
Cu(II) Y	79	71	11	0

mately 0.19 wt.%, or approximately 0.07 wt.% on a sulfur basis. The results are summarized in Table 3.

It is clear that the performance of Cu(I) Y zeolite is superior to Cu(II) Y zeolite in all cases. Only in the case of the alkane-only fuel is the adsorption near-complete, however. It is notable that the adsorption of thiophene by Cu(II) Y is also significant with both iso-octane and fuel blend 1, which suggests that a π -bonding mechanism may not be required for adsorption of thiophene. When aromatics and/or olefins are present, adsorption of thiophene over both zeolites is severely compromised. In this latter case, the Cu(I) Y adsorbent changed color to dark upon contact with the hydrocarbon–sulfur mixture, whereas the Cu(II) adsorbent did not.

We then switched our attention to desulfurization of commercial gasoline. A sample of low sulfur gasoline was obtained at a local ARCO gasoline station. This sample contained only 5 ppmw sulfur by our measurements. The majority of the sulfur was present as thiols and sulfides, primarily ethane- and propane-thiol. The sample contained virtually no thiophenic sulfur compounds. According to the vendor, the sample contained approximately 1 vol.% olefins and 1.5 vol.% benzene. The sulfur SCD trace is provided in Fig. 1.

For this gasoline desulfurization study, we were interested in understanding the role of the various hydrocarbon species in the gasoline in affecting the ability of the copper-exchanged zeolites

Table 1

Elemental analysis of copper-exchanged Y zeolite, Cu(II)Y, as determined by SEM/EDS

Element	wt.%	at.%
Si	36.30	30.54
Al	12.72	11.14
Na	2.17	2.22
Cu	14.28	5.31

Both wt.% and at.% values have estimated accuracy within $\pm 1\%$.

Table 2

Composition of prepared fuel blends spiked with thiophene

	Iso-octane (wt.%)	Methyl-cyclohexane (wt.%)	Xylene (wt.%)	1-Pentene (wt.%)	Thiophene (ppmw)
Iso-octane	100	0	0	0	30
Fuel blend 1	95	5	0	0	28.5
Fuel blend 2	75	5	20	0	22.5
Fuel blend 3	74	5	20	1	30

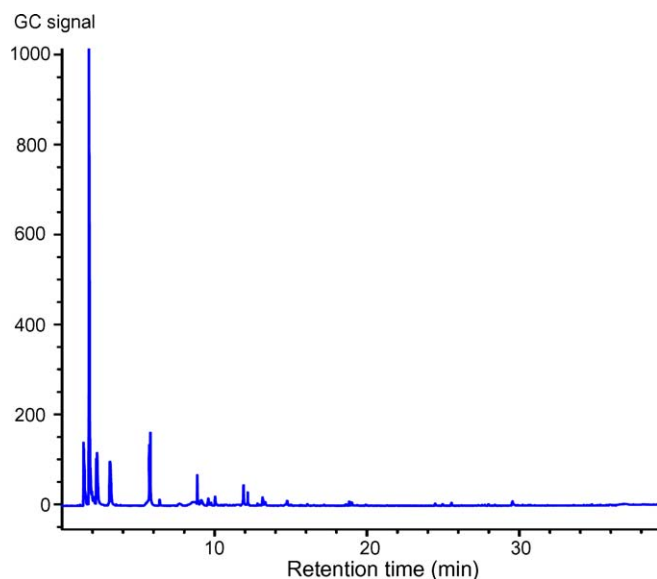


Fig. 1. Distribution of organo-sulfur species in low sulfur gasoline using SCD.

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