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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.

Keywords: Copper-exchanged zeolite; CuY; Cu(I); Cu(II); Desulfurization; Thiophene; Disulfides; Thiolate

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 Cu^{2+} 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 approximately 0.19 wt.%, or approximately 0.07 wt.% on a sulfur basis. The results are summarized in Table 3.

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

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 ±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

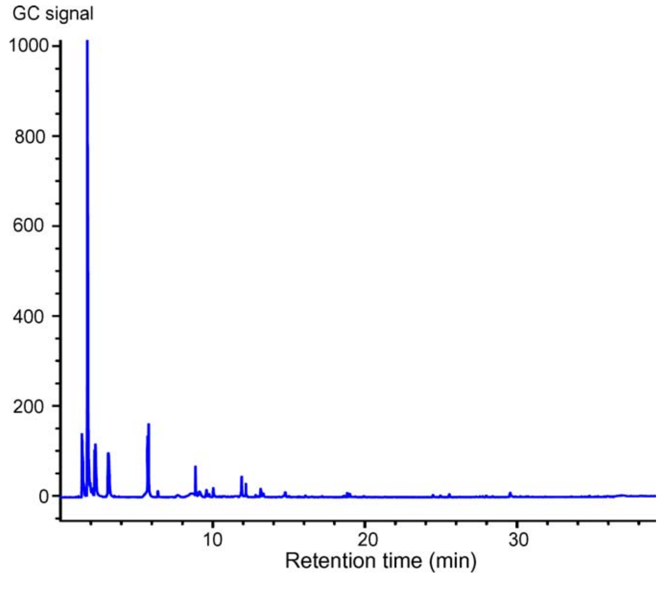

Fig. 1. Distribution of organo-sulfur species in low sulfur gasoline using SCD.

to remove sulfur. Due to the low concentration of sulfur and the lack of thiophenic components in this gasoline sample, we felt that our understanding of sulfur adsorption would be quite limited. Thus, we intentionally spiked the gasoline with 3 ppmw of the following compounds: (i) thiols–ethanethiol (A), 2-propanethiol (B), and 2-methyl-2-propanethiol (C); (ii) single ring thiophenes–thiophene (D), 2-methylthiophene (E), 3-methylthiophene (F), and 2,5-dimethlythiophene (G); (iii) arylthiophenes–benzothiophene (H) and dibenzothiophene (I). Fig. 2 shows the SCD trace for the spiked gasoline sample. The vertical scale in Fig. 2 is twice that of Fig. 1.

We began by adding a 0.1 g sample of Cu(I) Y zeolite to 10 ml of the sulfur spiked gasoline shown in Fig. 2 and stirred the mixture overnight. Analysis of this sample showed disappearance of the thiol compounds and very limited (∼3%) removal of the thiophenic compounds. A new series of peaks with a retention time between 10 and 17 min were observed. The SCD trace is shown in Fig. 3. We believe that the newly generated peaks are disulfides catalyzed by the Cu(I) Y zeolite, as will be further discussed below.

We repeated the same experiment with Cu(II) Y zeolite, and obtained virtually the same results as with Cu(I) Y, the main difference being that the former was completely inert toward the thiophenic compounds, whereas the latter showed a small affinity as indicated by the approximately 3% removal measured. We then proceeded to carry out a ‘‘blank run’’ utilizing NaY zeolite that had not been ion exchanged with copper. The resulting SCD trace looked virtually identical to that obtained with Cu(II) Y zeolite. Recognizing that if the new compounds formed were indeed disulfides, then these would be formed by an oxidative process. We re-ran the NaY zeolite experiment, but first purged the spiked gasoline and the zeolite sample vigorously with nitrogen prior to the adsorption test, in order to remove any oxygen in solution or entrapped oxygen within the zeolite that might facilitate the oxidative pathway. With that treatment, approximately 70% of the thiols were removed, but no new sulfur compounds were formed. This provides supporting evidence to the assignment of these new peaks as disulfides, which are formed via an oxidative coupling process with co-production of H_2O. The ∼70% thiol removal with NaY indicates that these sulfur compounds are quite easily removed, possibly by an acid–base interaction. We then re-ran the Cu(I) and Cu(II) Y adsorption experiments with spiked gasoline, but this time vigorously purged the zeolite samples and the hydrocarbon with nitrogen as we had the NaY case. The results obtained were the same as those obtained with the non-purged samples, i.e., new sulfur compounds were still formed with both Cu(I)Y and Cu(II)Y.

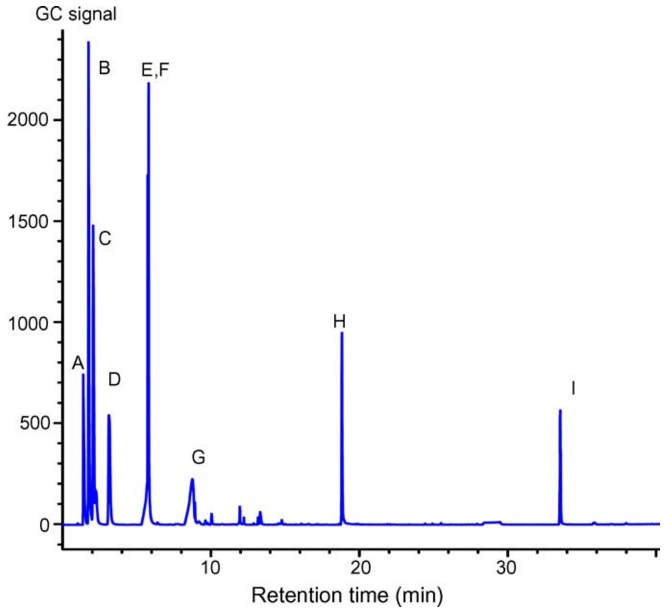

Fig. 2. SCD trace of gasoline spiked with various sulfur-bearing organics. Spiked components: (A) ethanethiol; (B) 2-propanethiol; (C) 2-methyl-2-propanethiol; (D) thiophene; (E) 2-methylthiophene; (F) 3-methylthiophene; (G) 2,5-dimethylthiophene; (H) benzothiophene; (I) dibenzothiophene.

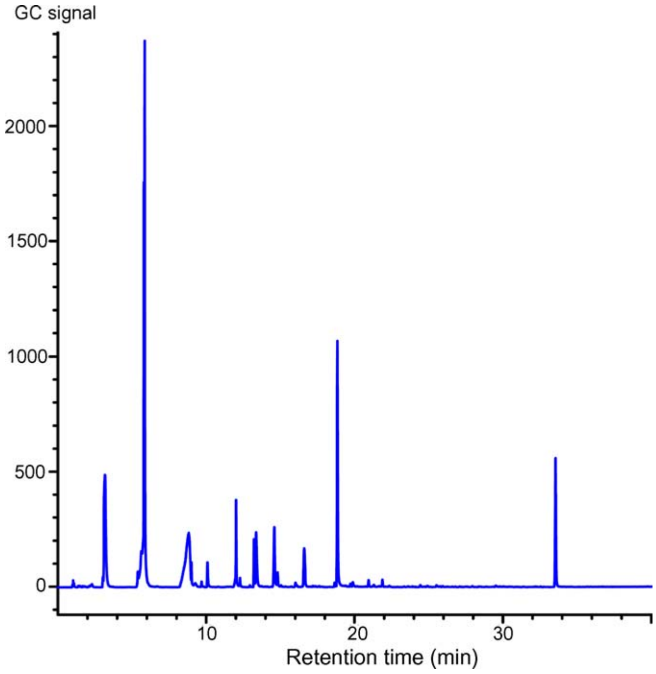

Fig. 3. SCD trace of spiked gasoline following treatment with Cu(I) Y zeolite at ambient temperature.

4. Discussion

We have observed that Cu(I) Y zeolite is effective in removing thiophene from iso-octane, however the presence of added olefin and aromatic compounds resulted in significantly compromised adsorption performance in our batch adsorption tests. The immediate change to a dark color upon its addition to fuel blends 2 and 3 indicate that additional chemical reactions are occurring between fuel components and the copper cation, possibly leading to reduced copper metal. Such a color change was not observed with Cu(II)Y or NaY zeolite with these same fuel blends.

Although the performance of Cu(I) Y was superior to Cu(II) Y in removing thiophene, in iso-octane both adsorbents were capable of removing thiophene. This suggests two possibilities:

a π-bonding interaction is not the sole method by which thiophene may be removed, or possibly some level of reduction of Cu(II) occurs during the course of the reaction in the hydrocarbon solvent at ambient temperature. Although the latter may be possible, especially since the overnight experiments suggest a long residence time, we prefer the former explanation, especially in light of the color change with Cu(I) that was not observed with Cu(II).

The new sulfur compounds that are produced with gasoline samples we assign to dialkyl disulfides. Oxidation of thiols to disulfides by metals oxides including cupric oxide has long been established [8], although we have not found references for this reaction occurring with copper-exchanged zeolites. Supported copper oxides have been found to react with thiols to produce disulfides along with copper (I) thiolate complexes [9], the latter which have been found to decompose at higher temperatures (190 °C) to dialkylsulfides and Cu_2S [10]. Based on prior literature findings, the observed formation of disulfides is most likely catalyzed by Cu^{+2} cations present in both Cu(II)Y and Cu(I)Y:

$$2Cu^{2+} + 2RSH \rightarrow RSSR + 2Cu^{+} + 2H^{+}. \quad (1)$$

It is possible that Cu^{+}, initially present in Cu(I)Y or produced by reaction (1), also contributes to the desulfurization via formation of thiolates:

$$2Cu^{+} + 2RSH \rightarrow 2RS\text{-}Cu + 2H^{+}. \quad (2)$$

In this latter case, stable copper thiolate complexes may remain in the zeolite at the low reaction temperatures employed, contributing to the removal of sulfur but not to the production of disulfide products. Decomposition of the thiolates to monosulfides and Cu_2S is thought to be unlikely at the low temperatures employed, but cannot be excluded without a more detailed analysis of the reaction products:

$$2RS\text{-}Cu \rightarrow RSR + Cu_2S. \quad (3)$$

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