

Desulfurization of Diesel Fuels by Adsorption via π -Complexation with Vapor-Phase Exchanged Cu(I)-Y Zeolites

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Removal of sulfur-containing compounds from liquid fuels is currently achieved by using hydrodesulfurization (HDS) with a Co-Mo/Al₂O₃ or Ni-Mo/Al₂O₃ catalyst.¹ HDS is highly efficient in removing thiols, sulfides, and disulfides but is less effective for aromatic thiophenes, especially those containing functional groups that hinder the sulfur atoms (i.e., 4,6-dimethyl-dibenzothiophene). To reduce the sulfur content to meet the new federal government regulations,^{2,3} the reactor size needs to be increased by factors of 5–15.⁴ The new challenge is to use adsorption to selectively remove these sulfur compounds.

Recently, Hernández-Maldonado and Yang showed that aqueous-phase copper(II)-exchanged Y-zeolites, when autoreduced to Cu(I)-Y, are capable of removing 0.20 mmol of organo-sulfur species from a commercial diesel fuel (297.2 ppmw total sulfur) per gram of zeolite.^{5–7} This corresponds to about 3 thiophenic molecules per unit cell. Afterward, the fuel contained a total sulfur content of less than 1 ppmw-S. The deep-desulfurization levels were obtained because of a π -complexation between the Cu⁺ ions (1s²2s²2p⁶3s²3p⁶3d¹⁰4s⁰) and the thiophenic aromatic rings. As seen in Figure 1, through the π -complexation mechanism the cations can form the σ bonds with their empty s-orbitals and, in addition, their d-orbitals can back-donate electron density to the antibonding π -orbitals (π^*) of the sulfur rings. Experimental data and molecular orbital (MO) calculations have shown that π -complexation with cuprous ions is stronger with organo-sulfur molecules (i.e., thiophenic molecules) than with aromatics without sulfur (e.g., benzene).⁸

The copper zeolites used in previous studies were prepared by liquid-phase ion exchange (LPIE) of Na-Y with copper(II) nitrate (followed by reduction to Cu⁺) and had a unit cell composition of Cu₂₁Na₁₄[Al₅₆Si₁₃₆O₃₈₄]. If all the copper is reduced to Cu⁺, then 38% of the charge compensation comes from cuprous ions, and the other 62% comes from sodium ions and free hydroxyl groups or extra lattice oxygen (ELO).^{9,10} Complete ion exchange in aqueous phase is usually difficult because of the hydration state of the cupric ions and because of complex hydrolysis mechanisms that arise during the process. Thus, other means of introducing copper(I) ions directly are essential. Guidry and Price¹¹ and Spoto et al.^{12,13} used vapor-phase ion exchange (VPIE) techniques to fully exchange ZSM-5 (MFI) zeolites with copper(I) ions. Afterward, the zeolite needed to be oxidized to a Cu²⁺ state before exposing it to atmospheric air. This avoids disproportionation of Cu⁺ to Cu²⁺ and Cu⁰.¹¹ The Cu⁺ species are then recovered by traditional reduction methods. Here we report the use of these techniques to synthesize a faujasite zeolite containing almost 57 copper ions per unit cell and use of the same to desulfurize a commercial diesel fuel.

H-Y was first obtained by heating a NH₄-Y zeolite powder (Si/Al = 2.40, Strem Chemicals) in air at 450 °C at 1 °C/min. Layers of the proton-form zeolite and CuCl (99.99%, Sigma-Aldrich) were loaded into a reactor each separated by thin quartz wool walls. Direct contact of the zeolite and salt is not desired

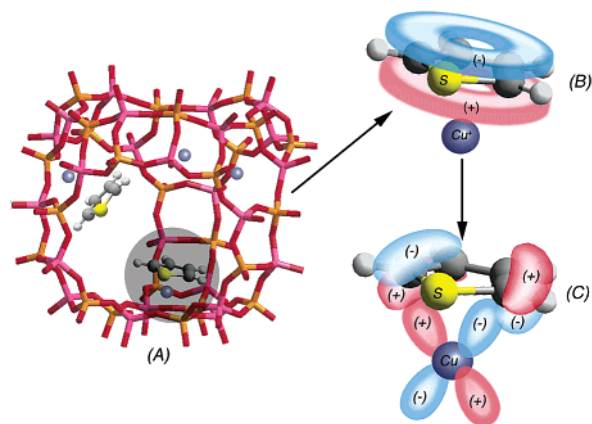


Figure 1. Faujasite supercage with copper ions occupying 6-ring windows sites (A); σ -donation of π -electrons of thiophene to the 4s orbital of copper(I) (B); d- π^* back-donation of electrons from 3d orbitals of copper(I) to π^* orbitals of thiophene. Here 3d represents d_{xy}, d_{yz}, or d_{xz}, or 3 of the 5 3d orbitals.

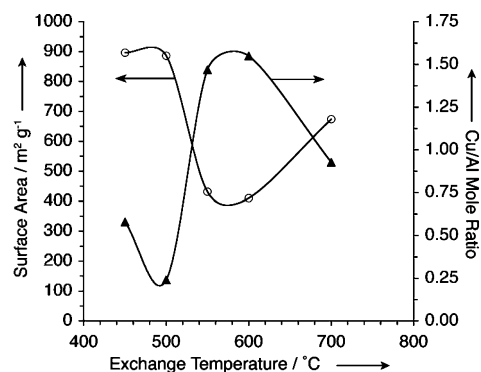


Figure 2. Cu(I)-Y (VPIE) surface area and copper concentration as a function of exchange temperature.

because of hydrolysis of the copper species in the presence of adsorbed water. The reactor was then heated in an inert, dry atmosphere, from room temperature to 200 °C at 1 °C/min and the temperature held at that point for 4–6 h. Afterward, the temperature was slowly increased above the normal melting point of CuCl (430 °C) and kept at a specific temperature for another 10 h. The zeolite was then treated in oxygen at 200 °C for 4 h before cooling down to room temperature. During the oxidation stage the cupric ions react to form oxonium ions [Cu-O-Cu]²⁺, which could further interact with moist air to form stable [Cu(OH)]⁺ ions.¹¹ After recovery, all the as-prepared zeolites were analyzed for elemental composition using neutron activation analysis (NAA). In addition, liquid nitrogen adsorption at -196 °C provided sorbent surface area information.

Figure 2 shows copper-to-aluminum molar ratio and surface area data as a function of VPIE temperature. At lower temperatures,

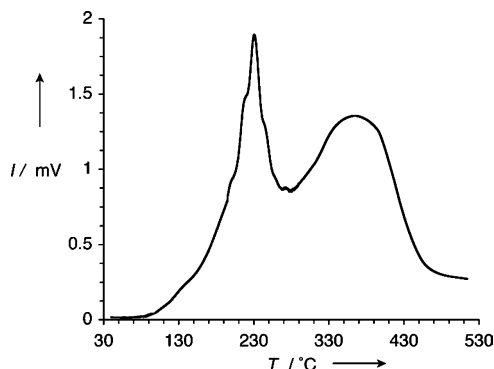


Figure 3. Temperature-programmed reduction of VPIE copper–Y zeolite with 5 vol % H₂ (in He) at a heating rate of 10 °C/min.

the amount of copper(I) chloride evaporated was not sufficient for complete exchange, and this was evident from the CuCl material left in the corresponding reactor section. Increasing the VPIE temperature to 550 or 600 °C resulted in zeolites with Cu/Al ratios greater than unity. This was due to a temperature not high enough to evaporate the CuCl excess from within the voids/cages of Y-zeolite. Clear evidence of this is the noticeable decrease in surface area between 550 and 600 °C (see Figure 2). However, a temperature of about 700 °C results in almost 95% ion exchange (Cu₅₄H₃[Al₅₇Si₁₃₅O₃₈₄]) and a higher surface area. At 700 °C, CuCl excess is completely evaporated, and this was corroborated by the absence of the salt from its original reactor location at the end of the VPIE process and by a white crystalline ring formed at the reactor outlet. Spoto et al.¹³ also made these observations during a VPIE process to produce Cu(I)–ZSM-5. The Cu(I)–Y (VPIE@700 °C) surface area is not as high as the original H–Y one, but this is due to the high copper loading. Trigueiro et al.¹⁴ studied the effect of metal ion exchange high loading on the surface area of faujasite zeolites, and their results agree well with ours.

The reduction temperature profile for Cu(II)–Y (VPIE) was studied using temperature-programmed reduction (TPR). The experiments were performed using an inert gas containing approximately 5% hydrogen (by volume) and a custom-made vertical reactor fitted with a heating jacket. The temperature was increased at 10 °C/min and the hydrogen consumption measured with a thermal conductivity detector (TCD). Figure 3 shows the resulting TPR profile for Cu(II)–Y (VPIE). The profile shows two major peaks: the first one corresponds to reduction of Cu(II) to Cu(I), while the second indicates reduction of Cu(I) to copper metal. Stepwise reduction of copper(II) ions in liquid-phase exchanged zeolites and dispersion on activated alumina supports have been reported before.^{11,15,16} In general, a reduction temperature of about 231 °C is sufficient to obtain the cuprous species required for π -complexation.

The desulfurization capability of the Cu(I)-Y (VPIE) zeolite was tested using a commercial diesel fuel (297.2 ppmw total S). Activation of the zeolite to obtain Cu(I)–Y (VPIE) was performed in situ in a vertical reactor as follows: heating to 350 °C in oxygen to remove bulk and adsorbed water, followed by cooling to room temperature, and then followed by heating to about 231 °C at 10 °C/min in an inert gas stream containing 5 vol % hydrogen. The last temperature leg was held for 15 additional minutes before cooling down to room temperature. The sorbent bed was then washed with a sulfur-free hydrocarbon (e.g., *n*-octane) to remove any entrapped gas. After allowing the liquid hydrocarbon head to disappear, the diesel was allowed to contact the bed. The effluent was sampled periodically and the sulfur concentration measured

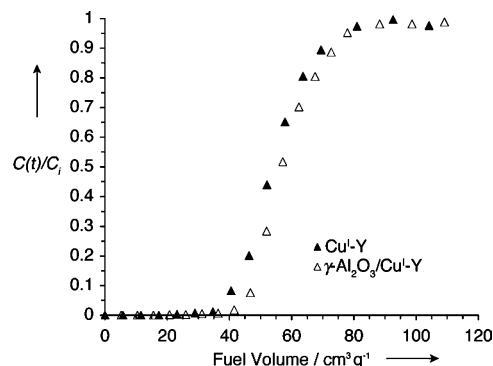


Figure 4. Breakthrough of total sulfur in a fixed-bed adsorber with Cu(I)–Y (VPIE) or γ -Al₂O₃/Cu(I)–Y (VPIE) adsorbents, for diesel feed at room temperature. C₁ is the total sulfur concentration of the feed.

with a GC–FPD system. Thorough information about the sulfur species identification and total content analyses can be found elsewhere.⁵ Figure 4 shows a total sulfur breakthrough curve for the diesel fuel treated with a VPIE cuprous zeolite.

The new sorbent provides a desulfurization capacity of 0.29 mmol of sulfur per gram of zeolite. This corresponds to about 5 thiophenic molecules per unit cell. After treating 18 cm³ of fuel, the cumulative average sulfur concentration detected was 0.032 ppmw-S. This evidences the presence of additional exposed cuprous ions (in sites II and III), which were not as abundant in the Cu(I)–Y (LPIE). The sulfur adsorption capacity was increased by 14% after a thin layer of activated alumina was placed on top of a fresh zeolite bed (Figure 4.) Hernández-Maldonado and Yang showed that activated aluminas are capable of adsorbing large thiophenic molecules, but not to deep desulfurization levels.¹⁷

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