Desulfurization of Gasoline and Diesel by Adsorption with Cu(I)–Y Zeolite

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The objectives of this work were to fabricate Cu(I)–Y zeolite nanoparticles for the desulfurization of commercial gasoline and diesel using fixed-bed adsorption processes at room temperature. The Cu(I)–Y zeolite prepared in the present study showed that the breakthrough capacities of 21 and 9 mg/g of adsorbents of diesel and gasoline, respectively at 298 K for sulfur removal. Under the same experimental conditions, the saturation loadings were 36 and 23 mg/g for diesel and gasoline, respectively. Moreover, the structural morphology, crystallinity, fine structure and characteristics of the adsorbents were also systematically investigated. TPR profile of Cu(II)–Y zeolite indicated that the two reduction steps at 462 and 509 K, respectively were observed. A reduction temperature of about 462 K is sufficient to obtain the cuprous species required for π -complexation. EXAFS spectra showed that the bond distances of Cu–S in Cu₂S and CuS were 2.35 and 2.47 Å, respectively in the sulfur-adsorbed Cu–Y adsorbent.

Introduction

Deep desulfurization of commercial gasoline and diesel fuels (CGDFs) has become an important topic due to the upcoming legislative regulations to reduce sulfur content all over the world. These liquid fuels contain various organic-sulfur compounds, which not only contribute to air pollution, but also cause serious hazardous impact on environmental risk and safety. Consequently, the sulfur level in CGDFs must be reduced from current maximum 500 to 15 ppmw in the USA and to 10 ppmw in the EU by 2010 (Kim *et al.*, 2006). Further lower limitation of sulfur or sulfur free CGDFs are required for the near future. Moreover, CGDFs are considered as potential liquid fuels for portable fuel cell (FC) system and automobiles due to their ready availability, proven safety for easily delivery or storage, and higher energy density. However, the levels of organic sulfur present in CGDFs and the generated H₂S from them during reforming process are sufficient to significantly reduce the activity and lifetime of catalysts as well as electrode catalysts for a FC processor. It is generally agreed that the sulfur concentration in CGDFs has to be reduced to less than 0.1 ppmv for fuel cell applications (Song, 2003; Kim *et al.*, 2006; Xue *et al.*, 2006).

The removal of sulfur containing compounds present in gasoline and diesel fuels is an important op-

eration in the petroleum refinery. Industrially, majority of sulfur is eliminated through the hydrodesulfurization (HDS) process (Babich and Moulijn, 2003). HDS uses Co-Mo/Al₂O₃, Ni-Mo/Al₂O₃ or Ni-W/Al₂O₃ catalysts. This process has also some disadvantages such as the catalytic processes operated at elevated temperatures (300–400°C) and elevated pressures (20–100 atm of H₂). Moreover, HDS process is highly efficient for the removal of sulfur compounds such as thiols, sulfides and thiophenes, but less effective for removing thiophene derivatives: benzothiophene (BT), dibenzothiophene (DBT), and their alkyl derived as 4-methyldibenzothiophene (MDBT) which are abundant especially in diesel and can lead the sulfur concentration up to 400 ppmw (Schulz *et al.*, 1999; Baeza *et al.*, 2008; García-Gutiérrez *et al.*, 2008).

At present, several alternative approaches have been tested, such as selective adsorption, bio-desulfurization, oxidative desulfurization, and extraction by ionic liquid (Song, 2003; Hernández-Maldonado *et al.*, 2005a, 2005b; Bhandari *et al.*, 2006; Caero *et al.*, 2006; Al-Shahrani *et al.*, 2007). Adsorptive desulfurization is a new and highly efficient method for this purpose and also a widely used technology, due to its simplicity and adaptability to different fuel processors. In addition, it can be accomplished relatively at lower pressure and temperature even at ambient conditions (Tang *et al.*, 2008). A distinguished amount of adsorbents have been reported for the removal of sulfur compounds from the CGDFs. Many works have focused on the porous materials such as charcoal (Mikhail *et al.*, 2002), mesoporous SBA-15,

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adsorbents based on transition metal complex supported on porous materials (zeolites) (Salem, 1994; Hernández-Maldonado and Yang, 2003; Velu *et al.*, 2003; Yang *et al.*, 2003; Hernández-Maldonado *et al.*, 2005a; Ma *et al.*, 2005), or transition metals, on mixed metal oxides, on activated carbon (AC), and transition metal compound supported on a porous silica gel (Ma *et al.*, 2002). Several works have developed new adsorbents to remove the thiophenic compounds from CGDFs via π -complexation, most of them published by Yang and collaborators (Velu *et al.*, 2003; Yang *et al.*, 2003; Hernández-Maldonado *et al.*, 2005a). The π -complexation adsorption is currently the most promising alternative. Molecular orbital (MO) calculations and experiments have shown that the refractory compounds (MDBT and DMDBT) bind strongly through the π -complexation due to a better electron donation/back-donation ability. In the π -complexation mechanism the cations can form the usual σ bonds with their *s*-orbitals while their *d*-orbitals can back-donate electron density to the antibonding π -orbitals of the sulfur rings. The metals that can form strong π -complexation bonding are those that possess empty *s*-orbitals and the electron density available at the *d*-orbitals necessary for back donation. Some literatures reported that π -complexation ion-exchanged Y zeolite sorbents obtained with Cu(I), Ni(II) or Zn(II) cations using different techniques have been studied for their usefulness in desulfurization of diesel, especially the copper Cu(I) for its electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^0$ (Hernández-Maldonado *et al.*, 2005b). These sorbents desulfurization performance decreased as following: Cu(I)-Y > Ni(II)-Y > Zn(II)-X > Zn(II)-Y. Molecular orbital calculations also indicated that these sorbents performance decreased as following: Cu(I) > Ni(II) > Zn(II) (Hernández-Maldonado *et al.*, 2005b). Therefore, the main objective was to investigate the desulfurization of commercial gasoline (76 ppmw S) and diesel (49 ppmw S) by π -complexation ion-exchanged adsorbents of Cu(I)-Y zeolite in a fixed-bed adsorber. Morphologies, crystallinity, and microstructures of this Cu(I) sorbent was also identified and characterized by TPR, N_2 adsorption isotherms (BET surface area), FE-SEM/TEM, XRD, Elemental Analyzer (EA), and X-ray absorption near edge structure/extended X-ray adsorption fine structure (XANES/EXAFS) techniques.

1. Experimental

1.1 Sorbents preparation

The sorbents used in the present work were nanophase H-Y zeolite particles (Si/Al = 10; surface area = 640 m²/g; total pore volume = 0.318 cm³/g; framework density = 1.25 g/cm³). The framework structures of Y zeolites are characterized by the double 6-ring (D6R). The pore of zeolite Y that is restricted by 12-membered oxygen rings (Wang *et al.*, 1999). Zeolites Y has a three-dimensional channel structures with

pore sizes of 7.4–8.1 and therefore useful as adsorbents for relatively large molecules such as gasoline and diesel. The zeolites were modified by liquid phase ion exchange (LPIE) technique (Bhandari *et al.*, 2006) and π -complexation [Cu(I)-Y] zeolite was prepared with 0.5 M Cu(NO₃)_{2(aq)} for 48 h followed by reduction of Cu(II) to Cu(I). A typical ion exchange procedure of H-Y with Cu(NO₃)_{2(aq)} was carried out at 298 K and at pH 5 for 9–10 h. The ion exchange process was repeated two times, each time for a period of 3 h to ensure desired level of ion exchange. The amount of copper in the ion exchange solution was equivalent to a 5-fold cation exchange capacity. After the ion exchange, the H-Y zeolite sorbents were filtrated, washed with deionized water to remove the excess solution, and then dried at 373 K for over 24 h. The average copper concentration over the H-Y zeolite was around 3 wt% identified using ICP/MS method. Autoredution of Cu(II) to Cu(I) was also conducted under a flowing inert He gas at 723 K for over 18 h (Hernández-Maldonado and Yang, 2003; Hernández-Maldonado *et al.*, 2005b; Yang *et al.*, 2001, 2003). The Cu(I)/Cu(II) ratio in the activated Cu-Y zeolite sorbent was ranged of 0.5–0.7 measured by Cu K-edge XANES techniques. A quartz-tube furnace was used for activating the H-Y zeolite adsorbents under well controlled conditions. After activation, the adsorbents were cooled down to room temperature under a flowing He gas. All the adsorbents were carefully activated in order to avoid any exposure to moisture. For Cu zeolites, this step is critical since Cu(I) species are highly unstable. Since Y zeolite adsorbent is recognized to be highly hydrophilic (water uptake >20 wt% at ambient conditions), helium gas was initially passed through a 3A molecular sieve column to remove moisture before use. The unit cell composition for the dehydrated H-Y zeolite sorbents prepared using LPIE methods is Cu₂₁Na₁₄(A)₅₆Si₁₃₆O₃₈₄) (Wang *et al.*, 1999; Hernández-Maldonado *et al.*, 2005b).

1.2 Fixed-bed adsorption/breakthrough

All adsorption/breakthrough experiments were conducted in a vertical quartz adsorber equipped with a supporting glass frit. The setup consisted of a low-flow liquid pump, Kynar and Teflon compression fittings, feed tanks, and a heating jacket. About 2.0 g H-Y zeolite sorbent was loaded inside the adsorber tube with a diameter of 5 mm (I.D.) and a length of 10 cm. The sorbents were heated at 723 K and then cooled down to room temperature under a flowing He gas. A sulfur-free hydrocarbon was flowing through the sorbents for 10 min to order to wet and clean the adsorbed bed previously. Finally, the feed was switched to CGDFs at a flow rate of 0.5 mL/min. Effluent liquids were collected until the saturation point was achieved. The typical compositions of CGDFs are shown in Table 1.

1.3 Characterization methods

All the CGDFs samples collected during breakthrough experiments were analyzed using gas chromatography/flame photometric detection (GC/FPD, 6890N

with FPD, Aligent Technologies Inc.) with an EC-5 capillary column (I.D. = 0.32 mm; L = 30 m). The average concentration of Cu species in H–Y zeolite sorbents was measured by ICP/MS (Perkin-Elmer SCIEX-ELAN 6100 DRC, PerkinElmer Inc.). The concentrations of Cu ions were calculated after calibrating individual measured curve by its corresponding standard Cu solution at ten different concentrations. The surface area of the as-synthesized Cu(I)–Y zeolite was measured using BET (Brunauer–Emmett–Teller) nitrogen adsorption method (ASAP Micromeritics 2010 Instrument). A conventional temperature programmed reduction (TPR) apparatus was used for the investigation of the reducibility of the Cu catalysts. TPR measurement was conducted using a flow rate of 30 mL/min of H₂/Ar mixture (30 vol% H₂) at 1 atm. 0.5 g of catalyst samples was tested each time and a heating rate of 10 K/min was performed from 298 to 800 K. Proximate and ultimate analyses of Cu(I)–Y zeolite were performed using traditional elemental analyzer (EA, F002-heraeus CHN–O rapid) as a tool. The morphologies, crystallinity, and microstructures of Cu(I)–Y zeolite was determined by FE-SEM/EDS (S–4700 Type II, Hitachi Ltd.). In addition, catalyst samples were dispersed on a carbon film supported by a copper grid for TEM (Model Zeiss 10C) observation. Structural investigations of the as-prepared products were carried out in a transmission electron microscope working at 200 kV. With regard to the identification of the solid phases and crystallinities of Cu(I)–Y zeolite, XRD was performed (MXP18, MAC Science Co. Ltd.). The sample was therefore scanned from 20 to 60° (2θ) with a scan rate of 4° (2θ)/min and monochromatic CuK α radiation. The specific peak intensities and 2θ values recorded can be further identified by a computer database system (Joint Committee on Powder Diffraction Standards, JCPDS of International Centre for Diffraction Data statistical Process Co.).

XANES/EXAFS spectra were collected at Wiggler 17C1 beam line of Taiwan National Synchrotron Radiation Research Center (NSRRC). The electron storage ring was operated with the energy of 1.5 GeV and a current of 100–200 mA. A Si(111) double crystal monochromator (DCM) was used for providing highly monochromatized photon beams with energies of 1 to 15 keV. The double crystal monochromators employing at selected X-rays with energy resolving power ($E/\Delta E$) better than 7000, sufficient for most XAS measurements. Data were collected in fluorescence or transmission mode with a Lytle ionization detector (Lytle, 1999) in the region of the Cu (8979 eV) for K edge experiments at room temperature. The EXAFS function was derived from the raw absorption data through the pre-edge and post-edge background subtraction and then normalized with respect to the edge jump by using program package AUTOBK. After being k^2 -weighted (k -range = 2.5–12.5^{–1}), where k is the photoelectron wavenumber, the EXAFS function was Fourier transformed from k -space to r -space. Local structural pa-

Table 1 A typical composition of commercial gasoline or diesel fuel in Taiwan

Parameter	Gasoline	Diesel
Boiling range [K]	315–478	503–622
Average sulfur content [ppmw]	76	49
Aromatics [vol%]	30–31	16–17
Olefins [vol%]	1.8	5.0
<i>n</i> -Alkanes [vol%]	17.5	Nil
Available branched alkanes [vol%]	32	Nil
Cycloalkanes [vol%]	5	Nil
Saturates [vol%]	Not available	78

Table 2 Breakthrough and saturation loadings of total sulfur from gasoline or diesel fuel on Cu(I)–Y zeolite nanoparticles

Parameter	Gasoline	Diesel
Breakthrough loading [mg/g]	9	21
Saturation loading [mg/g]	23	36

rameters such as the bond distance R , coordination number N , and Debye–Waller factor σ , for different coordination shells surrounding the absorbing atoms were obtained through non-linear least-square fitting routine. All the computer programs were implemented in the software package UWXAFS 3.0 (University of Washington Office of Technology Transfer). The phase shifts and backscattering amplitudes were theoretically calculated by using FEFF 8.20 code based on the crystallographic data of individual species (Zabinsky *et al.*, 1995; Lytle, 1999).

2. Results and Discussion

After the activation of Cu(I)–Y zeolite sorbent, desulfurization of commercial gasoline (76 ppmw S) and diesel (49 ppmw S) were performed by π -complexation ion-exchange in a fixed-bed adsorber conducted at ambient temperature and pressure. The composition of commercial gasoline and diesel were analyzed shown in **Table 1** and the results showed that average sulfur content of gasoline was 76 ppmw and 49 ppmw of diesel.

Breakthrough adsorption curves of gasoline and diesel fuel on Cu(I)–Y zeolite adsorbents were generated using plotting the transient total sulfur concentration normalized by the feed total sulfur concentration versus cumulative fuel volume normalized by total adsorbent weight. The adsorption amounts (normalized per adsorbent weight) were obtained after integrating for the areas above the breakthrough curves. The total sulfur concentrations in the fixed-bed adsorber effluent were monitored periodically as a function of time. **Table 2** summarized that the Cu(I)–Y zeolite had higher thiophenic sulfur removal capacity (~36 mg/g) from diesel liquid fuels. Sim-

Fig. 1 Breakthrough of total sulfur in a fixed-bed adsorber: Cu(I)-Y zeolite nanoparticle for the commercial gasoline and diesel feed using fresh activated Cu(I)-Y zeolite nanoparticles at 298 K and 1 atm (initial total sulfur concentration: commercial gasoline (76 ppmw) and diesel (49 ppmw))

ilarly, high sulfur removal capacity (~ 23 mg/g) was also found for commercial gasoline. The adsorption amounts (normalized per adsorbent weight) were obtained after calculating the integrated equation based on the value of area above the breakthrough curves at any time t (Seader and Henley, 1998).

Figure 1 showed that the total sulfur breakthrough curve obtained during treatment of the commercial gasoline and diesel using fresh activated Cu(I)-Y zeolite nanoparticles at 298 K and 1 atm. The sulfur concentrations of effluent fuel liquids was 4 and 72 ppmw at breakthrough (145 mL) and saturation (310 mL) conditions for the commercial gasoline, respectively, while the sulfur concentrations of effluent fuel liquids was 3 and 47 ppmw at breakthrough (420 mL) and saturation (720 mL) conditions for the commercial diesel, respectively. The different sulfur compounds in these two fuels may have an effect of the sulfur capacity. However, the sulfur capacity was clearly equilibrium limited, i.e., the saturated sorbents were in equilibrium with the feed solution. The higher total sulfur content in the commercial gasoline (76 ppmw S) and diesel (49 ppmw S) resulted in higher sulfur capacities.

As shown in **Table 3**, GC/FPD results also indicated that the sorbents selectively adsorbed highly substituted thiophenes, benzothiophenes, and dibenzothiophenes from CGDFs. It represented that the major sulfur compounds existing in current CGDFs are the alkyl dibenzothiophenes with one or two methyl groups at 4- and 6-positions, which are the refractory sulfur compounds in CGDFs due to the space interference of the methyl groups in HDS process.

The FE-SEM image of Cu(I)-Y zeolite has shown in **Figure 2(a)**. It showed a pellet-like shape of Cu(I)-Y zeolite nanoparticles formed with diameters of approxi-

Table 3 GC/FPD analyses of typical sulfur compounds/relatives in the fresh commercial gasoline/diesel and the residues of fuels after desulfurization on Cu(I)-Y zeolite adsorbents

Sulfur compounds and relatives	Gasoline	Diesel
Fresh	Thiophene derivatives: BT, DBT, BT, DBT, 4,6-DMDBT; Alkyl derivatives: 4-MDBT	BT, DBT, 4,6-DMDBT, 4-MDBT
After desulfurization	Trace	Trace

mately 50–80 nm. **Figure 2(b)** also indicated that the ion-exchanged Cu(I)-Y zeolite nanoparticle was well crystalline but it aggregated in the calcination processes at high temperature (above 700 K).

The XRD patterns of Cu doped Y zeolite are shown in **Figure 3** with sulfur adsorption in different conditions. The XRD spectra showed that the crystal structure of the fresh Cu(I)-Y zeolite was changed after sulfur adsorption in gasoline and diesel as the two strong peaks at 2θ of 35.58° and 38.76° were disappeared, which indicated that the presence of CuO in the Cu-doped Y zeolite catalyst (Massarotti *et al.*, 1998). Furthermore, characteristic peaks at the region of $2\theta = 45$ to 48° remain identical for CuO. Moreover the adsorbent calcined at 523 K in air showed some strong new peaks. It might be due to higher order crystal structure formed in higher temperature. But calcined at the same temperature in hydrogen atmosphere did not show these type of peaks represented in **Figure 3(a)**.

The reduction temperature profile for Cu(II)-Y zeolite was studied using TPR technique. The experiments were performed using an inert gas containing approximately 30 vol% hydrogen and a custom-made vertical reactor fitted with a heating jacket. The temperature was increased at $10^\circ\text{C}/\text{min}$. The TPR effluent from the bed of the sample was analyzed by a gas chromatograph. The intensity measured by the thermal conductivity detector (TCD) indicated H_2 consumption. **Figure 4** shows the resulting TPR profile for Cu(II)-Y zeolite. The profile shows two major distinct peaks at 462 K and 509 K. These two peaks corresponded to two reduction steps. The first peak at 462 K indicated the reduction from Cu(II) to Cu(I), while the second peak indicated the reduction from Cu(I) to copper metal. The difference in intensities of the two peaks was likely caused by incomplete conversion of Cu(I) to copper metal. From the above result, it was determined that 462 K was the appropriate temperature for reduction to Cu(I). Stepwise reduction of Cu(II) ions in liquid-phase exchanged zeolites and dispersion on activated alumina supports have been reported before (Rouco, 1994; Guidry and Price, 1999; Takahashi

Table 4 Elemental analysis for S total content of nanopahse Cu(I)–Y zeolite adsorbents at different activated conditions for the commercial gasoline

Activated condition of adsorbent	Net S [mg/g]
Fresh adsorbent before adsorption	0
In H ₂ atmosphere and at 523 K	5.8
In air and at 523 K	16.8
In air and at 393 K	8.6

Fig. 2 Image of nanophase Cu(I)–Y zeolite adsorbent calcined under a flowing He gas at 723 K: (a) FE-SEM and (b) TEM

et al., 2000). A reduction temperature of about 462 K is sufficient to obtain the cuprous species required for π -complexation.

The results of sulfur elemental analyses of the Cu(I)–Y zeolite adsorbent at different activated conditions the commercial gasoline are shown in **Table 4**. It showed that the sulfur content of Cu(I)–Y zeolite was higher under air at 523 K. It also indicated that the sulfur content at same environment but lower temperature (393

Fig. 3 XRD patterns of Cu(I)–Y zeolite adsorbent of (a) reduced under H₂ at 523 K, (b) calcined under air at 523 K, (c) calcined under air at 393 K, and (d) the fresh catalyst before calcination used for the desulfurization of CGDFs

Fig. 4 TPR curve of Cu–Y zeolite adsorbent under a flow rate of 30 mL/min of H₂/Ar mixture and a heating rate of 10 K/min

K) was lower than that of elevated temperature. The net weights of sulfur content of catalyst were 16.8 and 8.6 at 523 and 393 K respectively at air atmosphere. It might be due to the higher crystal order formed of the Y zeolite adsorbent at elevated temperature and moreover, for the π -complexation, about 462 K (from Figure 4) was required. But, 393 K was not sufficient to convert the Cu(II) to Cu(I) state which was the main requirement for the π -complexation ion exchange. The Cu(I) ions may be oxidized in the presence of H₂O or O₂ and that the process was accelerated in the simultaneous presence of both oxidative species. This result should apply also for Cu–Y zeolite adsorbent, reinforcing the need for proper activation of the zeolites to maintain the maximum possible

Fig. 5 XANES spectra of fresh activated Cu(I)-Y zeolite, sulfur-adsorbed Cu(I)-Y zeolite adsorbent, Cu_2S , CuS , Cu_2O , and CuO standards ("ads" denotes "Cu(I)-Y zeolite adsorbent")

amount of Cu(I) ions before desulfurization processes. Furthermore, the air atmosphere was more favorable for the sulfur adsorption than hydrogen.

For Cu(II)-Y, the activation was conducted at 723 K under a flowing He gas to enhance auto-reduction of Cu(II) to Cu(I) species, which is needed for π -complexation. For sulfur removal using π -complexation to be successful, it is necessary for the copper to be in the Cu(I) state. Actually, treatment in dry air, which should yield only Cu(II) species. Takahashi *et al.* (2000) found that Cu(II)-Y zeolite adsorbents can be auto-reduced in He gas at 723 K under moisture free and O_2 free conditions. 50% of the original Cu(II) ions were reduced to Cu(I) ions after 1 h activation process. Therefore, activation time plays a crucial part in obtaining more Cu(I) species. Lower temperature activation to obtain Cu(I) ions may not result in the formation of as many Cu(I) ions either. This results indicated that there were not as many Cu(I) ions present in the 623 K He-treated adsorbent as compared to the 723 K treated adsorbent. It should be noted that, after several hours of auto-reduction, the color of Cu(I)-Y zeolite was pale green, compared to a bluish green typically observed in Cu(II)-Y.

To investigate the structure of the copper species in Y zeolite, X-ray absorption spectra of the catalyst were also performed. The XANES spectra of Cu-Y zeolite for sulfur adsorption from gasoline were represented in **Figure 5**. The preedge XANES spectrum of Cu-Y zeolite exhibits very weak absorbance feature for the $1s$ to $3d$ transition which is forbidden by the selection rule in the case of perfect octahedral symmetry. There is a shoulder at 8981–8983 eV which is due to the dipole-allowed of $1s$ to $4p_{xy}$ electron transition. It confirms that the existence of Cu(I) in the catalyst. The intensity of the $1s$ to $4p_{xy}$ transition is proportional to the amount of Cu(I) in Cu-Y

Fig. 6 Fourier transform (FT) spectra of (a) Cu(II)- and (b) reduced Cu(I)-Y zeolite adsorbent calcined under a flowing He gas at 723 K. The best fitting of the EXAFS spectra are expressed by the dotted lines

zeolite. An intense feature at 8992–8996 eV are attributed to the $1s$ to $4p_{xy}$ transition that indicates the existence of Cu(II) species in Cu-Y zeolite. From the XANES spectra, the coexistence of Cu(I) and Cu(II) in the Cu-Y zeolite was found (Lin and Wang, 1999, 2000a, 2000b).

Generally, Cu K-edge EXAFS spectroscopy can provide the information on the atomic arrangement of sorbents in terms of bond distance, bond angle, coordination number and kind of neighbors. A high reliability of the EXAFS data fitting for Cu species in Y zeolite was obtained. The data were collected several times and the standard deviation also calculated from the averaged spectra. The Fourier transformation was performed on k^2 -weighted oscillations over the range of 2.5 and 12.5 $\text{\AA}^{-1}$.

As shown in **Figure 6(a)**, a central Cu atom has a Cu(II)-S bonding of organosulfur complex with a bond distance of 1.81 ± 0.05 and a coordination number of 3.8 in Cu(II)-Y zeolite nanoparticles. It is likely that the

Table 5 Fine structural parameters of Cu(I)–Y zeolite adsorbent analyzed by EXAFS

Analyzed item	Bonding pair	CN ^a	R ^b (±0.05)	$\Delta\sigma^2(\text{\AA}^2)^c$
Copper standard				
CuO	Cu–O	2.1	1.95	0.0035
Cu ₂ O	Cu–O	2.1	1.86	0.0065
Cu in fresh Cu(I)–Y zeolite (no reduction)				
CuO	Cu–O	3.55	1.96	0.004878
Cu ₂ O	Cu–O	3.58	1.96	0.004894
Doped S in Cu(I)–Y zeolite (reduction)				
Cu	Cu–Cu	5.29	2.48	0.014726
CuS	Cu–S	1.64	2.39	0.005548
sulfur	S–S	1.47	2.27	0.006792
Cu(I)–Y zeolite with adsorbed S				
CuS	Cu–S	1.85	2.47	0.001411
Cu ₂ S	Cu–S	3.04	2.35	0.009419

Notes: ^aCoordination number; ^bBond distance; ^cDebye–Waller factor

Cu(II)–Y zeolite was formed in ion-exchanging process with 0.5 M Cu(NO₃)_{2(aq)} for 48 h. More Interestingly, using EXAFS spectra, the Cu(I)–S organosulfur species possess a Cu(I)–S bond distance of 1.98 Å with a coordination number of 1.2 shown in **Figure 6(b)**. This result may offer a further explanation of an autoreduction of Cu(II) to Cu(I) which was found under a flowing inert He gas at a higher temperature of 723 K.

The structural parameters of the copper oxide, copper sulfide clusters obtained from the best fit to the EXAFS data are shown in **Table 5**. The Debye–Waller factors ($\Delta\sigma^2$) in all EXAFS data were less than 0.015 Å. The standard Cu–O bond distances in CuO and Cu₂O were 1.95 and 1.86 Å, respectively with the coordination number of 2.1 in both cases. In the fresh Cu(I)–Y zeolite Cu–O bond distances in CuO and Cu₂O are very much similar to that of standard bond distance (1.96 Å) but with the different coordination numbers 3.55 and 3.58, respectively.

After doping sulfur on the Cu(I)–Y zeolite the Cu–Cu and Cu–S bond distances were found 2.48 and 2.39 and the coordination numbers were 5.29 and 1.64, respectively. After adsorbing sulfur from the gasoline the Cu–S bond distances in CuS and Cu₂S were 2.47 and 2.35 Å with the coordination number 1.85 and 3.04, respectively. It showed that the bond distance of Cu–S increased with adsorption of sulfur on to the copper surface and predominated that Cu–O and Cu–Cu are the main oxidation active sites in the Y zeolite channels for the adsorption of sulfur.

Conclusions

This work has demonstrated that copper-exchanged Y-type zeolites are excellent adsorbents for the removal

of thiophene from gasoline and diesel fuel, based on fixed bed adsorption. It was capable of reducing the sulfur content to lower values for long periods of time. Cu(I)–Y zeolite provided the best adsorption capacity both at breakthrough point and at saturation. Our experimental results, demonstrate that organic sulfur compounds in gasoline and diesel fuel can be removed by selective adsorption using a transition metal compound loaded on a porous support. More studies will be needed in order to fully understand the effect of copper loading and the relation between copper and sulfur include thiophenes, which are abundant in commercial liquid fuels.

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