

Desulfurization by adsorption with copper supported on zirconia

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Abstract

Copper supported on zirconia was used to separate low thiophene concentration from a mixture of 2000 ppmw of thiophene in *n*-octane at room temperature and atmospheric pressure. The results show that the capacity of copper on zirconia to adsorb thiophene increases as the copper content increases, reaching a maximum at a concentration of 3% of copper. The adsorption capacity also depends on the treatment used, and the higher capacities are observed in adsorbents treated with a flow of N₂O at 90 °C. These samples possess a notable saturation adsorption capacities of 0.49 mmol of thiophene per grams of adsorbent.

Keywords: Adsorption; Copper; Zirconia; Thiophene

1. Introduction

The removal of sulfur containing compounds present in transportation fuels is an important operation in the petroleum refinery. Industrially the elimination of sulfur is carried out through the process called hydrodesulfurization (HDS). HDS uses Co–Mo/Al₂O₃, Ni–Mo/Al₂O₃ or Ni–W/Al₂O₃ catalysts. The disadvantages of this process are: a) the catalytic processes operated at elevated temperatures (300–400 °C) and elevated pressures (20–100 atm of H₂), and b) the 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) [1,2].

The new environmental legislation will require substantial reductions in the sulfur content. In US Environmental Protection Agency sulfur standards require that the sulfur contents in gasoline and diesel fuels will be 30 and 15 ppm, respectively [3]. Deep desulfurization, or removal of

“refractory” sulfur compounds, can be achieved by using the new unsupported Mo–W–Ni HDS trimetallic catalyst known as NEBULA. It was synthesized for ExxonMobil, Akzo Nobel and Nippon Ketjen, and it is three times better than current HDS catalysts and can produce a diesel with a sulfur content of 10 ppmw [4]. However, the NEBULA catalyst requires greater hydrogen consumption. Another important issue is how the organic sulfur is adsorbed on HDS catalysts. In this case the adsorption occurs through the sulfur atom, and depending on the substituents in the organic molecule close to the S atom, there can be strong steric hindrance. Desulfurization by HDS is extremely difficult for the least reactive derivatives of DBT with methyl groups in positions adjacent to S, as MDBT and 4,6 dimethyldibenzothiophene (DMDBT) [5]. Thus, the use of adsorption to selectively remove the sulfur compounds at environmental conditions is an excellent option over HDS.

Several works have developed new adsorbents to remove the thiophenic compounds from commercial fuels via π -complexation, most of them published by Yang and collaborators [6–11], or adsorption by chemisorption at elevated temperatures [12–14]. The π -complexation adsorption is currently the most promising alternative. Molecular

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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 [6]. 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 [15], especially the copper Cu(I) electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^0$.

In this paper, we present preliminary results of new promising sulfur adsorbents of copper supported on zirconia, and the adsorption capacity of these materials to remove thiophene from a mixture of thiophene in *n*-octane (2000 ppmw) at ambient conditions. This work also demonstrates the strong dependence of the absorption capacity on the treatment to reduce the copper oxide present on the zirconia surface to Cu^{+1} species.

2. Experimental

2.1. Adsorbents preparation

The adsorbents were prepared by dry impregnation of zirconium oxide with aqueous solutions of copper nitrate (Merck p.a.) containing the required amount of salt to render Cu concentrations between 1% and 6% for the copper supported on zirconia. Zirconium oxide (specific surface area BET $36 \text{ m}^2 \text{ g}^{-1}$, average pore diameter 92 \AA) was obtained by calcination of a commercial zirconium hydroxide (FZO922 MEI Chemical Corporation, USA) at $700 \text{ }^\circ\text{C}$ during 3 h, composed for a mixture of 17% of tetragonal zirconia and 83% of monoclinic zirconia [16]. After impregnation of supports, the adsorbents were dried at $105 \text{ }^\circ\text{C}$ for 12 h, and then calcined at $500 \text{ }^\circ\text{C}$ for 3 h in a muffle furnace.

2.2. Adsorption experiments

Adsorption experiments were performed in a vertical Pyrex adsorber reactor equipped with a supporting glass porous disk. A bed of 500 mg of adsorbent was placed in the reactor and oxidized in situ at $300 \text{ }^\circ\text{C}$ during 1 h under a 20 mL min^{-1} flow of pure O_2 . After oxidation, the reactor was cooled down to room temperature and purged with pure He during 30 min. Then, two treatments were used to generate the Cu^{+1} species which, as will be shown below, is the active species for the adsorption of the sulfur compounds. The first treatment method (method A) consists in reducing the oxidized sample by treating at $180 \text{ }^\circ\text{C}$ for 1 h under a 20 mL min^{-1} flow of a mixture of 5% H_2/He , and then cooling down to room temperature. The second treatment method (method B) consists in reducing completely the oxidized sample (calcined at $300 \text{ }^\circ\text{C}$ for 1 h), treating it at $300 \text{ }^\circ\text{C}$ for 1 h under a 20 mL min^{-1} flow of a 5% H_2/He mixture, cooling down to $90 \text{ }^\circ\text{C}$, partially reox-

idizing with a 20 mL min^{-1} flow of pure N_2O for 30 min, and cooling down to room temperature.

For the adsorption experiments, the liquid flow was driven into the reactor by means of a peristaltic variable flow mini-pump. The experiment was performed using a mixture of 2000 ppmw of thiophene in *n*-octane (C_8H_{18}) at a feed rate of 0.5 mL min^{-1} . Samples were collected at regular time intervals until saturation was achieved, which depended on the amount of adsorbent. In the case of the adsorbent with the larger capacity for adsorption of thiophene, *n*-octane was replaced by toluene to compare the competitive adsorption between the sulfur compounds and the aromatic compound.

The samples were analyzed by gas chromatography using a Perkin-Elmer Autosystem XL equipped with an HP-5 capillary column (L 30 m, I.D. 0.53 mm, Film $0.88 \mu\text{m}$) and the following conditions: detector at $300 \text{ }^\circ\text{C}$, injector at $275 \text{ }^\circ\text{C}$, and carrier flow, 15 mL min^{-1} (He). The column temperature was set to increase from $40 \text{ }^\circ\text{C}$ to $200 \text{ }^\circ\text{C}$ at $15 \text{ }^\circ\text{C min}^{-1}$ rate. $0.5 \mu\text{L}$ of the sample volume was injected for each GC-FID run. The sensibility (limit detection) is 2 ppm.

2.3. Adsorbents characterization

The adsorbents samples were studied by temperature programmed reduction (TPR) experiments in a 5% H_2/Ar stream, with the purpose to determinate the different copper species over zirconia surface. In these experiments, 0.2 g of catalyst were loaded in a quartz reactor and oxidized in situ in a $20 \text{ cm}^3 \text{ min}^{-1}$ stream of pure O_2 at $300 \text{ }^\circ\text{C}$ for 1 h. The temperature was then reduced to room temperature, the reactor purged during 30 min with pure He, the reducing mixture is introduced at $20 \text{ cm}^3/\text{min}$, and heating started using a $10 \text{ }^\circ\text{C}/\text{min}$ temperature ramp. The H_2 consumption was determined using a thermal conductivity cell.

The fraction of zirconia surface covered by copper in different Cu/ZrO₂ adsorbents was estimated using the electrophoretic migration technique in a Zeta Meter Inc. equipment, model 3.0, provided with an automatic sample transfer unit. In each measurement 30 mg of sample were suspended in 300 mL of solution 10^{-3} M of KCl, adjusting the pH with solutions of KOH or HCl 0.1 M, as required, obtaining the isoelectric point of copper oxide and zirconium oxide, and the corresponding point of zero charge of each adsorbent [17,18]. The sample is used directly after calcination in a muffle furnace at $500 \text{ }^\circ\text{C}$ for 3 h, without any further treatment, so the sample is expected to be in an oxidized state.

3. Results and discussion

3.1. Adsorbents characterization

Fig. 1 shows the TPR curves obtained for Cu/ZrO₂ adsorbents with different copper contents. For the 1%

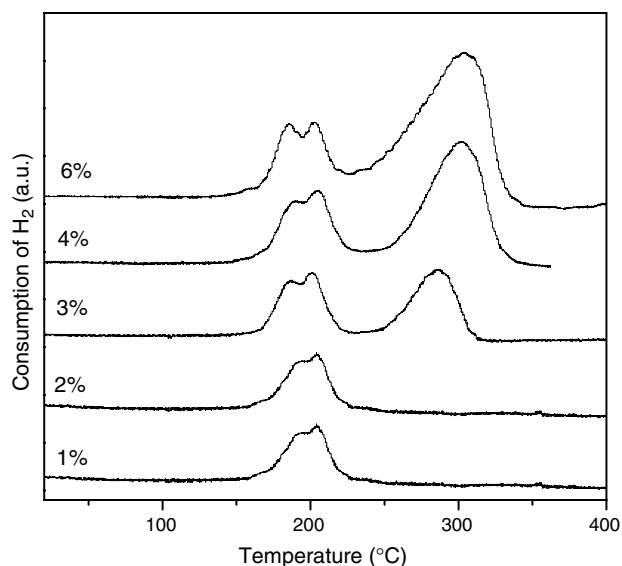


Fig. 1. TPR results of adsorbents with different Cu loading supported on ZrO_2 . The metal content is indicated in the figure.

Cu/ZrO_2 adsorbent, two overlapped peaks are clearly seen, with apparent maxima at 180 °C and 200 °C. A result very similar has been reported by Liu et al. [19] for the reduction of CuO supported on tetragonal zirconia. They pointed out that these peaks correspond to the reduction of highly dispersed Cu^{2+} species. These species would be first reduced to Cu^{1+} and then to Cu^0 , giving rise to two different peaks observed in the TPR curves. Zhou et al. [20] also reported the presence of two reduction peaks at relatively low temperatures, one centered around 177 °C (alpha peak) and a second one around 195 °C (beta peak), for CuO catalysts supported on zirconia. Both peaks were attributed by those authors to the reduction of highly dispersed copper species. For the adsorbent with 3% Cu, the TPR spectrum shows the appearance of a third reduction peak at about 270 °C, while the low temperature peaks show only a slight increase of their area with no shift of the reduction temperature. This third peak has been assigned to the reduction of bulk CuO species [20,21]. Increasing the Cu loading to 6% shows that the high temperature peak associated with bulk CuO , keeps growing and displaces its maximum to higher temperatures, which indicates an increasing presence of bulk CuO . The low temperature peaks, however, do not grow with the Cu concentration, as it has been previously reported [20].

The results of the isoelectric point measurements of the support and the copper oxide used for estimating the fraction of ZrO_2 surface covered by copper oxide are shown in Table 1. Additionally, the PZC (potential of zero charge) values of the adsorbent and the fraction of support surface area covered by copper oxide, estimated from the adsorbent PZC, are included. It can be seen that the values of the fraction of surface covered increase with the metallic content until reaching a maximum at a copper loading of 3% w/w. At higher metallic contents the surface coverage

Table 1

Results of zeta potential measurements: isoelectric point (IEP), potential of zero charge (PZC) and fraction of covered surface (X_M) for the different Cu/ZrO_2 adsorbents prepared

Sample	Cu loading (% w/w)	IEP	PZC	X_M
ZrO_2 Support	–	3.92	–	0.00
1% Cu/ZrO_2	1.0	–	4.32	0.07
2% Cu/ZrO_2	2.0	–	5.32	0.23
3% Cu/ZrO_2	3.0	–	6.94	0.49
4% Cu/ZrO_2	4.0	–	7.09	0.52
6% Cu/ZrO_2	6.0	–	7.21	0.54
CuO	–	10.07	–	–

does not increase, indicating that maximum copper dispersion over zirconia is reached at loadings close to 3% Cu, and above this amount, tridimensional copper species start forming.

3.2. Adsorption tests

In the adsorption tests, the mixture of thiophene in *n*-octane was passed through a Cu/ZrO_2 bed (size 500–850 μm) diluted in SiC 1:1 v/v placed in a vertical Pyrex reactor. The outlet concentration was monitored by GC as a function of time in order to determine the cumulative effluent per gram of adsorbent. Initial adsorption experiments using Cu/ZrO_2 samples pretreated with only a pure O_2 flow of 20 $mLmin^{-1}$ at 300 °C for 1 h gave a completely oxidized adsorbent, and treated with a 5% H_2/He flow of 20 $mLmin^{-1}$ at 300 °C for 1 h, gave a completely reduced adsorbent, showing that under these conditions there was no thiophene adsorption. This agrees with literature results for copper supported on zeolite [6,7], which indicate that Cu^0 and Cu^{2+} species do not adsorb thiophene, and the active species in the adsorption is Cu^{1+} . In order to generate the Cu^{1+} species two treatment were used, as described in the experimental part. Fig. 2 shows the adsorption curves for Cu/ZrO_2 samples with different copper content, pretreated at 300 °C with O_2 as described previously, and reduced partially with a 5% H_2/He mixture at 180 °C (method A). The objective of this treatment was to increase the amount of Cu^{1+} species in the adsorbent, assuming that the lower temperature peak of the TPR curves (near 180 °C) for highly dispersed Cu species corresponds to the $Cu^{2+} \rightarrow Cu^{1+}$ step (see Fig. 1). The fraction of thiophene adsorbed by the Cu/ZrO_2 samples is expressed as $1-(S_t/S_i)$, where S_t and S_i are the thiophene concentrations in the outlet and in the mixture samples, respectively. It is seen that adsorption clearly depends on the copper content, and the adsorption capacity increases as copper content increases, with maximum adsorption capacity at Cu loads around 3%, while at higher Cu content the capacity does not increase significantly. The maximum sulfur adsorption obtained at copper loads close to 3% can be related to the maximum Cu dispersion on the zirconia surface (representing a ZrO_2 surface coverage of around 50%) estimated by zeta potential measurements.

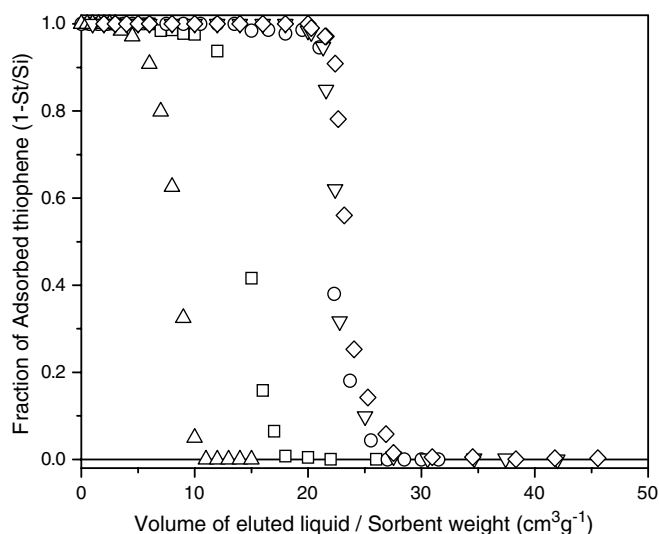


Fig. 2. Adsorption of thiophene in bed of Cu/zirconia with different copper contents reduced with H_2 at $180\text{ }^\circ\text{C}$, a liquid feed containing 2000 ppmw (S_i) of thiophene in n -octane. (Δ) 1%, (\square) 2%, (\circ) 3%, (∇) 4% and (\diamond) 6% of copper.

Fig. 3 shows the adsorption curves for Cu/ZrO₂ samples reduced with a 5% H₂/He mixture at 300 °C, followed by oxidation with pure N₂O at 90 °C (method B). It has been suggested that treatment with N₂O would produce a larger amount of Cu¹⁺ species on the support surface [22]. Similarly to the results observed in the previous case, the adsorption capacity depends on the copper content and reaches a maximum close to 3% Cu. In addition, it can be observed that after treatment with N₂O, the samples present higher adsorption capacities. By integrating the area under the adsorption curves the saturation adsorption capacities can be estimated. When the 3% Cu/ZrO₂ adsorbent is treated with N₂O this capacity is 0.49 mmol of thiophene per grams of adsorbent, higher than the saturation

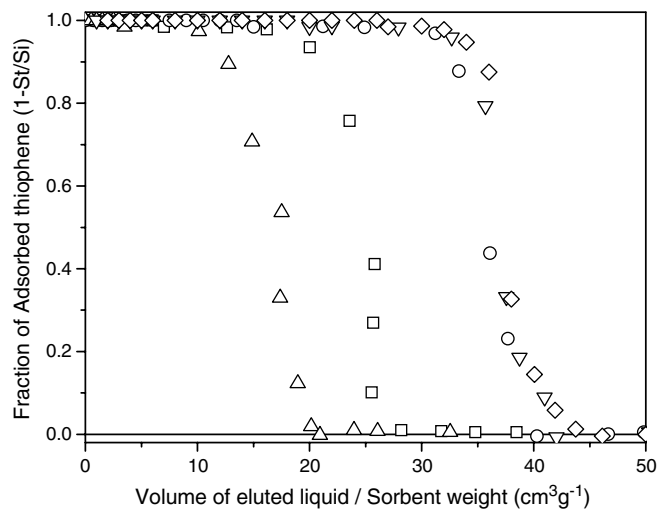


Fig. 3. Adsorption of thiophene in bed of Cu/zirconia with different copper contents reduced with H_2 at $300\text{ }^\circ\text{C}$ and then oxidized with N_2O at $90\text{ }^\circ\text{C}$, a liquid feed containing 2000 ppmw (S_i) of thiophene in n -octane. (Δ) 1%, (\square) 2%, (\circ) 3%, (∇) 4% and (\diamond) 6% of copper.

adsorption capacity calculated for the samples only reduced with H_2 at $180\text{ }^\circ\text{C}$ (0.30 mmol per grams). A summary of the saturation adsorption capacities for the different Cu/ZrO₂ adsorbents prepared is shown in Table 2. When the reaction was carried out with a mixture of 2000 ppm of thiophene in toluene, the adsorption capacity decreased to 0.18 mmol of thiophene per gram of 3% Cu/ZrO₂ adsorbent. A similar decrease in adsorption capacity was found by Hernández-Maldonado et al. in the case of copper supported on zeolite [6].

Hernández-Maldonado et al. [8] have informed the regeneration of Cu(I)-Y zeolites sulfur adsorbents with different methods, suggesting the best method to be flowing air at high temperature to remove the sulfur atoms as a gas effluent (SO₂). In this work the adsorbents regeneration was carried out using pure O₂ at 300 °C for 1 h. The results of adsorption tests after regeneration are showed in Fig. 4. A decrease of the adsorption capacity is evident for the 3%

Table 2
Saturation adsorption capacities of thiophene estimated for the different Cu/ZrO₂ adsorbents prepared

Sample	Cu loading (% w/w)	Adsorption capacity (mmol Thiophene (g of Adsorbent) ⁻¹)
<i>Reduced with H₂ at 180 °C</i>		
1% Cu/ZrO ₂	1.0	0.11
2% Cu/ZrO ₂	2.0	0.19
3% Cu/ZrO ₂	3.0	0.30
4% Cu/ZrO ₂	4.0	0.30
6% Cu/ZrO ₂	6.0	0.30
<i>Reduced with H₂ at 300 °C, and then oxidized with N₂O at 90 °C</i>		
1% Cu/ZrO ₂	1.0	0.22
2% Cu/ZrO ₂	2.0	0.32
3% Cu/ZrO ₂	3.0	0.49
4% Cu/ZrO ₂	4.0	0.49
6% Cu/ZrO ₂	6.0	0.49

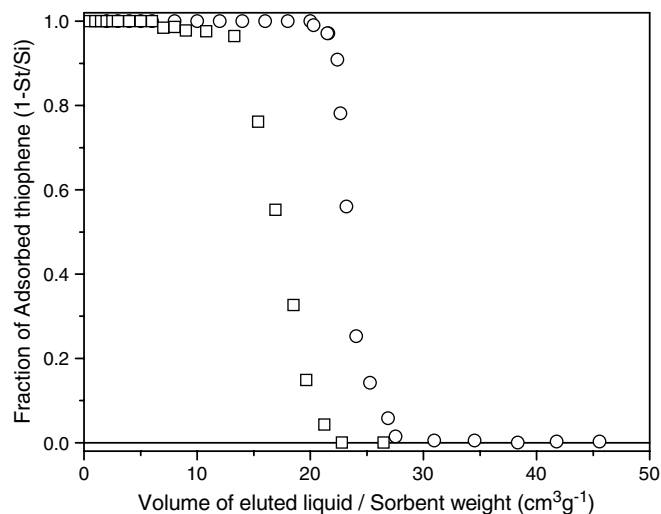


Fig. 4. Adsorption of thiophene in bed of 3% Cu/ZrO₂ sample reduced with H_2 at $180\text{ }^\circ\text{C}$ (\circ), and second cycle regenerated with O_2 (\square). Liquid feed containing 2000 ppmw (S_i) of thiophene in n -octane.

Cu/ZrO₂ sample after regenerated with a flow of O₂. The saturation adsorption capacity decreases from 0.30 to 0.26 mmol of thiophene per grams of fresh and regenerated adsorbents, respectively.

The results previously shown demonstrate that this samples of Cu supported on zirconia are prominent adsorbents in the desulfurization of sulfur organic compounds, with possible applications in the deep desulfurization of petroleum.

4. Conclusions

The preliminary results presented in this work indicate that samples of Cu supported on zirconia posses a significant adsorption capacity of sulfur-containing compounds, even though the amount of copper of the analyzed samples is relatively low. Further work is underway to verify if these materials could be used as sulfur adsorbent, in particular to study their adsorption capacity of molecules larger than thiophene, as DBT derived molecules, considering that zirconia has larger pore size compared with zeolite. These new adsorbents constitute a new generation of copper based materials oriented to carry out the deep desulfurization, based on π -complexation adsorbents, in later stages of the catalytic hydrodesulfurization.

Acknowledgments

This work has been financed under FONDAP Project 11980002. Donation of hydrous zirconia by Magnesium Elektron Inc. MEI (USA) is gratefully acknowledged.

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