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The chemistry of copper-containing sulfur adsorbents in the presence of mercaptans

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Abstract

A brief review of the chemistry of copper and thiols is given and a contrast is made to the behavior of copper-containing adsorbents used for the desulfurization of liquid hydrocarbon streams that are routinely treated in refinery processes. A study was made of the chemistry between copper adsorbents and model liquid feed streams containing mercaptans. It was found that sulfur capacity can be quite high, greater than 8% by weight, and is dependent on the dispersion of the copper oxide on the adsorbent. In addition, it is shown that bulk copper is involved in the adsorption of mercaptans, as there is significantly more sulfur than there is copper on the surface. At a temperature of approximately 150 °C, very well formed lamellar crystals of copper(I) thiolate are formed, which indicates that the copper migrates from the surface of the catalyst to expose bulk copper for further reaction. When the temperature is raised to 190 °C, there is evidence that the copper(I) butanethiolate decomposes to copper(I) sulfide. Reaction mechanisms are proposed for the process of desulfurization of liquid hydrocarbon streams containing mercaptans when using a copper-containing adsorbent.

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1. Introduction

In refineries, straight run gasoline and naphtha feed streams are hydrotreated before going to the catalytic reformers and isomerization units. Often times, the hydrotreater sufficiently reduces the sulfur in the streams to acceptable levels of approximately 0.5 ppm_w sulfur, which is typically composed of more mercaptans than thiophenic sulfur compounds. Depending on the type of reformer (conventional, semi-regenerable, or continuous) or isomerization unit, often less than 0.1 ppm_w sulfur is required. To achieve these lower levels of sulfur, a guard bed is utilized after the hydrotreater. Ni-based adsorbents are quite effective at elevated temperatures at removing sulfur species from liquid hydrocarbon streams, especially when refractory sulfur compounds are present. Still, situations do occur when lighter and more reactive sulfur compounds are prevalent, such as H₂S and mercaptans, where Cu-based adsorbents are acceptable. Copper oxide adsorbents are normally quite unreactive with thiophenic sulfur compounds, while in contrast, they readily react with and adsorb mercaptans (also known as thiols), see for example the recent work by King et. al. in Ref. [1]. It is well known that Cubased adsorbents are less efficient than Ni-based, and often sulfur is observed to leak from this type of guard bed.

The purpose of this study is to provide a description of the reaction mechanism between CuO and thiols, with a proposed explanation for the sulfur leakage through this type of adsorbent bed. It is desirable to understand the chemistry involved between copper oxide and thiols, especially as copper oxide has such unique performance characteristics in a guard bed. In contrast, one may consider sulfur compounds simply chemisorbing onto the surface of reduced nickel particles, albeit in an irreversible manner under the restraints of existing reactors, and that a typical bed of adsorbent will have been spent when an adsorption front of sulfur has passed through to the end of the bed. On the other hand, thiols act in a very different manner with copper oxide, where an irreversible redox reaction takes place, converting the thiol and Cu^{2+} into copper(I) thiolate, which has been reported to be a two-step process [2]:

Step(1): $2RSH + 2CuO \rightarrow RSSR + Cu_2O + H_2O$

Step(2): $2RSH + Cu_2O \rightarrow 2RSCu + H_2O$

where in the first step, reduction/oxidation occurs between the thiol and CuO to form a disulfide and copper(I) oxide.

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The reaction continues as the thiol reacts with the surface copper(I) oxide to form copper(I) thiolate. Similar chemistry occurs between the surface of copper metal and thiol, according to the following reaction, where in this case, the copper metal serves as a reducing agent to liberate H₂:

$$2RSH + 2Cu \rightarrow 2RSCu + H_2$$

It is well known that thiols will self-assemble into strictly arranged monolayers (commonly known as SAMs) onto the surface of the coinage metals, especially gold, silver, and copper [2]. These SAMs are intensely researched and are of great interest due to the unique properties of the resulting surfaces, including stabilization and passivation to electrochemistry and other reactions. While much of the study of copper/thiol chemistry has been restricted to the formation and properties of SAMs, it has been shown that multilayers can form into independent lamellar structures (Fig. 1) [3–5]. It was discovered in this study that under the right conditions, these types of layered compounds can be formed in a sulfur guard bed at elevated temperature and pressure, and in the presence of a hydrocarbon solvent.

The redox chemistry of Cu^{2+} and mercaptans has long been known, and actually a process to sweeten gasoline has been used since the early 20th century based upon this chemistry [6]. In the so-called "Perco" process, copper(II) chloride is placed in an air percolating bed with gasoline, and the foul smelling mercaptans are converted to the less offensive disulfides. In this case, the Cu^{2+} is not consumed in the process because the oxygen from the air percolation reoxidizes the partially reduced Cu^+ back to Cu^{2+} , according to the following reaction scheme.



Fig. 1. Simple representations of (A) self-assembled monolayer (SAM) of butanethiol on the surface of copper metal, and (B) self-assembled multilayers of copper(I) butanethiolate.

Table 1						
Characterization	of SC	copper	products	tested	for Cu	S-trap

Perco sweetening process:

 $\begin{aligned} \text{Step}(1): \quad 2\text{HSR} + 2\text{Cu}^{2+} &\rightarrow \text{RSSR} + 2\text{Cu}^{+} + 2\text{H}^{+} \\ \text{Step}(2): \quad 2\text{Cu}^{+} + \frac{1}{2}\text{O}_{2} + 2\text{H}^{+} &\rightarrow 2\text{Cu}^{+} + \text{H}_{2}\text{O} \\ \text{net reaction}: 2\text{HSR} + \frac{1}{2}\text{O}_{2} &\rightarrow \text{RSSR} + \text{H}_{2}\text{O} \end{aligned}$

Notice that in the Perco sweetening process, the copper is never allowed to form the stable $\operatorname{copper}(I)$ thiolate compound.

Finally, the routine synthesis of copper(I) thiolate, such as that made from butanethiol, is done with mixed aqueous and organic phases, where the aqueous phase contains a Cu^{2+} salt and the organic phase contains the thiol. These procedures vary and are reported in reference literature [4], but the general procedure only illustrates the common way of synthesizing copper(I) thiolate crystals. What is shown with the present work is that these layered materials may also be formed at conditions similar to those used in sulfur trap beds in refineries.

2. Experimental

Copper-containing materials used in this study were prepared by the Süd-Chemie group by conventional methods of impregnation (sample A) or co-precipitation (samples B and C). Sample A was simply prepared by first forming high surface area alumina into carrier extrusions followed by calcination at temperatures as high as 730 °C until an approximate surface area of $200 \text{ m}^2/\text{g}$ was reached. The calcined extrusions were then impregnated with copper nitrate solution of 15% by weight copper. The impregnated extrusions were then recalcined to drive off nitrate and moisture. Sample B was prepared by coprecipitation of a copper nitrate and zinc nitrate solution at a Cu/Zn molar ratio of two by mixing with a solution of sodium carbonate. The resulting precipitate was filtered and washed free of nitrate with deionized water, after which it was dried and calcined to drive off carbonate. Alumina was then mixed with the calcined precipitate as a binder, and the mixture was formed into extrudates. The preparation of Sample C is described by the patent in Ref. [7]. The important aspect of this type of preparation is to control the precipitation of Cu. Zn. and Al to form a hydrotalcite-like phase. As pointed out in the patent, a precursor of this type can result in a significantly higher Cu specific surface area. For the purpose of this study, these materials are considered representative of Cu-based adsorbents that are used in refinery processes. Characterization of the fresh materials (shown in Table 1) includes metals analysis, Cu surface area, BET surface area, and mercury pore volume. Copper surface area was measured by first reduction in H₂, and

		-				
Adsorbent ID	Туре	Cu (wt.%)	Cu/Zn ratio	Cu surface area (m ² /g)	BET surface area (m ² /g)	Mercury pore volume (cm ³ /g)
A	CuO/Al ₂ O ₃	20	_	2.0	178.4	0.626
В	CuO/ZnO/Al ₂ O ₃	41.0	1.99	5.6	61.0	0.216
С	CuO/ZnO/Al ₂ O ₃	38.5	1.89	19	95.5	0.302

Table 2 Desulfurization test conditions

	Test 1	Test 2
Temperature	150 °C	190 °C
Pressure	10 bar	10 bar
LHSV	5	4
Feed	Naphtha	Naphtha
Sulfur	200 ppm_{w} butanethiol	50 ppm _w hexanethiol

then decomposition of nitrous oxide, which was pulsed over the copper surface to produce stoichiometric amounts of N_2 gas [8].

Two accelerated performance tests were conducted in a dual fixed bed unit with the conditions listed in Table 2. The adsorbent material was granulated and sized to roughly 16×20 mesh, and loaded into the reactor in four relatively equal sized beds. These beds where analyzed separately to determine the degree of sulfur distribution throughout the whole bed. The reactors were configured for down-flow of the liquid feed stream.

Sulfur analysis of liquid hydrocarbons was performed on an Antek 7000 and of solid samples on a LECO SC444. As well as sulfur analysis on liquid and solid samples, powder XRD and FE-SEM analysis was performed on fresh and spent materials.

3. Results and discussion

In sulfur adsorption performance Test 1, for the three copper-containing adsorbents, the adsorption profiles were very unique, as can be seen in Fig. 2. After the initial breakthrough, the sulfur reached an equilibrium level in the exit stream of approximately 80% of the inlet concentration, where it was stable for the majority of the run. This type of breakthrough curve is indicative of a more complex mechanism of adsorption than just simple molecular chemisorption onto the surface of the material. Furthermore, it was found that the total amount of sulfur adsorbed on these materials increased with the total copper specific surface area (Table 3). Therefore, it is clear that



Fig. 2. Sulfur breakthrough curves for adsorbents: (\blacktriangle) Sample A, CuO/Al₂O₃; (\blacksquare) Sample B, CuO/ZnO/Al₂O₃; (\bigcirc) Sample C, CuO/ZnO/Al₂O₃. Test conditions: *T* = 150 °C, *P* = 10 bar, 5.0 LHSV. Feed composition: 200 ppm_w butanethiol in naphtha.

Table 3	
Performance summary of conner adsorben	ts in Test 1

			11			
Adsorbent D	Sulfur	(wt.%)	Atomic ratio ^a			
	Bed 1	Bed 2	Bed 3	Bed 4	Whole bed	(S _{adsorbed} /Cu _{surface})
4	5.3	2.4	1.4	1.2	4.8	38
3	14.8	4.7	3.6	2.9	6.4	29
2	12.4	13.2	7.8	5.3	9.6	6

^a Atomic ratio is calculated for the top bed 1 portion only.

copper surface area plays a role in the effectiveness of an adsorbent.

Along with the unique adsorption profiles, the spent material removed from the test reactor had changed in appearance, showing signs of crystal formation. An investigation of the material by FE-SEM revealed long flat rod-like or sheet-like crystals were formed during the adsorption process (Fig. 3). A closer inspection of the sheet-like crystals revealed that these sheets were made up of conjoined flat rods or plank-like crystals. The dimensions of the plank-like crystals are estimated to be approximately: depth 1–3 μ m, width 10–50 μ m, and length 1000 μ m. The sheet-like crystals could be as wide as 1000 μ m, with similar depths and widths. Furthermore, the crystals were found to be completely segregated from the adsorbent particles, and as seen in the figure, they might actually have grown in contact and between particles.

Analysis of the spent adsorbent material by powder X-ray diffraction revealed very strong reflections with preferred orientation of copper(I) butanethiolate crystals (Fig. 4). The strongest intensity was measured for the top most bed, with intensities as high as 35,000 cps, indicating relatively large crystal formation. Similar diffraction patterns are shown for other thiolate crystals in reference [4], but with what seems to be much lower intensities, confirming the redox chemistry between Cu²⁺ and the butanethiol in the naphtha feed stream. By using Bragg's law of diffraction and the peak positions for the crystals, the interlayer spacing for the layered copper(I) butanethiolate crystals was found to be 15.3 Å, which is in close agreement with reference literature value of 15.875 Å [4].

The sulfur distribution throughout the entire bed revealed that in most cases, the majority of the sulfur was adsorbed in the top most portion of the bed (Table 3). Again, this is also confirmed in the diffraction patterns of each of the separate beds, where the only observable species in the top bed was the copper(I) butanethiol with much less or none found in the subsequent beds. Also, the rest of the beds showed the typical reflections of CuO and ZnO from the fresh material. Furthermore, it was found that the amount of sulfur that was adsorbed onto the material was far above the amount of copper that was determined to be on the surface. This is not surprising when considering how the copper(I) butanethiolate crystals are formed apart from the adsorbent molecules as seen in the SEM micrographs. Therefore, the conclusion is that the bulk copper is also utilized in this process, though as already shown, the dispersion of the copper particles enhances the total capacity for sulfur adsorption. It should be expected that since the copper is effectively leached from the adsorbent particles to crystallize



Fig. 3. Scanning electron micrographs produced from secondary electrons of copper(I) butanethiolate crystals formed in performance Test 1. (A) Thin sheet made of conjoined narrower planks. (B) Bundle of thin rods or planks. (C) Bundle of thin rods or planks viewed end on. (D) Small crystals of copper(I) butanethiolate that have grown between and among adsorbent particles.



Fig. 4. Representative XRD patterns for spent adsorbent materials, in this case for Sample B, CuO/ZnO/alumina, where very large reflections for the lamellar crystalline compound copper(I) butanethiolate is seen at the top of the bed (flow of the feed is top to bottom) (XRD patterns are offset for clarity.)

elsewhere in the bed, an increase in pressure drop may occur, though this was not noticeable in any of these tests.

In light of the above observations and comparing this data with the chemical mechanisms that were reviewed in the introduction, Fig. 5 is provided as an illustration of a proposed primary mechanism for adsorption of mercaptans onto copper-



Fig. 5. Proposed reaction mechanism occurring at 150 $^{\circ}$ C and 10 bar between copper(II) oxide and butanethiol to form crystals of copper(I) butanethiolate. (1) Reduction/oxidation to form a disulfide and Cu₂O. (2) Displacement to form a self-assembled monolayer of butanethiol on the surface of the CuO. (3) Dissolution of the copper(I) butanethiolate to expose fresh surface of the material. (4) Crystallization of self-assembled multilayers of copper(I) butanethiolate.

containing adsorbents at these conditions. First, the well-known redox chemistry occurs between the CuO and mercaptan, resulting in a disulfide and a Cu₂O site on the surface. This is followed by a displacement reaction of the Cu₂O with the mercaptan, in this case, forming copper(I) butanethiolate on the surface. It should be noted that at this point, effectively a SAM has been formed on the surface. Indeed, SAM formation on the surface of CuO has been reported to occur [2,9]. Since copper(I) butanethiolate crystals were formed separate from the adsorbent materials, it is necessary for the surface species to dissolve into the feed liquid stream and migrate to crystallize at another site. This mechanism is therefore quite effective in uncovering bulk CuO in the material, making it available to participate in the adsorption of the mercaptan. Possibly the complete conversion of the mercaptan to disulfides and the differences in adsorptivities between the mercaptan and disulfides might explain the constant 80% breakthrough of sulfur for the more effective adsorbents CuO/ZnO/alumina. This was somewhat confirmed when an analysis of the exit streams revealed that all of the mercaptan had disappeared, and the sulfur that did breakthrough appeared to be a disulfide.

As a possible secondary reaction mechanism, the disproportionation of Cu_2O to CuO and Cu^0 may occur, as reported in a number of references, for example see [10,11]. It was reported that this occurs at elevated temperatures in the presence of water. According to the above mechanism, the amount of water created in the process would be stoichiometric to the amount of thiol adsorbed or converted, that is, one molecule of water is produced for every two thiol molecules that react. If this occurs, then as pointed out in the introduction, Cu^0 may also react further with the thiol to form copper(I) thiolate, which can then continue in the primary mechanism outlined above.

As a further effect on the mechanism, competing adsorption reactions with aromatic compounds and with nitrogen and



Fig. 6. Sulfur breakthrough curves for adsorbents: (\bigcirc) Sample A, CuO/Al₂O₃; (\blacksquare) Sample B, CuO/ZnO/Al₂O₃. Test conditions: T = 190 °C, P = 10 bar, 4.0 LHSV. Feed composition: 50 ppm_w hexanethiol in naphtha.

sulfur heterocyclic compounds should be considered. It has already been noted that thiophenic compounds are relatively unreactive with CuO as compared to thiols. Recently, it has been shown that aromatics and heterocyclics can form moderately strong bonds with Cu(I) through π -complexation at lower temperatures [11,12]. Therefore, it is possible that the presence of these types of molecules may impede or prevent the mechanism to proceed, especially once Cu₂O is formed. Still, it is expected for the temperatures at which these current tests were performed, the effect from these types of interactions should be small, especially when compared to the apparent ease of reaction between copper and thiol.

Somewhat different results are obtained when using the conditions for sulfur adsorption performance Test 2. Fig. 6 shows the breakthrough curves for samples A and B. It was also found that a steady state was reached where approximately 30%



Fig. 7. XRD patterns for spent adsorbent materials: (A) Sample A–CuO/alumina; (B) Sample B–CuO/ZnO/alumina. Notice the lack of copper(I) hexanethiol, but instead, crystalline forms of Cu_2S are present at the top portions of the bed. Also, all of the CuO has disappeared, as it has been converted to Cu_2O by the mercaptan.

 Table 4

 Performance summary of copper adsorbents in Test 2

Adsorbent ID	Sulfur	(wt.%)	Atomic ratio ^a			
	Bed 1	Bed 2	Bed 3	Bed 4	Whole bed	(Sadsorbed/Cu _{surface})
A	5.2	5.0	3.0	0.7	3.5	31
В	12.3	3.5	0.3	0.1	4.2	24

^a Atomic ratio is calculated for the top bed 1 portion only.

of the sulfur leaked from the bed, though this is much lower than the leakage at the conditions for Test 1. It is well known that Cu²⁺ can easily react with alkanethiols with longer alkyl chains, and so it is not likely that the mercaptan has made an effect on this observation [4,5]. Instead, it is proposed that an increase of the temperature has changed the adsorptivity as well as altered the chemical mechanism. This is confirmed when observing the XRD patterns for the spent materials (Fig. 7). First, it is found that there is no longer any copper(I) thiolate crystals in the spent material, but at the top of the bed, crystalline forms of Cu2S are found. Another difference between the two conditions is that all of the CuO was converted to Cu₂O throughout the bed. When comparing the amount of sulfur adsorbed with the amount of surface copper, once again, there is significantly more sulfur adsorbed on the top of the bed than surface copper (Table 4).

It is proposed that the reaction mechanism that occurs at the conditions for Test 2, namely at the higher temperature, is similar to that already discussed. Since there was no more CuO in the spent material, but Cu₂O, the redox chemistry between CuO and the mercaptan must be more favored at the higher temperature. Also, since Cu₂S was present in the top portions of the bed instead of copper(I) thiolate, it is proposed that the copper(I) thiolate is not stable at the higher temperature, but decomposes to Cu₂S and a sulfide, according to the following reaction mechanism:

$$2RSCu \xrightarrow{neat} Cu_2S + RSR$$

Since it is observed in Test 1 that separate copper(I) butanethiolate crystals are well formed in and among adsorbent particles in the fixed bed, the conclusion is that there is a certain, but low, solubility of the copper(I) thiolate in the naphtha stream. There was some concern that copper might leach from the adsorbent bed into the exit stream. Therefore, the exit stream was periodically sampled and monitored for the presence of copper by AES-ICP, and found that trace levels did indeed exit the bed. Furthermore, once the bed reached a certain level of sulfur adsorption then significantly more copper was seen exiting the bed (Fig. 8). Still, it was observed that at any time during the test, only 0–5 ppm Cu was in the exit stream. Therefore, it is concluded that copper can leach from a sulfur adsorbent bed, but at only extreme conditions of adsorption and close to the end of the life of the bed.

Regarding the type of materials tested, it cannot be concluded that the ZnO present in the samples B and C contributed directly to the adsorption of mercaptans, or in the reaction mechanism between CuO and mercaptan. If there is



Fig. 8. Copper leakage is compared to the sulfur pickup in samples: (\blacksquare) Sample B, CuO/Al₂O₃/alumina; (\bullet) Sample C, CuO/ZnO/Al₂O₃. Note that at the same level of sulfur pickup, copper leakage is relatively low indicated by the two thin arrows.

any influence, it would only be indirectly, as the presence of Zn has long been known to stabilize the copper phase and increase its dispersion [13]. It has already been shown that high dispersion is effective in increasing the sulfur capacity.

4. Conclusions

The chemistry of copper oxide with mercaptans has been studied at similar guard bed conditions used in typical refinery operations and found that redox chemistry occurs between the copper oxide and mercaptans to form disulfides, and at certain conditions, a copper(I) thiolate crystalline compound is formed. Furthermore, the efficiency of this reaction seems to be dependent on the total and copper specific surface areas. This is especially true for highly dispersed copper on CuO/ ZnO/alumina materials. This unique chemistry allows for bulk copper to be involved in the adsorption process, and also allows for a relatively stable level of sulfur to leak from the guard bed.

During the formation of the crystals of the copper(I) butanethiolate, the copper is leached from the catalyst particles and they migrate to nearby areas in the bed to crystallize. Also, at these conditions it was found that all of the mercaptans in the feed stream were converted to disulfides as described in the equations above. Furthermore, during the process of growing crystals of copper(I) butanethiolate, the copper oxide surface of the catalyst continues to be refreshed, allowing bulk copper to react with the sulfur-containing feed. It is conceivable that if copper/thiol complexes are able to migrate away from catalyst particles, that it would be possible for the copper to leach from the beds. This was found to be the case, though it should be stressed that this has occurred at extreme conditions of high sulfur content in the feed (much higher than what is expected in typical refinery processes) and at close to end of run.

At a higher temperature of 190 °C with 50 ppm hexanethiol, the copper thiolate crystals do not form, presumably because the higher temperature does not allow this. Nevertheless, there is evidence that the above chemistry occurred since the CuO has been reduced to different crystalline forms of Cu_2S .

Overall, when ranking the effectiveness of the different Cucontaining materials, the samples with high copper content and dispersion performed the best, which in this case, was a CuO/ ZnO/alumina material, as opposed to CuO/alumina [14]. According to the parameters of these tests, overall pickup of mercaptan was two times larger than that for CuO/alumina. Still, no matter what the material tested, the redox chemistry described occurs, converting the mercaptan to a disulfide, and at the right conditions, the mercaptan may also form a copper thiolate crystalline compound. A portion of the disulfide formed in the reactor, having a different adsorption coefficient, passes through the bed on a consistent basis.

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