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Selective Oxidation of H_2S over CuO/Al_2O_3: Identification and Role of the Sulfurated Species formed on the Catalyst during the Reaction

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A CuO/Al_2O_3 catalyst was used for selective oxidation of hydrogen sulfide into sulfur at low temperature (383 K). H_2S is totally consumed during the 28 first hours of the reaction, without detection of SO_2 nor S_n. The decrease of H_2S conversion is concomitant with the detection of sulfur at the bottom of the reactor. Analysis of the catalyst evidenced the presence of several sulfurated species, such as sulfate, sulfur, and especially sulfide species. The sulfide/copper molar ratio varies versus reaction time and reaches values greater than 1, which suggests the formation of polysulfide species. Its maximum value (3.5) is concomitant with the conversion decrease and the formation of S_n. Complementary reactivity experiments show that the active phase cannot be a simple copper sulfide CuS and underline the peculiar role of oxygen in the network. It finally seems that the oxidation step can be divided into three parts: adsorption of H_2S to create the active copper oxysulfide phase, insertion of S^0 from oxidation of H_2S leading to the creation of polysulfide species, desorption of S_n sulfur when the polysulfide chain becomes too long. Deactivation of the catalyst can be due to the storage of sulfur in its porosity or to the impoverishment of the network oxygen. Regeneration treatment at 603 K under water leads to the removal of S_n and sulfate species.

INTRODUCTION

The Claus process (1, 2) is the most commonly employed technique for removing sulfur from natural gas, crude oil, or industrial and combustion streams. However, the catalytic reaction $SO_2 + 2\,H_2S \leftrightharpoons 3/n\,S_n + 2\,H_2O$ being an equilibrium, the best sulfur recovery efficiency of Claus plants units does not exceed 97–98% (3). The remaining H_2S has to be eliminated and one of the most promising possibilities is the direct H_2S oxidation to elemental sulfur:

$$H_2S + 1/2\,O_2 \rightarrow 1/n\,S_n + H_2O.$$

Recently, Elf and Lurgi together developed a tail gas process, called Doxosulfreen (4), based on the direct oxidation reaction of H_2S into sulfur below the dewpoint of sulfur, with an overall recovery of 99.9%. This process involves two catalytic beds, the first for performing the Claus reaction and the second for the transformation of the H_2S remaining downstream by direct oxidation. Both of these beds operate in a cyclic mode, with the adsorption reaction conducted between the dew point of water and that of sulfur (i.e., between 363 and 413 K). The sulfur produced is trapped in the optimized porous network of the catalyst carrier. Regeneration is carried out at approximately 573 K, leading to the sulfur removal from the catalyst.

New catalysts have been developed by Procatalyse for this oxidation step, one of them being CuO/Al_2O_3. To optimise its performances in the industrial process, better understanding of the involved oxidation mechanism and of the efficiency of the regeneration step has to be achieved. The aim of this work was to identify and study the role of the species formed on the catalyst during the oxidative step of H_2S into sulfur. Among them, sulfate, sulfide, and sulfur species were expected. It was therefore necessary first to define the best analytical methods for detecting and to quantifying them. Capillary electrophoresis was used to analyze sulfate, thiosulfate, and sulfite species. Attempts to use IR spectroscopy to differentiate copper, alumina, and mixed sulfate species (5) were unsuccessful, due to the lack of transparency of the IR beam. S_n was quantified by UV spectrometry, after extraction in chloroform. The total amount of sulfide species was determined by complexometry method (6). Attempts to characterize polysulfide species by Raman technique, according to Perrin *et al.* (7), failed because of the instability of the samples under the laser beam. Yet, their presence was evidenced by calculation of sulfide/copper molar ratio. Sulfur balances were obtained by comparison between total sulfur estimated from addition of these analysis results and total sulfur quantified by elemental microanalysis. The variation of these several species amount has been followed with time on stream, in order to establish reaction mechanisms. The role of sulfide and sulfate species has been particularly studied.

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EXPERIMENTAL

The CuO/Al_2O_3 catalyst was provided by Procatalyse: its copper content was 17.3 (wt%) and its specific area 136 $m^2\ g^{-1}$.

The catalytic tests were carried out in a fixed bed continuous flow quartz microreactor under atmospheric pressure, at 383 K. The reactor was heated externally with a furnace and the temperature of the catalyst bed was controlled by a thermocouple being localized close to the wall of the quartz tube. For each experiment, 4 g of catalyst was heated up to 383 K in the stream of reactants. The feed was a mixture of $H_2S/O_2/H_2O = 0.9/2/30$ diluted in N_2. The total flow rate was 53.5 mL/min (W/F $= 28\ g \cdot h\ mol^{-1}$). For regeneration, the CuO/Al_2O_3 catalyst was heated up to 603 K under a mixture of nitrogen and water vapor (≈25%).

At the end of each experiment, the catalyst was cooled under nitrogen flow and was then kept in a glove box under dry nitrogen for subsequent analysis.

The quartz or Teflon tubes of the catalytic test were heated to avoid water or sulfur condensation. Water and sulfur produced by the reaction were trapped at room temperature; remaining traces of water were condensed by magnesium perchlorate. Gaseous products were analyzed by gas chromatography (Varian 3400 CPG equipped with a FPD detector using a 25-m Porapak Q column). The conversion of hydrogen sulfide and the sulfur selectivity were calculated using the following equations:

$$\text{conversion (\%)} = (\text{mol } H_2S \text{ reacted})/(\text{mol } H_2S \text{ fed}) \times 100\%$$

$$\text{sulfur selectivity (\%)} = (\text{mol } H_2S \text{ reacted} - \text{mol } SO_2 \text{ formed})/(\text{mol } H_2S \text{ reacted}) \times 100\%.$$

Analytical Methods

Total amount of sulfur. After each experiment, the sulfur content of all the sulfurated species forms was systematically quantified by the Vernaison CNRS microanalysis center. Burning the samples at 2073 K under oxygen flow transformed the whole sulfurated species into SO_2, which was further titrated using IR spectroscopy.

Sulfate, thiosulfate, and sulfite species titration. Sulfate, thiosulfate, and sulfite species analysis was performed using a *lone* technique, the capillary electrophoresis, which made it possible to separate ionized compounds in relation with their own mobility under an electric potential (4). The system used (Waters) was equipped with a capillary (Supelco, 75 μm × 60 cm) made of fused silica. The applied potential was 20 kV, with a current intensity around 18 μA. The injection was performed by hydrostatic mode, with an injection time of 30 s. Analyses were realized at room temperature. Due to its instability, the electrolyte had to be prepared just before each analysis. It was prepared from a mere solution of sodium chromate (0.1 M), obtained from dissolution of $Na_2CrO_4, 4H_2O$ into ultrapurified water; 5 mL of this solution was added to 2.5 mL of a commercial solution of OFM (Osmotic Flow Modifier) which is specific for anionic analysis. The pH of the so-obtained solution was higher than 9. After adding ultrapurified water until 100 mL, the electrolyte was evacuated for 15 min. The detection mode was an inverted UV spectrometer, which was equipped with a mercury lamp, at a wavenumber of 285 nm. The samples were diluted in a NaOH solution (pH 9), stirred at 323 K for 10 min, and filtered. It was checked by a subsequent analysis that all of the sulfur has passed into the filtrate.

Sulfide species titration. The method used is related in ISO 4284 (6), for spaths fluor sulfide analysis. Its principle is first to dissociate the M–S bonds by an acidic attack: a mixture of boric and chlorhydric acids (respectively 500 mg and 50 ml of a 400 g L^{-1} solution) with tin chloride (10 ml of a 200 g L^{-1} solution) was added to 500 mg of sample previously finely ground. The H_2S evolved being, under nitrogen flow, trapped in a cadmium acetate solution, leading to CdS cadmium sulfide formation. The reaction of this latter solution with 10 mL of an acidic iodine solution (0.0086 N) liberates H_2S, which reacts with I_2 stoichiometrically. Titration of the iodine excess by a sodium thiosulfate solution (0.01 N) allows one access to the H_2S evolved and so to the amount of sulfide species initially present.

S_n species titration. Samples 500 mg were ground in an agate mortar and then added to 50 mL of $HCCl_3$ (Prolabo). The obtained mixture was stirred and heated to 323 K for 5 h. After two successive washings, the mixture was filtered, transformed into methylene blue, and analyzed using a Beckman UV spectrometer, equipped with a deuterium lamp, the maximum S_n absorbance being above 280 nm.

XRD characterization. X-ray diffractograms were registered in the 5–70° 2θ range on a Philips PW 1800 diffractometer (scan 0.02°, accumulation time 2 s) equipped with a Cu anticathod ($\lambda = 1.5406$ Å).

RESULTS AND DISCUSSION

CuO/Al_2O_3 Catalyst, Adsorption Step

A first experiment has been performed for 50 h on the CuO/Al_2O_3 catalyst according to the above-described oxidation conditions. The evolution of the H_2S consumption is reported in Fig. 1. During the first 28 h, H_2S is totally consumed; then the conversion progressively decreases to reach 64% after 50 h. In any case, no SO_2 has been detected.

Moreover, sulfur formation is observed after 28 h: it appears at the cool bottom of the reactor, since the water trapped is no longer clear. The decrease of the H_2S conversion into sulfur via the selective oxidation reaction is concomitant with the formation of sulfur. It could be noticed

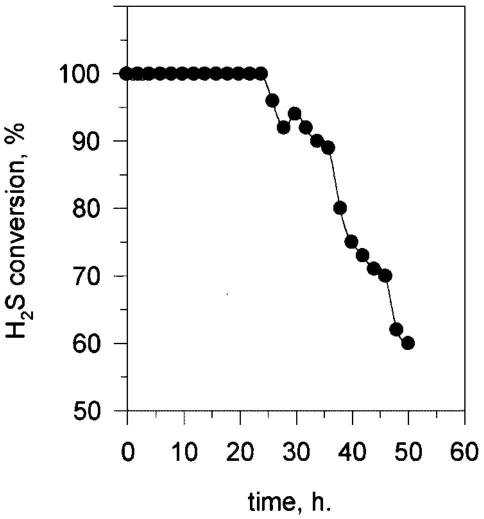

FIG. 1. H_2S conversion (%) versus time on stream (h).

that its coloration has passed from gray before the experiment to black after the reaction. This observation suggests that sulfidation phenomena have occurred during the reaction. Analysis results show that the total amount of sulfate, thiosulfate, and sulfite species remains low ($\approx$3.4%). Content of S_n is also very low (6%), since the major part of sulfurated species (24.4%, i.e., more than 70% of the whole sulfurated species) are sulfide ones. Thus, the sulfur balance, defined as the ratio between the addition of these results and the elemental sulfur amount (34.5%), leads to a ratio of 0.98. It can thus be concluded that the analytical methods used are convenient for the titration of the sulfurated species on CuO/Al_2O_3 after reaction.

In order to follow the variation of the amount of sulfided species formed with time on stream, several experiments were performed and stopped at different times on stream. Corresponding analyses were performed. As shown in Fig. 2, the amount of sulfide species increases during the first hours of the reaction to reach a maximum value near 28 h of reaction (30 wt% of S per 100 g of catalyst). It is further stabilized around 25%. Moreover, no S_n is detected in the catalyst before 28 h of reaction, showing that the sulfur appearance visualized at the bottom of the reactor or in water corresponds to the beginning of its formation. After 28 h of time on stream, the difference between the amount of total sulfur and that of sulfide species is due to the formation of a low amount of sulfate species and to the formation of S_n remaining on the catalyst, as shown by results after 50 h on stream. We can therefore suspect a link between the sulfur storage and the beginning of deactivation, as already mentioned in the literature (8). Actually, the sulfate amount is too low to provoke catalyst deactivation and we have checked that the H_2S selective oxidation effectively occurs on a presulfated catalyst. The total amount of sulfur (as H_2S) passed over the catalyst is also reported in Fig. 2. One can actually define a second sulfur balance, taking into account in one hand the H_2S inlet starting from the beginning of the experiment and in the other hand the amount of total sulfur and especially the quantity of sulfide species formed. This balance is very good up to 28 h (see Fig. 2). The subsequent deficit (after 28 h) is related to the S_n trapped at the bottom of the reactor, whose amount can be estimated to 14% (grams of S per gram of catalyst) after 50 h of experiment.

Finally, the main result is relative to the evidence of sulfide species formation. In order to get information about their structure, the molar ratio between sulfide and copper has been calculated and reported in Fig. 2. It shows that sulfide species are progressively enriched in sulfur, to reach a maximum of 3.5 mol of sulfide per mol of copper at 28 h of adsorption time. This value clearly indicates that there is formation of polysulfide species. Once a maximum of polysulfide condensation is reached, elemental sulfur S_n appears and so the S/Cu ratio decreases. One must thus conclude that the complexometry method used to analyze sulfide species also titrates polysulfide species. Since metal polysulfides are not commercially available, it was not possible to check this point. However, it is well known that copper is likely to form polysulfide chains (9). X-ray diffraction patterns (see Fig. 3) have been performed on the fresh catalyst, after 28 h of experiment, and at the end of the reaction (50 h on stream). The pattern of fresh catalyst evidences the presence of the two main characteristic lines of copper oxide (10). Their intensity decreases with time on flow and only a

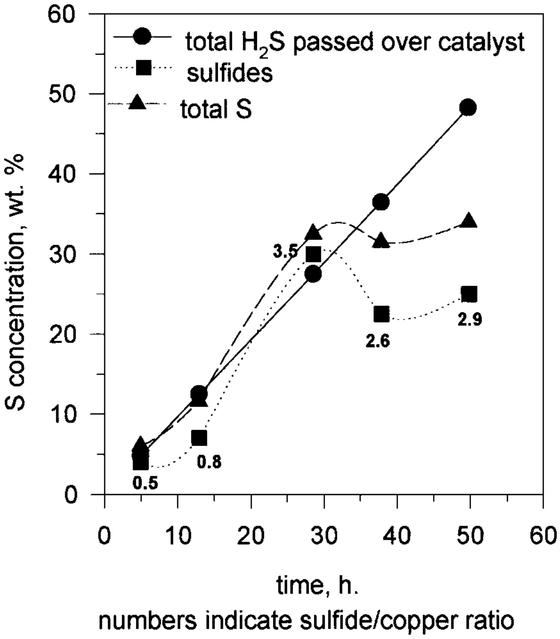

FIG. 2. Total sulfur and sulfide amount (wt%) on the CuO/Al_2O_3 catalyst compared to S stream (corresponding to total H_2S passed over the catalyst). S/Cu, sulfide/copper molar ratio.

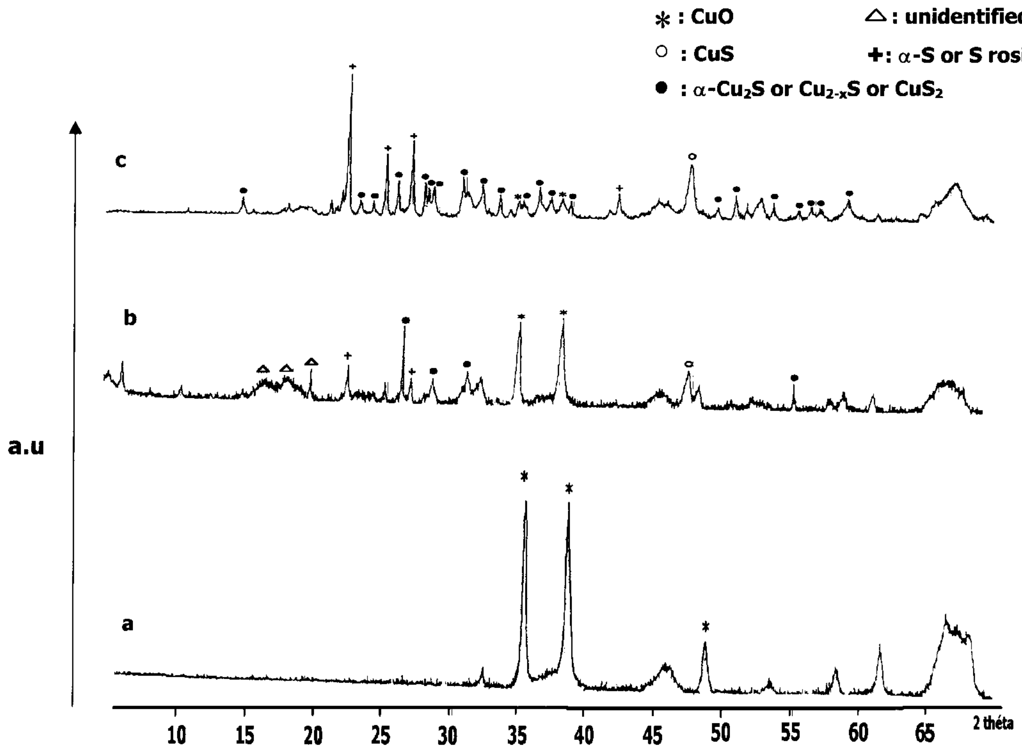

FIG. 3. XRD spectra of CuO/Al_2O_3: (a) fresh, (b) after 28 h of time on stream, (c) after 50 h of time on stream.

very small amount of copper oxide still remains on the catalyst at the end of the experiment. The middle-reaction catalyst pattern presents several lines, which can be attributed to different sulfided phases such as CuS, $Cu_{2-x}S$, α-Cu_2S, and CuS_2. However, two unknown lines absent from the two other diffractograms arise ($2\theta = 16.97$ and 20.39°). This corresponding transient phase could be relative to copper polysulfide not referenced in literature, since it was already noticed that the amount of sulfided species reaches a maximum value precisely at 28 h of reaction. At the end of the experiment, the copper oxide phase remains very minor. Several sulfided phases still remain, since lines relative to S_n have grown, which is in agreement with the analytical results obtained on the catalyst and previously detailed.

The sulfur formation mode could consist first of sulfidation of some copper sites and then S^0 formation through H_2S oxidation, followed by S^0 incorporation, creating a polysulfide chain. When this chain reaches a critical length, S_n is desorbed. In this feature, a copper sulfide phase should be efficient to transform H_2S into S_n. Two kinds of experiments have been performed, starting from a CuO/Al_2O_3 presulfided sample or from a CuS/Al_2O_3 sample.

Comparison with Oxidation Performed on a CuO/Al_2O_3 Presulfided Sample

The CuO/Al_2O_3 catalyst was first pretreated under H_2S flow (2.2% in N_2) without oxygen, under the conditions previously described. H_2S is first totally consumed up to 45 min, before being progressively released. The total equivalent consumption of H_2S corresponds to 0.003 mol g^{-1} of sulfur, which is 10 times lower than that needed to reach the maximum polysulfide condensation in the previous experiment (0.034 mol g^{-1} of sulfur after 28 h). The obtained S/Cu ratio (0.28) and the absence of oxygen in the flow suggest that formation of a sulfide phase such as CuS_xO_y.

Starting from this presulfided catalyst, the oxidation reaction was then performed under the same oxidative conditions (0.9% H_2S and 2% O_2) as for the first experiment. H_2S is first totally consumed, without any formation of elemental sulfur. After 22 h, sulfur appears and H_2S is partially released: this corresponds to a new consumption of 0.026 mol g^{-1} of H_2S. The H_2S consumption and the equivalent S/Cu ratio are reported in Table 1. It clearly appears that the molar ratio S/Cu is above 1 in both experiments,

TABLE 1

S/Cu Molar Ratio at H_2S Release Time

	H_2S consumption (mol g^{-1})	S/Cu
CuO/Al_2O_3, first experiment		
Oxidative treatment	0.034	3.15
CuO/Al_2O_3, second experiment		
Presulfidation step	0.003	0.28
Oxidative treatment	0.026	2.41

reaching 3.15 in the first one and 2.69 in the second. These results confirm that a high S/Cu ratio has to be reached before the catalyst produces sulfur. Moreover, the second experiment clearly shows that the presence of oxygen in the flow is necessary for the consumption of a large amount of H_2S without formation of S_n. Indeed, oxygen is consumed to oxidize the sulfur present in H_2S into sulfur S^0 which will be incorporated into the polysulfide chain. This experiment confirms the formation of polysulfides as intermediate toward sulfur S_n formation. The mechanism could thus involve, first, an adsorption step leading to a partial sulfidation of the catalyst and, second, an oxidation step which leads to polysulfide formation. S_n production could finally result from the breaking of the $(–S–)_x$ chains.

A second experiment has been performed starting from a commercial CuS/Al_2O_3 catalyst (S/Cu = 1, wt% of Cu = 10.4) in order to determine the role of the oxygen atoms initially present in CuO/Al_2O_3. According to the above proposed mechanism, we expect that this CuS/Al_2O_3 catalyst presents a good activity toward H_2S oxidation and behaves exactly in the same way as CuO/Al_2O_3, without of course the first adsorption step. The H_2S release time has been compared for the both catalysts. In the case of CuO/Al_2O_3, H_2S release time is reached once 8500 μmol g^{-1} of H_2S has been consumed. In the case of CuS/Al_2O_3, the very short H_2S release time corresponds to only 420 μmol g^{-1} of H_2S (equivalent to 700 μmol g^{-1} for a CuS/Al_2O_3 sample containing 17.4 wt% of copper). The comparison between the two values (700 and 8500 μmol g^{-1}) clearly shows that CuS/Al_2O_3 leads to the formation of fewer condensed polysulfides than CuO/Al_2O_3 and is therefore less effective in H_2S transformation. This experiment emphasizes the peculiar importance of the network oxygen of the CuO phase. The active phase is thus not simply a single copper sulfide, but a copper oxy-sulfide. H_2S release time could thus depend on the oxygen storage available in the network.

Besides, we have shown that the ratio $O_2/H_2S = 2.2$ is not a limiting factor since its increase promotes the recovery of the activity after 40 h of reaction, as shown by the following experiment: the experiment was first performed under the conditions previously described, till a significant deactivation was observed (84% of conversion after 38 h of experiment). Then the reactor was bypassed and some of the catalyst was taken for analysis. The O_2/H_2S ratio was then increased from 2.2 to 3, and the stream led once again to the reactor. As shown in Fig. 4, the increase of oxygen rate in the inlet flow leads to an increase of H_2S conversion (around +6%). The analysis of the samples at 38 h of experiment and at the end of the process show an increase of 5% of sulfide and polysulfide species. It therefore appears that O_2 increase enhances the reaction rate. The conversion finally decreases because of the loss of active phase due to S_n present in the pores. As expected, the increase of O_2/H_2S ratio enhances the sulfate species formation (from 3% before changing the ratio to 5% after). But it is important to note that, as observed in the case of a pre-sulfated catalyst, the increase of sulfate amount does not affect the performance of the catalyst. This ability to maintain good catalytic performances in spite of the presence of sulfates, in particular an excellent selectivity, constitutes the uniqueness of the catalyst, contrary to many other catalysts previously studied, especially NiO/Al_2O_3 (11, 12). This suggests that the mechanism of H_2S selective oxidation and particularly the reactive species might be thus different in the case of CuO/Al_2O_3 relative to that of NiO/Al_2O_3.

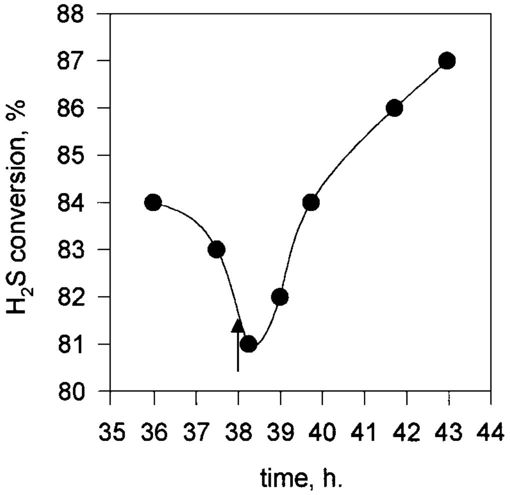

FIG. 4. Influence of the O_2/H_2S molar ratio on H_2S conversion (%) versus time (h). The arrow corresponds to the changing of the O_2/H_2S ratio.

The promoting role of oxygen could be explained involving polysulfide reactivity, as reported in the literature (13). Actually, if one considers that the reaction of H_2S oxidation is ruled by a radical mechanism (14), oxygen would preferentially react with the radicals present at the end of the sulfur chain, to create $S_x–S–O–O^\circ$ species extremely reactive with H_2S present in the flow. When the O_2/H_2S ratio is increased, the excess of oxygen could weaken the –S–S– bond, resulting in a cleavage of this latter, as previously explained by Steijns (15) and Dudzik (16). This cleavage could induce S_n and SO_2 formation and liberate an active copper site, boosting then the H_2S conversion. Nevertheless, the latter interpretation is not convenient for two main reasons: (i) SO_2 is not observed even when the gaseous oxygen amount is increased, and (ii) it does not explain the importance of oxygen contained in the oxy-sulfide active phase. One could also consider, as suggested by Zhenglu *et al.* (17), that a Mars and Van Krevelen mechanism (18) is involved in the H_2S-selective oxidation reaction. The oxygen of the active phase CuS_xO_y network would allow sulfur species oxidation (and H_2O formation) and the subsequent polysulfide formation; it would be regenerated by gaseous oxygen. Consequently, the observed deactivation could be

TABLE 2

Concentrations of Different Sulfurated Species (wt%) in the Catalyst Pretreated in Different Ways

	Sulfide	Sulfate	Elemental sulfur
After oxidation reaction	24.5	3.5	6.0
After 3 h of regeneration treatment	4.8	1.8	0.0
After 14 h of regeneration treatment	3.9	0.0	0.0

partly due to the progressive decrease of oxygen content in the oxy-polysulfide active phase, as shown by the decreasing intensities of CuO diffraction lines versus time (Fig. 3). This hypothesis could also explain the low performances of CuS/Al_2O_3, which contains much fewer oxygen atoms. Increasing O_2/H_2S ratio may enhance gaseous oxygen incorporation in the oxy-polysulfide phase and thus partly inhibit the deactivation.

Regeneration Step

Because of the unavoidable decrease of conversion, mainly due to sulfur S_n storage in the pores, the catalyst has to be regenerated regularly in order to eliminate elemental sulfur or even sulfate species. Table 2 reports analysis results gathered from a CuO/Al_2O_3 catalyst after an oxidation step and during the regeneration step. The total amount of sulfur present on the regenerated samples is much lower than that on the nonregenerated one. In particular, no more S_n elemental sulfur remains on samples, which is expected since the regeneration temperature is much higher than the sulfur dewpoint. Most of sulfide species are removed, since only 3.9% remains after regeneration (versus 24.4% after the oxidation step). Sulfate species are also eliminated. We have already studied the reduction of sulfate species on promoted alumina such as CuO/Al_2O_3. This study showed that these species are partially reducible by H_2S as low as 573 K (19) but that water alone has no effect on their stability. Since the regeneration flows contain only N_2 and H_2O, the decrease of sulfate species amount is certainly due to their reduction by H_2S formed by a reverse Claus reaction. Indeed, emissions of SO_2 (920 μmol g^{-1}) and H_2S (400 μmol g^{-1}) during the regeneration step were observed by CPG, as described in Fig. 5. The experimental H_2S/SO_2 ratio is different from the stoichiometry of a reverse Claus reaction (0.4 versus 2). This discrepancy could be attributed to H_2S consumption due to sulfate reduction.

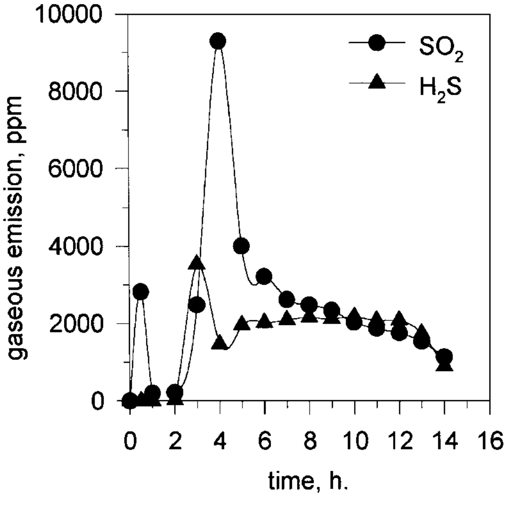

FIG. 5. Emissions of SO_2 and H_2S during the regeneration by $N_2 + H_2O$ and corresponding temperature profile.

CONCLUSION

CuO/Al_2O_3 catalyst was shown to be very selective for the H_2S selective oxidation reaction, since SO_2 has never been detected. Results imply that the formation of sulfide and even polysulfide species on the surface of the catalyst is a result of simple sulfur adsorption and the oxidation of S^{-II} to S^0, respectively. Elemental sulfur S_n appears after several hours, resulting from the cleavage of too-long polysulfides chains. Concomitantly, H_2S is no longer totally consumed, because of the loss of active surface due to sulfur accumulation inside the alumina pores. Oxygen plays a fundamental role in the formation of polysulfide species and in the enhancement of the reaction.

The remarkable characteristics of CuO/Al_2O_3 presently studied are its poor ability to form sulfate species and its excellent selectivity in sulfur, even with an excess of oxygen. Moreover, sulfates are not poisons of the selective H_2S oxidation. This constitutes, with the formation of polysulfide chains, a second uniqueness of this catalyst.

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