ELSEVIER

Applied Catalysis A: General 173 (1998) 185–192

APPLIED CATALYSIS
A: GENERAL

The effect of water in the low-temperature catalytic oxidation of hydrogen sulfide to sulfur over activated carbon

Alessandra Primavera, Alessandro Trovarelli*, Paolo Andreussi, Giuliano Dolcetti

Dipartimento di Scienze e Tecnologie Chimiche, Universita di Udine, via Cotonificio 108, 33100 Udine, Italy

Abstract

This study investigates the use of low-temperature catalytic oxidation for the removal of H_2S from tail gases originating from geothermal plants, with special focus on the effect of water on the overall performance of the activated carbon catalyst. It is shown that water strongly influences the reaction rate and the total amount of sulfur that can be adsorbed on the catalyst prior to regeneration. It is suggested that the reaction takes place in a thin water layer, inside the carbon pores, from the reaction of dissolved H_2S with chemisorbed oxygen.

1. Introduction

Hydrogen sulfide originating from various sources (coal-based power plants, natural-gas processing, refineries, smelter operation) can be regarded as a major air pollutant entering the atmosphere and causing acid rain. Several processes have been described and developed at various stages for the elimination of H_2S from products or off-gases. Some employ transition-metal oxides and mixed oxides for the catalytic oxidation of H_2S [1–3], whereas others utilize activated carbon in various forms as adsorbent and/or catalyst [4–7]. Under these conditions, hydrogen sulfide can either be transformed into sulfur dioxide or oxidized to elemental sulfur

$$H_2S + 1.5O_2 \rightarrow SO_2 + H_2O \qquad (1)$$

$$H_2S + 0.5O_2 \rightarrow S + H_2O \qquad (2)$$

although additional side reactions producing sulfur compounds at various stages of oxidation can occur, depending on conditions [6]. The choice of reaction parameters, particularly reaction temperature and type of catalyst/promoter, will affect the main reaction pathways and, generally, activated carbon at low temperatures (293–323 K) promotes the oxidation of H_2S to S, in accordance with reaction (2). In the presence of oxygen, H_2S can be converted catalytically to water and sulfur, which remains adsorbed on the spent catalysts and can be then recovered by regeneration with inert gases or steam. This process is particularly suitable for dealing with gas streams presenting an H_2S concentration ranging from 300 to 10 000 ppm.

Several studies have described the use of carbon as catalyst for H_2S oxidation to S/SO_2 and kinetic data for this reaction are also available [6,8]. As a result of the wide range of experimental conditions used for this reaction (type of carbon, reaction temperature, concentration of reagents, etc.), the literature data are somewhat conflicting and the effect of some variables (like the presence of water) on the overall efficiency of the process, and on the kinetics, are not covered in

---

*Corresponding author.

0926-860X/98/$ – see front matter © 1998 Elsevier Science B.V. All rights reserved.
PII: S0926-860X(98)00178-1

detail. However, despite these discrepancies, it clearly appears that water plays an important role in the process by enhancing the performance of carbon for the low-temperature oxidation of H_2S to S while leaving almost unaffected the reaction rate at higher temperatures, when SO_2 becomes the main product.

In the present paper, we analyze in detail the low-temperature oxidation of H_2S to sulfur over a fixed activated carbon bed, with special focus on the role of water in the process. In particular, the effect of water in the activation of the catalyst and in the amount of S that can be stored are considered. The experimental conditions used are adapted to better simulate the composition of mixtures from tail gases of geothermal plants (i.e. 10 000–30 000 ppm of H_2S in CO_2 rich gases with a water content close to 100% of relative humidity). The kinetics of H_2S oxidation, both in the presence and absence of water, is also investigated.

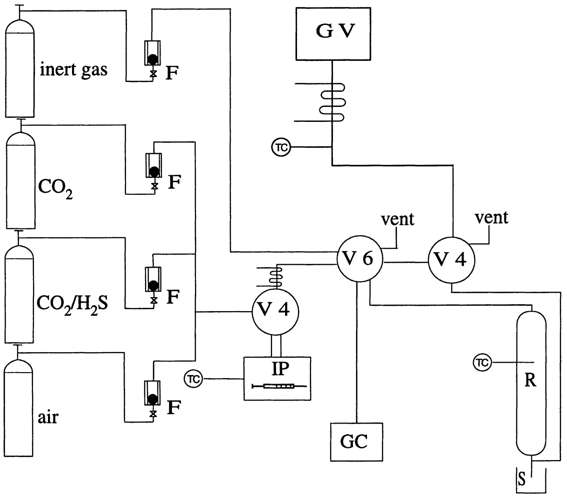

Fig. 1. Schematic diagram of the apparatus used for catalytic experiments.

2. Experimental

2.1. Apparatus

The oxidation of H_2S was carried out in a fixed-bed microreactor. A schematic representation of a laboratory test plant is illustrated in Fig. 1. The reactor (R) consists of a U-shaped (9 mm ID, 250 mm long) glass tube immersed in a thermostatic bath maintained at a fixed temperature. The catalyst is loaded from the top of the reactor and supported on a layer of glass wool placed 20 mm away from the bottom. The reactor used for oxidation of H_2S is also used for the regeneration of the spent carbon catalyst. For this purpose, an on/off valve is placed at the bottom of the reactor; the valve connects the glass tube to a cold trap, where sulfur can be collected (S). A thermocouple (TC) is placed in the reactor, immersed in the catalyst bed, to continuously monitor the temperature. The gas flow is regulated by means of electronic flow meters (F). Upstream of the reactor, a 4-way valve (V4) connects the dry reagents to an infusion pump (IP) for the introduction of a known amount of water. To avoid problems arising from excess pressure, a pressure check and relief valve (10 psi) is placed between the liquid pumps and the reactor. A 6-way valve (V6) allows the gas mixture to be fed into the reactor or analyzed directly at the gas chromatograph (GC). In this way, it is possible to check the composition of the reagent and product mixtures at any time within the same experimental run. Another 4-way valve allows switching between normal operation (oxidation cycle) and regeneration of the spent catalyst with vapor using a vapor generator (GV) or heated inert gases. All lines, valves and connections are made of 1/8" stainless-steel tubing and can be heated up to 250°C with high potential heating tapes. Analysis of the gases is performed on-line by means of an HP-5890 A gas chromatograph using a Hayesep-C column and a thermal conductivity detector.

2.2. Reaction conditions

The oxidation of H_2S was studied at temperatures ranging from 298 to 343 K with an H_2S content varying from 1 to 3%. Excess or stoichiometric oxygen was supplied to the catalysts; the inert gas as balance was CO_2, to simulate the composition of off-gases from geothermal plants. Water content was varied between 0 and 90 RH%. A total flow of $\approx$250 ml/min was used with a GHSV of 7000 h^{-1} and a catalyst weight of 1 g. Kinetic experiments carried out under differential conditions were performed at a GHSV of 13 0000 h^{-1} ($\approx$30 mg of catalyst) by keeping the conversion lower than 5–10%. The absence of mass-transfer limitation was con-

Table 1
Characteristics of activated carbon catalyst

Apparent density	460 g/l
BET surface area	940 m^2/g
Water content	9wt%
Trace metals (2–5 ppm) [a]	Fe, Mn, Al, Cr, V

[a] Determined by ICP-MS.

firmed by looking at the conversion with different W/F values (weight of catalyst/total flow of reagents) and with a variable particle diameter of the catalyst.

2.3. Materials and analytical methods

The catalyst used was a commercial sample of an activated carbon obtained from Norit (Norit, RFN-2 sample A-6280) whose characteristics are reported in Table 1. Morphology of the catalysts was studied by scanning electronic microscopy (SEM). Samples for SEM were mounted on stubs and metallized with gold by a sputtering system device (S150A Edwards). They were observed by a Stereoscan 250 scanning electronic microscope (Cambridge Instrument). Textural properties were measured with a Carlo Erba Sorptomatic 1900 instrument using the BET method.

3. Results and discussion

Fig. 2 reports the percentage conversion of hydrogen sulfide feed in CO_2, water and air stream at a temperature of 298 K for a typical run. At the same time, the amount of sulfur produced and deposited on the catalyst is indicated. The amount of sulfur was calculated by integrating the hydrogen sulfide conversion vs. time curve and then compared with the values obtained by weighing the catalyst after reaction and by elemental analysis of the unloaded catalyst. The three measurements agree to within 7%, indicating that under these conditions there is no further oxidation of S to SO_2 and that sulfate formation on the catalyst is negligible. This is consistent with previous studies, which found formation of SO_2 and other sulfur-containing products only at higher temperatures [6,9,10].

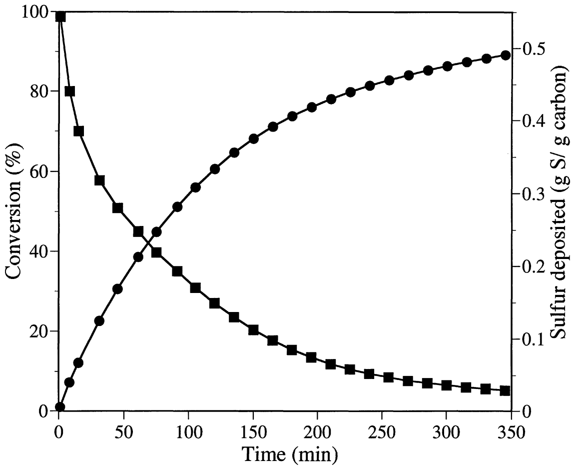

Fig. 2. (■) Conversion of H_2S, and (●) amount of sulfur deposited on the catalyst during reaction. Reaction conditions: GHSV 7000 h^{-1}, 1 g catalyst, $P(H_2S)=13.5$ torr, $P(O_2)=20.1$ torr and $P(H_2O)=11.9$ torr; balance CO_2.

The cause of deactivation is the loss of active surface area, which occurs by the progressive filling of the catalyst pores with sulfur. Fig. 3 shows the drop in BET surface area from 944 m^2/g down to a few m^2/g after ≈0.6 g_{sulfur}/g_{carbon} is deposited on the catalyst. Most of the surface area is lost in the first two hours of reaction. Regeneration of the spent catalyst is accomplished at a temperature of 673 K in inert gas flow for 2 h. After the first run, a decrease in the amount of sulfur deposited is observed. This remains constant in subsequent runs, as can be seen in Table 2. Similarly, the residual surface area stabilizes at higher values.

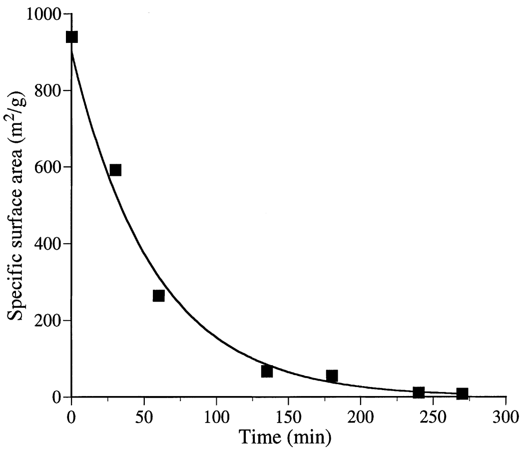

Fig. 3. Surface area of carbon measured at various times during reaction.

Table 2
Effect of regeneration of carbon

Sample [a]	Surface area (*f*) [b] (m^2/g)	Sulfur deposited (g_{sulfur}/g_{carbon})	Surface area (*s*) (m^2/g)
Fresh	944	0.54	15
I	899	0.36	113
II	913	0.38	81
III	877	0.38	69

[a] Fresh and regenerated carbon. Regenerated once (I), twice (II) and thrice (III).
[b] (*f*) Fresh carbon; (*s*) spent carbon.

SEM analyses of the fresh and spent carbon are reported in Fig. 4(a–b). No major modifications of the external morphology are evidenced after reaction, indicating that sulfur is unlikely to be adsorbed on the large macropores. A similar morphology is observed over samples subjected to regeneration. The rapid decrease in BET surface area during the beginning of reaction would indicate that the sulfur is first deposited on the micropores which account for most of the carbon surface in agreement with earlier findings [11]. Different patterns are observed if large macropores are filled first, followed by filling up of micropores [12]. The reasons for the reduced performance of the regenerated catalyst may be due to some irreversible fixation of residual sulfur on the active site of the catalyst which cannot be removed under our conditions and/or to the loss of ca. 5–10% of the initial surface area after the first regeneration. Although the amount of sulfur that can be removed over a regenerated catalyst is still comparable to that observed on a fresh catalyst, the initial conversion of a regenerated catalyst shows quite an unusual behavior. The initial high conversion drops in the first hour of reaction to lower values and, then, is partially recovered to follow a normal behavior pattern (see Fig. 5). This effect is not observed if the catalyst is first treated with water. We attribute this behavior to the absence of water in the first stage of reaction, and suggest that, during the course of the reaction, water fed and water generated by the process accumulate inside the pores of the catalysts up to a point where catalytic activity is recovered. This effect is particularly evident after regeneration of the catalyst with inert, dry gases. After regeneration, the carbon does not contain any additional water and the drop in activity is consistent with the time needed to refill the pores with water. Over a fresh catalyst, which contains $\approx$10% by weight of H_2O, this behavior is not observed. Another explanation for this fast deactivation in the first hour of reaction may be related to the adsorption of H_2S on the carbon. Under these conditions, the disappearance of H_2S would not be due to the reaction and consequent deposition of sulfur, but only to H_2S adsorption, and the reaction would start only in the presence of a sufficient amount of adsorbed H_2O. However, adsorption of H_2S, though possible, is likely to be followed by fast reaction with chemisorbed oxygen present on the surface.

It appears from these data that water plays a key role in the oxidation of H_2S at low temperatures. A more detailed investigation on the effect of H_2O on the amount of sulfur produced and on the reaction rate was, therefore, carried out to better reveal its role in the process. The dramatic effect of water on sulfur adsorbed is reported in Figs. 6 and 7, which show the dependence of the conversion of H_2S vs. sulfur deposited at increasing concentrations of water in the feed. In these experiments, the relative humidity (RH%) was varied between 0 and 90 and the temperature between 298 and 323 K. As may be observed, the presence of water strongly modifies the amount of sulfur which can be adsorbed on the catalyst during the reaction. At low RH% (0–20) a rapid decrease in conversion is observed with sulfur deposition, either at 298 or at 323 K. At higher RH% values (>75), an almost linear, less marked decrease of conversion is observed. With RH%=50, an intermediate situation is observed, which depends on temperature. Therefore, after deposition of a given amount of sulfur (e.g. 0.2 g_{sulfur}/g_{carbon}) the conversion is strongly dependent on the amount of water fed. Since the adsorption characteristics of carbon are the same, it is not likely that the small amount of sulfur adsorbed at low water content is responsible for the loss in catalytic activity. The surface area after adsorption of this amount of S is ca. 300 m^2/g and much of the carbon surface is still available for reaction. An interesting finding is that it is not only water in the feed that influences the total loading of sulfur but also water initially present in the catalyst. The results reported in Fig. 8 were obtained by using carbon catalyst previously loaded with different amounts of water and fed with a stream not containing H_2O. As can be seen, a catalyst without H_2O (either preloaded or added in the feed) exhibited

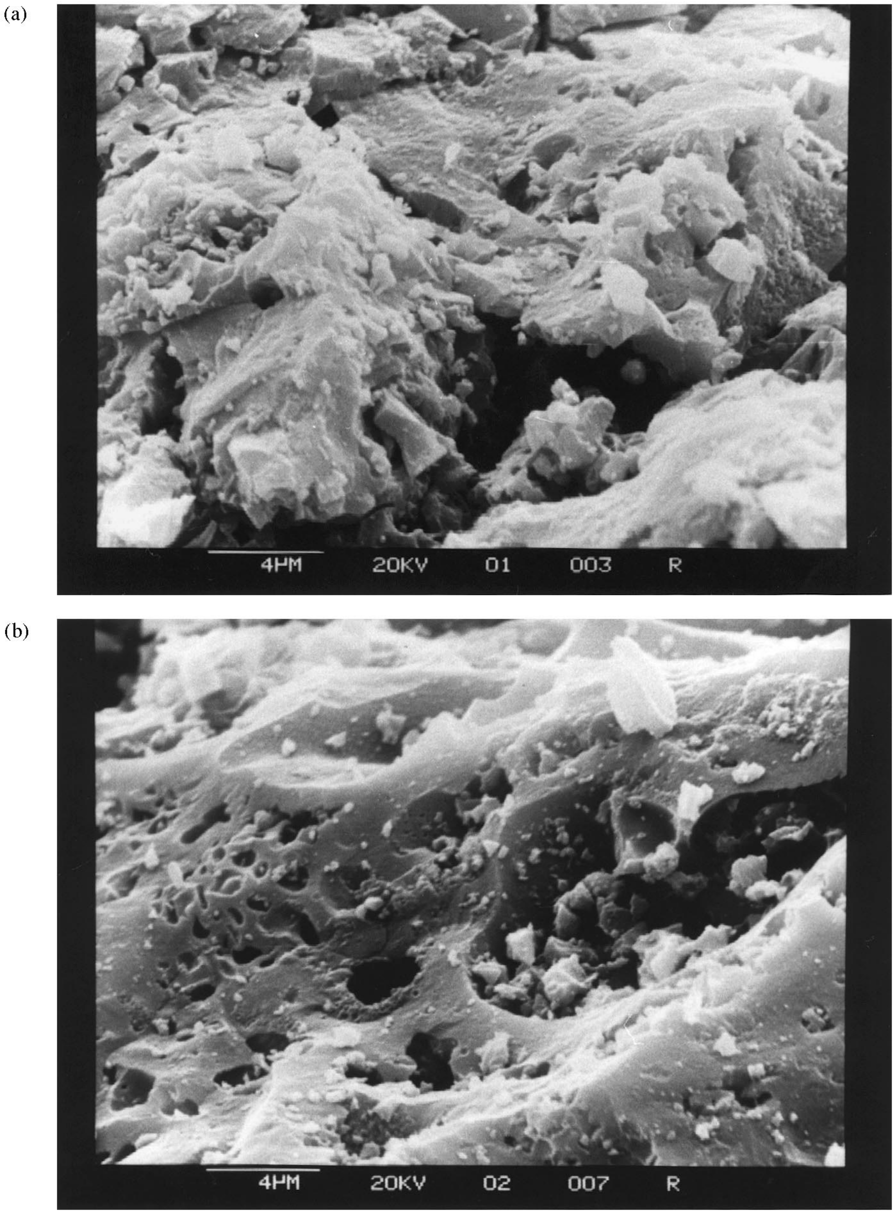

Fig. 4. SEM micrographs of (a) fresh carbon and (b) spent carbon.

very poor behavior and the total S adsorbed is $<0.2\ g_{sulfur}/g_{carbon}$, almost three times lower than the value measured with carbon containing 30% by weight of H_2O. This behavior, therefore, implies that in the presence of water, different mechanisms might affect the reaction path: (i) the catalytic reaction may take place in the water phase (faster than on the catalyst surface) within the pores of the catalyst by dissolving O_2 and H_2S in a water film, as previously suggested [6,13]; and (ii) the presence of water slows down the deactivation process, for example, by promoting deposition and adsorption of sulfur in different carbon sites and/or by mechanically removing sulfur from active sites.

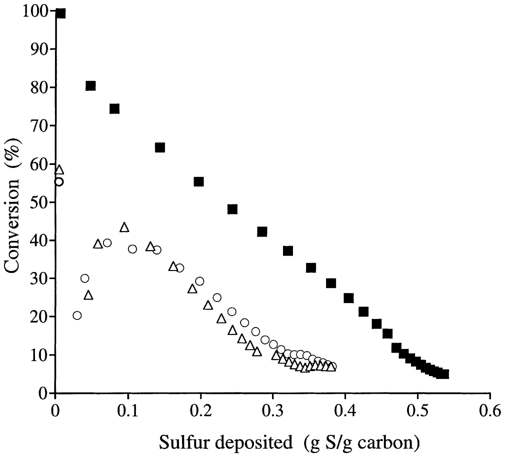

Fig. 5. Hydrogen sulfide conversion vs. sulfur content of the carbon: (■) New Carbon; (△) carbon regenerated once; and (○) carbon regenerated twice. Reaction conditions same as in Fig. 2.

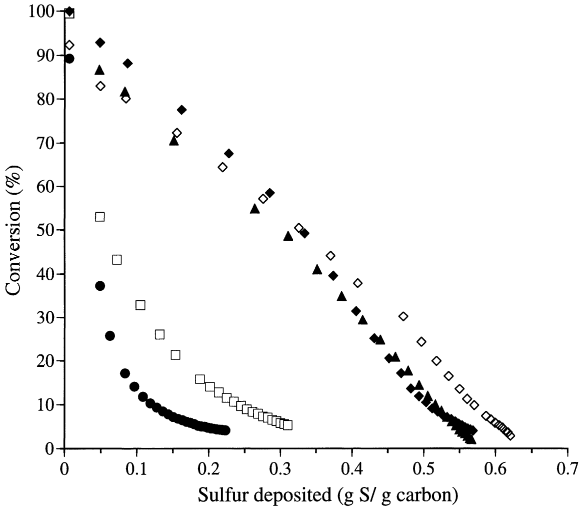

Fig. 6. Hydrogen sulfide conversion vs. sulfur content of the carbon at different RH% (●, 0; □, 20; ▲, 50; ◇, 75; ◆, 90; and T=298 K).

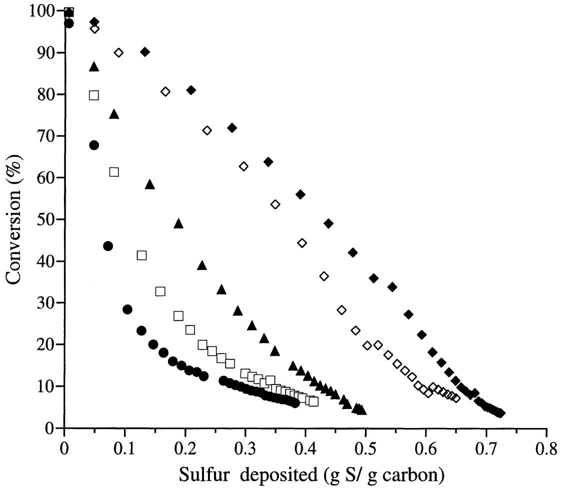

Fig. 7. Hydrogen sulfide conversion vs. sulfur content of the carbon at different RH% (●, 0; □, 20; ▲, 50; ◇, 75; ◆, 90; and T=343 K).

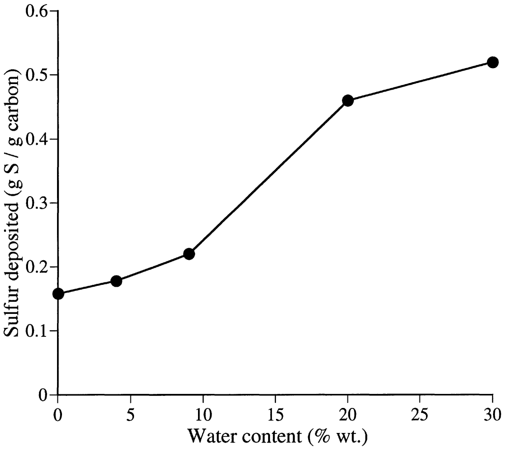

Fig. 8. Sulfur deposited in exhausted carbon at various water contents (% of water initially present on the carbon). Reaction conditions: GHSV=7000 h^{-1}, 1 g catalyst, $P(H_2S)$=13.5 torr, $P(O_2)$=20.1 torr; balance CO_2.

To gain further evidence on the role of water, we carried out a more detailed kinetic analysis on the effect of oxygen, H_2S and H_2O. The detailed measure of kinetic parameters over this system requires a knowledge of the effect of sulfur on reaction rate, for it has been reported that the deposited sulfur has an autocatalytic effect on the reaction and, especially for materials with low intrinsic activity, deposited sulfur can strongly influence the reaction rate [11,14]. Specifically, depending on the type of catalyst used, the profile of reaction rate vs. sulfur deposition can show a maximum before reaching a steady-state value. In our case, the profile of reaction vs. sulfur content was of type B [14], i.e. activity decreased with sulfur deposition and the maximum was not observed. This indicates that the intrinsic activity of our catalyst is much higher than the autocatalytic effect of sulfur, which should not affect the kinetic results. The reason for this behavior is connected with the presence of traces of metals (particularly Fe) in our activated commercial carbon. It has been demonstrated that even slight traces of metals make the observation of a maximum in the oxidation rate impossible [13,14]. However, it should be also noted that previous investigations were carried out at higher temperatures (403–473 K), where the autocatalytic effect of sulfur is more pronounced. Other factors which could affect the reaction rate in the present case are a gradual decrease in the number of active sites due to their physical covering by sulfur and a continuous change in the effectiveness factor due to textural variation during reaction. Therefore, for every kinetic experiment, the reaction rate vs. time data were fitted with empirical relationships [15] and the value of the rate at the beginning of reaction was calculated. From these experiments, rate data were obtained for the oxidation of H_2S at 298 K with a 0.5–4% of H_2S in the gas stream. Activation energy was 16.8 kJ/mol, in agreement with previous results [8].

Fig. 9 gives the results of rate dependence on hydrogen sulfide and oxygen concentrations. An almost zero order dependence was observed for H_2S content, while for oxygen the order varies from 0.57 at low O_2 concentration to zero at high concentrations.

The dependence of reaction rate on H_2O concentration has a more complicated behavior. We observed that the oxidation rate of H_2S shows a maximum as a function of the amount of water fed into the reactor. The position and intensity of the maximum are dependent on the partial pressure of water and temperature (Fig. 10). On increasing the temperature, an increase in maximum rate is observed. This is accompanied by a slight shift in the maximum at higher water pressures. However, if we report the results as relative humidity at a given temperature, the maximum is observed at the same RH% values (Fig. 11). These results indicate that water strongly influences oxidation rate at an RH% value of ca. 20. Lower or higher water contents do not produce the same enhancement of reaction rate. The lowest value is observed in the absence of water. We can distinguish three different regions of the curve, as indicated in Fig. 11. In the first part, at low water concentrations, the reaction rate increases with time and this is due to the catalytic effect of water deposited in the pores. This effect is probably related to the presence of a liquid-phase layer, where the reaction is accelerated. In region II, a decrease in activity is observed, which can be related to the filling of micropores. In region III, a kind of stationary activity level is reached and the reaction is probably running inside larger pores or on the outer surface of particles.

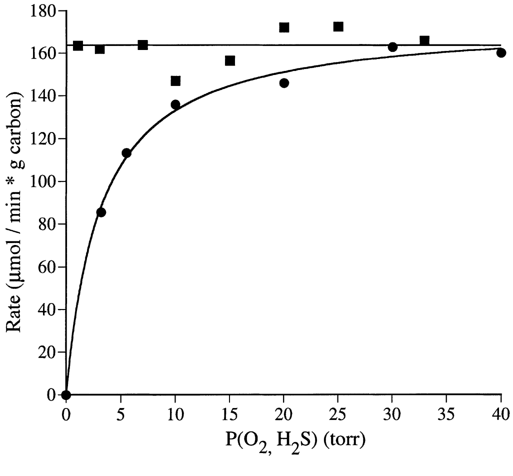

Fig. 9. Rate of hydrogen sulfide oxidation at different (●) oxygen, and (■) H_2S pressures.

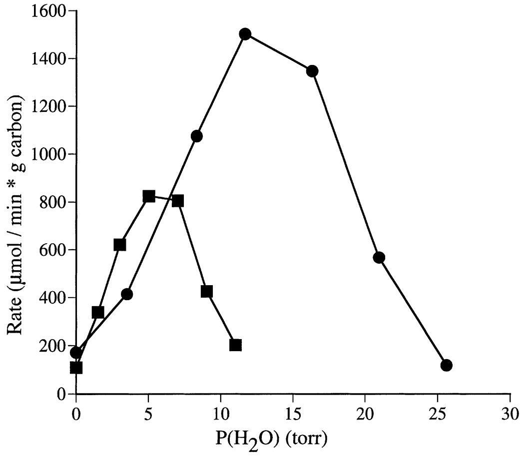

Fig. 10. Rate of hydrogen sulfide oxidation at different H_2O pressures. Reaction conditions: (■) T=298 K, (●) T=313 K; GHSV=134 200 h^{-1}, 30 mg catalyst, $P(H_2S)$=26.1 torr, $P(O_2)$= 14.5 torr; balance CO_2.

From the results shown above, it is clear that H_2O acts as an efficient medium for the oxidation of H_2S over activated carbon. An indication of the promotion

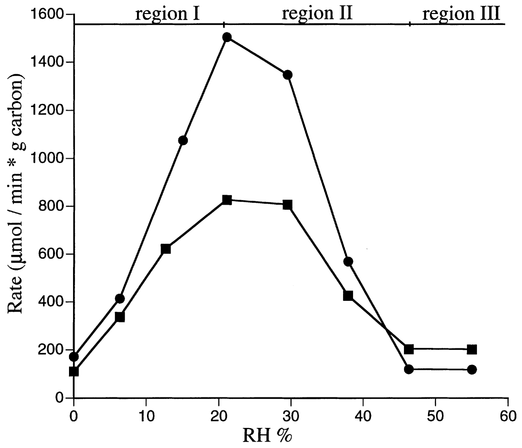

Fig. 11. Rate of hydrogen sulfide oxidation at different RH%: (■) T=298 K, (●) T=313 K. Reaction conditions: GHSV= 134 200 h^{-1}, 30 mg catalyst, $P(H_2S)$=26.1 torr, $P(O_2)$=14.5 torr; balance CO_2.

of the catalytic activity operated by water was already present in the literature. It had been reported that the complete exhaustion of carbon can occur only if the feed gas has a relative humidity of at least 50%, and Klein and Henning proposed a mechanism whereby the catalytic reaction occurs inside a water film on the surface of carbon [6].

These findings, however, have not previously been corroborated by kinetic measurements of the effect of water. From our kinetic results, we can state that water has a catalytic effect, acting in a manner similar to that found with sulfur but at lower temperatures, when H_2O retains its liquid phase. At higher temperatures, the effect of water, above its boiling point, is reported to be very poor and the presence of liquid sulfur in these conditions may also affect the results. A positive reaction order with oxygen implies that the actual catalytic step is the activation of O_2 by the carbon surface. The influence of water also implies that the formation of a liquid layer inside the pores of the carbon is an important requirement for the catalytic reaction. It is hypothesized that chemisorbed oxygen or oxygen radicals will react with chemisorbed or dissolved/dissociated H_2S. The experimental observation of almost zero order in H_2S points to a reaction with dissolved H_2S which, under these conditions, is partially dissociated into protons and hydrosulfide ions.

4. Conclusions

The use of active carbon as catalyst is an effective medium for the removal of low concentrations of H_2S (1–3%) from H_2O-rich tail gases after a geothermal plant. The presence of water has a beneficial effect on the overall catalyst performance. In particular, it enhances the reaction rate and the amount of sulfur that can be loaded before regeneration. Kinetic data for the oxidation of H_2S agree with a model where reaction occurs in a liquid layer by means of reaction of adsorbed oxygen with dissolved H_2S.

Acknowledgements

Financial support from CEE under Joule program (JOU2-CT92-0067) and by ENEL is gratefully acknowledged. Alessandra Primavera is grateful to Consorzio Pisa Ricerche for providing a grant.

References

[1] K.T. Li, C.S. Yen, N.S. Shyu, Appl. Catal. A: Gen. 156 (1997) 117.
[2] M. Novak, M. Zdrazil, Collect. Czech. Chem. Commun. 56 (1991) 1893.
[3] R.J.A.M. Terörde, P.J. van den Brink, L.M. Visser, A.J. van Dillen, J.W. Geus, Catal. Today 17 (1993) 217.
[4] J.J. Choi, M. Hirui, M. Shoda, Appl. Catal. A: Gen. 79 (1991) 241.
[5] A.N. Kaliva, J.W. Smith, Can. J. Chem. Eng. 61 (1983) 208.
[6] J. Klein, K.D. Henning, Fuel 63 (1984) 1064.
[7] H. Katoh, I. Kuniyoshi, M. Hirai, M. Shoda, Appl. Catal. B: Env. 6 (1995) 255.
[8] O.C. Cariaso, P.L. Walker Jr., , Carbon 13 (1975) 233.
[9] A.I. Chowdhury, E.L. Tollefson, Can. J. Chem. Eng. 68 (1990) 449.
[10] A.K. Dalai, A. Majumdar, A. Chowdhury, E.L. Tollefson, Can. J. Chem. Eng. 71 (1993) 75.
[11] M. Steijns, P. Mars, J. Catal. 35 (1974) 11.
[12] R. Sreeramamurthy, P.G. Menon, J. Catal. 37 (1975) 287.
[13] I. Coskun, E.L. Tollefson, Can. J. Chem. Eng. 58 (1980) 72.
[14] M. Steijns, F. Derks, A. Verloop, P. Mars, J. Catal. 42 (1976) 87.
[15] H.S. Fogler, Elements of Chemical Reaction Engineering, Prentice-Hall Int. Inc., London, 1992.