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Oxidation of H_2S on Active Carbon Catalyst[1]

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The air oxidation of H_2S to sulfur on activated coconut shell charcoal as catalyst was studied at 65–100°C. The pattern of sulfur deposition on the catalyst was followed from changes in surface area, pore-size distribution, reactivity and electron probe microanalysis. The first amounts of S are deposited in layers of over 20 S atoms thick in the larger pores accounting for about 70% of the catalytic activity. This is followed by a gradual filling of the micropores with a 4-atom thick layer of sulfur.

The reaction is quantitative for removal of H_2S from air and for recovery of sulfur. At temperatures above 120°C the molten sulfur flows down the catalyst bed and can be tapped off and the catalyst remains active for days or weeks.

This system was also used for following the advancing maxima in temperature profiles and rate profiles in a rapidly fouling catalyst bed in an exothermic reaction. These profiles are important for the effective use and life of such catalyst beds.

INTRODUCTION

The role of active carbon as a catalyst for oxidation of hydrogen sulfide to elemental sulfur or sulfur dioxide has been recognized only recently (*1–4*) though its properties as a good adsorbent have been known for more than a century. Swinarski and Siedlewski (*2*) have reported that the deposit of sulfur formed in the reaction,

$$H_2S + \tfrac{1}{2}O_2 = H_2O + S,$$

first covers the catalyst pores of 80–300 Å diameter and this does not affect the catalytic properties of the catalyst (charcoal). Puri *et al.* (*5*) have studied the fixation of sulfur by coconut shell charcoal and sugar charcoal on treatment with CS_2 and H_2S at high temperatures (100–800°C); they have found that the amount of sulfur fixed decreases with decrease in the hydrogen and oxygen contents of the charcoal. We undertook a detailed study (*6*) of the oxidation of H_2S by air on active carbons as catalyst in view of its potentialities for both the elimination of H_2S from water gas, synthesis gas, stack or flue gases, etc., and the subsequent recovery of sulfur. Our main results are presented below.

This oxidation was found to be an ideal reaction for following the temperature profiles and rate profiles in a rapidly fouling catalyst bed in an exothermic reaction. Such profiles measured by us have been published elsewhere (*7,8*).

EXPERIMENTAL METHODS

Since the sulfur formed in the oxidation of H_2S is deposited on the carbon catalyst, the progress of the reaction could be easily followed from the increasing weight of the catalyst. The apparatus (Fig. 1) consists of a simple McBain sorption balance with a quartz spiral of maximum load (10 g) and

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sensitivity (2.0 cm/g). The catalyst (1-5 g) was taken in a basket of fine stainless steel wire gauze and suspended from the quartz spiral with a thin stainless steel wire. The elongation of the spiral relative to a fixed reference point was measured correct to 0.01 mm with a cathetometer. A stream of H_2S was mixed with nitrogen (diluent) and air, preheated and sent over the catalyst. The product gas was passed through a calcium chloride U-tube or tested for H_2S or SO_2 as required. The lower part of the sorption balance containing the catalyst was kept in an aluminum-block furnace with a control of ±0.1°C on the set temperature.

The temperature rise of the catalyst bed was measured by keeping a thin-stem thermometer in the middle of the catalyst layer, suspending the catalyst basket from a glass rod instead of the quartz spiral, and using the same amount of carbon catalyst and same flow conditions as for the rate studies. Thermocouples could not be used for this purpose since they would be attacked by H_2S or they would readily catalyze the oxidation of H_2S.

Surface areas of the carbon catalysts were determined by benzene adsorption in a dynamic system using Rubinshtein's apparatus (*9*), taking the molecular area for benzene as 41 Å^2. Surface areas of active carbons determined by benzene adsorption are sufficiently reliable (*10,11*) and comparable (*12*) with the areas obtained from nitrogen adsorption in a conventional volumetric apparatus.

Materials

Hydrogen sulfide taken from a normal Kipp's apparatus was washed free of acid vapors and dried over anhydrous calcium chloride. Nitrogen and air were drawn from gas cylinders and dried over anhydrous calcium sulfate ("Dryal") and silica gel. In special adsorption experiments in the absence of any oxygen, the nitrogen was freed of traces of oxygen by first bubbling through alkaline pyrogallol and then passing over copper turnings at 350°C and finally dried over Dryal and silica gel.

Several types of active carbons were tried as catalysts: these included various grades of carbon made from coke, carbon from a Shell naphtha gasification unit in Madras, and activated coconut shell charcoal. Of these the most active catalyst was activated coconut shell charcoal, made in a pilot plant of our laboratory and marketed under the name Hykol-CSG. Hence all

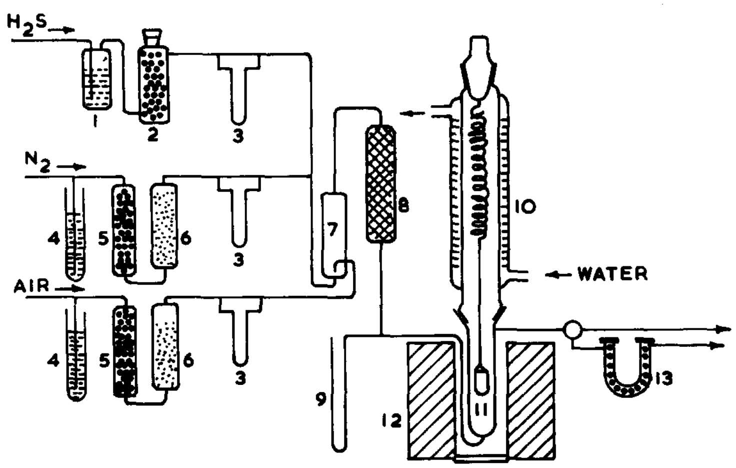


FIG. 1. Sorption balance setup for H_2S oxidation studies. (1) water scrubber, (2) anhydrous calcium chloride, (3) capillary flowmeter, (4) water leg, (5) anhydrous calcium sulfate, (6) silica gel, (7,8) gas mixers, (9) manometer, (10) sorption balance, (11) catalyst basket, (12) furnace and (13) calcium chloride tube.

further work was carried out with this catalyst (2–4 mm particles, 490 m^2/g).

RESULTS AND DISCUSSION

The increase in weight of the carbon catalyst as a function of time for experiments at furnace temperatures of 65–100°C is shown in Fig. 2. The sulfur deposition on the catalyst is higher at higher temperatures. However, the expected exponential increase with temperature in the rate of the reaction is not observed, obviously due to mass transfer limitations from gas phase to the surface of the catalyst, particularly since the major part of the reactant gas can bypass the catalyst basket in the sorption balance setup. Preliminary experiments have shown that (a) no sulfur is deposited on the walls of the reactor tube, (b) sulfur powder taken in the catalyst basket has no catalytic activity for H_2S oxidation under these conditions, (c) no SO_2 is formed at these temperatures, and (d) the adsorption of water (the product of the oxidation reaction) on the catalyst at these temperatures is negligibly small; since the carbon has been initially dried only at 110°C, it is only to be expected that further adsorption of water at about this temperature cannot be appreciable.

Assuming that the weight increase of the catalyst is exclusively due to the sulfur deposited (and not partly due to adsorption of H_2S), the rate of the oxidation reaction can be calculated from data similar to that given in Fig. 2. The rates are given in mg S/(g carbon hr). The rate–time plots are characterized by a sharp maximum during the first hour, followed by a progressive decrease in the rate as the surface of the carbon is covered more and more by sulfur (Fig. 3).

Temperature Rise in the Catalyst Bed

From the heats of formation of H_2S and H_2O, the heat of the reaction can be calculated as 53 kcal/mole. Due to this highly exothermic reaction the temperature of the catalyst rises rapidly during the reaction (Fig. 3). The time–temperature profile of the catalyst at different furnace temperatures is given in Fig. 4. It is also observed that at a fixed flow rate the rise in temperature of the catalyst depends on the amount of carbon taken. In a fixed catalyst bed with 10 g carbon and without diluent nitrogen, even at a furnace temperature of 100°C the catalyst temperature rose abruptly within a few minutes to over 350°C, the carbon started to burn and the

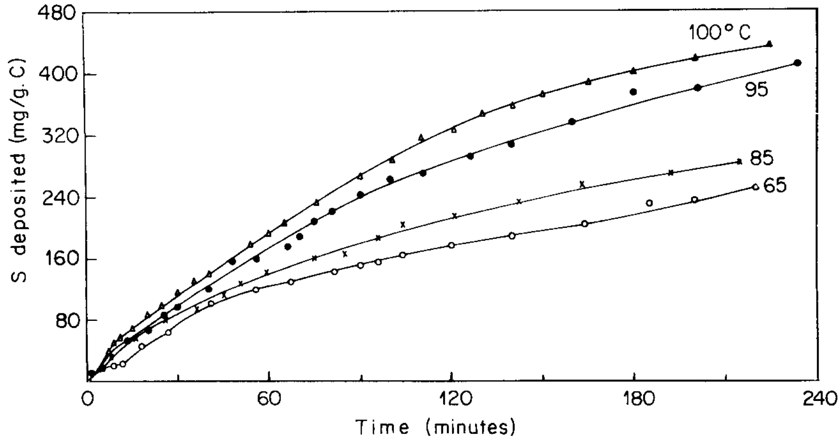


FIG. 2. Weight increase of the catalyst (due to sulfur deposition) as a function of time at different furnace temperatures.

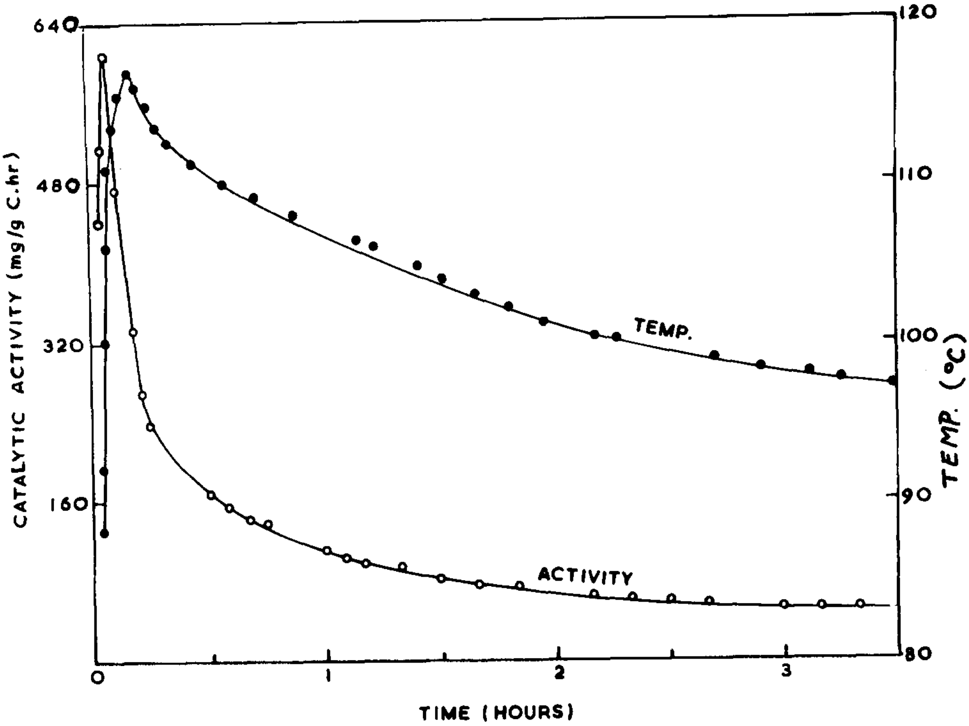


FIG. 3. Variation of catalytic activity and catalyst temperature with time at a furnace temperature of 85°C. Gas flow: H_2S, air, N_2, 2, 5, 25 liters/hr.

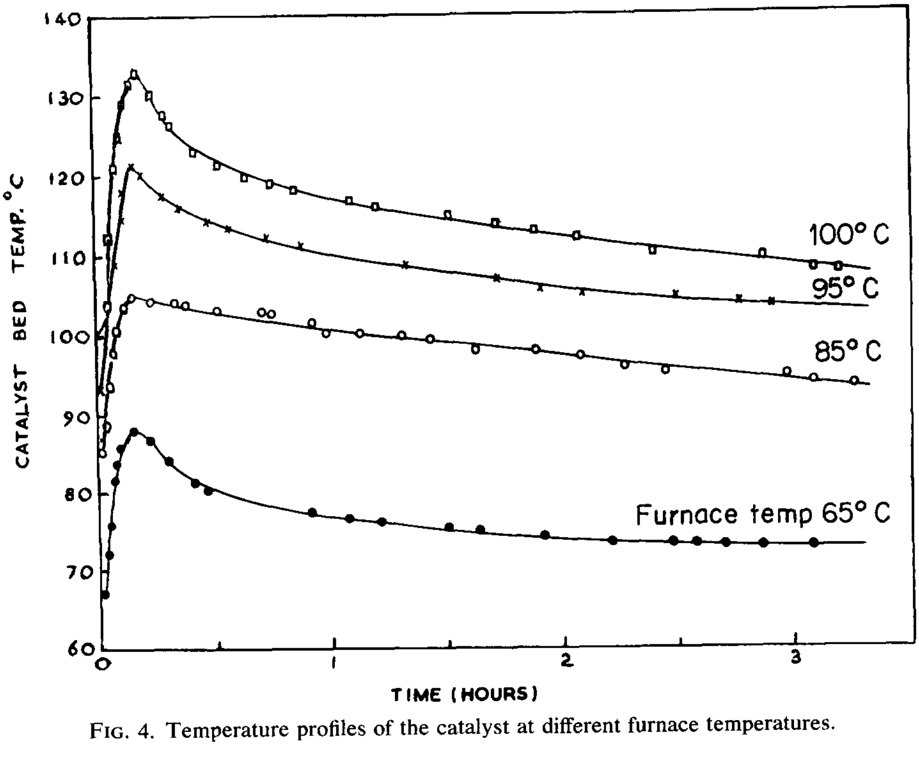


FIG. 4. Temperature profiles of the catalyst at different furnace temperatures.

whole catalyst mass became red hot. (N. B. Catalyst temperature in this context means only the temperature of the gas measured in the catalyst bed; the surface temperature of the catalyst particles can be much higher, but this is not easy to measure accurately in a packed bed of catalyst particles of 2–4 mm size.)

The above experiments made it imperative (a) to dilute the gas stream considerably with nitrogen and (b) to take only a small quantity of catalyst so as to reduce this temperature rise of the catalyst during any kinetic study of the reaction. The effect of dilution with nitrogen on the temperature rise of the catalyst showed that the peak in the time–temperature curve was considerably lowered by dilution, though the steady temperature attained after 1.5–2 hr was not at all affected by it. Up to 25 liters/hr of N_2 could be used as diluent with 2 liters/hr H_2S and 5 liters/hr air, without affecting the weighing by the sorption balance.

Both the temperature of the catalyst and the catalytic activity (weight increase of the catalyst in mg/g carbon/hr) show a steep maximum within 30 min of starting the experiment (Fig. 3). The high initial activity of the catalyst may partly be attributed to the increased temperature of the catalyst. But it has been repeatedly found in experiments in the range 60–120°C that the maximum in the rate curve is reached 5–20 min before that in the temperature–time curve, as shown in Fig. 3. This could be partly due to the time lag involved in the measurement of temperature. More probably, by the time the catalyst reaches the maximum temperature, part of its surface is already covered by the deposited sulfur and the reaction rate has already decreased considerably. This suggests that part of the carbon surface is extremely active and the vigorous reaction on this part raises the catalyst temperature, which in turn accelerates the reaction. However, the sulfur formed as

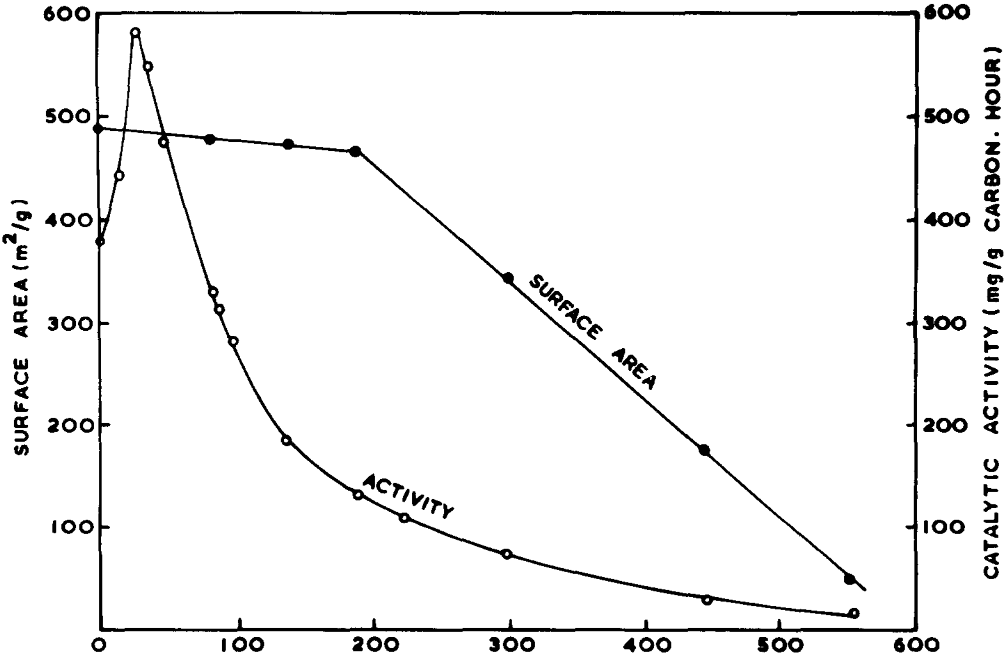


FIG. 5. Change in catalytic activity and surface area of catalyst with increasing sulfur deposition.

product of the reaction soon covers this highly active surface and the catalytic activity decreases rapidly, thereby lowering the catalyst temperature as well.

Changes in Texture of the Catalyst

Several catalyst samples taken in the sorption balance were exposed to the H_2S–N_2–air mixture at 100°C for different periods so that known amounts of sulfur could be deposited on them. Their surface areas were then determined by benzene adsorption. (It was ascertained beforehand that sulfur itself does not adsorb benzene to any appreciable extent.) The results are shown in Fig. 5. The change in catalytic activity for different amounts of sulfur deposited at 100°C on the same weight of catalyst is also shown in Fig. 5. For the deposition of the first 160 mg S/g catalyst, the surface area is reduced by about 5%, but the catalytic activity is reduced to about 30% of the original. It is the higher accessibility (larger pores, as shown in Fig. 6) of this 5% of the total surface that raises the catalyst temperature which in turn accelerates the reaction. Thereafter the reaction proceeds slowly, but the remaining surface area decreases more rapidly since this area is in the predominant smaller micropores (Table 1).

The pore-size distributions of catalyst samples exposed to an H_2S–air–N_2 stream at 100°C for 0, 45, 100 and 240 min were determined from water desorption isotherms of the catalyst samples. These results are shown in Fig. 6. The first amounts of sulfur (up to 45 min) are deposited in the relatively large pores, scarcely affecting the main micropore region which accounts for the predominant part of the

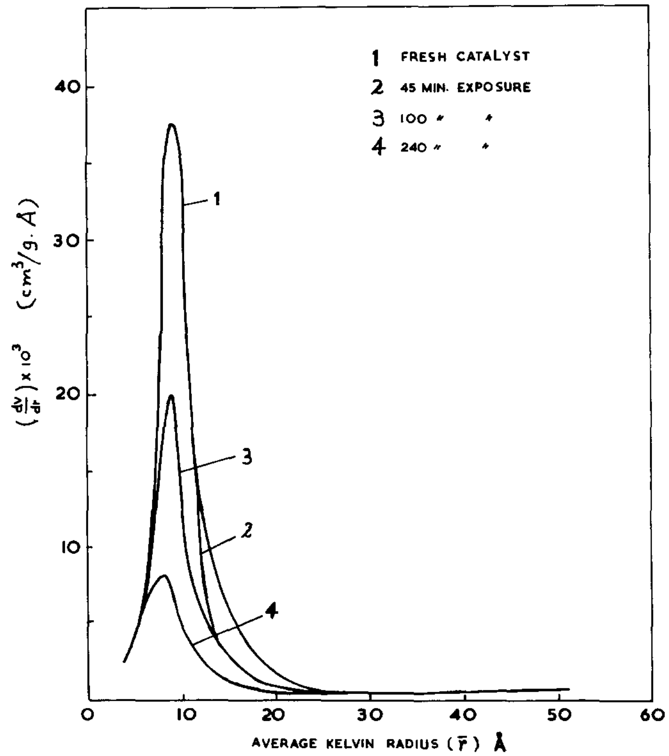


FIG. 6. Pore-size distribution of the catalyst samples exposed to H_2S–air–N_2 mixture for various periods. Samples 1–4 contain 0, 155, 290 and 440 mg S/g catalyst, respectively, deposited on them.

TABLE 1

EFFECT OF S DEPOSITION ON S-FREE SURFACE AREA[a]

Exposure time (min)	Sulfur deposited (mg S/g C)	Decrease in S-free surface area (m^2/g)	S mg/m^2 of S-covered surface
11	82	11	7.32
25	96	14	6.76
45	103	24	4.30
115	199	147	1.35
300	361	316	1.14
720	572	448	1.28

[a] Carbon taken, 1 g; H_2S/N_2/air, 2/5/25 liters/hr; Temp. 100°C.

surface area of active carbon. Further deposition of sulfur progressively fills up the micropores in the carbon. These changes in pore-size distribution readily explain the observed pattern of surface area variation on sulfur deposition (Fig. 5).

It may be argued that the rapid weight increase of the catalyst during the first hour (from which a high rate of reaction is inferred) is only due to adsorption of H_2S on the carbon and not due to reaction and consequent deposition of sulfur. However, experiments carried out with H_2S and also with H_2S diluted with oxygen-free nitrogen, in the absence of air, indicate that most of the H_2S adsorbed is readily oxidized by chemisorbed oxygen invariably present on the carbon surface. This was evident, for instance, from the temperature rise of the catalyst and from the water formed (collected over anhydrous calcium chloride and weighed) even during these "adsorption" measurements. The sulfur deposited could also be extracted by carbon disulfide. The weight of the catalyst did not decrease when it was evacuated at 25°C after its use in the oxidation reaction for 4–5 hr, indicating that there was no physically adsorbed H_2S remaining on the catalyst surface. Even if some H_2S was present in the chemisorbed state, it should be negligible compared to the total weight increase of 300–400 mg/g catalyst in a run.

Electron spin resonance studies of the interaction of H_2S with evacuated samples of the present active carbon catalyst also show (*13*) that adsorbed H_2S readily reacts with the residual surface oxygen on the carbon, thereby liberating free radicals on the carbon surface. On opening the sample tube to air, the ESR signal disappears completely, oxygen annihilating the free radicals instantaneously.

X-Ray Study

Samples of catalyst exposed to H_2S–N_2–air mixture for various periods were subjected to an X-ray study. No sulfur pattern was seen, apparently because the deposited sulfur is in an amorphous state.

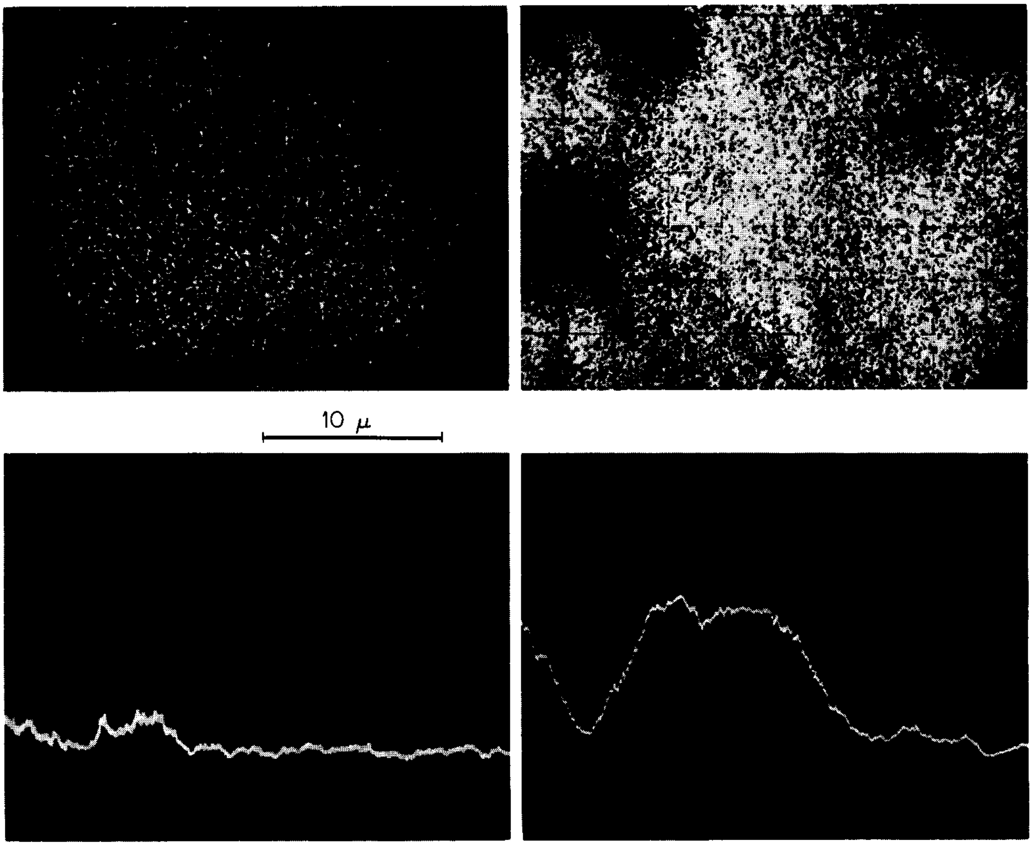
Electron Probe Microanalysis

An electron probe microanalysis (EPMA) study of sulfur on the carbon catalyst was carried out by one of us (P.G.M.) in 1968 in the Department of Mechanical Engineering, Twente University of Technology, Enschede, The Netherlands. Details of this apparatus have been given in an earlier study by Menon and Prasad (*14*). The EPMA photos show the concentration of sulfur in a 1μm thick layer of the catalyst surface after exposure to the H_2S–N_2–air mixture for 30 min and for 4 hr (Fig. 7). A scan of the sulfur profile along the central horizontal line of the two photos is also shown in Fig. 7. Sulfur is formed in the early stages in lumps or as islands, not as a continuous film.

Analogy to Coke Formation on Catalysts

It is possible to draw here a parallelism between sulfur deposition on carbon catalyst and coke lay-down on catalysts used in many hydrocarbon reactions like cracking, isomerization and hydrocracking. As early as 1945 Voorhies (*15*) obtained a relation between coke on the catalyst, C_c, and the process time t for catalytic cracking:

$$C_c = A_1\, t^{1/2} \tag{1}$$



30 min

4 hrs

FIG. 7. Electron probe microanalysis of sulfur in a 1 μm thick layer on the catalyst surface after 0.5 hr and 4 hr exposure to H_2S–air–N_2 mixture at 100°C. The scan of sulfur profiles along the central horizontal line of the photographs is shown in the oscilloscope traces in the lower photographs.

From Blanding's data (*16*) it is possible to derive a similar relation between catalyst activity k and t:

$$k = A_2/t^{1/2}. \qquad (2)$$

Combining these two relations leads to

$$k = A_3/C_c, \qquad (3)$$

where A_1, A_2 and A_3 are constants.

According to Van Zoonen (*17*) this inverse proportionality between the rate of coke formation and the amount of coke already present on a catalyst is of a general character and of wide applicability, and the assumption that the rate-determining step in this reaction is the diffusion of the reactants through coke-filled pore entrances is a plausible hypothesis to explain this phenomenon. Froment and Bischoff (*18*), however, propose that a gradual physical covering of the active sites by coke can explain the above empirical equations. [Equation (3) assumes infinite activity at zero time and hence this equation should be applied only after the first unit of time]. Whatever may be the exact mechanism, our data on sulfur deposition on active carbon catalyst also fit Eq. (1), (2) and (3) satisfactorily. A typical plot of catalyst activity vs reciprocal of sulfur deposited [Eq. (3)] is shown in Fig. 8.

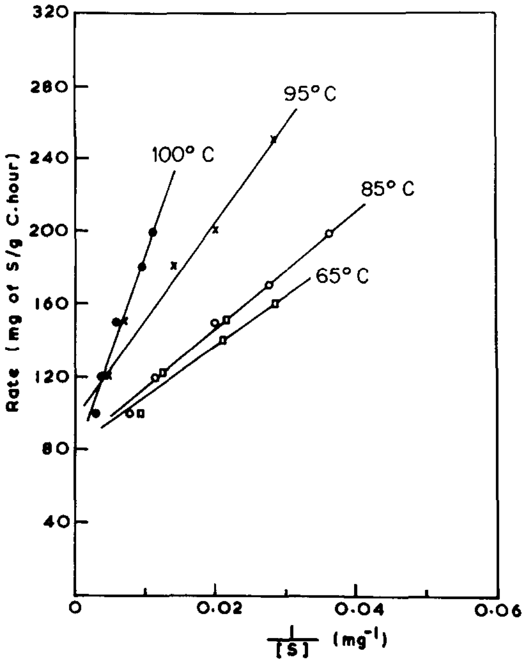


FIG. 8. Dependence of reaction rate on the reciprocal of sulfur already present on the catalyst at various reaction temperatures.

Kinetics of H_2S Oxidation

Catalyst fouling usually leads to anomalous kinetic results. In the present case, the reaction rate is affected by (a) the continuous change in the effectiveness factor due to the texture of the catalyst changing as a result of sulfur deposition and (b) the gradual decrease in the number of active sites due to their physical covering by sulfur. From experiments on pelleted and powdered catalysts, made from the same active carbon used in the present studies, rate data have been obtained for the oxidation of H_2S in the temperature range 70–100°C with 1–4% H_2S in the gas stream. The data can be expressed in terms of a Langmuir–Hinshelwood model, incorporating a term for catalyst fouling, similar to that proposed by Otake *et al.* (*19*). Details of this kinetic study will be published separately.

Temperature Profiles and Rate Profiles in a Packed Catalyst Bed for H_2S Oxidation

The oxidation of H_2S has also served as an ideal system to observe the maxima in temperature profiles and rate profiles in a rapidly fouling catalyst bed used for an exothermic reaction and to follow the progress of these maxima through the catalyst bed as a function of process time. Such advancing maxima, first predicted theoretically by Froment and Bischoff (*18*) in 1961, have been experimentally measured in the present studies and published earlier (*7,8*). These studies were carried out in an 11 × 1½ in. catalyst bed in a glass reactor with provision for determining the temperature and the sulfur laydown in successive layers of the catalyst bed (*8*). From the relatively more accurate

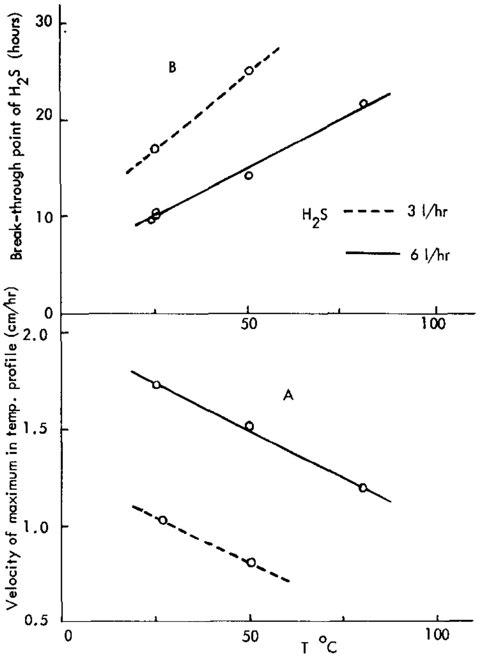


FIG. 9. Temperature dependence of (A) velocity of maximum in temperature profile and (B) breakthrough point of H_2S. Experiments with a catalyst bed of 11 × 1½ in. For experimental details see text and Ref. (*7,8*).

temperature profiles, the velocity of the advancing maximum or peak in the profile could be calculated. This peak velocity is constant for a given reactor-wall temperature and gas flow rate. It increases with increasing H_2S concentration and decreasing reactor temperature. The effective life of the catalyst bed was measured from the breakthrough of H_2S at the exit end of the reactor. Typical data on peak velocities and breakthrough points for H_2S are shown in Fig. 9. The effective life of the catalyst bed naturally increases with decreasing peak velocity.

Continuous Operation

By keeping the catalyst bed at 120°C or above it was possible to run the oxidation of H_2S as a continuous process. Then molten sulfur from the catalyst flows down the bed and can be tapped off at the bottom of the reactor. Such catalyst beds remain active for complete and quantitative removal of H_2S from gas streams for several days or weeks depending on the concentration of H_2S in the gas stream. Thus active carbon as a catalyst is very useful both for removal of low concentrations of H_2S from gas streams or air and for recovery of sulfur.

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REFERENCES

1. Bankowski, O., and Pasternak, R., *Ger. (East) Pat.* 12,805, Mar. 1, 1957; *Chem. Abstr.* **53,** 3624 (1959).
2. Swinarski, A., and Siedlewski, J., *Gaz. Woda Tech. Sanit.* **31,** 462 (1957); *Chem. Abstr.* **52,** 783 (1958); *Chem. Stoso.* **5,** 211 (1961); *Actes Congr. Catal., 2nd, 1960* **2,** 2345 (1961).
3. Siedlewski, J., and Trawinski, S., *Rocz. Chem.* **9,** 1347 (1964).
4. Storp, K., *DECHEMA (Deut. Ges. Chem. Apparatewesen) Monogr.* **64,** 91 (1971).
5. Puri, B. R., Jain, C. M., and Hazra, R. S., *J. Indian Chem. Soc.* **43,** 67 (1966).
6. Sreeramamurthy, R., PhD thesis, Andhra University, India, 1972.
7. Menon, P. G., and Sreeramamurthy, R., *J. Catal.* **8,** 95 (1967).
8. Menon, P. G., Sreeramamurthy, R., and Murti, P. S., *Chem. Eng. Sci.* **27,** 641 (1972).
9. Rubinshtein, A. M., and Klyachko-Gurvich, A. L., *Kinet. Catal. (USSR)* **5,** 523 (1962).
10. Davies, R. G., *Chem. Ind. (London)* 160 (1952).
11. Hassler, J. W., "Activated Carbon," p. 212. Chem. Publ., New York, 1963.
12. Kuczynski, W., Andrzejak, A., Wesolowski, J., Fiedorow, R., and Dziewanowska, *Int. Chem. Eng.* **4,** 413 (1964).
13. Menon, P. G., Nieuwenhuise, B., and Mars, P., unpublished data.
14. Menon, P. G., and Prasad, J., *J. Catal.* **17,** 238 (1970).
15. Voorhies, A., *Ind. Eng. Chem.* **37,** 318 (1945).
16. Blanding, F. H., *Ind. Eng. Chem.* **45,** 1186 (1953).
17. Van Zoonen, D., *Proc. Int. Congr. Catal., 3rd, 1964* p. 1319 (1965).
18. Froment, G., and Bischoff, K. B., *Chem. Eng. Sci.* **16,** 189 (1961).
19. Otake, T. O., Tone, S., Yokota, Y., and Yoshimura, K., *J. Chem. Eng. Jap.* **4,** 155 (1971).