

## The Mechanism of the Catalytic Oxidation of Hydrogen Sulfide

### II. Kinetics and Mechanism of Hydrogen Sulfide Oxidation Catalyzed by Sulfur<sup>1</sup>

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The kinetics of the catalytic oxidation of hydrogen sulfide by molecular oxygen have been studied in the temperature range 20–250°C. The primary reaction product is sulfur which may undergo further oxidation to SO<sub>2</sub> at temperatures above 200°C.

From the kinetics of this autocatalytic reaction we derived an oxidation–reduction mechanism. The two rate influencing steps are the chemisorption of oxygen and the reaction between dissociatively chemisorbed H<sub>2</sub>S and chemisorbed oxygen.

The high activation energy for the formation of SO<sub>2</sub> (120 kJ mol<sup>-1</sup>) explains the high selectivity towards sulfur, although SO<sub>2</sub> is thermodynamically the most favored product. At temperatures above 300°C, where the formation of SO<sub>2</sub> occurs readily, the SO<sub>2</sub> may be an intermediate in the reaction of H<sub>2</sub>S with O<sub>2</sub> leading to S and H<sub>2</sub>O.

#### INTRODUCTION

In Part I (1) we concluded that sulfur is a catalyst for the oxidation of hydrogen sulfide. Sulfur deposits in the pores of porous materials and causes an autocatalytic effect. On the basis of some ESR measurements we proposed that sulfur radicals are the sites for oxygen chemisorption. From kinetic data we obtained evidence for a dissociative adsorption of hydrogen sulfide.

Kinetic data on this reaction are scarce. A survey of the more important publications is given in Table 1. Some of the work (2–5) could be affected by the large exothermicity of the reaction at high concentration and conversion levels. Sreeramamurthy (6) and Cariaso (7) tried to fit their

kinetic data on activated carbon into a mechanism. Cariaso concluded that the chemisorption of oxygen by the carbon surface is the first step in the mechanism, but that the second step, the impact of H<sub>2</sub>S with chemisorbed oxygen, determines the overall rate. Sreeramamurthy supposed that H<sub>2</sub>S and O<sub>2</sub> both chemisorb on the carbon surface. The chemisorption of oxygen is dissociative. The reaction between the chemisorbed species leading to sulfur and water is rate determining.

The possibility that SO<sub>2</sub> is an intermediate was also discussed by some authors. The opinion of Brodsky and Pagny (3) is that SO<sub>2</sub> is not an intermediate; Prettre and Sion (4), on the other hand, asserted the contrary. Cariaso (7) excluded SO<sub>2</sub> as an intermediate on the basis of thermodynamic calculations assuming that S<sub>2</sub> is the predominant species in the gas phase at

<sup>1</sup> This publication is the second in a series on the mechanism of hydrogen sulfide oxidation; see (1) for Part I.

TABLE 1  
Survey of Literature Data on the Kinetics of H<sub>2</sub>S Oxidation

	Catalyst	Temp range (°C); concn (vol%)	Activation energy $E^a$ (kJ mol <sup>-1</sup> ); reaction orders in O <sub>2</sub> and H <sub>2</sub> S	Remarks
1. Brodsky and Pagny (3)	a. Pumice	a. $T$ , 260–420 H <sub>2</sub> S, 2.5–3.0 O <sub>2</sub> , 1.5–7.9	a. $E^a = 22.6$ –34.4 $n_{O_2} = 0.0$ –0.1 (300°C)	a. At high temperatures and high oxygen concentration formation of SO <sub>2</sub> occurs
	b. Pumice + iron oxide	b. $T$ , 200–300 H <sub>2</sub> S, 2.5–3.0 O <sub>2</sub> , 1.5–16.0	b. $E^a = 27.2$	b. Impregnation with iron oxide leads to an increase of the activity with a factor 10
2. Prettre and Sion (4)	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> $S_{BET} = 220$ m <sup>2</sup> /g $V_p = 0.15$ cm <sup>3</sup> /g	$T$ , 40–150 H <sub>2</sub> S, 0.5 <sup>b</sup> O <sub>2</sub> , 0.2–1.5	$E^a = 33.5$ ( $T < 120^\circ\text{C}$ ) $E^a = 14.7$ ( $T > 120^\circ\text{C}$ ) $n_{H_2S} = 0.5$ $n_{O_2} = 0.85$	No SO <sub>2</sub> is formed even at O <sub>2</sub> /H <sub>2</sub> S = 3.
3. Puri <i>et al.</i> (5)	a. Active charcoal $S_{BET} = 300$ –400 m <sup>2</sup> /g	a. $T$ , 120–240 H <sub>2</sub> S, 5 <sup>b</sup> O <sub>2</sub> , 5–80	a. $E^a = 25.1$ $n_{O_2} = 0.1$	a + b. A part of the sulfur formed is bound irreversibly by the carbon
	b. Carbon black $S_{BET} = 25$ –45 m <sup>2</sup> /g	b. $T$ , 120–240 H <sub>2</sub> S, 5 <sup>b</sup> O <sub>2</sub> , 30	b. $E^a = 12.6$ –16.8	
4. Sreeramamurthy (6)	Active carbon $S_{BET} = 320$ m <sup>2</sup> /g	$T$ , 70–100 H <sub>2</sub> S, 4 <sup>b</sup> O <sub>2</sub> , 2 <sup>b</sup>	$E^a = 6.7$ –29.3 $n_{O_2} = 0.5$ $n_{H_2S} = 1$	Low activation energy is caused by diffusional influence according to the author
5. Cariaso (7)	Carbon molecular sieve (CMS)	$T$ , 100–160 H <sub>2</sub> S, 0.25–0.5 O <sub>2</sub> , 1.0	Measured, $E^a = 20.1$ Caled, $E^a = 40.2$ $n_{H_2S} = 1$ $n_{O_2} = 0$	Diffusional limitations <sup>c</sup>

<sup>a</sup> Energy of activation calculated from reaction rates and not from rate constants.

<sup>b</sup> The concentration is varied around this value.

<sup>c</sup> We calculated that the rates were largely determined by the diffusion rate of H<sub>2</sub>S through the hangdown tube of the thermobalance to the catalyst sample.

150°C. It is known, however, that under Cariaso's conditions S<sub>3</sub> is the main S-species (8). Summarizing, it can be concluded that from the literature data it is not possible to prefer one mechanism.

The present paper describes experiments on concentration and temperature dependences of the H<sub>2</sub>S oxidation rate on different porous materials. A mechanism is proposed which covers most of the kinetic data. The oxidation of sulfur was studied to investigate the consecutive reaction leading to SO<sub>2</sub> and SO<sub>3</sub>. The role of SO<sub>2</sub> as an intermediate is also discussed.

## METHODS

### Apparatus

The fixed-bed reactor system and the thermobalance have already been described (1). All our experiments were carried out

under near differential conditions; the highest conversions of H<sub>2</sub>S or O<sub>2</sub> were 0.25. Also the sulfur, deposited during reaction, was equally distributed over the catalyst bed. The uniform yellow color of the bed in the case of a zeolite catalyst pointed to this equal distribution of sulfur. Temperature effects were negligible because the maximum (i.e., adiabatic) increase in temperature amounts to only 3°C in the case of 10% conversion of 0.5 vol% H<sub>2</sub>S.

### Catalysts

In Table 2 the catalysts used are listed and some properties relating to their pore structure are given. The surface area was calculated by applying the BET equation to argon adsorption data obtained at -196°C. The pore volume was calculated from the difference between the apparent

TABLE 2  
Catalyst Data

Catalyst	Manufacturer	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore vol (cm <sup>3</sup> g <sup>-1</sup> )
Molecular sieve 13X	Union Carbide	470	0.24
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Peter Spence	190	0.34
	Degussa	78	0.78
Carbon molecular sieve (CMS)	Seifert K. G.	1000	—
Activated carbon RBWI <sup>a</sup> (sugar)	Norit	950	0.81
	Our lab.	1050	0.45

<sup>a</sup> This catalyst was extracted with dilute sulfuric acid to remove the inorganic impurities.

catalyst volumes in mercury and methanol at room temperature.

Carbon molecular sieve (CMS) is a very pure carbon with a pore radius mainly in the range of 10–12 Å. The material is prepared by carbonization of vinylidene chloride polymer.

## RESULTS

Kinetic experiments were carried out not only on different materials (Table 2) but also at different sulfur contents of these porous materials. As we already pointed out in Part I (1) the oxidation rate of H<sub>2</sub>S can be strongly dependent on the amount of sulfur deposited in the micropores. For materials which have a low intrinsic oxidation activity (= initial oxidation rate), the characteristic course of the activity as a function of sulfur uptake by the material is given in Fig. 1. There are three distinct ranges, A, B, and C. In range A the activity increase with reaction time is due to the autocatalytic activity of the sulfur deposited in the pores. In range B a decrease of the activity is observed because pores become filled up with sulfur which results in a considerable decrease of the specific surface area of sulfur. A stationary activity level is reached in range C, when the amount of sulfur formed equals the amount of sulfur desorbed from the large pores left

unfilled and from the outer surface of the particles. In case a material possesses a high intrinsic activity compared to the autocatalytic activity, deposition of sulfur lowers the activity and branch A is not observed.

For experiments in the regions A or B where the activity did not attain a stationary level as a function of reaction time, the rate data are always compared at the same sulfur content. The sulfur content is calculated by integration of the H<sub>2</sub>S oxidation rate in the fixed-bed experiments. The desorption rate of sulfur is in this case much smaller than the oxidation rate.

At a stationary activity level (region C), the sulfur content of the material does not change further. For some materials it is even possible to vary concentrations and temperature in a limited region without

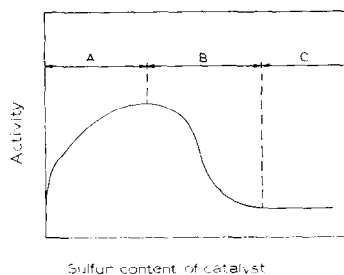


FIG. 1. Catalytic activity as a function of the amount of sulfur deposited in the porous material.

TABLE 3  
Rate Dependence on the Oxygen Concentration

Catalyst	S [g (g cat) <sup>-1</sup> ]	T (°C)	Vol%		Reaction order
			H <sub>2</sub> S	O <sub>2</sub>	
MS 13X	0.08	130	1.27	0.087-0.403	1.05
	0.16	130	1.27	0.087-0.403	1.02
MS 13X <sup>a</sup>	0.304 <sup>a</sup>	151	1.20	0.11-0.78	0.83
MS 13X	0.304	22	0.25	1.04-5.78	0.60
Norit RBWI	0.12	180	1.0	0.15-0.63	% O <sub>2</sub> > 0.35, 0.0 % O <sub>2</sub> < 0.35, 0.85
CMS	0.15	200	0.75	0.075-0.375	% O <sub>2</sub> > 0.15, 0.5
	0.30	200	0.75	0.075-0.375	% O <sub>2</sub> < 0.15, 0.75
Carbon (sugar) <sup>a</sup>	0.70 <sup>a</sup>	130-150	0.30	0.65-1.76	0.23 ± 0.10
	0.70 <sup>a</sup>	170-190	1.68	0.07-0.57	0.79 ± 0.10
γ-Al <sub>2</sub> O <sub>3</sub> (Degussa) (Peter Spence)	0.05-0.40	80	1.0	0.17-0.50	0.95
	0.40	115	0.74	0.10-0.60	1.0

<sup>a</sup> Stationary activity level of branch C in Fig. 1.

changing the amount of adsorbed sulfur. Such a material is molecular sieve 13X, where the amount of sulfur adsorbed corresponds with the volume filling of supercages in the aluminosilicate framework. In a separate experiment we found that the relative sulfur pressure ( $P_{rel}$ ) can be varied in the range  $P_{rel} = 0.005-0.25$  without changing the amount of adsorbed sulfur significantly.

In the case of the fixed-bed experiments the kinetic parameters can be derived from

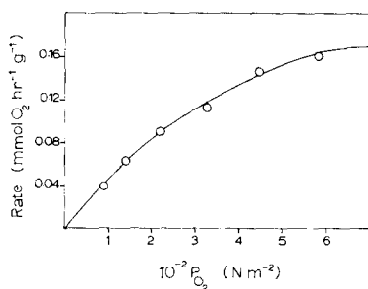


Fig. 2. Oxygen concentration dependence of the rate on activated charcoal prepared from sugar. Catalyst at stationary level;  $T = 170^\circ\text{C}$ ;  $P_{H_2S} = 6.8 \times 10^2 \text{ N m}^{-2}$ ; sulfur content:  $0.7 \text{ g (g carbon)}^{-1}$ .

the conversions of oxygen and hydrogen sulfide. At temperatures below  $200^\circ\text{C}$  the selectivity towards sulfur is always above 90% assuming that the main by-product is  $\text{SO}_2$ .

#### Oxygen Concentration Dependence of the Rate

A part of the results is summarized in Table 3. The amount of sulfur adsorbed on the catalyst does not affect the reaction order significantly. The oxidation rate of  $\text{H}_2\text{S}$  is, however, a function of the sulfur charge of the material.

The oxidation rate on zeolite 13X shows a first order dependence on the concentration over a wide concentration and temperature range. Only at a high excess of oxygen (10-50 times the stoichiometric amount) can a lower order be observed.

For the active carbons the observed reaction order varies from zero to one. As a typical example the rate on activated charcoal prepared from sugar is plotted in Fig. 2 as a function of oxygen concentration. The transition of first order to zero

TABLE 4  
Rate Dependence on the Hydrogen Sulfide Concentration

Catalyst	S[g(g cat) <sup>-1</sup> ]	T (°C)	Vol%		Reaction order	
			H <sub>2</sub> S	O <sub>2</sub>		
MS 13X	0.12	130	0.24	-0.64	0.25	0.10
MS 13X <sup>a</sup>	0.305 <sup>a</sup>	150	0.14	-0.62	0.26	0.04
γ-Al <sub>2</sub> O <sub>3</sub> (Degussa) (Peter Spence)	0.04-0.40	80	0.23	-1.47	0.50	0.05
	0.40	115	0.11	-0.55	0.23	0.06
Norit RBWI	0.12	180	0.5	-1.25	0.51	0.5
CMS	0.10	185	0.135-0.5		0.25	0.73
	0.20	185	0.135-0.5		0.25	0.50
	0.25	180	0.125-0.5		0.50	0.50
	0.50	180	0.125-0.5		0.50	0.44
Active carbon <sup>a</sup> (sugar)	0.70 <sup>a</sup>	130-150	0.11	-0.65	1.50	0.60 ± 0.06
	0.70 <sup>a</sup>	170-190				

<sup>a</sup> Stationary activity level of branch C in Fig. 1.

order was also observed for other types of activated charcoal. The activated charcoal prepared from sugar was free of inorganic impurities and available in batches of uniform composition. The autocatalytic effect of sulfur was very pronounced for this material, which made it especially attractive for kinetic studies.

#### Hydrogen Sulfide Concentration Dependence of the Rate

Table 4 gives a survey of the results. A zero order dependence was observed for the oxidation rate on zeolite 13X and γ-Al<sub>2</sub>O<sub>3</sub>. For the active carbons the order varies from approximately 0.5 at low H<sub>2</sub>S concentrations to zero at high concentrations.

In Fig. 3 the oxidation rate on activated carbon prepared from sugar is plotted versus the square root of the hydrogen sulfide pressure.

#### DISCUSSION

##### Oxidation-Reduction Mechanism for the Oxidation of H<sub>2</sub>S

When the results of the kinetic experiments (Tables 3 and 4) are compared, and

the observed differences in reaction orders are noted, the conclusion can be drawn that the mechanism is not the same for all the materials. In Part I (1) we reported on the autocatalytic effect of sulfur in different materials. Therefore, it is very likely that sulfur adsorbed in the micropores of the 13X molecular sieve catalyzes the oxidation reaction in the same manner as sulfur adsorbed in porous carbons. Any mechanism proposed should be in accordance with the observed variation of reaction mechanisms, and an oxidation-reduction mechanism can

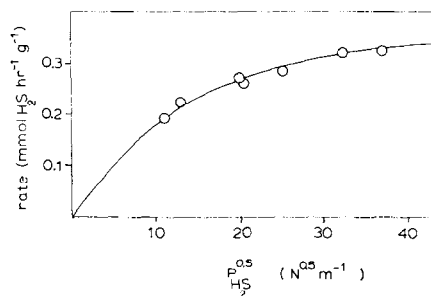
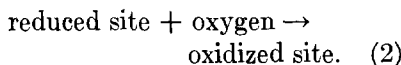
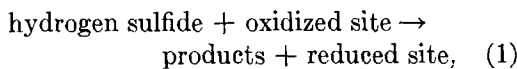


FIG. 3. H<sub>2</sub>S oxidation rate on activated sugar charcoal as a function of the square root of the partial pressure of H<sub>2</sub>S. T = 190°C; P<sub>O<sub>2</sub></sub> = 2.2 × 10<sup>-2</sup> N m<sup>-2</sup>; sulfur content: 0.7 g (g carbon)<sup>-1</sup>.

satisfy this condition. This mechanism of two chemical resistances in series has been observed for many different oxidation reactions, e.g., on vanadium oxide (9a, b). The two reactions involved in the oxidation of hydrogen sulfide could be:



If these two chemisorption steps occur in series then both reaction orders should vary between zero and one, depending on the partial pressures of oxygen and H<sub>2</sub>S. Our experiments show that this is only true for the order in oxygen but not for the order in H<sub>2</sub>S. The maximum half order in H<sub>2</sub>S observed indicates that H<sub>2</sub>S is not directly involved in the reduction step [Eq (2)]. A dissociative adsorption of H<sub>2</sub>S is likely. We launched this idea in Part I (1). From the literature it is known that the reaction of H<sub>2</sub>S with sulfur forming polysulfides (H<sub>2</sub>S<sub>x</sub>, x ≥ 2) proceeds very fast already at room temperature (10). Golyland *et al.* (10) observed a high rate of isotopic exchange between radioactive H<sub>2</sub>S and sulfur deposited in the pores of active carbon:

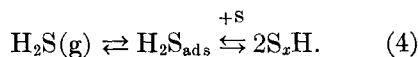


asterisk = radioactive.

The maximum half order in H<sub>2</sub>S is in accordance with a reduction step which is a surface reaction between adsorbed oxygen and dissociatively adsorbed hydrogen sulfide. Although the formation of water from adsorbed oxygen occurs in several steps, only one of these steps is the rate-determining reduction step. Assuming that the rate of this reduction reaction is proportional to the degrees of occupation of the specific sites on the sulfur surface with oxygen and hydrogen sulfide, respectively, θ<sub>O</sub> and θ<sub>SH</sub>, then

$$-\frac{dP_{H_2S}}{dt} = k_{\text{red}}'' \cdot \theta_{\text{SH}} \cdot \theta_{\text{O}}. \quad (3)$$

θ<sub>SH</sub> can be related to the partial pressure of H<sub>2</sub>S if there is an equilibrium between H<sub>2</sub>S in the gas phase and dissociatively adsorbed H<sub>2</sub>S:



The equilibrium constant (K) for reaction (4) is:

$$K = \frac{\theta_{\text{SH}}^2}{P_{H_2S} \cdot (1 - \theta_{\text{SH}})}.$$

If θ<sub>SH</sub> ≪ 1 and the equilibrium is established then:

$$\theta_{\text{SH}} = K \cdot P_{H_2S}^{0.5} \quad (5)$$

Substituting Eq. (5) in (3):

$$-\frac{dP_{H_2S}}{dt} = k_{\text{red}}' \cdot P_{H_2S}^{0.5} \cdot \theta_{\text{O}}. \quad (6)$$

For the oxidation step the rate of reoxidation of sites reduced by H<sub>2</sub>S is proportional to the oxygen partial pressure and the fraction of sites not covered by oxygen, i.e.,

$$\frac{-dP_{O_2}}{dt} = k_{\text{ox}}' \cdot P_{O_2} \cdot (1 - \theta_{\text{O}}). \quad (7)$$

For the oxidation of one mole of H<sub>2</sub>S to sulfur a half mole of oxygen is required, so that:

$$-0.5 \frac{dP_{H_2S}}{dt} = \frac{-dP_{O_2}}{dt}. \quad (8)$$

In the steady state:

$$\begin{aligned} 0.5 \cdot k_{\text{red}}' \cdot P_{H_2S}^{0.5} \cdot \theta_{\text{O}} \\ = k_{\text{ox}}' \cdot P_{O_2} \cdot (1 - \theta_{\text{O}}). \end{aligned} \quad (9)$$

Solving Eq. (9) for θ<sub>O</sub> and substituting in (6) gives:

$$\begin{aligned} \frac{-dP_{H_2S}}{dt} \\ = \frac{1}{(1/k_{\text{red}}' \cdot P_{H_2S}^{0.5}) + (1/2 \cdot k_{\text{ox}}' \cdot P_{O_2})}. \end{aligned} \quad (10)$$

There may exist two limiting cases:

a. If  $k_{\text{red}}' \cdot P_{\text{H}_2\text{S}}^{0.5} \gg 2 \cdot k_{\text{ox}}' \cdot P_{\text{O}_2}$ , then

$$\frac{-dP_{\text{H}_2\text{S}}}{dt} = 2 \cdot k_{\text{ox}}' \cdot P_{\text{O}_2}$$

b. If  $k_{\text{red}}' \cdot P_{\text{H}_2\text{S}}^{0.5} \ll 2 \cdot k_{\text{ox}}' \cdot P_{\text{O}_2}$ , then

$$\frac{-dP_{\text{H}_2\text{S}}}{dt} = k_{\text{red}}' \cdot P_{\text{H}_2\text{S}}^{0.5}$$

These two extremes are indeed observed (Tables 3 and 4). The general expression relating the oxidation rate of  $\text{H}_2\text{S}$ , expressed as  $\text{mmol H}_2\text{S g}^{-1} \text{hr}^{-1}$  to the partial pressures of  $\text{H}_2\text{S}$  and  $\text{O}_2$  is:

$$V_{\text{H}_2\text{S}} = -A \cdot \frac{dP_{\text{H}_2\text{S}}}{dt} = \frac{1}{(1/k_{\text{red}} \cdot P_{\text{H}_2\text{S}}^{0.5}) + (1/2 \cdot k_{\text{ox}} \cdot P_{\text{O}_2})} \quad (11)$$

$A$  is a constant.

Kinetic data from experiments on activated sugar charcoal are plotted in Fig. 4 to verify the applicability of Eq. (11). As shown, the experimental data fit Eq. (11). This is also the case with the results obtained with activated sugar charcoal at different temperatures in the range 130–200°C. These results and also the experimental data on zeolite 13X were in accordance with Eq. (11). The applicability of the equation was not tested for all the materials, but as can be seen from Tables 3 and 4 most of the apparent reaction orders represent extreme cases of the oxidation-reduction model.

The rate constants  $k_{\text{ox}}$  and  $k_{\text{red}}$  were calculated for some materials under various conditions. From the temperature dependence of these rate constants we derived  $E_{\text{ox}} = 37 \pm 4 \text{ kJ mol}^{-1}$  and  $E_{\text{red}} = 52 \pm 5 \text{ kJ mol}^{-1}$  for active carbon. For zeolite 13X both values were higher, i.e.,  $E_{\text{ox}} = 55 \pm 5 \text{ kJ mol}^{-1}$  and  $E_{\text{red}} = 65 \pm 5 \text{ kJ mol}^{-1}$ . These differences in activation energies point to an influence of the chemical nature of the porous material.

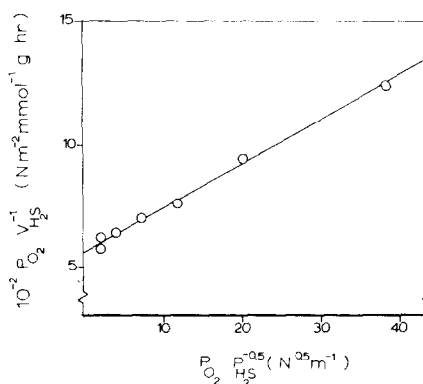
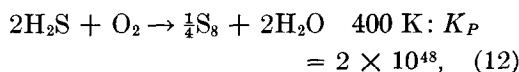


FIG. 4. Test for the applicability of Eq. (11) to the experimental data on activated sugar charcoal.  $T = 190^\circ\text{C}$ ; sulfur content: 0.7 g (g carbon) $^{-1}$ .

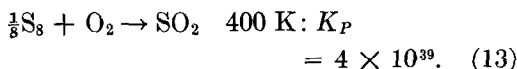
Literature data on the kinetics of the reaction (Table 1) show that some authors corroborate a part of our results. The zero order in oxygen for pumice (3) and active carbon (5) fits in the mechanism. Also the half order in  $\text{H}_2\text{S}$  reported by Prettre and Sion (4) for  $\gamma\text{-Al}_2\text{O}_3$  is consistent. The rate data of Sreeramamurthy (6) are not in accordance with our model. The activation energies found by this author vary from 6.7 to 30  $\text{kJ mol}^{-1}$ . These low values could indicate that there is in most experiments a large influence of diffusion in the observed rates. Also the rates reported by Cariaso (7) are largely influenced by diffusion. From the data presented by Cariaso (7) we calculated that in most experiments the diffusion rate of  $\text{H}_2\text{S}$  to the carbon catalyst was the limiting factor. The mechanism proposed by Cariaso is in fact an oxidation-reduction mechanism. However, he considers the carbon surface as the only surface which is active in the catalysis of  $\text{H}_2\text{S}$  oxidation.

#### Considerations Regarding the Possible Role of $\text{SO}_2$ as an Intermediate

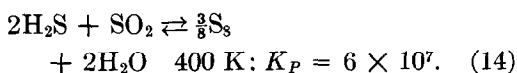
The oxidation of  $\text{H}_2\text{S}$  according to the reaction,



is not the only reaction which may occur at the catalyst surface. Especially at high temperatures ( $T > 200^\circ\text{C}$ ) and high excess of oxygen a consecutive reaction occurs:



From thermodynamic calculations we learned that at 400 K this  $\text{SO}_2$  can be further oxidized to  $\text{SO}_3$ . We will not consider this reaction because in practice this compound is only formed in traces. The  $\text{SO}_2$  formed according to Eq. (13) will react with unconverted  $\text{H}_2\text{S}$  via the fast reaction:



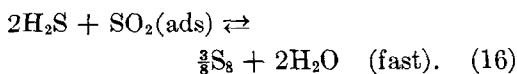
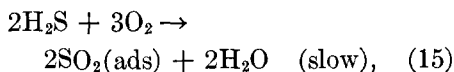
From the equilibrium constants calculated for the different reactions it can be concluded that the possibility exists that  $\text{SO}_2$  is an intermediate.

To check this possibility we performed a few experiments on the oxidation of adsorbed elemental sulfur by molecular oxygen. In the temperature region  $100\text{--}200^\circ\text{C}$  we observed that the formation rate of sulfur dioxide was at least a factor 100 smaller than the oxidation rate of hydrogen sulfide. At temperatures above  $300^\circ\text{C}$  the order of magnitude of the rates is equal. This is because the energy of activation for S oxidation ( $125 \pm 10 \text{ kJ mol}^{-1}$ ) found by us is much higher than that for  $\text{H}_2\text{S}$  oxidation ( $\sim 40 \text{ kJ mol}^{-1}$ ). The energy of activation for oxidation of adsorbed sulfur has the same value as for pure liquid sulfur, i.e., literature values:  $120 \text{ kJ mol}^{-1}$  (11) and  $116 \text{ kJ mol}^{-1}$  (12).

Combining the thermodynamic data with the kinetic data on sulfur and hydrogen sulfide oxidation it can be concluded that at temperatures above  $300^\circ\text{C}$   $\text{SO}_2$  may be an intermediate in the reaction. Below  $200^\circ\text{C}$  the rate of sulfur oxidation is too low to make a contribution to  $\text{H}_2\text{S}$  oxidation. The high selectivity of  $\text{H}_2\text{S}$  oxidation towards sulfur at temperatures below  $200^\circ\text{C}$  and even excess oxygen implies also that

formation of  $\text{SO}_2$  is a slow reaction. The main reason is the relatively high energy of activation for sulfur oxidation. Wiewirowski and Slater (11) assumed that this activation energy is related to the dissociation energy of a terminal sulfur-sulfur bond in a sulfur chain molecule. This assumption points to a reaction of oxygen with the ends of sulfur chains, which contain the unpaired electrons.

Physically adsorbed  $\text{SO}_2$  is postulated as an intermediate in  $\text{H}_2\text{S}$  oxidation on  $\gamma\text{-Al}_2\text{O}_3$  at  $100^\circ\text{C}$  by Prettre and Sion (4). The following reactions should occur:



Here a direct oxidation of  $\text{H}_2\text{S}$  to  $\text{SO}_2$  occurs, something which is not very likely at  $100^\circ\text{C}$ . At excess oxygen and a high conversion level  $\text{SO}_2$  should appear in the off gases. Prettre and Sion reported, however, the complete absence of  $\text{SO}_2$  in the gas leaving the reactor even with  $\text{O}_2/\text{H}_2\text{S} = 3$ . For this reason we doubt that there is physisorbed  $\text{SO}_2$  present at the surface of alumina which is an intermediate.

There still remains the question as to what is the nature of the product of the reaction between sulfur and oxygen. We discuss the nature of the oxidized catalyst site  $\text{S}_x\text{O}_y$  in Part III (13).

## CONCLUSIONS

1. Kinetic data for the oxidation of  $\text{H}_2\text{S}$  on various materials agree with the kinetics of an oxidation-reduction model.

2. The oxidation step is a reaction between molecular oxygen and adsorbed sulfur. The reduction step is a reaction between dissociatively adsorbed  $\text{H}_2\text{S}$  and a chemisorbed oxygen, yielding water and sulfur. The kinetics are formulated in Eq. (11).



3. Below 200°C the formation of SO<sub>2</sub> is slow compared with the oxidation of H<sub>2</sub>S into sulfur. This causes the high selectivity towards sulfur. Above 300°C cleavage of S-S bonds occurs readily and an alternative route wherein SO<sub>2</sub> acts as an intermediate begins to contribute to the overall reaction rate.

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