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Kinetics of Cobalt-Molybdate-Catalyzed Reactions of SO_2 with H_2S and COS and the Hydrolysis of COS[1]

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The following reactions:

$$SO_2 + 2H_2S \rightleftharpoons 2H_2O + 3/xS_x, \qquad (a)$$

$$SO_2 + 2COS \rightleftharpoons 2CO_2 + 3/xS_x, \qquad (b)$$

$$COS + H_2O \rightleftharpoons CO_2 + H_2S, \qquad (c)$$

which are important in Claus sulfur recovery process were studied over a commercial cobalt-molybdate catalyst. At 250°C, which is close to the operating temperature for Claus catalytic reactors, the rate constants for the above reactions were 75:1:5. Considerable irreversible adsorption of SO_2 and H_2S on the catalyst was observed. Kinetically all reactions were similar in that the strongly adsorbed reactant (SO_2 and H_2O) was zero order and the other reactant (H_2S and COS) was first order. H_2S–SO_2 reaction (Claus reaction) appeared to be diffusion controlled with an activation energy of 5.5 kcal/mole. No poisoning by CO_2 was observed for the COS reactions.

INTRODUCTION

Cobalt-molybdate-on-alumina catalyst is sometimes added to the first stage of a conventional Claus sulfur-recovery plant (*2*) in order to improve the conversion of carbonyl sulfide and carbon disulfide which are often present along with hydrogen sulfide. The relevant reactions are

$$2COS + SO_2 \rightleftharpoons 2CO_2 + 3/xS_x, \qquad (1)$$

and

$$CS_2 + SO_2 \rightleftharpoons CO_2 + 3/xS_x. \qquad (2)$$

In addition, since there is usually considerable water vapor present, hydrolysis reactions are also possible

$$COS + H_2O \rightleftharpoons CO_2 + H_2S, \qquad (3)$$

$$CS_2 + 2H_2O \rightleftharpoons CO_2 + 2H_2S. \qquad (4)$$

The hydrogen sulfide produced by reactions (3) and (4) then reacts according to the principal Claus reaction:

$$2H_2S + SO_2 \rightleftharpoons 2H_2O + 3/xS_x, \qquad (5)$$

to give the same overall effect as reactions (1) and (2).

The bulk of the catalyst in a Claus reactor is either bauxite or alumina. Reaction (5) is thermodynamically limited so that 2 to 4 catalyst stages, with intervening sulfur removal, are required at the normal operating temperatures of 250–300°C to achieve total conversions of 95–98%. Reactions (1)–(4) are thermodynamically favorable but are slow at Claus operating temperatures so that any carbonyl sulfide or carbon disulfide (which may be present initially along with hydrogen sulfide, or may be formed by reaction with traces of hydrocarbon during the partial combustion in the furnace preceding the catalytic stages) tends to pass unchanged through the catalytic reactors and contribute to the sulfur content of the tail gas which is flared.

As part of a more extensive study of the

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[1] Contribution No. 634 from the Research Council of Alberta, Canada (*1*).

Claus reaction that is underway in these laboratories, a number of observations have been made of reactions (1), (3), and (5) over a commercial cobalt-molybdate catalyst. It was hoped that the reactions of carbonyl sulfide would be indicative of those of carbon disulfide [reactions (2) and (4)].

Experimental and Results

Apparatus

The fixed bed integral flow reactor was made out of ¼ in. (i.d.) 316 stainless steel tubing except for the reactor assembly and sulfur condensor (Fig. 1). Helium with about 1% added nitrogen (marker) was the carrier gas. Reactants (H_2S or COS and SO_2) were bled into the helium stream by means of micrometering valves. Water vapor when required was introduced into the reactor by allowing helium to pass through a saturator. Ballast volume and mixing chamber were placed in the reactant flow line to produce a feed of uniform composition. A separate helium line was used for gc analysis. Provision was made to monitor feed and product stream.

The reactor was 1 × ⅜ in. (i.d.) and had a 100 mesh stainless steel screen to support the catalyst granules (generally 20–30 mesh). A thermocouple was located approximately in the center of the catalyst bed. The reactor was operated in the range of 240–450°C and up to 1.3 atm. The reactants entered the reactor after passing through a preheater (5 × ⅜ in. i.d.) packed with stainless steel shavings and no corrosion of the shavings was detected.

A thermocouple placed in the stream just ahead of the reactor measured the temperature of the reactants. Both the reactor and preheater were heated by the same furnace which was a porcelain tube with resistance wire wound around it and kept in a Dewar flask. The furnace was controlled by an F and M Model 240 temperature programmer. The thermocouple output could be read to ±2°C by means of a DANA multimeter (Model 4300). The catalyst was heated at the rate of 3°C/min during activation. The furnace could easily be removed and replaced by a Dewar cylinder of liquid nitrogen to permit measurement of nitrogen adsorption at $p/p_0 = 0.06$ by the usual dynamic method (*3*). The temperature of the apparatus was kept above the melting point of sulfur at 125°C (G and K in Fig. 1).

The sulfur condenser was a 16 × 1 in.

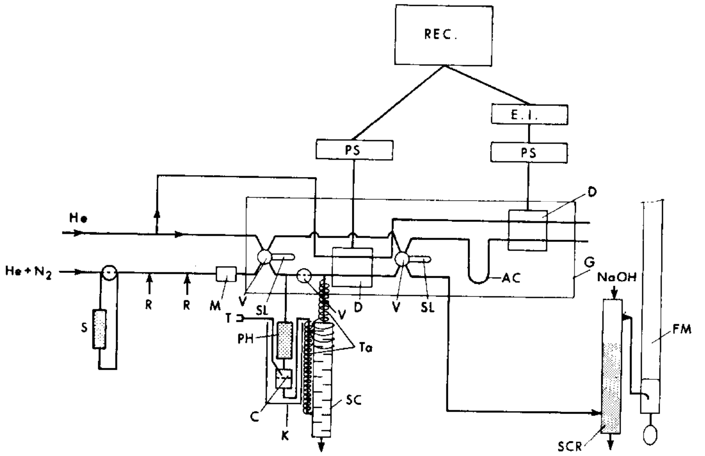

FIG. 1. Schematic diagram of the apparatus used. Flow reactor: (S) saturator; (R) reactants (M) mixing chamber; (V) valve; (SL) sampling loop; (PH) preheater; (C) catalyst; (T) thermocouple; (D) detector TC; (AC) analytical column; (PS) power supply; (EI) electronic integrator; (K) dewar with furnace inside; (Ta) heating tape, 125°C; (REC) recorder; (SCR) scrubber; (FM) flow meter; (SC) sulfur condensor; (G) thermostated box.

(i.d.) stainless steel tube and had baffles every inch to facilitate sulfur condensation. Sulfur condensing was critical. Experiments with an unheated condensor caused sulfur to condense at the exit of the condenser and into the sampling section resulting in unreliable conversions. No attempt was made to keep the sulfur above the melting point in the condenser as this has been reported (*4*) to catalyze the Claus reaction. As a result of extended experimentation it was found that if the connecting tube from the reactor outlet and part of the condenser exit section were kept around 150°C (the temperature in the unheated section of the condenser was around 60°C), satisfactory sulfur condensing could be accomplished and this procedure was followed. This arrangement was quite sufficient to condense most of the sulfur except at high flow rates, when sulfur mist escaped into other parts of the system. Periodically the condenser and other parts of the system had to be heated to drain the sulfur.

The analyses of the feed and product streams, carried out when the catalyst was bypassed, showed that no other part of the system was catalyzing the reaction, even when appreciable condensed sulfur was present in the condenser.

The effluent of the reactor was scrubbed with a 2 *M* solution of NaOH to remove sulfur compounds before venting to the atmosphere.

Flow rates measured with a 500 ml soap bubble meter following the scrubber, were expressed as mmoles/sec of dry helium.

As shown in the schematic diagram, there are two thermal conductivity detectors (Teflon-coated filaments and thermostated at 125°C). One is located immediately after the catalyst and is used to measure retention volume and surface area. The second detector is located after the analytical column and is used for analysis of feed and product samples. This detector output at maximum sensitivity was fed to a Hewlett-Packard electronic integrator (No. 3370A) as well as to a conventional strip chart recorder. The detector–integrator system was calibrated by injecting 2.0 ml samples of pure reactants at different pressures (measured by a digital manometer) ahead of the analytical column.

The apparatus was provided with sampling loops (5.0 ml) so that both feed and product streams could be monitored. By operating a seven-port sampling valve, the separate gc helium stream would sweep the contents of the sampling loop onto the analytical column which consisted of 8 ft × ⅛ in. Poropak Q (50–80 mesh) followed by 2 ft × ⅛ in. Poropak T (50–80 mesh). The column was operated at 125°C and provided good separations of N_2, CO_2, H_2S, COS, H_2O, and SO_2 in about 5 min (Fig. 2). It was observed that the analytical column after prolonged use had turned yellow (at 125°C sulfur condensation is very unlikely). However, this did not interfere with the efficiency of the analysis.

Adsorption measurements using frontal chromatography were studied in another apparatus. The TC detector used was similar to the one used for gc analysis. Further, adsorption of SO_2 and the BET surface area of the catalyst were determined on a Cahn RG electrobalance.

Materials

The catalyst used in this study was a commercial cobalt-molybdate on γ-alumina (Girdler G-35) manufactured and kindly supplied by Chemetron Corp., Louisville, KY. It was reported to have 3.5% CoO and 10.0% MoO_3. The catalyst, which was ⅛ × ⅛ in. tablets, was crushed and sieved to 20–30 mesh granules for kinetic studies. It had a measured surface area of 180 m^2/g using the one point isotherm, compared to 192.5 m^2/g by the BET method. This catalyst is used mainly for hydrodesulfurization [cf. the excellent comprehensive review by Schuit and Gates (*5*)].

The chromatographic firebrick used in the saturator was Chromosorb A manufactured by Johns-Manville. It was washed and sieved to 20–30 mesh before use.

Reactants

H_2S, SO_2, and COS were supplied by Matheson and had reported purity of more than 99 mole%. Traces of CO_2 were present in all gases.

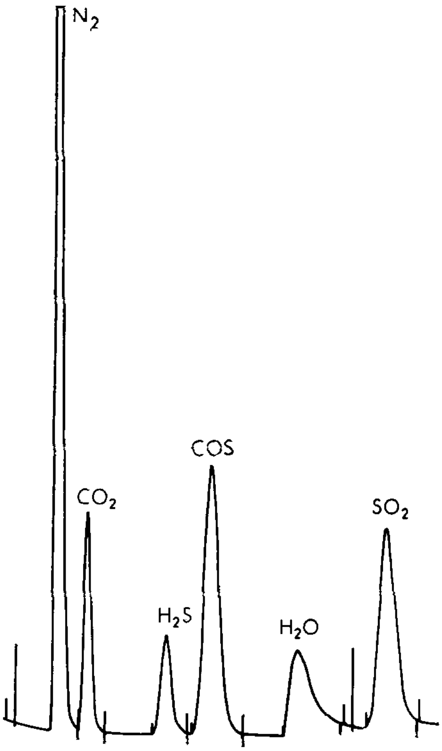

FIG. 2. Sample chromatogram: Anal. column: 8 ft × ⅛ in. (50–80 mesh) Poropak Q, followed by 2 ft × ⅛ in. (50–80 mesh) Poropak T. Column and TC detector thermostated at 125°C, 250 mA and 1.34 ml/sec of helium flow rate.

The catalyst was activated in flowing helium at 450°C for 16 hr. The surface area of the catalyst was checked prior to the reaction and then periodically during the reaction.

For hydrolysis studies or investigating the effect of water on the reaction rate, water was introduced into the reactor by allowing helium to pass through a saturator which contained about 20 g chromatographic firebrick (20–30 mesh) loaded with 30% water. By controlling the temperature of the bath around this saturator, constant partial pressure of water vapor in the helium could be maintained. By means of frontal chromatography it was possible to measure the amounts of water adsorbed by the catalyst under various partial pressures of water vapor in the helium stream. From the volume of helium passed before the waterfront appeared at the postcolumn detector, the amount of water taken up by the catalyst could be calculated. The breakthrough was fairly sharp, indicating rapid adsorption of water. The calibration of the detector was based on the known partial pressure of water in the saturator. During the experiment wet helium flowed through the apparatus.

Kinetic Studies

Kinetic measurements were made at two or three flow rates after steady state conditions were established, based on successive analysis being within 0.5% (about 10 min). Since the SO_2 and H_2O peaks had tails (Fig. 2) and the CO_2 peak was not quite reproducible, conversions were calculated from the disappearance of COS or H_2S. Several repeat analyses were made for each set of conditions, the conversion ranging between 5–30% with an uncertainty of ±2%. The initial rate was obtained by fitting the experimental data to the expression

$$x = C \tanh[D(\mathrm{W/F})],$$

where x is the fractional conversion of reactant, W/F in g, sec/mmoles reactant, and C and D are constants.

This expression has been demonstrated by Mezaki and Kittrell (*6*) to be a convenient and relatively nondiscriminating way to extrapolate to zero conversion.

The range of partial pressures (Torr) of reactants used were H_2S, 4–10; COS, 4–20; SO_2, 0.5–10; and H_2O, 5–23.

The initial rate (mmoles of H_2S or COS reacted/sec, g) was fitted to the expression

$$r_0 = kp_{\mathrm{A}}{}^a p_{\mathrm{B}}{}^b,$$

where a and b are kinetic orders with respect to reactants A and B. The following aspects of the kinetics were investigated on the basis of initial rates

(a) Diffusional effects
(b) Order of reaction
(c) Activation energy
(d) Effect of H_2O

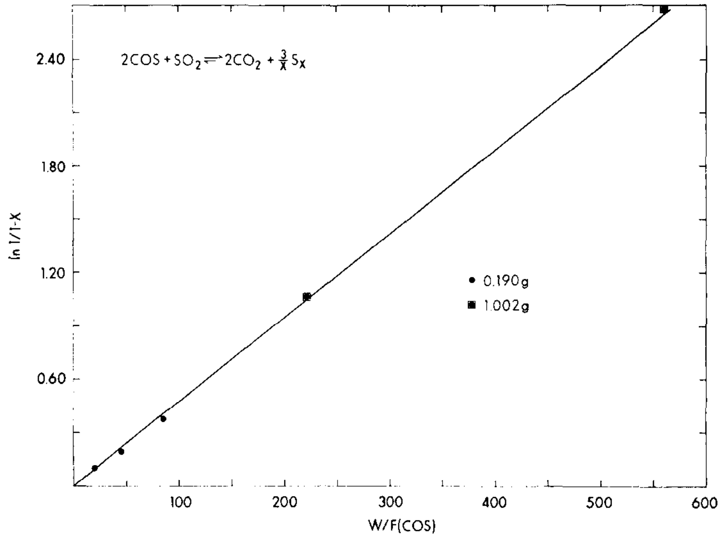

FIG. 3. Test for first-order reaction and film diffusion for COS–SO_2 reaction.

Diffusional Effects

For COS–SO_2 reaction at 350°C fractional conversion of COS obtained for 0.190 and 1.002 g catalysts fitted into the same first-order plot (Fig. 3), indicating that film diffusion was negligible under the conditions of operation. It was assumed to hold true for the other reactions as well.

Pore diffusion was considered negligible for COS hydrolysis reaction since decreasing the particle size did not increase the initial rate (Table 1). For COS–SO_2 reaction the initial rate increased as the particle size was decreased (Table 2). However, the increase was not pronounced for particles ≤ 1.02 mm diameter indicating that the influence of pore diffusion for the catalyst used in this study (1.02 mm) may not be serious.

TABLE 1
HYDROLYSIS OF COS, TEST FOR PORE DIFFUSION, 350 ± 2°C

d_p[a]	pCOS[b]	pH_2O[b]	r_0[c]
1.69	1.99	4.6	0.0011
1.02	2.01	4.6	0.0013
0.72	1.99	4.6	0.0013

[a] Average particle diameter (mm).
[b] Average partial pressure (Torr).
[c] mmoles reacted/sec, g.

However, for the H_2S–SO_2 reaction, the initial rate increased with decrease in particle size (Table 3) [the increase in rate could not be related to the expected increase in the external surface area of the catalyst], and the reaction is probably diffusion controlled.

Reactions were carried out using 20–30 mesh granules as the pressure drop on smaller particles was high.

Reaction Orders and Activation Energies

Kinetic orders were determined at different temperatures (250, 300, and 350°C).

TABLE 2
TEST FOR PORE DIFFUSION, COS–SO_2 REACTION, 350 ± 2°C

d_p	pCOS	pSO_2	x[a]	W/F[b]	r_0
1.69	3.97	2.02	0.112	35.5	0.0035
	4.01	2.02	0.152	54.7	
1.02	4.01	2.02	0.103	22.0	0.0054
	3.98	2.01	0.160	45.0	
	4.02	1.99	0.080	14.8	
0.72	3.98	2.02	0.107	18.5	0.0059
	4.01	1.99	0.188	35.0	
0.51	4.00	1.98	0.250	48.1	0.0062
	4.02	2.03	0.098	14.4	

[a] Fractional conversion based on H_2S (or COS).
[b] g, sec/mmole reactant.

TABLE 3
TEST FOR PORE DIFFUSION IN H_2S–SO_2 REACTION AT 350 ± 2°C

d_p	pH_2S	pSO_2	x	W/F	r_0	Relative rate	Relative external area
1.69	4.02	1.99	0.180	23.6	0.0087	1.0	1.0
	3.97	2.01	0.270	46.6			
1.02	4.01	1.96	0.130	17.6	0.0117	1.3	1.7
	3.98	2.01	0.124	11.2			
0 51	4.01	1.98	0.305	20.6	0.0147	1.7	4.1
	4.02	1.99	0.160	11.7			

From the variation in initial rate with the partial pressure of reactants it was observed that the kinetic order with respect to SO_2 was zero (0.02 and 0.08) and that with respect to H_2S was one (0.93 and 0.96) for Claus reaction (Table 4). Experiments involving 0.5 and 2.0 Torr SO_2 (4.0 Torr H_2S) showed that the kinetic order in SO_2 was about 0.5 indicating that for the zero order in SO_2 observed (2–10 Torr) the surface was fully covered with adsorbed SO_2.

The same pattern was observed for COS–SO_2 reaction in that the kinetic orders were zero (−0.05) and one (1.15) with respect to SO_2 and COS (Table 5) [the same kinetic orders were observed by Naber, Wesselingh, and Groenendaal (7) for the reduction of SO_2 to H_2S over a cobalt-molybdate catalyst]. COS hydrolysis was zero order in H_2O (0.11) and first order (1.07) in COS (Table 6). Since the overall reaction (for all three reactions) appeared to be first order, the conversion data was plotted in the usual first-order form [(log $1/1 - x$) against W/F (reactant)]. In all cases the points fell on a straight line through the origin (e.g., Fig. 3) indicating that for the relatively wide range of conversions tested here, the rate for the reac-

TABLE 4
KINETIC DATA ON CLAUS REACTION OVER COBALT–MOLYBDATE CATALYST

t (°C)	pH_2S	pSO_2	x	W/F	r_0 (computed)
350 ± 2	3.96	2.01	0.275	12.4	0.0238
	4.01	2.02	0.370	19.3	
	4.00	10.17	0.406	16.7	0.0278
	4.02	10.12	0.265	9.3	
	10.20	1.99	0.188	3.6	0.0598
	10.30	2.01	0.116	2.0	
250 ± 2	4.00	10.30	0.284	20.9	0.0148
	3.98	9.71	0.106	7.8	
	3.99	10.22	0.178	11.8	
	4.04	1.98	0.336	29.9	0.0144
	4.00	2.00	0.235	18.0	
	4.01	2.01	0.179	13.2	
300 ± 2	1.98	1.97	0.184	54.4	0.0043
	1.98	2.02	0.128	29.7	
	8.52	2.02	0.095	5.7	0.0168
	8.70	2.00	0.200	12.3	

TABLE 5
Kinetic Data, COS-SO_2 Reaction

pCOS	$p$$SO_2$	x	W/F	r_0
3.99	2.01	0.103	22.0	0.0054
3.95	2.01	0.168	45.2	
3.98	1.98	0.080	14.8	
4.04	21.02	0.139	34.4	0.0048
4.01	20.80	0.082	17.7	
4.04	21.01	0.178	52.5	
11.07	2.02	0.195	13.8	0.0157
11.05	2.01	0.095	6.2	

tions H_2S–SO_2, COS–SO_2, and COS–H_2O can be expressed as $r = kp_A$, where A is H_2S or COS.

From the temperature coefficient of the rate constant, the activation energies were determined to be 5.5; 12.0, and 18.0 kcal/mole for H_2S–SO_2 reaction, COS hydrolysis and COS–SO_2 reaction, respectively (Fig. 4). Figure 4 also shows the relative rates of reaction; the H_2S–SO_2 reaction is the fastest of the three. This is consistent with it being also the one showing marked diffusional resistances and the low apparent activation energy probably refers to the diffusion step.

Effect of Water on H_2S–SO_2 Reaction

Since water is a product of the reaction, an attempt was made to study the effect of water on the reaction by equilibrating the catalyst with different partial pressures of water vapor and carrying out Claus reaction over the wet catalyst (Table 7). It was observed that water retards the reaction and the effect can be described by an adsorption term in the denominator to give an empirical rate expression as follows:

$$r = \frac{kpH_2S^{1.0}pSO_2^{0}}{(1 + 0.10pH_2O)}$$

TABLE 6
Hydrolysis of COS at 350 ± 2°C

pCOS	$p$$H_2O$	x	W/F	r_0
1.99	4.6	0.220	53.9	0.0043
1.98	4.6	0.127	30.1	
8.42	4.6	0.130	6.9	0.0202
8.38	4.6	0.245	16.0	
2.02	22.3	0.223	58.5	0.0052
2.05	22.3	0.130	27.0	

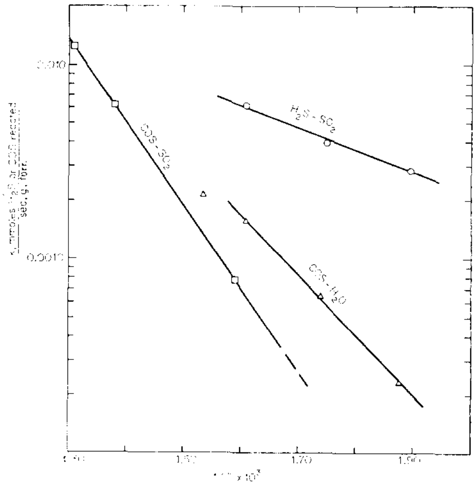

Fig. 4. Arrhenius plot for the reactions. (□) COS–SO_2; (△) COS–H_2O; (○) H_2S–SO_2.

The effect of water on the COS + SO_2 reaction was not investigated as the COS will be hydrolyzed to H_2S which then reacts much faster on this catalyst.

Effect of CO_2 on COS Reaction

Since strong poisoning by CO_2 for the COS–SO_2 reaction has been reported by Chuang, Dalla Lana, and Liu (*8*) on alumina, we attempted to investigate the effect of CO_2 on COS–SO_2 reaction by adding 12 Torr CO_2 to the reaction at 425°C when COS conversion was 45%. CO_2 was allowed to flow over the catalyst for 20 min and CO_2 was turned off before checking the steady state conversion of COS. There was no change in conversion, suggesting that under these conditions CO_2 did not poison the catalyst.

A similar experiment with the COS hydrolysis reaction also was negative, indicating the lack of poisoning of CO_2 on the rate of hydrolysis. These results are in contrast to the strong poisoning of alumina by carbon dioxide (*8*). It is possible that CO_2 is not adsorbed strongly on cobalt molybdate under these experimental conditions.

TABLE 7
EFFECT OF WATER ON CLAUS REACTION AT 350 ± 2°C

pH_2S	pSO_2	pH_2O	x	W/F	r_0	K_{H_2O}[a]
3.96	2.01	—	0.275	12.4	0.0238	
4.01	2.02	—	0.370	19.3		
4.10	2.01	4.6	0.222	15.8	0.0157	0.11
4.06	1.98	4.6	0.122	8.0		
4.00	2.02	22.3	0.101	15.8	0.0070	0.10
4.10	2.01	22.3	0.071	9.1		

[a] In the expression $r = kp_{H_2S}/1 + K_{p_{H_2O}}$.

State of the Catalyst During Reaction

In the course of each of the reactions studied, the catalyst turned black, probably indicating the formation of sulfide. Heating the used sample with dilute HCl and exposing lead acetate paper to the vapor did not always indicate sulfidation. Heating the sample in air evolved SO_2 (either desorbed SO_2 or oxidized H_2S). The surface area of the used catalyst had not decreased by more than 10%.

Adsorption of Reactants

Frontal chromatography was used for the adsorption of H_2S, COS, SO_2, CO_2, and H_2O at 350°C, generally on the sulfided catalyst. Sulfidation was accomplished by heating the catalyst at 400°C in 60 Torr H_2S for 3 hr. The catalyst turned black from the original deep blue color, due to sulfidation. Heating the sulfided catalyst in air or oxygen restored the catalyst to the oxide form. Four to 16 g of the sulfided catalyst (20–30 mesh) were used and the catalyst was packed in a ¼ in. stainless steel tube 6 in. long in the form of a U-tube. The partial pressure of the adsorbate was measured by diverting a sample through a calibrated thermal conductivity detector. The adsorption was not reversible as desorption at the same temperature indicated that 40–60% of the material was irreversibly adsorbed, especially for H_2S and SO_2 (Tables 8 and 9). Temperature programming to 450°C desorbed some of the material and this was followed for each adsorption. The maximum adsorption of H_2S and SO_2 on the oxide catalyst was 0.06 and 0.04 mmole/g at 350°C (Fig. 5) and on the sulfided catalyst it was 0.04 and 0.07 mmole/g at the same temperature (Figs. 5 and 6). The adsorption of 0.04 mmole/g SO_2 corresponds to about 3% surface coverage (taking the total surface as 180 m^2/g). Per unit surface area the adsorbate concentration is 10^{13} sites/cm^2.

Adsorption of SO_2 on a fresh sample of cobalt molybdate catalyst was measured by a Cahn microbalance. At 350°C and 5 Torr SO_2 the adsorption was very slow; at the end of 72 hr the adsorption was not complete. Comparing the results of frontal chromatography with that of microbalance,

TABLE 8
MATERIAL BALANCE, OXIDE CATALYST, 350°C[a]

pH_2S (Torr)	Q (mmole/g)
17.4	0.068
Desorption at 350°C	0.014
Temp programming to 450°C	0.012
Total recovery	0.026 (38%)

[a] Approximately 60% of the material is irreversibly adsorbed.

TABLE 9
MATERIAL BALANCE, OXIDE CATALYST, 350°C[a]

pSO_2 (Torr)	Q (mmole/g)
4.6	0.019
Desorption at 350°C	0.006
Temp programming to 450°C	0.006
Total recovery	0.012 (63%)

[a] Approximately 40% irreversibly adsorbed.

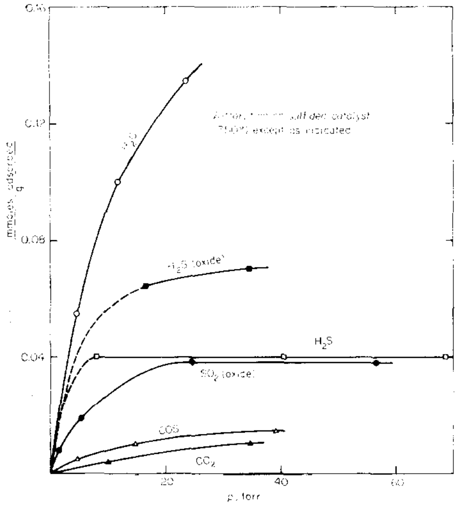

FIG. 5. Adsorption on the sulfided catalyst at 350°C except SO_2 and H_2S (■) which are on the oxide catalyst.

it appears that the latter was about 3 times more than the chromatographic results. At 20 Torr SO_2, 84% of the SO_2 was irreversibly adsorbed. The catalyst at the end of the experiments with the microbalance was found to be black. This material was found to have the same activity as a fresh sample of cobalt-molybdate for Claus reaction.

DeRosset, Finstrom, and Adams (*9*) investigated adsorption of H_2S on γ-alumina. For samples activated at 500°C and adsorption measured at 300–360, the saturation coverage (defined as the reciprocal of the limiting slope of Langmuir plot) was around 0.05 mmoles/g, almost identical with our results on the sulfided catalyst. This represents about 3% surface coverage.

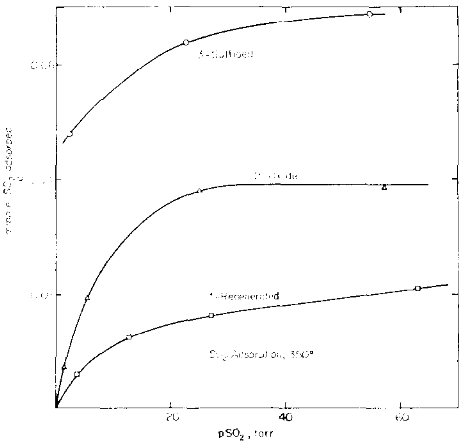

FIG. 6. Adsorption isotherm for SO_2 at 350°C. (○) Sulfided catalyst; (△) oxide catalyst; (□) sulfided catalyst regenerated with 60 Torr SO_2 at 450°C.

The gas chromatographic breakthrough curves indicated that surface penetration followed the same pattern for both reactants; fast adsorption was followed by slow desorption although tailing appeared to be more severe with SO_2. Sulfur dioxide adsorption on the sulfided catalyst showed two breakthroughs before SO_2 broke through. These could be water and sulfur from the Claus reaction as well as from reaction:

$$2CoS + SO_2 \rightleftharpoons 2CoO + 3/xS_x.$$

Attempts to regenerate the sulfided catalyst to the oxide form with SO_2 (60 Torr) at 450°C were not very successful. The catalyst was cooled in helium to 350°C and the SO_2 adsorption on this regenerated catalyst (curve 1, Fig. 6) was about half that on the oxide catalyst. It is possible that some of the adsorption sites may have been irreversibly destroyed by the regeneration procedure as the surface area of the regenerated catalyst was only 100 m^2/g compared to 180 m^2/g of the oxide form. It is also possible that regeneration with SO_2 was not complete. Regeneration with air was not attempted.

H_2O adsorption on the sulfided catalyst was more nearly reversible as close to 75% adsorbed water can be desorbed at the same temperature (350°C). Before H_2O broke through, some H_2S was desorbed (identified by gc analysis) formed probably by reaction such as:

$$CoS + H_2O \rightleftharpoons CoO + H_2S.$$

The maximum adsorption of water on the sulfided catalyst was about 0.2 mmole/g, about 5 times more than H_2S adsorption. This corresponds, assuming the molecular area of H_2O to be 12.1 Å^2 (*10*), to a surface coverage of about 8% at this temperature.

COS adsorption was relatively small, the maximum being 0.014 mmole/g, about a third of H_2S adsorption. There was always some CO_2 produced by the catalytic decomposition of COS.

$$COS + O_{(ads)} \rightleftharpoons CO_2 + S.$$

Molecular oxygen adsorbed on the oxide catalyst is suggested to be responsible for the above reaction (*11*). On the sulfided catalyst, the following reaction may have occurred:

$$2COS \rightleftharpoons CO_2 + CS_2.$$

We were not able to identify CS_2 in the effluent. CO_2 adsorption was similar to COS but lower. Adsorption isotherms are shown in Figs. 5 and 6.

Attempts to measure the limiting heat of adsorption of reactants on the catalyst using gas chromatographic retention volume measurements were not very successful. For SO_2 the first few slugs were irreversibly adsorbed and the retention volumes were not reproducible, and the gas chromatographic peak had severe tail indicating that adsorption desorption equilibrium was not attained. For H_2S and COS the same behavior was observed although to a lesser extent.

Discussion

The important aspect of our results is the striking similarity in the kinetic expressions for the three reactions, which suggests that the effective concentration of SO_2 or H_2O is independent of the partial pressure, while the other reactant, H_2S or COS, is either linearly or negligibly adsorbed. This, however, is not consistent with our adsorption results. Perhaps much of the adsorption is on nonreactive sites.

The zero-order dependency in SO_2 (2–10 Torr) that we observed can be explained on the basis that SO_2 is strongly adsorbed on the catalyst (for gas chromatographic retention volume measurements the first few slugs were irreversibly adsorbed). Consequently the surface of the catalyst is fully covered with adsorbed SO_2 under our experimental conditions. Zero order in SO_2 for the reduction of SO_2 to H_2S over a cobalt-molybdate catalyst has been reported (*7*). For the H_2S–SO_2 reaction different kinetic orders have been proposed (*12, 13*).

The decrease in the rate of H_2S–SO_2 reaction over the wet catalyst indicates competition for adsorption sites between H_2O and other reactants.

The low activation energy of 5.5 kcal/mole (for H_2S–SO_2 reaction) is indicative of a diffusion controlled reaction. With the limited data on the Arrhenius plot, a curvature is not evident at the high temperature region where diffusion control becomes more evident. With low partial pressure of reactant and high rates, pore diffusion can be expected. Landau, Molyneux and Houghton (*14*) studied H_2S–SO_2 reaction over a bauxite catalyst and concluded that the reaction was controlled by pore diffusion. COS hydrolysis did not appear to be diffusion controlled. However, Namba and Shiba (*15*) concluded that COS hydrolysis over an alumina catalyst was diffusion controlled above 230°C and an activation energy of 2.9 kcal/mole was determined for the diffusion controlled reaction. They reported that the kinetic order with respect to COS was one.

Lepsoe (*16*) investigated COS–SO_2 reactions over an alumina catalyst and his findings were similar to ours in that the reaction was first order with an activation energy of 14 kcal/mole in the temperature range 300–600°C. Poisoning of alumina catalyst by CO_2 for this reaction has been reported (*8*). We have not been able to detect any irreversible poisoning by CO_2 for this reaction over the cobalt molybdate catalyst. Assuming that H_2S–SO_2 reaction and COS–SO_2 reaction proceed by Langmuir–Hinshelwood mechanism, the difference in rate probably reflects the difference in adsorption of H_2S and COS. It is quite possible that most of the active sites were poisoned by CO_2 during the initial stages of the reaction of COS and the reaction was taking place on the low energy sites requiring high activation energy for the reaction.

The rate constants for COS–SO_2 reaction and COS hydrolysis are about the same at 400°C which is reported to be the temperature in the first catalytic converter containing cobalt-molybdate catalyst (*2*). The rates of these reactions in the plant operation would also be similar. Hence COS and CS_2 would be used up by these two reactions in Claus plants using cobalt molybdate.

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