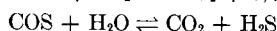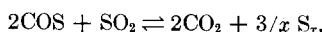# Effect of Catalyst Basicity for COS–SO$_2$ and COS Hydrolysis Reactions*

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The effect of catalyst basicity on the following reactions:

$$2COS + SO_2 \rightleftharpoons 2CO_2 + 3/x \, S_x,$$
$$COS + H_2O \rightleftharpoons CO_2 + H_2S$$

was investigated by loading NaOH on to Chromosorb-A (a commercial gas chromatographic support) and a cobalt–molybdate catalyst and determining the relative activities of these catalysts on the basis of initial rates. It was observed that the catalyst basicity increased the rate for COS hydrolysis but not for COS–SO$_2$ reaction. A mechanism involving the participation of basic sites and the presence of abstractable protons in the reactants is postulated for these reactions.

INTRODUCTION

In a previous publication from this laboratory (*1*), the kinetics of the following reactions (which are important in Claus sulfur recovery operations) were investigated over a commercial cobalt–molybdate catalyst.

$$2H_2S + SO_2 \rightleftharpoons 2H_2O + 3/x \, S_x, \quad (1)$$
$$2COS + SO_2 \rightleftharpoons 2CO_2 + 3/x \, S_x, \quad (2)$$
$$COS + H_2O \rightleftharpoons CO_2 + H_2S. \quad (3)$$
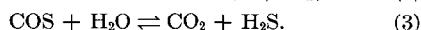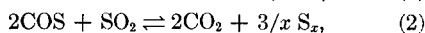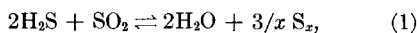
It was also shown that bases enhanced the catalytic activity of a relatively inactive material towards Claus reaction (*1*). For example, at 240°C, the catalytic activity of Chromosorb-A could be increased 10^3 (on the basis of initial rates) by depositing 3.9% NaOH on the sample (*2*). An attempt was therefore made to study the effect of catalyst basicity for reactions (2) and (3) and the results are summarized in this report.

EXPERIMENTAL AND RESULTS

The reactants COS and H$_2$O or COS and SO$_2$, diluted with He, were passed over

the catalyst which was contained in a 3/8 in. (i.d.) 316 stainless steel tube by a 100 mesh stainless steel screen. As shown in Fig. 1, provision was made for analysis of reactant and product streams, for preheating the reactants before contacting the catalyst and for condensing the product sulfur. Since the details of these operations are given in a previous publication (*1*), only brief descriptions are provided here. The preheater was 5 × 3/8 in. (i.d.) packed with stainless steel shavings and gave adequate preheating up to 60 ml/sec of helium. The preheater and the reactor were heated by the same furnace and this could easily be removed and replaced by a Dewar cylinder of liquid nitrogen to permit measurement of nitrogen adsorption by the usual dynamic method (*3*), using a relative pressure $p/p_0 = 0.06$.

The sulfur condenser was a 16 × 1 in. (i.d.) stainless steel tube and had baffles every inch to facilitate sulfur condensation. Sulfur condensing was critical. Experiments with an unheated condenser 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
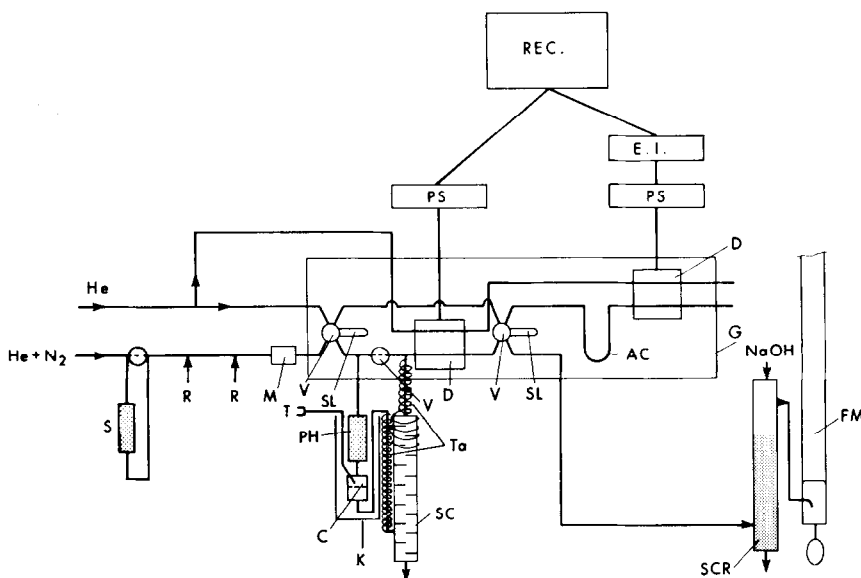
Fig. 1. Schematic diagram of flow reactor: (S) saturator; (R) reactants; (M) mixing chamber; (V) valve; (SL) sampling loop; (PH) preheater; (C) catalyst; (T) thermocouple; (D) detector T.C.; (AC) analytical column; (PS) power supply; (EI) electronic integrator; (K) Dewar with furnace inside; (Ta) heating tape, 125°C; (REC) recorder; (SCR) scrubber; (FM) flow meter; (SC) sulfur condensor; (G) thermostated box.

the melting point in the condenser as this could catalyze COS–SO₂ 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. Periodically the condenser and other parts of the system had to be heated to remove the sulfur.

Nitrogen was introduced with the reactants as a marker. The analyses of the feed and product streams, carried out when the catalyst was by-passed, showed that no other part of the system was catalyzing the reaction, even when appreciable condensed sulfur was present in the condenser.

The apparatus was provided with sampling loops (5.0 ml) so that both feed and product streams could be monitored. By operating a seven-part sampling valve, the separate gc helium stream would sweep the contents of the sampling loop onto the analytical column of 8 ft × ⅛ in. poropak

Q followed by 2 ft poropak T, maintained at 125°C. It provided good separations of N₂, COS, CO₂, H₂S, H₂O and SO₂ (1).

Materials

The chromatographic firebrick (Chromosorb-A) was manufactured by Johns-Manville, New York. It was washed, dried and sieved to 20/30 mesh before use. It had a measured surface area of 2.0 m²/g. The chemical analysis of Chromosorb provided by the manufacturer is (wt%): SiO₂, 90.6; Al₂O₃, 4.4; Fe₂O₃, 1.6; TiO₂, 0.3; P₂O₅, 0.2; CaO, 0.8; MgO, 0.7; Na₂O and K₂O, 0.5; loss on ignition, 0.3. Chromosorb-A was chosen as the support for NaOH loadings due to its low activity for the reactions, large pore openings (∼2000 Å) so that resistance to mass transfer would not be rate determining, and small surface area so that increase (rate/m²) can be determined.

The cobalt–molybdate on γ-alumina catalyst (Girdler G-35) was manufactured and kindly supplied by Chemetron Corp., Louisville, KY. It was reported to have 3.5% CoO and 10.0% MoO₃. 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 m²/g using the one point isotherm, (3) compared to 192 m²/g by the BET method.

Reactants

COS and SO_2 were supplied by Matheson and had a purity of more than 99 mole%. Traces of CO_2 were present in both gases.

For hydrolysis studies 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. The wet helium in turn passed through the catalyst at the reaction temperature. 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 (1). 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.

Deposition of Base

Deposition of NaOH was accomplished by soaking the catalyst granules in the appropriate solution and drying at 100°C. The exact loading was determined by leaching the adsorbate with hot distilled water (70°C, 72 hr) and titrating with 0.02 N HCl to pH 7. At base loadings up to 10%, the base could be leached from the catalyst and the approximate original activity restored. With higher base loadings (15–20%) the base reacted with the Chromosorb-A and also decreased the surface area of alumina catalysts and these materials were judged to be unsuitable for study. An attempt was made to determine if the NaOH (low loadings) was deposited uniformly over the catalyst surface. Scanning electron micrographs (5000×) of the catalysts with and without NaOH depositions did not reveal any significant differences indicating that under these low loadings, the exact nature of the deposition was difficult to detect.

The effect of catalyst basicity for the COS–SO_2 reaction and COS hydrolysis was investigated over Chromosorb-A and cobalt–molybdate catalysts.

Reversibility of NaOH Loading

The analytical method for determining the degree of base loading assumes that the base is totally extractable when the impregnated and activated catalyst is leached with hot water. An extraction experiment was performed on the cobalt–molybdate catalyst (3.9% NaOH) to check its catalytic activity. At 378°C, and a W/F of 53.9, the fractional conversion of COS was 0.208 compared to the expected 0.220 for the COS hydrolysis demonstrating reversibility of NaOH loading. However, after the catalyst had been used for 6 hr, the amount of extractable base was decreased by about 40%.

Degree of NaOH Loading vs Hydrolysis Reactivity

Samples of Chromosorb-A with loadings of 3.9, 7.2 and 10.5 wt% NaOH were prepared. The hydrolysis reaction was carried out at 230 ± 2°C, using 2.0 Torr COS and 4.6 Torr H_2O. Any variation in the partial pressure of reactants on the observed conversion was adjusted on the basis that the kinetic orders with respect to COS and H_2O were one and zero respectively (1). As the NaOH loading was increased, the rate went through a maximum.

Rate Studies

Rates of reactions, based on the disappearance of COS, were determined only after steady state conditions were established, as indicated by successive analyses being within 1.0%, usually about 10 min from start-up. Several flow rates were used, with conversions between 5 and 30% with an uncertainty of ±2%. The initial rate was obtained by fitting the experimental data to the expression

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

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

The derivative of the above function with respect to W/F is:

$$\frac{dx}{d(W/F)} = (C)(D)(\mathrm{sech}^2[D(W/F)]).$$

At $W/F = 0$, which is equal to the initial rate (r_0), the above derivative reduces to CD. The best values of C and D were obtained by a gradient search using a digital PDP-9 computer. This expression has been demonstrated by Mezaki and Kittrell (4) to be a convenient and relatively nondiscriminating way to extrapolate to zero conversion.

The range of partial pressures (Torr) of reactants used were COS, 2.0–4.0; SO₂, 2.0; and H₂O, 4.6.

Adsorption of Reactants

Adsorption of SO₂ on the cobalt–molybdate catalyst using frontal chromatography as well as microbalance measurements indicate that 40–80% of the SO₂ is irreversibly adsorbed at 350°C (1).

COS adsorption was characterized by the production of CO₂ (1) by reaction:

$$COS + O \text{ (ads)} \rightarrow CO_2 + S. \qquad (4)$$
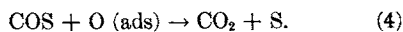
CO₂ adsorption was reversible.

H₂O adsorption at reaction temperature was more nearly reversible as close to 75% of the adsorbed water could be desorbed at the same temperature. H₂O adsorption was much greater than SO₂ or COS adsorption on cobalt–molybdate.

Adsorption of SO₂ on the Chromosorb-A (containing 3.9% NaOH) using frontal chromatography at 230°C and 2 Torr SO₂ was 0.031 mmole/g compared to 0.014 mmole/g without NaOH. For COS adsorption the presence of NaOH increased its adsorption from 0.011 to 0.018 mmole/g at 230°C (2 Torr COS).

Adsorption of reactants on cobalt–molybdate containing NaOH was not attempted. Increase in adsorption of reactants can be expected.

Determination of Catalyst Basicity

The method of determining catalyst basicity consisted of making a suspension of about 0.50 g of the catalyst in 25.0 ml of benzene to which was added 1.0 ml of the indicator solution (0.128 g of bromothymol blue in 100.0 ml of benzene). If the catalyst possessed basic sites the yellow dye reacted with the base (transfer of electrons) to yield the color of the conjugate base (green). The suspension was then titrated against $0.01 N$ benzoic acid in benzene until the green color of the granules disappeared. The details of the method are given by Tanabe and Yamaguchi (5). For the Chromosorb-A containing 3.9 wt% NaOH, maximum basicity (0.27 mmole/g) was developed after activation for 3 hr at 500°C in dry helium.

TABLE 1
HYDROLYSIS OF COS OVER COBALT–MOLYBDATE CATALYST

t (°C)	pCOS^a	pH₂O^a	x	W/F (COS)^b	r_0 (computed)^c
302 ± 2	2.0	4.6	0.076	60.3	
	2.0	4.6	0.172	150.7	0.0015
	2.0	4.6	0.088	31.3	
348 ± 2	2.0	4.6	0.174	57.0	0.0028
	2.0	4.6	0.335	125.0	
378 ± 2	2.0	4.6	0.127	30.1	
	2.0	4.6	0.220	53.9	0.0040

^{a} Partial pressure (Torr).

^{b} g, sec/mmole reactant.

^{c} Initial rate for 230°C (extrapolated) = 3.8×10^{-4} (mmoles COS reacted/sec g).
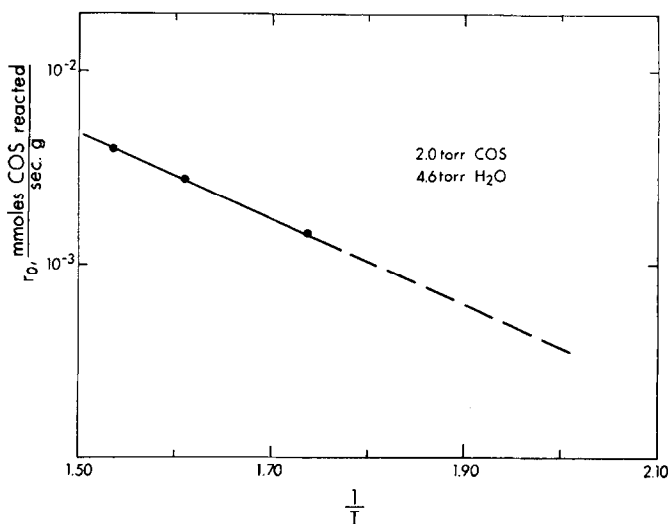
FIG. 2. Arrhenius' plot for COS hydrolysis over cobalt-molybdate catalyst.

The method could not be applied for the cobalt–molybdate catalysts due to the intense blue color of the granules.

Effect of CO_2 on COS Reactions

CO_2 is a product of COS–SO$_2$ and COS–H$_2$O reactions and since it is reported that CO_2 poisons the catalytic activity of γ-alumina for the former reaction (6), attempts made to investigate the effect of CO_2 on the above reactions indicated that CO_2 did not affect the rates over the cobalt–molybdate catalyst. In fact the advantage of the mixed oxides (CoO, MoO$_3$) on γ-alumina appears to be related to its resistance to poisoning by CO_2 produced in reactions (2) and (3).

1. COS Hydrolysis

In Table 1 the kinetic data for the hydrolysis of COS over cobalt–molybdate

catalyst are given. The initial rate for 230°C was obtained by the extrapolation of the data (Fig. 2). In Table 2, the data for the hydrolysis over the cobalt–molybdate catalyst containing 3.9% NaOH are given. It is seen that at 230°C, the initial rate for hydrolysis has increased from 3.8×10^{-4} to 9.3×10^{-3}, i.e., a 25-fold increase in rate.

For the hydrolysis reaction over Chromosorb-A at 230°C, no conversion of COS could be observed at a W/F (COS) of 1100. However, on the 3.9% NaOH loaded Chromosorb-A, the initial rate at 230°C was 4.5×10^{-5} (Table 3). The rate then went through a maximum (9.0×10^{-5}) at 7.2% NaOH loading and decreased to 3.3×10^{-5} at 10.5% NaOH loading. The decrease in rate at higher base loading could be due to the loss in surface area of Chromosorb-A at high base loadings. The one point isotherm used to measure the

TABLE 2

HYDROLYSIS OF COS OVER COBALT–MOLYBDATE
CONTAINING 3.9 wt% NaOH AT 230 ± 2°C[a]

pCOS	pH$_2$O	x	W/F (COS)	r_0 (computed)
2.0	4.6	0.152	20.5	
2.0	4.6	0.265	38.5	9.3×10^{-3}
2.0	4.6	0.485	102.0	

[a] At the end of the reaction 1.8% NaOH was extracted from the catalyst.

TABLE 3

HYDROLYSIS OF COS OVER CHROMOSORB-A
CONTAINING 3.9% NaOH AT 230 ± 2°C[a]

NaOH loading	x	W/F	r_0 (computed)
3.9%	0.070	1750	4.5×10^{-5}
	0.122	3872	

[a] pCOS, 2.0 Torr; pH$_2$O, 4.6 Torr.

TABLE 4

COS–SO₂ Reaction Over Chromosorb-A
at 415 ± 2°C

pCOS	pSO₂	x	W/F	r_0 (computed)
4.0	2.0	0.067	75.7	0.0015
4.0	2.0	0.115	143.1	

TABLE 6

COS–SO₂ Reaction Over Cobalt–Molybdate
at 359 ± 2°C

pCOS	pSO₂	x	W/F	r_0 (computed)
4.0	2.0	0.102	15.4	
4.0	2.0	0.204	31.2	0.0066
4.0	2.0	0.300	46.9	

surface area was not sufficiently sensitive to detect such losses in surface area. A similar decrease in rate at high base loadings was observed for Claus reaction (*2*).

2. COS–SO₂ Reaction

In Table 4 the data for the COS–SO₂ reaction over Chromosorb-A are given. In Table 5 the data for the same catalyst containing 6.0 wt% NaOH are given. The initial rate for the NaOH loaded catalyst was 0.0020 compared to 0.0015 for the same catalyst without NaOH indicating the presence of NaOH does not significantly affect the rate.

The data for the COS–SO₂ reaction over the cobalt–molybdate catalysts at 359°C are given in Tables 6 and 7. The initial rates were 0.0062 and 0.0066 for the catalyst with and without NaOH indicating again that NaOH on the catalyst does not significantly influence the rate.

DISCUSSION

The important finding in this study is the increase in rate of COS hydrolysis by the presence of base (NaOH) on the catalyst and the absence of such an effect for COS–SO₂ reaction.

It was shown in this study that at 230°C,

the initial rate of COS hydrolysis can be increased 25 times by depositing 3.9 wt% NaOH on the cobalt–molybdate catalyst. A similar effect was also observed for Chromosorb-A (Table 3). It was also shown that the initial rate for Claus reaction at 240°C can be increased as much as 10³-fold by depositing 3.9 wt% NaOH on Chromosorb-A (*2*). However, the presence of base did not affect the rate of COS–SO₂ reaction (Tables 4–7).

The increased rate for COS–H₂O and H₂S–SO₂ reactions when the catalyst was pretreated with base and the absence of such an effect for the COS–SO₂ reaction, can be explained in terms of the increased participation of basic sites (on the catalyst surface) and the presence of abstractable protons in the reactants. These conditions are satisfied for the H₂S–SO₂ and H₂O–COS reactions but not for SO₂–COS reactions, hence the lack of effect in the latter case.

It is proposed therefore that the hydrolysis of COS proceeds by a concerted mechanism similar to that already suggested for H₂S–SO₂ reaction (*2*).

The surface of the catalyst containing base (for hydrolysis) will be partially covered with OH⁻,

TABLE 5

COS–SO₂ Reaction Over Chromosorb-A
Containing 6.0 wt% NaOH
at 415 ± 2°C[a]

pCOS	pSO₂	x	W/F	r_0 (computed)
4.0	2.0	0.072	61.8	0.0020
4.0	2.0	0.135	123.7	

[a] 3.2% NaOH was left on the catalyst at the end of the reaction.

TABLE 7

COS–SO₂ Reaction Over Cobalt–Molybdate
Containing 5.0 wt% NaOH
at 359 ± 2°C[a]

pCOS	pSO₂	x	W/F	r_0
4.0	2.0	0.152	24.0	0.0062
4.0	2.0	0.242	40.0	

[a] 1.9% NaOH was left on the catalyst at the end of the reaction.

$$HOH + [B(s)*] \rightleftharpoons [BH^+(s)] + OH^-, \quad (5)$$

as well as by adsorbed H_2O {*[B(s)]: basic site on the surface of catalyst}. COS may be adsorbed on the base-loaded catalyst by an ion–dipole interaction (dipole moment of COS is 0.72×10^{-18} esu) or in the manner described by Chuang, Dalla Lana and Liu (6) on the alumina based catalysts. This adsorbed surface complex can react with an adsorbed H_2O [Eq. (7)].

$$(6)$$

$$(7)$$

$$\underset{(ads)}{SH^\ominus} + H_2O \rightleftharpoons \underset{(ads)}{H_2S} + OH^-. \quad (8)$$
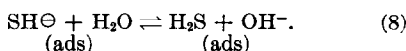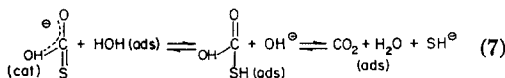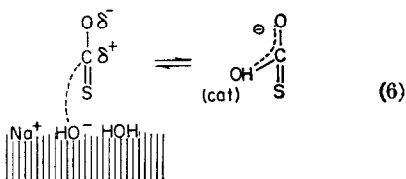
The difference between COS–H_2O and H_2S–SO_2 reaction is that the former reaction is zero order in H_2O and the latter is zero order in SO_2 but this may merely reflect the different strengths of chemisorption.

Chuang, Dalla Lana and Liu (6) studied the adsorption of COS on γ-alumina. At room temperature, the surface OH of γ-alumina (infrared vibrations occur at 3785, 3720 and 3680 cm^{-1}) was unaffected on adsorbing COS showing that COS is not adsorbed on the OH of the catalyst. A new band observed at 2000 cm^{-1} was ascribed to the C–O stretching vibration of the physically adsorbed (linear) COS, adsorbed via the sulfur atom. On heating the adsorbed COS to 237°C, sulfur was condensed on the infrared cell and catalyst wafer and bands due to adsorbed CO_2 (2360, 1800 and 1500 cm^{-1}) were detected. Argano, Randhava and Rehmat (7) adsorbed COS on Pt (1%) supported on γ-alumina. They observed chemisorbed COS (1920 cm^{-1})
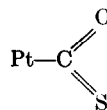
in addition to physisorbed COS.

It would be interesting to examine the ir spectra under reaction conditions to confirm the presence of the surface complexes postulated in the above mechanism. However, this would probably be complicated by the deposition of sulfur, adsorption of H_2S (bands at 1685, 1565, 1460, 1370, 1260 and 1140 cm^{-1}) and CO_2 (bands at 2360, 1800 and 1500 cm^{-1}) on alumina catalysts. Further the active surface complex will be transient and the concentration may not be sufficiently high to be detectable by infrared spectroscopy.

It has been shown by Liu (8) that treatment of γ-alumina with NaOH under the conditions used in this study does not lead to the formation of significant amounts of $NaAlO_2$.

The number of basic sites indicated by SO_2 adsorption is about one tenth of the sites determined by benzoic acid titration.

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