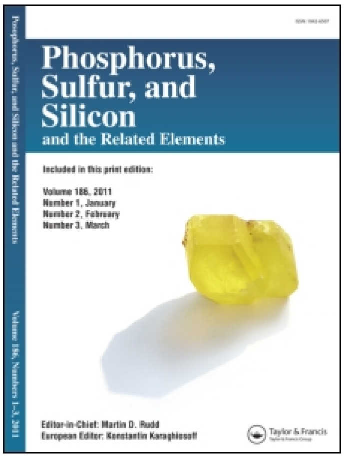

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ADVANCES IN CLAUS REACTION AND RELATED REACTIONS

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ADVANCES IN CLAUS REACTION AND RELATED REACTIONS*

by

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CONTENTS

I. INTRODUCTION

During the sweetening of sour natural gas H_2S and other contaminants are separated from natural gas. The conversion of H_2S and other sulfur compounds to sulfur is accomplished by the well known Claus process in which H_2S and SO_2 are allowed to react catalytically over an alumina-based catalyst at around 250°C. The Claus reaction is thermodynamically limited so that 2-4 catalytic stages, with intervening sulfur removal, are required to achieve total conversions of 95-98%. There is considerable research activity into all phases of sulfur recovery operations with the major emphasis on maximizing the overall sulfur recovery. This report summarizes the developments in Claus reaction and attempts to focus attention on potential areas for future research.

II. CLAUS REACTION AND RELATED REACTIONS

In the original Claus process[2] H_2S is mixed with the necessary amount of air and passed over a red-hot iron oxide catalyst where the Claus reaction takes place:

$$3H_2S + 1.5O_2 \rightleftharpoons 3H_2O + \frac{3}{x}S_x \qquad (1)$$

at 250°C $\Delta H = -145$ to -173 kcal/mole

Since the reaction is highly exothermic and the equilibrium concentration of sulfur is adversely affected by high temperatures, the process is generally carried out in two stages; one third of the H_2S is oxidized in a free flame with air in the so-called "front-end furnace", and the resultant SO_2 reacted with the residual H_2S over an alumina-based catalyst at about 250°C.

$$H_2S + 1.5O_2 \rightleftharpoons H_2O + SO_2 \qquad (2)$$

at 250°C $\Delta H = -124$ to -138 kcal/mole

$$2H_2S + SO_2 \rightleftharpoons 2H_2O + \frac{3}{x}S_x \qquad (3)$$

at 250°C $\Delta H = -21$ to -35 kcal/mole

Some complication in the chemistry of this modified Claus process arises in the front-end furnace due to the

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* *Alberta Research Contribution No. 743.*

conversion of hydrocarbon and CO_2 impurities in the H_2S into COS and CS_2. These compounds may undergo hydrolysis

$$COS + H_2O \rightleftharpoons CO_2 + H_2S \tag{4}$$

or Claus type oxidation

$$2COS + SO_2 \rightleftharpoons 2CO_2 + \frac{3}{x} S_x \tag{5}$$

While thermodynamically favorable, the rates of these reactions are low under normal operating conditions in the Claus units[3] and COS and CS_2 are frequently the source of significant plant loss of sulfur to the atmosphere.

Since almost all the work on Claus reaction now refers to the modified Claus reaction, the term Claus reaction or process used here refers to the modified Claus reaction, *i.e.* the catalytic reaction between H_2S and SO_2. Since reactions (3), (4), and (5) take place in the Claus catalytic converters, all three reactions will be considered in this report. It is assumed that the reactions of CS_2 will be similar to those of COS.

$$CS_2 + SO_2 \rightleftharpoons CO_2 + \frac{3}{x} S_x \tag{6}$$

$$CS_2 + 2H_2O \rightleftharpoons CO_2 + 2H_2S \tag{7}$$

III. THERMODYNAMICS

Gamson and Elkins have done extensive thermodynamic calculations on Claus and related reactions.[4] Recently, the free energy minimization technique developed by White, Johnson and Dantzig[5] has been used by Liu,[6] and by Mohtadi and Dingle[7] to predict equilibrium conversions of SO_2 in Claus and related reactions.

IV. KINETICS

A. H_2S–SO_2 Reaction

Dalla Lana and students at the University of Alberta have done considerable work on the catalytic reaction of H_2S with SO_2 and the other related reactions. They used a recycle flow reactor to study the kinetics of Claus reaction under conditions similar to that of an actual Claus plant operation. Dalla Lana, McGregor, Liu, and Cormode[8] reported that Claus reaction over a bauxite catalyst was not diffusion controlled and that the kinetic orders were 1.0 and 0.5 in H_2S and SO_2, respectively. Various rate expressions were tested, and their results are best explained by the rate expression:

$$r = \left(\frac{k p_{H_2S}^{1.0} p_{SO_2}^{0.5}}{1 + 0.00423 p_{H_2O}} \right) e^{-7400/RT} \tag{8}$$

They also observed that molten sulfur as well as condensed water catalyzed the Claus reaction.

George studied the kinetics of Claus reaction over a commerical cobalt-molybdate catalyst (Girdler G-35) on the basis of initial rates using a fixed-bed integral flow reactor, low partial pressure of reactants (2.0 torr SO_2 and 4.0 torr H_2S) and low conversions.[3] The kinetic orders in H_2S and SO_2 were determined to be 1.0 and zero respectively. The reaction was found to be diffusion controlled (pore) and an activation energy of 5.5 kcal/mole was determined for the Claus reaction. His rate expression was:

$$r = \frac{k p_{H_2S}^{1.0} p_{SO_2}^{0}}{(1 + 0.10 p_{H_2O})} \tag{9}$$

The value for the rate constant k at 315°C was 0.0050 (mmol H_2S reacted/sec.g. torr).

Taylor and Wesley[9] studied the Claus reaction over pyrex glass and derived the following rate expression:

$$-r_{H_2S} = k p_{H_2S}^{1.5} p_{SO_2}^{0} \tag{10}$$

The rate was found to be proportional to the surface area of the catalysts. Murthy and Rao[10] studied Claus reaction over metallic sulfides at room temperature and noticed that the reaction would not proceed in the absence of water but, in the presence of water, the overall reaction was found to be second order.

The variation in the kinetics of Claus reaction over different catalysts might only reflect the adsorption properties of the different catalysts. Further, mass transfer resistance could have a significant effect on the overall kinetics.

B. COS–SO_2 Reaction

Lepsoe[11] studied the reaction between COS and SO_2 (5) over an alumina catalyst and concluded that the overall reaction was first order with an activation energy of 14 kcal/mole in the temperature range of 300-600°C.

Chuang, Dalla Lana and Liu[12] carried out extensive studies into the COS–SO_2 reaction over an alumina catalyst. In their kinetic experiments they observed that the conversion of COS, which was about 70% at the beginning (285°C), decreased to a negligible amount in about one hour. The chemisorption of CO_2 (product) was regarded as responsible for the poisoning of the catalyst. In another experiment a fresh sample of the catalyst was exposed to 7 torr CO_2 for one hr, and then the COS–SO_2 reaction was attempted. No conversion of COS was detected. Further, ir study of CO_2 adsorption indicated that indeed CO_2 was chemisorbed and poisoned the catalyst for the COS–SO_2 reaction.

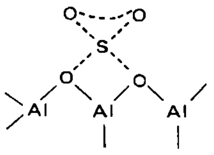
George studied the COS–SO_2 reaction over a cobalt-molybdate catalyst and observed that the overall reaction was first order (zero order in SO_2 and first order in COS) and an activation energy of 18.0 kcal/mole was determined. The reaction was not diffusion controlled. No poisoning of the catalyst by CO_2 was detected.[3]

C. Hydrolysis of COS

Namba and Shiba[13] studied the hydrolysis of COS (4) over an alumina catalyst and concluded that the reaction was diffusion controlled above 230°C and an activation energy of 2.9 kcal/mole was determined for the diffusion controlled reaction. The reaction was found to be first order with respect to COS. George, on the other hand, concluded that the reaction was not diffusion controlled and an activation energy of 12.0 kcal/mole was determined for the hydrolysis reaction.[3] Again, the kinetic orders were similar to those of the previous reactions considered, (3) and (5) in that the kinetic order with respect to the strongly adsorbed reactant (H_2O) was zero and that with respect to the other reactant (COS) was first order. It was also shown that at 250°C, close to the operating temperature of Claus catalytic converters, the rate constants *k* for the Claus reaction, COS hydrolysis and COS–SO_2 reaction were in the ratio 75 : 5 : 1.

V. ADSORPTION OF H_2S, SO_2, COS, CO_2 AND H_2O

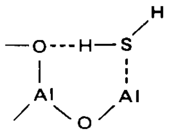
Deo, Dalla Lana, and Habgood[14] studied the adsorption of H_2S and SO_2 on zeolite and alumina catalysts by ir spectroscopy. They concluded that both reactants were hydrogen bonded to the catalyst surface. Further, SO_2 was found to be chemisorbed on alumina and the following structure has been proposed for the chemisorbed SO_2



(11)

They also suggested that the principal role of the catalyst is to bring the reactants into a suitable orientation to react.

Slager and Amberg[15] studied the adsorption and decomposition of H_2S on alumina-supported molybdenum sulfide by ir spectroscopy and suggested the following structure for the hydrogen bonded H_2S:



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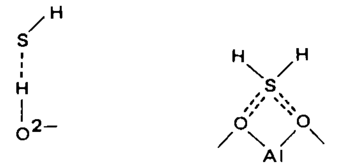
George[16] has suggested the following structures for H_2S adsorption on basic sites:



(Chemisorbed)

(13)

Dalla Lana, *et al.*,[17] studied the adsorption of H_2S, CS_2, and COS on γ-alumina using ir spectroscopy and concluded that the following oxidation reactions took place:

$$H_2S + [O] \rightleftharpoons H_2O + S_x \quad (14)$$

$$CS_2 + [O] \rightleftharpoons CO_2 + S_x \quad (15)$$

$$COS + [O] \rightleftharpoons CO_2 + S_x \quad (16)$$

Adsorbed oxygen on the catalyst was postulated as responsible for the above reactions.

George[3] has measured the adsorption of H_2S, SO_2, COS, CO_2, and H_2S on the cobalt-molybdate catalyst using frontal chromatography. Adsorption of H_2S and SO_2 was characterized by the very large amount (as much as 80%) of irreversible adsorption. SO_2 adsorption was also measured by experiments using a Cahn microbalance. It was observed that SO_2 adsorption was a very slow process; at 350°C using 20 torr SO_2, the equilibrium adsorption was not yet attained at the end of 72 hrs. As a result of SO_2 adsorption the molybdate catalyst turned black; however, this catalyst had the same activity as a fresh sample of the catalyst for Claus reaction. H_2S and SO_2 adsorptions were also measured on the sulfided catalyst (heating the catalyst at 100 torr H_2S for 4 hours at 400°C). SO_2 adsorption on the sulfided catalyst was higher than on the oxide catalyst and the frontal chromatographic adsorption showed breakthrough for H_2O, sulfur and SO_2.[3] 4 torr adsorption of H_2S and SO_2 on the oxide catalyst at 350°C amounted to 0.04 mmol/g corresponding to a surface coverage of about 3%.

DeRosett, Finstrom and Adams[18] studied the adsorption of H_2S on γ-alumina. For samples activated at 500°C and adsorption measured at 300-360°C, the saturation coverage (defined as the reciprocal of the limiting slope of Langmuir plot) was 0.05 mmol/g. This represents about 3% surface coverage.

Irreversible adsorption of H_2S and SO_2 was also observed in attempts to measure the heat of adsorption by measuring gas chromatographic retention volumes.[3] The first few slugs were irreversibly adsorbed, and the retention volumes were not reproducible.

Glass and Ross measured the heat of adsorption of SO_2 on alumina and H_2S on silica gel using calorimetry.[19,20] For SO_2 adsorption at low surface coverages the heat of adsorption was 48.0, 59.0, and 85.0 kcal/mol for the catalyst activated at 500, 700, and 900°C respectively. The heat of adsorption of H_2S on silica gel for the 240° to 550°C heat-treated samples was a maximum of 30.0 kcal/mol (0.005 μmol/m^2). The heat of adsorption decreased with surface coverage[20].

COS adsorption on the cobalt molybdate resulted in the production of CO_2.[3] The following reactions are possible

$$COS + [O] \rightleftharpoons CO_2 + S_x \tag{17}$$

$$COS \rightleftharpoons CO + S_x \tag{18}$$

$$2COS \rightleftharpoons CO_2 + CS_2 \tag{19}$$

At 350° to 450°C large amounts of CO_2 and smaller quantities of CO were observed. No CS_2 was detected. When the catalyst was reduced in hydrogen at 500°C, the ratio of CO_2/CO was reversed; however as the reaction progressed, the CO_2/CO ratio became almost identical to that observed with the oxide catalyst.

Haas and Khalafalla[21] studied the catalytic decomposition of COS. They observed that the CO_2/CO ratio, which was high in the temperature range 300-600°C, became low above 600°C. It was assumed that reaction (19) had occurred. Detection of CS_2 was not reported. The catalytic decomposition was not dependent on the catalyst; the decomposition was invariant with the surface area of the catalyst (5-500 m^2/g). The extent of decomposition depended only on the temperature.

Thermal and catalytic decomposition of H_2S (to sulfur and hydrogen) was investigated by Raymont.[22] For the thermal decomposition, 25 mol % of hydrogen was obtained at 1 130°C. For the catalytic decomposition (sulfided molybdenum and cobalt-molybdate catalysts) higher hydrogen production (than by thermal decomposition) was observed at 450-850°C.

Haas and Khalafalla[23] studied the decomposition of H_2S (to sulfur and hydrogen) in an electrical discharge. A threshold voltage of 1-3 kV was required to decompose H_2S at atmospheric pressure. Above this voltage the H_2S conversion increased with increasing voltage, decreasing temperature, decreasing H_2S concentration, and decreasing H_2S flow rate. The extent of H_2S decomposition increased significantly in the presence of chlorotrifluoroethylene.

VI. FACTORS AFFECTING CLAUS REACTION

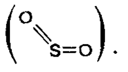
Wiewiorowski[24] carried out the reaction between H_2S and SO_2 in molten sulfur. The reaction was followed by ir spectroscopy. At 140°C (molten sulfur) no reaction between H_2S and SO_2 was observed. However, when 50 ppm of ethylenediamine was added to the system, very fast reaction between H_2S and SO_2 was observed.

During the course of his investigation into the properties of a good Claus catalyst, George observed that deposition of acids (H_2SO_4, H_3PO_4) on Chromosorb A (a gas-chromatographic solid support which is relatively inactive towards Claus reaction) did not enhance the catalytic activity of chromosorb for Claus reaction. The same conclusion was also arrived at from his experiments using zeolite catalysts (NaY zeolite was more active than NaHY zeolite for Claus reaction). However, when bases (NaOH, LiOH, and KOH) were deposited on the Chromosorb-A (3-5 wt%), a dramatic increase in Claus activity was observed. For example, for Chromosorb A that had 3.9% NaOH deposited on it, the activity for Claus reaction (on the basis of initial rates at 300°C) was increased 10^3 times compared to the sample which had no NaOH on it.[16] When the same experiment was repeated on alumina-based catalysts, the increase in activity was about 30%. The effect of catalyst basicity for the hydrolysis of COS and COS–SO_2 reaction has also been investigated. Whereas Claus reaction and COS hydrolysis reaction rates were enhanced on the base-loaded catalyst, no increase was observed for the COS–SO_2 reaction.[25]

Hyne and Mehmet[26] studied the reaction between H_2S and sulfoxides

$$H_2S + RSOR' \rightarrow H_2O + S_8 + RSR' \tag{20}$$

This generalized reaction also includes the Claus reaction if R and R′ in the sulfoxide are replaced by a single oxygen atom



The experiment consisted of bubbling H_2S through the sulfoxide solution. The reaction was followed by the continuous recording of the rise in product sulfur absorption near 320 nm. Their proposed mechanism involves the formation of ionic intermediates:

$$RSOR' + H_2S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Intermediate} \xrightarrow{\text{non-reversible}} RSR' + \tfrac{1}{8}S_8 + H_2O \qquad (21)$$

In a recent paper Burns, Lippert and Kerr[27] discussed the objective evaluation of Claus catalysts. Factors controlling catalyst quality include chemical composition, particle size and pore volume. Experimental data relating these factors to Claus reaction, $COS-SO_2$ reaction, and COS hydrolysis (including reactions of CS_2) showed that bauxite has the most effective composition and that the best phyisical characteristics are those that generate the highest ratio of pore-volume to particle size.

Kerr and Rankine[28] proposed that unprecedented efficiency levels can be achieved in Claus sulfur recovery operation by carefully controlling the operating variables. They predicted that more than 99% conversion is theoretically possible with a 4-stage Claus catalytic converter by controlling the following parameters:

1) Methods of reheat that introduce sulfur compounds into the main gas stream must be avoided.

2) Each sulfur condensor must be operated at around 127°C.

3) Mist elimination devices should be installed in each condensor.

In the actual plant operation 99.1% conversion was reported.

VII. LOW TEMPERATURE CLAUS REACTION

Struck, Kulik, and Gorin[29] have described the reaction between H_2S and SO_2 (about 2 torr H_2S, 1 torr SO_2) over an alumina catalyst at around 100°C. The catalyst was heated in N_2 to desorb the condensed sulfur. Sustained high conversions were reported. Commerical processes such as CBA[30] and Sulfreen[31] for the desulfurization of stack gas depend on this process.

VIII. POISONING OF CLAUS CATALYST

Pearson[32] has discussed the poisoning of Claus catalyst by carbon deposition, sulfur condensing, and sulfation. The drop in catalyst activity was shown to be proportional to the sulfate on the catalyst. The performance of a superior alumina catalyst that had excellent resistance to poisoning was demonstrated. Regeneration of the poisoned Claus catalyst has not been very successful due to the formation of aluminum sulfate which is not a catalyst for the Claus reaction.

Graulier and Papee[33] have discussed the sulfation of Claus catalysts. The reaction between SO_2, OH groups on the catalyst, and oxygen was suggested responsible for the sulfation which was indicated to increase with temperature and the partial pressure of oxygen. The regeneration of the sulfated catalyst was possible with dilute H_2S or H_2S/SO_2 mixture at around 300°C.

IX. REACTION BETWEEN H_2S AND SO_2 IN SOLUTION

Dry SO_2 and H_2S do not react at room temperature, or do so only slowly by catalytic processes. When such a catalytic reaction does occur the water formed in the reaction probably becomes a center of autocatalysis. Although dilute aqueous solutions of H_2S and SO_2 are stable for a few days, concentrated solutions rapidly form colloidal sulfur, polysulfur oxides $(S_2O)_x$, $H_2S_4O_6$, $H_2S_6O_6$, H_2SO_4, and higher polythionic acids. The reaction between H_2S and SO_2 is characterized by an induction period that is attributed to the initial formation of thiosulfurous acid which exists in equilibrium with H_2S and SO_2[34]:

$$H_2S + SO_2 \rightleftharpoons H_2S_2O_2 \qquad (22)$$

The unsymmetric form of thiosulfurous acid slowly rearranges to its tautomer HO–S–S–OH. Subsequently the major part of the elemental sulfur comes from attack of HS^- and/or H_2S on $H_2S_2O_2$,

$$H_2S_2O_2 + HS^- \xrightarrow{H^+} 3S + 2H_2O \qquad (23)$$

$H_2S_2O_2$ also readily condenses with H_2SO_3 to form tetrathionic acid,

$$HO{-}SS{-}OH + 2H_2SO_3 \rightarrow H_2S_4O_6 + 2H_2O \qquad (24)$$

Upon standing, further reactions involving electrophilic substitution reactions yield other polythionates and additional sulfur.[35]

$$H_2SO_3 + S \rightarrow H_2S_2O_3 \qquad (25)$$

$$H_2S_2O_2 + 2H_2S_2O_3 \rightarrow H_2S_6O_6 + 2H_2O \qquad (26)$$

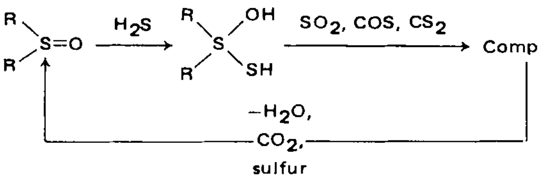
$$S_4O_6^{=} + HSO_3^{-} \rightleftharpoons S_3O_6^{=} + S_2O_3^{=} + H^+ \qquad (27)$$

$$H_2S_6O_6 \rightarrow H_2S_5O_6 + S \qquad (28)$$

Mathieu[36] has reported on the more practical apsects of the reaction between H_2S and SO_2 in aqueous solution. These results indicate that various technological aspects such as reactor design and intimacy of gas-liquid contact profoundly affect the efficiency of liquid phase reactions. Under such conditions a maximum of 85% of the input sulfur could be recovered at the most favorable H_2S concentration of 20% ($H_2S/SO_2 = 2$). Below 5% H_2S the efficiency of sulfur recovery drops significantly and the reactions leading to sulfur formation are slow. When the reaction is carried out in distilled water the sulfur formed remains colloidal. In order to obtain sulfur having good settling characteristics, brine solutions which are extremely corrosive are employed.

Diah, *et al.*,[37] studied the Claus reaction in organic solvents. The best solvent was a mixture of ethylene monoethyl ether (83%), water (15%) and dibutylamine (2%). The reaction was studied at 18, 26 and 41°C. Water was reported to be a co-catalyst as the reaction did not proceed in the absence of water. The gas stream was composed of 35% H_2S, 15% SO_2, and 50% N_2.

Another process that has potential for the Claus tail gas clean up is the Sulfoxide process developed by Hyne and Rennie.[38] The process consists of absorbing both H_2S and SO_2 into an organic sulfoxide solution which acts both as a solvent and catalyst. Preferred operating temperatures are below the melting point of sulfur where conversions as high as 99% are possible with high reaction rates. An added advantage of the process is the ability to convert COS and CS_2 to CO_2 and sulfur. The process can be represented:



(29)

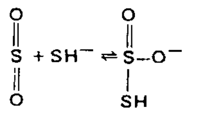
The process is reported to operate efficiently up to water loading of 20 mole %. Processes such as Townsend,[39] IFP,[40] Bumines citrate,[41] and Giammarco-Vetrocoke[42] operate on the above principle.

A very large number of dry non-aqueous solvents catalyze the reaction between H_2S and SO_2. These have been categorized on the basis of their ability to react within specified time limits, apparently to form a visible amount of sulfur. While the explanations for the various reactivities are tentative and not altogether satisfying, Albertson and McReynolds[43] have proposed that such reactivity is based upon the strength of the H_2S-solvent hydrogen bond, *i.e.* the liquid acts as a Brønsted base toward H_2S thereby producing HS^- as the reactive species. Such a suggestion explains, for example, why methyl benzoate is catalytic whereas methyl salicylate, which forms internal hydrogen bonds, is inactive. Kinetic studies in such non aqueous systems are complicated by the colloidal nature of the sulfur formed and the autocatalytic effect of product water.

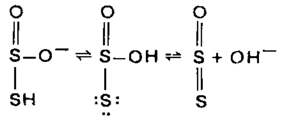
X. MECHANISM OF CLAUS REACTION

Hammar[44] from his experiments of Claus reaction over a cobalt-molybdate catalyst concluded that both reactants are adsorbed on the catalyst and the proposed mechanism for Claus reaction involved the dissociative adsorption of H_2S (H^+ and HS^-). George[16] has proposed a mechanism based on his observation that catalyst basicity enhanced the rates of Claus reaction and COS hydrolysis but not that of COS–SO_2 reaction. The mechanism involves the participation of basic sites (of the catalyst) and the presence of abstractable protons in the reactants:

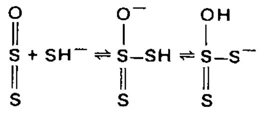
$$\mathrm{H{-}S{-}H} + [\mathrm{B(S)}^{a}] \rightleftharpoons \mathrm{SH^-} + \mathrm{BH^+} \qquad (30)$$



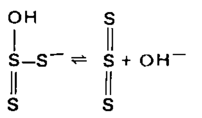
$$\mathrm{O{=}S{=}O} + \mathrm{SH^-} \rightleftharpoons \mathrm{O{=}S(SH){-}O^-} \qquad (31)$$



$$\mathrm{O{=}S(SH){-}O^-} \rightleftharpoons \mathrm{O{=}S(:\!S\!:){-}OH} \rightleftharpoons \mathrm{O{=}S{=}S} + \mathrm{OH^-} \qquad (32)$$



$$\mathrm{O{=}S{=}S} + \mathrm{SH^-} \rightleftharpoons \mathrm{{}^-O{-}S({=}S){-}SH} \rightleftharpoons \mathrm{HO{-}S({=}S){-}S^-} \qquad (33)$$



$$\mathrm{HO{-}S({=}S){-}S^-} \rightleftharpoons \mathrm{S{=}S{=}S} + \mathrm{OH^-} \qquad (34)$$

[a] [B(s)•] basic site on surface of the catalyst.

XI. SOME AREAS FOR FUTURE RESEARCH

A. Kinetics and Mechanism

Considerable effort has been put into the study of the kinetics of Claus reaction and related reactions. There are some apparent discrepancies in the kinetic order in SO_2, diffusional resistance and the adsorption equilibrium constant of water, (8) and (9), which may only reflect different properties of the two catalysts used[3,8]. The relative rate constants for Claus reaction, COS hydrolysis, and COS–SO_2 reaction are in the ratio 75 : 5 : 1 [reactions (3), (4), and (5)] as reported above. A catalyst over which the rates of reactions (4) and (5) are enhanced, without sacrificing Claus catalytic activity, would reduce the concentrations of COS and CS_2 in the effluent gases. Attempts to design such a catalyst would therefore be worthwhile.

The first step in heterogeneous and homogeneous Claus reaction appears to be the generation of HS^- (hydrosulfide) ions. It would be informative to investigate if the same mechanism is operative in both cases.

B. Catalyst Poisoning and Regeneration

Even though it is reported that catalyst activity for Claus reaction is lost by carbon deposition, sulfur condensation, and sulfation, very little data is available for the exact cause of deactivation. It is reported, for example, that whereas one Claus reactor can function efficiently for prolonged periods, the same feed to another reactor could result in rapid deactivation. It would be very valuable therefore to evaluate the precise factors that cause deactivation under Claus plant operating conditions. It would also be worthwhile to investigate methods of regenerating a deactivated catalyst. If regeneration can be achieved, this could lead to substantial savings in time and cost.

C. Factors that Affect Claus Activity

Total surface area, pore volume, pore diameter, and basicity of the catalyst are some of the factors that contribute to the overall Claus activity. However, these have not been investigated in a systematic way. If the relationship among the various catalyst parameters is established, it may be possible to make a Claus catalyst with excellent activity and longer life.

D. Superiority of Cobalt-Molybdate Catalyst

CO_2 poisons γ-alumina for the COS–SO_2 reaction and CO_2 has been found to chemisorb on alumina. However, cobalt-molybdate is not poisoned by CO_2 for the COS–SO_2 reaction (5) or the CO–SO_2 reaction[45] (stack gas clean-up)

$$2CO + SO_2 \rightleftharpoons 2CO_2 + 1/x\ S_x \qquad (35)$$

It is possible that CO_2 is not chemisorbed on cobalt-molybdate; this can be investigated by ir spectroscopy.

E. Surface Chemistry

Investigation of Claus reaction and related reactions by, for example, Photoelectron spectroscopy, may provide valuable information concerning the nature of the adsorbed species on the catalyst surface.

XII. CONCLUSIONS

In recent years, extensive studies of Claus catalysis have centered around kinetics, reactor design, and improvement of equilibrium conversions. However, there are areas that still need further research and development. These include the poisoning and regeneration of alumina-based Claus catalysts, the development of more efficient catalysts for the removal of COS and CS_2, and the study of the properties of a good Claus catalyst. Evaluation of the catalysts under Claus plant conditions would be essential.

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