JOURNAL OF CATALYSIS 63, 72–82 (1980)

Electron Donor Properties of Claus Catalysts[1]

I. Influence of NaOH on the Catalytic Activity of Silica Gel

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Received February 15, 1978; revised November 20, 1978

The influence of electron donor properties of catalysts on the Claus reaction was investigated by impregnating relatively inactive silica gel with NaOH and observing the formation of SO_2^- anion radicals by ESR spectroscopy and determining the corresponding Claus catalytic activity by the initial rate of the Claus reaction. A good correlation between the electron donor properties and the Claus activity was observed for silica gel impregnated with varying amounts of NaOH. As the NaOH impregnation was increased, the ESR signal intensity of SO_2^- and the rate of reaction went through a maximum. SO_2^- which appears to be a reaction intermediate reacted rapidly with H_2S both in the static system and under Claus reaction conditions. The use of SO_2 as a test molecule for evaluating electron-donor properties of catalysts has been proposed.

INTRODUCTION

The modified Claus reaction, Eq. (1), involves the catalytic reaction between H_2S and SO_2 to produce sulfur and water:

$$2H_2S + SO_2 \rightleftharpoons 2H_2O + 3/xS_x, \quad (1)$$

ΔH at 250°C = −21 to −35 kcal/mole and x represents the sulfur species in equilibrium. Many materials have been reported to catalyze the Claus reaction. These include iron oxide, titanium iron oxide, bauxite, manganese dioxide, alumina, glass, alumino-silicates, activated carbon, silver, cobalt–molybdate on alumina, cobalt–thiomolybdate, alkalized alumina as well as the sulfides of silver, cobalt, and molybdenum (*1*). Alumina-based catalysts, notably activated alumina and bauxite, are the ones used commercially.

Although the Claus reaction has been studied recently by Pearson (*2*), Dalla Lana *et al.* (*3*), Blanc *et al.* (*4*), Kerr *et al.* (*5*), and George (*6–11*) the reaction mechanism is not fully established. George observed that when a relatively inactive material such as Chromosorb was impregnated with a small amount of an alkaline reagent (NaOH), the catalytic activity of this solid for H_2S–SO_2 reaction was increased significantly (*8*). Further, Dudzik and Bilska-Ziolek observed that sodium faujasites are very active for H_2S oxidation indicating electron donor properties of these catalysts (*12*). Preliminary studies of commercial Claus alumina and zeolite catalysts by electron spin resonance spectroscopy using SO_2 as the electron-acceptor molecule indicate that these materials possess strong electron-donating properties (*13*). For investigating the influence of NaOH on the electron-donating properties and its attendent Claus catalytic activity, silica gel (Davison grade 407) was chosen as it exhibits only a vestigial ESR signal in the magnetic field region investigated and has relatively low Claus activity. Catalytic activity comparisons were made on the basis of initial rates. The results of these investigations are summarized in this report.

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0021-9045/80/050072-11$02.00/0

EXPERIMENTAL

Rate Measurements

A fixed-bed integral flow reactor (Fig. 1) was made out of 0.32-cm (i.d.) 316 stainless-steel tubing except for the reactor assembly and sulfur condenser which were made out of larger diameter stainless-steel tubing. Helium containing about 2% nitrogen as a marker was the carrier gas. Reactants, H_2S and SO_2, were introduced into the helium stream by means of micrometering valves. Water vapor when required was introduced into the reactor by allowing the helium to bubble through a water saturator. By controlling the temperature of the water saturator, the partial pressure of water in the feed stream could be maintained constant. The reactants were allowed to go through a mixing chamber located just ahead of the reactor and this enabled a uniform feed composition to be maintained. A separate helium line, as shown in Fig. 1, was used for gc analysis. Provision was made for the analysis of feed and product stream.

The reactor was 2.54 × 0.95 cm (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 180–400°C and at an absolute pressure of up to 1.3 atm. The reactants entered the reactor after passing through a preheater 12.7 × 0.95 cm (i.d.) packed with stainless-steel shavings and no corrosion of the shavings was detected.

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 catalyst was generally heated to 180°C at the rate of 3°/min during activation in flowing dry helium. Activation at 450°C did not show any significant difference in Claus

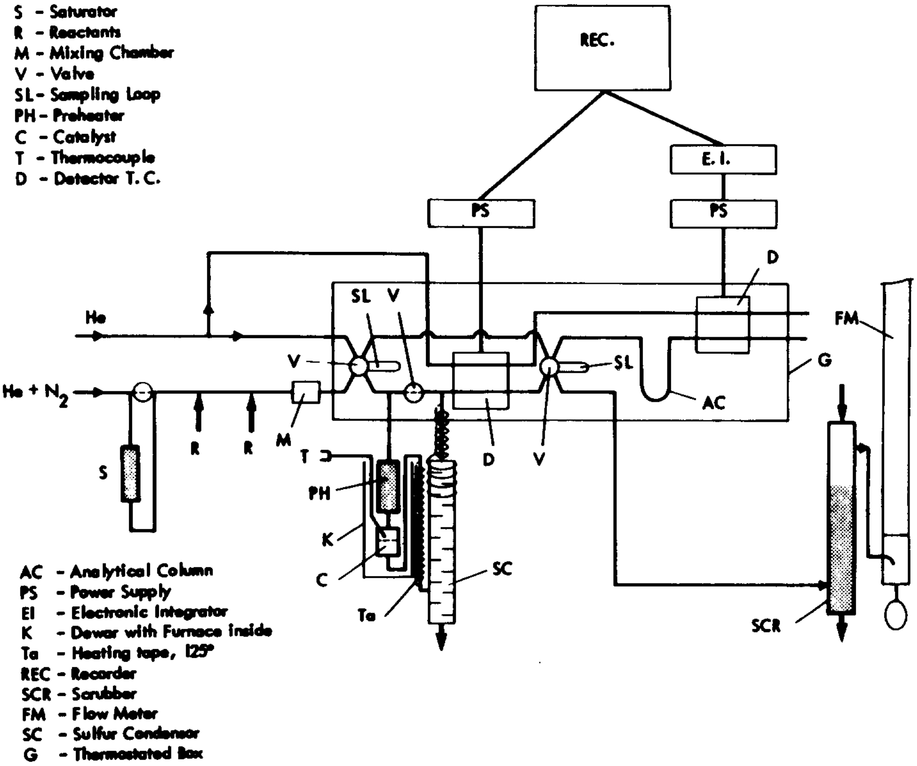

FIG. 1. Flow reactor (schematic).

activity compared to the 180°C activation. The furnace could easily be removed and replaced by a Dewar vessel with liquid nitrogen to permit measurement of nitrogen adsorption at $p/p_0 = 0.06$ by the usual dynamic method (*14*) for surface area measurements. The temperature of the apparatus was kept above the melting point of sulfur at 125°C.

The sulfur condenser was a 40.6 × 2.54-cm (i.d.) stainless-steel tube and had baffles every 2.5 cm to facilitate sulfur condensation. Further details are given in a previous publication (*6*). Periodically the condenser and other parts of the system have 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 nonparamagnetic elemental 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. The flow rates measured with a 500-ml soap bubble meter following the scrubber were expressed as millimoles per second of dry helium.

As shown in the schematic diagram (Fig. 1), there are two thermal conductivity detectors 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 (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 (2.0 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 which consisted of 20.3-cm × 0.32-cm Poropak Q (50–80 mesh) followed by 5.1- × 0.32-cm Poropak T (50–80 mesh). The column was operated at 125°C and provided good separations of N_2, CO_2, H_2S, H_2O, and SO_2 in about 5 min (Fig. 2). It was observed that the analytical column after prolonged use had turned yellow. This, however, did not interfere with the efficiency of the analysis.

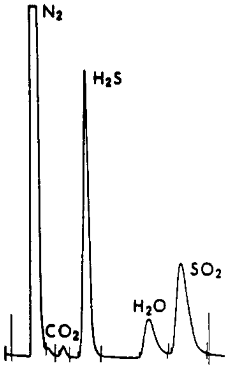

FIG. 2. Gas chromatogram of analysis product stream. Analysis column: 20.3 × 0.32-cm (50–80 mesh) Poropak Q, followed by 5.1 × 0.32-cm (50–80 mesh) Poropak T. Column and thermal conductivity detector thermostated at 125°C, 250 mA, and 1.34 ml/sec of helium flow rate.

BET surface areas of catalysts were determined on a Quantasorb sorption apparatus (Quantachrome Corp., U.S.A.)

ESR Studies

Both static and flow experiments were performed. In the static system, 50 mg of the catalyst (particles 20–30 mesh or finer) was placed in a 3-mm (i.d.) quartz reactor (Fig. 3b) and heated at 400°C for 18 hr under 10^{-4} Torr. H_2S, SO_2, or a 2 : 1 mixture of the above reactants from a volume of 300 ml was introduced into the reactor at temperatures ranging from −14 to +300°C.

For the flow experiments, the reactor and sulfur condensers employed for the kinetic experiments were replaced by the quartz flow reactor (Fig. 3a) which contained 100 mg of 40 to 60-mesh catalyst. The catalyst

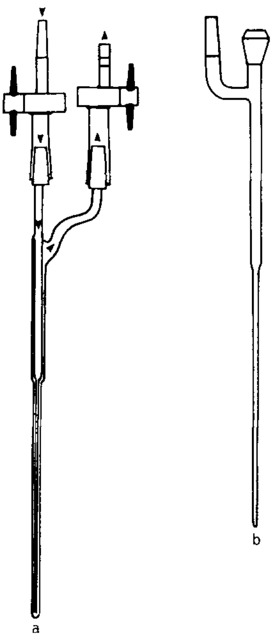

FIG. 3. Reactors for ESR measurements. (a) Flow; (b) static.

was activated at 180°C in flowing helium overnight. The experiments were identical to the conventional flow experiments as described later on. The product stream was not analyzed, but from the temperature, partial pressure of reactants, and W/F(g sec/mmole H_2S), H_2S conversion could be extrapolated. At the end of the experiment the stopcocks were closed and the furnace removed and replaced by a Dewar of liquid nitrogen. Spectra were recorded during the initial stage of the reaction and after the catalyst had attained steady-state activity (5 min and 2 hr respectively). Most of the spectra were obtained at liquid-nitrogen temperature. The g factors were determined relative to a standard sample containing cellulose char with $g = 2.00276$ (*15*) and using a Micro-Now Gaussmeter (Model 515-1). The amount of free spins in the samples was determined by comparing their signals with that from Varian Standards (VP-01 = 3×10^{15} and VP-02 = 1×10^{13} spins/cm cavity). The ESR spectra were obtained using a Varian E-line, X-band spectrometer with the field modulation of 100 kHz and recorded on a Hewlett-Packard X-Y recorder.

Materials

Most of the kinetic experiments were carried out on silica gel (Davison Chemicals, Grade 407) crushed and sieved to 20–30 mesh. Commercial Claus alumina catalyst (Kaiser Alumina S-201) was purchased from Travis Chemicals, Calgary, Alberta. Silica gel and alumina had BET surface areas of 520 and 260 m^2/g with average pore diameter estimated to be about 15 and 70 Å respectively.

Impregnation of Catalyst with NaOH

Since silica gel contained trace amounts of carbonaceous materials and these interfered with the ESR signal for SO_2^-, they were removed by heating to 400°C in a flow of oxygen for 2 hr prior to NaOH impregnation. An aliquot of the catalyst was added to an appropriate NaOH solution, sufficient to wet the granules, heated and evaporated to dryness at around 80°C in a Teflon beaker. Exact NaOH impregnation was determined by leaching and sodium by atomic absorption.

Reactants

H_2S and SO_2 were purchased from Matheson and had reported purity of more than 99 mole%. Traces of CO_2 were present in both gases.

Catalyst Samples Investigated

Most of the experiments were performed on silica gel containing varying amounts of NaOH. Comparative studies were made using γ-alumina and low-surface alumina as well as zeolites.

RESULTS

A. RATE STUDIES

Kinetic measurements were made at three or more flow rates after steady-state conditions were established, based on successive analysis being within 2% (about 4 hr from the start-up). Since the SO_2 and H_2O gc peaks had "tails," conversions were calculated from the disappearance of H_2S. Several repeat analyses were made for each set of conditions, the conversion ranging from 10 to 50%.

Initial-Rate Determinations

Generally, the conversion (X) of a reactant (A) is plotted against W/F_A (space time) of the reactant. The initial rate determined usually by measuring the slopes at the origin graphically is subject to errors, especially when there is scatter in the experimental data. The method used in this investigation is briefly described.

Rate expressions for the Claus reaction reported by Dalla Lana *et al.* (*3*), Blanc *et al.* (*4*), and George (*6*) are of the general form

$$r = \frac{k pH_2S^a pSO_2^b}{(1 + K pH_2O)} \qquad (2)$$

which pertains to the hyperbolic model as discussed by Kittrell (*16*). In this study we have attempted to fit our experimental data to a hyperbolic tangent expression and determine the initial rate by analytically differentiating the curve at the origin.

In general, for a flow reactor the rate of reaction for a unit mass of catalyst may be expressed as

$$r_A = \frac{dx_A}{d(W/F)}. \qquad (3)$$

where

r_A = mmole of reactant A converted per unit time and unit mass of catalyst

F = flow rate of feed, mmole per unit time

W = mass of catalyst

x_A = fractional conversion of reactant A.

The initial reaction rates were obtained by fitting the conversion–space time data to the hyperbolic function

$$x = C \tanh [D(W/F)] \qquad (4)$$

and analytically differentiating the function at the origin. In this expression x refers to the fractional conversion of H_2S, W/F to g sec/mmole H_2S and C and D are constants. The derivative of Eq. (3) with respect to W/F is

$$\frac{dx}{d(W/F)} = (C)(D)(\mathrm{sech}^2 [D(W/F)]. \qquad (5)$$

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 PDP-9 computer. This expression has been used by Mezaki and Kittrell (*17*) as a convenient and relatively nondiscriminating way to extrapolate to zero conversion to obtain initial rates. Conversion–space time data have also been fitted to an exponential function or by a third-degree polynomial to obtain initial rates (*18*). Sample values of C and D in this study were 0.00108 and 0.44003 respectively. The initial rate of the Claus reaction (r_0) is expressed as mmole H_2S reacted/sec g. Most of the experiments were performed employing 4.0 Torr H_2S and 2.0 Torr SO_2.

Initial rates of the Claus reaction determined at 180°C on silica gel impregnated with varying amounts of NaOH are shown in Fig. 4. This figure also demonstrates the surface area of silica gel as a function of NaOH loading. It can be seen from Fig. 4 that as the NaOH impregnation is increased, the Claus activity attains a maximum at 1.0–1.4 wt% NaOH loading and then declines rapidly. Further, a correlation between Claus activity and surface area is evident at NaOH loading over 1.4 wt%. Moreover, where maximum Claus catalytic activity is achieved, about 60% of the original surface area is retained. The enhanced Claus initial rate achieved with silica gel impregnated with 1.0–1.4 wt% NaOH was 12.3×10^{-4} mmole H_2S reacted/sec g compared to 20.1×10^{-4} for the commercial Claus alumina catalyst.

Stability of NaOH-Impregnated Silica Gel

In order to compare the sustained Claus activity of NaOH-impregnated silica gel

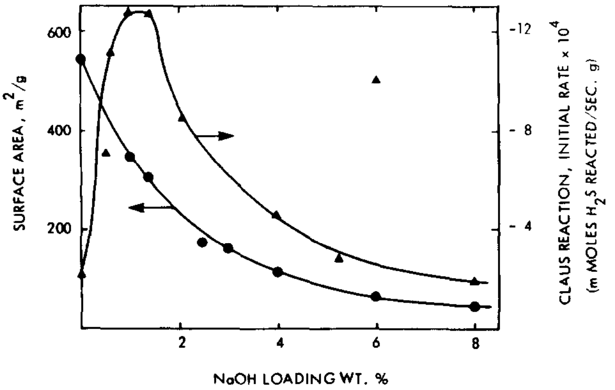

FIG. 4. Claus reaction initial rate at 180°C vs NaOH loading and surface area. (●) surface area (▲) initial rate.

(1.4 wt%) with that of commercial Claus alumina catalysts, the Claus reaction was carried out for up to 5 days at a fixed W/F under conditions that are similar to that of a third converter in an actual Claus plant (180°C, 4.0 Torr H_2S, 2.0 Torr SO_2, and 200 Torr water) and compared with commercial alumina catalysts under the same conditions. The results indicated that these two catalysts exhibited an initial decline in Claus activity followed by similar sustained activity. Sodium determination of the used silica gel catalyst indicated almost no loss of sodium during the reaction.

Reversibility of NaOH Loading

In an attempt to determine the nature of NaOH impregnation, a 2.0-g sample of silica gel containing 1.4% NaOH was leached for 48 hr at 80°C with 500 ml distilled water. The sodium content of the leachate determined by atomic absorption indicated that 50% of the initial NaOH had been leached out. The Claus activity of this leached sample was 18.0×10^{-4} (S.A. = 400 m^2/g) compared to 12.3×10^{-4} for the sample containing 1.4% NaOH. An aliquot of this leached sample was further leached with 1 M HNO_3 as before and the results of Na determination indicated that almost all the sodium had been leached out (S.A. = 450 m^2/g). The initial rate for the Claus reaction on this sample was 3.0×10^{-4} compared to 2.0×10^{-4} for the fresh silica gel. NaOH appears to have been adsorbed at least in two forms: a loosely bound form, which is removed by water leaching and which appears to block some of the catalytically active sites, and a tightly bound form on which a significant portion of the Claus reaction occurs.

B. ESR MEASUREMNTS

1. Static System

Activated silica gel showed a very weak ESR signal in the magnetic field region investigated (Fig. 5a). On adsorbing 20 Torr SO_2 on silica gel samples in the temperature range of 0–300°C, formation of SO_2^- anion radicals was observed. In Fig. 5 adsorption of SO_2 on silica gel (nonimpregnated) is summarized. The shape of the SO_2^- anion radical signal and g factors are different from those on the NaOH-impregnated sample (Fig. 6). It is probable that an unidentified narrow single line ($g = 2.0097$) is superimposed on the SO_2^- signal (Fig. 5b). This signal was not observed before SO_2 adsorption and disappeared completely on adsorbing H_2S (Fig. 5c). SO_2 adsorption on NaOH-impregnated silica gel is summarized in Fig. 6. The g factors for SO_2^- on this sample were 2.0014, 2.0101, and 2.0041 and these agree with the reported values for

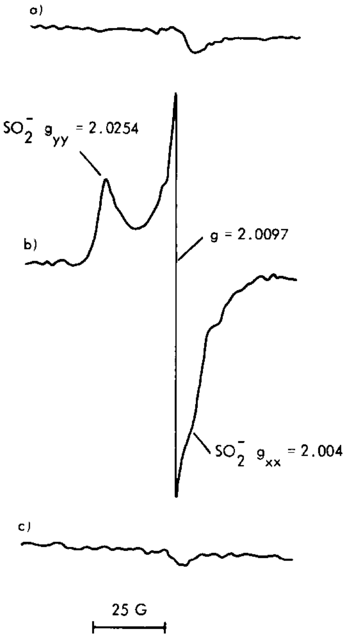

FIG. 5. ESR spectra, silica gel (nonimpregnated). (a) Background; (b) SO_2^- anion radical, 20 Torr SO_2, 0°C, 27 hr; (c) after adsorbing 40 Torr H_2S, 0°C, 2 min on (b).

SO_2^- on zeolites (*12, 13, 19, 20*) and on alumina (*13, 21*).

The changes in SO_2^- signal intensity with NaOH content and adsorption time investigated at 0 and 26°C are presented in Fig. 7. One arbitrary unit corresponds to approximately 2×10^{13} spins/g. Maximum signal intensity for SO_2^- was obtained on the sample containing 1.4 wt% NaOH.

II. Flow System

The ESR signals of SO_2^- on silica gel and silica gel impregnated with 1.4, 4.0, and 12.0 wt% NaOH were investigated employing the ESR flow reactor (Fig. 3a) during the initial stage of the Claus reaction and at steady state. Figure 8 is a typical example for the NaOH-impregnated sample. The important observation from these experiments was that SO_2^- was generated in a dynamic manner on the impregnated sample.

Reactivity of SO_2^- toward H_2S. On adsorbing 40 Torr H_2S at 0°C onto a silica gel sample (no impregnation) that had preadsorbed SO_2, the SO_2^- signal disappeared completely (Fig. 5c). However, on the NaOH-impregnated sample approximately 50% decrease in intensity was observed under similar conditions. No substantial changes in the intensity of SO_2^- signal were observed on varying H_2S contact time. Further, with the decrease in SO_2^- signal intensity, a concomitant ESR signal for sulfur-chain radicals was detected.

DISCUSSION

The significant feature of our results is the good correlation between SO_2^- anion radical concentration measured by ESR spectroscopy and the corresponding Claus catalytic activity as measured by the initial rate of reaction (Figs. 7 and 4) for silica gel containing varying amounts of NaOH. SO_2^- is likely to be formed on electron transfer from the catalyst surface and we have used this property as a probe to evaluate the electron donor property and the attendant catalytic activity of Claus catalysts. In the static system up to 10% of SO_2 was adsorbed as SO_2^-. Whereas H_2S reacted completely and instantly with SO_2^- formed on silica gel (no impregnation) at

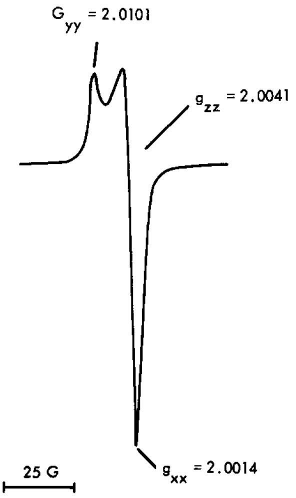

FIG. 6. ESR spectra of SO_2^- generated on silica gel containing 1.0 wt% NaOH, 20 Torr SO_2, 0°C.

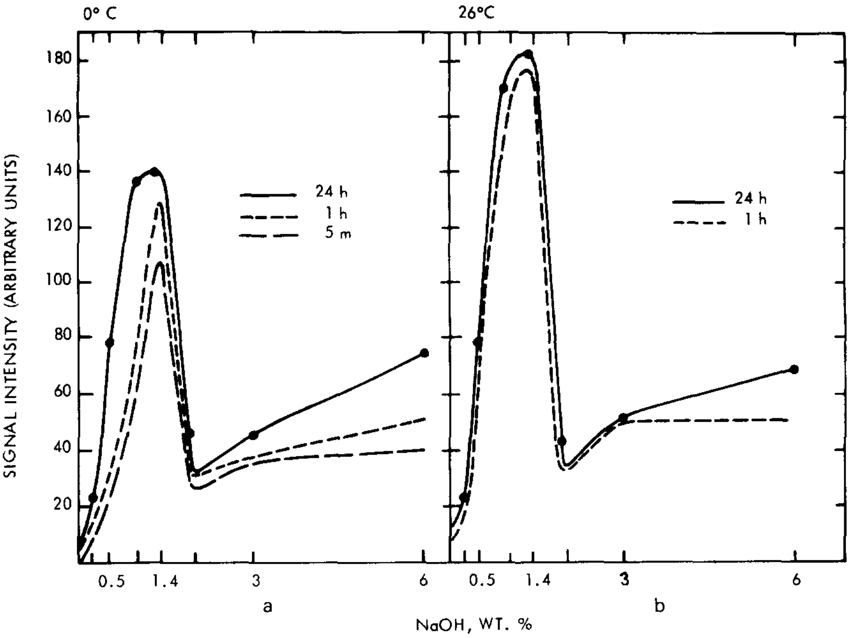

FIG. 7. Silica gel. Effect of NaOH concentration and SO_2 adsorption time on the intensity of SO_2^- anion radical. 20 Torr SO_2. (a) 0°C; (b) 26°C.

0°C, only about 50% of SO_2^- reacted with H_2S at 0°C on the impregnated samples, depending on the amount of NaOH retained on the silica gel. The *g* factors for SO_2^- on these samples were also different (Figs. 5 and 6). These differences in SO_2^- (reactivity toward H_2S and *g* factors) may be attributed to the degree of stabilization of SO_2^- on these surfaces by the Na^+ cations introduced during impregnation. The *g* factors of SO_2^- generated on the NaOH-impregnated sample (Fig. 6) are very close to those reported for SO_2^- stabilized by Na_4^{+3} complexes of Na-reduced NaY zeolite (*20*). Even though the *g* factor for the narrow single line on the nonimpregnated sample (Fig. 5b, $g = 2.0097$) was higher than that reported by Ben Taarit and Lunsford for SO_3^- on MgO (*22*), the fact that *g* factors for SO_2^- on the nonimpregnated sample were also higher (compare Figs. 5 and 6) coupled with our observation that this signal disappeared completely on adsorbing H_2S, leads us to assign this signal to SO_3^-.

ESR spectra of silica gel catalysts under Claus reaction conditions at 180°C (flow experiment) indicate that SO_2^- is formed in a dynamic manner and reacts readily with H_2S both during the initial stage and at steady-state conditions (Fig. 8). Since H_2S conversion under these conditions amounted to 57%, a significant amount of water[3] would be present in the reaction medium and no measurable effect of water on SO_2^- was detected. SO_2^- species are probably reaction intermediates, and the rate-controlling step in the Claus reaction over these catalysts appears to be the reaction between SO_2^- and H_2S. Further, a rate of reaction is proportional to $[SO_2^-]$ on the surface which is related to the ESR signal intensity for SO_2^-.

Whereas the catalytic activity increased with NaOH concentration up to 1.4 wt%, the ESR signal intensity for SO_2^- increased up to 2.0 wt%. This difference (reaction rate vs SO_2^- intensity) could be due, at least in part, to the extent of stabilization of

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[3] A mole of water is formed per mole of H_2S reacted in the Claus reaction (Eq. (1)).

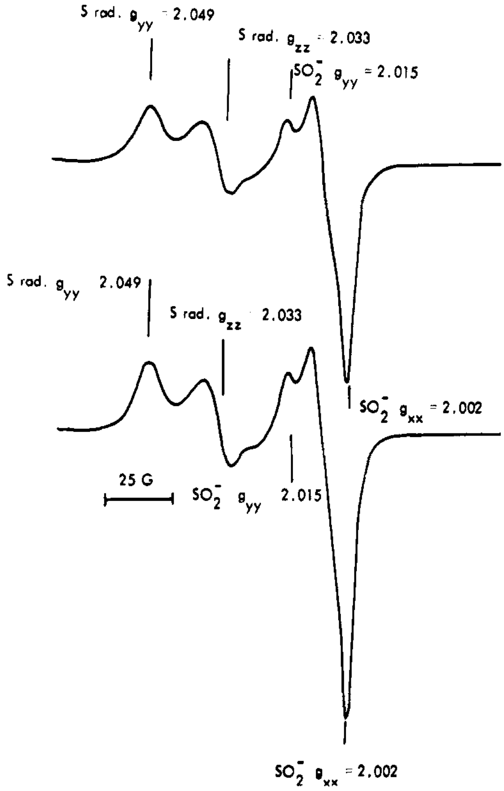

FIG. 8. ESR spectra during the Claus reaction. ESR flow rector. Silica gel containing 1.4 wt% NaOH, 180°C, 4.0 Torr H_2S and 2.0 Torr SO_2 in helium: (top) after 5-min flow (initial stage of reaction); (bottom) after 2-hr flow (steady-state reaction).

the SO_2^- anion radical. The initial rate for the sample containing 6.0 wt% NaOH is significantly higher than expected (Fig. 4). Even though we have no simple explanation at this time, experiments are under way to establish the presence of more than one maximum in such a plot.

In a previous study it was shown that when a relatively inactive material was impregnated with NaOH, a significant increase in Claus reactivity resulted (*8*). In this study we have demonstrated that the enhanced activity is related to the corresponding electron donor property of the NaOH-impregnated catalysts. Activated alumina (industrial Claus catalyst) and other active catalysts are very effective in forming SO_2^- (on SO_2 adsorption), suggesting that the electron donor property is one of the prerequisites for an efficient Claus catalyst.

It is probable that silica gel had all the other requirements for an efficient Claus catalyst except for its limited electron donor property. The enhancement of Claus activity with increasing NaOH loading during the initial stages can be explained in terms of increased electron donor capacity. Maximum catalytic activity achieved with silica gel containing 1.0–1.4% NaOH is equivalent to about 20-Å thickness of NaOH, assuming a uniform coverage. At the maximum Claus activity, silica gel retained 60% of its initial surface area. Activation experiments with Chromosorb (*8*) as well as sintered alumina (*13*) (both possessing only about 3 m^2/g) suggest that large surface area is not a requisite for enhanced Claus activity.

The electron transfer from the surface of NaOH-impregnated silica gel to adsorbed SO_2 occurs quite easily. The amount of SO_2^- formed at 0°C after 24 hr is on the average about 12% smaller than the SO_2^- formed at 26°C. At 180°C no substantial increase in SO_2^- formation was observed.

The second paramagnetic species present on the active catalyst surface during the Claus reaction in both static and flow systems has been identified as sulfur-chain radicals (Fig. 8). They appear to be stable on the catalyst surface and probably recombine to form sulfur rings after removal from the catalyst. These sulfur-chain radicals are highly reactive toward H_2S and may play a significant role in the Claus reaction mechanism. The presence of S_3^- anion radicals cannot be excluded. This radical has *g* factors similar to those of sulfur-chain radicals (*23*). S_3^- anion radicals are stable and may be formed as a result of the reaction between sulfur radicals and the OH groups on the catalyst (*23*).

Sulfur dioxide, which possesses strong electron affinity and is also a Claus reactant, was especially valuable for evaluating electron donor properties of Claus catalysts. Furthermore, the SO_2^- anion radical has a characteristic ESR spectrum and has been identified on many simple oxides (*13, 21, 24–27*) as well as on zeolites (*12, 19, 20*).

Additional experiments involving electron spectroscopy are needed to elucidate the nature and composition of the stable surface species. We observed a marked increase in Claus activity when the loosely bound NaOH was removed from the catalyst surface by water leaching, indicating that excess NaOH blocked some of the active sites for the catalytic reaction and its removal resulted in greater reactivity. This aspect of the Claus reaction is under investigation in our laboratories.

NaOH pellets and silica gel impregnated with 12.0 wt% NaOH have only limited Claus activity and do not exhibit the strong ESR signal for SO_2^- associated with active Claus catalysts. The catalytically active electron-donating phase originates as a result of interaction between sodium hydroxide solution and silica gel. Other electron-donating reagents such as carbonates of alkali metals may also enhance Claus catalytic activity. It has been reported recently by Kijenski and Malinowski (*28*) that when MgO was impregnated with NaOH solution, its electron-donating activity was increased.

The nature of electron-donating sites associated with the NaOH-impregnated silica gel is not properly understood. It is probably related to the O^{2-} anions in the low-coordination sites and OH^- groups on the surface (*29*). Experiments relating to the nature of NaOH on the surface of silica gel (and other catalysts), catalyst activation by other molecules, Claus catalysis by zeolites, etc., are under investigation in these laboratories.

ACKNOWLEDGMENTS

Excellent technical assistance was provided by J. Bodeux, Mrs. E. Dudzik, and Ms. L. Schneider. Surface areas were measured by H. A. Hamza, Energy, Mines and Resources, Edmonton. Valuable discussions with H. W. Habgood, D. Currie, A. T. Blades, and K. Schulz of the Alberta Research Council and H. Karge and the Fritz-Haber-Institut der Max-Planck-Gesellschaft, West Berlin are gratefully acknowledged.

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