

Infrared Studies of the Adsorption and Surface Reactions of Hydrogen Sulfide and Sulfur Dioxide on Some Aluminas and Zeolites

A. V. DEO AND I. G. DALLA LANA

Department of Chemical and Petroleum Engineering, University of Alberta

AND

H. W. HABGOOD

Research Council of Alberta, Edmonton, Alberta*

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Adsorption of hydrogen sulfide, sulfur dioxide, and their mixtures on four different catalysts has been studied by infrared spectroscopy of the catalyst surfaces. The four catalysts, which show a wide range of acidity and are all active for the Claus reaction ($2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 3\text{S} + 2\text{H}_2\text{O}$), were γ -alumina (the main constituent of commercial bauxite catalysts), γ -alumina doped with NaOH, sodium Y zeolite, and hydrogen Y zeolite. All catalysts showed physical adsorption of both reactants with strong hydrogen bonding to surface OH groups. This would suggest that the role of the catalyst is primarily to bring the reactants together in suitable orientation. On the other hand, γ -alumina shows, on heating with SO_2 , a chemisorbed SO_2 species which may be a reaction intermediate. The NaOH-treated γ -alumina shows a second chemisorbed SO_2 species which is irreversibly adsorbed and thus may be a catalyst poison.

INTRODUCTION

Infrared spectroscopy as a technique for studying adsorption phenomena on solid surfaces, e.g., gases on solid catalysts, has become extensively used since Eischens early work (1). The reaction of hydrogen sulfide and sulfur dioxide to form elemental sulfur and water is known to respond to many different catalysts (2). Because this reaction is an important commercial process for sulfur recovery from sour gases, and little has been reported about the detailed nature of the reaction or the chemical qualities of good catalysts, this study using the infrared technique was initiated. The most common catalysts in commercial use are derived from aluminum oxide or na-

tural bauxite. The molecular-sieve zeolites (crystalline alumino-silicates) are also catalytically active and have been suggested for such an application (3). The zeolites have been employed for hydrogen sulfide removal from sour gases. This paper describes the results from infrared studies of the adsorption and surface reactions of hydrogen sulfide and sulfur dioxide on four catalysts: γ -alumina, γ -alumina treated with sodium hydroxide, sodium Y zeolite, and hydrogen Y zeolite.

EXPERIMENTAL

Technique

The technique for examining the spectra of adsorbed gases is well known (4) and involves preparing the finely powdered adsorbent into a thin wafer that can be in-

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served into the infrared light beam of the spectrometer, adding the desired gaseous adsorbates, and observing the changes produced in the transmission spectrum of the wafer as a result of adsorption. The catalyst wafer is contained in a vacuum-tight glass *in situ* cell (5, 6) with infrared-transparent windows. A separate section of the cell is covered with external resistance heater windings, and the wafer can be moved into this section for thermal treatment. The cell is connected to a conventional vacuum and gas-handling system so that gases can be introduced and removed as required. The wafers of "catalyst" are prepared by pressing the finely ground powder in a steel die at a pressure of around 12 t/in.² The wafer diameters used in this work were either 3/4 in. or 1 in., and their weight was in the range 8–25 mg/cm.²

A conventional high resolution double-beam spectrometer is normally used for these measurements with the catalyst pellet inserted into the sample beam. Both Perkin-Elmer 621 and Beckman IR-12 infrared spectrophotometers were used in the present study. Because of scattering of the infrared beam by the wafer, especially at the high frequency end of the infrared spectrum, the transmission may be considerably reduced to anywhere between 0.5 to 40%. This was compensated for by attenuating proportionally the reference beam, and by using wider slits, and slower scanning speeds. In order to obtain a spectrum due solely to the combination of catalyst and added adsorbate, it is necessary to correct for any spectral absorption due to the gas phase present in the cell. Often the cell pressures are low enough that the gas-phase spectrum is negligible, but if it is appreciable, it must be eliminated, and this is most conveniently done by using in the reference beam of the spectrometer a similar cell with no wafer but containing gaseous adsorbate at the same pressure. Most oxide adsorbents and catalysts show strong infrared absorption at frequencies below 1200 to 1000 cm⁻¹, and this forms a lower limit to the useful frequency range for such adsorption studies.

Before the initial addition of adsorbate,

the catalyst wafer was always pretreated. The pretreatment involved degassing at an elevated temperature of 450 to 500°C for a prolonged period of 8–10 hr for removal of any adsorbed water. The wafer was then heated in oxygen two or three times (at 100–200 Torr of oxygen each time) for 2 hr at 450°C to remove traces of adsorbed organic materials. This was then followed by further prolonged degassing at the same elevated temperature. The wafer was then cooled to room temperature and the spectrum transmitted by the wafer alone (in the evacuated cell) was recorded to obtain a base line spectrum. The desired gaseous adsorbates were then added, various cycles involving heating the system, pumping off excess adsorbate, etc. were followed as described later, and the spectra were recorded at room temperature after each step. The figures which will be examined in this article show selected spectra in the regions of interest and are shifted along the transmission scale for clarity.

Materials

Aluminum oxide was Alon C (from Cabot Corporation, U. S. A.), a γ -alumina with a surface area of approximately 50–100 m²/g. Wafers prepared directly from this fine powder had a transmission of about 40% at 4000 cm⁻¹. The γ -alumina doped with sodium hydroxide was prepared by adding 2% by wt of sodium hydroxide to Alon C, with a minimum amount of water to make a thick slurry. The water was removed by heating at 110°C and the resulting cake crushed into fine powder and pressed into wafers. The sodium content was approximately 1.15%, corresponding to roughly 4 Na⁺ per 100(Å)² (the maximum possible OH concentration on the alumina surface is 13/100 (Å)²). The particle size of this doped material was greater than that of the original Alon C so that the wafers exhibited a lower transmission, about 10% at 4000 cm⁻¹.

Sodium Y zeolite powder was obtained from the Linde Division of Union Carbide Corporation (Lot SK40). In some cases it was washed several times with 1 N NaCl solution to remove traces of calcium or

other ions; this did not seem to make any difference in the spectra. Hydrogen Y zeolite was prepared in the usual fashion by heating NH_4Y , obtained by aqueous ion-exchange, to temperatures between 400 and 600°C. As discussed later, the higher temperature led to some dehydroxylation and possibly also some loss of crystallinity. The sodium content of this sample was not determined. The zeolites had a larger particle size ($1\ \mu$) than did the aluminas (0.01 – $0.04\ \mu$), and the transmission of the zeolite wafers was in the range 0.5–5% at $4000\ \text{cm}^{-1}$ but was always greater than 30% at lower wave numbers.

Hydrogen sulfide and sulfur dioxide were obtained from Matheson and dried before use by passage through a desiccant. The purities of the test gases were checked by infrared spectroscopy. No detectable impurities were found in the sulfur dioxide. Some lots of hydrogen sulfide had significant amounts of carbon dioxide (a few percent) which was found to chemisorb and thus interfere with these studies. The results reported here were obtained with hydrogen sulfide substantially free of carbon dioxide.

RESULTS AND DISCUSSION

I. Background Spectra of Catalysts:

Al_2O_3 , NaOH-doped $\gamma\text{-Al}_2\text{O}_3$, NaY, and HY Zeolites

The base line for pure γ -alumina (Curve a of Fig. 1), after prolonged degassing and oxygen treatment at 450°C, shows three (broad) bands at 3785, 3720, and 3680 cm^{-1} . These bands are attributed to the three different types of free surface hydroxyl groups present on the surface of γ -alumina. According to Peri (7), the number (as high as five), the intensity, and the sharpness of these bands depend mainly on the temperature of degassing. In the model proposed by Peri (8), these bands are attributed to the vibrations of distinct classes of surface OH groups that differ in the number and orientations of neighboring oxide (O^{2-}) and aluminum (Al^{+3}) ions.

When pure γ -alumina is doped with sodium hydroxide (8) and pretreated in the

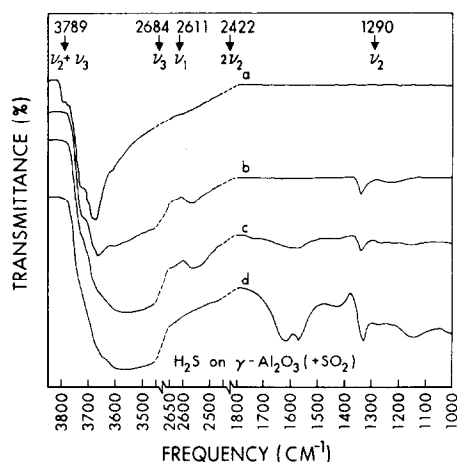


FIG. 1. Spectra of H_2S on γ -alumina. The arrows at the top show the frequencies for the gaseous molecules. (a) Base line spectrum of activated wafer. (b) Exposed to 100 Torr H_2S at room temperature. (c) Heated to 400°C in steps of 100° (in presence of 100 Torr H_2S), then pumped at room temperature for 1 hr. (d) Then exposed to 1 Torr SO_2 . (In Figs. 1–4 the region 1800–1000 $^{-1}$ is shown as the differential spectrum between the base line and the adsorbed spectrum. Useful transparency of the wafer extends to 1000 cm^{-1} .)

same way, the base line (Curve a of Fig. 2) shows an apparent decrease in the total adsorption in the OH region with complete disappearance of the high frequency vibration at 3785 cm^{-1} . The larger particle size of the NaOH-treated material means that scattering increases strongly with increasing frequency and it is difficult to decide on an absolute basis whether the apparent decrease of the low frequency OH bands is real or merely a result of the varying scattering. The two lower frequency bands are well separated and the middle band is shifted from 3720 to 3740 cm^{-1} . The complete disappearance of the high-frequency band could suggest that the NaOH chemically reacts preferentially with the OH groups responsible for this vibration to give =Al—O—Na . Peri (8) has reported that the band at the lower frequency of 3680 cm^{-1} corresponds to the most acidic of the three free surface hydroxyl groups, because of the greater ease with which it exchanges hydrogen. On the other hand, the elimination of the high frequency band by sodium hydroxide doping suggests that the

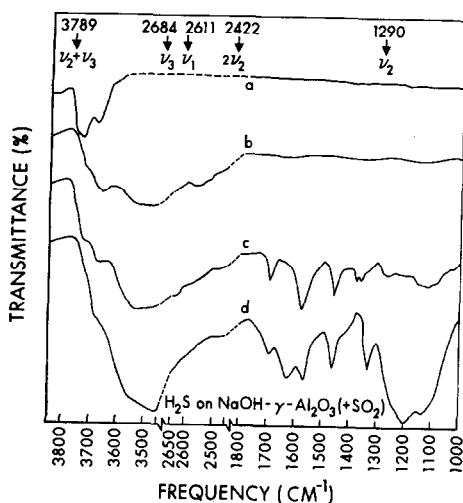


Fig. 2. Spectra of H_2S on NaOH-doped γ -alumina. (a) Base line. (b) Exposed to 100 Torr H_2S at room temperature. (c) Heated to 400°C in steps of 100° (in the presence of 100 Torr H_2S), then pumped at room temperature for 1 hr. (d) Then exposed to 1 Torr SO_2 .

high frequency band is the most acidic one. To add to this inconsistency, as will be discussed subsequently in this paper, adsorption of either H_2S or SO_2 (both "acid" gases) on $\gamma\text{-Al}_2\text{O}_3$ causes the same 3785 cm^{-1} band to disappear and leaves the two lower frequency hydroxyl bands still well separated and distinguishable. These observations, from a chemical reaction with sodium hydroxide or from hydrogen bonding of H_2S and SO_2 , suggest that the acidity behavior of the surface hydroxyl groups on γ -alumina is more complicated than previously considered. Adsorption studies of different species varying widely in their reactivity as acids or bases might be revealing.

In contrast to alumina, the dehydrated sodium Y zeolites have only low concentration of structural hydroxyl groups so that the hydroxyl bands appearing in the zeolite background (Curves a and e of Fig. 5) are very weak. The ideal zeolite crystal should have no OH groups at all. The principal band at 3750 cm^{-1} is considered to represent Si-OH groups at the crystal edges.

Hydrogen Y zeolite differs from sodium Y zeolite primarily due to the replacement

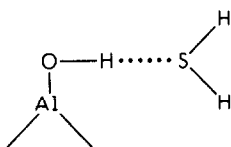
of Na by H. A sample prepared by decomposition of NH_4Y at 400°C showed two strong bands of about equal intensity at 3650 and 3550 cm^{-1} that are due to acidic OH groups and a much weaker band at 3750 cm^{-1} similar to that on the NaY. Most of the spectra in the present study were obtained after the same wafer had been heated to 600°C . The resultant background spectrum (Fig. 6a) showed a relative decrease in the intensity of the 3550 cm^{-1} band probably due to partial dehydroxylation and an increase in the 3750 cm^{-1} band, which may be an indication of partial loss of crystallinity.

II. Adsorption of H_2S on γ -Alumina

Figure 1 shows the results of adsorption of H_2S on γ -alumina. As soon as H_2S is adsorbed on the surface at room temperature, the white color of the catalyst wafer changes to a bright violet. The high-frequency hydroxyl band at 3785 cm^{-1} (Curve 1b) completely disappears, while the other two hydroxyl bands do not change in frequency and are still distinguishable, along with the formation of a large broad band around 3500 cm^{-1} due to hydrogen bonding of H_2S molecules with the surface hydroxyl groups. Because various molecular interactions associated with hydrogen bonding will result in spectral changes in the region of this broad band, their explicit interpretation is difficult. Nonetheless, the spectra do reveal that hydrogen bonding has occurred between surface hydroxyl groups and the H_2S molecules.

The principal adsorption bands of adsorbed H_2S are found at 2560 and 1335 cm^{-1} , and these remained even after room temperature pumping. The infrared adsorption bands for gaseous H_2S molecules are shown at the top of Figs. 1 and 2 with their positions and modes of vibration (9). The 1335 cm^{-1} band probably represents the ν_2 vibration of H_2S (a scissor-like bending vibration of the two SH bonds) reported for the free molecule at 1290 cm^{-1} (9). The 2560 cm^{-1} band may include contributions from the SH stretching vibrations (ν_1 and ν_3 , 2611 , and 2684 cm^{-1} for the free molecule) and the first overtone of the bending

vibration ($2\nu_2$, 2422 cm^{-1} for the free molecule). The broad and asymmetrical shape of this band suggests that it might be a combination of two or more bands. The shift of the SH stretching frequency to a lower value and of the HSH bending frequency to a higher value is similar to the shifts observed in the spectrum of water (a molecule of analogous structure), the result of associations in condensed phases (10). Consequently, the most likely representation of adsorbed H_2S is given by the following structure,

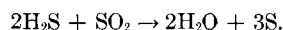


Such a structure, however, inadequately explains the change in color of the catalyst on adsorption. This color change, which was observed only for the system H_2S -pure γ -alumina, is indicative of a strong electronic perturbation for which we have no specific explanation at this time. From conjecture, it may be due to disintegration of the H_2S molecule or some higher polymeric forms of sulfur, S_x . A similar color change to cobalt-blue was reported by Kerr and Johnson (12) when they exposed 13x Linde molecular sieve to a stream of H_2S and air.

This band structure remained unchanged for γ -alumina heated with 100 Torr H_2S up to a temperature of 400°C except for a gradual broadening and increase in intensity in the hydrogen-bonding region. No change was produced by pumping off the H_2S for 1 hr at room temperature (Curve 1c).

The catalyst wafer was then exposed to a very small pressure of sulfur dioxide (1 Torr), and the color of the wafer immediately turned yellowish. The hydrogen-bonding region increased considerably (Curve 1d), and both bands due to H_2S adsorption (2560 and 1335 cm^{-1}) disappeared. Two new bands appeared at 1565 cm^{-1} (with a broad band at 1625 cm^{-1}) and 1330 cm^{-1} . The 1330 cm^{-1} band is much more intense than the previous 1335 cm^{-1} band and for this reason is considered to

represent a new species. The increase in the hydrogen-bonding region along with the appearance of the broad band at 1625 cm^{-1} , which is the ν_2 (bending) band of water, indicates the formation of water, and the yellow color indicates the formation of free sulfur according to the usual Claus reaction,



The bands at 1565 and 1330 cm^{-1} , which are part of the spectrum of adsorbed SO_2 , will be discussed later.

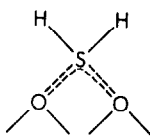
III. Adsorption of H_2S on NaOH-doped γ - Al_2O_3

Figure 2 shows the results of adsorption of H_2S on sodium hydroxide-doped γ -alumina. On adsorption at 10 Torr at room temperature, the pellet immediately turned yellowish in contrast to the violet color observed on pure γ -alumina. The two surface free hydroxyl bands shifted towards the lower frequency side with the appearance of a broad hydrogen-bonded hydroxyl region, though much smaller in intensity than the one on pure γ -alumina. The 2560 cm^{-1} broad band appeared although it was weaker than with γ -alumina, but the band at 1335 cm^{-1} was completely absent. These observations suggest a lesser degree of adsorption of H_2S on the doped alumina as compared with the pure alumina. With increase in pressure up to 100 Torr, no further change was observed (Curve 2b).

When the wafer was heated in the presence of 100 Torr H_2S , new bands appeared in the spectrum, at 1685 , 1565 , 1460 , and 1370 cm^{-1} , and two shallow bands appeared around 1260 and 1140 cm^{-1} , increasing in intensity with increasing temperature up to 400°C . There was also an increase in the OH region, although less pronounced than that found for pure alumina. Pumping at room temperature eliminated the 2560 cm^{-1} band, and pumping at successively higher temperatures up to 400°C caused only small decreases in intensity of the remaining bands (Curve 2c). Addition of a small pressure of SO_2 at room temperature produced an increase in the hydrogen-bonded hydroxyl region, a broad band at

about 1625 cm^{-1} , with the 1370 cm^{-1} band intensifying and shifting to 1330 , and the two shallow bands developed into deep and broad bands at 1200 and 1140 cm^{-1} , but otherwise there was no change in the rest of the band structure (Curve 2d). Further heating to 200°C produced no change.

The complex band structure described in the preceding paragraph suggests the simultaneous presence of both a chemisorbed H_2S and, because of similarities with spectra obtained on heating SO_2 with the two alumina samples (see below), a chemisorbed SO_2 . Chemisorbed H_2S might have a structure of the sort,



indicating reaction with the oxide ions of the alumina lattice. Such a species might reasonably be expected to react with SO_2 to form water and sulfur. Although water was indeed observed, the chemisorption bands did not disappear. The production of chemisorbed SO_2 from H_2S would require an oxidation step that could involve either chemisorbed molecular oxygen or removal of oxygen ions from the alumina lattice. Chemisorption of oxygen is clearly sufficient on the zeolite catalysts to oxidize significant amounts of H_2S to S and H_2O , but no chemisorption bands of the present type were found in this case. This reaction should produce an equivalent amount of water but water bands were not observed during the development of the chemisorption bands. On the other hand, the initial slightly yellowish color of the wafer may have indicated some complete oxidation to elemental sulfur. The species should be resistant to treatment with SO_2 , as indeed it was, but the observed production of water during this step could be explained only by surmising the simultaneous presence of H_2S adsorbed in amounts too small to be detectable.

There is the further possibility that this chemisorption band structure arises from SO vibration of chemisorbed sulfur atoms

to give SO_2 -like species with the lattice oxide ions.

In our opinion, the most plausible explanation of these chemisorption bands is the formation of chemisorbed SO_2 similar to that found on the reaction of SO_2 with the aluminas as described below.

IV. Adsorption of SO_2 on γ -Alumina

Figure 3 shows the results of adsorption of SO_2 on pure γ -alumina. The infrared absorption bands for SO_2 molecules are shown at the top of Figs. 3 and 4 with their posi-

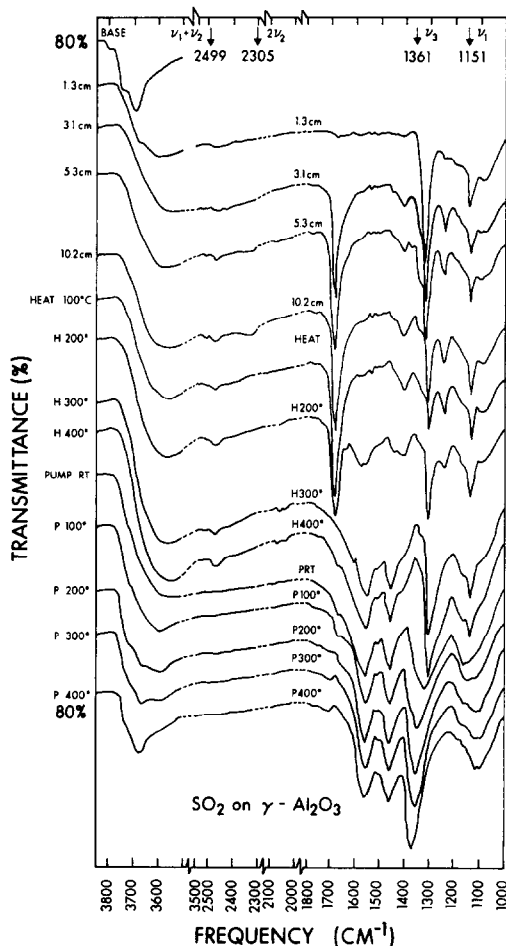


FIG. 3. Spectra of SO_2 on γ -Alumina. The curves in order from the top show the base line, successive additions of SO_2 at room temperature up to 100 Torr, and heating successively at temperatures up to 400°C . The subsequent addition of H_2S removed all bands in the region 1800 – 1000 cm^{-1} (no spectrum shown).

tion and modes of vibrations (12). The most striking feature of the SO_2 spectrum is a pair of absorption bands representing symmetric and antisymmetric SO vibrations. These occur in the gas phase at 1360 (ν_3) and 1151 cm^{-1} (ν_1) and are also found in the spectrum of SO_2 adsorbed at room temperature and low pressure at 1330 and 1140 cm^{-1} , values similar to those observed for liquid SO_2 . The weaker bands found in the gas phase at 2499 ($\nu_1 + \nu_2$) and 2305 cm^{-1} ($2\nu_1$) are observed with adsorbed SO_2 at 2470 and 2340 cm^{-1} . The shift to a higher frequency of the $2\nu_1$ vibration is somewhat unexpected. Accompanying the low pressure adsorption of SO_2 is a disappearance of the high frequency OH vibration of the alumina and the appearance of a broad band at 3500 cm^{-1} due to hydrogen-bonded OH. Obviously the SO_2 is adsorbed by hydrogen bonding to surface hydroxyl groups. There was no change in color of the wafer on adsorption.

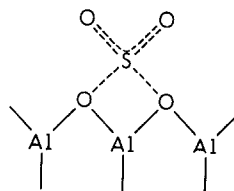
At higher pressures of SO_2 , up to 100 Torr, a new pair of bands at 1685 and 1240 cm^{-1} appear, and their shapes and relative intensities suggest that they might be the ν_3 and ν_1 vibrations of a perturbed SO_2 . A second but weaker pair of bands at 1410 and 1090 cm^{-1} may indicate another perturbed adsorbed SO_2 species.

On heating the wafer, a further pair of bands was observed at 1570 and 1440 cm^{-1} , the relative intensities approximately equal in this case, in contrast with the stronger absorption of the high frequency member in each of the other pairs of bands.

When heating was extended to 400°C and the system subsequently was pumped at temperatures up to 400°C (lower 7 curves of Fig. 3), the 1685 – 1240 and the 1410 – 1090 pairs of bands disappeared; the 1330 – 1140 pair gradually broadened and shifted to 1375 and 1110 cm^{-1} ; the 1570 – 1440 pair intensified and stabilized at 1570 and 1470 cm^{-1} , and the original OH band structure of alumina substantially reappeared.

The final spectrum clearly represents some form of chemisorbed SO_2 . One interpretation treating the spectrum as two pairs of absorption bands, as has been done

above, would postulate two separate chemisorbed species, each a bent O–S–O structure adsorbed on the surface and vibrating with its own characteristic set of frequencies. Another interpretation is that a sulfate-like structure has been produced,



with the oxide ions of the surface, and that this species has a spectrum similar to that observed for inorganic sulfates in an unsymmetrical field, such as found for example in bisulfates (14).

A similar band structure, at 1565 and 1330 cm^{-1} , was observed when H_2S -treated γ -alumina was exposed to SO_2 . These two bands may correspond to the two pairs observed here, 1570 – 1470 cm^{-1} and 1375 – 1110 cm^{-1} . The appearance of bands, not in pairs, but as single bands in the case of the H_2S -treated surface may be attributed to the smaller concentrations of such a species.

In any case, the molecular species of greatest interest in the Claus reaction are those found at high temperatures and the physically adsorbed (and hydrogen-bonded) SO_2 , which will be present even at high temperatures under high partial pressures of SO_2 . On exposing such a surface to a small pressure of H_2S , it was observed that the above bands all disappear giving only the usual bands around 3500 and 1650 cm^{-1} , due to water, as expected for the reaction of H_2S and SO_2 .

V. Adsorption of SO_2 on NaOH-treated γ -Alumina

The spectra of SO_2 on the NaOH-doped alumina (Fig. 4) are significantly different from those on pure alumina. Initial low pressure adsorption at room temperature yielded the two strong bands at 1330 and 1135 cm^{-1} , but these were almost from the beginning accompanied by another pair at 1380 and 1185 cm^{-1} . With increasing pressure and subsequent heating the 1330 cm^{-1}

band shifted to 1305 cm^{-1} , but otherwise, there was little change in the band structure apart from the disappearance of an initial very broad band at 1640 cm^{-1} .

The intensity of the hydrogen-bonded OH absorption was somewhat less than that found with pure alumina, but the disappearance of the original OH bands seemed to be more complete although these bands returned on final pumping. The combination and overtone bands at 2480 and 2340 cm^{-1} are more intense than in the spectra from pure alumina.

Pumping with heating finally yielded a single pair of bands at 1260 and 1180 cm^{-1}

which, as before, represents a chemisorbed SO_2 species.

Two very similar bands at 1260 and 1140 cm^{-1} were observed on H_2S -treated NaOH -doped γ -alumina surface along with other bands due to chemisorbed H_2S . The similarity in their shapes and band positions suggest that the same type of chemisorbed structure occurs in both of the cases when H_2S or SO_2 are adsorbed on sodium hydroxide-doped γ -alumina surface.

It was distinctive however, that this final chemisorbed species was not removed when small amounts of H_2S were added. It possibly represented, in practical terms, the formation of an irreversible product which could act as a poison by the elimination of active sites.

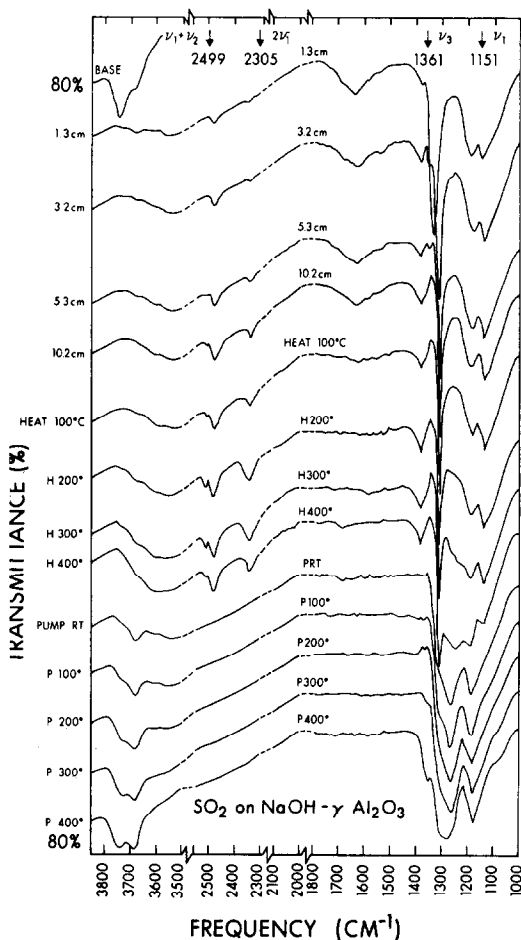


FIG. 4. Spectra of SO_2 on NaOH -doped γ -alumina. The curves follow the same sequence as in Fig. 3. Subsequent addition of H_2S did not produce any change in the band structure of the bottom curve.

VI. Adsorption of a Mixture of H_2S and SO_2 on Aluminas and Zeolites

When a 2:1 mixture of H_2S and SO_2 was admitted to either alumina sample at room temperature, both wafers became yellow from free sulfur and the spectra showed only the bands due to water, indicating the occurrence of the expected Claus reaction. The same results were observed on both the zeolites. None of the chemisorption bands discussed above were observed. This observation suggests that the main purpose of the catalyst may be just to bring the reactants together in a suitable orientation, most probably through the hydrogen bonding, observed prominently in all of the experiments.

VII. Adsorption of H_2S and SO_2 on NaY Zeolite

Figure 5 shows spectra for additions of H_2S and of SO_2 to NaY zeolite. Addition of H_2S produced only a slight darkening and not the bright violet color found with alumina. The combination ν_1 , ν_3 , and $2\nu_2$ band was encountered at a slightly different frequency than that on alumina, 2575 cm^{-1} , and no band was observable near 1330 as expected for the ν_2 bending vibration. A small increase in molecular water is shown by bands near 3690 , characteristic of water on zeolites (15), and one near

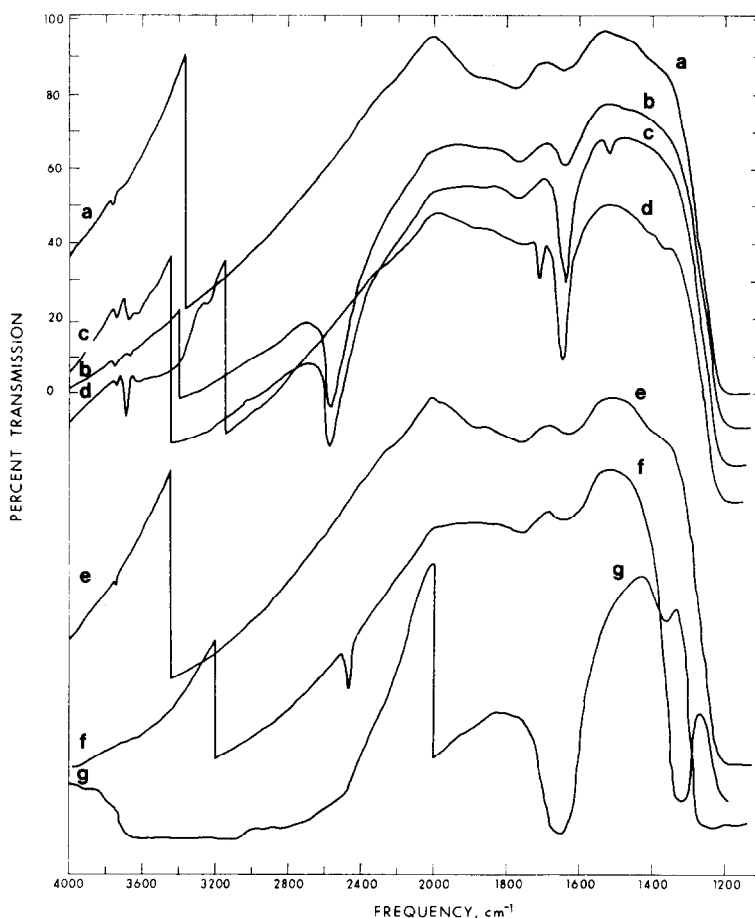


FIG. 5. Spectra obtained with NaY zeolite. (a) Background. (b) Exposed to 98 Torr H_2S at room temperature. (c) Then heated at 400°C overnight. (d) Then pumped at room temperature. (e) Then pumped at 400°C . (f) Then exposed to 20 Torr SO_2 at room temperature (no change on heating to 400°C overnight). (g) Then added 40 Torr H_2S .

1650 cm^{-1} . This water is considered to be the result of oxidation of H_2S by chemisorbed oxygen on the surface. Heating in H_2S at 400°C increased the apparent amount of water and also led to a new band near 1520 cm^{-1} . This differs from the bands found on alumina, both in frequency and in the fact that it disappeared after pumping.

No explanation is offered for the band near 1720 cm^{-1} formed transiently when the system was pumped at room temperature.

The adsorption of SO_2 onto the evacuated surface gave a strong band at 1330 cm^{-1} and a weaker band at 2470 cm^{-1} similar to those found on alumina, but the results differed from those with alumina in that

no further bands were observed after the system had been heated.

The adsorption of SO_2 onto the evacuated surface (Curve 5b) gave the expected strong band at 1330 cm^{-1} . The accompanying band at 1150 cm^{-1} was not visible because the background absorption by the zeolite cut off the transparency of the wafer in this region. The combination band at 2470 cm^{-1} was clearly seen, but the band at 2340 cm^{-1} was not observed (possibly because of interference from the 2350 cm^{-1} CO_2 band in the long light path of the IR 12 spectrometer).

No hydrogen-bonding interaction is possible on the NaY zeolite because of the absence of structural hydrogens. This did not significantly affect the frequencies of

the physically adsorbed SO_2 . Since the adsorption of H_2S produced some water which did show hydrogen bonding (Curves 5c and 5d), it is not possible to comment on the spectrum of H_2S adsorbed in the absence of hydrogen bonding.

The final curve in Fig. 5 shows the spectrum of water produced by the addition of H_2S to the wafer containing SO_2 . Here also the Claus reaction occurred rapidly when two reactants were contacted with the catalyst.

VIII. Adsorption of H_2S and SO_2 on HY Zeolite

The results with hydrogen Y zeolite differed from those with NaY primarily in the OH region, and this is illustrated in Fig. 6 for the wafer that had been deammoniated and partially dehydroxylated at 620°C . The addition of H_2S produced a small decrease in the intensity of the structural —OH bands at 3650 and 3550 cm^{-1} and the formation of a broad, well separated hydrogen-bonded adsorption near 3200 cm^{-1} (spectrum 6b). This hydrogen-bonding shift is considerably greater than that found with alumina indicating a stronger degree of hydrogen bonding. Preliminary observations of H_2S added to the wafer that was deammoniated at 400°C also showed the broad 3200 cm^{-1} band which in this case was accompanied by a small relative decrease in the intensity of the band at 3550 cm^{-1} . In contrast to the experiments with NaY, there appeared to be no oxidation of H_2S on HY, which would be revealed by the appearance of molecular water (in particular the band at 1650 cm^{-1}), indicating a much lesser degree of chemisorption of oxygen on HY. The addition of SO_2 (to the outgassed wafer) decreases the 3650 cm^{-1} band somewhat and gives a broad hydrogen-bonded band near 3500 cm^{-1} (spectrum 6e) similar to that found on alumina.

For the rest of the spectral region, the principal adsorption bands, 2575 cm^{-1} for H_2S and 2470 and 1330 cm^{-1} for SO_2 , were the same as on NaY, and there was no evidence of the presence of chemisorbed species under any conditions of heating.

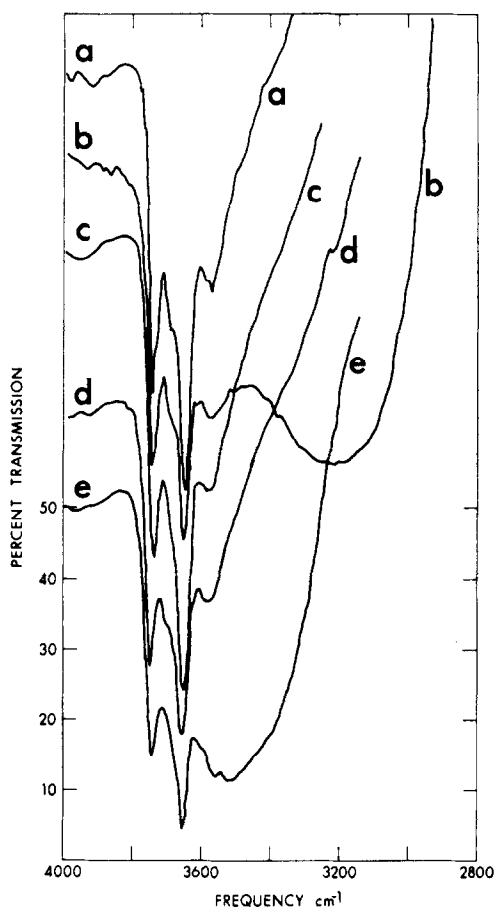


FIG. 6. Spectra obtained with HY zeolite (high frequency region only). (a) Background, wafer outgassed at 620°C (partial dehydroxylation). (b) Exposed to 30 Torr H_2S at room temperature. (c) Heated to 250°C and pumped at 250°C . (d) Heated with pumping to 450°C . (e) Then added SO_2 .

IX. Reaction of H_2S with Deuterated HY Zeolite

In order to investigate further the interaction between HY and H_2S , the HY wafer was exhaustively deuterated by repeated exposure to D_2O vapor. The spectrum of the almost completely deuterated material is shown as (a) in Fig. 7.

The absorption bands at 3750 , 3650 , and 3550 cm^{-1} due to OH— stretching vibrations have been replaced by OD bands at 2757 , 2689 , and 2640 cm^{-1} . The addition of H_2S to this wafer brought about a rapid reaction with the 2689 cm^{-1} OD band converting it into the 3650 cm^{-1} OH band. The other

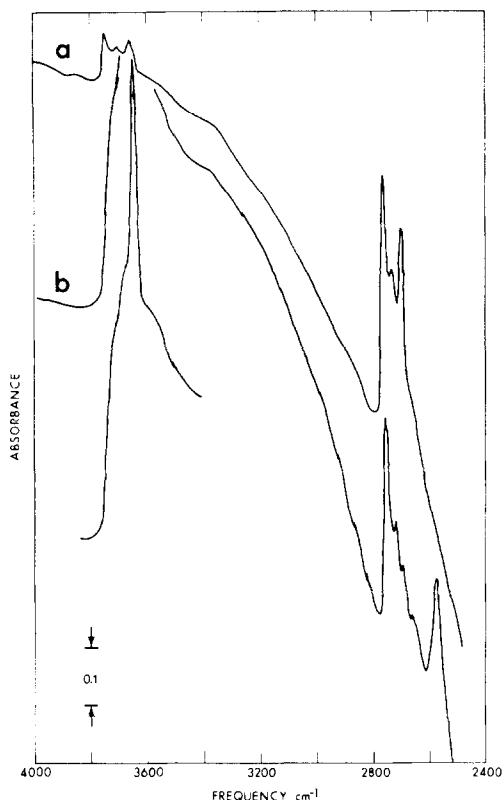


FIG. 7. Spectra showing reaction of H_2S with deuterated HY zeolite. (a) HY zeolite treated several times with D_2O vapor then pumped at 450°C . (b) Then added 6 Torr H_2S at 100°C .

OD bands were substantially unchanged. Thus the H_2S molecule shows rapid H-D exchange with the surface OH group to which it is most strongly hydrogen bonded (3650 cm^{-1}).

A further large addition of H_2S (spectrum not included in Fig. 7) gave relatively little more reduction in the OD absorption, but led to disappearance of the 3650 cm^{-1} OH band, and to a massive broad band centered around 3300 cm^{-1} , similar to that shown in Fig. 6d. In this last case, a rather weak band near 1870 cm^{-1} may have been due to the expected ν_1 vibration of D_2S (1891 cm^{-1} in the gas phase).

These results and those of the previous section confirm the strong interaction of H_2S with acidic hydrogen.

GENERAL CONCLUSIONS

The infrared evidence indicates that SO_2 and H_2S show significant physical ad-

sorption on most of the catalysts examined. The shifts in band frequencies are comparable to those observed in going from gas to liquid. Where possible, a strong hydrogen-bonding interaction between the OH groups of the catalyst and H_2S or SO_2 can occur, but not all catalysts contain significant numbers of such OH groups (although in a steady reaction state at atmospheric pressure, some or much water could be present on any catalyst surface). These results would lead one to believe that the function of the catalyst in the Claus process reaction step is primarily to bring the reactants together in a suitable orientation.

This simple interpretation is not the entire story because, on the surface of γ -alumina, a chemisorbed SO_2 type of species was observed to form when either adsorbed H_2S or SO_2 was heated. Furthermore, this chemisorbed species will react with H_2S , suggesting that it might be regarded as a reaction intermediate even though it is not present in detectable concentration on the other catalyst.

A second chemisorbed species is formed from both H_2S and SO_2 on NaOH-doped γ -alumina surface. In contrast to the chemisorbed SO_2 type of species, this one does not react further with the other reactant akin to the Claus reaction step. This irreversibly formed product is either a combination with excess sodium hydroxide or a catalytic "sulfation" product which could cause irreversible loss of catalytic activity.

Although the four catalysts studied exhibit a great variation in acidity: Hydrogen Y is a strong protonic acid, and sodium Y has a relatively weak to negligible protonic acidity; γ -alumina is both a Lewis acid and probably when wet, a weak Brønsted acid, and the NaOH-treated γ -alumina is similar, but with reduced Brønsted acidity; acidity does not seem to be the primary factor responsible for their catalytic activity in the Claus reaction. Indeed, some preliminary results from kinetic studies suggest that both the sodium Y zeolite and the sodium hydroxide-treated γ -alumina are slightly more active catalysts than their more acidic counterparts. A direct comparison of the catalytic

activities of zeolites and aluminas has not been completed as yet, but kinetics studies now in progress should provide a means of correlating their relative catalytic activities with the view of surface mechanisms being developed by infrared spectroscopy.

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