

Infrared Studies of SO₂ on γ -Alumina

CHARLES C. CHANG

Department of Physical Chemistry, General Motors Research Laboratories, Warren, Michigan 48090

Received June 27, 1977; revised February 23, 1978

Sulfur dioxide (SO₂) adsorption on a γ -alumina (Al₂O₃) catalyst was found to be affected by two factors: the number of hydroxyl groups present and the temperature of the catalyst. Sulfur dioxide chemisorbed more readily on a well-dehydrated surface. The SO₂ uptake decreased as the temperature of the alumina catalyst was increased. At 600°C SO₂ underwent disproportionation to form aluminum sulfate [Al₂(SO₄)₃] which could be thermally decomposed at 800°C. The application of infrared spectroscopy disclosed that SO₂ first adsorbed on Al₂O₃ in the form of a sulfite species (SO₃) yielding an infrared band at 1060 cm⁻¹, which could be removed at 600°C. SO₂ also chemisorbed to yield a band at 1326 cm⁻¹ at moderate surface coverage, which could be removed at 100°C. In the presence of oxygen, SO₂ could be oxidized on Al₂O₃ to form aluminum sulfate, as demonstrated by the formation of paired bands in the regions of 1400 and 1100 cm⁻¹.

INTRODUCTION

Deo *et al.* (1) studied the adsorption of H₂S and SO₂ on alumina and zeolite by means of infrared spectroscopy. They showed that physical adsorption of both reactants occurred with strong H bonding to surface OH groups. Chemisorption of SO₂ was achieved after heating alumina at 400°C. Formation of sulfatelike species was suggested as an interpretation of the infrared spectrum generated by SO₂ chemisorption. Later, Glass and Ross (2) studied the heats of SO₂ adsorption by means of calorimetry. The initial heats of adsorption were 48, 59, and 85 kcal mol⁻¹ on γ -alumina preheated at 500, 700, and 900°C, respectively. These high heats of adsorption clearly revealed that chemisorption had occurred at low surface coverage. These workers also proposed that a sulfatelike species was formed on the γ -alumina surface.

Some concern has been raised about the formation of sulfates from the SO₂ in engine

exhaust by automotive emission control catalysts. Oxidation reactions involving sulfur oxides and sulfuric acid emissions have been extensively studied over alumina-supported catalysts under various experimental conditions using simulated exhaust systems (3, 4). Reaction products have been analyzed for SO₂ and SO₃, and the reaction mechanisms have been considered (3, 4). The reaction of SO₂ was in general accompanied by storage of sulfur in the catalyst (3, 5). Since information about the nature and structure of surface species, as well as the intrinsic changes of the catalysts, would be of mechanistic significance and potential utility, studies have been undertaken using infrared spectroscopy to investigate SO₂ adsorption on γ -alumina.

EXPERIMENTAL

The γ -alumina (Alon) catalyst used in this study was obtained from Cabot Corporation in powdered form. The powder was pressed by 42 MPa (3 tons/in²) into

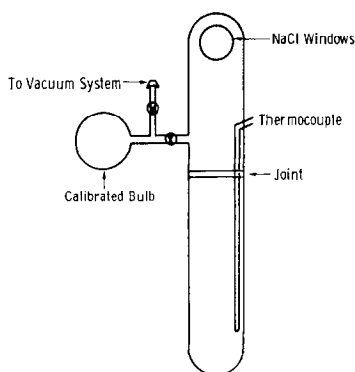


FIG. 1. Quartz infrared cell.

self-supporting disks which were 20 mm in diameter and weighted about 100 mg. BET measurements of the disk catalyst yielded a surface area of 96 m² per gram of samples. The porosity characteristics, as measured by the American Instrument Co., indicated that the sample is of a bimodal support with a micropore diameter of 150 Å and a macropore diameter of 4×10^5 Å. The pore volume is 0.475 cm³/g. For infrared experiments, the sample disks were always first evacuated at room temperature for 1 hr below 10^{-5} Torr, and the temperature was then gradually increased to 700°C in 2 hr. The residual pressure was always below 10^{-5} Torr before experimentation.

Research grade SO₂ (Matheson) was distilled from a liquid nitrogen trap three times, and only the middle fractions of the distillate were stored for use. Mass spectrometric analysis of the stored SO₂ showed that it was 99.9% pure. Also, infrared analysis of the stored SO₂ showed only absorption bands due to SO₂.

Sulfur trioxide vapor was collected from liquid Sulfan obtained from Allied Chemical. The aluminum sulfate [Al₂(SO₄)₃ \cdot *n*H₂O] was from Baker.

The infrared cell was made of quartz. A schematic diagram is given in Fig. 1. The advantage of using this type of cell is that the sample can be easily pretreated at high temperatures *in vacuo* and can then be transferred *in vacuo* to the NaCl window

mounts for infrared investigation. Infrared spectra were always obtained at room temperature with a Perkin-Elmer 180 grating instrument. An equally activated and identical alumina disk was used as reference for the region between 3000 and 1000 cm⁻¹. Although the reference sample compensated for most of the alumina absorption, the match was not perfect, particularly near the 1000 cm⁻¹ region. Accordingly, all spectra shown in the infrared figures have had the background subtracted out. The region below 1000 cm⁻¹ was not scanned, owing to complete absorption by the alumina.

A number of adsorption experiments were carried out on a BET system with a 1-g sample of catalyst from the same batch as that used for the infrared experiments. This catalyst was pretreated in the same way as the catalyst used in the infrared studies. To match as closely as possible the conditions used in the infrared experiments, the sample for the BET studies was first pressed into disks similar to those used in the ir studies and then broken into large chunks for the adsorption measurements.

RESULTS

BET Measurements

Adsorption experiments with the BET system were performed on a larger (1-g) sample than that used in the ir studies in order to permit quantitative measurements to be made. To investigate the effect of OH groups on SO₂ uptake, the sample was first evacuated for 24 hr at 200°C in order to remove all the weakly adsorbed OH groups. SO₂ was then added to the sample at 25°C. An isotherm was determined and is shown in Fig. 2 (curve A'); the maximum amount chemisorbed was 3.8 cm³/g (1.06×10^{18} molecules/m²), which was determined by extrapolation of the SO₂ equilibrium pressure to zero (shown by the dotted line in Fig. 2). The sample was then evacuated while the temperature was slowly increased

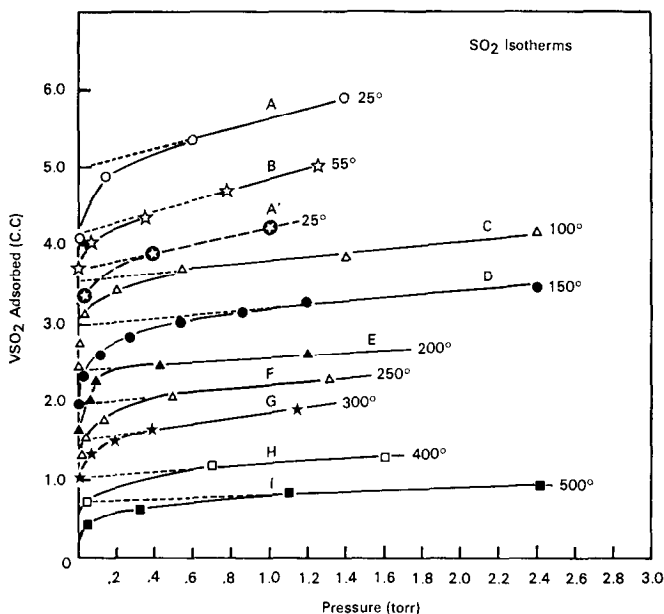


FIG. 2. SO₂ adsorption isotherms on γ -Al₂O₃.

to 600°C in order to remove the adsorbed SO₂. The sample was further evacuated for 1 hr at 700°C, so that additional OH groups were removed (6). SO₂ was then adsorbed on the sample at 25°C. The isotherm for the adsorption is shown in Fig. 2 (curve A); the maximum amount chemisorbed was 5.0 cm³/g (1.40×10^{18} molecules/m²). The SO₂

uptake was significantly increased when the surface was better dehydrated.

Adsorption measurements were also carried out at increasingly higher temperatures on the sample preheated 2 hr each time at 700°C. Isotherms were determined at 55, 100, 150, 200, 250, 300, 400, and 500°C, and are plotted as curves B, C, D,

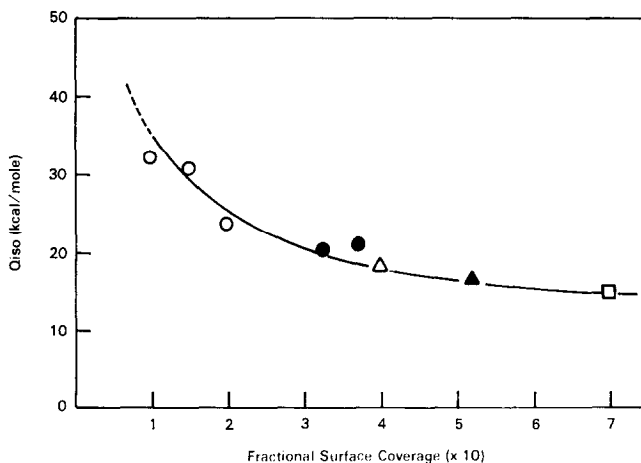


FIG. 3. Heats of SO₂ adsorption against surface coverage: (○) from 400 and 500°C isotherms; (●) from 250 and 300°C isotherms; (△) from 200 and 250°C isotherms; (▲) from 150 and 200°C isotherms; (□) from 100 and 150°C isotherms.

TABLE 1
COLLECTIONS OF ADSORBED SO₂ BY STEPWISE TEMPERATURE INCREMENTS^a

Isotherm temperature	Desorption temperature						
	25°C	100°C	200°C	300°C	400°C	500°C	600°C
25°C	(1.11)	0.92	1.14	0.72	0.78	0.46	0.20
55°C		(1.77)	1.27	0.76	0.62	0.46	0.25
100°C		(1.16)	1.17	0.91	0.69	0.46	0.25
150°C			(1.71)	1.03	0.82	0.35	0.19
200°C			(0.69)	0.91	0.72	0.45	0.21

^a Amounts are expressed in cm³ (1 cm³ = 2.69 × 10¹⁹ molecules of SO₂ measured at STP) that are removed at the indicated temperatures. Figures in parenthesis include gas-phase SO₂.

E, F, G, H, and I, respectively in Fig. 2. As can be seen, the uptake decreased with increasing temperature. Isothermic heats of adsorption were calculated from these isotherms at selected surface coverages by application of the Clausius–Clapeyron equation and are shown in Fig. 3. The data indicated that the heat values decreased with increasing coverage. These results agree well with those reported by Glass and Ross (2).

During the adsorption measurements, one noted feature was that it took several hours to reach equilibrium at low surface coverage and equilibrium pressures in the micrometer ranges. This phenomenon, which suggested that SO₂ was adsorbing on the surface very slowly, will be dealt with further below.

Desorption measurements followed each adsorption isotherm. Quantitative desorption results are shown in Table 1. The results show that SO₂ adsorbs on γ -alumina with different strengths. The weakly adsorbed SO₂ was removed by room temperature evacuation. The more strongly adsorbed SO₂ was removed at relatively higher temperature. Nearly all the adsorbed species were removed by evacuation at 600°C.

Effect of OH Groups on SO₂ Adsorption

Since the OH groups on the alumina surface are believed to play an important role

in surface reactions (7), SO₂ chemisorption was first investigated using ir spectroscopy to follow the change of the intensity, shape, and position of the OH band at 3699 cm⁻¹ after measured amounts of SO₂ were added to the γ -alumina. Figure 4 shows a series of changes in the ir bands when successive doses were added to the surface. Spectrum

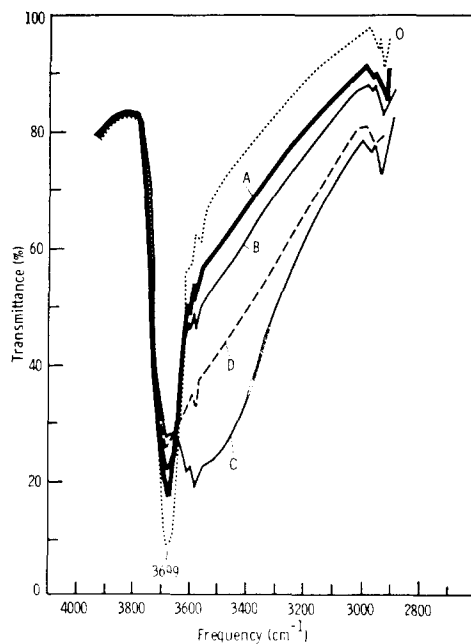


FIG. 4. Effect of SO₂ adsorption on the changes of the infrared spectra owing to OH absorption: (A) 1.5 cm³/g SO₂ (4.20 × 10¹⁷ molecules/m²); (B) 3.0 cm³/g (8.40 × 10¹⁷ molecules/m²) SO₂; (C) 5.0 cm³/g SO₂ (1.40 × 10¹⁸ molecules/m²); (D) approximately 4 cm³/g SO₂ (1.12 × 10¹⁸ molecules/m²).

O represents the original OH band at 3699 cm^{-1} prior to SO_2 adsorption. When $1.5\text{ cm}^3/\text{g}$ (4.20×10^{17} molecules/ m^2) SO_2 was added to the sample, the intensity of the OH band was slightly reduced as shown in spectrum A, and the lower frequency side of the band was slightly increased in intensity. These changes indicated slight H-bonding of the OH groups with the adsorbed SO_2 . When another $1.5\text{ cm}^3/\text{g}$ (4.20×10^{17} molecules/ m^2) SO_2 was added, a similar change was observed (spectrum B). A total of $3\text{ cm}^3/\text{g}$ (8.40×10^{17} molecules/ m^2) SO_2 adsorption constituted about 60% of the maximum surface coverage but did not cause a sizeable distortion of the OH band. Pronounced distortion occurred only when the surface was covered by physically adsorbed SO_2 at saturation

coverage. This is shown in spectrum C. Prolonged evacuation at room temperature removed all the weakly adsorbed SO_2 and restored most of the OH band to its original shape and position (spectrum D). A complete restoration of the OH band at 3699 cm^{-1} was achieved when the surface was heated to 600°C . Thus, these results suggest that most of the chemisorbed SO_2 is interacting directly with the surface sites rather than with the OH groups.

Infrared Spectra of SO_2 on γ -Alumina

Figure 5 shows the infrared spectra for adsorbed SO_2 on γ -alumina as successive doses of SO_2 were added to the disk sample. For a small $0.3\text{ cm}^3/\text{g}$ (8.40×10^{16} molecules/ m^2) dose, one band at 1060 cm^{-1} immediately became evident, and a weak band also appeared at 1326 cm^{-1} , as shown in spectrum A. Addition of another $0.3\text{ cm}^3/\text{g}$ (8.40×10^{16} molecules/ m^2) dose produced spectrum B. The intensity of both bands was increased; however, the increase in intensity for the band at 1326 cm^{-1} after the second dose was more than twice that generated by the first dose. In contrast, the increase for the band at 1060 cm^{-1} from the second dose was less than that generated by the first dose. This fact seemed to suggest that the SO_2 contributed more intensity to the 1326 cm^{-1} band from the second dose than from the first dose. This reverse distribution trend became more pronounced in spectrum C, when another $0.6\text{ cm}^3/\text{g}$ (1.68×10^{17} molecules/ m^2) dose was added to the sample. Therefore, the reverse trend in the distribution of intensity to the two bands between the first dose and the following doses suggests that the two bands stem from differently adsorbed forms of SO_2 . In other words, SO_2 molecules first adsorbed predominantly in a form to yield the band at 1060 cm^{-1} . As more SO_2 molecules were adsorbed, some adsorbed in another form to yield a band at 1326 cm^{-1} . This distribution became more evident as additional

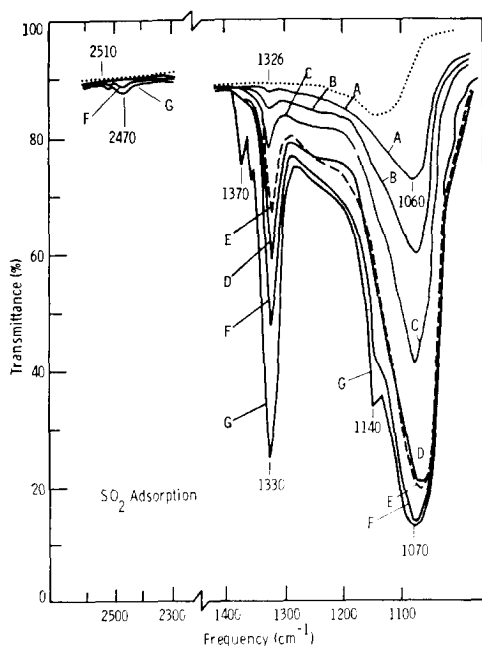


FIG. 5. Infrared spectra of SO_2 adsorbed on Alumina: (A) after $0.3\text{ cm}^3/\text{g}$ SO_2 (8.4×10^{16} molecules/ m^2); (B) after $0.6\text{ cm}^3/\text{g}$ SO_2 (1.68×10^{17} molecules/ m^2); (C) after $1.2\text{ cm}^3/\text{g}$ SO_2 (3.36×10^{17} molecules/ m^2); (D) after $2.2\text{ cm}^3/\text{g}$ SO_2 (6.16×10^{17} molecules/ m^2); (E) after 2 hr, standing; (F) after approximately $4\text{ cm}^3/\text{g}$ SO_2 (1.12×10^{18} molecules/ m^2); (G) after approximately $8\text{ cm}^3/\text{g}$ SO_2 (2.24×10^{18} molecules/ m^2).

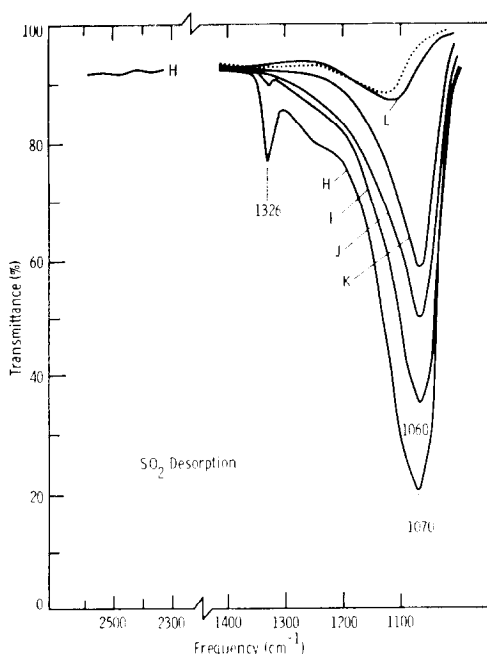


FIG. 6. Infrared spectra of SO₂ after stepwise desorption: (H) after 1 hr at 25°C; (I) after 30 min at 100°C; (J) after 30 min at 200°C; (K) after 30 min at 300°C; (L) after 30 min at 600°C.

doses were added to the sample. It was also noted that both bands tended to shift to higher frequencies—to 1330 and 1070 cm⁻¹, respectively—when the surface was saturated with adsorbed SO₂. Addition of a fourth dose (1 cm³/g or 2.80 × 10¹⁷ molecules/m²) to give a total of 2.2 cm³/g (6.16 × 10¹⁷ molecules/m²) yielded spectrum D. Further intensification of the two bands indicated that the surface was still adsorbing SO₂. This system was then left at room temperature for 2 hr. A rescanning of this system (spectrum E) showed a reduction of intensity for the band at 1326 cm⁻¹ and an increase of intensity for the band at 1060 cm⁻¹. Apparently, conversion of the surface species from a weakly adsorbed form to a strongly adsorbed form was taking place during the 2 hr of standing. This conversion, therefore, confirmed that there were at least two forms of SO₂ species on the surface. This result might also account for the extremely slow approach to equi-

librium in the micrometer pressure ranges previously observed in the BET measurements. Further successive addition of SO₂ caused these two bands to grow until a new band at 1140 cm⁻¹ started to appear as a shoulder on the 1070 cm⁻¹ band. The formation of this 1140 cm⁻¹ band was, in fact, accompanied by the formation of some other bands at 2470, 1370, and 1375 cm⁻¹, as shown in spectrum F. Addition of excess SO₂ intensified these bands as well as the 1330 cm⁻¹ band and also generated another small band at 2510 cm⁻¹ and shifted the 1140 cm⁻¹ band to 1147 cm⁻¹, as shown in spectrum G. The appearance of the gaseous SO₂ bands at 2499 (V₁ + V₃), 1130 (V₃), and 1151 (V₁) cm⁻¹ (8) indicated that the surface was saturated with SO₂ species.

Figure 6 shows the spectra after the system was evacuated at various temperatures. Spectrum H was obtained when the system was evacuated 1 hr at room temperature. The disappearance of the bands at 2510, 2470, 1370, 1375, and 1147 cm⁻¹, along with some reduction of the intensity of the band at 1330 cm⁻¹, indicated that all the gaseous and weakly adsorbed SO₂ was removed from the system. The intensity of the 1070 cm⁻¹ band, however, was essentially intact after such evacuation. Prolonged room temperature evacuation for 80 hr did not further change the shape and intensities of the bands at 1326 and 1070 cm⁻¹. Thus, the persistence of these two bands indicates that these two adsorbed forms of SO₂ species are firmly bound to the surface. Evacuation of the system at 100°C for 30 min, however, essentially removed the band at 1326 cm⁻¹ and also shifted the 1070 cm⁻¹ band to 1060 cm⁻¹, as well as causing some reduction of its intensity, as shown in spectrum I. Further removal of the intensity of the 1060 cm⁻¹ band was only achieved by evacuation at elevated temperatures. Spectra J and K were obtained when the system was evacuated at 200 and 300°C, respectively. The remaining SO₂ was removed by evacuation

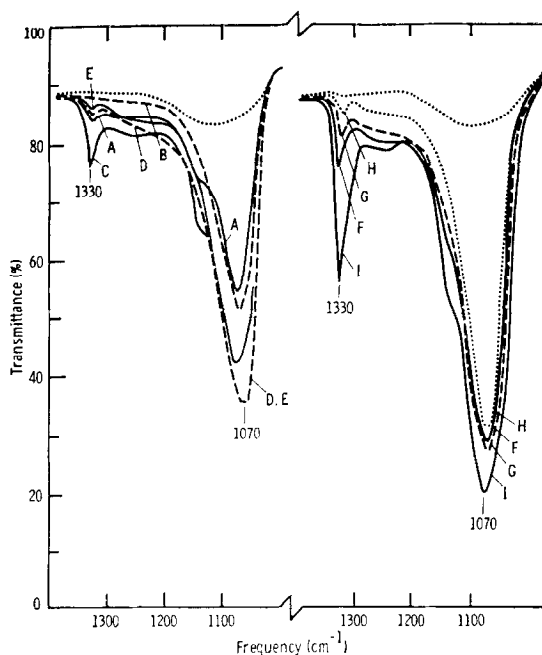


FIG. 7. Annealing of SO_2 adsorbed at room temperature: (A) after $1.5 \text{ cm}^3/\text{g}$ SO_2 (4.20×10^{17} molecules/ m^2); (B) after 30 min at 200°C in a closed system; (C) after $3.0 \text{ cm}^3/\text{g}$ SO_2 (8.40×10^{17} molecules/ m^2); (D) after 30 min at 200°C in a closed system; (E) after 1 hr evacuation at 100°C ; (F) after addition of another $1 \text{ cm}^3/\text{g}$ SO_2 (2.80×10^{17} molecules/ m^2); (G) after 30 min at 200°C in a closed system; (H) after 1 hr evacuation at 100°C ; (I) after addition of another $1 \text{ cm}^3/\text{g}$ SO_2 (2.80×10^{17} molecules/ m^2).

for 1 hr at 600°C . This was evidenced by the disappearance of the band at 1060 cm^{-1} , as shown in spectrum L. As can be seen, the initially adsorbed species was bound most tightly to the surface and was desorbed last at higher temperature.

Annealing Experiments

Since the adsorbed SO_2 species changed dramatically from one form to another at room temperature, as evidenced by the decrease in intensity of the 1326 cm^{-1} band and the concomitant increase in intensity of the 1060 cm^{-1} band, this suggests that SO_2 first adsorbed on the surface in two forms, and in time the weakly adsorbed form transformed into the strongly adsorbed form. To characterize this transformation, the following experiment was carried out: The disk sample was first

exposed to a measured amount of SO_2 , the spectrum was scanned, the sample was then heated for 30 min at 200°C in a closed system, and the spectrum was scanned again. The system was then degassed for 1 hr at 100°C , and the spectrum was taken again. After this treatment, another measured dose was added, and the entire procedure was repeated until no further changes in the intensity of the ir bands occurred.

Figure 7 shows the spectra taken after each step. When $1.5 \text{ cm}^3/\text{g}$ (4.20×10^{17} molecules/ m^2) SO_2 was admitted into the system, spectrum A, as expected, showed the formation of two bands at 1326 and 1060 cm^{-1} . The sample was then heated and yielded spectrum B, which shows the disappearance of the 1326 cm^{-1} band and an intensification of the 1060 cm^{-1} band. After evacuation, the resulting spectrum

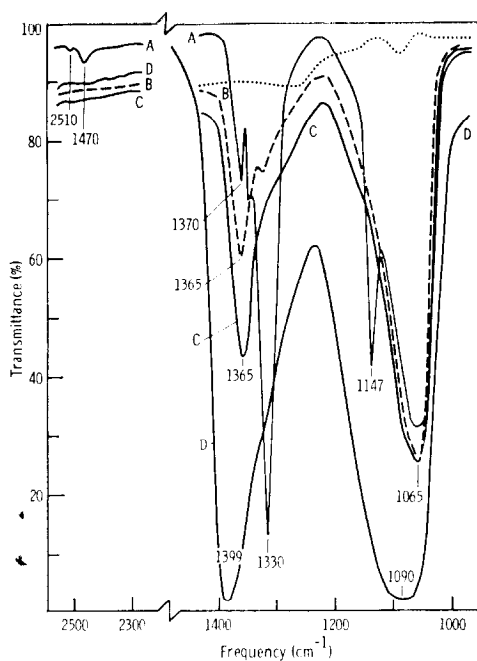


FIG. 8. Infrared spectra from a mixture of 7 Torr SO₂ and 7 Torr O₂: (A) initial spectrum at 25°C; (B) after 1 hr at 400°C; (C) after 3 hr at 400°C; (D) after 10 hr at 500°C.

turned out to be identical to the spectrum taken before evacuation. This fact revealed that the adsorbed SO₂ species yielding the 1060 cm⁻¹ band was strongly bound to the surface. Addition of another 1.5 cm³/g (4.20×10^{17} molecules/m²) SO₂ yielded spectrum C, which showed a further growth for the two bands. Heating for 30 min at 200°C resulted in spectrum D, again showing the reduction (not a disappearance) of the 1326 cm⁻¹ band and an intensification of the 1060 cm⁻¹ band. Obviously, the intensification of the 1060 cm⁻¹ band was achieved at the expense of the intensity of the 1326 cm⁻¹ band. The failure to render a complete removal of the 1326 cm⁻¹ band by heating, however, suggested that the surface was probably close to saturation with the species responsible for the 1060 cm⁻¹ band. Therefore, it was not so easy for the second heating to achieve a complete conversion in the limited length of time as in the previous heating. Evacuation of the

system yielded spectrum E. Now the intensity of the band at 1060 cm⁻¹ was unchanged, but the intensity of the band at 1326 cm⁻¹ was reduced, which indicates that some of the species had been pumped out of the system. Further addition of 1 cm³/g (2.80×10^{17} molecules/m²) SO₂ generated spectrum F, which again shows an increase in the intensity for both bands. The 1060 cm⁻¹ band shifted to 1070 cm⁻¹. The incremental increase for the 1060 cm⁻¹ band was quite small, however, but the incremental increase for the 1326 cm⁻¹ band was substantial relative to its previous intensity. Obviously, more SO₂ molecules from this dose were adsorbed in the weak form. Heating yielded spectrum G, which showed a further reduction in intensity for the band at 1326 cm⁻¹ and a slight increase in intensity for the band at 1070 cm⁻¹. Apparently, the amount transferred by heating was insignificant. This fact revealed that the surface was reaching its maximum capacity for the strongly adsorbed species. Evacuation generated spectrum H, which showed a reduction in intensity for both bands. It seemed that, at high surface coverage, the 1070 cm⁻¹ band could be slightly removed by 100°C evacuation. Further addition of 1 cm³/g (2.80×10^{17} molecules/m²) SO₂ (Fig. 7, curve I) still caused these two bands to grow and also shifted the 1326 cm⁻¹ band to 1330 cm⁻¹. Actually, the spectra developed in exactly the same manner as previously observed in Fig. 5. Desorption of these adsorbed species at various temperatures also yielded the spectra similar to the desorption spectra obtained from the desorption process as previously shown in Fig. 6.

SO₂ Oxidation on γ -Alumina

Addition of a mixture of 7 Torr SO₂ and 7 Torr O₂ to the sample yielded spectrum A in Fig. 8, which was similar to the spectrum when SO₂ alone was in the system. This result showed that O₂ did not

interfere with SO_2 adsorption on γ -alumina. No oxidation reaction was detected until the catalyst was heated to 400°C . After 1 hr at 400°C , a new band was observed at 1365 cm^{-1} , along with an intense band at 1060 cm^{-1} (spectrum B). The 1365 cm^{-1} band continued to grow as the oxidation reaction continued. Spectrum C shows the 1365 cm^{-1} band after the system was heated for 3 hr at 400°C . Heating the sample for 10 hr at 500°C , however, greatly sped up the oxidation reaction and caused a drastic change in the surface, as shown by the presence of the two broad and intense bands around 1400 and 1100 cm^{-1} (spectrum D). Thermal desorption studies disclosed that these two bands could not be removed until the sample was heated at 800°C . It was also observed that these two bands declined in concert during the 800°C heating of the sample. The concurrent declination of these two bands suggests that they stem from the same species. These

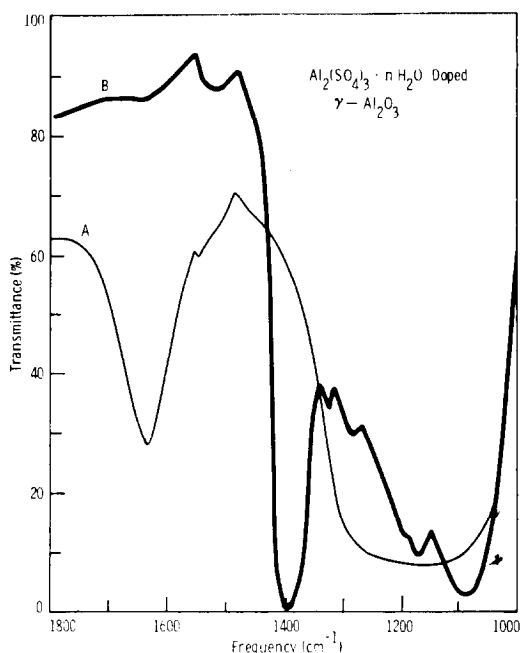


FIG. 10. Infrared spectra from aluminum sulfate-doped γ -alumina: (A) initial spectrum; (B) after 2 hr at 600°C .

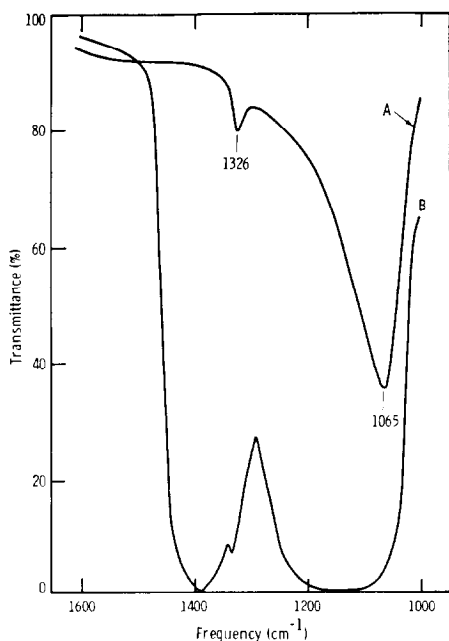


FIG. 9. Infrared spectra from SO_3 adsorption on $\gamma\text{-Al}_2\text{O}_3$: (A) initial spectrum, from a small amount of SO_3 ; (B) final spectrum, from a large amount of SO_3 .

results, therefore, suggest that aluminum sulfate was formed from the oxidation of SO_2 .

Spectra from SO_3 Adsorption and $\text{Al}_2(\text{SO}_4)_3$ -Doped γ -Alumina

Figure 9 shows the room temperature spectra from a γ -alumina sample exposed to gaseous SO_3 . When the alumina sample was exposed to a small amount of SO_3 , two bands at 1326 and 1065 cm^{-1} appeared in the infrared spectra (spectrum A). These two bands corresponded well to the V_3 and V_1 vibrations of gaseous SO_3 molecules (9). They were also similar to the two bands obtained from initial SO_2 adsorption on the catalyst (Fig. 5). Unlike SO_2 adsorption, however, when more SO_3 was added, these two bands rapidly changed into two broad and intense bands around 1400 and 1100 cm^{-1} (spectrum B), which are nearly identical to the paired bands obtained from the oxidation of SO_2 over the alumina catalyst.

Figure 10 shows the room temperature spectra when the fresh γ -alumina sample was doped with 5% hydrated aluminum sulfate [$\text{Al}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$]. Spectrum A was obtained from the original sample; the band at 1630 cm^{-1} was due to the absorption of water in the catalyst. The broad and unresolved band at 1200 cm^{-1} was due to the sulfur oxide absorption. Heating the sample for 2 hr at 600°C removed the water and generated a number of bands (spectrum B) at 1400, 1322, 1280, 1192, 1170, and 1100 cm^{-1} . The presence of the two major bands around 1400 and 1100 cm^{-1} strongly suggests that they were generated by sulfate absorption.

DISCUSSION

A considerable amount of information is available about the absorption bands arising from different sulfur species. The absorption bands produced by the S-O linkage can be usually recognized from the characteristic location and intensity of the bands. Thus, when a sulfite or sulfate compound is adsorbed on the catalyst surface, it can be identified. The gas-phase vibrations of SO₂, for example, appear at $1375\text{ (V}_3\text{)}$ and $1165\text{ (V}_1\text{)}\text{ cm}^{-1}$, with the V₃ intensity twice V₁ (8). Upon initial adsorption of SO₂ to the alumina surface, however, the appearance of a band at 1060 cm^{-1} , rather than around the expected 1375 and 1165 cm^{-1} region, suggests that a new surface species was formed. This new surface species is characterized by the fact that it yields high heats of adsorption and is desorbed at high temperature. The requirement of high temperature to desorb the first-on-and-last-off species is also consistent with the result of high initial heats of adsorption for SO₂ as computed from the adsorption isotherms. But our inability to investigate the region below 1000 cm^{-1} (because of the appearance of a broad absorption band from alumina) for the S-O vibration makes it difficult to give a

definitive assignment to this new species. However, we might consider the following: adsorption of SO₂ of MgO (10, 11a) and CaO (11b) to form sulfite species has been shown by the formation of infrared bands at 1060 and 960 cm^{-1} . The confirmation was based on the fact that the free SO₃²⁻ ion (C_{3v}) has a nondegenerate vibration, V₁, at 960 cm^{-1} and a doubly degenerate vibration, V₃, at 1010 cm^{-1} (12). Splitting of the degenerate V₃ occurs in sulfite complexes (12, 13). If the SO₃ ion is bonded with its sulfur atom toward the surface, the C_{3v} symmetry would be preserved. The coordination through the sulfur atom shifts the S-O stretching bands to higher frequencies (12). If the SO₃ ion is bonded with its oxygen atoms toward the surface, the symmetry would be lowered to C_s; this type of coordination shifts the band to lower frequencies relative to the free ion (12). Baldwin (13) first found V₁ at 988 cm^{-1} and the two split bands of V₃ in the regions of 1093 to 1070 cm^{-1} and 1036 to 1042 cm^{-1} in sulfite complexes coordinated through sulfur to the surface. When adsorbing SO₂ on MgO, Lunsford and Schoonheydt (10) found the V₁ band at 975 cm^{-1} and the V₃ bands around 1040 cm^{-1} with a shoulder at 1070 cm^{-1} . Thus, they concluded that a surface SO₃²⁻ species was formed. Low and co-workers reached a similar conclusion from SO₂ adsorption on MgO (11a) and CaO (11b). For SO₂ adsorption on Al₂O₃, the appearance of this intense and broad band around 1060 cm^{-1} coincided with the V₃ region of SO₃²⁻ surface species as reported on MgO and in sulfite complexes. Since the overall adsorption mechanism and behavior of SO₂ on Al₂O₃ were quite similar to those on MgO and CaO, it is reasonable to conclude, by analogy, that a SO₃²⁻ surface species was formed on Al₂O₃ to yield a V₃ band at 1060 cm^{-1} , even though bands below 1000 cm^{-1} could not be observed.

After the 1060 cm^{-1} band reached its maximum intensity, further addition of

SO₂ led to more adsorption and generated a new band at 1326 cm⁻¹. The fact that this 1326 cm⁻¹ band could only be removed by 100°C evacuation strongly indicated that this SO₂ was chemisorbed on Al₂O₃. Since chemisorption generally shifts bands to lower frequencies (14), the 1326 cm⁻¹ band was assigned to the asymmetrical V₃ of the SO₂ vibration. Similar assignments were made by Lunsford *et al.* (10) and Low *et al.* (11a) on MgO and CaO (11b). The failure to detect the symmetrical V₁ band around 1125 cm⁻¹ was attributed to the fact that the V₁ band was less intense than the V₃ band, in fact, was much less intense than the 1060 cm⁻¹ band. Therefore, the V₁ band was blocked by the broad 1060 cm⁻¹ band.

Weakly adsorbed SO₂ was detected by the appearance of the bands at 1330 and 1140 cm⁻¹ at high surface coverage. They corresponded well to the gas phase bands of 1362 (V₃) and 1151 (V₁) cm⁻¹ (8). Thus, they could be assigned to V₃ and V₁ vibrations of SO₂, respectively. The weak intensity of the 1140 cm⁻¹ band might also serve as an explanation for the failure to detect the V₁ band which accompanied the 1326 cm⁻¹ (V₃) band for the chemisorbed SO₂ at the moderate surface coverage.

The fact that S-O linkage gives rise to more than one characteristic band has been found in many sulfate compounds. For example, Bellamy and Williams (15) reported that a sulfonyl group (-SO₂-) usually yielded a symmetrical S-O absorption (V₁) around 1160 to 1140 cm⁻¹ and an asymmetrical absorption (v₃) around 1300 to 1350 cm⁻¹. Any change in the symmetrical frequency, V₁, was accompanied by a proportional change in the asymmetrical frequency, V₃. They also pointed out that the -SO₂- stretching frequencies were essentially free from mass and coupling effects and that exact positions of V₁ and V₃ depended on the electronegativity of the substituents attached to the sulfonyl group. It was found that the more electro-

negative the attached substituents, the stronger the S=O bond, and hence the higher the vibrational frequencies. Later, Robinson (16) found more examples which supported the validity of these simple relations.

When a sulfonyl group (-SO₂-) is attached to two oxygens, a sulfate compound is formed. For an organic covalent sulfate, the bands usually appear in the region from 1230 to 1150 cm⁻¹ for V₁ and from 1140 to 1350 cm⁻¹ for V₃ (17). For example, strong bands were observed at 1193 and 1412 cm⁻¹ for V₁ and V₃, respectively, of dimethyl sulfate (18). For inorganic sulfates, however, these two bands were found at 1090 and 1390 cm⁻¹ for (NH₄)₂SO₄ (19). Since nearly identical bands at 1090 and 1390 cm⁻¹ were observed from Al₂(SO₄)₃-doped Al₂O₃, it is believed that Al₂(SO₄)₃, like (NH₄)₂SO₄, yielded V₁ and V₃ bands at 1090 and 1390 cm⁻¹, respectively. The formation of these two bands at 1090 and 1390 cm⁻¹ from SO₃ adsorption on Al₂O₃ further supported the belief that they stemmed from sulfate absorption, because it has been reported that SO₃ readily reacts with alumina at room temperature to form aluminum sulfate (20). There is no aluminum sulfite [Al₂(SO₃)₃] (21). Therefore, the generation of these two bands at 1090 and 1390 cm⁻¹ from SO₂ oxidation over alumina at 400°C confirms the formation of aluminum sulfate in the alumina catalyst.

REFERENCES

1. Deo, A. V., Dalla Lana, I. G., and Habgood, H. W., *J. Catal.* **21**, 270 (1971).
2. Glass, R. W., and Ross, R. A., *Canad. J. Chem.* **50**, 2537 (1972).
3. Taylor, K. C., *Ind. Eng. Chem.* **15**, 264 (1976).
4. Summers, J. C., Paper to be presented at the SAE meeting, February 24-March 4, 1977, in Detroit, Mich.
5. Chang, C. C., unpublished results.
6. Peri, J. B., *J. Phys. Chem.* **69**, 211 (1965).
7. Peri, J. B., *Proc. 2nd Int. Cong. Catal.*, Paris, 1960, Vol. 1, p. 1333, 1961.

8. Nickless, G., "Inorganic Sulfur Chemistry," p. 373. Elsevier, New York, 1968.
9. Herzberg, G., "Infrared and Raman Spectra of Polyatomic Molecules," p. 178. Van Nostrand, New York, 1945.
10. Schoonheydt, R. A., and Lunsford, J. H., *J. Catal.* **26**, 261 (1972).
11. (a) Goodsel, A. J., Low, M. J. D., and Takezawa, N. *Environ. Sci. Technol.* **6**, 268 (1972), (b) *ibid.*, **5**, 119 (1970).
12. Nakamoto, K., "Infrared Spectra of Inorganic and Coordination Compounds," pp. 173-177. Wiley, New York, 1970.
13. Baldwin, M. E., *J. Chem. Soc.* 3123 (1961).
14. Chang, C. C., and Kokes, R. J., *J. Amer. Chem. Soc.*, **93**, 7107 (1971).
15. Bellamy, L. J., and Williams, R. L., *J. Chem. Soc.* 863 (1957).
16. Robinson, E. A., *Canad. J. Chem.* **39**, 247 (1961).
17. Bellamy, L. J., "The Infrared Spectra of Complex Molecules," p. 351. Wiley, New York, 1958.
18. Schreiber, K. C., *Anal. Chem.* **21**, 1168 (1949).
19. Miller, F. A., and Wilkins, C. J., *Anal. Chem.* **24**, 1253 (1952).
20. Hammerle, R. H., and Mikkor, M., Paper presented at the ACS Annual Meeting in Chicago, Ill., August 1975.
21. Bailar, J. C., Jr., Emeleus, H. J., Nyholm, R., and Trotman-Dickenson, A. F., "Comprehensive Inorganic Chemistry," Vol. 1, p. 1055. Pergamon Press, Oxford, 1973.