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ISBN 0-612-16474-8

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UNIVERSITÉ D'OTTAWA
UNIVERSITY OF OTTAWA

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ABSTRACT

This thesis has been concerned with some aspects of the reactions of SO_2 and H_2S over various catalysts, and it has been peripherally concerned with the use of probe molecules to study the surface structure of silica. The major experimental technique has been infrared spectroscopy, sometime supported by data obtained from Raman spectroscopy, mass spectroscopy, temperature programmed desorption and gravimetric measurements.

Most of the work has been related to the Claus reaction, $2\text{H}_2\text{S} + \text{SO}_2 \longrightarrow 2\text{H}_2\text{O} + \frac{3}{n}\text{S}_n$. In Chapter 3 this reaction has been studied over Al_2O_3 catalysts, in Chapter 4 over sodium impregnated Al_2O_3 catalysts, in Chapter 5 over sodium impregnated SiO_2 catalysts, and in Chapter 6 over Y type zeolites.

Chapter 7 is concerned with a study of the oxidation of SO_2 over spinel (magnesium aluminate, MgAl_2O_4) with the view of examining the suitability of this material for adsorption of SO_x ($\text{SO}_2 + \text{SO}_3$) during the regeneration of fluidized catalytic cracking (FCC) catalysts.

Chapter 8 is concerned with a study of the adsorption of NO_x and of NO_x/SO_2 mixtures over Al_2O_3 and $\text{CuO}/\text{Al}_2\text{O}_3$ catalysts, with respect to the Selective Catalytic Reduction (SCR) of NO_x species.

The last Chapter, 9, is related to a very different study, an IR examination of the use of antimonypentamethyl, SbMe_5 , as a molecule for probing the structure and accessibility of surface silanol (SiOH) groups on silica.

A brief summary of the work above, headed by the relevant chapter in this thesis, is given below.

Chapter 3:

The dissociative chemisorption of H_2S on alumina gives rise to infrared bands which have been attributed to OH, Al-SH and Al-S species. The interaction occurs with AlOH groups and coordinatively unsaturated acidic Al and basic O sites which are created by the thermal activation under vacuum when Al_2O_3 is heated at temperatures above about 300°C . Physical adsorption also occurs on Al sites and via hydrogen bonding to AlOH groups.

The chemisorption of SO_2 on alumina produces two species, one being a sulfite like species, probably AlOSO_2 having an infrared band in the range from 1070 to 1050 cm^{-1} . This occurs via the interaction of SO_2 with O^{2-} sites. A second species, a hydrogensulfite probably having the structure AlOSO_2H has an IR band at 1010 cm^{-1} and occurs via a reaction with basic surface OH groups. Physical adsorption gives rise to species having infrared or Raman bands near 1330 and 1150 cm^{-1} , close to the frequencies for the antisymmetric and symmetric SO stretching modes of the parent SO_2 . Two unidentified species of unknown structure are in evidence as shown by very weak infrared bands near 1250 and 1200 cm^{-1} .

Under static reaction conditions, preadsorbed SO_2 reacts with gaseous H_2S to give sulfur. On the other hand, preadsorbed H_2S does not react with SO_2 but instead, preadsorbed H_2S is displaced by the stronger acid SO_2 . We have concluded that the mechanism of the Claus reaction over Al_2O_3 mainly involves a reaction between adsorbed SO_2 and gaseous H_2S .

The adsorption of a 2:1 mixture of gaseous $\text{H}_2\text{S}/\text{SO}_2$ on Al_2O_3 has been investigated for the first time. The Claus reaction appears to occur readily at room temperature on Al_2O_3 and on several other oxide catalysts and a single species can be detected as the reaction proceeds, characterized by a sharp IR band at 1028 cm^{-1} and a pair of bands near 1200 cm^{-1} . The sharp band is observed for all oxides and its wavenumber does not depend on the quantity of water present. On the other hand, the wavenumber of the pair of bands near 1200 cm^{-1} depends on the nature of the oxide and on the quantity of water present. Tentatively, all of these IR bands have been attributed to polythionate species which are generated during the Claus process, and it may correspond to an intermediate of Wackenroder's solution ($\text{H}_2\text{S}/\text{SO}_2$ in water).

Chapter 4:

At room temperature, sulfur dioxide reversibly adsorbs on Al_2O_3 , $\text{Na}/\text{Al}_2\text{O}_3$ as well as $\text{Cs}/\text{Al}_2\text{O}_3$, and we have concluded that weak basic sites are implicated in the physisorption process. In addition, at least two strongly chemisorbed species are produced. The major species on Al_2O_3 and $\text{Na}/\text{Al}_2\text{O}_3$ has a strong IR band near 1050 cm^{-1} and has been attributed to an adsorbed sulfite type species, probably involving an AlOSO_2 bond. This species is somewhat reactive with gaseous H_2S and leads to the formation of water and sulfur, two products of the modified Claus reaction. More sulfite is formed on $\text{Na}/\text{Al}_2\text{O}_3$ than on Al_2O_3 . However, the sulfite on the more basic $\text{Na}/\text{Al}_2\text{O}_3$ catalyst is more strongly chemisorbed than on pure Al_2O_3 , and it is less reactive with gaseous H_2S .

Sulfur is formed when gaseous H_2S is contacted with chemisorbed SO_2 , but not when gaseous SO_2 is contacted with chemisorbed H_2S . The decrease of reactivity after impregnation with a large quantity of sodium or cesium can be attributed to the greater stability of the sulfite species adsorbed on the more basic sites of alkali-containing catalysts than the stability on pure Al_2O_3 , these sulfite species being considered as intermediates in the modified Claus reaction. Others have proposed that the lower activity of a high sodium loaded alumina catalyst relative to pure alumina was due to either (i) the catalyst being too basic with excessive sodium or (ii) the need to have both acid and base sites, and sodium poison the acid sites. We conclude that hypothesis (i) is more plausible; a greater basicity is not necessarily a favourable factor for the modified Claus reaction.

Chapter 5:

Silica is inert in the Claus reaction. Therefore, the work in this chapter has been related to a study of the Claus reaction over a sodium on silica catalyst in an attempt to elucidate the role of sodium in this process. The results are very complex, but as with the other studies, sulfur was only produced after a reaction with pre-adsorbed SO_2 and gas phase H_2S and not in the reverse sequence. However, with Na/SiO_2 , thiosulfate was a stable product of the reaction and it is believed that these were generated from less stable polythionates of the general formula $\text{S}_m\text{O}_6^{2-}$.

When a 2/1 mixture of $\text{H}_2\text{S}/\text{SO}_2$ was contacted with the catalyst, sulfur was produced and polythionates and thiosulfates were the major stable surface products detected. Various reaction schemes have been postulated which lead to the generation of thiosulfate which can subsequently lead to the generation of sulfur when H_2S and SO_2 and H_2O are present.

Chapter 6:

The adsorption capacity of the zeolites NaY and HY for SO_2 or for H_2S is considerably greater than Al_2O_3 , $\text{Na}/\text{Al}_2\text{O}_3$ or Na/SiO_2 . This can be attributed to the microporous nature of zeolites. However, the adsorption is mainly physical and there is little evidence for chemisorption of either reactant. None the less, the acidity of the zeolite does influence the quantity and strength of physically adsorbed species, this being lower for HY, as would be expected for the physical adsorption of acidic molecules on an acidic surface. On NaY, SO_2 adsorption is primarily believed to occur via coordination to sodium sites.

In common with Al_2O_3 , $\text{Na}/\text{Al}_2\text{O}_3$ and Na/SiO_2 , the Claus reaction occurs when mixtures of H_2S and SO_2 are contacted with NaY; no significant reaction occurs on HY. The primary role of the zeolite appears to be to bring the weakly held reactants together in a suitable orientation for reaction to occur. As with Al_2O_3 and Na/SiO_2 , it would appear that polythionates, $\text{S}_m\text{O}_6^{2-}$, are generated in the Claus reaction.

Chapter 7:

The sulfation of magnesium aluminate spinel, MgAl_2O_4 , via oxidation of SO_2 in excess oxygen in the temperature range from 350 to 650 °C has been studied using infrared spectroscopy and vacuum microbalance techniques. The major conclusions are:

(1). At least two types of surface sulfate species are formed for low doses of SO_2 , but at higher doses, ionic like sulfate species become incorporated into the bulk of the spinel.

(2). The quantity of sulfate formed for a given dose of SO_2 increases with the temperature of oxidation (for a fixed time of oxidation) or with the time of oxidation (for a fixed temperature). The presence of the water vapour will increase the sulfate species, mainly bulk species.

(3). All types of sulfate species are thermally stable under vacuum to about 800°C but are removed when heated in the range from 800 to 900°C .

(4). In excess hydrogen, all sulfates are removed during heating from about 550 to 640°C .

(5). The thermal stability and reducibility of sulfated spinel (3 and 4 above) have been compared with those of sulfated Al_2O_3 , TiO_2 , ZrO_2 and MgO . We have concluded that, of these materials, spinel is a superior FCC (fluid catalytic cracking) transfer catalyst by virtue of its high sorption capacity for sulfate species, and because the catalyst can be easily regenerated in H_2 at moderately low temperatures.

Chapter 8:

The adsorption of NO_2 and NO_2/SO_2 mixture on Al_2O_3 and $\text{CuO}/\text{Al}_2\text{O}_3$ catalysts has led to the following conclusions:

(1). Al_2O_3 has a catalytic capacity to reduce NO_2 to NO and NO^+ . The higher the activation temperature, the more NO and NO^+ are found. The reduction sites may involve two coordinatively unsaturated Al^{+3} ions. The adsorption of NO_2 on Al_2O_3 to form NO_3^- species is so strong that the catalytic capacity is reduced. The assignments of different coordinated NO_3^- are also obtained.

(2). Preadsorption of SO_2 increases the ability of Al_2O_3 to reduce NO_2 to NO and NO^+ . On the other hand, preadsorption of NO_2 on Al_2O_3 increases the amount of SO_2 adsorbed. It gives strong bands at 1150 and 1370 cm^{-1} , which belong to sulfate species.

(3). For the CuO/Al₂O₃ catalyst investigated here (containing 1% Cu), there mainly exist Cu²⁺ cations in the CuO phase, Cu²⁺ ions in aluminate types, very few isolated Cu²⁺ in the Al₂O₃ lattice, and a few Cu⁺ ions in Cu⁺-O-Cu^{x+} (x=1,2) states as well as a few Cu⁰ sites.

(4). Addition of copper greatly increases the ability of alumina to reduce NO₂ to NO. The possible mechanism might involve the reaction ($2\text{Cu}^+ + \text{NO}_2 \longrightarrow 2\text{Cu}^{2+}(\text{O}) + \text{NO}$), which suggests that increase of the Cu⁺ content greatly promotes the reduction activity of the catalysts. The impregnated sample also greatly decreases the stability of NO₃⁻ toward to SO₂.

(5). It seems SO₂ mostly adsorbs on surface basic sites which are connected with Cu²⁺ ions of CuO phase to form surface sulfate species and leave aluminate like Cu²⁺ cations (CuAl₂O₄) free to adsorb NO.

(6). SO₂ can be adsorbed on Cu⁰ sites to dissociate to SO and O species.

(7). Sulfated copper species on the surface can promote the reduction of NO₂ to NO, NO⁺ and N₂O.

Chapter 9:

Infrared spectroscopy has been used to study the chemisorption of pentamethylantimony, SbMe₅, on silica. For temperatures of activation from room temperature to 1000°C, a single chemisorbed product is formed, ≡SiOSbMe₄. The hydrogen-bonded silanols react to completion faster than the isolated silanols. Unlike other reactive metal-alkyl compounds, there was no evidence for a significant reaction with siloxane sites. The chemisorbed species does not react with water vapor at room temperature or at 100°C. However, upon heating under vacuum to 250-300°C it decomposes to yield surface SiOMe groups and gaseous SbMe₃. Finally, the silanol groups can be regenerated when surface SiOSbMe₄ reacts with gaseous HCl to yield SbMe₄Cl, the reaction being: $\text{SiOSbMe}_4 + \text{HCl} \longrightarrow \text{SbMe}_4\text{Cl} + \text{SiOH}$.

ACKNOWLEDGEMENTS

First of all, I wish to express my deepest and most sincere appreciation to my supervisor, Professor B. A. Morrow, for his guidance, encouragement and patience throughout the course of my Ph. D. work.

I would also thank Professor J. C. Lavalley for a fruitful cooperation between our two research groups.

I would like to thank the friends and colleagues in Professor Morrow's lab. They have supported me in both a scientific way and a personal way throughout the course of my graduate studies in Ottawa. They are Carl, Andy, Bruce, Lyn, Steve, Dang and Dave. I really have a good time in working with them.

Finally, my thanks goes to my wife, Baoling, and my daughter, Rui, for their love, inexhaustible support and patience. I am equally very grateful to my parents who have always given support and encouragement towards everything I have done in my life and career.

Chapter 1

INTRODUCTION

Sulfur dioxide (SO₂) and several oxides of nitrogen (NO_x) are the major pollutants in the atmosphere. Both contribute to the generation of acid rain, which exerts a harmful effect on the environment. Photolytic decomposition of NO₂ in the atmosphere may result in ozone formation.

In this thesis, infrared spectroscopy has been used to study the modified Claus reaction ($\text{SO}_2 + 2 \text{H}_2\text{S} \rightleftharpoons 2 \text{H}_2\text{O} + \frac{3}{n} \text{S}_n$) on some metal oxides. Some NO_x reactions on various metal oxide surfaces were also investigated. The characterization of the oxide surfaces plays an important role in heterogeneous catalysis. Various probe molecules were used to study the surface properties of the metal oxides and silica.

FTIR spectroscopy is a powerful tool for investigating the mechanisms of the interaction between a gas and a solid catalyst, and the *in situ* technique is particularly useful in this situation. The progressive decrease or growth of the IR bands shows the progressive loss or formation of some species on the surface. IR spectroscopy can also provide information on composition and structure of the surface compounds. These are the primary requirements for us to understand the mechanisms of interaction between surface groups and adsorbed species or reactants. The Claus reaction is a heterogeneous process involving gas-solid adsorption, and FTIR spectroscopy is perfectly suited for this investigation. SO₂ gas has adsorption bands at 1360 and 1151 cm⁻¹, while H₂S gas has a relatively weak band at about 2570 cm⁻¹. Many oxysulfur compounds are known and some have been identified by IR. The S-O stretching vibrational modes mainly lie from 1300 to 900 cm⁻¹, while S-O-S and S-S-O deformation vibrational modes lie in 800 to 400 cm⁻¹ spectral region. This is well suited for our mid-infrared spectroscopic study. Although

sulfur, one of the final products of the Claus process, has S-S vibrations below 500 cm^{-1} , we can use Raman spectroscopy to overcome this problem. The NO , NO_2 , NO_3^- species also have vibrational modes in $2000\text{-}1000\text{ cm}^{-1}$ region. The oxides used here were Al_2O_3 , SiO_2 , ZrO_2 , MgO and various zeolites. Most of these oxides are transparent from 4000 to about $1000\text{-}800\text{ cm}^{-1}$. Therefore, most features of the adsorbed SO_x and NO_x species are "visible" by means of IR. Besides IR, vacuum microbalance techniques were also used in this thesis.

1. CLAUS REACTION

Besides its emission from volcanoes or other natural sources, the principal sources of sulfur dioxide are coal combustion (about 70% of the total from industrial sources), oil combustion and refining (20%), and metal ore smelting and others (10%) [1]. Industrial sulfur dioxide emissions are estimated at about 1.6×10^8 tons a year. The oxidation of SO_2 in the atmosphere is a very complex process and can be induced homogeneously by several oxidants such as $\text{OH}^\bullet$, O_3 , H_2O_2 , or it can be catalyzed by some metal ions like Fe^{3+} , Mn^{2+} , Cu^{2+} and some gases like NO_x [2]. The foremost chemical reaction of SO_2 in the atmosphere is oxidation to SO_3 , which takes about 3-7 days depending on the weather conditions. Then SO_3 will react with water to give sulfuric acid. SO_2 can also dissolve in water and it can be subsequently oxidized to H_2SO_4 . Relatively pure rain water has a pH value around 5.5 - 5.7, but owing to the formation of acid rain, its pH can drop to as low as 2. The acid rain may result in the acidification of waters and soils, and in damage to buildings. It has been recognized as a global problem.

H_2S is another pollutant. It is very toxic and has very bad smell. Concerning the human activity, H_2S mainly comes from: (a) catalytic hydrodesulfurization (HDS) of crude oil (which contains about 0.2-5.0% sulfur); (b) fluid catalytic cracking (FCC) catalyst regeneration; (c) gasification of coal (0.3-3.0% by volume); (d) natural gas (about 1-5 mole percent of H_2S). For each 20,000 barrels of crude oil with a high sulfur content, like that from Kuwait (containing 2.5~4% of sulfur), approximately 45 tons of H_2S is formed under HDS treatment.

In the pioneer work by Carl Friedrich Claus in 1890 [3,4], hydrogen sulfide was partially oxidized to elemental sulfur and water by stoichiometric amount of air:



The original Claus reaction took place in a single reactor on a bauxite catalyst. A big problem in this process was that the heat liberated was large and temperature control was very difficult. (The temperature in the reactor could reach about 1200 °C.) In 1938, I. G. Farben introduced the split-flow concept in the Claus process, that is, instead of single reactor, two reactors were used [5]. First, one third of hydrogen sulfide was burned completely to sulfur dioxide in a waste heat boiler (reaction 1-2):



The gases were cooled to about 160 °C. The sulfur dioxide produced then reacted with the remaining two thirds of the hydrogen sulfide over the catalyst in a converter (reaction 1-3):



S_n species include S_2 , S_4 , S_6 , S_8 and S_λ , which may exist in a complicated equilibrium. The advantage of the modified Claus process was that only about one fifth of total heat was evolved in the catalytic converter (comparing ΔH_3 with ΔH_1). The reaction can be easily controlled and higher equilibrium conversions are obtained at the lower operating temperatures. Reaction (1-3) is strictly known as the modified Claus reaction, but it is commonly called 'the Claus reaction' today.

Despite the simple stoichiometric equation, the modified Claus reaction is very complicated.

- (i). The dry sulfur dioxide gas does not react with dry hydrogen sulfide in the absence of catalysts below 400 °C [6]. Suitable catalysts are necessary to let mutual oxidation and reduction take place in lower temperatures.
- (ii). Since the modified Claus reaction (reaction 1-3) is an

equilibrium, conversion in the catalytic stage is never complete. The reactions involve a large amount of heat, and from the thermodynamic point of view, a lower temperature favours the conversion of H_2S ; however, this lower temperature must make the reaction go at a workable rate. Therefore, there will be a balance between the conversion of H_2S and the reaction rate. The activity of the catalyst at a low temperature is a crucial factor in determining the efficiency of the conversion. (iii). It is well known that the Claus reaction occurs over alumina and other solid oxide catalysts. But this reaction also occurs in the gaseous phase with a trace of water and in the liquid phase without a catalyst [7], although it might involve a different mechanism. Therefore, the real process might involve the gas reactions as well as heterogeneous catalyzed process. (iv). A further limitation on the conversion is also imposed by side process such as the formation of carbonyl sulfide, COS, and carbon disulfide, CS_2 . These gases are produced by the interaction between H_2S , CO and hydrocarbons which are naturally present. (v). Finally, the chemistry of oxysulfur compounds is very complex and is not well understood [8, 9]. Therefore, although the Claus reaction has been known for over a century and the modified process has been known for over fifty years, details of the reaction are little understood.

Public awareness calls for stronger regulations to limit emissions of SO_2 and H_2S . It is estimated that to build a new coal-fired generating plant, about 30% of the total cost will go toward mandated environmental control [10]. Therefore, there is a requirement for more efficient methods to control emissions, and in turn, for more efficient catalysts.

Among Claus catalysts, pure alumina is widely used. In chapter 3, the modified Claus reaction on pure Al_2O_3 will be investigated. Although alumina as a Claus catalyst has been investigated by many reporters [11-20], the conclusions are usually vague and many controversies exist. We have reinvestigated the adsorption of SO_2 and H_2S on $\gamma\text{-Al}_2\text{O}_3$. In order to get more information, a series of alumina samples differing in activating temperature were studied. We also tried to introduce the gas in a very small quantity which lead to a very low coverage on the surface of the catalyst. The samples were made as thin as possible to overcome poor IR transmission below 1000 cm^{-1} .

Virtually all previous work has dealt with the reactions of preadsorbed SO_2 with gaseous H_2S , or of preadsorbed H_2S with gaseous SO_2 . However, in the modified Claus process, a 2:1 mixture of $\text{H}_2\text{S}/\text{SO}_2$ is used. A unique feature of this thesis has been an examination of the reaction of various $\text{H}_2\text{S}/\text{SO}_2$ mixtures over Al_2O_3 and other oxide catalysts (MgO , ZrO_2 , TiO_2 and zeolites). By this means we have been able to tentatively identify more intermediates in the Claus process. This work is mainly discussed in Chapters 3 and 5, and the work relative to zeolites is described in chapter 6.

Although an alumina catalyst displays relatively high activity towards the Claus reaction, it is not sufficiently active towards carbonyl sulfide (COS) hydrolysis, which is necessary in the Claus process to eliminate undesired by-products like COS . Alumina may also be deactivated by sulfation, which happens if the conditions in the converter accidentally become oxidizing. Therefore, some additives were investigated to improve the performance of pure alumina. Some additives, like sodium and cesium, were added to alumina and these new catalysts were compared with pure alumina by spectral differences. Basic alkali metals were used because many reports have shown that the active sites for the Claus reaction are basic. It is well known that the addition of sodium increases the basicity of alumina, and it also increases the rate of the Claus reaction [21]. But it has also been shown that a higher sodium content on alumina gave rise to a very basic catalyst which was less active for the Claus process. This gave rise to the question of whether there might exist an optimum basicity, and the presence of excess sodium goes beyond the optimum making the catalyst too basic so as to not favour the Claus reaction. A second possibility is that the reaction needs both of basic and acidic sites to complete the catalytic process, and that the latter are poisoned by the presence of excess sodium. A comparison of these basic catalysts with pure alumina will reveal some factors concerning the adsorption of the SO_2 and H_2S on basic or acid sites, and whether the Claus process occurs on basic sites or on both sites. This project is studied in the chapter 4.

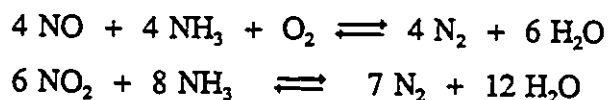
In view of the possible role of sodium as a base modifier of Al_2O_3 catalysts for the Claus reaction, we have attempted to study the effect of sodium alone on this reaction. To this end, we have supported sodium on SiO_2 , and we have studied the adsorption of SO_2 and H_2S and their

reactions over this material. Silica is inert for the chemisorption of either of the reactants, or their mixtures, and by this means we have attempted to be able to study the role of sodium alone in the Claus process. This work is described in Chapter 5.

Zeolites are interesting catalysts because of their special properties such as acidity, Si/Al ratio, ion exchange modification, etc. Zeolite-Y is an intermediate silica-to-alumina ratio zeolite (about 2.0 to 5.0) and has a very high surface area, over 800 m²/g. Comparing the activities of Na-Y and H-Y zeolite for the Claus reaction, we can acquire a knowledge about the role of acidity. H-Y zeolite calcined at 480 °C has only Brønsted acidic sites [22] and this investigation might provide an opportunity to determine the role of Brønsted acidic sites in the Claus process. This study is described in the chapter 6.

2. NO_x REACTIONS

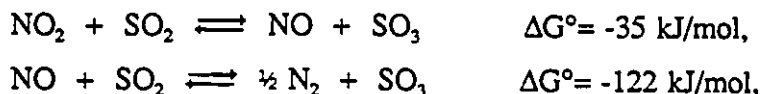
It is reported that the concentration of SO₂ in the atmosphere is gradually decreasing while that of nitrogen oxides, NO_x, is increasing [2, 23-25]. The amount of NO_x (NO, NO₂, N₂O) which comes from human activity is about 6.0x10⁷ tons/year [23]. Removal of NO_x from emission gas is becoming more and more important. So far, no technology exists that is completely satisfactory for the conversion of NO_x components in the emission gas. Although many papers have been published, most of them were concerned on the so-called selective catalytic reduction (SCR) by NH₃. The reactions which occur during the SCR process are:



The catalysts used in the above process are usually a metal oxide supported on TiO₂, such as V₂O₅/TiO₂, or on zeolite. The main problem in the SCR process is the poisoning of the catalysts by SO₂ which usually accompanies NO_x in most cases. The SCR process also consumes a lot of ammonia. Using NH₃ as the reductant has some drawbacks. One is the cost and another one

is that unreacted NH_3 is also environmentally objectionable. It is important to find ways to reduce NO_x with a N-free reducing agent [26].

In most exhaust streams, both SO_2 and NO_x are present. The current removal methods are complex and expensive, with many unwanted byproducts. While the reactions,



are thermodynamically favourable, no catalysts are known for these reactions and there are not many published accounts of the SO_2 - NO_x reaction on surfaces. Although the oxides of nitrogen are unstable thermodynamically, they are extremely stable in the kinetic sense [26,27]. In chapter 8, we have examined the species formed by the adsorption of NO, NO_2 , SO_2 on Al_2O_3 and $\text{CuO}/\text{Al}_2\text{O}_3$. The $\text{CuO}/\text{Al}_2\text{O}_3$ catalyst was made by impregnation of $(\text{CH}_3\text{COO})_2\text{Cu}$ on Al_2O_3 . After activation, the catalyst mainly contains CuO on the surface and Cu is 1% by mass. We choose to study $\text{CuO}/\text{Al}_2\text{O}_3$ because copper based catalysts are among the most intensively investigated catalysts for NO_x reduction [26, 28]. In the NO_x reduction process, it is important to develop catalysts which are heat resistant and alumina based catalysts are suitable for this purpose. To remove NO_x and SO_x simultaneously is a large project [29], and this chapter is a preliminary study of these reactions.

3. OTHER SYSTEMS

OH groups are present on the surface of solid oxides and these can have a strong influence on its catalytic properties. Some agents react with surface OH groups on an oxide and substitute the hydrogen atoms; these chemicals are usually called hydrogen sequestering (HS) agents. These substitution reactions result in an important area of surface chemistry, which can involve chemical synthesis, surface modification and catalysis. On silica, the surface silanol groups play an important role in the adhesive bonding of organic groups. Therefore, accessibility of the surface silanols is an important property of silica. Hydrogen sequestering agent, SbMe_3 , has been

used to study the accessibility and reactivity of the surface silanol groups of silica. This study is presented in chapter 9.

In the petroleum industry, there is an important process called catalytic cracking. Catalytic cracking, in general, may be regarded as a method for converting high-boiling petroleum fractions into gasoline and other low-boiling fractions. The most widely used process is fluid catalytic cracking (FCC). However, during the cracking, organosulfur compounds are deposited on the catalyst, which remarkably reduces the catalyst's activity. Therefore, the catalyst is continuously withdrawn from the bottom of the reactor and moved into a regenerator. In order to regenerate a FCC catalyst, oxygen is introduced to burn off the deposited organosulfur compounds and coke, and a mixture of SO_x ($\text{SO}_2 + \text{SO}_3$) is emitted. The mixture usually contains 90% SO_2 and 10% SO_3 . The emitted SO_x can be reduced by some gases such as methane [30], CO [31], or by H_2S in the Claus process. The Claus reaction has many advantages, e. g. elemental sulfur is a byproduct and the process is carried out under dry conditions. So, one way to control the emission of SO_x is to add to the FCC catalyst a so-called SO_x transfer catalyst. The transfer catalyst is capable of trapping the SO_x species and turns them to relatively stable sulfates. Then, this transfer catalyst is re-activated by some reducing process and the sulfur compounds released in the reduction are collected in a safe way. It is evident that an ideal transfer catalyst should have a high trapping ability, and easily facilitate the oxidation of SO_2 to SO_3 . The sulfates formed on transfer catalysts should also have a suitable stability so as not to decompose during the main catalytic process, but they must be easily reduced during the regeneration process. The regeneration is usually carried out by reducing the sulfates to hydrogen sulfide which is then treated via the modified Claus process to give elemental sulfur. Through infrared spectroscopy and vacuum microbalance techniques, we have investigated the potential of using magnesium aluminate spinel, MgAl_2O_4 , as a FCC transfer catalyst. This work is described in chapter 7.

References

- [1]. Fergusson, J. E., 'Inorganic Chemistry and the Earth', Pergamon Press, 1982, Oxford.
- [2]. Brandt, C. and van Eldik, R., Chem. Rev., 95, 119(1995).
- [3]. Gamson, B. W. and Elkins, R. H., Chem. Eng. Pro., 49, 203(1953).
- [4]. Lagas, J. A., Borsboom, J. and Berben, P. H., Oil & Gas Journal, Oct 10, 68(1988).
- [5]. Lagas, J. A., Borsboom, J. and Berben, P. H., Oil & Gas Journal, Oct 10, 69(1988).
- [6]. Barnett, E. de Barry and Wilson, C. L., "Inorganic Chemistry", Longmans Green and Co, second edition, London, 1957, p499.
- [7]. Miaskiewicz, K. and Steudel, R., J. Chem. Soc. Dalton Trans., 2919(1994).
- [8]. Schmidt, M., in "Sulfur in Organic and Inorganic Chemistry" (Ed. by Senning, A.), Vol. 2, Marcel Dekker Inc., New York, 1972, p71.
- [9]. Lyons, D. and Nickless, G., in "Inorganic Chemistry" (Ed. by Nickless, G.), Elsevir, Amsterdam, 1968, p509.
- [10]. C & EN, June 17, 1991, p33.
- [11]. Datta, A., Cavell, R. G., Tower, R. W. and George, Z. M., J. Phy. Chem., 89, 443(1985).
- [12]. Datta, A. and Cavell, R. G., J. Phys. Chem., 89, 450(1985).
- [13]. Datta, A. and Cavell, R. G., J. Phys. Chem., 89, 454(1985).
- [14]. Kasumov, F. B., Kinetics and Catalysis, 33, 302(1992).
- [15]. Karge, H. G. and Dalla Lana, I. G., J. Phys. Chem., 88, 1538(1984).
- [16]. Srinivasan, S., Narayanan, C. R., Biaglow, A., Gorte, R. and Darye, A. K., Appl. Catal. A: General, 132, 271(1995).
- [17]. Mendioroz, S., Munoz, V., Alvarez, E. and Palacios, J. M., Appl. Catal. A: General, 132, 111(1995).
- [18]. George, Z. M., in "Sulfur Removal and Recovery from Industrial Processes" (Ed. by Pfeiffer, J. B.), Adv. Chem. Series 139, p75, Washington, D. C., 1975.
- [19]. Lavalley, J. C., Mohammed Saad, A. B., Tripp, C. P. and Morrow, B. A., J. Phys. Chem., 90, 981(1986).
- [20]. Dalla Lana, I. G., Karge, H. G. and George, Z. M., J. Phys. Chem., 97, 8005(1993).

- [21]. Karge, H. G., Tower, R. W., Dudzik, Z. and George, Z. M., Stud. Surf. Sci. catal., 7, 643(1981).
- [22]. Ward, J. P., J. Catal., 13, 321(1969).
- [23]. Ismagilov, Z. R. and Kerzhentsev, M. A., Catal. Rev. - Sci. Eng., 32, 51(1990).
- [24]. Hedin, L. O., Likens, G. E. and Bormann, F. H., Nature, 325, 244(1987).
- [25]. Walker, G., Nature, 368, 175(1994).
- [26]. Shelef, M., Chem. Rev., 95, 209(1995).
- [27]. Shelef, M., catal. Rev.- Sci. Eng., 11, (1975).
- [28]. Gopalakrishnan, R., Stafford, P., Davidson, J., Hecher, W. C. and Bartholomew, C. H., Appl. Catal. B, 2, 207(1993).
- [29]. Acres, G. J. K. in "Perspectives in Catalysis", Edited by Thomas, J. M. and Zamaraev, K. I., Blackwell Scientific Publications, 1992, p359.
- [30]. Mulligan, D. J. and Berk, D., Ind. Eng. Chem., prod. Res. Dev., 28, 926(1989).
- [31]. Hibbert, D. B., Catal. Rev.- Sci. Eng., 34, 391(1992).

Chapter 2

EXPERIMENTAL SECTION

1. INSTRUMENTATION

The work involving infrared spectra was carried out on two infrared spectrometers: a Bomem DA3-02 spectrometer and a Bomem Michelson MB-100 instrument. Both are Fourier transform infrared (FTIR) spectrometers.

The DA3-02 instrument has two sample chambers, one with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector and the other has an ambient temperature deuterated triglycine sulphate (DTGS) detector. The instrument is capable of maximum resolution of 0.02 cm^{-1} and can record infrared spectra in the mid-infrared region from 5000-400 cm^{-1} . Because the MCT detector has a higher sensitivity, the work on DA3-02 was mostly done using this detector. The spectral resolution was 4 cm^{-1} and normally 100 scans were acquired which required about 40 to 50 seconds.

The MB-100 instrument has a single DTGS detector and was used for most of the work reported in this thesis. The spectra were recorded using a resolution of 4 cm^{-1} with 15 scans requiring 42 seconds. Most experiments on this instrument were carried out by acquiring 5 to 25 scans prior to Fourier transformation, depending on the reaction requirements, but the experiments involving thin film samples usually needed 100 or more scans.

All spectra are shown in absorbance against wavenumber (cm^{-1}). Unless otherwise noted, all spectra were plotted as they were recorded without additional smoothing. Difference spectra were obtained by subtracting the background spectrum from the spectrum of interest.

The Raman spectra were obtained on a Jobin-Yvon HG-2 Raman spectrometer with the resolution at 8 cm^{-1} . The sample irradiation was achieved by using an argon ion laser (488 nm) with a laser power at the sample ranging from 50 to 500 mW. These spectra were obtained in our laboratory by Carl Tripp and were reported in his thesis [1].

The B.E.T. measurements were carried out gravimetrically using an electronic vacuum microbalance to measure the quantity of N_2 adsorbed at 77 K. The equipment is a model Sartorius 4433 and has a symmetrical two-arm configuration.

2. SAMPLE CELL

The infrared cell used in this laboratory has been described previously by Morrow and Ramamurthy [2] and is shown in Fig 2.1. The cell body was made of either pyrex or quartz depending on whether high heating temperatures (above $500\text{ }^\circ\text{C}$) were employed. The lower part of the IR cell has a furnace and two windows which were either NaCl, KBr or ZnSe, depending on the reaction conditions inside the cell, because some chemicals might react with the windows. ZnSe windows, for example, are inert to water, SO_2 and H_2S , and, therefore, were used in studying the Claus reaction. The furnace region was wound with nichrome wire at a density of about four turns per centimetre. This was insulated by a layer of alumina. The pyrex cell could be heated to $500\text{ }^\circ\text{C}$, the quartz cell to $1200\text{ }^\circ\text{C}$. The upper part of the cell was made of pyrex. The two parts of the cell body were lubricated with the grease "Apiezon H". The windows of the cell were cooled by a fan when the sample was heated at high temperatures. The temperature of the cell was measured by a chromel-alumel thermocouple which was encased in a thin quartz tube and was inserted between the insulation mat and the heating wire. Inside the cell there was a sample holder which was made of quartz. The sample holder could be moved to or from furnace region by external magnets.

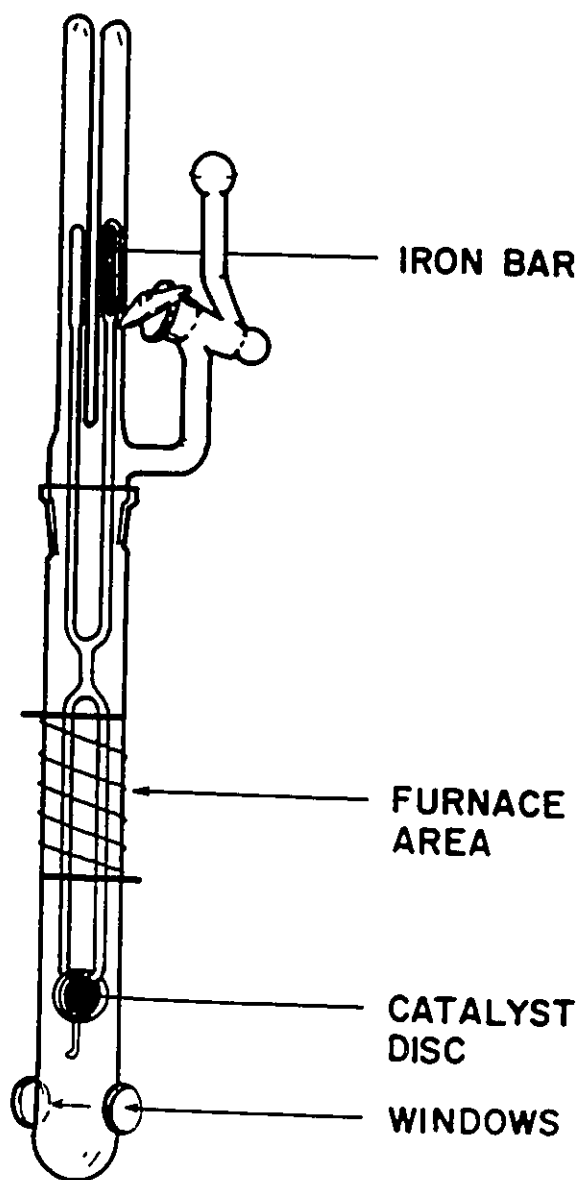


Fig 2.1 The infrared cell used in this work

3. VACUUM LINE

The vacuum line consisted of pyrex manifold, an oil diffusion pump and a mechanical pump. A liquid nitrogen trap was placed between the diffusion pump and the main manifold. The vacuum line was designed so that the IR cell and various gas containers could be easily connected. In this way, the infrared cell could be evacuated and various gas could be added in a known amount to the infrared cell. All stopcocks were constructed of pyrex and teflon. The grease "Apiezon N" was used to attach the vacuum line to the sample cell via ball joints. The base pressure with this system was 10^{-6} Torr, the pressure being measured by means of capacitance manometers and a Pirani gauge. The whole vacuum line was attached to a portable cart so that it could be moved close to the infrared spectrometer for *in situ* studies.

4. MATERIALS

(1). Solid oxides

The alumina, Degussa Alumin Oxid C, was from Degussa A.G. Frankfurt. The specific surface area was reported as nominally $100 \text{ m}^2/\text{g}$ and was found to be $105 \text{ m}^2/\text{g}$ in our laboratory. This alumina was mainly γ -alumina.

The silica was an aerosil type, Cab-O-Sil HS-5, which was obtained from Cabot Inc., U.S.A. The B.E.T. (N_2) surface area was $325 \text{ m}^2/\text{g}$.

The spinel (magnesium aluminate spinel) used was provided by DOW Chemical Co., as a product called Cernel. According to DOW, at least 99% of the Mg and Al atoms had the spinel structure, the rest being in the form MgO and Al_2O_3 . The specific surface area reported by DOW is $120 \text{ m}^2/\text{g}$. However, a B.E.T. analysis using nitrogen in our laboratory showed the values reported in Table 2.1 as a function of the temperature of activation in vacuum. An X-ray analysis showed that the sample remained as a normal spinel regardless of the temperature of activation used (up to 1100°C) but that the diffraction peaks became narrower as the temperature of activation was increased, suggesting a higher degree of crystallinity for a higher activation temperature.

Table 2.1 Surface area of spinel as a function of the temperature of activation*

T (°C)	22	150	450	600	800	1000
Area (m ² /g)	142	183	183	178	140	36

* Sample was under evacuation for 1 hour at each temperature.

The zeolite-Y was in the sodium form (NaY, Union Carbide lot number 9680801014). Hydrogen-Y zeolite (HY) was prepared in the usual fashion by heating NH₄Y which was obtained by 2N NH₄⁺ aqueous ion exchange of NaY. Heating NH₄Y in vacuum at 120 °C for 0.5 hour and then at 450 °C for another 0.5 hour (pressure is about 10⁻⁵ Torr) evolves NH₃ leading to the hydrogen form, HY.

Zirconium dioxide (ZrO₂) is from Degussa as an "experimental product". It had a B.E.T. surface area 45 m²/g after vacuum activation at 450 °C. Gallium oxide (Ga₂O₃) was purchased from Alpha Ventron of Danvers, MA. This sample contains about 99.99% of pure Ga₂O₃ and the measurement surface area was 13 m²/g.

The solid oxide samples for infrared studies were prepared as self-supported discs which could be easily mounted in the sample holder. A preweighed amount of oxide was put in a 2.5 cm diameter stainless steel die which was then pressed under a desired pressure ranging from 10⁶-10⁸ Pa depending on the particular oxide and on the mass used. For example, a lower pressure (10⁶ Pa) was used to make a silica disc while a higher pressure, 10⁸ Pa, had to be used to make a Ga₂O₃ disc. The quantity of oxide in a given disc is expressed in mg/cm². For the alumina and spinel samples, the disc often adhered to the surface of the stainless steel die after pressing. In order to prevent this, lens paper or thin mica plates were placed between the die faces and oxide powder before pressing. The lens paper or mica plates could be easily removed from the discs later. Sometimes, in order to acquire a better knowledge of some spectral regions where the substrate is strongly absorbing, the thin film technique was used. A small quantity of oxide powder was uniformly put on a stainless steel die or on a clean quartz window. Then a

ZnSe window was placed above the powder and was gently rotated and pressed by hand so that the oxide adhered to the ZnSe window. This thin film usually contained 0.1 to 0.5 mg/cm² of oxide and could be mounted in the sample holder together with the ZnSe window. The film could be activated under vacuum up to 450 °C.

(2). Gaseous chemicals

The gases used were mostly from commercial sources. If necessary, gases could be purified before use by repeated freeze-pumping cycles and the purity was checked by infrared or mass spectroscopic analysis. For SO₂ and H₂S, impurities like water and CO₂ had to be removed. Water could be removed by distilling SO₂ or H₂S. The removal of CO₂ was done by passing SO₂ or H₂S through dried alumina (dried at 150 °C) several times. These were done in a vacuum line by freezing one container with liquid nitrogen and warming another container while the alumina powder was placed between them. NO and NO₂ were from Matheson. Purification of NO₂ was carried out with fresh P₄O₁₀ and could be checked by its infrared spectrum [3]. Commercial nitrogen dioxide usually contained traces of N₂O₃. This could be verified by condensing the gas at liquid nitrogen temperature. The trace of N₂O₃ would give a blue colour. In this case, the NO₂ gas had to be purified by mixing NO₂ with pure O₂, and reacting for at least one hour. N₂O₃ would react with O₂ to give NO₂. After reaction, the gas was passed through P₄O₁₀ to remove water. Then, the gas was frozen at liquid nitrogen temperature and evacuated to remove excess O₂. At this stage, pure NO₂ was obtained as a colourless product. To purify NO, it was first passed through P₄O₁₀ on the vacuum line in order to remove water, and then it was distilled several times until it was colourless [4].

(3). Other chemicals

SbMe₃ was kindly provided by Dr. Frank J. Feher, Professor of Chemistry, University of California, Irvine. All other chemicals used here which are not mentioned were obtained from standard commercial sources.

References

- [1]. Tripp, C., Ph. D. Thesis, April, 1988, Univ. of Ottawa.
- [2]. Morrow, B.A. and Ramamurthy, P., J. Phys. Chem., 77, 3052 (1973).
- [3]. Angelici, Robert J., "Synthesis and Technique in Inorganic Chemistry", W. B. Saunders Company, Philadelphia, 1977, p90.
- [4]. Morrow, B. A. and Moran, L. E., J. Catal., 62, 294 (1980).

Chapter 3

ALUMINA CATALYST

1. INTRODUCTION

Alumina is a widely used catalyst in the modified Claus process and many papers about the properties of Al_2O_3 and its use in the Claus process have been published. Among them, there are no lack of controversies. In this chapter, the adsorption of SO_2 and H_2S have been studied in detail and, especially, we have investigated the behaviour of gaseous mixtures of $\text{H}_2\text{S}/\text{SO}_2$ on Al_2O_3 . To our knowledge, this is the first time that infrared spectra of the mixture ($\text{H}_2\text{S}:\text{SO}_2 = 2:1$) adsorbed on oxide catalysts has been reported.

(1). Alumina

Alumina (Al_2O_3) is an important catalyst and catalyst support because of its high thermal stability and relatively high surface area. It exists in a number of crystalline forms which usually come from the dehydration of aluminum hydroxide $[\text{Al}(\text{OH})_3]$ or oxyhydroxide $[\text{AlO}(\text{OH})]$. These varieties of alumina are based on the many different close packing structures of oxygen atoms and on the arrangements of Al^{3+} cations in octahedral and tetrahedral voids. The value of the radius ratio of $r_{\text{Al}^{3+}}/r_{\text{O}^{2-}}$ in $\gamma\text{-Al}_2\text{O}_3$ (about $0.407 \text{ \AA}$) is very close to the critical radius ratio value of the octahedral structure ($0.414 \text{ \AA}$), so Al^{3+} cations can enter either octahedral voids or tetrahedral voids. Among these crystalline forms, γ -alumina is most commonly used. It has a defect spinel structure.

The structure of spinel (Al_2MgO_4) is one of the important structural forms of A_2BO_4 , in which oxygen atoms form cubic-closest-packed ($ABCABC\dots$) layers. In the unit cell there are 32 oxygen atoms, and 24 cations. In total there are 64 tetrahedral voids of which only 8 are occupied by B atoms, and 32 octahedral voids of which 16 are occupied by A atoms. A and B

are different atoms or the same atoms but in different environmental positions.

The structure of γ -alumina is very similar to that of spinel. Oxygen atoms form a close packed structure and there are 32 oxygen atoms and $21\frac{1}{3}$ Al^{3+} cations (electrical neutrality satisfied) in the unit cell. Among the 24 occupied metal cation positions of the spinel, $2\frac{2}{3}$ positions are vacant, and this is the so-call defect spinel structure [1]. The structural formula can be expressed as: $(\text{Al}^{3+}_{8/9}\odot_{1/9})_2(\text{Al}^{3+}_{8/9}\odot_{1/9})\text{O}_4$, where $\odot$ represent a vacant position.

In the powder diffraction X-ray spectra of $\gamma\text{-Al}_2\text{O}_3$, the spectral lines coming from the oxygen crystal lattice are sharp and other lines, especially those from Al^{3+} cations in tetrahedral positions are broad. This suggests that the distribution of Al^{3+} in $\gamma\text{-Al}_2\text{O}_3$ is random. The structure of $\gamma\text{-Al}_2\text{O}_3$, which is the most important alumina catalytically, is not well determined and the surface of the $\gamma\text{-Al}_2\text{O}_3$ is still a mystery [2].

Usually, $\gamma\text{-Al}_2\text{O}_3$ is obtained in a form of a powder. The particle size can be very small, so the specific surface area of γ -alumina is usually very large.

Alumina is among the most important catalysts in the modified Claus reaction because of its low cost, high durability and high activity. Marshneva *et al.* [3] reported that among 21 oxides, TiO_2 , MgO , V_2O_5 and Al_2O_3 were most active catalysts for Claus reaction. In fact, activated alumina is used industrially as the catalyst in Claus plants to purify natural gas [4], and a typical Bauxite catalyst (Engelhard Industries Ltd.) which is widely used in Claus process contains mostly Al_2O_3 [5]:

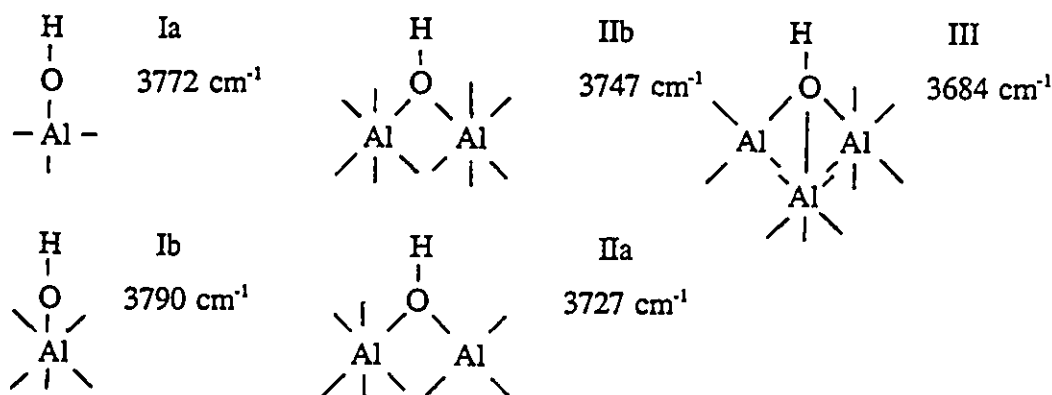
Al_2O_3	87%	Fe_2O_3	1.4%
TiO_2	1.7%	SiO_2	6.0%
insoluble	3.9%		

(2). Hydroxyl groups on Al_2O_3

Peri [6] reported that after evacuation for 100 hours at 25°C , there still existed about 13

molecules of water on $100 \text{ \AA}^2$ of surface of alumina. Although much of this water exists in the form of hydroxyl groups on the surface, some of the water remains in the molecular form. And after heating at 120°C , there were 8.25 molecules left. At this state, we can see, using infrared spectroscopy, a broad band in the OH stretching region indicating that the hydroxyl groups on surface must be hydrogen-bonded. Only after heating above 150°C , do isolated hydroxyl groups begin to appear (see Fig 3.1).

According to reports [1] there are at least five different types of hydroxyl on $\gamma\text{-Al}_2\text{O}_3$. If these hydroxyls are not hydrogen-bonded, their stretching vibrations have defined positions (see Fig 3.1).



The infrared intensities of these hydroxyl vibrations depend on their relative concentrations on the alumina surfaces. And these hydroxyl concentrations depend largely upon the exposed area on the different crystal faces [(100), (110) or (111)] to the total surface. So, the relative intensities of the hydroxyl vary with different samples.

For the infrared band assignments, Jones [7] suggested that the OH stretching frequency increased with the increasing negative charge on the oxygen atom of OH groups. According to this assignment, Ib has the highest wavenumber and the III mode has the lowest wavenumber. On the other hand, if one considers the residual negative charges left on the oxygen of the hydroxyl and stabilities of them when the proton is removed, the Brønsted acidities seems in the order: $\text{III} > \text{IIa} > \text{IIb} > \text{Ia} > \text{Ib}$ [1].

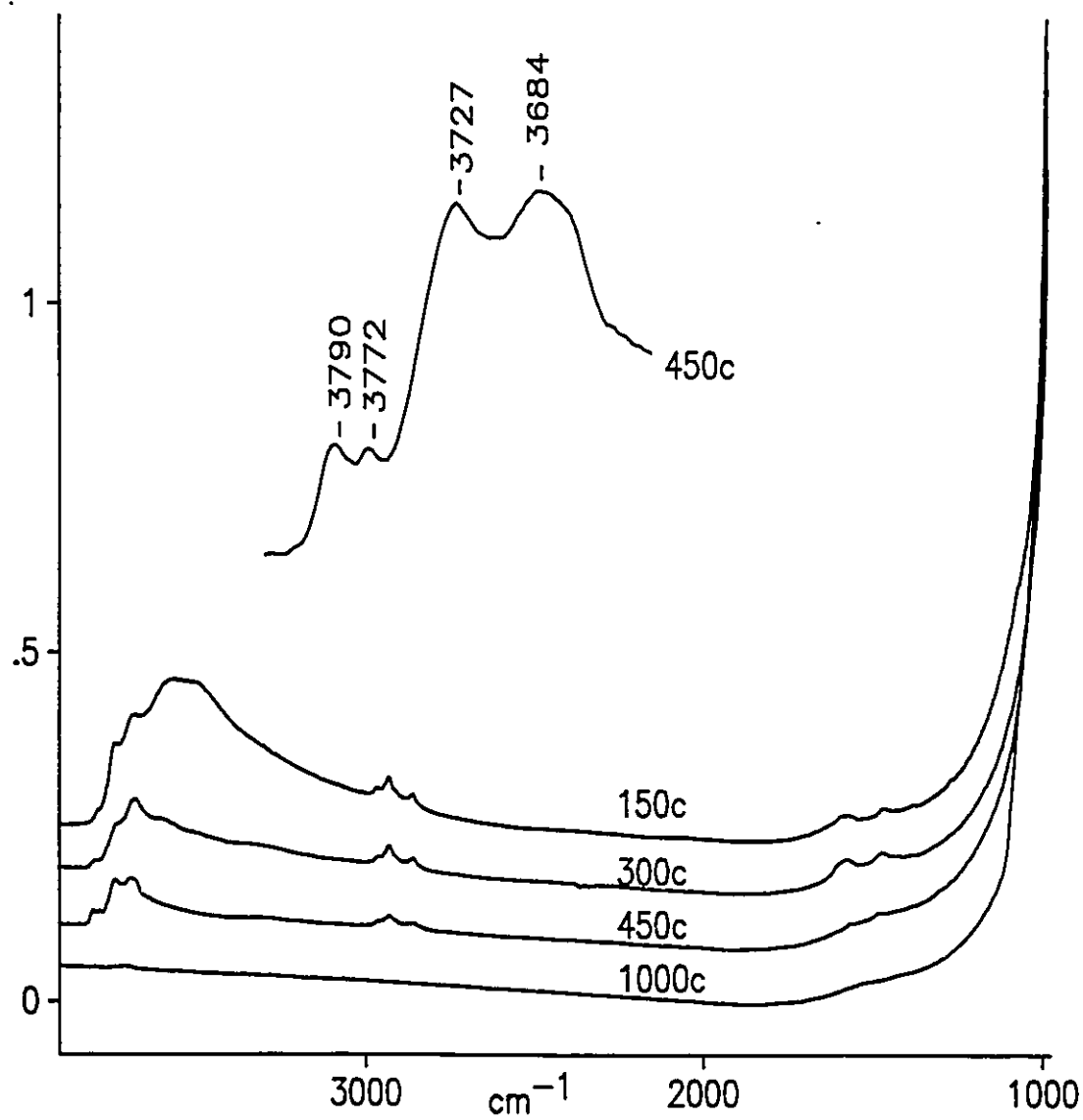
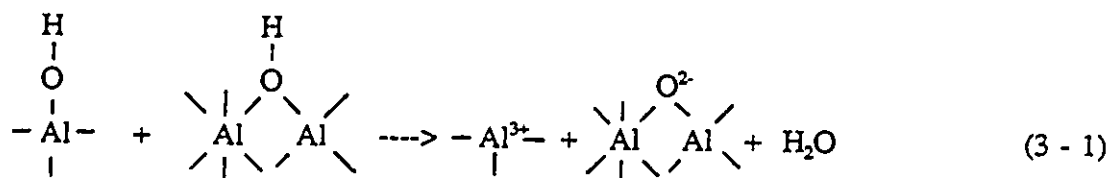


Fig 3.1 Infrared spectra of $\gamma\text{-Al}_2\text{O}_3$ (6 mg/cm²) which had been degassed at different temperatures for 1-2 hours.

Dehydroxylation may occur when samples are heated. When this happens, bare Al^{3+} and O^{2-} sites are created. It appears that the bare Al^{3+} comes more likely from Ia or Ib sites, and O^{2-} sites comes from III, II sites. For example, Ia and IIa sites condense as follows:



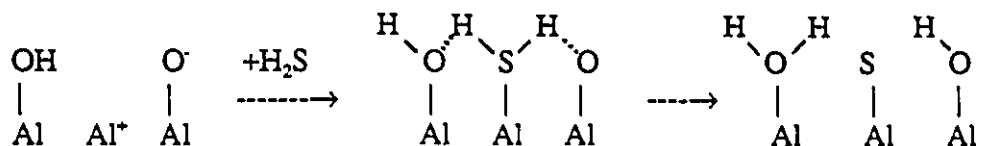
Al^{3+} is a weak Lewis acid site and O^{2-} is a base site. It was suggested that the dehydroxylation of alumina below 400 °C produced weak Lewis acid and basic sites. Heating above 400 °C produced very strong Lewis acid sites by so-called irregular dehydroxylation leading to surface defects [8].

As a catalyst, $\gamma\text{-Al}_2\text{O}_3$ has a high activity only after dehydroxylation above 300 °C, which suggests that the Lewis acid and base sites produced by dehydroxylation are responsible for this. When heated at 700 °C, alumina can have 45% of -OH removed relative to alumina heated at 400 °C [9].

In this thesis, Al_2O_3 was activated under vacuum at different temperatures in order to investigate how the activities varied. For convenience, the alumina catalysts will be denoted as Al(C) where "C" is the activation temperature in degrees Celsius. For example, Al(450) is a $\gamma\text{-Al}_2\text{O}_3$ catalyst which has been activated in vacuum at 450 °C.

(3). Literature review

In a series of studies, Datta and Cavell [10] concluded that H_2S adsorbed on alumina in two different forms, the dissociative form and undissociative form. The former came from the interaction between H_2S and an aluminum ion with an adjacent hydroxyl, as well as an oxide ion. Water was produced:



It yielded a Al-S species and the IR band should be below 1000 cm^{-1} which could not be detected by IR spectroscopy (see Fig 3.1, lower limit of transmission is about 1000 cm^{-1}). The undissociated form involved an aluminum ion and yielded a Al-SH₂ species. This species had a pair S-H bands at 2570 cm^{-1} (SH₂ stretch) and 1334 cm^{-1} (HSH deformation). There were also other bands at 1624 and 1570 cm^{-1} . The band at 1624 cm^{-1} was postulated to be due to the water which came from the above reaction. The band at 1570 cm^{-1} was assigned by others as the species of Al=O [11]. But Lavalley [12] and Carl Tripp [13] showed that this was due to absorbed CO₂ which was present as an impurity in the H₂S. In studying H₂S on Al₂O₃, Kasumov [14] suggested that reaction (3-2) occurs:



In this reaction, Kasumov suggested that the sulfur ions of H₂S exchange with oxygen ions of the γ -Al₂O₃ surface. This dissociative species was active towards SO₂ and the reaction leads to the formation of elementary sulfur.

Although several papers about the adsorption of SO₂ on alumina have been published, the interpretation of the spectra is still quite ambiguous.

Gaseous SO₂ has absorption bands at 1361 cm^{-1} (strong) and 1151 cm^{-1} (medium) due to the antisymmetric and symmetric SO₂ stretching modes respectively. Deo *et al.* [15] observed two bands at 1330 and 1140 cm^{-1} after the adsorption of SO₂ on alumina. The band at 1330 cm^{-1} was assigned to the ν_3 asymmetric stretching vibration, and the 1140 cm^{-1} band to the ν_1 symmetric stretch of weakly adsorbed SO₂. Chang [16] reported two additional bands at 1326 and 1050 cm^{-1} . The band at 1326 cm^{-1} was stable to evacuation at 100°C , and the band at 1050 cm^{-1} was attributed to SO₃²⁻ species which could be removed only after heating up to 800°C . Karge and

Dalla Lana [17] studied the site blocking effect by preadsorbed bases and acids on alumina. They assigned the band at 1050 cm^{-1} to chemisorption of SO_2 on basic cusO^{2-} [cus $\equiv$ coordinatively unsaturated sites], and the bands at 1330 , 1326 , 1150 cm^{-1} were due to SO_2 physically adsorbed on acidic cusAl^{3+} sites (weak adsorption). SO_2 could also be adsorbed on the basic hydroxyl groups. Datta and Cavell [18] showed that there were probably five distinct forms of adsorbed SO_2 on Al_2O_3 . The band at 1050 cm^{-1} was attributed to sulfite like species (SO_3^{2-}) which was strongly chemisorbed on an acidic surface site. The bands at 1255 and 1189 cm^{-1} , which were very weak in intensity, were attributed to two species which resulted from the chemisorption of SO_2 on Al^{3+} acid sites. The pair of bands at 1322 and 1140 cm^{-1} were implicated in the perturbation of the AlOH species absorbing at 3680 cm^{-1} whereas the pair absorbing at 1334 and 1148 cm^{-1} appeared to be associated with a shift of the AlOH absorbing at 3730 cm^{-1} ; therefore, both species were thought to be due to hydrogen-bonded SO_2 . The band at 1050 cm^{-1} increased in intensity with higher activation temperatures above 140°C . In another report [19], Dalla Lana *et al.* used TPD to show that the chemisorbed SO_2 existed in both undissociated and dissociated forms. SO_2 could be dissociated to SO on alumina. That is to say, both H_2S and SO_2 can be chemically dissociated on the surface of alumina.

2. RESULTS AND DISCUSSION

(1). Adsorption of H_2S

We will first consider the changes in the OH stretching vibrational region. On $\text{Al}(450)$, with the first dose of 0.09 Torr (about $90\text{ }\mu\text{mol/g}$) H_2S , the bands from 3750 - 3790 cm^{-1} decrease and among them, the band around 3772 cm^{-1} decreases more quickly. With another dose of H_2S , the decrease in the 3790 cm^{-1} band becomes more evident. The bands around 3750 and 3727 cm^{-1} decrease slower than the bands around 3772 and 3790 cm^{-1} (Fig 3.2 A). The change of the band around 3750 cm^{-1} can be seen in this alumina only by the difference spectra as shown in Fig 3.2 B. [In all spectra the $\text{Al}(450)$ background has been subtracted. Unless otherwise stated, all further spectra are difference spectra after background subtraction.] As the band at 3675 cm^{-1} increases, the broad background from 3650 - 3200 cm^{-1} also increases. A weak band at 3700 cm^{-1} appears as more H_2S is added.

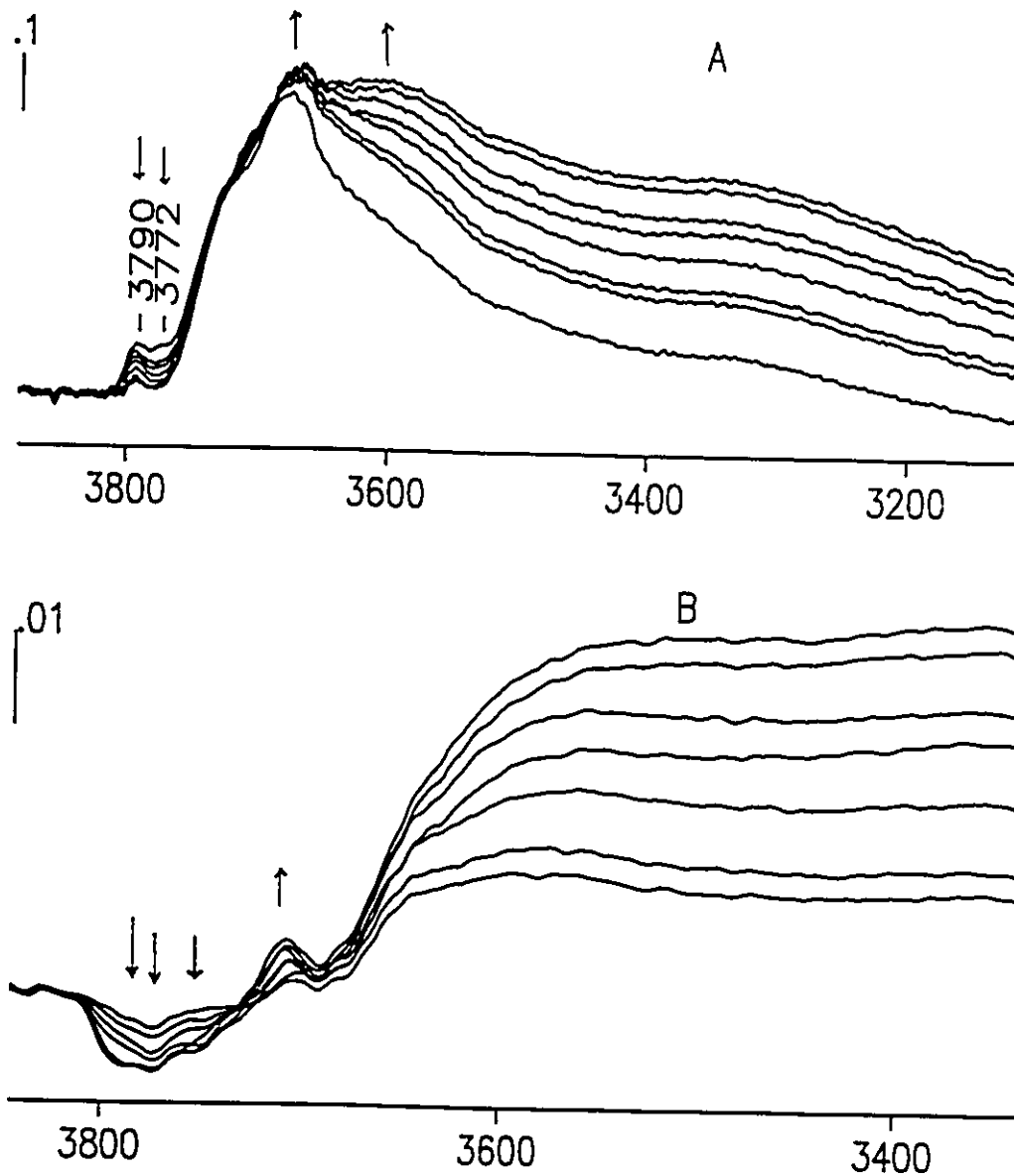
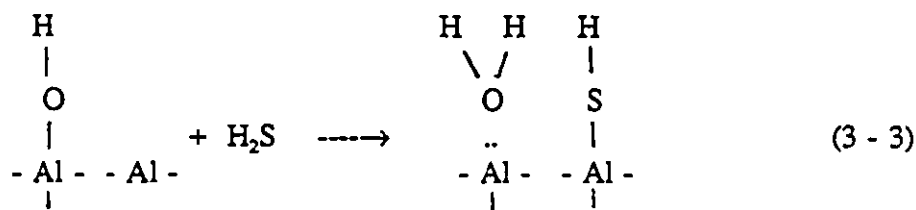


Fig 3. 2 Adsorption of H₂S on Al(450) in OH stretching region
 (A). Addition of H₂S from 0.09 Torr to 3.70 Torr (the lowest one is the alumina background).
 (B). The difference spectra of (A), after subtraction of the alumina background.

The change of the hydroxyl bands indicates that the isolated hydroxyls have different reactivities toward H_2S . The background from 3650 to 3200 cm^{-1} increases, indicating that some hydrogen-bonded hydroxyls are formed and some water is produced (adsorbed water has a band in this region). Even with a large dose of H_2S , the 3790, 3772 cm^{-1} bands are still present, although of low intensity. It appears that there is an isosbestic point at 3650 cm^{-1} . That is to say, there are isolated OH groups above 3650 cm^{-1} and hydrogen-bonded OH groups below 3650 cm^{-1} . The reason why the band around 3772 cm^{-1} is more reactive toward H_2S than the band at 3790 cm^{-1} is still not very clear. Type Ia may be more accessible to H_2S than type II or III hydroxyls.

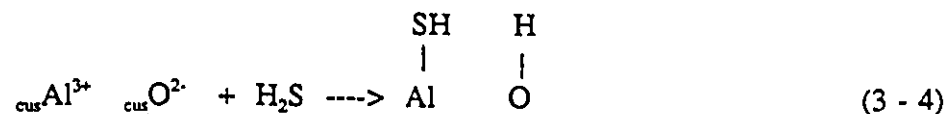
In the region from 2600-1600 cm^{-1} there is a broad band centred at 2570 cm^{-1} whose intensity increases with the quantity of H_2S added (Fig 3.3). This broad band probably has three peaks at 2540, 2567 and 2580 cm^{-1} (Fig 3.3). With more H_2S , the band at 2567 cm^{-1} becomes the dominant one. With evacuation, all bands decrease in intensity but that at 2580 cm^{-1} decreases less and, in this situation, is finally the most intense one. There is also a weak band at 1620 cm^{-1} (bending vibration of water); it is evident that water is formed when H_2S is added.

In accounting for the decrease of the isolated hydroxyl bands at 3790, 3772 and 3750 cm^{-1} and the increase of the band at about 3550 cm^{-1} with the first dose of H_2S , we can suggest that the isolated OH groups react with H_2S as follows:



The water so produced has bands at 3550 and 1620 cm^{-1} and it desorbs following evacuation.

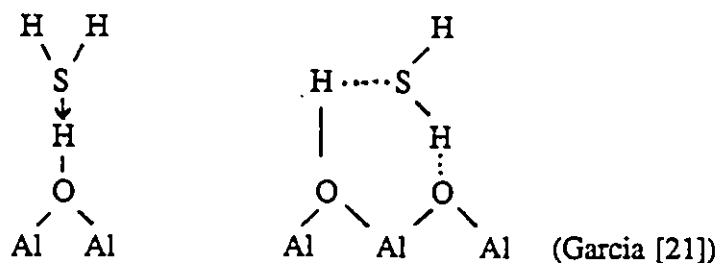
The band at about 3700 cm^{-1} increased in intensity with the addition of H_2S . Lavalley *et al.* [20] suggested that the 3700 cm^{-1} band was due to a new OH species formed from the reaction:



With further H_2S addition, the 3700 cm^{-1} band decreased in intensity while those at 3200 cm^{-1} and at about 2567 cm^{-1} increased in intensity. This might suggest that this OH group (at 3700 cm^{-1}) is involved in the formation of 2567 cm^{-1} species. When evacuated, the band at 3700 cm^{-1} increased in intensity while the band at 3200 cm^{-1} decreased in intensity. We assume that this chemisorption involves strong acidic Al^{3+} sites which are created by the thermal activation.

The 2580 cm^{-1} band which remains after evacuation lies in the spectral region associated with S-H stretching vibrations and is assigned to Al-S-H, which is produced in reactions (3-3) and (3-4). The reaction (3-4) may contribute more to this Al-SH species. This is supported by the evidence that on high temperature activated catalysts, those which contain fewer OH groups, the 2580 cm^{-1} band was more intense (Fig 3.4).

We might also expect some undissociated (physical) adsorption to occur. This may occur on basic sites O^{2-} or through H-bonding with OH groups on surface:



The hydrogen-bonded S-H species should have lower vibrational frequencies than free S-H species, and the 2540 cm^{-1} band is so assigned. The free S-H band of physically adsorbed ($\text{Al:S}\ddot{\text{H}}_2$) might have a vibration at about 2567 cm^{-1} . Any of the isolated OH groups (I, II and III types, as well as the new OH groups adsorbing at 3700 cm^{-1}) might be involved in hydrogen bonding.

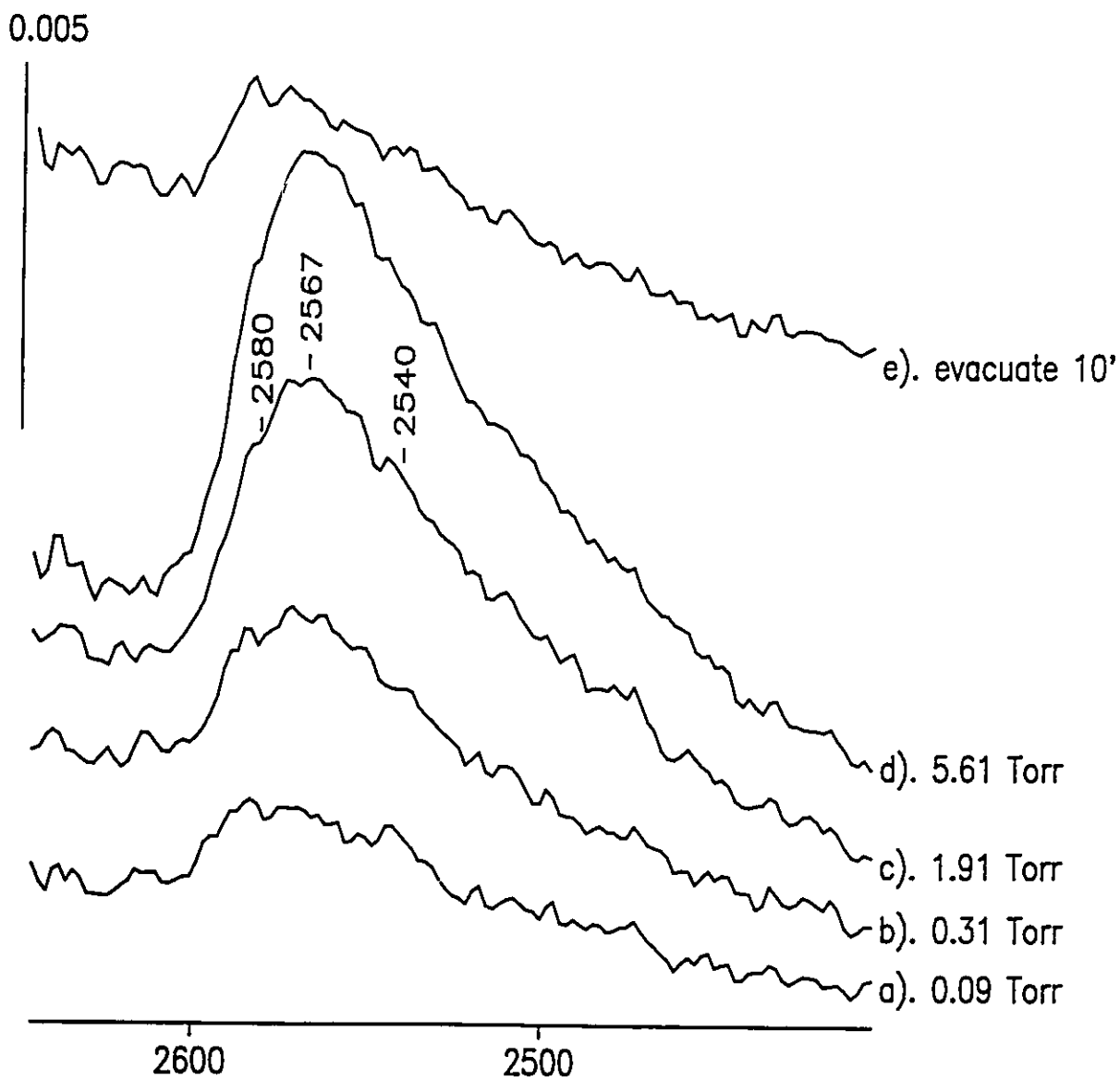


Fig 3. 3 IR spectra of the adsorption of H_2S on Al_2O_3 (30 mg, activated at 450°C).

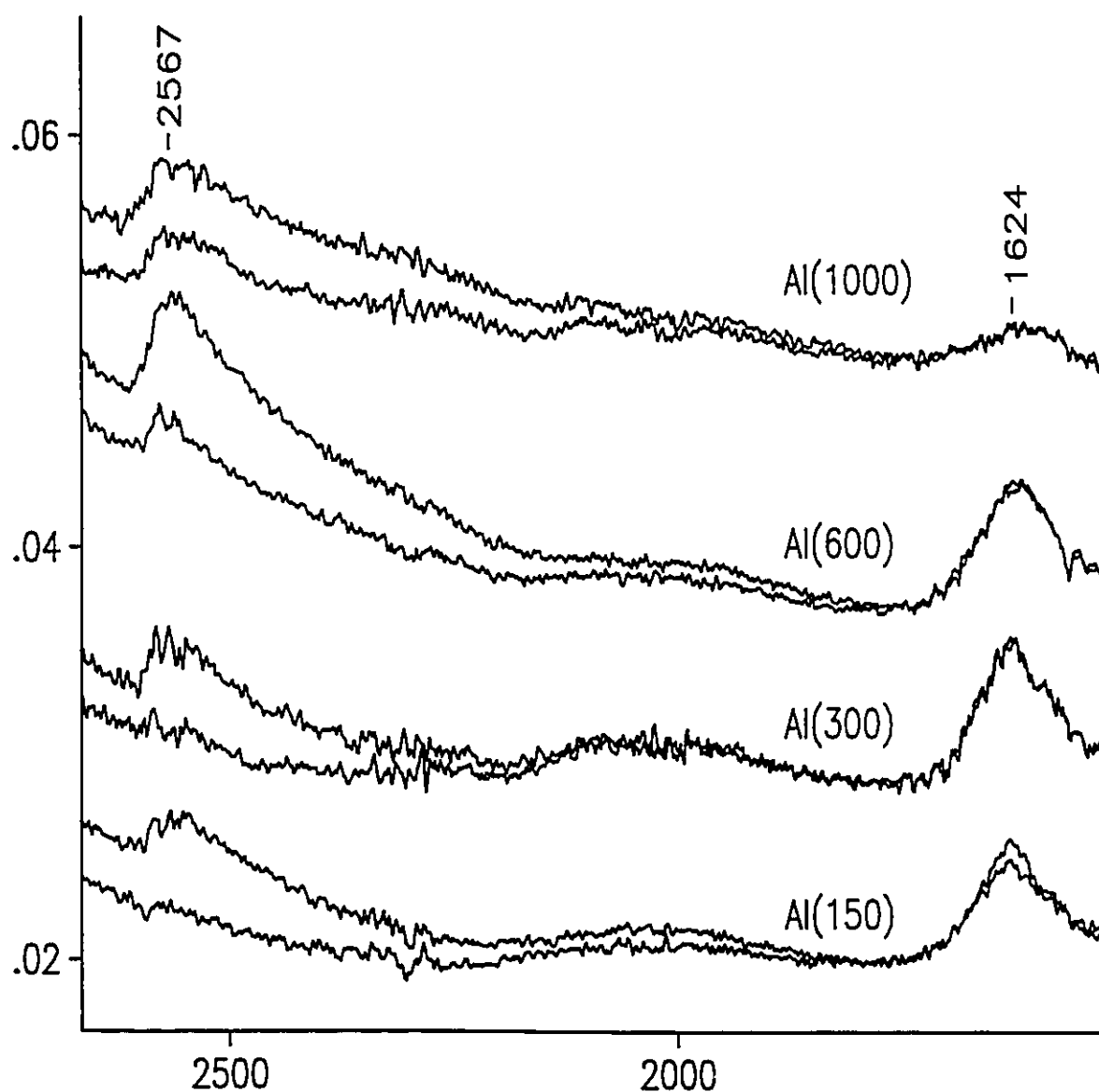
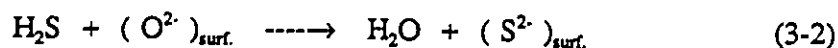


Fig 3. 4 The difference IR spectra of limited H_2S on $\text{Al}(\text{C})$

On each catalyst, $\text{Al}(\text{C})$, there are two spectra. The top one is the alumina on which about 3.20 Torr of H_2S was adsorbed, and the lower one is after evacuation then for 5 minutes.

The band at about 1620 cm⁻¹ is definite evidence of the formation of water. This may occur from the reaction of OH groups with H₂S (reaction 3-3) or via direct reaction with basic oxygen:

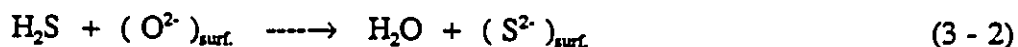
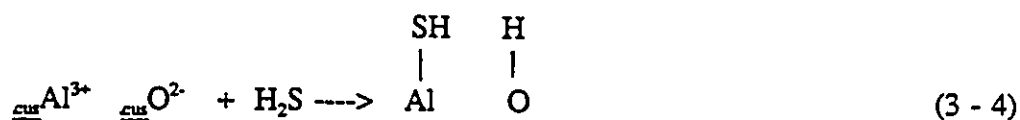
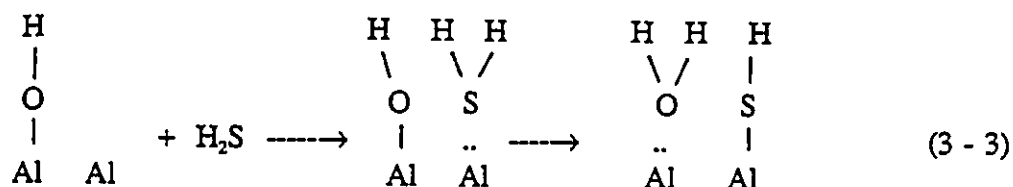


Using different Al(C) catalysts and with the same small amount of H₂S (about 3 Torr), the higher temperature activated catalysts produced more chemisorbed species (Fig 3.4). On Al(150), there was only a weak band at about 2570 cm⁻¹, and after evacuation, no band was left. On the other hand, with Al(1000), the band from 2585 to 2530 cm⁻¹ decreased in intensity only slightly after evacuation. Al(1000) contains no OH groups on the surface, yet water was still produced, probably via reaction (3-2).

When Al₂O₃ is heated above 400 °C, a peak near 1020 cm⁻¹ appears which has been reported by Lavalley *et al.* [22] to be a strained Al-O-Al bridged site which was formed during the process of the dehydroxylation (Fig 3.5). After addition of H₂S, this new peak disappears. It is probably the result of reaction (3-4).

Through the discussion above, we conclude that the adsorption of H₂S on Al₂O₃ gives:

(i). Dissociative adsorption (or chemisorption):



AlS-H has an IR band at about 2580 cm⁻¹.

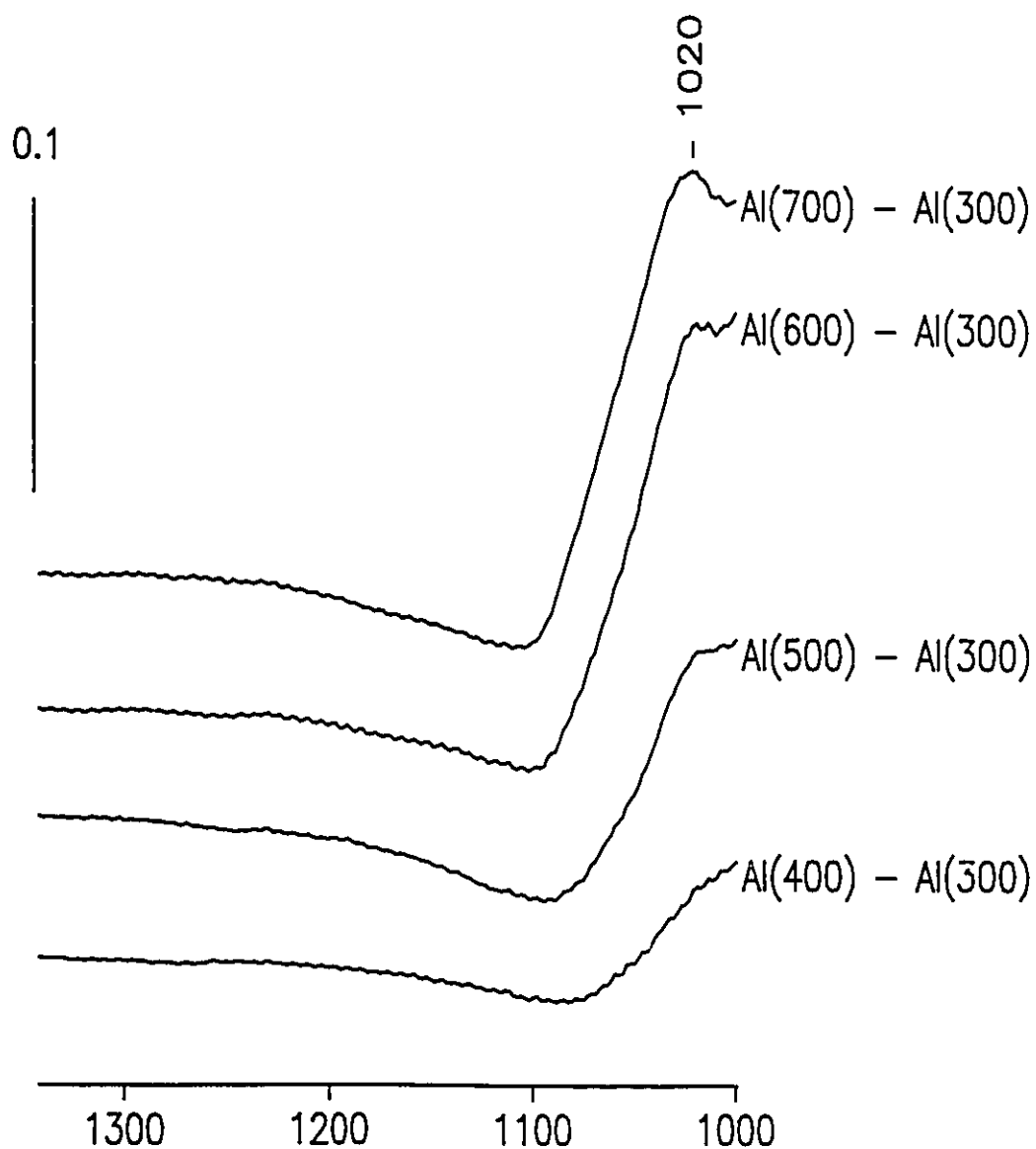
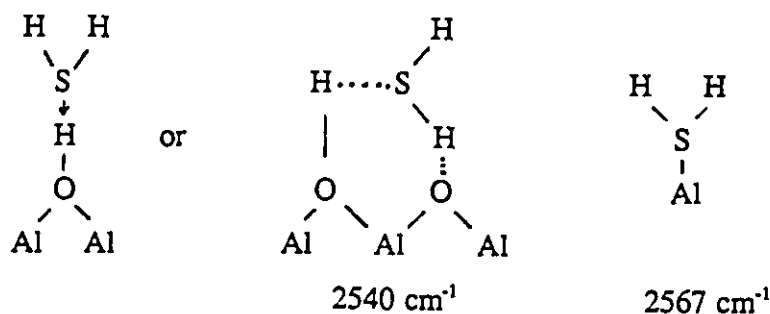


Fig 3. 5 The gradual formation of the band at 1020 cm^{-1} is shown from the difference spectra. The activation temperatures are from $300\text{ }^{\circ}\text{C}$ to $700\text{ }^{\circ}\text{C}$.

(ii). Nondissociative adsorption:



The free S-H bands have their IR vibration at about 2567 cm^{-1} and hydrogen-bonded S-H have a vibration at about 2540 cm^{-1} . According to Marshneva *et al.* [23], there may exist another kind of adsorbed species on oxides. H_2S may adsorb on a $(\text{S}^{2-})_{\text{surf}}$ site, which comes from the complete decomposition of H_2S on the surface of oxides like Bi_2O_3 . However, considering there are very few $(\text{S}^{2-})_{\text{surf}}$ sites available on Al_2O_3 , this adsorption might not be important in this work.

(2). Adsorption of SO_2

In this thesis, most experiments have been done using Al(450). When a small dose of SO_2 (0.08 Torr) was added (Fig 3.6 a), there were two broad bands at 1050 and 1010 cm^{-1} and three very weak bands at 1200 , 1250 and 1325 cm^{-1} . With further doses of SO_2 , new bands at 1147 , 1361 and 1375 cm^{-1} appeared and the 1325 cm^{-1} band shifted to 1330 cm^{-1} . (The 1375 and 1361 cm^{-1} peaks are the R and Q branches respectively of gas phase SO_2). When evacuated, the bands at 1375 , 1361 , 1330 and 1147 cm^{-1} disappeared and all others decreased slightly.

In the hydroxyl-stretching region, after activating at 450°C , as discussed before, the residual hydroxyl bands are at 3790 , 3772 , 3727 and 3684 cm^{-1} (Degussa, Aluminosilicate C, see Fig 3.1). When SO_2 was added, all of the residual hydroxyls decreased in intensity and a weak but broad band between 3600 - 3000 cm^{-1} formed (Fig 3.7 A). In the difference spectra, the positions of the hydroxyl groups were much clearer. After adding about 1.20 Torr of SO_2 , the intensities of the isolated hydroxyl groups did not decrease much further, but the broad band around 3500 cm^{-1} increased very quickly (Fig 3.7 B). Even with very large dose of SO_2 , weak isolated hydroxyl

peaks were still evident.

With H_2S , as discussed before, the peaks at 3790 , 3772 cm^{-1} decreased but that at 3727 cm^{-1} almost did not change and that at 3675 cm^{-1} increased. However, following SO_2 adsorption, all isolated OH peaks decreased in intensity. There is also an isosbestic point at 3650 cm^{-1} .

We will discuss the bands at low wavenumber with reference to specific species.

(a). The bands between $1100\text{-}980\text{ cm}^{-1}$

We have confirmed that a peak near 1020 cm^{-1} appeared after heating alumina over $400\text{ }^\circ\text{C}$ (Fig 3.5). Lavalley [22] suggested that a strained Al-O-Al bridged site formed, which could be destroyed with the addition of H_2O , and also with H_2S . Therefore, when H_2S was added, a "negative" peak showed at about 1020 cm^{-1} . With a small dose of SO_2 , alumina showed a small valley between 1050 and 1010 cm^{-1} (see Fig 3.6). This gives rise to the question whether the two peaks at 1050 and 1010 cm^{-1} are really due to two species, or whether this is one broad band with a negative "valley" in between.

The band around $1020\text{-}990\text{ cm}^{-1}$ can be recognized only by difference spectra. We will show that the bands at 1050 and 1010 cm^{-1} are real. (i). The two peaks at 1050 and about 1010 cm^{-1} were also observed following SO_2 adsorption on $\text{Al}_2\text{O}_3(300)$. However, it is known that the reactive AlOAl site responsible for the negative artefact at 1020 cm^{-1} is not present when Al_2O_3 has only been activated at $300\text{ }^\circ\text{C}$. (ii). With different alumina samples and discs of different weight, these two bands are always present (Degussa alumina or Rhône-Poulenc alumina).

The band at 1050 cm^{-1} has been assigned to a surface sulfite species of unknown structure in all previous studies of the adsorption of SO_2 on Al_2O_3 [17, 24, 25]. Although it is frequently formulated as " SO_3^{2-} ", this is probably not strictly correct as this implies a sulfite species having C_{3v} symmetry, as in ionic sulfites. None the less, in the description below, we will continue to use this formula for convenience where it is to be understood that no particular mode of bonding to the surface is implied. We will show indeed that this species is likely a "sulfite" or SO_3

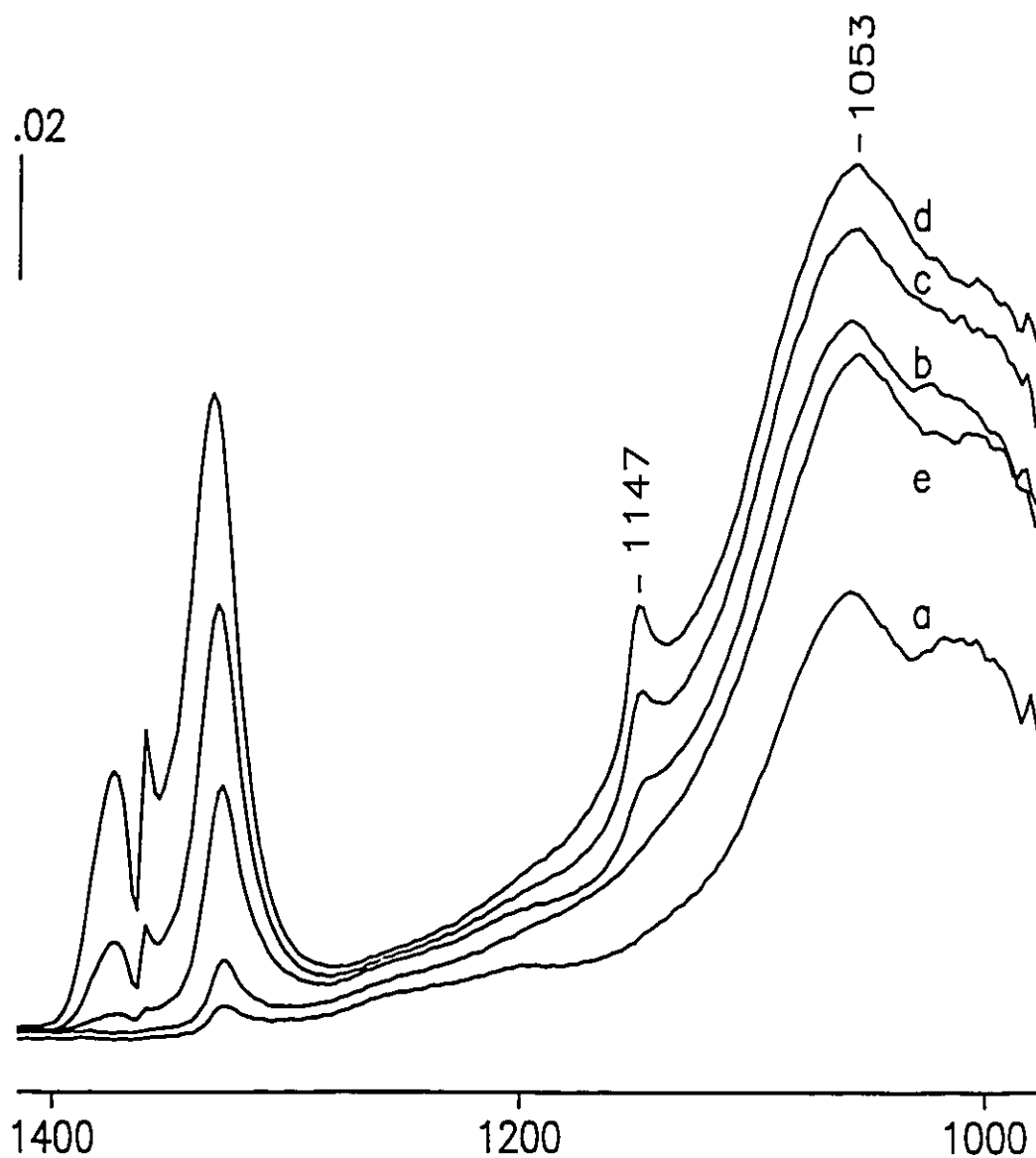


Fig 3. 6 IR spectra of the adsorption of SO₂ on Al(450) (difference spectra)

- (a). add 0.08 Torr (50- μ mol/g) SO₂ and 10'.
- (b). add 0.14 Torr SO₂ and 10'.
- (c). add 0.46 Torr SO₂ and 10'.
- (d). add 1.20 Torr SO₂ and 10'.
- (e). evacuate for 10'.

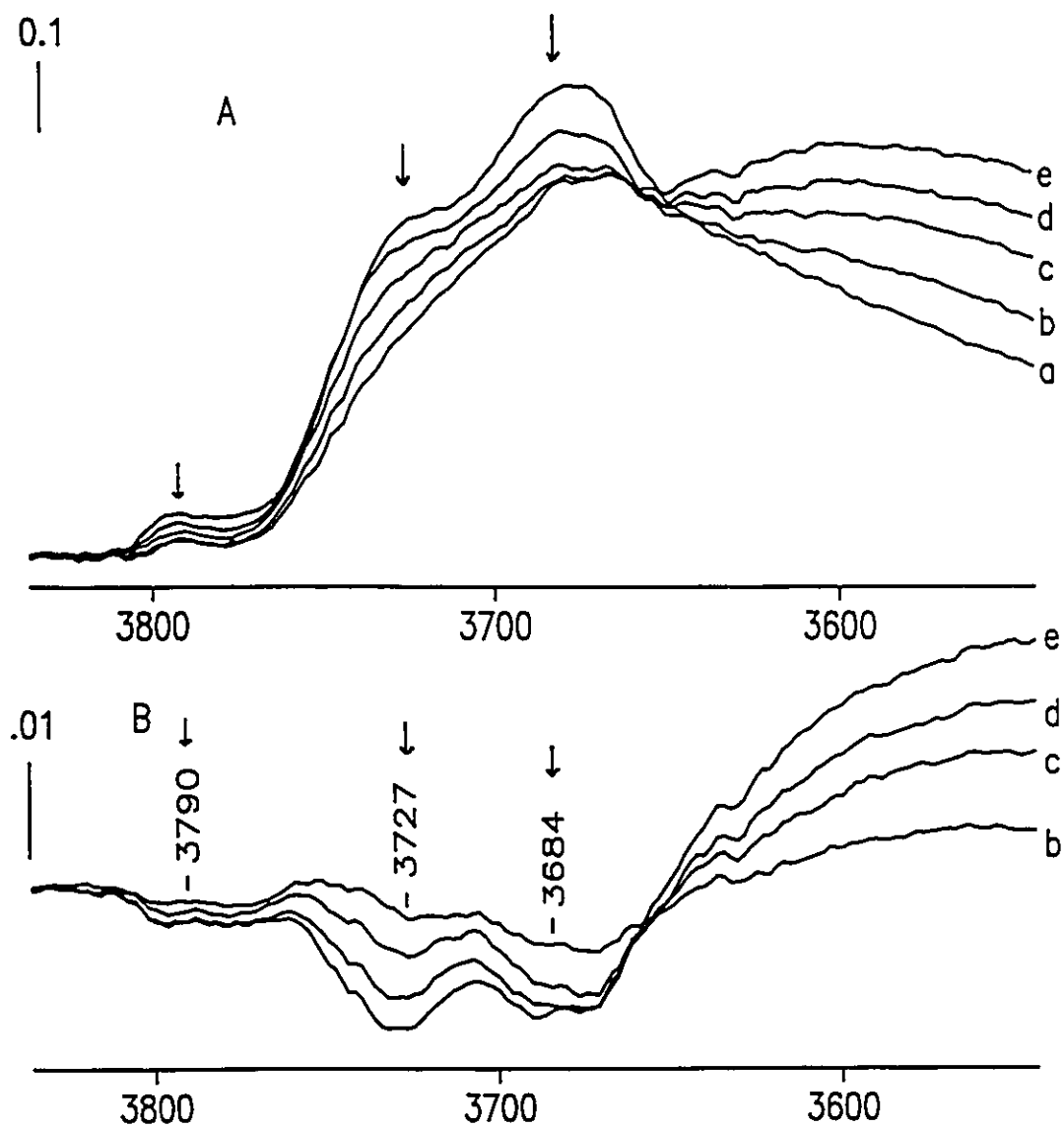


Fig 3.7 IR spectra of adsorption of SO_2 on Al(450) in OH stretching region

- (A). Adsorption spectra (no background subtraction): (a) Al_2O_3 which has been activated at 450 °C; (b) in contact with 0.08 Torr of SO_2 ; (c) in contact with 0.14 Torr of SO_2 ; (d) in contact with 0.46 Torr of SO_2 ; (e) in contact with 1.20 Torr of SO_2 .
- (B). Difference spectra of (A). The background spectrum, Al_2O_3 (a), has been subtracted from the subsequent spectrum.

containing species. On the other hand, the lower wavenumber band at about 1010 cm^{-1} is probably due to a hydrogensulfite like species, HSO_3^- , and we will also use this formulation without necessarily specifying a mode of bonding or even a mode of attachment of H (which could be to an O or S atom).

Gas phase SO_2 has vibrations at 1361 (ν_3), 1151 (ν_2). As a strong acidic reagent, SO_2 can react with basic O^{2-} sites, and SO_3^{2-} can be formed. Free SO_3^{2-} has a C_{3v} symmetry, and has a doubly degenerate vibration ν_3 at 1010 cm^{-1} , and a non-degenerate ν_1 at 960 cm^{-1} . When SO_3^{2-} forms a complex the doubly degenerate vibration will be split. Newman and Powell [24] reported that three bands were at region 1093-1070 cm^{-1} and 1036-1024 cm^{-1} as well as 988 cm^{-1} . On MgO, adsorption of SO_2 gave bands at 1070, 1040, 975 cm^{-1} [25], and on CaO, bands at 1050 and 960 cm^{-1} were reported [16]. When Al_2O_3 has been activated at high temperatures so as to eliminate all OH groups, this (the band near 1060 cm^{-1}) is the only IR band which can be observed in this spectral region. Therefore, the band at 1050 cm^{-1} is assigned to SO_3^{2-} species.

The band at 1010 cm^{-1} could be due to another sulfite species, possibly having a different structure. However, this band was more intense the lower the temperature of activation of the Al_2O_3 , conditions under which the OH concentration is higher. This suggests that this species might be formulated as HSO_3^- . However, true salts of HSO_3^- are rare and most of the common light alkali metal bisulfites are, in reality, salts of the disulfite ion, $\text{S}_2\text{O}_5^{2-}$. That is, attempts to concentrate solutions of HSO_3^- invariably lead to the formation of disulfite via the equilibrium:



We will return to the question of the assignment of this band later.

The band noted above at 1050 cm^{-1} for Al(450) was also observed for different temperatures of activation of the alumina, and the peak maximum was at a higher wavenumber the higher the activation temperature (Fig 3.8). The peak maximum was near 1070 cm^{-1} for Al(600), 1040 cm^{-1} for Al(300) and at 1020 cm^{-1} for Al(150).

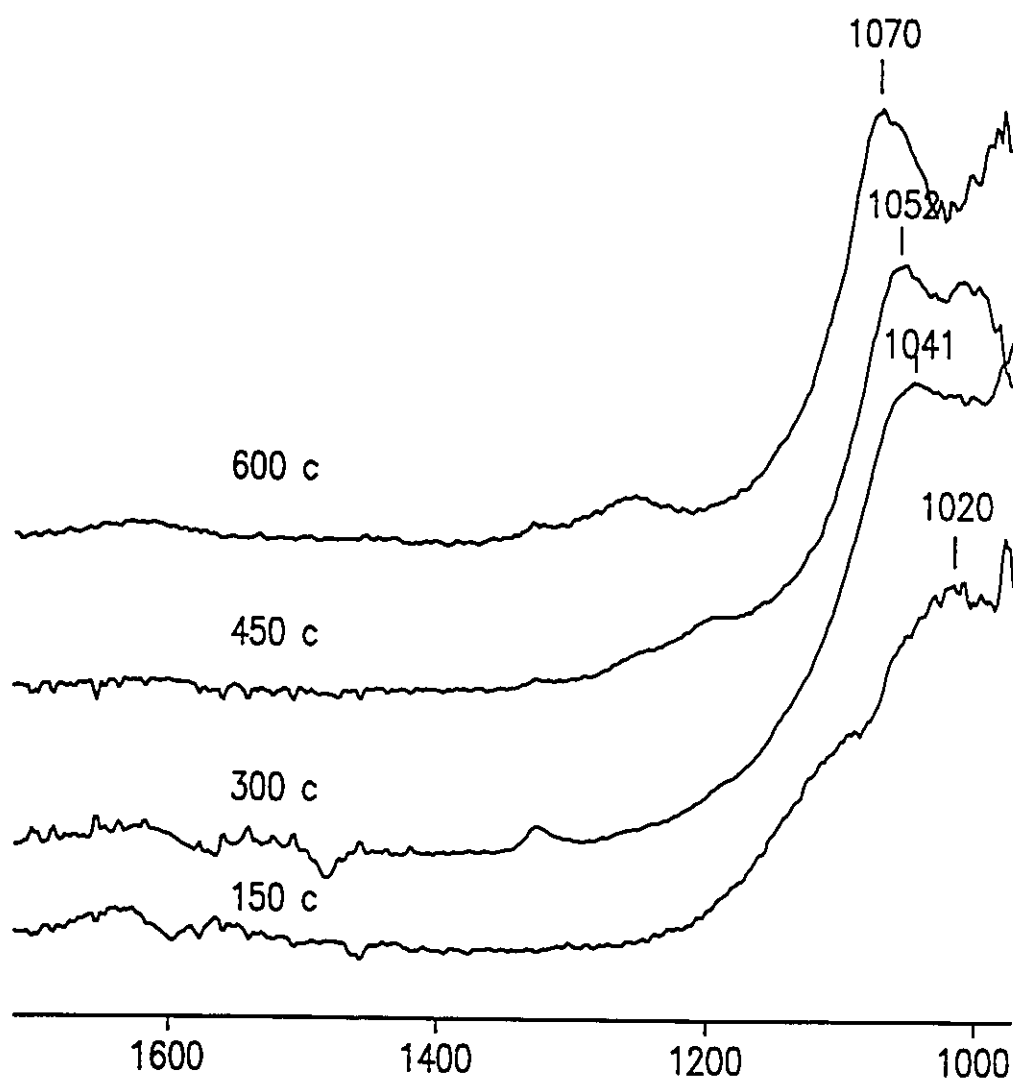


Fig 3.8 IR spectra of adsorption of SO_2 on Al(C)
 On Al(600), the highest band is at 1070 cm^{-1} , while on Al(450), it is at 1052 cm^{-1} , and near 1040 cm^{-1} for Al(300), near 1020 cm^{-1} for Al(150).

(b). The bands at 1330 and 1150 cm^{-1}

These bands are from physisorbed SO_2 since they are very close to the stretching modes of SO_2 in gas phase and they could be removed by brief evacuation at room temperature. Datta *et al.* [18] suggested that they came from the interaction between SO_2 and hydroxyl groups. The $\nu(\text{O-H})$ region changed upon physisorption of SO_2 and the 1330/1150 cm^{-1} bands were more intense on Al(300) than on Al(600), the former having a higher OH content. However, the adsorption of SO_2 on totally dehydroxylated alumina also showed the 1330/1150 cm^{-1} bands. Therefore, these two bands might also be due to weakly physically adsorbed SO_2 on Al^{3+} sites as found by Karge during selective poisoning experiments when adsorption of SO_2 was inhibited as the Lewis acid sites were blocked by adsorbed pyridine [26]. On the other hand, with increased basicity of the alumina (e.g. $\text{Na}/\text{Al}_2\text{O}_3$ and $\text{Cs}/\text{Al}_2\text{O}_3$, see chapter 4), the quantity of physisorbed SO_2 (1330/1150 cm^{-1}) increased. Therefore, one can conclude that, on alumina, these species (1330/1150 cm^{-1}) may involve the sites of Al^{3+} and O^{2-} as well as OH which are weakly basic. The greater contribution of these two bands may come from OH sites because more intense bands are found on lower activated catalysts. A more precise assignment is difficult.

Raman spectra showed bands at 1150 and 1330 cm^{-1} due to weakly adsorbed SO_2 and a very weak broad band near 1060 cm^{-1} (see Fig 3.9). The 1150/1330 cm^{-1} bands were eliminated by evacuation.

(c). The bands at 1200 and 1250 cm^{-1}

The band at 1200 cm^{-1} was always very weak, and we also observed another very weak band at 1250 cm^{-1} , which was more apparent when the alumina had been activated at high temperature [see Fig 3.8 for Al(600)]. It has been attributed by Datta to a species coordinated to Al clusters, $(\text{Al})_n\text{SO}_2$ [18]. We can conclude nothing regarding these species because they are so weak in intensity.

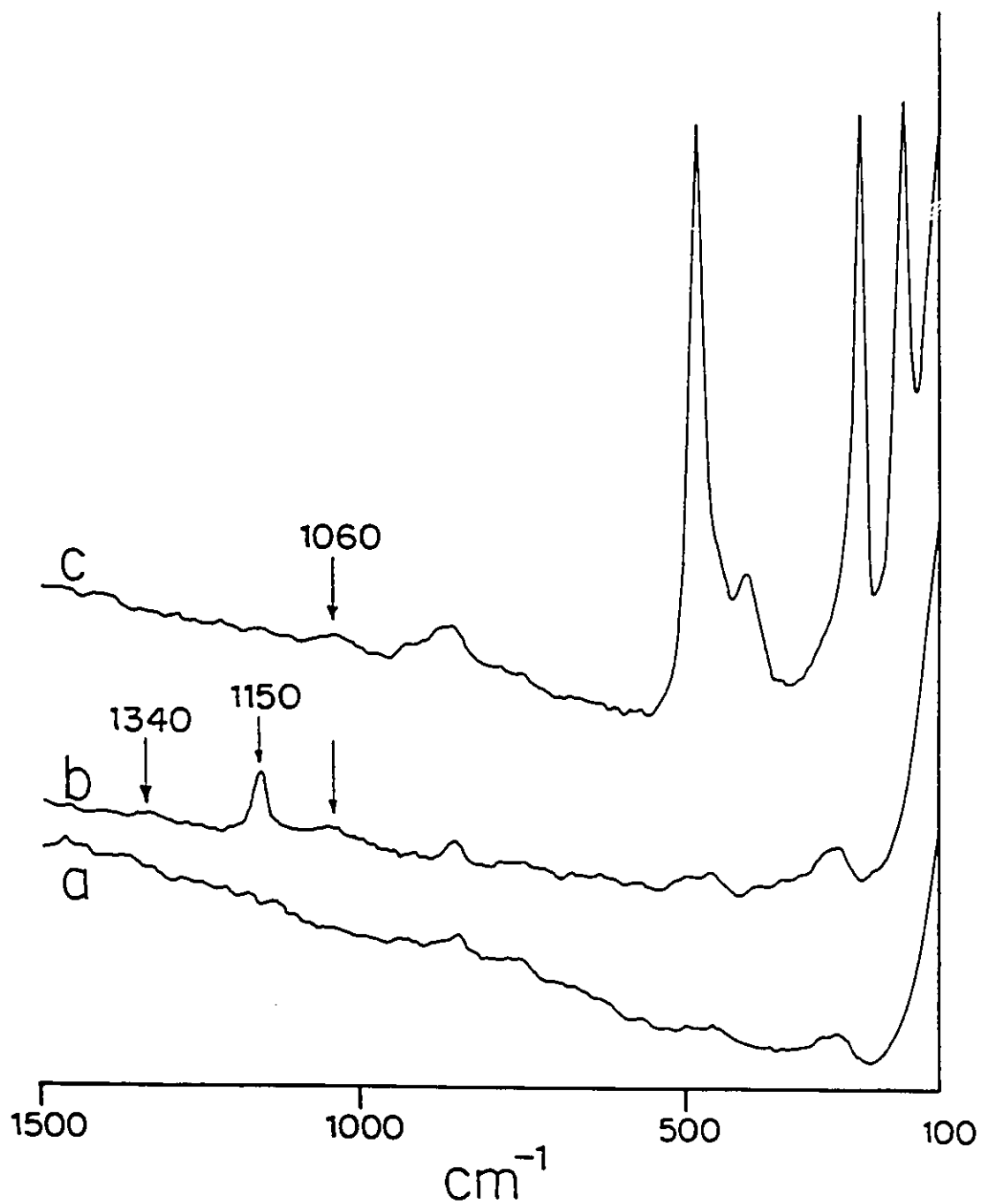


Fig 3.9 Raman spectra

- (a) Background Raman spectrum of Al(500);
- (b) After the addition of 2 Torr of SO_2 ;
- (c) After evacuation for 5', followed by the addition of 1 Torr of H_2S .

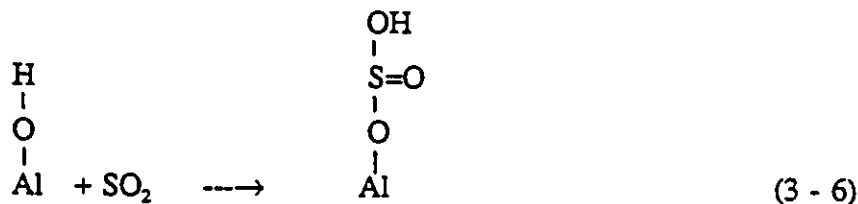
(d). Surface reactions

Fig 3.10 shows the time evolution of the spectral changes following the adsorption of 100 $\mu\text{mol/g}$ of SO_2 on $\text{Al}(300)$. Initially, there are bands at 1325, 1147, 1054 and 1016 cm^{-1} . With increasing time of contact the bands at 1325 and 1147 cm^{-1} decrease while the peaks at 1057 and 1016 cm^{-1} increase. After about 60 minutes, the 1057 and 1017 cm^{-1} bands merge into one peak around 1040 cm^{-1} . It seems that physically absorbed SO_2 (1325 and 1147 cm^{-1}) gradually changes to sulfite or sulfite-like species.

From Fig 3.8, we can see that with the different temperatures of activation the peak maximum at about 1070 cm^{-1} on $\text{Al}(600)$ shifts to 1020 cm^{-1} on $\text{Al}(150)$. Further, there are more surface OH groups on the low temperature activated catalyst. Therefore, we tend to assign band near 1010 cm^{-1} to $\text{S}_2\text{O}_3^{2-}$ or HSO_3^- species.

In aqueous solution, it has been postulated that SO_2 reacts with H_2O to form $\text{H}-\text{S}-\text{O}-\text{O}^\cdot$,
 $\text{O}^\cdot$
 O
 O
hydrogen sulfite, which has a S-H linkage [27]. Another structure, $\text{H}-\text{O}-\text{S}-\text{O}$, does not exist in solution, but the $\text{HOSO}_2^\cdot$ radical is known [28]. Its O-H stretching vibration is at 3540 cm^{-1} , and a band at 1309 cm^{-1} is the SO_2 asymmetric stretching vibration, and a band at 1097 cm^{-1} is the SO_2 symmetric stretching vibration.

We do not observe a $\nu(\text{S-H})$ band but there is a broad $\nu(\text{O-H})$ band. Lavalley *et al.* [29] suggested that a band at 1020 cm^{-1} was due to adsorbed HOSO_2 and not to HSO_3^- :



We have found that the preadsorption of SO_2 on alumina hinders the subsequent adsorption of CO_2 , which indicates that SO_2 and CO_2 adsorb on common sites. Carbon dioxide is acidic and

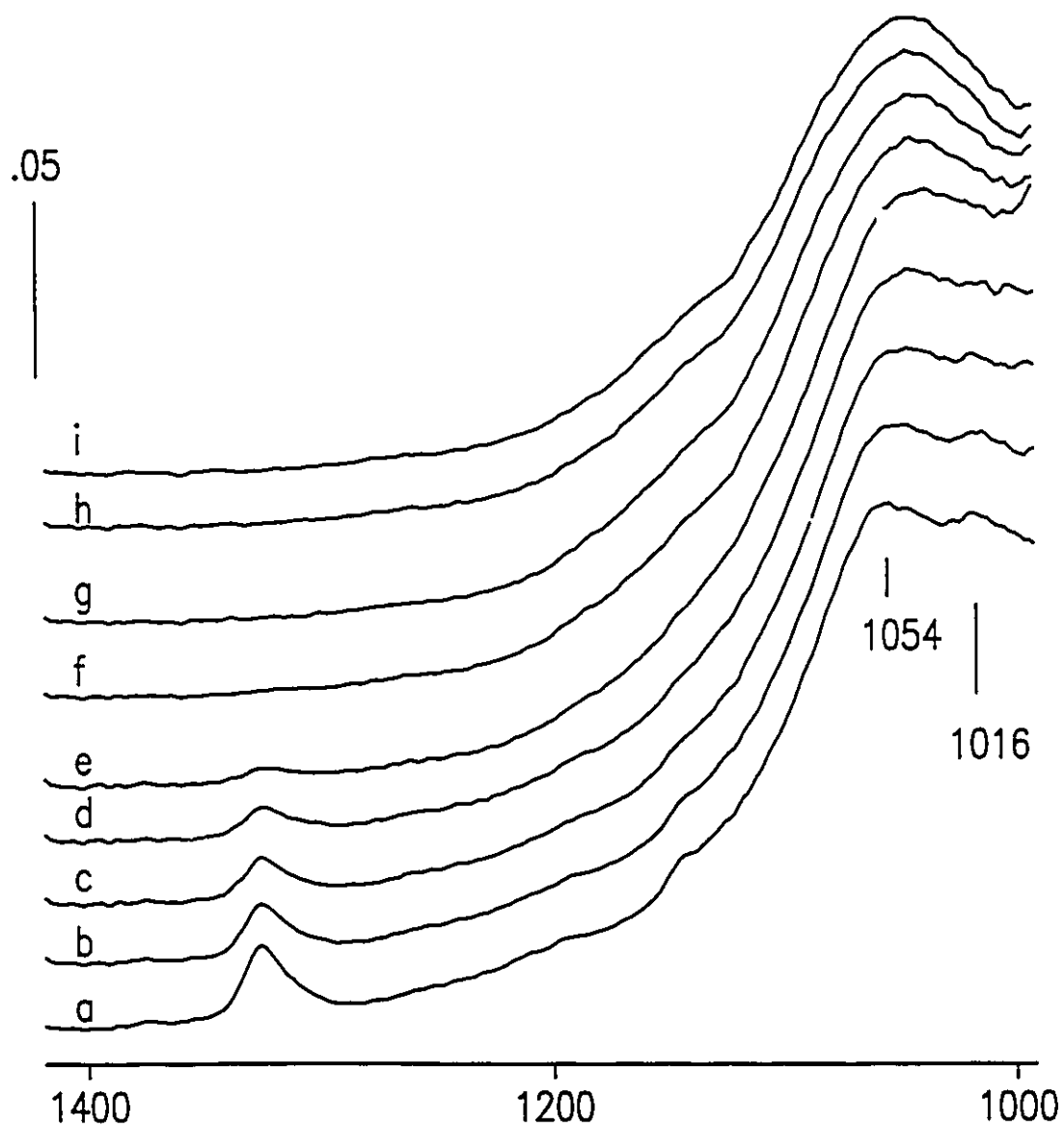
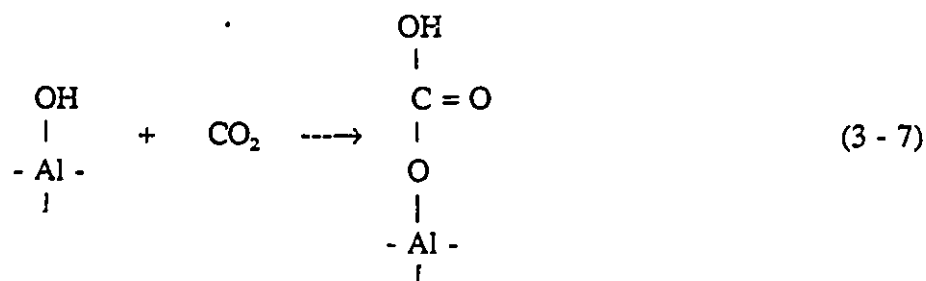


Fig 3.10 Adsorption of SO_2 and H_2S on $\text{Al}(300)$ (difference spectra)

- | | | |
|---|--------------------|--------------------------|
| (a). add 0.20 Torr (about $100 \mu\text{mol/g}$) SO_2 . | (b). after 5 min. | (c). after 15 min. |
| (d). after 30 min. | (e). after 1 hour. | (f). evacuate for 5 min. |
| (g). add 0.20 Torr H_2S (about $100 \mu\text{mol/g}$). | (h). after 10 min. | (i). after 20 min. |

it will be expected to adsorb on basic sites. On basic hydroxyl groups, chemisorbed CO_2 can form a hydrogencarbonate species:



If the alumina has been pretreated by SO_2 , a stronger acid than CO_2 , the hydrogencarbonate species formed by adsorption of CO_2 are not detected. It is believed that, among the different types of OH groups existing after activation, the more basic OH groups attached to one of the coordinatively unsaturated aluminum cations are involved in the formation of hydrogencarbonate. Therefore, we expect that SO_2 will react with AlOH type Ia (3772 cm^{-1}) and AlOH type Ib (3790 cm^{-1}) to form hydrogensulfite. These two kinds of OH groups are more basic than the others. But, definitive vibrational assignments are difficult because of the limit of sample transparency near 1000 cm^{-1} . The main peak near 1050 cm^{-1} has been attributed to the surface sulfites in many reports [17, 24, 25]. As the temperature of activation is lowered, the peak shifts to lower wavenumber, which means that its formation could arise from an interaction with OH groups which are more prevalent on samples activated at lower temperatures. The CO_2 adsorption experiments confirm that these basic hydroxyls give HCO_3^- species. From the evidence above, we attribute the band near 1010 cm^{-1} to the possible formation of a hydrogensulfite species of unknown structure.

To summarize, the adsorption of SO_2 on alumina gives sulfite species which may form on cusO^{2-} sites (band at 1050 cm^{-1}) and hydrogensulfite species (1010 cm^{-1}) which might be produced at surface basic OH groups (probably OH types I and II). There are weakly physisorbed forms of SO_2 (bands at 1330 and 1150 cm^{-1}) which are attributed mainly to OH sites but might also partly arise from adsorption on acid cusAl^{3+} sites and on basic cusO^{2-} sites. Finally, there are two unknown species which have very weak and broad bands near 1250 and 1200 cm^{-1} .

(3). The static reaction between SO₂ and H₂S.

(a) Adsorption of SO₂ then H₂S:

Fig 3.11A shows a typical spectrum following adsorption and evacuation of SO₂ on Al(450). When H₂S was added, the 1325 cm⁻¹ band disappeared and a band at 1620 cm⁻¹ (H₂O) appeared (Fig 3.11B). When more H₂S was added, the band at 1620 cm⁻¹ further increased (spectrum not shown). This suggests that the Claus reaction is taking place. In Raman studies, the bands near 1330 and 1150 cm⁻¹ due to physically adsorbed SO₂ disappeared following evacuation at room temperature. When H₂S was added, intense Raman bands at 151, 220 and 480 cm⁻¹ characteristic of S₈ [30] were observed (Fig 3.9).

An AlSH band at 2570 cm⁻¹ was never observed in IR or Raman spectra when any quantity of H₂S was added to preadsorbed SO₂. It is apparent that the Al³⁺ sites which would normally be adsorption centres for H₂S were occupied by SO₂, sulfur or H₂O.

In IR spectra, the bands at about 1000 and 1050 cm⁻¹ decreased with time following addition of H₂S, the 1000 cm⁻¹ band at a faster rate (Fig 3.11). At this stage, adding CO₂ produced a small quantity of hydrogen-carbonate species (bands at 1650, 1445 and 1230 cm⁻¹), which indicated that some sites previously occupied by SO₂ species were available for CO₂ adsorption (Fig 3.11 E,F).

(b). Adsorption of H₂S, then SO₂:

On Al(450), addition of H₂S gave rise to the weak peak at 3700 cm⁻¹ (AlO-H), and broad bands around 2570 cm⁻¹ (AlS-H). After evacuation, there was only a very weak band near 2580 cm⁻¹. Upon adding SO₂, the 2580 cm⁻¹ band disappeared immediately, and a very weak band appeared at 1620 cm⁻¹ due to H₂O (much weaker than that which was previously observed when H₂S was added to preadsorbed SO₂), along with bands at 1050 cm⁻¹ (SO₃²⁻) and at about 1000 cm⁻¹. If more SO₂ was added, bands at 1330 and 1150 cm⁻¹ appeared, and the overall spectrum was virtually identical to that which was observed previously for adsorbed SO₂ alone on Al(450).

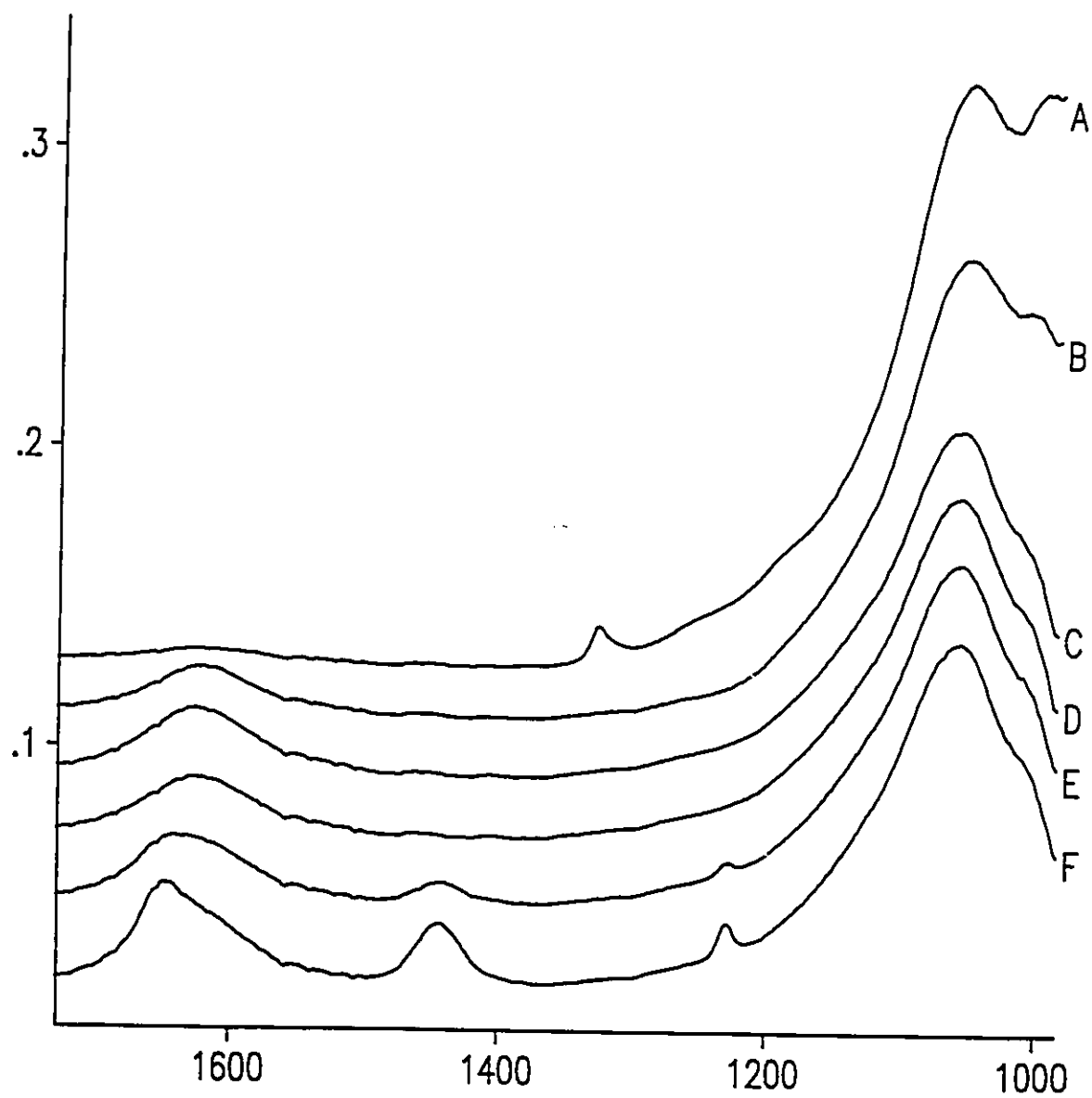


Fig 3. 11 Adsorption of SO_2 , then H_2S (difference spectra)
 (A). add 2.20 Torr SO_2 to Al(450) and after 15', then evacuate for 5'.
 (B). add H_2S 2.33 Torr.
 (C). after 15'.
 (D). evacuate for 5'.
 (E). add CO_2 3.34 Torr.
 (F). after 15'.

In Raman spectroscopic experiments, when SO₂ was added to preadsorbed H₂S on Al(500), no Raman bands due to S₈ were detected and the spectrum resembled that which was previously observed when SO₂ alone was added to Al₂O₃. However, when the SO₂ was evacuated and more H₂S added, S₈ bands at 151, 220 and 480 cm⁻¹ were clearly detected.

(c) Summary:

With respect to the mechanism of the Claus reaction on Al₂O₃, Karge *et al.* [17] suggested that the process involved adsorbed SO₂ and gaseous H₂S. However, Datta and Cavell [31] suggested that the reaction could equally take place between adsorbed H₂S and SO₂ gas. Kasumov [14] reported that SO₂ gas also reacted with surface S²⁻ species which formed from the dissociative adsorption of H₂S.

In the present study, no sulfur was produced when SO₂ was added to preadsorbed H₂S. The Raman results have clearly shown that the generation of sulfur requires the presence of chemisorbed SO₂ insofar as S₈ was only detected if H₂S was added to preadsorbed SO₂, and not if SO₂ was added to preadsorbed H₂S. Therefore, we conclude that Al-S, as suggested by Kasumov [14], does not contribute significantly to the Claus reaction under these circumstances. On the other hand, the SH band from preadsorbed H₂S did disappear when SO₂ was added. However, SO₂ is a stronger acid than H₂S and one might expect SO₂ to displace adsorbed H₂S. When H₂S was readded, S₈ was generated, and the infrared spectrum was virtually identical to that which was observed when only SO₂ was added to Al₂O₃. Therefore, we conclude that the Claus process does not occur to a significant extent via a reaction between pre-adsorbed H₂S and gaseous SO₂ but, rather, the reaction mainly involves a reaction of chemisorbed SO₂ with gaseous H₂S.

(4). *Adsorption of a mixture of H₂S and SO₂.*

The stoichiometry of the Claus reaction between H₂S and SO₂ is 2:1 (2H₂S + SO₂ ⇌ 2H₂O + $\frac{3}{8}$ S₈). However, most previous spectroscopic studies have only examined the reaction of either H₂S or SO₂ alone, or one gas after the other. Only Datta reported an infrared

spectroscopic study of a 2:1 H₂S/SO₂ mixture on alumina but the gases were added separately and with a low coverage [31]. In their report, when SO₂ was added followed by H₂S to give a mixture on alumina, only the 1060 cm⁻¹ band was found. Because the real reaction is under the stoichiometry of 2:1, we have reinvestigated the reaction under these conditions.

The gases were mixed with the desired proportion just before addition to the cell. The basic result, for a 2:1 mixture, is shown in Fig 3.12 A-F. There was the appearance of a very sharp peak at 1028 cm⁻¹, two broader ones at 1230 and 1186 cm⁻¹, and a band at 1627 cm⁻¹ due to the deformation mode of H₂O, all of which grew in intensity with increasing contact time. On the other hand, the spectrum of gas phase and physically adsorbed SO₂ near 1330 cm⁻¹ decreased in intensity with time. Accompanying these spectral changes, the disc progressively became yellow.

Evacuation produced the spectra shown in the Fig 3.12 G-J; although most bands in this region decreased slightly in intensity, the band at 1186 cm⁻¹ immediately shifted to 1175 cm⁻¹ whereas that at 1230 cm⁻¹ appeared to shift to 1285 cm⁻¹ and intensified. That is, the 1230/1186 cm⁻¹ bands apparently shifted to 1285/1175 cm⁻¹ upon evacuation. The readdition of water completely regenerated the original spectrum which was formed before evacuation (see Fig 3.12 K).

The γ -Al₂O₃, used for this investigation has a surface area 105 m²/g. It was necessary to have at least an initial pressure of 1.7 to 1.8 Torr of the 2:1 mixture in the 300 ml volume cell in order to observe the above spectra. The mass of the disc was about 30 mg. This is important relative to the number of surface sites which absorb SO₂. For less than 1.7 Torr we only observed the normal spectrum of adsorbed SO₂, and all gas phase bands disappeared. For greater pressures, we could easily observe the decrease in the intensity of gas phase SO₂ as the reaction proceeded. This may be a partial explanation of why other studies have not reported this result.

The same bands were also observed if slightly different ratios of H₂S/SO₂ were used. We only used ratios from 1.5 to 3, but as long as there was excess gas phase SO₂, the same infrared spectrum was observed. For example, using a pressure of about 2.8 Torr and a 3:1 mixture, no

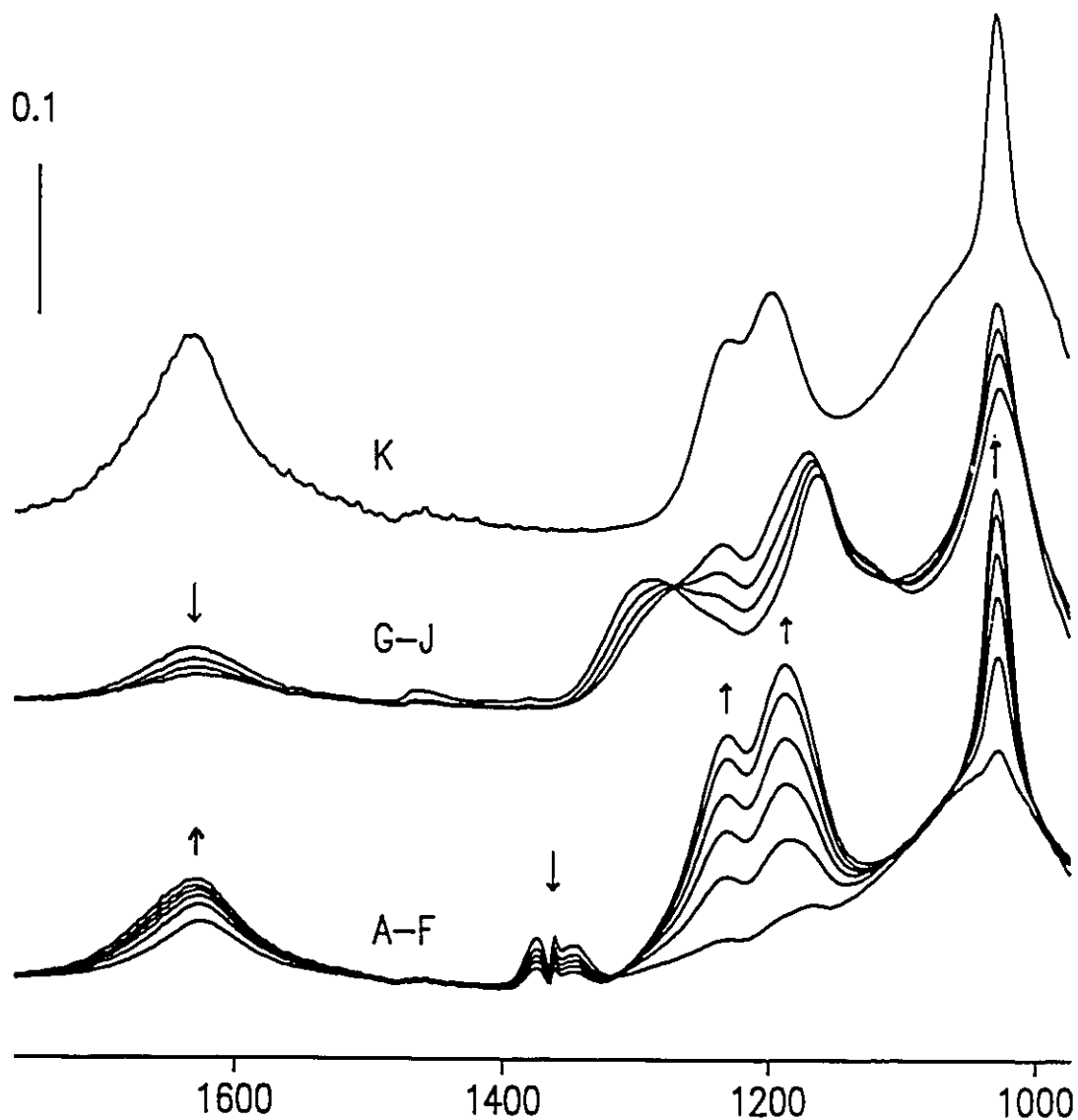


Fig 3.12 The adsorption of a mixture ($\text{H}_2\text{S}/\text{SO}_2=2/1$) on Al(450)

A-F. The spectra show the adsorption of a mixture (4.8 Torr) on ZrO_2 , the contact time being from 5 minutes to 1.5 hour.

G-J. Subsequently evacuate for 5 minutes to 18 hours.

K. Re-add water vapor to (J).

gas phase SO_2 was detected and the spectrum resembled that which was observed for SO_2 alone adsorbed on Al_2O_3 .

Using D_2S in place of H_2S , there was no shift of the 1028 cm^{-1} band. The 1230 cm^{-1} band appeared at the same frequency, but the 1186 cm^{-1} band was now strongly overlapped by the D_2O deformation mode.

The addition of water before the introduction of the mixture gave the same results except that the peaks in this region increased more rapidly, which suggests that the adsorption of water facilitates the reaction. It is evident that water plays an important role in the formation of the species responsible for these bands.

A similar infrared spectrum was observed following the adsorption of the 2:1 mixture on zirconia, ZrO_2 . However, ZrO_2 is more transparent than Al_2O_3 to lower wavenumber, the limit of transmission being about 900 cm^{-1} . Fig 3.13A shows a spectrum of SO_2 alone adsorbed on $\text{ZrO}_2(450)$; this is dominated by a very broad band between about 1050 and 900 cm^{-1} with a single sharper peak at 927 cm^{-1} . The spectrum did not change with time. Figure 3.13B-G shows the spectral features observed following admission of a 2:1 mixture to $\text{ZrO}_2(450)$. There was the growth of a sharp band at 1028 cm^{-1} and of water at 1612 cm^{-1} and a decrease in the intensity of the bands due to SO_2 near 1330 cm^{-1} . This is qualitatively similar to that which was observed using Al_2O_3 . However, although bands near 1200 cm^{-1} also appeared on ZrO_2 , their frequencies were different, being at $1257/1157\text{ cm}^{-1}$. Evacuation did not alter the spectrum.

The addition of water produced a significant spectral change, as shown in Fig 3.13H. There was an intensification of the 1028 cm^{-1} band, and the pair near 1200 cm^{-1} shifted to $1234/1184\text{ cm}^{-1}$, almost identical to that observed under these conditions for Al_2O_3 . Finally, evacuation resulted in a broadening of the 1028 cm^{-1} band (Fig 3.13I) and the 1200 cm^{-1} pair shifted back to $1257/1157\text{ cm}^{-1}$.

With both oxides, we measured the shifts of the peaks for partial or complete replacement

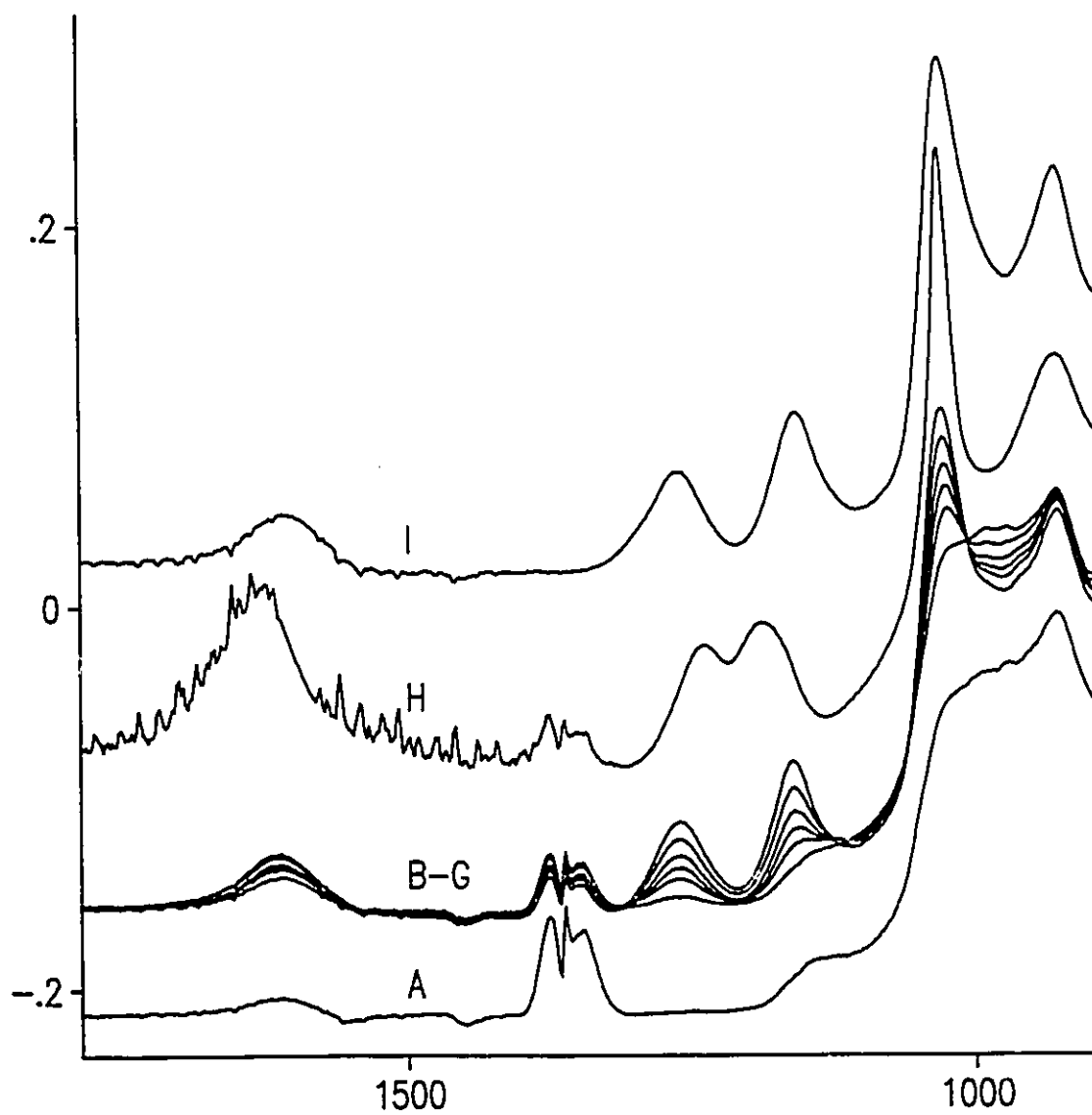
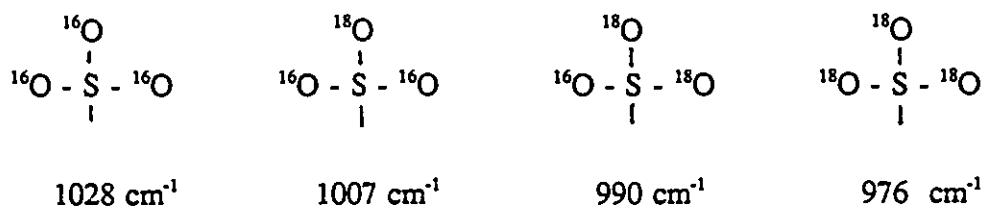


Fig 3.13 The Adsorption of SO_2 , mixture ($\text{H}_2\text{S}/\text{SO}_2$) and H_2O on $\text{ZrO}_2(450)$

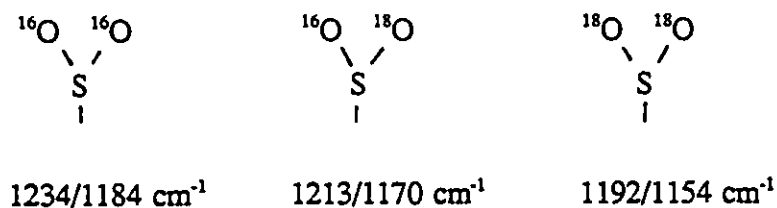
- A. SO_2 alone adsorbed on ZrO_2 .
- B-G. A 2:1 mixture adsorbed on ZrO_2 .
- H. H_2O vapor (8 Torr) adsorbed on (G).
- I. evacuate (H) for 5 minutes.

of oxygen-16 by oxygen-18. This was accomplished by using $S^{18}O_2$ in place of $S^{16}O_2$ in a 2:1 mixture and following its adsorption on an unexchanged or on an oxygen-18 exchanged Al_2O_3 . The progressive shift of the bands for replacement of oxygen-16 by oxygen-18 could also be followed for Al_2O_3 or ZrO_2 if 99% $H_2^{18}O$ was added after the normal bands due to the adsorption of the mixture were developed. A sequence of spectra developed by the latter method on ZrO_2 for a nearly 100% ^{16}O , about 50% each of $^{16}O/^{18}O$ and about 90% ^{18}O are shown in Fig 3.14.

For either Al_2O_3 or ZrO_2 , the most noticeable effect of oxygen-18 exchange was the appearance of a total of four bands for the sharp 1028 cm^{-1} band for partial exchange. The dominant band for 90% ^{18}O substitution was at 976 cm^{-1} , whereas for about 50% exchange the frequencies were at $1028, 1007, 990$ and 976 cm^{-1} . For 50% exchange, the relative intensities were approximately in the ratio of 1:3:3:1. This is clear evidence that an SO_3 unit is the functional group responsible for the generation of the 1028 cm^{-1} band, the four species for partial or complete exchange being as follows:



The shifts of the $1234/1184\text{ cm}^{-1}$ pair of bands is ambiguous because of the greater breadth of the bands. The general pattern is also shown in Fig 3.14 and it appears that although both bands shift by about 40 cm^{-1} to low wavenumber for complete substitution of ^{16}O by ^{18}O [$1234/1184$ shifting to $1193/1154\text{ cm}^{-1}$], for intermediate substitution it appears that the bands are at about $1213/1170\text{ cm}^{-1}$. This could suggest that these bands arise from the antisymmetric and symmetric stretching modes of an SO_2 unit as follows:



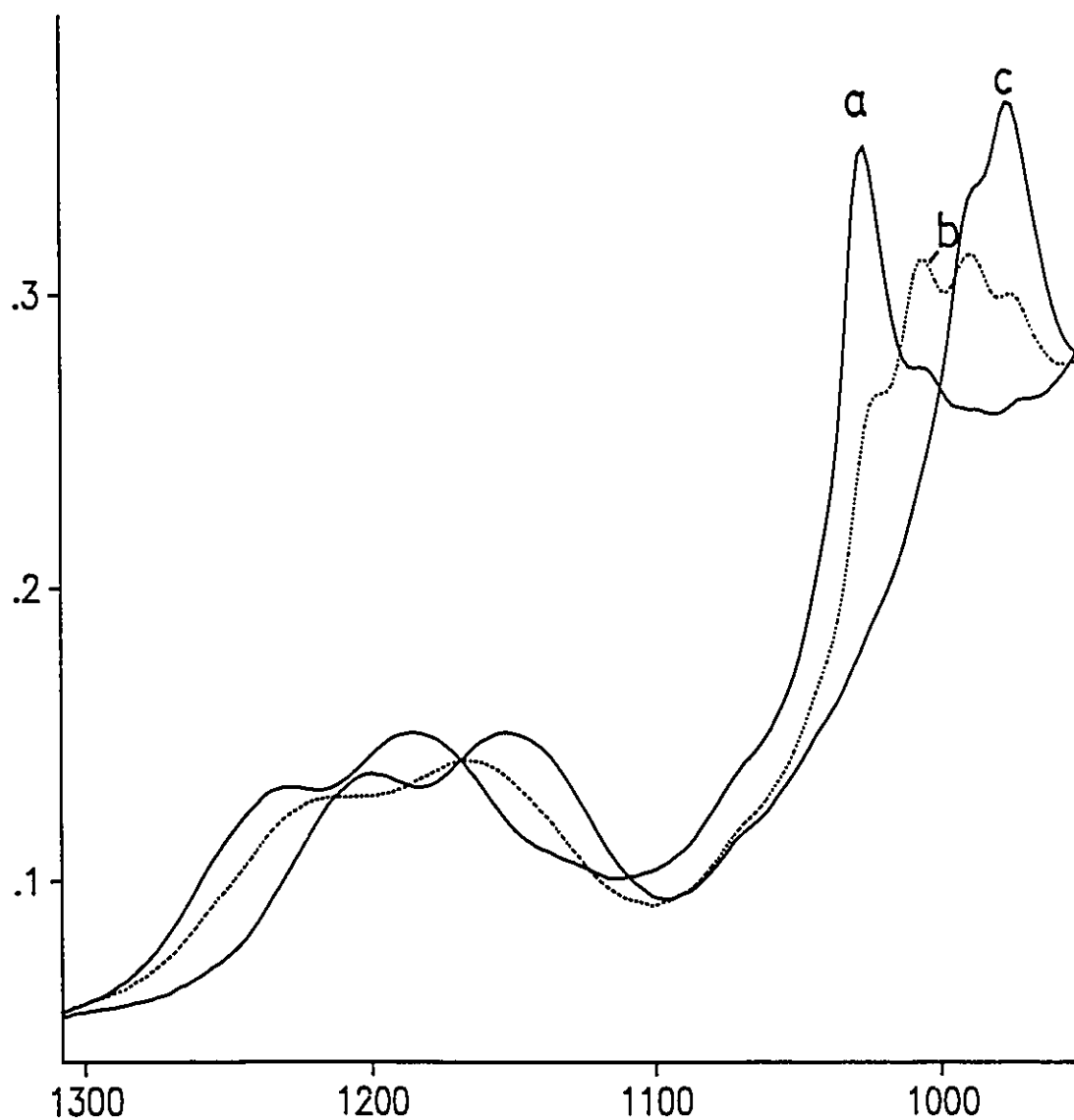


Fig 3.14 The adsorption of a mixture ($\text{H}_2\text{S}/\text{SO}_2=2$) on $\text{ZrO}_2(450)$
 The bands in $900\text{--}1300\text{ cm}^{-1}$ spectral region shift with ^{18}O substitution. (a) nearly 100% ^{16}O ; (b) about 50% $^{16}\text{O}/^{18}\text{O}$; (c) about 90% ^{18}O .

We have noted the similarities and differences between the IR spectra of the mixture adsorbed on alumina and on zirconia, that is, a strong band at 1028 cm^{-1} which was not sensitive to the presence of water, and a pair of bands near 1200 cm^{-1} which were sensitive to water. These spectral features were also observed for the adsorption of the mixture on other oxides. The frequencies in the presence of water are as follows: Ga_2O_3 1028, 1232/1190 cm^{-1} , TiO_2 1028, 1234/1188 cm^{-1} , MgO 1028, 1242/1196 cm^{-1} . The spectral changes for Ga_2O_3 were virtually identical to those observed for alumina, whereas those for TiO_2 , were similar to ZrO_2 , the '1200 pair' after evacuation being at 1253 and 1168 cm^{-1} .

It is apparent that the frequencies of the observed bands, and particularly that at 1028 cm^{-1} , are largely unaffected by the nature of the surface, even a strongly basic one such as MgO . On the other hand, the surface does play a role, because no IR bands were observed when the mixture was adsorbed on silica, an oxide which is inert in the Claus reaction (see Chapter 5). For the other oxides, the bands developed slowly, in parallel with the IR band due to water; therefore, it is evident that water is important, and water is an initial product of the Claus reaction.

One of the yet unsolved problems of sulfur chemistry is the composition of aqueous solutions of H_2S and SO_2 , the so-called Wackenroder's solution. This solution, which gradually turns milky upon standing because of the formation of colloidal sulfur, defies chemical analysis and complete understanding. What is known is that an extremely complex mixture of polythionates are formed, $\text{S}_n\text{O}_6^{2-}$, and the corresponding thionic acids, $\text{H}_2\text{S}_n\text{O}_6$, in various amounts depending on the reaction conditions. It is believed that the first stable product of the reaction is tetrathionic acid, $\text{H}_2\text{S}_4\text{O}_6$. In common with most thionic acids, only salts have been characterized by spectroscopic techniques, the acids themselves cannot be isolated and positively identified.

It is not fruitful to review all of the speculative literature [32, 33] on the subject because most of the postulated intermediates leading eventually to sulfur in Wackenroder's liquid have not been identified, such as thiosulfuric acid, $\text{H}_2\text{S}_2\text{O}_3$, or thiosulfurous acid, $\text{H}_2\text{S}_2\text{O}_2$. What is clear is that the observed infrared spectrum is very similar to those which have been observed

by Steudel *et al.* [34], for a series of polythionate salts of the formula $S_nO_6^{2-}$, $n = 4-6$. These species have 4 to 6 sulfur atoms linked in a linear chain with two terminal SO_3 groups. A single sharp band near 1028 cm^{-1} is attributed to the symmetric SO_3 stretching mode and a doublet near 1200 cm^{-1} is assigned to the antisymmetric SO_3 stretching modes. The spectra are remarkably similar to those observed in the present work and we believe that we are in some sense looking at the infrared spectrum of the polythionate products of Wackenroder's liquid. The tentative observation that the pair of bands near 1200 cm^{-1} had ^{18}O shifts which appeared to be consistent with a SO_2 group is not really relevant if in fact this band is due to nearly degenerate antisymmetric stretching modes of an SO_3 unit [and the breadth of the bands in any case made it difficult to accurately assess the number of components generated by partial oxygen exchange].

It is tempting to assign the observed spectral features to two or more unknown reactive intermediates in the generation of elemental sulfur. The facts do not bear this out. First, the three bands grow in unison, suggesting that a single species is generated (or at least all species are generated with the same concentration). Second, the species generated is very stable, it is not desorbed by prolonged evacuation, and the re-addition of water simply regenerates the original spectrum. This is not a characteristic of a reactive and difficult to detect intermediate, hitherto unidentified.

It is apparent from the above that there exist many unanswered questions. That the high wavenumber pair of bands depends on the nature of the surface and on the quantity of water present is a particular puzzle. On zirconia, little water is generated from the reaction itself when compared to alumina; however, when water was added, the wavenumbers of these bands was identical on both oxides. This lends further support to the notion that these bands are indeed associated with Wackenroder's liquid when excess water above a certain minimum quantity is present. Upon evacuation, the species is possibly more perturbed by the surface, or by deprotonation. This aspect needs clarifying in the future and more oxides will have to be examined before firm conclusions can be reached.

Another aspect which needs further study is the question of the effect of the H_2S/SO_2 ratio.

In this work, only a few experiments were carried out due to time limitations but it would be desirable to fully examine the effect of ratio of the reactants in relation to the total pressure used. This study used ratios no higher than 3 and pressures no greater than about 8 Torr. In a future study, using the more transparent ZrO_2 , this laboratory will look into the question of whether or not additional IR bands can be observed when reactant ratios much greater than or much less than 2 are used. We also want to look at the effect of the degree of hydroxylation of the surface and the number of surface hydroxyl groups present. Studies of this nature are necessary before any mechanistic conclusions can be reached.

3. CONCLUSION

The dissociative chemisorption of H_2S on alumina gives rise to infrared bands which have been attributed to OH, Al-SH and Al-S species. The interaction occurs with AlOH groups and coordinatively unsaturated acidic Al and basic O sites which are created by the thermal activation under vacuum when Al_2O_3 is heated at temperatures above about 300°C . Physical adsorption also occurs on Al sites and via hydrogen bonding to AlOH groups.

The chemisorption of SO_2 on alumina produces two species, one being a sulfite like species, probably AlOSO_2 having an infrared band in the range from 1070 to 1050 cm^{-1} . This occurs via the interaction of SO_2 with cusO^{2-} sites. A second species, a hydrogensulfite probably having the structure AlOSO_2H has an IR band at 1010 cm^{-1} and occurs via a reaction with basic surface OH groups. Physical adsorption gives rise to species having infrared or Raman bands near 1330 and 1150 cm^{-1} , close to the frequencies for the antisymmetric and symmetric SO stretching modes of the parent SO_2 . Two unidentified species of unknown structure are in evidence as shown by very weak infrared bands near 1250 and 1200 cm^{-1} .

Under static reaction conditions, preadsorbed SO_2 reacts with gaseous H_2S to give sulfur. On the other hand, preadsorbed H_2S does not react with SO_2 but instead, preadsorbed H_2S is displaced by the stronger acid SO_2 . We have concluded that the mechanism of the Claus reaction over Al_2O_3 mainly involves a reaction between adsorbed SO_2 and gaseous H_2S . In contradiction

with the study of Kusamov [14], Al-S species do not appear play a significant role in the Claus reaction over Al_2O_3 .

The adsorption of a 2:1 mixture of gaseous $\text{H}_2\text{S}/\text{SO}_2$ on Al_2O_3 has been investigated for the first time. The Claus reaction appears to occur readily at room temperature on Al_2O_3 and on several other oxide catalysts and a single species can be detected as the reaction proceeds, characterized by a sharp IR band at 1028 cm^{-1} and a pair of bands near 1200 cm^{-1} . The sharp band is observed for all oxides and its wavenumber does not depend on the quantity of water present. On the other hand, the frequencies of the pair of bands near 1200 cm^{-1} depends on the nature of the oxide and on the quantity of water present. Tentatively, the bands have been attributed to a polythionate species which is generated during the Claus process, and it may correspond to an intermediate of Wackenroder's solution. Further research is necessary in order to elucidate the structure of the species responsible for these bands.

References

- [1]. Knozinger, H., Ratnasamy, P., Catal. Rev-Sci. Eng., 17, 13(1978).
- [2]. Henrich, V. E. and Cox, P. A., "The Surface Science of Metal Oxides", Cambridge University Press, 1994, p64.
- [3]. Marshneva, V. I. and Mokrinskii, V. V., 4(29), part 2, 854(1988).
- [4]. Parnell, D., Hydrocarbon Process., 9, 114(1985).
- [5]. EL Masry, Applied Catalysis, 16, 301(1985).
- [6]. Peri, J. B., J. Phys. Chem., 69, 211(1965).
- [7]. Jones, L. H., J. Chem. Phys., 22, 217(1954).
- [8]. Della Gatta, G., Fubini, B., Ghiotti, G. and Morterra, C., J. Catal., 43, 90(1976).
- [9]. Kiselev, A. V. and Lygin, V. I., "Infrared Spectra of Surface Compounds", Wiley and Sons, 1972.
- [10]. Datta, A. and Cavell, R. G., J. Phys. Chem., 89, 450(1985).
- [11]. Slager, T. L. and Amberg, C. H., Can. J. Chem., 50, 3416(1972).

- [12]. Lavalley, J. C., Travert, J., Chevreau, T., Lamotte, J. and Saur, O., J. Chem. Soc., Chem. Comm., 146(1979).
- [13]. Tripp, C. P., Ph. D. thesis, University of Ottawa, Canada, 1988.
- [14]. Kasumov, F. B., Kinetics and Catalysis, 33, 302(1992).
- [15]. Deo, A. V., Dalla Lana, I. G. and Habgood, H. W., J. Catal., 12, 270(1971).
- [16]. Chang, C. C., J. Catal., 53, 374(1978).
- [17]. Karge, H. G. and Dalla Lana, I. G., J. Phys. Chem., 88, 1538(1984).
- [18]. Datta, A., Cavell, R. G., Tower, R. W. and George, Z. M., J. Phys. Chem., 89, 443(1985).
- [19]. Dalla Lana, I. G., Karge, H. G. and George, Z. M., J. Phys. Chem., 97, 8005(1993).
- [20]. Berbed, P. H., Kappers, M. J. and Geus, J. W., Mikrochimica Acta, 15(1988).
- [21]. Garcia, C. L. and Lercher, J. A., J. Phys. Chem., 96, 2230(1992).
- [22]. Lavalley, J. C. and Benaissa, M., J. Chem. Soc., Chem. Commun., 908(1984).
- [23]. Marshneva, V. I., Dubkov, K. A., Mokrinskii, V. V., Paukshtis, E. A. and Davydov, A. A., Kinetics and Catalysis, 31, 1051(1991).
- [24]. Newman, G. and Powell, D. B., Spectrochimica Acta., 19, 213(1963).
- [25]. Schoonheydt, R. A. and Lunsford, J. H., J. Catal., 26, 261(1972).
- [26]. Karge, H. G., Tower, R. W., Dudzik, Z. and George, Z. M., Stud. Surf. Sci. Catal., 7, 643(1981).
- [27]. Simon, A. and Waldmann, K., Z. Anorg. Allg. Chem., 281, 113(1955).
- [28]. Hashimoto, S., Inoue, G. and Akimoto, H., Chem. Phys. Lett., 107, 198(1984).
- [29]. Lavalley, J. C., Janin, A. and Preud'homme, J., React. Kinet. Catal. Lett., 18, 85(1981).
- [30]. Currel, B. R., Williams, A. J., Mooney, A. J., and Nash, B. J., "New Use of Sulfur", Ed. by West, J. R., Amer. Chem. Soc., Washington, D. C., 1975.
- [31]. Datta, A. and Cavell, R. G., J. Phys. Chem., 89, 454(1985).
- [32]. Schmidt, M., in "Sulfur in Organic and Inorganic Chemistry" (Edited by Senning, A.), Vol. 2, Marcel Dekker Inc., New York, 1972.
- [33]. D. Lyons and G. Nickless in "Inorganic Sulfur Chemistry", Ed. G. Nickless, page 509, Elsevier, Amsterdam, 1968.
- [34]. R. Steudel, T. Gobel and G. Holdt, Z. Naturforsch. 43b, 203(1988).

Chapter 4

THE EFFECT OF BASICITY ON AN ALUMINA CATALYST

1. INTRODUCTION

Alumina is the most commonly used catalyst for the modified Claus reaction. The active sites for this reaction, as discussed in chapter 3 and elsewhere [1, 2], are basic. In chapter 5 we will show that silica impregnated with NaOH demonstrates some Claus activity while pure silica is inert. It is known that the addition of sodium increases the basicity of alumina [3, 4]. While prior studies have also shown that a catalyst which contained 3.9 mass percent sodium on Al_2O_3 gave rise to a very basic catalyst, it was only moderately active for the modified Claus reaction [5]. Therefore, two explanations have been proposed for this behaviour: (i) the greatly augmented basicity makes the catalyst less active for this reaction (i.e., there exists an optimum basicity, and the presence of sodium goes beyond the optimum making the catalyst too basic), or (ii) the reaction needs basic and acid sites, the latter being poisoned by the presence of excess sodium.

The purpose of the present investigation is two-fold: firstly to study the effect of sodium on the adsorption of SO_2 on Al_2O_3 ; secondly to compare the reactivity of the adsorbed SO_2 species with gaseous H_2S on Al_2O_3 and on sodium impregnated Al_2O_3 ($\text{Na}/\text{Al}_2\text{O}_3$) catalysts. The catalysts are gamma Al_2O_3 and gamma Al_2O_3 impregnated with 0.13 mole sodium per 100 g of sample (equal to 3 mass percent sodium). A limited number of infrared spectroscopic experiments were done with cesium impregnated Al_2O_3 ($\text{Cs}/\text{Al}_2\text{O}_3$) in order to compare the effect of using a more strongly basic dopant than sodium. The cesium doped alumina was made by the same impregnation method with 0.13 mole per 100 g of catalyst, which corresponds to about 17 mass

percent. The techniques used are gravimetry, infrared (IR) and Raman spectroscopies, and temperature programmed desorption (TPD).

2. EXPERIMENTAL

The gamma alumina sample, provided by Rhône-Poulenc, France, was used for all of the gravimetric and temperature programmed desorption (TPD) studies reported herein. It had a BET surface area of 244 m²/g and a pore volume of 0.52 cm³/g after vacuum activation at 350 or 600 °C. Sodium impregnated alumina, used in gravimetric and TPD studies, containing 0.13 mole Na per 100 g of sample after drying, was prepared by mixing Rhône-Poulenc alumina with a solution of sodium acetate. This wet sample was dried at 120 °C and was calcined in air overnight at 450 °C. After calcining the sample had a BET surface area of 235 m²/g and a pore volume of 0.45 cm³/g. The alumina, used in infrared and Raman studies, was a Degussa alumina (Aluminumoxid C) which had a BET surface area of 105 m²/g. The impregnated Al₂O₃, used in IR and Raman studies, was made by the same method but with Degussa alumina. Some of the infrared work was also carried out using Rhône-Poulenc alumina and no significant spectral differences were noted.

The cesium impregnated alumina was prepared by mixing Al₂O₃ with a cesium hydroxide solution so as to give a sample which, after drying, contained 0.13 mole of cesium per 100 g of dry catalyst (17 mass percent Cs). However, during the normal calcining process at 450°C, this very basic catalyst adsorbed atmospheric CO₂ and the surface was contaminated with carbonates. These could be eliminated if the calcined catalysts was heated at 700°C under vacuum, after which it was contacted with the vapour pressure of water at room temperature (to rehydroxylate the sample). This was then reactivated in vacuum at the desired temperature. The Cs/Al₂O₃ sample was only used in infrared studies in order to compare the quantity of SO₂ adsorbed on this material with respect to the less basic Al₂O₃ and Na/Al₂O₃.

Prior to use, samples were activated by heating under vacuum for about 1 to 3 hours at a specific temperature, during which time the base pressure dropped to less than 10⁻⁴ Torr. For

convenience as before, the various samples will denoted below as $\text{Al}_2\text{O}_3(\text{C})$, $\text{Na}/\text{Al}_2\text{O}_3(\text{C})$ or $\text{Cs}/\text{Al}_2\text{O}_3(\text{C})$ where 'C' is the activation temperature in degrees Celsius, i.e. $\text{Na}/\text{Al}_2\text{O}_3(450)$ is a sample of sodium on alumina which has been activated in vacuum at 450 °C.

Infrared studies were carried out using Nicolet MX1 FTIR, Bomem DA3-02 or Bomem Michelson MB FTIR spectrometers at a resolution of 4 cm^{-1} . Raman spectra were recorded using a Jobin-Yvon HG2 instrument (8 cm^{-1} resolution) and sample irradiation was achieved using an argon ion laser (488 nm) with laser power ranging from 50 to 500 mW.

For TPD studies, about 5 kPa of SO_2 (about 37.5 Torr) were contacted with the activated sample at room temperature ($22 \pm 1\text{ }^\circ\text{C}$) and after 20 minutes the sample was evacuated at room temperature for 1 hour. It was then heated ($5\text{ }^\circ\text{C}/\text{min}$) under a helium flow ($20\text{ cm}^3/\text{min}$) and the desorbed gases were analyzed quantitatively and qualitatively by gas chromatography. Gravimetric measurements were done using a McBain thermobalance.

All of the gravimetric and TPD experiments were performed by A. B. Mohammed Sadd in the laboratory of J. C. Lavalley, Caen, France.

3. RESULTS

(1). Gravimetry:

A series of gravimetric measurements were made on Al_2O_3 and $\text{Na}/\text{Al}_2\text{O}_3$ samples by contacting each sample with 40 Torr of SO_2 at room temperature. The total quantity adsorbed, and the quantities physically or chemically (irreversibly) adsorbed are shown in Table 4.1. The total quantity adsorbed represents both physically and chemically adsorbed species. The amount chemically adsorbed was determined to be that which remained following evacuation for 2 hours at room temperature, the difference being the quantity physically adsorbed.

Table 4.1
Gravimetric measure of the quantity of SO₂ adsorbed (molecule/nm²)
as a function of the temperature of activation

	Al ₂ O ₃ (350)	Na/Al ₂ O ₃ (350)	Al ₂ O ₃ (600)	Na/Al ₂ O ₃ (600)
SO ₂ total	3.1	4.3	3.0	4.4
SO ₂ chemisorbed	1.8	2.8	2.0	2.8
SO ₂ physisorbed	1.3	1.5	1.0	1.6

These results show that the quantity adsorbed is greater for the Na/Al₂O₃ samples but that there is not a large difference for the same catalyst but with different activation temperatures. We also measured the mass change of each sample after the evacuation at room temperature followed by heating at 2 °C/min up to 600 °C and found that the curves were quasi-parallel (Fig 4.1 A) indicating that the quantity of chemisorbed SO₂ was always greater on the Na/Al₂O₃ sample. Further, all SO₂ was desorbed from pure Al₂O₃ after heating to 600 °C whereas about 0.4 molecule/nm² remained on the Na/Al₂O₃.

(2). TPD experiments:

Fig 4.1B shows the TPD profiles following adsorption on the 600 °C activated samples. For both Al₂O₃ and Na/Al₂O₃ samples there was a relatively sharp desorption near 100-120 °C. Further, there was a tapering off of the desorption curve to high temperature, with a poorly defined peak near 290 °C for Al₂O₃ and a more distinct peak near 380 °C for Na/Al₂O₃(600). In agreement with the gravimetric results, all SO₂ desorbed from pure Al₂O₃ by 600 °C, but not from Na/Al₂O₃.

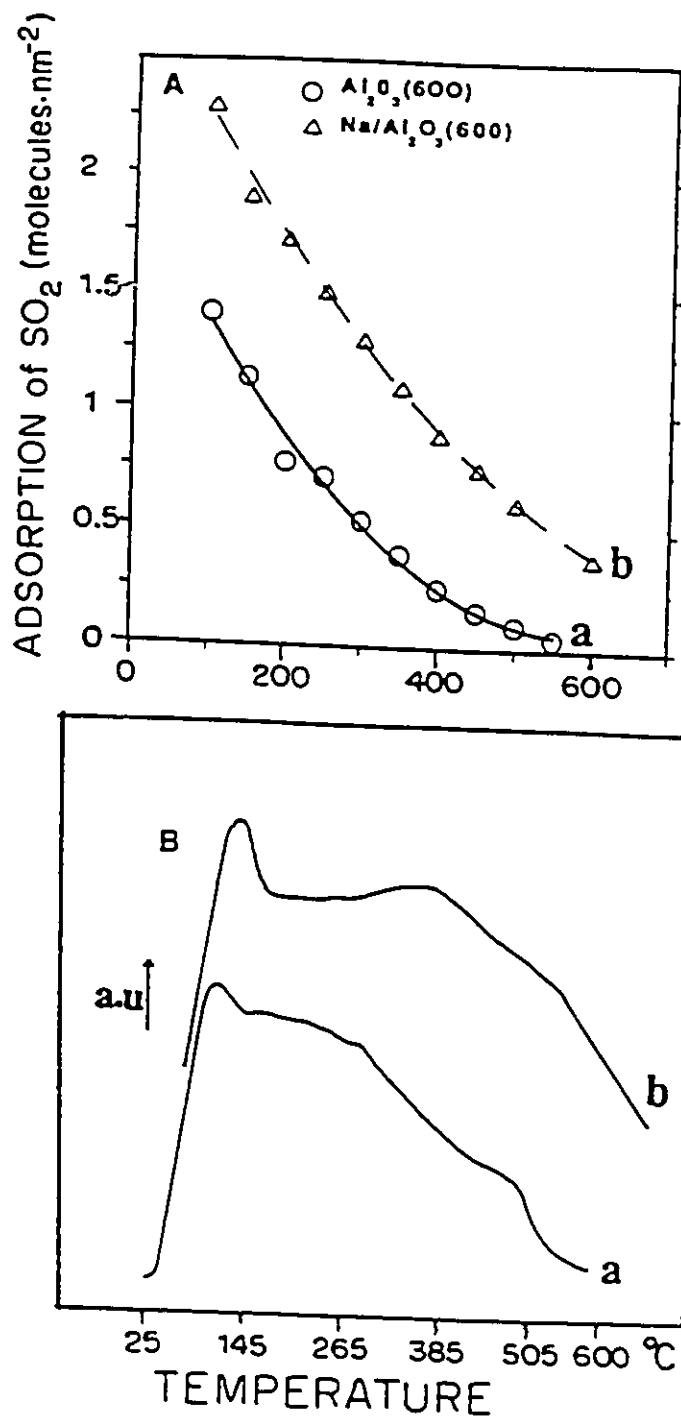


Fig 4. 1 (A) Effect of temperature of the mass of chemisorbed SO_2 on $\text{Al}_2\text{O}_3(600)$ (a) and $\text{Na}/\text{Al}_2\text{O}_3(600)$ (b). (B) TPD spectra of SO_2 adsorbed on $\text{Al}_2\text{O}_3(600)$ (a) and $\text{Na}/\text{Al}_2\text{O}_3(600)$ (b).

(3). *Infrared and Raman experiments of adsorbed SO₂:*

As discussed in chapter 3, gaseous SO₂ has absorption bands at 1361 (strong) and 1151 cm⁻¹ (medium) due to the antisymmetric and symmetric SO₂ stretching modes respectively [6]. Following the introduction of 20 Torr of SO₂ on Al₂O₃(450), Na/Al₂O₃(450) and Cs/Al₂O₃(450), IR bands near these frequencies were observed. After spectral subtraction of the contribution from the gas phase, relatively symmetrical bands at 1335 and 1148 cm⁻¹ for Al₂O₃(450), 1340 and 1150 cm⁻¹ for Na/Al₂O₃(450) or 1330 and 1147 cm⁻¹ for Cs/Al₂O₃(450) (Fig 4.2) were observed. Similar bands were also observed following addition of SO₂ to other catalysts which were activated at different temperatures. On Al₂O₃(350), these two bands (1137 and 1335 cm⁻¹) could be removed by evacuation for 5 minutes at room temperature, showing that they arose from physisorbed SO₂. [On Al₂O₃(450) or other high temperature catalysts, there is a very weak band at 1325 cm⁻¹ which remains after evacuation.] These two bands, 1147 and 1335 cm⁻¹, were most intense in the case of Cs/Al₂O₃. The relative integrated intensities (band areas) for all three samples are shown in Table 4.2. In agreement with the gravimetric results for Al₂O₃ or Na/Al₂O₃, we found that the activation temperature did not greatly influence the band areas if the activation temperature was not too high, but they were greater for the alkali-containing samples.

Table 4.2
Relative band areas (arbitrary units)
for physically adsorbed SO₂

	Al ₂ O ₃ (450)	Na/Al ₂ O ₃ (450)	Cs/Al ₂ O ₃ (450)
1147 cm ⁻¹	1.0	2.2	4.7
1335 cm ⁻¹	7.6	13.0	26.3

The spectra of the species which were irreversibly adsorbed (chemisorbed) at room temperature following evacuation are shown in Figure 4.3. (These are difference spectra, after background subtraction, Al₂O₃ being totally adsorbing below about 1000 cm⁻¹.) For Al₂O₃(450),

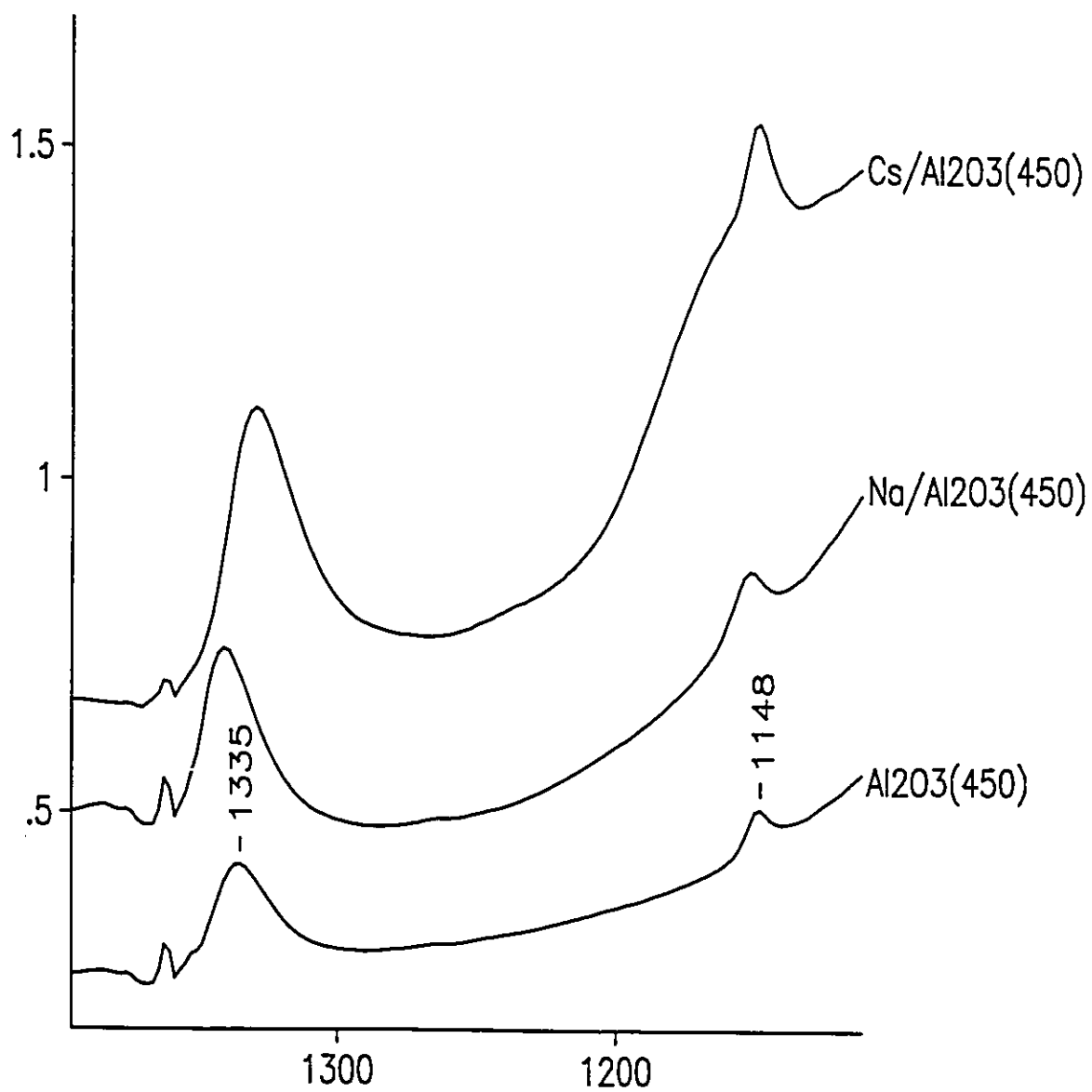


Fig 4. 2 Infrared spectra of physically adsorbed SO_2 on $\text{Al}_2\text{O}_3(450)$, $\text{Na/Al}_2\text{O}_3(450)$ and $\text{Cs/Al}_2\text{O}_3(450)$.

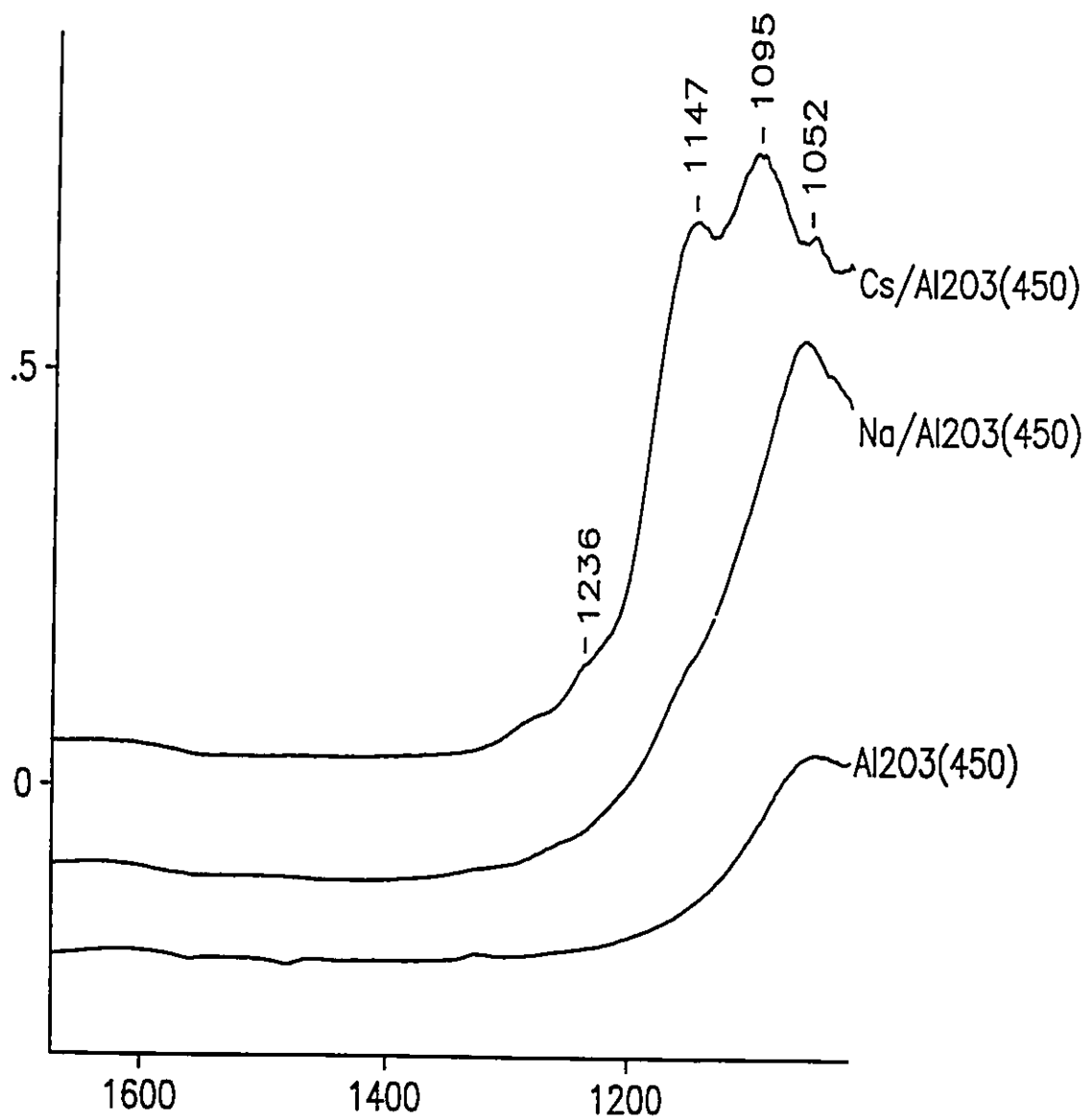


Fig 4. 3 Infrared spectra of chemisorbed SO_2 on corresponding catalysts (the background of Al_2O_3 , $\text{Na/Al}_2\text{O}_3$ and $\text{Cs/Al}_2\text{O}_3$ have been subtracted).

there was a broad band at 1050 cm^{-1} , while for $\text{Na/Al}_2\text{O}_3(450)$, there were a broad asymmetric band having a maximum near 1250 cm^{-1} and a shoulder near 1147 cm^{-1} . For each sample, there is a weak shoulder near 1200 cm^{-1} . For $\text{Cs/Al}_2\text{O}_3(450)$, a weak band at 1050 cm^{-1} and a strong band at 1095 cm^{-1} as well as a strong band at 1147 cm^{-1} . (Because of its strongly basic nature, there may be some unique Cs-sulfite species, and we will return this point later.) In agreement with the order of basicity, the amount of chemisorbed species is in the order $\text{Cs/Al}_2\text{O}_3 > \text{Na/Al}_2\text{O}_3 > \text{Al}_2\text{O}_3$.

In Raman spectroscopy, the behaviour of $\text{Na/Al}_2\text{O}_3$ is the same as Al_2O_3 (Al_2O_3 was shown in Fig 3.9). We observed the bands near 1150 and 1340 cm^{-1} which were due to physically adsorbed SO_2 on Al_2O_3 . These bands disappeared following evacuation at room temperature. But the very weak band near 1050 cm^{-1} for both catalysts (see Fig 3.9) was not removed by evacuation.

In the AlO-H spectral region, the IR of pure alumina after activation at 450°C showed distinct bands at $3790, 3772, 3727$ and 3684 cm^{-1} due to AlO-H vibrations, and for $\text{Na/Al}_2\text{O}_3(450)$ there was a sharp band centred near 3738 cm^{-1} and a shoulder at 3680 cm^{-1} , whereas for $\text{Cs/Al}_2\text{O}_3$, there was a weak band near 3700 cm^{-1} (Fig 4.4). Following adsorption of SO_2 , the sharper bands of Al_2O_3 in the $3800\text{-}3600\text{ cm}^{-1}$ spectral region decreased in intensity and were replaced by a very broad absorption extending from about 3600 to 2800 cm^{-1} . This effect is shown more clearly by the difference spectra in Figure 4.5 where the negative peaks in the O-H spectra region correspond to the decrease in intensity of the positive peaks in Figure 4.4 as a result of the adsorption of SO_2 . For any temperature of activation, this broad band (from 3600 to 2600 cm^{-1}) was much more intense for $\text{Na/Al}_2\text{O}_3$ and $\text{Cs/Al}_2\text{O}_3$ than for pure Al_2O_3 . However, in all cases there was a broad weak absorption near 2400 cm^{-1} though it was much less intense on pure Al_2O_3 .

(4). Comparison between adsorbed SO_2 and CO_2 :

In a previous study Lavalley *et al.* [7] and our laboratory (see chapter 3) showed that the

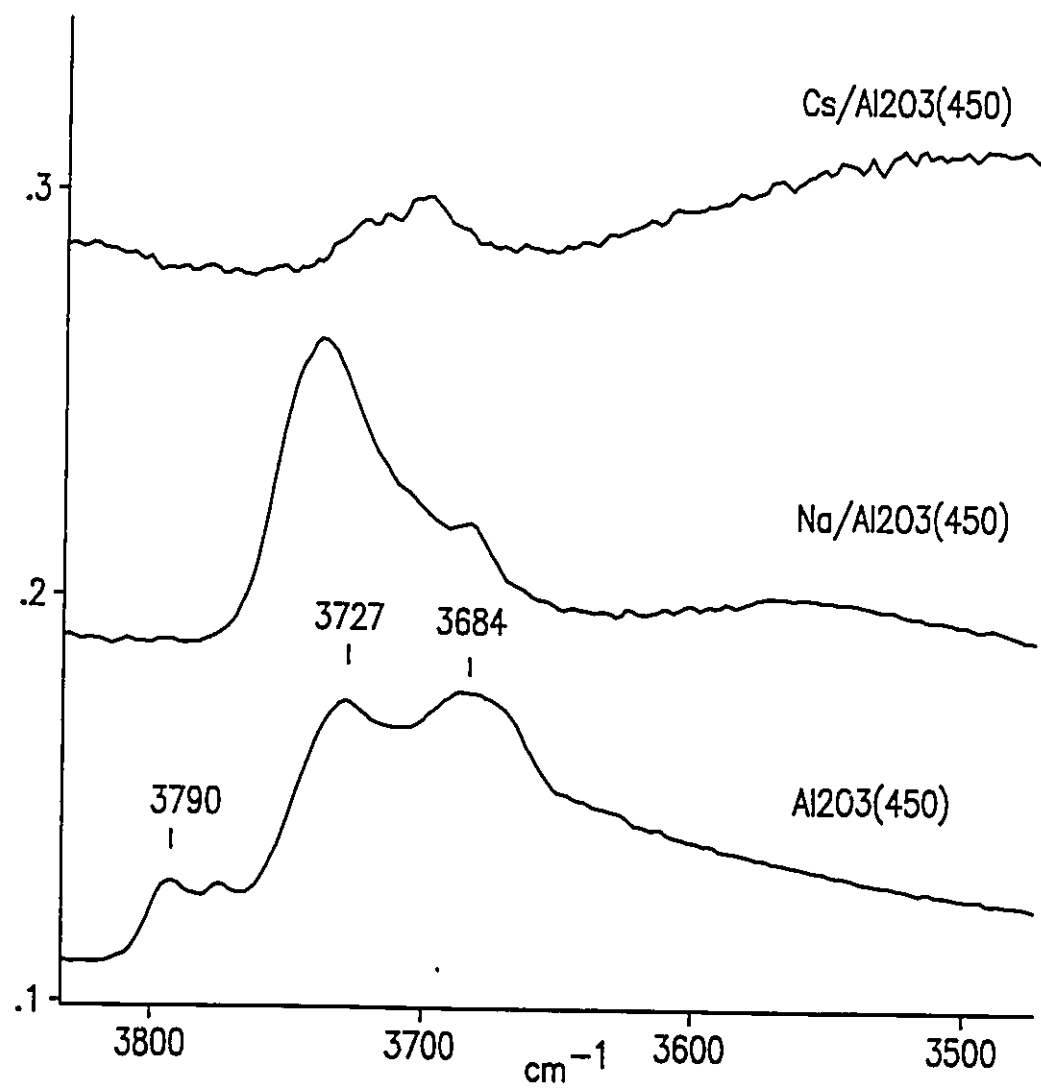


Fig 4. 4 Infrared spectra of the hydroxyl groups on Al₂O₃, Na/Al₂O₃ and Cs/Al₂O₃.

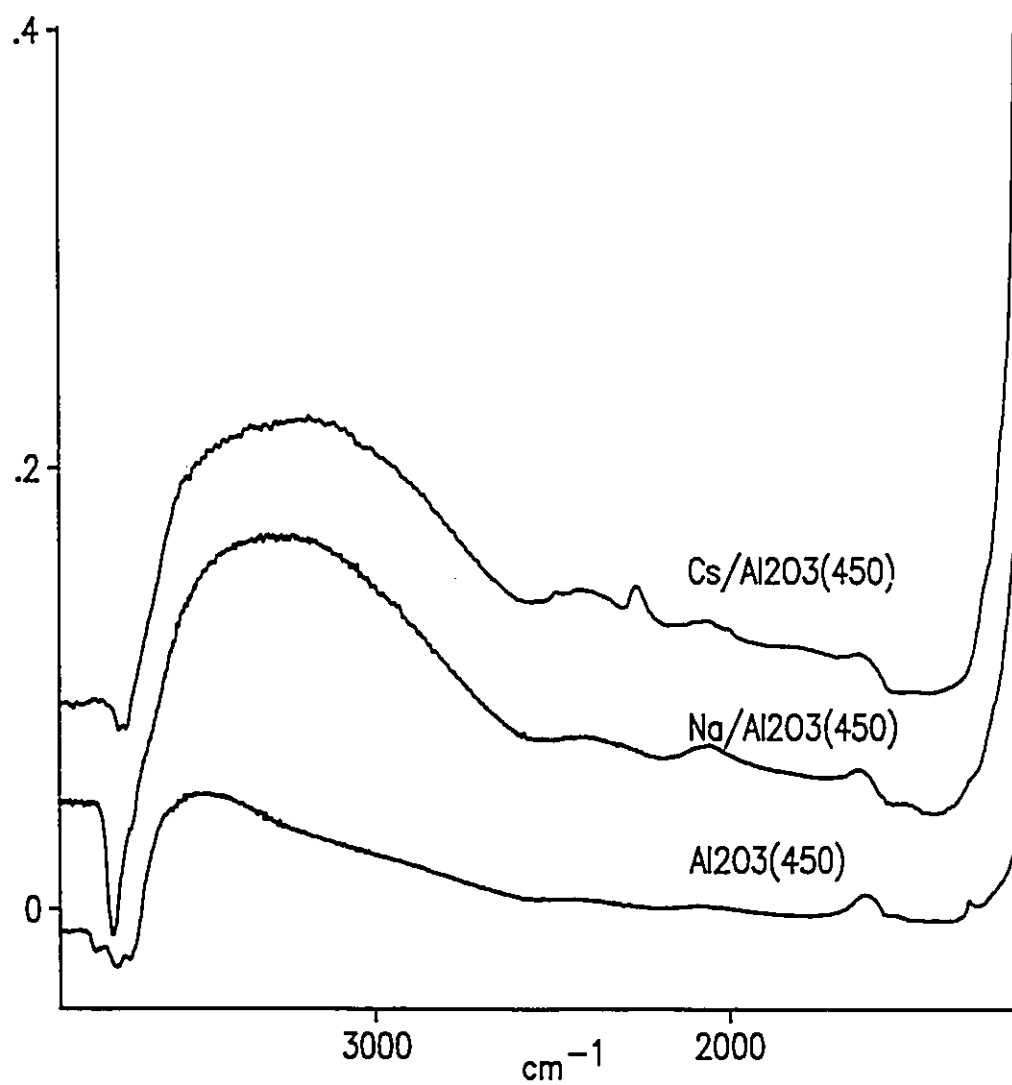


Fig 4.5 Difference spectra after the addition of SO_2 to Al_2O_3 , $\text{Na}/\text{Al}_2\text{O}_3$ and $\text{Cs}/\text{Al}_2\text{O}_3$.

preadsorption of SO_2 on Al_2O_3 blocked the subsequent adsorption of CO_2 (SO_2 is a stronger acid than CO_2) indicating that both of the probes SO_2 and CO_2 adsorbed on common sites. In particular, the hydrogencarbonate species formed by adsorption of CO_2 on the OH groups did not form if the alumina had been pretreated by SO_2 , suggesting that hydrogensulfite species might be formed by reaction with the same OH sites. Therefore, in order to further characterize the adsorption sites, we have studied the effect of addition of CO_2 on $\text{Al}_2\text{O}_3(450)$, $\text{Na}/\text{Al}_2\text{O}_3(450)$ and $\text{Cs}/\text{Al}_2\text{O}_3(450)$.

The adsorption of CO_2 on basic oxides gives rise to IR bands in the spectral region between 1200 and 1700 cm^{-1} due to carbonate or hydrogencarbonate species [8]. On Al_2O_3 , CO_2 adsorption mainly gives rise to hydrogencarbonates characterized by bands at 3610 cm^{-1} (ν_{OH}), 1650, 1480 and 1450 cm^{-1} (ν_{OCO}) and 1235 cm^{-1} (δ_{OH}). Such species are also formed on $\text{Na}/\text{Al}_2\text{O}_3$ (corresponding bands at 3620, 1650, 1435 and 1235 cm^{-1}) with additional carbonate species characterized by bands near 1600, 1345, 1090 and 1060 cm^{-1} . Progressive heating under vacuum in the temperature range from 100 to 350 $^{\circ}\text{C}$ resulted in the preferential removal of the bands due to hydrogencarbonate species. A higher temperature is necessary to eliminate all of the species from $\text{Na}/\text{Al}_2\text{O}_3$ than from pure Al_2O_3 (350 $^{\circ}\text{C}$ versus 250 $^{\circ}\text{C}$, respectively) demonstrating the greater basicity of the former catalyst.

The increased basicity of $\text{Na}/\text{Al}_2\text{O}_3$ was also demonstrated in a sequence of experiments whereby SO_2 was pre-adsorbed at room temperature followed by evacuation of SO_2 at a given temperature, and finally, CO_2 was added at room temperature. We found that it was necessary to evacuate the SO_2 treated Al_2O_3 at 150 $^{\circ}\text{C}$ before the subsequent addition of CO_2 produced a spectrum of hydrogencarbonates. However, using $\text{Na}/\text{Al}_2\text{O}_3$, evacuation at 250 $^{\circ}\text{C}$ was necessary before carbonates were observed. For $\text{Cs}/\text{Al}_2\text{O}_3$, evacuation below 150 $^{\circ}\text{C}$ caused no change in the spectrum of the sulfur-containing species and no carbonates formed with the addition of CO_2 . Only after evacuation at 200 $^{\circ}\text{C}$, were some sulfur-containing species lost and a trace of carbonates were formed when CO_2 was re-introduced into the cell. As in the case of $\text{Na}/\text{Al}_2\text{O}_3$, evacuation at 250 $^{\circ}\text{C}$ caused a large decrease in intensities of the bands due to sulfur-containing species and carbonates could be observed with the addition of CO_2 . This again demonstrates that

SO₂ is more tenaciously held on the more basic Na/Al₂O₃, Cs/Al₂O₃ than on pure Al₂O₃.

The significance of these results will be discussed in more detail later in connection with the H₂S/SO₂ reaction on these catalysts.

(5). Reaction between chemisorbed SO₂ and H₂S:

In order to study the reaction between chemisorbed SO₂ and gaseous H₂S, SO₂ was chemisorbed on Al₂O₃(450) (see chapter 3). The addition of H₂S to this sample resulted in the disappearance of the shoulder at 1200 cm⁻¹, a decrease in intensity of the 1050 cm⁻¹ band, and the appearance of a band at 1620 cm⁻¹, the latter being indicative of the formation of water. The addition of H₂S did not result in the appearance of a SH band as was previously observed for adsorption of H₂S alone on Al₂O₃ [9, 10]. Finally, heating caused a further decrease in the intensity of the 1050 cm⁻¹ band. Qualitatively similar results were found for the different Al₂O₃(C) samples.

In a separate experiment, after adsorption of SO₂ followed by H₂S, the gaseous H₂S was evacuated at room temperature, and then CO₂ (P_e = 2 Torr) was introduced. This resulted in the appearance of the spectrum of hydrogencarbonate species. Recall that under similar conditions, but without introduction of H₂S, CO₂ did not adsorb on Al₂O₃ pretreated with SO₂. Therefore, OH sites capable of interacting with CO₂ must have been created during the SO₂/H₂S reaction. These basic hydroxyls could have been formed either from the reaction of H₂S with the species responsible for the 1050 or 1200 cm⁻¹ bands, or as a result of the formation of water. However, when H₂O alone was added to chemisorbed SO₂ on Al₂O₃(450) the 1200 cm⁻¹ band disappeared and there was practically no effect on the band at 1050 cm⁻¹. Therefore, we conclude that the H₂O generated from the SO₂/H₂S reaction was not responsible for the decrease in the intensity of the 1050 cm⁻¹ band, but rather this resulted from a reaction with H₂S. We can make no conclusion regarding the reactivity of the species responsible for the 1200 cm⁻¹ band with H₂S.

The same series of experiments were carried out using SO₂ pretreated Na/Al₂O₃(450) which

has a band 1050 cm^{-1} and a shoulder 1150 cm^{-1} as well as very weak band at 1200 cm^{-1} (Fig 4.6a). The addition of H_2S caused the preferential disappearance of the 1150 cm^{-1} band and a decrease in the intensity of the 1050 cm^{-1} band, but less so than for pure Al_2O_3 . Species at 1200 cm^{-1} also disappeared. Water was also formed (1620 cm^{-1} , see Fig 4.6b) but less so than for pure Al_2O_3 . After evacuation at room temperature, the addition of CO_2 gave no bands due to carbonates or hydrogencarbonates, confirming that adsorbed SO_2 species are less reactive on $\text{Na}/\text{Al}_2\text{O}_3$ than on Al_2O_3 . And furthermore, heating caused much less decrease in the intensity of 1050 cm^{-1} (Fig. 4.6c-d) than that involving the pure Al_2O_3 catalyst.

Finally, for Al_2O_3 and $\text{Na}/\text{Al}_2\text{O}_3$, the appearance of a yellowish colour after the introduction of H_2S suggests formation of sulfur via the modified Claus reaction. Raman spectroscopy confirmed this conclusion. Following addition of H_2S to preabsorbed SO_2 on either catalyst, intense Raman bands at 151 , 220 and 480 cm^{-1} characteristic of S_8 were observed (Fig 3.9).

(6). *Reaction between chemisorbed H_2S and SO_2 :*

Details of the adsorption of H_2S alone on Al_2O_3 are reported in the previous chapter. In this chapter, we are concerned mainly with the adsorption of SO_2 and its subsequent interaction with H_2S so we can compare the behaviour of Al_2O_3 with that of $\text{Na}/\text{Al}_2\text{O}_3$. But the salient features to note are, in agreement with other work, that H_2S physically adsorbs on Al^{3+} sites and $\text{Al}-\text{OH}$ sites of alumina to produce IR bands at 2567 and 2540 cm^{-1} , and that it additionally dissociated to give AlOH (3700 cm^{-1}) and AlSH (2580 cm^{-1}) species, or to give S^{2-} species (see chapter 3).

On $\text{Na}/\text{Al}_2\text{O}_3$ more complex spectra were observed after addition of H_2S . NaSH species were produced, as shown by IR spectroscopy (2585 cm^{-1}), as well as H_2O on $\text{Na}/\text{Al}_2\text{O}_3$ (1630 cm^{-1} , HOH deformation mode) and there was evidence for the presence of surface sulfides [11]. Finally, about 50% more H_2S was adsorbed (either physically or irreversibly) on $\text{Na}/\text{Al}_2\text{O}_3$ than on pure Al_2O_3 [11]. Although more H_2S was adsorbed by $\text{Na}/\text{Al}_2\text{O}_3$ than Al_2O_3 there was no significant increase in the intensity of the HS band.

After having chemisorbed H_2S at room temperature on $\text{Al}_2\text{O}_3(450)$, SO_2 was added. This

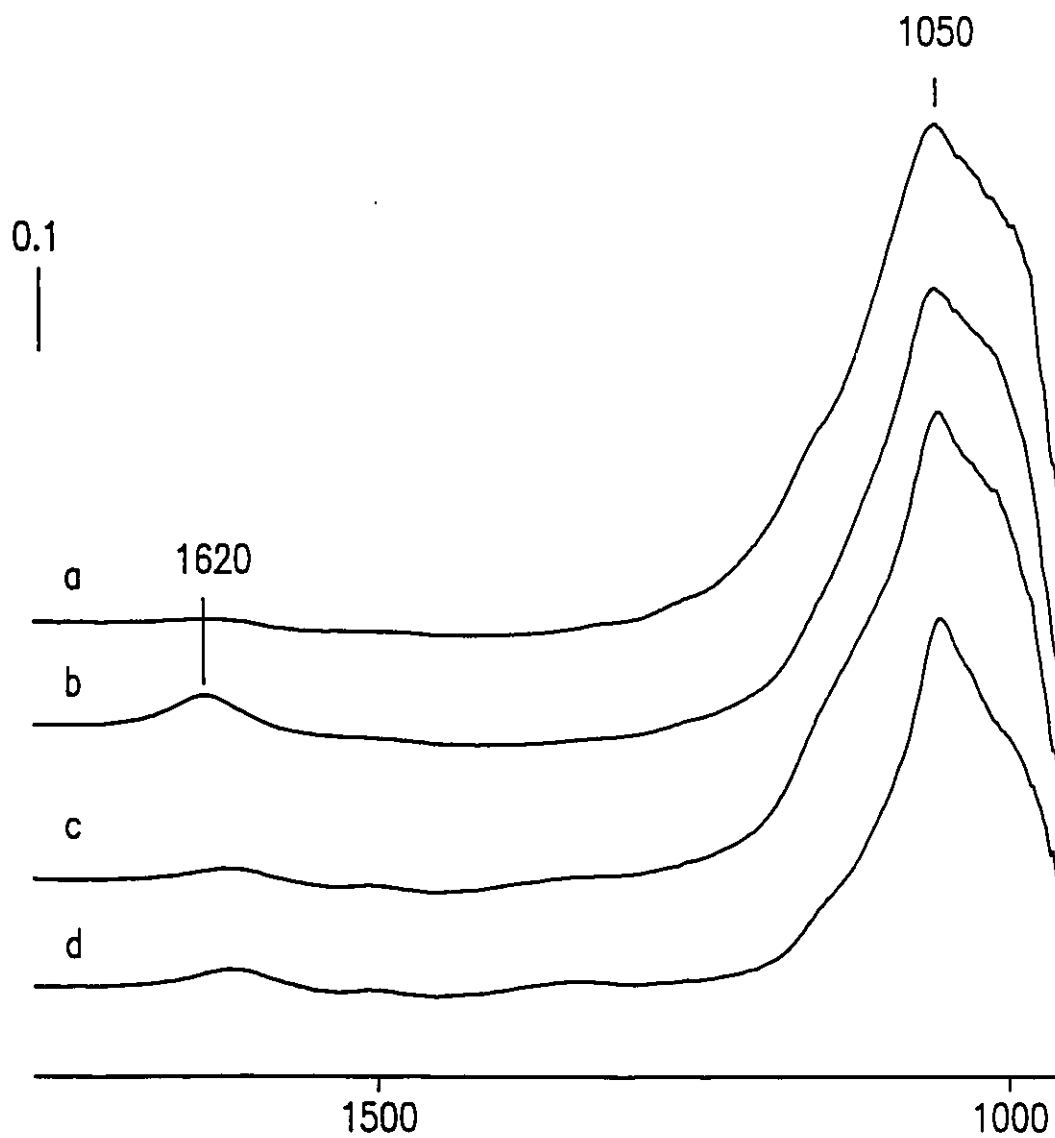


Fig 4. 6 (a) Infrared spectrum of Na/Al₂O₃(450) after addition of excess SO₂, followed by evacuation (background subtracted); (b) After addition of H₂S to (a) (P_r = 3 Torr) at room temperature for 30 minutes; (c) After heating (b) at 100 °C under evacuation; (d) After heating (c) at 200 °C under evacuation.

caused the disappearance of the $\nu(\text{SH})$ band but did not hinder the chemisorption of SO_2 , giving rise to a broad band near 3550 cm^{-1} , and appearance of a band near 1050 cm^{-1} . The band resulting from the formation of water was hardly visible. We conclude that there is some interaction, but that the conditions are not favourable for the modified Claus reaction to take place. The same conclusion was reached using Raman spectroscopy. Preabsorbed H_2S did not react with SO_2 to produce Raman bands characteristic of S_8 . Conversely, if H_2S was re-added after the above addition of SO_2 , then S_8 was again detected. Similar results were observed using $\text{Na}/\text{Al}_2\text{O}_3$. Although more H_2S was adsorbed on $\text{Na}/\text{Al}_2\text{O}_3$, no S_8 was found, we suggest that surface Na_2S species do not react with SO_2 .

4. DISCUSSION

(1). *Nature of the catalysts:*

The IR spectra of our gamma Al_2O_3 in the OH stretching vibrational region are similar to those reported in the literature [12-15]. However, given that the surface structure of gamma Al_2O_3 from the surface science point of view is largely unknown [16], it would be inappropriate to attempt a detailed description of the $\text{Na}/\text{Al}_2\text{O}_3$ or $\text{Cs}/\text{Al}_2\text{O}_3$ surface. Impregnation with alkali results in the removal of most of the fine structure in the OH stretching region (e.g. Fig 4.4). In agreement with other work relative to $\text{Na}/\text{Al}_2\text{O}_3$, the disappearance of the high and low wavenumber OH bands at 3790 and 3690 cm^{-1} shows that Al-O-Na groups are formed, and this suggests that the sodium is well dispersed on the surface [3, 17]. However, XPS or zero point of charge (z.p.c.) measurements on similar materials have shown that, at sodium coverage similar to ours, there could also be islands of Na_2O or of sodium aluminate [18]. Ivanov *et al.* also reported that a very small amount of Na_2O was on the surface of $\text{Na}/\text{Al}_2\text{O}_3$ [19]. In our case, we do not believe that the formation of this species is excessive because the surface area and the pore volume was not significantly changed by the addition of sodium. Further speculation concerning the nature of the surface is unwarranted.

Finally, Fledorow *et al.* [20] studied the surface properties of the alumina samples which contain 2 to 5 mass percent of NaOH or LiOH by impregnation. The results show the alkali

metal ions can react not only with Brønsted acid sites but also with Lewis acid sites (LAS). The poisoning effect upon LAS will increase with increasing ionic radius of the metal alkali ion. Considering our experiments with Na and Cs, the impregnation will cause the catalysts have the LAS order: $\text{Al}_2\text{O}_3 > \text{Na}/\text{Al}_2\text{O}_3 > \text{Cs}/\text{Al}_2\text{O}_3$. And the basicity order should be: $\text{Cs}/\text{Al}_2\text{O}_3 > \text{Na}/\text{Al}_2\text{O}_3 > \text{Al}_2\text{O}_3$.

(2). *Physisorbed SO₂*:

As discussed in chapter 3, the two stretching modes of SO₂ in the gas phase are at 1361 cm⁻¹ (ν_a , antisymmetric SO₂ stretch) and at 1151 cm⁻¹ (ν_s , symmetric SO₂ stretch). The complexation of SO₂ with some acids and bases has been studied [21]. With strong electron pair acceptors (Al or Ga halides), an Al:OSO or Ga:OSO interaction arises and ν_a and ν_s shift to near 1450 and 1090 cm⁻¹, respectively. With strong electron pair donors such as pyridine or triethylamine, a N:SO₂ interaction arises and these modes shift to near 1275 and 1125 cm⁻¹, respectively.

In the present study, the IR or Raman bands of physisorbed SO₂ on Al₂O₃ are very close to those of the free molecule, showing that the interaction with the surface is weak. As has been discussed in chapter 3, the interaction with Al₂O₃ is mainly via the AlOH groups and on Al³⁺ sites. We also note (Table 4.1) that there is more physisorbed SO₂ on Al₂O₃(350) than on Al₂O₃(600), the former having a higher OH content.

The gravimetric (Table 4.1) and IR (Table 4.2) studies show that more SO₂ is physisorbed on Na/Al₂O₃ than on Al₂O₃ alone. In a previous study, Waqif *et al.* showed that the quantity of physisorbed SO₂ increased as the sodium loading was increased in 0.05% increments from 0.0% to 3% [22]. The IR bands were observed at 1335 and 1147 cm⁻¹, very close to those reported for SO₂ complexation with very weak bases such as ethylene, ethanol dioxane and water [21]. Therefore, we assume that adsorption occurs on basic O²⁻ or OH⁻ on Na/Al₂O₃. The peaks due to physical adsorption of SO₂ on Cs/Al₂O₃ had the greatest intensity (Fig 4.2). In the spectrum of Cs/Al₂O₃, there were fewer OH groups than on Al₂O₃ or on Na/Al₂O₃, so the higher adsorption capacity probably comes from basic O²⁻ sites reacting with SO₂. On Al₂O₃, Karge and Dalla Lana

[23] studied the adsorption of SO_2 after poisoning the catalyst with different acid or base probes. Because NH_3 and pyridine partly hindered observation of the 1334 cm^{-1} band, and BF_3 , HCl or CH_3COOH did not, they concluded that physisorbed species mainly reside on acidic sites. The present results show that physisorption also occurs on basic sites.

For both Al_2O_3 and $\text{Na}/\text{Al}_2\text{O}_3$, the TPD results show that the physisorbed species are desorbed at a relatively low temperature, $100\text{--}120\text{ }^\circ\text{C}$.

(3). Chemisorbed SO_2 :

These species can be attributed to IR bands which remain after evacuation. Both the IR and gravimetric results show that the number of these species is greater for sodium loaded alumina than for Al_2O_3 . (We will discuss $\text{Cs}/\text{Al}_2\text{O}_3$ later.) The species with or without Na are characterized by a strong broad band near 1050 cm^{-1} , accompanied by a shoulder to higher wavenumber, near 1150 cm^{-1} for $\text{Na}/\text{Al}_2\text{O}_3$ and a very weak band near 1200 cm^{-1} for both Al_2O_3 and $\text{Na}/\text{Al}_2\text{O}_3$. The TPD results show that the chemisorbed species desorbed in a wide temperature range, having a maxima from 290 to $350\text{ }^\circ\text{C}$, thus demonstrating their greater thermal stability relative to the physisorbed species.

The main peak near 1050 cm^{-1} on $\text{Al}_2\text{O}_3(450)$ has been universally attributed to the formation of a surface sulfite on alumina, probably of structure Al-O-SO_2 , as discussed in chapter 3 and in many reports [23-26]. The adsorption of SO_2 on $\text{Na}/\text{Al}_2\text{O}_3$ has only been the subject of a few studies. Zotin and Faro [5] showed that the presence of Na on alumina increased the quantity of SO_2 irreversibly adsorbed at $100\text{ }^\circ\text{C}$. It went from 0.49 mmol/g on pure gamma Al_2O_3 to 0.76 mmol/g on $3.9\%\text{ Na}/\text{Al}_2\text{O}_3$, which corresponds respectively to 1.5 and $2.6\text{ molecules/nm}^2$. These values are close to those found in the present study (Table 4.1), confirming the greater adsorption capacity of $\text{Na}/\text{Al}_2\text{O}_3$ relative to Al_2O_3 . We also found that the species formed were more thermally stable on $\text{Na}/\text{Al}_2\text{O}_3$, a result which will be discussed further below in connection with $\text{H}_2\text{S}/\text{SO}_2$ reaction. The increased basicity of $\text{Na}/\text{Al}_2\text{O}_3$ undoubtedly is responsible for both the increased number of sulfite species and their thermal stability. The 1050 cm^{-1} band observed in

the case of Na/Al₂O₃(450) is assigned to sulfite species on alumina whose basicity is increased by the presence of sodium. It is not possible to show that bulk Na₂SO₃ is formed because its characteristic IR band [6] at 970 cm⁻¹ is below the limit of transmission (about 1000 cm⁻¹) of Al₂O₃. However, the number of chemisorbed species does not depend significantly on the activation temperature of either catalyst (Table 4.1). This is not what one would expect if the interaction was only between SO₂ and O²⁻, the latter species being expected to be more abundant when the activation temperature leading to dehydroxylation is higher. Therefore, we assume that SO₂ can react with equal facility with O²⁻ or with OH⁻ to form sulfite, or even to form a hydrogensulfite species, HSO₃⁻ or HOSO₂⁻, or disulfite, S₂O₅²⁻.

The formation of HOSO₂⁻ could account for the very broad band in the 3500-3300 cm⁻¹ spectral region when SO₂ chemisorbs on Na/Al₂O₃(450) and Cs/Al₂O₃(450). Note that the formation of S₂O₅²⁻ has been observed when introducing SO₂ to a Na/SiO₂ catalyst (see chapter 5). This species is characterized by a band at 657 cm⁻¹. However, solid Na₂S₂O₅ has a strong band [27] in the IR at 1180 cm⁻¹ which might correspond to the weak shoulder near 1150 cm⁻¹ for Na/Al₂O₃.

Finally, in order to compare the effect of basicity, a more strongly basic catalyst Cs/Al₂O₃ was used. Further, some oxysulfur ions exist as cesium salts and not as sodium salts, for example, solid CsHSO₃ is a stable compound while solid NaHSO₃ does not exist [28]. Therefore, more species might be expected from the chemisorption of SO₂ on Cs/Al₂O₃ than on either Al₂O₃ or Na/Al₂O₃. This is confirmed. The band at 1147 cm⁻¹ was much stronger than that barely observed on Al₂O₃ or on Na/Al₂O₃, and, in addition to the 1050 cm⁻¹ band, there was a new strong feature at 1095 cm⁻¹. The overall intensity was considerably greater than that observed for the other catalysts (Fig 4.3). The identity of these species is as yet unknown, but we prepared a sample of CsHSO₃ and, in common with its Raman spectrum, the strongest IR band is near 1118 cm⁻¹, so that one of the 1147 or 1095 cm⁻¹ bands may be partially attributable to this species. The strongest band in the Raman spectrum of Cs₂S₂O₅ is 1050 cm⁻¹. Further speculation is unwarranted.

(4). Reaction between SO₂ and H₂S:

The major purpose of this part of this thesis has been to compare the adsorption of SO₂ on Al₂O₃, and Na/Al₂O₃ and to compare the reactivity of chemisorbed SO₂ with H₂S on these catalysts. For pure Al₂O₃, the decrease in the intensity of the band near 1050 cm⁻¹ with the concomitant formation of water when H₂S was added has been reported by others [23, 25, 29] and by our laboratory (see chapter 3). However, we have shown that this species, although present to a greater extent on Na/Al₂O₃ than on Al₂O₃ (gravimetric, IR and Raman results), is less reactive to H₂S on Na/Al₂O₃, an effect which can be attributed to greater basicity of the Na/Al₂O₃ catalyst. That is, the sulfite is more strongly chemisorbed on Na/Al₂O₃ and its reactivity with H₂S is accordingly reduced. The TPD results confirm this trend; higher temperature are required to desorb sulfite from Na/Al₂O₃.

For Al₂O₃ and Na/Al₂O₃ the Raman results have shown that the generation of sulfur required the presence of chemisorbed SO₂ insofar as S₈ was only detected if H₂S was added to preabsorbed SO₂, and not if SO₂ was added to preabsorbed H₂S. Moreover, in the latter instance, sulfur was generated following the re-introduction of H₂S after addition of SO₂. Noting that SO₂, being a stronger acid than H₂S, can displace adsorbed H₂S from some surface sites (the SH band disappears), we conclude that the reaction to produce sulfur at room temperature on both of these catalysts involves the reaction of gaseous H₂S with chemisorbed SO₂.

Further speculation concerning the mechanism of the reaction to generated sulfur is unwarranted in the absence of additional experimental evidence. For example, we have shown that the shoulder near 1150 or 1200 cm⁻¹ disappear after contacting chemisorbed SO₂ with either H₂S or H₂O, the latter being a product of the reaction. Quite apart from not knowing the structure of these species, we can conclude nothing *via-à-vis* their reactivity with H₂S.

5. CONCLUSIONS

At room temperature, sulfur dioxide reversibly adsorbs on Al₂C₃, Na/Al₂O₃ as well as Cs/Al₂O₃, and we have concluded that weak basic sites are also implicated in the physisorption

process. In addition, at least two strongly chemisorbed species are produced. The major species on Al_2O_3 and $\text{Na}/\text{Al}_2\text{O}_3$ has a strong IR band near 1050 cm^{-1} and has been attributed to an adsorbed sulfite type species, probably involving an AlOSO_2 bond. This species is somewhat reactive with gaseous H_2S and leads to the formation of water and sulfur, two products of the modified Claus reaction. More sulfite is formed on $\text{Na}/\text{Al}_2\text{O}_3$ than on Al_2O_3 . However, the sulfite on the more basic $\text{Na}/\text{Al}_2\text{O}_3$ catalyst is more strongly chemisorbed than on pure Al_2O_3 , and it is less reactive with gaseous H_2S .

Sulfur is formed when gaseous H_2S is contacted with chemisorbed SO_2 , but not when gaseous SO_2 is contacted with chemisorbed H_2S . The decrease of reactivity after impregnation with a large quantity of sodium and cesium can be attributed to the greater stability of the sulfite species adsorbed on the more basic sites of alkali-containing catalysts [5] than the stability on pure Al_2O_3 , these sulfite species being considered as intermediates in the modified Claus reaction [23, 25, 29]. Zotin and Faro [5] proposed that the lower activity of a high sodium loaded alumina catalyst relative to pure alumina was due to either (i) the catalyst being too basic with excessive sodium or (ii) the need to have both acid and base sites, and sodium poisons the acid sites. We conclude that hypothesis (i) is more plausible; a greater basicity is not necessarily a favourable factor for the modified Claus reaction.

References

- [1]. George, Z. M., "Sulfur Removal and Recovery from Industrial Process", Adv. Chem. Series, 139, Ed. by Pfeiffer, J.B., Amer. Chem. Soc., Washington D. C., 1975, p75.
- [2]. Karge, H. G., Tower, R. W., Dudzik, Z. and George, Z. M., Stud. Surf. Sci. Catal., 7, 643(1981).
- [3]. Scokart, R. O., Amin, A., Defosse, C. and Rouxhet, P. G., J. Phys. Chem., 86, 1406(1981).

- [4]. Berteau, P., Kellens, M.-A. and Delmon, E., J. Chem. Soc. Faraday Trans., 87, 1425(1991).
- [5]. Zotin, J. L. and Faro, A. C., Catal. Today, 5, 423(1989).
- [6]. Nakamoto, K., "Infrared and Raman spectra of Inorganic and Coordination compounds", 4th Edition, John Wiley & Sons, New York, 1986.
- [7]. Lavalley, J. C., Janin, A. and Preud'homme, J. React. Kinet. Catal. Lett., 18, 85(1981).
- [8]. Morterra, C., Zecchina, A., Coluccia, S. and Chiorino, A., J. Chem. Soc., Farad. Trans. I, 73, 1544(1977).
- [9]. Saur, O., Chevreau, T., Lamotte, J., Travert, J. and Lavalley, J. C., J. Chem. Soc., Farad. Trans. I, 77, 427(1981).
- [10]. Lavalley, J. C., Mohammed Saad, A. B., Tripp, C. P. and Morrow, B. A., J. Phys. Chem., 90, 908(1986).
- [11]. Mohammed Saad, A. B., Saur, O. and Lavalley, J. C., private communication.
- [12]. Knözinger, H. and Ratnasamy, P., Catal. Rev. Sci. Eng., 17, 31(1978).
- [13]. Morrow, B. A., Stud. Surf. Sci. and Catal., 57A, 161(1990).
- [14]. Zecchina, A., Coluccia, S. and Morterra, C., Appl. Spectrosc. Rev., 21, 250(1985).
- [15]. Mohammed Saad, A. B., Ivanov, V. A., Lavalley, J. C., Nortier, P. and Luch, F., Appl. Catal., 94, 71(1993).
- [16]. Henrich, V. E. and Cox, P. A., "The Surface Science of Metal Oxides", Cambridge University Press, Cambridge, U. K., 1994.
- [17]. Vordonis, L., Koutsoukos, P. G. and Lycourghiotis, A., J. Catal., 98, 296(1986).
- [18]. Deo, D. V., Dalla Lana, I. E. and Habgood, H. W., J. Catal., 21, 270(1971).
- [19]. Ivanov, V. A., Pieplu, A., Lavalley, J. C. and Nortier, P., Applied Catal. A: General, 131, 323(1995).
- [20]. Fledorow, R. and Dalla Lana, I. G., J. Phys. Chem., 84, 2779(1980).
- [21]. Belopukhov, S. L., Dmitrevsky, L. L., Knyazev, D. A., Kochits, V. A., Koord. Khim. USSR, 13, 1047(1987).
- [22]. Waqif, M., Mohammed Saad, A. B., Bensitel, M., Baxhelier, J., Saur, O. and Lavalley, J. C., J. Chem. Soc., Farad. Trans., 88, 1931(1992).
- [23]. Karge, H. G. and Dalla Lana, I. G., J. Phys. Chem., 88, 1538(1984).

- [24]. Chang, C. C., J. Catal., 53, 374(1978).
- [25]. Karge, H. G., Dalla Lana, I. G., Trevisan De suarez, S. and Zhang, Y., Proceed. 8th Intern. Congr. Catal., Berlin, 1984, vol. III, 453.
- [26]. Datta, A., Cavell, R. G., Tower, R. W. and George, Z. M., J. Phys. Chem., 89, 443(1985).
- [27]. Sato, S., Higuchi, S. and Tanaka, S., Appl. Spectrosc. 39, 822(1985).
- [28]. Meyer, B., Spectrochimica Acts, 53A, 345(1979).
- [29]. Datta, A. and Cavell, R. G., J. Phys. Chem., 98, 454(1985).

Chapter 5

SODIUM SILICA CATALYST (Na/SiO₂)

1. INTRODUCTION

It is known that pure silica is inactive for the Claus process but silica impregnated with sodium catalyzes the Claus reaction [1,2]. The purpose of this work is to find out the effect and the function of sodium on the Claus reaction. Another goal is to find possible common features between Na/SiO₂ and Al₂O₃ or Na/Al₂O₃, the last two having been discussed in the previous chapters. The advantage of using Na/SiO₂ in studying the Claus process is that this catalyst has "two windows" of partial transparency between 500 and 1000 cm⁻¹, which is important in identifying SO_x angle deformation vibrations (500-700 cm⁻¹) and S-S stretching vibrations (400-700 cm⁻¹). This region is opaque for Al₂O₃ and most other oxides used in Claus catalysis. In order to understand the Na/SiO₂ catalyst and prepare for the work to be described in chapter 9 in which surface hydroxyl groups will be studied, we will give here a brief review of the nature of silica.

(1). Silica

Synthetic amorphous silica is an important catalyst and catalyst support, and it is also used in other applications as rubber fillers, and as a stationary phase for chromatography. There are some excellent reviews about silica [3-7]. Natural silica has limited uses because of its low surface area (about 30 m²/g). Three kinds of synthetic silica exist, silica gel, precipitated silica and pyrogenic or aerosil silica. In this work, aerosil type silica has been used.

Precipitated silica and silica gel are prepared in the liquid phase. They are usually produced by the hydrolysis of Na₂SiO₃, SiCl₄ and Si(OC₂H₅)₄ under acid conditions. Aerosil silica, on the other hand, is produced in the gas phase by burning SiCl₄ in a hydrogen-oxygen flame at about

1000 to 1100°C. The ratio of the three components determines the particle size and surface characteristics of these so-called pyrogenic or fumed silicas [8].

For silica gel and precipitated silica, the properties depend on the sizes of the micropores and on the types of hydroxyl groups on the surface and in the pores [9-12]. For aerosil, because it lacks micropores its properties depended mainly on the particle size and on the concentration of the different types of hydroxyl groups on the surface.

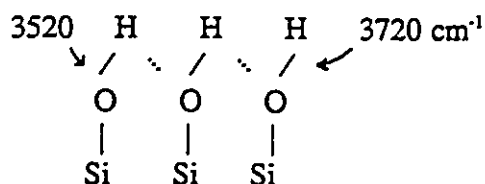
The bulk structure of all amorphous silicas consist of SiO_4 units which are covalently linked to each other by oxygen atoms in a continuous network but in a random way [13]. X-ray diffraction studies show clearly that there is no long range order and that the Si-O-Si bond angles may change considerably [14].

It has been found that aerosil has the following infrared bands (cm^{-1}) after activation at 50-150 °C [15-17]: (See Fig 5.1 and Fig 5.2)

<u>3747</u>	<u>3720</u>	<u>3650</u>	<u>3520</u>	<u>1850</u>	<u>1630</u>	<u>1100</u>	<u>800</u> cm^{-1}
O-H stretches				combinations		Si-O-Si stretches	

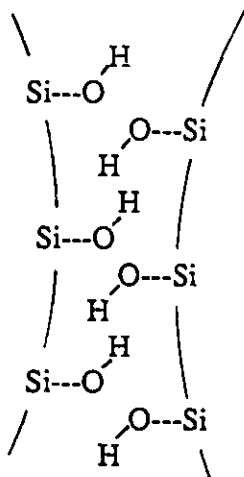
(a) The 3747 cm^{-1} band is well established as being due to isolated surface hydroxyl groups which do not interact with neighbouring hydroxyls [15-17].

(b) The 3720 and 3520 cm^{-1} bands are assigned as the free and H-bonded silanols of a pair or chain of adjacent silanols:

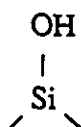


During thermal dehydroxylation, adjacent hydroxyls may condense to liberate water, a point which will be discussed further later.

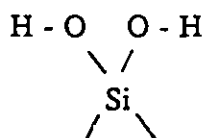
(c) The 3650 cm^{-1} band is relatively weak and broad and is attributed to hydroxyls which are perturbed due to interparticle contact. These hydroxyls are generally inaccessible to most hydrogen sequestering agents which are capable of reacting with other accessible hydroxyls [16, 18].



Any of the above hydroxyl groups may be singly attached to a silicon atom (single OH groups) or be doubly attached to a silicon atom (geminal hydroxyl groups) [6, 15-18]:



single



geminal

(d) The intense bands around 1100 and 800 cm^{-1} are due to bulk Si-O-Si stretching vibrations (Fig 5.2). X-ray diffraction has shown that Si-O-Si bond angle variation may be as large as 20° from the average angle of 144° [14].

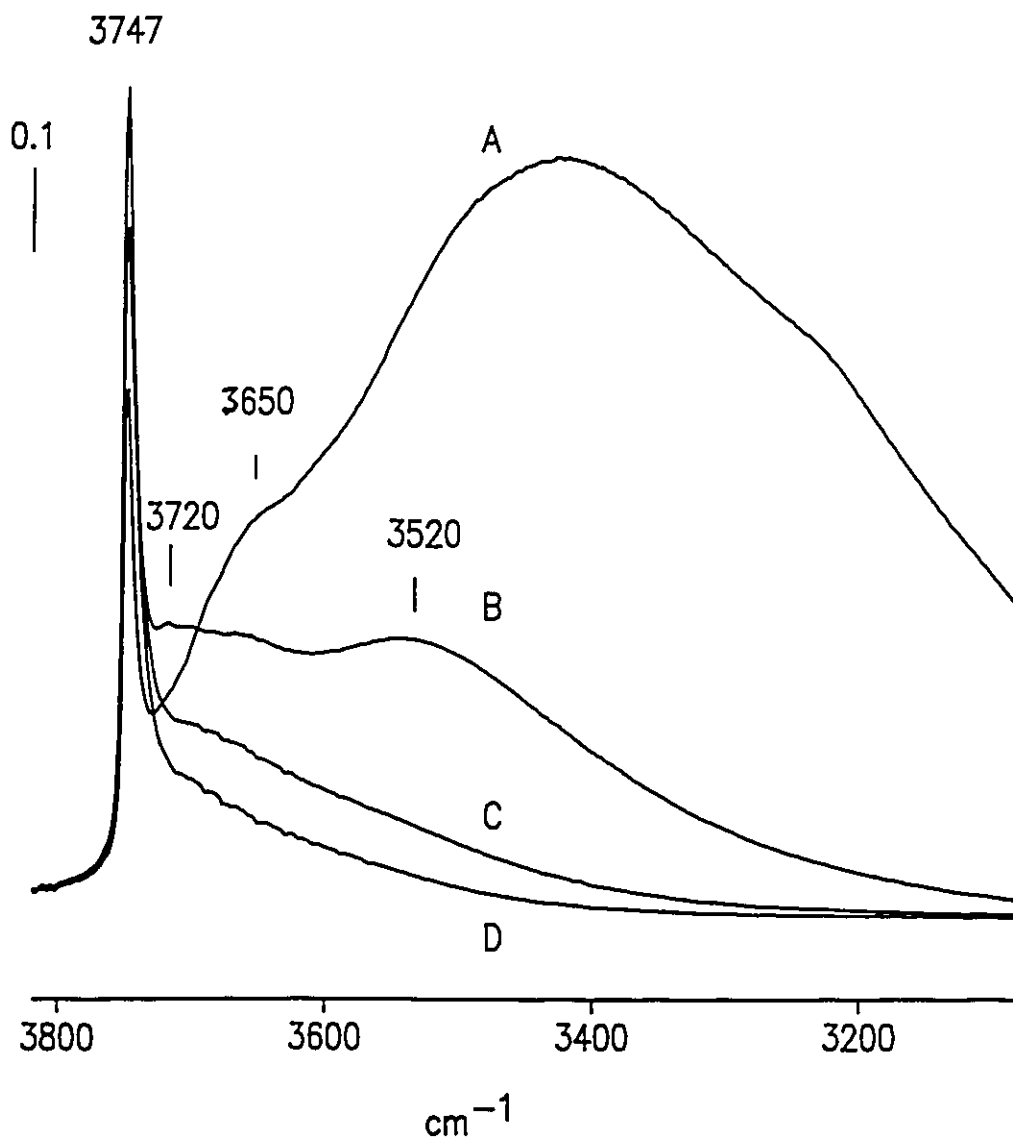


Fig 5.1 Infrared spectra of silica in SiO-H stretching region

- (A). 50 mg of SiO_2 (no treatment).
- (B). after evacuation for 1 hour at 25 °C.
- (C). after evacuation for 1 hour at 300 °C.
- (D). after evacuation for 1 hour at 450 °C.

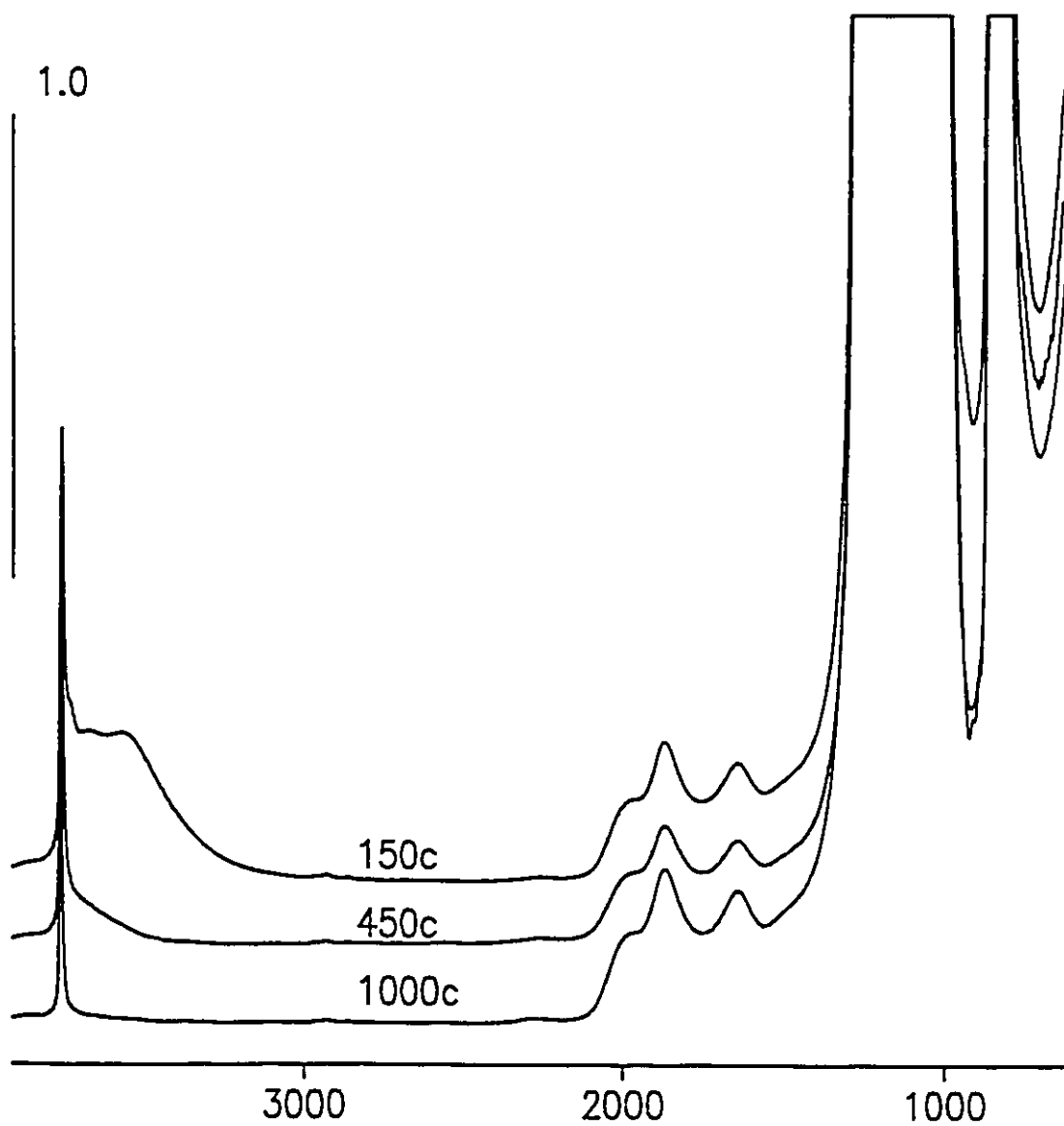
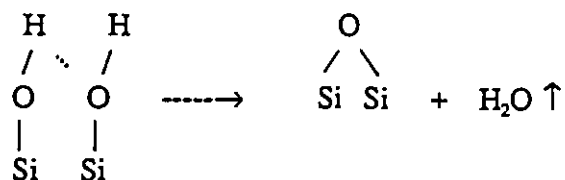


Fig 5. 2 Silica spectra
 SiO_2 (Cab-O-Sil) 50 mg, activated at different temperatures under vacuum.

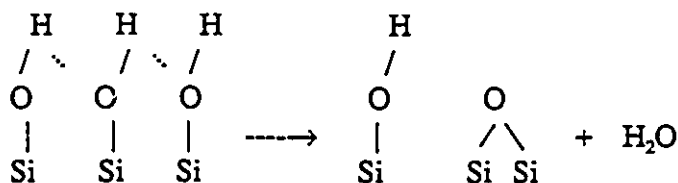
(2). Dehydroxylation of Silica

The infrared spectrum of water which is physically adsorbed on silica has a very a broad peak near 3450 cm^{-1} (symmetric and antisymmetric OH stretching modes, see Fig 5.1 A) and a band at 1620 cm^{-1} which is due to the angle deformation mode. The amount of adsorbed water depends on the concentration of surface hydroxyl groups. Physically adsorbed water can be desorbed from typical samples of aerosil type silicas after evacuation for 1 hour (Fig 5.1 B). This has been confirmed by infrared and gravimetric studies [18].

Further evacuation under vacuum in the temperature range from room temperature to about $150\text{ }^{\circ}\text{C}$ does not alter the infrared spectrum of aerosil [18]. However, evacuation at temperatures above $150\text{ }^{\circ}\text{C}$ results in the evolution of water which is generated by the collapse of hydrogen-bonded adjacent silanol groups, as follows: (see also Fig 5.1 C,D)

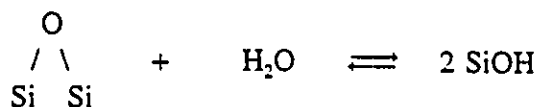


The majority of the H-bonded silanols are removed if the silica is heated for 1 h at 450°C , whereas evacuation up to this temperature has no effect on the initial number of isolated silanols (3747 cm^{-1} band). However, if there are an odd number of silanol groups, then after collapse of H-bonded pairs there is a residual isolated silanol and this results in an increase in the intensity of the isolated silanol band at 3747 cm^{-1} .

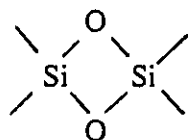


The elimination of the vicinal silanols at temperatures up to $450\text{ }^{\circ}\text{C}$ creates siloxane bridges

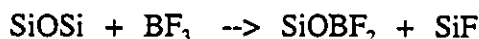
which can be reversibly rehydroxylated when water is added at room temperature.



On the other hand, heating under vacuum at temperatures above 450 °C, and particularly at 800 °C or higher, causes elimination of the isolated silanols and gives rise to the appearance of two new bands at 908 and 888 cm⁻¹ in the infrared spectrum which are due to highly strained four membered siloxane rings [15, 19, 20].



These groups are very reactive and the strained siloxane bond can be broken as a result of the dissociative chemisorption of some volatile metal halogen or metal alkyl type species, for example, the reaction with BF₃ being as follows [21]:



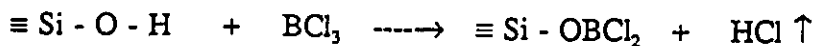
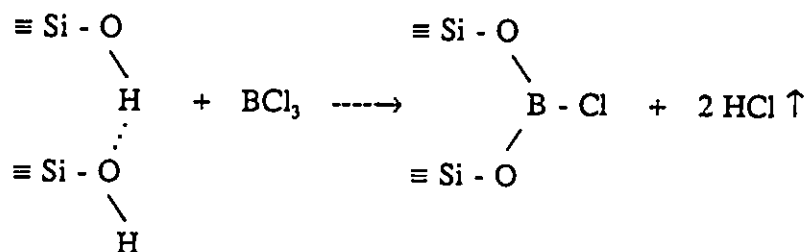
The site also reacts with NH₃ or alcohols (ROH) to produce SiOH and either SiNH₂ or SiOR [19,22].

(3). *Measurement of the -OH groups*

The hydroxyl concentration (OH groups per nm²) can be measured by a variety of methods, and a summary of the results for numerous silicas has been given by Zhuravlev [23]. It is apparent that the surface of all silicas of whatever origin, when fully hydroxylated, contain about 4.6 to 5 OH groups/nm². The silica used in this work contains about 1.4 OH groups per nm² after activation in vacuum at 450 °C [18].

Prior work in our laboratory has been aimed at measuring the number of hydroxyl groups which are accessible to various hydrogen sequestering agents of varying steric dimension, such as, AlMe₃, GaMe₃, BCl₃, TiCl₄, ZnMe₂ and (Me₃Si)₂NH [16,18]. For example, BCl₃ might react

with H-bonded or single hydroxyls differently, as illustrated below:



The work to be described in Chapter 9 is concerned with the measurement of the reactivity of antimony pentamethyl, SbMe_5 , with the silanol groups on silica.

2. EXPERIMENTAL

The Na/SiO_2 samples were prepared by impregnation of Cab-O-Sil HS-5 ($325 \text{ m}^2/\text{g}$) from the solutions of NaOH or CH_3COONa , the quantities of sodium compounds being chosen so as to give a dried sample which contain 3% sodium by weight. The wet slurries were dried overnight in an oven at about 110°C and the dried mass was ground in a mortar and stored for further use. Thereafter, different samples were prepared from this stock by calcining at different temperatures. For example, $\text{Na/SiO}_2(150)$ and $\text{Na/SiO}_2(450)$ samples were calcined in air at 150 or 450°C for 4 hours. A disc was then prepared and these samples were activated in vacuum for 1 h at 150 or 450°C respectively. After impregnation and drying at different temperature, the specific surface areas of the catalysts were as follows:

$\text{SiO}_2(\text{pure})$	450°C	$325 \text{ m}^2/\text{g}$
Na/SiO_2	150°C	$170 \text{ m}^2/\text{g}$
Na/SiO_2	450°C	$130 \text{ m}^2/\text{g}$

The Na/SiO_2 samples from CH_3COONa usually had a higher specific surface area than those from NaOH . For example, the $\text{Na/SiO}_2(450)$ from NaOH had a BET surface area $100 \text{ m}^2/\text{g}$ and

that from CH_3COONa was $130 \text{ m}^2/\text{g}$. For $\text{Na/SiO}_2(150)$ sample, NaOH is the only source of Na^+ because CH_3COONa molecule does not decompose at 150°C . No infrared differences between two kinds of $\text{Na/SiO}_2(450)$ were observed. The IR spectra shown in this chapter were all obtained from the sodium acetate preparation if activation temperature is over 300°C .

For infrared studies, sample discs containing about 6 to 10 mg/cm^2 of Na/SiO_2 were pressed in a die at a pressure of about 10^7 Pa before being mounted in the infrared cell. All of the reactants were obtained from commercial sources and precautions were taken to ensure that no water was present. Infrared spectra were recorded either on a Bomem DA3-02 or Michelson MB-100 FTIR at a resolution of 4 cm^{-1} .

Raman spectra were recorded using a dispersive Jobin-Yvon HG2 double monochromator using a Spectra Physics argon or krypton ion laser. Power level at the sample varied from about 30 mW to 1000 mW . In all cases a 90° scattering geometry was employed and the resolution was about 6 cm^{-1} . For studying the Raman spectra of sodium salts, a small quantity of each salt was generally pressed into a small disc which was inserted in a quartz cell for appropriate vacuum treatment. For studying the Na/SiO_2 samples, about 100 mg of catalyst was generally pressed into a 12 mm diameter disc and then mounted in the Raman cell. All of the Raman results were obtained by Carl Tripp in our laboratory [24].

3. RESULTS

(1). *Spectra of SiO_2 and Na/SiO_2*

The background spectrum of pure silica in the 500 to 4000 cm^{-1} spectral region after activation in vacuum at 150 , 450 and 1000°C are shown in Figure 5.2, and Figure 5.3 shows that of $\text{Na/SiO}_2(450)$ and $\text{Na/SiO}_2(150)$. The sharp band at 3747 cm^{-1} is due to isolated SiOH groups, and the strong totally absorbing broad features centred at 1150 and 800 cm^{-1} are due to SiOSi modes of silica. In both cases, the SiO-H band shapes were similar for both pure and Na doped SiO_2 but the SiO-H bands intensities were much lower on the Na doped SiO_2 , suggesting that SiOH may have been partially replaced by SiONa . Below 1300 cm^{-1} , the only accessible spectral

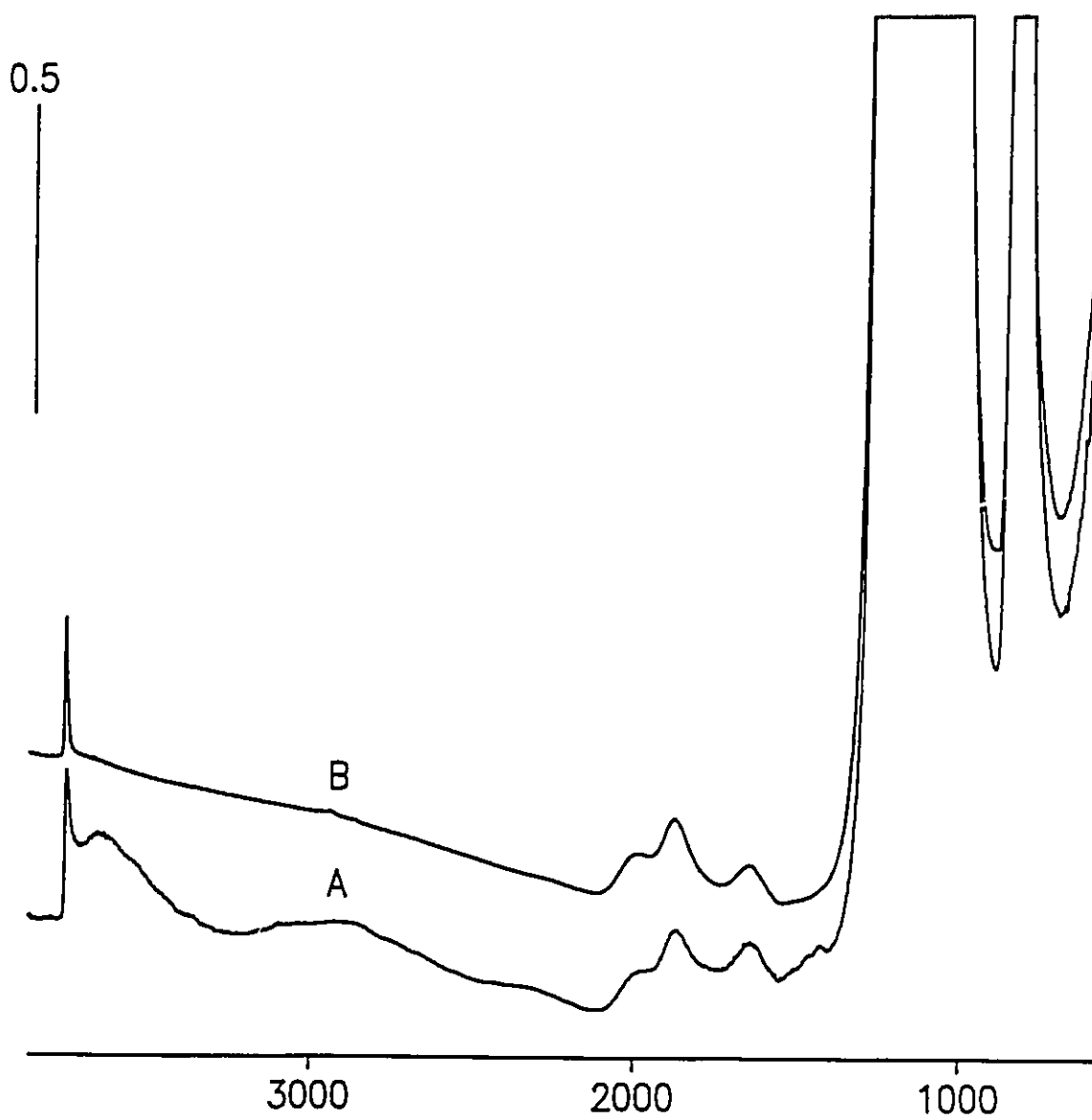


Fig 5. 3 Spectra of Na/SiO₂
(A). 50 mg, activated at 150 °C under evacuation for 1 hour.
(B). 50 mg, activated at 450 °C under evacuation for 1 hour.

regions are in the two 'windows' of partial transmission between 1000 and 870 cm^{-1} and from 750 to 550 cm^{-1} . As will be discussed further, the latter region proved to be the more useful from the diagnostic point of view.

We have verified that none of the reactants, SO_2 and H_2S alone or in any combination gave rise to new features in this region (1000-500 cm^{-1}) when absorbed on pure silica activated at any temperature (150 $^{\circ}\text{C}$ to 1000 $^{\circ}\text{C}$).

The characteristic vibrational frequencies associated with inorganic SO_x and SH containing species (whether ionic or not) are as follows: SH stretching vibrations, 2500-2600 cm^{-1} ; SO_x stretching vibrations, 950-1250 cm^{-1} ; SO_x angle deformation vibrations, 500-700 cm^{-1} ; S-S stretching vibrations, 400-700 cm^{-1} . Therefore, in view of the opacity of SiO_2 from about 1000 cm^{-1} to 1300 cm^{-1} , the infrared study of adsorbed sulfur species has been mainly restricted to the SH stretching region and to the S-S stretching and SO_x deformation region below 700 cm^{-1} . We will first discuss the results of various systems, and the basis of most of the spectroscopic assignments will from part of the Discussion.

(2). Adsorption of SO_2

The infrared spectrum following addition of SO_2 to Na/SiO_2 produced a well defined peak at 657 cm^{-1} accompanied by a broad absorption near 620 cm^{-1} , shown in Figure 5.4. (This feature can be seen more clearly after subtraction of the silica background (Fig 5.4 B-A) and the remaining IR spectra will be presented in this format.) Evacuation decreased the intensity of the 657 cm^{-1} band revealing more clearly a band at 635 cm^{-1} (Fig 5.5 C). Addition of water provoked an increase in the intensity of the 635 cm^{-1} band whereas that at 657 cm^{-1} decreased and finally disappeared (Fig 5.5 D-F). If this sample was subsequently heated under vacuum, the 635 cm^{-1} band only significantly started to decrease in intensity after heating at 300 $^{\circ}\text{C}$, but it was still distinctly present after heating at 500 $^{\circ}\text{C}$. Re-addition of SO_2 caused the reappearance of the 657 cm^{-1} band without a significant decrease in the intensity at 635 cm^{-1} . Finally, following adsorption of S^{18}O_2 , the 657 cm^{-1} band shifted to 640 cm^{-1} , and following addition of

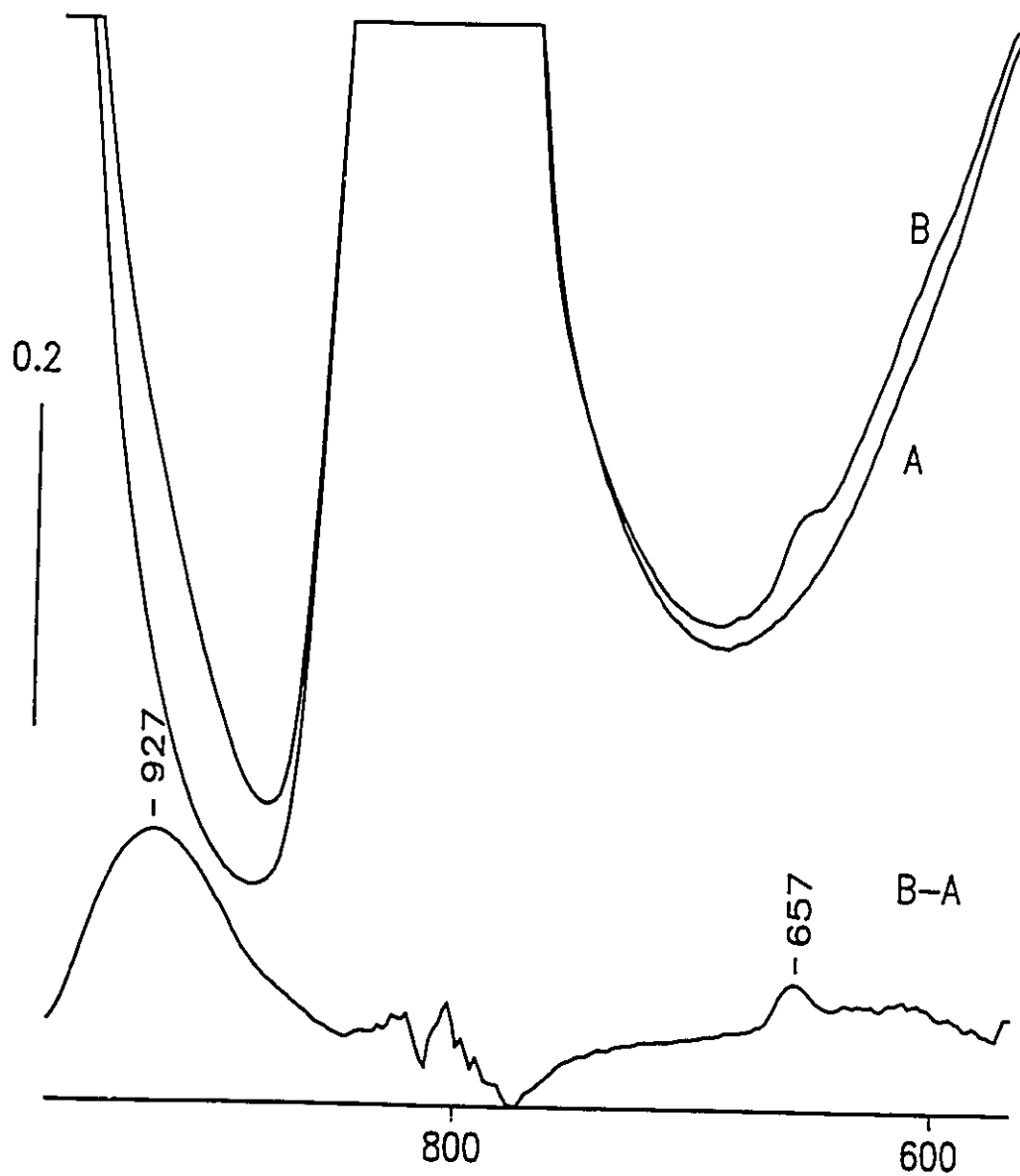


Fig 5. 4 The spectra of Na/SiO₂ in two "window" regions

- (A). Na/SiO₂ after activated at 450 °C.
- (B). add 4.32 Torr SO₂.
- (B-A). difference spectrum.

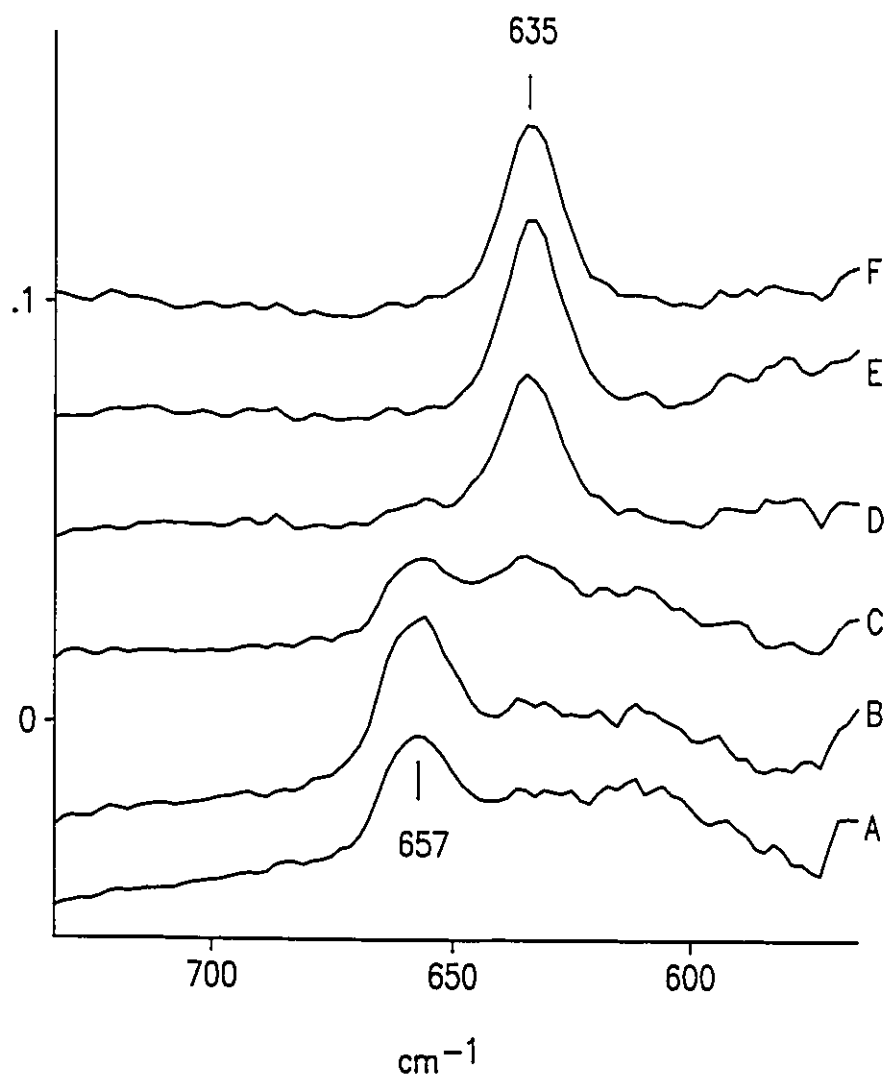


Fig 5. 5 Adsorption of SO_2 on Na/SiO_2 (difference spectra)

- (A). add 4.32 Torr of SO_2 on 30 mg SiO_2 .
- (B). after 30 minutes.
- (C). evacuate for 5 minutes.
- (D). add 1.71 Torr of H_2O .
- (E). after 30 minutes.
- (F). evacuate for 5 minutes.

H_2^{18}O , the 635 cm^{-1} band appeared at 611 cm^{-1} .

Saad [25] used Na/SiC instead of Na/SiO₂ in the same experiments. With the Na/SiC sample the region below 600 cm^{-1} is more accessible and it showed that, under the same experimental conditions, the 657 cm^{-1} band was accompanied by low wavenumber bands at 559 and 446 cm^{-1} . Introduction of successive doses of water confirmed that these bands diminished in intensity as new bands appeared at 635 and 495 cm^{-1} . The re-addition of SO₂ caused the bands at 657 , 559 and 446 cm^{-1} to reappear without a significant decrease in intensity at 635 cm^{-1} .

No new IR bands were observed above 1300 cm^{-1} and, in the 1000 to 850 cm^{-1} spectral region, only a broad continuous absorption was observed after spectral subtraction during adsorption of SO₂ (Fig 5.4 B-A). This broad band persisted during the experiments to be described later and no diagnostic information could be obtained. For this reason, only the spectra which were observed in the 750 - 550 cm^{-1} spectral region will be shown hereafter.

(3). Adsorption of H₂S

The addition of H₂S to Na/SiO₂ caused the appearance of very weak IR band at 2590 cm^{-1} which is due to a SH stretching mode, these modes being very weak in the infrared; there was also a very broad band near 3000 cm^{-1} and sharp band at 1620 cm^{-1} which indicates that water was formed as a reaction product (Fig 5.6). In the Raman spectrum, addition of H₂S to solid NaOH give rise to a very strong band at 2540 cm^{-1} . Solid NaSH has a strong Raman band at this wavenumber [24].

(4). Adsorption of SO₂ followed by H₂S

Figure 5.7A shows a characteristic spectrum of SO₂ chemisorbed on Na/SiO₂. It has a relatively distinct peak at 657 cm^{-1} with a weaker broad band to lower wavenumber. Following the addition of H₂S the spectrum was transformed into that shown in Fig 5.7C. It has two peaks at 645 and 680 cm^{-1} , and there was a band due to the deformation mode of water at 1620 cm^{-1}

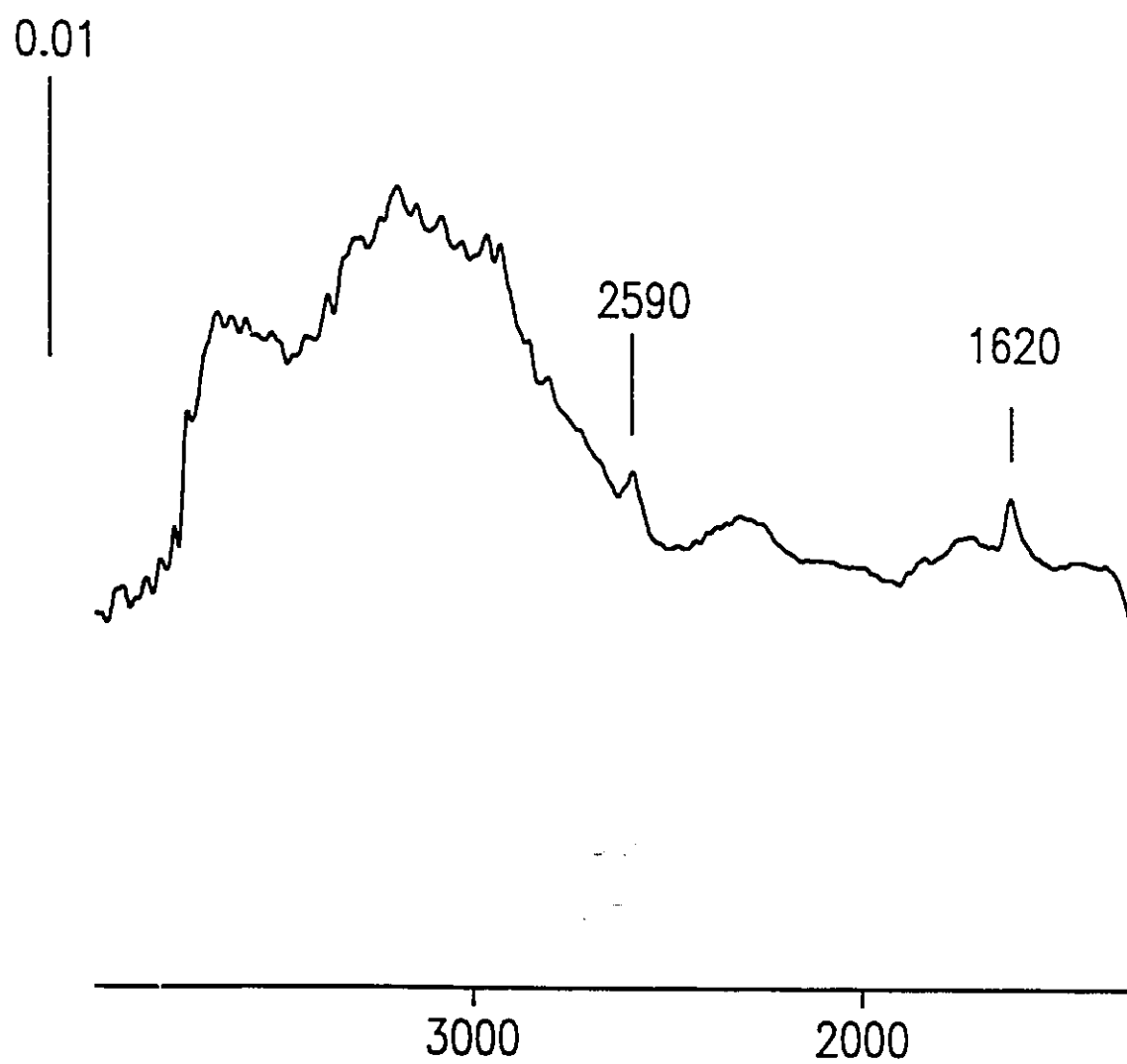


Fig 5.6 The adsorption of H_2S on $\text{Na/SiO}_2(450)$

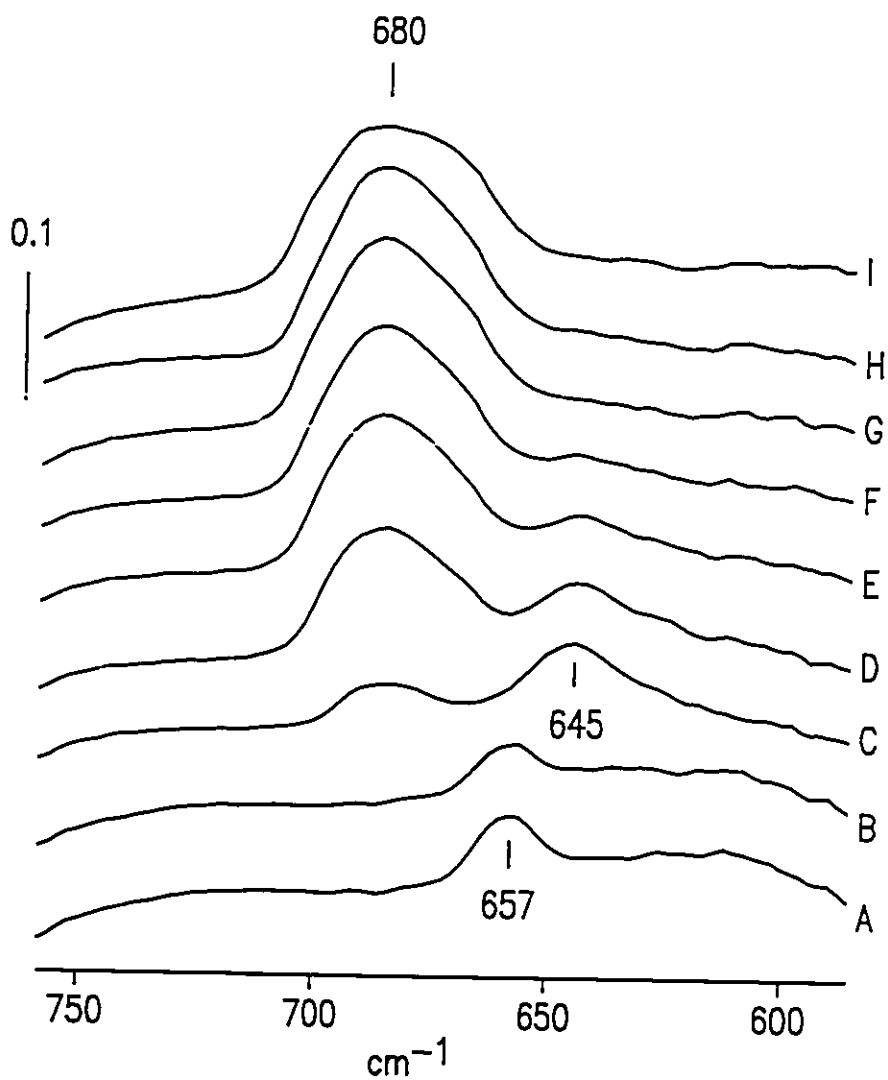


Fig 5.7 Adsorption of SO_2 , and then H_2S

(A). add 5 Torr of SO_2 and after 30'.
 (C). add 0.60 Torr of H_2S .
 (E). after 15'.
 (G). after 120'.
 (I). add 3.00 Torr of H_2O .

(B). after evacuation for 5'.
 (D). after 5'.
 (F). after 30'.
 (H). after evacuation for 30'.

(not shown). With longer contact time the 645 cm^{-1} peak gradually disappeared and those at 680 and 1620 cm^{-1} intensified (see Fig 5.7 C-G). The 680 cm^{-1} band did not change following evacuation, or following the addition of an excess of water vapour at room temperature, evacuation of the water, and subsequent heating to $150\text{ }^{\circ}\text{C}$. However, heating at near $200\text{ }^{\circ}\text{C}$ caused the 680 cm^{-1} band to diminish in intensity and it disappeared if heated in the range from $200\text{ }^{\circ}\text{C}$ to $300\text{ }^{\circ}\text{C}$ and a yellowish deposit appeared on the cell walls. The band positions did not change when D_2S was substituted for H_2S , whereas with S^{18}O_2 , the bands previously at 680 and 645 cm^{-1} after addition of H_2S now appeared near 668 and 630 cm^{-1} (not shown). Experiments with Na/SiC in Lavalley's laboratory [25] showed that the band noted above at 680 cm^{-1} was accompanied by a broad lower wavenumber band at 555 cm^{-1} .

We have also investigated the sensitivity of the 635 cm^{-1} band to H_2S . As discussed previously, the addition of H_2O to Na/SiO_2 pretreated with SO_2 gave a strong band at 635 cm^{-1} . Addition of H_2S at room temperature to this sample caused a slight decrease in the intensity at 635 cm^{-1} and the appearance of a weak band at 680 cm^{-1} (Fig 5.8). Notably, no band appeared at 645 cm^{-1} . With time, the 635 cm^{-1} band decreased in intensity and that at 680 cm^{-1} intensified and it was accompanied by a shoulder at 700 cm^{-1} . Heating to $50\text{ }^{\circ}\text{C}$ did not modify the spectrum, but upon heating at $100\text{ }^{\circ}\text{C}$ the 680 cm^{-1} band doubled in intensity and that at 635 cm^{-1} decreased. Finally, heating to about $200\text{ }^{\circ}\text{C}$ eliminated the 635 cm^{-1} band and approximately halved the intensity of that at 680 cm^{-1} .

(5). Adsorption of H_2S followed by SO_2

If SO_2 was added to chemisorbed H_2S on Na/SiO_2 the 680 cm^{-1} and 645 cm^{-1} bands appeared immediately although the latter was asymmetric to low wavenumber (Fig 5.9C). After 5 minutes a band emerged at 623 cm^{-1} followed by another near 605 cm^{-1} . With longer contact time, the band initially at 645 cm^{-1} shifted to about 650 cm^{-1} and decreased in intensity whereas those at 605 and 680 cm^{-1} intensified and that at 623 cm^{-1} weakened (Fig 5.9 A-H).

Evacuation at room temperature after 2 hours reaction did not alter the spectrum, except that

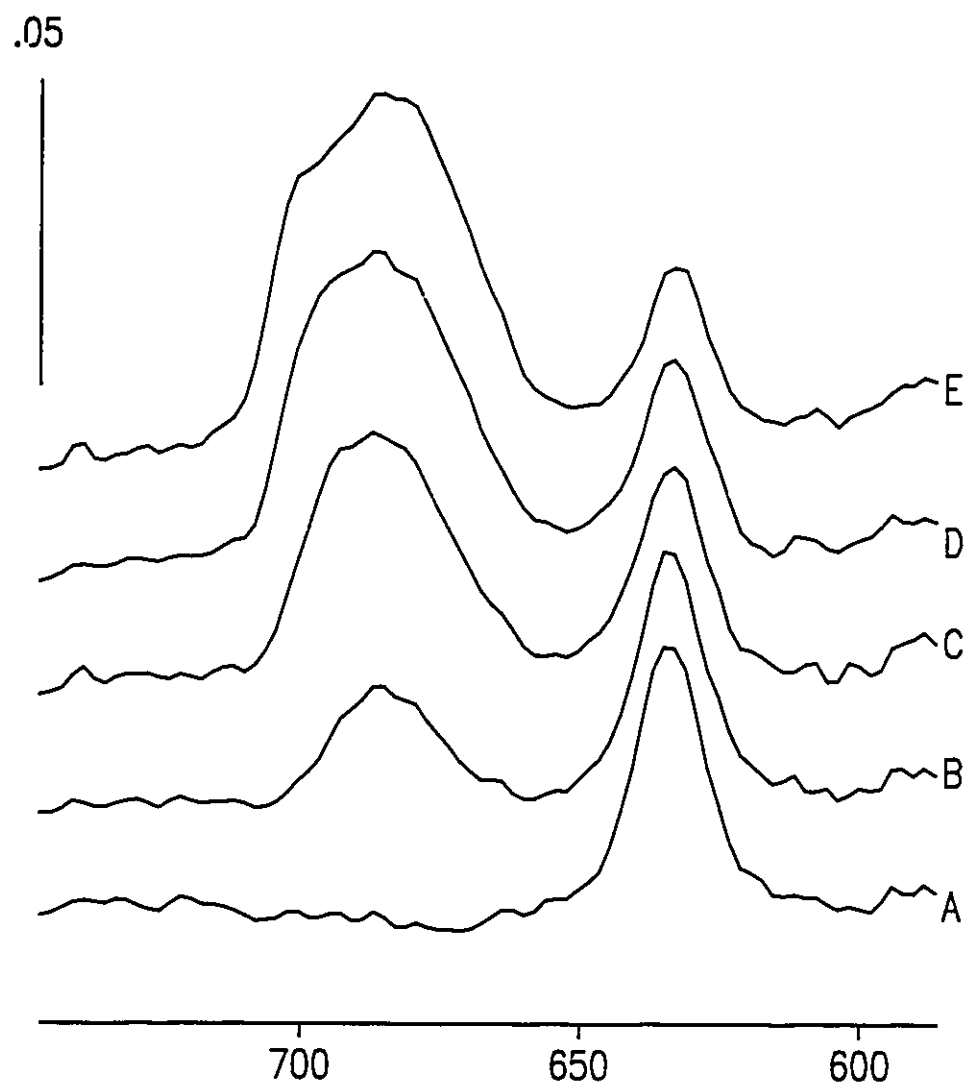


Fig 5. 8 Adsorption of SO_2 , then H_2O and H_2S

(A) After addition of 4.32 Torr of SO_2 and evacuation for 5', 1.71 Torr of H_2O is added to 20 mg of $\text{Na/SiO}_2(450)$; (B) after addition of 3.75 Torr of H_2S ; (C) 5' later; (D) 15' later; (E) 1 hour later.

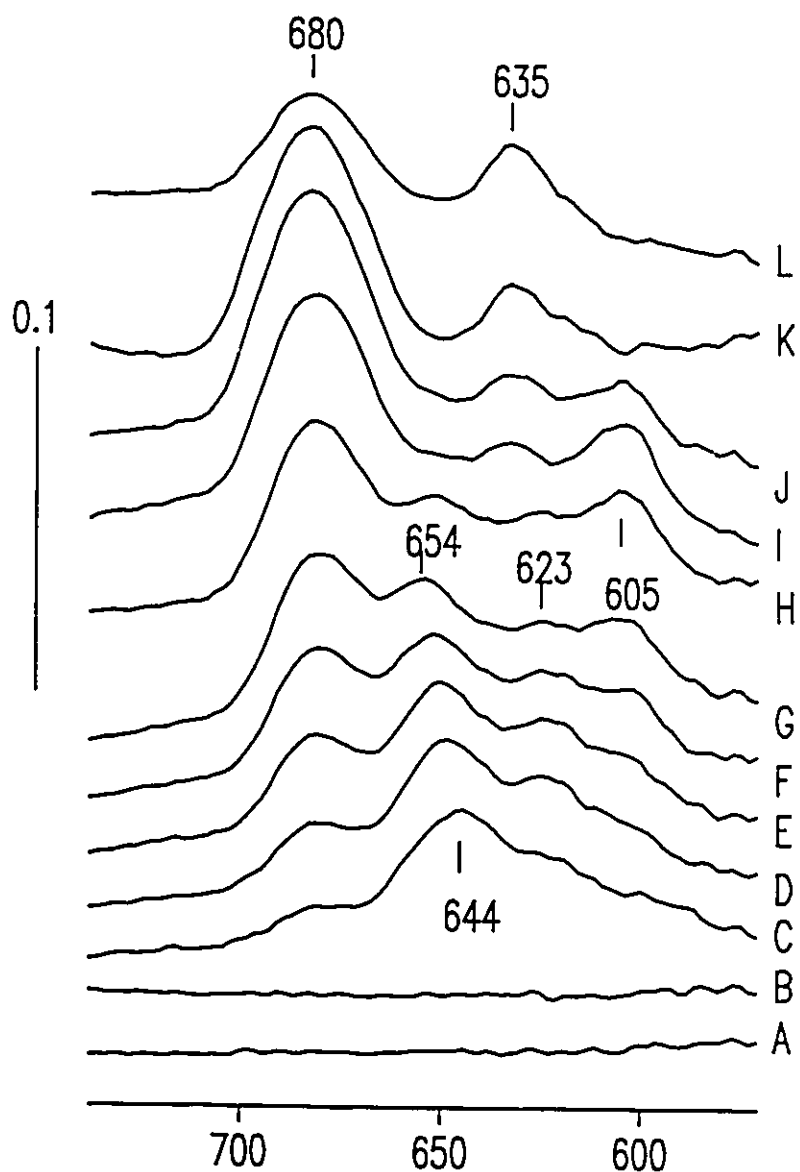


Fig 5.9 Adsorption of H_2S , then SO_2

- | | |
|---|-----------------------------------|
| (A). add 3.40 Torr of H_2S for 30'. | (B). evacuate for 5'. |
| (C). add 0.42 Torr of SO_2 . | (D). after 5'. |
| (E). after 15'. | (F). after 30'. |
| (G). after 60'. | (H). evacuate for 5'. |
| (I). heat at 50 °C for 0.5 hour. | (J). heat at 100 °C for 0.5 hour. |
| (K). heat at 150 °C for 0.5 hour. | (L). heat at 250 °C for 0.5 hour. |

water was removed (Fig 5.9H). Heating under vacuum at between 100 °C and 150 °C caused the disappearance of the bands at 650, 623 and 605 cm^{-1} (Fig 5.9 I-L) and the appearance of a new band at 635 cm^{-1} . Heating at about 300 °C resulted in the decrease in the intensity of the 680 cm^{-1} band as noted previously, whereas that at 635 cm^{-1} was present, albeit weaker, and it could be observed even after heating at 400 °C.

(6). *Adsorption of a mixture of $\text{H}_2\text{S}/\text{SO}_2$*

We have studied the adsorption of a 2:1 mixture of $\text{H}_2\text{S}/\text{SO}_2$ on Na/SiO_2 , and the spectra are shown in Fig 5.10. Bands at 645 and 680 cm^{-1} appeared immediately upon introduction of the mixture and there was little additional change over the following hour except for a general intensity increase and the appearance of a very weak band near 605 cm^{-1} and a shoulder at 623 cm^{-1} . Although not shown, the IR band due to water appeared initially and continued to grow in intensity over the following hour. The spectrum did not change after heating at 50 °C (Fig 5.10 G), but following heating at 150 °C the 645 cm^{-1} band disappeared, that at 680 cm^{-1} approximately doubled in intensity, and there was a yellow deposit of sulphur on the cell walls.

4. DISCUSSION

(1). *Spectra of known oxysulfur species*

In order to interpret the spectra observed from the adsorption of various sulphur species on the Na/SiO_2 catalysts, we have relied on the group frequency concept as it applies to sodium salts of known structure. It is important to realize that the solution chemistry of the oxyanions of sulfur is exceedingly complex and is still not well understood. For example, SO_2 when dissolved in water gives a complex mixture, sometime called sulfurous acid (H_2SO_3) for convenience, but this species has never been isolated and identified. Rather, the solution is reported to contain hydrated SO_2 and the ions H_3O^+ , $\text{S}_2\text{O}_3^{2-}$ and HSO_3^- with very small amounts of SO_3^{2-} and HOSO_2^- . Additionally, when H_2S and SO_2 are both dissolved in water, a complex solution, called 'Wackenroder's liquid' (see chapter 3) [26, 27] is produced which stoichiometrically leads to the formation of elemental sulphur via a reaction

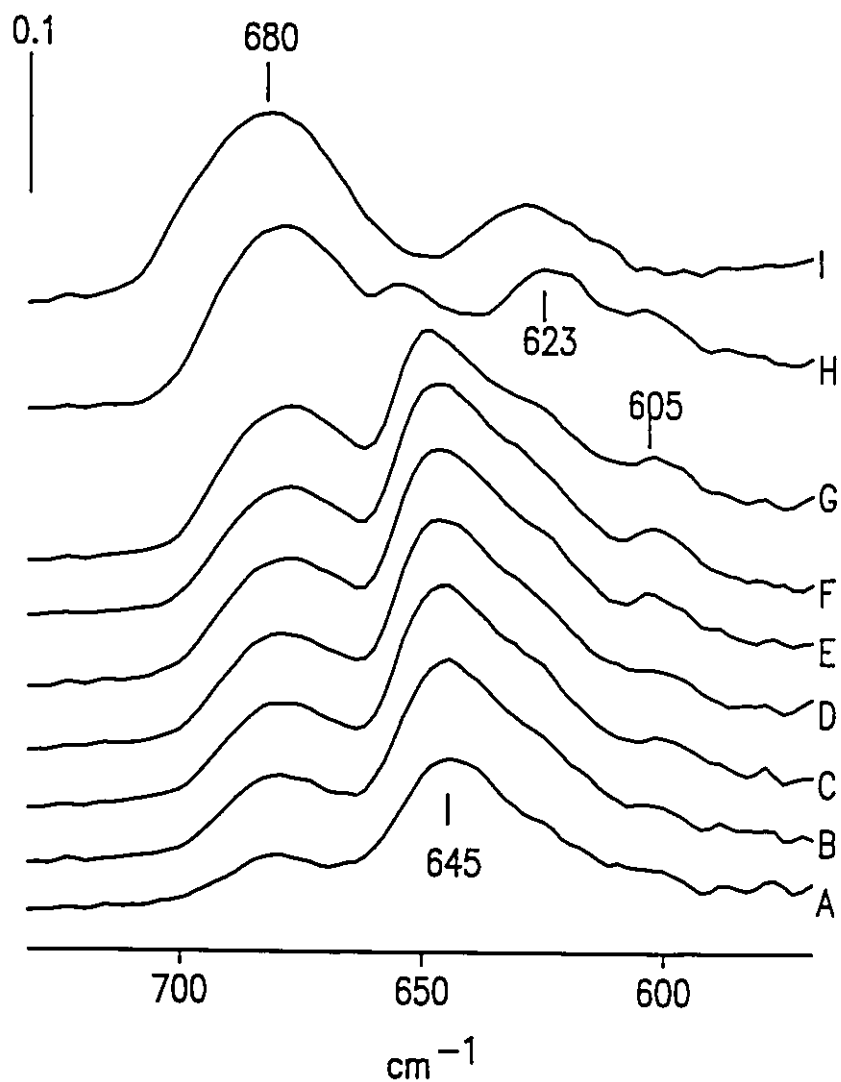
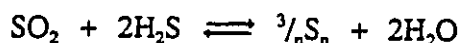


Fig 5.10 Adsorption of a mixture of $\text{H}_2\text{S}/\text{SO}_2$

- | | |
|------------------------------------|-------------------------------|
| (A). add 1.20 Torr of mixture gas. | (B). after 5'. |
| (C). after 15'. | (D). after 30'. |
| (E). after 60'. | (F). evacuate for 5'. |
| (G). heat at 50 °C for 1 hr. | (H). heat at 100 °C for 1 hr. |
| (I). heat at 150 °C for 1 hr. | |



The stoichiometry is deceptively simple and a large number of $\text{S}_x\text{O}_y^{n-}$ species (hydrated or not) have been detected or postulated, such as the thiosulfate ion, $\text{S}_2\text{O}_3^{2-}$, the tetrathionate ion, $\text{S}_4\text{O}_6^{2-}$, and various polythionates, $\text{S}_m\text{O}_6^{2-}$.

The sulfur in SO_2 is in the +4 oxidation state and on a catalyst surface, one might additionally have any of the +4 state ions SO_3^{2-} , HSO_3^- or $\text{S}_2\text{O}_5^{2-}$. However, during reduction to elemental sulfur in the Claus process, species having an oxidation state between +4 and 0 might appear as intermediates or as stable species. Some possible ionic species, with the average oxidation state in parentheses, follow (this list is not comprehensive): $\text{S}_3\text{O}_6^{2-}$ (+3.3), $\text{S}_2\text{O}_4^{2-}$ (+3), $\text{S}_4\text{O}_6^{2-}$ (+2.5) and $\text{S}_2\text{O}_3^{2-}$ (+2). Further, these species might be partially or completely protonated during the Claus reaction, e.g. HS_3O_6^- or $\text{H}_2\text{S}_3\text{O}_6$. Therefore, we have examined the infrared and Raman spectra of a number of $\text{S}_x\text{O}_y^{z-}$ salts. The characteristic SO stretching modes occur in the approximate range from 1250 to 950 cm^{-1} and the OSO angle deformation modes lie near 700 to 450 cm^{-1} .

In solution the dithionite ion ($\text{S}_2\text{O}_4^{2-}$) has a tendency to disproportionate to $\text{S}_2\text{O}_3^{2-}$ and HSO_3^- under acidic conditions, or to S^{2-} and SO_3^{2-} under alkaline conditions. The solid is reported to decompose in the absence of air if moisture is present to yield $\text{S}_2\text{O}_3^{2-}$ and HSO_3^- , and upon heating the solid generates $\text{S}_2\text{O}_3^{2-}$, SO_3^{2-} and SO_2 . This complexity perhaps explains why there are conflicting descriptions of the IR spectrum of sodium dithionite in the literature. Takahashi *et al.* [28] reported a pair of weak bands in the IR spectrum of solid $\text{Na}_2\text{S}_2\text{O}_4$ at 645 and 654 cm^{-1} (spectrum not shown) and at 640 and 652 cm^{-1} in the Raman spectrum. Sato *et al.* [29] showed an IR spectrum of $\text{Na}_2\text{S}_2\text{O}_4$ in KBr discs which had very weak bands at about 645 and 660 cm^{-1} . However, the Sadtler spectrum of this compound [30] in KBr shows no bands in this region but instead there was a very weak band near 620 cm^{-1} . We obtained a pure sample of $\text{Na}_2\text{S}_2\text{O}_4$ and confirmed that the spectrum was identical to the Sadtler spectrum.

Since any of the above ions, (and others not mentioned) might be expected in the Claus reaction when sodium is present, we have examined the infrared and Raman spectra of a number

of salts (in solution and as solids) and, because most of the spectra are already in the literature, we will not reproduce those spectra.

(a). Na_2SO_4

Na_2SO_4 salt with KBr is shown in Fig 5.11A. The main feature is three bands: 1131, 640 and 617 cm^{-1} .

(b). Na_2SO_3

The spectrum of Na_2SO_3 is in Fig 5.11B. We have the bands in interesting region at 1215(w), 1138(w), 1050(shoulder), 974, 632, 495 cm^{-1} . According the reference [31], the Raman frequencies for Na_2SO_3 are 990, 950, 639 and 499 cm^{-1} .

(c). $\text{Na}_2\text{S}_2\text{O}_3$

We have the spectra of both $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and $\text{Na}_2\text{S}_2\text{O}_3$ (Fig 5.11 C and D). The $\text{Na}_2\text{S}_2\text{O}_3$ is from the dehydration of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. Heating at 100 °C under evacuation should result $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ to loss five water molecules to form $\text{Na}_2\text{S}_2\text{O}_3$. The main features are at 1130, 1008, 684, 675, 555 cm^{-1} .

(d). $\text{Na}_2\text{S}_2\text{O}_5$

The infrared spectrum of $\text{Na}_2\text{S}_2\text{O}_5$ is shown in Fig 5.11E. There are bands at 1185, 1072, 1055, 982, 662, 654, and 567 cm^{-1} . The bands in the Raman spectrum, according to B. Meyer [32], are shown in Table 5.1.

(e). " NaHSO_3 "

According to Meyer *et al.* [31,32], NaHSO_3 and KHSO_3 do not exist except in solution. The commercial solid ' NaHSO_3 ' is in reality $\text{Na}_2\text{S}_2\text{O}_5$ and we have verified this by Raman spectroscopy. However, RbHSO_3 , CsHSO_3 and tetra-alkyl ammonium salts of HSO_3^- (HSO_3^- or SO_3H^-) do exist, and bands in Raman spectrum of these solids are reported near 625 and 510 cm^{-1} . The data of Raman spectra of RbHSO_3 and CsHSO_3 are in Table 5.1.

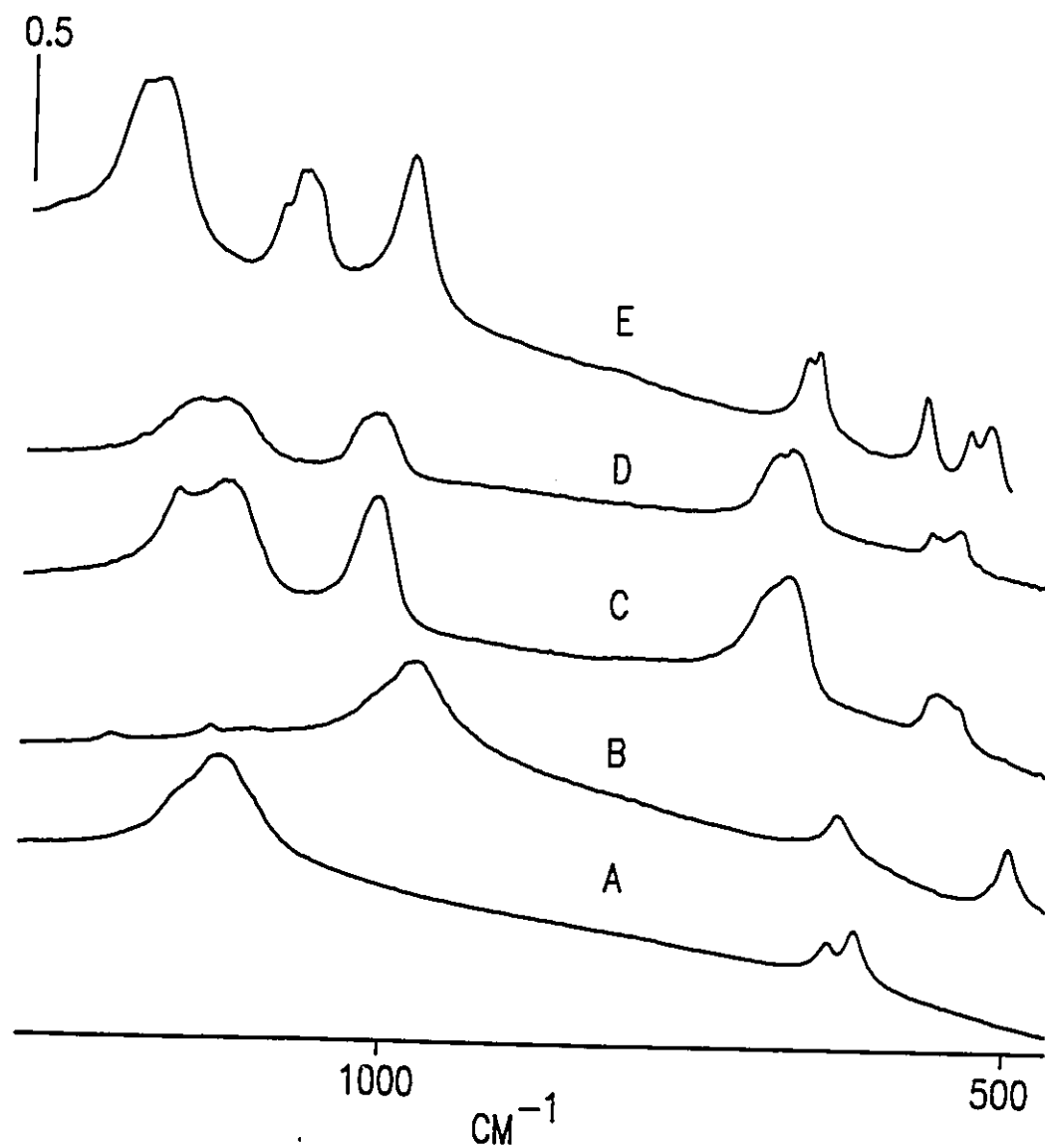


Fig 5.11 IR spectra of some oxysulfur species (2.5% in KBr)

- (A). Na_2SO_4 .
- (B). Na_2SO_3 .
- (C). $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.
- (D). $\text{Na}_2\text{S}_2\text{O}_3$.
- (E). $\text{Na}_2\text{S}_2\text{O}_5$.

(f). Other sulfur-oxygen compounds

A figure (Fig 5.12) of the characteristic Raman bands for oxygen-containing inorganosulfur compounds is from reference [29].

Table 5.2 gives a list of reported IR bands in the 1200 to 500 cm^{-1} spectral regions.

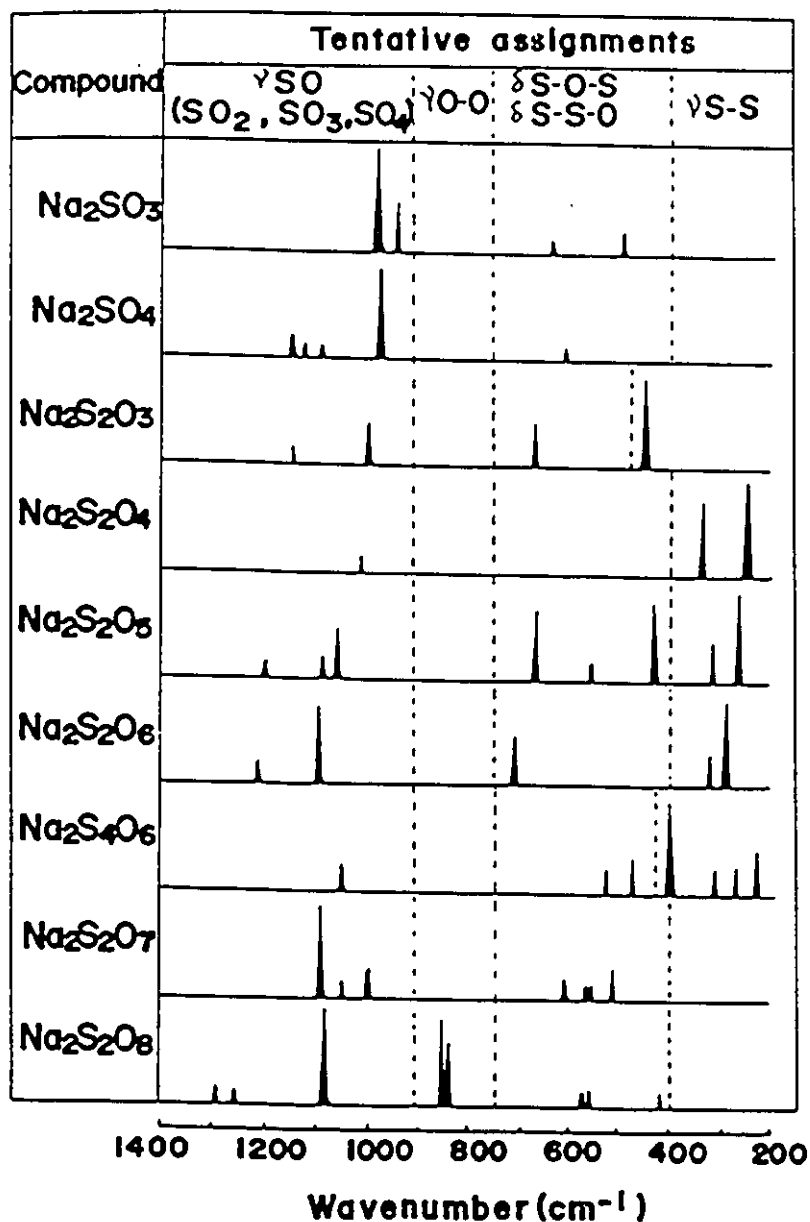


Fig 5. 12 Raman bands of oxysulfur compounds (from ref. 29)

Table 5.1. Raman spectra of $S_2O_5^{2-}$ and HSO_3^- [32]

$K_2S_2O_5$ (aqueous)	$Na_2S_2O_5$	$K_2S_2O_5$	$Rb_2S_2O_5$	$Cs_2S_2O_5$	$RbHSO_3$	$CsHSO_3$	Assignment
168 s.p							
200 s.p	224 m	217 m	220 m	224 m			A'
235 vs.p	268 vs	244 vs	242 vs	240 vs			A'
309 s.p	318 m	318 m	315 m	315 m			A'
395 w.dp							
424 s.p	432 s	434 s	432 s	435 s			A'
467 m.p							
					508 m	509 m	E(HSO_3^-)
					515 w	519 w	
510 w.dp	513 w	525 w	519 w	519 w			A"
	533 w						
558 w.dp	555 w	557 w	543 w	545 w			A"
	568 w		558 vw	558 vw			
587 w.dp							
					621 w	626 w	$A_1(HSO_3^-)$
637 w.dp	650 vw	643 vw	643 vw	643 vw			A"
655 s.p	659 vw	653 s	654 s	654 s			A'
709 m							
966 w.p	977 w	970 w	950 w	952 w			A'
1021 s.p					1037 s	1038 s	$A_1(HSO_3^-)$
1052 s.p	1064 s	1060 s	1047 s	1047 s			A'
1085 s.p	1083 w	1088 m	1068 w	1071 w			A'
	1088 w						
1128 m.dp					1132 s	1122 s	E(HSO_3^-)
1170 w. dp	1171 w	1178 m	1154 w	1155 w			A"
	1179 w						
1196 w.dp	1203 w		1188 w	1181 w	1188 w	1193 w	A"
					1242 vw	1250 vw	E(HSO_3^-)
2533 m.p					2602 m	2573 m	$A_1(HSO_3^-)$

Cationic vibrations omitted: vs = very strong; m = medium; w = weak; vw = very weak; p = polarize; dp = depolarized.

Table 5.2. IR Spectra of Oxysulfur Compounds

Na_2SO_3	Na_2SO_4	" NaHSO_3 "	NaHSO_4^*	$\text{Na}_2\text{S}_2\text{O}_3$	$\text{Na}_2\text{S}_2\text{O}_4^{**}$	$\text{Na}_2\text{S}_2\text{O}_5$	$\text{Na}_2\text{S}_2\text{O}_6^{*3}$	$\text{Na}_2\text{S}_2\text{O}_8^{*3}$
495 s					508 m			
		514 m				515 m		
		526 m				530 m	525 m	
				537 m	538 w			
				555 m				559 s
		567 m				567 m		
			575		580 w			
							605 s	595 m
	617 s	620 w	620					
					625 vw			
632 m		635 s						
	640 m						645 s	
		654 vw				654 m		
		662 vw				662 m		
				675 vs				
				684 vs				
								720 s
			850					
			872					
			885					
						910 vs		
			955					
974 vs		977 s			970 w			
						982 vs		
		990 m						
			1010	1008 vs			1010 s	
					1028 m		1030 vs	
					1040 vs			
1050 vw					1050 s	1055 w		
		1059 s						1068 s
			1070			1072 s		
1104 vw						1084 w		
		1122 s			1120 w			
1138 vw	1131 vs			1130 vs				
		1149 vs		1150 vs				
		1173 w	1170					
		1182 vw				1185 vs		
						1200 vs		

*. Data from Saad's thesis [25]; **. Data are come from Sadler IR spectra; *³. From ref.[29].
All others are from our lab.

(2). Adsorption of SO_2

Chemisorbed SO_2 initially gave rise to bands at 657 and 560 cm^{-1} which are also present in the spectrum of $\text{Na}_2\text{S}_2\text{O}_5$, and we attribute these to the presence of disulfite species. There was also a broad feature from about 635 to 615 cm^{-1} . A band at 635 cm^{-1} intensified at the expense of the 657 cm^{-1} band following evacuation, or following the addition of water. Eventually the 657 cm^{-1} species was eliminated, but re-addition of SO_2 re-generated the 657 cm^{-1} band. Because the 657 and 635 cm^{-1} bands showed a significant ^{18}O shift, these modes cannot be attributed to S-S vibrations.

The generation of disulfite probably arises from an interaction of SO_2 with sodium oxide, rather than surface NaOH . The spectrum in the OH region shows that a weak isolated SiOH peak is present after activation, but there is no evidence of a broad lower wavenumber trail which might be ascribed to H-bonded SiOH or NaOH (the O-H frequency of NaOH as recorded in our laboratory is at 3636 cm^{-1}). Without specifying a structure for this oxide of sodium (or whether sodium is bonded to silica or not), we assume that a reaction of the following type occurs:



That the addition of H_2O which generates a new species could be accounted for by postulating the following equilibrium:



There are several problems with this proposal. The species responsible for the 635 cm^{-1} band is extremely thermally stable, resisting evacuation even up to 500 $^\circ\text{C}$. One would expect evacuation to reverse this process. Further, although hydrogensulfite species are present in solution, sodium hydrogensulfite does not exist in the solid state (attempts to concentrate solutions of NaHSO_3 always reverse the above equilibrium leading solid $\text{Na}_2\text{S}_2\text{O}_5$). Therefore, the high thermal stability of the species responsible for the 635 cm^{-1} band is inconsistent with an attribution to a hydrogensulfite type species, based on the known chemistry of sodium salts of this ion. Finally, although no spectroscopic data exists for the HOSO_2^- ion, HSO_3^- salts of Cs and Rb exist. We prepared solid CsHSO_3 and recorded its IR spectrum; in this spectral region there was a sharp band at 623 cm^{-1} , close to that reported at 626 cm^{-1} in its Raman spectrum.

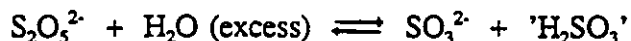
We found that prolonged evacuation also generates the 635 cm⁻¹ species, and that re-addition of gaseous SO₂ generates disulfite. This could be accounted for by the following equilibrium:



In this case, we would attribute the 635 cm⁻¹ band to the sulfite ion. There is some spectroscopic support for this assignment. Solid Na₂SO₃ has a sharp band at 630 cm⁻¹, accompanied by an equally intense sharp band at 495 cm⁻¹. We cannot observe the latter spectral region using Na/SiO₂, but using Na/SiC a sharp band at 495 cm⁻¹ appeared in concert with the generation of the 635 cm⁻¹ band.

If the above hypothesis is correct, we have to account for the formation of sulfite species when water is added to disulfite. It is to be noted that when SO₂ is added to Na/SiO₂ there is, in addition to the 657 cm⁻¹ band, a broad contour from about 635 to 615 cm⁻¹. We carried out the following supplementary experiment. Several drops of an aqueous solution of Na₂S₂O₅ were placed on an ZnSe window and allowed to dry in air. The spectrum recorded after visible traces of water had evaporated is shown in Fig 5.13A. There is a broad band with a maximum near 615 cm⁻¹, asymmetric to higher wavenumber, having shoulders near 630 and 660 cm⁻¹. Evacuation for 2 hours at room temperature resulted in no change. However, following heating in the closed cell at 100 °C, new IR bands appeared at 631 and 657 cm⁻¹, and at 200 °C the 631 cm⁻¹ feature dominated the spectrum (Fig 5.13 C). Using the more transparent CdTe as a support material, but now heating under vacuum at 100 °C, two distinct bands at 631 and 494 cm⁻¹ were the major spectral features (Fig 5.13 D). Although not shown, the spectra in the 900 to 1300 cm⁻¹ spectral regions for the samples corresponding to those shown in Figure 5.13D and C, were identical to that of sodium sulfite.

Bearing in mind that the chemistry of aqueous solutions of sodium disulfite is essentially that of aqueous sodium sulfite, or of SO₂ dissolved in water ($\text{H}_2\text{O} + \text{SO}_2 \rightleftharpoons \text{'H}_2\text{SO}_3\text{'}$), we postulate the following process when water is added to adsorbed SO₂ on Na/SiO₂:



In this case, evacuation eliminated the broad continuum near 620 cm⁻¹ as a result of the desorption of 'H₂SO₃' as water and SO₂, leaving the very stable sulfite species on the surface.

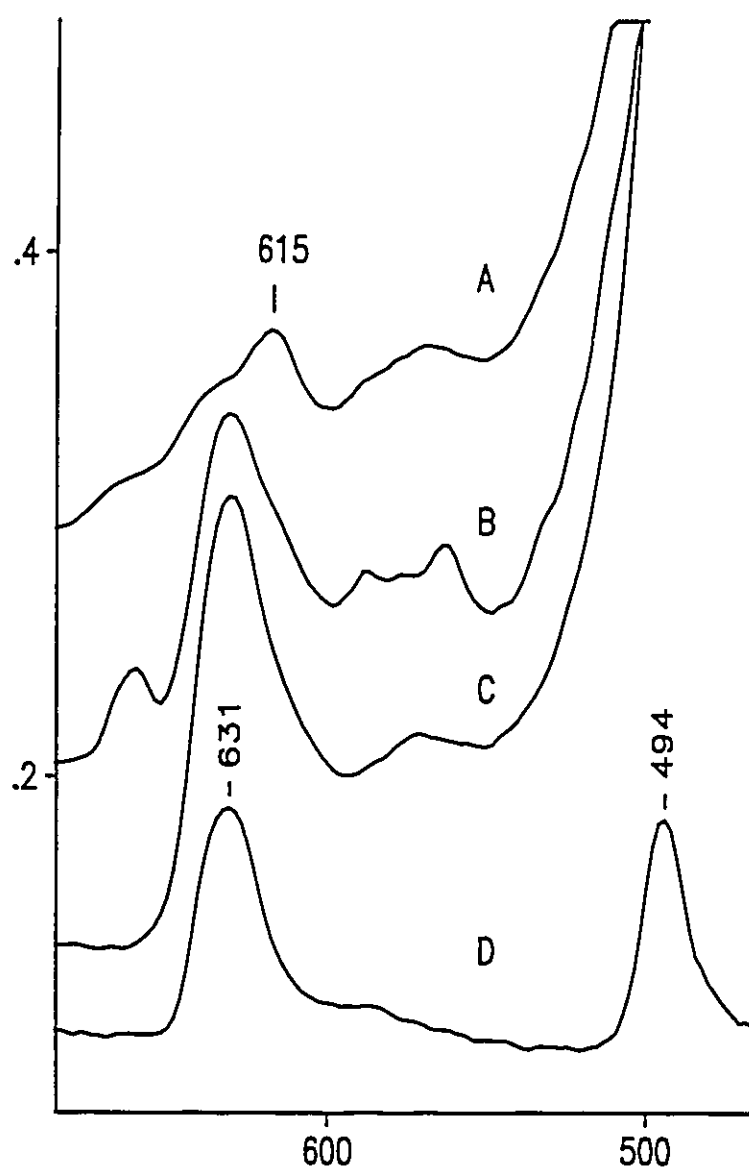


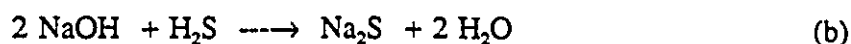
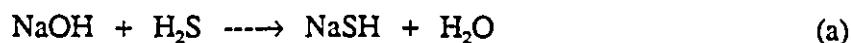
Fig 5. 13 $\text{Na}_2\text{S}_2\text{O}_5$ sample on ZnSe and CdTe windows

- A. IR spectrum observed after placing a few drops of an aqueous solution of $\text{Na}_2\text{S}_2\text{O}_5$ on a ZnSe window and allowing the excess water evaporated until a moist residue remained or following evacuation of this mixture for 1 hour (no spectral differences noted between the two cases).
- B. Heating A in closed cell at 100 °C for 2 h.
- C. Heating B in closed cell at 200 °C for 1 h.
- D. As for A, but deposit on a CdTe window, and evacuated for 1 h at 100 °C under vacuum.

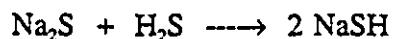
(3). *Adsorption of H₂S:*

The addition of H₂S to Na/SiO₂ gave rise to a very weak IR band at 2590 cm⁻¹, a broad band at 3100 cm⁻¹ and sharper band at 1630 cm⁻¹. In the Raman spectrum, addition of H₂S to solid NaOH gave rise to a very strong band at 2540 cm⁻¹ whereas no such band observed for the adsorption on solid Na₂O.

The above results might suggest that H₂S dissociates on Na/SiO₂(450) or on solid NaOH to produce water via the reactions:



However, Fuji and Takeda [33] found that the adsorption of H₂S on solid NaOH produced mainly NaSH and there were less than 5% sodium sulfide or polysulfide. Therefore, although reaction (b) might occur, there is probably a further reaction of the Na₂S as follows:



(4). *The Claus reaction*

The chemistry taking place during the interaction between H₂S and SO₂ on Na/SiO₂ is evidently very complex. Given that the chemistry of Wackenroder's liquid is not well understood we can only speculate about the identity of the some intermediates which manifest themselves by the appearance of infrared bands in the 500 - 700 cm⁻¹ spectral region.

For convenience, we will discuss the results in terms of the three major reaction sequences studied, designated as follows:

- (a) Adsorption of SO₂ followed by the addition of H₂S;
- (b) Adsorption of H₂S followed by the addition of SO₂;
- (c) Adsorption of a 2:1 mixture of H₂S and SO₂.

The observed spectral changes can conveniently be illustrated by Reaction Scheme A (RSA) in which the wavenumbers of the observed IR bands are indicated for each of the spectral

sequences above. RSA is intended to summarize the IR spectroscopic observations without any bias as to the identity of the species which are responsible for each observed band. For example, looking at the top horizontal line, this indicates that adsorption of SO_2 gives rise to an IR band at 657 cm^{-1} and when water is subsequently added, a new IR band at 635 cm^{-1} is generated. And so on for the remaining spectral changes for the various reaction sequences.

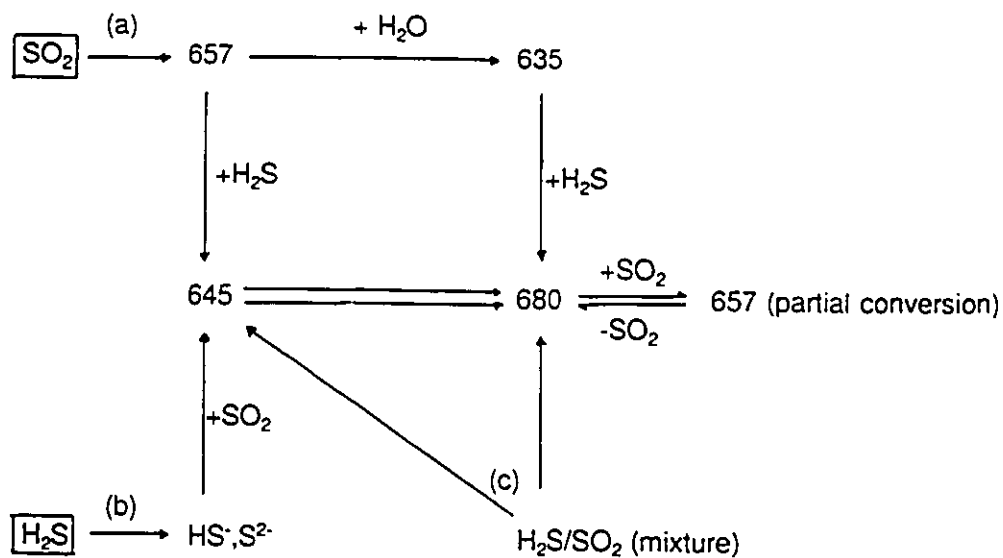
The Reaction Scheme B (RSB) shown below RSA contains the identity of some of the species which have been discussed previously; for example, the 657 cm^{-1} band can probably be assigned to $\text{S}_2\text{O}_3^{2-}$, and the 635 cm^{-1} band to SO_3^{2-} . The identity of the other species will be discussed below.

We have shown that a strong band appears near 680 cm^{-1} during all of the above reaction conditions. Because this band has a significant ^{18}O shift to lower wavenumber, this species is probably due to an SO_x deformation mode, and not to a S-S stretching mode. This band is at the same wavenumber and has the same band shape as that which we have observed for sodium thiosulphate and 1-3% by mass sodium thiosulfate supported on silica. Further, using SiC as a support, we observed the parallel growth of a band at 555 cm^{-1} which is also observed in the IR spectrum of $\text{Na}_2\text{S}_2\text{O}_3$. Heating the sample to about 300°C after generation of the 680 cm^{-1} band at room temperature caused its disappearance and the appearance of a yellowish deposit of sulphur on the cell walls. When supported $\text{Na}_2\text{S}_2\text{O}_3$ was heated to 300°C , the 680 cm^{-1} band disappeared and we observed the appearance the same yellowish deposit.

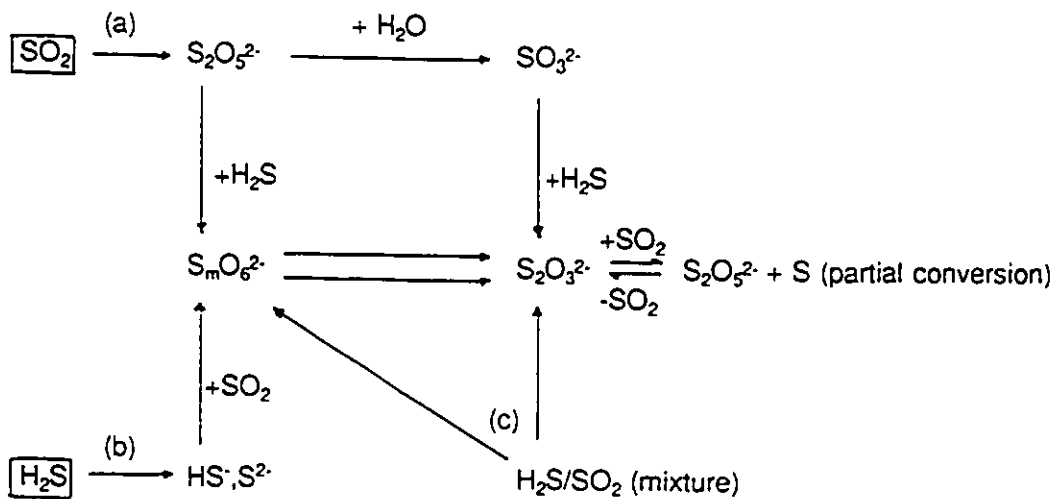
In a Raman investigation [24] of the $\text{SO}_2/\text{H}_2\text{S}$ reaction on Na/SiO_2 at low laser power (50 mW), no bands were observed. However, if the laser power was increased to 200 mW, strong peaks at 152 , 220 and 480 cm^{-1} characteristic of S_8 were observed. In a previous Raman study [24], it was reported that solid sodium thiosulfate decomposed to give sulfur with an argon ion laser operating at 700 mW whereas no decomposition occurred using a HeNe laser at 90 mW.

From the ensemble of results above, we conclude that 680 cm^{-1} band can be assigned to the thiosulphate ion, $\text{S}_2\text{O}_3^{2-}$. This is so indicated in RSB.

Reaction Scheme A (RSA)



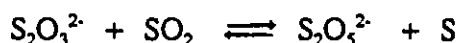
Reaction Scheme B (RSB)



- (a) Addition of SO_2 followed by evacuation of excess.
 (b) Addition of H_2S followed by evacuation of excess.
 (c) Addition of a 2:1 mixture of $\text{H}_2\text{S}/\text{SO}_2$.

Although thiosulfate is a stable product of the reaction at room temperature, a new IR band at about 645 cm⁻¹ appears to be due to a precursor species under reaction conditions (a) and (b) insofar as this band appeared immediately then decreased in intensity as that at 680 cm⁻¹ intensified. Under either of reaction conditions (a) or (b), there was a quasi isosbestic point between the 645 and 680 cm⁻¹ bands, showing a correspondence between the disappearance of the species responsible for the 645 cm⁻¹ band and the formation of thiosulfate (see Fig 5.14). However, during reaction condition (c) with a 2/1 stoichiometric mixture of H₂S/SO₂, the ratio of the intensities of the 645/680 cm⁻¹ bands remained almost constant as water was generated. Further, during the course of reaction, the originally white sample disc slowly turned greyish, suggestive of the formation of a small particle size solid deposit. This could be due to small particles of S₈, and only by heating to about 130 °C do these sublime to the cell walls and appear as a yellowish deposit.

The conversion of the 645 cm⁻¹ band to the 680 cm⁻¹ band during reaction sequence (a) could be stopped (the spectral changes ceased) if H₂S was evacuated. If SO₂ was subsequently readded, there was about a 20% decrease in the intensity of the 680 cm⁻¹ band and the band at 657 cm⁻¹ reappeared. Evacuation of SO₂ resulted in a reversal of this process, the 657 cm⁻¹ band disappeared and the 680 cm⁻¹ band reappeared. This process is indicated by the double arrows to the right of the position of the 680 cm⁻¹ band in RSA where the words 'partial conversion' have been included. In RSB we suggest that this is due to the possible equilibrium:



We will now discuss the origin of the 645 cm⁻¹ band. A mechanistic interpretation of the results would be difficult without the knowledge that the IR bands at 645 and 680 cm⁻¹ were also observed when the mixture was adsorbed on Na/SiO₂. Without these results, one would be tempted to attribute the 645 cm⁻¹ band to a relatively unstable intermediate in sequences (a) or (b) which ultimately results in the formation of thiosulfate, 680 cm⁻¹. However, during the adsorption of the mixture (sequence (c)), both the 680 and 645 cm⁻¹ bands grow in intensity in unison, and both bands remained unchanged in intensity or shape if the mixture was evacuated.

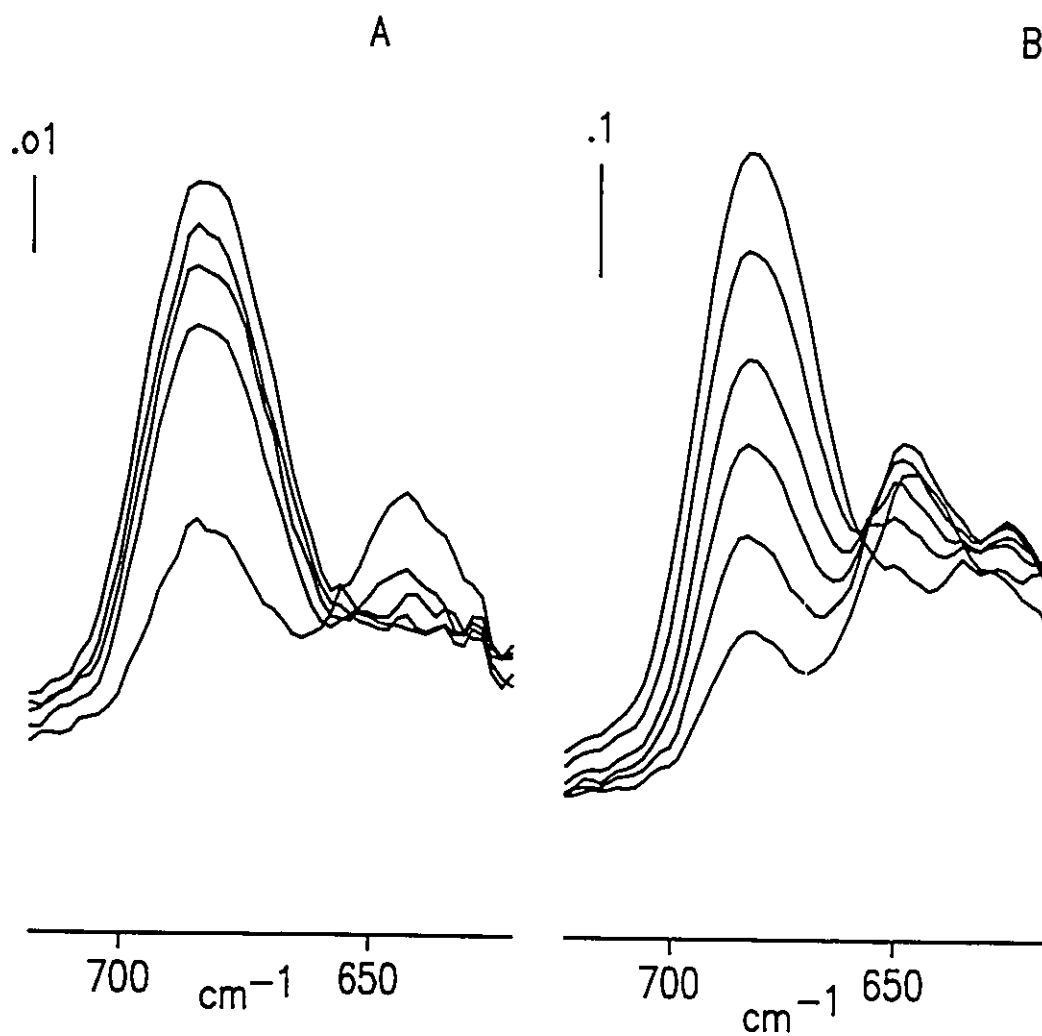


Fig 5. 14 Continuous reaction of H_2S and SO_2 on Na/SiO_2

(A). addition of SO_2 , evacuation, addition of H_2S ;
(B). addition of H_2S , evacuation, addition of SO_2 .

Therefore, the species responsible for the 645 cm^{-1} band cannot be an unstable intermediate. Indeed, even during the generation of the 680 cm^{-1} band in the static reaction between preadsorbed H_2S with gaseous SO_2 or in the reverse sequence, if the gaseous reactant was evacuated before the 645 cm^{-1} intensity had been reduced to zero, the reaction stopped and the 645 cm^{-1} remained with constant intensity at the point where the evacuation commenced.

Therefore, we are faced with the difficult situation of trying to devise a mechanism for a reaction which ultimately leads to the generation of thiosulfate when $\text{H}_2\text{S}/\text{SO}_2$ interact over Na/SiO_2 . Water is also formed. The pattern of spectral changes in the presence of the mixture is reminiscent of the reaction of the mixture over Al_2O_3 ; in the Na/SiO_2 case, IR bands due to water and the bands at 680 and 645 cm^{-1} increased in intensity in unison over a period of an hour.

The adsorption of the $\text{H}_2\text{S}/\text{SO}_2$ mixture provides a medium where Wackenroder's solution can develop. We can assume, as was postulated in the case of Al_2O_3 and ZrO_2 (and other oxides), that a polythionate, $\text{S}_m\text{O}_6^{2-}$, is formed, and we note that all of these have an IR band near 640 cm^{-1} [34]. The 645 cm^{-1} band is, therefore, assigned to $\text{S}_m\text{O}_6^{2-}$. The 645 cm^{-1} band shows evidence of shoulders to high and low wavenumber, and indeed, its peak maximum varied considerably according to the conditions of reaction, usually being in the range from 644 to 650 cm^{-1} . Some polythionates also have IR bands between 620 to 600 cm^{-1} , and during some of the reactions under static conditions there have been weak IR bands in this wavenumber region in addition to the major peaks at 645 and 680 cm^{-1} (e.g reaction sequence (b)).

Unlike the situation of Al_2O_3 and ZrO_2 where few experiments have been carried out, several thousand spectra have been recorded in this study of the Na/SiO_2 system. The system Cs/SiO_2 has also been examined in the hope that HSO_3^- species might be identified given that solid CsHSO_3 is a stable species having a known IR spectrum. No new insights were found.

It is evident that there is a mixture of oxysulfur species, protons and water on Na/SiO_2 and that the partially or totally protonated oxyanions of sulfur might be stabilized on the surface. The

IR spectra of most of these species are largely unknown, an exception being the Raman spectrum of the HS_2O_3^- ion which has recently been published [35]. In our case, we just do not know how the IR spectrum of a polythionate ion $\text{S}_m\text{O}_6^{2-}$ ion would be affected if it were to be partially or totally protonated.

The 645 cm^{-1} band did not appear under one set reaction conditions. If water was added to preadsorbed SO_2 , this eliminated the 657 band and caused the appearance of a relatively strong and sharp band at 635 cm^{-1} which was attributed to sulfite. Subsequent addition of H_2S resulted in a slow appearance of the band at 680 cm^{-1} , and a slow decrease in the intensity of the 635 cm^{-1} band; the band at 645 cm^{-1} was not detected. Having shown that the sulfite species is very thermally stable, we also conclude that it is not particularly reactive with H_2S , a conclusion which was also reached regarding the reactivity of sulfite species on sodium impregnated Al_2O_3 catalysts. We have to assume that the generation of $\text{S}_2\text{O}_3^{2-}$ from SO_3^{2-} does not involve a polythionate in this instance. Having previously suggested that ' H_2SO_3 ' is a product of this step, in the presence of H_2S this would yield elemental sulfur, and it is well established that thiosulfate can be formed directly from the reaction $\text{SO}_3^{2-} + \text{S} \rightarrow \text{S}_2\text{O}_3^{2-}$.

In summary, all works on sulfur chemistry comment on the incredible complexity of the $\text{H}_2\text{S}/\text{SO}_2/\text{H}_2\text{O}$ system [26, 27, 36]. Therefore, it is highly probable that other reactive intermediates exist on Na/SiO_2 but they are present in such low concentration that they escape detection. It is not worth speculating further.

REFERENCES

- [1]. Gallon, M. A. and Smith, J. M., *J. Catal.*, 38, 206(1975).
- [2]. Dudzik, Z. and George, Z. M., *J. Catal.*, 63, 72(1980).
- [3]. Hair, M. L., " *Infrared Spectroscopy in Surface Chemistry* ", Marcel Dekker Inc., New York, 1967.
- [4]. Little, L. H., " *Infrared Spectra of Adsorbed Species* ", Acad. Press, London, 1966.
- [5]. Kiselev, A. V. and Lygin, V. I., " *Infrared Spectra of Surface Compounds* ", Wiley, New York, 1975.
- [6]. McFarlan, A. J., Ph.D. Thesis, University of Ottawa (1991).
- [7]. Zecchina, A. and Arean, C. O., *Catal. Rev.-Sci. Eng.*, 35, 261(1993).
- [8]. Young, G. J., *J. Coll. Sci.*, 13, 67(1958).
- [9]. Hockey, J. A., *Chem. Ind.*, 57(1965).
- [10]. Snyder L. R. and Ward, J. W., *J. Phys. Chem.*, 70, 3941(1966).
- [11]. Kiselev, A. V., Nikitin, Y. S., Petrova, R. S., Shcherbakova K. D. and Yashi, Y. I., *Anal. Chem.*, 36, 1526(1964).
- [12]. McDonald, R. S., *J. Phys. Chem.*, 62, 1168(1958).
- [13]. Zachariasen, W. H., *J. Am. Chem. Soc.*, 50, 3841(1932).
- [14]. Mozzi R. L. and Warren, B. E., *J. Appl. Crystallogr.*, 2, 164(1969).
- [15]. Morrow, B. A., *Studies Surface Science and Catalysis*, 57A, 161(1990).
- [16]. Morrow, B. A. and McFarlan, A. J., *Amer. Chem. Soc. Adv. Chem. Ser.*, 234, 183(1994).
- [17]. Morrow, B. A. and McFarlan, A. J., *J. Non-Cryst. Solids*, 120, 61(1990).
- [18]. Morrow, B. A. and McFarlan, A. J., *Langmuir*, 7, 1695(1991).
- [19]. Morrow B. A. and Cody, I. A., *J. Phys. Chem.*, 80, 1995(1976).
- [20]. Grabbe, A., Michelska, T. A. and Smith, W. L., *J. Phys. Chem.*, 99, 4648(1995).
- [21]. Morrow B. A. and Devi, A., *J. Chem. Soc. Faraday Trans I*, 68, 403(1972).
- [22]. Morrow, B. A., Cody I. A. and Lee, L. S. M., *J. Phys. Chem.*, 80, 2761(1976).
- [23]. Zhuravlev, L. T., *Langmuir*, 3, 316(1987).
- [24]. Tripp, C. P., Ph. D. Thesis, University of Ottawa, Canada, 1988.
- [25]. Mohammed Saad, A. B., Thesis, Docteur de l'Université de Caen, Caen, France, 1991.

- [26]. Schmidt, M., " Sulphur in Organic and Inorganic Chemistry " (Ed. by Senining, A.), Vol. 2, p71, Marcel Dekker Inc., New York, 1972.
- [27]. Lyons, D. and Nickless, G. in "Inorganic Sulfur Chemistry", Ed. Nickless, G., Elsevier, Amsterdam, Page 509, 1968.
- [28]. Takashi, H., Kaneko, N. and Miwa, K., Spectrochimica Acta, 37A, 1147 (1982).
- [29]. Sato, S., Higuchi, S. and Tanaka, S., Applied Spectroscopy, 39, 822 (1985).
- [30]. Sadtler Standard Spectra, Sadtler Res. Lab., Philadelphia, U. S. A., 1965, Spectrum Y143, Inorganic Grating Spectra.
- [31]. Peter, L. and Meyer, B., Inorg. Chem., 24, 3071 (1985).
- [32]. Meyer, B., Spectrochimica Acta, 35A, 345 (1979).
- [33]. Fuji, K. O. and Takeda, E., Kagaku Kojo, 11, 81 (1967).
- [34]. Steudel, R., Gobel, T. and Holdt, G., Z. Naturforsch., 43b, 302(1988).
- [35]. Steudel, R. and Prenzel, A., Z. Naturforsch., 44b, 1499(1989).
- [36]. Greenwood, N. N. and Earnshaw, A., "Chemistry of the Elements", Pergamon Press, London, 1984.

Chapter 6

THE CLAUS REACTION ON ZEOLITES

1. INTRODUCTION

Alumina or bauxite are employed as the main catalysts in the Claus process on an industrial scale. Zeolites, however, are also interesting catalysts in view of their special properties such as Brønsted acidity, very high surface area, pore structure, variable Si/Al ratio and ion exchange modification. An investigation of the behaviour of zeolites on the Claus reaction might help us to expand our knowledge about this process and the role of the surface acidity and basicity.

There have been other studies of zeolites as Claus catalysts, but most investigations were focused on X-type zeolites. According to E. M. Flanigen [1], A and X zeolites belong to low Si/Al ratio zeolite (about 1 to 1.5); Y and L type zeolites are of intermediate Si/Al ratio (about 2 to 5); ZSM-5 is classed as a high Si/Al ratio zeolite (about 10 to 100). As discussed in previous chapters, pure silica is not a Claus catalyst but alumina shows a relatively high catalytic activity. An intermediate Si/Al ratio zeolite, zeolite-Y, should be a good candidate for studying the catalytic behaviour of zeolites and the role of the framework AlO_4 tetrahedra. And by comparing the zeolite NaY with zeolite HY which is a strong acidic catalyst, we may acquire some knowledge about the effect of surface acidity on Claus process whereas surface basic sites had been shown to be the Claus active centres on Al_2O_3 , $\text{Na}/\text{Al}_2\text{O}_3$ and Na/SiO_2 as discussed before.

Deo *et al.* [2] studied the adsorption and reaction of H_2S and SO_2 on γ -alumina, and on the zeolites NaY (Na^+ exchanged Y-type zeolite), HY (H^+ ion exchanged Y-type zeolite), and DY (D exchanged Y-type zeolite). The results lead them to believe that the functional step was primarily to bring the reactants together in a suitable orientation on zeolite. They found that the

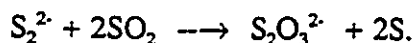
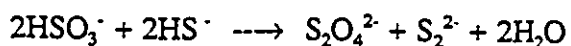
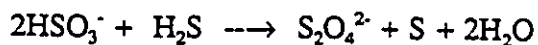
acidity did not seem to be the primary factor responsible for their catalytic activity in the Claus reaction. In Deo's report, no infrared information below 1300 cm⁻¹ was given because the transparency was cut off by the background adsorption of zeolite, being similar to that of silica.

Karge and Rasko studied H₂S adsorption on zeolites with systematically varied Si/Al ratios [3]. When Si/Al ratios were less than 2.5 or at least equal to 2.5, H₂S dissociated to give OH bands at 3650 and 3580 cm⁻¹ and an HS band at 2560 cm⁻¹. Na⁺ ions at the walls of supercage were the centres for dissociation of H₂S. NaY (Si/Al > 2.5) adsorbed H₂S but no dissociation occurred. The Si/Al ratio also had an affect on the oxidation of H₂S. In this paper, no Claus reaction was reported.

Ziolek observed the Claus reaction in a dynamic system [4]. X-type zeolites were found to adsorb more H₂S or SO₂ than the Y-type and this adsorption capacity increased also for ion exchanged zeolites, in the order K > Na > Li.

The adsorption of H₂S on some transition metal exchanged zeolite was studied by Howard and Kadir [5]. They concluded that ν_3 of H₂S and $\nu(\text{SH}^-)$ bands were very close to each other at about 2560 cm⁻¹.

Karge *et al.* [6,7] studied Claus reaction on zeolites by using IR and UV-visible spectroscopic techniques. During the adsorption process, acidic OH groups developed on MX (M = Li, Na, K, Rb, Cs), but they were not found on MY zeolites. SO₂ was adsorbed on NaX with traces of water to give HSO₃⁻, 1240 cm⁻¹, and H₂S was adsorbed to give HS⁻ species. And no matter which one was added first for SO₂ and H₂S, the results were the same, postulated to be:



S₂O₄²⁻, S₂²⁻ and S₂O₃²⁻ were the suggested intermediates in the Claus reaction. The starting point was the formation of HSO₃⁻. The band at 2560 cm⁻¹ was assigned as HS⁻ species; the band at 1240 cm⁻¹ as HSO₃⁻ species; the band at 1315 cm⁻¹ as physically adsorbed SO₂ species. No S₂O₄²⁻

IR bands was observed but 320 nm in UV/vis was assigned as the species of $\text{S}_2\text{O}_4^{2-}$ [6,7].

The adsorption of H_2S on ZSM-5 zeolite was reported [8]. The interesting aspect of this report was that the deconvolution of the 2620-2500 cm^{-1} spectral region showed three bands: asymmetric ν_3 , symmetric ν_1 , and stretching vibration of H_2S on extra lattice material ($\nu_3 > \nu_1 > \nu_{\text{extra}}$). H_2S was observed as molecular species on Na- and H-ZSM-5 zeolite surfaces.

Only Karge *et al.* [6] observed the band at 1240 cm^{-1} , no other paper has dealt with the region below 1200 cm^{-1} . In our experiments with thinner sample disc and with a FTIR spectrometer, we have shown clear bands about 1200 cm^{-1} , which is an important region for identifying S-O species, as was discussed in chapter 3.

2. EXPERIMENTAL

The zeolite-Y used was in the sodium form and will be designated as NaY. Hydrogen-Y (HY) was prepared in the usual fashion by heating zeolite NH_4Y which was obtained by 2N NH_4^+ aqueous ion exchange of NaY. The activation temperature for NaY was 450 °C under evacuation. To activate HY, two steps have to be followed. First, one heats the disc of NH_4Y in the IR cell under vacuum at 120 °C for half hour, and then, the temperature is raised to 450 °C under evacuation for another half hour. The infrared spectrum showed no NH_3 species remain on the HY sample after this activation.

3. RESULTS AND DISCUSSION

(1). Adsorption of SO_2

After activation at 450 °C for 1 hour, NaY has only a weak 3695 cm^{-1} band in OH stretching vibrational region while HY still has intense 3650, 3550 cm^{-1} bands and two very weak bands at 3745 and 3695 cm^{-1} (see Fig 6.1). The band at 3695 cm^{-1} is due to traces of water which are attached to the Na^+ ions, and the band at 3745 cm^{-1} is assigned to a Si-OH species (equal to 3747 cm^{-1} band on pure silica). The characteristic band at 3650 cm^{-1} on HY is reasonably ascribed to

framework hydroxyl groups in the supercages because it is accessible to most reagents. Another band at 3550 cm^{-1} is less certain and some conclude it is an OH in the sodalite-prism complex [9]. Because this weak band at 3695 cm^{-1} is found on HY, we conclude that the exchange of H^+ with Na^+ ions was not complete (usually 80% to 90% exchanged), which is normal.

The adsorption of SO_2 on HY causes a large change in OH stretching region. A new band at 3420 cm^{-1} appears but there is also a "negative peak" at about 3650 cm^{-1} (Fig 6.2, these being difference spectra, after subtraction of the background spectrum prior to adsorption, as will be done in succeeding figures). The band at 3550 cm^{-1} diminished a little only with larger doses of SO_2 . After evacuation, almost all bands due to adsorption of SO_2 are removed and the OH returns to that which was observed prior to adsorption. Following adsorption of SO_2 on NaY, the weak band at 3695 cm^{-1} decreases and a weak band at 3650 cm^{-1} appears (Fig 6.3). After evacuation, there is a weak band around 3650 cm^{-1} .

For both zeolites, there is a weak peak near 2500 cm^{-1} which is a combination mode of the symmetric and antisymmetric SO_2 stretching modes. Only the band due to the antisymmetric stretching mode of physically adsorbed SO_2 near 1330 cm^{-1} can be observed for adsorbed SO_2 because of the limited transmission below 1200 cm^{-1} . The band at 1330 cm^{-1} was considerably more intense for the same quantity of SO_2 than that which was observed for SO_2 adsorption on Al_2O_3 or on $\text{Na}/\text{Al}_2\text{O}_3$. After evacuation for 5 min, the 1330 cm^{-1} band was almost eliminated for HY, whereas this band was only reduced by about 50% for NaY. As will be discussed later, this is probably related to the greater acidity of HY relative to that of NaY, the adsorption of acidic SO_2 being weaker on the acidic zeolite. The enhanced adsorption capacity of the zeolite to that of Al_2O_3 is almost certainly related to the micropore structure of the zeolite which has a greater capacity for physically adsorbing a given molecule.

In $\delta(\text{H}_2\text{O})$ region, a weak peak at 1640 cm^{-1} appeared after adding SO_2 to NaY but this band was not found for SO_2 adsorption on HY.

For HY, the change in the spectrum of the OH groups, especially that at 3650 cm^{-1} , is quite

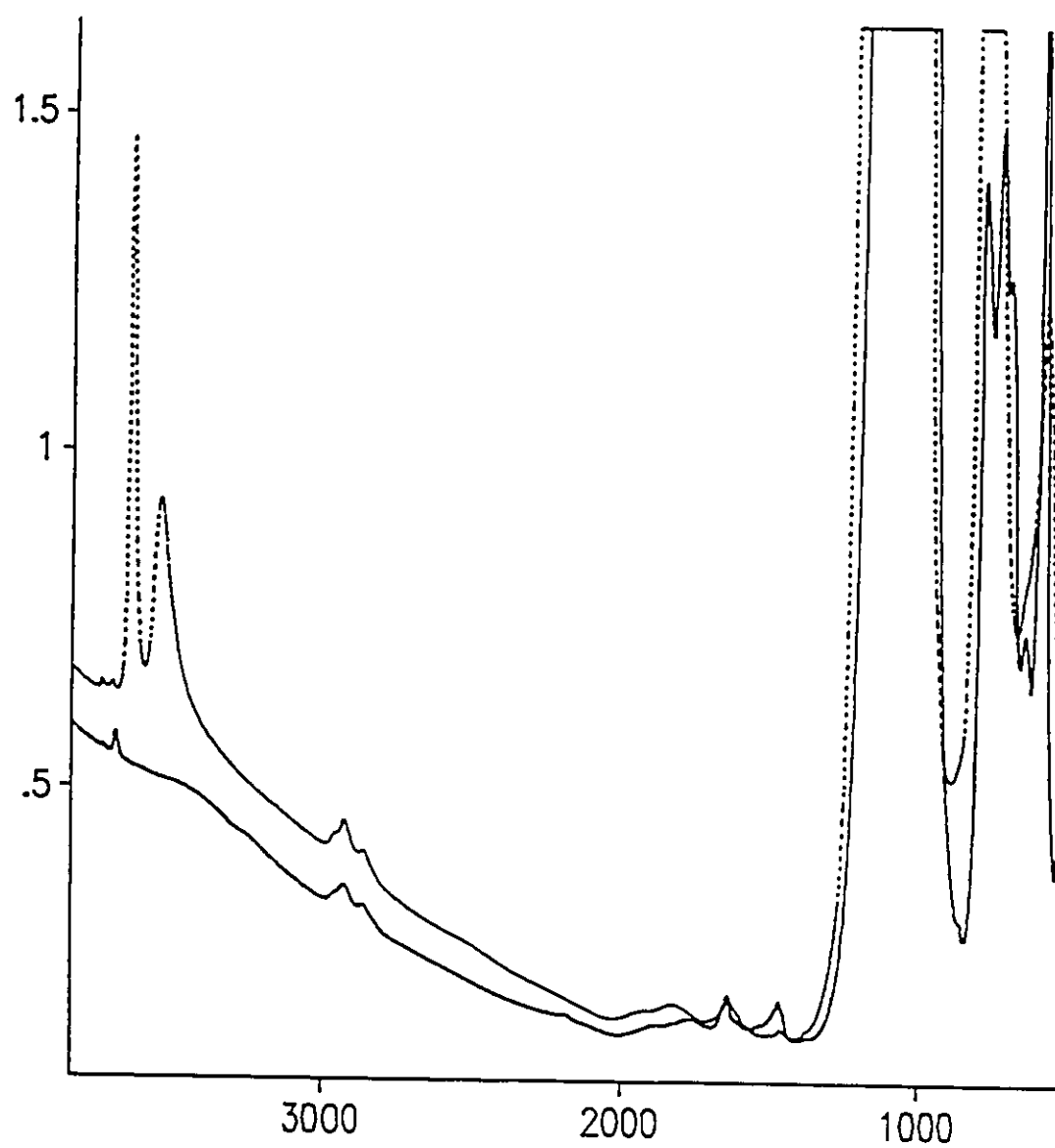


Fig 6. 1 IR spectra of HY (top curve) and NaY (lower curve)
30 mg of zeolite under evacuation at 450 °C and cool to room temperature.

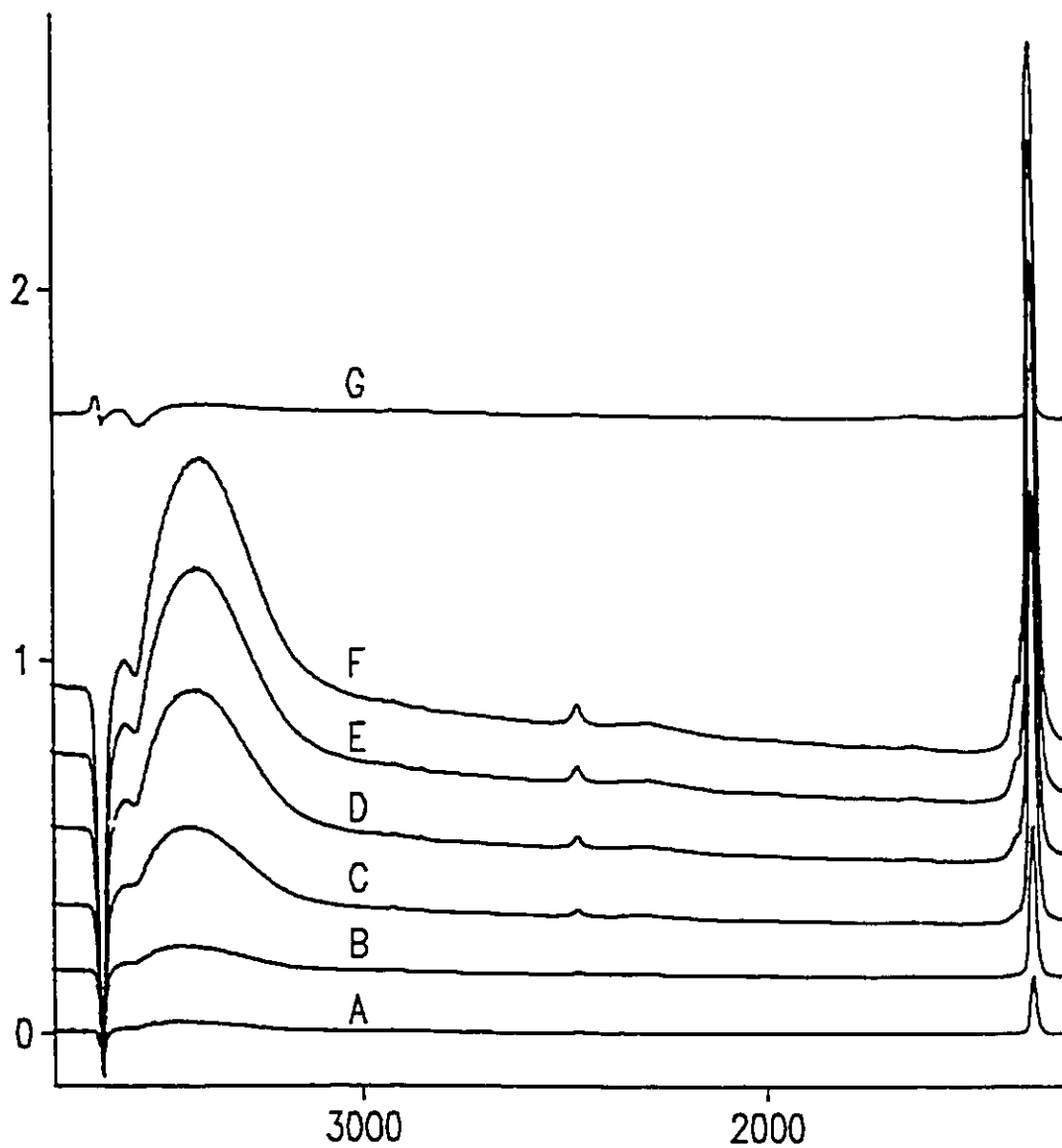


Fig 6. 2 Adsorption of SO₂ on HY

- (A). add 0.05 Torr of SO₂ (50 $\mu\text{mol/g}$).
- (B). add 0.15 Torr of SO₂ (150 $\mu\text{mol/g}$).
- (C). add 0.61 Torr of SO₂ (610 $\mu\text{mol/g}$).
- (D). add 1.34 Torr of SO₂ (1340 $\mu\text{mol/g}$).
- (E). add 2.40 Torr of SO₂ (2400 $\mu\text{mol/g}$).
- (F). add 4.40 Torr of SO₂ (4400 $\mu\text{mol/g}$).
- (G). evacuate for 5 minutes.

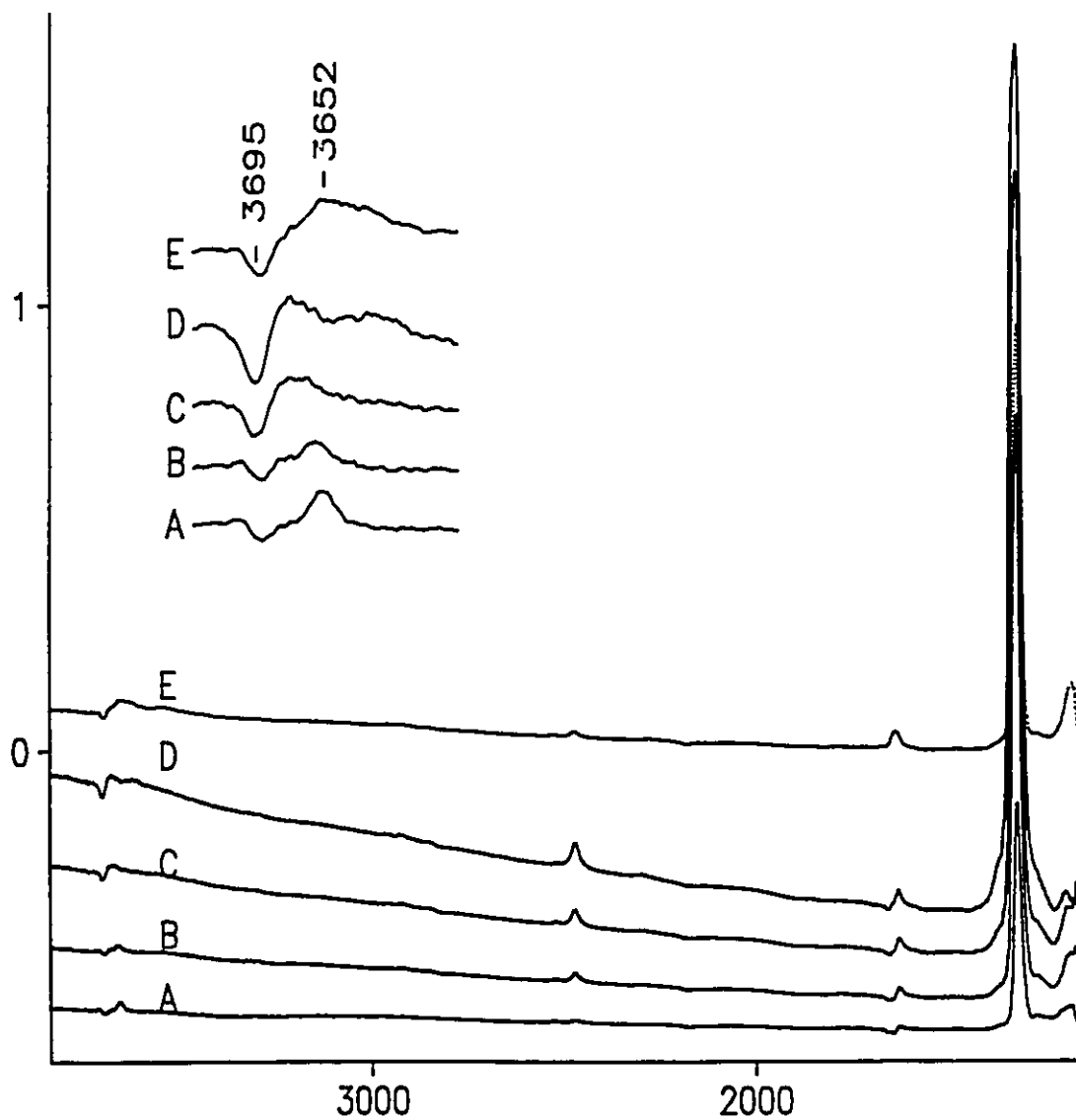


Fig 6. 3 Adsorption of SO₂ on NaY
 (A). add 0.12 Torr of SO₂ (120 μmol/g).
 (B). add 0.46 Torr of SO₂ (460 μmol/g).
 (C). add 0.96 Torr of SO₂ (960 μmol/g).
 (D). add 1.96 Torr of SO₂ (1960 μmol/g).
 (E). evacuate for 5'.

evident, but after evacuation almost the all OH bands return to their initial intensity. We suggest that SO_2 is adsorbed on OH sites through a weak hydrogen bond. Because the band at 1330 cm^{-1} is very symmetric on HY, it seems that there is only one kind of physisorption site. And this physically adsorbed SO_2 is in the supercages (responsible for the perturbation of the acidic OH groups absorbing at 3650 cm^{-1} in the supercages of HY [9]). After evacuation, there is a weak 1330 cm^{-1} band which may come from the fact that $\text{H}^+\text{-Na}^+$ exchange was not complete on HY. A HY zeolite calcined at $480\text{ }^\circ\text{C}$ has only Brønsted acidity [11, 12] and it is said that the Brønsted acidic sites are associated with the framework aluminum [13]. Our HY sample was activated at $450\text{ }^\circ\text{C}$ and it should contain mainly Brønsted acidic sites. There is no evidence that $[\text{HSO}_3^-]$ was produced. Once the H^+ ions are replaced by Na^+ ions, the adsorption capacity for SO_2 is somewhat increased and the strength is much greater. This might suggest that SO_2 is adsorbed on the framework $(\text{AlO}_4^-)\text{Na}^+$ sites. A possible species might be described as: $(\text{AlO}_4^-)\text{Na}^+:\text{SO}_2$. The van der Waals interaction force, which comes from the polarization of the interacting species, plays a major role in this interaction. The Coulombic interaction of the Na^+ ions plays a secondary role. This might explain why the adsorption capacity of ion exchanged zeolites is in the order $\text{K} > \text{Na} > \text{Li}$ [4].

Smaller ions like Li^+ and Mg^{2+} (diameters less than $1\text{ \AA}$), are mostly located inside the small cages of the zeolite, while larger ions, like K^+ and Rb^+ (diameters larger than $1\text{ \AA}$), are located in the supercages [14]. Na^+ ions, having a diameter of about $0.98\text{ \AA}$, are found in either the small cages or in the supercages. Considering the molecular size of SO_2 and the spectral change at 3650 cm^{-1} , we believe that the adsorption site is in the supercages, especially on the so-called S_{II} sites in the supercages [15, 16]. Then, the existence of Na^+ ions on the zeolite helps to stabilize adsorbed species.

To conclude, although a considerable quantity of SO_2 can adsorb on HY, because of the presence of Brønsted acid sites, only weak physisorption occurs in the supercages. The stronger adsorption of SO_2 on NaY occurs mainly on Na^+ sites associated with framework AlO_4^- . The quantity of SO_2 which is physically adsorbed on either zeolite is much greater than that which physically adsorbed on Al_2O_3 or on $\text{Na}/\text{Al}_2\text{O}_3$ for the same quantity of gas added, and this is

mainly a reflection of the high internal surface area (pore structure) of the zeolites.

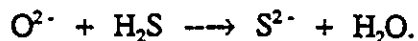
(2). *Adsorption of H₂S*

The spectrum of H₂S adsorbed on HY in the 3800 - 3000 cm⁻¹ spectral region is much like that of SO₂ adsorbed on HY except that the hydrogen bonded OH band is shifted to lower wavenumber, around 3115 cm⁻¹ (Fig 6.4). This suggests that H-bonded H₂S is more strongly held than is H-bonded SO₂. The band at 3650 cm⁻¹ decreased and the band at 3550 cm⁻¹ was almost unchanged. After evacuation, almost all OH bands recovered their initial intensity but the band at 3650 cm⁻¹ decreased slightly (Fig 6.4 A-F). The spectral change in the OH spectral region for H₂S on NaY was much smaller (Fig 6.5). With increasing dosage of H₂S the background between 3700-2800 cm⁻¹ increased in intensity. After evacuation, there was clearly a growth in the band at 3695 cm⁻¹ and there was a broad band near 3430 cm⁻¹ (Fig 6.5H).

In 2600-2300 cm⁻¹ ν (HS) spectral region, there is a broad band centred at 2575 cm⁻¹ on both zeolites (Fig 6.4, and Fig 6.5). For NaY, a careful analysis of the overlapping bands shows at least four different bands at 2605, 2575, 2565, and 2530 cm⁻¹. On HY, they are at 2605, 2585, 2575 and 2530 cm⁻¹ (see Fig 6.6). All of these bands are eliminated following evacuation, showing that they are from physisorption.

For both zeolites, there is a band at 1640 cm⁻¹, but the intensity on NaY is much higher than on HY (Fig 6.4 and Fig 6.5). In the 1400-1100 cm⁻¹ region, there is not much change and the background decreases in intensity below 1300 cm⁻¹.

After evacuation of H₂S on NaY, a band at about 1640 cm⁻¹ remained. Dry NaY has a strong adsorbability for water. We can not exclude the possibility of water desorbing from the cell walls to the zeolite but a blank test showed that such an intense band did not appear. Therefore, we suggest that the water found in this experiment is mainly from the reaction of H₂S with the surface. This possibly comes from the reaction of H₂S with some active O²⁻ sites. The reaction is:



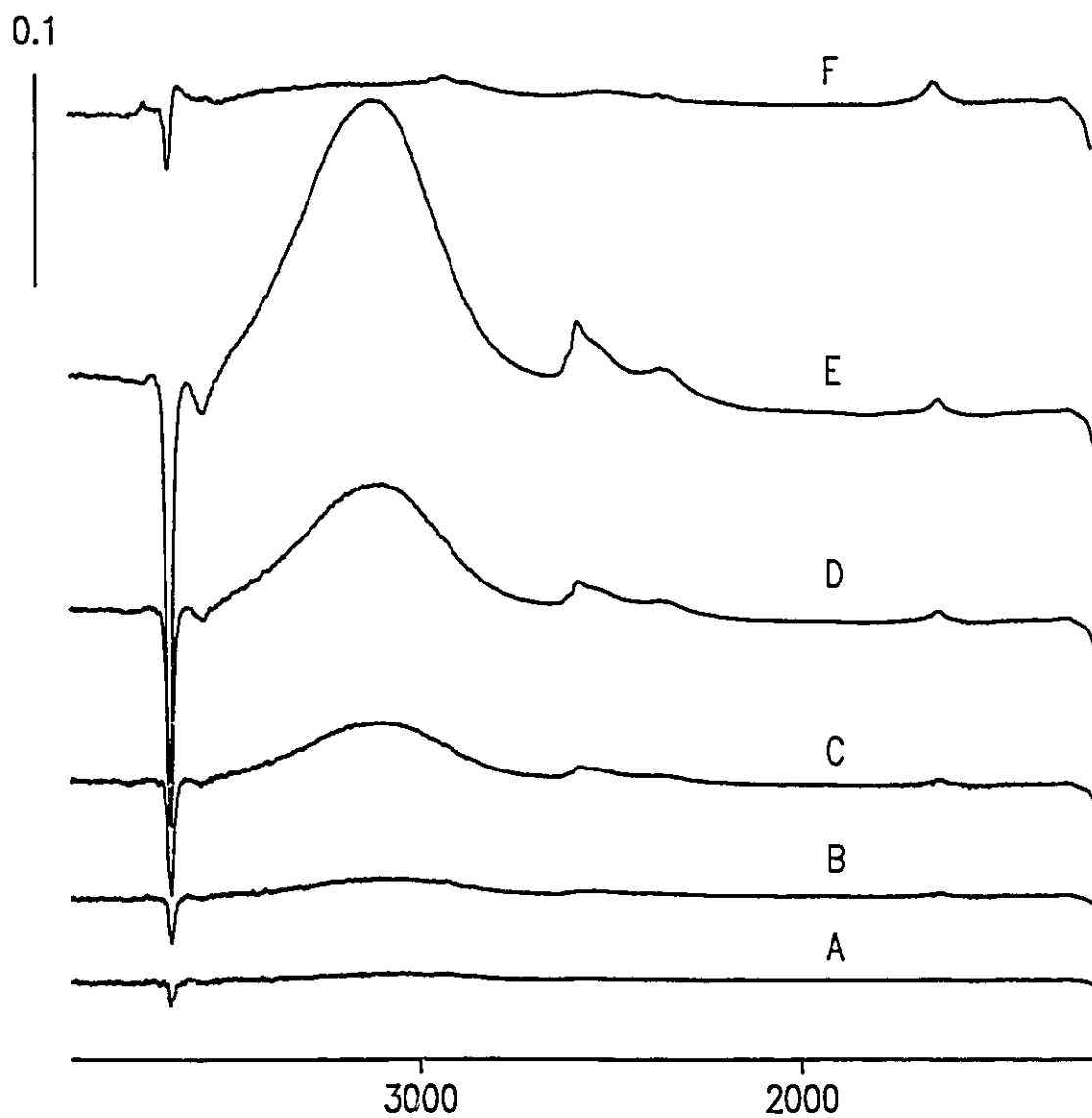


Fig 6.4 Adsorption of H_2S on HY
(A). add $60 \mu\text{mol/g}$ of H_2S . (B). add $150 \mu\text{mol/g}$ of H_2S .
(C). add $600 \mu\text{mol/g}$ of H_2S . (D). add $1400 \mu\text{mol/g}$ of H_2S .
(E). add $4000 \mu\text{mol/g}$ of H_2S . (F). after evacuation for 5 min.

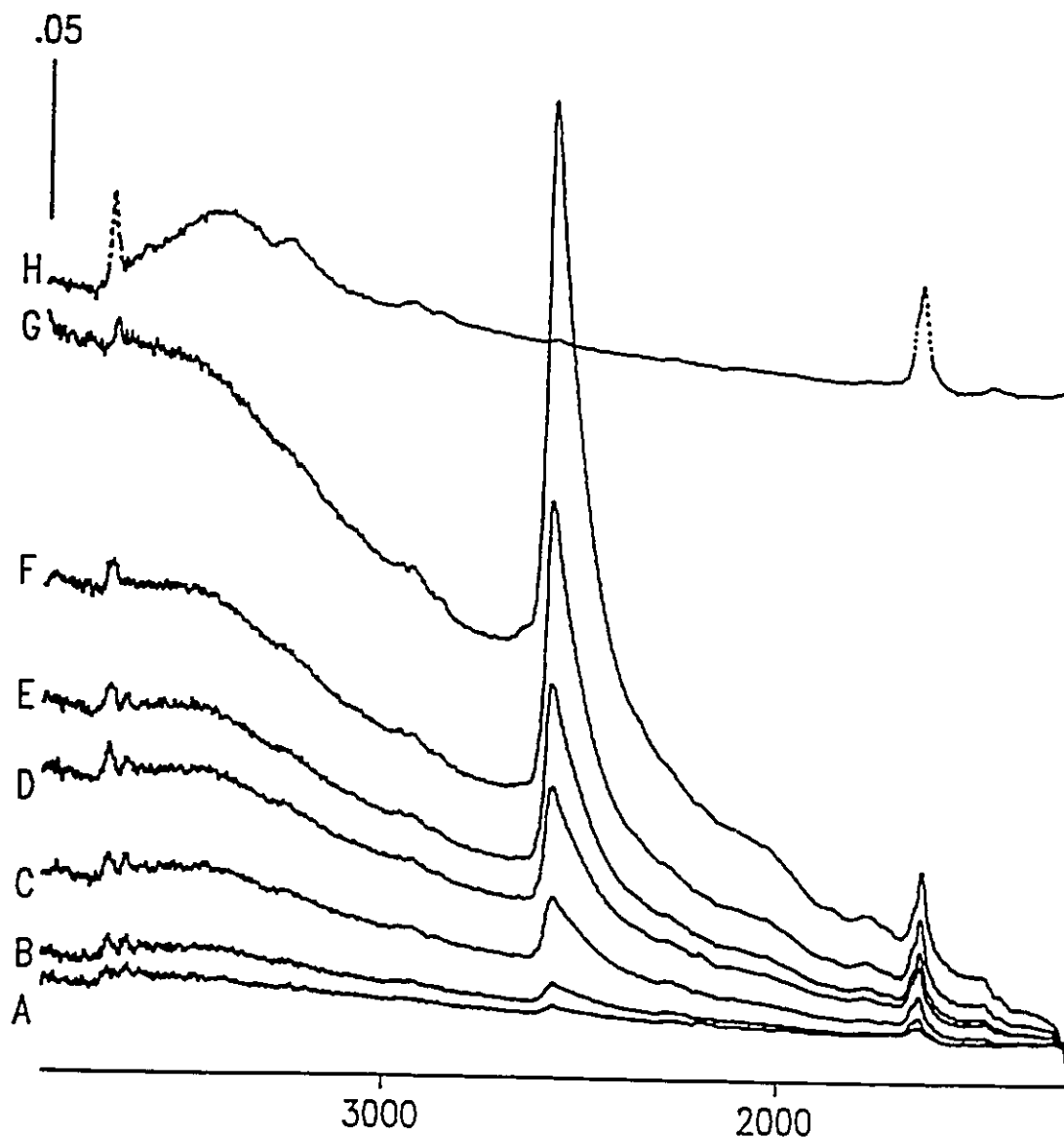


Fig 6. 5 Adsorption of H_2S on NaY
 (A). add 0.04 Torr of H_2S ($40 \mu\text{mol/g}$). (B). add 0.10 Torr of H_2S ($100 \mu\text{mol/g}$). (C). add 0.50 Torr of H_2S ($500 \mu\text{mol/g}$). (D). add 1.10 Torr of H_2S ($1100 \mu\text{mol/g}$). (E). add 2.00 Torr of H_2S ($2000 \mu\text{mol/g}$). (F). add 3.50 Torr of H_2S ($3500 \mu\text{mol/g}$). (G). add 10.00 Torr of H_2S ($10000 \mu\text{mol/g}$). (H). evacuate for 10 minutes.

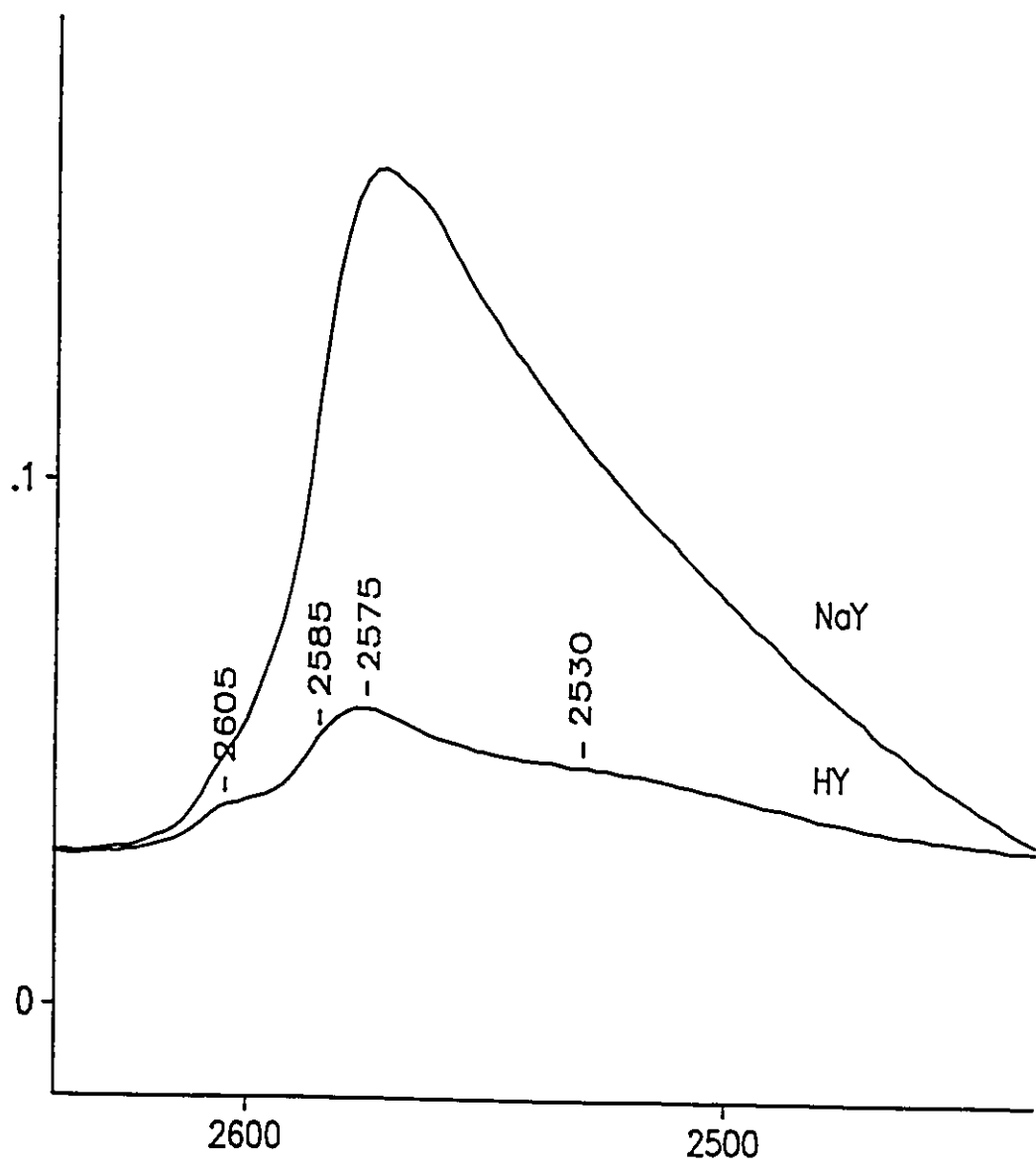


Fig 6. 6 The adsorption of H₂S on NaY and HY (about 4.00 Torr H₂S on 20 mg zeolites)

The IR bands between 2620 and 2300 cm^{-1} arise from physically adsorbed H_2S . They are more distinct with lower H_2S pressures and they can be resolved into four bands. On HY the situation is almost the same except the bands are much weaker, the intensities being about a quarter of that for NaY with the same pressure of H_2S . There is not much difference in the positions of these bands on NaY or HY. Because the bands at 2605 and 2530 cm^{-1} are observed at very low H_2S pressures, and the intensities do not change much with higher H_2S pressure, we assign them to the SH stretching vibrations of H_2S adsorbed on the Lewis acidic sites. It has been speculated that two kinds of Lewis acidic sites on zeolites; one is a pentagonal site and other is a tetrahedral site, both being associated with the nonframework aluminum residues [13]. These two bands (2605 and 2530 cm^{-1}) cannot be the asymmetric and symmetric SH vibrational modes of the same species because they are too far apart. The intensities of the bands at 2575 and 2565 cm^{-1} (or 2585, 2575 cm^{-1} on HY) increase in parallel with the increase of the pressure of H_2S , and they are assigned to the asymmetric and symmetric SH modes of H_2S molecules interacting with the OH groups or O^{2-} sites in the supercages. The serious perturbation of the band at 3650 cm^{-1} by the adsorption of H_2S on HY, and the formation of the new band at 3110 cm^{-1} support the notion that adsorption mainly occurs in the supercages. Further speculation is unwarranted.

In conclusion, H_2S physically adsorbs on zeolite-Y through OH or O^{2-} sites and on the Lewis acidic sites, but the dissociative chemisorption is found only on NaY. Water may be produced by replacement of O^{2-} by S^{2-} on the some active O^{2-} sites.

(3). Adsorption of SO_2 , evacuation, then addition of H_2S :

After evacuation of preadsorbed SO_2 on NaY, gaseous H_2S was added. Several OH bands appear at 3695, 3615, 3524, 3428, and 3245 cm^{-1} (Fig 6.7) and they intensify with increasing time of contact. The weak SO_2 combination band at about 2500 cm^{-1} disappears immediately and a $\nu(\text{HS})$ band at about 2570 cm^{-1} appears. A $\delta(\text{H}_2\text{O})$ band at 1640 cm^{-1} appears initially, and its intensity increases with the time. The band at 1330 cm^{-1} disappears. And new bands at 1252 and 1211 cm^{-1} grow initially, and then decrease with longer contact time. These new bands have not been reported before.

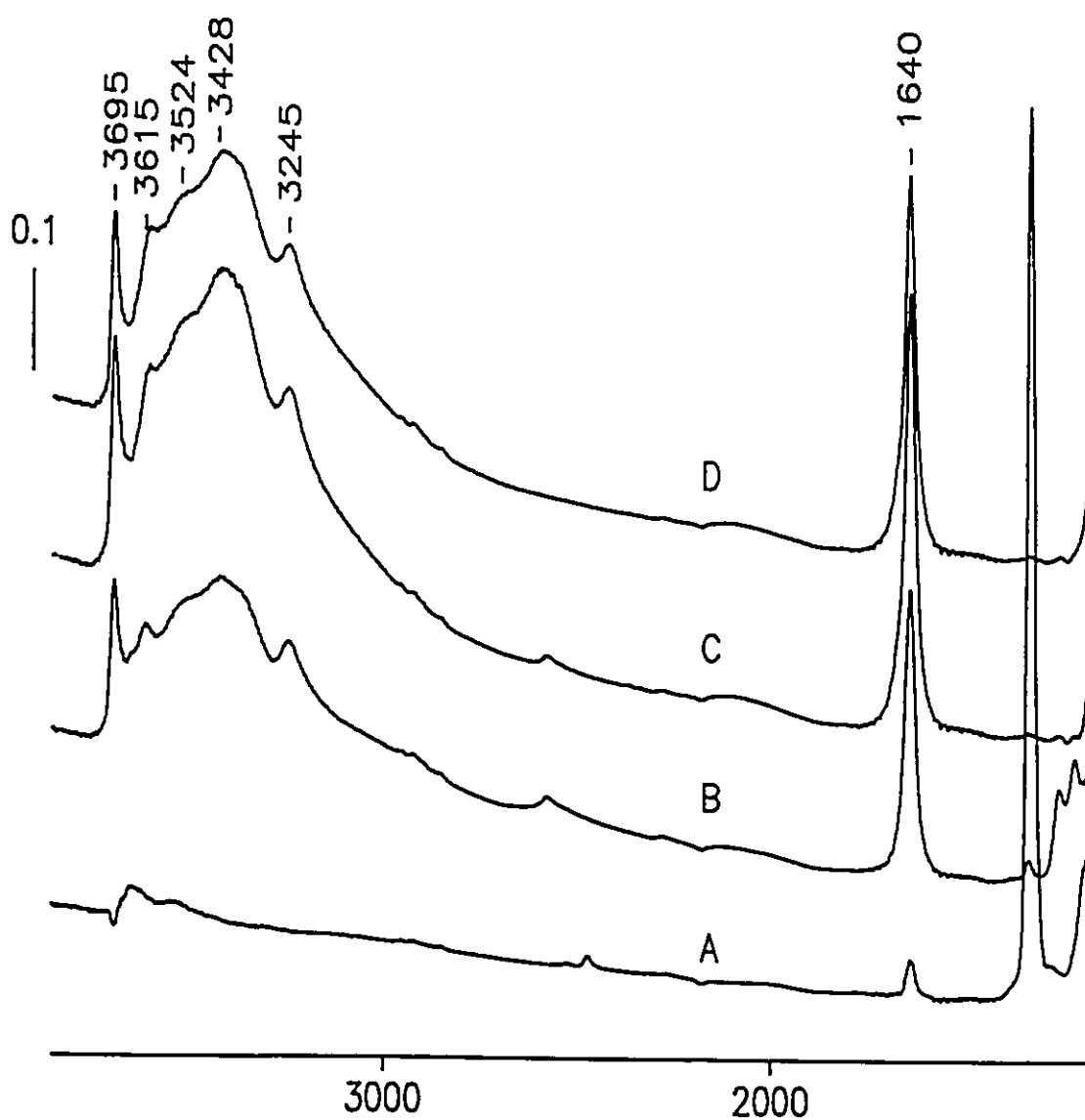
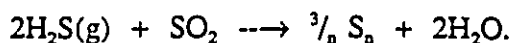


Fig 6. 7 Adsorption of SO_2 , then H_2S on NaY
 (A). add SO_2 2000 $\mu\text{mol/g}$, then evacuate for 5 min.
 (B). add H_2S 1350 $\mu\text{mol/g}$.
 (C). after 60 min.
 (D). evacuate for 5 min.

Because the band due to physically adsorbed SO_2 at 1330 cm^{-1} decreases in intensity quickly upon addition of H_2S and a strong $\delta(\text{H}_2\text{O})$ band at 1640 cm^{-1} grows, the Claus reaction between adsorbed SO_2 and gaseous H_2S probably occurs.



The water produced might react with excess H_2S to form many different hydrogen bonded OH groups ($3600\text{--}3200\text{ cm}^{-1}$). At this stage, the zeolite changed from white to light grey. After evacuation of the gas phase at room temperature, the sample was heated at about 170°C and sulfur was deposited on the cell walls.

The addition of H_2S to preadsorbed SO_2 on HY did not generate any new spectral features and the spectrum of adsorbed SO_2 on HY did not change. Therefore, the bands observed at 1250 and 1210 cm^{-1} are unique to NaY. They probably belong to the same species as was found for the adsorption of a $\text{H}_2\text{S}/\text{SO}_2$ mixture on Al_2O_3 ($1235/1190\text{ cm}^{-1}$), ZrO_2 ($1256/1155\text{ cm}^{-1}$), MgO ($1245/1203\text{ cm}^{-1}$). This point will be discussed further later in connection with the adsorption of the $\text{H}_2\text{S}/\text{SO}_2$ mixture. However, it is evident that the acidity of the surface has a strong influence on the Claus reaction. The HY zeolite is very acidic, and there was no evidence for this reaction.

(4). Adsorption of H_2S , evacuation, then addition of SO_2 :

We have seen that HY is a poor adsorbent of H_2S and after evacuation of preadsorbed H_2S all IR bands disappeared. The subsequent addition of SO_2 yielded a spectrum which was similar to that of SO_2 on HY. No additional reaction could be detected and, as was found in the previous section, HY is inactive for the Claus reaction.

In the same experiment using NaY, a new band at 3650 cm^{-1} formed when SO_2 was added but the band at 3695 cm^{-1} did not change much (Fig 6.8). In this case, there was only a weak combination band at about 2500 cm^{-1} . The band at 1640 cm^{-1} increased slightly and we conclude

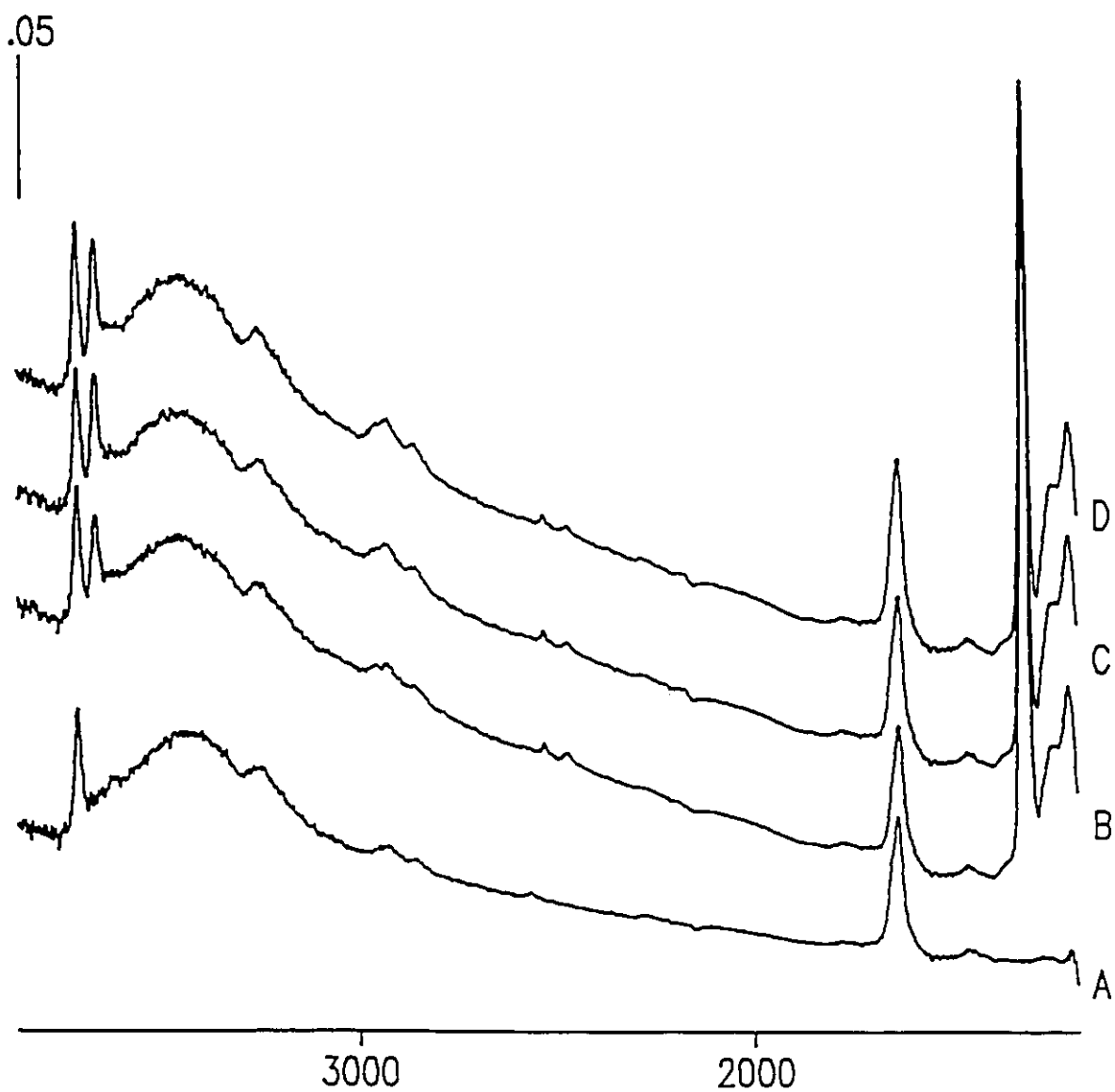


Fig 6. 8 Adsorption of H_2S , then SO_2 on NaY

(A). add 10 Torr (10000 $\mu\text{mol/g}$) of H_2S , then evacuate for 10 minutes (the same spectrum as in Fig 6.5H). (B). add 0.06 Torr (60 $\mu\text{mol/g}$) of SO_2 . (C). after 15'. (D). after 30'.

that only a little water was formed (compared with the situation of preadsorption of SO_2). A band at 1330 cm^{-1} appeared (physisorbed SO_2) along with bands near 1250 and 1215 cm^{-1} which were found for addition of H_2S to preadsorbed SO_2 on NaY. Following addition of a ten fold greater dose of SO_2 , the intensity of the water band increased by about 10% and the pair of bands at $1250/1215\text{ cm}^{-1}$ disappeared.

Therefore, the preadsorption of H_2S on NaY does not favour the Claus reaction, as was found for Al_2O_3 and $\text{Na}/\text{Al}_2\text{O}_3$. However, for NaY the explanation probably lies in the fact that H_2S does not apparently chemisorb on NaY, and that which is physically adsorbed is readily pumped away. The result agrees with the findings reported by Karge and Dalla Lana [18].

(5). Adsorption of a mixture of H_2S and SO_2 .

A low dose of the $\text{H}_2\text{S}/\text{SO}_2$ mixture ($\text{H}_2\text{S}:\text{SO}_2 = 2:1$) was added to NaY. Fig 6.9A shows that broad OH bands between 3000 to 3700 cm^{-1} appear. A sharp $\delta(\text{H}_2\text{O})$ band at 1640 cm^{-1} indicates that water is formed. Very weak bands at about 2600 cm^{-1} (H_2S) and 1330 cm^{-1} (SO_2) are shown, which indicates that little free H_2S and SO_2 exist. These bands disappeared after a few minutes reaction. Two bands at 1254 cm^{-1} and 1219 cm^{-1} are observed at the very beginning, and their absorbencies decrease with time. With about $500\text{ }\mu\text{mol/g}$ of the mixture, the $1254/1219\text{ cm}^{-1}$ bands disappeared after 1 hour of reaction, while both OH bands and $\delta(\text{H}_2\text{O})$ increased in their intensities. Compared with Al_2O_3 and other metal oxides, under the same conditions, the $1254/1219\text{ cm}^{-1}$ pair on NaY are less stable and converts faster to other species.

It is to be noted that the water band at 1640 cm^{-1} is more intense than that which was observed for adsorption of the same quantity of the mixture on Al_2O_3 , and ZrO_2 . Further, the two bands at $1254/1219\text{ cm}^{-1}$ are much weaker and eventually disappeared. With the other oxides, these two peaks usually increased in intensity with increasing time of contact. On the other hand, in the case of the spectra shown in Figure 6.9, although there was a weak band initially at 1330 cm^{-1} due to physically adsorbed SO_2 , this disappeared rapidly and there was no evidence of the presence of gas phase SO_2 . Fig 6.10A shows the IR spectrum observed when a much larger dose

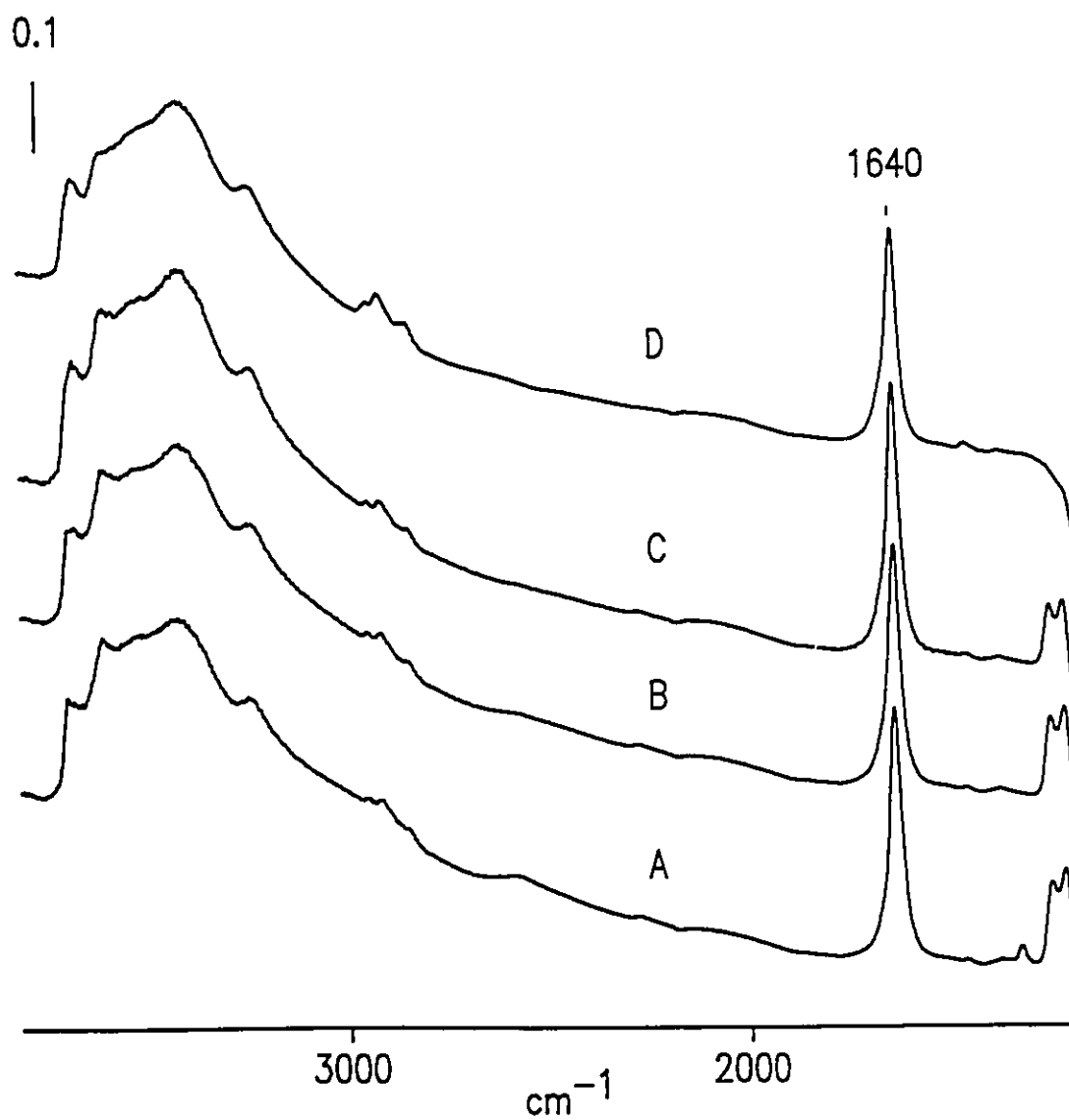


Fig 6. 9 The adsorption of a $\text{H}_2\text{S}/\text{SO}_2$ mixture on NaY

- (A). add mixture gas ($\text{H}_2\text{S}/\text{SO}_2=2$) 1200 $\mu\text{mol/g}$ on NaY.
- (B). after 5 min.
- (C). after 60 min.
- (D). evacuate for 5 min.

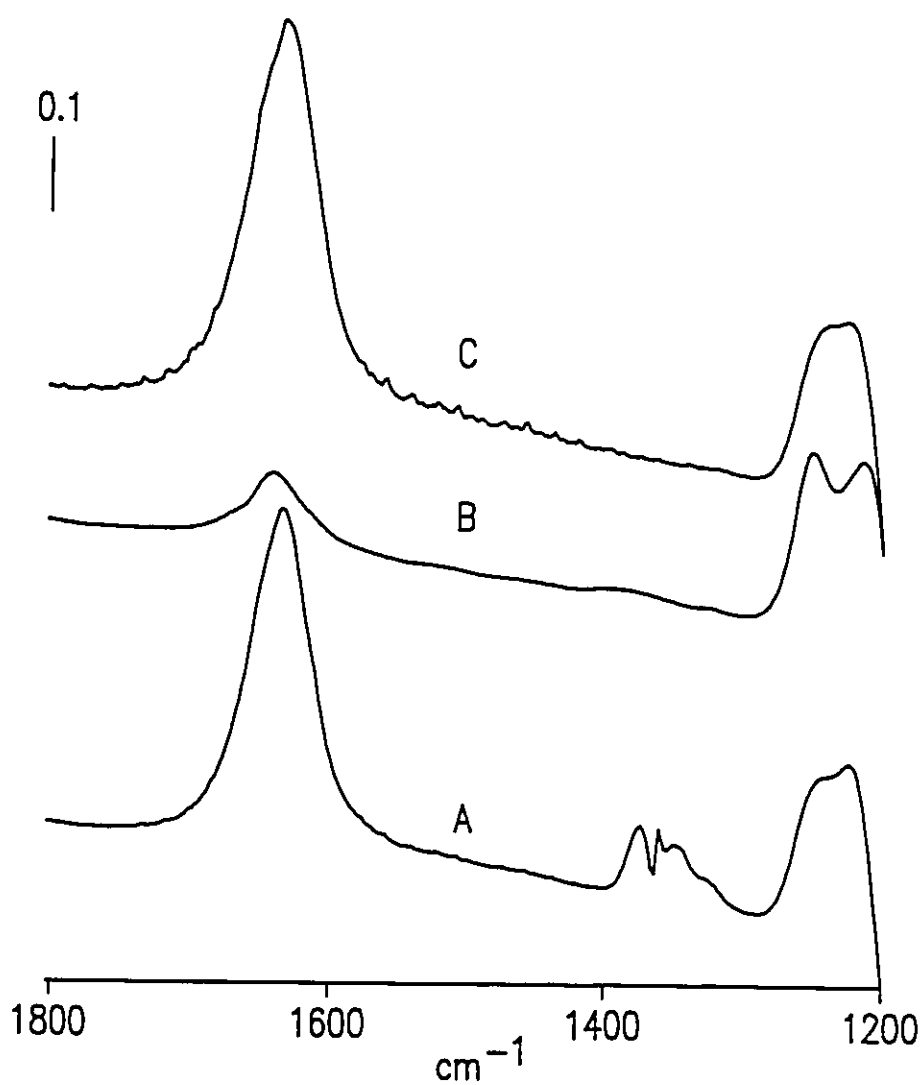


Fig 6.10 A large dose of $\text{H}_2\text{S}/\text{SO}_2$ mixture was added to NaY
(A). 24 Torr of mixture was added to NaY;
(B). after evacuation for 15 minutes;
(C). after adding 9 Torr of H_2O .

of the mixture was added, 24 Torr or 25 mmol/g. In this case the IR spectrum of gas phase SO_2 can be observed, the water band is very intense and the pair of bands near 1200 cm^{-1} are at $1240/1221\text{ cm}^{-1}$. None of the IR bands shown in Fig 6.10A changed in intensity with further time of contact. However, evacuation yielded the spectrum shown in Fig 6.10B; gas phase SO_2 is eliminated, the intensity of the water band diminishes and the pair of bands is now at 1254 and 1216 cm^{-1} . The shift to high and low wavenumber of the pair of bands near 1200 cm^{-1} upon evacuation was also observed following evacuation when the mixture was adsorbed on Al_2O_3 or on ZrO_2 . Upon re-addition of water the spectrum shown in Fig 6.10C was observed, this being qualitatively similar to that in Fig 6.10A (except for the absence of gas phase or physically adsorbed SO_2), again mimicking the behaviour which was observed for adsorption of the mixture on the other oxides.

It is apparent that the absorption capacity of NaY is much larger than Al_2O_3 or ZrO_2 , a direct manifestation of the microporous nature of zeolites. The same can be said of the adsorption of H_2S or SO_2 alone. The 1330 cm^{-1} band of physically adsorbed SO_2 on NaY (Fig 6.3) is very intense, as is the $\nu(\text{HS})$ mode for adsorbed H_2S (Fig 6.5) in comparison with those which were observed for adsorption of either gas on Al_2O_3 .

It would appear that, by virtue of its porous structure, NaY has much higher ability per gram of catalyst to adsorb and convert $\text{SO}_2/\text{H}_2\text{S}$ via the Claus reaction than does Al_2O_3 . The same cannot be said of the HY form of the zeolite; when the mixture was added, there was no evidence of the Claus activity, which is consistent with the weak adsorption of the acids H_2S or SO_2 on this acidic catalyst. Therefore, we can firmly conclude that although porosity is important as it relates to the quantity of an adsorbent which can be held by a catalyst, excessive acidity impedes this process and we assume that catalyst acidity has a very negative impact on the Claus reaction.

4. CONCLUSION

The adsorption capacity of the zeolites NaY and HY for SO_2 or for H_2S is considerably

greater than Al_2O_3 , $\text{Na}/\text{Al}_2\text{O}_3$ or Na/SiO_2 . This can be attributed to the microporous nature of zeolites. However, the adsorption is mainly physical and there is little evidence for chemisorption of either reactant. None the less, the acidity of the zeolite does influence the quantity and strength of physically adsorbed species, this being lower for HY, as would be expected for the physical adsorption of acidic molecules on an acidic surface. On NaY, SO_2 adsorption is primarily believed to occur via coordination to sodium sites which can act as active centre.

In common with Al_2O_3 , $\text{Na}/\text{Al}_2\text{O}_3$ and Na/SiO_2 , the Claus reaction occurs when mixtures of H_2S and SO_2 are contacted with NaY; no significant reaction occurs on HY. The primary role of the zeolite appears to be to bring the physically held reactants together in a suitable orientation for reaction to occur. As with Al_2O_3 and Na/SiO_2 , it would appear that polythionates, $\text{S}_m\text{O}_6^{2-}$, are generated in the Claus reaction.

References

- [1]. Flanigen, E. M., in "Zeolite: Science and Technology" (Editor: F. Ramoa Ribeiro et al.), Martinus Nijhoff Publishers, Hague, 1984.
- [2]. Deo, A. V., Dalla Lana, I. G. and Habgood, H.W., J. Catal., 21, 270-281(1971).
- [3]. Karge H. G. and Rasko, J., J. Colloid and Interface Science, 61, 522(1978).
- [4]. Ziolk, M., Bulletin of the Polish Academy of Sciences, Chemistry, 30, 285-290(1984).
- [5]. Horward, J. and Kadir, Z. A., Spectrochimica Acta., 41A, 825-831(1985).
- [6]. Karge, H. G., Zhang, Y., De Suarez, S. T. and Ziolk, M., Proc. Conf. Structure and Reactivity of Modified Zeolite, Prague, P. A. Jacobs et al. (Editors), Elsevier Science Publishers, Amsterdam, 1984, p49.
- [7]. Karge, H. G., Lanieki, M. and Ziolk, M., J. Catal., 109, 252-262(1988).
- [8]. Garcia, C. L. and Lercher, J. A., J. Phys. Chem., 96, 2230-2235(1992).

- [9]. Smith, J. V. in Rabo, J. A. (Editor), "Zeolite Chemistry and Catalysis", ACS monograph Series vol. 171, (1976) p52.
- [10]. Datta, A., Cavell, R. G., Tower, R. W. and George, Z. M., J. Phys. Chem., 89, 443 (1985).
- [11]. Ward, J. P., J. Catal., 13, 321(1969).
- [12]. Scherzer, J., "Octane-Enhancing Zeolitic FCC catalysis: Scientific and Technical Aspect", Marcel Dekker Inc., New York and Basel, 1990.
- [13]. Coster, D., Blumefeld, A. L., and Fripiat, J. J., J. Phys. Chem., 98, 6201(1994).
- [14]. Liu, S. b., Fung, B. M., Yang, T. C., Hong, E. C., Chang, C. T., Shih, P. C., Tong, F. H. and Chen, T. L., J. Phys. Chem., 98, 4393(1994).
- [15]. Klein, H., Kirschhock, C., and Fuess, H., J. Phys. Chem., 98, 12345(1994).
- [16]. Lin, Chiung-Fang and Chao, Kuei-Jung, J. Phys. Chem., 95, 9411(1991).
- [17]. Veloso, C. O., Monteiro, J. L. F. and Sousa-Aguiar, E. F., in "Zeolites and Related Microsporous Materials: State of the Art 1994", (Studies in Surface Science and Catalysis, Vol. 84), Ed. by Weitkamp, J. *et al.*, p1913, Elsevier, 1994.
- [18]. Karge, H. G. and Dalla Lana, I. G., J. Phys. Chem., 88, 1538 (1984).
- [19]. Barthomeuf, D., in "Zeolites: Science and Technology", Ed. by Ramôa, F. *et al.*, Martinus Nijhoff Publishers, The Hague, 1984, p291.

Chapter 7

AN EVALUATION OF MAGNESIUM ALUMINATE SPINEL AS A SULFUR DIOXIDE TRANSFER CATALYST

1. INTRODUCTION

Crude oil contains sulfur, the quantity ranging from about 0.2-5% by mass, depending on its source. The sulfur is mostly in the form of organosulfur compounds [1]. In petrochemical processes using fluidized catalytic cracking (FCC) catalysts, about 45-55% of the sulfur in the crude oil is converted to H_2S , 35-45% remains in the liquid products and about 5-10% is deposited on the catalyst as coke [2]. During the oxidative regeneration of an FCC catalyst when coke and occluded organosulfur deposits are 'burned off' in oxygen at elevated temperatures, a $\text{SO}_2 + \text{SO}_3$ mixture (SO_x) is generated [2-7]. The gas which comes from the catalytic cracker catalyst recovery furnace can be the largest source of particulate air pollution in a refinery operation. This is a serious pollutant gas because of its high concentration. Although SO_x emissions can be controlled by flue gas scrubbing or feedstock desulfurization, these are laborious and costly. A better strategy to control SO_x emissions (about 90% SO_2 and 10% SO_3) during regeneration is to add to the FCC catalyst a so-called SO_x transfer catalyst which is capable of trapping the SO_x species produced as sulfates. The ideal transfer catalyst should be able to easily facilitate the oxidation of SO_2 to SO_3 , have a high sorption capacity for the sulfur (VI) species produced, form relatively thermally stable sulfates, and be easily regenerated. The regeneration is carried out by reducing the sulfates to hydrogen sulfide which are then treated via the modified Claus process.

In this chapter, we report the results of an investigation on magnesium aluminate spinel (hereinafter referred to as spinel, MgAl_2O_4) as a potential SO_x transfer catalyst. The experiments are based on infrared spectroscopy and vacuum microbalance techniques to examine the sorption

ability of the spinel. We also study the possible sulfate structures formed on the spinel, and the stability of the sulfate toward heat and hydrogen. Many patents claim that spinel is an efficient SO_x transfer agent [8-11] and its role in a more complex system with cerium oxide has recently been discussed [2]. Our results are compared with those previously obtained for Al_2O_3 [12], TiO_2 [12], ZrO_2 [13], SiO_2 [14], and MgO [15] for which there is a wide range of stabilities and structures of the sulfate species formed. As will be discussed below, we conclude that spinel is a superior material as a SO_x transfer catalyst.

2. RESULTS

(1). *Surface properties of spinel*

The infrared spectrum of spinel activated in vacuum at 250 °C for 2 hours is shown in Fig 7.1. It is characterized by a broad and relatively featureless absorption from 3800 to 3400 cm^{-1} due to surface OH groups, two strong bands at 1545 and 1428 cm^{-1} due to carbonate species, and a region of total absorption below 950 cm^{-1} due to absorption by the lattice modes of MgAl_2O_4 . A carbon analysis revealed that the original sample contained 0.84% carbon. Progressive heating of the sample resulted in a decrease in the intensities of both the carbonate and OH peaks, with the latter showing some structure having infrared bands at 3750 (shoulder) 3737 and 3680 cm^{-1} (see Fig 7.1 for 450 and 750 °C), different from those of Al_2O_3 [16] and MgO [17]. Heating above 900 °C removed all traces of carbonate and hydroxyl species, but the surface area also started to decrease markedly (Fig 7.2). The results showed that the spinel surface structure was stable below 650 °C but that the surface area had a large change in a temperature range between about 700-900 °C. This suggests that spinel as transfer catalyst should be used and regenerated at a temperature below about 700 °C.

We have studied the adsorption of some probe molecules such as pyridine, CO, and CO_2 on spinel activated at 450 °C in order to assess the nature of the acid-base sites. The results were similar to those which have been reported by Morterra *et al.* [18] and will not be reported here except to note that this sample of spinel appears to be similar to that which has been investigated previously. That is, the Lewis acidity and basicity is intermediate between that of MgO and

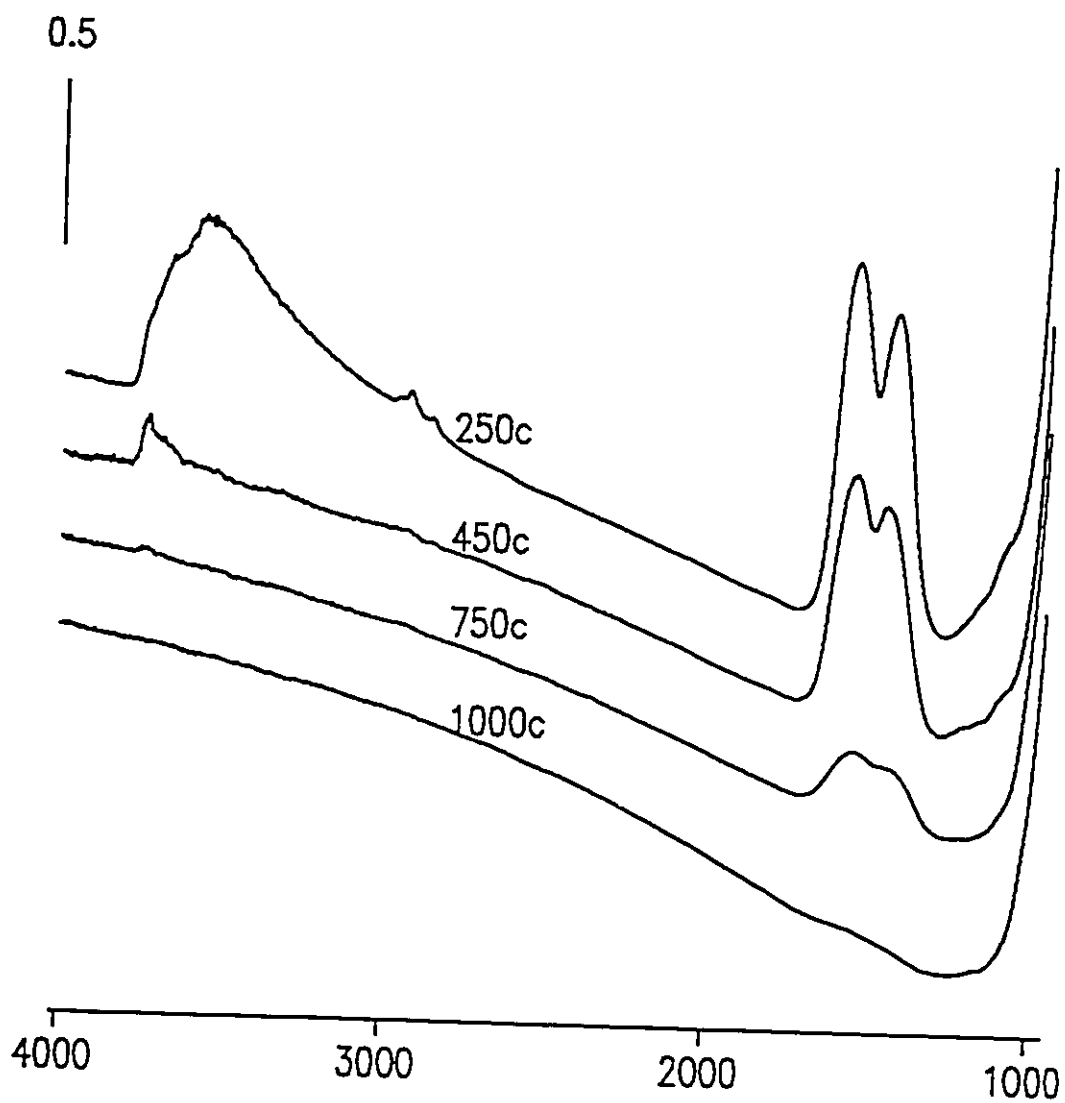


Fig 7.1 Infrared spectra of a 10 mg/cm² spinel sample after heating in vacuum at the indicated temperatures in °C.

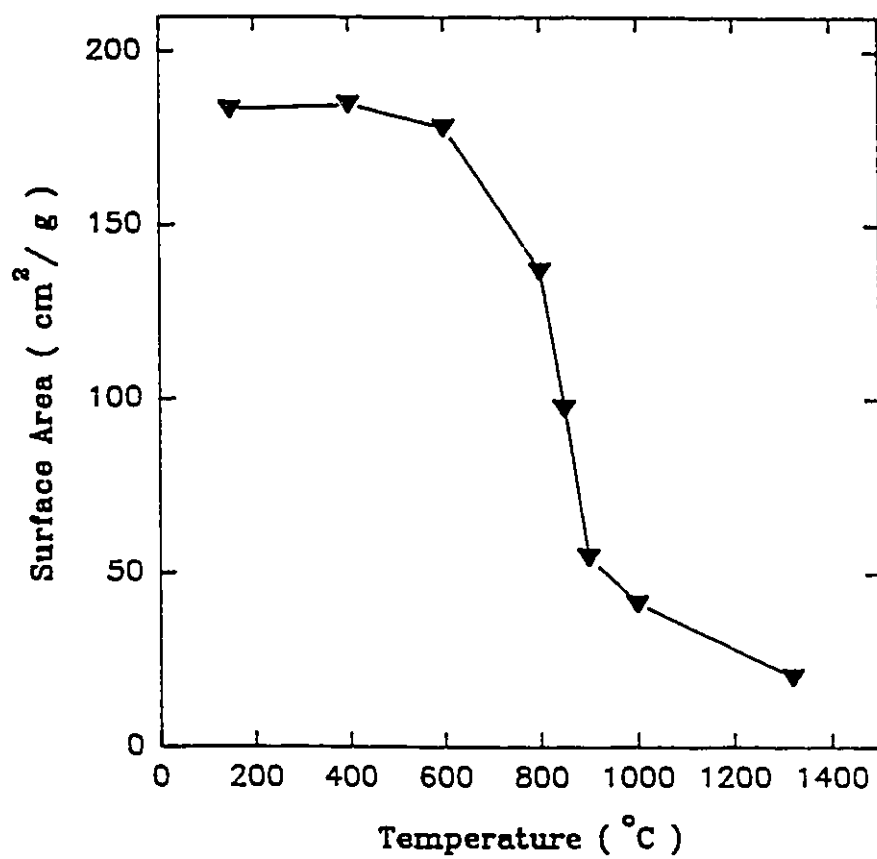


Fig 7.2 Surface area of spinel as a function of the temperature of activation
BET measurements are made up evacuation for 1 hour at each temperature.

Al_2O_3 , Al_2O_3 having the stronger Lewis acid sites and MgO having the stronger base sites. This stronger basicity of spinel relative to alumina is clearly demonstrated by the observation that carbonates readily form on spinel from the adsorption of carbon dioxide from the air, whereas this does not occur on Al_2O_3 . Accordingly, any spinel that is used as an industrial FCC transfer catalyst will likely contain carbonate initially, and for this reason, the sulfation experiments to be described below were carried out without attempting to remove these species. That is, the activation and sulfation temperatures were in the range from 450 to 650 °C.

(2). Sulfation

The sulfation process was carried out by introducing a known quantity of SO_2 or H_2S (expressed as $\mu\text{mol/g}$ of spinel) in a large excess of oxygen followed by heating at a specified temperature in a quartz cell. As has been found with other oxides (except for SiO_2), sulfation could arise from oxidation of H_2S or SO_2 , or via impregnation (including SiO_2) with ammonium sulfate followed by activation at 450-650 °C [12-15]. Fig 7.3 compares the infrared spectra observed via oxidation of SO_2 (400 $\mu\text{mol/g}$) at 450 °C with that obtained via impregnation using 400 $\mu\text{mol/g}$ of ammonium sulfate followed by activation at 450 °C. Unlike the situations with Al_2O_3 , TiO_2 or ZrO_2 , the spectra are quite different according to the mode of sulfation. Finally, the spectra in Fig 7.3 are superimposed upon the steeply rising background of spinel in the 1100 to 950 cm^{-1} spectral region. For the subsequent spectra, the background spectrum of the activated spinel has been subtracted from those obtained after sulfation so as to give a straight baseline (such a subtraction is not possible with the impregnated spinel).

Fig 7.4 shows the spectra observed following the oxidation of increasing quantities of SO_2 for 2 hours at 550 °C on a sample preactivated in vacuum at the same temperature. Three bands at 1350, 1135 and 1055 cm^{-1} are observed initially for 25 $\mu\text{mol/g}$ of SO_2 . For increasing quantities of SO_2 (Fig 7.4B, 4C) one notes the appearance of a shoulder at 1375 cm^{-1} , a band near 1290 cm^{-1} and a shoulder near 1025 cm^{-1} . For even greater quantities (Fig 7.4D, 4E), the peak in the centre of the spectrum increases in intensity and broadens with the appearance of a shoulder near 1175 cm^{-1} . Finally, the oxidation of the same quantities of H_2S (not shown here)

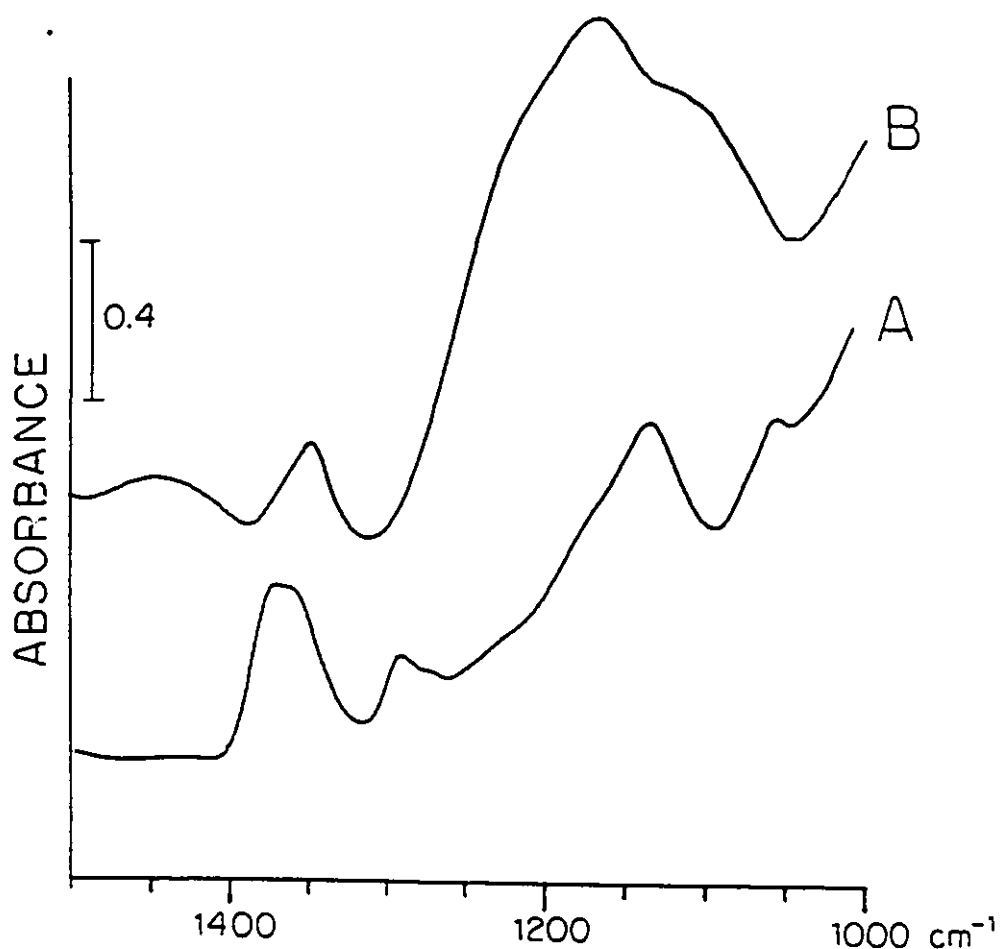


Fig 7.3 IR spectra of (A) spinel after oxidation at 450 °C of 400 $\mu\text{mol/g}$ of SO_2 in excess oxygen followed by evacuation at 450 °C. (B) IR spectrum of spinel after impregnation from solution with 400 $\mu\text{mol/g}$ ammonium sulfate followed by heating under vacuum at 450 °C. The increasing background absorption at the right of each curve is due to adsorption by spinel below 1000 cm^{-1} and in the remaining spectra (Figs 7.4-7.8), the background spectrum of the activated spinel has been subtracted.

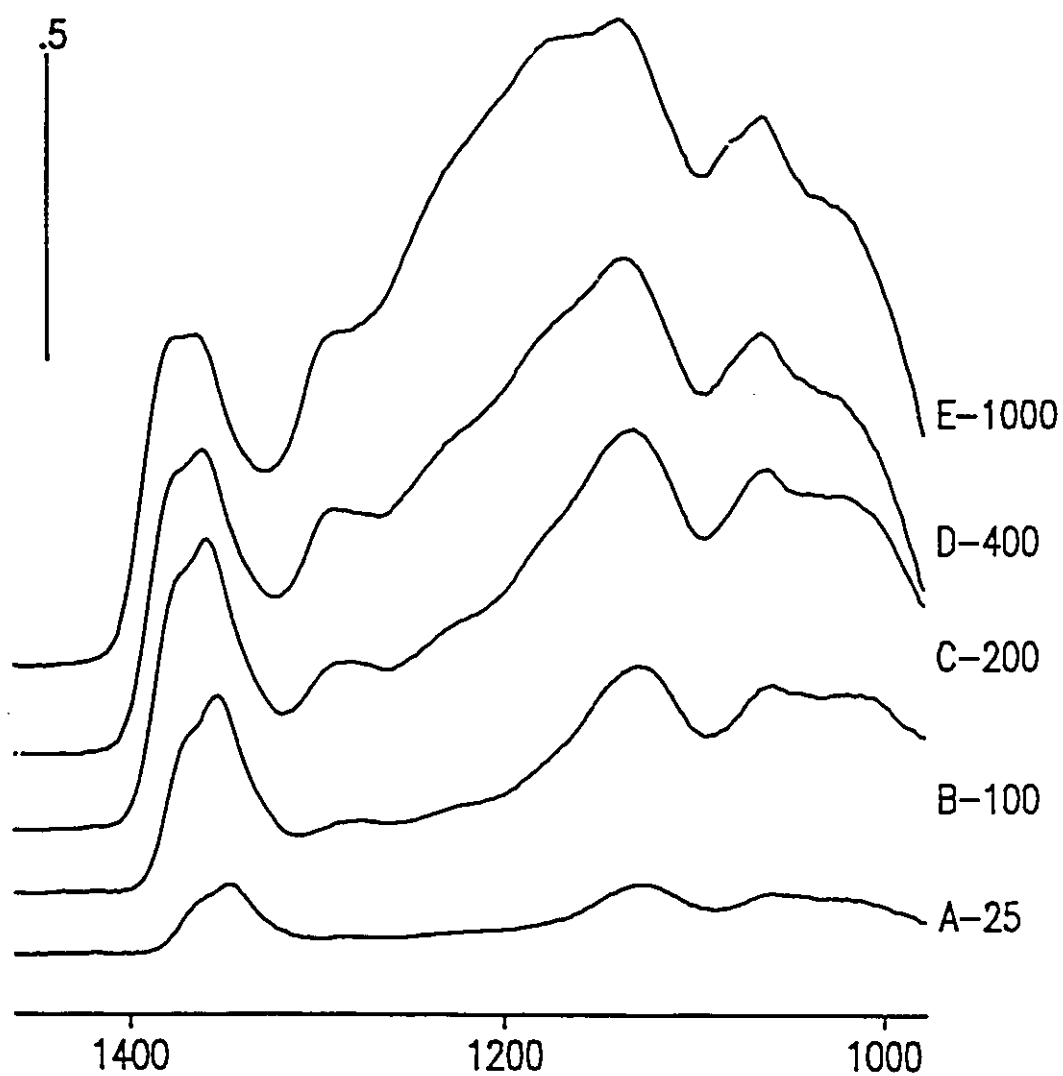


Fig 7.4 Infrared spectra of spinel after oxidation of the indicated quantities of SO_2 ($\mu\text{mol/g}$). In each case the oxidation was at 550°C for 2 hours and the sample was evacuated for 0.5 hour at 550°C afterwards.

under the same experimental conditions gave almost identical spectra although the shoulder at 1175 cm^{-1} was slightly more intense than in the case of SO_2 oxidation.

Fig 7.5A, B, C and D shows the effect of varying the temperature of oxidation of SO_2 while curves E, F and G show the effect of changing the time of oxidation at the same temperature. These curves show that there is an increase in the intensity of the intense central peak near 1175 cm^{-1} for either increasing in the temperature of sulfation from 300 to $650\text{ }^\circ\text{C}$, or the time of sulfation at a fixed temperature ($550\text{ }^\circ\text{C}$). Finally, Fig 7.6A shows the spectrum obtained with a spinel which was calcined in air at $1320\text{ }^\circ\text{C}$ (BET surface area $20\text{ m}^2/\text{g}$), activated at $600\text{ }^\circ\text{C}$ and then sulfated with $200\text{ }\mu\text{mol/g}$ of SO_2 in excess O_2 at $600\text{ }^\circ\text{C}$ for 18 hours. On this low surface area spinel, the spectrum is notable for the absence of bands in the $1400\text{-}1350\text{ cm}^{-1}$ spectral region, and presents major features at 1240 , 1175 , 1110 (doublet) and 1025 cm^{-1} . Subsequent spectra show the effect of evacuating the sample at increasing temperatures to $750\text{ }^\circ\text{C}$.

The results described are very different from those found for alumina and titania [12] insofar as the overall band profile for spinel changed considerably according to the quantity of SO_2 (or H_2S) oxidized, or with the time or temperature of oxidation, indicating that several sulfate type species were produced. Even on ZrO_2 , where three surface sulfate type species were found [13], the differences in the present case are much more pronounced as the overall spectral intensity increases. A further difference relative to other oxides is the presence, after long oxidation periods, or on low surface area samples, of a very intense band at 1175 cm^{-1} , a characteristic of bulk sulfate ions [19] which generally have an intense band in the spectral region from 1100 to 1200 cm^{-1} . A spectrum which was very similar to that shown in Fig 7.6 was also observed in a study of sulfation of SO_2 on MgO and this was attributed to bulk or ionic type sulfate species [15].

A vacuum microbalance study of the sulfation of spinel confirmed that the sorption capacity of this material is high. A 400 mg spinel sample (20 fold greater than that used in the IR studies) was activated at $650\text{ }^\circ\text{C}$ and sulfated with $1000\text{ }\mu\text{mol/g}$ of SO_2 at $550\text{ }^\circ\text{C}$ for 66 hours.

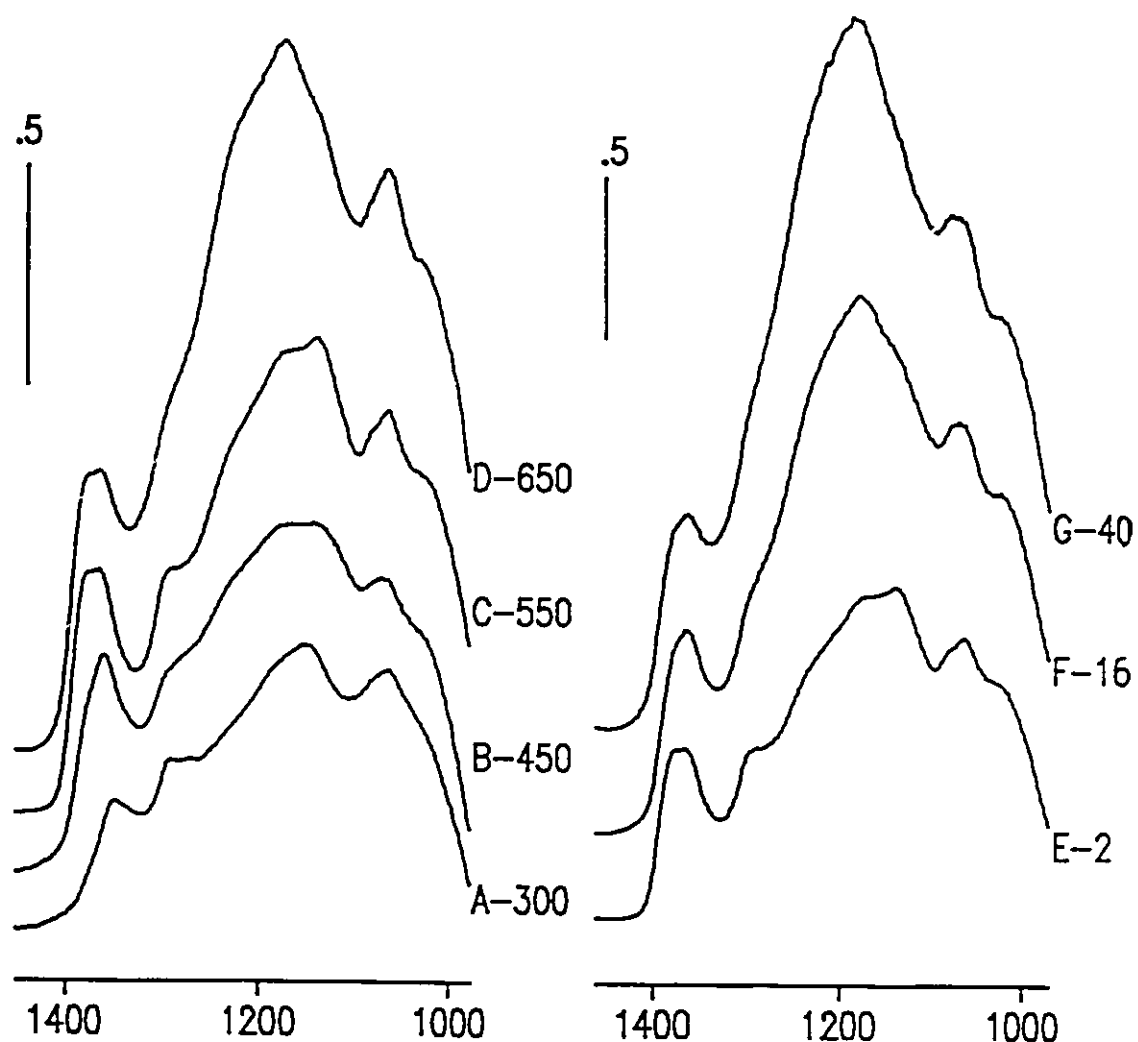


Fig 7.5 Infrared spectra of sulfated spinel (1000 μmol/g) showing the effect of temperature (curves A-D at the left) and time (curve E-G at the right) on the intensity of the sulfated bands. For curves A-D, the sulfation time was 2 hours and the temperature of sulfation was as indicated. For curves E-G, the temperature of sulfation was 550 °C and the time of sulfation in hours was indicated.

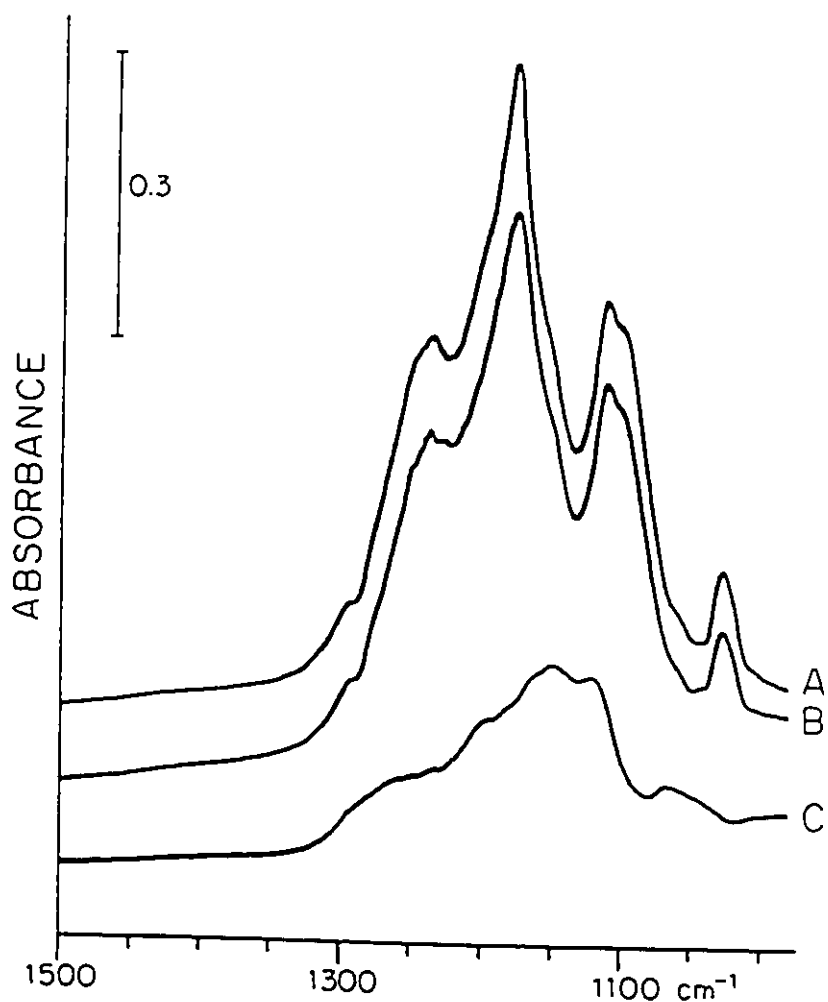


Fig 7.6 (A) Sulfation of a low surface area spinel at 600 °C with 200 $\mu\text{mol/g}$ of SO_2 for 14 hours followed by evacuation for 1 hour at 600 °C. (B) and (C), spectra observed after evacuation of (A) at 700 °C and then at 750 °C for 1 hour respectively.

After 60 hours the mass was constant and, assuming that SO_2 becomes oxidized to SO_3 which in turn adsorbed to give sulfate, the gain in mass corresponded to $872 \mu\text{mol/g}$. This number is probably to be considered a lower limit for the amount of sulfate formed from $1000 \mu\text{mol/g}$ of SO_2 because, during heating for 60 hours, some of the surface carbonates would certainly be displaced (as has been confirmed in other IR studies) giving rise to an opposing decrease in mass of the sample as sulfate is formed. Thus, practically all of added SO_2 can be transformed into sulfate under these conditions. In a similar experiment with $1000 \mu\text{mol/g}$ of SO_2 on alumina, the quantity of sulfate formed after 40 hours was $290 \mu\text{mol/g}$ and $310 \mu\text{mol/g}$ after 80 hours. In this case only 31% of the added SO_2 was converted to sulfate, clearly showing that the sorption capacity of alumina is less than that of spinel under the same conditions.

(3). Thermal stability and reducibility of sulfates

The thermal stability under vacuum and the reducibility of the various sulfate species was studied using 450 and 550°C sulfated samples, and the results were qualitatively similar in each case although for equal sulfation doses and equal sulfation times the infrared peaks were less intense in the 450°C case, as explained earlier. Fig 7.7A shows the effect of heating a sulfated spinel ($100 \mu\text{mol/g SO}_2$) at increasing temperatures after initial sulfation at 550°C followed by evacuation at 550°C . Between 550°C and 700°C the intensity of the 1375 cm^{-1} band increased whereas that at 1360 cm^{-1} remained practically constant and the only other change, which was more clearly seen in the subtracted spectra (not shown), was a slight decrease in intensity near 1175 , 1225 and 1290 cm^{-1} . Beyond 800°C there was a large decrease in all bands, leaving very weak peaks at 1375 , 1175 and 1025 cm^{-1} . Fig 7.7B shows a series for a sample which was similarly sulfated overnight with $400 \mu\text{mol/g}$ of SO_2 and which contained bulk sulfate species (1175 cm^{-1}) in addition to surface species. In this case the heating caused a large decrease in the intensity of the 1175 cm^{-1} band accompanied by an increase in the intensity of that at 1375 cm^{-1} . Finally, vacuum microbalance experiments confirmed that there was only a small loss in mass during heating of a sulfated spinel from 450 to 800°C (heating rate at 1°C/min), reconfirming that there is little decomposition up to 800°C and in accord with the infrared results.

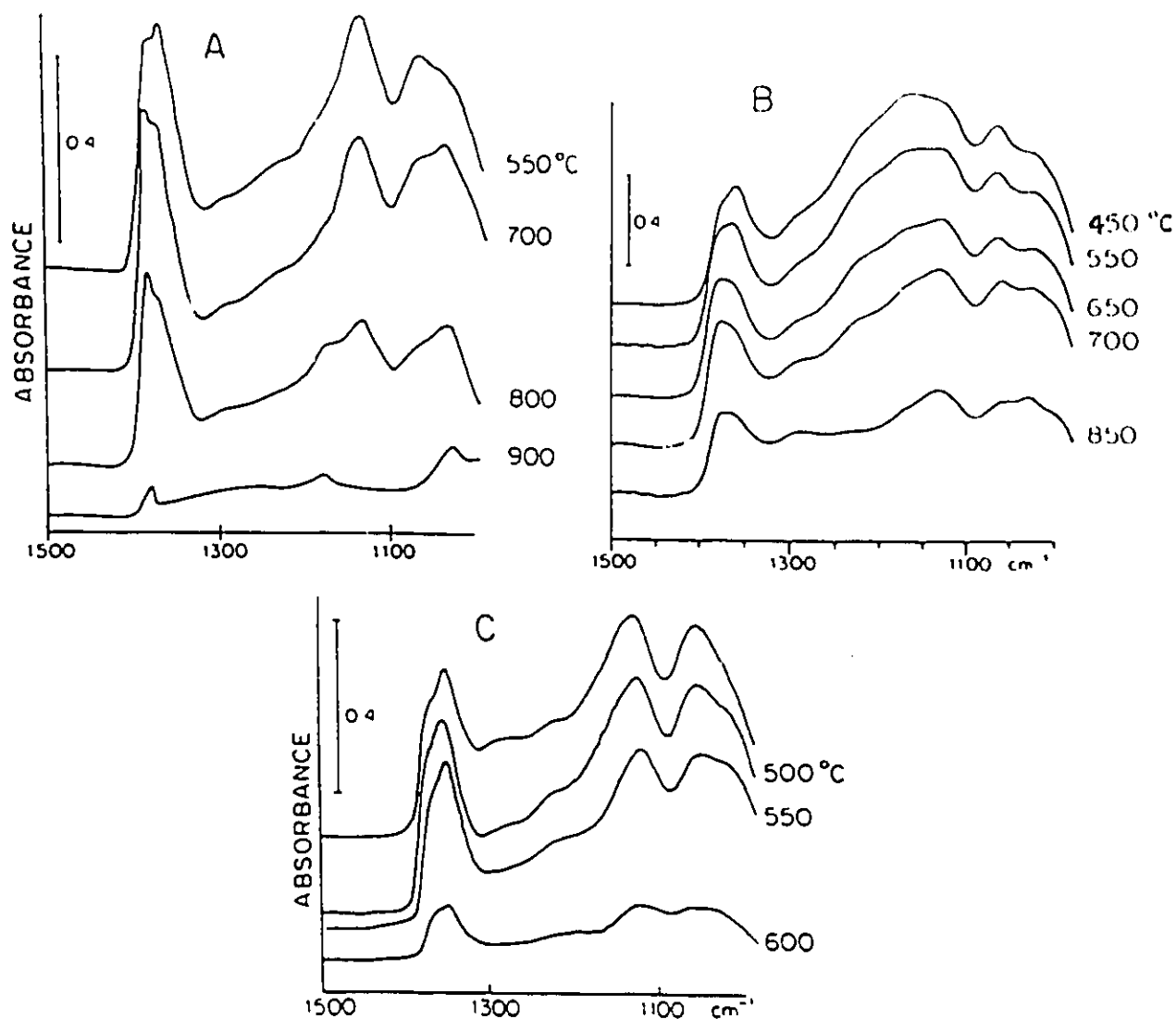
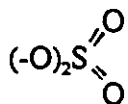


Fig 7.7 (A) The spinel was sulfated with 100 $\mu\text{mol/g}$ of SO_2 for 1 hour at 550 $^{\circ}\text{C}$ (top curve) followed by evacuation at the indicated temperatures in $^{\circ}\text{C}$. (B) The spinel was sulfated with 400 $\mu\text{mol/g}$ of SO_2 for 14 hours at 550 $^{\circ}\text{C}$ (top curve) followed by evacuation at the indicated temperatures in $^{\circ}\text{C}$. (C) The spinel was sulfated with 100 $\mu\text{mol/g}$ of SO_2 at 550 $^{\circ}\text{C}$ for 8 hours and then evacuated at 550 $^{\circ}\text{C}$ (top curve). Then, 40 Torr of hydrogen (1 Torr = 133.3 Pa) was added at 20 $^{\circ}\text{C}$ and the cell was heated for 1 hour at the indicated temperatures in $^{\circ}\text{C}$.

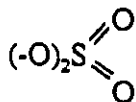
Fig 7.7C shows the affect of heating a sulfated ($100 \mu\text{mol/g SO}_2$) spinel in excess hydrogen gas at increasing temperatures. There is a small uniform decrease in intensities of all bands from initial state after heating at 450 to 550 °C and a very large change thereafter, all bands essentially disappearing after heating about 600 °C. It is apparent that under the presence of the hydrogen the sulfate species are much less stable on spinel. For large initial doses of SO_2 , where bulk sulfate was additionally present, there was also an almost uniform decrease in the intensities of all bands in the 550 to 650 °C temperature range. Microbalance experiments showed that a spinel sulfated with $200 \mu\text{mol/g}$ of SO_2 underwent no mass loss in a large excess of hydrogen up to 500 °C, but beyond this temperature there was a large decrease in mass between about 550 °C to 640 °C, and at higher temperatures the mass of the sample was essentially constant again. The temperature for 50% mass loss was 590 °C and with a more highly sulfated sample ($1000 \mu\text{mol/g SO}_2$) this temperature was 610 °C. These results are also in agreement with those observed via infrared spectroscopy, bearing in mind that the temperature was increased at a constant rate in the microbalance experiments whereas heating was at a series of fixed temperatures in the IR case.

(4). Discussion

The previous studies have shown that only surface sulfates were formed on Al_2O_3 [12], TiO_2 [12], and ZrO_2 [13] from the oxidation of SO_2 , and on SiO_2 [14] via impregnation with ammonium sulfate followed by vacuum activation. Further, three distinct sulfate types were found on ZrO_2 but a single type on the other oxides. Isotopic exchange using H_2^{18}O showed that the single sulfate species was type $(-\text{O})_3\text{S}=\text{O}$ on Al_2O_3 and TiO_2 , but of type



containing 2 equivalent $\text{S}=\text{O}$ bonds on SiO_2 . The infrared spectrum of sulfated spinel is more complex than that which was observed using the above oxides insofar as multiple species, both surface and bulk, can be formed. Only on MgO was there evidence for bulk as well as surface species, the surface species being of type



but containing non-equivalent S=O bonds [15].

For sulfated spinel, like the other oxides, the infrared bands in the region from 1375 to 1350 cm^{-1} must be attributed to surface species containing one or two S=O oscillators, and the strong peak at 1175 cm^{-1} , like MgO, must be attributed to bulk sulfate. At low coverage (Fig 7.4A) three bands are observed at 1350, 1135 and 1055 cm^{-1} which are probably attributable to a single species. Following H_2^{18}O exchange the 1350 cm^{-1} peak gave only one shifted component for partial exchange, suggesting that this species has the structure $(-O)_2S=O$ containing a single S=O oscillator.

The 1350 cm^{-1} peak, even at the lowest coverage has a shoulder to higher wavenumber. As the coverage increases, peaks at both positions intensify and appear to shift to higher wavenumber, eventually appearing at 1360 and 1375 cm^{-1} (Fig 7.4B-E). Accompanying this is the appearance of a shoulder at 1025 cm^{-1} and new weak peaks at 1225 and 1290 cm^{-1} . The experiments carried out on the thermal stability of the sulfated spinel show (Fig 7.7A) that the last peaks to disappear are those at 1375 and 1025 cm^{-1} , and these bands can, therefore, be assigned to a second surface species of unknown structure. (It is not possible to measure the O-18 shift of the 1375 cm^{-1} peak because it is always overlapped by that at 1360 cm^{-1}). The origin of the 1290 cm^{-1} and 1225 cm^{-1} peaks remains obscure because their intensities always are weak but they might be due to another surface sulfate like species. On MgO [10] the surface species having two non equivalent S=O oscillators gave rise to infrared bands at 1230 and 1420 cm^{-1} , but it is also true that the bulk sulfate species has a considerable shoulder at 1225 cm^{-1} (Fig 7.6). The latter is formed at the highest coverages, or when the surface area is very low, or via impregnation with $(\text{NH}_4)_2\text{SO}_4$ (Fig 7.3) and is characterized by a peak of considerable intensity at 1175 cm^{-1} . However, this species also has bands and shoulders at other frequencies which overlap with those which have been attributed to surface sulfates.

It is disappointing that we cannot positively identify the structures of some of the sulfates species, or indeed, even to specify exactly how many sulfate species form on spinel. However, the purpose of this work was not to determine the structure of the different sulfate species formed, which were expected to be numerous given the complexity of this mixed oxide system. Rather, the purpose of this work was to understand why spinel is used to remove SO_x from FCC flue gas. The infrared and gravimetric results provide information about the nature of sulfated spinel as compared to the other oxides studied, and this provides some insight into the relative possible utility of spinel as an FCC transfer catalyst.

If water vapour is present during the process of sulfation, the bulk like sulfate species are more abundant than that without water, shown at Fig 7.8.

The observation of infrared bands characteristic of bulk sulfate and the discovery that large quantities of sulfate can be incorporated into the bulk of the spinel show that this material has a high sorbet capacity for SO_x gas. This capacity for spinel is much greater than that of alumina because the latter only has surface sulfate species and its sorption capacity is, therefore, limited. On the other hand, bulk species also form on magnesia [15,20]. However, the ideal FCC transfer catalyst would be one where the sulfates are thermally stable but are easily reduced during regeneration process. This study has shown that the bulk and surface sulfates on spinel only decompose at relatively high temperatures. Moreover, the experiments with hydrogen show that there is no significant difference in the cases with which any of the sulfate species can be reduced. Both infrared and gravimetric measurements indicate that all are removed from the surface at about 550 to 640 °C.

Fig 7.9 shows schematically, via horizontal lines, the temperature ranges where the sulfate species on spinel and some other oxides [12, 13, 15] were either reduced in hydrogen (curve A) or were removed via desorption under vacuum (curve B). The shorter the line the narrower was the temperature range for complete removal. The vertical bar shows the approximate temperature at which half of the species had been removed. This figure shows that sulfates are more easily reduced on spinel than on magnesia [20]. And from Fig 7.2, we have shown that the surface area

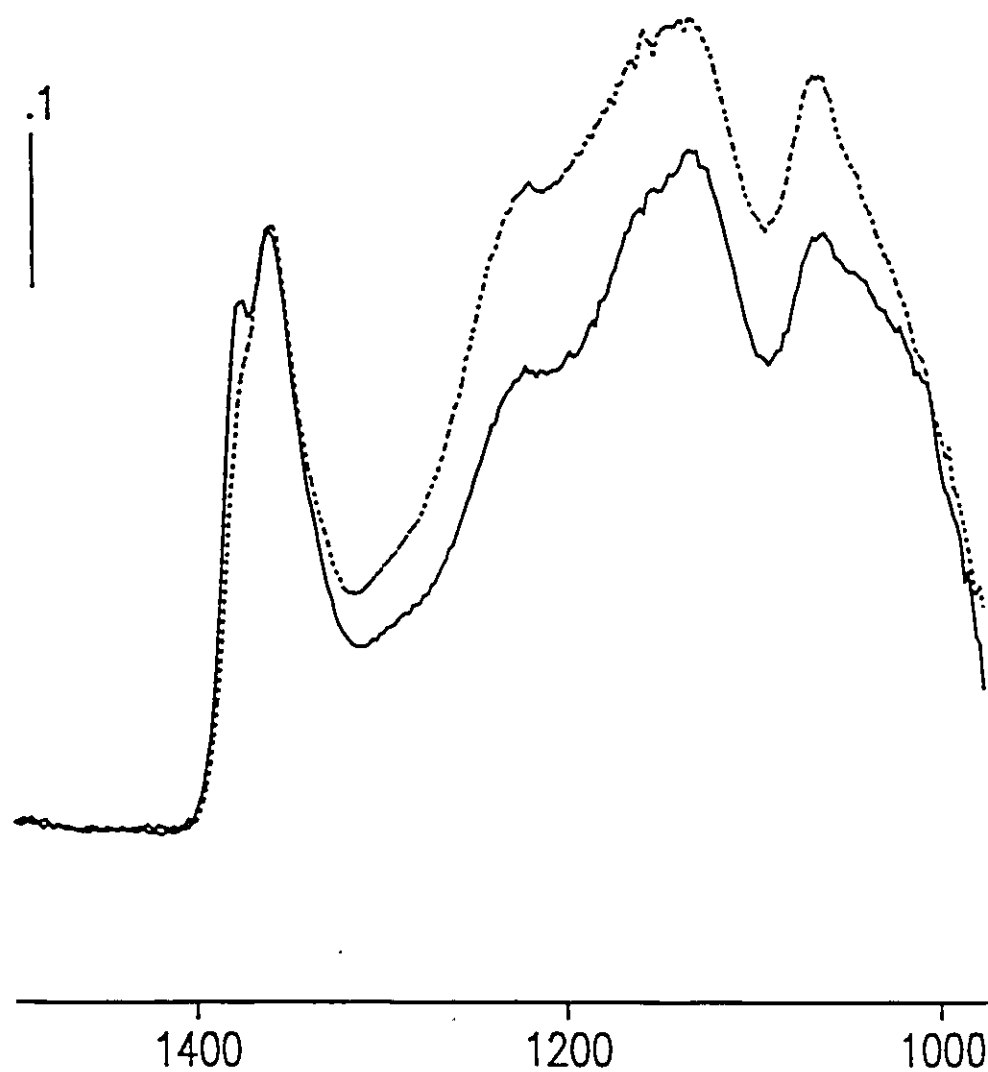
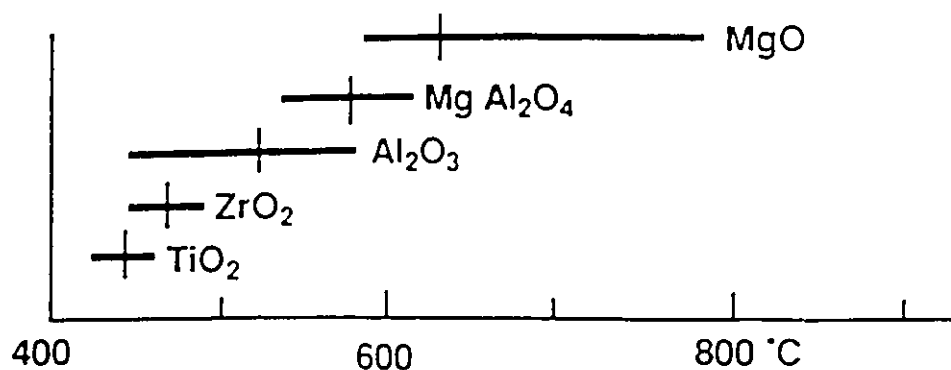


Fig 7.8 Effect of H_2O on the intensity of the sulfate bands. (—), spinel heated with $100 \mu\text{mol/g}$ SO_2 and excess O_2 . (...), spinel heated with $100 \mu\text{mol/g}$ SO_2 , $600 \mu\text{mol/g}$ H_2O and excess O_2 . Both were heated at 550°C for 2 hours, then evacuated at 400°C for another 0.5 hour.

(A) Reduction in H_2



(B) Thermal Stability

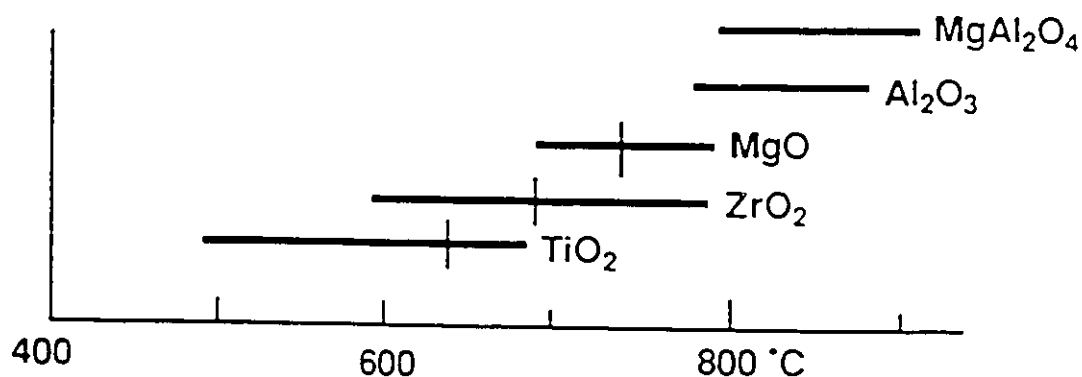


Fig. 7.9 Schematic showing the temperature ranges for reduction of sulfates in hydrogen on various oxides (Part A) and for thermal decomposition under vacuum (Part B), see text. The vertical bar indicates the approximate temperature at which about 50% of the sulfates had disappeared (this could not be determined with precision for temperature above 800 °C. the maximum attainable with the microbalance).

of the spinel does not change much at reduction temperature, about 620 °C. Therefore, in terms of the ability to be regenerated, spinel appears superior to MgO as an SO_x transfer catalyst. It is interesting to note that alumina has a thermal stability comparable to that of spinel, and the sulfates can be reduced in hydrogen at a slightly lower temperature range. However, as stated previously, its sorption capacity is inferior to that of spinel by virtue of not incorporating bulk sulfates. In conclusion, of the materials listed in Fig 7.9, spinel appears to be most suitable as an FCC SO_x transfer catalyst.

3. CONCLUSIONS

The sulfation of magnesium aluminate spinel, MgAl₂O₄, via oxidation of SO₂ in excess oxygen in the temperature range from 350 to 650 °C has been studied using infrared spectroscopy and vacuum microbalance techniques. The major conclusions are:

- (1). At least two types of surface sulfate species are formed for low doses of SO₂, but at higher doses, ionic like sulfate species become incorporated into the bulk of the spinel.
- (2). The quantity of sulfate formed for a given dose of SO₂ increases with the temperature of oxidation (for a fixed time of oxidation) or with the time of oxidation (for a fixed temperature). The presence of the water vapour will increase the sulfate species, mainly bulk species.
- (3). All types of sulfate species are thermally stable under vacuum to about 800 °C but are removed when heated in the range from 800 to 900 °C.
- (4). In excess hydrogen, all sulfates are removed during heating from about 550 to 640 °C.
- (5). The thermal stability and reducibility of sulfated spinel (3 and 4 above) have been compared with those of sulfated Al₂O₃, TiO₂, ZrO₂ and MgO. We have concluded that, of these materials, spinel is a superior FCC transfer catalyst by virtue of its high sorption capacity for

sulfate species, and because the catalyst can be easily regenerated in H₂ at moderately low temperatures.

REFERENCES

- [1]. Bond, G. C., " Heterogeneous Catalysis -- principles and applications ", Clarendon Press., Oxford, 1987.
- [2]. Bhattacharyya, A. A., Woltermann, G. M., Yoo, J. S., Karch, J. A. and Cormier, W. E, Ind. Eng. Chem. Res., 27, 1356(1988).
- [3]. Otterstedt, J. E., Gevert, S. B., Jaras, S. G. and Menon, P. G. Appl. Catal., 22, 159(1986).
- [4]. Anderson, S., Pompe, R. and Vannerberg, N.-G. Appl. Catal., 16, 49(1985).
- [5]. McArthur, D. P., Simpson, H. D. and Baron, K., Oil Gas J., 70(1983).
- [6]. Habib, E. T., Oil Gas J., 111(Aug. 8, 1983).
- [7]. Byrne, J. W., Speronello, B. K. and Leuenberger, E. L., Oil Gas J., 101(Oct. 15, 1984).
- [8]. Yoo, J. S. and Jaecker, J. A., U. S. patent 4 469 589 (1984).
- [9]. Yoo, J. S. and Jaecker, J. A., U. S. patent 4 472 267 (1984).
- [10]. Yoo, J. S. and Jaecker, J. A., U. S. patent 4 492 677 (1985).
- [11]. Yoo, J. S. and Jaecker, U. S. patent 4 492 678 (1985).
- [12]. Saur, O., Bensitel, M., Mohammed Saad, A. B., Lavalley, J. C., Tripp, C. P. and Morrow, B. A. J. Catal., 99, 104(1986).
- [13]. Bensitel, M., Saur, O., Lavalley, J. C. and Morrow, B. A., Mater. Chem. Phys., 19, 147(1988).
- [14]. Morrow, B. A., McFarlane, R. A., Lion, M. and Lavalley, J. C., J. Catal., 107, 232(1987).
- [15]. Bensitel, M., Waqif, M., Saur, O. and Lavalley, J. C., J. Phys. Chem., 93, 6581(1989).
- [16]. Knözinger, H. and Ratnasamy, P., Cat. Rev. Sci. Eng., 17, 31(1978).
- [17]. Coluccia, S., Marchese, L., Lavagnino, S. and Anpo, M., Spectrochim. Acta, 43A, 1573(1987).

- [18]. Morterra, C., Ghiotti, G., Boccuzzi, F. and Coluccia, S., J. Catal., 51, 299(1978).
- [19]. Hezel, A. and Ross, R. D., Spectrochim. Acta, 22A, 1949(1966).
- [20]. Bensitel, M., Thèse de l'Université de Caen, Caen, France, July 1988.

Chapter 8

THE INVESTIGATION OF NO₂ AND SO₂ ON Al₂O₃ AND CuO/Al₂O₃

1. INTRODUCTION

Nitrogen oxides (N_xO_y, most commonly NO and NO₂) are also noxious pollutants of the atmosphere. It is estimated that the amount of NO₂ produced by industrial and daily activities is about 60 × 10⁶ T/year [1, 2], and they are mainly produced by the combustion of fossil fuels. Nitrogen oxides are very toxic especially near the pollution sources because of higher concentrations. Like SO_x, they exist in flue gas and can also contribute to the formation of acid rain. It was verified that nitrogen oxides contribute to the ozone problem [3, 4].

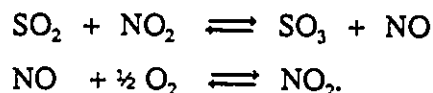
Because nitrogen forms a number of oxidation states many kinds of nitrogen oxides can exist, but NO and NO₂ are most important in air pollution. NO is the primary product while NO₂ is the secondary product of combustion processes ($\text{NO} + \frac{1}{2} \text{O}_2 \longrightarrow \text{NO}_2$).

In controlling NO_x pollution of flue gas, the most successful method is the so-called Selective Catalytic Reduction (SCR) process ($\text{NO}_2 + \text{NH}_3 \longrightarrow \text{N}_2 + \text{H}_2\text{O}$), which can remove about 95% of nitrogen oxides. However, larger capital investments and operating expenses are required for this. The catalysts in this process usually are metal oxides [2, 5]. Other methods are limited to about 60% removal [6].

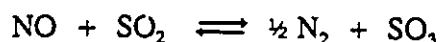
A catalytic process that simultaneously removes sulphur dioxide and nitrogen oxides would be highly desirable. According to published reports, there is a process to remove "simultaneously" NO_x and SO₂ [2, 7]. First, both NO_x and SO₂ gases are oxidized to their highest oxidation states by active oxygen-containing radicals, like O and OH. Then under an ammonia environment, ammonium salts [NH₄NO₃, (NH₄)₂SO₄] are formed, which can be used as fertilizers.

The removal of NO_x and SO₂ is reported to be about 70% and 40%, respectively. The high energy consumption, which is needed to produce the active oxygen-containing radicals, is one of the shortcomings of this process. This process is not a catalytic reaction between NO_x and SO₂.

It is well known that NO₂ can catalyze the oxidation of SO₂ to SO₃ by so-called lead chamber process:



And for NO, the thermodynamic data of the reaction



are favourable with $\Delta G = -156.69$ kJ/mol at 25 °C. This process seems to be more attractive because N₂ is not objectionable from an environmental stand point.

There has been little study of the SO₂-NO_x reaction on surfaces. This is unfortunate because SO₂ and NO_x both are in stack gas and can cause air pollution. If we can remove both in the same reaction, we "kill two birds with one stone". But so far, there is no catalyst in this field and only some minor progress has been made in liquid phase [8]. There is another reason why studying the SO₂-NO_x reaction is interesting. SO₂ must be oxidized to SO₃ or H₂SO₄ for acid-rain to be produced, and there are a number of mechanisms by which this can occur. The reaction may occur in the gas phase under photo-chemical initiation, or may be a heterogeneous process, catalyzed by particulates in the atmosphere. In either case an oxidizing agent must be present. This could be molecular oxygen, ozone or NO₂, if it is present. Thus, the study of the surface reaction of NO₂ and SO₂ is relevant to one of the possible mechanisms of production of acid rain.

CuO/Al₂O₃ has been used as the sorbent-catalyst for the simultaneous removal of SO₂ and NO_x [9]. It was thought that during the process, CuO/Al₂O₃ reacted with SO₂ to form a surface

sulfate, which then catalyzed the selective reaction of NH_3 with NO_x to form N_2 . This performance is still under investigation and the nature of the sorbent-catalyst and mechanism are not well understood. $\text{CuO}/\text{Al}_2\text{O}_3$ was also used as the catalyst in the reduction of NO with carbon monoxide [10, 11]. Copper catalysts and various alumina supported catalysts are also applied to control NO_x emission from automobile exhaust gas [12].

The adsorption behaviour of NO and CO on copper oxides has attracted a great deal of attention and many different surface sites have been found [10, 13, 14, 15]. The adsorption of SO_2 , CO and thiophene show that the $\text{CuO}/\text{Al}_2\text{O}_3$ catalyst has four different adsorption sites [13]. They are Cu^{2+} , Cu^+ sites in a matrix of Cu^{2+} , Cu^+ site in a matrix of Cu^+ and Cu^0 site. Leung *et al.* [16] investigated the adsorption of SO_2 on Cu(100) by Electron Energy Loss Spectroscopy. It was reported that on the Cu(100) surface, SO_2 dissociated to give SO and O, which will further react with other SO_2 molecules to produce adsorbed sulfite and sulfur species. To the best of our knowledge, no studies of NO_2 adsorption on copper-alumina catalysts have been reported.

Our aim is to investigate the surface compounds which are formed during the adsorption of SO_2 and NO_2 on Al_2O_3 and $\text{CuO}/\text{Al}_2\text{O}_3$, and their stabilities to thermal treatments and toward other gases. It will be beneficial to increase our knowledge of the interaction between these two gases in the presence of a catalyst, as this will aid in the design of new catalysts for preventing these pollutants from escaping into the atmosphere. In this report, we will show that the introduction of CuO to alumina greatly decreases the stability of NO_3^- species on the surface, therefore, NO_2 can be reduced much more easily. Using the probe molecules, CO and NO, the surface sites of the $\text{CuO}/\text{Al}_2\text{O}_3$ sample were also studied.

2. EXPERIMENTAL

$\text{CuO}/\text{Al}_2\text{O}_3$ catalysts were prepared by impregnation of Al_2O_3 (γ -type, Degussa Alumin Oxid C) from a solution of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$. The wet slurries are dried at 110 °C for several hours in a furnace and subsequently calcined in an oven at 450 °C for 2 hours. The dried sample contains 1% copper by weight.

For IR study, about 50 mg of $\text{CuO}/\text{Al}_2\text{O}_3$ was used. After the disc was activated at 450 °C for 0.5 hour under evacuation, 40 to 50 Torr of O_2 is introduced into the cell and the oxidation process took 2 to 3 hours at 450 °C. Before each experiment, the sample was evacuated at 450 °C for about 0.5 hour to remove O_2 and was then allowed to cool to room temperature.

3. RESULTS AND DISCUSSION

(1). *Surface characteristics of $\text{CuO}/\text{Al}_2\text{O}_3$*

IR spectra of $\text{CuO}/\text{Al}_2\text{O}_3$ background show not much difference from pure $\text{Al}_2\text{O}_3(450)$ after being activated at 450 °C under evacuation except that the impregnation sample lost most of the fine structure in the OH stretching region (not shown).

After the oxidation and subsequent evacuation, CO gas is introduced into the cell at room temperature to probe the catalyst surface. CO adsorption shows that the catalyst surface contains Cu^+ and Cu^0 sites, 2124 cm^{-1} band for Cu^+ -CO site and 2106 cm^{-1} band for Cu^0 -CO site (see Fig 8.1 A). There is also a very weak band around 2170 cm^{-1} , which is assigned as CO on Cu^{2+} sites. These assignments are made by comparison with previous publications [10, 14, 15]. The C-O stretching vibration of gaseous CO is at 2143 cm^{-1} . To explain a higher C-O vibration frequency (above 2143 cm^{-1}) on the surface of the some metal oxides, the reasonable theory is the σ -complex concept which involves adsorption of CO on cations (coordinatively unsaturated cations). Binding in such complexes is attained via the unshared electron pair at the C atom to unfilled metal orbitals. In this situation, C-O bond is strengthened and the frequency of ν_{co} shifts to higher wavenumber. Hence, the band at 2170 cm^{-1} is assigned as Cu^{2+} -CO. The appearance of carbonyl stretching frequencies lower than 2143 cm^{-1} is usually interpreted as being due to the donation of electron density from metal d -orbitals of suitable symmetry to previously vacant anti-bonding π^* -orbitals of CO. The ability of Cu to donate electron density should increase in the order $\text{Cu}^{+2} < \text{Cu}^+ < \text{Cu}^0$. Since accepting electron density into π^* orbitals decrease the strength of the carbonyl bond, the carbonyl stretching frequency of complexed CO is expected to decrease in the order $\text{Cu}^{+2} > \text{Cu}^+ > \text{Cu}^0$, in accord with the literature assignments. Another interpretation

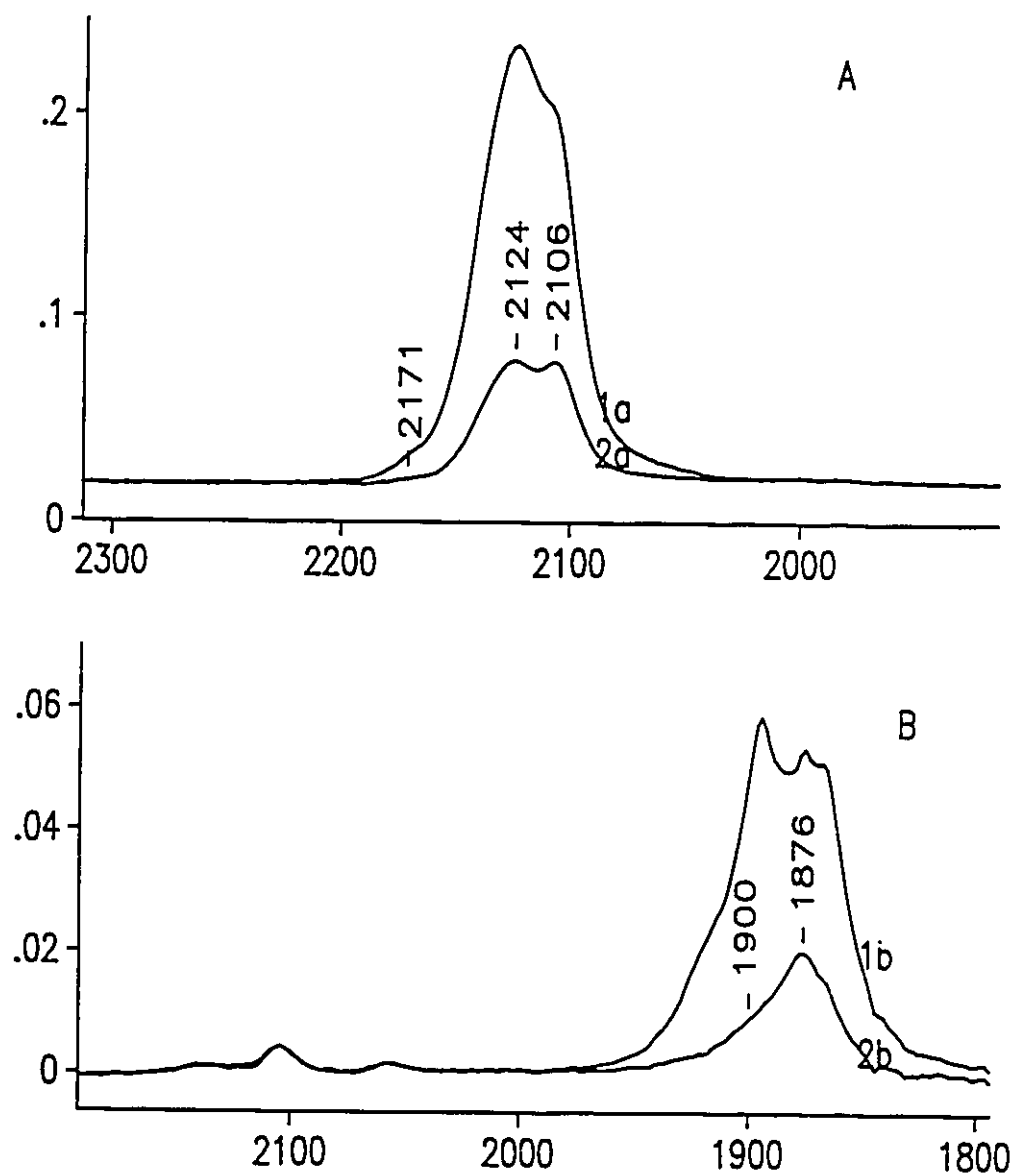


Fig 8.1 Difference IR spectra observed after CO or NO adsorption on CuO/Al₂O₃

A: 1a. 2 Torr of CO in contact with 50 mg CuO/Al₂O₃(450).
 2a. after evacuation for 5 min.

B: 1b. 1.6 Torr of NO in contact with 50 mg CuO/Al₂O₃(450).
 2b. after evacuation for 5 min.

is physical adsorption. Usually, physical adsorption shifts the adsorption band toward lower frequency [17].

In this experiment, addition of CO gas shows that Cu^+ and Cu^0 sites are present on the surface. Interaction of CO with $\text{CuO}/\text{Al}_2\text{O}_3$ catalyst in the temperature range 20 to 200 °C could result in the reduction of CuO to Cu^+ [17, p190]. It is not certain whether the Cu^+ or Cu^0 sites are the results of the reduction of Cu^{2+} by CO or whether they are produced during evacuation at 450 °C in the activation process. In the latter process some CuO may undergo reduction



But considering that the temperature is 450 °C and CuO (bulk) has a melting point of 1326 °C, the above process might only partly contribute to the formation of Cu^+ . We suggest that most of the Cu^+ sites are probably formed by reduction of surface Cu^{2+} sites by CO. For Cu^0 sites they might come from the further reduction of Cu^+ with CO. It is evident that some surface Cu^{2+} are more sensitive toward reduction. But, the surface of the sample mainly contains Cu^{2+} ions, as expected. The band of CO at Cu^{2+} sites ($\text{Cu}^{2+}\text{-CO}$), at 2170 cm^{-1} , is usually very weak, as shown in our experiment, and can be eliminated very easily by brief evacuation at room temperature.

Further, probing the surface of $\text{CuO}/\text{Al}_2\text{O}_3$ by NO, we find some bands between 1850-1950 cm^{-1} (Fig 8.1 B). After evacuation at room temperature, the feature at 1876 cm^{-1} is predominant. This band is due to $\text{Cu}^{2+}\text{-NO}$, in which the Cu^{2+} cation is in the CuO phase [17, 18]. The band at about 1900 cm^{-1} is from the adsorption of NO on surface Cu^{2+} ions of the aluminate-type (CuAl_2O_4). This band is weakly bonded and a brief evacuation can eliminate it. The appearance of a high frequency tail at about 1920 cm^{-1} with large dose of NO indicates that there are very few ionically bound Cu^{2+} cations which are located in Al_2O_3 lattice (isolated Cu^{2+}). In particular, the bands due to $\text{Cu}^+\text{-NO}$ (1740-1780 cm^{-1}) are undetectable when NO is added, and this further supports the interpretation that the surface Cu^+ and Cu^0 sites are mostly formed by CO reduction.

It is reported that the Cu^{2+} ions in associated sites ($\text{Cu}^{2+}\text{-O-Cu}^{2+}$) are more easily reducible than isolated Cu^{2+} ions [17, p73]. If Cu^+ sites on $\text{CuO}/\text{Al}_2\text{O}_3$ are mostly from CO reduction, Cu^+ sites should be in state of $\text{Cu}^+\text{-O-Cu}^{2+}$ or $\text{Cu}^+\text{-O-Cu}^+$ (in associated states). As there is only one

kind of Cu^+ -CO band (2124 cm^{-1}) detected in these experiments, we suggest that all Cu^+ ions are in these states whether they are from reduction by CO or from reduction by heating under vacuum. Hence the IR spectra of adsorbed NO and CO confirm that on this $\text{CuO}/\text{Al}_2\text{O}_3$ catalyst (1% of Cu), there are mainly Cu^{2+} cations on a CuO surface (responsible for ν_{NO} 1876 cm^{-1}), some Cu^{2+} sites of the aluminate type (CuAl_2O_4) and very few isolated Cu^{2+} . There are also few Cu^+ and Cu^0 sites mainly on the CuO surface.

(2). *NO_2 adsorption on Al_2O_3*

NO_2 is strongly adsorbed on alumina. The strongest adsorption bands occurred at about 1600 cm^{-1} and 1240 cm^{-1} . The following is the discussion of the spectra observed when NO_2 is adsorbed on pure Al_2O_3 .

(i). $3200\text{-}3800\text{ cm}^{-1}$ region

After activation at 450°C , pure alumina has OH bands at 3790 cm^{-1} (Ib), 3774 cm^{-1} (Ia), 3728 cm^{-1} (IIa), and 3684 cm^{-1} (III). When NO_2 is adsorbed on Al(450), the 3774 cm^{-1} band disappears first (Fig 8.2 top). It appears that NO_2 prefers to react with type Ia OH group first, then reacts with type Ib OH group (3790 cm^{-1}). Only after all Ia and Ib types have been reacted, then NO_2 reacts with other OH groups. As more NO_2 is added, the stretching bands of the isolated OH groups become poorly resolved, and the broad band at about 3600 cm^{-1} increases.

NO_2 is an acidic molecule and as expected, it will attack the basic sites of alumina surface. The observation of the change of OH groups might suggest occurrence of the hydrogen bonds or even HONO_2 species. The latter seems more likely and it will be verified by thermal treatment process later.

Why does NO_2 prefer to react with Ia instead of reacting with Ib? According to Knozinger and Ratnasamy's estimation the acidic order of hydroxyl groups on alumina surface is $\text{Ib} < \text{Ia} < \text{IIb} < \text{IIa} < \text{III}$. NO_2 gas, as an acidic oxide, would be expected to react first with most basic site, type Ib, rather than Ia. When CO_2 reacts with thorium dioxide, the hydrogen carbonates are

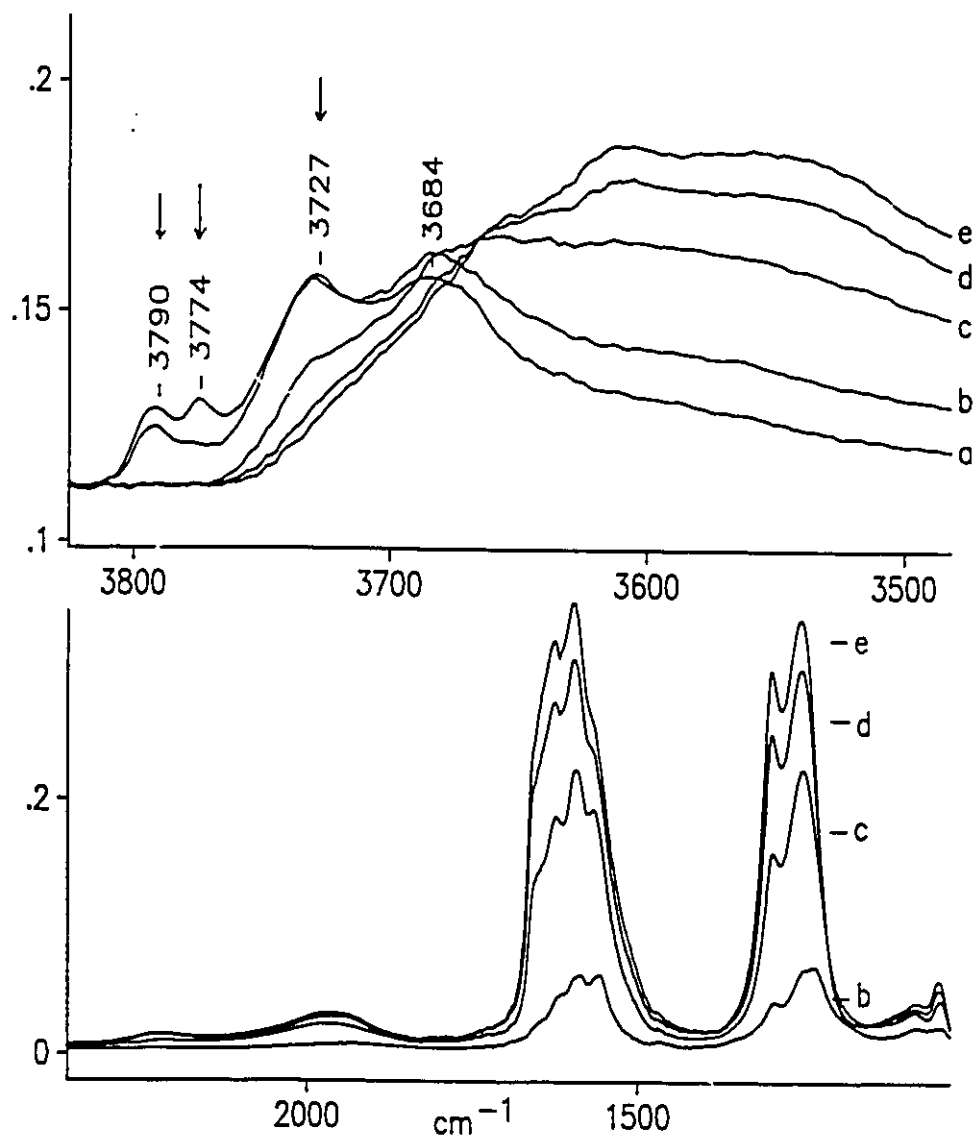


Fig 8.2 Adsorption of NO₂ on Al(450)

Top. IR spectra in OH stretching region (no Al₂O₃ background was subtracted). (a). 30 mg alumina, after activation at 450 °C. (b). add 0.11 Torr of NO₂. (c). add 0.41 Torr of NO₂. (d). add 1.02 Torr of NO₂. (e). add 1.72 Torr of NO₂.

Bottom. Difference spectra in 1000-2400 cm⁻¹ region. Al₂O₃ background (a) has been subtracted.

formed essentially from the OH groups having the highest wavenumber [19]. Also on ZrO_2 , CO_2 was found to react preferentially with the OH groups having the highest wavenumber OH bands ($\nu_{\text{OH}} = 3775 \text{ cm}^{-1}$). This OH group is considered to be most basic sites [20].

In this reaction, besides the basicity, there might be other factors that affect the reactivities of the surface hydroxyl groups. Because the detailed mechanism of the reactions of NO_2 with Al_2O_3 are not known, any interpretation of the observed order of reactivity can only be considered as speculative. Nevertheless, it is possible that type Ib OH groups are less sterically accessible than type Ia OH groups in some special surfaces.

On the other hand, it appears that the band at 3790 cm^{-1} is easier to restore than the band at 3774 cm^{-1} when the system is under evacuation at increasing temperatures (Fig 8.3). In Fig 8.3 the experiment shown in Fig 8.2 is continued. It is seen that upon increasing the temperature at which the sample is evacuated, the band at 3728 cm^{-1} reappears first, at about 200°C . The band at 3790 cm^{-1} reappears at about 300°C , and the band at 3774 cm^{-1} reappears at about 350°C . This is just the reverse order of the experiment in Fig 8.2. It is evident that the species formed by reaction with Ia site is more stable than the species formed by reaction with OH groups of type Ib.

(ii). $1900\text{-}2300 \text{ cm}^{-1}$ region

There are broad bands at about 1960 cm^{-1} on higher temperature activated alumina (Fig 8.4). The evacuation at room temperature lowers its intensity a little. Parkyns [21] assigned $1960\text{-}1970 \text{ cm}^{-1}$ to NO^+ , without conclusive evidence. When NO loses an electron, it is removed from an anti-bonding π^* -orbital, and a sharp increase in the vibrational frequency occurs. As we can see that NO^+ species in $\text{SnCl}_4\cdot\text{N}_2\text{O}_4$ is at 2216 cm^{-1} , in NO^+HSO_4 is at 2340 cm^{-1} , and in NO^+NO_2 is at 2240 cm^{-1} . All NO^+ species have bands over 2200 cm^{-1} [17]. Comparing with the table below and a frequency of free NO at about 1876 cm^{-1} , we tend to assign the band around 1960 cm^{-1} to NO species on Al^{3+} sites.

Stretching Frequencies of NO [22]

bond order	molecule	cm ⁻¹
3	NO ⁺	2345
2.5	NO	1876
2	NO ⁻	1353
1.5	NO ²⁻	897

The appearance of bands due to NO indicates that some of the NO₂ has decomposed on Al₂O₃ to yield NO.

The intensity at 1960 cm⁻¹ strongly depends on the activation temperature of alumina. On Al(800), the band at 1960 cm⁻¹ is much more intense than that on Al(450), while on Al(300) it is absent. On Al(800), the band is asymmetric and on Al(1000), there apparently exist two bands (see Fig 8.4). This can be observed much more clearly when SO₂ is added. When this is done two bands near 1939 cm⁻¹ and 1987 cm⁻¹ are seen apparently (see next parts), and we will show that there are no SO_x bands in this region. The appearance of the two bands suggests that NO is adsorbed on at least two distinct surface sites. (The difference in frequency may relate to differences in Lewis acidity in the surface sites. The more electron-withdrawing sites should accept more electron density from NO_x, leading to higher vibrational frequencies.) It is probable that high temperature activation creates different Lewis acid sites. Adsorption of NO on these sites could account for the presence of two bands.

There is a very weak band at 2250 cm⁻¹ in this region and it can be assigned to NO⁺ species adsorbed on Al sites because all NO⁺ species in inorganic complexes give frequencies above 2200 cm⁻¹. Parkyns assigned the band at 2250 cm⁻¹ to NO₂⁺, the but nitronium ion NO₂⁺ has its N-O antisymmetric stretching vibration (ν_3) above 2350 cm⁻¹ [22]. Davis *et al.* [23] studied the adsorption of NO₂ on SiO₂-Al₂O₃, and a 2280 cm⁻¹ band was assigned as NO⁺. In all experiments here, the band of NO⁺ species is very broad and weak. Preadsorption of SO₂ increases the intensity of the 2200 cm⁻¹ peak (discussed later).

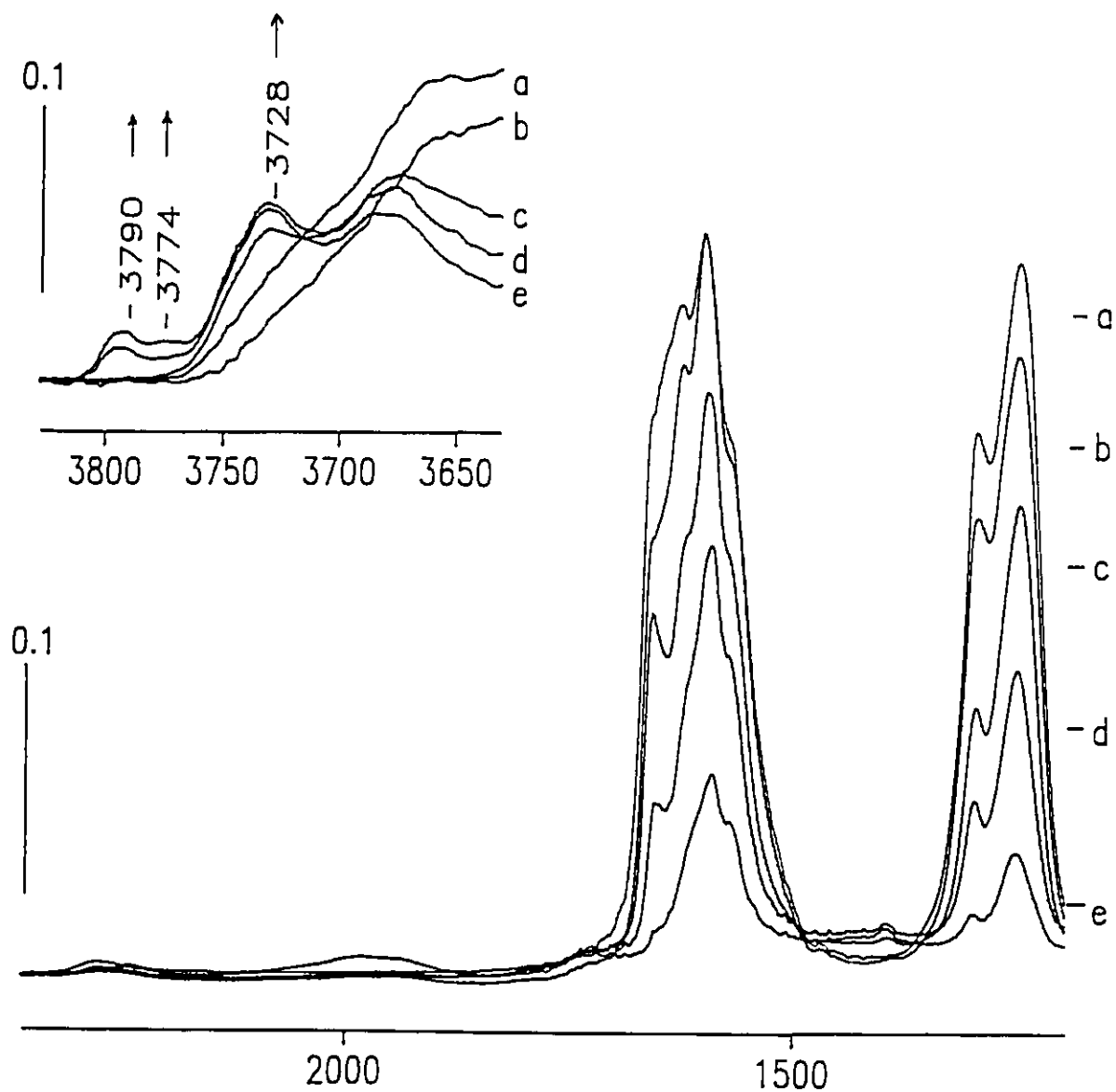


Fig 8.3 IR spectra of the species obtained by adsorption of 1.72 Torr NO_2 followed by evacuation at (a) 25 °C, (b) 100 °C, (c) 250 °C, (d) 300 °C, (e) 350 °C for 1 hour. The inset in the upper left corner shows the OH region of the spectrum during this experiment. This is the continuation of the experiment shown in Fig. 8.2

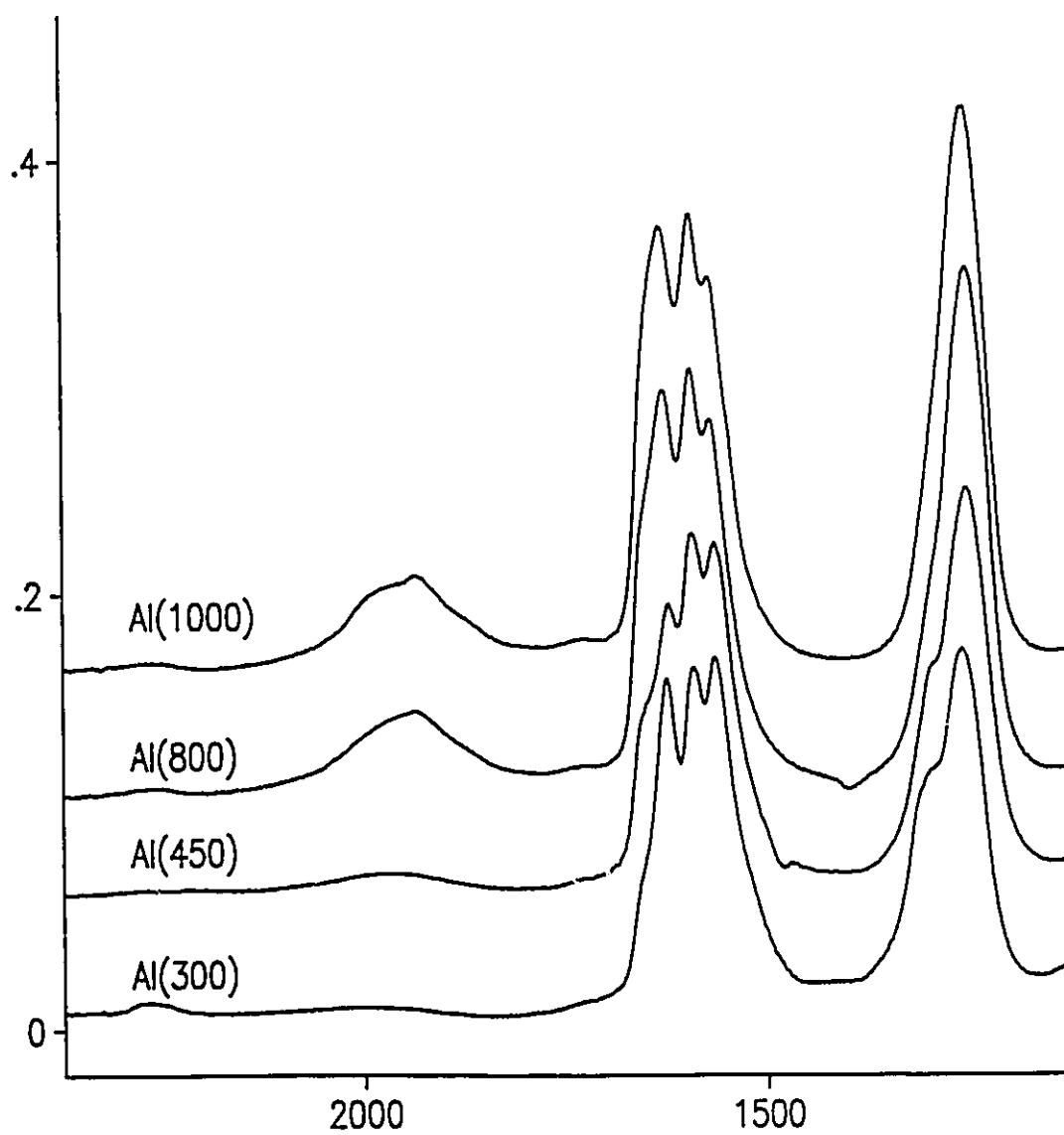


Fig 8.4 Adsorption of NO₂ (0.38 Torr) on Al₂O₃ (30mg)
These are difference spectra and the activated temperatures are shown in Al(C).

(iii). 1200-1700 cm^{-1} region

When nitrogen dioxide reacts with alumina strong bands at about 1240 and 1600 cm^{-1} are observed. With small doses of NO_2 , we clearly observe at least four bands at about 1600 cm^{-1} (1565, 1591, 1620 and 1655 cm^{-1}) and three bands at about 1250 cm^{-1} (1230, 1250 and 1292 cm^{-1}). When more NO_2 is added, the bands at 1655 and 1230 cm^{-1} broaden and become unresolved, and only 5 bands remain in this region (Fig 8.2 bottom part). To the best of our knowledge, no other authors have reported the appearance of the bands at 1655 and 1230 cm^{-1} . Using of $^{15}\text{NO}_2$ instead of $^{14}\text{NO}_2$ shifts these bands to lower wavenumbers. When a mixture of $^{14}\text{NO}_2$ and $^{15}\text{NO}_2$ is used, no bands attributable to species containing more than one nitrogen are observed. (Such species would be expected to have same band at a frequency between those observed for pure $^{14}\text{NO}_2$ and pure $^{15}\text{NO}_2$.)

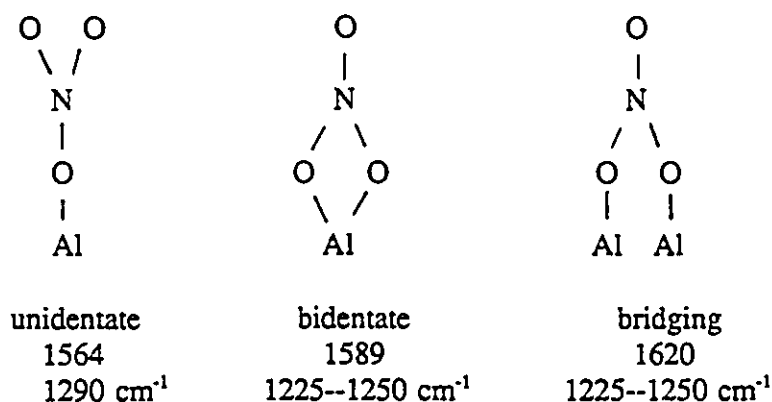
The activation temperatures of the alumina had a strong effect on the spectra. Some bands due to the surface species formed during adsorption of NO_2 are given in the following table and in Fig 8.4.

The frequencies of bands observed following NO_2 adsorption on Al_2O_3

Al(300)	Al(450)			Al(800)	Al(1000)
$^{14}\text{NO}_2$	$^{14}\text{NO}_2$	$^{15}\text{NO}_2$	Δ	$^{14}\text{NO}_2$	$^{14}\text{NO}_2$
1253	1250	1219	31	1250	1250
1292	1290	1272	18	-	-
1562	1564	1528	36	1566	1566
1289	1589	1553	36	1591	1591
1622	1620	1585	35	1624	1624
1655	1657(sh)	1620(sh)	37	-	-
-	1960	1930	30	1931,1956	1931,1960

For high temperature activated Al_2O_3 , above 800 °C, the band around 1290 cm^{-1} disappears, and the band at 1655 cm^{-1} may be covered by the stronger band at 1620 cm^{-1} .

Free NO_3^- has D_{3h} symmetry and has bands at 1400 (ν_3), 1053 (ν_1) and 720 cm^{-1} (ν_4). When NO_3^- is bonded to other atoms, the D_{3h} symmetry is lowered and ν_3 (E) splits to give two bands [9]. The bands around 1240 cm^{-1} and 1600 cm^{-1} are from the splitting of ν_3 [21, 24]. But with different bonding situations, these two bands might give different wavenumbers. Parkyns [21] assigned the bands at 1246, 1290 cm^{-1} to symmetric NO_2 stretching modes, the bands at 1564, 1589, 1620 cm^{-1} to antisymmetric NO_2 stretching modes. The latter three bands were assumed to be due to three possible modes of coordination of the nitrate ion:



According to Pozdnyakov *et al.* [24], the bands at 1245, 1600, 1620 cm^{-1} (no other bands were observed in this range in their experiments) were assigned to bridging nitrate. There is also an similar assignment of the stretching vibrations of NO_3^- in reference [15].

We find one more band at about 1655 cm^{-1} . This can be observed by carefully adding a small dose of NO_2 to the sample. If the pressure of NO_2 is a little higher, say about 2 Torr, the 1655 cm^{-1} band will be covered by the strong band at around 1620 cm^{-1} . With higher activation temperature alumina (over 800 °C), no 1655 cm^{-1} band can be found. Interestingly, we notice there is no 1290 cm^{-1} band either. We assume that 1657 cm^{-1} and 1290 cm^{-1} are from the same species, hydrogenonitrato HONO_2 . The reasons are: (a) addition of NO_2 causes the ν_{OH} bands at 3790 and 3774 cm^{-1} to disappear. It is clear that NO_2 reacts with type I OH group. The

products are not simply hydrogen-bonded species, because high temperatures, 300 to 350 °C, are needed to regenerate the OH groups; (b) the band at 1655 cm⁻¹ decreases with heating before 200 °C and 3728 cm⁻¹ increases a little at the same time, while other bands in 1500-1700 cm⁻¹ do not change so much with heating at an increasing temperature. It is generally believed that hydrogenonitrato (at 1655 cm⁻¹) is less stable toward heating (See Fig 8.3); (c) As the temperature of heating is increased, the 1655 cm⁻¹ band loses more intensity, and the loss is proportional to the gain in intensity of the AlOH bands at 3790 and 3774 cm⁻¹ which are being regenerated (Fig 8.3, c-e). When the bands at 3790 and 3774 cm⁻¹ almost completely recover their initial intensities, the species responsible for the 1655 and 1290 cm⁻¹ bands have been eliminated.

Note the relative intensities around 1600 cm⁻¹. As the activation temperature increase, the relative intensities of 1620 and 1591 cm⁻¹ are higher (Fig 8.4). When the samples are highly dehydroxylated, there will be more acid sites, and the formation of bidentate and bridging NO₃⁻ may be more favourable.

There are at least two bands near 1250 cm⁻¹ beside the 1290 cm⁻¹ band. With a small dose of NO₂ there are apparently bands at 1230 and 1250 cm⁻¹ (spectrum b in Fig 8.2 lower part). With more NO₂ is added, the strong 1250 cm⁻¹ band covers the band at 1230 cm⁻¹.

Thermal treatments usually can help us understand the bonding modes of surface species. All species in this region are relatively stable to thermal treatment. Under evacuation and heating over 200 °C, all these bands (around 1200-1700 cm⁻¹) decrease in intensity, and after heating over 350 °C, the bands around 1200-1700 cm⁻¹ can be eliminated. The order of thermal stability of the spectral features is: 1591 ≈ 1565 > 1620 > 1655 cm⁻¹ and 1250 ≈ 1230 > 1290 cm⁻¹.

From the above discussion, we tend to assign the bands as follows:

1565 - 1230 cm⁻¹ to unidentate NO₃⁻ ($\Delta\nu_3 \approx 330$ cm⁻¹),

1591 - 1250 cm⁻¹ to bridging (or polydentate) NO₃⁻ ($\Delta\nu_3 \approx 340$ cm⁻¹),

1620 - 1230 cm⁻¹ to bidentate NO₃⁻ ($\Delta\nu_3 \approx 390$ cm⁻¹),

1657 - 1290 cm^{-1} to HONO_2 . ($\Delta\nu_3 \approx 370 \text{ cm}^{-1}$).

The stabilities of NO_3^- toward SO_2 are in accord with this assignment [see part 4, 5]. After addition of SO_2 , the band at 1565 cm^{-1} will lose more intensity since unidentate species are less stable compared with the others.

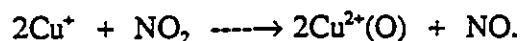
This conclusion is different from reference [21]. This assignment is also different from reference [17], in which bridging species were assigned to higher vibrational wave number.

Comparing with CO_2 on alumina [19], $\Delta\nu_3$ [$\Delta\nu_3 = \nu_s(\text{CO}_3) - \nu_s(\text{CO}_2)$] of unidentate carbonate is the smallest, and the $\Delta\nu_3$ of bidentate carbonates are larger than that of polydentate carbonates. In our assignments, $\Delta\nu_3$ of different species agree with this order though all these three $\Delta\nu_3$ values are not markedly different from each other.

(3). NO_2 adsorption on $\text{CuO}/\text{Al}_2\text{O}_3$

Adding NO_2 to $\text{CuO}/\text{Al}_2\text{O}_3$ (activated at 450 °C) also gives the bands around 1600 and 1240 cm^{-1} as on pure $\text{Al}(450)$, but copper impregnated sample shows some distinct bands between 1800-2300 cm^{-1} (Fig 8.5 b). This is quite different from pure alumina $\text{Al}(450)$ which has only weak bands around 1960 cm^{-1} (Fig 8.5 a). As from the previous discussion in section (2), the band around 1960 cm^{-1} is assigned to NO on Al^{3+} sites. NO in the gas phase has a band at about 1876 cm^{-1} , and NO^+ species have bands around 2300 cm^{-1} . (N_2O has bands at about 2215 and 2240 cm^{-1} .) The band found in this experiment at 2340 cm^{-1} (very weak) is assigned to NO^+ species at Cu^{2+} sites and the band at 2210 cm^{-1} is the vibration of N_2O on surface.

Apparently, the introduction of CuO on alumina greatly increases the reducing power. Without the existence of reductants, part of the NO_2 can be reduced to NO^+ and NO , or even lower oxidation states (like N_2O). The oxidation of surface Cu^+ to Cu^{2+} must be invoked to explain the reduction of NO_2 :



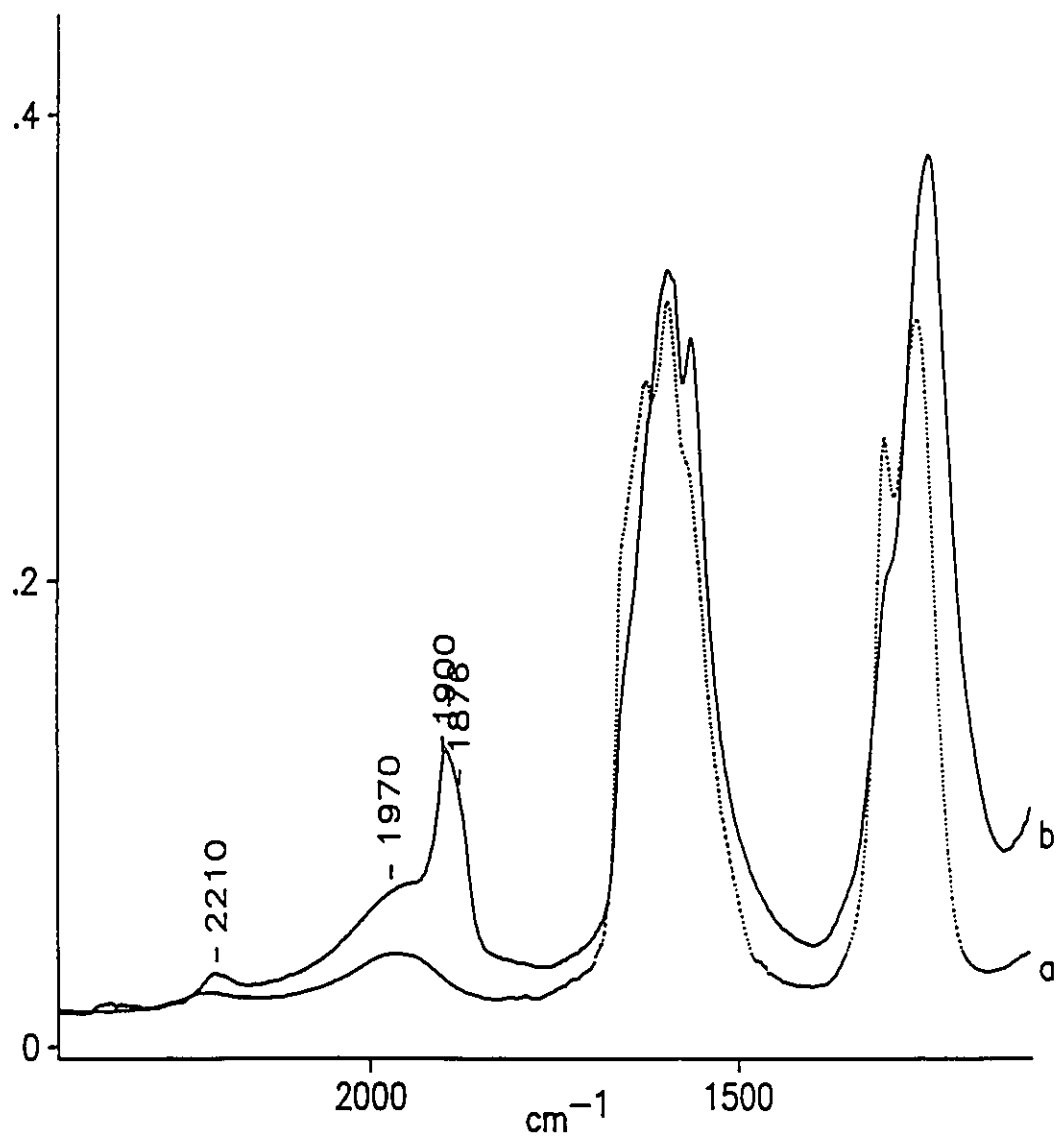
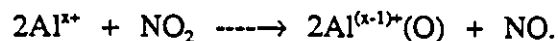


Fig 8.5 The adsorption of NO_2 (1.0 Torr) on pure Al_2O_3 (A), and on $\text{CuO}/\text{Al}_2\text{O}_3$ (B). Both catalysts have been activated at 450°C for 1 hour under evacuation.

The oxidation of Cu^+ and Cu^0 can be clearly demonstrated by adding CO to $\text{CuO}/\text{Al}_2\text{O}_3$ before or after introducing NO_2 . Adsorption of CO before gives bands due to Cu^+-CO (2126 cm^{-1}) as well as Cu^0-CO (2106 cm^{-1}). All these CO bands can be eliminated immediately if we then introduce NO_2 to cell (not shown). If CO is added after NO_2 preadsorption, no CO bands are observed. ($\text{Cu}^{2+}-\text{CO}$ band are very weak at room temperature. Some CO may react with NO_2 to produce NO, but the presence of the excess CO still does not produce a Cu^+-CO band). The formation of Cu^+-NO complex should produce an absorption band at about 1780 cm^{-1} . It is possible that all Cu^+ and Cu^0 sites are oxidized to Cu^{2+} by the addition of NO_2 . In probing $\text{Cu}/\text{Al}_2\text{O}_3$ with CO and NO (section 1), we found that there were only very few Cu^+ or Cu^0 species on the surface. Increasing the number of Cu^+ would increase the reducing power of the copper catalysts.

In section (2-ii), we noticed that some weak bands at about 1960 cm^{-1} , which were assigned to NO species, are found on the high temperature activated alumina. By comparison with the change from Cu^+ to Cu^{2+} on $\text{CuO}/\text{Al}_2\text{O}_3$ catalyst, it is possible that some similar process happens on pure alumina catalyst. Two neighbouring coordinately unsaturated aluminum ions may react with NO_2 to give NO:



The bond strength of O-NO is about 305 kJ/mol at 25°C and is even less than that of H-SH (381 kJ/mol) [25], which was found to be decomposed on Al_2O_3 . The cleavage of O-SO bond has also been observed on alumina [26] and the bond strength in this case is much higher, about 552 kJ/mol . Therefore, the reaction above is possible. It is evident that a high activation temperature favours the formation of coordinatively unsaturated surface Al ions, therefore, more intense NO bands can be found, as shown on Al(800) and Al(1000). This process must involve two adjacent Al ions and the abundance of this defect (coordinatively unsaturated Al ions adjacent to each other) is not expected to be large.

(4). *Adsorption of NO₂, then SO₂*

When SO₂ is added to an NO₂ treated Al₂O₃ sample, the bands due to preadsorbed NO₂ show surprisingly little change. Only after a longer contact time, do we observe a decrease in intensity in the NO₃⁻ vibration region (Fig 8.6). The band at 1565 cm⁻¹ decreases much more. It is consistent with our previous assignment that the band at 1565 cm⁻¹ is due to a unidentate NO₃ species and that it is less toward to SO₂. The addition of SO₂ on high temperature activation alumina pretreated with NO₂ usually splits the broad band at 1960 cm⁻¹ into two species, one being at 1938 cm⁻¹ and the other at 1987 cm⁻¹. They are assigned to NO adsorbed on different Al³⁺ sites.

Adding SO₂ to a Cu/Al₂O₃ sample with preadsorbed NO₂ causes all NO₃⁻ bands to decrease gradually, and an intense and broad band due to sulfur species is seen in the 1000-1400 cm⁻¹ region. The broad bands from 1860 to 2300 cm⁻¹ also become more intense (see Fig 8.7). After a longer contact time, there are strong bands around 1045, 1150 and 1370 cm⁻¹. Because these bands also appear when a mixture of (NO₂ + SO₂) is added to Al₂O₃, and they are strongly adsorbed on the surface, we tend to assign them to sulfate species. The bands around 1045 and 1370 cm⁻¹ are probably from the surface sulfate species, which can be confirmed by the sulfation of Al₂O₃ with SO₂ and O₂ or by impregnation of Al₂O₃ with Al₂(SO₄)₃•18H₂O [27]. The broad bands around 1150 cm⁻¹ may be assigned to the bulk sulfate ions [28]. Their presence suggests that some SO₂ gas has been oxidized to SO₄²⁻ species at the expense of NO₃⁻ species. The bands responsible for sulfate species are resistant to thermal decomposition up to 500 °C.

Interestingly, in the region from 1800 to 2300 cm⁻¹ in another experiment (see Fig 8.8), the broad band near 1970 cm⁻¹ disappears gradually and new broad bands at about 2080 cm⁻¹ are produced. Usually the broad band at 1900 cm⁻¹ is asymmetric, and at best we can observe at least two bands at about 1876 and 1898 cm⁻¹. With the adsorption of SO₂ the shoulder at 1876 cm⁻¹ gradually disappears and species at 1898 cm⁻¹ shifts to about 1900 cm⁻¹ and becomes symmetric.

The band at 1970 cm⁻¹ has been assigned to NO on an Al³⁺ site, but this species is less stable

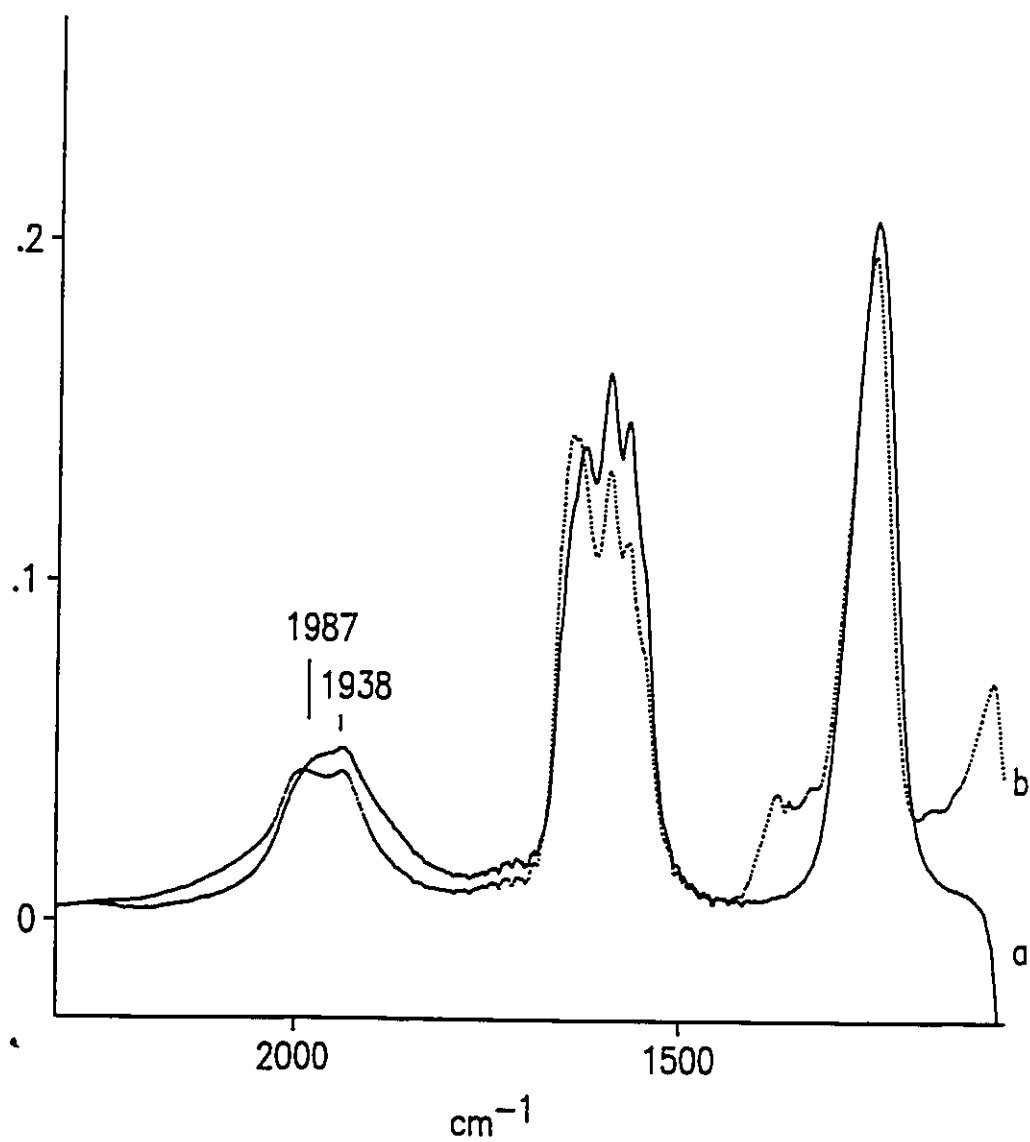


Fig 8.6 Adsorption of NO_2 , then SO_2 on Al_2O_3

- (a). 0.30 Torr of NO_2 in contact with $\text{Al}(1000)$ for 20', then evacuate for 10'.
 (b). 0.28 Torr of SO_2 is added to (a) for 20'.

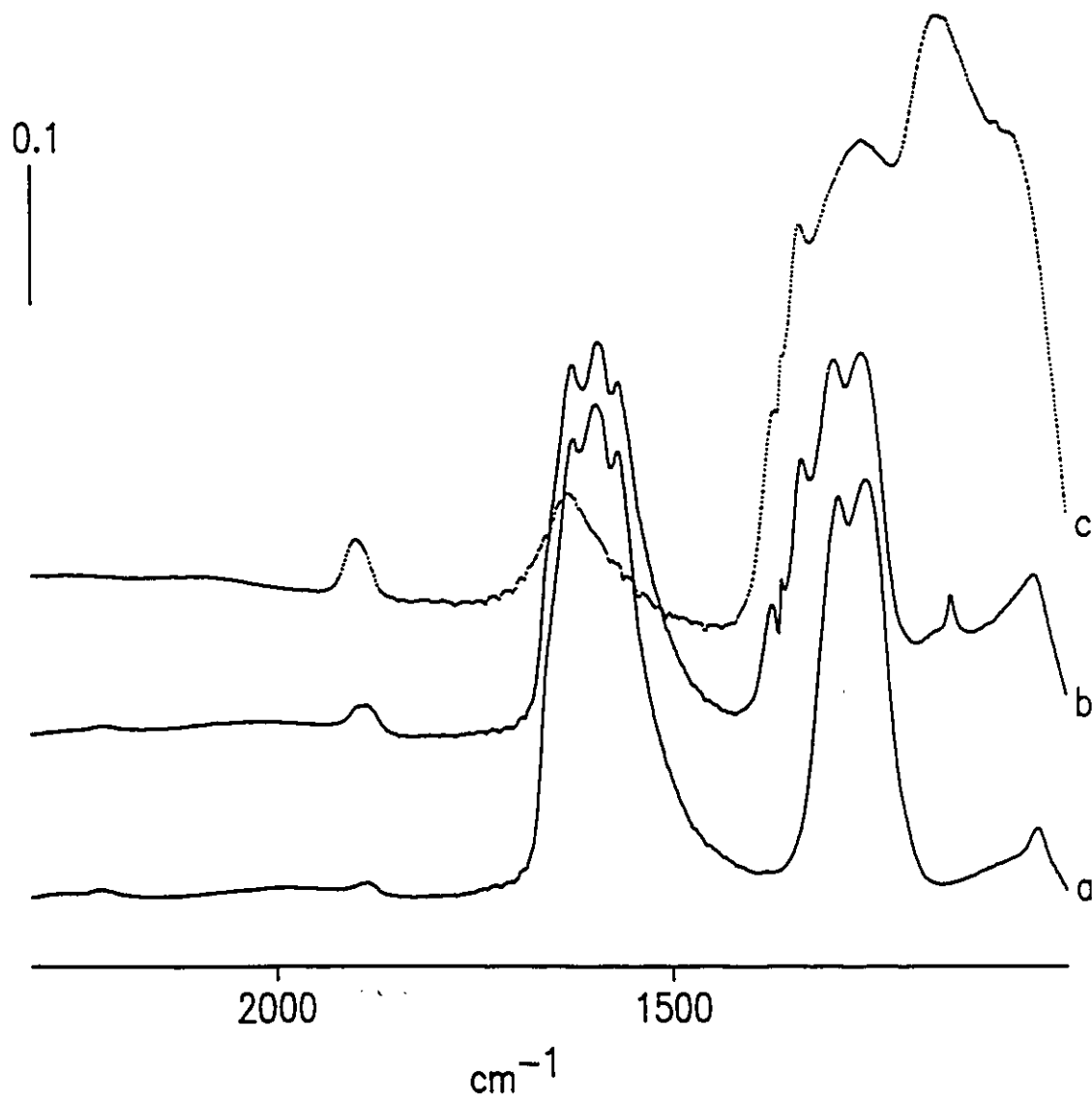


Fig 8.7 Adsorption of NO_2 , then SO_2 on $\text{CuO}/\text{Al}_2\text{O}_3$

- (a). 1.44 Torr of NO_2 in contact with $\text{CuO}/\text{Al}_2\text{O}_3(450)$ for 15', then evacuation for 5'.
(b). 1.74 Torr of SO_2 is added to (a).
(c). after 4 hours.

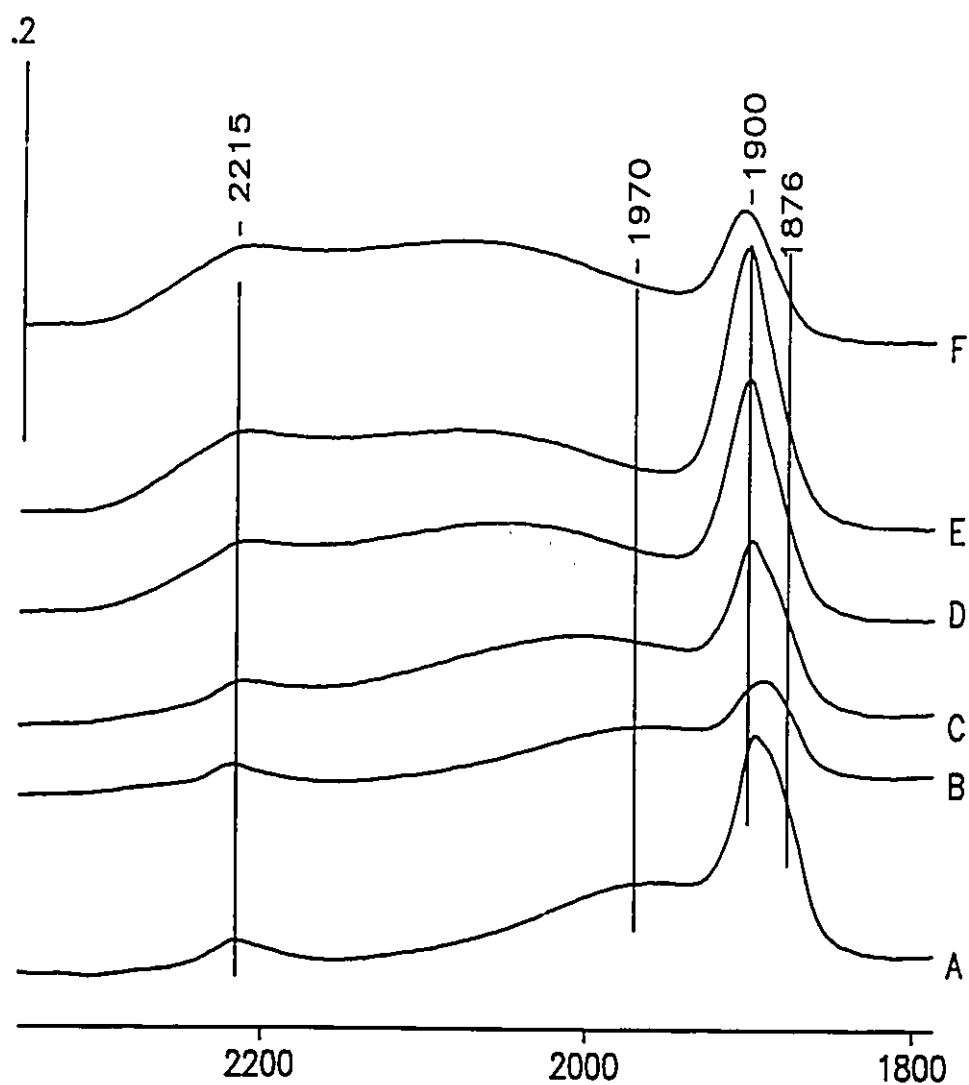


Fig 8.8 Adsorption of NO_2 , then SO_2 on $\text{CuO}/\text{Al}_2\text{O}_3$

(A). add NO_2 1.00 Torr and stand for 15 minutes. (B). evacuate for 5 minutes. (C). add SO_2 1.24 Torr. (D). after 15 minutes (E). after 45 minutes. (F). evacuate for 5 minutes.

and NO will transfer to Cu^{2+} sites to form a more stable Cu^{2+} -NO species, which results in an increase in intensity at about 1900 cm^{-1} . For longer contact time or with high pressure of NO_2 and SO_2 gases, the band peak at 2215 cm^{-1} will shift to higher wavenumber at about 2240 cm^{-1} . The bands at 2240 and 2215 cm^{-1} obviously belong to N_2O species. The broad band at about 2080 cm^{-1} has not yet been assigned.

We have observed that the surface Cu^{2+} ions are not in a uniform environment, and a broad band from 1875 to 1930 cm^{-1} appears when NO_2 is added. With the addition of SO_2 , the shoulder band at 1876 cm^{-1} disappears and a strong band at 1900 cm^{-1} becomes symmetric. This demonstrates that the SO_2 is predominantly adsorbed at basic sites which are connected with Cu^{2+} ions on the CuO surface. (And probably will react with isolated Cu^{2+} , but this species is so little in concentration that we couldn't make any conclusion.) The Cu^{2+} ions in CuAl_2O_4 type are still available for the adsorption of NO, which is responsible for the band at 1900 cm^{-1} .

(5). Adsorption of SO_2 , then NO_2

When SO_2 is added to pure Al_2O_3 , we observe the chemisorbed species at 1050 cm^{-1} and a weak band at 1325 cm^{-1} (as shown in chapter 3). The adsorption sites that produce the species to give the 1050 cm^{-1} band, as discussed before, are surface Lewis basic O^{2-} sites. On adding NO_2 , besides all NO_2 bands which appear when NO_2 is added alone, all SO_2 derived bands increase in intensity (not shown). There are also new bands near 1150 and 1350 cm^{-1} (broad). The bands around 2200 and 1960 cm^{-1} become more intense. This is especially noticeable with Al_2O_3 activated at higher temperatures.

It looks as if NO_2 and SO_2 absorb on Al_2O_3 on different sites and do not affect each other very much. However, SO_2 preadsorption promotes NO_2 interaction with alumina, producing more NO^+ and NO. It is also possible that preadsorption of SO_2 might create more acidic sites because SO_2 attacks Lewis basic sites. NO species attack acid sites, like surface cations, to give the intense bands around 1900 - 2250 cm^{-1} .

Adding SO_2 to $\text{CuO}/\text{Al}_2\text{O}_3$ gives a somewhat similar spectrum to that which was observed with pure alumina. However, the introduction of CuO provides more complicated micro-environments and increases the basicity of the surface. Therefore different adsorbed states are expected to occur. There are weak bands at about 1325 cm^{-1} . The 1050 cm^{-1} band which usually appeared on pure Al_2O_3 is now at 1040 cm^{-1} (see Fig 8.9 A). We have shown that SO_2 predominately adsorbs on the basic sites which are connected with Cu^{2+} ions of CuO phase, but not with the Cu^{2+} ions in CuAl_2O_4 forms. Adding CO on $\text{CuO}/\text{Al}_2\text{O}_3$, in another experiment, we get bands at 2170 (weak), 2122 and 2106 cm^{-1} . At this stage, adsorption of SO_2 eliminates the 2170 cm^{-1} band immediately, and the band at 2106 cm^{-1} decreases gradually and finally disappears, while the band at 2122 cm^{-1} shifts to 2130 cm^{-1} then gradually moves back to 2126 cm^{-1} (Fig 8.10). Because SO_2 first attacks the basic sites which connects Cu^{2+} ions in CuO phase, the Cu^{2+} - CO species at 2170 cm^{-1} (mainly from Cu^{2+} on CuO surface) is eliminated quickly. To explain why the band at 2122 cm^{-1} shifts to 2130 cm^{-1} with the addition of SO_2 , it is suggested that the electron density of the Cu^+ site is lowered by the formation of neighbouring $\text{O} \rightarrow \text{SO}_2$ species. In this way, the electron pair on the C atom moves more closely to the metal centre and strengthens the C-O bond, shifting the C-O frequency to higher wavenumber. As time passes, the band at 2130 cm^{-1} can move back to 2126 cm^{-1} . This may suggest that the environment of Cu^+ has been changed. For example, the $\text{Cu}^+ \text{--} \text{O} \text{--} \text{Cu}^{2+}$ bonds could break or some new sulfur species could be formed. There are many ways to try to account for the shift of this band, but speculation is unwarranted.

A most interesting observation is the behaviour of the band at 2106 cm^{-1} (see Fig 8.10). This Cu^0 - CO band gradually disappears, which suggests that the Cu^0 species has been oxidized. Because the band at 2126 cm^{-1} (due to $\text{Cu}^+ \text{--} \text{CO}$) does not increase, the Cu^0 species might be oxidized to Cu^{2+} . This transfer is a slow process. In the absence of NO_x or other oxidizing agents, the possible mechanism is that SO_2 dissociates on Cu^0 sites to give SO and O species. Leung *et al.* have demonstrated this phenomena on the $\text{Cu}(100)$ surface [16]. Our experiments also demonstrate that SO_2 is dissociated to SO and O atoms on Cu^0 sites in this $\text{Cu}/\text{Al}_2\text{O}_3$ catalyst.

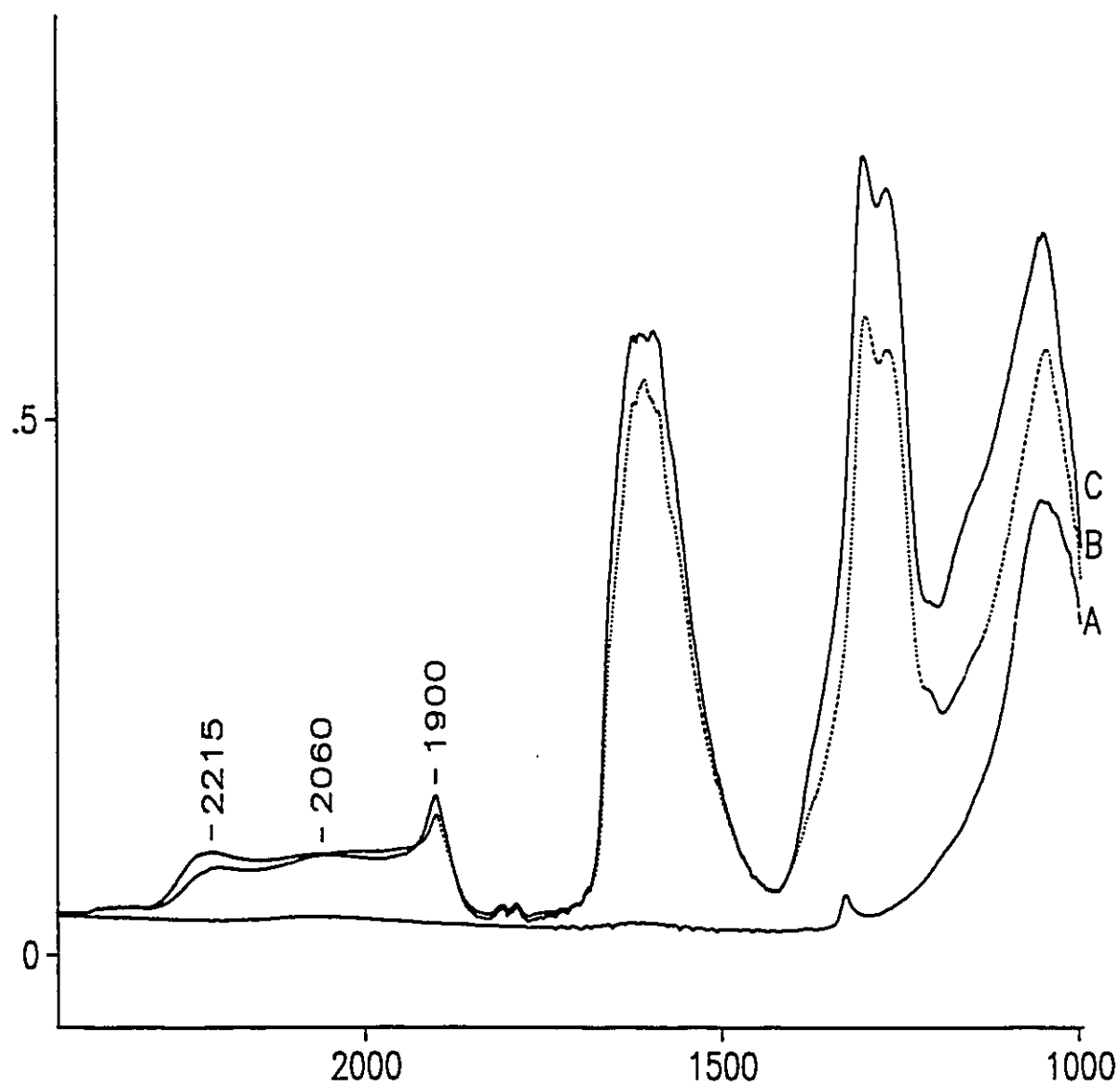


Fig 8.9 Adsorption of SO_2 , then NO_2 on $\text{CuO}/\text{Al}_2\text{O}_3$
(A). add SO_2 1.40 Torr and stand for 15 minutes, then evacuate for 5 minutes. (B). add NO_2 1.77 Torr. (C). after 30 minutes.

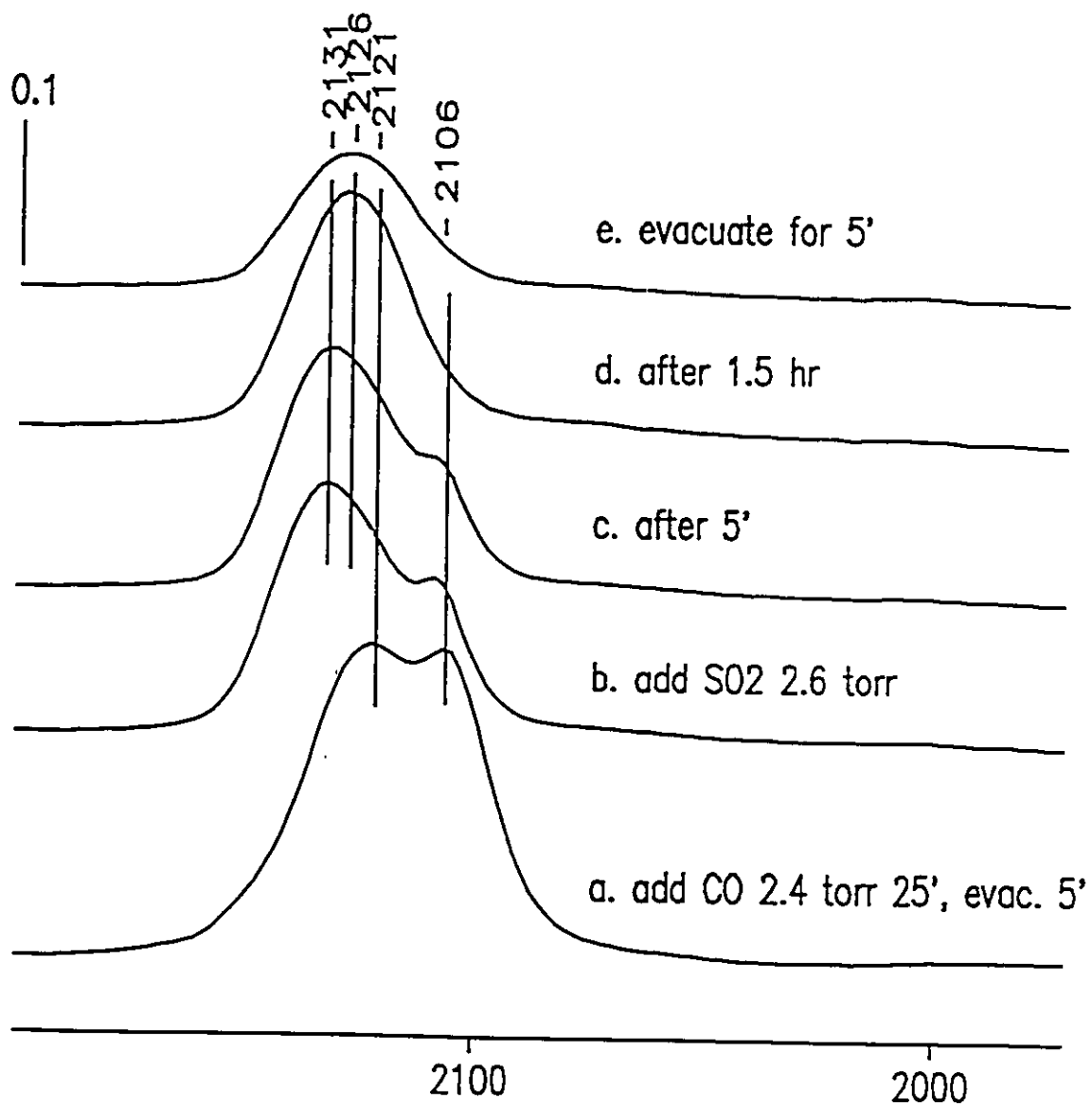


Fig 8.10 Adsorption of CO and SO₂ on CuO/Al₂O₃

Finally, adding NO_2 to a $\text{CuO}/\text{Al}_2\text{O}_3$ sample after SO_2 results in the formation of broad bands at about 1900, 2060 and 2215 cm^{-1} (Fig 8.9 B-C). The band at 1900 cm^{-1} is apparently symmetric. This observation also supports the fact that there is only one kind of surface Cu^{2+} ion available after SO_2 treatment. The Cu^{2+} ions on the CuO surface have been connected with SO_x species and Cu^{2+} in other sites are still free to adsorb NO to give a 1900 cm^{-1} band. Since the bands due to nitrogen containing species in lower oxidation states are more intense when SO_2 has been preadsorbed, it is suggested that surface copper sulfate species favour the reduction of NO_2 to NO or other lower oxidation state species.

4. CONCLUSION

(1). Al_2O_3 has a catalytic capacity to reduce NO_2 to NO and NO^+ . The higher the activation temperature, the more NO and NO^+ are found. The reduction sites may involve two coordinatively unsaturated Al^{+3} ions. The adsorption of NO_2 on Al_2O_3 to form NO_3^- species is so strong that the catalytic capacity is reduced. The assignments of differently coordinated NO_3^- are also obtained.

(2). Preadsorption of SO_2 increases the ability of Al_2O_3 to reduce NO_2 to NO and NO^+ . In the development of the SCR (Selective Catalytic Reduction) process, a number of problems exist. One of them is that the catalysts (customarily used for this process are metal oxides supported on TiO_2 and zeolite) are easily poisoned by SO_x . Alumina seems to have higher resistance to SO_x poisons. This may be useful in the SCR process in which NO_x are reduced by NH_3 to N_2 . On the other hand, preadsorption of NO_2 on Al_2O_3 increases the amount of SO_2 adsorbed. It gives strong bands at 1150 and 1370 cm^{-1} , which belong to sulfate species.

(3). For the $\text{CuO}/\text{Al}_2\text{O}_3$ catalyst investigated here (containing 1% Cu), there mainly exist Cu^{2+} cations on CuO phase, Cu^{2+} ions in aluminate types, very few isolated Cu^{2+} in Al_2O_3 lattice, and a few Cu^+ ions in $\text{Cu}^+-\text{O}-\text{Cu}^{x+}$ ($x=1,2$) states as well as a few Cu^0 sites.

(4). Addition of copper greatly increases the ability of alumina to reduce NO_2 to NO . The possible mechanism might involve the reaction ($2\text{Cu}^+ + \text{NO}_2 \longrightarrow 2\text{Cu}^{2+}(\text{O}) + \text{NO}$), which suggests that an increase of Cu^+ content would greatly promote the reducing activity of the catalysts. The impregnated sample also greatly decreases the stability of NO_3^- toward to SO_2 .

(5). It seems SO_2 mostly adsorbs on surface basic sites which are connected with Cu^{2+} ions of CuO phase to form surface sulfate species and leave aluminate like Cu^{2+} cations (CuAl_2O_4) free to adsorb NO .

(6). SO_2 can be adsorbed on Cu^0 sites to dissociate to SO and O species.

(7). Sulfated copper species on the surface can promote the reduction of NO_2 to NO , NO^+ and N_2O .

Elucidation of the detailed structure of the active centres and the mechanism proposed to account for these observations in this work call for further investigation.

References

- [1]. Fergusson, J. E., "Inorganic Chemistry and the earth", Pergamon Press, Oxford, 1982.
- [2]. Ismogilov, Z. R. and Kerzhentsev, M. A., Catal. Rev. - Sci. Eng., 32, 51(1990).
- [3]. Wark, K. and Warner, C. F., "Air Pollution: Its Origin and Control", 2nd Edition, Harper & Row, Publishers, New York, 1981.
- [4]. National Research Council of Canada, "Photochemical Air Pollution: Formation, Transport and Effects", Publications NRCC, Ottawa, 1975.
- [5]. Shelef, M., Chem. Rev., 95, 209(1995).
- [6]. Haggin, J., Chemical & Engineering News, p20, April 20, 1991.

- [7]. Frank, N. W., Kawamura, K. and Miller, G. A., Chem. Eng. Prog., 81(6), 30(1985).
- [8]. Haggin, J., Chemical & Engineering News, p25, July 25, 1994.
- [9]. Centi, G., Riva, A., Passarini, N., Brambilla, G., Hodnett, B. K., Delmon, B. and Ruwet, M., Chemical Engineering Science, 8, 2679 (1990).
- [10]. London, J. W. and Bell, A. T., J. Catal., 31, 96 (1973).
- [11]. Rewick, R. T. and Wise, H., J. Catal., 40, 301 (1976).
- [12]. Taylor, K. C., Catal. Rev.-Sci. Eng., 35, 457(1993).
- [13]. Padley, M. B., Rochester, C. H., Hutchings, G. J. and King, F., J. Catal. 148, 438(1994).
- [14]. Busca, G., J. Mol. Catal., 43, 225(1987).
- [15]. Fu, Y., Tian, Y. and Lin, P., J. Catal., 132, 85(1991).
- [16]. Leung, K. T., Zhang, X. S. and Shirley, D. A., J. Phys. Chem., 93, 6164(1989).
- [17]. Davydov, A. A., "Infrared Spectroscopy of Adsorbed Species on the Surface of Transition Metal Oxides " (Ed. Rochester, C. H.), John Wiley & Sons, 1990.
- [18]. Frieman, R. M., Freeman, J. J. and Lytle, F. W., J. Catal., 55, 10(1971).
- [19]. Lamotte, J., Lavalley, J-C., J. Chem. Soc., Faraday Trans. 1, 79, 2219(1983).
- [20]. Bensite, M., Moravek, V., Lamotte, J., Saur, O., Lavalley, J-C., Spectrochimca Acta, 43A, 1487(1987).
- [21]. Parkyns, N. D., " Proc. 5th Intern. Congr. Catal.", 1972, p12-255.
- [22]. Laane J. and Ohlsen, J. R., "Progress in Inorganic Chemistry", Vol. 27(Ed. by S. J. Lippard), John Wiley and Sons, 1980.
- [23]. Davis, S. Mark and Lunsford, Jack H., J. Colloid and Interface Science, Vol. 65, 352 (1978).
- [24]. Pozdnyakov, D. V. and Filimonov, V. N., Kinetics and Catalysis, 14, 655 (1973).
- [25]. "CRC Handbook of Chemistry and Physics", 69th Edition, 1988-1989. F-183.
- [26]. Dalla Lana, I. G., Karge, H. G. and George, Z. M., J. Phys. Chem., 97,8005(1993).
- [27]. Saur, O., Bensitel, M., Mohammed Saad, A. B., Lavalley, J. C., Tripp, C. and Morrow, B. A., J. Catal., 99, 104(1986).
- [28]. Ross, S. D., "Inorganic Infrared and Raman Spectra", McGraw-Hill, London, 1972.

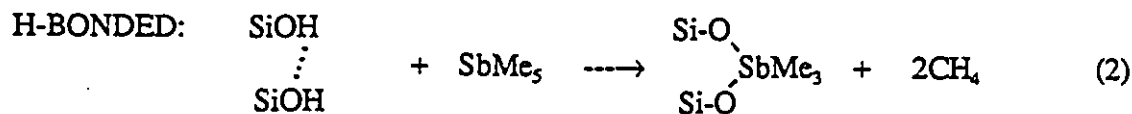
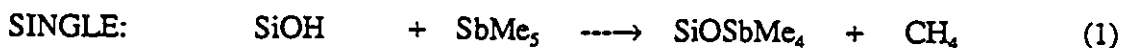
Chapter 9

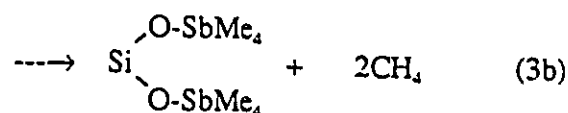
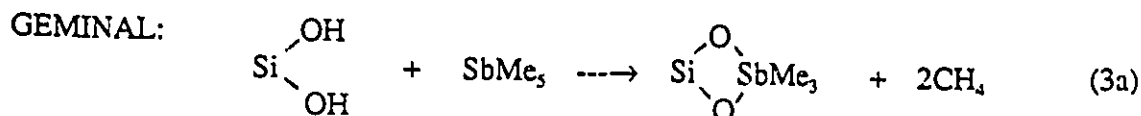
ADSORPTION OF PENTAMETHYLANTIMONY (SbMe_5) ON SILICA (SiO_2)

1. INTRODUCTION

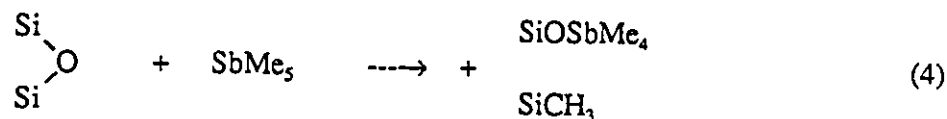
The chemical vapour deposition (CVD) of volatile organometallic compounds on oxide surfaces is a useful method for preparing novel mixed oxide catalysts [1-5]. When the organometallic species is an alkyl compound, additional information regarding the texture of the surface and the structure of the surface hydroxyl layer can be obtained [6,7]. Such organoalkyls are part of a class of compounds generally known as hydrogen sequestering (HS) agents by virtue of their ability to react with surface OH groups [7,8]. Reactions of surface OH groups with HS agents, in practice, are also important in many other areas of chemistry [9-14]. Examples are chemical synthesis, heterogeneous catalysis and surface modifications. Particular interest has been directed toward the use of methyl derivatives of Zn [15], Cd [16], Hg [17], Al [18], and Ga [19] because they are relatively small and they are capable of sequestering a large number of surface hydroxyl groups.

Pentamethylantimony, SbMe_5 , is a potential HS agent whose reactivity with oxides has not been explored, although its reaction with the hydroxyl groups on a partially condensed silsesquioxane has been confirmed [20]. Its reaction with various hydroxyl configurations on SiO_2 might be expected to occur as follows:





In addition, as has been previously found for AlMe_3 , SbMe_3 might react with siloxane sites as follows:



We report here a detailed study of the chemisorption of SbMe_3 on a fumed or pyrogenic silica, the thermal stability of the sequestered surface, and its reaction with H_2O , HCl and HBr .

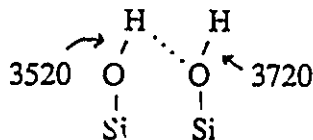
The silica used in these experiments was Cab-O-Sil grade HS-5, which is commercially available from Cabot Inc., U.S.A.. It had a BET surface area of $325 \text{ m}^2/\text{g}$ and was used "as received". This silica has been fully characterized previously in our laboratory, both with respect to the accessibility of the surface silanols to other HS reagents [6,7], and to H/D exchange probes of varying steric sizes [6]. The surface silanol density after activation at 150°C is $3.1/\text{nm}^2$ of which $2.5/\text{nm}^2$ can undergo H/D exchange using D_2O or ND_3 . About 1.1 of these are isolated silanols (single or geminal), 1.4 are hydrogen-bonded (single or geminal) and 0.6 are inaccessible due to interparticle contact. After vacuum activation at 450°C only isolated silanols remain, the density being about $1.4/\text{nm}^2$. Following vacuum activation at 1000°C the density of the silanols falls to about $0.5/\text{nm}^2$. In this text, as before, we will designate each silica sample by the symbol $\text{Si}(\text{C})$ where "C" is the temperature of activation in degrees Celsius.

The sample of SbMe_3 is kindly provided by Dr. Frank J. Fcher, Professor of the University of California, Irvine.

2. RESULTS

(1). Reaction between SbMe_3 and SiO_2

The infrared of Si(150) from 4000 to 2500 cm^{-1} is dominated by a sharp feature at 3747 cm^{-1} due to isolated non-interacting surface silanol groups. This peak is accompanied by broader features at 3720, 3650 and 3520 cm^{-1} (Figure 9.1, also see Chapter 5). The 3720 and 3520 cm^{-1} spectral features are due to H-bonded SiOH groups and the 3650 cm^{-1} band is due to silanols which are perturbed due to interparticle contact. The 3520 cm^{-1} band is assumed to be due to H-bonded SiOH groups that act as proton donors, while the band at 3720 cm^{-1} is assumed to be due to H-bonded accepting SiOH groups.



Heating under vacuum at 450 °C removes most of the H-bonded and perturbed silanols (eliminated by condensation of silanols to yield siloxane bridges and water) leaving an intense peak at 3747 cm^{-1} which is asymmetric to low wavenumber (Figure 9.1B). Finally, activation at 800 to 1000 °C results in the removal of the low wavenumber asymmetry leaving a relatively sharp and symmetric peak at 3747 cm^{-1} (Figure 9.1C).

The perturbed silanols (3650 cm^{-1}) are inaccessible to most HS agents whereas all of the isolated silanols react with typical HS agents [6,7]. Depending of the molecular size and the degree of steric hinderance, the H-bonded silanols are more or less accessible to most HS agents (and H/D exchange agents). Figure 1A', 1B' and 1C' show the resultant IR spectra after completely reaction (i.e. no further spectral changes can be found, usually after 1 hour of adsorption) of Si(150), Si(450) and Si(1000) respectively with excess SbMe_3 at room temperature, and after evacuation of the gas phase for 5 minutes.

In every case, new spectral features appeared in the CH_x stretching region from 3000 to 2800 cm^{-1} , the most intense peak being near 2970 cm^{-1} . Figure 9.2 shows the corresponding difference

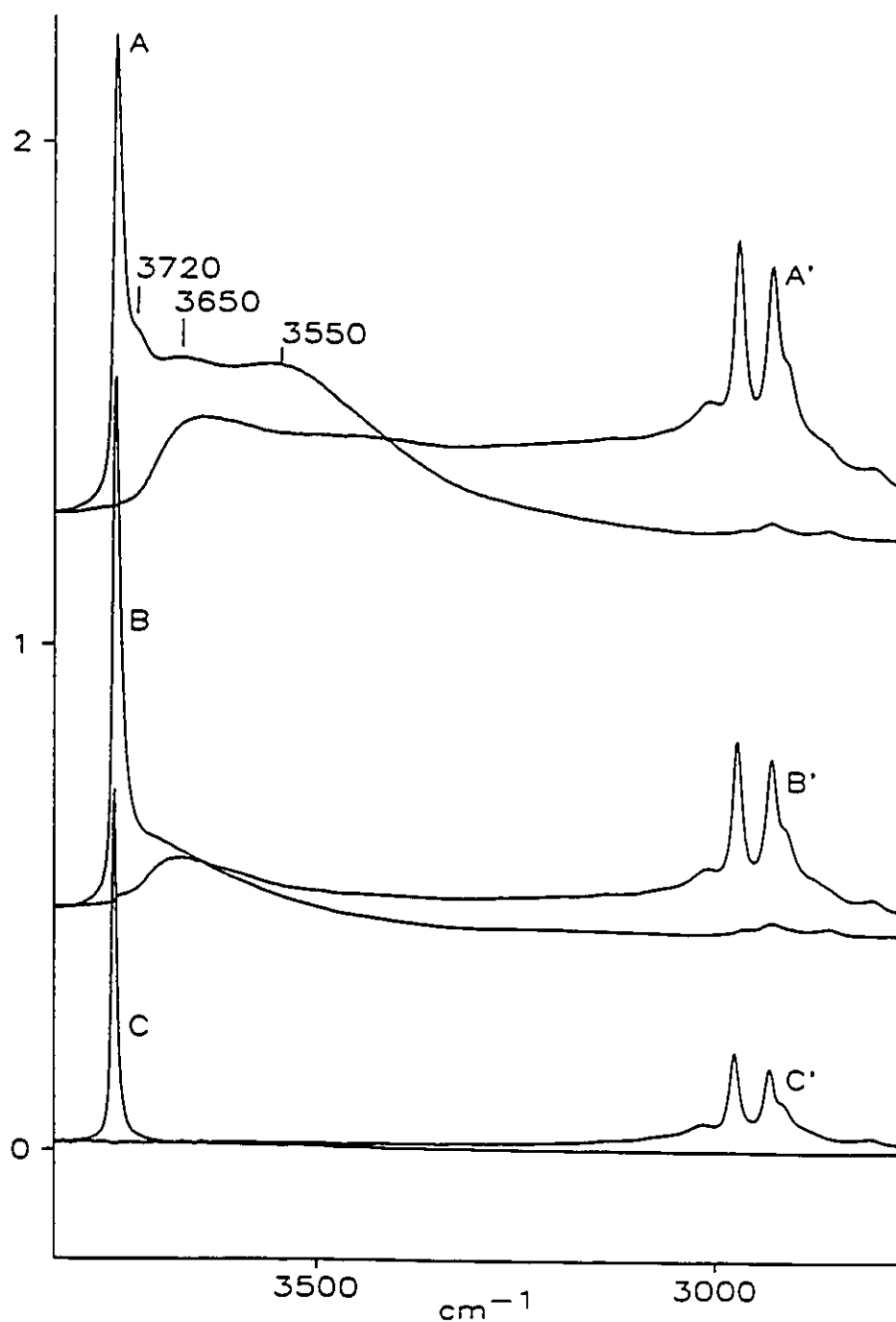


Fig 9. 1 Infrared spectra of silica after activation in vacuum for 1 hour at 150 °C (A), 450 °C (B) or 1000 °C (C). Curves A', B' and C' are the infrared spectra which were observed after complete reaction of each silica surface with excess SbMe_3 at room temperature followed by evacuation for 5 min. Figures A and B have been displaced for convenience of display.

spectra after subtraction of the spectra before reaction from that after complete reaction; peaks going down correspond to spectral features which have been eliminated by the reaction, those pointing upward correspond to the creation of new spectral features. The inset to Figure 9.2 shows the CH_x stretching region for each silica, each spectrum having been scaled so that the 2970 cm^{-1} peak has the same maximum intensity.

Activated temperatures of silica from 150 to $1000\text{ }^\circ\text{C}$ do not affect chemisorption spectra very much in the region 3200 to 500 cm^{-1} (there are two opaque regions below 1300 cm^{-1}). The spectra in the CH stretching region in Figure 9.2 are qualitatively similar, apart from minor shifts in wavenumber, suggesting that the same product distribution is formed regardless of the temperature of activation of the silica. The wavenumbers ($\pm 2\text{ cm}^{-1}$) of the observed features are 3010 , 2972 , 2930 , 2910 and 2800 cm^{-1} . Gaseous or physically adsorbed SbMe_3 has IR bands at 3010 , 2960 , 2915 and 2900 cm^{-1} . In each case, methane was the only gas phase product of the reaction. We will show later in discussion part that a single product, SiOSbMe_3 , is formed as a result of reaction (1) or (3b).

Thin silica disks are opaque to infrared radiation between about 1300 to 1000 cm^{-1} (Figure 9.3A). Outside of these regions, additional IR bands for $\text{SbMe}_3/\text{SiO}_2$ were observed at 1412 , 860 , 700 and 564 cm^{-1} (Figure 9.3B). The IR spectrum of gaseous or physically adsorbed SbMe_3 has several CH_3 deformation modes near 1412 cm^{-1} , four CH_3 rocking modes at 827 , 772 , 729 and 694 cm^{-1} (all very sharp and intense) and 516 cm^{-1} (IR active asymmetrical equatorial Sb-C stretching mode) [21].

For Si(450) or Si(1000), the course of the reaction is too fast to be followed using infrared spectroscopy when an excess of reactant is present. The band at 3747 cm^{-1} disappears in about five seconds, the time required to carry out a single scan. However, for Si(150), the interaction between SbMe_3 and SiO_2 surface is a relatively slow process. Then, the differences in the rate of reaction between isolated and hydrogen-bonded silanols can be seen if the quantity of reactant added is equal to the number of accessible silanols. Figure 9.4 shows such a series of spectra in the OH stretching region.

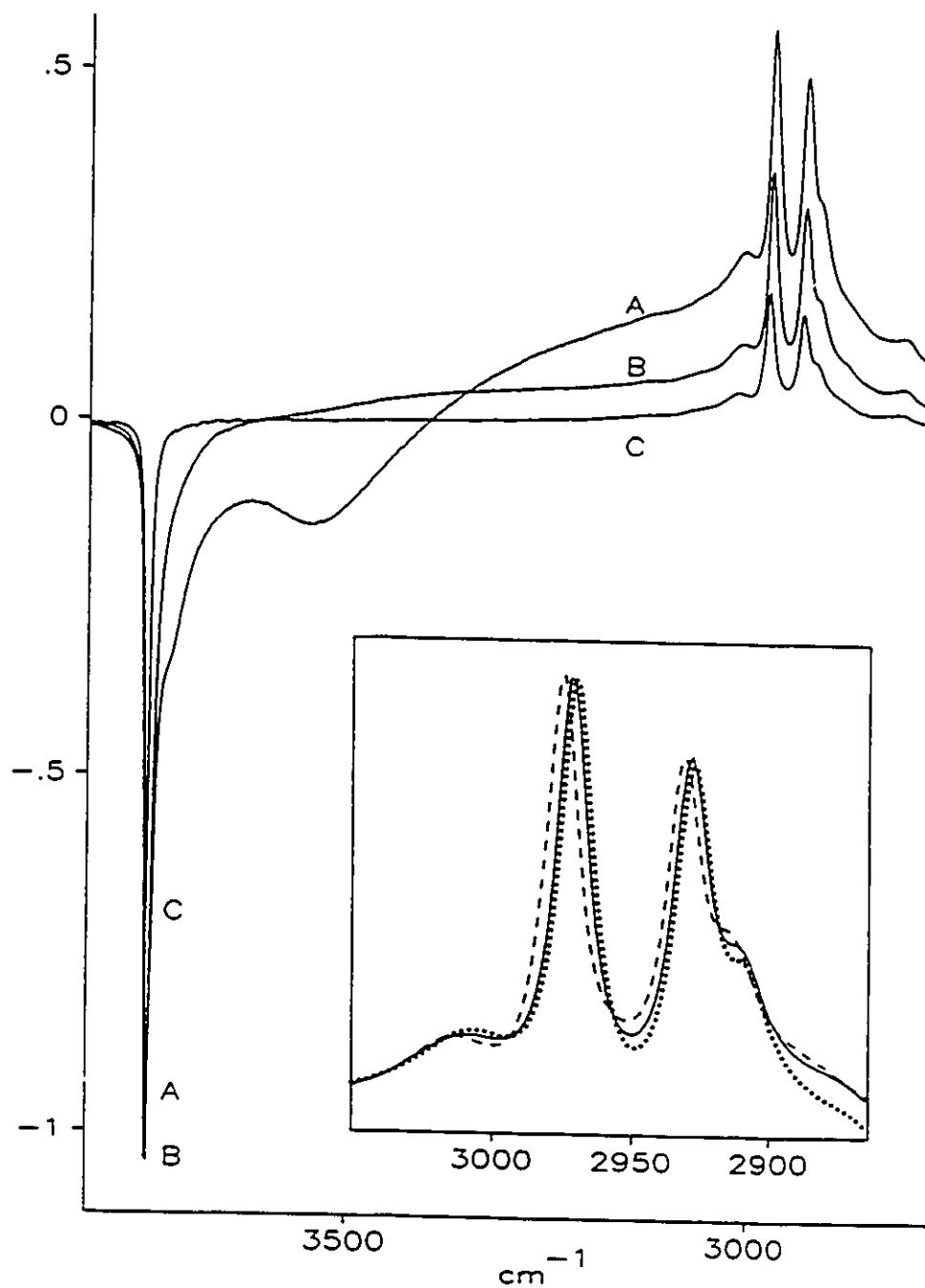


Fig 9. 2 Infrared difference spectra from Figure 1, showing the spectral changes observed following reaction with SbMe_3 . Curve A corresponds to $[A' \text{ minus } A]$ from figure 1. and so forth for B and C. The inset reproduces the above spectra in the CH stretching region after normalization so that the intensities of the strongest peak near 2970 cm^{-1} are equal.

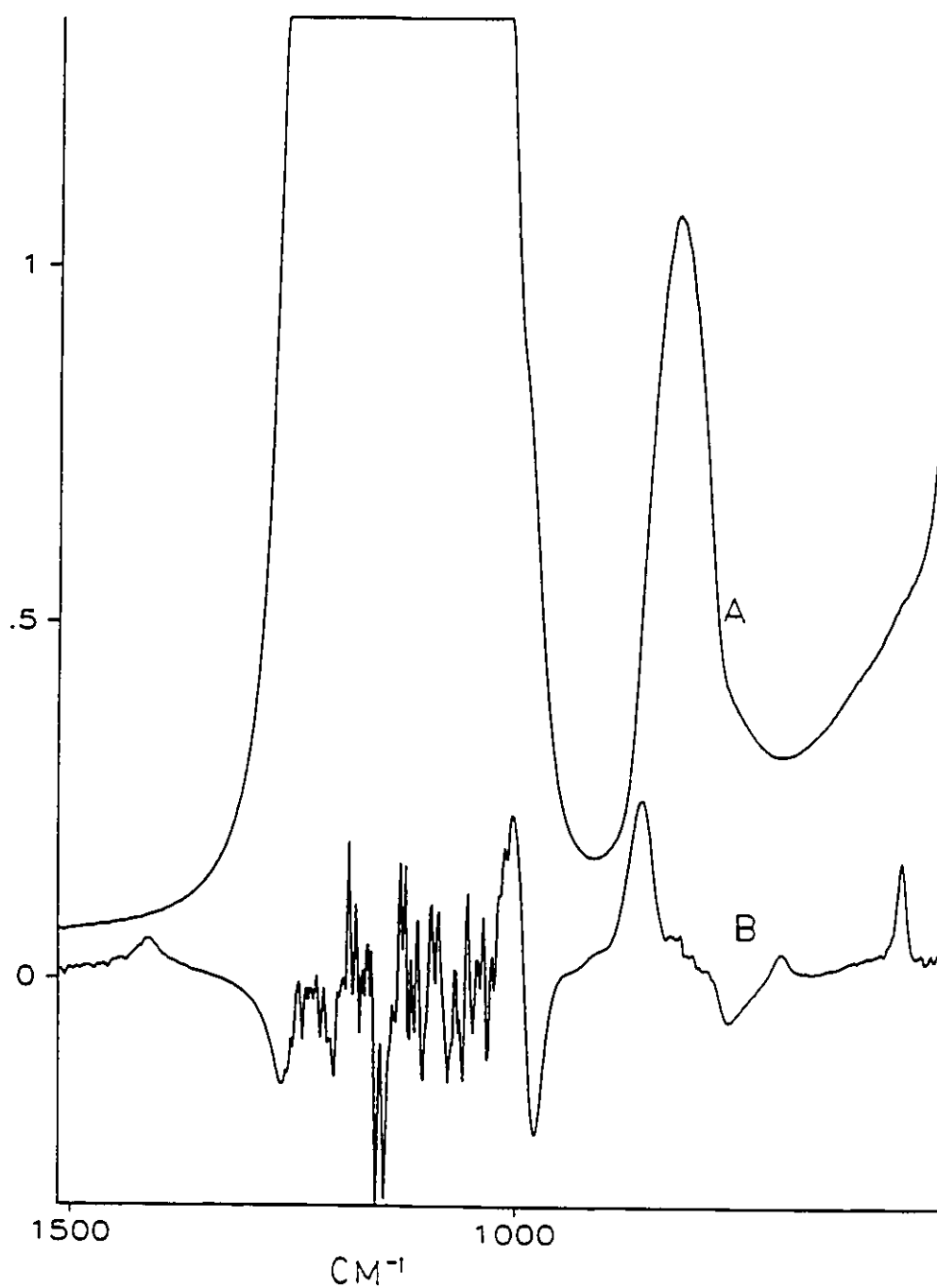


Fig 9. 3 A, background infrared spectrum of 4 mg/cm² Si(450). B, difference infrared spectrum (after subtraction of curve A) following complete reaction of the silica spectrum shown in curve A from that after reaction with SbMe₅. The excessive noise level between about 1250 and 1020 cm⁻¹ is due to the total absorption for both samples in this spectral region.

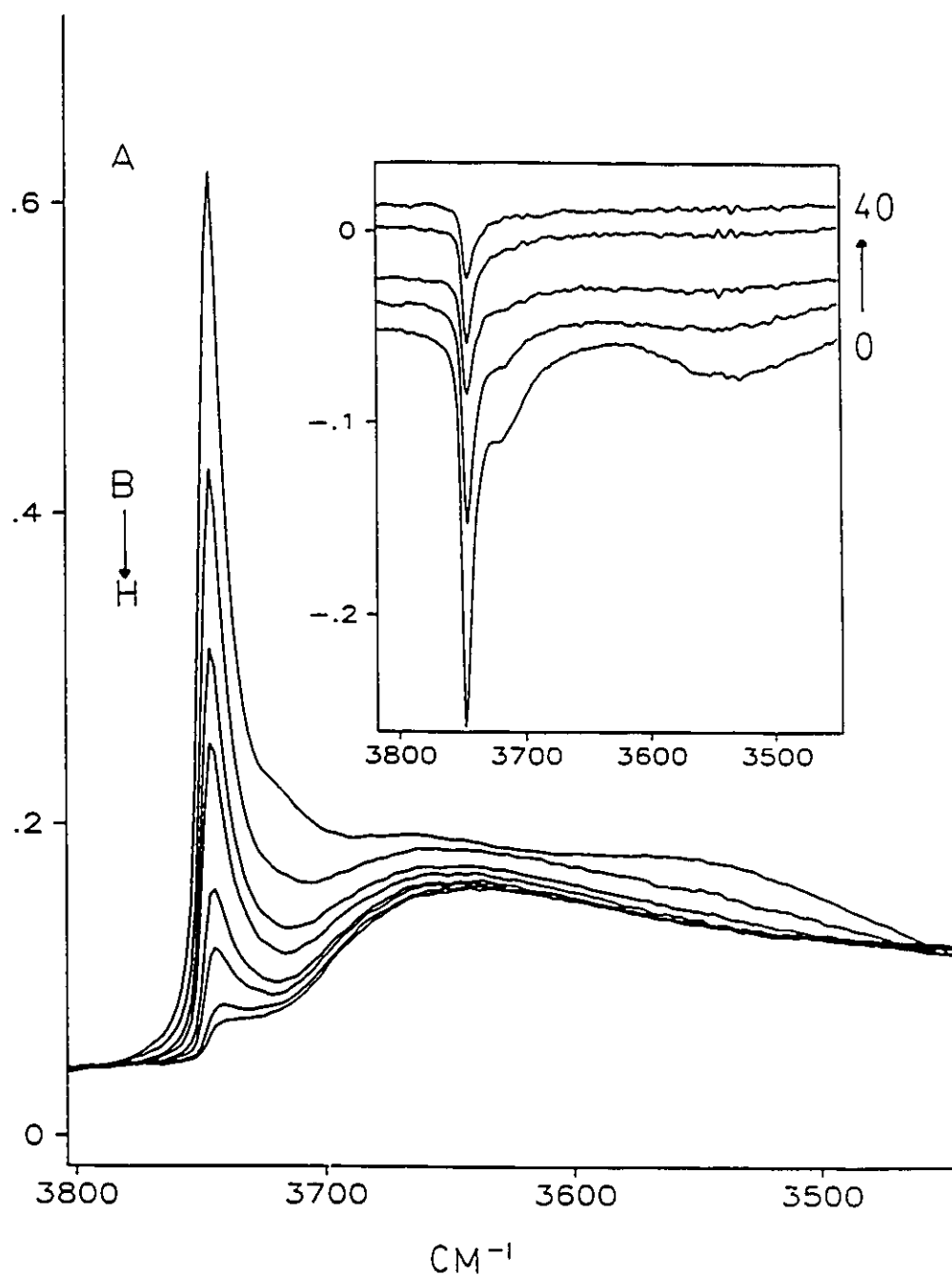


Fig 9. 4 A, infrared spectra of Si(150). B to H, infrared spectrum observed immediately after addition of SbMe_3 (Curve B) and, with decreasing intensity following curve B, after 10, 20, 40, 60, 120 and 180 seconds. Inset. From bottom to top, difference spectra showing the silanols which have reacted immediately after addition of SbMe_3 (bottom curve) and during 10 second intervals thereafter at 10, 20, 30 and 40 seconds.

Details of the reaction are more clearly seen in difference spectra which show what has 'reacted' during selected time intervals. The inset to Figure 9.4 shows such spectra recorded at 10 second intervals during the first 40 seconds of reaction. The peaks going down represent silanols which have reacted during each time interval. Note that although there was continuing reaction of the isolated silanols after about 30 seconds, there was essentially no further reaction of the hydrogen-bonded silanols, as evidenced by the bands at 3720 and 3520 cm^{-1} which reacted during the first three reaction intervals but not thereafter. This shows that the hydrogen-bonded hydroxyls are more active toward SbMe_3 . Finally, if the quantity of SbMe_3 added was twice the number of accessible silanols, the spectral features were qualitatively similar but the reaction rate was faster.

(2). Thermal stability

In the second part of experiment, the samples are heated at various temperatures after adsorption of SbMe_3 and after evacuation for five minutes.

A fully reacted Si(150) was heated under evacuation for 1 hour at 100 °C, 200 °C, 250 °C and 300 °C and spectra in the 3900 to 2700 cm^{-1} spectral region are shown in Figure 9.5. The most noticeable effects were the appearance of a sharp peak near 2858 cm^{-1} which particularly intensified after heating at or above 250 °C, and the partial reappearance of the 3747 cm^{-1} isolated silanol band. The bands at 3010 and 2910 cm^{-1} diminish and a new peak at 2959 cm^{-1} appears. After heating at 300 °C, the spectrum in the CH_x stretching region was virtually identical to that of a methoxylated silica containing surface SiOCH_3 groups [22]. There are bands at 2990, 2959, 2928 and 2858 cm^{-1} in CH_3 stretching vibration region. There is also 1466 cm^{-1} (does not show). For 250 °C heating the spectrum was a mixture of that due to the initially observed species and SiOCH_3 . A similar result was obtained if the silica had been activated at a higher temperature such that only isolated silanols were initially present. Finally, the gaseous products after heating to 300 °C were trapped and analyzed by infrared and mass spectroscopy. Both indicated that SbMe_3 was the sole gas phase product [23,24].

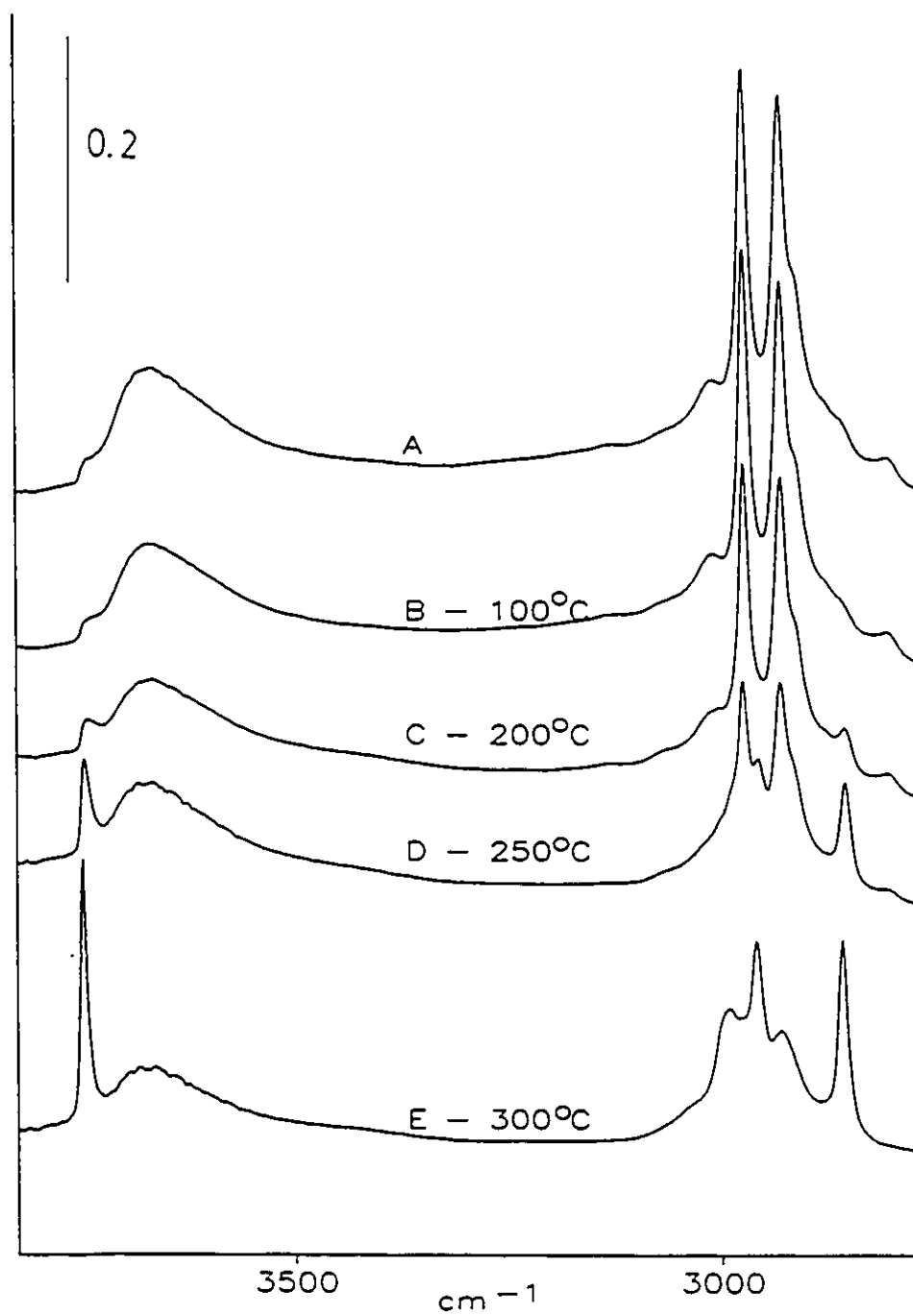


Fig 9. 5 A, infrared spectrum of Si(150) after complete reaction with SbMe_5 . Curves (B) - (E) show the IR spectra recorded after heating under vacuum for 1 h at the indicated temperature.

(3). Reaction with H_2O

Addition of water vapour (8 Torr) to $SbMe_3/SiO_2(450)$ system after complete reaction at room temperature did not alter the spectrum of "adsorbed $SbMe_3$ ". In OH stretching region, a broad band from 3000 cm^{-1} to 3660 cm^{-1} was formed (not shown). This is due to the physically adsorbed water, which has a characteristic vibration near 3400 cm^{-1} . Evacuation at $100\text{ }^\circ\text{C}$ removed physically adsorbed water and restored the initially spectrum in observation region. We conclude that the surface species is very stable toward water in room temperature.

(4). Reactions with HX

Treating $SbMe_3$ with HX gives methane and Me_4SbX [25]. In the same fashion, addition of excess HCl gas to $SbMe_3$ sequestered $Si(450)$ (Figure 9.6A) yielded the infrared spectrum shown in Figure 9.6B. Apart from the very broad and intense feature centred at 3150 cm^{-1} , there was partial restoration of the 3747 cm^{-1} peak and in the CH_x region there was a new band at 3025 cm^{-1} in addition to the sharp feature at 2930 cm^{-1} , and the shoulder near 2910 cm^{-1} had disappeared. Only unreacted HCl was seen in the gas phase spectrum. Heating at $100\text{ }^\circ\text{C}$ for 1 hour after evacuation of the gas phase caused a decrease in the intensity of all bands below 3700 cm^{-1} and a further increase in intensity of the 3747 cm^{-1} band (Figure 9.6C). These change progressed further after additional heating at $100\text{ }^\circ\text{C}$ (Figure 9.6D). Finally, heating at $150\text{ }^\circ\text{C}$ caused removal of virtually all $SbMe_3$ created features in the CH_x stretching region and complete restore of the 3747 cm^{-1} band to its intensity prior to reaction with $SbMe_3$ (Figure 9.6E).

In the low wavenumber spectral region, infrared bands near 1412 and 700 cm^{-1} changed slightly in intensity following addition of HCl but there was no frequency shift. The peak at 860 cm^{-1} shifted to 870 cm^{-1} , that at 564 cm^{-1} shifted to 570 cm^{-1} .

Finally, the spectra observed following addition of HBr in place of HCl. The spectrum was virtually identical to those as that happened with HCl in Figure 9.6.

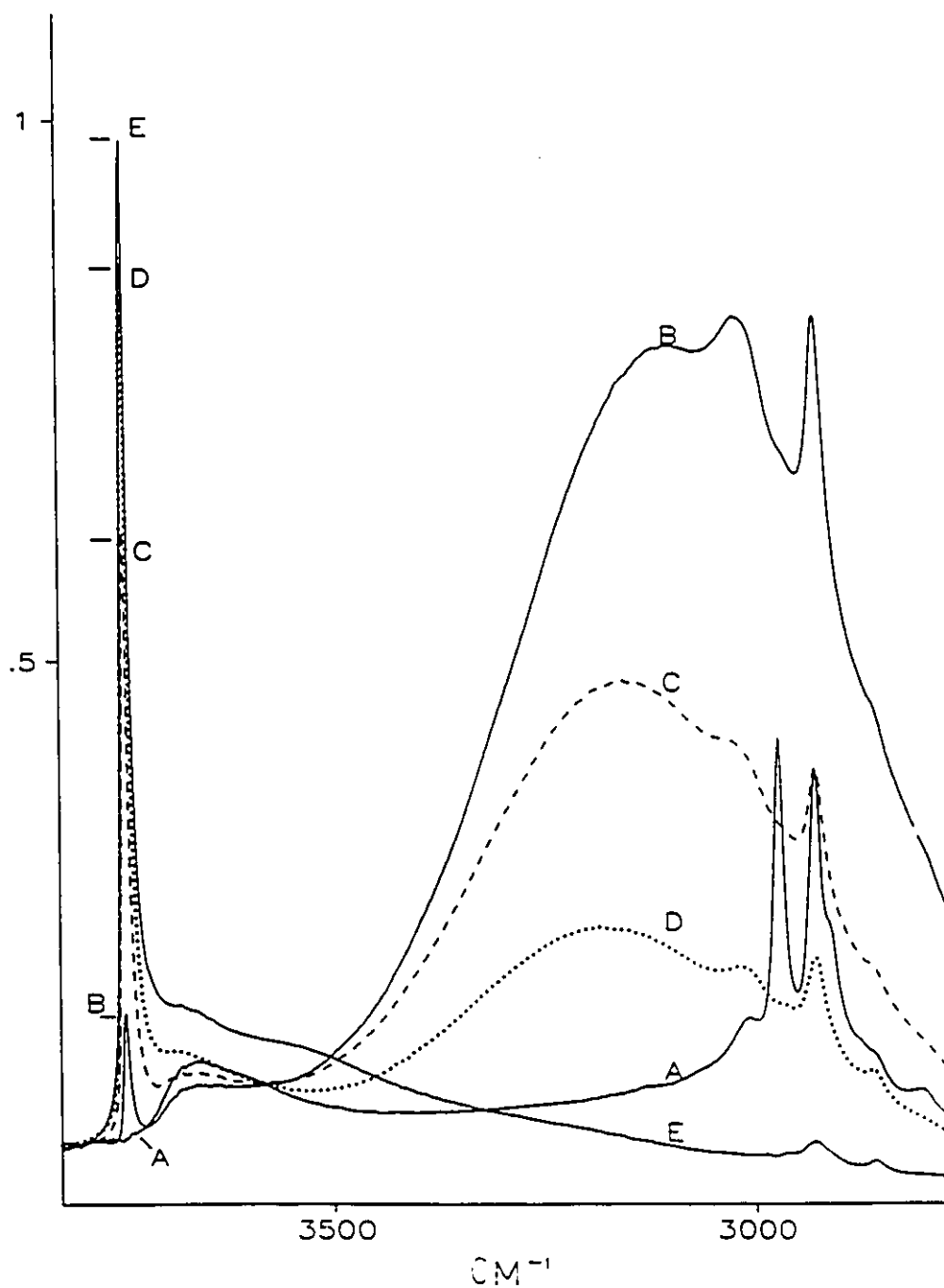


Fig 9. 6 A, infrared spectrum of Si(450) after complete reaction with SbMe_3 . B, infrared spectrum after addition of 9 Torr of HCl to A. C, spectrum after evacuation of B and heating under vacuum at 100°C for 1 h. D, heating after spectrum in C for an additional 1.5 h at 100°C . E, heating at 150°C under vacuum for 1 h.

3. DISCUSSION

(1). *Formation of the surface Si-OSbMe₄*

The reaction of SbMe₃ with silica appears to be remarkably simple. Regardless of the temperature of activation or the degree of hydrogen bonding of the silanols, the observed spectral features over the accessible range were the same. Four peaks in C-H stretching region for all silica samples are in constant proportion. Further, in experiments where small incremental doses of SbMe₃ were added, even at the first appearance of a spectrum in the CH_x region the relative intensities and frequencies of the observed bands were the same as those which were observed for saturation coverage (spectra not shown). This was also true in the case of Si(1000) where a reaction with siloxane sites might be expected. That is, there was no evidence for the formation of SiCH₃ and we conclude that reaction (4) does not occur to a significant extent. The spectral evidence (see below) suggests that SiOSbMe₄ is the major surface species formed, probably via reactions (1) and (3b). The activation temperature does not play an important role in this situation but on lower temperature activated silica, more OH groups are available and therefore, more surface antimony species are produced. There is no evidence for the formation of >SbMe₃ surface species via a reaction with geminal silanols as depicted in scheme (3a).

Further evidence for the formation of Si-O-SbMe₄ is that there is a band at 564 cm⁻¹. No matter what activation temperature is used, there is always a band at 564 cm⁻¹ when SbMe₃ is added. According to reference [26], the assignments for ν_s (MC, Sb-C₃ stretching modes) are:

(CH ₃) ₃ Sb	513 cm ⁻¹
(CH ₃) ₃ Sb ²⁺	582 cm ⁻¹
(CH ₃) ₄ Sb ⁺	574 cm ⁻¹
(CH ₃) ₅ Sb	516 cm ⁻¹ .

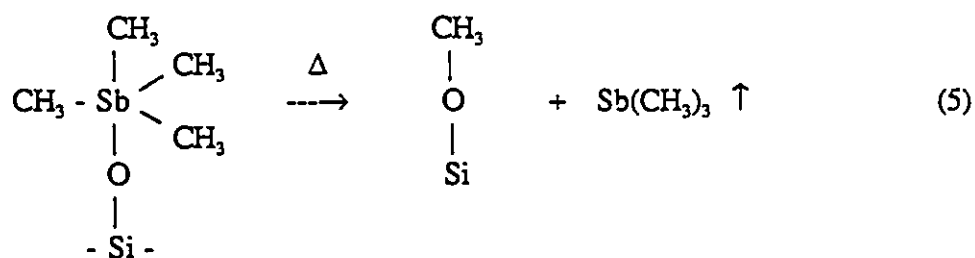
We observed 517 cm⁻¹ for SbMe₃ (gas phase), while the chemisorbed band at 564 cm⁻¹ is much closer to the band of (CH₃)₄Sb⁺ and this further supports our assignment to the sole product as SiOSbMe₄.

The rocking modes of SbMe_3 lie between 829 and 694 cm^{-1} and the new infrared bands observed in this spectral region for $\text{SbMe}_3/\text{SiO}_2$ at 858 and 700 cm^{-1} undoubtedly can be assigned to the rocking modes of SiOSbMe_4 . For example, Sb-CH_3 rocking modes in a series of XOSbMe_4 compounds [25] occur near 840 and 690 cm^{-1} . Finally, the 1412 cm^{-1} band which is common to most SbMe_x species is a CH_3 angle deformation mode, and the weak peak at 2800 cm^{-1} would most reasonably be the overtone.

In time resolved experiments (Figure 9.4) or in incremental titration experiments (not shown) where SbMe_3 was added to hydroxylated $\text{Si}(150)$, there was again no evidence for the formation of more than one chemisorbed Sb-methyl containing surface species. In the entire spectral range the bands created were identical regardless of the temperature of activation. Therefore, hydrogen-bonded silanols do not react according to reaction 2, but rather, as with most other reactive methyl containing HS agents [6,7], they react as depicted in scheme (1). However, the hydrogen-bonded silanols which are accessible to the reactant react faster than those which are isolated (disappearance of the $3720/3520\text{ cm}^{-1}$ bands, see Figure 9.4). A similar result was found by Feher for reaction of SbMe_3 with a partially condensed silsesquioxane [20].

(2). Stability to thermal treatment

Although the chemisorbed product is relatively thermally stable, heating at $300\text{ }^\circ\text{C}$ results in the formation of SiOCH_3 and gaseous SbMe_3 . The reaction is apparently:



According to Yates *et al.* [27], bands at 3000 , 2962 , 2857 , and 1470 cm^{-1} represent SiOCH_3 . (1466 cm^{-1} is the deformation frequencies of $-\text{OCH}_3$). It is very reasonable to believe that the

peaks at 2990, 2959, 2857, 1466 cm^{-1} in our experiments are come from Si-O-CH_3 .

(3). Stability to water vapour

The stability of the surface species to water vapour was somewhat surprising relative to other metal-methyl HS agents giving the normal propensity for the metal-carbon bond to cleave to yield methane and MOH. However, it seems that the OSbMe_4 species is remarkably stable to hydrolysis in other compounds (Me_4SbOH is stable in aqueous solution [24,28]).

(4). Formation of XSbMe_4

In the reaction with HCl, the intensity of the band due to isolated SiOH was restored after mild heating. The complete reaction would be:



We did not detect methane in the gas phase, instead, some FSbMe_4 type species was found on the sample and on cell windows. The compound FSbMe_4 has pronounced IR bands in the CH stretching region at 3018 and 2930 cm^{-1} [29], as compared to the bands at 3025 and 2930 cm^{-1} in the present case. A prominent peak in the range from 3000 to 3020 cm^{-1} is also a common feature of other XSbMe_4 or XOSbMe_4 compounds [30]. Infrared bands near 870 and 700 cm^{-1} are not inconsistent with the formation of ClSbMe_4 . This molecule would be expected to strongly interact with the generated SiOH groups giving rise to the broad band having a maximum near 3200 cm^{-1} . This disappears after heating under vacuum at about 150 $^{\circ}\text{C}$ as the ClSbMe_4 is removed from the reaction cell and the isolated SiOH peak is completely restored.

4. CONCLUSION

$\equiv\text{SiOSbMe}_4$ is the only detectable product of the reaction between silica and SbMe_5 regardless of the temperature of activation (room temperature to 1000 $^{\circ}\text{C}$). When present, the

hydrogen-bonded silanols react to completion faster than the isolated silanols. Unlike other reactive metal-alkyl compounds, there was no evidence for a significant reaction with siloxane sites. The chemisorbed species does not react with water vapour at room temperature or at 100 °C. However, upon heating to 250 to 300 °C it decomposes to yield surface SiOMe groups and gaseous SbMe₃. Finally, the surface OH groups can be regenerated by adding HX agents to SbMe₃/SiO₂ and heating at about 150 °C under evacuation.

As a final note, SbMe₃ reacts with accessible surface silanols to produce only one species, Si-O-SbMe₃. Therefore, SbMe₃ might be an ideal methyl containing HS agent for the accurate determination of the number of hydroxyl groups on Si(450) to Si(1000) because, unlike AlMe₃, there is no significant reaction with siloxane sites (reaction 4). Additionally, a gravimetric measure of the mass change following chemisorption would give a rapid measure of the OH concentration. Previously, the reaction of ZnMe₂ has been used for this purpose [15], but in a forthcoming publication we will show that the reaction of ZnMe₂ with silica is the most complex of all metal-alkyl HS agents and that these molecules are unsuitable for the determination of the silanol concentration.

References

- [1]. "Tailored Metal Catalysts", Iwasawa, Y., Ed., Reidel, Boston, 1986.
- [2]. Iwasawa, Y., Adv. Catal., 35, 186(1987).
- [3]. Sheng, T. C. and Gay, I. D., J. Catal., 145, 10(1994).
- [4]. Zecchina, A. and Aeran, C. O., Catal. Rev. Sci. Eng., 35, 261(1993).
- [5]. "Perspectives in Catalysis", Thomas, J. M. and Kamaraev, K. I., Editors, Blackwell Science Publishers, London, 1992.
- [6]. Morrow, B. A. and McFarlan, A. J., Langmuir, 7, 1695(1991).
- [7]. Morrow, B. A. and McFarlan, A. J., J. Non-cryst. Solids, 120, 61(1990).

- [8]. Morrow, B. A., *Stud. Surf. Sci. Catal.* 57A, A161(1990).
- [9]. Chmielowiec, J., Morrow, B. A., *J. Colloid Interface Sci.*, 94, 319(1983).
- [10]. Tripp, C. P. and Hair, M. L., *J. Phys. Chem.*, 97, 5693(1993).
- [11]. Kinney, J. B. and Stalry, R. H., *J. Phys. Chem.*, 87, 3735(1983).
- [12]. Ellestad O. H. and Blindheim, J. *Mol. Catal.*, 33, 275(1985).
- [13]. Low, M. J. D., Severida, A. G. and Chan, J., *J. Catal.*, 69, 384(1981).
- [14]. Sindorf, D. W., and Maciel, G. E., *J. Phys. Chem.*, 87, 5516(1983).
- [15]. (a). Galanskii, A. A. and Galich, P. N., *React. Kin. Catal. Lett.*, 38, 281(1989). (b). Nondek, L., *React. Kin. Catal. Lett.*, 2, 283(1975). (c). Vit. Z. and Nondek, L., *React. Kin. Catal. Lett.*, 24, 137(1984).
- [16]. Dodonov, V. A., Oleynik, A. A., Molotovshchikova, M. B., Lysenko, G. N. and Druzhkov, O. N., *Russ. Chem. Bull. (in English)*, 42, 1639(1993).
- [17]. Hohl, H. and Zust, W., *Colloids and Surfaces*, 11, 365(1984).
- [18]. (a). Soto, C., Wu, R., Bennett, D. W. and Tysoc, W. T., *Chem. Mater.*, 6, 1705(1994). (b). Kratochivila, J., Zadlc, Z., Kazda, A. and Salajka, Z. J., *Non-cryst. Solids*, 143, 14(1992). (c). Bartram, M., E., Michalske, T. A. and Rogers, J. W., *J. Phys. Chem.*, 95, 4453(1991). (d). Kinney, J. B. and Staley, R. H., *J. Phys. Chem.*, 87, 3735(1983).
- [19]. Morrow, B. A. and McFarlane, R. A., *J. Phys. Chem.*, 90, 3192(1986).
- [20]. Feher, F. J., Budzichowski, T. A., Rahimian, K. and Ziller, J. W., *J. Am. Chem. Soc.*, 114, 2859(1992).
- [21]. Downs, A. J., Schmutzler, R. and Steer, I. A., *Chem. Comm.*, 221(1966).
- [22]. Morrow, B. A., *J. Chem. Soc. Faraday Trans. I*, 70, 1527(1974).
- [23]. "EPA/NIH Mass Spectral Data Base", Volume 1, Heller, S. R. and Milne, G. W. A., Editors, U. S. Dept. Commerce, National Bureau of Standards, 1978.
- [24]. Rosenbaum, E. J. and Ashford, T. A., *J. Chem. Phys.*, 7, 554(1939).
- [25]. Eberwein, B., Ott, R., Weidlein, J., *Z. Anorg. allz. Chem.*, 431, 95-104(1977).
- [26]. Maslowsky, E., Jr., *Journal of Organometallic Chemistry*, 70, 153-227(1974).
- [27]. Yates, D. J. C., Dembinski, G. W., Kroll, W. R. and Elliott, J. J., *J. Phys. Chem.*, 73(4), 911(1969).
- [28]. Schmidbaur, H., *Angew. Chem. internat. Edid.*, 4(3), 201 (1965).

- [29]. Schmidbaur, H., Weidlein, J. and Mitschke, Karl-Heinz, Chem. Ber., 102, 4136 - 4146 (1969).
- [30]. Shindo, M. and Okawara, R., J. Ogaromet. Chem., 5, 537(1966).
- [31]. Feher, F. J., personal letter to Prof. B. A. Morrow, September 14, 1990.