

Mechanism of H₂S Oxidation by Ferric Oxide and Hydroxide Surfaces

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The interaction of H₂S with the surface of either α-Fe₂O₃ or amorphous ferric hydroxide at low temperatures has been characterized using FTIR and quantified using volumetric methods. The mechanism of the interaction of H₂S with either reagent is ionic and involves heterolytic dissociation of H₂S and exchange of S²⁻ and SH⁻ anions for O²⁻ or OH⁻. Subsequently water is eliminated and, in coupled redox reactions, sulfide is oxidized to elemental sulfur and Fe³⁺ cations are reduced to Fe²⁺. Initially, almost all the surface sites can interact readily with H₂S, to form a layer of iron sulfides. Over longer reaction times reaction occurs with deeper sites, to form bulk sulfides. Regeneration of ferric (hydr)oxide by oxidation with oxygen converts Fe²⁺ to Fe³⁺, and S²⁻ anions are replaced by O²⁻ with formation of elemental sulfur. The surface species involved in each reaction have been characterized using FTIR and, for the first time, direct evidence has been obtained for the presence of SH⁻ anions as very reactive intermediates.

Introduction

Iron oxides or hydroxides such as α- or γ-Fe₂O₃·H₂O are effective as reagents to remove H₂S either from waste gas streams from various chemical plants or from natural gas. A significant characteristic of these systems is that they can be regenerated readily at low temperatures in the presence of air and then recycled for further H₂S adsorption.¹

These systems have been known and investigated for several decades, yet there is still little known of the detailed mechanism for this important process, especially the nature of the initial stages of the molecular interaction between H₂S and iron (hydr)oxides at the gas–solid interface. Herein we report on spectroscopic and volumetric studies of the interaction of H₂S with the surfaces of α-Fe₂O₃ and amorphous ferric hydroxide, the nature of the intermediates involved, and the reaction mechanism. The choice of α-Fe₂O₃ rather than the monohydrate was made to provide data on the role of sites that neither contain nor are adjacent to hydroxyls.

Background

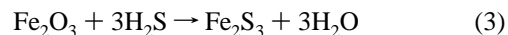
There exists a large body of information on the use of iron oxides or hydroxides to sweeten gas streams and the molecular and physical properties of the bulk materials involved, because of both the importance of such materials as reagents and their involvement in reactions in corrosion and the environment.^{1,2} The macroscopic aspects of H₂S absorption by iron (hydr)oxides have been the subject of several investigations, in large part because iron oxides are such excellent reagents for H₂S reaction, to a theoretical maximum of 0.6 g (H₂S)/g (Fe₂O₃).¹ The interaction of H₂S with iron (hydr)oxides and the regeneration of the (hydr)oxides by oxygen (or air) are normally described in terms of the stoichiometry of the reactions to the bulk products, as identified by XRD or other analytical methods.

The stoichiometries of the reactions for H₂S with ferric hydroxide are summarized in eqs 1 and 2, but the reactions are

much more complex and involve several intermediate species not shown by the equations.



It has been proposed that the principal reactant is Fe₂O₃, which reacts with H₂S to initially produce Fe₂S₃ (eq 3).³

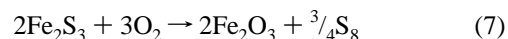
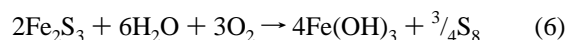
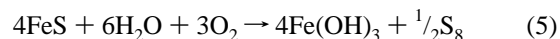


The Fe₂S₃ is thermodynamically unstable under these conditions and reacts further to form pyrite, which is acid-insoluble, and Fe₃S₄ (eq 4).

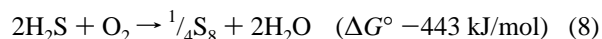


As the (hydr)oxide reacts to form sulfide, the power of the solid to react with H₂S decreases, until the reagent is exhausted.

The regeneration of reaction sites is accomplished by reaction with oxygen: the sulfide ions are displaced by oxide ions, and sulfur is liberated (eqs 5–7).^{1–3}



The overall stoichiometry of the process is therefore



The reactions of ferric (hydr)oxide with H₂S and the oxidative regeneration of the (hydr)oxide by reaction with oxygen can lead to sintering of the reagent.⁴ Co-feeding of oxygen with the H₂S prevents the accumulation of substantial amounts of FeS and Fe₂S₃ in the reactor.^{3,4}

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Clearly, schemes such as those above show only the stoichiometry of the proposed steps in the process and do not describe details of the reaction mechanism.

In contrast to the data on the bulk materials and the process, the existing spectroscopic data about the molecular aspects of the interaction of H₂S with solid ferric (hydr)oxides surfaces are limited. There is only one previous IR spectral investigation specifically addressing the interaction of gaseous H₂S with the solid surface,⁵ in which it was remarked that the most significant feature in the spectrum of H₂S chemisorbed on ferric (hydr)oxides is the formation of a hydroxyl IR band. The intensity of this band is about one-half that arising from chemisorbed water, which is consistent with the assumption that H₂S is chemisorbed at the surface to produce equal numbers of hydroxide and SH⁻ ions. The intensity of the SH stretching band will be significantly less than that of the OH stretching band, and consequently no prominent band would be observed for a system with such a small concentration of surface SH moieties.

No other detailed spectroscopic investigation specifically addressing the interaction of H₂S with iron (hydr)oxides has been reported, probably because of the significant experimental difficulties. The iron (hydr)oxides are colored, and the ions Fe³⁺ are paramagnetic. Thus neither UV nor EPR methods can be used effectively for the investigation of a small number of sites in a material containing several other unpaired electron features. Data concerning surface properties and the active sites of Fe₂O₃ have been obtained using IR as the spectroscopic method.^{6–10} The observed IR bands were attributed to terminal and bridging iron–oxygen species, and partially reducing species such as O₂⁻.

A significant feature of H₂S absorption by industrial iron-containing reagents is the required presence of either hydroxyls or water. Effective systems either contain hydrated iron oxides (hydroxides) or operate at low temperatures in the presence of both water and H₂S.^{1,2} This indicates that the gas–solid reaction shares some common characteristics with the reaction of iron oxides with aqueous H₂S.¹¹ Further, FTIR spectroscopic evidence exists for the formation of SH⁻ anions arising from the interaction of H₂ with anhydrous oxides of metals other than iron.¹²

In this report we will use IR spectroscopy and volumetric studies to obtain insights into (i) the activation of H₂S on the surfaces of ferric (hydr)oxides, (ii) the surface sites involved, and (iii) the intermediates formed; we will then compare the reactions of H₂S with ferric oxide and hydroxide with reactions of H₂S with other metal oxides.

Experimental Section

The samples of α -Fe₂O₃ were prepared by calcination of ferric hydroxide (specific surface area, S_{sp} , 10 m²/g) in an air stream at 723 K. Ferric hydroxide was precipitated from an aqueous solution of Fe(NO₃)₃ by neutralization with ammonia, washing the precipitate with water to remove all NO₃⁻, and finally drying the solid product at 80 °C for 24 h, in air. The samples were characterized as α -Fe₂O₃ (crystalline) and amorphous ferric hydroxide, respectively, by both XRD and IR in the region of the cutoff vibrations. Materials that had been used for interaction with H₂S and then regeneration in oxygen (5 times) were also so characterized.

The principal methods of investigation of the interaction between H₂S gas and either α -Fe₂O₃ or ferric hydroxide were infrared spectroscopy (FTIR) of the probe molecule to study

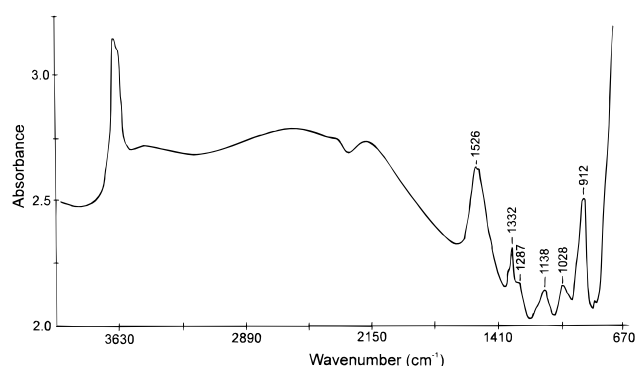


Figure 1. FTIR spectra of α -Fe₂O₃ treated at 673 K in O₂ for 2 h and then under vacuum for 2 h.

the surface phenomena and volumetric methods to quantify the adsorption of H₂S.

FTIR Spectroscopic Measurements. The samples were pressed into pellets (60–100 mg/cm²) and then placed in an IR cell designed for operation up to 773 K.¹³ Using this cell it was possible to investigate the nature of the surface of each reagent and its interaction with H₂S and examine adsorption or desorption of gases at different temperatures. The cell was attached to vacuum equipment capable of operation at pressures as low as 10⁻⁶ Torr. The samples of Fe₂O₃ were then treated under vacuum and in oxygen at 723 K. Samples of ferric hydroxide were treated under vacuum and then under oxygen at 373 K. FTIR spectra were obtained using a Nicolet-740 FTIR spectrometer. Direct in situ spectral measurements were made during the progress of the interaction (293–373 K) using a customized cell of the design described by Kiselev.¹³ The data so obtained were then used to determine the progress of the surface compound transformations.

Adsorption Measurements. The sample pellets were each pretreated in the cell by sequential treatment with vacuum and oxygen at 723 K, to remove potential impurities from the surface. Cleaning of the surfaces was monitored for each sample using FTIR spectroscopy. The gases (CO, NH₃) for adsorption were each purified carefully by storage over zeolites. The gases were adsorbed by exposing the pellets of each material to a series of aliquots of adsorbate. The size of each aliquot was controlled to ensure that it was smaller in quantity than the number of adsorption sites, as predetermined by optical density of adsorption bands (a.b.'s) in the IR spectra of adsorbed probe molecules CO and NH₃.

Results and Discussion

1. α -Fe₂O₃. The local geometry and electronic properties of the surface sites determined both the character and the interaction of adsorbed molecules with oxides and the type and properties of the surface compounds formed.¹⁰ α -Fe₂O₃ was selected as a subject for this investigation of the interaction of H₂S with iron oxides because of its known utility as a reagent with H₂S and the paucity of data available concerning the pertinent surface properties and active surface sites.

1.1. The Nature and Properties of the α -Fe₂O₃ Surface. The FTIR spectrum of α -Fe₂O₃ after calcination is shown in Figure 1. The absorption bands (a.b.'s) at 787, 850, and 914–920 cm⁻¹ have been assigned^{6–10} to vibrations of surface Fe–O–Fe and Fe=O bonds. The bands at 1028, 1138, and 1325 cm⁻¹ arise from either partially reduced oxygen species, such as O₂⁻ or combinations of lattice vibrations or excited states, and the a.b. at ~1530 cm⁻¹ arises from multiphoton absorption.^{6–10} For

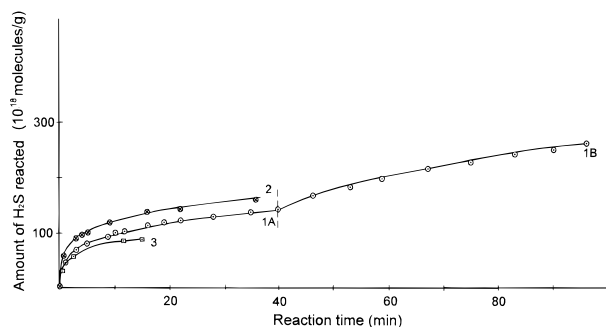


Figure 2. Kinetics of H₂S adsorption at room temperature on α -Fe₂O₃ pretreated at 723 K under vacuum for 6 h: (1) A, $P = 12.44$ Torr; B, $P = 27$ Torr; (2) after regeneration by O₂ and following evacuation to 5–10 Torr; (3) after three adsorption/regeneration cycles.

α -Fe₂O₃, two hydroxyl a.b.'s are usually observed at 3642 and 3610 cm⁻¹, as shown in Figure 1.

Lewis acid sites (Fe³⁺ cations) on the oxidized surface of α -Fe₂O₃ have been characterized and quantified by analysis of the infrared spectra of adsorbed NH₃. The a.b.'s at 1220 and 1620 cm⁻¹, which characterize δ_s and δ_{as} of coordinated NH₃,¹⁰ are observed in the IR spectrum of NH₃ coordinated at the surface of Fe₂O₃. The value for the δ_s band is sensitive to the electron acceptor properties of the cation, increasing with increase of the acceptor strength.¹⁰ The electron acceptor ability (X) of the Lewis acid site, calculated using the Wilmschurst equation,¹⁰ is 1.85 in this case. Such Lewis acid sites do not readily adsorb CO (weak electron donor), because of the high coordination saturation of the cations.

Even under mild reducing conditions (using CO at 373–423 K), α -Fe₂O₃ is partially reduced. The IR transmittance of the reduced sample is inferior to that of the original sample, because of the presence of free electrons.¹⁰ For a sample reduced under mild conditions the value of δ_s for coordinated NH₃ decreases to 1190 cm⁻¹. In this case the value for X is 1.5, which is characteristic for NH₃ adsorption on Fe²⁺ cations. The Fe²⁺ sites are coordinatively unsaturated and, in contrast to Fe³⁺ ions, adsorb weak electron donors including CO. The a.b. at ~ 2200 cm⁻¹ (ν CO) is characteristic of Fe²⁺–CO complex cations.

Deeper reduction of α -Fe₂O₃ by CO leads to total loss of the IR transmittance of the sample. This phenomenon is caused by the presence of large numbers of the free electrons (conductivity band) associated with the formation of clusters of Fe²⁺. Thus the change in the transmittance of the sample can be used to monitor the degree of Fe³⁺ reduction to Fe²⁺ and cluster formation. It is noteworthy that the interaction of α -Fe₂O₃ with H₂S, which is a stronger reducing agent than CO, does not lead to such substantial changes in transmittance. The ligands (S²⁻ or SO₄²⁻) also probably effect a change in character of the conductivity band for these samples, and the nature of the Fe²⁺ sites or clusters that are formed differs from the nature of sites created by reduction with CO.

1.2. Interaction of α -Fe₂O₃ with H₂S. Volumetric Measurements. Interaction between H₂S and α -Fe₂O₃ occurs readily, even at room temperature, and the total quantity of H₂S that is consumed is high (Figure 2). The maximum value depends on both the ferric oxide pretreatment conditions and H₂S pressure (Figure 2, curves 1A, 1B). At a H₂S pressure of ~ 10 Torr, the amount of H₂S adsorbed on the fresh or regenerated (up to three cycles) surfaces of α -Fe₂O₃ (n) is $\sim 1.5 \times 10^{19}$ molecules/m² (surface area 10 m²/g). Thus the interaction of H₂S with the surface is limited to a monolayer, because the capacity of one monolayer of H₂S on O²⁻ is $(1-2) \times 10^{19}$ atoms/m². Increasing the H₂S pressure 5-fold leads to doubling the amount of

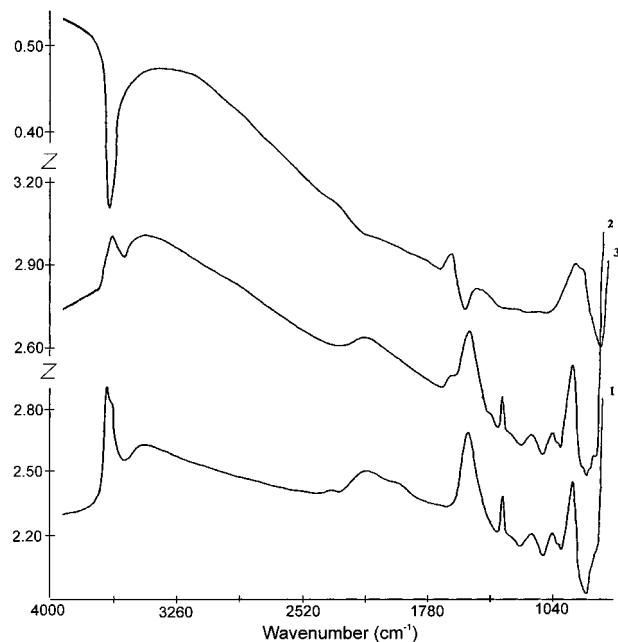


Figure 3. FTIR spectra of α -Fe₂O₃: (1) after treatment in O₂ (2 h) and then under vacuum at 723 K; (2) after H₂S adsorption ($P_0 = 2.55$ Torr); (3) difference spectrum 2 by subtraction of spectrum 1 from spectrum 2.

coverage by H₂S. Significantly, the main portion of the H₂S reacts in the first 10–15 min. Thereafter the rate of H₂S consumption is slower, but continues steadily for an extended time (Figure 2). These observations are consistent with rapid chemisorption of H₂S and a slower reaction of H₂S with Fe₂O₃ to form iron sulfides (vide infra).

1.3. Interaction of α -Fe₂O₃ with H₂S. FTIR Measurements. The IR spectra of the α -Fe₂O₃ surface after interaction with H₂S were obtained for each of the sample pretreatment conditions and H₂S partial pressures and show that H₂S interacts with essentially all available surface sites. Bands attributed to Fe–O–Fe, Fe=O, and surface hydroxyls each decrease in intensity or disappear after reaction with H₂S (Figure 3). It is noteworthy that preadsorption of CO or NH₃ does not significantly influence the reaction with H₂S as both CO and NH₃ coordinated to Fe²⁺ or Fe³⁺ sites are readily displaced by H₂S. Thus all types of anionic and cationic surface site are involved in the reaction with H₂S. The IR spectra obtained at the higher value of H₂S partial pressure are not informative, because the only features that appear immediately following the initiation of H₂S adsorption are intense absorptions with wide maxima at 3500 and 1620 cm⁻¹ (Figure 3), assigned to ν OH and δ HOH. The intensities of these a.b.'s increase during the progress of the interaction with H₂S and show that large quantities of water are formed as a product of the interaction of surface species with H₂S. No a.b. that can be assigned to ν SH is observed in the IR spectra of α -Fe₂O₃ treated with H₂S, in contrast with the IR spectra of Al₂O₃, TiO₂, MgO, and CaO treated with H₂S, for which an a.b. is observed in the range 2400–2600 cm⁻¹.^{12,14} However, it is not possible to conclude that ν SH bands are totally absent from these spectra, because there is an intense and broad hydroxyl stretching band in this region.

Both H₂S and, especially, SH⁻ groups bonded to the surface iron sites are highly reactive. Spectra with high signal-to-noise ratios were obtained by accumulation of a large number of scans, usually 500–1000. Therefore, if the SH⁻ ions were consumed more rapidly than the time taken to acquire this many scans, the bands due to SH⁻ ions would not show significant relative

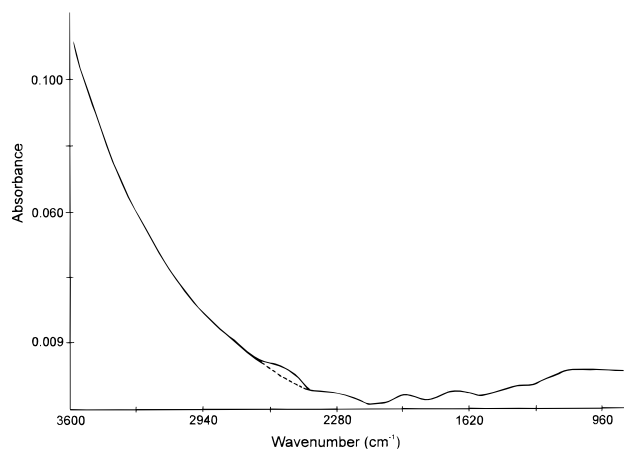


Figure 4. FTIR spectra of $\alpha\text{-Fe}_2\text{O}_3$ after H_2S adsorption at $P = 0.55$ Torr directly after H_2S adsorption (100 scans).

intensity in the IR spectra. Consequently, to detect SH^- groups on the surface, we have developed and used the following procedure. Typically, an initial small number of scans of the spectrum was accumulated. In these spectra a broad band at $2480\text{--}2540\text{ cm}^{-1}$, above noise level, has been detected for the difference spectrum between $\alpha\text{-Fe}_2\text{O}_3$ exposed to H_2S and the initial material (Figure 4). Although this band cannot be unambiguously assigned, it is in the correct region for νSH due to SH^- groups. However, the signal-to-noise ratio is high for the small number of scans accumulated, and so a degree of uncertainty remains. Further, it should be noted that the association of H_2S molecules with the oxide surface can be effected by the formation of different types of the H-bonds, or the H_2S can be fully dissociated, or both, because the νHSH mode is not observed even when the amount of H_2S adsorbed on $\alpha\text{-Fe}_2\text{O}_3$ is high. It is anticipated that the H_2S molecules will be adsorbed in more than one type of interaction, especially for high surface coverage. H-bonded H_2S molecules will experience significant weakening of S–H bonds, can interact with several types of surface site at the same time, and will be converted rapidly to S^{2-} .

Thus, to further examine the initial stages of the H_2S interaction with ferric oxide, to establish whether or not SH groups are formed as intermediates on the surface, and to determine the mechanism of initial formation of water, additional designed experiments were performed in which the surface was sequentially exposed to several very small amounts of H_2S . The data (Figure 5) show that water is formed immediately on interaction of the H_2S with the surface. The initial appearance of water is attributed to direct exchange of O^{2-} ions by S^{2-} or SH^- ions, which occurs *without* participation of the surface hydroxyl groups (FTIR). This interpretation is consistent with the absence of changes to the bands assigned to surface hydroxyl groups until after a significant amount of H_2S had been adsorbed and reacted. The most basic sites, O^{2-} , will be the first to react with H_2S , forming SH^- and some S^{2-} ions by heterolytic dissociation. However, during this time the a.b. at $\sim 3500\text{ cm}^{-1}$ due to νOH of the water molecules appears and increases in intensity. The anticipated δHOH band is not observed under these conditions because its extinction coefficient is smaller than the coefficient for νOH . Only after the concentration of water on the surface has increased, as a consequence of increase in the H_2S adsorbed, is any change observed in bands assigned to the surface hydroxyl groups. The changes observed in the hydroxyl region of the spectra may also result from interactions of surface ions with the water molecules produced. No change

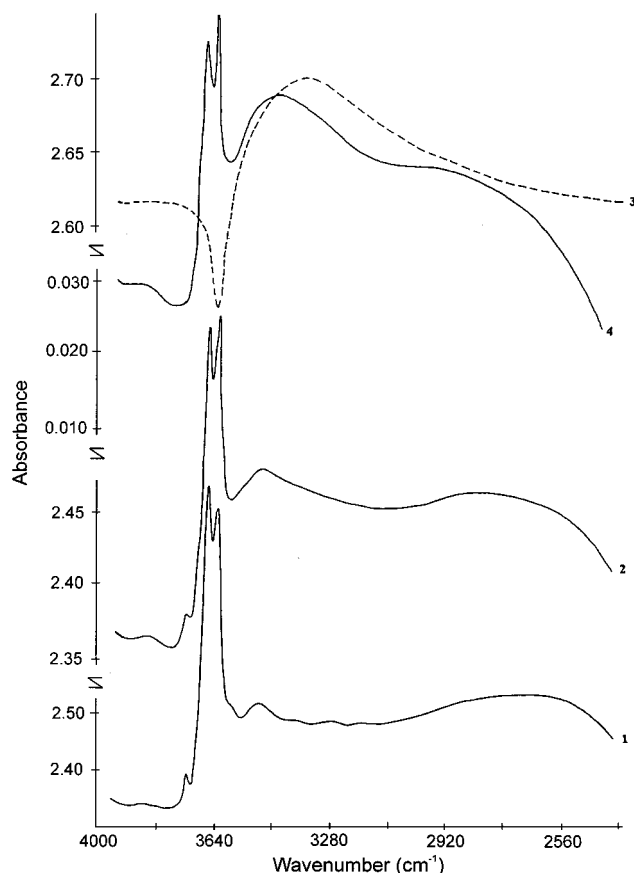
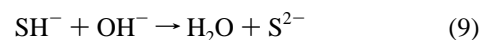


Figure 5. FTIR spectra of $\alpha\text{-Fe}_2\text{O}_3$: (1) after H_2S adsorption at different pressures; (2) 0.55 Torr; (3) spectrum 2 after subtraction of spectrum 1; (4) 0.8 Torr.

in concentration of surface OH groups (FTIR) was observed that can be ascribed with confidence to H_2S adsorption and the subsequent reaction:



At this stage of the reaction the interaction of the adsorbed portion of H_2S with the surface must involve essentially all OH groups of the oxide.

Analysis of both the IR and X-ray diffraction data of the solid after interaction of $\alpha\text{-Fe}_2\text{O}_3$ with H_2S shows that the phase structure of the bulk solid has not been changed by the interaction. Elemental sulfur is formed, probably due to the coupled redox reactions $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ and $\text{S}^{2-} \rightarrow \text{S}_x$. Although the degree of H_2S reduction is high, there is no significant change of the system's optical properties similar to that which occurs when $\alpha\text{-Fe}_2\text{O}_3$ is reduced by CO. The replacement of O^{2-} by S^{2-} or SH^- probably does not effect formation of Fe^{2+} clusters, in contrast to the behavior during reduction of Fe^{3+} by CO.

The high reactivity of H_2S toward the oxide is a consequence of two factors. First, H_2S is both highly reactive and a strong reducing agent. Second, S–H bond heterolytic rupture is facile because the hydrogen in this moiety has a high mobility ($\text{pK}_a = 7.04$). Further factors that are significant are that H_2S readily forms donor–acceptor complexes and has a low ionization potential.

Thus the interaction of H_2S with all surface sites effects a replacement of Fe–O bonds with Fe–S bonds. Oxide ions are replaced by S^{2-} with formation of water, and elemental sulfur is formed by redox reactions. With increasing contact time the

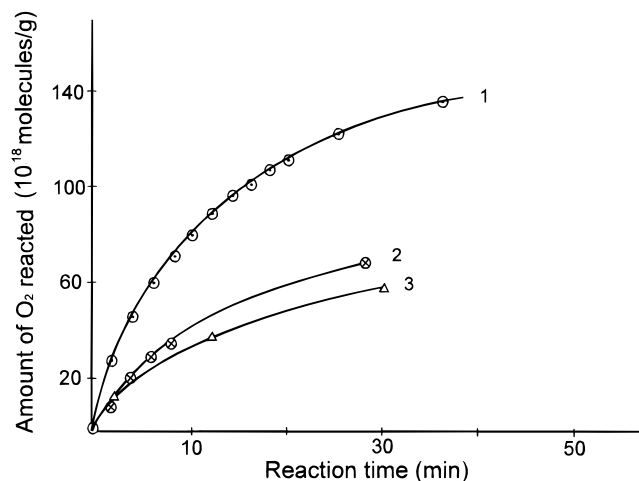


Figure 6. Kinetics of O₂ adsorption on α -Fe₂O₃ after interaction with H₂S: (1) first cycle; (2) second cycle; (3) third cycle.

reaction is extended to include replacement of O²⁻ by S²⁻ at sites below the surface layer and, after several hours contact at high H₂S pressure, forms bulk iron sulfides. Exchange of SH⁻ for O²⁻ and OH⁻ has also been proposed for the mechanism of reductive dissolution of hematite suspended in aqueous solutions of H₂S.¹¹

IR and XRD spectral results show that the samples were completely covered by sulfur after four or five cycles, but that there was no significant amount of FeS formed.

1.4. Interaction between Sulfided α -Fe₂O₃ and Oxygen. Volumetric Measurements. The interaction of a sulfided sample with oxygen can be examined in a manner similar to study of a stage of contact regeneration, because the interaction with the oxidant must lead to the oxidation of Fe²⁺ ions. The oxidation–reduction potential for Fe²⁺ \rightarrow Fe³⁺ is low, and therefore is favorable for the interaction of Fe²⁺ with H₂S and, in particular, elimination of elemental sulfur.¹

The adsorption of oxygen at the surface through treatment of the sample at room temperature is at least as strong as adsorption of H₂S. The amount of oxygen adsorbed at room temperature depends on the amount of preadsorbed H₂S, increases with increasing the partial pressure of oxygen, and depends on the age of the reagent (Figure 6). The molar amount of adsorbed oxygen is similar to the value for H₂S, $(1.2\text{--}1.65) \times 10^{20}$ molecules·g⁻¹, for the first three cycles and increases with increasing temperature (Figure 7). This dependence on temperature shows that the reaction proceeds initially at the surface, but also occurs at deeper layers as the reaction progresses. The main process for sulfur formation in this system is considered to be electron transfer from S²⁻ ions to ferric oxide Fe³⁺ ions, effecting the redox reaction Fe³⁺ \rightarrow Fe²⁺ in the solid volume.

A common conductivity band is formed even by weak reduction of the oxide, which shows that the electrons from the bulk of the solid are involved in the progress of the reaction. Thus the amount of sulfur that can be formed, even during the first stage of the interaction with H₂S, can correspond to an amount up to half of the total number of Fe³⁺ ions in the solid.

1.5. Interaction with Oxygen. FTIR Measurements. During treatment of sulfided ferric oxide with oxygen under mild conditions a new a.b. at ~ 985 cm⁻¹ appears in the spectra, and the intensity of the a.b. at ~ 915 cm⁻¹ increases (Figure 8). These observations indicate that additional Fe³⁺–O bonds (a.b. 915 cm⁻¹) are formed during contact oxidation, either by means of direct oxidation or by back exchange of a fraction of the S²⁻

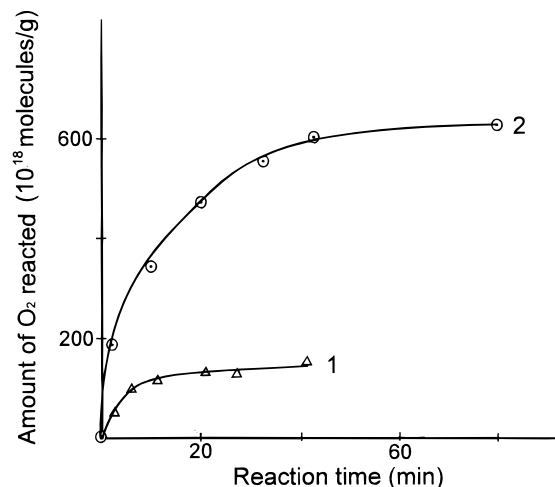


Figure 7. Kinetics of O₂ adsorption on sulfided α -Fe₂O₃: (1) 293 K; (2) 573 K.

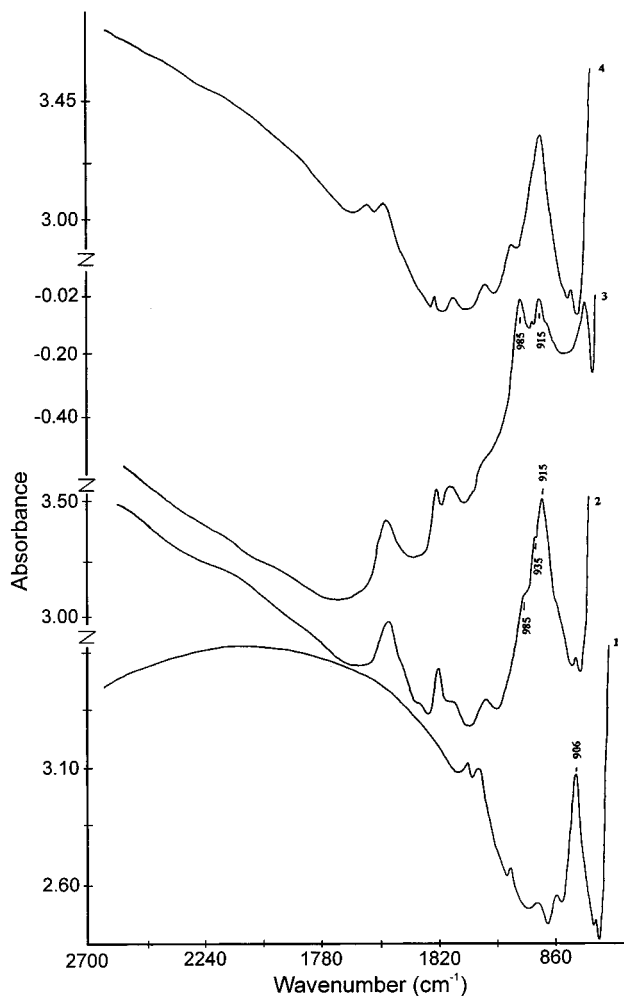


Figure 8. FTIR spectra of α -Fe₂O₃: (1) after interaction with H₂S ($P_0 = 5.5$ Torr); (2) following interaction with O₂; (3) difference spectrum by subtraction of spectrum 1 from spectrum 2; (4) following interaction with H₂S ($P_0 = 7.5$ Torr).

ions with O²⁻. The new band at 985 cm⁻¹ decreases in intensity and then disappears with increasing either the interaction temperature or time on stream. Further, the a.b. at 985 cm⁻¹ is absent in the spectra of samples contacted with oxygen at 100 °C or higher temperatures. Therefore it is proposed that the band at 985 cm⁻¹ arises from formation of peroxide ions (O₂²⁻) under mild conditions.^{10,15} The formation of O₂²⁻ ions would

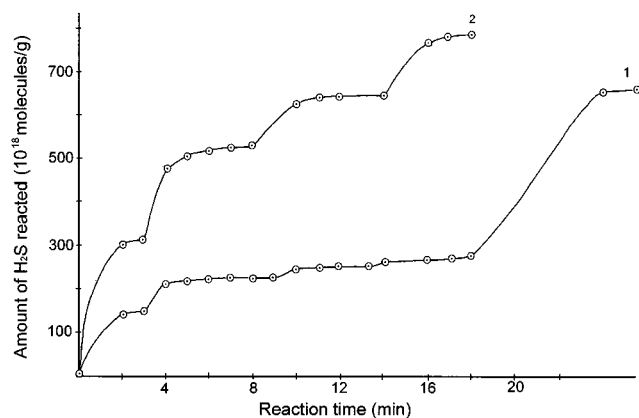


Figure 9. Kinetics of H_2S adsorption: (1) on fresh amorphous ferric hydroxide at room temperature; (2) after regeneration by O_2 .

thus represent the first stage of the interaction between oxygen and the surface of sulfided ferric oxide. Subsequently, reaction of the O_2^{2-} with Fe^{2+} would result in $\text{Fe}^{3+}-\text{O}$ bond formation.

The ready sequential conversion of adsorbed oxygen via peroxide to oxide $\text{O}_2 \rightarrow \text{O}_2^{2-} \rightarrow \text{O}^{2-}$ at room temperature is a consequence of the high electron affinity of oxygen (0.43 eV).

2. Amorphous Ferric Hydroxide. *2.1. Interaction with H_2S : Volumetric Measurements.* As shown in Figure 9, amorphous ferric hydroxide reacts with more H_2S than does the same mass of $\alpha\text{-Fe}_2\text{O}_3$. The amount of H_2S consumed increases with increasing H_2S pressure to a higher degree than for $\alpha\text{-Fe}_2\text{O}_3$. This greater dependency on partial pressure is expected, because the specific surface area of amorphous ferric hydroxide ($\sim 100 \text{ m}^2/\text{g}$) is 10 times higher than that for $\alpha\text{-Fe}_2\text{O}_3$. Consequently, the total quantity of gas reacted per unit area is approximately the same, but the rate of H_2S consumption is significantly higher. The main portion of the gas is adsorbed and reacts on ferric hydroxide during the first 2–3 min (Figure 9). The same dependency exists for the amount of O_2 consumed during regeneration (Figure 10), but the oxygen reacts more slowly. The amount of sulfur observed on the surface of this sample is significantly greater than for $\alpha\text{-Fe}_2\text{O}_3$ and shows that the interaction of H_2S with the surface involves the redox reaction as well as any initial adsorption interaction.

The recycle process can be effected at room temperature for ferric hydroxide, and so this material can be used as a reagent for capture and conversion of H_2S and can be readily regenerated.

2.2. Interaction with H_2S : FTIR Measurements. In situ spectral investigations of the interaction between H_2S and ferric hydroxide were performed using the same protocol as was used for $\alpha\text{-Fe}_2\text{O}_3$, except that the temperature for pretreatment of each sample was different (373 K). This temperature was selected to avoid excessive dehydroxylation of the hydroxide. The process was studied at low pressure of H_2S , and small number of scans were used to obtain the IR spectra.

Evolution of water was observed immediately upon commencement of the reaction with H_2S . The concentration of water increased as the reaction progressed. However, unlike the reaction with $\alpha\text{-Fe}_2\text{O}_3$, isolated SH groups were not detected in the IR spectra, even using the procedures outlined above. Thus, if any such groups are formed, they must be considerably more active than on $\alpha\text{-Fe}_2\text{O}_3$, and they must react rapidly with OH^- to form S^{2-} and water. Elemental sulfur is observed on the samples, both visually and in the IR spectra, and so Fe^{3+} centers must also be reduced to Fe^{2+} .

If they are indeed formed as intermediates, the anticipated isolated SH^- groups will be more active in the case of iron

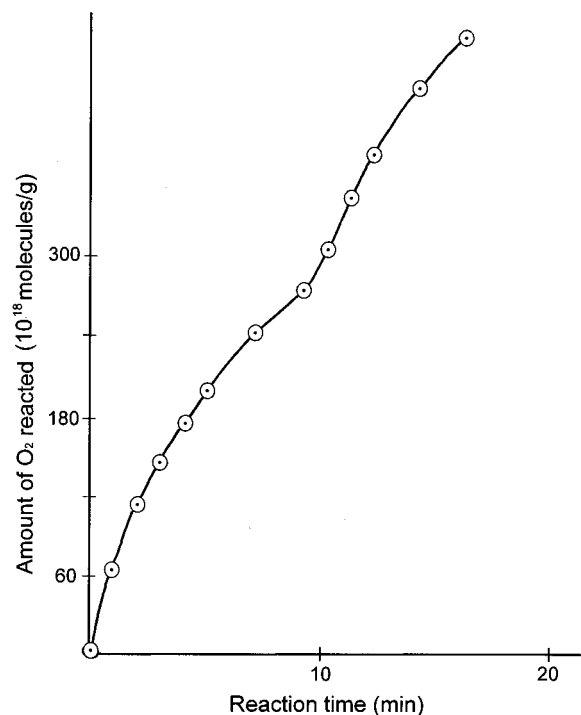


Figure 10. Kinetics of O_2 adsorption on sulfided amorphous ferric hydroxide.

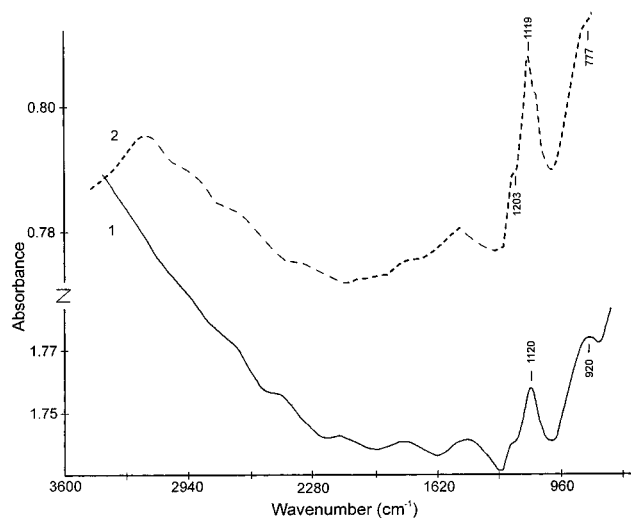


Figure 11. FTIR spectrum of (1) $\alpha\text{-Fe}_2\text{O}_3$ and (2) fresh amorphous ferric hydroxide, after several cycles of the interaction with H_2S and O_2 at room temperature.

hydroxide than for $\alpha\text{-Fe}_2\text{O}_3$ because of the favorable composition of the material. The nature of the reagent ensures that OH^- groups exist throughout the material. Therefore interaction of the OH^- with SH^- groups will be much more facile than for $\alpha\text{-Fe}_2\text{O}_3$, and H_2O and S^{2-} ions will be more readily formed. In contrast, for a bulk oxide such as $\alpha\text{-Fe}_2\text{O}_3$, only a small part of the surface comprises such active centers (OH^-) at which the reaction can proceed by the proposed mechanism.

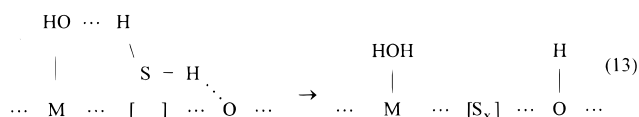
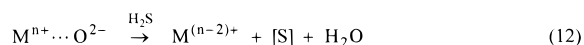
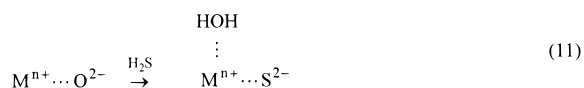
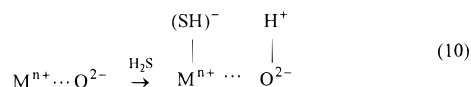
It is significant that from the initial cycle for either sample, oxide or hydroxide, the appearance of ionic sulfates was observed (a.b. 1120 cm^{-1}).¹⁶ As shown in Figure 11, the amorphous reagent has a higher propensity to form ionic sulfates. However, the reasons and conditions for the formation of sulfates appear to depend on different parameters, which have not been a subject of this investigation.

The data obtained from both adsorption and XRD methods show that the amount of H_2S reacted increases with increasing

contacting time and increasing pressure. The amount of H₂S adsorbed in the first cycle is 7.0×10^{21} molecules·g⁻¹, and the amount of oxygen that is adsorbed during the first regeneration reaction is 1.1×10^{21} molecules·g⁻¹. It is known that iron sulfides are formed under these reaction conditions.^{1,2}

3. Mechanism of the Reactions. The volumetric data show that the interaction of H₂S with ferric oxide or hydroxide is extensive over the surface at room temperature and that the reaction occurs more readily and more extensively for the hydroxide than for the oxide. After prolonged time the reaction extends to involve bulk oxide sites as well as surface sites. Sulfur is formed by the coupled oxidation of S²⁻ and reduction of Fe³⁺ to Fe²⁺. The spectroscopic data show that essentially all cationic and anionic sites are involved, or affected, by the initial interaction of H₂S with the surface, that oxygen species are displaced by sulfur species, and that water is formed immediately from the initiation of the reaction. On the basis of these data, and the observation for the first time of SH⁻ as an intermediate, conclusions can be drawn regarding the mechanism of the reactions.

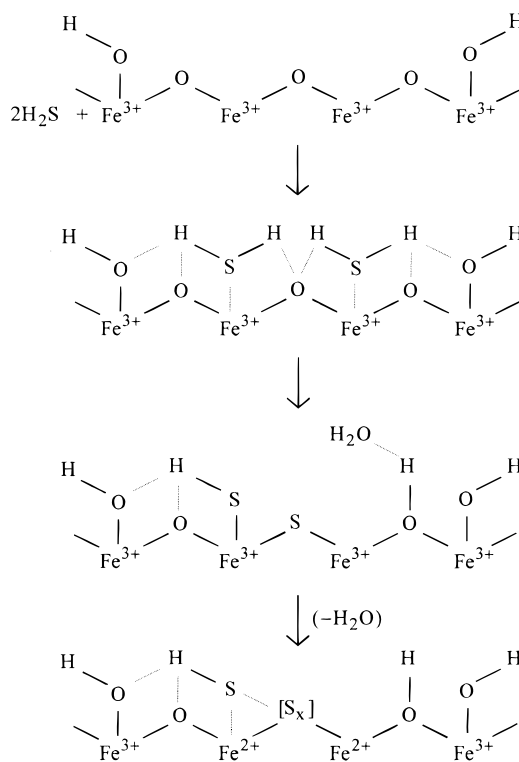
The reaction of H₂S with the surface of the oxides Al₂O₃, MgO, CaO, ZnO, and SnO₂ has been shown to occur through interaction with ion pairs (eqs 10–12) or defect sites (eq 13).^{12,14} In each case the reaction involves heterolytic S–H bond cleavage, and formation of S²⁻ and SH⁻, with S²⁻ substituting for the original O²⁻ ions.



The data now obtained are consistent with similar initial interactions of H₂S with the surface of oxides or hydroxides of metals other than iron. The major difference is in the extent of the reaction. Whereas the volumetric and spectroscopic data show that essentially all the surface of ferric oxide or hydroxide interacts with H₂S, the amount of H₂S interacting with γ-Al₂O₃, for example, corresponds to approximately 10% of a monolayer.¹⁴ This latter amount in turn corresponds with the number of coordinately unsaturated centers. This difference in behavior is attributed to the difference in metal–oxygen bond strengths.¹⁷ The lower value for Fe–O compared to the above metal oxides allows for ready substitution of S²⁻ for O²⁻. Similarly, the OH⁻ in ferric hydroxide is readily displaced by sulfide. In neither case is it observed that molecular H₂S is coordinated to a surface site.

The reaction of H₂S with Fe₂O₃ is rapid and water is evolved, but the residual surface hydroxyls are not immediately affected in a significant manner (FTIR). The anion SH⁻ is observed at the initiation of the reaction, but is then rapidly consumed. These data suggest that the initial reaction is as shown in reaction 10, followed by rapid progress to reaction 11. The elimination of

SCHEME 1. Interaction of H₂S with α-Fe₂O₃



sulfur then involves a redox reaction similar to reaction 12. However, defect sites are expected to be present on the surface of ferric oxide,^{12,14} and so reaction 13 may also play a role.

The absence of any FTIR observation of molecular H₂S coordinated to a surface site is attributed to one or both of two effects. The initial interaction of H₂S with the surface involves multiple sites, both anionic and cationic, and so no monocoordinated H₂S is present. The production of water is immediate, showing that reaction of the H₂S with the surface species rapidly follows the initial interaction. Thus there is virtually no molecular H₂S present on the surface at any time (Scheme 1). This process occurs until all oxide is transformed to sulfide, as previously observed for the Sn/Mo catalyst system.^{18,19}

The anion SH⁻ is not observed in the reaction of H₂S with ferric hydroxide. This observation is consistent with the very rapid consumption of SH⁻ by reaction with the high concentration of OH⁻ present on the surface. This result contrasts with the data for oxides of Al, Ti, Mg, or Ca, for which the SH⁻ species formed on reaction with H₂S are stable, and hence the presence of SH⁻ is persistent and is more easily observed.^{12,14}

The regeneration of the surface by oxygen appears to occur in two stages. Peroxide ions are observed as intermediates, Fe²⁺ centers are oxidized to Fe³⁺, and elemental sulfur is generated. These data suggest that surface S²⁻ ions are displaced by O₂²⁻ and then O²⁻ ions. The reduction of the oxygen effects the oxidation of both sulfide to sulfur and Fe²⁺ to Fe³⁺.

Conclusions

The initial reaction of H₂S with the surface of either α-Fe₂O₃ or amorphous ferric hydroxide involves the replacement of O²⁻ anions with S²⁻ and SH⁻, without affecting the surface hydroxyls already present. Subsequently, reaction of the highly reactive SH⁻ with hydroxyls forms water and S²⁻, and reduction of Fe³⁺ to Fe²⁺ is accompanied by oxidation of S²⁻ to elemental sulfur.

Regeneration of the sorbent by oxygen is accomplished by oxidation of Fe^{2+} to Fe^{3+} , and formation of elemental sulfur by replacement of S^{2-} by O^{2-} anions.

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