

The Mechanism of the Catalytic Oxidation of Hydrogen Sulfide

III. An Electron Spin Resonance Study of the Sulfur Catalyzed Oxidation of Hydrogen Sulfide¹

M. STEIJNS, P. KOOPMAN, B. NIEUWENHUIJSE, AND P. MARS

Department of Chemical Engineering, Twente University of Technology, Enschede, the Netherlands

Received July 4, 1975; revised October 29, 1975

ESR experiments on the oxidation of hydrogen sulfide were performed in the temperature range 20–150°C. Alumina, active carbon and molecular sieve zeolite 13X were investigated as catalysts. For zeolite 13X it was demonstrated that the reaction is autocatalytic and that sulfur radicals are the active sites for oxygen chemisorption. The intensity of the sulfur radical ESR signal, which is related to the degree of conversion of these radicals, by oxygen, fits in with an oxidation–reduction mechanism.

The sulfur–oxygen radical species, which appear when oxygen is admitted to sulfur radicals, are assigned to sulfur chains containing one or two oxygen atoms at the end of the chain. It is very likely that these sulfur–oxygen radicals are intermediates in the proposed mechanism. The formation of the byproduct SO₂ from S₂O₂^{·-} at temperatures above 175°C is also visible in the ESR spectrum.

On the basis of the experiments it is concluded that in the mechanism of H₂S oxidation on active carbons, carbon radicals do not play an important role.

INTRODUCTION

In Part I (1), we presented the results of some preliminary ESR investigations relating to H₂S oxidation. The presence of sulfur radicals under reaction conditions on an alumina catalyst was demonstrated. We obtained strong evidence that these radicals were involved in the chemisorption of oxygen, an essential step in the oxidation. In Part II (2), we reported on the kinetics and the mechanism of the H₂S oxidation. The kinetic data fit with an oxidation–reduction mechanism.

Other investigators (3, 4) have also used the ESR technique to study the mechanism of H₂S oxidation. They mainly studied ac-

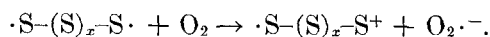
¹ This publication is the third in a series on the mechanism of hydrogen sulfide oxidation, see (1) and (2) for parts I and II.

tivated carbon catalysts and they were interested especially in the role of the carbon radicals. The importance of free radicals of carbon is demonstrated by Siedlewski and Trawinski (3); they reported a linear increase of the oxidation rate of H₂S with an increase of the number of free radicals. Krause (5) developed a mechanism on the basis of work done by Siedlewski and Swinarski (6, 7). Also Sreeramamurthy (4) concluded from his ESR experiments that the carbon radicals are the active sites for H₂S oxidation.

The presence of sulfur radicals at the surface of different porous materials has been reported by several authors (8–12). Dudzik and Preston (13) studied the effect of oxygen on these sulfur radicals adsorbed in different forms of molecular sieves. For the

Linde zeolites 5A and 13X they observed a disappearance of the sulfur signal upon admission of oxygen. Habgood and Imai (9) found that an oxygen radical at the surface of molecular sieve NaY has the capability to oxidize H₂S.

In a recent paper (8) Dudzik *et al.* reported on the oxidation of H₂S over Linde zeolite 13X. During the reaction of H₂S with molecular oxygen, sulfur radicals are formed, even at temperatures as low as -80°C. The radicals are supposed to react further with oxygen, forming an oxygen anion radical:



This oxygen radical should react with H₂S yielding water and sulfur radicals.

The aim of our paper is to report ESR experiments on various porous materials. The molecular sieve 13X is studied in detail. We examined the influence of reaction time, temperature, oxygen and H₂S concentrations upon the ESR spectrum. Separately we studied the reaction of oxygen with sulfur radicals and the reduction by H₂S of the resulting sulfur-oxygen surface complex. The oxidation-reduction mechanism, developed on the basis of kinetic data, has been tested and extended with the aid of the ESR experiments.

EXPERIMENTAL METHODS

CATALYTIC REACTOR

A catalytic fixed-bed reactor (diam, 4 mm) was placed in the cavity of the ESR spectrometer. In all experiments a combination of the gases N₂, H₂S, O₂, or SO₂ was led through 0.1-0.2 g catalyst with a flow rate of 500 cm³ min⁻¹. The conversions of H₂S and O₂ were always lower than 20%. This was checked in a separate fixed-bed experiment where the gas streams entering and leaving the reactor were analyzed.

The materials studied were γ -Al₂O₃ (Ketjen-AKZO), Carbon molecular sieve (CMS) and Linde zeolite 13X (NaX). In-

formation on the surface area and the pore structure is given in Part II (2).

The diameter of the particles was between 0.3 and 0.6 mm for all materials. Catalyst samples were heated at 150°C in a nitrogen flow (500 cm³ min⁻¹) during at least 1 hr to remove most of the adsorbed water.

The reactor tube was placed in an insert dewar to prevent extensive heating of the cavity. The reactor was heated by a stream of hot nitrogen gas (300 liters hr⁻¹). The temperature was controlled with a Varian variable temperature accessory (V 4540). ESR spectra were measured at reactor temperatures of 22 and 150°C. The accuracy of the reactor measurement was not very high, i.e., temperature differences of 10°C may exist between the setting temperature and the temperature in the catalyst bed.

ESR SPECTROMETER

Absorption spectra were recorded as first derivatives with a Varian E-12 spectrometer, equipped with a Varian E-231 cavity, at a frequency of 9148-9152 MHz (X-band). All experiments were performed at a field modulation amplitude of 1 G, a modulation frequency of 100 kHz and a microwave power of 20 mW. In the first instance the magnetic field was calibrated with the aid of a DPPH standard sample. Later on an AEG NMR magnetic field meter, equipped with a HP electronic counter, became available for this purpose. Microwave frequencies were measured with a HP frequency counter. *g* values, calculated from $g = h\nu/\beta H$, have an uncertainty of ± 0.002 .

The concentration of the free radicals was determined by comparison with a standard sample of 0.1% pitch in KCl ($g = 2.0028$, $\Delta H = 1.7$ G). The spin concentration of this sample was 3×10^{15} cm⁻¹ of length. The intensity was defined as: $I = \text{signal height} \times (\text{signal width})^2$.

Signal height and width are taken as peak-to-peak distances (mm). According

TABLE 1
Results of ESR Experiments on Different Materials ($T = 150^\circ\text{C}$)

Material	Reactor feed	Signals ^a	ΔH (G)	Leg- end	Assignment
Alumina	a. N ₂ or 2% O ₂ in N ₂	a. $g = 2.002$ $g = 4.244$	650 40	A } B }	Iron impurities (20)
	b. 1% H ₂ S in N ₂ or a mixture: 97% N ₂ , 2% O ₂ , 1% H ₂ S	b. A + B $g = 2.026$	60	C	
Physical mixture 92 wt% SiO ₂ 5.9 wt% CMS 2.1 wt% S	a. N ₂ or N ₂ /H ₂ S	a. $g = 2.002$	3.3	D	Carbon radicals (17)
	b. N ₂ /O ₂ or N ₂ /O ₂ /H ₂ S	b. $g = 2.002$	3.3–40	D	Signal broadening with increasing vol% O ₂
Molecular sieve 13X	a. N ₂ or N ₂ /O ₂	a. $g = 2.002$ $g = 4.244$	800 170	A } B }	Iron impurities (20)
	b. 1% H ₂ S in N ₂ or N ₂ /O ₂ /H ₂ S	b. A + B $g = 2.028$	ca. 50	C	
	c. N ₂ /O ₂	c. A + B + C $g = 2.005$ $g = 2.013$	ca. 5 ca. 10	E } F }	

^a Uncertainty in the last digit 2.

to Ayscough (14) a good assumption is that 80% of the absorption occurs in the central half of the cavity (1.145 cm). This means that the 0.1% pitch signal is due to $3 \times 10^{15} \times 1.145 \times 100/80 = 4.2 \times 10^{15}$ spins. The accuracy of the determination of the spin concentration is ± 25 –50%.

The reproducibility of all experiments was verified by repeating every experiment at least once.

1. Experiments on Different Catalysts, at a Reactor Temperature of 150°C

A survey of our results on different materials and conditions is given in Table 1.

1.1 Alumina ($\gamma\text{-Al}_2\text{O}_3$, Ketjen-AKZO). In nitrogen the material showed a broad signal at $g = 2.002$ (A) and a minor signal at $g = 4.244$ (B). The spectrum did not change when 2 vol% O₂ was admixed with the N₂. After purging with N₂ a stream of 1% H₂S in N₂ was introduced. In consequence of this a new signal appeared at $g = 2.026$ (C). According to the literature

(15, 16) this signal must be attributed to a sulfur species. After this H₂S treatment, admission of a N₂-O₂ mixture led to the disappearance of the sulfur signal.

When a mixture of 97% N₂, 2% O₂, and 1% H₂S was flowed through the reactor containing pure Al₂O₃ a sulfur signal was detected. The intensity, however, was smaller than in the case of H₂S alone. The signals already present in the pure $\gamma\text{-Al}_2\text{O}_3$ did not change in the presence of O₂ and/or H₂S.

1.2. Carbon molecular sieve (CMS). Because of high dielectric losses of the carbon bed it was impossible to carry out ESR measurements on undiluted carbon samples. To diminish the conductivity we used a physical mixture of 92.0 wt% SiO₂, 5.9 wt% CMS, and 2.1 wt% S.

In a separate experiment we found that the SiO₂ used as a diluent had no activity for H₂S oxidation and did not give rise to an ESR signal upon admission of H₂S and/or O₂.

In a nitrogen atmosphere the carbon-silica-sulfur bed gave one strong signal at $g = 2.002$ (D).

In the presence of oxygen the signal width increased and the signal height decreased; the intensity of the signal decreased to 70% of the initial value when nitrogen was replaced by air. The oxygen effect was completely reversible. On the basis of literature data (17) we assign the signal at $g = 2.002$ (D) to carbon radicals. H_2S had no influence on this signal, neither in the presence nor in the absence of oxygen, although CMS is an active catalyst for H_2S oxidation. A sulfur signal could not be detected because of the strong and very broad signal due to carbon radicals.

1.3. *Molecular sieve 13X*. In a nitrogen atmosphere the pure material gave absorption peaks at $g = 2.002$ (A) and $g = 4.244$ (B). These signals, only stronger, were also observed for alumina.

ESR spectra at various conditions are given in Fig. 1; the very broad but weak signals (A) and (B) are not visible in Fig. 1.

In an atmosphere of 1% H_2S in nitrogen the signal due to sulfur radicals arose at the slightly shifted g value of $g = 2.028$ (C). When 0.25% H_2S and 0.18% O_2 were admixed with the nitrogen the same signal but with a larger intensity was observed. The intensity of the signal increased as a function of reaction time and reached a constant value when the zeolite was nearly saturated with sulfur. This saturation was also demonstrated by the deposition of sulfur in the cooler parts of the reactor outlet. Thereupon a nitrogen-oxygen mixture was admitted to the sulfur containing zeolite. The intensity of the sulfur signal [$g = 2.028$ (C)] became smaller by a factor of 20 and minor signals appeared at $g = 2.005$ (E) and $g = 2.013$ (F) (see Fig. 1). When in this experiment oxygen was replaced by H_2S the sulfur signal at $g = 2.028$ (C) reappeared. Then the signals at $g = 2.005$ (E) and $g = 2.013$ (F) became hardly detectable.

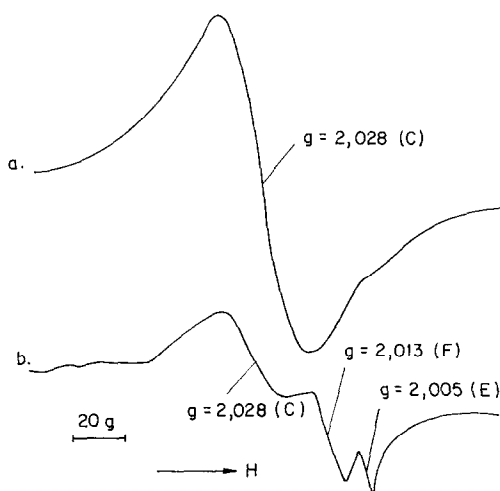


FIG. 1. ESR spectra of molecular sieve 13X under various conditions, $T = 150^\circ C$. (a) 1% H_2S in N_2 or a mixture of 0.25% H_2S and 0.18% O_2 in N_2 . The line shape for both conditions is the same, but the intensities are different. (b) 10 min after admission of a mixture of 0.18% O_2 in N_2 to (a).

2. Experiments on the Influence of Reaction Conditions on the Reaction on Molecular Sieve 13X

2.1 *Influence of temperature*. At room temperature the sulfur signal is observed when only H_2S is led over the zeolite. The increase of the intensity of the sulfur signal as a function of reaction time was much slower at room temperature than at $150^\circ C$.

If H_2S and O_2 were both present, a triplet signal at $g_1 = 2.043$, $g_2 = 2.033$ and $g_3 = 2.023$ was observed. When heated to $150^\circ C$ under N_2 this triplet signal formed one signal with $g = 2.028$ (C). The intensity of the signal is plotted as a function of reaction time at 22 and $150^\circ C$ in Fig. 2. The time needed to obtain a constant signal intensity was much longer at $22^\circ C$. At room temperature part of the water formed was retained by the zeolite. Sometimes this water made it impossible to record ESR spectra, due to the high dielectric losses.

At $150^\circ C$ this difficulty is negligible, because the adsorption of water is much smaller.

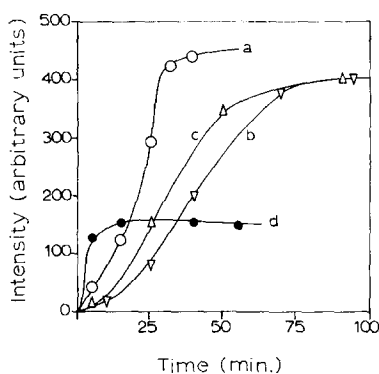


FIG. 2. Intensity of the sulfur signal as a function of reaction time at various conditions (Zeolite 13X). (a) $T = 150^{\circ}\text{C}$, feed: 0.25% H_2S and 0.18% O_2 in N_2 . (b) $T = 22^{\circ}\text{C}$, feed: 0.30% H_2S and 0.18% O_2 in N_2 . (c) $T = 22^{\circ}\text{C}$, feed: 1.50% H_2S and 0.18% O_2 in N_2 . (d) $T = 22^{\circ}\text{C}$, feed: 0.30% H_2S and 2.0% O_2 in N_2 .

2.2 Influence of concentrations. In Fig. 2 the sulfur signal intensity is plotted as a function of time after the introduction of the feed gases with various compositions. An increase of the H_2S concentration by a factor of five did not change the rate of increase of the sulfur signal nor the intensity of the signal in the stationary state. However, an increase of the O_2 concentration by a factor of 11 gave a different picture. In the latter case the initial intensity increased much faster, but the maximum intensity is a factor of three lower.

Alternate admission of $\text{H}_2\text{S}/\text{N}_2$ and O_2/N_2 mixtures gave rise, respectively, to an increase and decrease of the signal assigned to sulfur. From the strong decrease of the signal in an oxygen-nitrogen atmosphere it is concluded that at least 90% of the sulfur radicals can combine with oxygen.

In another series of experiments the concentration of the reactants were varied for a molecular sieve with only the micropores saturated with sulfur. From separate fixed-bed experiments it was known that this material had reached a stationary activity level, i.e., the sulfur formed desorbs completely. The number of sulfur radicals was determined as a function of H_2S and O_2 con-

centrations. The results of these experiments will be used to verify the proposed oxidation-reduction mechanism (2).

2.3. Experiments with SO_2 . A series of experiments was performed to study the role of SO_2 in the mechanism of H_2S oxidation. SO_2 is a by-product at high temperatures and high oxygen concentrations.

Admission of a mixture of 0.76 vol% SO_2 in nitrogen to a zeolite 13X at room temperature led to a broad ESR signal at $g = 2.0099$ ($\Delta H = 15$ G). Then the temperature was raised to 150°C . The signal narrowed ($\Delta H = 3$ G) and shifted to $g = 2.0058$. This signal is connected with the presence of SO_2 : in pure N_2 it disappears. Replacement of SO_2 by H_2S at 150°C led to the appearance of the well-known sulfur signal.

This effect is reversible: when SO_2 substitutes the H_2S the broad signal mentioned above reappeared.

DISCUSSION

1. The Signal of Sulfur

The main signal present during the oxidation of H_2S at 150°C is a sulfur signal in view of the g values ($g = 2.028 \pm 0.002$); compare Tables 1 and 2. Another argument is that the intensity of this signal reaches a constant value in case of saturation of the zeolite, when sulfur condensation starts in the cooler parts of the reactor outlet. Moreover, the adsorbed substance shows the well-known behavior of sulfur radicals, namely the transition of a triplet signal at room temperature ($g_1 = 2.043$, $g_2 = 2.033$, $g_3 = 2.023$) to one signal at higher temperatures ($g = 2.021$ – 2.031). The triplet signal is caused by anisotropy, as explained by Kurita and Gordy (18). The value 2.023 which we found for g_3 is high compared to literature data, which are mostly about 2.002; see Table 2. Another difference with the literature data (Table 2) is our observation of a triplet signal at room temperature. Usually this triplet arises at lower tempera-

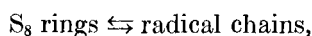
tures (-196°C). These differences may be connected with the adsorbed state of the sulfur.

It is remarkable that the three signals of triplet do not appear at the same time when O_2 and H_2S are led over a zeolite; the sequence is first g_2 , and then g_1 and g_3 . Also remarkable is that admission of an O_2/N_2 mixture at room temperature made g_1 and g_3 disappear first. The reason for this phenomenon is not fully understood.

Most authors (Table 2) believe that the radicals are chains of sulfur atoms with unpaired electrons at the ends. These chains cause the high viscosity of polymer sulfur above 160°C . From Table 2 it can be seen that the g value of the free electron located on sulfur is not affected by the presence of neighboring atoms or atom groups like H or CH_3 . On the basis of our experiments we cannot exclude the possibility that some atom, e.g., hydrogen, is bonded to sulfur atoms containing an unpaired electron.

Further we cannot discriminate between short or long chains of sulfur atoms. For our experiments at 22°C we calculate 3×10^4 sulfur atoms/spin. If all the sulfur was in the radical form, the average chain length would be 10^4 – 10^5 atoms. One chain molecule would occupy a volume of 10^6 \AA^3 . This value is of course very large for sulfur adsorbed in micropores. Therefore, we believe that the most of the sulfur produced will not be in the radical form, but rather in the form of S_8 rings. Seff (19) found that, when type A zeolites are impregnated with sulfur, two S_8 rings are accommodated in each zeolite supercage.

For pure elemental sulfur at 150°C Koningsberger (16) found 3.5×10^7 atoms/spin. For sulfur adsorbed at 25°C in zeolite 13X we calculated an atom/spin ratio of 3×10^4 . Our conclusion is that the equilibrium,



shifts to the right side for adsorbed sulfur.

TABLE 2
ESR Data on Sulfur Radicals

g_1	g_2	g_3	Description	Ref.
	2.024		S liquid ($T > 185^{\circ}\text{C}$)	(15)
2.039	2.025	2.000	S liquid	(27)
	2.025		S liquid (180– 350°C)	(28)
2.050	2.031	2.003	S in melting salt	(29)
2.0405	2.0259	2.0023	S at 2°K	(30)
2.039	2.024	2.002	S cooling down (145 \rightarrow -160°C)	(16)
2.053	2.030	2.000	S on Co Mo- γ - Al_2O_3	(11)
2.047	2.032	2.010	S in zeolite 3A (-196°C)	(13)
	2.0286		S in zeolite 3A (25°C)	(13)
	2.0275		S in zeolite 13X (25°C)	(13)
2.054	2.032	2.003	S in zeolite 5A (-196°C)	(12)
2.042	2.028	2.002	S in decomposition of COS	(31)
	2.028		S in ultramarine	(32)
2.050	2.029	1.998	S on Mo- γ - Al_2O_3	(33)
2.055	2.025	2.003	S after radiation of 3,3'-di- thiopropionic acid	(34)
2.0499	2.0319	2.0026	$\text{S}_3 \cdot^-$ in KCl	(35)
	2.026		S CH_2	(25)
	2.024		S $\text{CH}_2 \text{CH}_3$	(25)
	2.024		S $\text{CH}_2 \text{C}_6\text{H}_5$	(25)
	2.028		S $\text{CH}_2 \text{CH NH}_2 \text{COOH}$	(25)

2. The Oxidation of H_2S by the Pure Materials in the Absence of Oxygen

Interesting is the formation of a sulfur radical, in the presence of H_2S and in the absence of oxygen, on pure alumina and zeolite. Moreover, the color of the catalyst turns yellow, which is an indication of the formation of sulfur.

Also in this case the atom-spin ratio of the deposited sulfur was lower, i.e., about 10^3 times lower than in sulfur not adsorbed. The rate of increase of the S-signal indicates that the oxidation rate of H_2S in the absence of O_2 is much lower than in the presence of O_2 . The signal at 20°C in the absence of O_2 was hardly detectable.

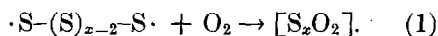
The question arises as to what causes the oxidizing properties of the porous material. A first possibility is that impurities such as iron ions are responsible. The ESR signals which we found in the pure materials at $g = 2.0016$ and $g = 4.244$ are very similar to the data reported by Derouane *et al.* (20) for iron impurities in the Linde SK40 zeolite. We observed that both signals did not change upon admission of H_2S , so it is unlikely that these iron ions react. Another

possibility might be the reaction of H_2S with a chemisorbed oxygen species like $\text{O}\cdot^-$ or $\text{O}_2\cdot^-$. The oxidation of H_2S by these oxygen species has already been reported for $\gamma\text{-Al}_2\text{O}_3$ (11) and zeolite NaY (9). However, from the ESR experiments we did not obtain evidence for the presence of these oxygen radical species. In contrast with our observations Dudzik *et al.* (8) report no oxidation activity of the pure material, i.e., zeolite 13X. One reason may be their activation temperature of 350°C , compared to 150°C for our experiments. This could result in a lower concentration of oxygen species which may be responsible for the oxidation activity. A second reason may be the low intensity of the sulfur signal at their measuring temperature, i.e., room temperature.

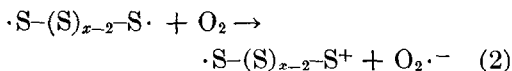
3. Oxidation-Reduction Mechanism for the Oxidation of H_2S on Zeolite 13X

The dependence of the radical concentration on reaction time is an S-shaped curve (Fig. 2). This reflects the autocatalytic character of the reaction as reported in Part I (1).

One of the most interesting features is that the oxidation of H_2S is in fact a two-step process, involving an oxidation and a reduction step. The oxidation step is the reaction of molecular oxygen with sulfur radicals which causes the observed decrease in the S-signal.

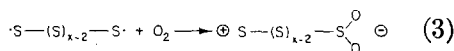


Because we do not know very much about the nature of the reaction product, we use the notation $[\text{S}_x\text{O}_2]$. At room temperature 90–95% of the radicals disappear upon admission of a mixture of $\text{O}_2\text{-N}_2$. In the literature (8) the following reaction is mentioned:



As discussed in Sect. 4 below, it is indeed quite possible that there is an electron trans-

fer from the sulfur radical to the oxygen molecule. Another possibility is that both free electrons at the ends of one sulfur chain are involved in the chemisorption of one oxygen molecule:



This reaction could explain the disappearance of the sulfur signal without formation of a new oxygen radical species. We discuss below the possible role of the weak signals E ($g = 2.005$) and F ($g = 2.013$) as intermediates.

The second step in the mechanism is the reduction of $[\text{S}_x\text{O}_2]$ with H_2S , yielding sulfur and water. From the observed half order in H_2S found in the kinetic experiments (2), it may be concluded that H_2S reacts first with sulfur, forming SH groups.

The results of the kinetic experiments on zeolite 13X agree very well with the ESR experiments:

a. When comparing Fig. 2b and c, it is clear that the H_2S concentration hardly influences the radical concentration as a function of reaction time and especially the signal concentration in the stationary state. In separate kinetic experiments we found an apparent zero order in H_2S for the same set of conditions used in the ESR experiments.

b. An increase of the oxygen concentration results in a marked increase of the formation rate of sulfur radicals (compare Fig. 2b and d). In kinetic experiments we found an apparent first order with respect to oxygen. The lower intensity of the sulfur signal in the stationary state, at high oxygen concentrations, shows that the degree of occupation of sulfur radicals with oxygen is high.

The proposed oxidation-reduction model (2) can be verified quantitatively with a series of experiments at constant temperature. The intensity of the sulfur signal was measured as a function of the partial pres-

sures of oxygen (P_{O_2}) and hydrogen sulfide (P_{H_2S}). All experiments were performed at a constant activity level of the zeolite.

From Eq. (9) in Part II (2) we obtained:

$$\frac{\theta}{1 - \theta} = \frac{2k_{ox}}{k_{red}} \cdot \frac{P_{O_2}}{P_{H_2S}^{0.5}} \quad (4)$$

Although the intensity of the signal represents all radicals, including those in the bulk, we assume that the intensity I is a measure of the number of radicals at the surface. This assumption is discussed below. The relation between the degree of occupation and the intensity of the sulfur signal is:

$$1 - \theta = A \cdot I, \quad (5)$$

A is a constant. Combination of Eqs. (4) and (5) gives:

$$\frac{1}{I} = A + A \cdot \frac{2k_{ox}}{k_{red}} \cdot \frac{P_{O_2}}{P_{H_2S}^{0.5}} \quad (6)$$

A plot of I^{-1} vs $P_{O_2} \cdot P_{H_2S}^{-0.5}$ gives a straight line (Fig. 3).

This is another proof for the applicability of an oxidation-reduction mechanism. A value for the ratio k_{ox}/k_{red} was determined from Fig. 3 and amounted to $3.8 \times 10^{-3} \text{ N}^{-\frac{1}{2}} \text{ m}$ at 130°C . This is in good agreement with values between 3.1×10^{-3} and $6.2 \times 10^{-3} \text{ N}^{-\frac{1}{2}} \text{ m}$ which we found under the same conditions in our previous kinetic experiments (2).

We mentioned already the disappearance of 90–95% of the sulfur radicals when only O_2-N_2 is present at room temperature. At 130°C all sulfur radicals react with oxygen within some minutes, even when the zeolite has a micropore volume completely filled with sulfur. Our conclusion is that it is possible that free electrons can diffuse rapidly by cleavage and combination of S-S bonds in an interconnecting net of sulfur chains and rings. This mobility means that the equilibrium between the concentrations of surface radicals and bulk radicals will be established rapidly after a change of reac-

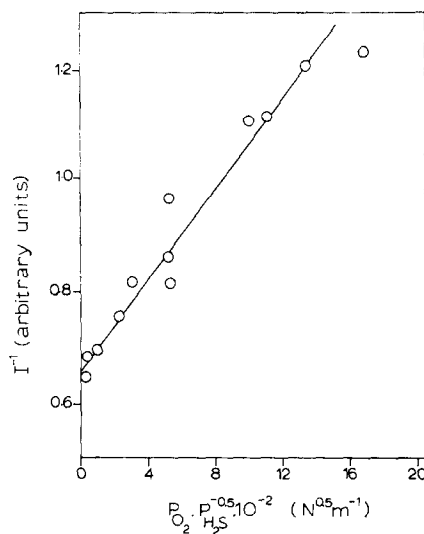


FIG. 3. Test for the oxidation-reduction mechanism. $T = 130^\circ\text{C}$, variable P_{H_2S} and P_{O_2} , zeolite 13X micropores filled with sulfur: 0.3 g S (g zeolite) $^{-1}$.

tion conditions. The assumption made before that the concentration of bulk sulfur radicals is proportional to the concentration of surface sulfur radicals is therefore acceptable.

Dudzik and Preston (13) observed that, when oxygen is admitted at room temperature to zeolite 3A impregnated at 400°C with sulfur, the signal assigned to sulfur radicals did not change. This will be caused by the fact that there is no net of interconnecting sulfur in this small pore (3 Å diam) zeolite, so that the free electrons cannot move to the surface.

4. Sulfur-Oxygen Signals in the ESR Spectra

Special attention was paid to some minor ESR signals which could possibly reveal something about the nature of the so-called "oxidized sulfur": $[S_xO_2]$.

Admittance of an oxygen-nitrogen mixture to sulfur radicals results in a decrease of the sulfur signal intensity and an increase of the intensity of some weak signals at $g = 2.013$ (F) and $g = 2.005$ (E). In

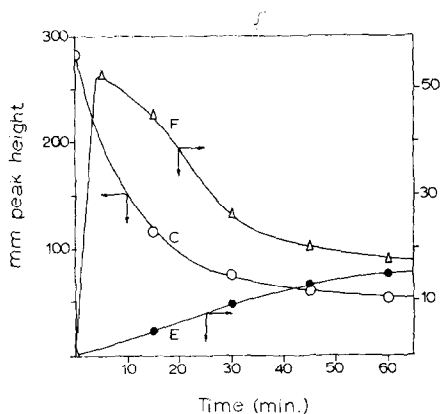


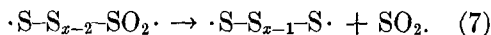
Fig. 4. Signal intensities as a function of time after admission of 0.7% O₂ in N₂ at 22°C. The sulfur is formed by reaction of 0.3% O₂ and 0.3% H₂S in N₂ at 22°C during 80 min on a zeolite 13X. (C) g = about 2.030, sulfur radicals $\cdot S_x\cdot$; (E) g = 2.005, $S_xO_2\cdot^-$; (F) g = 2.013, $S_xO\cdot^-$. The signal intensity is correlated with the peak height, a quantitative comparison of the signal intensities is therefore impossible.

Fig. 4 the intensities of the various signals are given as a function of time after admission of oxygen to sulfur radicals. The intensity of the signal at $g = 2.005$ (E) reaches a constant value at the same time as that of the sulfur signal. An important observation is that heating in nitrogen above 175°C leads to the disappearance of signal E and an appearance of the sulfur signal. From separate fixed-bed and infrared measurements we know that the formation of SO₂ from oxygen and adsorbed sulfur starts at 175°C.

The signal at $g = 2.005$ (E) is also formed when only SO₂ is adsorbed on a pure zeolite. The g value of the signal shifts from 2.0099 to 2.0058 when the temperature is increased from 22 to 150°C.

The signal which arises at $g = 2.0057$ when SO₂ is adsorbed on TiO₂ or ZnO is assigned to SO₂·⁻ (21). The same radical ($g = 2.0055$) is observed during the thermal decomposition of Na₂S₂O₄ (22). Irradiation of thiosulfate gives rise to an ESR signal at $g = 2.0054$, which is assigned to S₂O₂·⁻ (23). On the basis of these literature data we conclude that the signal of $g = 2.005$ (E) represents S₂O₂·⁻, i.e., a

sulfur chain terminated with an SO₂ group. At higher temperatures cleavage of the S-S bond may occur and SO₂ is formed.



Admission of SO₂ to sulfur radicals at room temperature led to the disappearance of the sulfur signal and the appearance of a signal with $g = \text{ca. } 2.005$ (E). This is a clear indication that the reverse reaction occurs at low temperatures.

SO₂ shows a behavior towards sulfur radicals which is very similar to oxygen, i.e., admission of SO₂ results in a strong decrease of the sulfur signal intensity and an increase of signal E and admission of H₂S (SO₂ absent) results in a strong increase of the sulfur signal and a decrease of signal E. When both H₂S and SO₂ are present the Claus reaction occurs and no sulfur signals are visible in the spectrum, which indicates that the reduction by H₂S in this case is the rate-determining step. In a separate experiment we found that the water formed by the reaction of H₂S and SO₂ is not responsible for the absence of a sulfur radical signal.

Morton (23) reports the discovery of an S₂O·⁻ radical with a g value of 2.0143. During the polymerization of S₂O an ESR signal is observed at $g = 2.010$, probably belonging to S₂O·⁻ (24). These literature data are close to the g value of 2.013, observed for signal F (Fig. 4). The fact that the intensity of signal F as a function of time (Fig. 4) has a maximum, suggests that F is an intermediate between S_x· and S_xO₂·⁻. Therefore, we assign the signal of $g = 2.013$ (F) to S_xO·⁻.

When oxygen and hydrogen sulfide react the signals E and F are only detectable when the O₂/H₂S ratio is above 2.

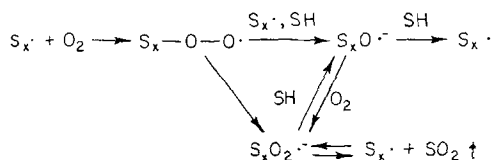
Admission of an O₂/N₂ mixture at 22°C to sulfur radicals which have been heated at 100°C in N₂ results in a new signal $g = 2.0083$ (G). This signal is only visible for a short time and is a precursor for the signals E and F. In Fig. 5 the intensities of the various signals are plotted as a function

of time. The signal at $g = 2.0083$ (G) was observed already by Dudzik and Preston (13) after adsorption of O_2 to sulfur radicals at room temperature. They assign the signal to an $O_2\cdot^-$ species, and they do not consider the possibility that it might be a sulfur-oxygen radical species. Chen (25) calculated g values for a $SO_2\cdot^-$ species with a so-called sp hybrid model and a so-called π -electron model. The π -electron model gave $g = 2.0053$, which is in accordance with our assignment of signal E to $S_2O_2\cdot^-$. For the sp hybrid model he calculated $g = 2.0078$, which is close to $g = 2.0083$ (G).

An explanation for the behavior of the various signals on the admission of oxygen to the sulfur radicals might be the following. Oxygen reacts with the sulfur radicals, signal C, and this leads to a decrease of the intensity of the sulfur signal C. In the sulfur-oxygen complex formed, two oxygen atoms terminate a chain of S atoms. The complex is a kind of peroxide radical $S_x-O-O\cdot$ (signal G), which reacts with chemisorbed hydrogen sulfide or with other sulfur radicals to give the $S_xO_2\cdot^-$ (signal F) species. This species can be reduced with chemisorbed H_2S to sulfur.

A rearrangement of the peroxide radical could yield $S_xO_2\cdot^-$; this species dissociates at high temperatures into sulfur and sulfur dioxide.

A scheme of this mechanism would be:



This scheme could explain the time-dependences of the various signals after O_2 admission (see Figs. 4 and 5) and is in accordance with the chemical structures assigned to the various signals. However, it should not be concluded with certainty that all the observed radical species play an important role in the mechanism. Also it is possible that there exist sulfur-oxygen com-

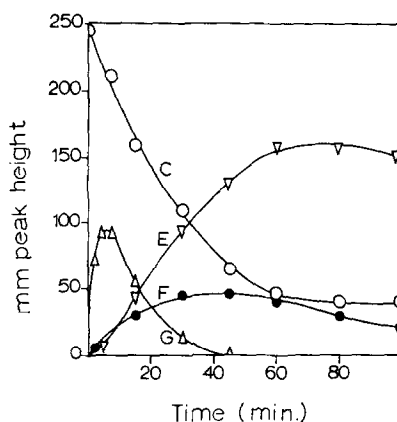


Fig. 5. Signal intensities as a function of time after admission of 2.9% O_2 in N_2 at $22^\circ C$. The sulfur is formed by reaction of 0.3% O_2 and 0.3% H_2S in N_2 at $150^\circ C$; the zeolite 13X with sulfur radicals is cooled down in an N_2 stream to $22^\circ C$. (C) $g =$ about 2.030; (E) $g = 2.005$; (F) $g = 2.013$; (G) $g = 2.0083$.

plexes, which are not radicals, but which still play a role in the mechanism.

5. The Role of Carbon Radicals in H_2S Oxidation on Active Carbon

Although we were not able to detect sulfur radicals in active carbons, there is great evidence that also here sulfur radicals have to be present. The initial increase of the oxidation rate caused by an autocatalytic effect of sulfur and the oxidation-reduction mechanism found for carbons as well as for zeolites point to the presence of sulfur radicals in carbons. In the literature (3, 4) most authors conclude that the carbon radicals play an important role in the mechanism. For the active carbons studied, the role of these carbon radicals does not seem to be important in this respect, because Norit RBW 1 carbon does not contain carbon radicals, but is a good catalyst for H_2S oxidation.

According to Armstrong *et al.* (17), the broadening of the carbon signal when gas-phase oxygen is present is caused by a physical interaction. The fact that this so-called "oxygen effect" (26) vanishes completely in pure nitrogen is also an indication

of the rather weak interaction between the carbon radicals and oxygen.

Because the interaction between oxygen and carbon radicals is so weak we do not expect that carbon radicals are the active sites for H₂S oxidation in active carbons.

CONCLUSIONS

1. In the sulfur adsorbed in zeolite 13X only a fraction is in the form of radical chains. The atom to spin ratio for this adsorbed sulfur is lower by a factor 10³ than for elemental sulfur at the same temperature.

2. The reaction of sulfur radicals with oxygen gives rise to at least three radical species. ESR signals due to sulfur chains terminated with one or two oxygen atoms may be distinguished. The place of these species in the network of reaction steps is outlined.

3. The by-product SO₂ is formed from an oxygen-sulfur complex which is observed in the ESR spectrum. At temperatures above 175°C rupture of an S-S bond in the complex occurs, and SO₂ is liberated.

4. The intensities of the sulfur signal as a function of the partial pressures of oxygen and H₂S point to an oxidation-reduction mechanism. From ESR data obtained for zeolite 13X at 130°C we calculate a value $k_{\text{ox}}/k_{\text{red}} = 3.8 \times 10^{-3} \text{ N}^{-\frac{1}{2}} \text{ m}$, which is in good agreement with those from kinetic measurements, i.e., between 3.1×10^{-3} and $6.2 \times 10^{-3} \text{ N}^{-\frac{1}{2}} \text{ m}$.

5. Our investigations show that the contribution of carbon radicals in the mechanism of H₂S oxidation on active carbon is not important.

ACKNOWLEDGMENT

We thank Mr. J. Venselaar for carrying out part of the experimental work. The investigations were supported by Chemical Research Netherlands (SON) with the financial aid of the Dutch Organization for Pure Research (ZWO).

REFERENCES

1. Steijns, M., and Mars, P., *J. Catal.* **35**, 11 (1974).

2. Steijns, M., Derks, F. W., Verloop, A., and Mars, P., *J. Catal.* **42**, 87 (1976).
3. Siedlewski, J., and Trawinski, S., *Int. Chem. Eng.* **7**, 35 (1967).
4. Sreeramamurthy, R., PhD thesis, Andhra Univ., 1972.
5. Krause, A., *Rocz. Chem.* **36**, 779 (1962).
6. Siedlewski, J., and Swinarski, A., *Rocz. Chem.* **35**, 999 (1961).
7. Siedlewski, J., *Int. Chem. Eng.* **5**, 293 (1965).
8. Dudzik, Z., Biliska, M., and Czeremuzinska, J., *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **22**, 307 (1974).
9. Habgood, H., and Imai, T., *J. Phys. Chem.* **77**, 925 (1973).
10. Dudzik, Z., *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **15**, 583 (1967).
11. LoJacono, M., Verbeek, J. L., and Schuit, G. C. A., *Proc. Int. Congr. Catal., 5th, 1972*, **2**, 1409 (1973).
12. Dudzik, Z., and Cvetanović, R. J., *Proc. Int. Congr. Catal., 4th 1968*, **2**, 175 (1969).
13. Dudzik, Z., and Preston, K. F., *J. Colloid Interface Sci.* **26**, 374 (1968).
14. Ayscough, P. B., "Electron Spin Resonance in Chemistry," p. 142. Methuen, London, 1967.
15. Gardner, D. M., and Fraenkel, G. K., *J. Amer. Chem. Soc.* **78**, 3279 (1956).
16. Koningsberger, D., PhD thesis, Eindhoven, 1971.
17. Armstrong, J. W., Jackson, C., and Marsh, H., *Carbon* **2**, 239 (1964).
18. Kurita, Y., and Gordy, W., *J. Chem. Phys.* **34**, 282 (1961).
19. Seff, K., *J. Phys. Chem.* **76**, 2601 (1972).
20. Derouane, E. G., Mestdagh, M., and Vielvoye, L., *J. Catal.* **33**, 169 (1974).
21. Lunsford, J., in "Advances in Catalysis" (D. D. Eley, H. Pines and P. B. Weisz, Eds.), Vol. **22**, p. 265. Academic Press, New York, 1972.
22. Janzen, E. G., *J. Phys. Chem.* **76**, 157 (1972).
23. Morton, J., *J. Phys. Chem.* **71**, 89 (1967).
24. Schenk, P., and Steudel, R., *Z. Anorg. Allg. Chem.* **342**, 253 (1966).
25. Chen, I., *J. Chem. Phys.* **45**, 3526 (1966).
26. Austen, D., and Ingram, D., *Chem. Ind.* 981 (1956).
27. Radford, H., and Rice, F. O., *J. Chem. Phys.* **33**, 774, (1960).
28. Van Aken, J., *Physica* **39**, 107 (1968).
29. Giggensbach, W., *Inorg. Chem.* **10**, 1308 (1971).
30. Châtelain, A., *Helv. Phys. Acta* **42**, 117 (1969).
31. Stiles, D., *Can. J. Chem.* **43**, 2442 (1965).
32. Wells, P. B., *J. Catal.* **19**, 372 (1970).
33. Seshadri, K. S., Massoth, F. E., and Petrakis, L., *J. Catal.* **19**, 95 (1970).
34. Kurita, Y., *Bull. Chem. Soc. Jap.* **40**, 94 (1967).
35. Schneider, J., *Phys. Status Solidi* **13**, 141 (1966).