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THE RATE OF OXIDATION OF HYDROGEN SULPHIDE BY OXYGEN TO ELEMENTAL SULPHUR OVER NaX AND NaY ZEOLITES AND THE ADSORPTION OF SULPHUR.

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ABSTRACT

The rate of oxidation of H_2S by O_2 over synthetic sodium faujasite zeolites to produce elemental sulphur has been studied at partial sulphur load of the zeolite using a gravimetric method. The rate of sulphur accumulation on a sample exposed to an atmosphere of about 1.0 vol % H_2S and 0.5 vol % O_2 in nitrogen has been measured. The rate of oxidation of H_2S to sulphur has been derived for three different NaY type zeolites, i.e. with an Si/Al ratio of 1.70, 2.07 and 2.40 respectively, at temperatures from about 120 to 200 °C. The activation energy of the rate constant appears to be the same for these zeolites and amounts to about 53 kJ mol^{-1}. The reaction rate increases substantially with a decreasing Si/Al ratio of the zeolite. So the NaX type zeolite is clearly more active in the H_2S oxidation than the NaY type. The frequency factor of the rate constant is found to increase linearly with the number of H_2S adsorption sites described previously by Karge and Rasko. This suggests that these sites act as reactive sites in the oxidation of H_2S over sodium faujasite zeolites. By the same micro-weighing technique the rate of desorption of sulphur from sulphur loaded zeolites has been determined at a temperature of about 300 °C. The sulphur vapour pressure close to the zeolite surface has been derived from the rate of weight loss by mass transfer calculations. It appears to be slightly lower for NaX zeolite than for NaY zeolite. In general, the relative sulphur vapour pressure is well below 10^{-2} for all zeolites we tested, unless the maximum adsorption capacity has been approached closely. Because of the high activity and the low relative sulphur pressures observed for NaX type zeolite, this zeolite is preferable as a catalyst in the oxidation of H_2S with O_2 if sulphur should be recovered in an adsorbed state.

INTRODUCTION

The oxidation of hydrogen sulphide with molecular oxygen is known to be the overall reaction in the production of elemental sulphur in the Claus process [1]. The primary reaction involved is:

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$$H_2S + \frac{1}{2} O_2 = S + H_2O \qquad (1)$$

Below about 500 °C this oxidation reaction requires the use of catalysts for improvement of reaction rate. Active carbons, aluminas and zeolites are frequently mentioned as useful catalysts. Among these catalysts, synthetic zeolites such as NaX exhibit superior activity and selectivity towards elemental sulphur [2,3].

In the Claus process, H_2S is converted to sulphur vapour by substoichiometric combustion and by reaction with the SO_2 produced, over alumina-based catalysts, according to the reaction:

$$2H_2S + SO_2 = 3S + H_2O \qquad (2)$$

In processes such as CBA [4,5] and Sulfreen [5] sulphur is recovered from low-H_2S gases by reaction 2 at temperatures below the dew point of sulphur. Sulphur condenses on the catalyst bed and is removed periodically by heating.

We are currently investigating a similar desulphurization process which is based, however, on reaction 1. The present paper is part of this study and deals with the rate of reaction of the H_2S oxidation over zeolites such as NaX, and the adsorption and desorption behaviour of sulphur. Based on the findings of the present work a study has been initiated on zeolite catalysts, modified to the application in fluidized bed systems. In that way the development of a continuous desulphurization process over a moving catalyst is enabled. On this subject we shall report elsewhere [6].

As a part of a larger study on different catalysts, Steijns and Mars [7] investigated the oxidation of H_2S over NaX zeolite and found an autocatalytic effect of the sulphur adsorbed. In ESR experiments Steijns et al. [8] observed a most strong signal of sulphur for NaX zeolite exposed to H_2S and O_2 mixtures. From kinetic measurements up to 200 °C, they determined reaction orders of H_2S and O_2 [8], but only a few values of the reaction rate were presented. Oxidation of H_2S over synthetic X and Y zeolites was studied also by Dudzik and Ziolek [9]. They reported different activities for NaX and NaY zeolites, but gave no data on the reaction rate or the activation energy.

The adsorption of sulphur vapour on NaX zeolite was studied by Barrer and Whiteman [10] and by Steijns and Mars [11]. These authors reported remarkably high adsorption capacities of about 0.35 and 0.30 kg sulphur per kg zeolite respectively at relative sulphur pressures as low as 10^{-2}, i.e. sulphur vapour pressures of a factor 100 lower than the equilibrium pressure of liquid sulphur. On the other hand, no data are available in literature on the adsorption of sulphur on NaY zeolites.

In this study, we focused on the reaction rate of the oxidation of H_2S to sulphur over various NaX and NaY zeolites. Using a gravimetric method, we determined the rate of deposition of sulphur, and hence the rate of the oxidation of H_2S, on a catalyst sample in an atmosphere of about 1.0 vol % H_2S and 0.5 vol % O_2. We looked for autocatalytic phenomena caused by the adsorbed sulphur and shall discuss the influence of the Si/Al ratio of the zeolite on the reaction rate. Furthermore, we studied the adsorption and desorption behaviour of sulphur from the H_2S oxidation. Using the same micro-weighing apparatus, we investigated both the maximum sulphur adsorption capacity of the different NaX and NaY zeolites and the desorption behaviour of the sulphur adsorbed.

EXPERIMENTAL

Experimental set-up

Sulphur adsorbed in the micropores of e.g. NaX zeolite evaporates very slowly, because the relative sulphur vapour pressure is below 10^{-2} even at a sulphur load close to the maximum adsorption capacity [11]. Due to this low volatility of adsorbed sulphur, the rate of the H_2S oxidation can be studied gravimetrically by measuring the rate of weight accumulation of a catalyst sample in a H_2S and O_2 containing atmosphere.

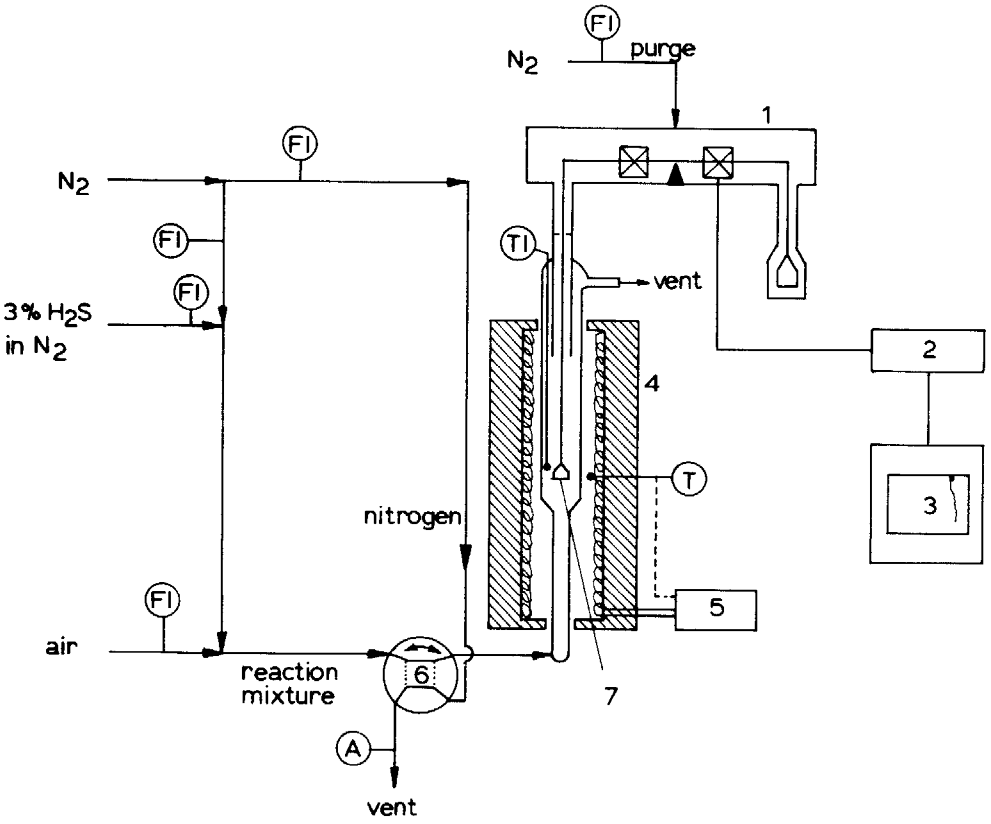
The experimental set-up used in this study is shown in Figure 1. It consisted of a Sartorius 4406 microbalance provided with a quartz hangdown tube inserted in a vertically mounted tubular furnace (heated length 0.30 m, internal diameter 30 mm). Catalyst samples were contained in a shallow quartz sample pan (diameter 10 mm) in the middle of the oven. The electronic controller of the microbalance was connected to a recorder for continuous registration of the sample weight and the temperature of the gas in the vicinity of the sample pan.

Reaction gas

A gaseous reaction mixture of about 1.0 vol % H_2S and 0.5 vol % O_2 in nitrogen was made by adding together flows of dry air and nitrogen containing H_2S. The composition of the gas mixture was adjusted by calibrated flowmeters and checked by chromatographic analysis for each experiment. The reaction mixture was fed to the bottom of the hangdown tube at a flowrate of $3.3*10^{-6}$ m^3s^{-1} (at 20 °C and atmospheric pressure).

Catalysts

Small amounts of pure zeolite powder, i.e. 1 to 10 mg, were used as a catalyst and these were carefully spread on the bottom of the sample pan. NaX was a commercial grade Linde molecular sieve, type 13X. NaY(1.70, see below) powder was supplied by P.A. Jacobs (Katholieke Universiteit Leuven, Belgium).



1. Microbalance
2. Balance controller
3. Recorder
4. Furnace
5. Temperature controller
6. Gas flow switch valve
7. Sample pan

Figure 1 Experimental set-up.

The other NaY catalysts were provided by Akzo Chemie bv (Research Centre Amsterdam). Chemical analysis of the Si and Al content was performed and the resulting Si/Al ratios were added in parentheses to the zeolite names: NaX(1.15), NaY(1.70), NaY(2.07) and NaY(2.40) respectively.

Experimental procedure

Before the experiments, the catalyst sample was dried in a nitrogen flow (high purity, > 99.98% N_2; flow rate $3.3*10^{-6}$ m^3s^{-1} STP) at increasing temperature (heating rate about 0.2 °C s^{-1}) up to 400 °C. When, after cooling to the measurement temperature, both isothermal conditions and a constant weight were attained, nitrogen was replaced by the reaction mixture to start the experiments. Unless mentioned otherwise, only fresh catalyst samples have been used.

RESULTS

Accumulation of sulphur

When the reaction gas mixture of about 1 vol% H_2S and 0.5 vol% O_2 in N_2 was introduced to the hangdown tube of the microbalance, elemental sulphur was formed from the oxidation of H_2S over the catalyst sample and deposited on the catalyst. Formation of sulphur as the main product of the H_2S-O_2 reaction was also shown in our experiments with fluid bed reactors (see [6], p. 151). In the microbalance, the presence of sulphur was apparent from the yellowish colour of the zeolite and the sustained increase of the sample weight recorded. A typical example of a weight versus time plot is given in Figure 2. Accumulation of weight is observed about 45 seconds after the beginning of the experiment (A), which delay period is caused by the residence time in the tubing and in the preheating zone of the hangdown tube. After a certain time of reaction the weight increase of the catalyst holds at a level roughly corresponding to the maximum uptake of sulphur reported by others [10,11]. As a matter of fact, the reaction rate of the H_2S oxidation decreases when the maximum sulphur load is reached, owing to the decreasing available surface area [7, 12]. In addition to this, desorption of sulphur may also become important because of the rapid increase of the relative sulphur vapour pressure at the maximum filling of the zeolite pores [10]. As a result, an equilibrium between the formation of sulphur from the H_2S oxidation and the desorption of sulphur is established, as is shown in Figure 2. Replacing the reaction mixture by nitrogen (C) stops the formation of sulphur and, due to desorption of sulphur, the weight of the catalyst slowly decreases. On account of the lower sulphur vapour pressure at slightly lower sulphur load, the rate of desorption of sulphur becomes negligibly small within a few minutes and an apparently stable weight is observed (D).

In the course of the deposition of sulphur also water, produced by the

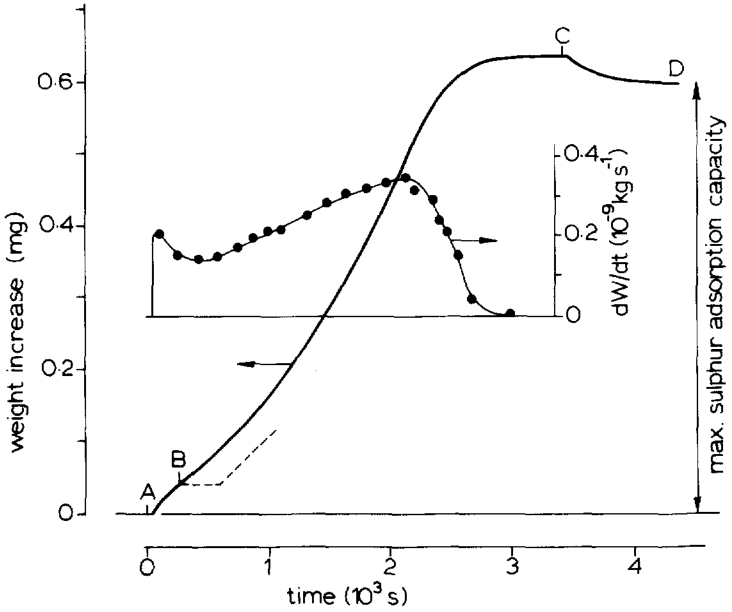


Figure 2 Typical weight registration of sulphur accumulation NaY(2.40) zeolite, 1.65 mg, 188 °C.

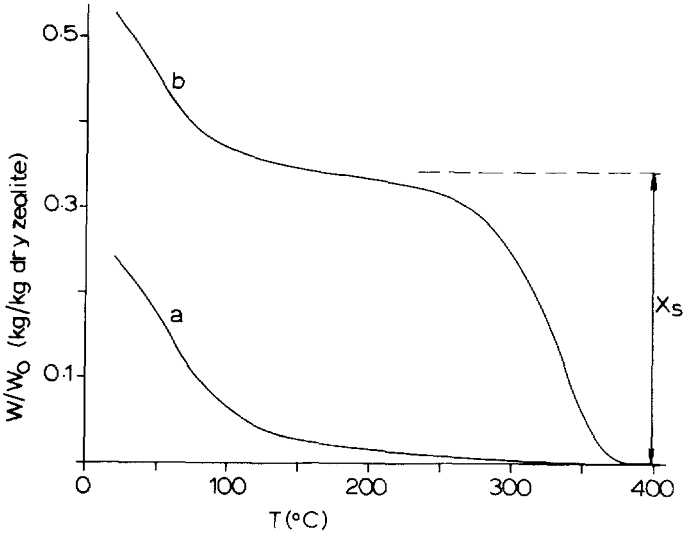


Figure 3 Thermoanalysis of NaY(2.40) (1.65 mg, heating rate 0.17 °C s^{-1}). (a) fresh. (b) containing 0.34 kg sulphur per kg dry zeolite.

reaction, might have been adsorbed simultaneously with the sulphur, because zeolites are known to strongly adsorb water molecules [13]. Thermogravimetric analysis of a fresh NaY(2.40) sample, as given in Figure 3a, shows a significant weight loss due to dehydration below 100 °C, while even up to 200 °C a gradually decreasing weight is observed. Similarly, a sulphur loaded sample shows a marked loss of weight in the range where dehydration of the fresh catalyst occurred (Figure 3b), although this weight loss is slightly lower. At temperatures above 200 °C a second weight loss is observed, which is obviously caused by the desorption of the sulphur adsorbed. Consequently, between about 100 and 200 °C all the sulphur remains on the catalyst, while water is not likely to adsorb substantially. And so the net increase of weight obtained eventually at D in Figure 2 can be considered the maximum sulphur adsorption capacity of the zeolite.

Maximum sulphur adsorption capacity

At temperatures above 100 °C several values of the maximum sulphur capacity of the NaX and NaY zeolites have been determined. The results are presented in Figure 4. The NaX(1.15) zeolite appears to adsorb less sulphur than the NaY zeolites. The adsorption capacity of NaX(1.15) is clearly independent of temperature, while for NaY zeolites a slight decrease at increasing temperature can be seen.

Adsorption of sulphur takes place in the supercages of the zeolite structure, because the apertures to the other cages are too narrow to allow the passage of most molecules [13]. Consequently the maximum number of sulphur atoms adsorbed in a supercage can be calculated from the maximum adsorption capacity. We determined for NaX(1.15) zeolite a value of about 14 sulphur atoms adsorbed per supercage, whereas the NaY zeolites adsorb up to 21 sulphur atoms per cavity. Seff [14] has studied sulphur adsorption complexes in the supercages of NaA zeolite. Such a zeolite has supercages similar to those of NaX zeolite and about the same Si/Al ratio. By an X-ray diffraction study the presence of two parallel S_8 rings in each supercage of the NaA zeolite has been proven. From the maximum sulphur adsorption capacity we calculated for NaX(1.15) zeolite about the same number of sulphur atoms per supercage, namely 14. For NaY zeolites a higher amount of sulphur atoms per cavity is observed. This might indicate the absence of the sulphur complexes mentioned above, or it might be caused by a larger volume available for sulphur adsorption because of a lower cation concentration in the supercages of the NaY zeolites as will be substantiated below.

Steijns and Mars [11] reported a maximum sulphur adsorption capacity of NaX zeolite of about 0.30 kg sulphur per kg zeolite at 260 °C, which is somewhat higher than we have found for the NaX(1.15) zeolite. This can be ex-

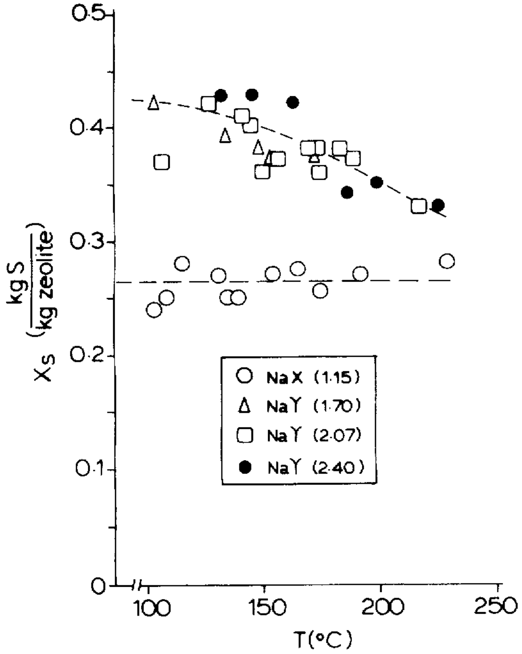


Figure 4 Maximum sulphur adsorption capacity of NaX and NaY zeolites versus temperature.

plained, however, by suggesting that the Si/Al ratio of their zeolite sample might have been slightly higher. Unfortunately the Si/Al ratio was not stated by them.

The rate of oxidation of H_2S

The increase of weight observed in Figure 2 obviously depends on the rate of oxidation of H_2S to sulphur. However, the rate of weight increase might be influenced by simultaneous adsorption of water produced also by the H_2S oxidation. According to the thermogravimetric analysis (cf. Figure 3) relatively low amounts of adsorbed water are to be expected above 100 °C if the atmosphere consists of nitrogen. But in the course of the H_2S oxidation, higher amounts of water might be present on the catalyst, because a substantial water concentration resulting from the H_2S oxidation, is likely to be present within the catalyst layer. By intermediate interruption of the H_2S - O_2 feed, which causes the desorption of any possible water adsorbed, it could be observed (cf. Figure 2, dotted curve at B) that this amount is less than one per cent of the catalyst weight, if the temperature is above about 120 °C. Therefore, under these conditions the weight change of the catalyst sample corresponds almost completely to the rate of the deposition of sulphur and hence to the rate of the oxidation of H_2S. As a matter of fact, the rate of the H_2S oxidation then follows from the tangent to the weight versus time plot according to:

$$r_{H_2S} = 2 * r_{O_2} = \frac{r_S}{M_S} = \frac{dW}{dt} * \frac{\rho}{W_o M_S} \tag{3}$$

From these results, useful data on the reaction rate of the H_2S oxidation can be evaluated only if the H_2S and O_2 concentration at the catalyst are close to the known feed gas concentrations and if temperature effects are absent. We studied the mass and heat transfer phenomena in detail as is described in the Appendix. Accordingly, we have estimated that in most experiments the concentration of both reactants at the catalyst is at least 80 per cent of the feed gas concentration and that the ultimate temperature rise of the catalyst bed is less than 4 °C. An exception has to be made for the experiments on the NaX(1.15) zeolite. Although in this case an activity in the H_2S oxidation was measured, the rate of the weight increase was always that high that it has been influenced by serious mass transfer limitations. But for the NaY zeolites the rate of reaction could be determined satisfactorily, i.e. under approximately gradientless conditions.

The rate of oxidation of H_2S was calculated from the weight signal as described above, and was plotted versus the sulphur load. Figure 5 shows a typical example (curve a). The rate data appear to be poorly reproducible

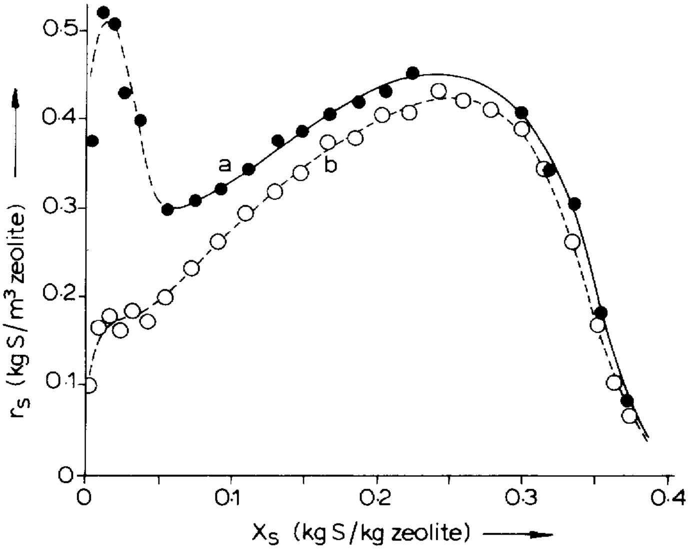


Figure 5 Reaction rate of the oxidation of H_2S with O_2 versus the sulphur load (zeolite NaY(1.70), 150 °C)(a) first experiment (b) fourth experiment.

below a sulphur load of about 5 wt %, whereas the data obtained at a higher load are significant and, for example, also persistent in the course of several cycles with regeneration by heating in nitrogen to about 400 °C and subsequent accumulation of sulphur at the original reaction temperature again (see Figure 5, curve b).

The nature of the high activity at low sulphur load, i.e. below about 5 wt %, is not very clear. We looked for the adsorption of H_2S from an O_2-free mixture on the fresh catalyst, but as is shown in Table 1, only small amounts, i.e. less than 1.0 wt %, were found, which cannot explain the initial peak in the activity satisfactorily. Because the activity at higher sulphur load contributes considerably more to the overall activity of the catalyst, we did not attempt to describe the initial activity extensively.

TABLE 1

Adsorption data for H_2S (1.0 vol.%)

Catalyst	Weight increase (wt %)	Temperature (°C)
NaX(1.15)	1.0	98
NaY(1.70)	0.4	101
NaY(2.07)	0.4	108
NaY(2.40)	0.3	133

TABLE 2

Iron content of the zeolites

Catalyst	Iron content, dry base (wt %)
NaX(1.15)	0.02
NaY(1.70)	0.03
NaY(2.07)	0.05
NaY(2.40)	0.08

At high sulphur load a maximum in the reaction rate is observed. This phenomenon has previously been reported by Steijns and Mars [7] with regard to an NaX catalyst and has been described by them as the autocatalytic effect of sulphur adsorbed in the micropores of the catalyst.

Data on the reaction rate of the H_2S oxidation obtained at different temperatures between 120 and 200 °C, are summarized in Figure 6. Autocatalytic phenomena are generally apparent. The reaction rates observed at a sulphur load of 0.01, 0.03 and 0.05 kg S per kg zeolite respectively are given in the Arrhenius plot presented in Figure 7. A first order rate equation has been assumed in accordance with data of Steijns et al. [8] who have found that the kinetics of the H_2S oxidation on aluminas and 13X molsieve are approximately first order in O_2 and zero order in H_2S. Reasonably parallel lines are obtained, from which an activation energy of the rate constant of about 53 kJ mol^{-1} is derived. This agrees fairly well with values of the activation energy of the reaction rate over a 13X catalyst reported by Steijns, viz. about 55 kJ mol^{-1}.

Based on the autocatalytic effect of sulphur adsorbed on purified active carbons, Steijns et al. derived a general mechanism for the oxidation of H_2S over sulphur adsorbed in porous materials [7,8]. They showed that the oxida-

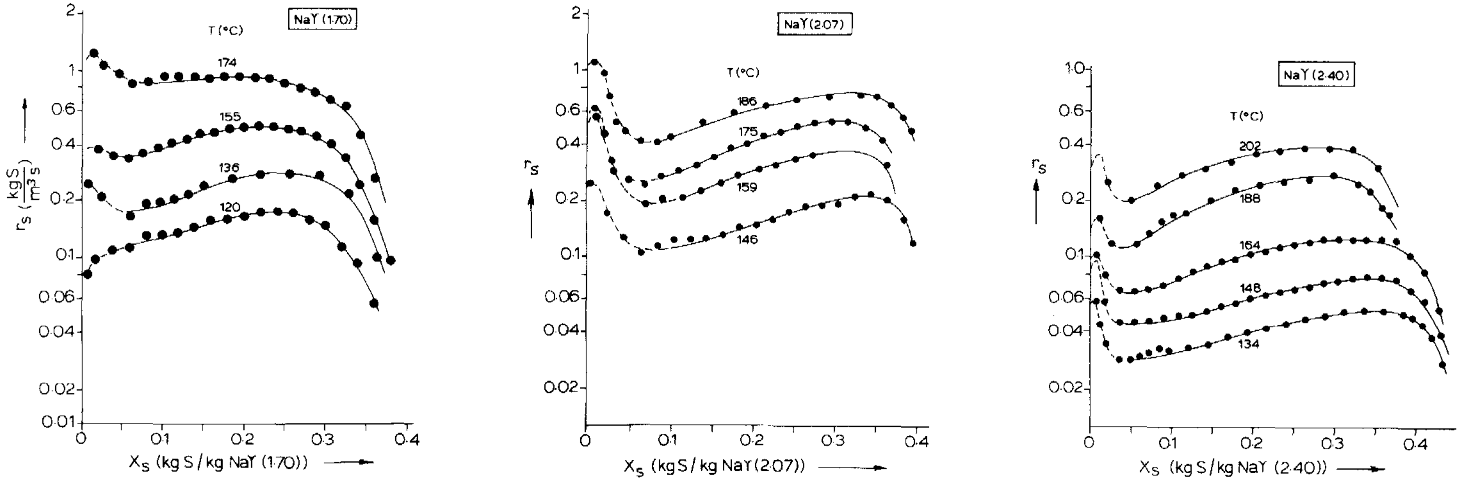


Figure 6 Reaction rate of the oxidation of H_2S with O_2 versus the sulphur load. (a) NaY(1.70). (b) NaY(2.07). (c) NaY(2.40).

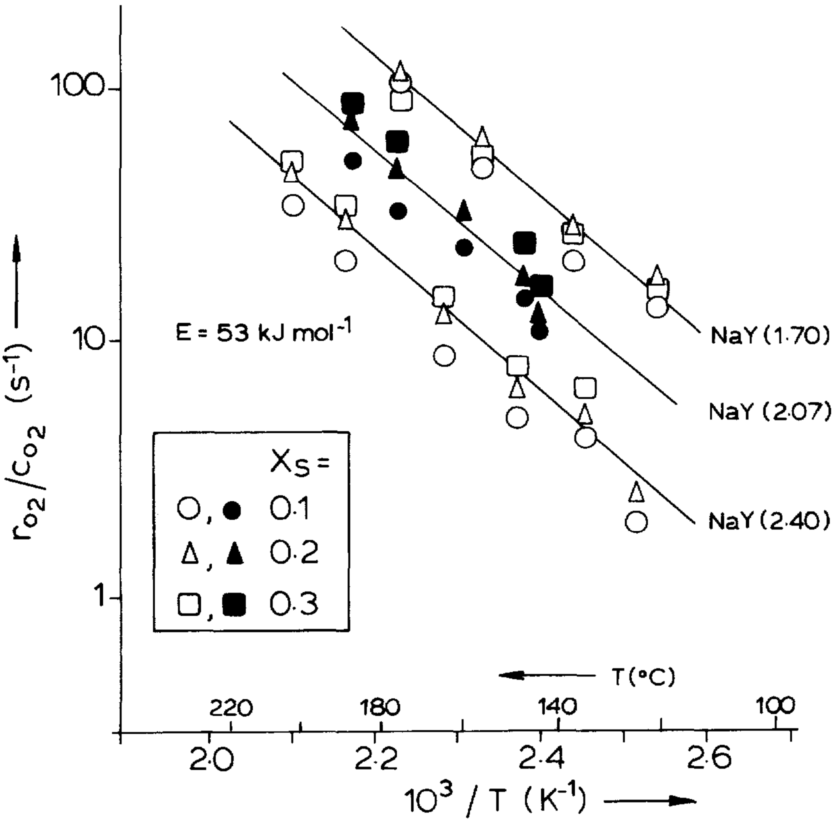


Figure 7 Arrhenius plot of reaction rate constants.

tion rate over an NaX zeolite is related to the specific sulphur surface area [12], which clearly reflects the autocatalytic role of sulphur. On the other hand, they found a high activity of sulphur adsorbed on a 13X zeolite, in comparison with sulphur on an active carbon catalyst. We have found substantial differences in the reaction rate over the NaY zeolites. Because of the similarity of the zeolite structure, large differences in sulphur surface area are unlikely and, therefore, sulphur adsorbed on zeolites with a low Si/Al ratio seems to be more active. Steijns suggested that iron impurities might be causing a higher activity [7,12]. Chemical analysis of the zeolites has, however, shown low iron contents (see Table 2) and, additionally, an increasing iron content is attended by a decreasing activity of the catalyst. Obviously, more parameters are involved in the oxidation of H_2S over NaX and NaY zeolites than those considered by Steijns [15].

Dudzik and Ziolek discussed a mechanism of the H_2S oxidation over NaX and NaY zeolites, which comprises an interaction of adsorbed reactants and the zeolite surface [9]. The chemisorption of H_2S is suggested as an essential step, at least during the initial stage of the reaction. Adsorption of H_2S on NaX and NaY zeolites has been described by many authors [16,17,18]. By IR spectroscopy of zeolites with systematically varied Si/Al ratios, Karge and Rasko [17] determined the dissociative nature of the H_2S adsorption on alumina-rich zeolites, and suggested that this adsorption takes place preferentially on unlocated Na^+ cations near the walls of the supercages. The concentration of these cations strongly depends on the Si/Al ratio. The number of Na^+ cations per unit cell is equal to the number of alumina tetrahedra per unit cell, but cations preferentially occupy the well-coordinated positions inside the small cages [19], i.e. sodalite cages and hexagonal prisms. The remaining cations are located near the walls of the supercages, where the oxidation of H_2S is likely to proceed. Consequently, the number of these cationic sites per unit cell has been proposed by Karge and Rasko as being equal to:

$$n_{Na^+} = \frac{192}{1 + Si/Al} - 56 \qquad (4)$$

They have found a good correlation between the concentration of dissociatively adsorbed H_2S molecules and the number of cationic sites according to the equation above. Consequently, if the H_2S adsorption sites act as reactive sites in the oxidation reaction, the reaction rate is related to the number of Na^+ cations in the supercages and thus depends on the Si/Al ratio of the zeolite. The frequency factor k_o of the Arrhenius equation, which can be calculated from the reaction rate data presented in Figure 7, is plotted in Figure 8 as a function of the Na^+ cation concentration calculated by equation 4. The value of k_o is found to increase rather linearly with an increasing concentration of H_2S adsorption sites in accordance with the suggested reac-

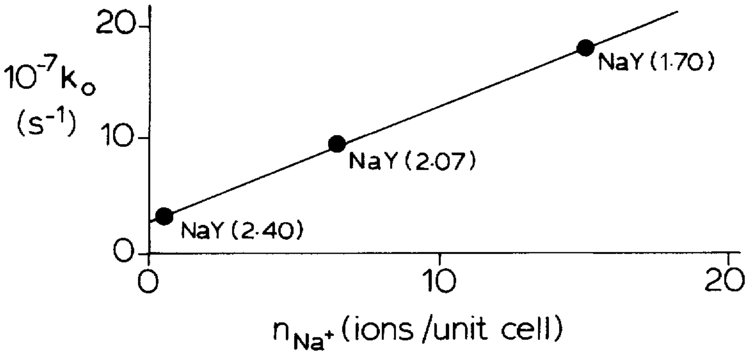


Figure 8 Frequency factors of the Arrhenius equation versus the calculated Na^+ concentration in the supercages.

tive sites model. Figure 8 predicts a residual activity in the absence of Na^+ cations, which would imply an additional activity of e.g. other sites. However, this can also be explained by a possibly lower value of the constant 56 in equation 4, in correspondence with the apparently higher number of cations available for dissociative H_2S adsorption suggested by other workers [18].

Ziolek and Dudzik have elaborated a relation between the catalytic activity of the H_2S oxidation over NaX and NaY zeolites and the Si/Al ratio [20]. They suggested a direct correlation with the number of alumina tetrahedra (AlO_4^-) per unit cell, which equals the total number of Na^+ cations per unit cell. This is not very likely, because only a fraction of Na^+ cations is located on supercage sites and are thus likely to participate in the H_2S adsorption process.

Sulphur desorption

After heating to about 300 °C, sulphur which was accumulated during the H_2S oxidation, desorbs slowly from the catalyst bed. Eventually over 90 per cent of the sulphur accumulated during the H_2S oxidation could be removed by this treatment. Noteworthy is the fact that sulphur adsorbed in subsequent sulphur accumulationdesorption cycles, could be removed from the zeolite about completely. On the fresh zeolite, obviously, some irreversibly adsorbed or chemisorbed sulphur species are formed, while the main part of the sulphur accumulated during the H_2S oxidation desorbs at moderate heating.

As is described in detail in the Appendix, the sulphur vapour pressure at the surface of the catalyst bed can be determined from the rate of the weight loss. We measured the rate of the weight loss as a function of the sulphur load in the desorption experiments and as a result, data on the vapour pressure of sulphur at each sulphur load were obtained. These data are presented in Figure 9.

Barrer and Whiteman [10] have investigated the adsorption and desorption of sulphur and phosphorus on different zeolites and have mentioned a relatively rapid release of sulphur from NaX zeolite. Therefore, we might expect no important concentration gradients inside the catalyst bed. Moreover, we used very small bed heights of less than half a millimeter, and the mass fluxes were very low, i.e. it took about two to six hours to reach the minimum sulphur load. So the sulphur vapour pressure at the interface might be considered the equilibrium pressure of sulphur at the actual sulphur load.

In agreement with the sulphur sorption isotherms on NaX zeolite determined by Steijns and Mars [11], S-shaped isotherms are found indicating an adsorbate-adsorbate interaction of the adsorbed sulphur molecules. The sulphur vapour pressure also depends on the adsorbing zeolite material. At increasing Si/Al ratio, the desorption of sulphur proceeds more rapidly, which might be

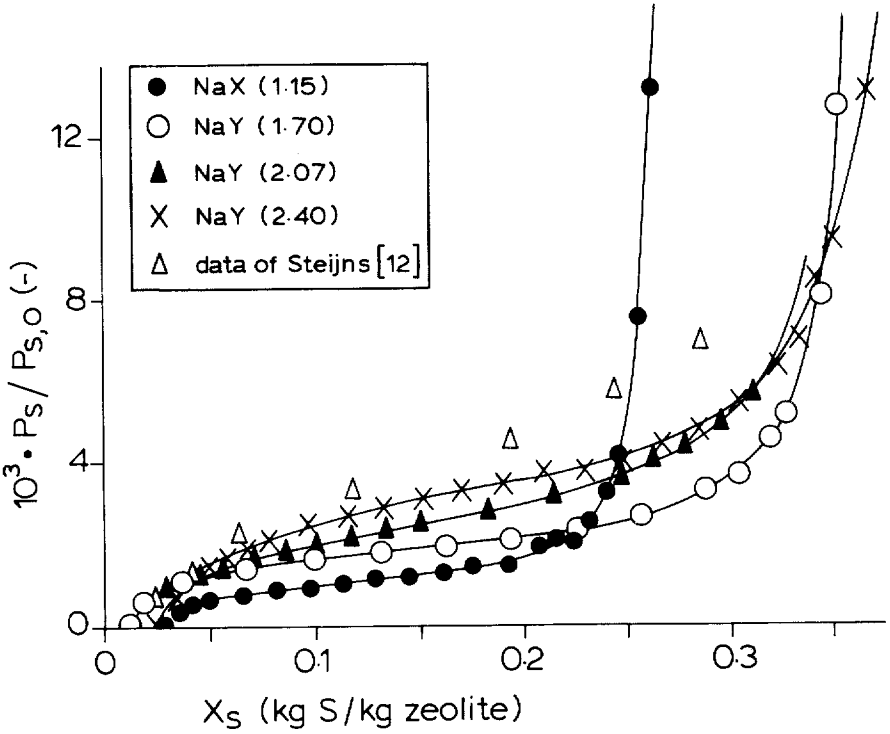


Figure 9 Relative sulphur vapour pressure for desorption of sulphur from NaX and NaY zeolites.

explained by the lower concentration of cations on the walls of the supercages. These Na^+ cations may interact with adsorbed sulphur molecules [14], which thereby might intensify the interaction of sulphur with the zeolite surface.

The data of Steijns and Mars [11] of the sulphur adsorption isotherm on NaX are also shown in Figure 9. Our vapour pressure data are obviously somewhat lower, especially those on NaX(1.15). The shape of their adsorption isotherm resembles that of the NaY zeolites rather than that of NaX(1.15). This agrees with the higher Si/Al ratio of their NaX suggested before on account of the high maximum sulphur adsorption capacity compared to our NaX(1.15) zeolite. Nevertheless, some discrepancies in the values of the sulphur vapour pressure as obtained in our experiments, and literature data remain unexplained by the suggestions above. Although experimental inaccuracies of both techniques could have been responsible, some hysteresis in the sulphur adsorption and desorption might cause such differences too.

CONCLUSIONS

The reaction rate of H_2S and O_2 to elemental sulphur over synthetic faujasite zeolites has been determined by measuring the rate of sulphur accumulation on the zeolite with a microbalance apparatus. At reaction temperatures between 120 and 200 °C desorption of sulphur can be neglected and simultaneous adsorption of water, which is the other reaction product, has only little influence on the rate of weight increase. By mass transfer experiments it has been determined that the rate of the H_2S oxidation over NaY zeolites could be measured without substantial mass transfer limitations. On the other hand, an NaX zeolite with an Si/Al ratio of 1.15 appeared to be too active to prevent concentration and temperature gradients.

Although the zeolite framework is practically identical for all the zeolites, the maximum sulphur adsorption capacity is rather different. The zeolites with an Si/Al ratio of at least 1.70, i.e. the NaY type zeolites, may adsorb up to about 0.42 kg sulphur per kg (dehydrated) zeolite, whereas the NaX zeolite having an Si/Al ratio of 1.15, adsorbs only about 0.27 kg sulphur per kg zeolite.

The rate constant of the oxidation of H_2S has about the same activation energy for the three NaY zeolites we tested, viz. about 53 $kJ\ mol^{-1}$, irrespective of the sulphur load of the zeolite. On the other hand, substantial differences in the rate of the H_2S oxidation over the different zeolites are observed. NaY zeolites with a lower Si/Al ratio, i.e. a higher aluminum and, accordingly, a higher cation content, show a higher activity.

It is suggested that the increased reaction rate of the zeolites with a higher aluminum content is related to a higher concentration of reactive sites on the zeolite material. We assumed that the active sites can be identified with the places where according to other workers [17,18] a dissociative adsorption of H_2S molecules takes place. A linear relationship was found between the reaction rate of the H_2S oxidation and the concentration of these H_2S adsorption sites.

Sulphur adsorbed on NaX and NaY zeolites in the course of the oxidation of H_2S, desorbs to a large extent from the zeolite at temperatures around 300 °C. Eventually, at least 90 weight per cent of the maximum sulphur load can be removed from the zeolite.

By mass transfer calculations we have determined the sulphur vapour pressure at the surface of the zeolite layer on the sample pan. It was found that the lowest relative sulphur pressure occurs over the NaX(1.15) zeolite and that the vapour pressure is increasing with increasing Si/Al ratio. Since no substantial vapour pressure gradients inside the zeolite sample are expected, it can be concluded that NaX zeolite is adsorbing sulphur relatively stronger than NaY zeolite. Generally, the relative sulphur pressure is always well below 10^{-2}, except for sulphur loads approaching the maximum sulphur adsorption capacity closely.

In spite of the lower sulphur adsorption capacity, the NaX zeolite is preferable as a catalyst in the oxidation of H_2S to elemental sulphur when the sulphur has to be removed in an adsorbed state, because of the higher activity and the lower relative vapour pressure of sulphur. Therefore, NaX zeolite was selected as the active catalyst in the subsequent process development work, described elsewhere [27], on a dry desulphurization process for gases containing low concentrations of H_2S.

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NOTATION

A	surface area of the catalyst bed	m^2
c	concentration	$mol\ m^{-3}$
$\bar{c}$	bulk concentration	$mol\ m^{-3}$
d	diameter of sample pan	m
D	diffusion coefficient	$m^2\ s^{-1}$
E	activation energy	$kJ\ mol^{-1}$
ΔH_r	enthalpy of reaction	$kJ\ mol^{-1}$
k_m	mass transfer coefficient	$m\ s^{-1}$
k_r	reaction rate constant	s^{-1}
k_o	frequency factor of the rate constant	s^{-1}
M_S, M_{S_8}	molecular weight of atomic and octatomic sulphur respectively	$kg\ mol^{-1}$
n_{Na^+}	Na^+ ion concentration, see eq. 4	(unit cell)$^{-1}$
P	partial pressure	Nm^{-2}
$P_{S,o}$	sulphur vapour pressure of liquid sulphur	Nm^{-2}
r_{H_2S}, r_{O_2}	reaction rate	$mol\ m^{-3}\ s^{-1}$
r_S	rate of sulphur formation	$kg\ S\ m^{-3}\ s^{-1}$
R	gas constant	$kJ\ mol^{-1}\ K^{-1}$
Re	Reynolds number	-
Sc	Schmidt number	-
Sh	Sherwood number	-
t	time	s
$T, \Delta T$	temperature, temperature increase	°C
T_o	reference temperature, eq. A12	K

v	gas velocity	$m\ s^{-1}$
V	volume	m^3
W	weight	kg
W_o	weight of dry catalyst sample	kg
X_S	sulphur load	kg S(kg zeolite)$^{-1}$
α	heat transfer coefficient	$W\ m^{-2}\ °C^{-1}$
η_g	viscosity of gas	$N\ s\ m^{-2}$
λ	thermal conductivity of gas	$W\ m^{-1}\ °C^{-1}$
ϕ''_h	heat flux	$kW\ m^{-2}$
ϕ''_m	mass flux	$mol\ m^{-2}\ s^{-1}$
ϕ	Thiele modulus	-
ρ_g	density of gas	$kg\ m^{-3}$
ρ	density of zeolite particle	$kg\ m^{-3}$

Subscripts

eff	effective
i	at the interface

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