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The Specific Catalytic Activity of Sodium Faujasites in H_2S Oxidation

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The H_2S oxidation reaction with molecular oxygen on sodium faujasites was investigated in a flow system within the temperature range 0–300°C and using ESR and UV methods. Elemental sulfur is the primary product, but at temperatures above 20°C substantial amounts of SO_2 were observed in the reaction products. At higher temperatures (70–300°C) NaY is distinctly more active than NaX. The specific high catalytic of sodium faujasites in the H_2S oxidation reaction was observed. This activity is due to the generation of the zeolite surface of radicals such as $\cdot S_x\cdot$, $HS_x\cdot$, $O_2\cdot^-$, $SO_2\cdot^-$, $SO_3\cdot^-$, and $H_2S_2\cdot^-$. These species take part in the reaction as intermediate compounds, and their concentrations strongly influence the reaction rate. On the basis of the results of kinetic and catalytic experiments and literature data, hypotheses concerning some initial reaction steps are presented and discussed.

INTRODUCTION

The reaction of hydrogen sulfide and oxygen to form elemental sulfur and water is known to respond to many different catalysts. The most common catalysts are silica gels, silicates (mainly Fe), activated carbon, alkali and alkaline earth metals, oxides and sulfides, and especially catalysts derived from aluminum oxide or natural bauxite (*1*, *2*).

The oxidation reaction of H_2S on these catalysts in a dynamic system proceeds at relatively high temperatures, mainly within the range of 250–400°C. Using a static system and special reaction conditions (efficient outgassing of the samples, low or relatively low pressures of H_2S), Deo *et al.* (*3*) observed the oxidation of H_2S at room temperature on γ-alumina and zeolite NaY, and Slager and Amberg (*4*) made similar studies on η- and γ-alumina. Kerr and Johnson (*5*), while passing gaseous hydrogen sulfide over a powdered 13X molecular sieve in air at room temperature, observed free sulfur deposited on the catalyst surface. One of us (*6*) investigated the oxidation of H_2S to elemental sulfur in a static system on NaX (Linde 13X) zeolite and observed that this reaction occurs even at −80°C. Immediately after admission of O_2 at −80°C to activated NaX zeolite containing H_2S adsorbed at room temperature, the sample became strongly paramagnetic and the ESR spectrum showed the presence of sulfur biradicals $\cdot S-(S)_x-S\cdot$. The sulfur–, oxygen–, and sulfur–oxygen radicals taking part in the H_2S oxidation reaction as intermediate compounds have been identified and described in earlier papers (*7*, *8*).

The mechanism of the catalytic oxidation of H_2S was investigated also by Steijns *et al.* (*9–11*). These authors concluded that the catalytically active phase in this process is liquid sulfur which may be deposited on

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different matrices. They proposed a redox model for this process in which the reaction between oxygen molecules and deposited sulfur is the oxidation stage, and the reaction between dissociatively adsorbed H_2S and chemisorbed oxygen is the reduction stage.

The aim of this paper is to synthesize the former (*7*, *8*) and the new results and to present on the basis of ESR and catalytic experiments some proposals concerning the initial steps of the H_2S oxidation reaction with molecular oxygen on sodium faujasites.

EXPERIMENTAL

The continuous flow technique was used for the measurements of catalytic activity. The U-shaped Pyrex glass reactor (i.d., 12 mm; total volume, 24 ml) fitted with Teflon stopcocks and containing 1.1 g of zeolite in dehydrated form was mounted in an ultrathermostat (for experiments carried out in the temperature range 0–200°C) or in an electric furnace (200–300°C). A 37-ml/min gas flow containing 2.7% vol of H_2S and different amounts of O_2 and N_2 passed through the reactor to a gas chromatographic assembly. The O_2:H_2S ratio was 1:1, or 7.5:1. A 70-cm glass column (i.d., 4 mm) containing Porapak Q, 120–150 mesh at 80°C, served to separate the products (carrier gas, N_2; 40 ml/min), which were subsequently detected and measured by a flame photometric detector (Jeol JGC-1100 FPD) and amplifier. H_2S was Fluka research grade. NaX was Linde 13X Lot No. 1360027 and NaY was Linde SK-40 Lot No. 3606411, both supplied in powder form. In the ESR experiments the zeolites were used in powder form, activated under a 10^{-4}-Torr vacuum at 350°C for 3 hr. In the kinetic experiments the zeolite crystallites were tableted under pressure, ground, sieved to the 1- to 1.5-mm diameter range and activated in flowing helium at 350°C for 4 hr.

The ESR spectra were obtained with a Varian T-line spectrometer and accessories, and uv spectra with a Unicam SP-700 spectrometer.

RESULTS

Hydrogen sulfide was oxidized at 70 and 300°C with molecular oxygen on NaX zeolite and on sodium silica–alumina obtained from the full collapse of the zeolite structure after 12 hr of heating of the NaX zeolite at 920°C. The O_2:H_2S ratio was 7.5:1. Results presented in Fig. 1 indicate the strong influence of the faujasite structure on this reaction when conducted at 70°C.

The H_2S oxidation reaction on NaX and NaY zeolites was carried out at an O_2:H_2S ratio of 7.5:1 at temperatures 0, 20, 70, 140, 185, 230, 270, and 300°C. H_2S was oxidized to elemental sulfur, partially in the paramagnetic form (sulfur chain radicals: $\cdot S_x \cdot$, $HS_x\cdot$), SO_2, also partially in the paramagnetic form ($SO_2\cdot^-$), and water. H_2S_n and H_2SO_3 are also present in the reaction products. As reaction intermediates, we identified $SO_3\cdot^-$, $O_2\cdot^-$, and $H_2S_2\cdot^-$. The details of various identifications are given below.

The ultraviolet spectra of all the samples of the NaX zeolite used as catalysts in H_2S oxidation reaction were subsequently measured. The spectra of these samples used in reactions carried out at an O_2:H_2S ratio equal to 7.5:1 in the temperature range 0–300°C, showed strong absorbance in the 200- to 400-nm region (Fig. 2a). Comparing these spectra with the spectra obtained by Feher and Munzer (*12*) and utilizing the results of the Hückel calculations of Meyer and Spitzer (*12*), we attribute this absorbance to the H_2S_n-type species. Only the sample used in the reaction conducted at 185°C at an O_2:H_2S ratio equal to 1:1 had a spectrum with a distinct peak with a maximum at ~315 nm (Fig. 2b). This peak was attributed to sulfur rings (*12*).

In Fig. 3 are plotted the amounts of H_2S removed from the flow and amounts of H_2S oxidized to SO_2 (all data obtained at the stationary state) vs temperature. In the

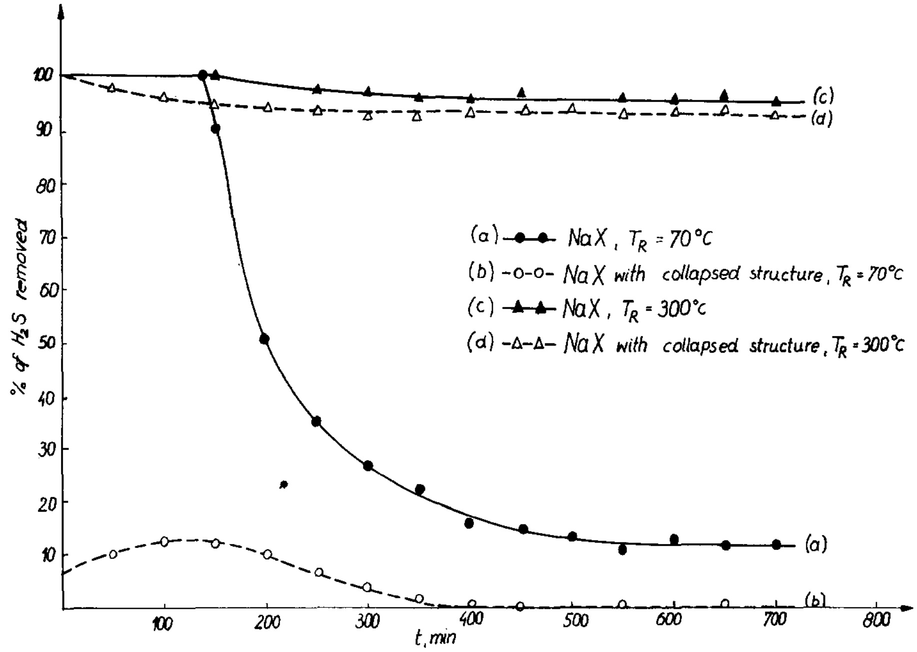

FIG. 1. Faujasite structure influence on H_2S conversion.

temperature region 0–70°C the catalytic activities of NaX and NaY zeolites at the stationary state are almost the same. At temperatures higher than 70°C the silica-rich faujasite (NaY) is more active.

At 0 and 20°C, SO_2 was not observed in reaction products. In the temperature region 70–185°C on both NaX and NaY zeolites all H_2S converted at the stationary state is oxidized to SO_2.

In the temperature region 185–270°C substantial amounts of elemental sulfur were formed. Again, at 300°C, nearly all H_2S converted is oxidized to SO_2.

Investigations of the excess oxygen influence at a 70°C reaction temperature proved that the reaction rate decreases with an increase of the $O_2:H_2S$ ratio (Fig. 4, curves a and b). At 300°C we observed a different picture. The increase in $O_2:H_2S$ ratio causes a moderate increase in reaction rate (Fig. 4, curves c and d). On NaY, the influence of excess oxygen is much smaller at 70°C (Fig. 5).

Results of ESR investigations of the H_2S oxidation reaction conducted in a static system are presented in Figs. 6 and 7. ESR measurements were carried out at liquid nitrogen temperature.

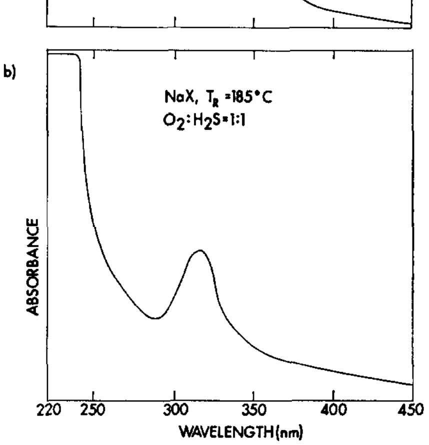

FIG. 2. The uv spectra of NaX samples used as catalysts in the $H_2S + O_2$ reaction.

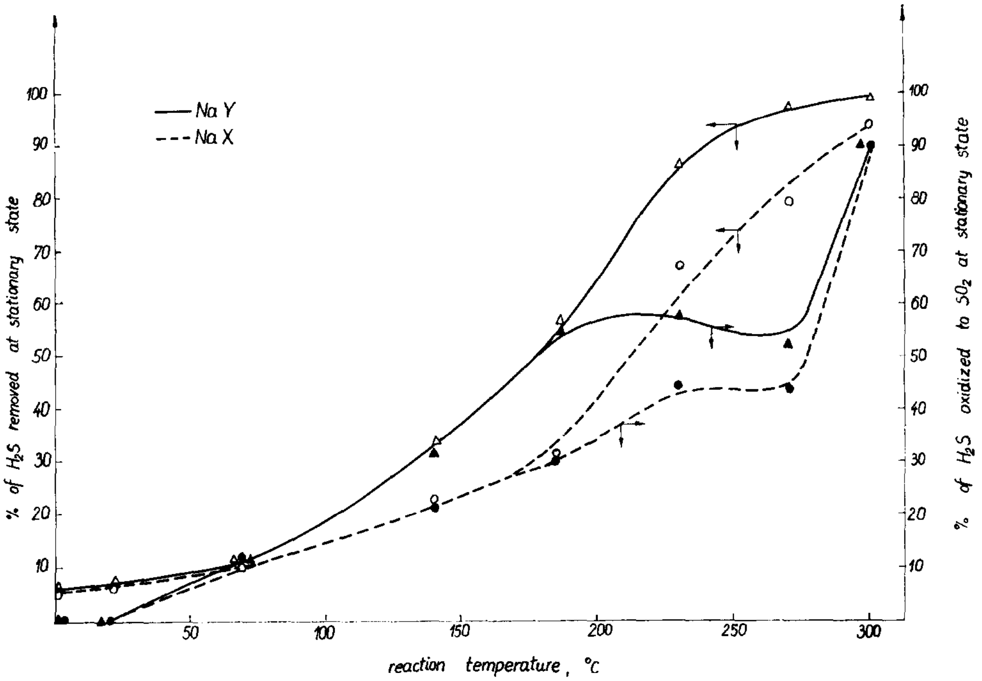

FIG. 3. Catalytic activity of NaX and NaY zeolites in the H_2S oxidation reaction. O_2:H_2S = 7.5:1.

After H_2S adsorption on NaX at room temperature no ESR signal was observed. The spectrum shown in Fig. 6, curve a was detected immediately after admission of H_2S and O_2 (ratio 1:2) to activated NaX at room temperature. This spectrum shows

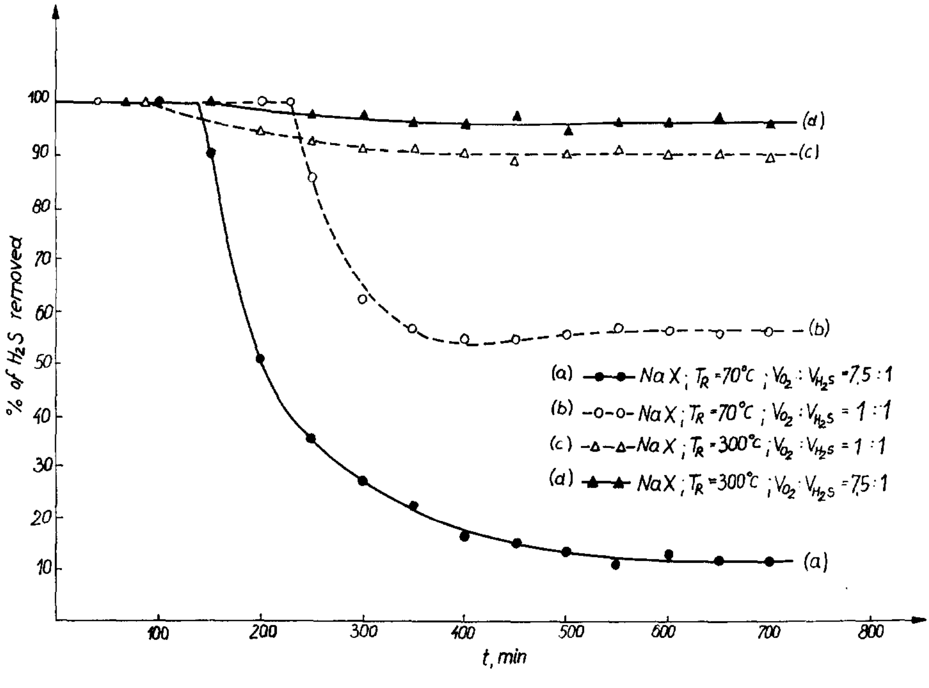

FIG. 4. The influence of excess oxygen on the H_2S conversion on NaX.

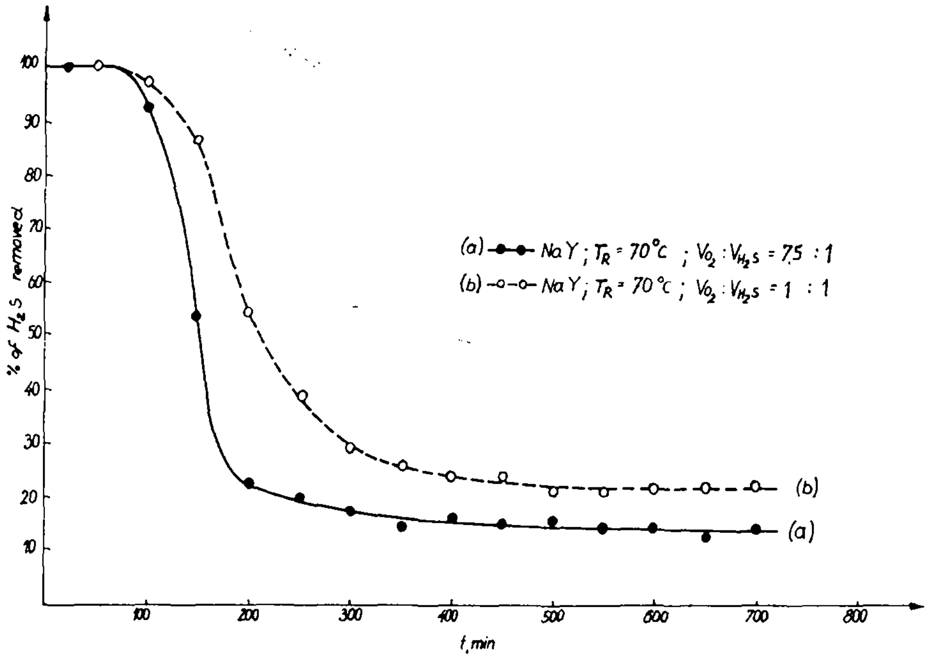

FIG. 5. The influence of excess oxygen on the H_2S conversion of NaY.

the presence of $\cdot S_x \cdot$ or $HS_x \cdot$ radicals (a triplet characterized by the g factors 2.0525, 2.0325, and 2.002) (*13*) and small amounts of $O_2\cdot^-$ radicals (g factors = 2.083, 2.007, and 2.002) (*14*). After admission at room temperature of additional oxygen up to 300 Torr and heating the sample to 150°C, no changes in signal shape and intensity were observed. Only when the sample was heated in oxygen at 230°C did the intensity of the signal of the sulfur-chain radicals substantially decrease, and a new strong signal characterized by a g factor of 2.0039 due to $SO_3\cdot^-$ appeared (Figure 6, curve b). Subsequent evacuation of the sample and heating to 330°C for 3 hr caused the disappearance of the $SO_3\cdot^-$ signal and formation of a new signal with g factors 2.0097, 2.0054 and 2.0017 (Fig. 6, curve c). This signal is identical with the signal obtained after admission of SO_2 at room temperature to activated NaX zeolite and is due to the presence of $SO_2\cdot^-$ ion-radicals (*8*). The $SO_2\cdot^-$ radicals generated on decationated Y zeolite have been investigated by Ono *et al.* (*15*). They observed two types of these radicals: One gives an ESR signal with $g_{\parallel} = 2.008$ and $g_{\perp} = 2.002$, is unstable at temperatures greater than 300°C, and reacts with oxygen at 200°C; the other gives an ESR signal with $g_{\parallel} = 2.010$ and $g_{\perp} = 2.002$, is stable up to 500°C, and does not interact with oxygen. Our spectrum (Figure 6, curve c) resembles the latter, and the signal does not change after heating under vacuum at 330°C for 3 hr.

Investigating the role of $O_2\cdot^-$ radicals in H_2S oxidation on NaX zeolite, we admitted oxygen to activated NaX samples and irradiated them with γ rays. In this way, $O_2\cdot^-$ radicals were generated on the zeolite surface (*16*). Thirty minutes after admission of H_2S to the sample containing $O_2\cdot^-$ at −196°C, we observed an ESR signal with $g_{\perp} = 2.014$ and $g_{\parallel} = 2.002$ (Fig. 7). This signal, attributed to $H_2S_2\cdot^-$ ion-radicals, is nearly identical with the signal described by Lin and Lunsford (*17*). They obtained it after admission of H_2S to MgO irradiated in hydrogen.

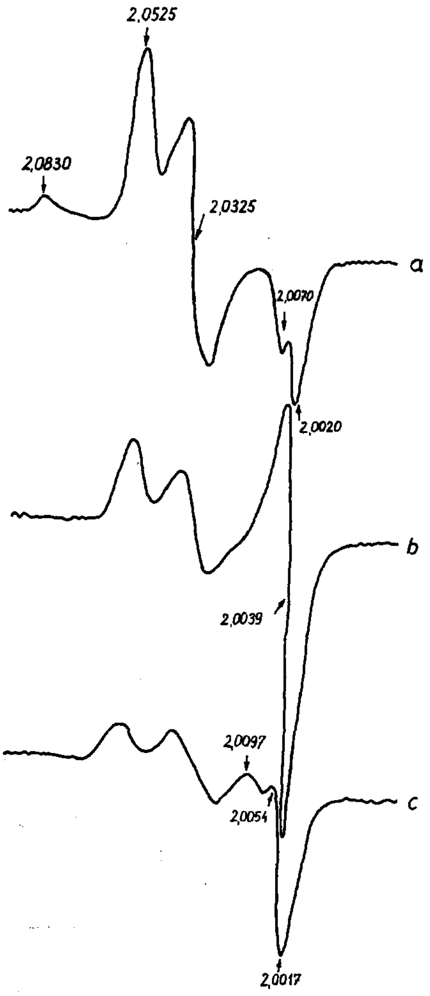

FIG. 6. ESR spectra of the radial intermediates of H_2S oxidation reaction on NaX. (a) H_2S and O_2 (1:2) admitted at room temperature; (b) additional O_2 admitted, heating up to 230°C; (c) sample evacuated, heated at 330°C.

DISCUSSION

In the first stage of H_2S oxidation on sodium faujasites before reaching stationary state the zeolite is acting simultaneously as an adsorbent and catalyst. When the stationary state is reached, physical adsorption no longer contributes to the removal of H_2S from the flow, and the percentage of H_2S removed is equivalent to the percentage of H_2S converted.

Sodium faujasites show a specific catalytic activity for the oxidation of H_2S particularly at lower temperatures. At temperatures higher than 250°C the reaction proceeds very easily, and the influence of the faujasite structure is diminished. This is illustrated in Fig. 1. At the reaction temperature of 70°C there is a very distinct difference between the catalytic activity of NaX zeolite and the activity of the collapsed NaX. On sodium silica–alumina such as this, there is no H_2S conversion at 70°C (Fig. 1, curve b). The small amounts of H_2S removed from the flow during the first 6 hr are merely adsorbed. At 300°C the amounts of H_2S oxidized are practically the same on both catalysts.

In the 0–70°C temperature region the main products of the H_2S oxidation on sodium faujasites are elemental sulfur, water, and (at temperatures higher than 20°C) SO_2. Nearly all S_{el} and substantial amounts of water remain in the zeolite cavities blocking centers active in this reaction. This may be the explanation for the observed equal catalytic activity of NaX and NaY in this temperature region.

At higher temperatures the reaction products are partially or fully removed from the zeolite cavities and then NaY is distinctly more active (Fig. 3). In the 70–185°C region the desorption of sulfur from zeolite cavities is still slow. Therefore most of the elemental sulfur which originated on the zeolite surface as the primary product of H_2S oxidation is subsequently catalytically oxidized to SO_2.

In the region 185–270°C sulfur leaves the zeolite surface quite rapidly, and at this temperature the noncatalytic oxidation of sulfur had not yet occurred. Therefore in the reaction products we observed both elemental sulfur and SO_2.

At 300°C sulfur is oxidized catalytically (on the zeolite surface) and noncatalytically (in the reactor volume) to SO_2. Therefore SO_2 predominates again in the reaction products. Steijns *et al.* (*10*) observed SO_2 in the reaction products only a temperatures higher than 200°C. They postulated that

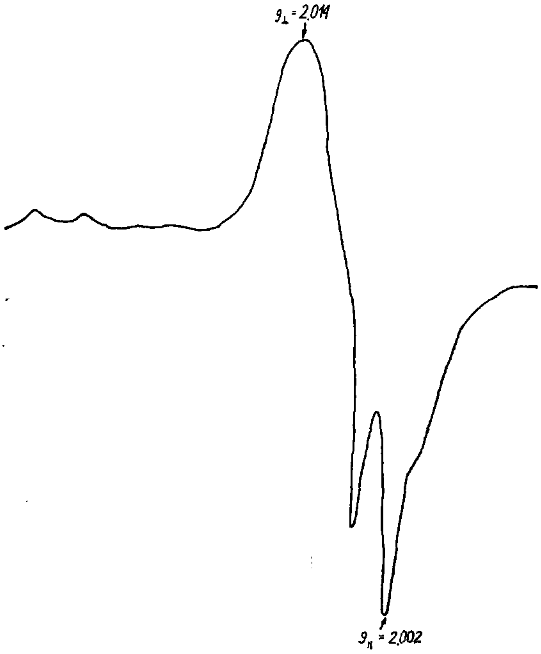

FIG. 7. The ESR spectrum obtained after admission of H_2S at −196°C to NaX zeolite irradiated in presence of O_2.

in the temperature region 100–200°C the formation rate of SO_2 is at least a factor 100 smaller than the oxidation rate of H_2S. We observed substantial amounts of SO_2 even at 70°C, and in the region 100–200°C SO_2 was the main reaction product. The formation of SO_2 and H_2S conversion depend strongly on reaction conditions. In the experiments summarized in Fig. 3 we used a large excess of oxygen ($O_2:H_2S = 7.5:1$) and a relatively long contact time. When we used a contact time approximately five times shorter (a 200-ml/min gas flow and the same amounts of H_2S and O_2 as previously), the H_2S conversion on NaX at 70°C was distinctly higher than the H_2S conversion on NaY at 185°C.

The differences in catalytic activity between NaX and NaY zeolites, i.e., zeolites which have the same structure and differ only in Si/Al ratio and in amounts of Na^+ cations per unit cell, can be explained in terms of different types of H_2S chemisorption. Karge and Rasco (*18*) used ir spectroscopy for investigations of H_2S chemisorption on faujasite-type zeolites. They found that on the alumina-rich faujasites (type X) heterolytic dissociative chemisorption occurs:

$$H_2S_{ads} \rightarrow HS^- + H^+,$$

H^+ forming a surface hydroxyl with the lattice oxygen. The amount of H_2S dissociated in this manner decreases with increasing Si/Al ratio, and on NaY the bands due to formation of HS^- and surface hydroxyls were not observed.

Imai and Habgood (*14*) observed, after H_2S adsorption at room temperature on silica-rich faujasite-type zeolite (NaY) activated and treated with H_2, an ESR spectrum which showed on orthorhombic *g*-tensor and which had hyperfine splitting due to an H atom. Consequently, we presume that on NaY another type of dissociative chemisorption may occur:

$$H_2S_{ads} \rightarrow HS\cdot + H\cdot$$

Conducting the H_2S oxidation reaction on NaX at 70°C, we observed a rather unusual effect. The high excess of oxygen distinctly lowered the reaction rate. The excess of oxygen influence is not clear yet. Probably it lowers the concentration of the active radical-type reaction intermediates and increases the amount of species (e.g., SO_3^-) blocking surface active centers. On NaY zeolite the negative influence of excess oxygen is not so distinct (Fig. 5).

During the initial stage of $H_2S + O_2$ reaction H_2S is oxidized to elemental sulfur. We did not observe SO_2 in the reaction products for a long time from the beginning of the reaction at $O_2:H_2S = 1:1$ (at 70°C, for 240 min; at 185°C, for 60 min) (*8*). Karge and Rasco (*18*) did not observe SO_2 in ir spectra after adsorption of H_2S and O_2 on NaX zeolite and heating the sample up to 400°C. On the basis of kinetic studies Steijns *et al.* (*11*) concluded that the primary reaction product is sulfur.

All the results discussed above suggest that on sodium faujasites H_2S is oxidized first to elemental sulfur and subsequently sulfur is oxidized to SO_2. On these catalysts the H_2S oxidation proceeds in a different way than was postulated for bauxite-type catalysts (*1*), i.e., H_2S oxidation to SO_2 and formation of elemental sulfur in the Claus reaction ($H_2S + SO_2$).

Sulfur dioxide formed in faujasite cavities from the oxidation of elemental sulfur is chemisorbed with the formation of an SO_3 complex (one oxygen of this complex belongs to the zeolite lattice), and after electron addition the ion-radical $SO_3\cdot^-$ is formed (Fig. 6, curve b). The nature of the electron-donor centers is still not clear. They may be Fe^{2+} impurities, lattice defects, or anion-type reaction intermediates. The strong signal of $SO_2\cdot^-$ obtained after adsorption of SO_2 on NaX even at room temperature (*8*) indicates that at the faujasite surface electrons are available.

Steijns *et al.* (*11*) postulate an oxidation–reduction mechanism for the oxidation reaction of H_2S on NaX zeolite. In this proposed mechanism there is first the oxidation step:

$$\cdot S - (S)_{x-2} - S\cdot + O_2 \rightarrow [S_xO_2]$$

The second step in the mechanism is the reduction of $[S_xO_2]$ with H_2S yielding sulfur and water (the equation was not written). This mechanism is based mainly on two observations:

(i) Sulfur chain radicals were detected in the ESR spectra of activated NaX zeolite after admission of H_2S at 150°C in N_2 flow. But, as Steijns *et al.* mention, the activation procedure used may still allow some oxygen species to exist on the zeolite surface. Other authors (*18*, *20*), and we ourselves, did not detect the elemental sulfur after H_2S adsorption on sodium faujasites in the complete absence of oxygen at temperatures up to 300°C.

(ii) Steijns *et al.* observed that after admission of a nitrogen–oxygen mixture at 150°C to a NaX zeolite containing sulfur, the intensity of the paramagnetic sulfur signal ($g = 2.028$) became smaller by a factor of 20. Two minor signals appeared which were attributed to $S_xO_2\cdot^-$ ($g = 2.005$) and $S_xO\cdot^-$ ($g = 2.013$). A signal with $g = 2.005$ was observed also after admission of SO_2 to NaX zeolite. It is our opinion, however, that the generation of $S_xO_2\cdot^-$ radicals after SO_2 sorption is not very probable. ESR investigations of SO_2 adsorption on faujasite-type zeolites (*8*, *15*) proved that in this process $SO_2\cdot^-$ ion-radicals are formed. We presume that the mechanism of H_2S oxidation with molecular oxygen on NaX, especially at the initial stage of the reaction, is more complicated. At the beginning of the reaction there is no elemental sulfur present on the zeolite surface. The reaction has to start from the interaction between adsorbed reactants. As was mentioned before (*18*, *20*), on NaX zeolite, the H_2S is chemisorbed dissociatively:

$$H_2S_{ads} \rightarrow HS^- + H^+, \qquad (1)$$

and the proton will form a hydroxyl with the lattice oxygen. Oxygen is adsorbed on Na^+ cations and it was found that O_2 molecules so adsorbed trap electrons very efficiently, giving rise to an ESR signal characteristic of the superoxide ion $O_2\cdot^-$ (*14*, *19*). Therefore if the Na^+ O–O electron trap and HS^- are in close proximity, the following reaction may occur:

$$HS^- + O_{2\text{ads}}(Na^+) \rightarrow HS\cdot + O_2\cdot^-(Na^+). \quad (2)$$

Takahashi (*21*) suggested that the most probable reaction of HS·radicals is:

$$2HS\cdot \rightarrow H_2S + \cdot S\cdot. \quad (3)$$

Also very probable are two other reactions of HS·:

$$2HS\cdot \rightarrow HSSH \quad (4)$$

$$HS\cdot + HS^- \rightarrow H_2S_2\cdot^- \quad (5)$$

Both intermediates were observed by us, H_2S_2 by uv spectra and $H_2S_2\cdot^-$ by ESR spectra (Figs. 2 and 7). $H_2S_2\cdot^-$ ought to react with oxygen:

$$H_2S_2\cdot^- + O_2 \rightarrow H_2S_2 + O_2\cdot^-. \quad (6)$$

We observed all these reaction intermediates except HS·. The difficulties with HS· indentification are probably connected with some similarity of this spectrum with the spectrum of sulfur chain radicals ($HS_x\cdot$ or $\cdot S_x\cdot$). This latter signal is one or a few orders of magnitude stronger during the H_2S oxidation reaction.

The reaction steps leading to formation of water are still only hypothetical. One possible way is the reaction between $O_2\cdot^-$ and physically adsorbed H_2S:

$$H_2S_{\text{ads}} + O_2\cdot^- \rightarrow HS\cdot + HOO^-. \quad (7)$$

This reaction step is very probable. Lunsford (*22*) reported that the $O_2\cdot^-$ radical easily takes a hydrogen atom from olefin molecules. The C–H bond energy in olefins ($\simeq$359 kJ/mol) is higher than the energy of the H–S bond in H_2S ($\simeq$343 kJ/mol). Even more probable is the reaction:

$$H_2S_2 + O_2\cdot^- \rightarrow HSS\cdot + HOO^-. \quad (8)$$

The HOO^- ions may react with H^+ supplied by surface hydroxyls [Eq. (1)]:

$$HOO^- + H^+ \rightarrow H_2O_2. \quad (9)$$

Samples of NaX and NaY, fresh and after 12 hr reaction time, have been tested for acidity using a titration method. We did not observe any appreciable changes in sample acidity before and after the H_2S oxidation reaction. Therefore some reaction step involving proton addition is obvious. The H_2O_2 will easily decompose

$$H_2O_2 \rightarrow H_2O + O, \quad (10)$$

and atomic oxygen will oxidize next the H_2S molecule.

The H_2S oxidation reaction on NaY will start differently. Probably the HS· radicals are formed after H_2S adsorption.

The considerable number of radicals, ion-radicals, and ions identified so far as intermediates in the H_2S oxidation reaction on sodium faujasites indicates that the mechanism of this reaction is rather complicated. Additional investigations involving ESR, ir, and uv measurements are necessary to elaborate the complete reaction mechanism.

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