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Catalytic Oxidation of Hydrogen Sulfide on Polynaphthoquinone

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The catalytic oxidation of H_2S was studied on a polynaphthoquinone in both a closed circulating system and a usual flow system in the temperature range 45–200°C. H_2S was rapidly decomposed to elemental sulfur in the presence of O_2. One atom of the product sulfur per quinone group had almost no effect on the catalytic activity while two atoms of sulfur per quinone group as the activie site markedly decreased the reactivity of the quinone group in the polynaphthoquinone. H_2S oxidation attained a steady state conversion of about 40% at 200°C. The polynaphthoquinone has been demonstrated to have a relatively well-defined surface with highly distributed quinone groups as active sites. H_2S molecule behaved as a good hydrogen donor to the quinone group, while oxygen acted as a hydrogen acceptor for the hydroquinone group. H_2S was catalytically oxidized by two successive hydrogen transfer reactions in conjunction with the redox cycle of quinone group active sites. The polynaphthoquinone was shown to have not only a favorable structure for pulling two hydrogen atoms from H_2S but also a highly conjugated π-electron system which may electronically promote the hydrogen transfer reaction.

INTRODUCTION

The desulfurization of waste gases is a major problem which remains to be solved from the point of view of air pollution as well as being of chemical interest catalytically. In the last two decades the removal of sulfur-containing compounds, especially hydrogen sulfide, in dry and wet systems has been extensively studied from various standpoints. Hydrogen sulfide is known to be adsorbed in the pores of materials as active carbons, zeolites, alumina, silica, etc. (*1*). In some cases the adsorption mainly depends upon the porosity of adsorbents (*2*). The adsorption of H_2S by these porous materials is one of the easiest methods for removing H_2S from effluent gases. However, its catalytic removal may be chemically more interesting. Industrially H_2S is oxidized to elemental sulfur by the Clauss process, $H_2S + \frac{3}{2} O_2 \rightleftharpoons SO_2 + H_2O$, $2 H_2S + SO_2 \rightleftharpoons 3 S + 2 H_2O$. Most adsorbents like active carbons (*3, 4*), molecular sieves (*4, 5*), alumina (*6*), etc., for example (*7*), also work as catalysts for oxidation of H_2S by O_2. Obscure mechanisms have been proposed for the reactions over these catalysts, especially on active carbons. Little attention has been paid to the dynamical state at active sites of catalysts during the course of the reactions. Less fruitful models for mechanisms seem to be derived from ill-defined active sites whose chemical state for a given catalyst may be changed by the reaction conditions or by impurities contained in the catalysts. It is still not understood why these catalysts are active in the decomposition of H_2S. Only selected catalysts having well-defined surface sites may be suitable for the investigation of the behavior of both admolecules on the catalysts and these sites.

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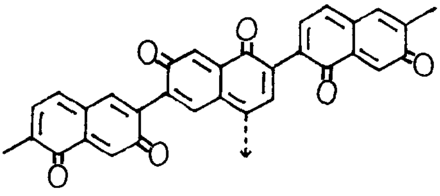
It has been demonstrated (*8*) that polynaphthoquinone has a relatively well-defined surface with uniformly distributed active sites. Polynaphthoquinone which is a porous, insoluble and thermostable quinone polymer, has been found to be a highly active catalyst for the dehydrogenations of many substrates (*9*). The quinone groups of the catalyst function as active sites where the oxidative dehydrogenations take place in conjunction with the redox cycle of each active sites. It was also found (*10, 11*) that catalytic hydrogen transfer reactions between both hydrogen donating and accepting compounds take place on polynaphthoquinone. The oxidation of H_2S, as the hydrogen donor, by O_2 was studied as an application of this hydrogen transfer system in connection with desulfurization of waste gases (*11*). In the present study a detailed discussion is given of the oxidation of H_2S on the polynaphthoquinone in connection with the behavior of active sites.



where the arrow implies partial cross-linkage.

EXPERIMENTAL METHODS

The decomposition of H_2S by oxygen was carried out in the temperature range 45–81°C in a glass-closed circulating system (185 cm^3) using 0.3 g of a polynaphthoquinone catalyst. The decomposition in a closed circulating system was always investigated in a mixture of H_2S and O_2 in the presence of N_2 as a diluent. The given pressures of H_2S, O_2 and N_2 were mixed in the preliminary circulating system prior to each run. The decomposition of H_2S by O_2 to form elemental sulfur over 0.5–1 g of a polynaphthoquinone was also studied in an ordinary flow system in the temperature range 30–200°C.

The adsorption of H_2S on the polynaphthoquinone was volumetrically measured in the same closed system as that used for the reaction, taking account of the adsorption of H_2S by the apparatus, in the temperature range 45–72°C.

The polynaphthoquinone used as a catalyst was obtained from 1,7-naphthalenediol by a similar procedure to that previously described (*8, 9*). 1,7-Naphthalenediol was purified by recrystallization from an ethanol–acetone–water solvent mixture. The polynaphthoquinone was heated at 340°C for 3 hr in a flow of nitrogen or treated at 340°C for 3 hr in vacuum before use as a catalyst.

The polynaphthoquinone thus obtained was suggested to be a planar molecule by transmission electron microscopy (*12*). This polymer is tightly aggregated to form a porous insoluble polynaphthoquinone catalyst which has a surface area of 73 ± 5 m^2/g. The TGA and DTA curves (*12*) (the rate of temperature promotion: 5°C/min) of polynaphthoquinone show that this polymeric quinone-type catalyst is a very thermostable organic polymer which does not decompose in a flow of nitrogen until 450°C.

H_2S with 99.5% purity was used without further purification. Oxygen, air and nitrogen gases were supplied to the reaction system through silica gel cooled with a dry ice-methanol trap.

All the reaction products were quantitatively analyzed by gas chromatography using a column of 5 m dioctyl phthalate (on Celite 454) at 95°C for H_2S, H_2O, SO_2, and O_2 (or $O_2 + N_2$). The same column was also used at 35°C to detect the formation of CO_2. O_2 in ambient gases during the oxidation of H_2S was analyzed by a 5A molecular sieve column after removing H_2S and H_2O by a liq. N_2 trap.

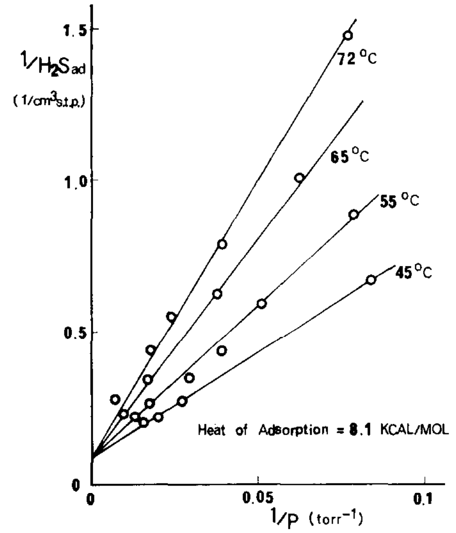


FIG 1. Linear Langmuir plots of the adsorption of H_2S on 0.3 g of polynaphthoquinone.

The gas products were also identified by ir spectroscopy.

RESULTS

Adsorption of H_2S

The adsorption of H_2S on 0.3 g of polynaphthoquinone was studied under the same condition as the reaction in the closed circulating system (185 cm^3) in the temperature range 45–72°C. The volumes of the reversible H_2S adsorption were determined by manometry, taking account of the adsorption by the apparatus itself. The H_2S adsorption on the polynaphthoquinone was very rapid and the adsorption was almost complete within 5 min, more than 90% of the adsorption occurring within 3 min. Under these conditions the change of the pressure by the H_2S adsorption on a catalyst can be distinguished from the pressure change accompanying the decomposition. The effect of O_2 present in the system on the adsorbed amount of H_2S was negligible although the H_2S adsorption was slightly increased by the presence of O_2. The Langmuir plots for the results at various temperatures are given in Fig. 1 which indicates that the H_2S adsorption on the polynaphthoquinone is of Langmuir type. The adsorbed amount, $(H_2S)_{ad}$, may accordingly be expressed as the function of the saturation mass of adsorption (b) and the equilibrium constant of adsorption (K) under certain ambient pressure of H_2S (P) by the following equation; $(H_2S)_{ad} = bKP/(1 + KP)$. The saturation mass was independent of temperature in Fig. 1. Its value was calculated from the Langmuir plots to be 37.4 cm^3 STP/g-cat. and the isosteric heat of adsorption was determined to be 8.1 kcal/mol.

The Oxidation of H_2S in a Closed Circulating System

H_2S was decomposed to produce elemental sulfur on the polynaphthoquinone

TABLE 1

The Oxidation of H_2S by O_2 on 0.3 g of Polynaphthoquinone[a]

$(H_2S)_0$ (Torr)	$(O_2)_0$ (Torr)	Temp (°C)	$\Delta(H_2S)$[b] (cm^3 STP)	$\Delta(O_2)$[b] (cm^3 STP)	$\frac{\Delta(H_2S)}{\Delta(O_2)}$
49.2	37.4	45	0.45	0.22	2.0_4
125.8	32.5	45	0.78	0.38	2.0_5
65.9	22.0	55	1.00	0.50	2.0_0
25.6	26.0	65	0.51	0.25	2.0_4
73.2	19.4	72	1.59	0.80	1.9_9

[a] The Amounts of H_2O and O_2 used in 20 min.

[b] *Vol of reactants consumed.*

in the presence of O_2 in the temperature range 45–81°C. N_2 was employed as a diluent gas since the oxidation of H_2S with O_2 is a highly exothermic reaction. The reaction was always carried out in the presence of 200 Torr of N_2. N_2 pressure in the range 100–450 Torr has no effect on the rate of the reaction. No sulfur dioxide was observed during the course of the oxidation of H_2S. The oxidation of H_2S by O_2 without a catalyst was negligible under the same condition. The amounts of both H_2S and O_2 used within 20 min are given in Table 1. The stoichiometry of the overall reaction of the H_2S decomposition is expressed as follows; $2\ H_2S + O_2 \rightarrow 2\ S + H_2S$.

The initial stage of the reaction was studied in order to examine the reactivity of the quinone groups as active sites in the catalyst and to determine the mechanism of the decomposition of H_2S by O_2. The initial rate (v_0), $-d(H_2S)/dt$, was determined from the initial slope in the reaction curve (the volume of the consumed H_2S vs reaction time). The initial rates of the H_2S oxidation were linearly dependent upon the amounts of adsorbed H_2S determined volumetrically prior to each reaction. These graphs at various reaction temperatures are shown in Fig. 2. The initial rates under various conditions are plotted against the pressure of O_2 in Fig. 3 which shows that the initial rates are independent of the O_2 pressure, indicating that the oxidation is zero order in oxygen. The results show that the initial rates, v_0, are expressed by the equation, $v_0 = k(H_2S)_{ad}$, which is equal to $kbKP/(1 + KP)$ from the Langmuir equation for the H_2S adsorption.

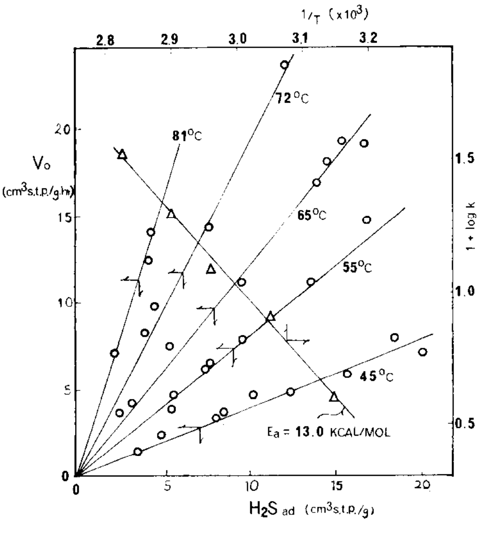


FIG. 2. Dependence of initial rates of the H_2S oxidation upon amounts of H_2S adsorbed on polynaphthoquinone, and activation energy.

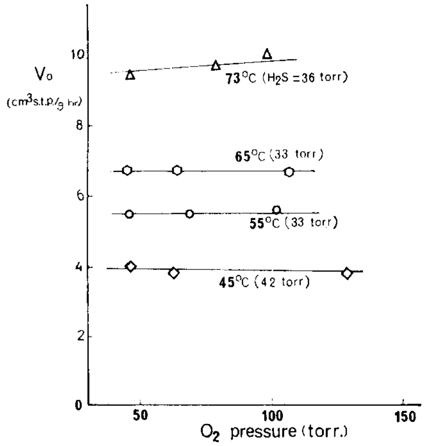


FIG. 3. Dependence of initial rates upon oxygen pressure.

The activation energy was obtained from the Arrhenius plots of the rate constants (k), $v_0/(H_2S)_{ad}$, at various temperatures as given in Fig. 2. The value was found to be 13.0 kcal/mol. The precoefficient in the Arrhenius equation was also calculated to be 3.5×10^8 hr^{-1}. Accordingly, k is expressed as $3.5 \times 10^8 \exp(-13{,}000/RT)$ hr^{-1}.

The Effect of Products on the Oxidation Rate of H_2S

The effect of added water on the oxidation rate is shown in Fig. 4, where initial rates of the reaction are plotted against the amount of added water. A slight increase in the rate was observed when small

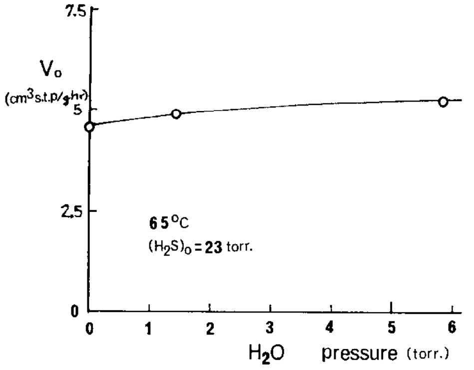


FIG. 4. Effect of added H_2O on the initial rate of the H_2S oxidation.

amounts of water were added, but the increase was below 15%.

Sulfur was deposited on the catalyst surface as the reaction proceeded. Figure 5 shows the dependence of the initial rates of the H_2S oxidation upon the known amounts of sulfur deposited on the catalyst. The initial rates of the reaction were almost not changed until at least 0.64 mmol of sulfur/g-cat. was deposited on the polynaphthoquinone; the concentration represents a ratio of 0.8 atom of sulfur to one effective quinone group (Q) as discussed below. When sulfur was deposited more than 0.8 mmol/g-cat. or one atom/Q, the reaction rate markedly decreased. The amounts of H_2S adsorbed did not drastically decrease with an increase in the amount of deposited sulfur as shown in Fig. 5.

The Distribution of Sulfur Deposited on Polynaphthoquinone

Sulfur deposited on the surface of the polynaphthoquinone catalyst during the course of the H_2S oxidation was observed by means of electron microscopy. Figure 6a is the electron scanning micrograph of the polynaphthoquinone on which 1.6 mmol/g-cat. of sulfur was deposited by the H_2S decomposition at 65°C. The electron probe microanalysis showed clearly the high distribution of the sulfur deposited on the catalyst surface in Fig. 6b where the distribution of the deposited sulfur is shown as the bright spots by electron probe microanalysis using the characteristic X-ray of sulfur element.

The Oxidation of H_2S in a Flow System

The decomposition of H_2S on 0.5–1.0 g of polynaphthoquinone was studied using

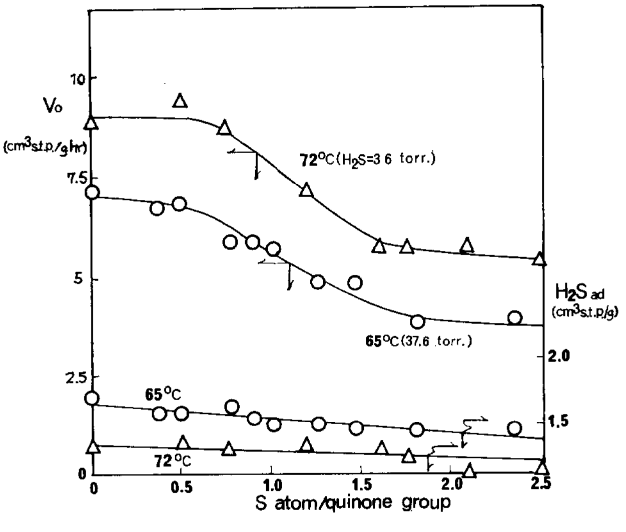


FIG. 5. Variation of the initial rate and the amount of H_2S adsorbed, with the amount of sulfur deposited on the catalyst.

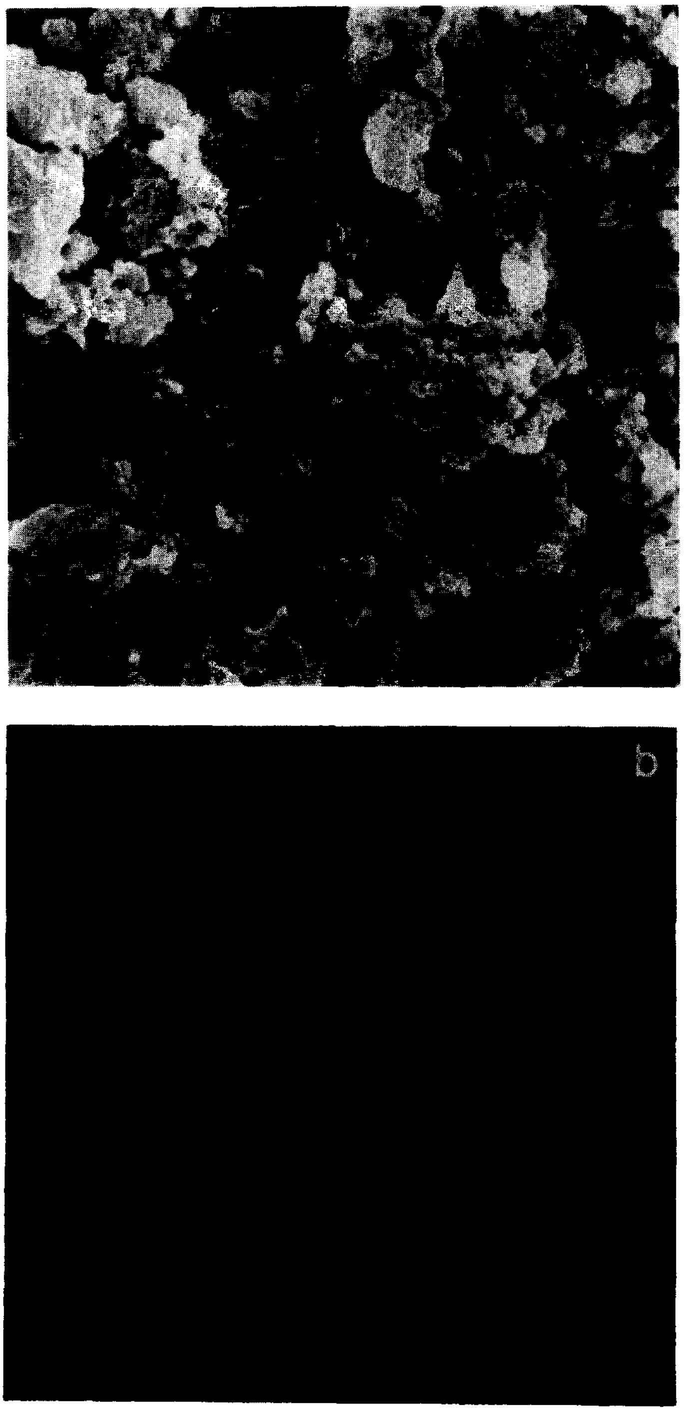


FIG. 6. Electron probe micrographs (×3000): (a) polynaphthoquinone; (b) sulfur deposited on polynaphthoquinone.

a conventional flow system with a view to the application of our catalyst to industrial procedure. The polynaphthoquinone acted as highly effective catalyst in the presence of O_2 for removing H_2S in a flow system.

The oxidation of H_2S by O_2 on the polynaphthoquinone in a flow system at 100°C is given in Fig. 7, where the conversion of H_2S to sulfur was plotted against the reaction time. Almost all of the H_2S molecules admitted into the system were removed in the initial stage of the reaction where the rate of the oxidation was nearly controlled by diffusion of H_2S to the catalyst surface. However, the conversion decreased with the time and eventually the decomposition of H_2S completely stopped because most of the sulfur formed as reaction product was deposited on the catalyst surface. The surface area of the catalyst after the reaction stopped was found to be about 1 m^2/g, implying that the surface of the polynaphthoquinone available for reaction was saturated with sulfur. Approximately one-half to two-thirds of the deposited sulfur were recovered by heating up to 350°C in a flow of N_2 after the H_2S decomposition. The rest of the sulfur was very slowly removed from the surface, its complete removal by heat alone being very difficult. The deposited sulfur reacted easily with oxygen in the temperature range 240–275°C to form sulfur dioxide. The catalytic activity of the polynaphthoquinone was completely restored by the oxidation of the catalyst by air in the temperature range 260–275°C. It is to noted that H_2S was completely converted to sulfur dioxide at 250°C in a large excess of O_2 over H_2S.

The 95% of H_2S admitted onto the polynaphthoquinone at 200°C was removed in the initial stage of the reaction and the activity of the catalyst did not reduce with the reaction time as rapidly as that at 100°C as shown in Fig. 7. The H_2S oxidation at 200°C proceeded without stopping at a conversion above 37% for at least 3 hr. Sulfur was observed to come out of the reactor during the reaction at 200°C. Thus sulfur was continuously recovered. Any product except for sulfur and water could not be detected. The selectivity of the oxidation of H_2S to sulfur was found to be 100%.

DISCUSSION

The oxidation of H_2S by O_2 in the absence of the polynaphthoquinone under the conditions employed was negligible.

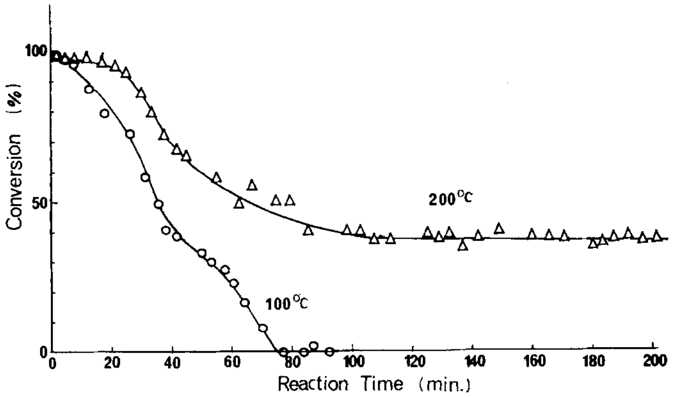
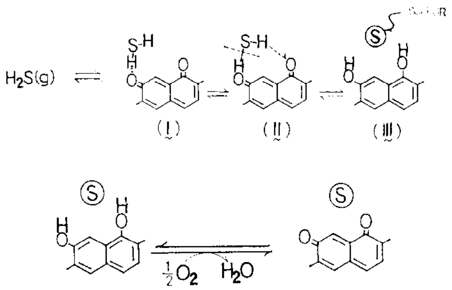


FIG. 7. Oxidation of H_2S on 0.5 g of polynaphthoquinone in a flow system: (○) $T = 100°C$, SV = 3780 cc/g·hr, $H_2S = 0.048$ atm, $H_2S:O_2:N_2 = 1:2:18$, (△) $T = 200°C$, SV = 2880 cc/g·hr, $H_2S = 0.063$ atm, $H_2S:O_2:N_2 = 1:1:14$.

Pure graphite containing neither quinone groups nor other surface oxides showed no catalysis for the decomposition of H_2S under the same conditions. It was found that the polynaphthoquinone with active quinone groups rapidly decomposed H_2S in the presence of O_2 in a closed circulating system as well as in an ordinary flow system.

The hydrogen donating compound like ethyl alcohol adsorbs on the quinone groups of the catalyst, forming the hydrogen bond for which the heat of adsorption was reported to be 8.7 kcal/mol (*8*). H_2S could be hydrogen bonded to the catalyst as indicated by ir spectroscopy for zeolites and alumina by Deo *et al.* (*1*). The isosteric heat of adsorption of H_2S of 8.1 kcal/mol determined in this investigation indicates that H_2S physically adsorbs on the quinone group, forming the hydrogen bond (see reaction scheme). The higher the pressure of H_2S, the more the H_2S molecules are adsorbed on the adjacent quinone group as in the case of ethyl alcohol (*8*). This means that two molecules of H_2S per pair of (adjacent) quinone groups may be adsorbed at saturation. The saturation mass of adsorption was found to be 37.4 cm^3 STP/g-cat. Therefore it is concluded that one-eighth of the total number of the quinone groups contained in the catalyst functions as effective sites for the adsorption of H_2S. One-eighth of the quinone groups in the catalyst work as active sites for the dehydrogenations as previously confirmed (*8*, *9*). These results indicate that both the adsorption and the reaction take place on the same sites, that is, the "effective" quinone groups in the polynaphthoquinone.

The initial rates of the oxidation of H_2S by O_2 at various temperatures were proportional to the amounts of H_2S adsorbed as shown in Fig. 2, while they showed the zero order dependence in O_2 pressure as shown in Fig. 3. These results and the behavior of adsorption indicate that the surface unimolecular reaction is the rate-determining step in the reaction sequence for the H_2S oxidation. Consequently the reaction may be expressed by the following scheme:



(I) in the scheme represents the adsorption of H_2S forming hydrogen bond; at the full coverage another H_2S molecule will also adsorb on the adjacent quinone group. The adsorption of H_2S on the quinone group by hydrogen bonding is the first step for the H_2S oxidation since the hydrogen bonding may be the most likely interaction for a reaction which proceeds via hydrogen transfer from H_2S to the quinone groups. The break of the S–H bond of the H_2S molecule adsorbed on the quinone group of the catalyst takes place in the rate-determining process. The transition state of this step is shown in (II) of the scheme. It is not obvious whether the second fission of another S–H bond in the same H_2S molecule will occur at the same time as the break of the first S–H bond or in a subsequent step. The polynaphthoquinone has a structure favorable for abstracting two hydrogen atoms from the substrate, where one quinone group electronically affects the adjacent quinone group. Therefore, the break of the first S–H bond may be followed rapidly by the break of the second S–H bond. Thus two hydrogen atoms in a H_2S molecule are trapped on the quinone group in the polynaphthoquinone forming hydroquinone groups as represented in (III) of the scheme, while elemental sulfur is formed. No hydrogen was evolved during the reaction. In the presence of O_2 the hydroquinone groups were rapidly oxidized to form quinone groups with the simultaneous formation of water. Thus the activity of the catalyst is completely restored. The oxidation of hydroquinone groups by oxygen may proceed through the formation of H_2O_2 which is rapidly decomposed to H_2O and O_2 on the polynaphthoquinone (*8*). Consequently the oxidation of H_2S with O_2 on the polynaphthoquinone was explained by two successive stoichiometric hydrogen transfer reactions; the first was the hydrogen transfer from the H_2S molecule to the quinone groups of the catalyst (dehydrogenation of H_2S) and the subsequent hydrogen transfer step from the hydroquinone group to oxygen (reoxidation process of the catalyst). Thus the decomposition is catalytically repeated on each quinone group in the polynaphthoquinone.

Figure 6b shows the high distribution of the deposited sulfur on the polynaphthoquinone catalyst given in Fig. 6a. The deposited sulfur was also observed as dark black spots by the transmission electron microscopy (*12*). It was concluded from these micrographs that nearly all the polynaphthoquinone particles (their surface) work uniformly in the oxidation of H_2S and the deposited sulfur is evenly distributed on the surface of each catalyst particle. The elemental sulfur produced by the decomposition of H_2S may be located near the active site as shown in the scheme under a low temperature of 65°C where the amount of the deposited sulfur in Fig. 6b was only 2.0 molecules of sulfur per one quinone group (effective quinone) in the catalyst. Thus the location of the sulfur produced by the reaction may correspond to location of the quinone active sites in the catalyst particles. Figure 6b is accordingly considered to show that the active sites are highly distributed on the polynaphthoquinone surface.

Figure 5 shows that the deposited amounts of sulfur corresponding to one atom of sulfur per one quinone group had almost no effect on the catalytic activity while the location of two atoms of sulfur close to a quinone group as the active site markedly decreased the reactivity of the quinone group in the polynaphthoquinone. The rate of the H_2S oxidation at 65°C on the catalyst having 2.0 S-atoms/Q reduced to half value of the rate on the catalyst without deposited sulfur. The amount of adsorbed H_2S was not drastically changed with the amount of sulfur deposited as shown in Fig. 5. H_2S adsorbs on sulfur as found by Golyland *et al.* (*13*) and Wiewiorowski (*14*). H_2S may adsorb not only on the quinone active sites but also on the deposited sulfur as the amount of deposited sulfur increases. Steijns *et al.* (*4*) demonstrated the critical role of the sulfur deposited on molecular sieve 13X (20–250°C) and active carbons (>130°C) in the H_2S oxidation by kinetics and ESR study, while Sreeramamurthy and Menon (*3*) reported that the sulfur did not catalyze the reaction in the temperature range 65–100°C. Sulfur is known to slowly dehydrogenate some hydrocarbons above 200°C [for example, Ref. (*15*)]. Sulfur deposited on a catalyst was proposed as one of reactive species for ethylbenzene dehydrogenation above 450°C (*16*). Our data on the polynaphthoquinone did not show the catalysis of the deposited sulfur in the H_2S oxidation in the temperature range 30–200°C. The sulfur deposited on the polynaphthoquinone may partly play a role in the oxidation of H_2S above 200°C.

The slight increase in the initial rate by the addition of water was observed in Fig. 4. Storp (*17*) reported the large effect of water on the activity of active carbons in the H_2S oxidation below 50°C.

The difference in the effect of water and sulfur on the polynaphthoquinone and on active carbons depends on the properties of the two catalysts. It is known that there are various surface functional groups such as quinone groups, carboxyl groups, hydroxyl groups, other surface oxides and radical species, on the surface of active carbons (*3*, *18*). On the other hand, the polynaphthoquinone is considered to have relatively well-defined surface with quinone groups as highly distributed active sites.

H_2S was rapidly oxidized even at 65°C in the presence of O_2 in a flow system in Fig. 7. Most of the produced sulfur was not removed from the catalyst surface below 150°C and the activity of the catalyst decreased fairly rapidly to 0% conversion as the reaction proceeded. Nevertheless the total amount of H_2S decomposed at 100°C corresponded to 10 times the population of quinone group active sites. This fact indicates that H_2S was catalytically oxidized to sulfur on the quinone groups of the polynaphthoquinone.

As shown in Fig. 7, the H_2S decomposition at 200°C did not stop within the reaction period investigated although the amount converted reduced to 40%. The amount of H_2S decomposed in 200 min at 200°C corresponded to 18 times the population of quinone sites. At the point where the reaction proceeds continuously at a conversion of about 40%, the rate of the oxidation of H_2S by O_2 may be controlled by the rate of the desorption of the sulfur deposited on the polynaphthoquinone surface. The turnover of the reaction at the initial stage is calculated to be 1.6×10^{-1} molecules/min/site, while it is 6.7×10^{-2} molecules/min/site at the steady state keeping a conversion of 40%. The present results demonstrate that the polynaphthoquinone has a higher activity than active carbons although the H_2S decompositions were made out in different conditions. No sulfur dioxide was produced under the reaction condition having the ratio, 1:0.5–1.0, of H_2S to O_2 at 200°C. Thus the selectivity towards sulfur was shown to be 100%.

The polynaphthoquinone has been demonstrated to have the quinone groups as active sites combined with the highly conjugated π-electron system by which the catalytic activity of the polynaphthoquinone for the hydrogen or electron transfer reactions may electronically be promoted. It was consequently found that the polynaphthoquinone behaved as a typical heterogeneous catalyst with a high activity which has a relatively well-defined surface and highly distributed active sites on which hydrogen transfer reactions take place catalytically to decompose H_2S in the presence of O_2.

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