

# Catalytic Decomposition of Hydrogen Sulfide

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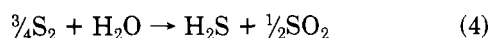
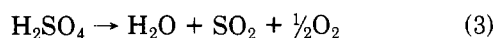
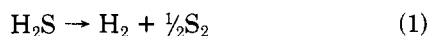
The decomposition of hydrogen sulfide on molybdenum disulfide and tungsten disulfide catalyst was studied at 500–800 °C. It has been found that molybdenum disulfide catalyst decomposes hydrogen sulfide effectively into hydrogen and elementary sulfur over the whole range of temperature employed in this study, and that it is possible to convert more than 95% of the hydrogen sulfide fed to the reaction system into hydrogen and sulfur by continuous removal of sulfur and intermittent separation of hydrogen from the reaction gas mixture at 800 °C.

## Introduction

The thermal decomposition of hydrogen sulfide to produce hydrogen and elementary sulfur has recently become of a great interest from the viewpoints of (1) effective utilization of hydrogen sulfide produced in such industrial processes as hydrodesulfurization of heavy oil and coal gasification and (2) research and development on a hydrogen energy technology.

Nowadays hydrogen sulfide produced in a petroleum refinery is in general subjected to the partial oxidation treatment, called Claus process, to obtain elementary sulfur. In this case hydrogen in hydrogen sulfide cannot be recovered and is finally wasted in the form of water. On the other hand, it is generally accepted that the important variables for the cost performance of hydrodesulfurization processes would be those of catalysts and hydrogen. The decomposition of hydrogen sulfide involves a disadvantage requiring an energy input owing to the fact that the reaction is endothermic, while it has a great advantage in providing two saleable products, hydrogen and sulfur. The disadvantage would be compensated in the future by the economic value of recovered hydrogen.

Attention is also paid to the decomposition of hydrogen sulfide because of its possibility to make up a key reaction in a thermochemical water splitting cycle. A number of thermochemical water splitting cycles have been proposed, of which the so-called Mark 4 process (Marchetti et al., 1970, 1971, 1972) includes the decomposition of hydrogen sulfide in its hydrogen-forming step. Kotera (1976) has proposed a "Sulfur Cycle" expressed by the equations



The latter cycle has also been proposed independently by Bowman in 1975.

There have been only a few fundamental and industrial studies on the thermal decomposition of hydrogen sulfide (Taylor and Pickett, 1927; Kingman, 1936; Darwent and Roberts, 1953; Inaba and Kono, 1955; Raymont, 1975). It has been found by the present authors that the disulfide of molybdenum or tungsten decomposes hydrogen sulfide at 500–800 °C effectively into hydrogen and elementary sulfur (Kotera et al., 1976). In this paper, the catalytic activities of molybdenum disulfide and tungsten disulfide for the decomposition of hydrogen sulfide have been examined and the effect of product separation on the yield of hydrogen has been studied.

## Experimental Section

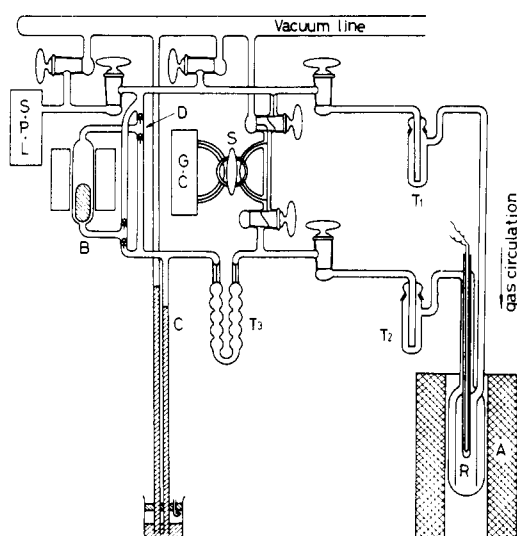
The apparatus employed in this study is a closed circulating system for reduced pressure gas reaction made from Pyrex glass as shown in Figure 1. The dead volume of the apparatus is 943 mL at room temperature with a reaction vessel being maintained at 800 °C. Hydrogen sulfide was reserved in a sample reservoir in advance from a liquefied hydrogen sulfide cylinder (purity: 99.99%) and a known amount of hydrogen sulfide was introduced in the reaction system when necessary. The reaction gas was circulated through the reaction vessel by a magnetic pump.

Since the equilibrium conversion of hydrogen sulfide into hydrogen and sulfur is at most of the order of several mole percent below 800 °C, it is necessary to separate and to remove any product from the circulating gas mixture to obtain hydrogen in higher concentration than predicted thermochemically. Consequently the reaction was carried out with continuous removal of elementary sulfur evolved by condensing gaseous sulfur into a trap cooled to ice temperature.

The analysis of hydrogen and hydrogen sulfide was carried out by means of gas chromatography using a Deactigel (Applied Science Laboratories, Inc., State College, Pa.) column for the separation of hydrogen sulfide and a molecular sieve column for the separation of hydrogen. Elementary sulfur collected in a trap was weighed after some experimental runs.

Molybdenum disulfide used as a catalyst was provided from Nippon Inorganic Colors and Chemicals Co., Tokyo, Japan, in a powder form (average particle size: 4 μm) made from the flotation and purification of molybdenite ore obtained from the Shimane Prefecture of Japan. The purity is 99.5% and the impurities are silica, 0.02%; ferric oxide, 0.19%; moisture, 0.1%; water soluble substances, 0.15%; and oil content, 0.09%. The sample of molybdenum disulfide used in this study has been revealed to have a hexagonal structure and a preferred orientation parallel to the (001) plane ( $l = 3, 6, 9$ , and  $12$ ) by means of X-ray diffraction. The surface area was 4.1 m<sup>2</sup>/g determined by the BET method.

The alumina-supported molybdenum disulfide catalyst was prepared by the impregnation of γ-alumina (spherical, diameter: 3–4 mm; surface area: 250 m<sup>2</sup>/g, manufactured by Catalysts and Chemicals Ind. Co., Tokyo, Japan) in an aqueous alkaline solution of ammonium thiomolybdate, and was followed by a reduction at 370 °C under a hydrogen stream. The catalyst thus prepared was calcined at 750 or 1140 °C under a nitrogen stream for 6 h prior to use. The amount of molybdenum disulfide supported was 8 wt % determined by an X-ray fluorescence method, and the surface areas were 202 and 47 m<sup>2</sup>/g for catalysts



**Figure 1.** Reaction apparatus for the decomposition of  $\text{H}_2\text{S}$ : A, electric furnace; R, reaction vessel; S, gas sampler;  $T_1$  and  $T_2$ , traps (cooled to ice temperature during reaction);  $T_3$ , trap (cooled to liquid nitrogen temperature on separation of hydrogen from hydrogen sulfide); G, gas chromatograph; S-P-L, sample reservoir.

**Table I.** Data for Figure 3

reaction temperature, °C	500	550	550 (blank)
catalyst weight, g	27.6	26.8	—
$\text{H}_2\text{S}$ introduced, mL (STP)	120.7	132.8	139.3
circulation rate of reaction gas, mL/min	732	530	530
total pressure, mmHg	100	97	135

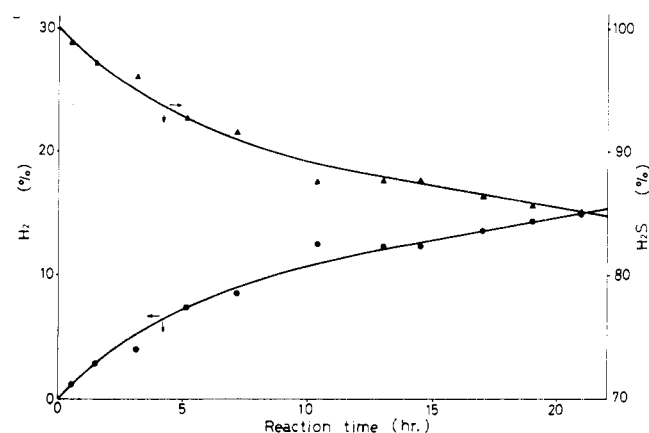
calcined at 750 and 1140 °C, respectively.

Tungsten disulfide powder (purity: 99.5%) used as a catalyst was obtained from Research Organic/Inorganic Chemicals Co. Its average particle size was 2  $\mu\text{m}$  and the surface area was 4.4  $\text{m}^2/\text{g}$ .

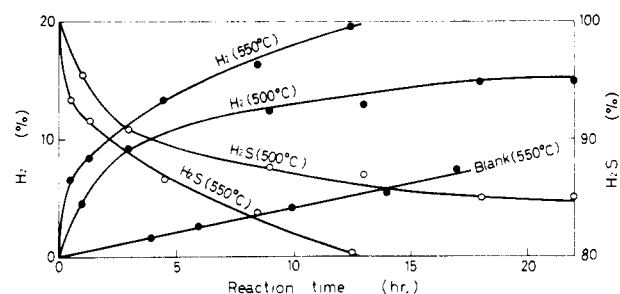
## Results

Typical results on the unsupported tungsten disulfide catalyst at 500 °C and on the unsupported molybdenum disulfide catalyst at 500–800 °C are given in Figures 2, 3, and 4, where the concentration of hydrogen in a circulating reaction gas is plotted against the reaction time. (For the experimental details of Figures 3 and 4, see Tables I and II, respectively.) It should be noted that the curves showing the change of hydrogen concentration with time do not correspond to the formation of hydrogen in the general sense of chemical kinetics but show only an accumulation of hydrogen in the gas phase, since elementary sulfur evolved is continuously removed from the circulating gas mixture and more concentrated hydrogen is accumulated than expected from thermochemical equilibrium.

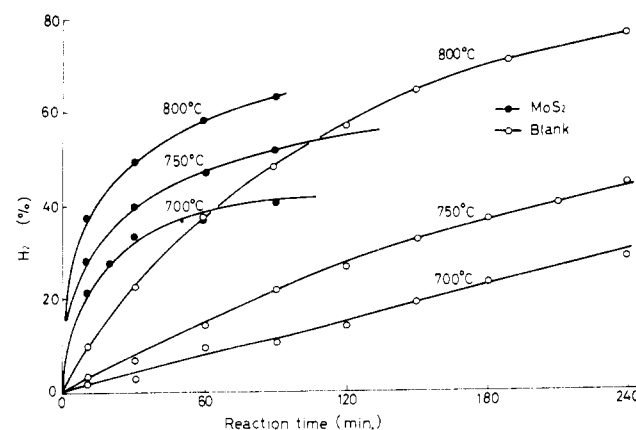
Since the initial slopes of the curves in Figures 2–4 are related to the initial rates of the decomposition of hydrogen sulfide, it is possible to evaluate approximately the catalytic activity of molybdenum disulfide by comparing with the results of the noncatalytic decomposition. The result of comparison is shown in Table III. The theoretical values of hydrogen concentration after 10 min were 18 and 31 mol % at 700 and 750 °C, respectively, calculated by assuming an equilibrated conversion at each passage



**Figure 2.** Decomposition of hydrogen sulfide on tungsten disulfide: reaction temperature, 500 °C; catalyst weight, 38.5 g; total surface area, 169.8  $\text{m}^2$ ;  $\text{H}_2\text{S}$  introduced, 325.6 mL (STP); total pressure of reaction gas, 40 mmHg; circulation rate of reaction gas, 732 mL/min.



**Figure 3.** Decomposition of hydrogen sulfide on unsupported  $\text{MoS}_2$  catalyst. (For experimental data, see Table I.)



**Figure 4.** Decomposition of hydrogen sulfide on unsupported  $\text{MoS}_2$  catalyst. (For experimental data, see Table II.)

through the catalyst bed under the same reaction conditions as in Figure 4. These values are nearly equal to observed ones shown in Figure 4. This result suggests that the catalytic activity of molybdenum disulfide is high enough to make the reaction proceed to its equilibrium under the reaction conditions indicated in Figure 4, and that the actual ratios of initial rates are greater than those shown in Table III. As seen from the table, the catalytic effect of molybdenum disulfide is remarkable, and the lower the reaction temperature the more significant the

**Table II.** Data for Figure 4

reaction temperature, °C	700	700 (blank)	750	750 (blank)	800	800 (blank)
catalyst weight, g	19.7	—	19.7	—	19.7	—
$\text{H}_2\text{S}$ introduced, mL (STP)	94.7	37.2	103.8	62.5	75.8	43.0
circulation rate of reaction gas, mL/min	940	940	940	940	940	940
total pressure, mmHg	92	34	60	56	70	40

Table III. Evaluation of Catalytic Activity of Unsupported Molybdenum Disulfide

temp, °C	initial rate (cat.), <sup>a</sup> mol %/min (A)	initial rate (noncat.), <sup>b</sup> mol %/min (B)	A/B
450	0.04	≈0 <sup>c</sup>	-
500	0.08	≈0 <sup>c</sup>	-
550	0.35	0.007	50
700	4.37	0.13	34
750	7.20	0.30	24
800	9.15	1.10	8

<sup>a</sup> Catalytic reaction on unsupported MoS<sub>2</sub>. <sup>b</sup> Noncatalytic reaction. <sup>c</sup> The formation of hydrogen was unmeasurable in the reaction period employed in this study.

Table IV. Data for Figure 5 (All Amounts of H<sub>2</sub> and H<sub>2</sub>S in mL (STP))

	time					
	initial	A	B	C	D	end
H <sub>2</sub> S introduced	132.8	-	-	-	-	-
H <sub>2</sub> produced	-	20.1	30.3	52.4	20.9	27.7
H <sub>2</sub> removed	-	16.3	24.6	52.4	20.9	27.7
H <sub>2</sub> S added	-	34.0	63.9	0	0	0
total amount of H <sub>2</sub> S introduced	132.8	166.8	230.7	230.7	230.7	230.7
total amount of H <sub>2</sub> produced	0	20.1	46.6	93.3	114.2	141.9

effect of the catalyst becomes. This is due to the difference between the activation energies for the catalytic reaction and for the noncatalytic reaction. The activation energies obtained using initial slopes were 26.8 kcal/mol for the catalytic reaction and 42.0 kcal/mol for the noncatalytic reaction, respectively. An almost similar result has been obtained for tungsten disulfide catalyst. An important feature of tungsten disulfide catalyst is that a much greater

amount of adsorption of hydrogen sulfide on the catalyst surface or absorption in the catalyst was observed during the reaction as compared with that on molybdenum disulfide.

The results given in Figures 2-4 show that the conversion of hydrogen sulfide by passage through the catalyst bed continues to decrease with an increasing number of gas circulation cycles if hydrogen remains unremoved in the reaction gas mixture. If hydrogen is removed together with elementary sulfur, then the conversion ought to keep the same value in every successive cycle as in the first cycle. To obtain hydrogen advantageously, therefore, it is desirable that the hydrogen formed be continuously or at least intermittently separated from the reaction gas. The problem of the separation of products under a reaction condition is brought forward from this point of view. In this study, an intermittent removal of hydrogen was attempted to examine the reproducibility of an initial state of the reaction and to observe the change of catalytic activity with time as well as to obtain hydrogen in high yield. For simplicity in the experiment, the separation of hydrogen was accomplished in the manner that the gas mixture consisting of hydrogen and hydrogen sulfide was cooled by a liquid nitrogen bath to trap out hydrogen sulfide alone and the hydrogen remaining in the gas phase was moved into a hydrogen reservoir or was evacuated. The experimental results on the effect of hydrogen removal are shown in Figure 5 and Tables IV, V, and VI. In the experiment for Figure 5, hydrogen was partially removed at time  $t = A$  and  $B$  and fresh hydrogen sulfide was added to the reaction gas. At  $t = C$  and  $D$ , all of the hydrogen was removed. As seen from Figure 5, the initial state of the reaction is clearly reproduced in repeated runs. This result indicates at the same time that there is no significant decrease in catalytic activity over a period of about 180 h at 550 °C. In the experiment for Table V the separation

Table V. Decomposition of Hydrogen Sulfide on Unsupported MoS<sub>2</sub> Catalyst with Intermittent Removal of Hydrogen<sup>a</sup>

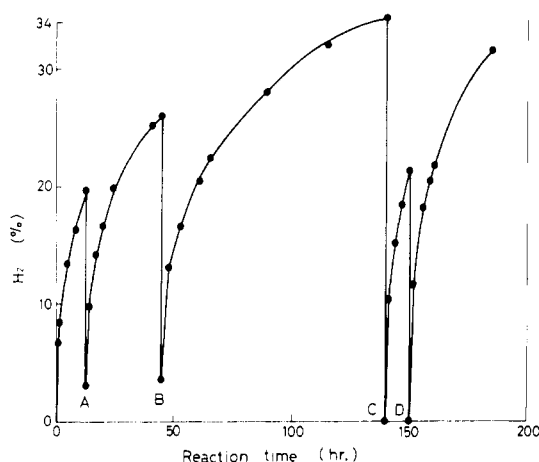
	run				
	1	2	3	4	5
amount of H <sub>2</sub> S introduced initially, mL (STP)	107.7	-	-	-	-
added H <sub>2</sub> S, mL (STP)	-	19.0	8.9	15.8	17.0
total amount of H <sub>2</sub> S introduced, mL (STP)	107.7	126.7	135.6	151.4	168.4
reaction time, h	4	4	4	4	4
hydrogen concentration, mol %	14.0	12.4	15.1	15.2	15.1
amount of H <sub>2</sub> produced, mL (STP)	15.0	14.0	16.2	16.3	16.3
total amount of H <sub>2</sub> produced, mL (STP)	15.0	29.0	45.2	61.5	77.8
amount of H <sub>2</sub> removed, mL (STP)	15.0	14.0	16.2	16.3	16.3
conversion into hydrogen based on the total amount of H <sub>2</sub> S, %	13.9	22.9	33.3	40.6	46.2

<sup>a</sup> Reaction temperature, 550 °C; catalyst weight, 26.8 g; circulation rate of reaction gas, 530 mL/min.

Table VI. Decomposition of Hydrogen Sulfide on Unsupported MoS<sub>2</sub> at 800 °C with Intermittent Removal of Hydrogen<sup>a</sup>

	run									
	1	2	3	4	5	6	7	8	9	10
amount of H <sub>2</sub> S introduced initially, mL (STP)	74.6	-	-	-	-	-	-	-	-	-
added H <sub>2</sub> S, mL (STP)	-	65.2	49.2	45.8	41.8	41.7	51.5	48.2	34.1	47.6
total amount of H <sub>2</sub> S introduced, mL (STP)	74.6	139.8	189.0	234.8	276.6	318.3	369.8	418.0	452.1	499.7
reaction time, min	120	90	90	90	90	90	90	90	90	90
hydrogen concentration, mol %	70.7	62.0	60.7	59.5	60.0	60.7	59.3	59.5	62.8	62.9
amount of H <sub>2</sub> produced, mL (STP)	50.3	53.2	58.2	62.8	59.6	57.9	61.0	61.2	49.1	49.6
total amount of H <sub>2</sub> produced, mL (STP)	50.3	92.7	139.5	189.8	236.0	281.1	329.7	377.8	426.9	476.5
amount of H <sub>2</sub> removed, mL (STP)	39.5	41.8	45.7	49.8	46.8	45.5	47.9	61.2	49.1	44.6
conversion into H <sub>2</sub> based on the total amount of H <sub>2</sub> S introduced, %	67.4	66.3	73.8	80.8	85.3	88.3	89.2	90.4	94.4	95.4

<sup>a</sup> Catalyst weight, 19.7 g; circulation rate of reaction gas, 590 mL/min.



**Figure 5.** Decomposition of hydrogen sulfide on unsupported  $\text{MoS}_2$  catalyst at  $550^\circ\text{C}$  with intermittent removal of hydrogen: catalyst weight, 26.8 g; circulation rate of reaction gas, 530 mL/min. (For experimental data, see Table IV.)

of hydrogen was carried out every 4 h and the hydrogen sulfide remaining was combined with freshly supplied hydrogen sulfide and substantially the same amount of hydrogen sulfide as used in the initial run was sealed in the reaction system. The same operations were repeated five times. The results show that 46.2% of all the hydrogen sulfide introduced into the reaction system was converted into hydrogen. The percent conversion based on the amount of hydrogen sulfide fed to the reactor was 15.1% when the reaction was continued for 12.5 h without separation of hydrogen from hydrogen sulfide as shown in Figure 2. Within substantially the same reaction period (by the third run), the percent conversion increased to 33.3% by two times of hydrogen separation. The effect of hydrogen separation on a conversion of hydrogen sulfide at  $800^\circ\text{C}$  is represented in Table VI where the hydrogen separation was carried out every 90 min except for the first run in which it was done after 120 min. The initial state of the reaction is obviously reproducible even at such a high temperature as  $800^\circ\text{C}$ . The percent conversion based on the total amount of hydrogen sulfide introduced reached 95.4% in a total of ten runs. In a separate experiment, the reaction was continued for 7.5 h at  $800^\circ\text{C}$  without removal of hydrogen, where 98.2 mL (STP) of hydrogen sulfide was initially sealed in the reaction system. The concentration and amount of hydrogen reached 80.0% and 78.6 mL (STP) at the end point of the reaction, respectively. Comparing this result with that shown in Table VI it is clear that the whole amounts of hydrogen sulfide treated and hydrogen obtained increased by three times by the addition of four times of hydrogen separation, while the percent conversion of hydrogen sulfide remained at almost the same level within about the same reaction period (by the fifth runs).

The amount of elementary sulfur collected in the sulfur condenser through the experiments for Figure 5 and for Table V was 0.326 g, which corresponds to 228.3 mL (STP) of hydrogen. The total amount of hydrogen formed in those two experiments was 219.7 mL (STP). The result, therefore, indicates that hydrogen sulfide was stoichiometrically decomposed into hydrogen and elementary sulfur.

### Discussion

It is well known that at elevated temperatures, hydrogen sulfide is dissociated into hydrogen and sulfur as indicated by the formula

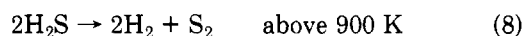
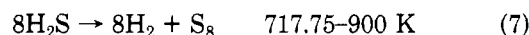
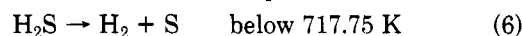


**Table VII.** Equilibrium Concentration of Hydrogen in the Decomposition of Hydrogen Sulfide under 1 atm (Calculated)

temp, K	equilibrium concn, mol %
400	$1.3 \times 10^{-3}$
500	$6.1 \times 10^{-3}$
600	$2.0 \times 10^{-2}$
700	$4.8 \times 10^{-2}$
900	1.9
1200	13.1
1400	25.6
1600	37.7
1800	47.0

where  $\text{S}_x$  denotes the allotropes of elementary sulfur such as solid and liquid sulfur,  $\text{S}$ , and gaseous sulfur,  $\text{S}_2$ – $\text{S}_8$ .

Although some complex system including all of sulfur allotropes may appear in an actual dissociation equilibrium, an assumption could be made without leading to serious errors that only thermodynamically the most stable species of elementary sulfur is included in the reaction system depending on the temperature range. Thus, on the basis of thermodynamic data (Barin and Knacke, 1973) reaction formula 5 can be developed as



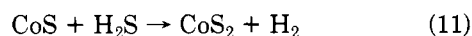
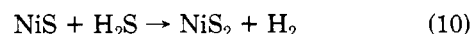
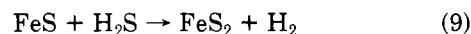
The concentration of hydrogen at equilibrium under 1 atm is given in Table VII.

As seen from Figures 2–4, much more concentrated hydrogen than those shown in Table VII can be obtained by continuous removal of sulfur and by circulating a gas mixture consisting of hydrogen and unreacted hydrogen sulfide repeatedly through the catalyst bed.

Molybdenum disulfide and tungsten disulfide have been found to be significantly effective as catalysts for the decomposition of hydrogen sulfide. The X-ray diffraction patterns showed that these two sulfides employed as catalysts in this study have a preferred orientation for the (001) plane ( $l = 3, 6, 9$ , and  $12$ ). Recently the hydrogenation and the hydrogen exchange reaction of ethylene on molybdenum disulfide has been studied by Okuhara et al. (1975), and the layer structure of molybdenum disulfide has been suggested to play an important role in those catalytic reactions. It is interesting to examine whether or not such a characteristic of the crystal lattice is related to the catalytic properties of these sulfide catalysts.

The effect of catalysts decreased with increasing temperature as shown in Table III. Although the data in Table III do not extend above  $800^\circ\text{C}$ , the data which do appear should reasonably be extrapolated to  $1000^\circ\text{C}$  where they tend to confirm the result reported by Raymont in 1975 to the effect that the catalyst has no additional effect on the reaction rate.

Sulfides of transition metals other than molybdenum and tungsten can be presumed to be effective as catalysts for the decomposition of hydrogen sulfide. It is, however, well known that such lower sulfides as  $\text{FeS}$ ,  $\text{NiS}$ , and  $\text{CoS}$  are likely to be easily converted into higher sulfides by contact with hydrogen sulfide at elevated temperatures according to the equations



Those higher sulfides are assumed to have poor or no

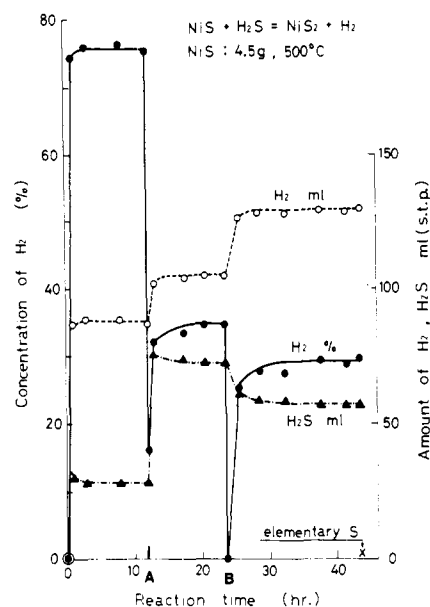


Figure 6. Sulfurization of nickel monosulfide by hydrogen sulfide at 500 °C.

catalytic activities for the decomposition of hydrogen sulfide. To certify the above assumption, the catalytic activity of nickel sulfide has been examined at 500 °C using the same apparatus as in the study on molybdenum disulfide catalyst. Nickel sulfide powder was provided from Research Organic/Inorganic Chemicals Co., being sealed under an argon atmosphere. X-ray diffraction pattern revealed the sample to be NiS. The result is shown in Figure 6, where the concentration of hydrogen, the amount of hydrogen sulfide in the gas phase, and the total amount of hydrogen produced are plotted against the reaction time. At  $t = A$  and  $B$ , a part and the whole amounts of hydrogen were removed from the reaction system, respectively, and fresh hydrogen sulfide was added to the reaction system. Since the amount of elementary sulfur collected in the sulfur trap throughout the reaction was found to be almost a trace quantity, it can be concluded that the whole amount of hydrogen produced has been derived from the sulfurization of nickel monosulfide according to eq 10. In practice a rapid sulfurization of NiS was observed at each introduction of fresh hydrogen sulfide as shown in Figure 6, but the apparent sulfurization rate quickly became much slower and in this stage the decomposition of hydrogen sulfide virtually could not be observed. A sample of nickel sulfide after the reaction was found to be a mixture of NiS and NiS<sub>2</sub> by X-ray diffraction analysis. These results suggest that the catalytic activity of nickel disulfide is much lower as compared with those of molybdenum disulfide and tungsten disulfide and that the complete sulfurization of NiS particle is considerably difficult while its surface layer can be easily sulfurized by hydrogen sulfide. In the case of molybdenum disulfide and tungsten disulfide, there are higher sulfide species such as MoS<sub>3</sub> and WS<sub>3</sub>. In this study, however, the X-ray diffraction study showed these disulfides not to be converted into trisulfides by contact with hydrogen sulfide under the reaction conditions.

Work is in progress to develop a sophisticated catalyst for an industrial application. In a preliminary experiment along this line, the activity of an alumina-supported molybdenum disulfide catalyst was compared with that of the unsupported one used in this study. In this experiment a much smaller surface area than those in the foregoing experiments was used to maintain the conversion

Table VIII. Comparison of Catalytic Activities of Alumina-Supported MoS<sub>2</sub> and Unsupported MoS<sub>2</sub> for the Decomposition of Hydrogen Sulfide<sup>a</sup>

catalyst	H <sub>2</sub> concentration in reaction gas, mol %		
	after 15 min	after 60 min	after 120 min
unsupported MoS <sub>2</sub>	13.5	27.6	37.1
MoS <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> calcined at 750 °C	10.5	23.3	30.4
MoS <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> calcined at 1140 °C	17.7	34.1	44.3

of hydrogen sulfide to a low extent. The result is summarized in Table VIII. It is obvious from the table that the alumina-supported catalyst calcined at 1140 °C is more active than that calcined at 750 °C and the unsupported one. This preliminary observation may indicate one of the approaches for the development of a highly active catalyst for practical use.

Many processes have been proposed for the production of hydrogen from hydrogen sulfide, including two-step closed cycles (Weiner and Leggett, 1961; Nishimoto et al., 1975), multistep open cycles (Nixon, 1965; Schuman, 1968; Shell Intern. Res., 1965), electrolysis (Lee, 1958), catalytic decomposition on metallic tungsten (Massey, 1961), and the decomposition by electric discharge (Kawamura, 1965; Haas et al., 1976). One of the reasons to design such apparently complex processes is due to the fact that the equilibrium conversion of hydrogen sulfide at generally available temperatures, for example below 1000 °C, is very low because of endothermic reaction. As shown by the results obtained in this study, however, it is possible to obtain hydrogen in high yield from hydrogen sulfide by a simple catalytic decomposition if the separation of the reaction products can be carried out efficiently. There are industrially established conditions for the separation of hydrogen sulfide from hydrogen by scrubbing with selected solvents such as methanol used in the Rectisol process, and these general procedures may be economically feasible by proper selection and design of operating temperatures and the processing of a side stream from the circulating reactants. However, these methods would be unfavorable unless a large amount of low cost heat is available, since the thermal efficiency of the separation processes is considerably lowered owing to the repeated cycles of heating and cooling of a large quantity of reactants. Another possibility for product separation is an application of some diffusion membrane which makes it possible to separate hydrogen from hydrogen sulfide and sulfur vapor under the reaction conditions. This technique has not yet been established industrially and a search for such an effective diffusion membrane usable especially under high temperature and corrosive conditions seems to be an important research subject for a future study.

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## Mixture Adsorption Equilibria of Ethane and Ethylene on 13X Molecular Sieves

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Pure gas adsorption isotherms of ethane and ethylene on 13X molecular sieves were determined at 25 and 50 °C. Data for the binary adsorption equilibria of these two gases were collected at the same temperatures and a pressure of 1033.9 mmHg (20 psia). With these data, models based on the following types of approaches have been evaluated: assuming the adsorbed phase is a thermodynamically ideal solution, assuming the adsorbed phase has a quasicrystalline structure (lattice solution model), treating the adsorbed phase as a two-dimensional gas, and applying simplified statistical thermodynamics to the adsorption process. For these systems the thermodynamically ideal adsorbed solution model gave the best results overall, while the two-dimensional gas model and the statistical thermodynamic approach also gave reasonably good predictions.

### Introduction

In spite of the widespread use of molecular sieves in both industries and laboratories, fundamental knowledge of adsorption phenomena remains limited. This deficiency is particularly prominent in adsorption involving gas or liquid mixtures. A number of experimental studies on the adsorption of mixtures have been reported, but only a few of them use molecular sieves as the adsorbent. This lack of data has made it difficult both to develop new models of adsorption and to evaluate models already presented in the literature.

Earlier studies (Barrer and Robins, 1953; Lederman and Williams, 1964; Dorfman and Danner, 1975) have shown that the simple theories which have been so useful for pure gas adsorption, such as the Langmuir and BET methods, are not adequate when extended to gas mixtures. More recent methods are examined with the new data that were collected in this work.

### Experimental Section

**Apparatus.** The apparatus was of the volumetric type. The total quantity of each gas admitted to the system and the amount of each gas in the vapor remaining after adsorption equilibrium was established were determined by appropriate  $P$ - $V$ - $T$  measurements and analysis by a gas chromatograph. The adsorbed phase parameters were then determined by the difference between the quantities of admitted and remaining gases. Details of the equipment and operating procedures are described in the previous publication of Dorfman and Danner (1975).

**Materials.** The adsorbent used in the experiments was Linde Molecular Sieves Type 13X, in the form of  $1/16$ -in. pellets containing 20% by weight of inert clay binder and eighty percent NaX synthetic zeolite. The pore volume of NaX (Si/Al = 1.25) zeolite was about 0.3 cm<sup>3</sup>/g of adsorbent determined from adsorption of  $n$ -pentane at 25

°C (Breck, 1974). The surface area determined by the BET method with nitrogen at -196 °C was about 525 m<sup>2</sup>/g (Breck, 1974). For Molecular Sieves Types 13X pellets, these values had to be decreased by 20% to account for the presence of the inert binder. The sieves were regenerated at 300 °C under vacuum for a period of at least 12 h between each run.

The gases used in this mixture adsorption study were research grade ethane and ethylene. The impurity contents reported by the manufacturer were 580 ppm for ethane and 75.5 ppm for ethylene. Ethane and ethylene were chosen because they are quite similar in size, molecular weight, and physical properties, but differ significantly in their degree of saturation, boiling point, and polarizability. Since the sizes of both gases were much smaller than the effective pore size of the molecular sieves, selectivity due to a molecular sieving effect was nonexistent.

### Experimental Results

**Pure Gas Adsorption.** Pure gas adsorption isotherms of ethane and ethylene on 13X molecular sieves were determined at 25 and 50 °C. The experimental equilibrium data of adsorption and desorption are plotted in Figures 1 and 2 and tabulated in Tables I-IV. As expected no hysteresis was observed in any of this work.

The volumes of ethane adsorption at 1033.9 mmHg (20 psia) were 49 and 43 cm<sup>3</sup> STP/g of adsorbent at 25 and 50 °C, respectively. The volumes of ethylene adsorbed at the same pressure and temperatures were 62 and 57 cm<sup>3</sup> STP/g.

**Gas Mixture Adsorption.** Adsorption equilibrium data of ethane-ethylene on Molecular Sieves Type 13X were taken at both 25 and 50 °C and 1033.9 mmHg (20 psia) total pressure. The experimental data are presented in the form of adsorption phase diagrams in Figure 3 and