The Study of Thermochemical Hydrogen Preparation. VI.[1] A Hydrogen-evolving Step through the H_2S–CO Cycle

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A two-step decomposition process of hydrogen sulfide was studied. The process is constituted from a hydrogen-evolution step ($CO+H_2S \xrightarrow{ca.\ 200\ ^\circ C} H_2+COS$) and a carbonyl sulfide-decomposition step ($COS \xrightarrow{ca.\ 830\ ^\circ C} CO+1/x\cdot S_x$). Almost an equilibrium amount of hydrogen could be produced in the first reaction (*ca.* 40%, 200 °C, 1 atm, $CO/H_2S=2.2$) with a cobalt sulfide or nickel sulfide catalyst. In the second reaction, an almost equilibrium amount of carbonyl sulfide (45%) could also be decomposed into carbon monoxide and elementary sulfur at 830 °C under 1 atm with a sufficient reaction rate and selectivity without using any catalysts. Carbon dioxide was formed as a by-product in the second reaction: however, its yield was only 5% of the carbon monoxide produced. From these results, it may be concluded that this two-step decomposition process of hydrogen sulfide can produce more hydrogen than that produced by the direct decomposition of hydrogen sulfide. In the second reaction, however, the recombination of carbon monoxide with elementary sulfur can not be neglected. Thus, a rapid separation of sulfur from carbon monoxide is required.

The recovery of hydrogen form hydrogen sulfide is of industrial importance in relation to the thermochemical splitting of water[2] and to the desulfurization of oil and coal.[3] It has been found by the present authors that molybdenum(IV) sulfide and tungsten(IV) sulfide effectively decompose hydrogen sulfide into hydrogen and elementary sulfur at 500—800 °C:[4]

$$H_2S \longrightarrow H_2 + 1/x\cdot S_x. \qquad (1)$$

The yield of hydrogen was, however, thermochemically limited, and only 5.5% of hydrogen could be produced even at 1000 K under 1 atm.

There have been many investigations undertaken in an attempt to overcome such a thermochemical disadvantage by using the external energies—for example, by α-ray,[5] by γ-ray,[5] by electron beam,[6] by UV irradiation,[7] by electric discharge,[8] or by electrolysis.[9] Besides these methods, it has been proved that the hydrogen can be separated selectively from hydrogen sulfide in the reaction zone by using a micro porous Vycor-type glass as an effusion barrier.[10] Such a process makes possible the production of more hydrogen than the equilibrium amount of Reaction 1.

Besides these single-step methods, several two-step cycles[11] and multi-step open cycles[12] have been proposed.

The present authors have previously reported a method for the production of hydrogen and carbonyl sulfide from hydrogen sulfide and carbon monoxide according to Reaction 2.[13] A closed cycle could be set up for the production of hydrogen and elementary sulfur from hydrogen sulfide if carbonyl sulfide could be decomposed selectively into carbon monoxide and sulfur:

$$\begin{array}{ll} H_2S + CO \longrightarrow H_2 + COS, & (2) \\ COS \longrightarrow CO + 1/x\cdot S_x, & (3) \\ \hline H_2S \longrightarrow H_2 + 1/x\cdot S_x. & (1) \end{array}$$

In this study, experiments were performed on Reaction 2, 3, and 4 in order to examine the possibility of this cycle:

$$CO + S \longrightarrow COS \qquad (4)$$

Experimental

Reaction 2. The apparatus employed in this study was made of Pyrex glass and was a flow reactor under atmospheric pressure, as is shown in Fig. 1. The catalyst was placed in the reactor, A. A mixture of hydrogen sulfide and carbon monoxide ($CO/H_2S=2.2$) was introduced into the reactor, A, at two different constant rates (Table 1). The reactor was then kept at certain given temperatures between 170—380 °C (Table 1). The effluent gas from the reactor was cooled at the trap, E, where the produced sulfur was condensed out; then it was introduced into the two-stage gas chromatograph in order to determine the composition of the reaction mixture. The first stage of the gas chromatograph was equipped with a Deactigel column (Applied Science Co.) in order to separate the mixture of hydrogen and carbon monoxide from the carbonyl sulfide and hydrogen sulfide, while a molecular-sieve column was used in the second stage for the separation of the hydrogen from the carbon monoxide.

Catalyst. The catalysts employed in Reaction 2 were as same as those employed in a previous work.[13]

Reaction 3. This reaction was a non-catalytic thermal decomposition reaction. The apparatus shown in Fig. 1 was used again except that the A reactor was changed to a quartz reactor, B. The carbonyl sulfide gas was introduced

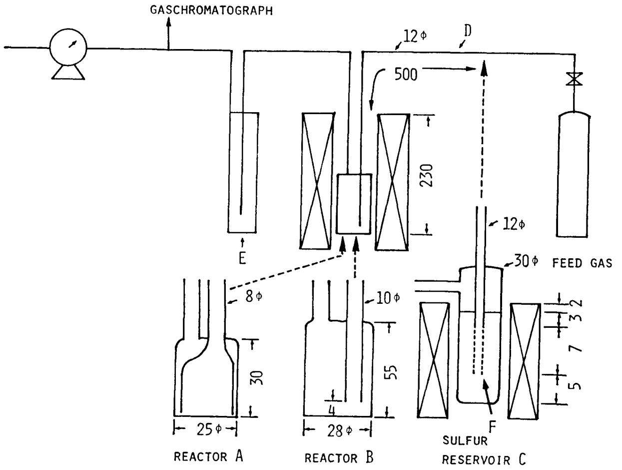

Fig. 1. Apparatus.

TABLE 1. RESULTS OF REACTION 2

Catalyst	Weight g	Surface area m^2	Reaction temp °C	Flow rate ml/min	H_2 concn %	H_2S conversion %	Reaction[b] ratio %
NiS	1.60	4.9	350	11.6	9.5	28.8	73.3
	1.60	4.9	250	11.6	5.0	15.8	37.3
Co_9S_8	2.94	93.1	300	14.2	12.1	38.7	94.4
	2.94	93.1	260	14.2	13.0	41.8	99.5
	2.94	93.1	220	14.2	13.3	42.9	97.7
	2.94	93.1	170	14.2	12.7	39.8	87.6
V_3S_4	3.00	12.0	350	14.2	7.5	24.0	61.1
	3.00	12.0	250	14.2	2.2	7.0	16.6
FeS	3.23	25.2	380	14.2	10.5	32.7	84.9
(FeS_2[a])	3.23	25.2	300	14.2	8.3	26.5	60.4
	3.23	25.2	250	14.2	3.3	10.7	25.2
Cr_2S_3	3.00	28.2	330	14.2	10.7	34.5	86.5
	3.00	28.2	280	14.2	6.5	20.8	50.2
MoS_2	4.24	14.0	380	14.2	11.8	37.6	97.7
	4.24	14.0	300	14.2	6.8	21.7	52.9
Ti_5S_4	3.22	349.0	350	14.2	8.4	26.9	68.4
	3.22	349.0	250	14.2	1.5	4.8	11.3

a) Minor component. b) (experimental conversion)/(equilibrium conversion).

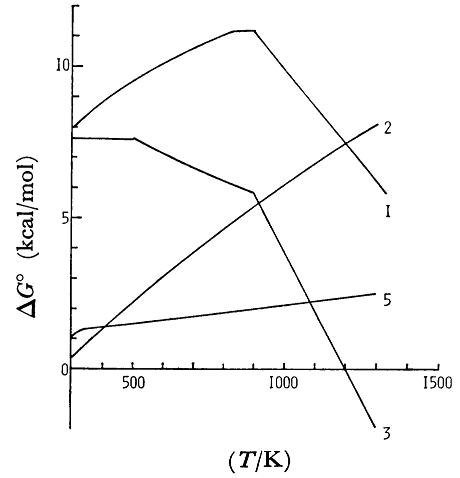

Fig. 2. Temperature dependence of ΔG° of Reactions 1,2 , 3, and 5. Reaction 1: $H_2S \rightarrow H_2 + 1/x \cdot S_x$, Reaction 2: $H_2S + CO \rightarrow COS + H_2$, Reaction 3: $COS \rightarrow CO + 1/x \cdot S_x$, Reaction 5: $COS \rightarrow 1/2 \cdot CO_2 + 1/2 \cdot CS_2$.

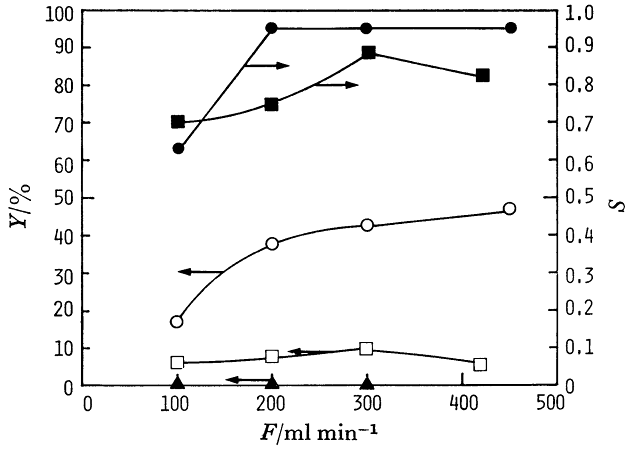

Fig. 3. Yields and selectivity against flow rate in Reaction 3. F: Flow rate, S: selectivity=(CO)/(CO $+2CO_2$), Y: yield=(CO)/(COS). ●, ○: 830 °C, ■, □: 630 °C, ▲: 430 °C.

at the given flow rates (Fig. 3). The reactor, B, was kept at 630, 730, and 830 °C. The composition of the each reaction mixture was determined by the same two-stage gas chromatograph.

Reaction 4. Reaction 4 was also performed in the same apparatus as Reaction 3, but now a sulfur reservoir, C, was attached to the apparatus shown in Fig. 1. The glass pipe, D, between the reactor, B, and the sulfur reservoir, C, was kept at 250 °C to prevent the condensation of the sulfur. The sulfur reservoir and the reactor were kept at the given temperatures (Figs. 4 and 5). In some cases, the inner pipe, F, of the sulfur reservoir was elongated (broken line in Fig. 1) in order to check the effect of the sulfur reservoir on Reaction 4. The carbon monoxide was introduced into the apparatus at certain given flow rates (Figs. 4 and 5). The carbon monoxide was made to react with sulfur in the sulfur reservoir, C, in the pipe, D, and in the reactor, B. The composition of the reaction mixture was determined by the two-state gas chromatograph.

Reagents. The purities of hydrogen sulfide, carbon monoxide, carbonyl sulfide, and sulfur were 99.99, 99.9, 99.9, and 99.5% respectively.

Results and Discussion

Table 1 represents the data for the various metal sulfide catalysts of Reaction 2 obtained at the reaction temperature of 170—380 °C and with the CO/H_2S ratio of 2.2 in the mixture of reactants. The results for Cu_2S, ZnS, and MnS were excluded from the table because the reactions on these catalysts did not proceed with a measurable velocity at 170—380 °C. As can be seen from Table 1, hydrogen and carbonyl sulfide can generally be obtained from hydrogen sulfide and carbon monoxide by using transition metal sulfides as catalysts at 170—380 °C. In the case of cobalt sulfide,

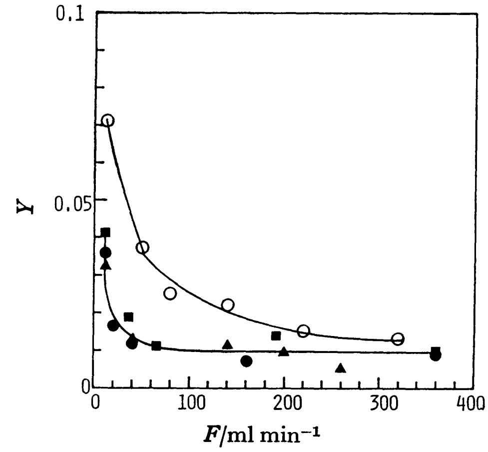

Fig. 4. Yield of Reaction 4 against flow rate (1). *F*: Flow rate, *Y*: yield=(COS)/(CO). Temperature of reactor: ○ 500 °C, ■ 450 °C, ● 400 °C, ▲ 300 °C. Temperature of sulfur reservoir: 200 °C.

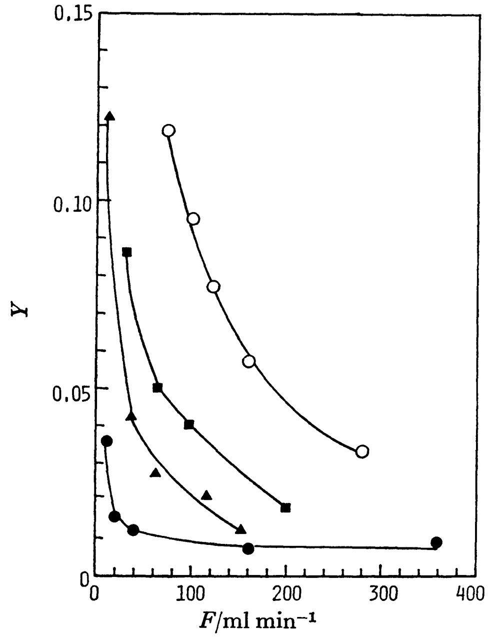

Fig. 5. Yield of Reaction 4 against flow rate (2). *F*: Flow rate, *Y*: yield=(COS)/(CO). Temperature of reactor: 400 °C. Temperature of sulfur reservoir: ○ 400 °C, ■ 300 °C, ▲ 200 °C, ● 200 °C.

hydrogen can be obtained in an amount as much as the equilibrated amount even at 220 °C. It should be noted that, in spite of the small surface area of the nickel sulfide catalyst, the conversion of hydrogen sulfide significantly high; thus, the reaction can proceed nearly to the equilibrium below 200 °C if a sufficient amount of a catalyst is employed.

Assuming that it is possible to separate each constituent from the produced gas mixture and that the selective decomposition of carbonyl sulfide into carbon monoxide and elementary sulfur can be performed, a two-step closed cycle for the decomposition of hydrogen sulfide can be constructed by the combination of Reactions 2 and 3.

Figure 2 represents the temperature dependence of the free energy changes of Reactions 1, 2, 3, and 5, which were calculated from the published thermochemical data.[14]

Figure 2 shows that the equilibrium conversions of Reactions 2 and 3 are much higher than that of Reaction 1. If Reaction 1 can be divided into Reactions 2 and 3, the additional yield of the two reactions can exceed that of Reaction 1. This is the most important reason to make up a multi-step cycle for the decomposition of hydrogen sulfide.

Unfortunately, carbonyl sulfide undergoes thermal decomposition by two reaction paths; one is the cracking reaction into carbon monoxide and elementary sulfur, as is expressed by Reaction 3, and the other is the disproportionation reaction to form carbon dioxide and carbon disulfide, as is expressed by Reaction 5.[15] Thus, the selectivity of the decomposition of carbonyl sulfide between Reaction 3 and Reaction 5 becomes a serious problem.

$$2COS \longrightarrow CO_2 + CS_2 \qquad (5)$$

Figure 3 shows the results obtained for the thermal decomposition of carbonyl sulfide. As can be seen in Fig. 3, the selectivity of carbon monoxide formation, which is represented by $CO/(CO+2CO_2)$, was as high as 95%, while that of carbon dioxide was as low as 5% at 830 °C when the flow rate of carbonyl sulfide was 420 ml min⁻¹. This selectivity seems to be sufficient to constitute a two-step closed cycle. Moreover, it must be emphasized that the yield and the selectivity of the carbon monoxide formation depended on the flow rate of the reactant carbonyl sulfide at 830 °C. The more carbon monoxide was produced, the faster the flow rate of the carbonyl sulfide. It was possible to obtain an almost equilibrated amount of carbon monoxide (*ca.* 45%) at 830 °C with the flow rate of 420 ml min^{-1}, without using any catalyst. On the other hand, the yield and selectivity of carbon monoxide were low at 630 and 430 °C over a wide range of flow rates.

When the flow rate was 100 ml min^{-1} at 830 °C, the yield and the selectivity of carbon monoxide formation were as low as that at 630 °C. From this fact, it may be concluded that Reaction 3 is very fast in both forward and reverse directions; thus, when the flow rate is slow, the reverse reaction occurs at the cooler part of the reactor, thus reducing the yield of carbon monoxide. The quenching of the gas mixture produced is, therefore, required in order to prevent the reverse reaction (Reaction 4).

In order to elucidate this reverse reaction more precisely, Reaction 4 was studied. In Fig. 4, the yields (COS/CO) of Reaction 4 are plotted against the fow rates of carbon monoxide at various temperatures of the reactor, B (300, 400, 450, and 500 °C). Below 450 °C, the yields were found to be as small as 1% at flow rates higher than 40 ml min^{-1}. At 500 °C, some increase in the yield was observed; however, the yield could be reduced to be less than 2% by raising the flow rate. Thus, Reaction 4 may be made negligible by increasing the flow rate. These results were obtained when the sulfur reservoir was kept at 200 °C and when the inner pipe, F, was dipped into the liquid sulfur to a depth of *ca.* 3 cm. Then, in order to estimate the effect of the sulfur reservoir more precisely, the inner pipe, F, was elongated to *ca.* 7 cm and the temperature of the reservoir was raised from 200 to 400 °C, while the temperature of the reactor, B, was kept at 400 °C. The results are shown in Fig. 4. The solid circles in Fig. 5 are the same data as those in Fig. 4. The results in Fig. 5 show that the yield of carbonyl sulfide increased when the carbon monoxide was mixed well with the liquid sulfur in the sulfur reservoir and when the temperature of the reservoir was elevated. The yield of carbonyl sulfide, however, depended greatly on the flow rate of the carbon monoxide. Thus, these results show that the recombination of carbon monoxide and liquid sulfur can be eliminated as negligible if the reaction mixture of Reaction 3 can be cooled promptly and if the separation of carbon monoxide from liquid can be carried out rapidly.

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