JOURNAL OF CATALYSIS 49, 379–382 (1977)

Catalytic Activity of Metal Sulfides for the Reaction, $H_2S + CO = H_2 + COS$

Today, it is widely recognized that the design of an adequate catalyst must be one of the most important objectives in industrial and academic research on catalysts. From such a point of view, much interest has been focused on the correlations between the catalytic properties and the physical and chemical properties of solid catalysts. The so-called twin-peaked activity pattern found for the catalytic activity of a series of oxides of 3*d* transition metals is a good example (*1*). This activity pattern has been found in various catalytic reactions, such as the dehydrogenation of propane, the disproportionation and dehydrogenation of cyclohexane (*2*), and the isomerization of *cis*-2-butene (*3*). A theoretical explanation for this activity pattern was given by Dowden and Wells (*4*, *5*) on the basis of crystal field theory. According to this explanation, a similar pattern with twin-peaked activity would be found for the sulfides of 3*d* transition metals in some catalytic reactions, provided that suitable surface coordination is accessible.

Dowden (*5*) has also reported a similar activity pattern for 3*d*-series metal sulfides in the hydrogenolysis of carbon disulfide, which is shown by the following equation:

$$CS_2 + 4H_2 = CH_4 + 2H_2S. \quad (1)$$

In this case, however, it should be noted that the maximum and minimum positions of the activity pattern are not in accordance with those for the oxide system. Thus, it seems worthwhile to obtain detailed information about the activity pattern of 3*d*-series metal sulfides.

In this study the catalytic activities of these metal sulfides have been examined, using the following reaction as a test reaction:

$$H_2S + CO = H_2 + COS. \quad (2)$$

EXPERIMENTAL

The reaction rate was followed by measurement of the concentrations of hydrogen, hydrogen sulfide, carbon monoxide, and carbonyl sulfide in the effluent gas, using a flow reactor under atmospheric pressure. The effluent gas was analyzed by a two-stage gas chromatograph, which was equipped with a Deactigel (Applied Science Co.) column in the first stage for separation of the mixture of hydrogen and carbon monoxide from carbonyl sulfide and hydrogen sulfide according to the method described by Thornsberry (*6*), while a molecular sieve column was used in the second stage for separation of hydrogen and carbon monoxide.

The purity of hydrogen sulfide and carbon monoxide was 99.99 and 99.9%, respectively.

Each catalyst was pretreated in a hydrogen sulfide stream at 380°C for several hours prior to use. All experiments were carried out under the following reaction conditions: reaction temperature, 170–380°C; $CO:H_2S$ in the reactant gas mixture = 2.2:1.

Cr_2S_3 was prepared by the sulfurization of $CrCl_3$ by a hydrogen sulfide stream in a quartz tube at 600–650°C. FeS was prepared in the following manner: Ammonium

ISSN 0021-9517

TABLE 1

Crystal Phases and Surface Areas of Various Catalysts

Crystal phase of catalyst			Surface area[b] m^2/g
Original[a]	After pretreatment	After reaction	
TiS_2	Ti_5S_4	Ti_5S_4	108.4
V_3S_4	V_3S_4	V_3S_4	4.0
Cr_2S_3	Cr_2S_3	Cr_2S_3	9.4
β-MnS	α-MnS	α-MnS	—
FeS	$FeS(FeS_2)$[c]	$FeS(FeS_2)$[c]	7.8
$CoS_{1.097}$	$CoS_{1.097}$	Co_9S_8[d]	31.7
NiS	NiS	NiS	3.1
Cu_2S	Cu_2S	Cu_2S	—
ZnS	ZnS	ZnS	—

[a] Original materials were obtained from the preparation described in the text or from commercial sources.

[b] Determined after the reaction.

[c] Mixture in which FeS_2 was a minor component.

[d] X-Ray diffraction patterns were the same before and after the reaction, except for that of cobalt sulfide.

sulfide solution was mixed with ferric chloride solution, and the resultant precipitate was washed and dried in an inert atmosphere. From the X-ray diffraction pattern observed after the pretreatment it was shown that the main component was FeS; other lines indicated the presence of FeS_2 as a minor component. V_3S_4 was prepared by the sulfurization of ammonium metavanadate by a hydrogen sulfide stream in a quartz tube at 700°C. Cu_2S was prepared by the sulfurization of Cu_2O by a hydrogen sulfide stream at about 400°C. ZnS, NiS, MnS, TiS_2, and $CoS_{1.097}$ were obtained from commercial sources. The crystal phase of each catalyst was determined by means of X-ray diffraction before and after pretreatment and after the reaction, and its surface area was determined by the BET method after the reaction. The results are summarized in Table 1.

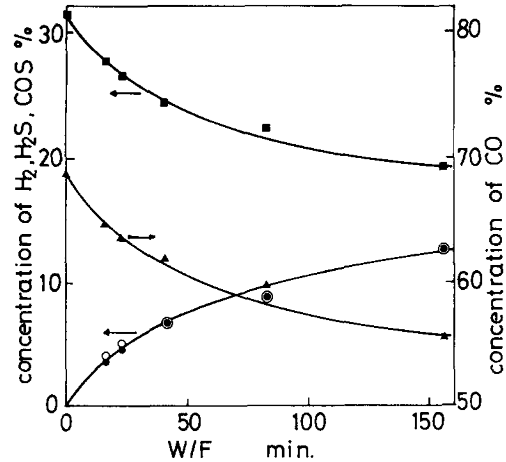

FIG. 1. The reaction, $H_2S + CO = H_2 + COS$, on Co_9S_8 at 170°C. W, weight of catalyst (2.94 g); F, weight of reactant gas mixture fed to the reactor per minute (g/min.). The concentrations of H_2(●), H_2S(■), CO(▲), and COS(○) are plotted against W/F.

RESULTS AND DISCUSSION

A typical result for cobalt sulfide at 170°C is given in Fig. 1, in which the concentrations of hydrogen, hydrogen sulfide, carbon monoxide, and carbonyl sulfide in the effluent gas from the reactor are plotted against W/F, where W is the weight of catalyst set in the reaction vessel, and F is the flow rate of reactant gas mixture expressed in terms of the weight of the gas mixture fed to the reactor per minute. At the initial stage of the reaction on cobalt sulfide, the evolution of a larger amount of carbonyl sulfide than of hydrogen was observed; this may have resulted from a reduction of $CoS_{1.097}$ to Co_9S_8 by carbon monoxide. At the stationary state, the carbon balance was observed to be closed, and the amounts of hydrogen and carbonyl sulfide were found to be substantially equal, as shown in Fig. 1. The initial rate of hydrogen formation was found to be expressed by the following equation:

$$d(H_2)/dt = k[(H_2S) - (H_2S)_{eq}] \times [(CO) - (CO)_{eq}], \quad (3)$$

where $(\ )_{eq}$ and t represent the equilibrium concentration and W/F, respectively. The values of the rate constants obtained are listed in Table 2. The rate constants calculated from the data listed in Table 2, at the reaction temperatures of 170, 250, and 380°C, are plotted in Fig. 2 for the series of sulfides, to compare their catalytic activities. As can be seen from Fig. 2, twin-peaked activity patterns similar to those observed for the oxide system have been obtained. That is, in this sulfide series ranging from Ti_5S_4 to Cu_2S, two peaks of activity were found, the first for Cr_2S_3 and the second represented by NiS at 170 and 250°C or by CO_9S_8 at 380°C. These two peaks of activity are separated by the low-activity sulfide, MnS. It is clear from Table 2 that almost the same activity pattern is obtained when the activation energy is adopted as a measure of catalytic activity.

The reaction rate at a definite temperature or at the temperature at which the reaction rate reaches a definite value has often been adopted as a measure of catalytic activity (*1–3*). However, De and Stone (*7*) emphasized the importance of taking into account the temperature dependence of the reaction rate for a comparison of catalytic activity on the ground that the activity patterns of Ti_2O_3, V_2O_3, and Cr_2O_3 for the hydrogen–deuterium exchange reaction changes, when sintered oxides are used at high temperatures. Under these conditions, Ti_2O_3 and V_2O_3 were found to become more active than Cr_2O_3, as reflected by the much larger activation energies of Ti_2O_3 and V_2O_3 compared to that of Cr_2O_3. The twin-peaked activity pattern for the first-series transition metal sulfides found in this study is valid over the range of reaction temperature of 170–380°C.

TABLE 2

Initial Rate Constants of Various Catalysts

Catalyst	Rate constant k (mole $\%\cdot min^{-1}\cdot m^{-2}$)
NiS	$0.186\cdot\exp(-7{,}800/RT)$
Co_9S_8	$2.09\cdot\exp(-10{,}500/RT)$
V_3S_4	$13.6\cdot\exp(-16{,}800/RT)$
FeS(FeS_2)	$316\cdot\exp(-18{,}300/RT)$
Cr_2S_3	$419\cdot\exp(-18{,}100/RT)$
Ti_5S_4	$1.20\cdot\exp(-17{,}900/RT)$
MnS[a]	$\simeq 0$
ZnS[a]	$\simeq 0$
Cu_2S[a]	$\simeq 0$

[a] Reaction does not proceed with a measurable rate at 170–380°C.

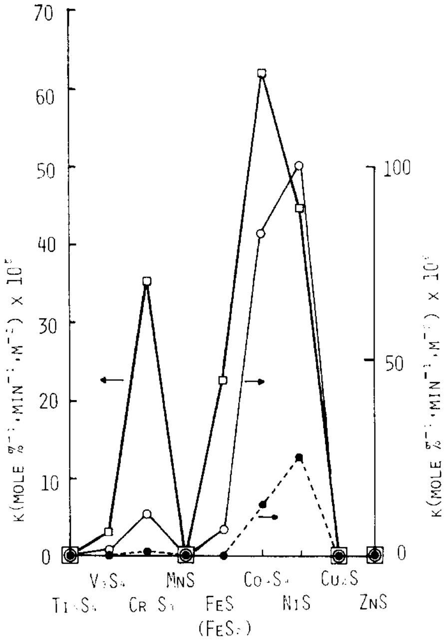

FIG. 2. Activity pattern of metal sulfide catalysts for the reaction, $H_2S + CO = H_2 + COS$. k: rate constant of Eq. (3) at 170 (●), 250 (○), and 380°C (□).

In the case of solid sulfides, the crystal phases are more numerous and the structures are more complex than those of oxides at relatively low temperature. Consequently, the principles described by Dowden and Wells (*4, 5*) for the oxide system may not necessarily be applicable to the sulfide system. In this study it was found that the chemical composition of cobalt sulfide changed during the reaction, that is, the initial composition $CoS_{1.097}$ was reduced to Co_9S_8 during the reaction. It is suggested, however, from the material balance between the reaction gas components that the change of chemical composition of cobalt sulfide was complete at the very initial stage of the reaction, and the stationary state was reached rapidly. Consequently, it seems most probable that the active catalyst component at the stationary state is CO_9S_8.

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Received September 30, 1976; revised May 27, 1977