The Formation Process of Cobalt Sulfide from Tricobalt Tetraoxide Using Sulfur Dioxide as a Sulfidizing Agent

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The products obtained by heating a mixture of Co_3O_4 and carbon in a SO_2 stream were CoO and $CoSO_4$ at 400—600 °C, $Co_{1-x}S$ and CoO at 650—700 °C, and $Co_{1-x}S$ ($Co_{0.90}S$) at 750—800 °C. Sulfur was obtained outside the heating zone throughout the temperature range. The possible reactions during the above process were also examined. Further, thermodynamical consideration was made of the formation of $Co_{1-x}S$. The formation process of $Co_{1-x}S$ ($Co_{0.90}S$) from Co_3O_4 can be represented as follows: The reaction of carbon with SO_2 occurs at first to form sulfur. Above *ca.* 400 °C, the reaction of Co_3O_4 with SO_2 occurs to form CoO and $CoSO_4$. Above *ca.* 500 °C, the reductions of Co_3O_4 with carbon and with sulfur also occur to form CoO. Above *ca.* 600 °C, the reduction of $CoSO_4$ with carbon occurs to form CoO. Above *ca.* 650 °C, $Co_{1-x}S$ is formed by the reaction of CoO with sulfur, both of which had been formed by the above reactions.

There have been several reports on the formation of cobalt sulfide by the reaction of cobalt with sulfur[1] or hydrogen sulfide,[2] and by the reaction of cobalt monooxide (CoO) with hydrogen sulfide.[3] Regarding the synthesis of cobalt sulfide using sulfur dioxide (SO_2) as a sulfidizing agent, however, little information has been available apart from the report of Pechkovskii and Mal'tseva.[4] They performed the differential thermal analysis of a mixture of tricobalt tetraoxide(Co_3O_4) and carbon (Co_3O_4:C=1:5 by molar ratio) in a SO_2 stream. They observed the formation of cobalt(II) sulfate($CoSO_4$) and CoO above 450 °C and of cobalt sulfide in addition to these products above 600 °C. The sample which they obtained after heating up to about 970 °C was a mixture of cobalt sulfide and CoO containing no residual carbon. They also reported that the cobalt sulfide formed was CoS below 700 °C and Co_9S_8 at 750—1000 °C. But, the formation process of cobalt sulfide from Co_3O_4 using SO_2 has not yet been revealed. This process is not only interesting from the viewpoint of the synthesis of the sulfide itself, but is also important for the further utilization of SO_2.

In this work, the reactions of Co_3O_4 with SO_2 and of Co_3O_4 with SO_2 in the presence of carbon were examined. In order to elucidate the formation process of cobalt sulfide from Co_3O_4, the reactions of Co_3O_4 with carbon and with sulfur were examined. Also, the reaction of $CoSO_4$, formed during the reaction process of Co_3O_4 with SO_2 in the presence of carbon, with carbon and the reaction of CoO, formed during the reaction process, with sulfur in a SO_2 stream were examined. Further, thermodynamical consideration was made of the Co–S–C–O system.

Experimental

The Co_3O_4 used was prepared at 800 °C by the thermal decomposition in the air of pentacobalt(II) dicarbonate hexahydroxide($Co_5(CO_3)_2(OH)_6$), which had been prepared by adding sodium carbonate solution to cobalt(II) nitrate solution.[5] The CoO was prepared by the thermal decomposition of the $Co_5(CO_3)_2(OH)_6$ at 800 °C in an argon stream.[5] The $CoSO_4$ was prepared by the dehydration of the guaranteed reagent cobalt(II) sulfate heptahydrate at 400 °C and was β-form(orthorhombic: low-temperature form).[6] The carbon was prepared by the thermal decomposition of the guaranteed reagent D-glucose. The above materials were used as powders under 150 mesh.

A mixture of Co_3O_4 and carbon at a specified ratio in a quartz boat (length: 72 mm, width: 16 mm, depth: 9 mm) was placed in a transparent, quartz reaction tube (inner diameter: 28 mm, length: 1000 mm). Gaseous SO_2 was then introduced into the reaction tube at a flow-rate of 100 cm³/min. The sample part was positioned in the middle of the tubular electric furnace (heating length: 300 mm) maintained at a specified temperature for 1 h. The temperature of the sample part was controlled within ±2 °C. After heating, the sample was quenched rapidly, and then heated at 100 °C for 1 h in an argon stream in order to release the SO_2 adsorbed on unreacted carbon.[7] The reactions of Co_3O_4 with carbon and with sulfur and of $CoSO_4$ with carbon in an argon stream, and the reaction of CoO with gaseous sulfur in a SO_2 stream were examined in a similar manner.

The X-ray analysis of the sample was performed with an X-ray powder diffractometer equipped with a proportional counter using Ni filtered Cu radiation. The thermogravimetry (TG) was performed by using a thermal balance with a quartz helix. The sensitivity of the quartz helix used was approximately 94 mm/g. The heating rate of 2.5 °C/min was employed, and a flow-rate of SO_2 was maintained at 50 cm³/min.

Concerning the chemical analysis of the cobalt sulfide formed, the sample was oxidatively decomposed in HNO_3 with $KClO_3$. Then, the cobalt content was determined by the chelatometric titration[8] and sulfur content by the gravimetric method as $BaSO_4$. In the case of a mixture of cobalt sulfide, unreacted carbon, and sulfur adsorbed on the carbon, the sample was oxidatively decomposed, and the contents of cobalt and total sulfur were determined by the above techniques. Then, after dissolving the cobalt sulfide in the sample selectively with dilute HNO_3, the undissolved residue, which consisted of unreacted carbon and the sulfur adsorbed on it, was oxidatively decomposed in HNO_3 with $KClO_3$, and the amount of sulfur adsorbed on the carbon was gravimetrically determined. The amount of sulfur due to the cobalt sulfide in the sample was calculated as the difference between the above total sulfur and the sulfur adsorbed on the carbon.

Results and Discussion

Reaction of Co_3O_4 with SO_2. The TG of Co_3O_4 (0.3 g) in a SO_2 stream was carried out. The TG

TABLE 1. PRODUCTS OBTAINED BY HEATING A MIXTURE OF Co_3O_4 AND CARBON IN A SO_2 STREAM AT VARIOUS TEMPERATURES

Temp / °C	Sample in the boat	Amount of sulfur obtained outside the heating zone/g
350	Co_3O_4	Trace
400	$Co_3O_4 > CoO > CoSO_4[\beta]$	Trace
450	$Co_3O_4 > CoO > CoSO_4[\beta]$	Trace
500	$CoO > Co_3O_4 > CoSO_4[\beta]$	Trace
550	$CoO > CoSO_4[\beta > \alpha]$	Trace
600	$CoO \gg CoSO_4[\alpha]$	Trace
650	$CoO > Co_{1-x}S$	Trace
700	CoO, $Co_{1-x}S$	0.01
750	$Co_{1-x}S$	0.55
800	$Co_{1-x}S$	2.40

TABLE 2. X-RAY DIFFRACTION DATA OF THE $Co_{1-x}S$ FORMED

d/Å	I/I_1	hkl
2.927	60	100
2.549	70	101
1.941	100	102
1.689	45	110
1.489	5	103
1.410	10	201
1.297	5	004
1.274	40	202
1.117	<5	203
1.082	10	211
1.028	15	114
1.017	20	212

TABLE 3. EXPERIMENTAL RESULTS FOR THE REACTION OF Co_3O_4 WITH CARBON IN AN ARGON STREAM

Temp / °C	Weight loss/%	Sample in the boat
450	—	Co_3O_4
500	0.2	$Co_3O_4 \gg CoO$
600	1.3	$Co_3O_4 > CoO$
700	4.3	$CoO \gg Co_3O_4$
750	6.3	$CoO \gg Co[\beta]$
800	15.4	$Co[\beta] > CoO$

curve showed that the sample weight increased continuously above about 400 °C and reached a constant value at about 670 °C. The sample heated up to 700 °C was found to be a mixture of CoO[9] and α-$CoSO_4$ (orthorhombic: high-temperature form)[10] by X-ray analysis. The final weight gain was 26.5%. This value was in good agreement with the value, 26.60%, which was calculated based on the reaction: $Co_3O_4(s) + SO_2(g) \rightarrow 2CoO(s) + CoSO_4(s)$. These results indicate that Co_3O_4 reacts with SO_2 above about 400 °C to form CoO and $CoSO_4$.

Reaction Products of Co_3O_4 with SO_2 in the Presence of Carbon. The reaction products of Co_3O_4 with SO_2 in the presence of carbon as a reducing agent were examined. Based on the results of preliminary experiments on the suitable amount of carbon to be mixed, the products obtained by heating a mixture of 2.00 g of Co_3O_4 and 2.00 g of carbon at various temperatures for 1 h in a SO_2 stream at a flow-rate of 100 cm^3/min were examined. The results are shown in Table 1. The sample in the boat was identified by X-ray analysis.[6,9–13] The modification of the $CoSO_4$ formed is represented in the brackets.

The formation of CoO and $CoSO_4$ was observed above 400 °C. Above 650 °C, the formation of $Co_{1-x}S$ was observed in addition to that of CoO. $Co_{1-x}S$ was obtained at 750—800 °C. Sulfur was obtained outside the heating zone throughout the temperature range in this experiment, and the amount of sulfur markedly increased above about 750 °C.

The X-ray diffraction data of the $Co_{1-x}S$ obtained are shown in Table 2. The $Co_{1-x}S$ phase is known to have a NiAs structure. The lattice constants of the $Co_{1-x}S$ formed were calculated from the X-ray diffraction data, shown in Table 2, to be $a_0 = 3.380$ Å and $c_0 = 5.185$ Å. The composition of the $Co_{1-x}S$ formed was determined by chemical analysis. The analysis gave Co 42.5%; S 25.7% for the sample obtained at 750 °C, and Co 61.3%; S 37.2% at 800 °C. From these results, the composition of the $Co_{1-x}S$ formed was determined to be $Co_{0.90}S$.

The formation of $Co_{1-x}S$ with the Co/S atomic ratio of 0.90 by the reaction of Co_3O_4 with SO_2 in the presence of carbon at 650—800 °C seems to be reasonable in terms of the phase diagram for the Co–S system, reported recently by Rau.[14] As mentioned before, Pechkovskii and Mal'tseva[4] described that Co_9S_8 was formed by heating a mixture of Co_3O_4 and carbon in a SO_2 stream at 750—1000 °C. But Co_9S_8 is unstable above 830 °C according to the above phase diagram.[14]

Reaction Process of Co_3O_4 with SO_2 in the Presence of Carbon. To elucidate the reaction process of Co_3O_4 with SO_2 in the presence of carbon, the following experiments were carried out under conditions similar to those described above.

Reaction of Co_3O_4 with Carbon: The products formed by heating a mixture of Co_3O_4 (2.00 g) and carbon (2.00 g) at various temperatures in an argon stream (100 cm^3/min) for 1 h were examined by X-ray analysis.[9,11,15] The results are shown in Table 3.

These results indicate that the reduction of Co_3O_4 with carbon proceeds above about 500 °C to form CoO, and that above about 750 °C CoO formed is further reduced with carbon to β-cobalt.

Reaction of Co_3O_4 with Sulfur: As seen from Table 1, when the mixture of Co_3O_4 and carbon was heated in a SO_2 stream, sulfur was formed. The reaction of carbon with SO_2 occurs even at 350 °C to form sulfur and this reaction proceeds markedly above about 700 °C, as reported by the present authors.[7] Therefore, the reaction of Co_3O_4 with gaseous sulfur was examined.

Co_3O_4(2.00 g) was heated in a stream of argon (100 cm^3/min) containing a specified amount of gaseous sulfur at various temperatures for 1 h. Prior to

Table 4. Products obtained by heating Co_3O_4 in a stream of argon containing gaseous sulfur

Temp/°C	Weight loss/%	Sample in the boat
450	—	Co_3O_4
500	0.1	$Co_3O_4 \gg CoO$
550	0.2	$Co_3O_4 \gg CoO$
600	0.5	$Co_3O_4 > CoO$

Table 5. Experimental results for the reaction of $CoSO_4$ with carbon in an argon stream

Temp/°C	Weight loss/%	Sample in the boat
500	—	$CoSO_4[\beta]$
550	—	$CoSO_4[\beta > \alpha]$
600	12.6	$CoSO_4[\beta > \alpha]$, CoO
650	27.8	CoO
700	28.7	CoO

this experiment, the amounts of sulfur formed by heating 2.00 g of carbon at various temperatures for 1 h in a SO_2 stream at a flow-rate of 100 cm^3/min were measured. Based on these experimental results, the amount of sulfur introduced at various temperatures was controlled to be 0.01 g for the experiments below 550 °C, and 0.04 g at 600 °C. The experimental results are shown in Table 4.

These results indicate that the reduction of Co_3O_4 with gaseous sulfur proceeds gradually above about 500 °C to form CoO.

Reaction of $CoSO_4$ with Carbon: As seen from Table 1, when the mixture of Co_3O_4 and carbon was heated in a SO_2 stream, $CoSO_4$ was formed above about 400 °C. Therefore, the reaction of $CoSO_4$ with carbon was examined.

The products obtained by heating a mixture of $CoSO_4$ (2.00 g) and carbon (2.00 g) in an argon stream (100 cm^3/min) for 1 h were examined. The results are shown in Table 5.

These results indicate that the reduction of $CoSO_4$ with carbon occurs above about 600 °C to form CoO.

The process of formation of the CoO on heating the mixture of Co_3O_4 and carbon in a SO_2 stream can be explained as follows: The reaction of Co_3O_4 with SO_2 occurs above about 400 °C to form CoO and $CoSO_4$. Above about 500 °C, the reductions of Co_3O_4 with carbon and with sulfur also occur to form CoO. Above about 600 °C, the $CoSO_4$ formed is reduced with carbon to CoO.

Formation Reaction of $Co_{1-x}S$ from CoO: As seen from Table 1, when the mixture of Co_3O_4 and carbon was heated in a SO_2 stream, $Co_{1-x}S(Co_{0.90}S)$ was formed above about 650 °C. Above this temperature, Co_3O_4 was reduced to CoO. Therefore, the reaction of CoO with gaseous sulfur in a SO_2 stream was examined.

Table 6. Products obtained by heating CoO in a stream of SO_2 containing gaseous sulfur

Temp/°C	Weight gain/%	Sample in the boat
600	—	CoO
650	2.2	$CoO \gg Co_{1-x}S$
700	7.5	$CoO > Co_{1-x}S$
750	15.4	CoO, $Co_{1-x}S$
800	19.4	$Co_{1-x}S > CoO$

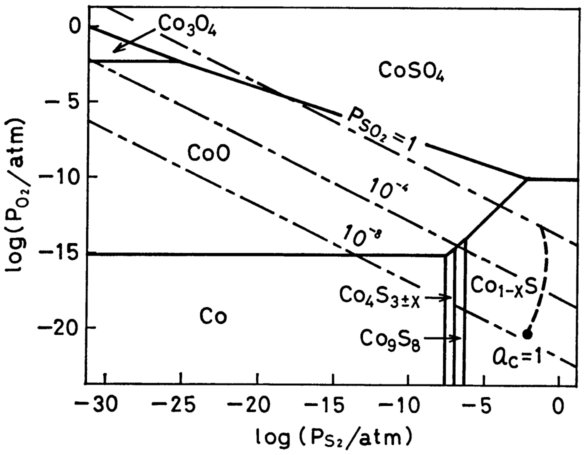

Fig. 1. Chemical potential diagram for the Co–S–C–O system at 800 °C (1 atm=101325 Pa).

The products formed by heating CoO (2.00 g) for 1 h in a stream of SO_2 (100 cm^3/min) containing a specified amount of gaseous sulfur at various temperatures were examined. The amounts of sulfur introduced were controlled to be 0.04 g for the experiment at 600 °C, 0.12 g at 650 °C, 0.58 g at 700 °C, 1.62 g at 750 °C, and 3.34 g at 800 °C, based on the results obtained for the amounts of sulfur formed by heating 2.00 g of carbon at various temperatures for 1 h in a SO_2 stream at a flow-rate of 100 cm^3/min. The experimental results are shown in Table 6.

These results indicate that the reaction of CoO with gaseous sulfur proceeds above about 650 °C to form $Co_{1-x}S$. The composition of the $Co_{1-x}S$ formed was evaluated to be $Co_{0.90}S$ by X-ray analysis (Table 2) and chemical analysis.

As seen from Table 3, CoO was reduced with carbon above about 750 °C to cobalt. In the Co–S system, the presence of Co_9S_8 and $Co_4S_{3\pm x}$ in addition to $Co_{1-x}S$ has been known as the lower sulfides. Therefore, thermodynamical consideration was made of the Co–S–C–O system, in order to discuss whether CoO was converted to $Co_{1-x}S$ *via* $Co_4S_{3\pm x}$, Co_9S_8 or cobalt, or without the formation of the lower sulfides or cobalt. The chemical potential diagrams for the Co–S–C–O system were constructed in a manner similar to that described by Yazawa[16] on the basis of the available thermodynamic data[17,18] and phase relations.[14] As an example, the diagram at 800 °C is shown in Fig. 1. The broken curved line shows the oxygen and sulfur potentials in the gas phase formed by the reaction of carbon with SO_2, depending on the carbon content in the gas phase. The activity of carbon, a_c, is unity at the dot mark. In these calculations, CO, CO_2, O_2, COS, CS_2, SO_2, SO_3, S_2, S_4, S_6, and S_8

were assumed to be gaseous products of carbon with SO_2.

The results shown in Fig. 1 indicate that CoO is converted to $Co_{1-x}S$ *via* cobalt, $Co_4S_{3\pm x}$, and Co_9S_8 under a pressure of SO_2 below *ca.* 10^{-5} atm, *via* $Co_4S_{3\pm x}$ and Co_9S_8 under a pressure of SO_2 at *ca.* 10^{-5}—10^{-4} atm, and *via* Co_9S_8 under a pressure of SO_2 at *ca.* 10^{-4}—10^{-3} atm, and that CoO is converted to $Co_{1-x}S$ without any formation of cobalt, $Co_4S_{3\pm x}$, and Co_9S_8 under a pressure of SO_2 above *ca.* 10^{-3} atm. Considering the experimental conditions in this work, the results in Fig. 1 show that $Co_{1-x}S$ is formed from CoO without any formation of the lower sulfides and cobalt.

From the results mentioned above, the process of formation of $Co_{1-x}S(Co_{0.90}S)$ by the reaction of Co_3O_4 with SO_2 in the presence of carbon can be represented as follows: On heating a mixture of Co_3O_4 and carbon in a SO_2 stream, the reaction of carbon with SO_2 occurs at first to form sulfur. Above about 400 °C, the reaction of Co_3O_4 with SO_2 occurs to form CoO and $CoSO_4$. Above about 500 °C, the reductions of Co_3O_4 with carbon and with sulfur also occur to form CoO. Above about 600 °C, the reduction of $CoSO_4$ with carbon occurs to form CoO. Above about 650 °C, $Co_{1-x}S$ is formed by the reaction of CoO with sulfur, both of which had been formed by the above reactions.

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