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The Formation of Molybdenum Disulfide by the Reaction between Molybdenum Trioxde and Sulfur Dioxide in the Presence of Carbon

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The reaction products obtained by heating a mixture of MoO_3 and carbon in a SO_2 stream at various temperatures were examined. The possible reactions during the above process were also studied. Further, thermodynamical consideration was made of the formation of MoS_2. When a mixture of MoO_3 and carbon was heated in a SO_2 stream, MoO_2 was formed above 400 °C. At 500—550 °C, the formation of a small amount of Mo_4O_{11} was also observed. Above 700 °C, the formation of MoS_2 in addition to MoO_2 was observed, and MoS_2 alone was obtained at 1000 °C. Sulfur was obtained outside the heating zone throughout the temperature range in this experiment. The process of the formation of MoS_2 by the reaction between MoO_3 and SO_2 in the presence of carbon can be represented as follows: The reaction between carbon and SO_2 occurs at first to form sulfur. Above *ca.* 400 °C, the reductions of MoO_3 with carbon and with sulfur occur to form MoO_2. Above *ca.* 700 °C, MoS_2 is formed by the reaction between MoO_2 and sulfur, which are formed by the above reactions.

As sulfidizing agents for synthesizing molybdenum disulfide (MoS_2), hydrogen sulfide and sulfur have been well known. But there has been no report on the chemical process for synthesizing MoS_2 from molybdenum trioxide (MoO_3) using sulfur dioxide (SO_2) as a sulfidizing agent. It is not only interesting from the viewpoint of the synthesis of the sulfide itself, but also important for the development of SO_2 utilization, to obtain knowledge of the above chemical process.

In this work, the reaction products between MoO_3 and SO_2 in the presence of carbon at various temperatures were examined. In order to elucidate the reaction process between MoO_3 and SO_2 in the presence of carbon, the reactions of MoO_3 with carbon and of MoO_3 with gaseous sulfur in a SO_2 stream were examined. Also, the reactions of MoO_2, formed during the reaction process between MoO_3 and SO_2 in the presence of carbon, with carbon and of MoO_2 with gaseous sulfur in a SO_2 stream were examined. Further, thermodynamical consideration was made of the formation of MoS_2.

Experimental

The MoO_3 used was prepared by the thermal decomposition of the guaranteed reagent ammonium paramolybdate at 600 °C. The carbon was prepared by the thermal decomposition of the guaranteed reagent D-glucose. The above materials were used as powders under 150 mesh. Gaseous SO_2 was dried by passing it through concd H_2SO_4 and over P_2O_5.

A mixture of MoO_3 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. 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 held at 100 °C for 1 h in an argon stream in order to release the adsorbed SO_2 on unreacted carbon.[1)] The reactions of MoO_3 with carbon in an argon stream, of MoO_3 with gaseous sulfur in a SO_2 stream, of MoO_2 with carbon in an argon stream, and of MoO_2 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 72 mm/g, and the heating rate of 2.5 °C/min was employed.

The molybdenum content in the sample was determined gravimetrically as $PbMoO_4$ after the fusion of the sample with a mixture of Na_2CO_3 and K_2CO_3. The sulfur content in the sample was determined gravimetrically as $BaSO_4$ after decomposing the sample with HNO_3 and $KClO_3$.

Results and Discussion

Reaction Products between Molybdenum Trioxide and Sulfur Dioxide in the Presence of Carbon. The TG of MoO_3 (0.3 g) in a SO_2 stream at a flow-rate of 50 cm^3/min was carried out. The heating temperature of the sample was limited to below 700 °C, since MoO_3 vaporized above this temperature. No weight change was observed, and the sample after the heating was found to be unreacted MoO_3 by X-ray analysis.[2)] These results indicate that MoO_3 does not react with SO_2.

The reaction between MoO_3 and SO_2 in the presence of carbon was then examined. First, the products obtained by heating a mixture of 2.00 g of MoO_3 and 1.20 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, together with the weight changes in the samples. The sample in the boat was identified by X-ray analysis.[2–5)]

The formation of MoO_2 was observed above 400 °C, and a small amount of Mo_4O_{11} in addition to MoO_2 was also observed at 500—550 °C. The formation of MoS_2 was observed at 700 °C. A small amount of sulfur was obtained outside the heating zone throughout the temperature range in this experiment. The slight increase in the sample weight at 350—400 °C was due to the adsorption of the sulfur formed by the reaction on the unreacted carbon.[1)]

In addition to the above observations, it was observed

Table 1. Products obtained by heating a mixture of MoO_3 and carbon in a SO_2 stream at various temperatures

Temp / °C	Weight change/%	Sample in the boat	Amount of sulfur obtained outside the heating zone/g
350	+0.1	MoO_3	Trace
400	+0.1	$MoO_3>>MoO_2$	Trace
450	−0.1	$MoO_3>>MoO_2$	Trace
500	−4.7	$MoO_2>MoO_3>Mo_4O_{11}$	Trace
550	−7.2	$MoO_2>>MoO_3>Mo_4O_{11}$	Trace
600	−8.8	MoO_2	0.00_5
650	−8.9	MoO_2	0.03
700	−7.8	$MoO_2>>MoS_2$	0.09

that a small amount of unreacted MoO_3 vaporized and deposited outside the heating zone at 700 °C. As seen from Table 1, all the MoO_3 used was converted to nonvolatile MoO_2 above 600 °C. The reactions at temperatures above 800 °C were examined by using a mixture of MoO_2 and carbon. When a mixture of 2.00 g of MoO_2 and 1.20 g of carbon was heated in a SO_2 stream (100 cm^3/min) at 800 °C for 1 h, unreacted carbon was not observed in the sample obtained after the heating. This result is considered to be due to the fact that the reaction between carbon and SO_2 proceeds markedly.[1)] 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 MoO_2 and 5.00 g of carbon in a SO_2 stream (100 cm^3/min) at various temperatures above 800 °C for 1 h were examined. The mixture of MoO_2 and carbon was prepared by adding fresh carbon to a mixture of MoO_2 and carbon, obtained by the reduction of MoO_3 with carbon at 700 °C. The results are shown in Table 2.

Table 2. Products obtained by heating a mixture of MoO_2 and carbon in a SO_2 stream at various temperatures

Temp / °C	Weight loss/%	Sample in the boat	Amount of sulfur obtained outside the heating zone/g
800	34.3	$MoO_2 \approx MoS_2$	3.90
900	54.0	$MoS_2>MoO_2$	4.86
950	57.6	$MoS_2>MoO_2$	5.04
1000	64.2	MoS_2	5.66

Chemical analysis of the sample obtained at 1000 °C showed it to contain 59.8% Mo and 39.9% S. Chemical analysis also proved that sulfur was not adsorbed on the unreacted carbon at 1000 °C. From these results, the sulfur was found to be due to the sulfide formed. The atomic ratio of Mo : S in the sample was calculated to be $1 : 2.0_0$. The results indicated that all the MoO_2 used was sulfidized to MoS_2 at 1000 °C.

Reaction Process between Molybdenum Trioxide and Sulfur Dioxide in the Presence of Carbon. To elucidate the reaction process between MoO_3 and SO_2 in the presence of carbon, the following experiments were carried out under conditions similar to those described above.

Reaction between MoO_3 and Carbon: The products formed by heating a mixture of MoO_3 (2.00 g) and carbon (1.20 g) at various temperatures in an argon stream (100 cm^3/min) for 1 h were examined. The results are shown in Table 3.

Table 3. Experimental results for the reaction between MoO_3 and carbon in an argon stream

Temp / °C	Weight loss/%	Sample in the boat
350	—	MoO_3
400	0.2	$MoO_3>>MoO_2$
450	0.9	$MoO_3>>MoO_2$
500	5.2	$MoO_2>MoO_3$
600	9.7	$MoO_2>>MoO_3$
700	9.7	MoO_2

These results indicate that the reduction of MoO_3 with carbon to form MoO_2 proceeds above about 400 °C.

Reaction between MoO_3 and Sulfur in a SO_2 Stream: As seen from Table 1, when the mixture of MoO_3 and carbon was heated in a SO_2 stream, sulfur was formed. The reaction between carbon and 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.[1)] Therefore, the reaction between MoO_3 and gaseous sulfur was examined in a SO_2 stream.

MoO_3 (2.00 g) was heated in a stream of SO_2 (100 cm^3/min) containing a specified amount of gaseous sulfur at various temperatures for 1 h. The amounts of sulfur introduced at various temperatures were controlled so as to be the same as those obtained by heating 1.20 g of carbon in a stream of SO_2 at a flow-rate of 100 cm^3/min for 1 h: the amounts were 0.01 g for the experiments below 550 °C, 0.03 g at 600 °C, 0.09 g at 650 °C, and 0.25 g at 700 °C.[1)] The results are shown in Table 4.

These results and the fact that MoO_3 does not react with SO_2 as described before show that the reaction between MoO_3 and gaseous sulfur proceeds above about 400 °C and that MoO_3 was reduced to MoO_2.

Table 4. Products obtained by heating MoO_3 in a stream of SO_2 containing gaseous sulfur

Temp / °C	Weight loss/%	Sample in the boat
350	—	MoO_3
400	0.2	$MoO_3>>MoO_2$
450	0.3	$MoO_3>>MoO_2$
500	0.5	$MoO_3>>MoO_2>Mo_9O_{26}$, Mo_4O_{11}
550	0.7	$MoO_3>>MoO_2>Mo_9O_{26}$, Mo_4O_{11}
600	1.0	$MoO_3>MoO_2>Mo_9O_{26}>Mo_4O_{11}$
650	4.2	$MoO_3>MoO_2>Mo_9O_{26}>>Mo_4O_{11}$
700	8.2	$MoO_2>>MoO_3>Mo_9O_{26}$, Mo_4O_{11}

These experimental results showed that the MoO_2 formed by heating a mixture of MoO_3 and carbon in a SO_2 stream (Table 1) was formed by the reductions of MoO_3 with carbon and with sulfur. As seen from Table 1, the formation of a small amount of Mo_4O_{11} in addition to MoO_2 was observed at 500—550 °C. As seen from Table 3, no formation of any intermediate oxide was observed in the reaction between MoO_3 and carbon. As seen from Table 4, however, the formation of intermediate oxides (Mo_4O_{11},[4] Mo_9O_{26}[6]) in addition to MoO_2 was observed during the reaction between MoO_3 and sulfur. It has been reported that on heating a mixture of MoO_3 and a sufficient amount of carbon in an argon stream, no intermediate oxide is formed.[7] These facts suggested that the Mo_4O_{11} formed by heating a mixture of MoO_3 and carbon in a SO_2 stream was due to the reduction of MoO_3 with sulfur.

Formation Reaction of MoS_2 from MoO_2: As mentioned before, when a mixture of MoO_3 and carbon was heated in a SO_2 stream, MoS_2 was formed above about 700 °C. Above this temperature, MoO_3 was reduced to MoO_2. Therefore, the reactions of MoO_2 with carbon in an argon stream and of MoO_2 with gaseous sulfur in a SO_2 stream were examined.

The products formed by heating a mixture of MoO_2 (2.00 g) and carbon (5.00 g) at various temperatures for 1 h in an argon stream (100 cm^3/min) were examined. The results are shown in Table 5.

TABLE 5. EXPERIMENTAL RESULTS FOR THE REACTION BETWEEN MoO_2 AND CARBON IN AN ARGON STREAM

Temp / °C	Weight loss/%	Sample in the boat
700	—	MoO_2
750	0.7	$MoO_2 \gg Mo_2C > Mo$
800	2.0	$MoO_2 > Mo_2C > Mo$
900	7.6	$Mo_2C > MoO_2 > Mo$
1000	11.3	$Mo_2C > Mo$

The results indicate that the reaction between MoO_2 and carbon proceeds above about 750 °C to form molybdenum[8] and dimolybdenum carbide (Mo_2C).[9] The Mo_2C was considered to be due to the reaction between the molybdenum formed and the carbon.[7]

The products formed by heating MoO_2 (2.00 g) in a stream of SO_2 (100 cm^3/min) containing a specified amount of gaseous sulfur at various temperatures for 1 h were examined. The MoO_2 used was prepared by the hydrogen reduction of MoO_3 at 600 °C,[10] because the reduction of MoO_3 with carbon gave a mixture of MoO_2 and unreacted carbon, as described in the previous paragraph.

Prior to this experiment, the amounts of sulfur formed by heating 5.00 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.[1] Based on the experimental results, the amounts of sulfur introduced at various temperatures were controlled to be 0.43 g for the experiment at 650 °C, 0.81 g at 700 °C, 4.79 g at 800 °C, 5.46 g at 900 °C, and 6.59 g at 1000 °C. The experimental results are shown in Table 6. These results indicate that the reaction between MoO_2 and gaseous sulfur proceeds above about 700 °C to form MoS_2.

TABLE 6. PRODUCTS OBTAINED BY HEATING MoO_2 IN A STREAM OF SO_2 CONTAINING GASEOUS SULFUR

Temp / °C	Weight gain/%	Sample in the boat
650	—	MoO_2
700	4.2	$MoO_2 > MoS_2$
800	10.8	$MoO_2 \approx MoS_2$
900	17.6	$MoS_2 > MoO_2$
1000	22.9	$MoS_2 \gg MoO_2$

As shown in Table 5, on heating a mixture of MoO_2 and carbon in an argon stream, MoO_2 was reduced to molybdenum, and Mo_2C was also formed. Thermodynamical consideration was made on the Mo–S–C–O system, in order to discuss whether MoO_2 was converted to MoS_2 *via* molybdenum or without molybdenum formation. The chemical potential diagrams for the Mo–S–C–O system were constructed in a manner similar to that described by Yazawa[11] on the basis of the available thermodynamic data[12] and phase relations.[13] As an example, the digram at 1000 °C is shown in Fig. 1. The broken line shows the oxygen and sulfur potentials in the gas phase formed by the reaction between carbon and SO_2, depending on the carbon content in the gas phase. The activity of carbon 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 between carbon and SO_2.

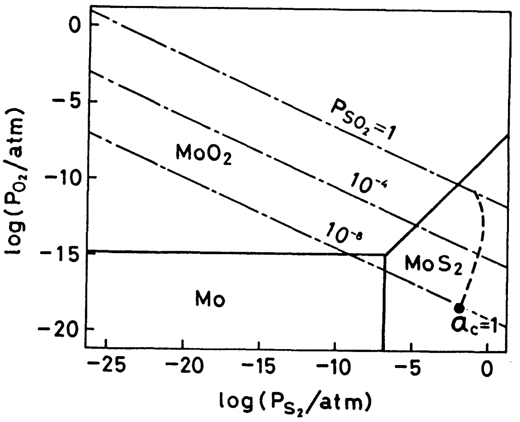

Fig. 1. Chemical potential diagram for the Mo–S–C–O system at 1000 °C.

The results shown in Fig. 1 indicate that MoO_2 is converted to MoS_2 *via* molybdenum under a low pressure of SO_2 below *ca.* 10^{-7} atm, and that MoO_2 is converted to MoS_2 without molybdenum formation under a higher partial pressure of SO_2. Considering the experimental conditions in this work, the results in Fig. 1 show that MoS_2 is formed from MoO_2 without any formation of molybdenum.

The process of formation of MoS_2 by the reaction between MoO_3 and SO_2 in the presence of carbon can be represented as follows: On heating a mixture of MoO_3 and carbon in a SO_2 stream, the reaction between carbon and SO_2 occurs at first to form sulfur. Above about 400 °C, the reductions of MoO_3 with carbon and with sulfur occur to form MoO_2. Above about 700 °C, MoS_2 is formed by the reaction between MoO_2 and sulfur, which are formed by the above reactions.

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