

Reaction Process between Zinc Oxide and Sulfur Dioxide in the Presence of Carbon

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The reaction products obtained by heating a mixture of ZnO and carbon in a SO₂ stream at various temperatures were examined. The possible reactions during the above process were also examined. When a mixture of ZnO and carbon was heated in a SO₂ stream, the formation of ZnS was observed above 600 °C. At 800 °C, all the ZnO used was converted to ZnS. Sulfur was also obtained outside the heating zone, and its amount increased markedly above ca. 750 °C. The ZnS formed was a mixture of α -ZnS and β -ZnS regardless of the reaction temperature. The process of formation of ZnS can be represented as follows: the reaction between carbon and SO₂ occurs at first to form sulfur. Above ca. 600 °C, the reaction between ZnO and the sulfur occurs to form ZnS. In addition to these reactions, the reduction of ZnO with carbon occurs slightly to form zinc, which then reacts with sulfur to form ZnS.

The chemical process for synthesizing metal sulfides from the oxides using sulfur dioxide (SO₂) as a sulfidizing agent is not only interesting from the viewpoint of the synthesis itself, but also important for the development of SO₂ utilization. In this work, the reaction process between zinc oxide (ZnO) and SO₂ in the presence of carbon was examined in order to understand the above chemical process.

Regarding the reaction between ZnO and SO₂ in the presence of carbon, little information has been available apart from the work of Pechkovskii,¹⁾ who reports that zinc sulfide (ZnS) is formed at 650–800 °C by heating a mixture of ZnO and carbon in a SO₂ stream and that 91.8% of the charged ZnO is sulfidized at 800 °C by using a 4 : 1 mixture of carbon and ZnO (molar ratio). The formation process of ZnS and the modification of ZnS formed have not been described.

In this work, the reaction products between ZnO and SO₂ in the presence of carbon at various temperatures were examined. The reactions between ZnO and carbon, between ZnO and gaseous sulfur in a SO₂ stream, and between zinc and gaseous sulfur in a SO₂ stream were also examined in order to elucidate the reaction process between ZnO and SO₂ in the presence of carbon.

Experimental

The ZnO used was prepared by the thermal decomposition of tetrazinc monocarbonate hexahydroxide monohydrate (Zn₄CO₃(OH)₆·H₂O), which was prepared by adding ammonium carbonate solution to zinc nitrate solution, at 600 °C.²⁾ The carbon was prepared by the thermal decomposition of the guaranteed reagent D-glucose. The above materials were used as powders under 150 mesh. Zinc (guaranteed reagent, sandy form) was used after washing with acetone and with dilute hydrochloric acid. Gaseous SO₂ was dried by passing it through concd H₂SO₄ and over P₂O₅.

A mixture of ZnO 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 SO₂ was then introduced into the reaction tube. The sample part was positioned in the middle of a tubular electric furnace (heating length: 300 mm) maintained at a specified temperature for 1 h. The tempera-

ture 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 SO₂ on unreacted carbon.³⁾ The reactions between ZnO and carbon in an argon stream, between ZnO and gaseous sulfur in a SO₂ stream, and between zinc and gaseous sulfur in a SO₂ 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.

Results and Discussion

Reaction Products between ZnO and SO₂ in the Presence of Carbon.

Prior to the examination of the reaction products between ZnO and SO₂ in the presence of carbon, the thermogravimetry of ZnO in a SO₂ stream was carried out in the temperature range up to 900 °C. The sample of ZnO (0.3 g) was heated at a rate of 2.5 °C/min and the flow-rate of SO₂ was maintained at 50 cm³/min. The sensitivity of the quartz helix used was approximately 72 mm/g. No weight change was observed, and the sample after the heating was found by X-ray analysis⁴⁾ to be unreacted ZnO. These results indicate that ZnO does not react with SO₂.

The products obtained by heating a mixture of 2.00 g of ZnO and 1.20 g of carbon at various temperatures for 1 h in a SO₂ stream at a flow-rate of 100 cm³/min were examined. The results are shown in Table 1, together with the weight changes in the samples. The

TABLE 1. PRODUCTS OBTAINED BY HEATING A MIXTURE OF ZnO AND CARBON IN A SO₂ STREAM AT VARIOUS TEMPERATURES

Temp /°C	Weight change/%	Sample in the boat	Amount of sulfur obtained outside the heating zone/g
550	+ 0.1	ZnO	Trace
600	+ 1.5	ZnO >> ZnS[α > β]	Trace
650	+ 2.1	ZnO >> ZnS[α > β]	< 0.01
700	+ 2.7	ZnO > ZnS[α > β]	< 0.01
750	– 3.0	ZnS[α > β] > ZnO	0.24
800	– 24.9	ZnS[α > β]	1.59

Note; α = α -ZnS, β = β -ZnS.

sample in the boat was identified by X-ray analysis.⁴⁻⁶⁾ The modification of the ZnS formed is represented in the brackets.

The formation of ZnS was observed above 600 °C, and no unreacted ZnO was observed at 800 °C. Sulfur was obtained outside the heating zone throughout the temperature range in this experiment, and the amount of sulfur markedly increased above *ca.* 750 °C. The sample weight also markedly decreased above *ca.* 750 °C. The slight increase in the sample weight at 550 °C was due to the adsorption of the sulfur formed by the reaction on the unreacted carbon.³⁾

The ZnS formed was a mixture of α -ZnS (high-temperature form, hexagonal) and β -ZnS (low-temperature form, cubic) at all temperatures.

Chemical analysis of the sample in the boat at 800 °C showed that the atomic ratio of zinc to sulfur³⁾ to be 1.0₀. From this result, it is confirmed that all the ZnO used was sulfidized at 800 °C.

Reaction Process between ZnO and SO₂ in the Presence of Carbon. To elucidate the reaction process between ZnO and SO₂ in the presence of carbon, the following experiments were carried out under conditions similar to those described in the preceding paragraph.

Reaction between ZnO and Carbon: The experimental results obtained by heating a mixture of ZnO (2.00 g) and carbon (1.20 g) in an argon stream (100 cm³/min) for 1 h at various temperatures are shown in Table 2.

TABLE 2. EXPERIMENTAL RESULTS FOR THE REACTION BETWEEN ZnO AND CARBON IN AN ARGON STREAM

Temp /°C	Weight loss/%	Amount of Zn obtained outside the heating zone/g	Conversion of ZnO to Zn/%
600	0.1	Detectable	Not calculated
650	0.2	0.001	<0.1
700	0.3	0.003	0.2
800	1.1	0.021	1.3

The samples after heating at all the temperatures were found to be unreacted ZnO by X-ray analysis. Zinc deposited outside the heating zone above 600 °C was dissolved in dilute nitric acid, and was determined by chelatometric titration.⁷⁾ The percentages of ZnO converted to zinc were calculated from the amounts of the zinc deposited.

These results indicate that a slight reduction of ZnO with carbon to zinc occurs above *ca.* 600 °C under the conditions in this experiment.

Reaction between ZnO and Sulfur in a SO₂ Stream: As seen from Table 1, when the mixture of ZnO and carbon was heated in a SO₂ stream, sulfur was formed. The reaction between carbon and SO₂ occurs even at 350 °C to form sulfur. This reaction proceeds markedly above *ca.* 700 °C, as reported by the present authors.³⁾ Therefore, the reaction between ZnO and sulfur was examined in a SO₂ stream.

ZnO (2.00 g) was heated in a stream of SO₂ containing a specified amount of gaseous sulfur at various temperatures for 1 h. The gaseous sulfur was formed by heating liquid sulfur and was carried by a stream of SO₂ (100

cm³/min). Based on the experimental results for the reaction between carbon and SO₂, reported by the present authors,³⁾ the amounts of sulfur introduced at various temperatures were controlled to be 0.01 g for the experiments below 550 °C, 0.03 g at 600 °C, 0.25 g at 700 °C, and 1.90 g at 800 °C, since the experimental conditions (the amount of carbon, the flow-rate of SO₂, *etc.*) in this work were identical to those for the experiment on the reaction between carbon and SO₂. The results are shown in Table 3. The percentages of ZnO converted to ZnS shown in Table 3 were calculated from the weight gains in the samples.

TABLE 3. PRODUCTS OBTAINED BY HEATING ZnO IN A STREAM OF SO₂ CONTAINING GASEOUS SULFUR

Temp /°C	Sample in the boat	Conversion of ZnO to ZnS/%
550	ZnO	—
600	ZnO >> ZnS[α > β]	2
700	ZnO > ZnS[α > β]	12
800	ZnS[α > β] > ZnO	74

These results and the fact that ZnO does not react with SO₂ as described above show that the reaction between ZnO and sulfur proceeds above *ca.* 600 °C to form ZnS under the conditions in this experiment. The ZnS formed was a mixture of α -ZnS and β -ZnS, similar to the ZnS obtained by the reaction between ZnO and SO₂ in the presence of carbon as described above.

Reaction between Zinc and Sulfur in a SO₂ Stream: As mentioned in the previous paragraph, on heating ZnO and carbon, ZnO was slightly reduced with carbon to form zinc above *ca.* 600 °C. It has been briefly reported in the early literature⁸⁾ that zinc powder vigorously reacts with sulfur in a SO₂ atmosphere. But no details of the reaction were given.

The products obtained by heating zinc (1.00 g) at various temperatures for 1 h in a stream of SO₂ (100 cm³/min) containing a specified amount of sulfur were examined. The amounts of sulfur introduced were controlled so as to be the same as those in the experiment on the reaction between ZnO and sulfur in a SO₂ stream described above. The experimental results are shown in Table 4.

TABLE 4. PRODUCTS OBTAINED BY HEATING ZINC IN A STREAM OF SO₂ CONTAINING GASEOUS SULFUR

Temp /°C	Sample in the boat	Conversion of Zn to ZnS/%
350	Zn	—
400	Zn >> ZnS[β]	<1
500	Zn >> ZnS[β]	1
600	Zn > ZnS[β]	2
700	Zn > ZnS[β]	3
800	Zn > ZnS[β]	6

These results show that on heating zinc in a stream of SO₂ containing gaseous sulfur, the reaction between zinc and sulfur proceeds above *ca.* 400 °C to form β -ZnS.

Although there has been a report⁹⁾ which describes that ZnO, ZnS, ZnSO₄, and ZnSO₄·ZnO are formed on heating zinc and SO₂ in a sealed tube at 500–800 °C, the formation of these compounds except ZnS is not observed in this experiment.

From the above-mentioned experimental results, the reaction process between ZnO and SO₂ in the presence of carbon can be represented as follows: On heating a mixture of ZnO and carbon in a SO₂ stream, the reaction between carbon and SO₂ occurs at first to form sulfur. Above *ca.* 600 °C, the reaction between ZnO and the sulfur occurs to form ZnS. In addition to these reactions, the reduction of ZnO with carbon occurs slightly to form zinc, which then reacts with sulfur to form ZnS.

It has been reported that the $\beta \rightleftharpoons \alpha$ transition temperature of ZnS is 1020 °C.¹⁰⁾ The temperature range in this work was below the transition temperature, and β -ZnS was only formed by the reaction between zinc and sulfur in a SO₂ stream, as shown in Table 4. While, the ZnS formed by heating the mixture of ZnO and carbon in a SO₂ stream was found to be a mixture of α -ZnS and β -ZnS, as shown in Table 1. The percentages of α -ZnS and β -ZnS were calculated to be α -ZnS 75% and β -ZnS 25% at 700 °C, and α -ZnS 70% and β -ZnS 30% at 750 and 800 °C, by the method reported by Bansagi *et al.* (the reproducibility: *ca.* $\pm 2.5\%$).¹¹⁾ Also, the ZnS formed by the reaction between ZnO and sulfur in a SO₂ stream was found to be a mixture of α -ZnS and β -ZnS, as shown in Table 3. And the percentages of α -ZnS and β -ZnS were calculated to be α -ZnS 70% and β -ZnS 30% at 700 and 800 °C.

The variation of the modification of ZnS, formed by heating the mixture of ZnO and carbon in a SO₂ stream or by the reaction between ZnO and gaseous sulfur in a SO₂ stream, with the reaction time (0.5–3 h) was examined. The ZnS formed by both processes was a mixture of α -ZnS and β -ZnS, and the wide variation in the percentages of α -ZnS and β -ZnS with the reaction time was not observed.

Regarding the formation of α -ZnS in the temperature

range at which β -ZnS is stable, it has been reported that when ZnO having the wurtzite (α -ZnS) structure is present in ZnS, the metastable growth of α -ZnS can be promoted below the $\beta \rightleftharpoons \alpha$ transition temperature,¹²⁾ and that on heating β -ZnS mixed with a small amount of ZnO¹²⁾ or CdS,¹³⁾ both having the wurtzite structure, a part of the β -ZnS is transformed into α -ZnS even below the $\beta \rightleftharpoons \alpha$ transition temperature. Considering the above reports, the formation of a mixture of α -ZnS and β -ZnS observed in this work is due to the presence of ZnO during the formation of ZnS.

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