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Selective removal of H_2S from coke oven gas

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Abstract

The catalytic performance of some metal oxides in the selective oxidation of H_2S in the stream containing water vapor and ammonia was investigated in this study. Among the catalysts tested, V_2O_5/SiO_2 and Fe_2O_3/SiO_2 catalyst showed good conversion of H_2S with very low selectivity to undesired SO_2. Hydrogen sulfide could be recovered as harmless solid products (elemental sulfur and various ammonium salts), and distribution of solid products was varied with types of catalyst and compositions of reactant. XRD and FT-IR analysis revealed that the salt was mixture of ammonium–sulfur–oxygen compounds. It was noteworthy that V_2O_5/SiO_2 catalyst produced elemental sulfur and ammonium thiosulfate, and that elemental sulfur was principal product on Fe_2O_3/SiO_2 catalyst. Small amount of ammonium sulfate was obtained with the Fe_2O_3/SiO_2 catalyst. In order to elucidate the reaction path, the effects of O_2/H_2S ratio and concentration of NH_3 and H_2O are also studied with the V_2O_5/SiO_2 catalyst. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogen sulfide; Ammonia; Water; Ammonium thiosulfate; Elemental sulfur; Catalytic oxidation

1. Introduction

Developing SO_x emission control technology has received significant attention since legal regulation becomes more severe. Now, a large amount of SO_x results from H_2S that is released from refineries of crude oil, natural gas and coke oven of steel industry. The coal liquefaction process is considered to be the major source of H_2S emissions in the near future. H_2S is usually recovered as elemental sulfur by the well-known Claus process [1,2] in which H_2S is partly oxidized to SO_2 and their mixture is further converted to elemental sulfur. However, the sulfur recovery rate in Claus plant is only 95–98% due to thermodynamic limitations. Since SO_x emission limits have been more strict over the years, it is necessary to treat supplementary residual gas of Claus installation, so-called tail gas. Although various tail gas treatments (TGT) have been developed, the majority of them are based on sorption technology. Those have need to treat secondary wastes and to regenerate the sorbent. From view point of environmental concern, the best choice would be the selective oxidation of H_2S to elemental sulfur which is readily to treat, handle and transport [3,4]. High conversion can be obtained in the selective oxidation of H_2S because it is not a thermodynamic reversible reaction.

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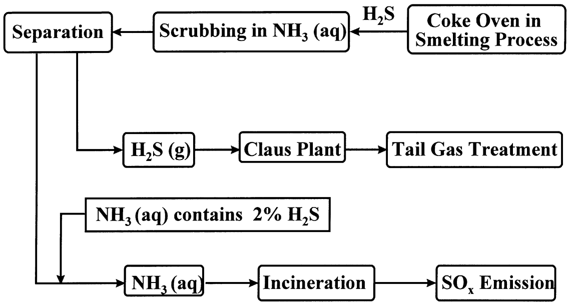

Fig. 1. H_2S emission control in steel production process.

On the other hand, H_2S in the coke oven gas released from the steel smelting process is scrubbed and concentrated using aqueous ammonia as shown in Fig. 1. Concentrated H_2S that is separated from aqueous ammonia is transferred to Claus plant to convert it into elemental sulfur, and remaining aqueous ammonia is usually incinerated. However, the separation of H_2S from the aqueous ammonia is not perfect. Remaining aqueous ammonia stream contains about 2% H_2S which in turn causes the SO_x emission problem during the incineration. In this case, the control of SO_x emission is difficult because the stream contains not only excess water vapor but also high concentration of ammonia.

In this study, we investigated the development of catalysts for selective removal of H_2S in the stream containing both of ammonia and water. Hydrogen sulfide was completely converted to the mixture of ammonium salt and elemental sulfur without considerable sulfur dioxide emission. This offers a new solution for the treatment of emission gas released from coke oven in steel production.

2. Experimental

2.1. Preparation of catalysts

Metal oxides (γ-Al_2O_3, TiO_2, V_2O_5, Fe_2O_3, SnO_2) were used as purchased without further purification. All supported catalysts were prepared by impregnating aqueous solutions of metal salts (ammonium metavanadate, iron citrate) onto SiO_2 support (JRC-SIO-6) followed by drying. The impregnated catalysts were dried in a vacuum oven at 130°C for 12 h and calcined under an air flow at 500°C for 5 h. The loading was fixed at 10 wt% on their oxide form basis.

2.2. Measurement of catalytic activity and analysis

Catalytic activities were checked using a continuous flow fixed-bed reactor that is made of a Pyrex glass tube. A condenser was attached at the effluent side of the reactor, and its temperature was constantly maintained at 110°C to condense only solid products (elemental sulfur+ammonium salt). A line filter was installed after the condenser to trap any solid mist which had not been captured by the condenser. From the condenser up to gas chromatography, all the lines and fittings were heated above 120°C to prevent condensation of water vapor. The flow rate of gas was controlled by a mass flow controller (5850E, Brooks). Water vapor was introduced to the reactant stream using a steam evaporator filled with small glass beads, and its amount was controlled by a syringe pump (301A, Sage).

In a typical experiment the reactant mixture is consisted of 5 vol% H_2S, 2.5 vol% O_2, 10 vol% NH_3, 60 vol% H_2O (vapor) and balance helium. The content of effluent gas was analyzed by a gas chromatography (HP5890, Hewlett Packard) equipped with a thermal conductivity detector and Teflon column of Porapak T. The exit gas from the analyzer was passed through a trap containing a concentrated NaOH solution and vented out to a hood.

Solid products were first dissolved into distilled water then filtered to separate elemental sulfur, remaining water solution was dried in a vacuum drying oven at room temperature to obtain solid salts. The solid products were identified by X-ray diffraction crystallography with Cu Kα radiation (Rigaku, DMAX 2400) and FT-IR (React IR 1000, ASI). Selectivity to solid products is calculated by subtracting selectivity of SO_2 (S–SO_2) from 100% (X-H_2S depicting the conversion of H_2S).

3. Results and discussion

3.1. Screening test

In order to find active components for the selective removal of H_2S, screen tests were carried out for some

Table 1
Catalytic performance of various metal oxides at 260°C

Catalyst	Run (A)		Run (B)	
	X-H_2S (%)	S–SO_2 (%)	X-H_2S (%)	S–SO_2 (%)
γ-Al_2O_3	94.0	1.9	50.5	48.7
TiO_2	94.7	2.0	53.1	10.5
V_2O_5	95.1	2.5	78.7	0.0
Fe_2O_3	94.6	5.2	69.0	0.0
SnO_2	57.6	4.7	64.8	21.6
SiO_2–Al_2O_3	27.8	17.7	—	—
ZnO	28.3	32.3	—	—

Run (A): 5% H_2S, 2.5% O_2, 92.5% He, Run (B): 5% H_2S, 2.5% O_2, 10% NH_3, 60% H_2O, 22.5% He.

metal oxides. Table 1 shows the catalytic performance of various metal oxides at two different reaction conditions: Run: (A) 5 vol% H_2S and 2.5 vol% O_2; (B) 5 vol% H_2S, 2.5 vol% O_2, 10 vol% NH_3 and 60 vol% H_2O. Bulk metal oxides of γ-Al_2O_3, TiO_2, V_2O_5 and Fe_2O_3 showed good conversion of H_2S without any considerable amount of SO_2 emission. TiO_2 and γ-Al_2O_3 are main components of commercial catalysts for sulfur recovery process. However, in the coexistence of water and ammonia, TiO_2 and γ-Al_2O_3 showed remarkable decrease of H_2S conversion and great increase of SO_2 emission. It is interesting to note that H_2S with concentration over 60% can only be removed on metal oxide such as V_2O_5, Fe_2O_3 and SnO_2 at 260°C. Relatively strong acidic and basic support, like SiO_2–Al_2O_3 and ZnO, respectively, showed very low conversion of H_2S even in the absence of water and ammonia.

3.2. Solid product distribution

Table 2 shows the variation of catalytic activity with temperature for 10 wt% Fe_2O_3/SiO_2 and 10 wt% V_2O_5/SiO_2 catalysts. The conversion of H_2S decreased with increasing the reaction temperature. This is in accordance with the results of thermodynamic calculation for selective oxidation of H_2S.

$$2H_2S + O_2 \rightarrow (2/n)S_n + 2H_2O \quad (1)$$

It is noteworthy that SO_2 was not emitted at all even up to 340°C for the two catalysts. It is believed that all the produced SO_2 are consumed to form solid product (elemental sulfur and white salts) in the presence of ammonia and water. XRD and FT-IR analysis revealed that the salt was mixture of ammonium–sulfur–oxygen compounds. It had a molecular formula of $(NH_{2w})_xS_yO_z$, where the values of w, x, y and z were dependent upon the catalyst employed.

Fig. 2 shows the distribution of solid products (elemental sulfur and white salt) with 10 wt% V_2O_5/SiO_2 and 10 wt% Fe_2O_3/SiO_2 catalysts. Distribution portion of solid products was varied with the types of catalyst, and the portion of salts was higher for 10 wt% V_2O_5/SiO_2 than 10 wt% Fe_2O_3/SiO_2. The XRD patterns in Fig. 3 confirmed the formation of ammonium thiosulfate ($(NH_4)_2S_2O_3$). Therefore, in all the following experiments filtrate was carefully dried

Table 2
Effects of temperature on catalytic activity

Temperature (°C)	10% V_2O_5/SiO_2		10% Fe_2O_3/SiO_2	
	X-H_2S (%)	S–SO_2 (%)	X-H_2S (%)	S–SO_2 (%)
260	81.4	0.0	94.7	0.0
280	80.9	0.0	92.1	0.0
300	78.5	0.0	88.8	0.0
340	70.6	0.0	82.5	0.0
360	69.1	0.0	79.5	0.8

(5% H_2S, 2.5% O_2, 10% NH_3, 60% H_2O, GHSV=60 000 h^{-1}).

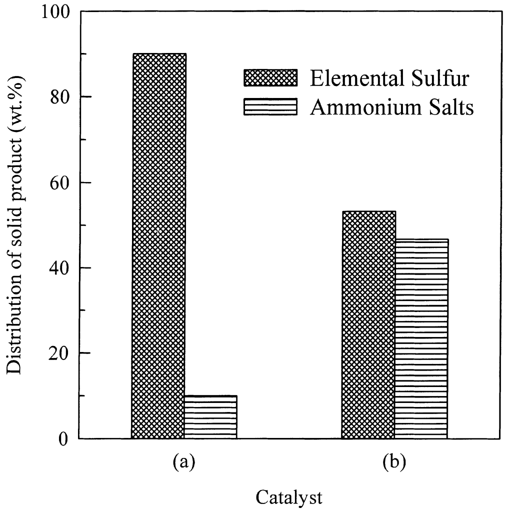

Fig. 2. Solid product distribution for: (a) 10% Fe_2O_3/SiO_2 and (b) 10% V_2O_5/SiO_2 catalysts. (Reactant composition=5% H_2S; 2.5% O_2; 10% NH_3; 60% H_2O; T=260°C; GHSV=60 000 h^{-1}.)

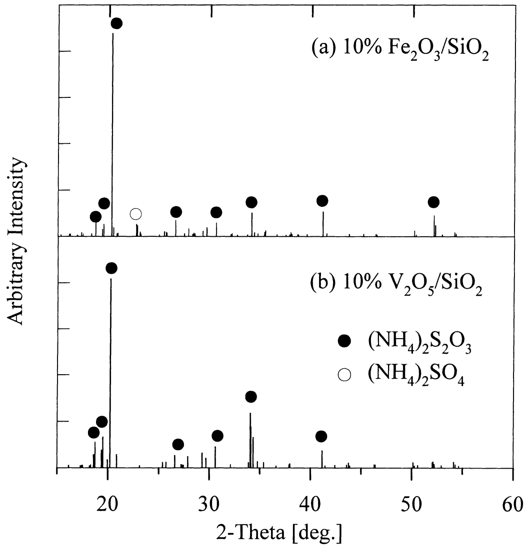

Fig. 3. XRD patterns of solid salt for Fe_2O_3/SiO_2 and V_2O_5/SiO_2 catalysts.

in a vacuum oven below 30°C since ammonium thiosulfate is easily decomposed into ammonium sulfate ($(NH_4)_2SO_4$) above 45°C. It is interesting to note that the salt produced with V_2O_5/SiO_2 and Fe_2O_3/SiO_2 catalyst is almost pure ammonium thiosulfate. Only trace amount of ammonium sulfate was observed in the Fe_2O_3/SiO_2 catalyst.

3.3. *Effect of oxygen concentration*

To study the influence of the partial pressure of oxygen, oxygen concentration in the feed was varied from 2.5 to 20 vol% while maintaining the concentration of other gases at the standard condition (5 vol% H_2S, 10 vol% NH_3, 60 vol% H_2O). Table 3 shows the conversion of H_2S and selectivity to SO_2 for 10 wt% V_2O_5/SiO_2 catalyst at various O_2/H_2S ratio. The conversion increased with increase of O_2/H_2S ratio and it reached up to 100% with O_2/H_2S ratio of higher than 2.0. When the O_2/H_2S ratio was 0.5, no SO_2 was produced. However, when O_2/H_2S ratio was greater than 0.5, undesirable SO_2 emission was increased with increasing the O_2/H_2S ratio. With an excess amount of oxygen in the feed, the production of SO_2 was inevitable according to the following consecutive (Eq. (2)) or parallel reaction (Eq. (3)).

Table 3
Effect of oxygen concentration on the conversion of H_2S and selectivity to SO_2 with 10% V_2O_5/SiO_2 catalyst at 260°C

O_2 (vol%)	O_2/H_2S ratio	X-H_2S (%)	S–SO_2 (%)
2.5	0.5	81.4	0.0
5	1.0	93.2	1.7
10	2.0	100	2.0
20	4.0	100	2.6

(5% H_2S, 2.5–20% O_2, 10% NH_3, 60% H_2O, GHSV=60 000 h^{-1}).

$$(1/n)S_n + O_2 \rightarrow SO_2 \qquad (2)$$

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O \qquad (3)$$

Therefore, higher amount of SO_2 production could be expected as it was the case of our previous work [5] on the selective oxidation of H_2S in the absence of NH_3 and water. But the selectivity to SO_2 was very low in the present work.

Fig. 4 shows the distribution of solid product for 10% V_2O_5/SiO_2 catalyst at various O_2 concentrations. The portion of ammonium thiosulfate in solid products increased with increasing the O_2 concentration up to 10 vol% and it was maintained constant over this range. Hartley and Matteson [6] and Hsunling et al. [7]

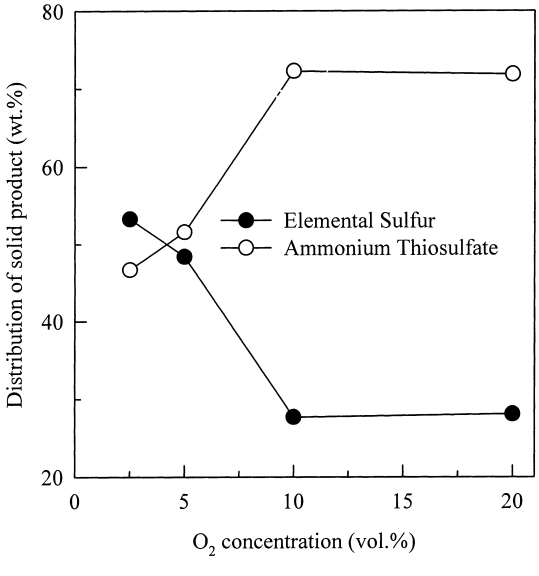

Fig. 4. Effect of O_2 concentration on solid product distribution for 10% V_2O_5/SiO_2 catalyst. (Reactant composition=5 vol% H_2S; 10 vol% NH_3; 60 vol% H_2O; T=260°C; GHSV=60 000 h^{-1}).

Table 4
Effect of ammonia concentration on the conversion of H_2S and selectivity to SO_2 with 10% V_2O_5/SiO_2 catalyst at 260°C

NH_3 (vol%)	X-H_2S (%)	S–SO_2 (%)
5	80.5	0.0
10	81.4	0.0
20	83.0	0.0
30	85.4	0.0

(5% H_2S, 2.5% O_2, 5–30% NH_3, 60% H_2O, GHSV=60 000 h^{-1}).

reported that SO_2 and NH_3 reacted in humid air to form ammonium sulfite (Eq. (4)) and ammonium sulfate (Eq. (5)) at room temperature:

$$SO_2 + 2NH_3 + H_2O \rightarrow (NH_4)_2SO_3 \quad (4)$$

$$(NH_4)_2SO_3 + (1/2)O_2 \rightarrow (NH_4)_2SO_4 \quad (5)$$

Ammonium thiosulfate is commercially produced by the reaction of ammonium sulfite with excess sulfur [8]:

$$(NH_4)_2SO_3 + S \rightarrow (NH_4)_2S_2O_3 \quad (6)$$

Therefore, it is believed that SO_2 formed during the reaction may be consumed to form ammonium thiosulfate.

3.4. *Effect of ammonia content*

To reveal the effect of partial pressure of ammonia on catalytic activity, reaction tests were carried out at different NH_3 concentrations using 10% V_2O_5/SiO_2 catalyst. As shown in Table 4, the conversion of H_2S increased with increasing the partial pressure of NH_3 but SO_2 was not produced at all. This also explains that SO_2 produced by the consecutive or parallel reaction is converted to ammonium thiosulfate with excess ammonia. However, Fig. 5 shows that the portion of ammonium thiosulfate in solid products decreased with increasing the partial pressure of NH_3. It was contrary to the effect of O_2 concentration on the salt distribution. Therefore, it can be suggested that excess ammonia reacts with H_2S to form an intermediate which finally decomposes to elemental sulfur. The intermediate may be a certain sort of ammonium sulfide. Ammonia is known to react easily with H_2S to form ammonium sulfide $(NH_4)_2S$ by Eq. (7), which can be oxidized to produce elemental sulfur (Eq. (8)) [9].

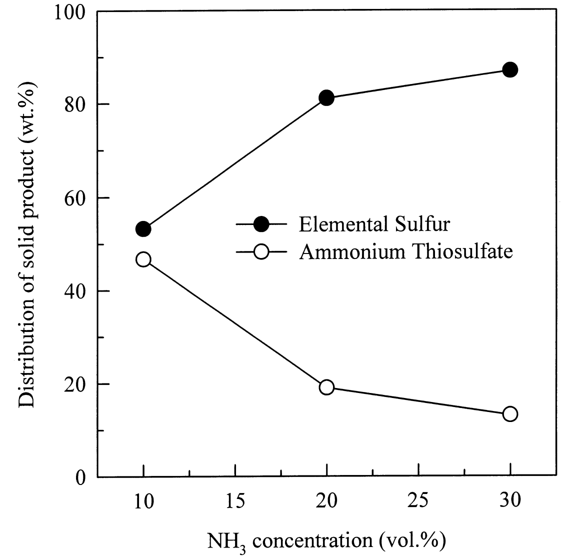

Fig. 5. Effect of NH_3 concentration on solid product distribution for 10% V_2O_5/SiO_2 catalyst. (Reactant composition=5 vol% H_2S, 2.5 vol% O_2, 60 vol% H_2O; T=260°C; GHSV=60 000 h^{-1}).

$$H_2S + 2NH_3 \leftrightarrow (NH_4)_2S \quad (7)$$

$$(NH_4)_2S + (1/2)O_2 \rightarrow S + 2NH_3 + H_2O \quad (8)$$

Different nature of the intermediate, formed by H_2S and NH_3 or that from SO_2 and NH_3, was examined by checking the distribution of solid product at various H_2S concentrations with fixed O_2 concentration of 2.5 vol%. As presented in Fig. 6, the ammonium thiosulfate portion in solid product was decreased with increasing the partial pressure of H_2S. The increase of H_2S concentration showed the same effect on the salt distribution as that of NH_3 concentration. Thus, one can conclude that ammonium thiosulfate is produced via an intermediate from NH_3 and SO_2, and that elemental sulfur can be produced via an intermediate from NH_3 and H_2S.

3.5. *Effect of water*

The effect of partial pressure of water vapor on the H_2S conversion and selectivity to SO_2 is shown in Table 5. Both the conversion and selectivity to SO_2 decreased with increasing H_2O concentrations. It is

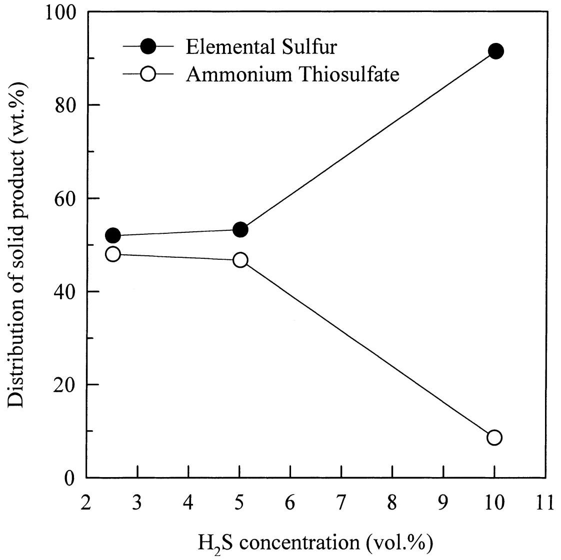

Fig. 6. Effect of H_2S concentration on solid product distribution for 10% V_2O_5/SiO_2 catalyst. (Reactant composition=2.5 vol% O_2, 10 vol% NH_3, 60 vol% H_2O; T=260°C; GHSV=60 000 h^{-1}).

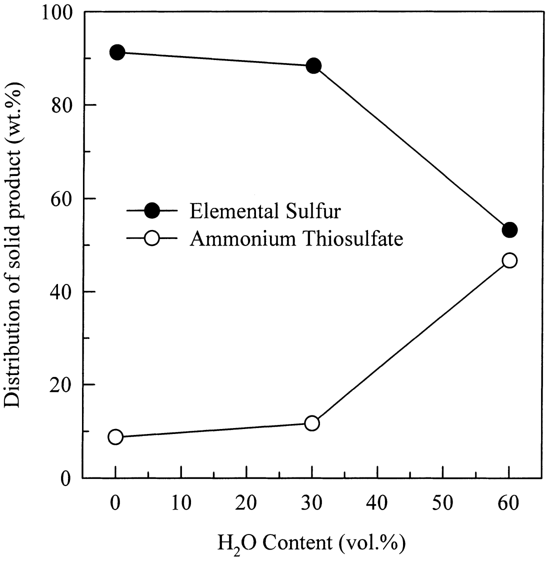

Fig. 7. Effect of H_2O concentration on solid product distribution for 10% V_2O_5/SiO_2 catalyst. (Reactant composition=5 vol% H_2S, 2.5 vol% O_2, 10 vol% NH_3; T=260°C; GHSV=60 000 h^{-1}).

Table 5
Effect of water vapor on the conversion of H_2S and selectivity to SO_2 with 10% V_2O_5/SiO_2 catalyst at 260°C

H_2O (vol%)	X-H_2S (%)	S–SO_2 (%)
0	93.0	4.5
30	87.5	0.6
60	81.4	0.0

(5% H_2S, 2.5% O_2, 10% NH_3, 0–60% H_2O, GHSV=60 000 h^{-1})

generally known that H_2O can react with elemental sulfur by reverse Claus reaction to form H_2S.

$$(3/n)S_n + H_2O \rightarrow 2H_2S + SO_2 \tag{9}$$

If H_2O affects only on this reaction the selectivity to SO_2 will increase with the H_2O concentration, but selectivity to SO_2 was decreased in Table 5. Fig. 7 shows the effect of water content on the salt distribution. The portion of ammonium thiosulfate was increased with the increase of H_2O content. This means that excess water vapor not only acts as a catalytic poison but also plays an important role in the production of ammonium thiosulfate probably by accelerating the reaction of NH_3 and SO_2 as pointed out by Hsunling et al. [7].

4. Conclusion

In this study, we investigated the development of catalysts for selective removal of hydrogen sulfide in the stream containing both of ammonia and water. As a result of the present studies one can conclude that Fe_2O_3 and V_2O_5 supported on silica are promising catalysts for the effective removal of H_2S containing the excess water and ammonia. We found the formation of ammonium thiosulfate, ammonium sulfate and elemental sulfur during the oxidation of H_2S in the presence of ammonia and water. Distribution of solid products varied with types of catalyst and compositions of reactant. SO_2 emission was closely dependent on the O_2/H_2S ratio and SO_2 formed during the reaction was consumed to produce ammonium salts with NH_3. Excess ammonia reacted with H_2S to form an intermediate which finally decomposed to elemental sulfur. Water vapor decreased H_2S conversion but it contributed to the formation of ammonium thiosulfate. Clarifying the salt product distribution and further kinetic studies would be very helpful to reveal essential features of the reaction mechanism.

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