

SELECTIVE OXIDATION OF H₂S IN THE PRESENCE OF AMMONIA AND WATER USING Co₃O₄/SiO₂ CATALYST

Sung Woo Chun, Jae Yeol Jang, Dae Won Park[†],
Hee Chul Woo* and Jong Shik Chung**

Department of Chemical Engineering, Pusan National University, Pusan 609-735, South Korea

*Department of Chemical Engineering, Pukyung National University, Pusan 608-737, South Korea

**Department of Chemical Engineering, Pohang University of Science and Technology, Pohang 790-784, South Korea
(Received 26 March 1997 • accepted 26 May 1997)

Abstract – The catalytic performance of some metal oxides in the selective oxidation of H₂S in the stream containing water vapor and ammonia was investigated in this study. Among the catalysts tested, Co₃O₄/SiO₂ was the most promising catalyst for practical application. It showed very small amount of SO₂ emission even in the presence of excess water and ammonia. The solid product formed in the reaction was a mixture of elemental sulfur, ammonium thiosulfate and ammonium sulfate.

Key words: Selective Oxidation, Hydrogen Sulfide, Ammonia, Water, Catalyst

INTRODUCTION

Recent environmental concern enforces tighter regulation for the emission limits of SO_x, since sulfur oxides are considered responsible for acid rain. In these days, a large amount of H₂S is released from crude oil, natural gas refineries and metal smelting process in steel production. The coal liquefaction process is considered to be the major source of H₂S emissions in the near future.

Hydrogen sulfide released from stationary source is usually removed by the well-known Claus process [Lagas et al., 1988; Wieckowska, 1995]. The Claus process consists of two steps; thermal oxidation and catalytic reaction. In the thermal oxidation step, one-third of the hydrogen sulfide is first burned with air to sulfur dioxide in a waste heat furnace (H₂S+O₂→SO₂+H₂O). In the subsequent catalytic reaction step, unconverted H₂S and SO₂ are reacted in a 2/1 ratio to elemental sulfur (2H₂S+SO₂↔3/n S_n+2H₂O) over an Al₂O₃ catalyst. However, due to thermodynamic limitations, typically 3 to 5 % H₂S is not converted into sulfur. As the legal regulation has been tightened, it is necessary to further treat the residual gas of the Claus installation, the so-called tail gas.

Various commercial tail gas treatment (TGT) processes have been developed. Conventional Claus TGT processes involved a hydrogen sulfide absorption step, in which a tail gas containing unreacted hydrogen sulfide is introduced into an alkaline solution bath. The most attractive process that has been recently developed is Modop (Mobil Direct Oxidation Process) process [Chopin et al., 1990; Kettner et al., 1982; Kettner and Liermann, 1983] or the Super Claus process [Brben and Geus, 1989; Brink and Geus 1990; Terorde et al., 1993], both of which are based on direct oxidation of H₂S to elemental sulfur.

Meanwhile, in steel industry, H₂S in the coke oven gas is

scrubbed and concentrated using aqueous ammonia. Concentrated H₂S that is separated from aqueous ammonia is transferred to Claus plant to be converted into elemental sulfur, and remaining aqueous ammonia is usually incinerated. However, the separation of H₂S from the aqueous ammonia is not perfect. Remaining aqueous ammonia stream contains typically about 2 % H₂S which in turn results in 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 gas.

In this study, we developed a new catalytic process for selective removal of H₂S in the stream containing both of ammonia and water. Hydrogen sulfide was effectively converted to ammonium sulfates and elemental sulfur without any considerable amount of sulfur dioxide emission. This gives a new solution for the treatment of emission gas released from coke oven in steel production process.

EXPERIMENTAL

Supported catalysts were prepared by conventional impregnation method onto a SiO₂ support (JRC-SIO-6) followed by drying for 12 hours in an oven at 120 °C. After impregnation, solvent was evaporated with a rotary vacuum evaporator at 80 °C. Then the catalysts were dried in a vacuum oven at 130 °C for 12 hours and calcined in flowing air at 500 °C for 5 hours. Metal oxides (γ-Al₂O₃, TiO₂, V₂O₅, Co₃O₄, SnO₂, SiO₂-Al₂O₃, and ZnO) were used as purchased without further purification.

Reaction tests were carried out in a continuous flow fixed-bed reactor. The reactor was made of a Pyrex® tube with an I. D. of 1 inch. 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 (sulfur+ammonium sulfates). A line filter was installed after the condenser to trap any solid mist which had not been captured by the condenser. From

*To whom correspondence should be addressed.

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 (Brooks MFC 5850E). 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. In a typical experiment the reactant composition consisted of 5 vol% H₂S, 2.5 vol% O₂, 10 vol% NH₃, 60 vol% H₂O (vapor) and balance He. The ratio of O₂/H₂S was varied from 0.5 to 4, and the gas hourly space velocity (GHSV) was varied from 3,000 to 60,000 (hr⁻¹).

The content of effluent gas was analyzed by a gas chromatography (HP 5890) equipped with a thermal conductivity detector and a 6 ft Porapak T column (80-100 mesh) at 100 °C. The exit gas from the analyzer was passed through a trap containing a concentrated NaOH solution and vented out to a hood. The conversion of H₂S and the selectivity to SO₂ are defined as follows:

$$\text{Conversion of H}_2\text{S} = \frac{[\text{H}_2\text{S}]_{\text{inlet}} - [\text{H}_2\text{S}]_{\text{outlet}}}{[\text{H}_2\text{S}]_{\text{inlet}}} \times 100 (\%)$$

$$\text{Selectivity of SO}_2 = \frac{[\text{SO}_2]_{\text{outlet}}}{[\text{H}_2\text{S}]_{\text{inlet}} - [\text{H}_2\text{S}]_{\text{outlet}}} \times 100 (\%)$$

RESULTS AND DISCUSSION

In order to find active components for the selective removal of H₂S, screen tests were carried out for some metal oxides which had shown good activity in our previous work [Chun et al., 1996] on H₂S oxidation in the absence of ammonia and water. Table 1 shows the catalytic performance of various metal oxides at three different reaction conditions: (a) 5 % H₂S and 2.5 % O₂, (b) in the presence of 10 % NH₃, (c) in the presence of 10 % NH₃ and 60 % water. TiO₂ and γ-Al₂O₃ are main components of commercial catalysts for Modop and Claus process, respectively. The conversion of H₂S on γ-Al₂O₃ was very high even in the presence of 10 % NH₃, while the conversion on TiO₂ decreased from 94.7 % to 76.7 % when ammonia was added in the standard reactant mixture of 5 % H₂S and 2.5 % O₂. But both of them showed remarkable decrease of the conversion

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

Metal oxide	H ₂ S+O ₂ ^a		H ₂ S+O ² +NH ₃ ^b		H ₂ S+O ² +NH ₃ +H ₂ O ^c	
	Conv.	Sele. ^d	Conv.	Sele. ^d	Conv.	Sele. ^d
	(%)	(%)	(%)	(%)	(%)	(%)
γ-Al ₂ O ₃	94.0	1.9	96.4	2.7	50.5	48.7
TiO ₂	94.7	2.0	76.7	3.3	53.1	10.5
V ₂ O ₅	95.1	2.5	97.6	5.7	78.7	0.0
Co ₃ O ₄	94.0	1.4	94.4	7.7	94.1	0.0
SnO ₂	57.6	4.7	87.1	0.9	64.8	21.6
SiO ₂ -Al ₂ O ₃	27.8	17.7	48.1	2.3	-	-
ZnO	28.3	32.3	21.7	11.4	-	-

a: H₂S=5 %, O₂=2.5 %, He=92.5 %

b: H₂S=5 %, O₂=2.5 %, NH₃=10 %, He=82.5 %

c: H₂S=5 %, O₂=2.5 %, NH₃=10 %, H₂O=60 %, He=22.5 %

d: selectivity to sulfur dioxide

GHSV=3,000 h⁻¹

and great increase of SO₂ emission in the coexistence of water and ammonia. It is interesting that above 60 % of H₂S was removed only on metal oxide such as V₂O₅, Co₃O₄ and SnO₂ at 260 °C. Relatively strong acidic and basic support, like SiO₂-Al₂O₃ and ZnO respectively, showed very low conversion of H₂S even in the absence of water and ammonia. Among the metal oxides tested, Co₃O₄ showed the highest conversion of H₂S and no emission of SO₂ in the presence of ammonia and water. Therefore, all the following experiments have been carried out using 10 wt% Co₃O₄/SiO₂ catalyst.

Table 2 shows the variation of catalytic activity as a function of reaction temperature. The conversion of H₂S was decreased with increasing the reaction temperature. It is noteworthy that the conversion was higher than 90 % and SO₂ was not produced at all even up to 340 °C. All the converted H₂S are transformed to elemental sulfur and a mixture of ammonium sulfates. Solid products were dissolved in water to separate ammonium sulfates from elemental sulfur and followed filtration. Filtrate was dried in vacuum oven below 30 °C carefully since ammonium thiosulfate [(NH₄)₂S₂O₃] is easily decomposed to ammonium sulfate [(NH₄)₂SO₄] above 40 °C. The X-ray diffraction patterns in Fig. 1 confirmed the formation of ammonium sulfate and ammonium thiosulfate. However, the exact distribution of the solid products has not yet been determined in the present work.

To study the influence of the partial pressure of oxygen, oxygen concentration in the feed was varied from 0.5 to 20 vol% while maintaining the concentration of H₂S to 5 vol%. Table 3 shows the conversion of H₂S and selectivity to SO₂ on 10 wt% Co₃O₄/SiO₂ catalysts at various O₂/H₂S ratio. The conversion reached up to 100 % in all the ranges of O₂/H₂S ratio tested with an exception of O₂/H₂S of 0.5. In catalytic oxidation of hydrogen sulfide, SO₂ emission results from the excess oxygen [Chun et al., 1996]. In this work, SO₂ emission closely depends on the O₂/

Table 2. Effects of temperature on the conversion of H₂S and selectivity to SO₂ for 10 wt% Co₃O₄/SiO₂ catalyst

Temp. (°C)	Conversion (%)	Selectivity of SO ₂ (%)
260	98.0	0.0
280	93.1	0.0
300	90.3	0.0
340	77.9	0.0
360	68.3	0.8

Reactant composition: H₂S=5 vol%, O₂=2.5 vol%, NH₃=10 vol%, H₂O=60 vol% GHSV=3,000 hr⁻¹.

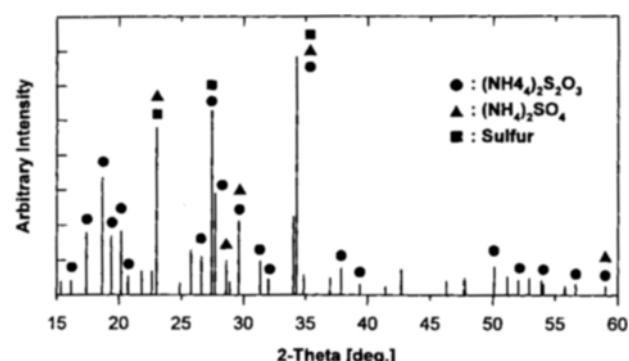


Fig. 1. X-ray diffraction patterns of products.

Table 3. Effect of partial pressure of oxygen on catalytic performance at 260 °C

O ₂ /H ₂ S ratio	Conversion (%)	Selectivity of SO ₂ (%)
0.5	98.0	0.0
1.0	100	2.0
2.0	100	14.1
4.0	100	29.6

Reactant composition: H₂S=5 vol%, O₂=2.5 vol%, NH₃=10 vol%, H₂O=60 vol%, GHSV=3,000 h⁻¹.

Table 4. Effect of NH₃ partial pressure on catalytic performance at 260 °C

NH ₃ conc.	Conversion (%)	Selectivity of SO ₂ (%)
5 %	67.9	7.7
10 %	70.4	4.2
20 %	75.3	2.5

Reactant composition: H₂S=5 vol%, O₂=2.5 vol%, H₂O=30 vol%, GHSV=30,000 h⁻¹.

H₂S ratio. When the O₂/H₂S ratio is 0.5, no SO₂ was produced. However, in case of O₂/H₂S ratio>0.5, undesirable SO₂ emission was increased with increasing the O₂/H₂S ratio.

To reveal the effect of partial pressure of ammonia on catalytic activity, reaction test was carried out with different NH₃ concentrations at GHSV=30,000 h⁻¹. The conversion was increased but the selectivity was decreased with increasing the partial pressure of NH₃. It is generally known, in the oxidation of H₂S, that increased conversion enhanced the consecutive reaction of elemental sulfur with oxygen to form SO₂ (1/n S_n→O₂+SO₂) [Chun et al., 1996]. Therefore, the decrease of SO₂ with increasing NH₃ concentration indicates that SO₂ produced by the consecutive reaction is converted to ammonium sulfates by reaction with excess ammonia. This is in agreement with the results of Hartley et al. [1975] who reported the formation of ammonium sulfates from SO₂ and NH₃ in humid air.

CONCLUSION

As a result of the present studies one can conclude that cobalt oxide supported on silica is a promising catalyst for the effective removal of H₂S containing the excess water and ammonia. We found the formation of ammonium thiosulfate, ammonium sulfates and elemental sulfur during the oxidation of H₂S in the presence of ammonia and water. Clarifying the solid product

distribution and further kinetic studies would be very helpful to reveal essential features of the reaction mechanism.

ACKNOWLEDGEMENTS

This work was supported by the Korea Science and Engineering Foundation (KOSEF) through the Research Center for Catalytic Technology of POSTECH.

REFERENCES

- Berben, P. H. and Geus, J. W., "Catalyst for the Selective Oxidation of Sulfur Containing Compounds to Elemental Sulfur", US Patent 4,818,740 (1989).
- Brink, P. J. and Geus, J. W., "Catalyst for the Selective Oxidation of Sulphur Compounds to Elemental Sulfur, Process for Preparing Such a Catalyst and Method for the Selective Oxidation of Sulfur Compounds to Elemental Sulfur", European Patent 409,353 (1990).
- Chopin, T., Hebrard, J. L. and Quemere, E., "Catalyst for Tail Gas Treatment and Process for Tail Gas Treatment", European Patent 422,999 (1990).
- Chun, S. W., Park, D. W., Woo, H. C., Hong, S. S. and Chung, J. S., "Removal of H₂S by Selective Catalytic Oxidation, II. Selective Oxidation of H₂S on TiO₂/SiO₂ Catalysts", *J. of Korean Ind. & Eng. Chemistry*, **7**, 645 (1996).
- Hartley, E. M. and Matteson, M. J., "Sulfur Dioxide Reaction with Ammonia in Humid Air", *Ind. Eng. Chem. Fundam.*, **14**, 67 (1975).
- Kettner, R. and Liermann, N., "New Claus Tail-Gas Process Provided in German Operation", *Oil & Gas J.*, Jan. **11**, 63 (1983).
- Kettner, R., Lubcke, T. and Liermann, N., "Process for the Reduction of the Sulfur Content in a Gaseous Stream", European Patent 78,690 (1982).
- Lagas, J. A., Borsboom, J. and Berben, P. H., "Selective Oxidation Catalyst Improves Claus Process", *Oil & Gas J.*, Oct. **10**, 68 (1988).
- Terorde, R. J. A. M., Brink, P. J., Visser, L. M. and Dillen, A. J., "Selective Oxidation of Hydrogen Sulfide to Elemental Sulfur Using Iron Oxide Catalysis on Various Supports", *Catalysis Today*, **17**, 217 (1993).
- Wieckowska, J., "Catalytic and Adsorptive Desulfurization of Gases", *Catalysis Today*, **24**, 105 (1995).