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Removal of H_2S and/or SO_2 by catalytic conversion technologies

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Abstract

Catalysts for selective oxidation and selective reduction of H_2S and SO_2 to elemental sulfur were developed using stoichiometric amounts of oxygen and hydrogen, respectively. Repetition of the two reactions, called the SPOR process, can be used for removing H_2S and/or SO_x in tail gas. The selective oxidation catalyst, V/SiO_2, exhibited about 95% of sulfur yield in the absence of water and about 86% in the presence of 30% water vapor in the feed at 225°C. The yield is comparable to that of Superclaus catalyst which uses 10 times excess oxygen over the stoichiometric amount. The selective reduction catalyst, CoMo/alumina, exhibited about 60–80% of sulfur yield depending on the SO_2 concentration. The presence of water did not affect the sulfur yield if the water content was kept below 11%. The overall reaction was composed of two independent reactions occurring on two different sites: complete hydrogenation of SO_2 to H_2S on metal phase; and the Claus reaction on acidic alumina support.

Keywords: Selective oxidation; Elemental sulfur; Removal of H_2S and/or SO_2

1. Introduction

Because of recent environmental concern, a more efficient method for removing SO_x and H_2S, major polutant species from stationary sources, needs to be developed. H_2S can be usually found in a desulfurization unit and can be best treated by the well-known Claus process [1], in which SO_2 produced after thermal oxidation of H_2S undergoes a condensation reaction over alumina catalyst to produce elemental sulfur.

$$H_2S + O_2 \rightarrow SO_2 + H_2O$$

$$2H_2S + SO_2 \leftrightarrow S + H_2O$$

Since the second reaction is reversible, usually two or three catalytic reactors are employed to get 90–98% conversion. To treat unrecovered Claus tail gas containing SO_2 and H_2S, there exist many commercial processes which are based on low temperature Claus reaction [2–4] or on the enrichment of H_2S by absorption and adsorption [5–7]. However, these processes re-

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quire batch or periodic operation and sometimes heavy installation cost [2]. Recently developed MODOP and Superclaus seems to be more attractive than the conventional processes since they can convert H_2S directly to elemental sulfur by selective catalytic oxidation and do not require periodic operation. Concerning catalytic activity, Superclaus seems to be superior to MODOP since the catalyst for the former can tolerate the presence of water. However, Superclaus uses ten times more oxygen than the stoichiometric amount for converting H_2S to sulfur, and cannot be applied for treating H_2S higher than 5%.

For treating SO_2, a throwaway process, such as lime or limestone scrubbing process, is prevailing now for oxygen-containing SO_2 (Flue gas desulfurization) [8]. For oxygen-free SO_2, there have been many efforts to find efficient catalysts and reductants in order to reduce it to elemental sulfur with a high yield. For various reductants, such as carbon, CO, hydrogen and methane, either the reaction temperature is too high (higher than 500°C) or the sulfur yield is not high enough as shown in Table 1.

Here, we report new catalysts developed for the selective reduction and oxidation of SO_2 and H_2S using stoichiometric amounts of hydrogen and oxygen, respectively. With these catalysts, it was possible to get high yields of sulfur at relatively low temperatures, around 220–300°C. Since the reactions were carried out using stoichiometric amounts of hydrogen or oxygen, the two reactions can be repeated as many times as necessary in order to get a high yield of sulfur. The process, called SPOR, can be attached to the Claus tail gas or may substitute for the rather expensive Claus process when H_2S concentration in the feed is not so high. Moreover, the SO_2 in oxygen-free gas can also be treated by applying the reduction step first, followed by the oxidation step.

Table 1
Literature survey for the reduction of SO_2 with various reducing agents

Reducing agent	Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)	Ref.
C	Coke	850–1200	50–99	– [a]	[8]
	Coke	800	96	96	[9]
H_2	V_2O_5	600–800	–	–	[10]
	Fe group metal sulfide				
	on porous material	275–325	–	–	[11]
	on Al_2O_3	480	77.4	45.8	[12]
	Bauxite	480	64.5	67.5	[13]
CO	Alumina, pyrrhotite	500–800	80	–	[8]
	Bauxite, chamotte	500–600	78–90	–	[14]
	Fe powder + alumina	500–600	78–90	–	[15]
	Surinam red mud, et al.	500–900	69	82	[16]
	Copper on alumina	450–580	86	87	[17]
	$LaCoO_3$, CeO_2–Co_3O_4, $CuCo_2O_4$	284–465	17–90	20–100	[18]
	$La_{0.5}Sr_{0.5}CoO_3$	500–700	90	90	[19]
Natural gas containing CH_4	Fe_2O_3 + MgO + CrO_2	500	–	–	[20]
	Activated alumina + bauxite + calcium sulfide	1000	56	90	[21]
	Alkaline earth molybdate + one of Co, Mg, Cu, Ce	575–645	70	–	[22]
	Activated alumina	650–750	–	–	[23]
	Transition metal sulfide, FeS_2, MoS_2, WS_2	650–750	–	–	[24]

[a] Not mentioned.

2. Experimental

Catalysts were prepared by impregnating aqueous solutions of metal salts (Alderich, cobalt nitrate, ammonium molybdate tetrahydrate and ammonium metavanadate) to silica gel (Davisil, grade 646, surface area 300 = m^2/g) or alumina support (Aldrich, surface area = 155 m^2/g). For the bimetallic compound of CoMo/alumina, molybdenum was impregnated first, this was followed by impregnation of cobalt after drying at 120°C overnight. The metal loading in the CoMo/Alumina was kept at 6 and 9%, respectively. After drying the impregnated sample at 120°C overnight, it was calcined at 400°C for 3 h before further use. For reaction test, catalyst was pelletized to a cylindrical form of 1 mm o.d. × 5 mm length.

SO_2 and H_2S (Solkatronic Chemical Inc., 99.98%) were used without further purification only after passing through a dust filter. Hydrogen and helium (KBOC, Korea, 99.999%) were further purified after passing through an oxygen-removing trap and a water-removing trap. Air (KBOC) was used without further purification. A vertical, fixed-bed flow reactor made of a 1.0-in. pyrex tube was used in this study. All reactions were carried out at atmospheric pressure. A mixture of sulfur dioxide and hydrogen or a mixture of hydrogen sulfide and air was diluted in helium using mass flow controllers. Water was injected by a syringe pump to the feed line located before the reactor, and vaporized in situ in the feed line before entering the reactor. A sulfur condenser was attached at the effluent side of the reactor; its temperature was maintained constant at 110°C to condense sulfur vapor without condensing water vapor. From the condenser up to the gas chromatograph, all the lines and fittings were heated above 125°C to prevent condensation of water vapor. A line filter was installed after the condenser to trap any sulfur mist that was not collected by the condenser. The gaseous products, SO_2, H_2S, and H_2O, were analyzed by a gas chromatograph (Hewlett Packard 5890) with a Porapak T column (80/100 mesh, 90 cm) and a thermal conductivity detector.

3. Catalyst for SO_2 reduction to sulfur

Table 2 shows the effect of reaction temperature on the conversion of SO_2 and the selectivity of sulfur for various concentrations of SO_2 at the stoichiometric SO_2/H_2 feed ratio of 0.5. With an increase in the reaction temperature, the conversion of SO_2 and the yield of sulfur increase while the selectivity for sulfur decreases. At the low concentration of 0.5% SO_2, the conversion of SO_2 was abruptly increased to 100%, while the selectivity of sulfur was de-

Table 2
The conversion of SO_2 and the selectivity of sulfur for various concentrations of SO_2 at SO_2/H_2 feed ratio of 1:2 (GHSV = 3000 l/kg cat./h)

Concentration of SO_2 (%)	Conversion and selectivity	Temperature (°C) 260	280	300	325	350
0.5	Conv. (%)	94.8	97.4	100.0	–	–
	Selec. (%)	86.4	71.7	58.5	–	–
2.5	Conv. (%)	46.3	54.7	59.0	62.5	62.7
	Selec. (%)	98.3	97.4	96.0	94.0	91.2
5.0	Conv. (%)	–	56.5	66.0	74.0	78.0
	Selec. (%)	–	97.6	95.6	94.0	89.6
10.0	Conv. (%)	–	58.0	70.8	80.4	–
	Selec. (%)	–	97.1	96.0	92.6	–
25.0	Conv. (%)	–	74.8	81.0	83.3	–
	Selec. (%)	–	92.0	88.4	87.0	–

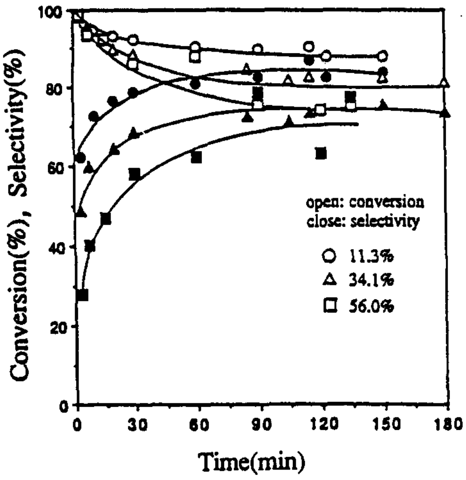

Fig. 1. Effect of water on the conversion and selectivity of sulfur (5% SO_2, GHSV = 4500 l/kg-cat./h, $T = 300°C$).

creased dramatically. Such a dramatic change at low SO_2 concentration suggests that the overall reaction is composed of multiple independent reactions and that one of those reactions can be diminished as SO_2 concentration becomes low. This point will be explained later. The low reaction temperatures around 300°C and the conversion and selectivity shown in Table 2 are much better than the results obtained by Doumani et al. [13], who reported 77% conversion and 46% selectivity at 480°C using Fe group metals supported on alumina.

Fig. 1 shows the effect of water content in the feed on the conversion and selectivity. When the water content was less than 11.3 vol.%, little decrease was observed in the sulfur yield. However, there were appreciable decreases in both conversion and selectivity as the water content increased beyond 11.3 vol.%. From the results, we assume that the reaction is composed of three reaction steps:

$$SO_2 + 2H_2 \rightarrow S + 2H_2O \quad (1)$$

$$S + H_2 \rightarrow H_2S \quad (2)$$

$$H_2S + SO_2 \rightarrow 3S + 2H_2O \quad (3)$$

$$SO_2 + 2H_2 \rightarrow S + 2H_2O \text{ (overall)} \quad (4)$$

Thermodynamic calculations [25] have shown that reactions (1) and (2) can be considered irreversible at low temperatures, around 300°C. The Claus reaction (3) is reversible, and the presence of water reduces the conversion of SO_2. In order to confirm the existence of the reaction steps proposed, the following experiment was carried out as shown in Fig. 2. When only alumina was used (case A), there were little conversion of SO_2 and zero selectivity of sulfur. $CoMoO_4$ (case B) hydrogenated SO_2 completely to H_2S, producing a negligible amount of sulfur. The case (C), in which the top bed of $CoMoO_4$ was separated from the bottom bed of alumina by a layer of glass wool, exhibited a high value of both sulfur dioxide conversion and sulfur selectivity. Since the top $CoMoO_4$ bed produces only hydrogen sulfide, the high sulfur selectivity in case (C) must result from a reaction catalyzed by the bottom alumina bed. Sulfur must be formed by the condensation reaction between hydrogen sulfide and sulfur dioxide (the Claus reaction). When the packing order in case (C) is reversed, locating the alumina bed on the top and $CoMoO_4$ below, as in case (D), the production of sulfur is negligible. In other words, the alumina bed is inert and only the $CoMoO_4$ bed produces hydrogen sulfide as in case (B) in which only $CoMoO_4$ is packed. The results in Fig. 2 establish that a metal sulfide phase in Co–Mo/Al_2O_3 hydrogenates sulfur dioxide and that the alumina

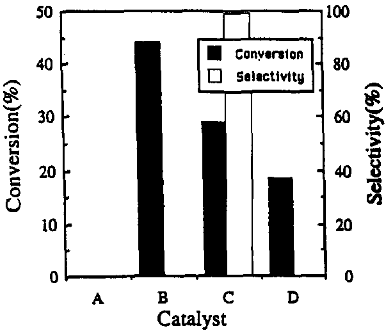

Fig. 2. Reaction tests on Al_2O_3, $CoMoO_4$, combined layers the two, and a physical mixture at 300°C (5% SO_2, $H_2/SO_2 = 3.0$, GHSV = 3000 l/kg-cat./h): A, Al_2O_3 (2 g); B, $CoMoO_4$ (2 g); C, $CoMoO_4$ (1 g)/glass wool/Al_2O_3 (1 g); D, Al_2O_3 (1 g)/glass wool/$CoMoO_4$ (1 g).

Table 3
Comparison of reaction conditions

	Fe/Silica [a]	V/silica
GHSV (h^{-1})	12000	48000
O_2/H_2S	5.0	0.5
H_2O content (%)	30	30
SO_2 concentration (%)	1	5

[a] From [27].

support catalyzes the Claus reaction between hydrogen sulfide and sulfur dioxide to produce elemental sulfur. The results coincide with the reaction mechanism proposed previously for cobalt/alumina catalysts [26]. X-ray analysis of the reacted catalysts showed the presence of MoS_2 and $CoMoO_4$ phases. As prescreening test of metal sulfide showed that CoS_2 was twice as active as MoS_2 for the reaction [25], we assume that a well dispersed Co–Mo–S phase is involved for the deep hydrogenation reaction.

4. Catalyst for H_2S oxidation to sulfur

Tables 3 and 4 show a comparison of the reaction conditions and the results of the reaction test between Fe/SiO_2 (known as Superclaus catalyst) and V/SiO_2, developed by us. The sulfur yield of V/SiO_2 is comparable to Fe/SiO_2, although the former has higher GHSV and much lower oxygen content in the feed. Recently, it is claimed that $Fe–Cr/SiO_2$ can give sulfur yield of more than 90% at the Superclaus condition [27]. The catalyst is known to have little decrease of the sulfur yield even in the presence of 30 vol.% water vapor in the feed. V/SiO_2 catalyst showed a decrease in the yield when excess water was introduced in the feed. The decrease of the sulfur yield can be kept at a minimum of 15% when the reaction temperature is kept low, as shown in Fig. 3. Anyhow, it can be seen from Table 4 that, despite of the decrease in the sulfur yield in the presence of water, the yield of V/silica catalyst is about the same as that of Superclaus catalyst. The use of a stoichiometric amount of oxygen with V/SiO_2 makes it possible to treat highly

Table 4
Results of reaction test

Temperature	Fe/silica [a]		V/silica	
(°C)	Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)
225	86	94	92	98
250	99	91	91	95
275	100	79	84	90
300	100	50	76	80
325	–	–	75	76

[a] From [27].

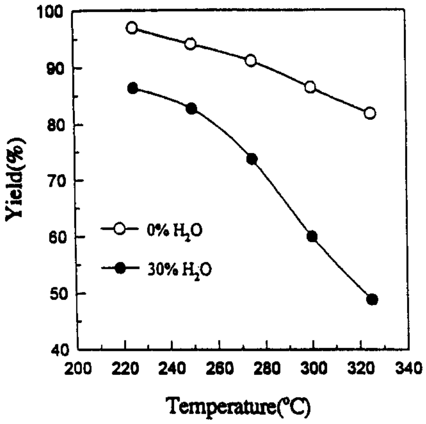

Fig. 3. Reaction tests of V (30 wt%)/SiO_2 catalyst at various temperatures (5% H_2S, $O_2/H_2S = 0.5$, GHSV = 3000/h).

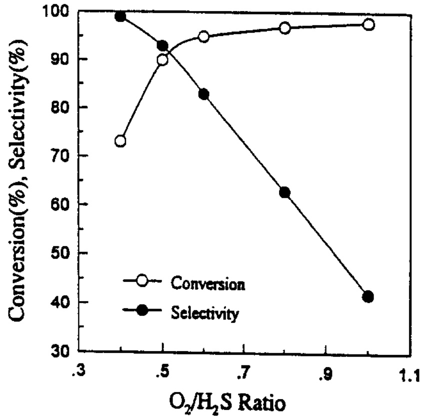

Fig. 4. Effect of O_2/H_2S feed ratio on the conversion of hydrogen sulfide and the sulfur selectivity (5% H_2S, 30% H_2O, GHSV = 96,000/h, $T = 225°C$).

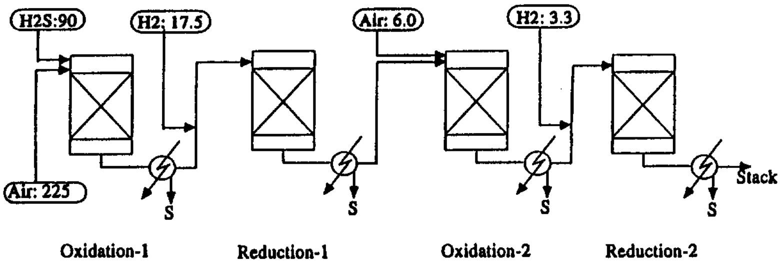

Fig. 5. SPOR process.

concentrated H_2S, whereas the Superclaus catalyst is limited to H_2S concentration less than 5 vol.%.

Fig. 4 shows the effect of O_2/H_2S ratio on the conversion of H_2S and the selectivity of sulfur. As the ratio increases, the conversion increases, while the selectivity decreases, indicating that main reaction for the conversion of H_2S is an irreversible series reaction, $H_2S \rightarrow S \rightarrow SO_2$. A separate calculation has shown that Claus reaction occupies about 10% at a low reaction temperature of 220°C, but reaches 30% at 350°C.

5. SPOR process

Based on catalytic systems [28–32] developed for the selective oxidation and selective reduction of H_2S and SO_2, respectively, we can devise a process, called SPOR (sulfur removal by partial oxidation and reduction), for solving SO_x problems in tail gas. Fig. 5 is a schematic diagram of the SPOR process. The oxidation and reduction cycle can be repeated as many times as necessary in theory. For practical applications, 2 or 3 stage catalytic reactor system is sufficient to give 98–99% recovery yield of sulfur. The process can be attached to the tail gas of Claus process with a single oxidation step like Superclaus process or with a two-stage oxidation–reduction combination. In the latter case, the sulfur recovery yield of SPOR is, of course, higher than that of Superclaus. When H_2S concentration in the feed is not so high (i.e., less than 20%), it is possible to apply the oxidation step to set up the feed composition of Claus reaction ($H_2S/SO_2 = 2.0$), as shown in Fig. 6. As can be seen in Fig. 4, the H_2S/SO_2 ratio of 2.0 can be obtained by increasing the O_2/H_2S ratio during the oxidation reaction. Therefore, the first oxidation reactor can substitute for the high temperature oven reactor in the conventional Claus process. The oven reactor is not only an expensive part of Claus plant, but is known to be difficult to keep in good maintenance. Especially at low H_2S concentrations, it is necessary to feed additional fuel to keep the oven temperature above 1100°C.

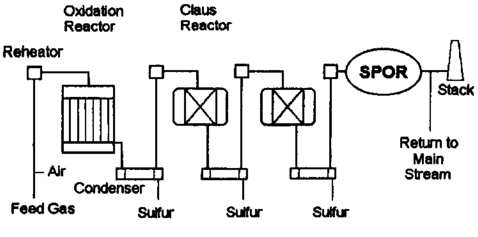

Fig. 6. Modified Claus process.

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