

## Phase Cooperation of V<sub>2</sub>O<sub>5</sub> and Bi<sub>2</sub>O<sub>3</sub> in the Selective Oxidation of H<sub>2</sub>S Containing Ammonia and Water

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**Abstract**—The selective oxidation of hydrogen sulfide containing excess water and ammonia was studied over vanadium oxide-based catalysts. The investigation was focused on the role of V<sub>2</sub>O<sub>5</sub>, and phase cooperation between V<sub>2</sub>O<sub>5</sub> and Bi<sub>2</sub>O<sub>3</sub> in this reaction. The conversion of H<sub>2</sub>S continued to decrease since V<sub>2</sub>O<sub>5</sub> was gradually reduced by treatment with H<sub>2</sub>S. The activity of V<sub>2</sub>O<sub>5</sub> was recovered by contact with oxygen. A strong synergistic phenomenon in catalytic activity was observed for the mechanically mixed catalysts of V<sub>2</sub>O<sub>5</sub> and Bi<sub>2</sub>O<sub>3</sub>. Temperature-programmed reduction (TPR) and oxidation (TPO) and two bed reaction tests were performed to explain this synergistic effect by the reoxidation ability of Bi<sub>2</sub>O<sub>3</sub>.

Key words: Hydrogen Sulfide, Selective Oxidation, Phase Cooperation, Vanadium Oxide, Bismuth Oxide

### INTRODUCTION

Since the international environmental regulations concerning the release of sulfur-containing gas are becoming more stringent, hydrogen sulfide contained in the acid gases should be effectively recovered before emission to the atmosphere. For many years, most of the hydrogen sulfide in petroleum refineries and natural gas plants has been removed by the well-known Claus process [Lell, 1985; Pieplu et al., 1998]. However, due to thermodynamic limitations, typically 3 to 5% H<sub>2</sub>S is not converted into sulfur. For treating a low concentration (less than 5 vol%) of sulfur-containing gas in the tail gas from the Claus plant or other emission sources, various commercial processes that are based on adsorption, absorption, and wet oxidation have been used. Among the processes, the most attractive process developed during the last 20 years is the dry catalytic oxidation of H<sub>2</sub>S to elemental sulfur after the hydrogenation of sulfur-containing gas to H<sub>2</sub>S. Commercially developed are MODOP process [Kettner et al., 1983, 1988], and Super Claus process [Lagas et al., 1988; van Nisselrooy and Lagas, 1993]. These processes are based on the following irreversible selective oxidation of H<sub>2</sub>S to S [Eq. (1)] as a main reaction, and other oxidation reactions [Eqs. (2) and (3)] and the reversible Claus reaction [Eq. (4)] as side reactions.



It is known that TiO<sub>2</sub>-based catalyst (MODOP process) is easily poisoned by the presence of water vapor. The iron-based catalyst

(Super Claus process) is resistant against water, but requires an excess amount of oxygen (10 times the stoichiometric amount). Catalyst containing vanadium oxide has also been reported to be active for the reaction both with a stoichiometric and an excess amount of oxygen. Bulk V<sub>2</sub>O<sub>5</sub> was most active over other bulk metal oxides [Li et al., 1996].

In previous works [Chun et al., 1988; Shin et al., 2001], we reported very high activity of TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> catalysts in the selective oxidation of hydrogen sulfide to elemental sulfur. Some binary metal oxides, such as Bi-V-O [Hass and Ward, 1985] or Fe-Cr-O [Berben et al., 1987] have also been reported as good catalysts for the gas phase conversion of H<sub>2</sub>S to sulfur. Li et al. [1996, 1997] reported a V-Mo, V-Bi, V-Mg, Fe-Sn and Fe-Sb mixed oxide catalyst system. However, it is difficult to isolate the role of each metal oxide since the coprecipitated mixed oxide catalysts can contain solid solution. The role of Bi<sub>2</sub>O<sub>3</sub> in the phase cooperation of binary mixed oxide system has been widely studied and very well reviewed by Weng and Delmon [1992]. Mechanical mixture of two pure metal oxides can offer much information about the phase cooperation of each metal oxide.

Although vanadium-based catalysts are widely used for selective oxidation reactions [Weng and Delmon, 1992; Kim and Yang, 2000], very little information is available about this catalyst system for the selective oxidation of H<sub>2</sub>S containing NH<sub>3</sub> and excess water [Chun et al., 1997]. The mixed gas of H<sub>2</sub>S, NH<sub>3</sub>, and water vapor is released from steel smelting process, where the H<sub>2</sub>S from coke ovens is generally scrubbed and concentrated by using aqueous ammonia solution. The concentrated H<sub>2</sub>S is separated from the solution and transferred to the Claus plant. However, the separation of H<sub>2</sub>S from the solution is not perfect and the remaining aqueous ammonia stream contains about 2% H<sub>2</sub>S which in turn causes the SO<sub>x</sub> emission problem during incineration. We reported a new vapor phase catalytic process for the selective conversion of H<sub>2</sub>S in the stream containing both ammonia and water [Park et al., 1998, 2001]. V<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> catalysts showed good cata-

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<sup>‡</sup>This paper is dedicated to Professor Wha Young Lee on the occasion of his retirement from Seoul National University.

lytic activities in the selective oxidation of the H<sub>2</sub>S to ammonium thiosulfate (ATS) and elemental sulfur. Recently, we also reported that Sb<sub>2</sub>O<sub>4</sub> increased the reoxidation of the partially reduced V<sub>2</sub>O<sub>5-x</sub> by supplying spillover oxygen [Park et al., 2002].

In this study, mechanical mixtures of V<sub>2</sub>O<sub>5</sub> and Bi<sub>2</sub>O<sub>3</sub> are used to further investigate the role of each metal oxide in the selective oxidation of H<sub>2</sub>S to ATS and elemental sulfur. Solid state modifications of the mixtures during the catalytic reaction tests are verified by the characterization of the catalysts before and after the reaction test by using XRD and XPS. Temperature programmed techniques (TPR and TPO) are also used to elucidate the phase cooperation mechanism in this reaction by spillover oxygen.

## EXPERIMENTAL

### 1. Catalyst Preparation

The mechanical mixture catalysts were prepared according to the literature [Weng and Delmon, 1992]. The pure V<sub>2</sub>O<sub>5</sub> (Junsei, SA=5.4 m<sup>2</sup>/g) and Bi<sub>2</sub>O<sub>3</sub> (Junsei, SA=1.37 m<sup>2</sup>/g) were dispersed in n-pentane (Merck, analytical purity). The suspension was stirred in an ultrasonic vibrator (Brasonic 32) for 10 min. n-Pentane was evaporated with agitation at 25 °C under vacuum. The remaining n-pentane was removed by drying in air at 80 °C for 20 h. Then, the sample was dried at 110 °C overnight and calcined at 500 °C for 5 h. The catalyst was designated as V<sub>2</sub>O<sub>5</sub>+Bi<sub>2</sub>O<sub>3</sub> (x : y) where x and y represents the weight ratio of V<sub>2</sub>O<sub>5</sub> and Bi<sub>2</sub>O<sub>3</sub>, respectively.

### 2. Reaction Test

Reaction tests were carried out in a continuous flow fixed-bed reactor. The reactor was made of a Pyrex<sup>®</sup> 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 thiosulfate). 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 chromatograph, 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 by using an evaporator filled with small glass beads, and its amount was controlled by a syringe pump.

The content of effluent gas was analyzed by a gas chromatograph (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 H<sub>2</sub>S and the selectivity to a special product are defined as follows:

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

$$\text{Selectivity (S) to a special product (SO}_2, \text{S, ATS)}$$

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

For the calculation of ATS selectivity, moles of ATS was multiplied by a factor of 2 because one mole of ATS can be obtained from two moles of H<sub>2</sub>S.

### 3. Characterization of Catalysts

The surface area of the individual oxides and their mechanical

mixtures was measured by N<sub>2</sub> adsorption method by using the BET technique (Micromeritics ASAP 2000). The phase analysis was performed by X-ray diffraction crystallograph with Cu-Kα radiation (Rigaku, DMAX 2400). The 2θ range between 5 and 90° was scanned at a rate of 2°/min. Identification of the phases was carried out by using JCPDS data base. XPS analyses were performed with an X-ray photoelectron spectrometer (VG, ESCALAB 220) with monochromatic Al-Kα radiation. The samples were pressed into self-supporting wafers without any binder followed by a pretreatment at an ultrahigh vacuum. The binding energies were calculated by using the C1s band as reference (284.6 eV). The recorded spectra were decomposed with a least squares fitting routine program. The element atomic concentration on the surface was calculated from the relative intensities of peaks by using different sensitivity factors supplied by the manufacturer. V2p<sub>3/2</sub> and Bi3d<sub>3/2</sub> were used for the calculation of V and Bi, respectively. In order to investigate the phase cooperation mechanism, TPR was performed. Before reduction, samples were pretreated by heating under air flow from 25 °C to 450 °C at 10 °C/min. Reduction was achieved under an H<sub>2</sub>/N<sub>2</sub> gas mixture (10 vol% H<sub>2</sub>). Gas flow was 20 mL/min and temperature program was from 25 °C to 700 °C at a heating rate of 10 °C/min. The amount of consumed H<sub>2</sub> was detected by mass spectroscopy (VG Quadrupole). After TPR experiment, the same sample was instantly tested in TPO under 2.5 vol% O<sub>2</sub> with helium gas balance.

## RESULTS AND DISCUSSION

### 1. Reaction over V<sub>2</sub>O<sub>5</sub>

In order to understand phase cooperation of V<sub>2</sub>O<sub>5</sub> and Bi<sub>2</sub>O<sub>3</sub>, pure V<sub>2</sub>O<sub>5</sub> was first investigated for its behavior in the selective oxidation of H<sub>2</sub>S. Fig. 1 shows the time variant conversion and selectivity to S and SO<sub>2</sub> with different treatment of feed at 220 °C. When a feed containing only H<sub>2</sub>S (5 vol% with balance helium) was passed over fresh catalyst (region A), the complete conversion that was

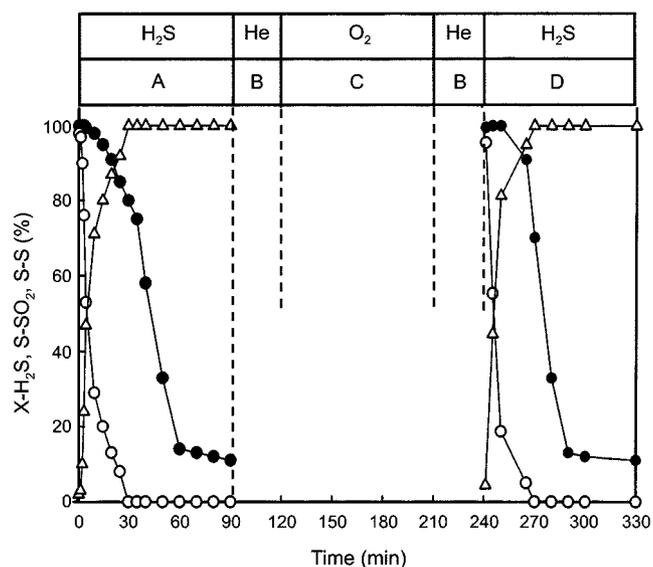


Fig. 1. Time variant profiles of X-H<sub>2</sub>S (●), S-SO<sub>2</sub> (○) and S-S (△) in square pulses: A/B/C/D=(5%H<sub>2</sub>S)/(He)/(O<sub>2</sub>)/(5%H<sub>2</sub>S), T=220 °C, GHSV=3,000 h<sup>-1</sup>.

achieved initially showed a dramatic decrease to 5% in about 60 min. The fresh  $V_2O_5$  catalyst produced only the complete oxidation product  $SO_2$  during less than 5 min. As the reaction proceeded, the sulfur production increased and 100% selectivity to sulfur could be achieved after 30 min. The results clearly show that an oxidized form of vanadium having very active surface oxygen produces only  $SO_2$ . When  $V_2O_5$  was reduced to a suboxide after the reaction for 30 min, the complete conversion continuously decreased and only sulfur was produced without  $SO_2$  emission probably due to the depletion of labile oxygen in vanadium. We therefore suggest that only less labile lattice oxygen in reduced vanadium oxides can produce sulfur via redox mechanism. After the reaction without oxygen for 90 min, the reactor was purged with helium [region (B)] for 30 min and the feed was switched to pure  $O_2$  for 90 min [region (C)]. When the feed was switched again to  $H_2S$  without oxygen [region (D)], the same response of the  $H_2S$  conversion and  $SO_2$  selectivity as that in the region (A) was observed again. It is interesting to note that oxygen treatment can recover the catalytic activity of  $V_2O_5$ . Reproducible performance in the conversion and selectivity was observed during repeated switching between region (A) and (C).

Fig. 2 shows the variation of conversion and selectivity to elemental sulfur and  $SO_2$  when a mixture of 5%  $H_2S$  and 2.5%  $O_2$  was passed over  $V_2O_5$  [region (E)] after introduction of  $H_2S$  and He as in Fig. 1. The conversion increased quickly and reached up to 92% with the presence of oxygen in the feed. When oxygen is present in the feed, the conversion seems to attain steady values after filling up the lattice oxygen from gas phase molecular oxygen. From the results, it can be suggested that the steady decrease in the conversion shown in the region (A) after 5 min of the reaction may be caused by a slow reduction of vanadium. We therefore conclude that the slow deactivation of catalyst observed for the oxidation of  $H_2S$  over vanadium based catalysts is caused by the steady reduction of  $V_2O_5$ , originating from the relatively slow rate of reoxidation of  $V_2O_5$  by gas phase oxygen.

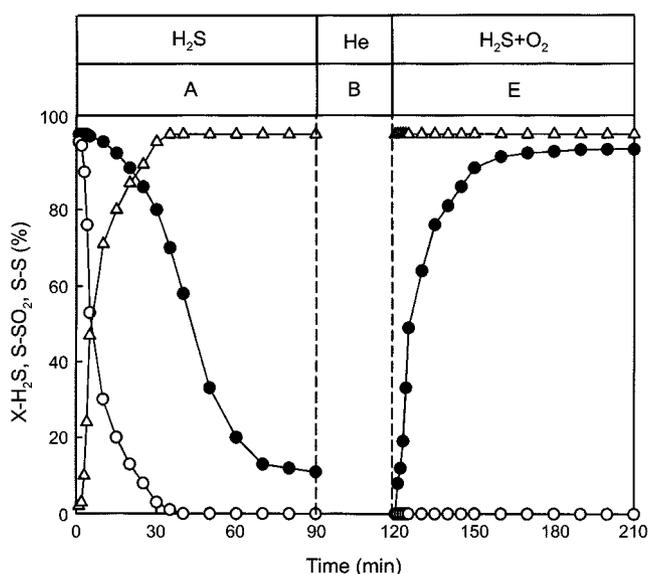


Fig. 2. Time variant profiles of  $X-H_2S$  (●),  $S-SO_2$  (○) and  $S-S$  (△) in square pulses: A/B/E=(5% $H_2S$ )/(He)/(5% $H_2S$ +2.5% $O_2$ ),  $T=220$  °C, GHSV=3,000  $h^{-1}$ .

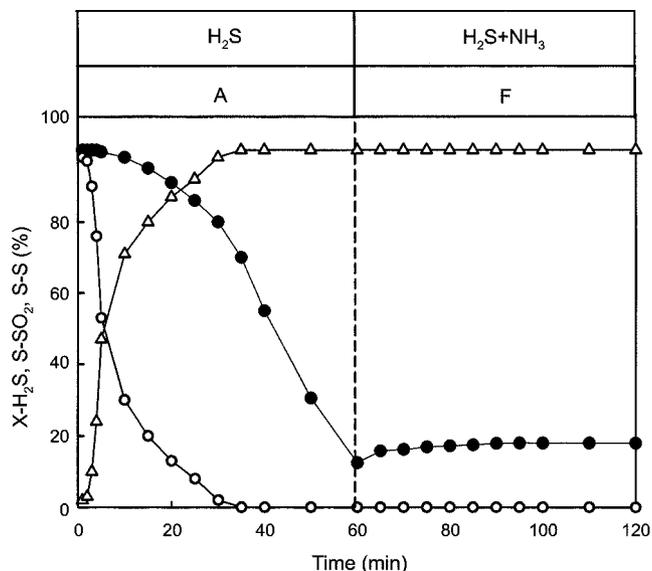


Fig. 3. Time variant profiles of  $X-H_2S$  (●),  $S-SO_2$  (○) and  $S-S$  (△) in square pulses: A/B/E=(5% $H_2S$ )/(He)/(5% $H_2S$ +5% $NH_3$ ),  $T=220$  °C, GHSV=3,000  $h^{-1}$ .

In Fig. 3, 5 vol% of  $NH_3$  was added to  $H_2S$  [region (F)] after 60 min of  $H_2S$  treatment in region (A). Comparing  $H_2S$  conversion at 60 min in region (A) of Fig. 2 with that in region (F) of Fig. 3, one can see that the  $H_2S$  conversion increased slightly with the introduction of  $NH_3$  to  $H_2S$ . This result implies that  $H_2S$  reacts with  $NH_3$  over  $V_2O_5$ .

## 2. Reaction over Mechanical Mixtures ( $V_2O_5+Bi_2O_3$ )

Mechanical mixture catalysts of  $V_2O_5$  and  $Bi_2O_3$  are used to study the phase cooperation phenomena with reactant composition of 5 vol%  $H_2S$ , 2.5 vol%  $O_2$ , 5 vol%  $NH_3$ , 60 vol%  $H_2O$  and the bal-

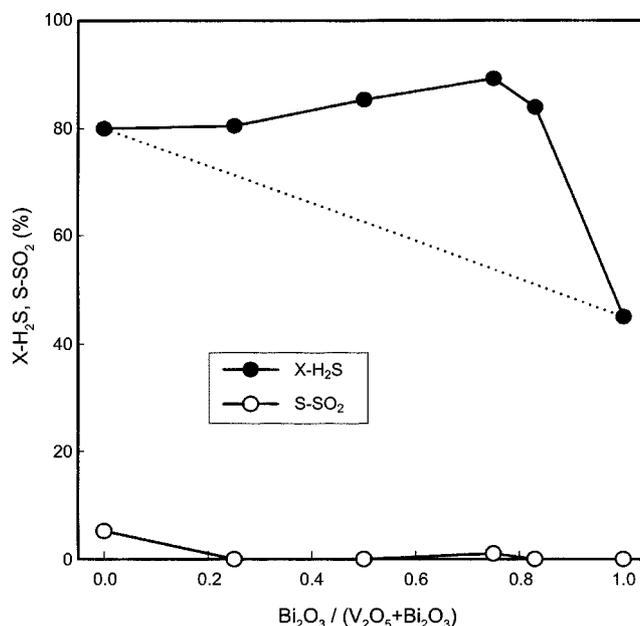


Fig. 4. Conversion of  $H_2S$  and selectivity to  $SO_2$  as a function of  $Bi_2O_3$  weight fraction for  $V_2O_5+Bi_2O_3$  mixtures at 260 °C ( $H_2S/O_2/NH_3/H_2O=5/2.5/5/60$ , GHSV=12,000  $h^{-1}$ ).

**Table 1. Conversion of H<sub>2</sub>S and selectivity to SO<sub>2</sub> for V<sub>2</sub>O<sub>5</sub> and V<sub>2</sub>O<sub>5</sub>+Bi<sub>2</sub>O<sub>3</sub> (1 : 3) at different temperatures**

Temp. (°C)	V <sub>2</sub> O <sub>5</sub>		V <sub>2</sub> O <sub>5</sub> +Bi <sub>2</sub> O <sub>3</sub> (1:3)	
	X-H <sub>2</sub> S (%)	S-SO <sub>2</sub> (%)	X-H <sub>2</sub> S (%)	S-SO <sub>2</sub> (%)
260	81.0	0.0	89.3	0.0
280	80.0	2.2	86.4	0.8
300	75.1	4.2	83.8	1.4
320	71.2	5.3	75.3	2.0
340	68.1	8.4	69.6	2.5

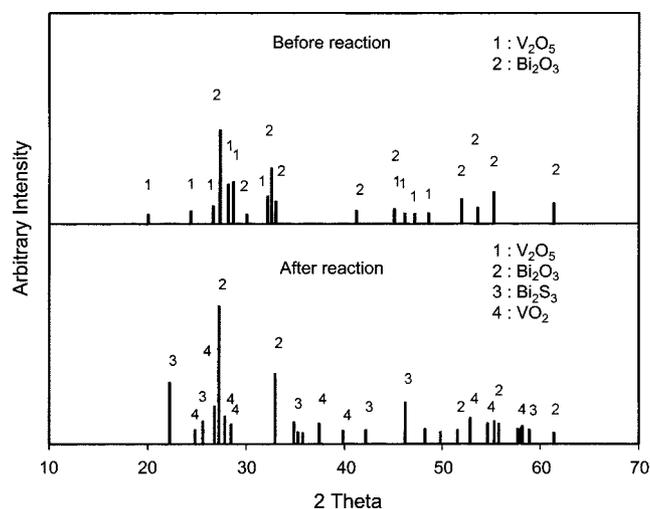
Reaction condition: H<sub>2</sub>S/O<sub>2</sub>/NH<sub>3</sub>/H<sub>2</sub>O/He=5/2.5/5/60/27.5, GHSV=12,000 h<sup>-1</sup>.

ance helium. The weight ratios of V<sub>2</sub>O<sub>5</sub>/Bi<sub>2</sub>O<sub>3</sub> were 1/0, 3/1, 1/1, 1/3, 1/5, and 0/1. Fig. 4 shows the H<sub>2</sub>S conversion and SO<sub>2</sub> selectivity as a function of mass ratio [V<sub>2</sub>O<sub>5</sub>/(V<sub>2</sub>O<sub>5</sub>+Bi<sub>2</sub>O<sub>3</sub>)] at 260 °C with GHSV of 12,000 h<sup>-1</sup>. Pure Bi<sub>2</sub>O<sub>3</sub> shows low conversion of H<sub>2</sub>S (45%). Considering the H<sub>2</sub>S conversion of 38% at 260 °C for the blank test, pure Bi<sub>2</sub>O<sub>3</sub> did not practically play any significant catalytic role in this reaction. The addition of V<sub>2</sub>O<sub>5</sub> into Bi<sub>2</sub>O<sub>3</sub> greatly increased H<sub>2</sub>S conversion. All the mechanical mixture catalysts (V<sub>2</sub>O<sub>5</sub>+Bi<sub>2</sub>O<sub>3</sub>) showed higher H<sub>2</sub>S conversion than the arithmetic average conversion (expressed as a dotted line in Fig. 4) of pure V<sub>2</sub>O<sub>5</sub> and pure Bi<sub>2</sub>O<sub>3</sub>; a strong synergy existed between V<sub>2</sub>O<sub>5</sub> and Bi<sub>2</sub>O<sub>3</sub>. But it was not easy to find any synergistic effect for the SO<sub>2</sub> selectivity because the SO<sub>2</sub> selectivities were very low for all the mixture catalysts. V<sub>2</sub>O<sub>5</sub>+Bi<sub>2</sub>O<sub>3</sub> (1 : 3) showed the highest H<sub>2</sub>S conversion. However, the cooperative effect has been known to depend on several parameters such as composition, ratio of surface area, number and quality of contacts of two components [Weng and Delmon, 1992]. A typical temperature dependence of the H<sub>2</sub>S conversion and SO<sub>2</sub> selectivity for V<sub>2</sub>O<sub>5</sub>+Bi<sub>2</sub>O<sub>3</sub> (1 : 3) catalyst and pure V<sub>2</sub>O<sub>5</sub> is shown in Table 1. The H<sub>2</sub>S conversion for V<sub>2</sub>O<sub>5</sub> and the mixture catalysts decreased with temperature. It is consistent with the previously estimated equilibrium calculations reported by Chun [1998] since the selective oxidation contains several reaction steps including the reverse Claus reaction. Over the whole temperature range, 260-340 °C, the mixture catalyst exhibits higher H<sub>2</sub>S conversion than pure V<sub>2</sub>O<sub>5</sub>. The SO<sub>2</sub> selectivities for the mixture catalyst were also lower than pure V<sub>2</sub>O<sub>5</sub>. Thus, the synergy for the mixture catalyst was confirmed over wide temperature ranges.

### 3. Phase Cooperation

The synergistic effect observed in mixed oxide catalysts is generally known [Weng and Delmon, 1992] to be from the three main reasons: (1) formation of new active phase by reaction between two phases, (2) increase of surface area, (3) formation of mobile oxygen species and some chemical action of the latter (remote control mechanism). In order to understand the phase cooperation for V<sub>2</sub>O<sub>5</sub>+Bi<sub>2</sub>O<sub>3</sub> catalyst, the first possibility was verified by XRD method. The X-ray diffraction patterns of V<sub>2</sub>O<sub>5</sub>+Bi<sub>2</sub>O<sub>3</sub> (1 : 3) catalyst are presented in Fig. 5.

Fresh catalyst shows only characteristic peaks of V<sub>2</sub>O<sub>5</sub> and Bi<sub>2</sub>O<sub>3</sub>. The spent catalyst, used for 8 h for the reaction, shows the existence of reduced phase of V<sub>2</sub>O<sub>5</sub> like VO<sub>2</sub>. Part of Bi<sub>2</sub>O<sub>3</sub> was also sulfided to Bi<sub>2</sub>S<sub>3</sub>. However, no new phase (principally V<sub>x</sub>Bi<sub>1-x</sub>O<sub>y</sub>) detectable by XRD was generated during the catalytic tests. Bismuth

**Fig. 5. XRD patterns of V<sub>2</sub>O<sub>5</sub>+Bi<sub>2</sub>O<sub>3</sub> (1 : 3) catalysts before and after reaction.**

vanadates (BiVO<sub>4</sub>, Bi<sub>4</sub>V<sub>6</sub>O<sub>21</sub>) are reported to be one of the most active phases in coprecipitated V-Bi-O mixed oxide catalyst used in selective oxidation reaction [Li et al., 1996; Moro-Oka, 1993]. Secondly, BET surface areas of the fresh and used V<sub>2</sub>O<sub>5</sub>+Bi<sub>2</sub>O<sub>3</sub> (1 : 3) catalyst were measured and they were 2.4 and 1.9 m<sup>2</sup>/g, respectively. The surface area of the fresh catalyst was nearly the same as the arithmetic average value of pure V<sub>2</sub>O<sub>5</sub> (5.4 m<sup>2</sup>/g) and Bi<sub>2</sub>O<sub>3</sub> (1.37 m<sup>2</sup>/g). The decrease in surface area of spent catalyst may be due to the increase of grain size. Therefore, the formation of new phase and increase of surface area can be excluded to explain the increase of H<sub>2</sub>S conversion in this study. These two phenomena are generally accepted to be not evident to describe synergistic effects in mechanically mixed catalysts.

The role of mobile oxygen species is extensively studied to explain phase cooperation in mechanically mixed catalysts. Weng and Delmon [1992] reviewed remote control effects of two phases in several selective oxidation catalysts. This remote control mechanism supposes that a mobile oxygen species (spillover oxygen) is formed from gas phase oxygen on the surface of one phase and migrates onto the other, where it creates and/or regenerates the active centers. They also reported Bi<sub>2</sub>O<sub>3</sub> could be a strong donor of mobile oxygen species. An attempt to verify the existence of the synergis-

**Table 2. The H<sub>2</sub>S conversion and product selectivities for three different operations with V<sub>2</sub>O<sub>5</sub>+Bi<sub>2</sub>O<sub>3</sub> catalysts at 260 °C**

Catalyst	Case	X-H <sub>2</sub> S (%)	S-SO <sub>2</sub> (%)	S-S (%)	S-ATS (%)
V <sub>2</sub> O <sub>5</sub> +Bi <sub>2</sub> O <sub>3</sub> (3 : 1)	A	70.4	0	80.2	19.8
	B	72.8	0	77.4	22.6
	C	73.3	0	71.5	28.5
V <sub>2</sub> O <sub>5</sub> +Bi <sub>2</sub> O <sub>3</sub> (1 : 3)	A	83.2	5.9	82.9	11.2
	B	86.1	3.3	61.0	35.7
	C	89.3	0.0	62.6	37.4

Reaction condition: H<sub>2</sub>S/O<sub>2</sub>/NH<sub>3</sub>/H<sub>2</sub>O/He=5/2.5/5/60/27.5, GHSV=12,000 h<sup>-1</sup>.

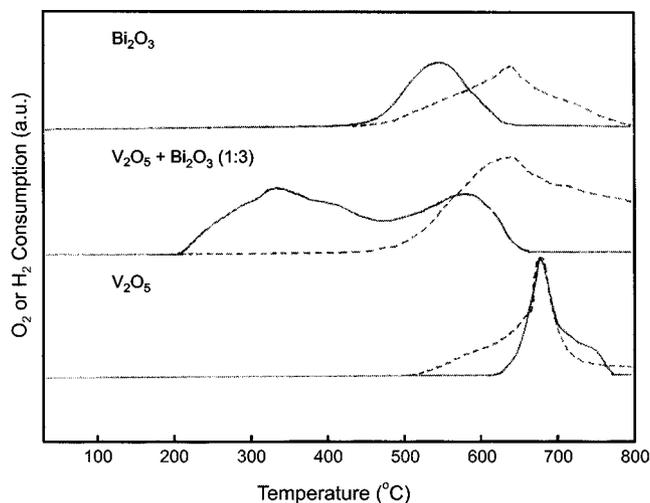


Fig. 6. TPR/TPO profiles of Bi<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, and V<sub>2</sub>O<sub>5</sub>+Bi<sub>2</sub>O<sub>3</sub> (1 : 3) catalysts (TPR: dashed line) and (TPO: solid line).

tic effect is to test the H<sub>2</sub>S oxidation in two-bed operation modes. The H<sub>2</sub>S conversion at three different operations for V<sub>2</sub>O<sub>5</sub>+Bi<sub>2</sub>O<sub>3</sub> catalysts of (3 : 1) and (1 : 3) is summarized in Table 2. In case A, the reactant mixture is first contacted with V<sub>2</sub>O<sub>5</sub> then Bi<sub>2</sub>O<sub>3</sub> before it comes out of the reactor. Case B is the reverse order of case A. In case C, uniform mixtures of V<sub>2</sub>O<sub>5</sub> and Bi<sub>2</sub>O<sub>3</sub> are placed together in the reactor. For both catalysts, the operation in case C, where uniform mixing is obtained, showed higher H<sub>2</sub>S conversion than case A and case B. Case B showed higher H<sub>2</sub>S conversion than case A. One conclusion to be drawn from this result is that Bi<sub>2</sub>O<sub>3</sub> is a donor phase and that V<sub>2</sub>O<sub>5</sub> is an acceptor phase for a mobile species, reaction intermediate or spillover oxygen.

In order to identify the real nature of this phase cooperation in V<sub>2</sub>O<sub>5</sub>+Bi<sub>2</sub>O<sub>3</sub> catalyst, TPR and TPO techniques are used in this study. Comparative temperature programmed reduction (TPR) and the following temperature programmed oxidation (TPO) are carried out for V<sub>2</sub>O<sub>5</sub>, Bi<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub>+Bi<sub>2</sub>O<sub>3</sub> (1 : 3), and the results are shown in Fig. 6. The reducibility of catalysts was first measured by using TPR method with hydrogen as a reductant. For the mixture catalyst, hydrogen consumption started from 440 °C, lower than that in the case of pure V<sub>2</sub>O<sub>5</sub> (500 °C). In the subsequent TPO experiment, the mixture catalyst showed better reoxidation property than pure V<sub>2</sub>O<sub>5</sub> and pure Bi<sub>2</sub>O<sub>3</sub>. The first maximum peak of O<sub>2</sub> consumption for the V<sub>2</sub>O<sub>5</sub>+Bi<sub>2</sub>O<sub>3</sub> (1 : 3) was 320 °C, much lower than V<sub>2</sub>O<sub>5</sub> (T<sub>max</sub> = 680 °C) and Bi<sub>2</sub>O<sub>3</sub> (T<sub>max</sub> = 550 °C). Therefore, it can be considered that the increase of H<sub>2</sub>S conversion in V<sub>2</sub>O<sub>5</sub>+Bi<sub>2</sub>O<sub>3</sub> mixture comes from the reoxidizing ability of Bi<sub>2</sub>O<sub>3</sub>.

The oxidation state of the vanadium in pure V<sub>2</sub>O<sub>5</sub> and V<sub>2</sub>O<sub>5</sub>+Bi<sub>2</sub>O<sub>3</sub> (1 : 3) is studied by XPS. Fig. 7 shows XPS spectra of V 2p<sub>3/2</sub> and V 2p<sub>1/2</sub> for the V<sub>2</sub>O<sub>5</sub> and the mixture catalyst before and after 8 h reaction at 260 °C with the standard reactant mixture and GHSV of 12,000 h<sup>-1</sup>. The standard XPS peaks of V 2p<sub>3/2</sub> for V<sup>5+</sup> and V<sup>4+</sup> are located at 516.9 and 515.6 eV, respectively. After reaction the XPS spectra were broadened and shifted to lower binding energy. It means that some of the fresh V<sub>2</sub>O<sub>5</sub> having only V<sup>5+</sup> state is reduced to V<sup>4+</sup> after the reaction. The full-width half-maximum (FWHM) value for the fresh V<sub>2</sub>O<sub>5</sub> was 1.65 eV, and that for used V<sub>2</sub>O<sub>5</sub> was

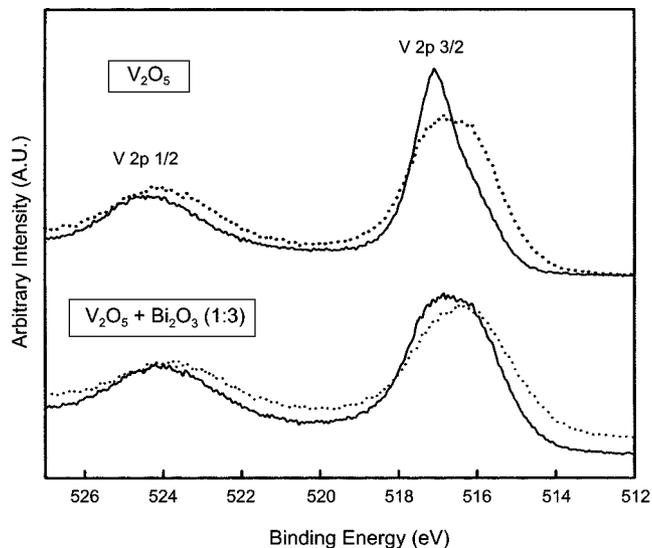


Fig. 7. XPS spectra of vanadium for V<sub>2</sub>O<sub>5</sub> and V<sub>2</sub>O<sub>5</sub>+Bi<sub>2</sub>O<sub>3</sub> (1 : 3) before (solid line) and after (dashed line) 8 h reaction at 260 °C.

2.55 eV. This corresponds to 54.5% increase in FWHM after reaction. However, the mixture catalyst showed 2.25 eV for fresh catalyst and 2.70 eV for the used catalyst, 20.0% increase in FWHM. Therefore, the mixture catalyst showed less reduction of vanadium oxide phase during the reaction. This can support the oxidizing ability of Bi<sub>2</sub>O<sub>3</sub> for the mixture catalyst.

The V<sub>2</sub>O<sub>5</sub>+Bi<sub>2</sub>O<sub>3</sub> mixed catalysts of other composition also showed the same results as V<sub>2</sub>O<sub>5</sub>+Bi<sub>2</sub>O<sub>3</sub> (1 : 3). Therefore, the possible explanation for the synergistic effect of V<sub>2</sub>O<sub>5</sub>+Bi<sub>2</sub>O<sub>3</sub> mixture catalyst will be the following sequence of the redox process. Since Bi<sub>2</sub>O<sub>3</sub> is a p-type semiconductor, electron transfer can occur from V<sub>2</sub>O<sub>5</sub> to Bi<sub>2</sub>O<sub>3</sub> at the boundary of these two metal oxides. Then, oxygen vacancy can be formed and it will promote the dissociative adsorption of O<sub>2</sub>. The oxygen ion O<sup>2-</sup>, therefore, can reoxidize the partially reduced active phase V<sub>2</sub>O<sub>5-y</sub>.



## CONCLUSIONS

The selective oxidation of hydrogen sulfide in the presence of excess water and ammonia was investigated in this study. V<sub>2</sub>O<sub>5</sub> catalyst was reduced during the reaction. The reaction proceeds via a redox mechanism: reduction by H<sub>2</sub>S and oxidation by gas phase oxygen. A synergistic effect on catalytic activity was observed for the mechanical mixture of V<sub>2</sub>O<sub>5</sub> and Bi<sub>2</sub>O<sub>3</sub>, and it originated from the reoxidation capacity of Bi<sub>2</sub>O<sub>3</sub> by supplying oxygen to the reduced vanadium oxide phase.

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