Korean J. Chem. Eng., **19**(4), 611-616 (2002)

Phase Cooperation of V_2O_5 and Bi_2O_3 in the Selective Oxidation of H_2S Containing Ammonia and Water

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(*Received 16 April 2002 • accepted 21 May 2002*)

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_2O_5, and phase cooperation between V_2O_5 and Bi_2O_3 in this reaction. The conversion of H_2S continued to decrease since V_2O_5 was gradually reduced by treatment with H_2S. The activity of V_2O_5 was recovered by contact with oxygen. A strong synergistic phenomenon in catalytic activity was observed for the mechanically mixed catalysts of V_2O_5 and Bi_2O_3. 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_2O_3.

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_2S 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_2S to elemental sulfur after the hydrogenation of sulfur-containing gas to H_2S. 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_2S 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.

$$H_2S+1/2O_2 \rightarrow 1/nS_n+H_2O \qquad (1)$$

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

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

$$2H_2S+SO_2 \leftrightarrow 3/nS_n+2H_2O \qquad (4)$$

It is known that TiO_2-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_2O_5 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_2 and V_2O_5 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_2S 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_2O_3 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_2S containing NH_3 and excess water [Chun et al., 1997]. The mixed gas of H_2S, NH_3, and water vapor is released from steel smelting process, where the H_2S from coke ovens is generally scrubbed and concentrated by using aqueous ammonia solution. The concentrated H_2S is separated from the solution and transferred to the Claus plant. However, the separation of H_2S from the solution is not perfect and the remaining aqueous ammonia stream contains about 2% H_2S which in turn causes the SO_x emission problem during incineration. We reported a new vapor phase catalytic process for the selective conversion of H_2S in the stream containing both ammonia and water [Park et al., 1998, 2001]. V_2O_5/SiO_2, Fe_2O_3/SiO_2 and Co_3O_4/SiO_2 catalysts showed good cata-

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‡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_2S to ammonium thiosulfate (ATS) and elemental sulfur. Recently, we also reported that Sb_2O_4 increased the reoxidation of the partially reduced V_2O_{5-x} by supplying spillover oxygen [Park et al., 2002].

In this study, mechanical mixtures of V_2O_5 and Bi_2O_3 are used to further investigate the role of each metal oxide in the selective oxidation of H_2S 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.

EXPERIMETAL

1. Catalyst Preparation

The mechanical mixture catalysts were prepared according to the literature [Weng and Delmon, 1992]. The pure V_2O_5 (Junsei, $SA=5.4\ m^2/g$) and Bi_2O_3 (Junsei, $SA=1.37\ m^2/g$) 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_2O_5+Bi_2O_3 (x : y) where x and y represents the weight ratio of V_2O_5 and Bi_2O_3, respectively.

2. Reaction Test

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 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_2S and the selectivity to a special product are defined as follows:

$$\text{Conversion of } H_2S(X) = \frac{[H_2S]_{inlet} - [H_2S]_{outlet}}{[H_2S]_{inlet}} \times 100(\%)$$

Selectivity (S) to a special product (SO_2, S, ATS)

$$= \frac{[\text{Product}]_{outlet}}{[H_2S]_{inlet} - [H_2S]_{outlet}} \times 100(\%)$$

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_2S.

3. Characterization of Catalysts

The surface area of the individual oxides and their mechanical mixtures was measured by N_2 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. $V2p_{3/2}$ and $Bi3d_{3/2}$ 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_2/N_2 gas mixture (10 vol% H_2). 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_2 was detected by mass spectroscope (VG Quadrupole). After TPR experiment, the same sample was instantly tested in TPO under 2.5 vol% O_2 with helium gas balance.

RESULTS AND DISCUSSION

1. Reaction over V_2O_5

In order to understand phase cooperation of V_2O_5 and Bi_2O_3, pure V_2O_5 was first investigated for its behavior in the selective oxidation of H_2S. Fig. 1 shows the time variant conversion and selectivity to S and SO_2 with different treatment of feed at 220 °C. When a feed containing only H_2S (5 vol% with balance helium) was passed over fresh catalyst (region A), the complete conversion that was

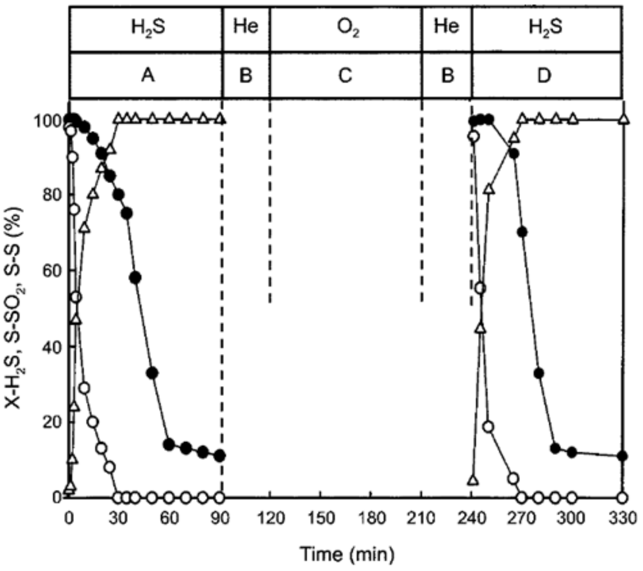

Fig. 1. Time variant profiles of X-H_2S (●), S-SO_2 (○) and S-S (△) in square pulses: A/B/C/D=(5%H_2S)/(He)/(O_2)/(5%H_2S), T=220 °C, GHSV=3,000 h^{-1}.

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.

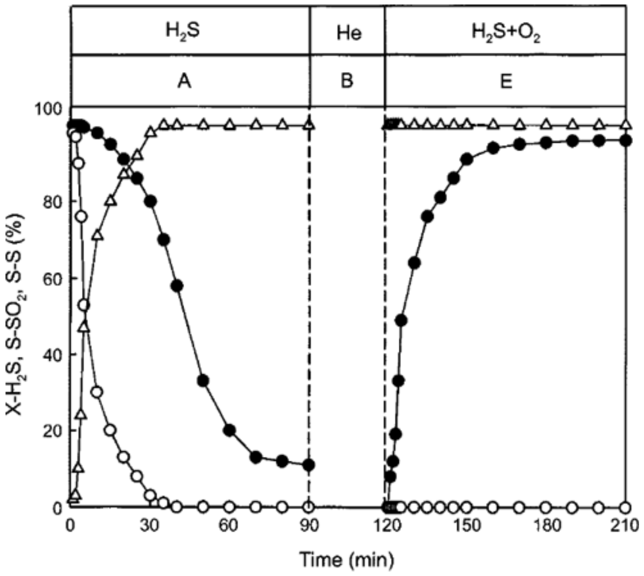

Fig. 2. Time variant profiles of X-H_2S (●), S-SO_2 (○) and S-S (△) in square pulses: A/B/E=(5%H_2S)/(He)/(5%H_2S+2.5%O_2), T=220 °C, GHSV=3,000 h^{-1}.

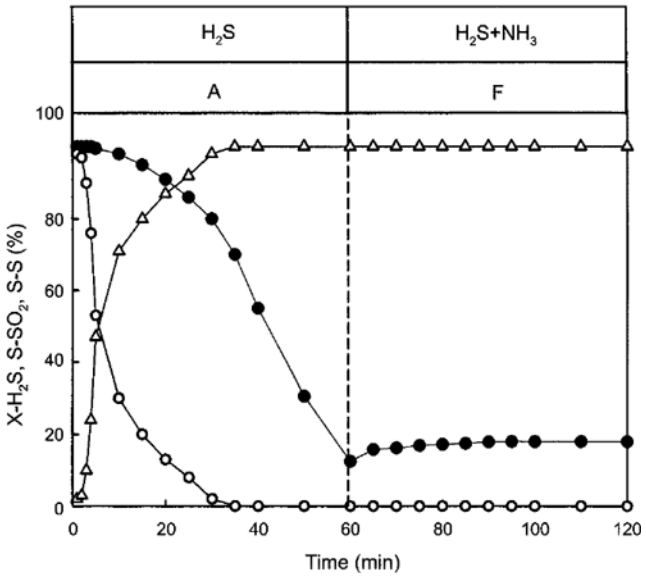

Fig. 3. Time variant profiles of X-H_2S (●), S-SO_2 (○) and S-S (△) in square pulses: A/B/E=(5%H_2S)/(He)/(5%H_2S+5%NH_3), T=220 °C, GHSV=3,000 h^{-1}.

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-

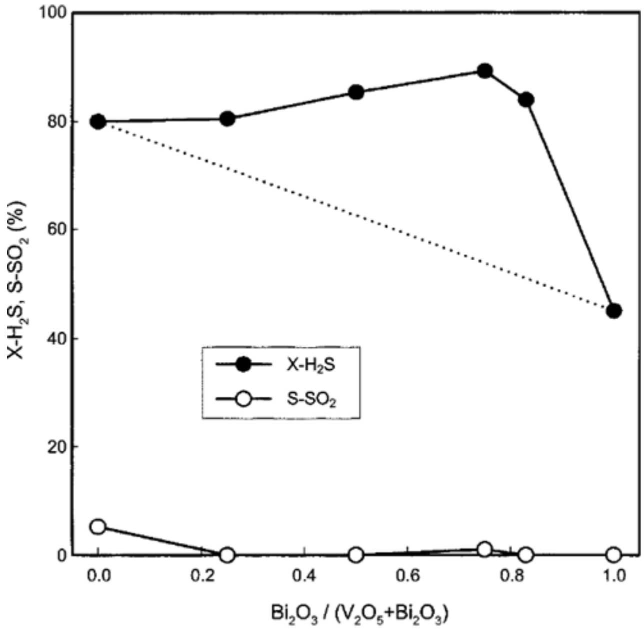

Fig. 4. Conversion of H_2S and selectivity to SO_2 as a function of Bi_2O_3 weight fraction for V_2O_5+Bi_2O_3 mixtures at 260 °C ($H_2S/O_2/NH_3/H_2O$=5/2.5/5/60, GHSV=12,000 h^{-1}).

Table 1. Conversion of H_2S and selectivity to SO_2 for V_2O_5 and V_2O_5 $+Bi_2O_3$ (1 : 3) at different temperatures

Temp. (°C)	V_2O_5		$V_2O_5+Bi_2O_3$(1:3)	
	X-H_2S (%)	S-SO_2(%)	X-H_2S (%)	S-SO_2(%)
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: $H_2S/O_2/NH_3/H_2O/He$=5/2.5/5/60/27.5, GHSV= 12,000 h^{-1}.

ance helium. The weight ratios of V_2O_5/Bi_2O_3 were 1/0, 3/1, 1/1, 1/3, 1/5, and 0/1. Fig. 4 shows the H_2S conversion and SO_2 selectivity as a function of mass ratio [$V_2O_5/(V_2O_5+Bi_2O_3)$] at 260 °C with GHSV of 12,000 h^{-1}. Pure Bi_2O_3 shows low conversion of H_2S (45%). Considering the H_2S conversion of 38% at 260 °C for the blank test, pure Bi_2O_3 did not practically play any significant catalytic role in this reaction. The addition of V_2O_5 into Bi_2O_3 greatly increased H_2S conversion. All the mechanical mixture catalysts ($V_2O_5+Bi_2O_3$) showed higher H_2S conversion than the arithmetic average conversion (expressed as a dotted line in Fig. 4) of pure V_2O_5 and pure Bi_2O_3; a strong synergy existed between V_2O_5 and Bi_2O_3. But it was not easy to find any synergistic effect for the SO_2 selectivity because the SO_2 selectivities were very low for all the mixture catalysts. V_2O_5 $+Bi_2O_3$ (1 : 3) showed the highest H_2S 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_2S conversion and SO_2 selectivity for $V_2O_5+Bi_2O_3$ (1 : 3) catalyst and pure V_2O_5 is shown in Table 1. The H_2S conversion for V_2O_5 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_2S conversion than pure V_2O_5. The SO_2 selectivities for the mixture catalyst were also lower than pure V_2O_5. 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_2O_5 $+Bi_2O_3$ catalyst, the first possibility was verified by XRD method. The X-ray diffraction patterns of $V_2O_5+Bi_2O_3$ (1 : 3) catalyst are presented in Fig. 5.

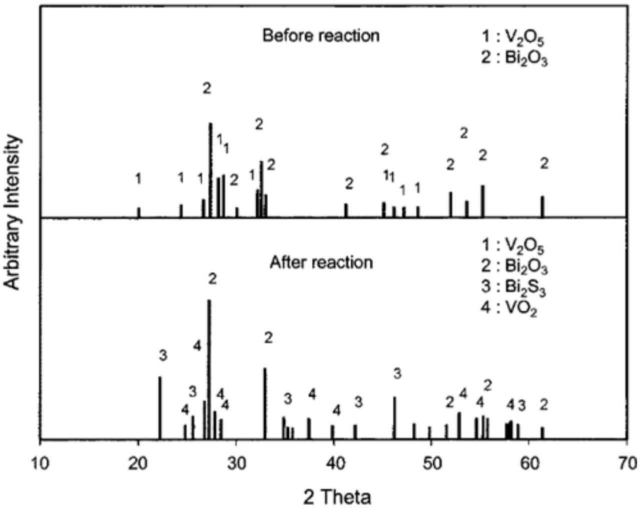

Fig. 5. XRD patterns of $V_2O_5+Bi_2O_3$ (1 : 3) catalysts before and after reaction.

Fresh catalyst shows only characteristic peaks of V_2O_5 and Bi_2O_3. The spent catalyst, used for 8 h for the reaction, shows the existence of reduced phase of V_2O_5 like VO_2. Part of Bi_2O_3 was also sulfided to Bi_2S_3. However, no new phase (principally $V_xBi_{1-x}O_y$) detectable by XRD was generated during the catalytic tests. Bismuth vanadates ($BiVO_4$, $Bi_4V_6O_{21}$) 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 $V_2O_5+Bi_2O_3$ (1 : 3) catalyst were measured and they were 2.4 and 1.9 m^2/g, respectively. The surface area of the fresh catalyst was nearly the same as the arithmetic average value of pure V_2O_5 (5.4 m^2/g) and Bi_2O_3 (1.37 m^2/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_2S 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_2O_3 could be a strong donor of mobile oxygen species. An attempt to verify the existence of the synergis-

Table 2. The H_2S conversion and product selectivities for three different operations with $V_2O_5+Bi_2O_3$ catalysts at 260 °C

Catalyst	Case	X-H_2S (%)	S-SO_2 (%)	S-S (%)	S-ATS (%)
$V_2O_5+Bi_2O_3$ (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
$V_2O_5+Bi_2O_3$ (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: $H_2S/O_2/NH_3/H_2O/He$=5/2.5/5/60/27.5, GHSV= 12,000 h^{-1}.

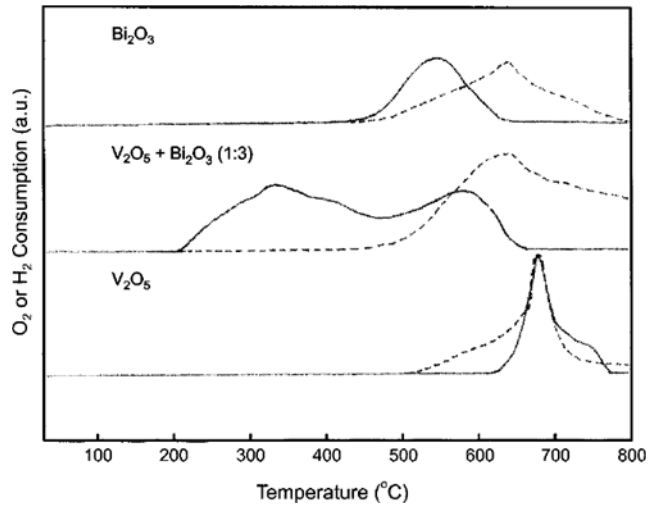

Fig. 6. TPR/TPO profiles of Bi_2O_3, V_2O_5, and V_2O_5+Bi_2O_3 (1 : 3) catalysts (TPR: dashed line) and (TPO: solid line).

tic effect is to test the H_2S oxidation in two-bed operation modes. The H_2S conversion at three different operations for V_2O_5+Bi_2O_3 catalysts of (3 : 1) and (1 : 3) is summarized in Table 2. In case A, the reactant mixture is first contacted with V_2O_5 then Bi_2O_3 before it comes out of the reactor. Case B is the reverse order of case A. In case C, uniform mixtures of V_2O_5 and Bi_2O_3 are placed together in the reactor. For both catalysts, the operation in case C, where uniform mixing is obtained, showed higher H_2S conversion than case A and case B. Case B showed higher H_2S conversion than case A. One conclusion to be drawn from this result is that Bi_2O_3 is a donor phase and that V_2O_5 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_2O_5+Bi_2O_3 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_2O_5, Bi_2O_3 and V_2O_5+Bi_2O_3 (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_2O_5 (500 °C). In the subsequent TPO experiment, the mixture catalyst showed better reoxidation property than pure V_2O_5 and pure Bi_2O_3. The first maximum peak of O_2 consumption for the V_2O_5+Bi_2O_3 (1 : 3) was 320 °C, much lower than V_2O_5 (T_{max} =680 °C) and Bi_2O_3 (T_{max}=550 °C). Therefore, it can be considered that the increase of H_2S conversion in V_2O_5+Bi_2O_3 mixture comes from the reoxidizing ability of Bi_2O_3.

The oxidation state of the vanadium in pure V_2O_5 and V_2O_5+Bi_2O_3 (1 : 3) is studied by XPS. Fig. 7 shows XPS spectra of V $2p_{3/2}$ and V $2p_{1/2}$ for the V_2O_5 and the mixture catalyst before and after 8 h reaction at 260 °C with the standard reactant mixture and GHSV of 12,000 h^{-1}. The standard XPS peaks of V $2p_{3/2}$ for V^{5+} and V^{4+} 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_2O_5 having only V^{5+} state is reduced to V^{4+} after the reaction. The full-width half-maximum (FWHM) value for the fresh V_2O_5 was 1.65 eV, and that for used V_2O_5 was 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_2O_3 for the mixture catalyst.

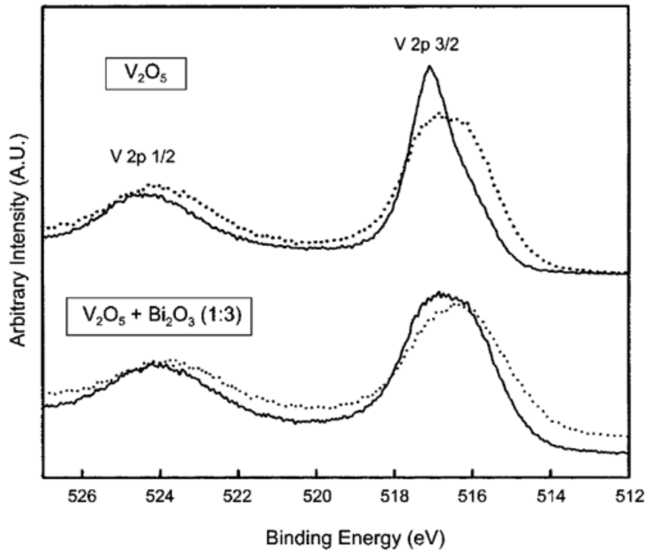

Fig. 7. XPS spectra of vanadium for V_2O_5 and V_2O_5+Bi_2O_3 (1 : 3) before (solid line) and after (dashed line) 8 h reaction at 260 °C.

The V_2O_5+Bi_2O_3 mixed catalysts of other composition also showed the same results as V_2O_5+Bi_2O_3 (1 : 3). Therefore, the possible explanation for the synergistic effect of V_2O_5+Bi_2O_3 mixture catalyst will be the following sequence of the redox process. Since Bi_2O_3 is a p-type semiconductor, electron transfer can occur from V_2O_5 to Bi_2O_3 at the boundary of these two metal oxides. Then, oxygen vacancy can be formed and it will promote the dissociative adsorption of O_2. The oxygen ion O^{2-}, therefore, can reoxidize the partially reduced active phase V_2O_{5-y}.

$$Bi^{3+}+x\,e^- \rightarrow Bi^{(3-x)+} \quad (5)$$

$$Bi^{(3-x)+}+x/4\;O_2 \rightarrow Bi^{3+}+x/2\;O^{2-} \quad (6)$$

$$V_2O_{5-y}+x/2\;O^{2-} \rightarrow V_2O_{5-y+x}+x\,e^- \quad (7)$$

CONCLUSIONS

The selective oxidation of hydrogen sulfide in the presence of excess water and ammonia was investigated in this study. V_2O_5 catalyst was reduced during the reaction. The reaction proceeds via a redox mechanism: reduction by H_2S and oxidation by gas phase oxygen. A synergistic effect on catalytic activity was observed for the mechanical mixture of V_2O_5 and Bi_2O_3, and it originated from the reoxidation capacity of Bi_2O_3 by supplying oxygen to the reduced vanadium oxide phase.

ACKNOWLEDGEMENTS

This work was supported by Korea Science and Engineering

Foundation (R 01200000326).

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