

Selective Oxidation of H_2S to Ammonium Thiosulfate and Elemental Sulfur Using Mixtures of V-Bi-O and Sb_2O_4

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Abstract—The selective oxidation of hydrogen sulfide in the presence of excess water and ammonia was investigated by using vanadium-bismuth based mixed oxide catalysts. Synergistic effect on catalytic activity was observed for the mechanical mixtures of V-Bi-O and Sb_2O_4 . Temperature programmed oxidation (TPO), X-ray photoelectron spectroscopy (XPS), and two separated bed reactivity test results supported the role of Sb_2O_4 for reoxidizing the reduced V-Bi-O during the reaction.

Key words: H_2S , Selective Oxidation, Ammonium Thiosulfate, V-Bi-O, Sb_2O_4

INTRODUCTION

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; Goar, 1975]. This process consists of two steps: thermal oxidation and catalytic reaction. In the thermal oxidation, one-third of H_2S is first burned with air to produce sulfur dioxide in a waste heat furnace, while unconverted H_2S reacts with SO_2 to elemental sulfur through the subsequent catalytic reaction over Al_2O_3 catalysts. However, due to thermodynamic limitations, 3-5% of H_2S is typically not converted to sulfur. Among various processes to improve the overall sulfur recovery efficiency, the Sulfreene [Cameron, 1974], Clauspol [Dezael and Kerdaon, 1994] and SCOT (Shell Claus Offgas Treating) processes are widely used ones. Recently, dry catalytic processes have been developed for the selective catalytic oxidation of H_2S to elemental sulfur. Examples of commercially developed ones for this purpose are the MODOP process [Kettner and Liermann, 1983, 1988] and Super Claus process [van den Brink and Geus, 1994; van Nisselrooy and Lagas, 1993]. In the MODOP process, H_2S is oxidized into elemental sulfur with a stoichiometric amount of oxygen over TiO_2 catalysts. One drawback of the MODOP process is that water should be removed from the tail gas before the reaction, due to the deactivation of catalysts in the presence of water. In the Super Claus process, tail gas can be treated without a dehydration step, since the Fe_2O_3/SiO_2 catalyst is not deactivated even in the presence of 30 vol% of water vapor. However, the Super Claus process cannot treat high concentrations of H_2S above 2 vol% because it is necessary to supply excess oxygen (usually 10 times the stoichiometric amount) to overcome the catalytic deactivation caused by water.

In previous work [Chun et al., 1998; 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 Sb_2O_4 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.

Hydrogen sulfide in the coke oven gas released from the steel smelting process is scrubbed and concentrated by using aqueous ammonia solution. Since the separation of H_2S from the aqueous ammonia is not perfect, the remaining aqueous ammonia stream contains about 2% H_2S , which in turn causes the SO_x emission problem during the incineration. 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].

One approach to resolving the problem is the selective catalytic oxidation of H_2S to ammonium thiosulfate (ATS) and elemental sulfur as reported in previous work [Park et al., 1998, 1999]. We reported a new vapor phase catalytic process for the selective conversion of H_2S in a stream containing both ammonia and water. V_2O_5/SiO_2 , Fe_2O_3/SiO_2 and Co_3O_4/SiO_2 catalysts showed good catalytic activities in the selective oxidation of H_2S to ATS and sulfur. We also reported the phase cooperation of V_2O_5 and Bi_2O_3 in the reaction [Cho et al., 2002]. The conventional process for the production of ATS is based on the liquid phase reactions. The ATS Claus Tail Gas Clean-up process [Zey et al., 1980] is divided into two sections: absorption of SO_2 from incinerator in aqueous ammonia and conversion of the intermediate product to ATS by sparging H_2S into the converter. In another ATS process [Benito, 1986], sulfuric acid is reacted with aqueous ammonia solution below 45 °C, then the

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[†]This paper is dedicated to Professor Hyun-Ku Rhee on the occasion of his retirement from Seoul National University.

mixture is contacted with H₂S to form ATS. Therefore, our process has the advantage of direct vapor phase operation compared to the above two processes.

In this study, we further tried to improve the performance of vanadium bismuth mixed oxide catalyst for the selective oxidation of H₂S in the stream containing both ammonia and water. Mechanical mixtures of V-Bi-O and Sb₂O₄ were prepared and used to understand the phase cooperation of metal oxides in the oxidation of H₂S. Solid state modifications of the mixtures during the catalytic reaction tests were studied by XRD and XPS. Temperature programmed techniques (TPR and TPO) and two separated bed operations were also used to elucidate the redox properties of this catalyst system.

EXPERIMENTAL

1. Catalyst Preparation

V-Bi-O catalyst was prepared by a coprecipitation method using ammonium metavanadate (NH₄VO₃, Junsei) and bismuth nitrate pentahydrate [Bi(NO₃)₃·5H₂O] as precursors. 5 wt% oxalic acid was used to dissolve the precursors. After evaporation at 80 °C, samples were dried at 110 °C overnight and calcined at 500 °C for 5 h. α-Sb₂O₄ (1.37 cm²/g) was produced by calcination of Sb₂O₃ (Merck, analytical purity) in air at 500 °C for 20 h. The mechanical mixture catalysts were prepared according to the literature [Weng and Delmon, 1992]. The V-Bi-O and α-Sb₂O₄ were dispersed in n-pentane (Merck, analytical purity). The suspension was stirred in an ultrasonic vibrator (Brasonic 32) during 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-Bi-O+Sb₂O₄ (x : y) where x and y represent the weight ratio of V-Bi-O and Sb₂O₄, 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 held 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 chromatography, all the lines and fittings were heated above 120 °C to prevent condensation of water vapor. The flow rates of gases were 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 the effluent gas (H₂S, SO₂ and NH₃) 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 solid products (ATS and sulfur) were dissolved in distilled water to separate them, and were weighed individually after drying in vacuum oven at 110 °C. The conversion of H₂S and the selectivity to a special product are defined as follows:

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

Selectivity (S) to a special product (SO₂, 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 were multiplied by a factor of two because one mole of ATS can be obtained from two moles of H₂S.

3. Characterization of Catalysts

The surface areas of the individual oxides and their mechanical mixtures were measured by N₂ adsorption method using the BET technique (Micromeritics ASAP 2000). The phase analysis was performed by X-ray diffraction crystallography with Cu-K α 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-K α 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). In order to investigate the phase cooperation mechanism, a temperature programmed reduction (TPR) experiment was also carried out. Before reduction, samples were pretreated by heating under air flow from 25 °C to 450 °C at a heating rate of 10 °C/min. Reduction was achieved under an H₂/N₂ gas mixture (10 vol% H₂). 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 H₂ was detected by mass spectroscopy (VG Quadrupole). After TPR experiment, the same sample was instantly tested in temperature programmed oxidation (TPO) under 2.5 vol% O₂ with helium gas balance.

RESULTS AND DISCUSSION

1. Catalytic Activity of Mixture Catalysts (V-Bi-O and Sb₂O₄)

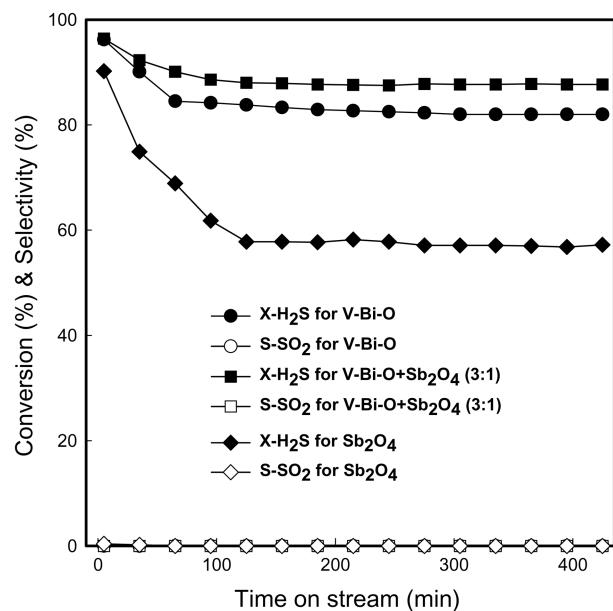


Fig. 1. Time variant conversion of H₂S and selectivity to SO₂ for V-Bi-O, V-Bi-O+Sb₂O₄ (3 : 1) and Sb₂O₄ at 260 °C (H₂S/O₂/NH₃/H₂O/He=5/2.5/5/60/27.5, GHSV=12,000 h⁻¹).

Mechanical mixture catalysts of V-Bi-O and Sb_2O_4 were used to study the phase cooperation phenomena with a reactant composition of 5 vol% H_2S , 2.5 vol% O_2 , 5 vol% NH_3 , 60 vol% H_2O and the balance helium. Fig. 1 shows time variant conversion of H_2S and selectivity to SO_2 for V-Bi-O, V-Bi-O+ Sb_2O_4 (3 : 1) and Sb_2O_4 at 260 °C with GHSV of 12,000 h^{-1} . The mechanical mixture catalysts showed the highest conversion of H_2S . All the catalysts showed very low formation of SO_2 . They maintained stable activities after about 5 hours of reaction time. However, a considerable decrease of H_2S conversion was observed up to about 1-1.5 h. In our previous study [Shin et al., 2000], when a feed containing 1 vol% of H_2S only (the balance helium, without oxygen) was passed over fresh pure V_2O_5 , complete conversion of H_2S was achieved initially and the fresh V_2O_5 produced only complete oxidation product, SO_2 . The result indicated that an oxidized form of vanadium having very active surface oxygen produced SO_2 , and only less labile lattice oxygen in partially reduced vanadium oxides could produce elemental sulfur via redox mechanism. The less severe decrease of initial conversion in V-Bi-O+ Sb_2O_4 (3 : 1) seems to be related to its good redox property, which will be discussed later.

Table 1 summarizes the H_2S conversion and SO_2 selectivity for five different catalysts with weight ratios of V-Bi-O/ Sb_2O_4 of 1/0, 3/1, 1/1, 1/3, and 0/1 at 260 °C. The addition of Sb_2O_4 into V-Bi-O increased H_2S conversion. All the mechanical mixture catalysts (V-Bi-O+ Sb_2O_4) showed higher H_2S conversion than the arithmetic average conversion (calculated from the weight ratio and H_2S conversion of V-Bi-O and pure Sb_2O_4); a strong synergy existed between V-Bi-O and Sb_2O_4 . V-Bi-O+ Sb_2O_4 (3 : 1) showed the highest value of H_2S conversion (88.8%). The increase of Sb_2O_4 in the mixture catalyst decreased sulfur selectivity, but increased ATS selectivity.

Table 2 shows H_2S conversion and SO_2 selectivity for V-Bi-O+

Table 1. Conversion of H_2S and product selectivity at 260 °C after 8 h of reaction

Catalyst	X- H_2S (%)	S- SO_2 (%)	S-S (%)	S-ATS (%)
V-Bi-O (Bi/V=1)	82.0	0.0	67.8	32.2
V-Bi-O+ Sb_2O_4 (3 : 1)	88.8	0.0	94.1	5.9
V-Bi-O+ Sb_2O_4 (1 : 1)	85.3	0.0	86.1	13.9
V-Bi-O+ Sb_2O_4 (1 : 3)	84.3	0.0	82.7	17.3
Sb_2O_4	57.1	0.0	96.5	3.5

Reaction condition: $\text{H}_2\text{S}/\text{O}_2/\text{NH}_3/\text{H}_2\text{O}/\text{He}=5/2.5/5/60/27.5$; GHSV = 12,000 h^{-1} .

Table 2. Conversion of H_2S and selectivity to SO_2 with various compositions of reactant mixture at 260 °C

Run	Reactant composition				V-Bi-O+ Sb_2O_4 (3 : 1)		Without catalyst	
	H_2S	O_2	NH_3	H_2O	X- H_2S	S- SO_2	X- H_2S	S- SO_2
A	5	2.5	-	-	90.1	1.9	8.8	21.9
B	5	2.5	5	-	92.5	2.1	13.1	30.2
C	5	2.5	5	60	88.8	0	30.2	0.3
D	5	-	5	-	20.4	-	8.0	-

Sb_2O_4 (3 : 1) catalysts with various compositions of reactant mixture at 260 °C. The corresponding reactivity data in blank experiments are also listed in Table 2. In cases A, B and C, the mechanical mixture catalysts showed high H_2S conversion without any appreciable amount of SO_2 emission. It is known that the following elementary reactions occur in the Claus process, where there is no existence of ammonia [Terorde et al., 1993].



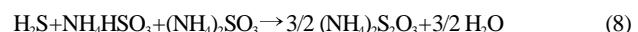
Ammonia is also known to react easily with H_2S to form ammonium sulfide $[(\text{NH}_4)_2\text{S}]$ which can be oxidized to produce elemental sulfur [Chang and McGaugh, 1988].



The higher value of H_2S conversion in run B, compared to run A, might be due to the reaction of H_2S and NH_3 [Eq. (5)]. The conversion of H_2S in run D was 20.4% and it supported the previous observation. In run C, where H_2S was present with excess water and ammonia, the conversion of H_2S was lower than that of run B probably because of inhibition by H_2O [Eq. (4)]. However, SO_2 was not produced at all. It is well known [Hartley and Matterson, 1975] that NH_3 and SO_2 reacts to form products such as NH_3SO_2 and $(\text{NH}_3)_2\text{SO}_2$ under anhydrous conditions. $(\text{NH}_4)_2\text{S}_2\text{O}_5$ could also be formed even at very low (50 ppm) water concentrations [Bai et al., 1992]. In the presence of enough water and ammonia, these products can be easily converted to NH_4HSO_3 and $(\text{NH}_4)_2\text{SO}_3$ [Zey et al., 1980; Bai et al., 1992]. Hartley and Matterson [1975] also reported the formation of ammonium bisulfite or ammonium sulfite [Eq. (7)] from the reaction of SO_2 and NH_3 in the presence of water.



Zey et al. [1980] reported the following reaction for the production of ATS in the Claus tail gas process.



Therefore, it is believed that SO_2 may be consumed to form ammonium thiosulfate. Ammonium thiosulfate (ATS) is commercially produced by the reaction of ammonium sulfite with excess sulfur.



ATS can also be produced by the reaction of ammonium sulfide, ammonium sulfite, and SO_2 :



A typical temperature dependence of the H_2S conversion and SO_2 selectivity for pure V_2O_5 , V-Bi-O+ Sb_2O_4 (3 : 1) and V-Bi-O is shown in Table 3. First, one observes an improvement of catalytic performance for V-Bi-O compared to the pure V_2O_5 . The incorporation of bismuth to vanadium oxide is known to increase the catalytic activity by several authors [Hass and Ward, 1985; Li et al., 1996]. V-Bi-O+ Sb_2O_4 catalyst showed higher H_2S conversion than V-Bi-

Table 3. Conversion of H₂S and selectivity to SO₂ for different catalysts

Temp. (°C)	V ₂ O ₅		V-Bi-O (Bi/V=1)		V-Bi-O+Sb ₂ O ₄ (3 : 1)	
	X-H ₂ S	S-SO ₂	X-H ₂ S	S-SO ₂	X-H ₂ S	S-SO ₂
240	79.3	0	81.5	0	86.9	0
260	81.0	0	82.0	0	88.8	0
280	80.0	2.2	81.1	0	87.5	0
300	75.1	4.2	77.2	2.4	82.6	2.0
320	71.2	5.3	73.3	5.3	75.9	3.2

Reaction condition: H₂S/O₂/NH₃/H₂O/He=5/2.5/5/60/27.5; GHSV = 12,000 h⁻¹.

O over the whole temperature ranges of 240–320 °C. The SO₂ selectivities for the mixture catalyst were also lower than V-Bi-O. Thus, the synergy for the mixture catalyst was confirmed over wide temperature ranges.

2. Phase Cooperation

The synergistic effect observed in mixed oxide catalysts is generally known [Weng and Delmon, 1992] to be from three main reasons: (1) formation of new active phase by reaction between two phases, (2) increase of surface area, and (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-Bi-O+Sb₂O₄ catalyst, the first possibility was verified by XRD method. The X-ray diffraction patterns of V-Bi-O+Sb₂O₄ (3 : 1) catalyst are presented in Fig. 2.

Fresh catalyst shows only characteristic peaks of Bi₄V₆O₂₁, BiVO₄ and Sb₂O₄. For the spent catalyst used for 8 h for the reaction, no new phase (principally V_xSb_{1-x}O_y) detectable by XRD was generated during the catalytic tests. Vanadium antimonate (VSbO₄) is reported to be one of the most active phases in coprecipitated V-Sb-O mixed oxide catalyst used in selective oxidation of H₂S to elemental sulfur reaction [Li and Shyu, 1997]. Therefore, the increase of H₂S conversion for the mixture catalyst was not due to the for-

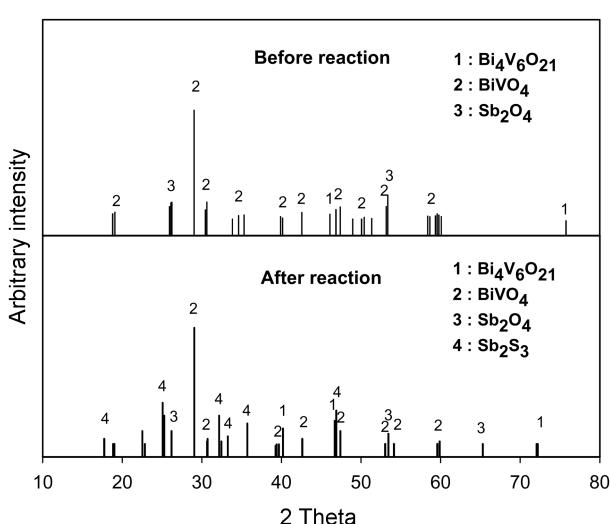
Table 4. Conversion of H₂S and product selectivities for three different operations with V-Bi-O and Sb₂O₄ catalysts at 260 °C

Case	X-H ₂ S (%)	S-SO ₂ (%)	S-S (%)	S-ATS (%)
A : V-Bi-O → Sb ₂ O ₄	82.7	0.0	73.8	26.2
B : Sb ₂ O ₄ → V-Bi-O	83.5	0.0	78.9	21.1
C : V-Bi-O+ Sb ₂ O ₄	88.8	0.0	94.1	5.9

mation of any new active site. After reaction, a part of Sb₂O₄ was sulfided to Sb₂S₃. Secondly, BET surface areas of the fresh and used V-Bi-O+Sb₂O₄ (3 : 1) catalyst were 1.95 and 0.43 m²/g, respectively. The surface area of the fresh catalyst was nearly the same as the arithmetic average value of V-Bi-O (2.61 m²/g) and Sb₂O₄ (1.37 m²/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 H₂S conversion in this study. These two phenomena are generally accepted to be not evident to describe synergistic effect 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 (oxygen donor) and migrates onto the other (oxygen acceptor), where it creates and/or regenerates the active centers. They also reported Sb₂O₄ could be a strong donor of mobile oxygen species. An attempt to verify the existence of the synergistic effect is to test the H₂S oxidation in two-bed operation modes. The H₂S conversions at three different operations for V-Bi-O+Sb₂O₄ (3 : 1) catalysts are summarized in Table 4. In case A, the reactant mixture is first contacted with V-Bi-O then Sb₂O₄ before it comes out of the reactor. The case B is the reverse order of case A. In case C, the uniform mixtures of V-Bi-O and Sb₂O₄ are placed together in the reactor. The operation in case C showed higher H₂S conversion than case A and case B. The case B showed higher H₂S conversion than case A. One conclusion can be drawn from this result: Sb₂O₄ is a donor phase and V-Bi-O is an acceptor phase for a mobile species, either reaction intermediate or spillover oxygen.

In order to identify the real nature of this phase cooperation in V-Bi-O+Sb₂O₄ (3 : 1) catalyst, TPR and TPO techniques were used in this study. Comparative temperature programmed reduction (TPR) and the following temperature programmed oxidation (TPO) were carried out for V-Bi-O, Sb₂O₄ and V-Bi-O+Sb₂O₄ (3 : 1). The reducibility of catalysts was first measured by using TPR method with hydrogen as a reductant. In the subsequent TPO experiment, oxygen was passed over the reduced catalyst. TPO results are shown in Fig. 3. The mixture catalysts showed better reoxidation property than V-Bi-O and pure Sb₂O₄. The maximum peaks of O₂ consumption for the mixture catalysts moved to lower temperature with the increase of V-Bi-O amount. The amount of hydrogen and oxygen consumption is summarized in Table 5. All the mixture catalysts showed higher amount of oxygen consumption than V-Bi-O and Sb₂O₄. V-Bi-O+Sb₂O₄ (3 : 1), the most active catalyst in Table 1,

**Fig. 2. XRD patterns of V-Bi-O+Sb₂O₄ (3 : 1) catalyst before and after reaction.**

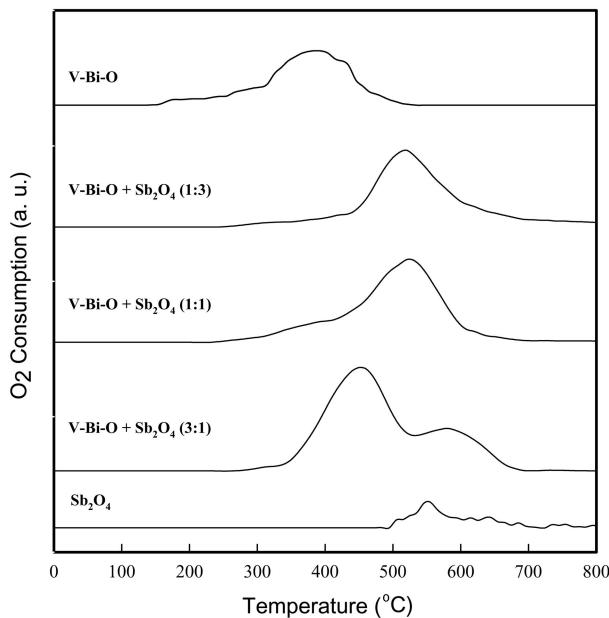


Fig. 3. TPO profiles of V-Bi-O, Sb_2O_4 , and V-Bi-O+ Sb_2O_4 catalysts.

Table 5. Desorbed amount of H_2 and O_2 in TPR and TPO experiments

Catalysts	H_2 ($\mu\text{mol/g-cat}$)	O_2 ($\mu\text{mol/g-cat}$)
V-Bi-O	52.3	51.6
V-Bi-O+ Sb_2O_4 (1 : 3)	29.5	72.1
V-Bi-O+ Sb_2O_4 (1 : 1)	31.9	78.2
V-Bi-O+ Sb_2O_4 (3 : 1)	36.8	99.9
Sb_2O_4	37.9	16.1

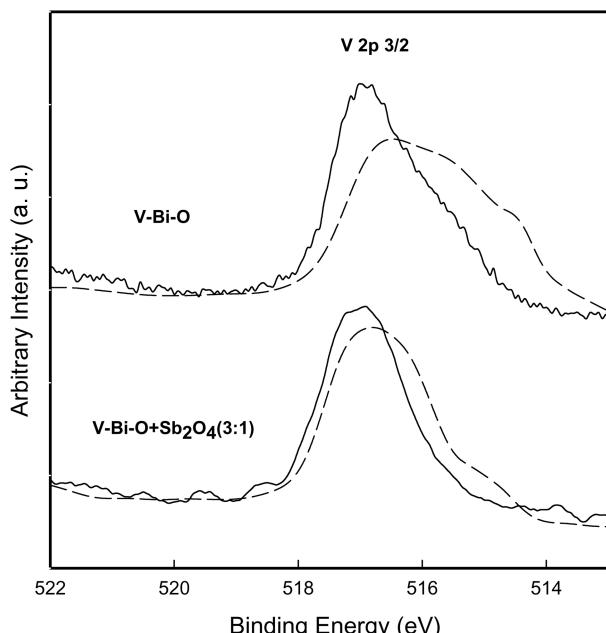


Fig. 4. XPS analyses of V-Bi-O and V-Bi-O+ Sb_2O_4 (3 : 1) before (solid line) and after (dashed line) reaction (H_2S 5 vol%, O_2 2.5 vol%, NH_3 5 vol%, H_2O 60 vol%, $\text{GHSV}=12,000 \text{ h}^{-1}$, $T=260^\circ\text{C}$).

showed the highest amount of oxygen consumption. However, the amount of hydrogen consumption was not so different from others. Therefore, the increase of H_2S conversion in V-Bi-O+ Sb_2O_4 mixture can be considered to come from the reoxidizing ability of Sb_2O_4 . An efficient method to maximize catalytic performance of active reducible oxide is to stabilize oxide surface at slightly reduced suboxide oxidation state allowing the reduction-oxidation cycle to proceed rapidly [Weng and Delmon, 1992].

The oxidation state of the vanadium in pure V-Bi-O and V-Bi-O+ Sb_2O_4 (3 : 1) was studied by XPS. Fig. 4 shows XPS spectra of V 2p_{3/2} for the V-Bi-O 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 peak of V 2p_{3/2} for V^{5+} and V^{4+} is 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-Bi-O having only V^{5+} state is reduced to V^{4+} after the reaction. The full-width half-maximum (FWHM) value for the fresh V-Bi-O was 1.72 eV, and that for used V-Bi-O was 2.37 eV. It corresponds to 37.8% increase in FWHM after reaction. However, the mixture catalyst showed 1.43 eV for fresh catalyst and 1.66 eV for the used catalyst, 16.1% increase in FWHM. Therefore, the mixture catalyst showed less reduction of vanadium oxide phase during the reaction. This can support the oxidizing ability of Sb_2O_4 for the mixture catalyst.

The possible explanation for the synergistic effect of V-Bi-O+ Sb_2O_4 mixture catalyst will be the following redox process sequence. Since Sb_2O_4 is a p-type semiconductor, electron transfer can occur from V-Bi-O to Sb_2O_4 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 of V-Bi-O.

CONCLUSIONS

The selective oxidation of hydrogen sulfide in the presence of excess water and ammonia was investigated in this study. Hydrogen sulfide was successfully converted into harmless ammonium thiosulfate and elemental sulfur without considerable emission of sulfur dioxide. Synergistic effects between V-Bi-O and Sb_2O_4 were observed for the mechanical mixtures of these catalysts. V-Bi-O+ Sb_2O_4 (3 : 1) showed the most improved catalytic performance. TPO and XPS results supported the role of Sb_2O_4 for oxidizing the reduced vanadium oxide phase during the reaction.

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