Selective Oxidation of Hydrogen Sulfide Containing Excess Water and Ammonia over Bi-V-Sb-O Catalysts

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Abstract—We investigated the selective oxidation of hydrogen sulfide to elemental sulfur and ammonium thiosulfate by using $Bi_4V_{2-x}Sb_xO_{11-y}$ catalysts. The catalysts were prepared by the calcination of a homogeneous mixture of Bi_2O_3, V_2O_5, and Sb_2O_3 obtained by ball-milling adequate amounts of the three oxides. The main phases detected by XRD analysis were $Bi_4V_2O_{11}$, $Bi_{1.33}V_2O_6$, $BiSbO_4$ and $BiVO_4$. They showed good H_2S conversion with less than 2% of SO_2 selectivity with a feed composition of $H_2S/O_2/NH_3/H_2O/He=5/2.5/5/60/27.5$ and GHSV=12,000 h^{-1} in the temperature ranges of 220-260 °C. The highest H_2S conversion was obtained for x=0.2 in $Bi_4V_{2-x}Sb_xO_{11-y}$ catalyst. TPR/TPO results showed that this catalyst had the highest amount of oxygen consumption. XPS analysis before and after reaction confirmed the least reduction of vanadium oxide phase for this catalyst during the reaction. It means that the catalyst with x=0.2 had the highest reoxidation capacity among the $Bi_4V_{2-x}Sb_xO_{11-y}$ catalysts.

Key words: Hydrogen Sulfide, Selective Oxidation, Ammonium Thiosulfate, $Bi_4V_{2-x}Sb_xO_{11-y}$

INTRODUCTION

In petroleum refineries and natural gas plants, hydrogen sulfide (H_2S) is typically collected by contact with amine-based solutions, and subsequently fed to a well known Claus plant [Goar, 1975; Lell, 1985]. However, total recovery of sulfur through the Claus process is not possible, due to limitations of thermodynamic equilibrium. As the environmental regulations become more stringent, it is necessary to further treat the residual (tail) gas of the Claus plants. H_2S in the tail gas of Claus plants or from other emission sources has been conventionally treated by various techniques such as adsorption, absorption, and wet oxidation.

Recently, a dry catalytic process has been developed for the selective catalytic oxidation of H_2S to elemental sulfur. Examples of commercially developed catalysts for this purpose are the titanium-based catalysts in the MODOP process [Kettner and Liermann, 1983, 1988] and the iron-based catalysts in the Super Claus process [van den Brink and Geus, 1994; van Nisselrooy and Lagas, 1993]. Vanadium-based mixed oxides [Li et al., 1996, 1997] and NaX-WO₃ mixtures [Pi et al., 2004] were also used as catalysts for the selective oxidation of H_2S to elemental sulfur.

Hydrogen sulfide in the coke oven gas released from the steel smelting process is scrubbed and concentrated using aqueous ammonia solution. Concentrated H_2S that is separated from aqueous ammonia is transferred to the Claus plant to convert it into elemental sulfur, and remaining aqueous ammonia is usually incinerated. In this case, the control of SO_x emission is difficult because the stream contains not only excess water vapor but also a high concentration of ammonia.

One approach to resolving the problem is the selective catalytic oxidation of H_2S to ammonium thiosulfate (ATS) and elemental

sulfur as reported in our previous works [Park et al., 1998, 1999; Cho et al., 2002; Kim et al., 2004]. 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 [Chun et al., 1997]. We reported improved performance of V-Sb-O/TiO_2 compared to V_2O_5/TiO_2 in the selective oxidation of H_2S to ATS and sulfur [Park et al., 2002].

It is well known that Bi_2O_3 exhibits a remarkable range of useful solid-state properties [Sammes et al., 1999]. Many multicomponent systems containing ternary oxides of Bi, such as bismuth vanadium molybdenum oxides (for example, $BiMo_{1-x}V_xO_4$) or bismuth vanadium oxide ($Bi_4V_2O_{11}$), are efficient selective oxidation catalysts for hydrocarbons [Aghabozorg et al., 1997]. Structural oxygen is released from the catalyst, thereby converting it to a nonstoichiometric solid. The anion deficiency is recovered when gaseous oxygen is taken up by the catalyst, in a Mars-van Krevelen mechanism [Pomonis et al., 1981].

The conventional processes for the production of ATS are 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 mixture is contacted with H_2S to form ATS. Therefore, our process has the advantage of direct vapor phase operation compared to the above two processes.

In the current work, we further examined the performance of $Bi_4V_{2-x}Sb_xO_{11-y}$ compounds for the selective oxidation of H_2S in the stream containing both ammonia and water. Solid-state modifications of the mixtures during the catalytic reaction tests were verified by characterization before and after the test by XRD and XPS. Temperature-programmed techniques (TPR and TPO) were also

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used to elucidate the redox properties of this catalyst system.

EXPERIMENTAL

1. Preparation of Catalysts

Bi-V-Sb-O catalysts of nominal formula $Bi_4V_{2-x}Sb_xO_{11-y}$, with x=0.2, 0.5, 1.0, and 1.7, were prepared following the procedure described previously [Aghabozorg et al., 1997]. The synthesis consisted in the calcination in air at 800 °C for 18 h of a homogeneous mixture of Bi_2O_3 (Aldrich, 99.9%), V_2O_5 (Aldrich, 99%) and Sb_2O_3 (Merck, analytical purity) obtained by ball-milling adequate stoichiometric amounts of the three oxides together.

2. Catalytic Activity Measurement

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 0.0254 m. 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 the gas chromatograph, 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 (H_2S, SO_2, and NH_3) was analyzed by a gas chromatograph (HP 5890) equipped with a thermal conductivity detector and a 1.83 m 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 H_2S (X) and the selectivity to a special product (SO_2, S, ATS) (S) are defined as follows:

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

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

For the calculation of ATS selectivity, moles of ATS was multiplied by a factor of 2 because 1 mol of ATS can be obtained from 2 mol of H_2S.

3. Characterization

The surface areas of the catalysts were measured by N_2 adsorption method using the BET technique (Micromeritics ASAP 2000). The phase analysis was performed by X-ray diffraction crystallography 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 database. 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 C 1s band as reference (284.6 eV). To investigate the phase cooperation mechanism, TPR was performed. Before reduction, samples were pretreated by heating under air flow from 25 to 450 °C at a heating rate of 10 °C/min. Re-

duction 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 to 700 °C at a heating rate of 10 °C/min. The amount of consumed H_2 was detected by mass spectroscopy (VG Quadrupole). After the TPR experiment, the same sample was instantly tested in TPO under 2.5 vol% O_2 with helium gas balance.

RESULTS AND DISCUSSION

1. Characterization of Catalysts

Powder XRD patterns for various values of the antimony doping level, x, are shown in Fig. 1. For samples with x=0.2 and x=0.5, the main peak corresponds to $Bi_4V_2O_{11}$. Small peaks of $BiVO_4$ phase was also observed for these catalysts. For samples with x≥1.0 some characteristic peaks of $BiSbO_4$ and $Bi_{1.33}V_2O_6$ were detected. Bi_2O_3 was also observed for the catalysts with x=1.7. As might be expected from the high annealing temperatures used to synthesize these catalysts, all the samples were highly crystalline, as evidenced by the narrow reflections observed in XRD. The above-found phases were also reported to exist in the Bi-V-Sb-O catalysts of Gaigneaux et al. [2001].

Table 1 shows BET surface area for the $Bi_4V_{2-x}Sb_xO_{11-y}$ cata-

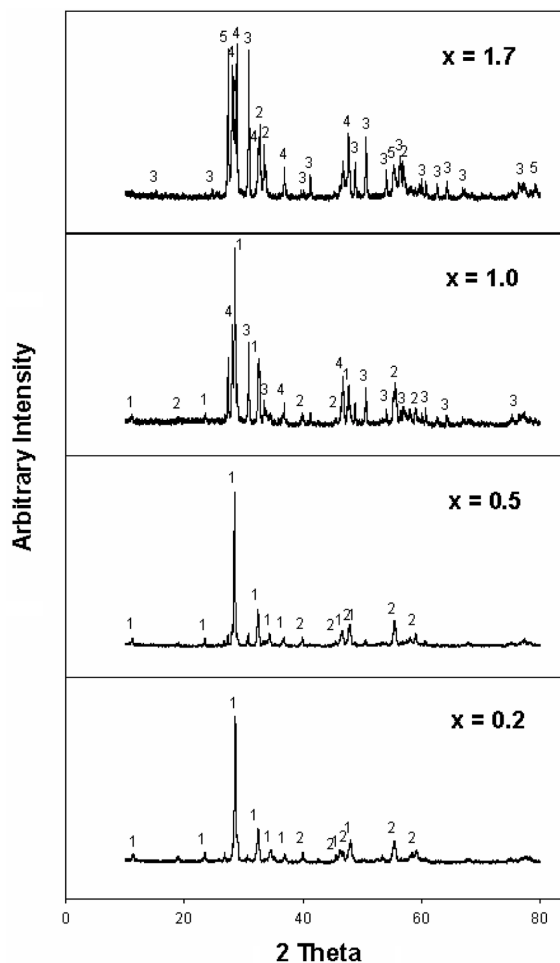Fig. 1. Powder XRD patterns recorded for the $Bi_4V_{2-x}Sb_xO_{11-y}$ catalysts (1: $Bi_4V_2O_{11}$, 2: $BiVO_4$, 3: $BiSbO_4$, 4: $Bi_{1.33}V_2O_6$, 5: Bi_2O_3).

Table 1. BET surface areas for $Bi_4V_{2-x}Sb_xO_{11-y}$ catalysts

$Bi_4V_{2-x}Sb_xO_{11-y}$	BET surface area (m^2/g)			
	x=0.2	x=0.5	x=1.0	x=1.7
Before reaction	0.53	0.58	0.62	0.63
After reaction	0.18	0.12	0.27	0.35

Table 2. Bulk nominal and experimentally determined surface concentration ratios for $Bi_4V_{2-x}Sb_xO_{11-y}$ catalysts

Catalyst ($Bi_4V_{2-x}Sb_xO_{11-y}$)	V/Bi		Sb/Bi		Sb/V	
	Bulk	XPS	Bulk	XPS	Bulk	XPS
Fresh (x=0.2)	0.450	0.258	0.050	0.049	0.110	0.129
Used (x=0.2)	0.450	0.265	0.050	0.070	0.110	0.173
Fresh (x=0.5)	0.375	0.247	0.125	0.089	0.330	0.229
Used (x=0.5)	0.375	0.147	0.125	0.085	0.330	0.351
Fresh (x=1.0)	0.250	0.120	0.250	0.101	1.0	0.453
Used (x=1.0)	0.250	0.136	0.250	0.210	1.0	0.629
Fresh (x=1.7)	0.075	0.066	0.425	0.232	5.67	0.811
Used (x=1.7)	0.075	0.083	0.425	0.374	5.67	0.868

lysts before and after reaction with a feed composition of $H_2S/O_2/NH_3/H_2O/He=5/2.5/5/60/27.5$ and GHSV=12,000 h^{-1} at 260 °C for 6 h. The surface areas were much lower than in a normal working catalyst material, typically in the range of 0.12-0.63 m^2/g. The used catalysts showed smaller surface area than the fresh catalysts probably due to the agglomeration of catalyst particle or the deposition of some sulfur on the catalyst surface during the reaction.

The surface chemical composition of the samples was checked by performing XPS over a range of binding energies. An experiment was carried out before and after performing the catalytic reaction on the catalysts. The O 1s peak overlaps the region in which the most intense peak for antimony (Sb $3d_{5/2}$) should appear. Therefore, the presence of antimony on the surface of samples should be probed by the Sb $3d_{3/2}$ peak. In addition, concerning vanadium, only the V $2p_{3/2}$ component can be accurately treated because the V $2p_{1/2}$ peak overlaps with the O 1s satellite peak.

Table 2 shows the surface chemical compositions of the catalysts before and after reaction test. The bulk chemical compositions, calculated from the amount of Bi_2O_3, V_2O_5, and Sb_2O_3 used for the preparation of catalysts, are also included in this table. Surface concentration ratios of V/Bi and Sb/Bi determined by XPS are smaller than their bulk concentration ratios. The Sb/V ratio on the surface of the fresh catalyst with x=0.2 was 0.129, higher than that in the bulk value of this compound, 0.110. Aghabozorg et al. [1977] reported that this trend was more evident for lower antimony doping level. However, this trend was inverse for the catalysts with x≥0.5. In addition, the XPS results of Sb/V ratio also show that the proportion of antimony after performing the catalytic reaction increases on the surface of catalysts. This may indicate a possible reconstruction of the surface of nominally orthorhombic samples to tetragonal during the catalytic reaction [Aghabozorg et al., 1977].

2. Catalytic Activity

Fig. 2 shows time variant conversion of H_2S(X-H_2S) and selectivity to SO_2(S-SO_2) for $Bi_4V_{2-x}Sb_xO_{11-y}$ catalysts with a reactant composition of 5 vol% H_2S, 2.5 vol% O_2, 5 vol%, NH_3, 60 vol%
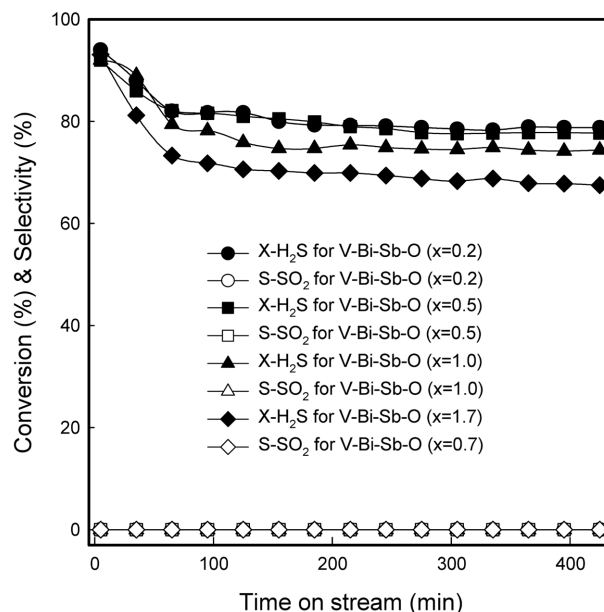
Fig. 2. Time variant conversion of H_2S and selectivity to SO_2 for $Bi_4V_{2-x}Sb_xO_{11-y}$ catalysts at 260 °C ($H_2S/O_2/NH_3/H_2O/He=5/2.5/5/60/27.5$, GHSV=12,000 h^{-1}).

H_2O and the balance helium at 260 °C with GHSV of 12,000 h^{-1}. The catalyst with x=0.2 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.

Table 3 summarizes the H_2S conversion and selectivities to SO_2, S and ATS for $Bi_4V_{2-x}Sb_xO_{11-y}$ catalysts after 8 h reaction at 260 °C. All the $Bi_4V_{2-x}Sb_xO_{11-y}$ catalysts showed higher H_2S conversion than $Bi_4V_2O_{11}$ (X=58.1%) and Sb_2O_4 (X=57.1%) did.

The $Bi_4V_{2-x}Sb_xO_{11-y}$ catalysts of x=0.2 showed the highest H_2S conversion. The increase of x resulted in an increase of ATS selec-

Table 3. Conversion of H_2S and product selectivity for $Bi_4V_{2-x}Sb_xO_{11-y}$ catalysts after 8 h of reaction at 260 °C

Catalyst	X-H_2S (%)	S-SO_2 (%)	S-S (%)	S-ATS (%)
$Bi_4V_2O_{11}$	58.1	0	61.7	38.3
x=0.2	81.4	0	96.0	4.0
x=0.5	80.5	0	93.3	6.7
x=1.0	77.4	0	92.4	7.6
x=1.7	71.9	0	87.2	12.8
Sb_2O_4	57.1	0	96.5	3.5

Reaction condition: $H_2S/O_2/NH_3/H_2O/He=5/2.5/5/60/27.5$, GHSV= 12,000 h^{-1}.

tivity at the expense of the decrease of sulfur selectivity. It is known that the following elementary reactions occur in the Claus process in the absence of ammonia [Terorde et al., 1993].

$$2H_2S + O_2 \rightarrow \frac{2}{n}S_n + 2H_2O \tag{1}$$

$$\frac{1}{n}S_n + O_2 \rightarrow SO_2 \tag{2}$$

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O \tag{3}$$

$$2H_2S + SO_2 \rightarrow \frac{3}{n}S_n + 2H_2O \tag{4}$$

Previous works [Bai et al., 1992; Hartley and Matterson, 1975] reported that the reaction of SO_2 with NH_3 occurred to form ammonium sulfite, and it was accelerated by the presence of water vapor:

$$SO_2 + 2NH_3 + H_2O \rightarrow (NH_4)_2SO_3 \tag{5}$$

Ammonium thiosulfate (ATS) is commercially produced by the reaction of ammonium sulfite with excess sulfur:

$$(NH_4)_2SO_3 + S \rightarrow (NH_4)_2S_2O_3 \tag{6}$$

ATS can also be produced by the reaction of ammonium sulfide [Chang and McGaugh, 1988], ammonium sulfite, and SO_2:

$$H_2S + 2NH_3 \rightarrow (NH_4)_2S \tag{7}$$
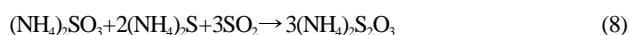
$$(NH_4)_2SO_3 + 2(NH_4)_2S + 3SO_2 \rightarrow 3(NH_4)_2S_2O_3 \tag{8}$$

Fig. 3 shows a typical temperature dependence of H_2S conversion for $Bi_4V_{2-x}Sb_xO_{11-y}$ catalysts. The catalyst with x=0.2 showed the highest H_2S conversion over the entire temperature ranges of 220-320 °C. The conversion increased up to 260 °C, then it decreased over this temperature. According to the estimated equilibrium calculations reported by Chun [1998], the equilibrium conversion of H_2S for the Claus process (Eqs. (1)-(4)) decreased with increasing reaction temperature [Park et al., 2002]. However, below 220 °C (not shown in Fig. 3) H_2S conversion decreased abruptly because

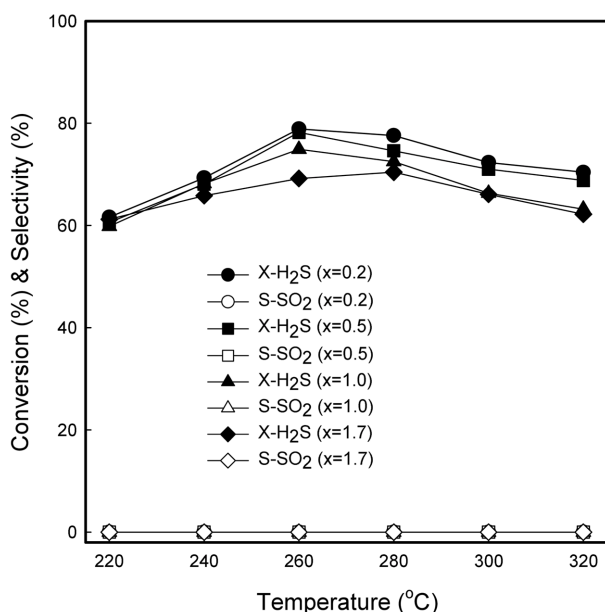**Fig. 3. Conversion of H_2S and selectivity to SO_2 for $Bi_4V_{2-x}Sb_xO_{11-y}$ catalysts at different temperatures ($H_2S/O_2/NH_3/H_2O/He= 5/2.5/5/60/27.5$, GHSV=12,000 h^{-1}).**
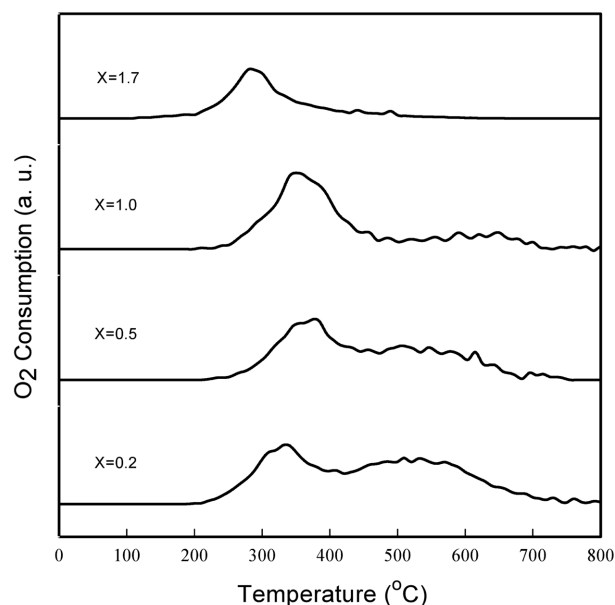
Fig. 4. TPO profiles of $Bi_4V_{2-x}Sb_xO_{11-y}$ catalysts.

Table 4. Desorbed amount of H_2 and O_2 in TPR and TPO experiments

Catalysts ($Bi_4V_{2-x}Sb_xO_{11-y}$)	H_2 (μmol/g-cat)	O_2 (μmol/g-cat)
x=0.2	27.6	53.0
x=0.5	23.2	42.0
x=1.0	27.9	36.9
x=1.7	25.7	24.4

of sulfur condensation on the surface of catalyst.

3. Redox Behaviour of Catalyst

To identify the highest activity for the catalyst with x=0.2, a comparative temperature-programmed reduction (TPR) followed by temperature-programmed oxidation (TPO) were carried out for $Bi_4V_{2-x}Sb_xO_{11-y}$. The reducibility of the catalysts was first measured by using TPR method with hydrogen as a reductant, and the TPO results are shown in Fig. 4. The amount of hydrogen and oxygen consumed is summarized in Table 4. In the TPO experiment, the catalyst with x=0.2 showed the best reoxidation property. The amount of oxygen consumption decreased with increasing x, which is in accordance with the order of H_2S conversion with the variation of x. However, the amounts of hydrogen consumption were not so different from others.

The oxidation state of vanadium in $Bi_4V_{2-x}Sb_xO_{11-y}$, was also studied by XPS. Fig. 5 shows XPS spectra of V $2p_{3/2}$ for these catalysts before and after 8 h of 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 516.9 and 515.6 eV, respectively. After the reaction, the XPS spectra were broadened and shifted to lower binding energy. It means that some of the catalyst surface having V^{5+} state is reduced to V^{4+} after the reaction. The full-width half-maximum (FWHM) value for the fresh catalyst with x=0.2 was 2.333 eV, and that for the used catalyst was 2.381 eV. It corresponds to 2.1% increase in FWMH after the reaction. However, the catalyst with x=0.5 showed 1.571 eV for the fresh catalyst and
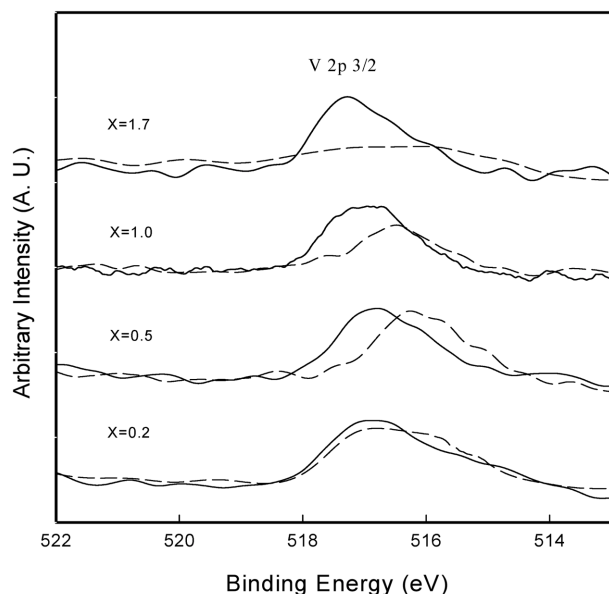
Fig. 5. XPS analyses of V 2p$_{3/2}$ for Bi$_4$V$_{2-x}$Sb$_x$O$_{11-y}$ catalysts before (solid line) and after (dashed line) the reaction: Reaction condition (H$_2$S/O$_2$/NH$_3$/H$_2$O/He=5/2.5/5/60/27.5, GHSV= 12,000 h^{-1}).

1.714 eV for the used one, 9.1% increase in FWMH. Therefore, after the reaction the catalyst with x=0.2 shows less reduction of vanadium phase than that of x=0.5. The degree of percentage increase in FWMH, implying the degree of reduction after reaction, increased with the increase of x. This can support the highest re-oxidation ability of the catalyst with x=0.2.

CONCLUSION

The selective oxidation of hydrogen sulfide in the presence of excess water and ammonia was investigated using Bi$_4$V$_{2-x}$Sb$_x$O$_{11-y}$ catalysts. Hydrogen sulfide was successfully converted into harmless ammonium thiosulfate and elemental sulfur without considerable emission of sulfur dioxide. The mixed oxide catalyst with x= 0.2 showed the highest conversion of H$_2$S. The TPO and XPS results supported the importance of reoxidation ability of this catalyst for the good conversion of H$_2$S.

ACKNOWLEDGMENT

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