바나듐계 촉매를 통한 H_2S의 선택적 산화에 대한 암모늄 티오설페이트와 황의 제조

황병하, 김봉국, 박대원
부산대학교 화학공학과

The Synthesis of Ammonium Thiosulfate and Sulfur by Selective Oxidation of H_2S over Vanadium-Based Catalysts

B. H. Hwang, B. G. Kim, D. W. Park
Dept. of Chemical Engineering, Pusan National University

Introduction

Since the international environmental regulations concerning the release of sulfur containing gas have become more strict, hydrogen sulfide contained in the acid gases should be effectively recovered before emission to atmosphere. For many years, most of hydrogen sulfide in petroleum refineries and natural gas plants has been removed by the well-known Claus process [1, 2]. The Claus process consists of two steps; thermal oxidation and catalytic reaction. However, due to thermodynamic limitations, typically 3 to 5% H_2S is not converted into sulfur. For this reason various tail gas treatment (TGT) technologies have been proposed. Conventional Claus TGT process involved a hydrogen sulfide absorption step, in which a tail gas containing unreacted hydrogen sulfide is introduced into an alkaline solution bath. The most attractive process that has been recently developed is Modop (Mobil Direct Oxidation Process) process [3-5] or Super Claus Process [6-8], both of which are based on direct oxidation of H_2S to elemental sulfur.

In our previous works, we reported a very high activity of V_2O_5 catalysts. In order to enhance catalytic activity, vanadium based mechanically mixed catalysts were investigated for selective removal of H_2S in the stream containing both of ammonia and water. Synergy effect is observed for mixed oxide catalysts.

In this study, we examined the performance of V-Bi-O+Sb_2O_4 and Bi-V-Sb-O catalysts for the selective oxidation of H_2S in the stream containing both of ammonia and water. Kinetic studies have been carried out to illustrate the reaction path.

Experimental

Mechanically mixed catalysts are composed of V_2O_5 (Aldrich, 99%) and Bi_2O_3 (Aldrich, 99.9%). Vanadium oxide (V_2O_5) and bismuth oxide (Bi_2O_3) were used as purchased without further purification. These catalysts were denoted as V_2O_5+Bi_2O_3 (x:y), where x and y indicate the amount of each pure oxide expressed in wt. ratio. Bi-V-Sb-O catalysts were prepared by the calcination in air at 800°C for 18h of a homogeneous mixture of Bi_2O_3, V_2O_5, and Sb_2O_3 (Merck, analytical purity) obtained by ball-milling adequate amounts of the three oxides. V-Bi-O was prepared by the coprecipitation method. V-Bi-O+Sb_2O_4 were also prepared using the method of dispersion followed by drying in air at 80°C. The reaction test was carried out at atmospheric pressure using a vertical continuous flow fixed bed reactor made of Pyrex glass tube (I.D. 1 inch). A sulfur condenser was attached at the effluent side of the reactor, and its temperature was constantly maintained at 110°C to condense only solid product (mixture of elemental sulfur and white salt). The flow rate of gases was controlled by a mass flow controller. Water vapor was fed to reactor via 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). The surface area of the individual oxides and their mechanical mixtures was 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). In order to investigate the phase cooperation mechanism, TPR was carried out. Before reduction, samples were pretreated by heating under air flow from 30°C to 450°C at 10°C/min. Reduction was achieved under a H_2/He gas mixture (10 vol.% H_2). Gas flow was 20cc/min and temperature program was from 30°C to 800°C at heating rate of 10°C/min. The amount of consumed H_2 was detected by a gas chromatograph (DS6200). After TPR experiment, the same sample was instantly tested in TPO under 2.5 vol.% O_2 with helium gas balance.

Results and Discussion

Table 1 shows H_2S conversion (X-H_2S) and selectivity to SO_2 (S-SO_2) for different catalysts. All the vanadium-based catalysts were effective for the conversion of H_2S to ATS and S. Comparing V_2O_5 and the mechanical mixture V_2O_5+Bi_2O_3 (1:3), increase of X-H_2S and decrease of S-SO_2 are observed over all the temperature range from 260-320°C. The slow reoxidation of V_2O_5 has been considered as a main cause of deactivation in the oxidation of

Table 1. Conversion of H_2S and selectivity to SO_2 for different catalysts.

Temp	V_2O_5		V_2O_5+Bi_2O_3(1:3)		V-Bi-O(Bi/V=1)		V-Bi-O+Sb_2O_4(3:1)	
(oC)	X-H_2S	S-SO_2	X-H_2S	S-SO_2	X-H_2S	S-SO_2	X-H_2S	S-SO_2
260	81.0	0.0	89.3	0.0	86.0	0.0	88.8	0.0
280	80.0	2.2	86.4	0.8	84.3	0.0	87.5	0.0
300	75.1	4.2	83.8	1.4	77.2	2.4	82.6	2.0
320	71.2	5.3	75.3	2.0	73.3	5.3	75.9	3.2

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

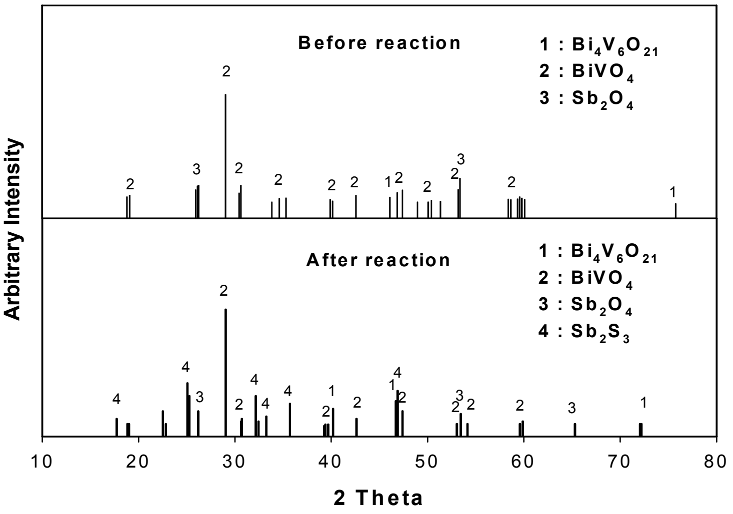

Fig. 1 XRD patterns of V-Bi-O+Sb_2O_4 (3:1) catalyst

H_2S. The mechanical mixture V-Bi-O+Sb_2O_4 (3:1) also showed synergistic effect in the activity of the selective oxidation of H_2S. XRD analyses revealed that V-Bi-O+Sb_2O_4 (3:1) catalyst had mainly $Bi_4V_6O_{21}$, $BiVO_4$ and Sb_2O_4 as shown in Fig. 1. These two mixed oxides have been reported to be major active phases for the oxidation of H_2S without NH_3. Sb_2O_4 is a p-type semiconductor and it can participate to reoxidize the partially reduced vanadium oxide active phase by dissociative adsorption of oxygen. Comparative temperature programmed reduction (TPR) and the following temperature programmed oxidation (TPO) are carried out for V-Bi-O, Sb_2O_4 and mechanically mixed V-Bi-O+Sb_2O_4 catalysts. The reducibility of the catalysts was first measured using TPR method with hydrogen as a reductant. In the subsequent TPO experiment, the mixture catalyst V-Bi-O+Sb_2O_4 (3:1) showed the best reoxidation property among all the catalysts as shown in Table 2. The maximum peak of O_2 consumption for the V-Bi-O+Sb_2O_4 (3:1) was 450°C. The reoxidation ability of Sb_2O_4 in the mechanical mixture of V_2O_5+Sb_2O_4 has been reported previously [9].

Table 2. Amount of hydrogen and oxygen in TPR/TPO experiments for V-Bi-O+Sb_2O_4 catalysts.

Catalyst (x)	H_2 (µmol/g-cat)	O_2 (µmol/g-cat)
V-Bi-O	25.5	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	16.3

Table 3. Catalytic activities and detected phases of $Bi_4V_{2-x}Sb_xO_{11-\mu}$ catalysts.

x (%)	X-H_2S (%)	S-SO_2 (%)	S-S (%)	S-ATS (%)	Phase
0.2	78.7	0.0	89.75	10.25	$Bi_4V_2O_{11}$, $BiVO_4$
0.5	78.0	0.0	93.00	7.00	$Bi_4V_2O_{11}$, $BiVO_4$
1.0	74.6	0.0	96.56	3.44	$Bi_4V_2O_{11}$, $BiVO_4$, $BiSbO_4$, $Bi_{1.33}V_2O_6$
1.7	68.8	0.0	94.05	5.95	$Bi_4V_2O_{11}$, $BiVO_4$, $BiSbO_4$, $Bi_{1.33}V_2O_6$, Bi_2O_3

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

Bi-V-Sb-O catalysts were also tested in the selective oxidation of H_2S to elemental sulfur and ammonium thiosulfate. Table 3 shows the H_2S conversion and selectivity to the products for Bi-V-Sb-O catalysts of different x values at 260℃ with $H_2S/O_2/NH_3/H_2O/He$=5/2.5/5/60/27.5 and GHSV of 12,000h^{-1}. The increase of x in $Bi_4V_{2-x}Sb_xO_{11-\mu}$ catalysts decreased the H_2S conversion and ATS selectivity, but the sulfur selectivity increased up to x=1.0. The main phases detected by XRD analyses were $Bi_4V_2O_{11}$, $Bi_{1.33}V_2O_6$, $BiSbO_4$, and $BiVO_4$. The highest conversion of H_2S was obtained for x=0.2. TPO results showed that this catalyst had the highest amount of oxygen consumption. It meant that the catalyst with x=0.2 had the highest reoxidation capacity in $Bi_4V_{2-x}Sb_xO_{11-\mu}$ catalysts.

Acknowledgement

This work was supported by the Korea Research Foundation (KRF E00076).

References

1. Lagas, J.A., Borsboom, J. and Berben, P.H., Oil&Gas J., Oct. **10**, 68 (1988).
2. Wieckowska, J., Catalysis Today, **24**, 105 (1995).
3. Chopin, T., Hebrand, J.L. and Quemere, E., EP 422999 (1990).
4. Kettner, R. and Liermann, N., Oil and Gas J. **11**, 63 (1983).
5. Kettner, R., Lubcke, T. and Liermann, N., EP 78690 (1982).
6. Brink, P.J. and Geus, J.W., US Patent 4818740 (1989).
7. Brink, P.J. and Geus, J.W., EP 409353 (1990).
8. Terorde, R.J.A.M., Brink, P.J., Visser, L.M. and Dillen, A.J., Catalysis Today, **17**, 217 (1993).
9. Park, D.W., Park, D.K. and Woo, H.C., Appl. Catal. A : Gen., 223, 215 (2002).