졸-겔법에 의해 제조된 TiO_2에 담지된 VO_x 촉매 상에서 과잉의 물과 암모니아를 포함한 H_2S의 선택적 산화반응

주월돈, 김문일, 김경훈, 박대원*, 홍성수[1]
부산대학교 화학공학과, [1]부경대학교 화학공학과
(dwpark@pusan.ac.kr*)

Selective oxidation of hydrogen sulfide containing excess water and ammonia using VO_x catalysts supported on TiO_2 prepared by sol-gel method

Wol-Don Ju, Moon-Il Kim, Kyung-Hoon Kim, Dae-Won Park*, Seong-Soo Hong[1]
Dept. of Chemical Engineering, Pusan National University
[1]Division of Applied Chemical Engineering, Pukyong National University
(dwpark@pusan.ac.kr*)

INTRODUCTION

In general, SO_x emission problem has been caused by H_2S released from crude oil and natural gas refineries. Hydrogen sulfide from stationary source is usually recovered as elemental sulfur by the Claus process [1]. Unfortunately about 3-5% of sulfur compounds is discharged due to thermodynamic limitations of Claus reaction. For this reason various tail gas treatment (TGT) technologies have been proposed. Most of wet Claus TGT processes involve hydrogen sulfide absorption step into an alkaline solution. In the same manner, H_2S contained in the coke oven gas of the steel smelting process is scrubbed and concentrated using aqueous ammonia solution. The concentrated H_2S separated from ammonia solution is generally transferred to the Claus plant, and remaining aqueous ammonia solution is incinerated without further treatment. Since the separation of H_2S is not perfect, the remaining aqueous ammonia contains about 2 % of H_2S which in turn can cause the SO_x emission problem during incineration. Hence, new technologies are being examined to remove H_2S in excess water and ammonia stream. One approach is the selective catalytic oxidation of H_2S to elemental sulfur and ammonium thiosulfate (ATS: $(NH_4)_2S_2O_3$) as reported in our previous work [2].

In this study, we examined the performance of VO_x/TiO_2 catalyst for the selective oxidation of H_2S in the stream containing both of ammonia and water.

EXPERIMENTAL

The preparation method of TiO_2 support was described in the previous paper [3]. The impregnation procedure used was the incipient wetness technique, in which the aqueous solution of NH_4VO_3 was slowly added to the support to obtain the desired metal content in the final catalyst.

Finally, all samples were dried and calcined at 500 ^{o}C for 12 h. The precipitation-deposition catalysts were prepared following the method described by Van Dillen et al. [4], in which the thermal decomposition of urea was used to raise homogeneously the pH of a suspension formed by the support in NH_4VO_3 solution. The pH of the solution was adjusted to 4 by addition of oxalic acid, and then continuously stirred at 90 ^{o}C for: 10 h for 1 wt.% V, 20 h for the catalyst up to 10 wt.% V. Finally, all catalysts were dried and calcined at 500 ^{o}C for 10 h.

The reaction test was carried out at atmospheric pressure using a vertical continuous flow fixed bed reactor. A sulfur condenser was attached at the effluent side of the reactor, and its temperature was constantly maintained at 110 ℃ 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).

RESULTS AND DISCUSSION

Fig. 1. shows XRD patterns of I-VO_x/TiO_2 catalysts prepared by the impregnation method and calcined at 500 ^{o}C. From the XRD results, all the catalysts show XRD peaks due to anatase titania with an intense peak at $2\Theta = 25.3$ ° corresponding to the [101] plane of titania. No reflection is observed at $2\Theta = 20.3$ ° corresponding to the most intense reflection of V_2O_5. This means that if a part of vanadium exists in the form of V_2O_5 clusters, these are not large enough to be detected by XRD. This result clearly indicates that vanadium oxide is present in a highly dispersed amorphous state on titania.

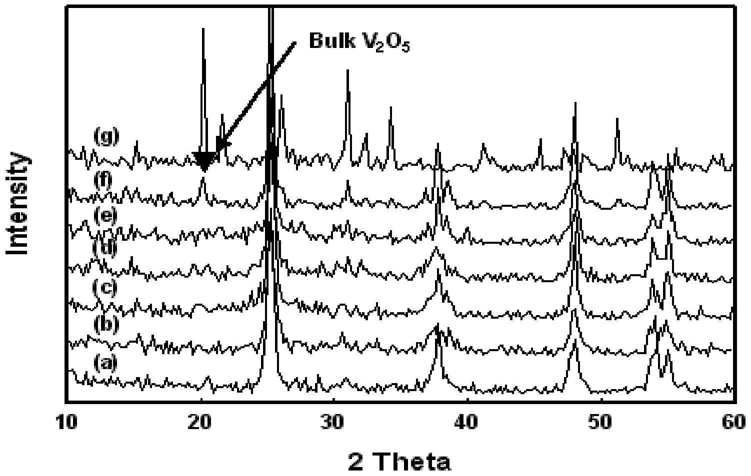

Fig. 1. XDR patterns of I-VOx/TiO_2 catalysts with different Vanadium loading.
(a) 1 wt.% (b) 3 wt.%(c) 5 wt.% (d) 7 wt.% (e) 10 wt.% (f) 13 wt.% (g) V_2O_5

To make further investigations, a series of TiO_2-supported vanadium oxide catalysts were prepared by impregnation and precipitation-deposition method with different vanadate loadings. VO_x/TiO_2 catalysts were tested in the selective oxidation of H_2S to elemental sulfur and ammonium thiosulfate. Table 1 and 2 show the H_2S conversion and selectivity to the products for the two differently prepared VO_x/TiO_2 catalysts at 260 ℃ with $H_2S/O_2/NH_3/H_2O/He$ = 5/2.5/5/60/27.5 and GHSV of 12,000 h^{-1}. BET results are also shown in Table 1. For all the catalysts in Table 1 and Table 2, surface area decreased as the vanadia loading increased. The surface area of P-VO_x/TiO_2 prepared by the precipitation-deposition method showed a little higher surface area than those prepared by the impregnation. In P-VO_x/TiO_2 catalysts (Table 1), the conversion of H_2S for 1 to 3 wt.% of vanadia loading were higher than 92 %, and there was no appreciable change in the H_2S conversion. However, the decrease of the H_2S conversion was notable for P-VO_x/TiO_2 catalysts of 7 wt.% and 10 wt.% of vanadia loading. Low value of the H_2S conversion for P-VO_x(10%)/TiO_2 might also be related to its low surface area. The surface coverage of vanadium for this catalyst will be higher than the monolayer deposition. Fig. 2 also shows that P-VO_x(10%)/TiO_2 has more severe activity decrease with process time. I-VO_x/TiO_2 catalysts in Table 2 also show that the H_2S conversion decreased with the vanadia loading. They have a little lower H_2S conversion than the P-VO_x/TiO_2 catalysts. This result suggests that the precipitation-deposition method can achieve a higher metal loading on the support and a high dispersion compared to the impregnation method.

Table 1. Conversion of H_2S and selectivities of SO_2, S and ATS for P-VO_x/TiO_2 catalysts.

Catalyst	Surface area(m^2/g)	X-H_2S (%)	S-SO_2 (%)	S-S (%)	S-ATS (%)
P-VOx(1%)/TiO_2	94	93.0	0	79.1	20.9
P-VOx(3%)/TiO_2	69	92.8	0	73.6	26.4
P-VOx(5%)/TiO_2	55	92.5	0	78.2	21.8
P-VOx(7%)/TiO_2	51	86.3	0	72.5	27.5
P-VOx(10%)/TiO_2	9	78.4	0	45.9	54.1

P : Precipitation deposition method

Table 2. Conversion of H_2S and selectivities of SO_2, S and ATS for I-VO_x/TiO_2 catalysts.

Catalyst	Surface area(m^2/g)	X-H_2S (%)	S-SO_2 (%)	S-S (%)	S-ATS (%)
I-VOx(1%)/TiO_2	59	90.8	0	87.6	12.4
I-VOx(3%)/TiO_2	49	89.2	0	77.4	22.6
I-VOx(5%)/TiO_2	43	87.7	0	69.3	30.7
I-VOx(7%)/TiO_2	34	84.2	0	71.5	28.5
I-VOx(10%)/TiO_2	29	82.1	0	59.6	40.4

I : Impregnation

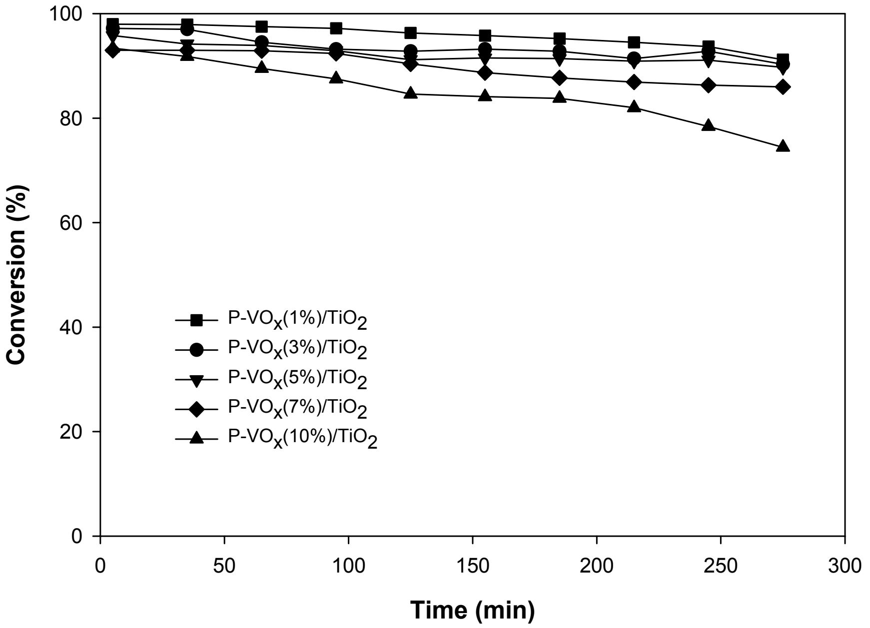

Fig. 2. Time variant conversion of H_2S for P-VOx/TiO_2 catalysts at 260 °C.

ACKNOWLEDGMENT

This work was supported by the Korea Science and Engineering Foundation (R05-2003-000-10050-0), and Brain Korea 21 and Brain Busan 21 program.

REFERENCES

1. Lagas, J.A., Borsboom, J. and Berben, P.H., "Selective Oxidation Catalyst Improves Claus Process", Oil&Gas J., Oct. **10**, 68 (1988).
2. Wieckowska, J., "Catalytic and Adsorptive Desulfurization of Gases", Catalysis Today, **24**, 105 (1995).
3. G.H. Lee, M.S. Lee, G.D. Lee, Y.H. Kim, S.S. Hong: J. Ind. Eng. Chem., **8**, 572 (2002).
4. J.A. Van Dillen, J.W. Geus, L.A.M. Hermans, J. Van Der Meijden: Proc. 6th Int. Congr. On Catal., London 1976.