황화수소의 선택적 산화반응에 대한 V_2O_5-TiO_2 촉매의 성능비교

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Comparitive Study of Differently Prepared V_2O_5-TiO_2 Catalysts for the Selective Oxidation of H_2S

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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, 2]. 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 [3-5]. The processes are based on the following reactions.

$H_2S + O_2 \rightarrow 2/n\ S_n + H_2O$ (Selective oxidation)
$S + O_2 \rightarrow SO_2$ (Sulfur oxidation)
$H_2S + 3/2O_2 \rightarrow SO_2 + H_2O$ (Deep oxidation)
$2H_2S + SO_2 \leftrightarrow 3/n\ S_n + 2H_2O$ (Claus reaction)

In this study, we examined the performance of VO_x/TiO_2 catalyst prepared by supercritical sol-gel method,non-hydrolytic so-gel method and by impregnation method for the selective oxidation of H_2S in the stream containing both of ammonia and water.
Vanadia supported catalyst shows high activity for the selective oxidation of H_2S.The best support is TiO_2- anatase, which provides high activity and resistance against poisonising by SO_2 .V_2O_5-TiO_2 catalysts are favored due to their high activity and stability. It was found that the textural property of V_2O_5-TiO_2 material varies with the method and conditions of synthesis. Surface vanadates and TiO_2 anatase phase are the crucial factors to obtain high catalytic activities. The surface area and pore volume exhibited by vanadia-titania catalyst are appreciable. The high catalytic activity showed by V_2O_5-TiO_2 catalyst may be due to their good surface area and better dispersion of vanadia species in the titania matrix.

EXPERIMENTAL

Vanadia-titania composite aerogel containing 5wt% vanadia were prepared by the sol-gel processing of ammonium vanadate and titanium tetraisopropoxide in the ethanol and subsequent continuous supercritical drying with CO_2 at 33 K and 20 MPa. The dried aerogel was subjected to a standard calcinations procedure, which consisted of heating in helium at 573 K and in oxygen at 773 K [6]. , V_2O_5-TiO_2 xerogel by non-hydrolytic sol-gel process and impregnated V_2O_5-TiO_2 catalyst were also prepared. The textures of the calcined mixed oxide were measured by N_2 adsorption method using the BET technique (Micromeritics ASAP 2000).

REANCTION TEST

Reaction test were carried out in a continuous flow fixed- bed reactor. The reactor was made of a Pyrex tube with an i.d of 0.0254m.A condenser was attached at the effluent side of the reactor and its temperature was constantly maintained at 110^0C to condense only solid products (sulphur+ammoniumthiosulphate). 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 120^0C 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 using an evaporator filled with small glass beads, and its amount was controlled by a syringe pump.

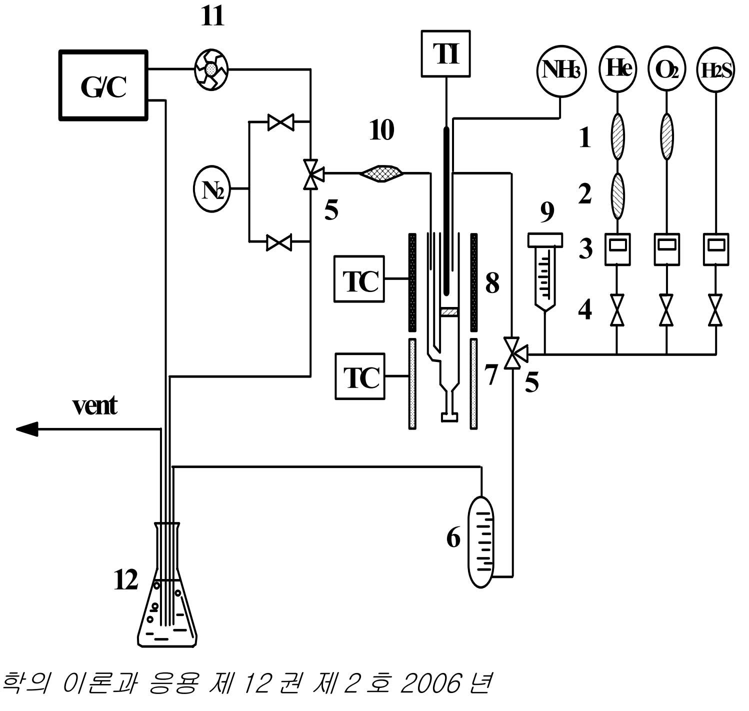
The content of effluent was analyzed by a gas chromatography (HP 5890) equipped with a thermal conductivity detector and a 1.83 m Porapak T column (80-100mesh) at 100^0C.The exist gas from the analyzer was passed through a trap containing a concentrated NaOH solution and vented out to a hood. The conversion of H_2S and the selectivity to a special product are defined as follows:

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

$$\text{Selectivity (S,\%) to a special product } (SO_2, S, ATS) = \{[\text{product}]_{outlet}/\{[H_2S]_{inlet} - [H_2S]_{outlet}\}\} \times 100$$

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

Schematic diagram of experimental apparatus



1. moisture trap
2. oxygen trap
3. mass flow controller
4. cut-off valve
5. 3-way valve
6. flow meter
7. sulfur condenser
8. reactor heater
9. syringe pump
10. sulfur removal filter
11. 6-way sampling valve
12. exhaust gas trap

RESULT AND DISCUSSION

The selective oxidation of hydrogen sulfide in the presence of ammonia and water was studied using 5wt% V_2O_5-TiO_2 catalysts. BET surface areas, pore volume, and average pore diameter are listed in Table-1.Aerogel catalysts prepared by supercritical drying process showed much higher surface areas and pore volumes than those of catalysts prepared by non-hydrolytic preparation method and by impregnated method. This may be due to the uniform dispersion of vanadia species in the titania matrix.

Table.1 Comparison of specific surface area(S_{BET}), total pore volume(V_p), and average pore size (Dp) of 5wt% V_2O_5-TiO_2 catalysts.

Catalyst	S_{BET} (m^2/g)	Vp (cm^3/g)	Dp(nm)
A	153	0.65	14.9
B	90	0.55	9.9
C	55	0.32	23.2

A: aerogel catalyst prepared by supercritical drying process, B: xerogel catalyst prepared by non-hydrolytic sol-gel method, C: vanadia impregnated on titania.

Table 2. Conversion of H_2S for vanadia- titania catalysts at different temperatures (^0C)

	H_2S conversion %				
Catalysts	220^0C	240^0C	260^0C	280^0C	300^0C
A	93.8	96.9	99.1	98.6	98
B	99.2	97.8	95.2	93	90.5
C	78.6	78.8	80.8	76.5	70.1

Reaction condition: $H_2S/O_2/NH_3/H_2O/He$ = 5/2.5/5/20/67.5, GHSV = 30,000 h^{-1}, reaction time = 6 h

Table 3. Conversion of H_2S and selectivity to products for 5 wt% V_2O_5-TiO_2 catalysts at 260^0C.

Catalyst	X-H_2S(%)	S-SO_2(%)	S-S(%)	S-ATS(%)
A	99.1	0	39.3	60.7
B	98.1	1.8	25.71	74.3
C	79.7	0	61.4	38.6

Reaction condition: $H_2S/O_2/NH_3/H_2O/He$ =5/2.5/5/20/67.5, GHSV =30,0000h^{-1}, reaction time=6h

Table-2 indicates the H_2S conversion of the three catalysts at different temperatures. The aerogel catalyst and xerogel catalyst showed higher H_2S conversion than catalyst prepared by impregnation method.Table.3 indicates that H_2S conversion at 260^0C given by aerogel catalyst 99.1% was higher than the 98.1% and 79.7% produced by non-hydrolytic method and by impregnation method respectively. In the presence of ammonia, the SO_2 produced from the oxidation of H_2S can react to form$(NH_4)_2SO_3$, then finally to produce ATS. Selectivity to ATS given by aerogel catalyst was also good. The high catalytic activity showed by vanadia-titania aerogel may be due to their increased surface area and better dispersion of vanadia species in the titania matrix.

CONCLUSIONS

The selective oxidation of hydrogen sulfide in the presence of excess water and ammonia was investigated in this study. V_2O_5-TiO_2 aerogel catalysts showed very high conversion of H_2S without any considerable amount of SO_2 emission. These catalysts showed much higher surface area and pore volume than the catalyst prepared by non-hydrolytic method and by impregnation method. Selectivity to ATS and sulfur is also very high. The high H_2S conversion and high selectivity to desired products exhibited by aerogel catalyst may be due to their increased surface area and better dispersion of vanadia species in the titania matrix.

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