Nb-Fe   H$_2$S

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The Synthesis of Ammonium Thiosulfate and Sulfur by Selective Oxidation of Hydrogen Sulfide over Nb-Fe Mixed Oxide Catalysts

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INTRODUCTION

In general, SO$_x$ emission problem has been caused by H$_2$S 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$_2$S contained in the coke oven gas of the steel smelting process is scrubbed and concentrated using aqueous ammonia solution. The concentrated H$_2$S 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$_2$S is not perfect, the remaining aqueous ammonia contains about 2% of H$_2$S which in turn can cause the SO$_x$ emission problem during incineration. The most attractive process that has been recently developed is Modop (Mobil Direct Oxidation Process) process [2-4] or Super Claus Process [5-7], both of which are based on direct oxidation of H$_2$S to elemental sulfur. Hence, new technologies are being examined to remove H$_2$S in excess water and ammonia stream. One approach is the selective catalytic oxidation of H$_2$S to elemental sulfur and ammonium thiosulfate (ATS: (NH$_4$)$_2$S$_2$O$_3$) as reported in our previous work [8].

The present work deals with the use of a iron-niobate catalysts for catalyzing the selective catalytic oxidation of hydrogen sulfide to sulfur in the stream containing both of ammonia and water, from which strong synergistic phenomena in both catalytic activity and catalytic selectivity have been observed for the iron-niobates.

EXPERIMENTAL

Iron-niobates with different atomic ratios (Nb/Fe = 1/0, 5/1, 3/1, 1/1, 1/2, 1/5, 0/1) were prepared by a coprecipitation method. Niobium pentachloride NbCl$_5$ (99%, Aldrich) and iron nitrate Fe(NO$_3$)$_3$·9H$_2$O (99.5%,

Katayama Chemical Company) were used as the starting materials. The products obtained were filtered, washed and dried at 383 K and then calcined in air at a range of temperature from 823 K for 2h. Nb-Fe binary oxide with Nb/Fe=1/1 atomic ratio was prepared by coprecipitation from alcoholic mixture using $NbCl_5$ and $Fe(NO_3)_3 \cdot 9H_2O$ as the starting materials. After filteration the solids were calcined in air at 550, 650 and 750 during 2h to obtain three catalysts denoted as NbFe-550, NbFe-650, NbFe-750, respectively. As a reference a single metal oxide system was also obtained. The obtained materials were characterized by XRD, XPS, BET and Temperature programmed techniques (TPR and TPO).

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   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/N_2 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 mass spectroscopy (VG Quadrupole). After TPR experiment, the same sample was instantly tested in TPO under 2.5 vol.% O_2 with helium gas balance. XPS analyses were performed with a 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 vaccum. The binding energies were calculated using the C1s band as reference (286.4 eV).

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 catalysts were effective for the conversion of H_2S to ATS and S. Compare with single Nb_2O_5 and Fe_2O_3, Nb-Fe binary oxides, increase of X-H_2S and decrease of S-SO_2 are observed over all the temperature range from 260-320°C. Nb-Fe mixed oxide catalysts showed synergistic effect in the activity of the selective oxidation of H_2S.
Fe_2O_3 can participate to reoxidize the partially reduced vanadium oxide active phase by dissociative adsorption of oxygen. TPR/TPO studies conformed the enhanced redox behaviors of Nb-Fe mixed oxide catalysts for several atomic ratio in Table 2. Comparative temperature programmed reduction (TPR) and the following temperature programmed oxidation (TPO) are carried out for single Nb_2O_5 and Fe_2O_3, Nb-Fe binary oxides of different atomic ratios (Nb/Fe = 1/0, 5/1, 3/1, 1/1, 1/2, 1/5, 0/1) and the results are shown. The reducibility of catalysts was first measured using TPR method with hydrogen as a reductant In the subsequent TPO experiment,

the Nb-Fe mixed oxide showed the best reoxidation property than other catalysts. The maximum peak of O_2

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

Temp (^{o}C)	N_2O_5		Fe_2O_3		Nb-Fe (Nb/Fe=1)	
	X-H_2S	S-SO_2	X-H_2S	S-SO_2	X-H_2S	S-SO_2
260	63.8	1.8	74.5	0.4	88.1	0.2
280	62.1	2.6	72.8	1.0	87.6	1.0
300	58.8	4.4	69.7	1.4	83.1	2.7
320	56.2	5.3	62.4	1.8	76.4	3.1

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

Catalyst (x)	H_2 (μ mol/g-cat)	O_2 (μ mol/g-cat)
Fe_2O_3	51.29	20.02
Nb-Fe(Nb/Fe=0.2)	53.75	25.54
Nb-Fe(Nb/Fe=0.5)	75.48	46.07
Nb-Fe(Nb/Fe=1.0)	75.62	37.08
Nb-Fe(Nb/Fe=3.0)	57.66	25.74
Nb-Fe(Nb/Fe=5.0)	49.84	21.35
Nb_2O_5	48.68	10.12

Table 2. TPR/TPO profiles for V-Sb-O-Bi_2O_3 catalysts.

consumption for the Nb-Fe(Nb/Fe=0.5) mixed oxide catalyst.

NbFe-550, NbFe-650, NbFe-750 catalysts were also tested in the selective oxidation of H_2S to elemental sulfur and ammonium thiosulfate. in Table 3 shows the H_2S conversion and selectivity to the products for NbFe-550, NbFe-650, NbFe-750 catalysts 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}. With increasing calcinations temperature, catalysts increased the H_2S conversion and ATS selectivity. The main phases detected by XRD analyses was amorphous for NbFe-550, NbFe-650 but FeNbO$_4$ for NbFe-750. Fig. 1 shows TPO curves of the three catalysts.

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

Catalysts	X-H_2S (%)	S-SO_2 (%)	S-S (%)	S-ATS (%)	Phase
NbFe-550	77.7	1.8	23.9	76.1	amorphous
NbFe-650	82.0	1.6	23.5	76.5	amorphous
NbFe-750	88.1	0.8	37.8	62.2	FeNbO$_4$

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

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. Nb-Fe mixed oxide catalysts showed good synergistic effect for the H_2S oxidation. Synergistic effects between Nb_2O_5 and Fe_2O_3 were observed Nb-Fe mixed oxide catalysts showed more improved catalytic performance than single Nb_2O_5 and Fe_2O_3. Nb-Fe binary oxides of different atomic ratios (Nb/Fe = 1/0, 5/1, 3/1, 1/1, 1/2, 1/5, 0/1) and the results that the highest conversion of H_2S was obtained for Nb/Fe = 1/2 since it showed the highest reoxidation capacity and the lowest reduction.
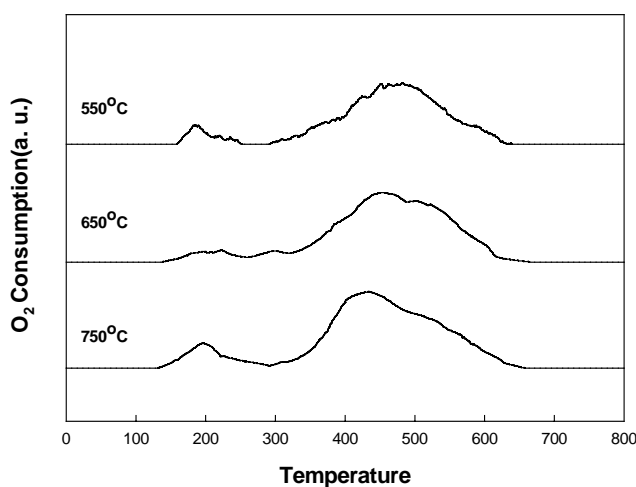

Fig. 1 TPO spectra of different calcinations temperature Nb-Fe catalysts

Acknowledgement

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