



Hydrogen sulfide oxidation on R_E ($R_E = \text{Sm, Y, La}$)-V-Sb catalysts: Effects of R_E size and electronegativity

Kuo-Tseng Li*, Chen-Hwa Huang

Department of Chemical Engineering, Tunghai University, No. 181, Section 3, Taichung Port Road, Taichung, Taiwan, ROC

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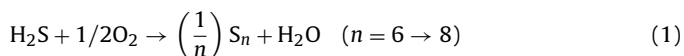
ABSTRACT

Three R_E -V-Sb (R_E was Sm, Y, and La) mixed-oxide catalysts were prepared for catalyzing the selective oxidation of hydrogen sulfide to sulfur. The multiphase R_E -V-Sb catalysts were characterized by TPR, XRD, SEM and BET techniques. Synergistic phenomena in sulfur yield were observed with the solid-state reaction between $R_E\text{VO}_4$ and $\alpha\text{-Sb}_2\text{O}_4$ (antimony oxide/ $R_E\text{VO}_4$ weight ratio = 1/3), which was ascribed to the formation of SbVO_4 species. Under identical reaction conditions, areal reaction rate decreased in the following order: $\text{Sm-V-Sb} > \text{La-V-Sb} \sim \text{LaVO}_4 > \text{Y-V-Sb} > \text{SmVO}_4 > \text{YVO}_4$. All R_E -V-Sb catalysts exhibited 100% sulfur yield in a certain temperature range. The temperature window width for 100% sulfur yield decreased in the following order: $\text{La} > \text{Sm} > \text{Y}$, which was the same as the order of decreasing ionic radius ($\text{La} > \text{Sm} > \text{Y}$) and the order of increasing R_E electronegativity ($\text{La} < \text{Sm} < \text{Y}$). The selectivity difference was explained in terms of active site isolation and product desorption effects. The rare earth cation size effect observed here for H_2S oxidation to elemental sulfur was similar to the alkali cation size effect reported for the hydrocarbon oxidation.

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1. Introduction

Hydrogen sulfide is a by-product of many industrial operations, such as hydrodesulfurization of crude oil, natural gas and coal [1]. It is usually converted to elemental sulfur in sulfur-recovery plants or so-called Claus plants. Due to thermodynamic limitation, the sulfur recovery offered by a Claus process is limited in practice to about 97%. About 1% of H_2S remains in the off-gas of a Claus plant [2]. Because of the strict air pollution regulations, a variety of Claus tail gas treatment (TGT) processes have been developed to increase the total sulfur-recovery efficiency [3]. Dry type Claus TGT processes have been developed which comprise a step of recovering elemental sulfur from Claus tail gas by selective oxidation of hydrogen sulfide using the following catalytic reaction [4,5]:



The method of partial catalytic oxidation of hydrogen sulfide to elemental sulfur, is also being increasing used in industry for treating H_2S -containing natural gases. This method does not require preliminary treatment of the gases and concentration of hydrogen sulfide, is more promising than the Claus method [6].

In addition to the production of sulfur in Eq. (1), sulfur dioxide can also be generated simultaneously due to side reactions (e.g., $(1/n)\text{S}_n + \text{O}_2 \rightarrow \text{SO}_2$). Therefore, a good hydrogen sulfide oxidation catalyst should be able to maximize the sulfur yield and to minimize the sulfur dioxide generation.

Rare earth element is the general name given to the 15 lanthanide elements together with Sc and Y elements. Characteristics of the rare earth elements lie in their relatively large ionic radii (1–1.17 Å) and small electronegativities [7]. Earlier work from our laboratory showed that several rare earth orthovanadates had better sulfur yield than vanadium oxide alone for the selective oxidation of hydrogen sulfide [8]. Sulfur yields of these rare earth orthovanadates were not high enough and their sulfur selectivities were sensitive to temperature change. It is therefore desired to develop catalysts with a higher sulfur yield and with a reasonable range of operation temperature, which can easily withstand inadvertent plant upsets.

In this work, selective oxidation of hydrogen sulfide to sulfur was carried out over three $R_E\text{VO}_4$ (R_E was Sm, Y, and La) with antimony oxide as an additive. We observed that the addition of antimony oxide significantly improved the sulfur yield of these rare earth orthovanadates, and all of the R_E -V-Sb catalysts exhibited 100% sulfur yield in certain temperature ranges. Temperature window width for 100% sulfur yield decreased in the following order: $\text{La} > \text{Sm} > \text{Y}$, which was the same as the order of decreasing ionic radius ($\text{La} > \text{Sm} > \text{Y}$).

* Corresponding author. Fax: +886 4 23590009.
E-mail address: ktli@thu.edu.tw (K.-T. Li).

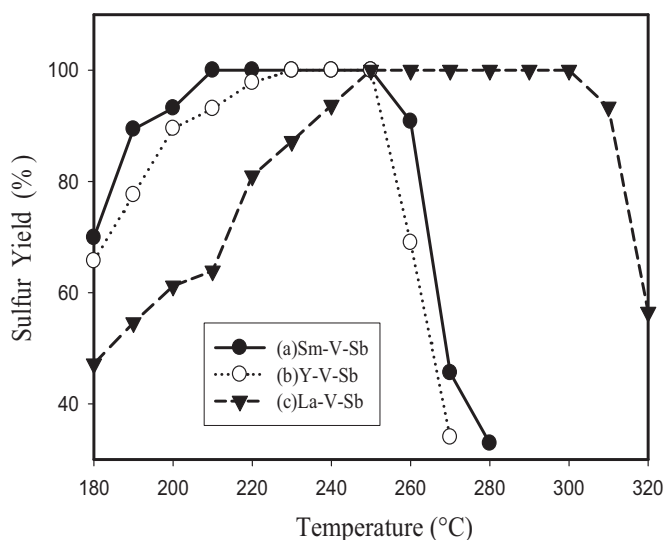


Fig. 1. Effect of reaction temperature on sulfur yield for Sm-V-Sb (curve a), Y-V-Sb (curve b), and La-V-Sb (curve c) catalysts.

2. Experimental

2.1. Catalyst preparation and characterization

R_E -V-Sb catalysts were prepared by mechanically mixing α - Sb_2O_4 with $R_EV_4O_{14}$ (α - $Sb_2O_4/R_EV_4O_{14}$ weight ratio=1/3) in *n*-pentane, followed by evaporation in vacuum (at 60 °C), drying (at 80 °C for 12 h), and calcination (at 600 °C for 144 h). $R_EV_4O_{14}$ was prepared by citrate method [9,10]. The starting materials were Sm_2O_3 (Strem), Y_2O_3 (Strem), La_2O_3 (ACROS Organics, Belgium) and NH_4VO_3 (Showa Chemicals, Tokyo). The main preparation steps were reported before [8]. Crystal structures of the catalysts were analyzed by X-ray diffraction crystallography on a Shimadzu XRD-6000 diffractometer with Cu K α radiation. Catalyst surface areas were determined by nitrogen adsorption with a Micromeritics BET surface area analyzer (Model ASAP2020). Catalyst reducibility was studied with temperature-programmed reduction (TPR) method, which was conducted using 0.15 g of catalyst in a stream of 10% hydrogen in argon and with a heating rate of 10 °C/min. The microscopic aspect of the catalysts was examined under a scanning electron microscope (TOPCON ABT-32).

2.2. Reaction studies

Selective oxidation of hydrogen sulfide to elemental sulfur was carried out in a continuous flow reactor containing 0.2 g of catalyst. Before the catalytic studies, catalysts were pretreated in an environment of 9 vol% hydrogen sulfide at 250 °C for 8 h. After the pretreatment stage, the reactor temperature was decreased to 180 °C and a gaseous feed consisting of 1 vol% hydrogen sulfide, 5 vol% oxygen and 94 vol% nitrogen was introduced into the reactor. The gaseous feed flow rate was 200 ml/min. The experimental data were taken 14 h after the catalyst pre-treatment stage. Experimental results confirmed the good reproducibility was achieved when the same reaction temperature was used, which indicated that the reaction reached the steady state during the tests of catalytic properties.

The gas products were dried and analyzed by a gas chromatograph using a 9-m-long Porapak Q column. Reaction conversion was defined as (moles of hydrogen sulfide reacted)/(moles of hydrogen sulfide fed) \times 100%. Sulfur selectivity was calculated as (moles of hydrogen sulfide reacted-moles of sulfur dioxide produced)/(moles

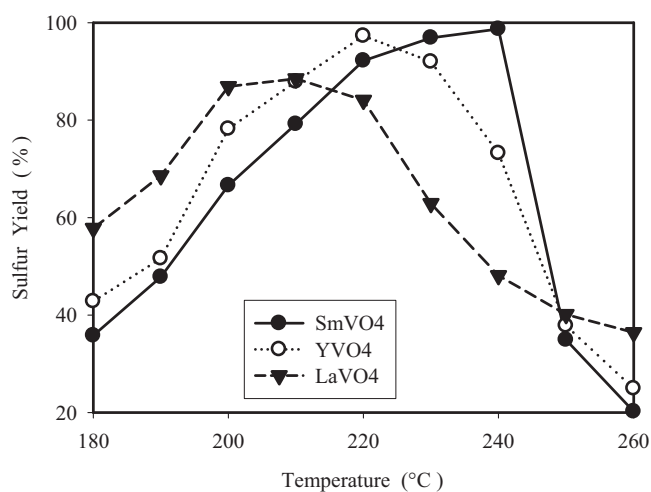


Fig. 2. Relationships between sulfur yield and reaction temperature for SmVO₄, YVO₄, and LaVO₄.

of hydrogen sulfide reacted) \times 100%. Sulfur yield was defined as conversion times selectivity.

3. Results and discussion

3.1. Oxidation of hydrogen sulfide

Figs. 1 and 2 present the relationships between sulfur yield and reaction temperature for R_E -V-Sb catalysts and for $R_EV_4O_{14}$ catalysts, respectively. The curves in Figs. 1 and 2 exhibit a volcano shape with a maximum sulfur yield because conversion increased with temperature while selectivity decreased with temperature. In certain temperature ranges, the maximum sulfur yield reached 100% for all R_E -V-Sb catalysts. The width of temperature window for 100% sulfur yield were 50 °C (in the temperature range of 250–300 °C), 30 °C (in the temperature range of 210–240 °C), and 20 °C (in the temperature range of 230–250 °C) for La-V-Sb, Sm-V-Sb, and Y-V-Sb catalysts, respectively. That is, the temperature window width for 100% sulfur yield decreased in the following order: La-V-Sb > Sm-V-Sb > Y-V-Sb.

For $R_EV_4O_{14}$ alone, the maximum sulfur yields obtained for LaVO₄, SmVO₄, and YVO₄ were 88.5% (at 210 °C), 98.7% (at 240 °C), and 97.3% (at 220 °C), respectively (shown in Fig. 2). For $R_EV_4O_{14}$ alone, the R_E radius size might change the extent of crystal lattice distortion and resulted in the differences in performances.

In order to minimize the emissions of both H₂S and SO₂, the maximum sulfur yield is the most important criterion for evaluating catalyst performance in the selective oxidation of hydrogen sulfide because sulfur yield = H₂S conversion \times sulfur selectivity. Hence, the results in Figs. 1 and 2 indicate that the catalytic performances of R_E -V-Sb samples were superior to those of $R_EV_4O_{14}$ alone, and R_E -V-Sb catalysts exhibited synergistic behavior in the catalytic performances for hydrogen sulfide oxidation.

The oxidation of H₂S may proceed as a sequential oxidation (H₂S \rightarrow S \rightarrow SO₂). The decrease of sulfur yield at the higher temperature range (shown in Figs. 1 and 2) suggest that the second reaction step (S \rightarrow SO₂) has greater activation energy than the first reaction step (H₂S \rightarrow S). In the lower temperature range, the second step reaction was not significant and the only product obtained was elemental sulfur. In the higher temperature range, the second step reaction became more significant and its rate increased rapidly with increasing temperature. Therefore, more sulfur was converted to sulfur dioxide and the sulfur selectivity and sulfur yield decreased with increasing temperature.

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