Effect of supports in hydrogen sulfide oxidation on vanadium-based catalysts

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Selective oxidation of hydrogen sulfide to sulfur was carried out over V_2O_5 and V–Sb–O mixed-oxide catalysts supported on TiO_2, ZrO_2 and γ-Al_2O_3. TiO_2-supported catalysts exhibited the highest sulfur yield and the highest areal rate. Catalyst reducibility was studied by temperature-programmed reduction.

Keywords: hydrogen sulfide oxidation, sulfur selectivity and yield, supported vanadium oxide catalysts, V_2O_5–TiO_2 interaction

1. Introduction

In petroleum refineries and natural gas-treating plants, hydrogen sulfide is usually converted to elemental sulfur by the Claus process [1]. The conversion of hydrogen sulfide in the Claus process is not complete (sulfur recovery of up to 97% can be typically achieved) due to thermodynamics limitation. The remaining hydrogen sulfide in the Claus effluent must be removed by additional costly tail-gas-treating (TGT) systems. Catalytic oxidation of hydrogen sulfide with molecular oxygen to elemental sulfur has been developed for the removal of H_2S in TGT processes. Comprimo's SuperClaus process [2] is an example of using a catalyst (α-alumina-supported iron oxide/chromium oxide) to catalyze the oxidation of H_2S in the Claus tail gas to sulfur via the reaction:

$$H_2S + (1/2)O_2 \rightarrow (1/n)S_n + H_2O \qquad (1)$$

In addition to the production of sulfur in the above reaction, sulfur dioxide may be generated as a major by-product. Therefore, a good catalyst for the selective oxidation of hydrogen sulfide should be able to maximize the sulfur yield and to minimize the sulfur dioxide generation.

Earlier work from our laboratory has shown that several unsupported vanadium-based mixed-oxide catalysts were effective for catalyzing the reaction between hydrogen sulfide and oxygen to elemental sulfur [3,4]. In the present work, the effect of supports on the catalytic performance of vanadium-based oxides for the selective oxidation of hydrogen sulfide to sulfur has been investigated, from which we have found that the sulfur yields of TiO_2-supported catalysts are much better than those of unsupported catalysts and other supported catalysts.

2. Experimental

Three materials were used as supports: γ-Al_2O_3, TiO_2, and ZrO_2. γ-Al_2O_3 (surface area = 86.7 m^2/g) and ZrO_2 (surface area = 24.6 m^2/g) were obtained from Strem Chemicals, while TiO_2 (surface area = 6 m^2/g) was supplied by ACROS Chemicals. Supported catalysts with 5 wt% V_2O_5 were prepared by impregnating the supports with an aqueous solution (pH = 6) of NH_4VO_3 (Riedel–deHaen, Germany) followed by drying at 120 °C for 18 h and then calcining in air at 450 °C for 5 h. Sb_2O_3 (ACROS) was added into the NH_4VO_3 aqueous solution for the preparation of supported V–Sb–O catalysts (5 wt% V_2O_5 with 2.5 wt% Sb_2O_3, i.e., Sb/V atomic ratio = 0.3).

Unsupported V_2O_5 and unsupported V–Sb–O mixed oxide (with Sb/V atomic ratio = 0.3) were also used for comparison. The unsupported V_2O_5 catalyst was obtained from Riedel–deHaen. The unsupported V–Sb–O mixed oxide was prepared by mixing appropriate amounts of NH_4VO_3 and Sb_2O_3 in 0.1 N oxalic acid solution (ACROS), followed by evaporation, drying and calcination.

Reduction characteristics of the catalysts were studied by the temperature-programmed reduction (TPR) method. 0.15 g catalyst was reduced in a 10% H_2/Ar gas flow (30 ml/min) at 1 atm. The reduction temperature was increased from room temperature to 800 °C with a heating rate of 10 °C/min. Water produced from the reduction was removed with small beads of molecular sieve. The hydrogen consumption was recorded as a function of reduction temperature using a thermal conductivity detector.

The catalytic test of hydrogen sulfide oxidation was conducted in a fixed-bed glass reactor. The weight of catalyst packing was 0.2 g. Before the measurement of catalytic properties, the catalyst was pretreated in an environment of 15 vol% hydrogen sulfide, 25 vol% oxygen, and 60 vol% nitrogen at 250 °C for 12 h. After the pretreatment stage, the reactor temperature was decreased to 180 °C and a

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gaseous feed consisting of 1 vol% hydrogen sulfide, 5 vol% oxygen and 94 vol% nitrogen was introduced into the reactor. The flow rate of gaseous feed was 200 ml/min. The data at 180 °C was taken at 12 h after the catalyst pretreatment stage and the data at 270 °C was taken at 21 h after the catalyst pretreatment stage. After the data at 270 °C was taken, the reactor temperature was decreased to 180 °C again, and data was taken at this temperature again. Experimental results confirmed that good reproducibility was achieved when the same reaction temperature was used.

Gaseous components in the reactor effluent were analyzed by gas chromatography. The conversion of hydrogen sulfide, sulfur selectivity, and sulfur yield were calculated using the following equations: conversion of hydrogen sulfide (%) $=$ (moles of hydrogen sulfide reacted/moles of hydrogen sulfide fed) $\times$ 100%; sulfur selectivity $=$ [(moles of hydrogen sulfide reacted – moles of sulfur dioxide produced)/moles of hydrogen sulfide reacted] $\times$ 100%; sulfur yield $=$ conversion of hydrogen sulfide $\times$ sulfur selectivity. In the lower reaction temperature range, sulfur yield is determined by hydrogen sulfide conversion, because sulfur selectivity is about 100% at low H_2S conversion. In the higer reaction temperature range, sulfur yield is mainly determined by sulfur selectivity.

3. Results and discussion

Figure 1 illustrates the relationship between sulfur yield and reaction temperature for H_2S oxidation over $V_2O_5/\gamma\text{-}Al_2O_3$, V_2O_5/ZrO_2, V_2O_5/TiO_2 and unsupported V_2O_5. With the increase of reaction temperature, H_2S conversion increases while sulfur selectivity decreases, therefore, there is a maximum sulfur yield for each catalyst. The maximum sulfur yield obtained for (a) unsupported V_2O_5 (V/Un), (b) $V_2O_5/\gamma\text{-}Al_2O_3$ (V/Al), (c) V_2O_5/ZrO_2 (V/Zr), and (d) V_2O_5/TiO_2 (V/Ti) is 79.5, 77.1, 83.2 and 90.4%, respectively. The results in figure 1 indicate that TiO_2-supported V_2O_5 catalyst has significantly better sulfur yield than other catalysts.

Figure 2 shows the sulfur yield as a function of reaction temperature for three supported V–Sb–O catalysts (the loading of V_2O_5 is 5 wt% and Sb/V atomic ratio 0.3) and one unsupported V–Sb–O catalyst (Sb/V atomic ratio 0.3). The addition of antimony oxide improves the catalyst performance significantly. The maximum sulfur yield obtained for (a) unsupported V–Sb–O (VSb/Un), (b) V–Sb–O/$\gamma\text{-}Al_2O_3$ (VSb/Al), (c) V–Sb–O/ZrO_2 (VSb/Zr), and (d) V–Sb–O/TiO_2 (VSb/Ti) is 90.3, 91.9, 100 and 100%, respectively. These sulfur yields are much higher than those obtained with the corresponding V_2O_5 catalysts.

It is worth noting that sulfur yields of the V–Sb–O/TiO_2 catalyst (curve (d) in figure 2) remain relatively constant (sulfur yields are in the range of 95–100%) between 200 and 250 °C, while the sulfur yields of other catalysts (curves (a)–(c) in figure 2) decrease rapidly after 210 °C. The results suggest that sulfur selectivity of the V–Sb–O/TiO_2 catalyst is less sensitive to temperature change. Hence, the V–Sb–O/TiO_2 catalyst has a much wider operating temperature window compared to other catalysts.

Table 1 presents the reaction rates per unit surface area for the supported catalysts at 180 °C. The results show that the areal reaction rate of the supported catalysts decreased in the order V–Sb–O/TiO_2 $>$ V_2O_5/TiO_2 $>$ V–Sb–O/ZrO_2 $>$ V_2O_5/ZrO_2 $>$ V–Sb–O/$\gamma\text{-}Al_2O_3$ $>$ $V_2O_5/\gamma\text{-}Al_2O_3$. That is, TiO_2-supported catalysts had the high-

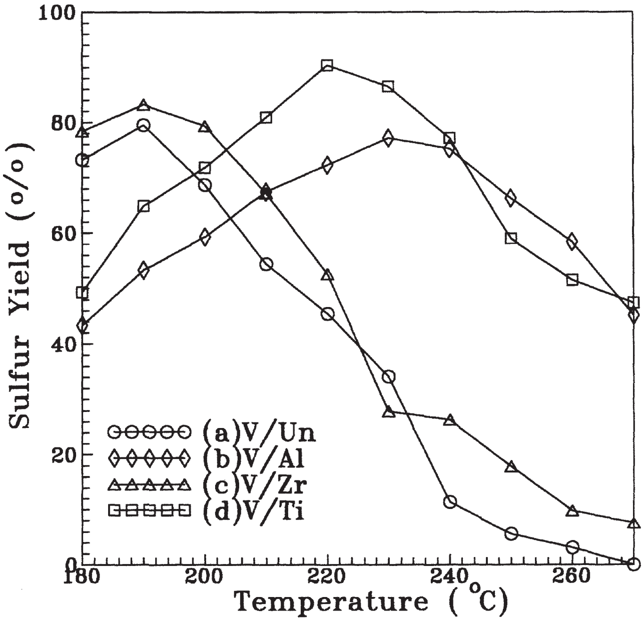

Figure 1. Sulfur yield of V_2O_5 catalysts: (a) unsupported V_2O_5 (V/Un), (b) $V_2O_5/\gamma\text{-}Al_2O_3$ (V/Al), (c) V_2O_5/ZrO_2 (V/Zr), and (d) V_2O_5/TiO_2 (V/Ti).

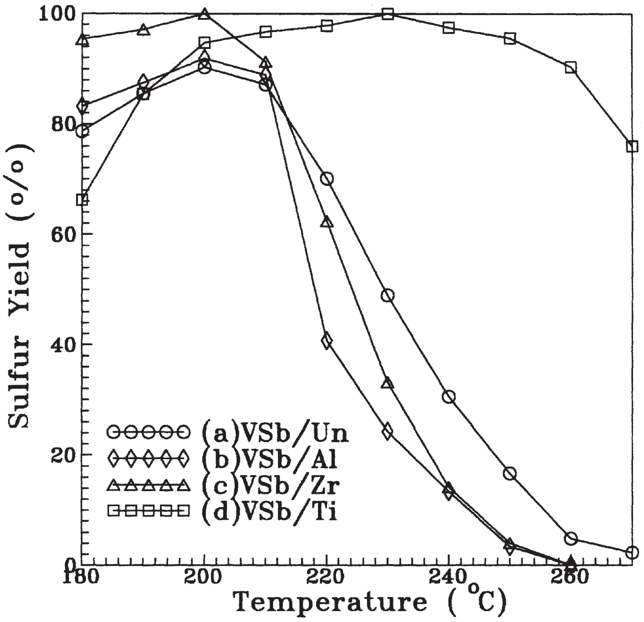

Figure 2. Sulfur yield of V–Sb–O catalysts: (a) unsupported V–Sb–O (VSb/Un), (b) V–Sb–O/$\gamma\text{-}Al_2O_3$ (VSb/Al), (c) V–Sb–O/ZrO_2 (VSb/Zr), and (d) V–Sb–O/TiO_2 (VSb/Ti).

Table 1
Catalytic activities of supported vanadia catalysts at 180 °C.

Supported catalyst	H_2S conversion (%)	BET surface area of used catalysts (m^2/g)	Reaction rate × 10^5 (gmol/(m^2 min))
V_2O_5/γ-Al_2O_3	43.4	58.9	0.3
V_2O_5/ZrO_2	78.4	20.3	1.58
V_2O_5/TiO_2	49.3	6.2	3.24
V–Sb–O/γ-Al_2O_3	83.2	68.4	0.5
V–Sb–O/ZrO_2	95.4	19.6	1.99
V–Sb–O/TiO_2	66.2	6.02	4.49

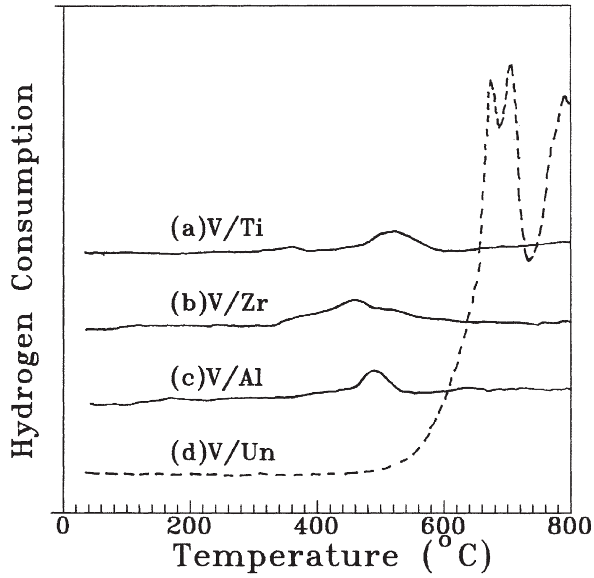

Figure 3. TPR profiles of V_2O_5 catalysts: (a) V_2O_5/TiO_2 (V/Ti), (b) V_2O_5/ZrO_2 (V/Zr), (c) V_2O_5/γ-Al_2O_3 (V/Al), and (d) unsupported V_2O_5 (V/Un).

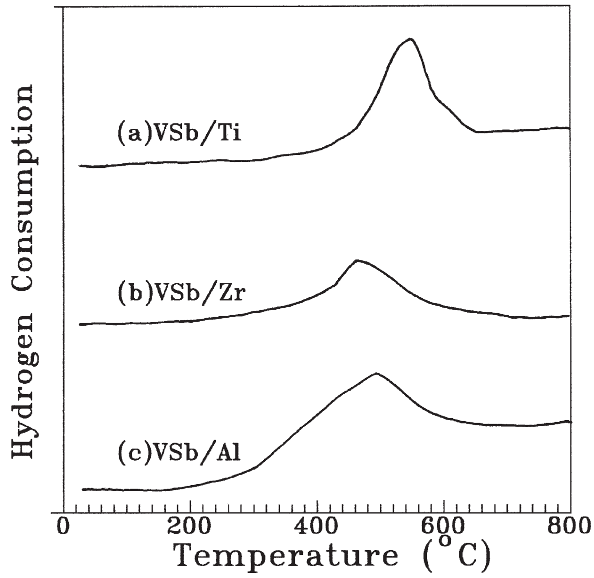

Figure 4. TPR profiles of supported V–Sb–O catalysts: (a) V–Sb–O/TiO_2 (VSb/Ti), (b) V–Sb–O/ZrO_2 (VSb/Zr), and (c) V–Sb–O/γ-Al_2O_3 (VSb/Al).

est areal rates and the catalytic activities of the supported V–Sb–O catalysts were significantly higher than those of the corresponding vanadia catalysts.

The higher activity and selectivity (i.e., better sulfur yield) for TiO_2-supported catalysts reported above might be due to the following two reasons: (1) the strong interaction between the surface of anatase TiO_2 and vanadium oxide which resulted in the stabilization of VO_x monolayer species [5,6]; (2) a close match between the structure of V_2O_5 and anatase TiO_2 [7].

Reducibility of the catalysts was measured using the temperature-programmed reduction (TPR) method with hydrogen as the reductant. Figure 3 shows the TPR profiles of V_2O_5 catalysts. The temperature of maximum hydrogen consumption ($T_{\max}$) obtained for (a) V_2O_5/TiO_2 (V/Ti), (b) V_2O_5/ZrO_2 (V/Zr), and (c) V_2O_5/γ-Al_2O_3 (V/Al) is 535, 455, and 483 °C, respectively. For unsupported V_2O_5 (V/Un, profile (d) in figure 3, represented by a dashed line), there are three peak maxima which occur at 650, 685, and 790 °C. The peak area of unsupported V_2O_5 is much larger than those of supported V_2O_5 catalysts, because the amount of V_2O_5 in unsupported sample is 20 times as large as those in supported samples (contained 5 wt% V_2O_5 only).

It is known that $T_{\max}$ depends strongly on the loading of V_2O_5 on the support. Bond and coworkers [8,9] found that the $T_{\max}$ for low-area TiO_2 with 5 wt% V_2O_5 was about 530 °C. They also found three peaks in the TPR profiles for pure V_2O_5, which occurred at about 670, 700, and 770 °C. Therefore, the $T_{\max}$ values we obtained in figure 3 for TiO_2-supported catalyst and unsupported catalyst are similar to those obtained by Bond and coworkers. Temperature-programmed reduction has also been recently used for studying V_2O_5/ZrO_2 by Albrecht et al. [10], and for studying V_2O_5/γ-Al_2O_3 by Blasco el al. [11]. Based on their data, the peak maximum temperature was about 460 °C for 5 wt% V_2O_5/ZrO_2, and around 500 °C for 5 wt% V_2O_5/γ-Al_2O_3. These peak temperature values are similiar to the $T_{\max}$ values we obtained in figure 3.

Figure 4 shows TPR profiles of the supported V–Sb–O catalysts. $T_{\max}$ values for (a) V–Sb–O/TiO_2 (VSb/Ti), (b) V–Sb–O/ZrO_2 (VSb/Zr), and (c) V–Sb–O/γ-Al_2O_3 (VSb/Al) are 540, 467, and 490 °C, respectively, which are similar to those obtained for supported V_2O_5 catalysts. The peak areas for the supported V–Sb–O catalysts are significantly larger that those of supported V_2O_5 catalysts, which should be due to the presence of additional 2.5 wt% antimony oxide in the supported V–Sb–O catalysts. Antimony oxide can be considered as oxygen donor [12] which may increase the amount of lattice oxygen available for the oxidation of hydrogen sulfide. This should be the major reason that V–Sb–O catalysts have higher catalytic activity than the corresponding V_2O_5 catalysts.

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