

Selective catalytic oxidation of H₂S using nonhydrolytic vanadia-titania xerogels

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Abstract—A series of vanadia-titania (V-Ti) xerogel catalysts were prepared by nonhydrolytic sol-gel method. These catalysts showed much higher surface area and total pore volumes than the conventional V₂O₅-TiO₂ xerogel. Two species of surface vanadium in the xerogel catalysts were identified by Raman measurements: monomeric vanadyl and polymeric vanadates. The selective oxidation of hydrogen sulfide in the presence of excess water and ammonia was studied over these catalysts. Xerogel catalysts from the nonhydrolytic method showed very high conversion of H₂S without harmful emission of SO₂. The conversion of H₂S increased with increasing vanadia loading up to 10V-Ti; however, it decreased at higher vanadia loading (12V-Ti and 18V-Ti) probably due to the formation of crystalline V₂O₅.

Key words: Hydrogen Sulfide, Selective Oxidation, Nonhydrolytic, Sol-gel Method, Vanadia-titania Xerogel, Ammoniumthiosulfate

INTRODUCTION

Developing SO_x emission control technology has received significant attention since legal regulation has become more severe. Now, a large amount of SO_x results from H₂S that is released from refineries of crude oil, natural gas and coke ovens of the steel industry. H₂S in the coke oven gas released from the steel smelting process is scrubbed and concentrated by using aqueous ammonia solution. Concentrated H₂S that is separated from aqueous ammonia is transferred to a Claus plant [1,2] to convert it into elemental sulfur, and the remaining aqueous ammonia is usually incinerated. However, the separation of H₂S from the aqueous ammonia is not perfect. Remaining aqueous ammonia stream contains about 2% H₂S, which in turn causes the SO_x emission problem during the incineration.

Although many works have been reported for the selective oxidation of H₂S without ammonia [3-12], very few have been reported for the conversion of H₂S containing excess water and ammonia.

One approach is the selective catalytic oxidation of H₂S to ammonium thiosulfate (ATS) and elemental sulfur as reported in our previous works [12-14]. We reported a new vapor phase catalytic process for the selective conversion of H₂S in the stream containing both ammonia and water. V₂O₅/SiO₂, Fe₂O₃/SiO₂ and Co₃O₄/SiO₂ catalysts showed good catalytic activities in the selective oxidation of the H₂S to ATS and sulfur. The conventional process for the production of ATS is based on the liquid phase reactions. The Claus tail gas clean-up process [15] is divided into two sections: absorption of SO₂ from incinerator in aqueous ammonia and conversion of the intermediate product to ATS by sparging H₂S into the converter. Therefore, our process has the advantage of direct vapor phase operation compared to the conventional process.

In sol-gel methods, which are based on the hydrolysis-conden-

sation of molecular precursors, such as metal alkoxides, the major problem is to control the reaction rates which are generally too fast, resulting in loss of microstructural control over the final oxide material [16]. An attractive solution is to use organic additives which act as chelating ligands (carboxylic acids, β -diketones, etc.) and modify the reactivity of the precursors [17]. One alternative strategy is provided by nonhydrolytic sol-gel processes, in which precursors, solvents, experimental conditions, catalysts, and reaction mechanisms are changed [18,19].

The preparation of V₂O₅-TiO₂ catalysts has been intensively studied during the last two decades [20]. Elaborate procedures have been used to increase the activity of vanadia-titania catalysts, such as multiple grafting, sol-gel synthesis using chemically modified precursors and 2-step procedures to improve the dispersion of vanadia species, or supercritical drying to increase the specific surface area of the catalyst [21,22]. The nonhydrolytic sol-gel process [23] offers a simple and efficient way to prepare mixed oxides [24]. This process is based on the condensation between chloride and alkoxide groups at moderate temperature (around 100 °C). The alkoxide groups can also be formed in situ, for instance, by reaction of chlorides with an organic ether, thus avoiding the use of expensive alkoxide precursors.

In this work, we report the nonhydrolytic sol-gel synthesis of vanadia-titania xerogels and their catalytic performance on the selective oxidation of H₂S to elemental sulfur.

EXPERIMENTAL

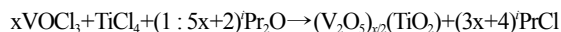
1. Preparation of V₂O₅-TiO₂ Xerogel

The catalysts were obtained by heating the reactants under autogenous pressure (about 6-7×10⁵ Pa) in a sealed tube (100 mL, heavy-wall Pyrex tube). Vanadyl (V) chloride (VOCl₃, Aldrich, 99%) was introduced first, then titanium (IV) chloride (TiCl₄, Acros Organics, 99.9%), and finally di-isopropyl ether (Pr₂O, Acros Organics, 99%) was added. No solvent was used, excepted for 6V-Ti, where a small amount of CH₂Cl₂ was needed to get a clear solution.

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$\text{V}_2\text{O}_5\text{-TiO}_2$ gels with vanadia loadings ranging from 6 to 18 wt% were prepared by nonhydrolytic condensation of VOCl_3 and TiCl_4 with Pr_2O at 383 K under autogenous pressure [25]:



The glass tube was frozen in liquid nitrogen and then sealed under vacuum; it was subsequently held at 383 K in an oven for 3 days. The tube was opened under argon and the gel (colored from dark brown to black) was first dried under vacuum at room temperature and then at 393 K during 12 h. Finally, the samples were calcined at 773 K (heating ramp 10 K min^{-1} , air flow $50\text{ cm}^3\text{ min}^{-1}$) for 5 h, turning into beige to green-brown powders. The samples were labeled as xV-Ti, where x refers to the (approximate) V_2O_5 weight percentage in the sample.

2. Characterization

The texture of the mixed oxide catalysts was studied by nitrogen physisorption at 77 K with a Micromeritics ASAP 2000 instrument; adsorption-desorption isotherms, specific surface area (S_{BET}), mean pore diameter ($D_p = 4V_p/S_{\text{BET}}$, where V_p is the total pore volume), and pore size distribution (using the BJH model for the desorption branch of the isotherms) were determined. Before measurement the samples were outgassed at 573 K to about 2 Pa. The elemental analyses were carried out at the Service Central d'Analyse du CNRS (Vernaison, France).

X-ray diffraction patterns were obtained on a Seifert powder diffractometer, in the 2θ range $19\text{--}90^\circ$, using Ni filtered $\text{Cu K}\alpha$ radiation, with the anode operating under 40 kV and 25 mA. The average size of the anatase crystallites was estimated from the broadening of the diffraction peak at $2\theta = 25.3^\circ$ by using the Debye-Scherrer formula.

FT-Raman analysis was done on a Labram 1B Confocal Jobin-Yvon spectrometer; excitation was provided by a 10 mW He-Ne laser at 632.8 nm.

3. Reactivity Test

Reaction tests were performed in a continuous flow fixed-bed reactor. The reactor was made of a Pyrex[®] tube with an i.d. of 1 inch. A condenser was attached at the effluent side of the reactor, and its temperature was constantly maintained at 110°C to condense only solid products (sulfur+ammonium thiosulfate). 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°C 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 by a stream evaporator filled with small glass beads, and its amount was controlled by a syringe pump. In a typical experiment the reactant mixture consisted of 5 vol% H_2S , 2.5 vol% O_2 , 5 vol% NH_3 , 20 vol% H_2O (vapor) and balance helium.

The content of effluent gas was analyzed by a gas chromatograph (HP 5890) equipped with a thermal conductivity detector and a 6 ft Porapak T column (80-100 mesh) at 100°C . The exit 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 SO_2 , S and ATS are defined as follows:

$$\text{Conversion of } \text{H}_2\text{S (X)} = \frac{[\text{H}_2\text{S}]_{\text{inlet}} - [\text{H}_2\text{S}]_{\text{outlet}}}{[\text{H}_2\text{S}]_{\text{inlet}}} \times 100(\%)$$

Selectivity (S) to a special product (SO_2 , S, ATS)

$$= \frac{[\text{Product}]_{\text{outlet}}}{[\text{H}_2\text{S}]_{\text{inlet}} - [\text{H}_2\text{S}]_{\text{outlet}}} \times 100(\%)$$

For the calculation of ATS selectivity, moles of ATS was multiplied by a factor of 2 because one mole of ATS can be obtained from two moles of H_2S .

RESULTS AND DISCUSSION

1. Characterization of Catalysts

Table 1 shows surface area, pore volume, and average pore diameter of the $\text{V}_2\text{O}_5\text{-TiO}_2$ xerogel prepared by the nonhydrolytic sol-gel method. When the vanadia loading increases, the specific surface area and the pore volume decrease. Average pore diameter decreases with increasing vanadia loading. This progressive disappearance of the smaller mesopores when the vanadia loading increases could result from the sintering of the anatase particles and also from the progressive filling with vanadia species of the mesopores between

Table 1. Physicochemical properties of V-Ti xerogels

Catalyst	V_2O_5 (wt%)	S_{BET} (m^2/g)	V_p (cm^3/g)	D_p (nm)
6V-Ti	6.5	87	0.30	13.8
8V-Ti	8.4	81	0.27	13.3
10V-Ti	10.6	78	0.24	12.3
12V-Ti	12.3	46	0.22	22.3
18V-Ti	18.3	26	0.22	33.8
Xerogel ^a	6.0	12	0.02	6.9
Impregnated ^b	6.0	50	0.28	23.0

^aConventional $\text{V}_2\text{O}_5\text{-TiO}_2$ xerogel catalyst with 6 wt% vanadium loading.

^bImpregnated $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst with 6 wt% vanadium loading.

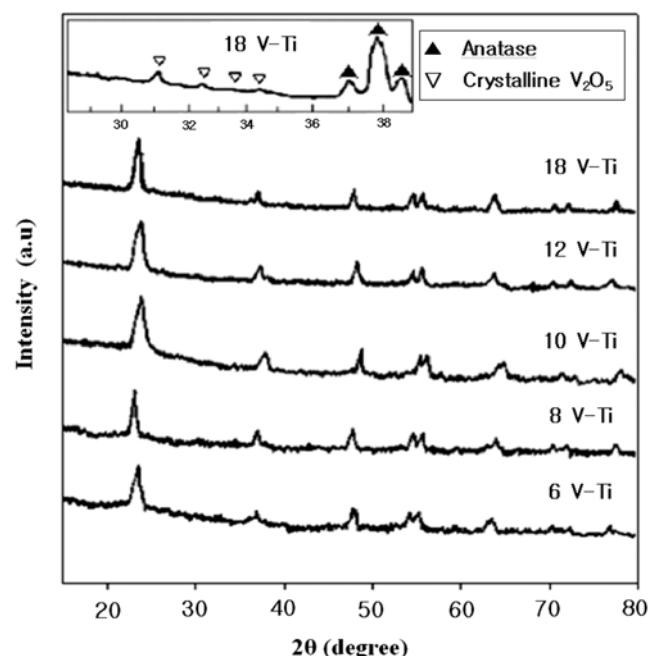


Fig. 1. X-ray diffraction patterns of different V-Ti xerogels.

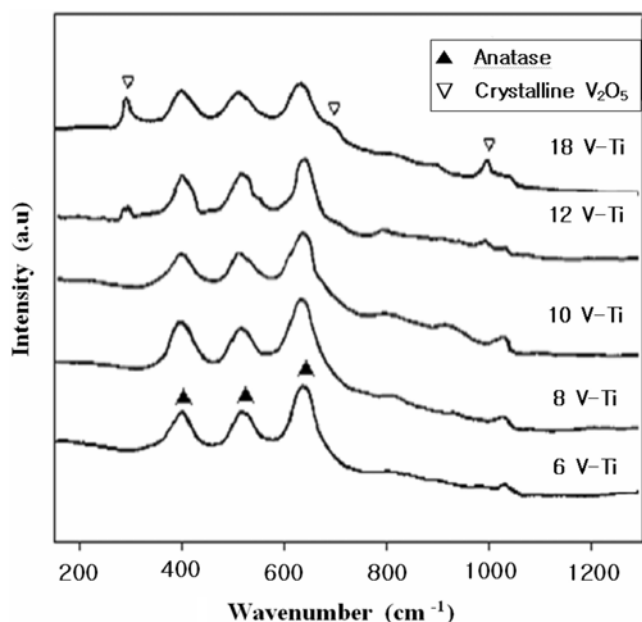


Fig. 2. Raman spectra of different V-Ti xerogels.

at relatively high V₂O₅ contents (78 m² g⁻¹ for 10V-Ti) despite the high calcination temperature (5 h at 773 K), which is not so common for V₂O₅-TiO₂ xerogels prepared by one-step processes.

The X-ray diffraction patterns of the V₂O₅-TiO₂ materials (Fig. 1) reveal the presence of TiO₂ anatase crystallites. The average sizes of these crystallites, estimated from the broadening of the diffraction peaks, increase from about 15 nm in samples 6V-Ti, 8V-Ti, and 10V-Ti, to about 25 nm in 12V-Ti and 35 nm in 18V-Ti. Whatever the composition, there is no evidence of the presence of TiO₂ rutile, although the powders were calcined at 773 K for 5 h. Crystalline V₂O₅ (scherbinaite) was detected only for the samples with the highest vanadia loadings (12 and 18 wt%).

Raman spectroscopy (Fig. 2) confirms these findings. For all of the samples, Raman bands at 390, 506, and 628 cm⁻¹ point to the presence of anatase and the lack of bands at 446 and 610 cm⁻¹ confirm the absence of rutile. In the spectra of 12V-Ti and 18V-Ti bands at 285, 703, and 997 cm⁻¹ indicate the presence of crystalline V₂O₅. Raman spectroscopy provides additional insight into the nature of vanadia species. Thus, the bands found in the spectra of samples 6V-Ti, 8V-Ti, and 10V-Ti around 930 cm⁻¹ (broad) and 1,030 cm⁻¹ (sharp) may be ascribed to polymeric and monomeric vanadia surface species, respectively. These results indicate that up to a critical V₂O₅ loading (about 12 wt%) all the vanadium is highly dispersed, whereas for higher loadings V₂O₅ crystallites form.

2. Selective Oxidation of H₂S

The selective oxidation of hydrogen sulfide was studied by using V₂O₅-TiO₂ xerogels of different vanadium loading. Fig. 3 shows H₂S conversion for these catalysts after 2 h of reaction at 220–300 °C with the reactant composition of H₂S/O₂/He=5/2.5/92.5, and GHSV=30,000 h⁻¹.

The H₂S conversion increases with increasing temperature from 220 to 240 °C, then it increases a little over 260 °C. When vanadia loading increases from 6V-Ti to 10V-Ti, the H₂S conversion increases. However, the H₂S conversion decreases for high loading of vana-

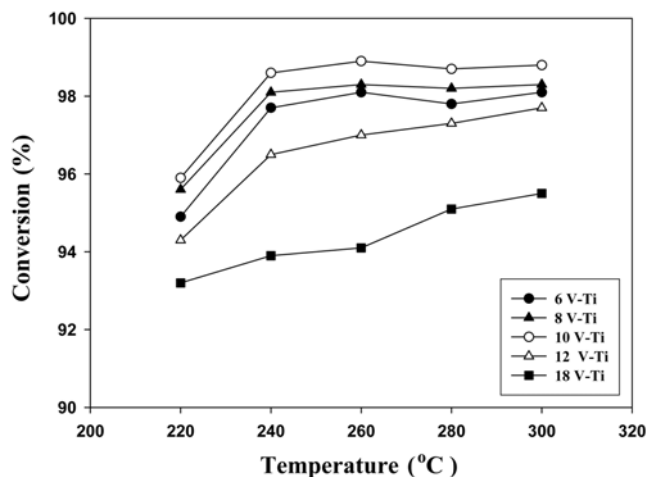


Fig. 3. The conversion of H₂S for V-Ti xerogels at different reaction temperatures (Reactant composition: H₂S/O₂/He (vol%) = 5/2.5/92.5, GHSV=30,000 h⁻¹, reaction time=2 h).

dia, 12V-Ti and 18V-Ti.

It is known that the following elementary reactions occur in the Claus process, where there is no existence of ammonia [26].



Reaction (1) is a main reaction and other oxidation reactions ((2) and (3)) and the reversible Claus reaction (reaction (4)) as the side reaction.

The role of TiO₂ in V₂O₅/TiO₂ catalyst has also been studied by several authors [27–30] and is well reviewed by Wachs and Weckhuysen [27]. The terminal V=O bonds have been proposed by many investigators to contain critical oxygen involved in hydrocarbon oxidation reactions over supported vanadia catalysts [31]. However, the combination of *in situ* Raman and hydrocarbon oxidation reactivity studies [32] suggests that the terminal V=O bonds and V-O-V bonds do not critically influence the oxidation reactions. The bridging V-O-support bond appears to be the most critical bond which can change the TOF for hydrocarbon oxidation reactions.

From the XRD and Raman results, crystalline V₂O₅ was formed for high vanadia loading (12V-Ti and 18V-Ti). Therefore, the decreases of H₂S conversion for the high vanadia loading catalysts could be ascribed to the presence of crystalline V₂O₅.

Fig. 4 shows the H₂S conversion at the same experimental condition of Fig. 3 except the reactant composition with water vapor: H₂S/O₂/H₂O/He=5/2.5/20/72.5. One can also observe the increase of H₂S conversion with increasing vanadia loading from 6V-Ti to 10V-Ti, and it decreases for high vanadia loading (12V-Ti and 18V-Ti). When compared to Fig. 3 (without H₂O), the H₂S conversions in Fig. 4 (with H₂O) for the same V-Ti catalyst showed lower values for all the catalysts. This might be explained by the presence of water vapor in the reactant mixture. The water vapor inhibits the forward reaction (1) and (3). It also accelerates the reverse reaction of the

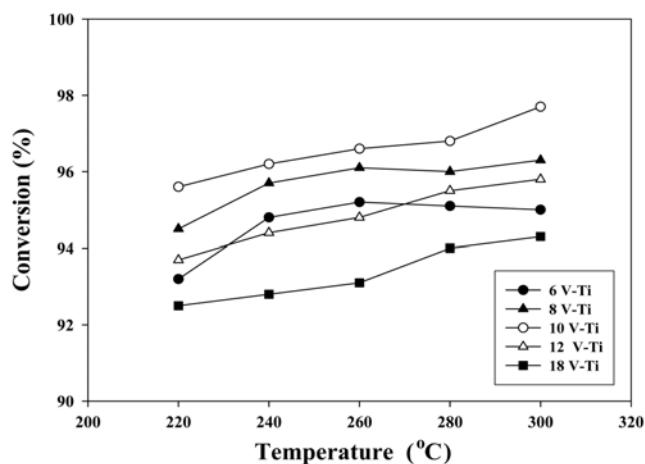


Fig. 4. The conversion of H₂S for V-Ti xerogels at different reaction temperatures in the presence of water vapor (Reactant composition: H₂S/O₂/H₂O/He (vol%)=5/2.5/20/72.5, GHSV=30,000 h⁻¹, reaction time=2 h).

Table 2. Conversion of H₂S and selectivities to products for 8V-Ti xerogel catalyst at different reaction temperatures

Temp. (°C)	X-H ₂ S (%)	S-SO ₂ (%)	S-S (%)	S-ATS (%)
220	88.6	0	45.3	54.7
240	93.7	0	38.9	61.1
260	98.2	0	26.3	73.7
280	96.8	0	23.2	76.8
300	95.9	0	20.1	79.9

Reaction condition: H₂S/O₂/NH₃/H₂O/He=5/2.5/5/20/67.5, GHSV=30,000 h⁻¹, reaction time=6 h.

Claus reaction (Eq. (4)).

The effects of temperature on the product selectivities were studied with 8V-Ti catalyst. Table 2 shows the H₂S conversion and selectivities of SO₂, sulfur, and ammonium thiosulfate (ATS) after 6 h of reaction with the presence of ammonia in the reaction mixture: H₂S/O₂/NH₃/H₂O/He=5/2.5/5/20/67.5.

The catalyst showed maximum H₂S conversion at 260 °C, then the activity decreased slightly with increasing temperature. Table 2 also shows that the S-ATS increased, but S-S decreased with increasing temperature. As reported in our previous works [33,34], higher temperature yielded more production of SO₂ and less production of elemental sulfur than low temperature did in the H₂S oxidation without NH₃. With the presence of NH₃, the produced SO₂ can react to form (NH₄)₂SO₃, then finally to produce ATS by the reaction (5) and (6).



The product distribution for different V-Ti catalysts with the same reaction mixture of Table 2 at 260 °C is shown in Table 3. The H₂S conversion and selectivity of ATS increased with increasing vanadia loading up to 10V-Ti. Then they decreased for 12V-Ti and 18V-Ti, probably due to the formation of crystalline V₂O₅.

All the V-Ti catalysts showed very high H₂S conversion without

Table 3. Conversion of H₂S and selectivities to products for different catalysts at 260 °C

Catalyst	X-H ₂ S (%)	S-SO ₂ (%)	S-S (%)	S-ATS (%)
6V-Ti	97.9	0	35.5	64.5
8V-Ti	98.2	0	26.3	73.7
10V-Ti	98.9	0	21.5	78.5
12V-Ti	96.3	0	24.6	75.4
18V-Ti	90.5	0	33.4	66.6
Xerogel ^a	80.2	8.1	34.8	57.1
Impregnated ^b	81.6	0	60.2	39.8

Reaction condition: H₂S/O₂/NH₃/H₂O/He=5/2.5/5/20/67.5, GHSV=30,000 h⁻¹ Temp=260 °C, reaction time=6 h.

^aConventional V₂O₅-TiO₂ xerogel catalyst with 6 wt% vanadium loading

^bImpregnated V₂O₅/TiO₂ catalyst with 6 wt% vanadium loading

any considerable emission of sulfur dioxide, which is known to be produced by either deep oxidation of sulfur or H₂S, or by the reverse Claus reaction (Eq. (4)). The produced SO₂ may be considered to react with ammonia to produce ATS via ammonium sulfite (reaction (6)). However, the conventional xerogel and impregnated catalysts showed much lower H₂S conversion than the xerogel catalysts prepared by nonhydrolytic sol-gel method. The high catalytic activity of the nonhydrolytic xerogel catalysts may be due to their high surface area and highly homogeneous VO_x dispersion on the surface. Conventional xerogel showed the undesired production of SO₂ with the selectivity of 8.8%.

CONCLUSION

The selective oxidation of hydrogen sulfide in the presence of excess water and ammonia was investigated in this study. V₂O₅-TiO₂ xerogel catalysts prepared by nonhydrolytic sol-gel method showed very high conversion of H₂S (98.9% for 10V-Ti at 260 °C) without any considerable amount of SO₂ emission. The surface area of these xerogel catalysts decreased with increasing vanadium loading from 6V-Ti to 18 V-Ti. 6V-Ti catalyst showed much higher surface area (87 m²/g) than the conventional xerogel catalyst (12 m²/g). The xerogel catalyst from the nonhydrolytic method showed higher H₂S conversion than the conventional xerogel and the impregnated catalysts did. The conversion of H₂S was maximum for 10V-Ti, and it decreased at higher vanadium content due to the formation of crystalline V₂O₅. The high catalytic performance of the nonhydrolytic xerogel catalysts originated from their highly dispersed VO_x species and high reducibility.

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