



Research paper

Catalytic performance of vanadia-doped alumina-pillared clay for selective oxidation of H₂S



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ABSTRACT

The catalytic oxidation of hydrogen sulfide over V₂O₅ supported on Al-pillared clay (V/Al-PILCs) was studied. The synthesized catalysts were examined using a variety of characterization techniques such as XRD, BET, XPS, ⁵¹V NMR, H₂-TPR and NH₃-TPD. A catalytic activity study performed by using V/Al-PILC catalysts showed that H₂S was successfully converted to elemental sulfur without considerable emission of sulfur dioxide. The H₂S conversion over V/Al-PILCs increased with the vanadia content up to 6 wt.%. This superior catalytic performance might be related to the uniform dispersion of vanadia species on the Al-PILC support.

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1. Introduction

Owing to very strict regulations on SO_x emissions, hydrogen sulfide (H₂S) contained in acid gases must be carefully controlled prior to their release into the atmosphere. The most common technology in current use for the removal of H₂S is the well-known Claus process (Lagas et al., 1988). However, because of thermodynamic limitations, 3–5% of the H₂S was not converted to sulfur. Therefore, various commercial processes have been developed to treat tail gases from the Claus plants or other emission sources (Goar, 1975; Naber and Wesselingh, 1973). The most attractive among these processes was the dry catalytic oxidation of H₂S to elemental sulfur after hydrogenation of the sulfur-containing gas to H₂S (van Nesselrooy and Lagas, 1993). Two important commercially developed processes are the Mobil direct oxidation process (MODOP) (Kettner and Liermann, 1982; Kettner et al., 1983) and the Super Claus process (Lagas et al., 1988; van Nesselrooy and Lagas, 1993). Both are based on the direct oxidation of H₂S to elemental sulfur. In the MODOP process, H₂S is oxidized into elemental sulfur with a stoichiometric amount of oxygen over TiO₂ catalysts (Kettner and Liermann, 1982). One drawback of this process is that water must be removed from the tail gas before the reaction, as it deactivates the catalysts (Kettner et al., 1983). In the Super Claus process, the tail gas can be treated without a dehydration step, since the iron-based catalyst is resistant to water, however, this process requires an excess amount of oxygen (10 times the stoichiometric amount) (van Nesselrooy and Lagas, 1993).

The manipulation of microstructure and surface reaction of the clay host and the guest components at a molecular level is a fast moving field (Zhou, 2011). Clays have long been used for catalysis, adsorption and ion-exchange, but their efficient use is limited by their lack of porosity and low thermal stability (Ahn et al., 2010; Ryu and Yeo, 2010; Zhou, 2010). Therefore, to improve upon these properties, modifications are made. An example of such a modification is that performed by using the pillaring process, which increases porosity and thermal stability. Pillared interlayered clays (PILCs) are two-dimensional zeolite-like materials that are prepared by exchanging the charge-compensating cations between clay layers with large inorganic cations, which are polymeric or oligomeric hydroxyl metal cations, formed by the hydrolysis of metal oxides or metal salts. Upon heating, the metal hydroxyl cations undergo dehydration and dehydroxylation, forming stable metal oxide clusters that act as pillars that maintain the separation between the silicate layers and create interlayer spaces of molecular dimensions (Chen et al., 1995; Gil et al., 2000; Klopogge, 1998; Valverde et al., 2003). A number of authors have reported works related to metal oxide pillared clays such as Fe-PILC (Rightor et al., 1991; Shamsudeen et al., 2004; Timofeeva et al., 2009; Wu et al., 2009; Yuan et al., 2006), Ti-PILC (Binitha and Sugunan, 2006; Chmielarz et al., 2003; Gil et al., 1996; Ouidri et al., 2010; Rezala et al., 2009), and Zr-PILC (Fetter et al., 2003; Ohtsuka et al., 1993; Pereira et al., 2001; Vinod and Anirudhan, 2002; Zyuzin et al., 2004).

Several studies also reported (Keller et al., 2001; Lee et al., 2005; Li and Chien, 1999; Shinkarev et al., 2009; Yasyerli et al., 2006) the selective catalytic oxidation of H₂S using a variety of catalyst. In our previous work (Bineesh et al., 2008; Park et al., 2002), we reported the good catalytic performance of a V₂O₅ catalyst for the selective

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oxidation of H₂S. We also studied the performance of V/Fe-PILC (Bineesh et al., 2011a, 2011b), V/Zr-PILC (Bineesh et al., 2009a, 2010), and V/Ti-PILC (Bineesh et al., 2009b, 2011c) for the selective oxidation of H₂S to elemental sulfur.

Al-pillared clays have received much attention as new materials that can be used as substitutes for zeolites, especially in the cracking process and in the selective catalytic reduction of NO by hydrocarbons, owing to their superior catalytic activities (Chae et al., 2001). Pan et al. (2008) reported the catalytic activity of Cu supported Al-PILC for the direct hydroxylation of benzene to phenol. Mishra and Ganga Rao (2005) studied the catalytic activity of ceria-containing Al-pillared clay in the dehydration of cyclohexanol. Colin et al. (2005) reported the catalytic activity of MoS₂ catalysts supported on alumina-pillared clays for the hydrogenation of naphthalene. Chmielarz et al. (2003) prepared Cu or Co modified Al-PILC catalysts and studied for the catalytic reduction of NO with ammonia.

In this work, we studied the catalytic performance of vanadia-doped alumina-pillared clays in the selective catalytic oxidation of H₂S to elemental sulfur. To date, however, there have been no reports of the use of vanadia-doped alumina-pillared clay in the selective catalytic oxidation of H₂S.

2. Experimental

2.1. Catalyst synthesis

The starting material was Na-montmorillonite, referred to as Na-MMT (Kunipia-F, Kunimine Industrial Company), with a cation exchange capacity of 120 meq/100 g. AlCl₃·6H₂O (99%, Sigma-Aldrich) was used as the aluminum ion source for the preparation of the alumina-pillared clay. The pillaring solution for the alumina-pillared clay was prepared by partial hydrolysis of an aluminum chloride solution using sodium hydroxide as a base. A suitable volume of 0.2 M NaOH was added dropwise into a stirred solution containing 0.2 M AlCl₃·6H₂O in order to obtain an OH/Al molar ratio of 2.0. The resulting solution was refluxed for 24 h and stored for 7 days at room temperature prior to the pillaring process. The pillaring processes were performed with a 2 wt.% clay slurry. The pillaring solutions were added drop wise to the aqueous clay suspensions with stirring to obtain a final Al/clay ratio of 20 mmol/g. The slurry was stirred for 24 h at room temperature. After aging for 12 h, the product was filtered, washed several times with distilled water, dried in air and then calcined at 400 °C for 3 h. The final product was referred to as Al-PILC. For the comparison of the metal pillared clays, Fe-PILC, Ti-PILC, and Zr-PILC were also prepared according to the previously reported procedures (Bineesh et al., 2009a, 2009b, 2011a).

Vanadia-loaded Al-PILCs containing 3, 6, 8, and 12 wt.% vanadia were prepared by the wet impregnation of Al-PILC supports with a solution of NH₄VO₃ (99%, Aldrich) dissolved in water acidified with oxalic acid. Finally, all the samples were dried at 80 °C for 20 h and calcined at 400 °C for 3 h in a stream of air. The samples were labeled as *x* wt.% V/Al-PILC, where *x* referred to the weight percentage of vanadia loading on the support used in the preparation step. We used a calculated amount of NH₄VO₃ for the preparation of the corresponding V/Al-PILC.

2.2. Characterization of the catalysts

The chemical composition of the samples was determined by X-ray fluorescence spectroscopy (XRF, Philips PW 2400). The X-ray diffraction (XRD) patterns were obtained on a Bruker Advanced D8 powder diffractometer, using Ni-filtered Cu K α radiation ($\lambda = 1.5404 \text{ \AA}$). A fixed power source (40 kV, 300 mA) was used, and the scan speed was $0.02^\circ 2\theta \text{ min}^{-1}$.

The surface areas were determined by N₂ adsorption at -196°C using a Micromeritics ASAP 2010 instrument. The samples were

outgassed under vacuum for 12 h at 110 °C prior to nitrogen adsorption. The specific surface areas were calculated using the BET equation. The total pore volumes were evaluated from the nitrogen uptake at a relative N₂ pressure of $P/P_0 = 0.99$. The *t*-plot method was used to determine the micropore volume.

XPS analyses were performed using an X-ray photoelectron spectrometer (VG, ESCALAB 250) with monochromatic Al K α radiation ($h\nu = 1486.6 \text{ eV}$). Samples calcined at 400 °C for 3 h were pressed into self-supporting wafers without a binder, followed by pretreatment in an ultrahigh vacuum. The binding energies (BE) were calculated using the C 1s band as the reference (284.6 eV).

The ⁵¹V spin-echo NMR spectra were obtained on a Bruker DSX 400 spectrometer ($\nu_0 = 105.2 \text{ MHz}$ for ⁵¹V resonance) with a field strength of 9.4 T. All chemical shifts were referenced to NaVO₃ as the external standard.

Temperature-programmed desorption of ammonia (NH₃-TPD) was performed with a BEL-CAT chemisorption apparatus (BEL, JAPAN). For NH₃-TPD, about 50 mg of the sample was pretreated at 400 °C for 2 h in a flow of He, and cooled to ambient temperature. Pure ammonia gas (50 mL/min) was adsorbed at 100 °C for 20 min. Desorption was carried out with a linear heating rate of 10 °C/min in a flow of He (20 mL/min). Temperature-programmed reduction by H₂ (H₂-TPR) was also performed with BEL-CAT chemisorption apparatus (BEL, JAPAN). For H₂-TPR, about 50 mg of sample was pretreated in an oxidative atmosphere (5% O₂ in He) at 400 °C for 30 min. After cooling to room temperature, the H₂-TPR (5% in He, flow rate 20 mL/min) was carried out from 100 to 700 °C at a heating rate of 10 °C/min.

2.3. Reaction tests

The reaction tests were carried out in a continuous flow fixed-bed reactor made of a Pyrex tube with 1-inch internal diameter. A mixture of gases of H₂S, O₂ and a balance of He with purity of 50%, 98%, and 99.999%, respectively were used. In a typical experiment, the reactant composition consisted of 5 vol.% H₂S and 2.5 vol.% O₂ with the balance being He. The gas hourly space velocity (GHSV) was fixed at $10,000 \text{ h}^{-1}$. Typically, 0.4 g of catalyst was used along with a total gas flow rate of 100 mL/min. Water vapor was introduced in the reactant stream using a steam evaporator filled with small glass beads, and its amount was controlled using a syringe pump. Before the measurement of catalytic activity, the catalyst was pretreated at 300 °C for 2 h.

The O₂, H₂S, and SO₂ contents of the effluent gas were analyzed by a gas chromatograph (HP 5890) equipped with a thermal conductivity detector and a 1.8-m 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 H₂S and the selectivity (%) to SO₂ and S were defined as follows:

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

$$\text{Selectivity to product (SO}_2\text{, S)} = \frac{[\text{Product}]_{\text{outlet}}}{[\text{H}_2\text{S}]_{\text{inlet}} - [\text{H}_2\text{S}]_{\text{outlet}}} \times 100(\%).$$

3. Results and discussion

3.1. Chemical composition

The chemical compositions of Na-MMT, Al-PILC and V/Al-PILCs are presented in Table 1. The pillaring of the initial clay by Al₂O₃ resulted in an increase in the Al₂O₃ content from 29.2 to 41.3 wt.%, with the complete replacement of the interlayer Na cations. The relative amounts of silica and magnesium remained constant in all samples

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