



Short communication

Influence of lanthanum promoter on vanadium catalyst for sulfur dioxide oxidation

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ABSTRACT

In this study, the catalytic properties of lanthanum modified V_2O_5 catalyst for SO_2 oxidation have been studied. Effects of La_2O_3 content and reaction temperature were investigated to optimize La_2O_3 loading on V_2O_5 catalyst. The samples were characterized by BET, FT-IR, Raman, XRD, SEM and TG/DSC. The results showed that the catalyst with 4 wt% La_2O_3 (VL4) possessed the highest catalytic performance, improving the mean SO_2 conversion at least 53% compared with the catalyst without La_2O_3 (VL0). Due to its excellent low-temperature and high-temperature activities, VL4 catalyst appears to be more efficient for the conversion of highly concentrated SO_2 gases.

1. Introduction

Sulfuric acid, produced by converting SO_2 into SO_3 over the supported liquid phase catalyst, is one of the most important products of chemical industries [1]. Vanadium catalyst, composed of active ingredient (V_2O_5), promoters (K_2SO_4 or Na_2SO_4) and support material (diatomite), is a typical supported liquid-phase catalyst used in sulfuric acid industry [2]. In correspondence with the significance of this contact process, a vast amount of researches have been conducted on application technologies and plant design as well as on catalyst composition, preparation and support materials [3,4]. Adding promoters such as lanthanide metals and alkali metals is considered to be one of the most effective ways to develop high-performance catalyst for SO_2 oxidation [5,6].

Among various promoters mentioned above, the effects of alkali metals promoters on V_2O_5 catalyst have been studied for decades [7]. Cs–V catalyst has shown high catalytic activity at low reaction temperature and can in turn decrease the operating cost and capital investment [8]. Due to the unique physical properties of lanthanide metal oxides, some researchers have put efforts to use these oxides over vanadium catalyst in SO_2 oxidation. Zhou et al. [9] studied the oxidation of SO_2 over cerium oxide cluster cations and found the weak bond strength of Ce–O and oxygen storage/release capacity of ceria were the key factors to SO_3 production. Mazidia et al. [10] studied the V_2O_5 catalyst promoted by ceria and found 7 wt% load of ceria can lead to the maximum catalyst activity. These reports showed that ceria can be a potential promoter of the catalyst for SO_2 oxidation in sulfuric acid

preparation, but lanthanum as a promoter over vanadium catalyst has never been studied.

La_2O_3 has been considered to be an effective promoter to improve the dispersion of active species and thus increase the stability and activity of the catalysts [11]. Recently, lanthanum has been used in fluid catalytic cracking process [12], reforming of methane by carbon dioxide to syngas [13], the reduction of NO [14] and water-gas shift reaction [15,16]. In this work, V_2O_5 catalyst and various amounts of La_2O_3 modified V_2O_5 (La_2O_3/V_2O_5) catalysts were prepared for SO_2 oxidation, and the effects of La_2O_3 modification on the catalytic performance of oxidation were also investigated.

2. Experimental

2.1. Catalyst preparation

The La_2O_3/V_2O_5 catalysts with various contents of La_2O_3 were prepared by ultrasonic mixing method [4,10]. Potassium hydroxide was mixed with deionized water and then mixed with V_2O_5 , H_2SO_4 and diatomaceous earth. $La(NO_3)_3 \cdot 6H_2O$ was dissolved in deionized water and impregnated in the paste. After 30 min of ultrasonic treatment, the paste was extruded as cylindrical rods with the size of $\Phi 5$ mm \times (6.0–6.5) mm by the TBL-2 catalyst extrusion molding machine. The cylindrical rods were dried at 110 °C for 1.5 h and were calcined at 550 °C for 3 h. The prepared vanadium catalyst contains 7% V_2O_5 , 20% K_2SO_4 , different contents of La_2O_3 and diatomite.

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2.2. Catalytic performance

The activity measurement was carried out based on the method described in China Chemical Industry Standard HG/T 2089–2007 (*Test method of activity for oxidizing sulfuric dioxide into sulfuric acid catalyst*) using a 32 mm i.d. fixed bed stainless steel tube microreactor [17]. The catalyst bed height was about 38 mm. The catalyst samples with the mesh size of 4.0–6.0 mm were charged into the microreactor. Catalyst performance was tested at 350–470 °C in the step of 20 °C and was calculated from the concentration change between inlet and outlet of the reactor. The sulfuric acid synthesis gas with composition of $10 \pm 0.1\%$ SO₂ and 90% air at a GHSV (gas hourly space velocity) of 3600 h^{-1} was used under atmospheric pressure. The rate and the concentration of the gas feeding the reactor were kept constant in all tests.

2.3. Catalyst characterization

FT-IR of KBr pellets were carried out by an AVATAR 370 Thermo Nicolet spectrophotometer in a scanning range of 4000 cm^{-1} to 400 cm^{-1} taking scan number of 32 with a resolution of 4 cm^{-1} . Raman spectroscopic measurements were carried out with a Renishaw in Via Raman Microscope system using a 532 nm Nd: YAG laser as the excitation source and was collected in the range of $50\text{--}1500 \text{ cm}^{-1}$ with 1 cm^{-1} resolution. To study the structure and crystallinity of the prepared samples, XRD was performed by a Rigaku D/max2500 diffractometer using a Cu K α radiation ($\lambda = 0.15405 \text{ nm}$, resolution 0.02°) within the 2θ scan range of $5\text{--}80^\circ$. Surface morphology of the catalysts was investigated by field-emission scanning electron microscope (FESEM, Hitachi S-4800) instrument. Elemental analysis was carried out by EDX (NORAN-System7, Thermo Fisher Scientific, USA). The BET surface area and the pore size distribution of samples were determined in a AUTOSORB-iQ2-MP apparatus by nitrogen adsorption and desorption at 77 K. Prior to the experiments, the catalyst samples were treated under vacuum at 573 K for 1 h to remove moisture from the surface. In addition, TG/DSC were carried out by a thermal analyzer (STA449C, NETZSCH Scientific Instruments Trading Ltd., Germany) in air atmosphere (100 ml/min) from 30 to 780 °C with a heating rate of $10^\circ\text{C}/\text{min}$.

3. Results and discussion

3.1. Catalytic performance

The catalytic performances for the oxidation of SO₂ over the V₂O₅ catalyst and the La₂O₃/V₂O₅ catalysts are compared at various temperatures of 350–470 °C as shown in Fig. 1. The catalytic activity is given, as percentage, in terms of SO₂ conversions. It can be seen that SO₂ oxidation over all catalysts has been ignited at 420 °C. SO₂ conversions of all the catalysts had an obvious increase with rising of the reaction temperature. However, the concentration of the La₂O₃ had significant effect on the catalytic activity. For example, at 450 °C, the conversion slightly increased from 61.6 to 77.6% with increasing the La₂O₃ loading from 0 up to 4 wt%. With more increasing in La₂O₃ content after exceeding 4 wt%, the activity decreased due to the pore blockage of the diatomite carrier, which can be seen in the BET and SEM results. Briefly, the trends of SO₂ conversion versus La₂O₃ promoter content at other temperatures were similar to the curve at 450 °C indicating that 4 wt% is the optimal content of La₂O₃ in composites. As expected, the low-temperature (below the ignition temperature) activity of the VLa4 catalyst was considerably higher than that of the VLa0 catalyst. This resulted from the presence of LaVO₄ crystalline phase and the formation of more potassium pyrosulfate in the VLa4 catalyst, which can be proved by the FT-IR, Raman and XRD results. Besides, VLa4 had excellent performance at high temperature, enhancing dramatically the mean SO₂ conversion at least 24% compared with

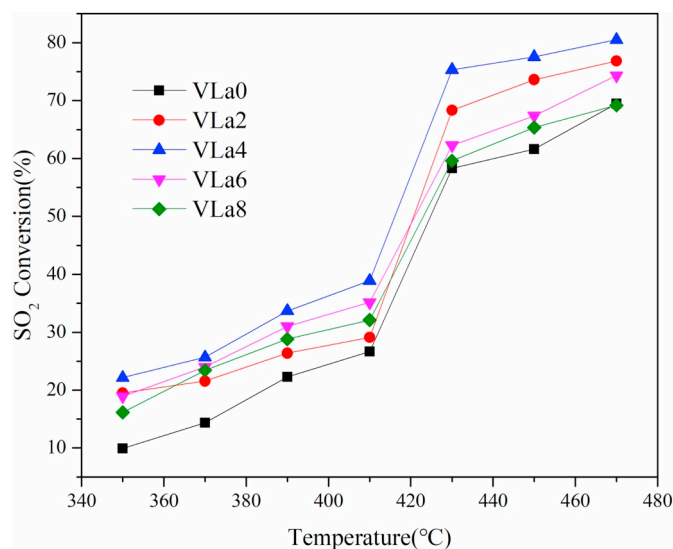


Fig. 1. Effect of La₂O₃ promoter concentration on SO₂ conversion at various temperatures from 350 to 470 °C.

Table 1

Composition and textural properties of the prepared catalyst samples with various contents of La₂O₃.

Sample	La ₂ O ₃ Loading (wt%)	BET(m ² /g)	Pore Volume ($\times 10^{-2} \text{ cm}^3/\text{g}$)
VLa0	0	3.5	0.65
VLa2	2.0	3.7	1.09
VLa4	4.0	4.3	1.31
VLa6	6.0	3.7	1.03
VLa8	8.0	3.6	1.05

the VLa0 catalyst.

3.2. N₂ adsorption/desorption analysis

The textural properties such as BET surface area and pore volume of the V₂O₅ catalyst and the La₂O₃/V₂O₅ catalysts are summarized in Table 1. The VLa4 had the highest surface area of about 4.3 m²/g and the highest pore volume of 0.0131 cm³/g. The doping of lanthanum may increase the dispersion of the active component V₂O₅ and the promoter K₂SO₄, thus improved the specific surface area. In addition, lanthanum can improve the thermal stability of diatomite and prevent the collapse of pore structure at high temperature, which can also be confirmed by Fig. A4. However, with the incorporation of La₂O₃ on V₂O₅ catalyst from 4 to 8 wt%, a considerable reduction in both BET area and pore volume was observed. This could result from migration of lanthanum promoter to the pores of the catalyst and clogging some pores by the addition of lanthanum promoter to V₂O₅ catalyst.

Table A.1 and Fig. A.1 show the pore-size distributions of the catalysts. Both kinds of the catalysts had a BJH pore-size distribution in the range of 0–150 nm and it slightly increased with increasing of the La₂O₃ loading from 0 up to 4 wt%, but reduced at the higher percentage of La₂O₃ content in the catalyst. More importantly, the VLa4 catalyst had the largest proportion of large macropores which was beneficial to the diffusion of the reaction gas.

Fig. 2 shows the N₂ adsorption-desorption isotherms of the catalysts. The N₂ adsorption/desorption isotherms were similar with each other and can be identified as type II, which is characteristic of adsorption on macroporous adsorbents with strong adsorbate-adsorbent interactions according to the IUPAC classification. Compared with other catalysts, the hysteresis loop of VLa4 catalyst occurred at a higher relative pressure (p/p^0) which was proportional to the large macropores in the catalyst [18].

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