Fuel 93 (2012) 385–390

Contents lists available at SciVerse ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Reversible removal of SO_2 at low temperature by L-α-alanine supported on γ-Al_2O_3

Renpan Deng, Lishan Jia *

Department of Chemical Engineering and Biochemical Engineering, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

ARTICLE INFO

Article history:
Received 14 October 2010
Received in revised form 6 October 2011
Accepted 9 November 2011
Available online 24 November 2011

Keywords:
L-α-Alanine
Adsorption
Gamma alumina
Sulfur dioxide
Flue gas desulfurization

ABSTRACT

L-α-Alanine was supported on γ-Al_2O_3 to remove SO_2 in this work. The effects of SO_2 concentration, water vapor and temperature on the removal of SO_2 were investigated. The experiment results showed that the activity of L-α-alanine on SO_2 removal increased significantly when supported on γ-Al_2O_3. SO_2 saturation capacity increased with increase SO_2 concentration, and kept about 57 mg/g when SO_2 concentration exceeded 1.7%. Water vapor promoted SO_2 removal and made SO_2 saturation capacity increase greatly. SO_2 saturation capacity decreased with increase in temperature, and room temperature was optimum. Raman spectroscopy analysis results revealed that SO_2 weakly adsorbed onto the adsorbent mainly due to the interaction of SO_2 and amino group via hydrogen bonds in the presence of water vapor. X-ray photoelectron spectroscopy (XPS) analysis results indicated that a small amount of SO_2 strongly adsorbed onto the adsorbent by forming aluminum sulfite. However, the strong chemical adsorption sites were saturated after the first adsorption and would no longer adsorb SO_2 afterwards. Ten continuous adsorption–desorption cycles showed that the adsorbent had an excellent regeneration performance.

1. Introduction

Air pollution has been a serious problem for years and has drawn increasing attention all over the world. SO_2, mainly emitted from fossil-fuel combustion, such as coals and oils, is one of major air pollutants, which have been linked with the formation of acid rain, urban smog and health hazards. Currently, flue gas desulfurization (FGD) is the most widely used techniques to control the emission of SO_2. Several conventional processes, such as wet FGD, dry FGD, semidry FGD, have been adopted in industry far and wide [1,2]. However, these methods have some disadvantages, for example, a large amount of water is required and by-products such as calcium sulfate are produced and these need to be treated further. Also, the absorbents used are difficult to regenerate [3–5].

Adsorption of SO_2 over solid sorbents is currently employed to remove large amounts of potential hazardous waste as it is a relatively simple process and consumes less water [6]. Generally, the adsorption desulfurization process would not cause secondary pollution. Moreover, adsorbents are usually easy to regenerate. A variety of solid materials, such as lignite [7], activated carbon [8], activated carbon fibers [9,10], zeolites [11,12], and metals or metal oxides, for example, Cu or CaO supported on porous materials [13,14], have been researched for SO_2 removal for years. Among these adsorbents, activated carbon and activated carbon fibers have been used in commercial units, however, the high cost limited their application to some extent. Most of other sorbents are still being at the phase of experimental research and have a long way to achieve industrial applications. Given this situation, it is urgently necessary to develop new sorbents of high efficiency, low cost, and excellent regenerative performance for FGD process.

Alkanolamines and amines, such as methyldiethanolamine and ethylenediamine [15,16], have been used for SO_2 removal for years. It has been demonstrated that the removal of SO_2 is related to amino groups in such materials. However, there are many difficulties in application of alkanolamines and amines due to their high volatility and toxicity. Amino acids have amino group, and are more environmentally friendly compared with alkanolamines and amines. Therefore, it could be a good choice to use amino acids as sorbent for SO_2 removal. In fact, there have been many reports about the interaction between amino acid and supports, for example, glycine supported on silica [17] and alanine supported on boehmite [18], etc. It was found that amino acid could support on various materials by different mechanisms, such as electrostatic adsorption, chemical adsorption or hydrogen-bond adsorption [19,20]. Garcia et al. studied the mechanism of L-α-alanine supported on γ-Al_2O_3 by vibrational spectroscopy. They found that L-α-alanine interacted with γ-Al_2O_3 by hydrogen-bonds [21], and the adsorption mechanism in the neutral immersed solutions is as follows:

$$\begin{aligned}&\mathrm{Al{-}OH_2^+} + {}^{-}\mathrm{OOC{-}CH(NH_3^+){-}CH_3}\\&\quad\rightarrow \mathrm{Al{-}OH_2^+}\cdots{}^{-}\mathrm{OOC{-}CH(NH_3^+){-}CH_3}\end{aligned}\tag{1}$$

Although there have been many related researches and reports, however, as far as we know, amino acids have not yet been applied as sorbents in the FGD process. In this work, we supported L-α-ala-

---

* Corresponding author. Tel.: +86 592 2188283; fax: +86 592 2184822.
E-mail address: Jials@xmu.edu.cn (L. Jia).

0016-2361/$ - see front matter Crown Copyright © 2011 Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.fuel.2011.11.024

nine on γ-Al_2O_3 (L-α-alanine/γ-Al_2O_3) and investigated its SO_2 adsorption property so as to develop a new renewable desulfurization adsorbent.

2. Materials and methods

2.1. Preparation of the adsorbents

In a typical immersed experiment [21], 1.0 g of γ-Al_2O_3 (40–60 mesh, calcined at 600 °C for 4 h in a muffle furnace. Specific surface area is 190.6 m^2/g) was immersed in 50 mL of 0.6 mol/L L-α-alanine solution and stirred at room temperature for 24 h. After the adsorption, the solid was separated by filtration, washed once with 50 mL of distilled water, and finally dried at 80 °C for 12 h. Under this condition, L-α-alanine loading determined by formaldehyde titration was 5.0 wt.%.

2.2. SO_2 removal experiments

The SO_2 removal experiments were performed in a glass-made jacketed fixed-bed reactor with 8 mm inside diameter, under isothermal conditions at required temperature. Approximately 0.3 g adsorbents were placed in the reactor to remove SO_2 from simulated flue gas. The simulated flue gas was a mixture of N_2, O_2 and SO_2 with the suitable concentration. Various simulated flue gas were introduced into the reactor after adding water vapor into the gas stream. Water vapor required for SO_2 removal was generated in a pressure-controlled boiler made of stainless steel and equipped with electric heating coils. The steam lines were insulated with heating belt to prevent condensation within the line and keep the temperature. For comparison, experiments were also carried out using dry simulated flue gas without adding water vapor. The flow rate of the mixture gas was kept at 15 mL/min. The SO_2 concentration changes at the outlet of the reactor were determined by iodine titration method (HJ/T 56-2000, a standard method of State Environmental Protection Administration of China). The amount of SO_2 adsorption capacity is expressed as milligram SO_2 per gram adsorbent (mg/g).

After saturation adsorption, the mixture gas was switched to N_2 and the temperature increased to 120 °C at a rate of 20 °C/min. The adsorbent was regenerated in the reactor under an N_2 flow at 120 °C until SO_2 in vent was not determined. The SO_2 concentration at outlet of the reactor was also determined by iodine titration method. The amount of desorbed SO_2 is also expressed as milligram SO_2 per gram adsorbent.

2.3. Specific Brunauer–Emmett–Teller (BET) surface areas

Specific surface areas of different adsorbents were calculated from nitrogen adsorption isotherms recorded at the temperature of liquid nitrogen on a Micromeritics Model ASAP 2000 (USA) using the Brunauer–Emmett–Teller (BET) equation.

2.4. Raman characterization

Confocal Raman microspectroscopy was conducted at room temperature with Renishaw UV–Vis Raman 1000 System, equipped with a CCD (charge couple device) detector and a Leica DMLM microscope. The line at 514.5 nm of an Ar^+ laser was used for excitation. The laser power was reduced to ∼1.0 mW to ensure that the sample is not damaged by laser irradiation.

2.5. X-ray photoelectron spectroscopy (XPS) analysis

So as to analyze the S species that are strongly adsorbed on the adsorbents, electronic binding energies for S2p peaks of L-α-alanine/γ-Al_2O_3 after desorbing SO_2 were measured by an X-ray photoelectron spectrometer. XPS analysis was performed on a PHI Quantum 2000 Scanning ESCA Microprobe with a monochromatised microfocused Al X-ray source. The binding energy was calibrated by C1s as reference energy (C1s = 284.6 eV).

3. Results and discussion

3.1. Activity of L-α-alanine/γ-Al_2O_3 on SO_2 removal

Fig. 1 illustrates the activity of L-α-alanine/γ-Al_2O_3 on SO_2 removal at 30 °C. L-α-alanine crystal exhibited very low activity on SO_2 removal, that is, SO_2 saturation capacity was only 6.7 mg/g. However, SO_2 saturation capacity increased about 8.5 times (57.2/6.7) when L-α-alanine was supported on γ-Al_2O_3, and compared with γ-Al_2O_3, SO_2 saturation capacity increased about 2.4 times (57.2/23.4). This indicated that the activity of L-α-alanine on SO_2 removal increased significantly when supported on γ-Al_2O_3. Table 1 gives the pore characteristics of different adsorbents, which could explain the phenomenon. The very low activity on SO_2 removal by L-α-alanine crystal may be due to the much low specific surface area (only about 0.5 m^2/g). However, the specific surface area of the adsorbents increased about 260 times when L-α-alanine was supported on γ-Al_2O_3. This could have greatly promoted the adsorption of SO_2 and caused a significant increase in SO_2 saturation capacity.

3.2. Effects of SO_2 concentration on SO_2 removal

Fig. 2 shows the effects of SO_2 concentration on SO_2 removal by L-α-alanine/γ-Al_2O_3 at 30 °C. The breakthrough time shortened with the increasing SO_2 concentration, and the breakthrough times were no more than one hour when SO_2 concentration was between 0.5% and 4.2%. This indicated the SO_2 adsorption rate was relatively fast. SO_2 saturation capacity increased with the increasing SO_2 concentration, however, the saturation capacity kept stable at about 57 mg/g when SO_2 concentration exceeded 1.7%. SO_2 saturation capacity could still maintain at about 40 mg/g when SO_2 concentration decreased to 0.5%, meaning that L-α-alanine/γ-Al_2O_3 could also be used to remove SO_2 under relatively low SO_2 concentration. The effects of SO_2 concentration on SO_2 removal may be due to dynamics and thermodynamics, that is, the concentration gradient between SO_2 and the adsorbents increased with the increasing SO_2

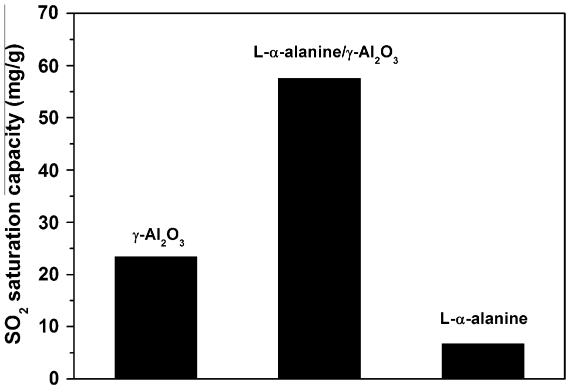

Fig. 1. Activity of L-α-alanine/γ-Al_2O_3 on SO_2 removal at 30 °C gas composition (vol.%): 1.7% SO_2; 5.0% O_2; 20% water vapor; balance gas: N_2.