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Reduction of SO₂ to elemental sulfur with H₂ and mixed H₂/CO gas in an activated carbon bed

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ARTICLE INFO

Article history:

Received 6 December 2016

Received in revised form 9 March 2017

Accepted 13 March 2017

Available online 21 March 2017

Keywords:

Sulfur dioxide reduction

Hydrogen

Elemental sulfur

Activated carbon

Catalysis

ABSTRACT

Experiments and thermodynamic equilibrium calculations were carried out on a H₂-SO₂ system. The effects of temperature, H₂/SO₂ ratio, and retention time on SO₂ reduction in an activated carbon bed were studied. The equilibrium calculations showed elemental sulfur to be the major S-containing product of SO₂ reduction at low H₂/SO₂ ratios. However, when the H₂/SO₂ ratio was greater than three, the calculations predicted that SO₂ would be completely reduced to H₂S with elemental sulfur completely absent from the reduction products. The experimental results showed that the starting temperature for reduction of SO₂ with H₂ is 600 °C. In the presence of activated carbon, the starting temperature decreased and an obvious increase in the SO₂ conversion and S yield was achieved at temperatures below 800 °C. The experimental results showed a lower SO₂ conversion and higher S selectivity than those predicted by the equilibrium calculations because equilibrium was not achieved under the experimental conditions. Higher H₂/SO₂ ratios and longer retention times were beneficial to SO₂ conversion. They also improved the S yield initially; however, subsequently, the yield decreased because an increase in S-containing byproduct formation after complete SO₂ conversion was achieved. The activity of mixed H₂/CO gas for SO₂ reduction was also probed. CO displayed a higher SO₂ reduction activity in comparison with H₂. COS was the major S-containing byproduct at lower temperatures, while H₂S was the main byproduct at 800 °C. At a H₂/CO ratio of 1, the optimum SO₂ conversion and S yield achieved were 99.3% and 79.3%, respectively, at 700 °C with a (H₂ + CO)/SO₂ ratio of 2.5.

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1. Introduction

Sulfur dioxide is the most important precursor of acid rain and one of the major contaminants generated from coal-fired power plants. Currently, the limestone-gypsum wet flue-gas desulfurization (WFGD) system is the most widely used method for removal of SO₂ from power-plant exhaust fumes. However, the gypsum byproduct of limestone-gypsum WFGD is often stockpiled (Liu et al., 2010). Desulfurization by adsorption on activated carbon is among a variety of alternative FGD technologies which can achieve sulfur recycling (Rubio et al., 1998; Liu et al., 2003). Commonly, SO₂ adsorbed on activated

carbon can be regenerated through heating or water scrubbing and recycled into sulfuric acid and liquid SO₂. However, the applications of liquid SO₂ are relatively limited and sulfuric acid is difficult to be stored and transported. Elemental sulfur is easier to be stored and transported, and it can be used as a raw material for almost all S-containing products (Bejarano et al., 2001; Humeres et al., 2002; Cha and Kim, 2001; Bejarano et al., 2003). Therefore, it is the ideal form of recovered sulfur.

Hydrogen is a common reducing agent widely utilized in various industrial sectors (Liu et al., 2016; Tahir et al., 2015). Recently, there has been a great deal of research on the reduction of SO₂ to elemental sulfur

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<http://dx.doi.org/10.1016/j.cherd.2017.03.014>

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Table 1 – Properties of the activated carbon.

Proximate analysis/%				Ultimate analysis/%					Bulk density/g/cm ³	Apparent density/g/cm ³
A _{ad}	M _{ad}	V _{ad}	FC _{ad}	N _{daf}	C _{daf}	H _{daf}	S _{daf}	O _{daf} ^a		
10.3	0.42	0.77	88.51	0.76	95.52	0.46	0.67	2.59	0.6384	1.142

^a Calculated as $O_{daf} = 100 - N_{daf} - H_{daf} - C_{daf} - S_{daf}$.

using H₂, with most studies focused on the development of catalysts. Ban et al. (2001) achieved 90% SO₂ conversion with H₂ and a Ru/Al₂O₃ catalyst at 500 °C. Ishiguro et al., 2002 used Ru/TiO₂ as a SO₂ reduction catalyst and reported a 90% elemental sulfur yield at 300 °C. Murdock and Atwood's research (Murdock and Atwood, 1974) on SO₂ reduction with hydrogen over an activated bauxite catalyst indicated that the SO₂ reduction process has two steps; the first step was reduction of SO₂ to elemental sulfur by H₂ and the second step was elemental sulfur reduction to H₂S by H₂. Paik and Chung, 1995 and Paik et al., 1997 found that Co-Mo/Al₂O₃ displayed a high catalytic activity towards SO₂ reduction, with an elemental sulfur yield above 80% achieved using a H₂/SO₂ molar ratio of three at 300 °C. They also found that the mechanism of Co-Mo/Al₂O₃ catalyzed SO₂ reduction proceeded via a H₂S intermediate; SO₂ was first reduced to H₂S on pre-sulfided Co-Mo/Al₂O₃, followed by a Claus reaction of the H₂S with SO₂ to produce elemental sulfur on the alumina support.

Activated carbon could be utilized as catalyst or catalyst support because of its large specific surface area, high degree of porosity, and surface functional groups (Xing et al., 2008; Han et al., 2016). In previous research, we found that activated carbon was catalytically active toward SO₂ reduction by CO (Feng et al., 2016). Meanwhile, the activated carbon was also the common reducing agent for SO₂ reduction (Humeres et al., 2002; Cha and Kim, 2001; Wang et al., 2007). However, the research on SO₂ reduction with H₂ in activated carbon bed has never been reported. In addition, H₂ is a primary component of the gas released during the preparation of activated carbon by fast pyrolysis of coal and, if successfully managed, this combination would provide a sustainable process for converting SO₂ to elemental sulfur (Zhang et al., 2014; Zhang et al., 2016; Li et al., 2008). Therefore, studying SO₂ reduction by H₂ in an activated carbon bed is essential and could be of great significance.

In this work, theoretical calculations were performed to determine the equilibrium thermodynamics of the H₂-SO₂ system and the influence of factors such as temperature, H₂/SO₂ ratio and retention time on SO₂ reduction in an activated carbon bed were evaluated experimentally. As CO is also a primary component of coal-pyrolysis gas, SO₂ reduction by a mixed H₂/CO gas was also probed.

2. Experimental section

2.1. Materials

A commercial coal-based activated carbon was used as the material in this study. Before experiments, the activated carbon was dried at 105 °C in an oven for 24 h, then crushed and sieved to a particle size of 0.70–0.84 mm (20–25 mesh). In order to avoid reactions between volatile components and SO₂ that may influence the experimental results, the activated carbon was heated at 1050 °C for 30 min under N₂ gas to eliminate tars and volatile components in advance (Ratcliffe and Pap, 1980). Some characteristics of this activated carbon are presented in Table 1.

2.2. Reaction system

A fixed-bed reactor system was employed for H₂ + SO₂ reaction tests, as shown in Fig. 1. A quartz tube of 20 mm diameter was fixed vertically in a tubular furnace fitted with an auto-

matic temperature control. The activated carbon was placed in the center of the tube and near a thermocouple used for measuring temperature to ensure a uniform and constant temperature was obtained. SO₂ and H₂ were mixed and diluted in N₂ using mass flow controllers (Beijing Sevenstar Company, CS200). The feed gas flow rate was 300 ml/min and the SO₂ concentration was 5 vol % for all runs. The outlet gas passed through a coiled condenser and a filter to separate the elemental sulfur and steam formed in the reaction. The outlet gas after condensing and filtering was collected by gas sampling bags, and then detected by gas analysis system immediately.

The H₂, CO₂, CO and N₂ gases among the gaseous products were analyzed by a refinery gas analyzer (PerkinElmer PE CLAUSE 500 GC). Moreover, the SO₂, H₂S and COS were analyzed by a gas chromatography–mass spectrometry (GC–MS) analyzer (Thermo ISQ) employing a GC–Carbonplot column (30 m × 0.32 mm × 3 μm). Injection was made in splitless mode with an injection volume of 1 ml and an injector temperature of 230 °C. The carrier gas, helium, was controlled at 1.0 ml/min. The column oven temperature was programmed to increase from an initial temperature of 40 °C, which was maintained for 2 min, followed by an increase to 120 °C at 5 °C/min, which was maintained for 3 min. The mass spectrometer was operated in elector impact (EI) mode with an ionization voltage of 70 eV. The ion source temperature was 230 °C and the transition line temperature was 250 °C. SO₂, H₂S and COS were the only S-containing products detected in the present study.

3. Results and discussion

3.1. Thermodynamic equilibrium calculations on a H₂-SO₂ system

3.1.1. Thermodynamic equilibrium prediction of product composition

The Equilib module of the thermodynamic software Factsage 6.4, which is based on Gibbs free energy minimization, was utilized to calculate the thermodynamic equilibrium compositions of the H₂-SO₂ system at various temperatures and H₂/SO₂ molar ratios. The Factsage software predicts all reaction products but only the products with a mole fraction above 10⁻⁴ are discussed in this work.

The primary equilibrium products of SO₂ reduction by H₂ contain H₂, H₂O, H₂S, SO₂ and elemental sulfur. The elemental sulfur exists in the form of S_x where the atom number, x, varies from 1–8. The atom number highly depends on temperature; at higher temperatures, S₂ is the major form of elemental sulfur while polyatomic molecules, with x from 6 to 8, are dominant at lower temperatures. For convenience of analysis, all elemental sulfur allotropes are expressed as S₁. The mole fractions of the other two S-containing products, SSO and H₂S₂, were predicted to be minor.

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