Chemical Engineering Science 61 (2006) 1854–1863

Chemical Engineering Science

www.elsevier.com/locate/ces

Capture of H_2S by limestone under calcination conditions in a high-pressure fluidized-bed reactor

Yongqi Hu[a, b], Masami Watanabe[a], Chizuko Aida[a], Masayuki Horio[a, *]

[a] *Department of Chemical Engineering, Tokyo University of Agriculture and Engineering, Koganei, Tokyo 184-8588, Japan*
[b] *College of Chemical and Pharmaceutical Engineering, Hebei University of Science and Technology, Shijiazhuang 050018, China*

Received 3 October 2004; received in revised form 27 September 2005; accepted 5 October 2005
Available online 1 December 2005

Abstract

The experiments on the sulfidation of CaO were carried out in a high-pressure and -temperature fluidized-bed reactor. The rate of CaO sulfidation decreased with the increase in total pressure under constant H_2S partial pressure. H_2O introduced in inlet gas and produced during reaction promoted the sintering of CaS or CaO, resulting in the decrease in both the rate of CaO sulfidation and final conversion. When the calcination of $CaCO_3$ and the sulfidation of CaO took place simultaneously, however, there was little influence of H_2O on the reaction. Both the calcination of $CaCO_3$ and sulfidation of CaO slowed down with increasing CO_2 partial pressure. The sulfidation of CaO was always slower than $CaCO_3$ calcination in the range of the experimental conditions. A shrinking unreacted-core model with variable effective diffusivity predicted well the sulfidation process accompanied by the calcination.

Keywords: Sulfidation; Calcination; Fluidization; Chemical reactor; Powder technology; Modeling

1. Introduction

Increasing interest is being focused on the capture of H_2S by Ca-based absorbent under high-temperature and -pressure due to the development of the advanced coal-fired electric power plant, such as the integrated gasification combined cycle (IGCC) and the advanced pressurized fluidized bed combustor (APFBC), which are both considered to be highly efficient and environmentally friendly power generating systems. In these systems, coal is gasified to produce the synthesis gas that is combusted in a gas turbine for power generation. During gasification, the sulfur contained in coal is released in the form of H_2S, COS and CS_2 due to the reduction circumstance. More than 90 wt% of the sulfur in the gas phase has been reported to be H_2S. It is necessary to remove these sulfur-containing components prior to the combustion of the synthesis gas in order to protect the gas turbine hardware and to comply with the environmental regulation. Sulfur removal under coal gasification conditions by in situ injection of limestone and dolomite can avoid cooling the synthesis gas, hence significantly increasing the thermal efficiency.

In gasification conditions, limestone can be calcined to CaO and CO_2 or remain $CaCO_3$ depending on whether the CO_2 partial pressure is lower or higher than the equilibrium pressure of limestone calcination

$$CaCO_3 = CaO + CO_2 \tag{1}$$

Both CaO and $CaCO_3$ can react with H_2S as the absorbents

$$CaO + H_2S = CaS + H_2O \tag{2}$$

$$CaCO_3 + H_2S = CaS + H_2O + CO_2 \tag{3}$$

The capture of H_2S by CaO has been found to be relatively rapid, and complete conversion of CaO has been reported (Attar and Dupuis, 1979; Fenouil and Lynn, 1995b; Efthimiadis and Sotirchos, 1992; Lin et al., 1995a). Lin et al. (1995a) studied the sulfidation of calcined limestone and uncalcined limestone using a TGA apparatus and concluded that sulfidation of limestone had a much lower initial reaction rate and final

---

[*] Corresponding author. Tel.: +81 42 388 7067; fax: +81 42 386 3303.
E-mail addresses: m_horiojp@yahoo.co.jp, masa@cc.tuat.ac.jp (M. Horio).

0009-2509/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ces.2005.10.006

conversion than that of the sulfidation of calcined limestone due to its less porosity. Yrjas et al. (1996) did experiments on the capture of H_2S with limestone in a pressurized thermogravimetric apparatus. The reaction was very slow and the highest amount of Ca converted to CaS after 120 min was less than 20% for 125–180 μm particles under the temperature range 998–1220 K. Borgwardt and Rocahe (1984) reported that over 60% conversion of $CaCO_3$ could be achieved only when particles were smaller than 3 μm.

In most cases, the calcination of $CaCO_3$ and sulfidation of CaO may simultaneously take place in the gasification circumstances. Fenouil and Lynn (1995b) studied simultaneous calcination and sulfidation of 1-mm limestone particles with differential tube reactor under atmospheric pressure. The results showed that the calcination was rapid enough not to interfere with the sulfidation reaction under 59 K over the calcination temperature, and slower than that of CaO sulfidation under 29 K over the calcination temperature. De Diego et al. (2004) did the experiments on the simultaneous calcination and sulfidation of 0.8–1 mm limestone and dolomite particles in a TGA at 0.1 MPa and in a differential reactor at 1 MPa, respectively. The H_2S retention process depended on the relative rate of the reactions of calcination, sulfidation of calcinated sorbents, and direct sulfidation.

Numerous researches have been carried out on the kinetics of CaO sulfidation. It has been reported by many research groups (Lin et al., 1995a,b; Squires et al., 1971; Westmoreland et al., 1977; Fenouil and Lynn, 1995a) that the reaction was the first order with respect to H_2S partial pressure. Large influence of the specific surface area of CaO was reported in some studies (Borgwardt et al., 1984; Chauk et al., 2000, Agnihotri et al., 1999a). Lin et al. (1995a) studied the effect of CO_2 and steam on the sulfidation of CaO. The presence of CO_2 inhibited both the initial reaction rate and the final conversion of the reaction. They attributed it to the fact that CO_2 accelerated sintering of CaO which in turn reduced the specific surface area of CaO. Only the initial reaction rate decreased with increasing steam concentration. Experiments on the effects of total pressure on the sulfidation with pressurized TGA and differential reactors (Matsukata et al., 1999; Chauk et al., 2000; Agnihotri et al., 1999b; Garcia-Labiano et al., 2004) showed that the sulfidation rate decreased with the increase in total pressure under constant H_2S partial pressure. Some researchers (Lin et al., 1995a; Heesink and Van Swaaji, 1995; Chauk et al., 2000) have also examined the effects of H_2 and CO on the reaction.

A sharp interface between the product CaS outer shell and the unreacted CaO core was found by Fenouil and Lynn (1995b) from SEM pictures of the inside of partially sulfided particles. Nguyen and Watkinson (1993) found the reaction appeared to be controlled by diffusion through the product layer after an initial stage of chemical control under atmospheric conditions and 1203 K. Agnihotri et al. (1999a) did the experiments on fine CaO particles (∼ 8 μm) under the temperature range 973–1173 K. They also concluded that overall sulfidation of CaO was controlled by the product layer diffusion at the later stage of the reaction and non-porous CaS product layer was formed. In the layer, S^{2-} ions migrated through the CaS product layer toward CaS/CaO interface. Fenouil et al. (1994) reported the sintering of CaS product layer, which played a significant role on the reaction rate and the utilization of sorbents.

The objective of this work was to analyze the capture of H_2S by Ca-based sorbents when calcination and sulfidation simultaneously took place. The experiments were made in a self-designed high-pressure and -temperature fluidized-bed reactor to simulate the reality in IGCC and APFBC system. The experiments were performed by using limestone under the CO_2 partial pressures lower than the equilibrium value. The effects of total pressure, CO_2 partial pressure and H_2O on the reaction were examined. A shrinking unreacted-core model (SCM) with variable effective diffusivity was proposed to describe the sulfidation process accompanied by the calcination.

2. Experimental

2.1. Apparatus

Fig. 1 shows the diagram of the experimental reactor. It involved an outer stainless vessel, an internal furnace and a dual-tube quartz reactor. The outer stainless shell sustained pressure while the temperature of its wall was low. The temperature of the quartz reactor was high while there was no pressure difference on it. It was designed to operate at pressure 1.0 MPa and temperature up to 1273 K. The internal heating furnace was placed between two adiabatic plates. The quartz reactor consisted of an outer tube in ϕ 28 mm ID and an inner tube in ϕ 18 mm ID. A sintered porous ceramic plate in the inner tube acted as both the bed holder and the gas distributor for the fluidized bed. The reactant gas first went through the annular space for preheating. The upper part of the inner tube was designed to enlarge to ϕ 30 mm ID for averting the entrainment of the particles. A pressurized sample reservoir installed at the top of the reactor could feed particles into reactor under high pressure. A thermocouple tube was inserted in the bed to detect the bed temperature directly. To avoid high temperature on

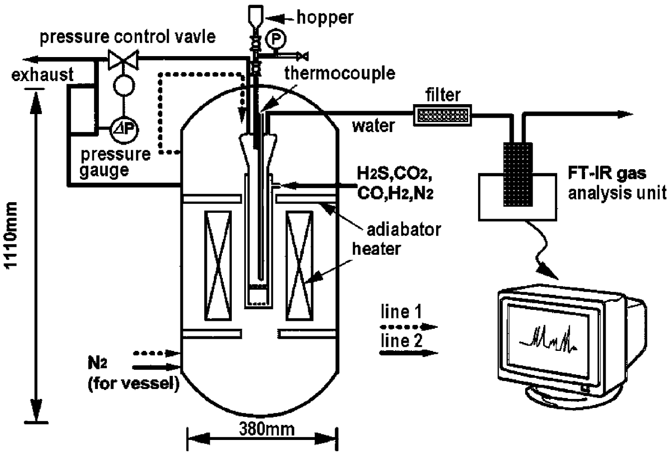

Fig. 1. The schematic of experimental setup.