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RESEARCH PAPER

Use of a Process Mass Spectrometer to Measure Rapid Changes of Gas Concentration

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Abstract: Experiments were conducted to investigate the suitability of a multistage in-situ reaction analyzer based on a micro fluidized bed (MFB-MIRA) for measuring rapid changes of gas concentration during gas-solid reactions. The results show that control of capillary temperature of a process mass spectrometer strongly influences the stability of on-line measurements. Based on observed regular patterns, the capillary temperature-control system was equipped with a precision controller that enabled a precision of ±0.2 °C to be achieved, and thereby guaranteed high stabilities of the sampling flow rate and chamber vacuum. Measurements using the modified gas-monitoring system showed that periodic fluctuations of the on-line measurement were eliminated and measurement stability significantly improved. The fluctuating range and relative standard deviation of the measured response to O_2 in air improved from 1.9% to 1.4% and 0.54% to 0.18%, respectively. A pressure-regulating device was also developed to control the absolute pressure at the gas sampling point. This achieved a control precision of ±0.02 kPa. The measured results showed that the response of the process mass spectrometer correlated positively with the absolute pressure at the sampling point, indicating the necessity for a pressure-regulating device. The accuracy and repeatability of the process mass spectrometer were improved. This work has enhanced the suitability of MFB-MIRA for studying rapid gas-solid reactions and broadened the scope of reliable applications of MFB-MIRA combined with a process mass spectrometer.

Key Words: Micro fluidized bed; Process mass spectrometry; Sampling flow rate; Vacuum; Stability

1 Introduction

Kinetic analysis of gas-solid reactions forms the foundation for the design of key industrial processes. On-line monitoring of gas release is an important tool in gas-solid reaction analysis and is helpful in describing the reaction process according to the gases released during a reaction process. Process mass spectrometry has many advantages, including a flexible sampling method, the wide range of concentrations that can be detected, high detection frequency, and efficient operation. Process mass spectrometry can also avoid the serious back-mixing that occurs in optical gas pools. This instrumentation therefore has strong potential application in measuring gas concentration changes in processes[1–4].

Xu *et al*[4–10] invented the micro fluidized-bed reaction analyzer (MFBRA). Its combination with a process mass spectrometer enables real-time analysis of isothermal differential gas-solid reaction processes under non-diffusion-controlled conditions. MFBRA has been widely used to study various types of reactions[7–16]. A newly developed gas-solid reaction analyzer is the multistage in-situ reaction analyzer based on a micro fluidized bed (MFB-MIRA)[17–19]. The MFB-MIRA is able to decouple a multistage gas-solid reaction at high temperature into a series of in-situ reaction processes by

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switching the reaction temperature and atmosphere, which allows the reaction processes to be efficiently analyzed.

Applications of MFBRA (or MFB-MIRA) involve numerous rapid gas-solid reactions (50% conversion reached in 3–30 s), such as coal combustion and limestone decomposition. Concentrations of the released gases change quickly during rapid gas-solid reaction processes, which results in steep concentration gradients and causes serious diffusion and back-mixing of gases in the system pipes; distortions of the concentration measurement are consequently generated[20–22]. A concentration-correction method based on the continuous stirred tank reactor (CSTR) concept can be used to calculate the actual gas concentration changes in the reactor[21]. This method requires derivatives of the measured concentration curves to be smooth, which, in turn, requires very small fluctuations of the measurement response of the process mass spectrometer. As discussed in detail in Section 3.1, early generation process mass spectrometers show periodic fluctuations (periods greater than 30 s) in their measurement responses and cannot meet the requirements for measuring rapid gas-solid reaction processes. In addition, transformation of both the gas flow value from the reactor and fluctuation of absolute atmospheric pressure will cause a change of absolute pressure at the sampling point of the spectrometer. Previous studies have indicated that software and hardware configurations, parameters, and operation of the mass spectrometer strongly influence the measurement results[23–25]. Improving the performance of the process mass spectrometer is one key to measuring rapid isothermal differential reaction processes (lasting only a few seconds) and obtaining high-order differentiable (smooth) concentration curves, as well as breaking through the limitations of existing analytical techniques.

The purpose of this study was to improve the suitability of a process mass spectrometer for measuring rapid changes in gas concentrations. Stability of measurement response and its influencing factors were specifically analyzed; the effect of absolute pressure at the sampling point on measurement response was also evaluated.

2 Experimental

2.1 Monitoring system

The original configuration of the system monitoring gas released from an MFB-MIRA is shown in Fig.1a. This consisted of a T-joint for sampling, a capillary tube (heat tracing system included), and an AMETEK Dycor-LC-D100M quadrupole process mass spectrometer (AMETEK, Inc., Pittsburgh, Pennsylvania, USA). The internal diameter, length, and temperature of the capillary tube were 50 μm, 1.1 m, and 180 °C, respectively. The gas supply and switching system (including a series of solenoid valves for switching gases[19] and several mass flow controllers), micro fluidized-bed reactor[17] and gas-release monitoring system were connected in series.

2.2 Samples and reagents

N_2, O_2, CO_2 and Ar were of high purity (99.999%). The mixed gases, e.g. 21% O_2/79% N_2 (*V/V*), were prepared from the high-purity gases using the gas supply and switching system that controlled the gas flow rates on-line. The calibrating gas concentrations were all balanced by Ar: for example, 4.01% CO volume concentration in Ar was denoted as 4.01% CO (calibrating gas). Preparation of Jincheng anthracite char (JC char) has been described previously[26]. The carbon mass fraction of JC char was 84.98%.

2.3 Experimental methods

2.3.1 Stability

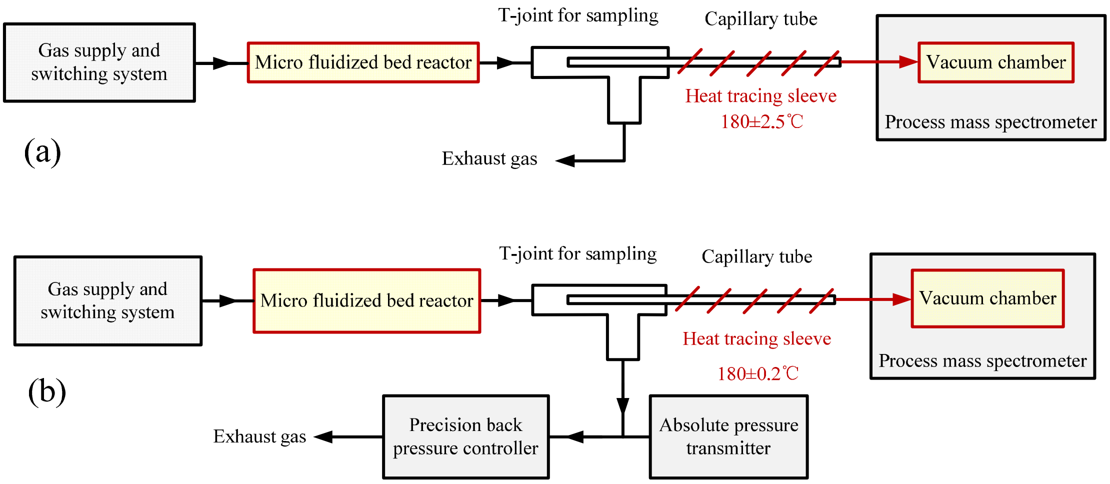

Fig.1 Schematic diagram of monitoring system for gas released from micro fluidized bed reactor: (a) original configuration, (b) improved configuration