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Measuring enthalpy of fast exothermal reaction with infrared thermography in a microreactor

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HIGHLIGHTS

- A microsystem integrated with infrared camera is developed to measure the reaction enthalpy.
- The reaction enthalpy can be determined from the temperature rise of the capillary.
- Two reactions including homogeneous and heterogeneous reactions are performed.
- It can provide a quick, safe and non-intrusive method to obtain the temperature profiles for fast exothermic reactions.

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ABSTRACT

In this paper, a microsystem integrated with infrared camera is developed to measure the reaction enthalpy of fast exothermic reactions. The microsystem is composed of a micromixer and a coiled capillary, which are all placed in a vacuum box to form an adiabatic environment. The fast exothermic reactions are started in the micromixer and then the temperature profiles of the capillary are measured via the infrared transparent window by the infrared camera. The reaction enthalpy can be determined from the temperature rise of the capillary. Two reactions which are homogeneous and heterogeneous respectively are performed with this method. The results show that the data obtained are in good agreement with the values reported in literature with the relative experimental errors less than 5%. Compared with the traditional calorimeter, the microsystem can provide a quick, safe and non-intrusive method to obtain the temperature profiles of the fast exothermic reactions.

1. Introduction

Over the last two decades microreactors have gained rapid development in carrying out efficiently numerous chemical reactions, of which the fast and exothermal reactions are thought to be one of the most suited reactions in microreactors [1–3]. Due to the characteristics of fast mixing, excellent heat and mass transfer, inherent safety in microreactors, it can bring many advantages: higher selectivity, faster reaction rate, better process control and increased safety. A lot of fast and exothermal have been performed in microreactors such as nitration [4], fluorination [5], rearrangement [6,7] and diazo reaction [8]. For such reactions, how to get a precise reaction enthalpy and temperature profiles in microreactors are crucial to control the reaction process and perform the process design. However, it is difficult to get these thermal information with conventional equipment considering the characteristic dimension smaller than 1000 μm in microreactors.

There have been many methods developed to measure the temperature profiles in microchannels. The thermocouple is simple and cheap, which is most widely used in microreactors [9,10]. But it has to be embed into the channel and may affect the flow behavior. Also, one thermocouple can only get one result at distinct points. As a result, non-intrusive methods have been proposed to acquire the reliable and accurate characterization of microdevices. The temperature sensitive tracers such as fluorescent dye [11,12] and liquid crystals [13] have been applied to measure temperature profiles in microchannels. However, the method is usually used in non-reacting systems as the tracers are also sensitive to the reacting conditions. In addition, the small measuring range also limits their application.

As a result, some technologically advanced methods based on Raman spectroscopy [14,15] and infrared thermometry [16–22] are attracting more and more attention. The methods can bring the advantages of recording the complete and continuous

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temperature field of a specified area. Ewinger et al. [15] used laser Raman spectroscopy to measure the temperature of water in microchannels with an accuracy of ±1.2 °C. The procedure had a lateral local resolution of approximately 15 μm and a depth resolution of 25 μm. Haber et al. [16] developed a microsystem with infrared thermometry and the temperature profiles of the fast exothermal hydrolysis of tetraethoxysilane were measured inside a microcapillary at different flow rates. Yi et al. [17] presented the thermal analysis of liquid containing Al_2O_3 nanoparticles in a microfluidic platform using an infrared camera, which allows the non-contact, three dimensional and high resolution capability for temperature profiling. However, there are two conditions required for the infrared thermometry, which limit its wide applications. One is the channel must be covered with infrared transparent materials, such as sapphire, silicon, germanium or zinc selenide [18]. The other is that the system needs a careful calibration due to the radiation losses by absorption or reflection of the IR signal.

In this work, a microsystem, including a micromixer, a coiled capillary, a vacuum box and the infrared camera was developed to measure the reaction enthalpy of fast exothermic reactions. The objective of this work is to provide a quick, safe and non-intrusive method to obtain the temperature profiles of the fast exothermic reactions with infrared thermography. The microsystem was first calibrated with a thermocouple. Two reacting systems which are homogeneous and heterogeneous respectively were tested at different conditions with the method. The temperature profiles of the capillary was recorded and then the reaction enthalpy could be calculated from the temperature profiles along the length of the capillary.

2. Materials and methods

2.1. Chemicals

Cyclohexanone oxime ($C_6H_{11}NO$, 98%) was purchased from J&K Scientific Ltd. (Beijing); Sulfuric acid (H_2SO_4, 98%) and sodium hydroxide (NaOH, analytical grade) were acquired from Sinopharm Chemical Reagent Beijing Co. Ltd.

2.2. Experimental setup

The experimental setup used for measuring the temperature profiles is shown in Fig. 1. It was composed of two pumps, a micromixer, a coiled capillary, a vacuum box and an infrared camera. The microreactor and the coiled capillary were both placed in the vacuum box which was vacuumized to a value below 10 kPa during the experiments. According to the reports in the literature [16], the value below 10 kPa is enough to suppress the convective heat transfer. The used infrared camera (PI400, Optris, Germany) had a resolution of 382 × 288 pixels with the frequency of 80 Hz. The measurement temperature range was −20 to 100 °C with a sensitivity of 0.08 °C. The system accuracy was ±2%. An infrared window (BGIR-75, Beijing Scitlion Technology Co.) with the diameter of 75 mm was fixed on the top of the vacuum box to make the capillary visible to the camera. The window is made of BaF_2, which provides a relatively high and constant transmissivity to the infrared ray [23]. As shown in Fig. 2, the high transmittance above 90% can be obtained for the material BaF_2 in the spectral range of 0.2–10 μm. When the wavelength is larger than 10 μm, transmittance is greatly decreased to a low value of 10% at 14 μm. According to Wien displacement law, it is more suitable to measure the temperature above 290 K (<10 μm). During our experiments, the temperature is usually above 293 K, which means high transmittance above 90% can be obtained using the material BaF_2. As a result, this material is quite suitable as the infrared window in our experiments. The losses of about 10% of the radiation due to the infrared window can lead to a slight deviation for the temperature measurement, which can be corrected by calibration as described in the next section.

The reactants were delivered separately by metering pumps (Beijing Satellite Co. Ltd.) through the steel capillaries immersed in a water bath to control the feeding temperature. Two commercial temperature sensors were integrated in the capillaries to calibrate the temperature measurement system. The feed streams were mixed in a T-shaped micromixer (VICI), which is made of stainless steel with an inner diameter of 0.25 mm. A stainless steel coiled capillary (1.0 m) with an inner diameter of 1 mm and an external diameter of 1.6 mm was connected directly downstream to the micromixer to perform the reaction. The inner diameter is so small that the temperature profile at radial direction can be ignored. During the experiments, the temperature profiles of the coiled capillary at the flow direction were recorded by the infrared camera via the infrared window. The camera was connected to the computer and controlled by the software (PI Connect). To get the variation of temperature versus time, we marked 5 measurement points every 0.2 m on the capillary. The temperature of these points would be calibrated as described in the next section. A typical temperature profile of the coiled capillary is shown in Fig. 3.

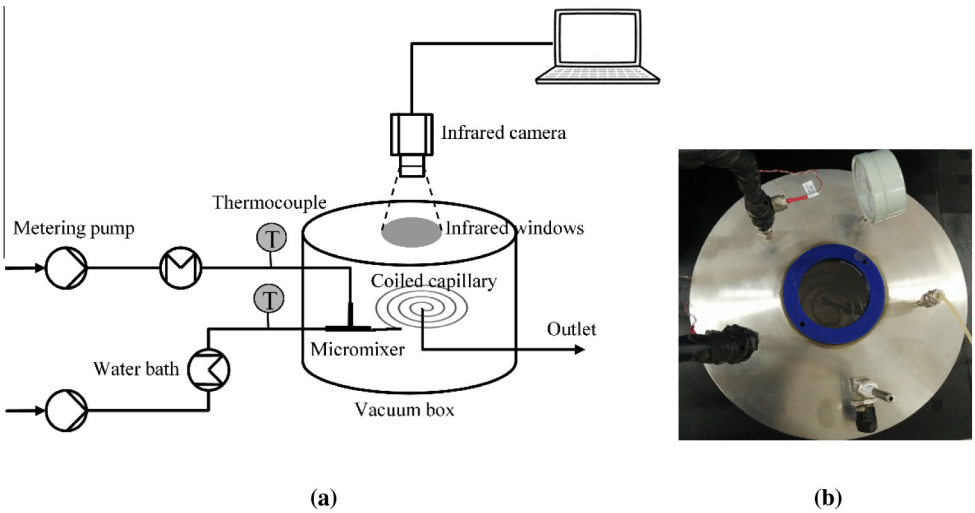

Fig. 1. The experimental setup used for measuring the temperature profiles. (a) Schematic overview, (b) the photograph.