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Measuring Enthalpy of Fast Exothermal Reaction with Micro-Reactor-Based Capillary Calorimeter

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This work presents a new micro-reactor-based capillary calorimeter for the enthalpy measurement of fast exothermal reactions. The new calorimeter was operated in the continuous way and the reaction enthalpy can be easily measured with the online temperatures from detached sensor chips. A standard reaction system and an industrial reaction system were selected to test this new calorimeter with homogeneous and heterogeneous reaction processes. The measurement was taken place at nearly adiabatic situations and the reaction enthalpy was calculated from the rising of temperature. High accuracy and good repeatability were obtained from this new calorimeter with relative experimental errors less than 3.5% and 2.4%, respectively. The temperature response was quick in this new calorimeter too, which was benefit to the low cost of reactive component. The fast and accurate measurement was contributed to the nice mixing performance and strict plug flowing in the calorimeter. © 2009 American Institute of Chemical Engineers *AIChE J,* 56: 1045–1052, 2010
Keywords: micro-reactor, reaction enthalpy, calorimeter, capillary

Introduction

During recent years, the applications of micro-device have received strongly growing interest in many areas.[1–3] Proceeding chemical process in micro-device, the mixing of fluids can be enhanced,[4] the storing volume of chemicals can be reduced,[5] the contact time can be shortened,[6] and the temperature can be reliably controlled.[7] On the basis of those advantages, micro-device has been widely used in the investigation of chemical reaction, especially for the fast reaction.[8] The active reactant can be quickly and uniformly mixed and the reaction time can be well controlled to several milliseconds in micro-reactor. The consumption of the reactant is low and the safety for some dangerous reactions can be ameliorated.

For the investigation of chemical reaction, one of the most important properties is the reaction enthalpy. Calorimeter is often used to measure the reaction enthalpy, and many different calorimetric systems have been developed during the last decades.[9,10] However, for the fast chemical reaction system, especially for the exothermal system, it is still difficult to characterize the reaction enthalpy in classical calorimetric system.[11] Indeed, it is better to study such reaction on a small scale, thus involving only small amount of very reactive compound and keep the safety of the reaction at an early stage of development. Besides, for the fast chemical reaction, rapid mixing as well as a precise control of the reaction time is mandatory. Such demands can be easily realized in micro-reactors.

In the recent years, there have been some reports about the enthalpy measurement with micro-reactors. Schneider and Stoessel combined a micro-chip reactor into a commercial calorimeter.[11] Their work innovatively introduced the micro-reactor into the study of fast exothermal reactions, but

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Correspondence concerning this article should be addressed to G. S. Luo at gsluo@tsinghua.edu.cn the reaction enthalpy was still measured from the commercial calorimeter. Moreover, most of the commercial calorimeters are batch reactors, but the micro-reactors work in the continuous way. The combination of the batch calorimeter and micro-reactor causes difficult to measure the whole energy released from reaction. Köhler and Zieren developed a chip-reactor-based calorimeter by integrating the reaction channel and sensitive thin-film thermoelements on a silicon chip.[12] Although the thermoelements could get the temperatures of the fluids online, the chip-reactor-based calorimeter was not operated on the continuous way either. The reason is that only a single chip was used in the calorimetric system and the thermoelements could be affected by the wall temperature, since heat can be transferred easily from high temperature region to low temperature region in the silicon chip. To get the total released heat from the reaction, impulse injection was used to feed reactants in that work.

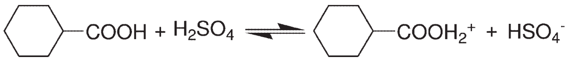
In this work, a new micro-reactor-based capillary calorimeter was designed to measure the enthalpy of fast exothermal reaction. The micro-reactor-based calorimeter has a simple structure and operated in the continuous way. The temperature sensors and the mixing channel of reactants are detached into different micro-chips and connected by the capillaries, making the recorded temperatures only represent the fluids. By using the energy conservation, the reaction enthalpy can be easily calculated from the online measured temperatures with high accuracy and good repeatability.

Experimental

Systems

Two working systems were introduced to test the micro-reactor-based capillary calorimeter. The reaction between NaOH and H_2SO_4 dilute aqueous solutions was chosen a standard reaction system. The initial concentration of NaOH was 1.6 mol/l and the initial concentrations of H^+ were changed from 0.143 to 0.744 mol/l.

The reaction between cyclohexanecarboxylic acid (CCA) and oleum, a crucial reaction in the SNIA Viscosa process, was chosen as an industrial reaction system to test this new calorimeter. [13] Two main reactions take place in this system.[14] One is the proton exchange reaction between CCA and sulfuric acid.



(I)

The equilibrium constant of this reaction given by Giuffre is infinity.[15] But according to our experimental result, it cannot reach to such a high level. Just at high feed ratio of CCA to H_2SO_4, H_2SO_4 can be consumed completely. The other reaction is between CCA and pyrosulfuric acid forming the mixed anhydride of cyclohexanecarboxylic acid with sulfuric acid.

(II)

The equilibrium constant of this reaction is 3.2×10^4 times higher than the proton exchange reaction, so the sulfur trioxide can be consumed completely during the reaction.[14] According to previous works,[16,17] those reactions are fast reactions. The reactant oleum is a reactive reactant, and the reaction is often operated by dripping oleum into large volume of CCA solution with strong stirring.

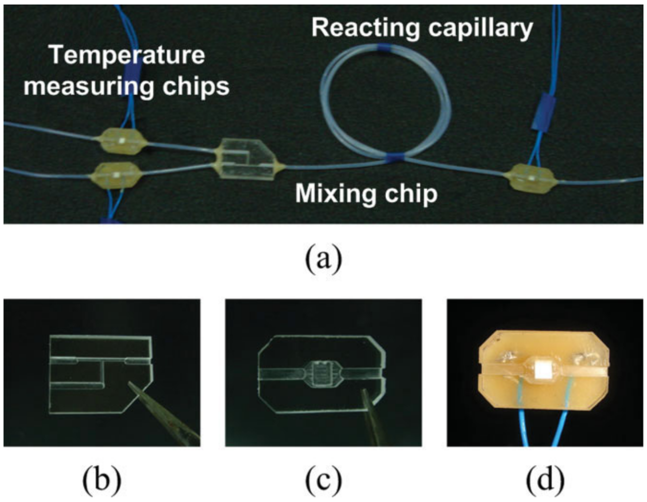


Figure 1. The plastic micro-reactor-based calorimeter and its detail structures.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

A side reaction takes place in this reaction system, transforming the mixed anhydride to undesirable by-product. But when the reaction conditions are well controlled, the yield of the side reaction products is low.[18] In this work, the selectivity of the main reactions was higher than 97%,[14] so the effect of the side reaction on the measurement can be neglected.

During the experiment, the proton exchange reaction and the mixed anhydride forming reaction were discussed separately; 68 wt % CCA/n-hexane solution was used at first to react with pure H_2SO_4 to form a homogeneous reaction system, and then olume with 62 wt % SO_3 was introduced to react with different concentrations of CCA/n-hexane solutions, 26–62 wt %, to form a liquid/liquid heterogeneous reaction system with olume as the dispersed phase.

Calorimeter design

To measure the reaction enthalpy of the standard reaction, a plastic calorimeter was made. The main structure of this micro-reactor-based capillary calorimeter is given in Figure 1a. A T-shaped micro-channel was used to mix the reactants, which was fabricated on a polymethyl methacrylate chip (PMMA) with end mill, as shown in Figure 1b. After fabrication, the chip was sealed with another PMMA plate to form a closed channel. The cross section of channel was 0.6 mm wide and 0.6 mm depth. Reaction will take place in this channel just after mixing, and a followed capillary was used to finish the reaction. The capillary was made of Teflon. The inner diameter of the capillary was 0.75 mm and the wall thickness was 0.2 mm. The length of the capillary was 0.5 m, which is long enough to finish the standard reaction. For the other reactions, the length of the capillary can be easily changed to adjust the reaction time. Besides, three measuring

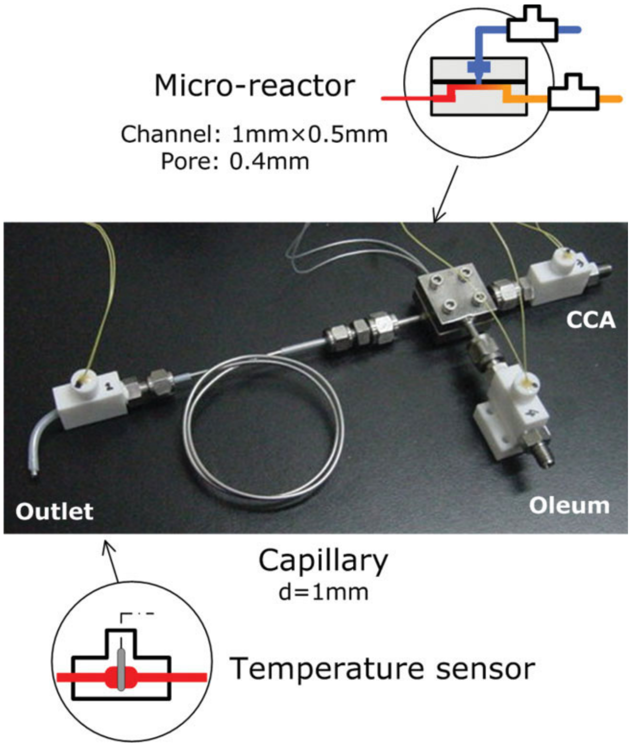


Figure 2. The stainless micro-reactor-based calorimeter and its detail structures.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

chips were placed at the inlets and outlet of the system to measure the temperatures of the fluids online. The measuring chip was made of PMMA too as shown in Figure 1c. Commercial PT 100 temperature sensors (1/3B, Germany) were embedded into the channel wall and fixed by resin bond as shown in Figure 1d. Since the inducting face of the sensor was just covered by a thin film of the resin bond (about 0.1 mm thick), the temperature can be inducted quickly. After embedding of the sensors, the measuring chip was sealed with another PMMA plate and connected with the capillary with resin bond.

For the industrial reaction system, a stainless steel calorimeter was produced to prevent corrosion, as shown in Figure 2. The main structure of this calorimeter was the same as the plastic one. Only a few changes were made in details. A T-shaped micro-pore dispersion device was used to mixing the reactants. The main channel of the mixing device was 1 mm wide and 0.5 mm depth. A micro-pore with a diameter of 0.4 mm was placed on the top of the main channel. A stainless steel capillary was used to complete the reaction. The length of the capillary was 0.6 m. The inner diameter of the capillary was 1 mm and the wall thickness was 0.3 mm. The temperature sensors were sealed by stainless steel coats too and embedded into three Teflon draw-in attachments.

In the experiment, the micro-reactor-based capillary calorimeter was placed in a self-made adiabatic room. The adiabatic room was made of NBR-PVC rubber foam and detached by three adiabatic chambers. The reaction unit and the temperature measuring chips were placed in different chambers to reduce disturbance from the thermal conductivity of air in the adiabatic room. Two water or oil bathes were used at the inlets to control the initial temperatures of the reactants. The initial temperatures of the standard reaction were fixed at 26°C and the industrial reactions were controlled between 25°C and 35°C. The effect of the initial temperature on the industrial reactions is little in this temperature interval. The temperature profiles of the fluids and the environment temperature were recorded by a data acquisition system (Riubohua, China). The temperature data were transformed to voltage signals in the data acquisition system. Figure 3 gives an exhibition map of the whole experimental set-up.

Temperature calibration

Before sealing the sensors, the temperature data acquisition system had to be calibrated. Both the sensors and a precision temperature thermometer were marinated in a constant

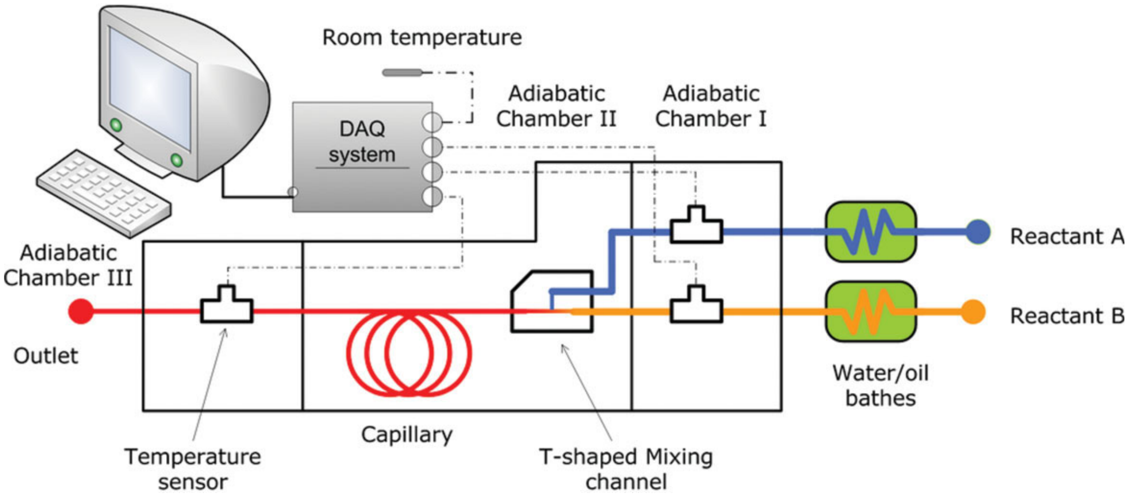


Figure 3. The whole experimental set-up.

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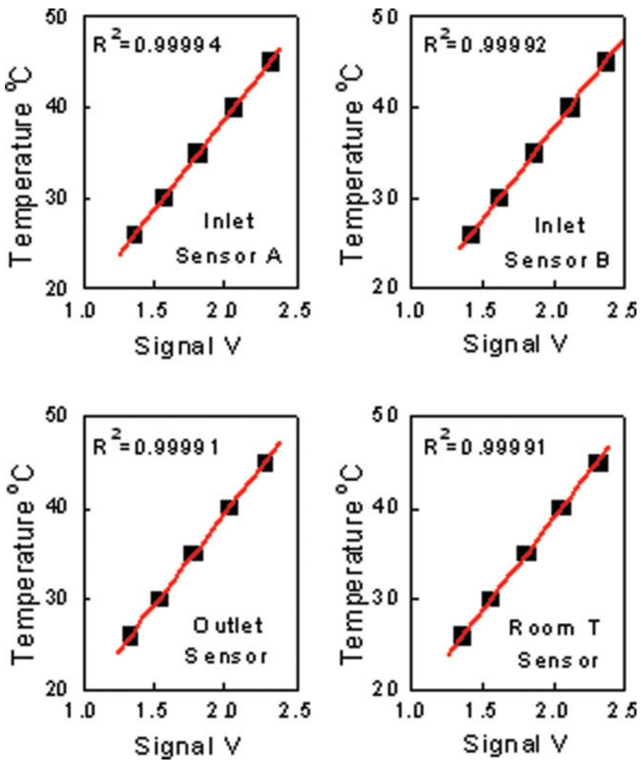

Figure 4. The linear relation between the voltage signals with the temperatures.

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temperature bath during the calibration, and the relationship between the temperatures and the signals were recorded. Figure 4 shows the liner relation between the signals and the temperatures of the four sensors used in the standard reactions and the lines fit well with the signals. The correlation coefficients are higher than 0.9999 for all the sensors used in the experiment.

Operation and calculation

The micro-reactor-based capillary calorimeter was operated in the continuous way and the online temperature was measured. In the standard reaction system, the NaOH solution was pumped into the straight channel of the mixing chip and the H_2SO_4 solution was pumped into the side channel. In the industrial reaction system, the CCA solution was pumped into the straight channel of the mixing device and the oleum or pure H_2SO_4 was pumped into the micro-pore. The reactants in the main channel were pumped into the devices first and then followed with the other. At the same time, the data acquisition system was started and the temperatures were recorded. After few minutes, the temperatures were stable and the measurement was finished.

The reaction enthalpies were calculated from the energy conservation in this work. As the reactions were taken place at nearly adiabatic condition, the released heat from the reaction was transformed to the thermal energy (temperature) rise of the reaction system. However, although adiabatic room was used, the thermal loss still existed. A blank experiment with hot fluid was made to evaluate the lost heat. By controlling the operating conditions, the thermal loss was first reduced to a low level and then calculated by a heat transfer equation as shown in Eq. 1.

$$Q_L = \mathrm{ha}\Delta T_m = \mathrm{ha}\frac{(\overline{T}_{in} - T_0) - (T_{out} - T_0)}{\ln\left[(\overline{T}_{in} - T_0)/(T_{out} - T_0)\right]} \qquad (1)$$

where Q_L is the thermal loss from the system, W; ha is the heat transfer coefficient, W/°C; ΔT_m is the log mean temperature difference between the system temperature with the environment temperature, °C; $\overline{T}_{in}$ is the mass average temperature of the inlet fluids, °C; T_{out} is the temperature of the outlet fluids, °C; and T_0 is the environment temperature, °C.

By adding the thermal energy rise and the thermal loss, the total heat released from the reaction could be calculated. The molar reaction enthalpy of the reaction was calculated by dividing the total released heat to the molar consumed dose of the reactant as shown in Eq. 2. Since both the two systems have an excessive reactant (NaOH and CCA), the consumed dose was actually the feed dose of the insufficient reactants.

$$\Delta_r H_m = -\frac{Q_L + \Delta H}{n_A} \qquad (2)$$

where ΔH is the thermal energy rise of the reaction system, W; and n_A is the molar feed rate of insufficient reactant A (H^+, pure H_2SO_4 or oleum), mol/s. The thermal energy rise was calculated from the heat capacity of the reaction system and the temperatures measured by the sensors. For the standard reaction between NaOH and H_2SO_4, the heat capacity of the whole system was estimated by the heat capacity of 0.8 mol/l NaOH since the flow rate of the initial NaOH solution was controlled the same as the H_2SO_4 solution. For the industrial reactions, the enthalpy rise was calculated by adding the thermal energy rises of all the reactants as shown in Eq. 3.

$$\Delta H = \begin{cases} \int_{\overline{T}_{in}}^{T_{out}} M\mathrm{Cp}_{solution}\,dT & \text{standard reaction} \\ \int_{T_{in}^{CCA}}^{T_{out}} (M_{CCA}\mathrm{Cp}_{CCA} + M_{C_6}\mathrm{Cp}_{C_6})\,dT & \\ + \int_{T_{in}^{S}}^{T_{out}} M_S\mathrm{Cp}_S\,dT & \text{industrial reaction} \end{cases} \qquad (3)$$

where, M is the total mass flow rate of the NaOH and H_2SO_4 solutions, g/s; M_{CCA} is the mass flow rate of CCA, g/s; M_{C6} is the mass flow rate of n-hexane, g/s; M_S is the mass flow rate of pure H_2SO_4 or oleum, g/s; $\mathrm{Cp}_{solution}$ is the heat capacity of the standard reaction, J/(g °C); Cp_{CCA} is the heat capacity of CCA, J/(g °C); Cp_{C6} is the heat capacity of n-hexane, J/(g °C); Cp_S is the heat capacity of pure H_2SO_4or oleum, J/(g °C), $\overline{T}_{in}$ is the

Table 1. The Heat Capacities of the Working System[19–21]

$\mathrm{Cp}_{solution}$	4.016 J/(g °C)	25–32°C
Cp_{CCA}	1.68 + 0.0068T J/(g °C)	25–60°C
Cp_{C6}	2.16 + 0.0043T J/(g °C)	25–60°C
Cp_{H2SO4}	1.37 + 0.0017T J/(g °C)	25–40°C
Cp_{oleum}	1.82 + 0.0025T J/(g °C)	25–60°C

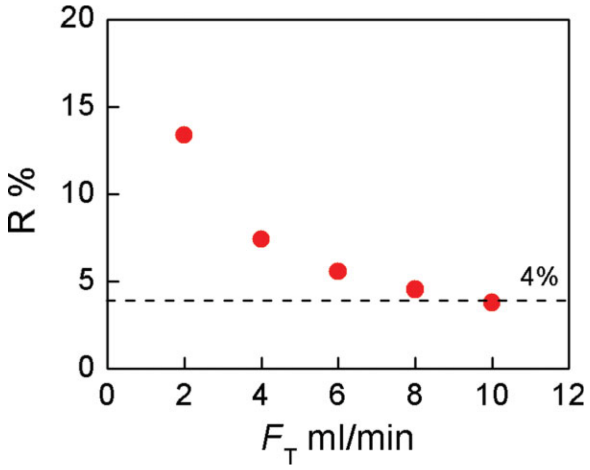

Figure 5. The thermal loss ratios at different flow rates.

F_T is the volumetric total flow rate of the two inlet fluids. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

mass average temperature of the entering NaOH and H_2SO_4 solutions, °C; $T_{in}{}^{CCA}$ is the temperature of the entering CCA/n-hexane solution, °C; and $T_{in}{}^{S}$ is the temperature of the entering pure H_2SO_4 or oleum, °C. The values of these heat capacities are given in Table 1.

Results and Discussion

Blank experiment

Blank experiments were done before the measurements to adjust the operating conditions and measure the thermal loss from the system with hot water and hot n-hexane. The plastic calorimeter is chosen as an example to introduce the blank experiment in this section. The main operating condition in enthalpy measurement is the flow rates of the two reactants. Proper rates should be found to have a low thermal loss. To simplify the process, the flow rates from the two inlets were the same as each other in the investigation of the standard reaction. The thermal loss is characterized by a value called thermal loss ratio, which is identified by the ratio of the lost heat to the total enthalpy flow rate in the calorimeter, as shown in Eq. 4.

$$R = \frac{\int_{T_{out}}^{\overline{T}_{in}} \mathrm{Cp_{water}} dT}{\int_{T_0}^{\overline{T}_{in}} \mathrm{Cp_{water}} dT} \times 100\% \tag{4}$$

where $\mathrm{Cp_{water}}$ is the heat capacity of water, J/(g °C). The enthalpy at environment temperature is seemed as zero in this work. The value of the thermal loss ratios at different flow rates are given in Figure 5. It is found that the thermal loss ratio decreases with the increase of the flow rate. The reason is that the total enthalpy flow rate increases with the increase of the flow rate, but the lost heat changes little. At a total flow rate of 10 ml/min, the thermal loss ratio is less than 4% and it is chosen as the flow rate for the standard reaction.

To keep the accuracy of the measurement, the thermal loss is considered in the calculation of the reaction heat, although it is lower than 4%. The thermal loss in the plastic calorimeter is calculated by the convectional heat transfer equation as shown in Eq. 5.

$$Q_L = \mathrm{ha}\Delta T_m = 0.0267\Delta T_m \tag{5}$$

For the stainless steel calorimeter, a similar blank experiment was done using n-hexane as the working system. When the total flow rate is about 80 ml/min, the thermal loss ratio can be reduced to 2%. The flow rate of 80 ml/min is chosen as the working flow rate of the industrial reaction and the convectional heat transfer equation is given in Eq. 6.

$$Q_L = \mathrm{ha}\Delta T_m = 0.029\Delta T_m \tag{6}$$

The standard reaction

The neutralization enthalpy of dilute acid and base solutions is a common reaction enthalpy, so it was used first to test this new calorimeter. According to the temperature difference between the inlet and outlet fluids the reaction heat can be calculated with Eqs. 2, 3, and 5. Excessive NaOH was used in the measurement, so the molar reaction enthalpy is calculated from the feed rate of the H^+, as shown in Eq. 7.

$$\Delta_r H_{mN} = -\frac{Q_L + \Delta H}{n_{H^+}} \tag{7}$$

where, $\Delta_r H_{mN}$ is the molar neutralization enthalpy measured from the new calorimeter, kJ/mol; and n_{H+} is the molar feed ratio of the H^+. The recorded temperature profiles are shown in Figure 6. It is found that the temperature difference is stabilized at about 300 s after the measurement was started at $C_{H+} = 0.744$ mol/l. After that the temperature difference changes little. For low H^+ concentration, the stable time is low too. This fast temperature response is benefit for the reducing of the reactant; 20 ml reactants are enough to complete the measuring process at $C_{H+} = 0.143$ mol/l.

The average temperature values between 400 s and 500 s are applied to calculate the reaction heat and the results are given in Table 2. The molar neutralization enthalpy of dilute acid and base solutions is −57.3 kJ/mol in literature.[19] The

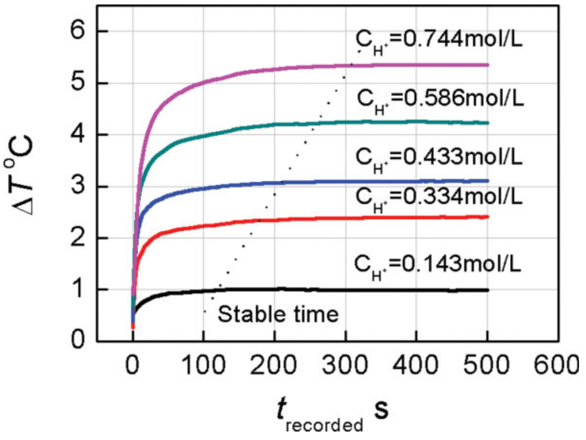

Figure 6. The time profiles of recorded temperatures.

ΔT is temperature difference between the outlet temperature and the mass average inlet temperature ($\Delta T = T_{out} - \overline{T}_{in}$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table 2. The Molar Reaction Enthalpies of the Standard Reaction Measured by the Micro-Reactor Based Calorimeter

C_{H+}	$\Delta_r H_{mN}$ (kJ/mol)	Relative Error (%)
0.143	−57.97	1.2
0.334	−59.14	3.2
0.433	−58.92	2.8
0.586	−58.65	2.4
0.744	−59.24	3.4

relative errors of the measured reaction enthalpy are given in Table 2. All the relative errors are less than 3.5%.

The fast and accurate measurement is contributed by the nice mixing performance and strict plug flowing in the calorimeter. In the micro-reactor-based capillary calorimeter, the heat transfer Peclet number at the outlet can be estimated by Eq. 8.

$$Pe = \frac{uL}{\alpha} = \frac{4F_T L}{\pi d^2 \alpha} \tag{8}$$

where, u is the average velocity in the capillary, m/s; L is the length of the capillary, m; α is the thermal diffusion coefficient of the solution, m^2/s; F_T is the volumetric total flow rate, m^3/s; and d is the inner diameter of the capillary, m. The Pe is 1.3×10^6 in this experiment, which shows a plug flowing in the calorimeter. The residence time in the calorimeter is just 1.33 s and the reaction time can be seemed as the residence time. Although the residence time is short, the reaction is completed due to the nice mixing performance in the calorimeter.

The industrial reaction—homogeneous reaction

Fast exothermal reactions are common reactions in the chemical engineering process, and it is important to know their thermodynamic characteristics. The reaction between CCA and H_2SO_4 was chosen as an industrial example to test the new micro-reactor-based capillary calorimeter. At feed ratio of CCA to H_2SO_4 higher than five, the reaction is a homogeneous reaction system. The molar reaction enthalpy is −13.58 kJ/mol.[22] As the reaction is a reversible reaction, excessive CCA was used in the measurement to avoid the effect of the chemical equilibrium on the consumption of H_2SO_4. To represent the heat released respect to the feed quantity of H_2SO_4 clearly, an apparent reaction enthalpy is defined as shown in Eq. 9,

$$\Delta_r \tilde{H}_{mP} = -\frac{Q_L + \Delta H}{n_{H_2SO_4}} \tag{9}$$

where $n_{H_2SO_4}$ is the molar feed rate of pure H_2SO_4, mol/s. A series of measurements at different feed ratios of CCA to H_2SO_4 were preceded with parallel experiments. The stabled temperatures were cut to calculate the apparent enthalpy and the results are given in Figure 7. The stable time of this experiment is between 2 and 3 min for one measurement. Figure 7 shows that at feed ratios lower than 12, H_2SO_4 is not consumed completely and the absolute value of apparent reaction enthalpy increases with the increase of the feed ratio. When the feed ratio is higher than 12, the apparent reaction enthalpy changes little with the variation of the feed ratios, which means H_2SO_4 is consumed completely and the molar reacted rate of H_2SO_4 is equal to the molar feed rate. The apparent reaction enthalpy is the real reaction enthalpy ($\Delta_r H_{mP}$) at this time. From the figure it can also be seen that the repeatability of the experiment is good. The largest relative error of the parallel trials is only 2.4%. The results given by the micro-reactor-based calorimeter fit well with the result from the literature.

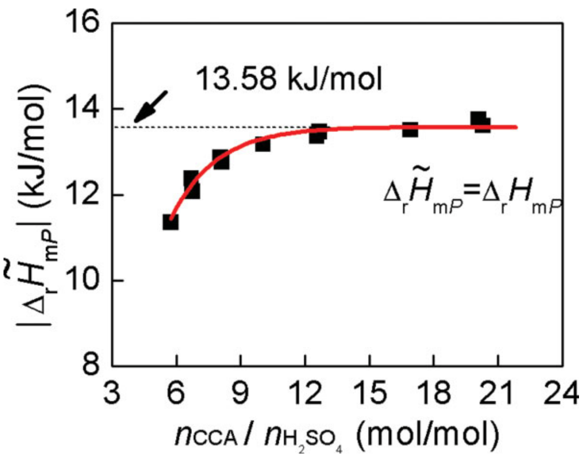

Figure 7. The apparent reaction enthalpy at different feed ratios of CCA to H_2SO_4.

The longitudinal coordinate is the absolute value of apparent reaction enthalpy. The flow rate of CCA solution is fixed at 78 ml/min and the flow rate of H_2SO_4 is changed from 1 to 3.6 ml/min in this experiment. The initial temperature was ranged from 25 to 35°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The industrial reaction—heterogeneous reaction

Besides homogenous reactions, many reactions in the chemical engineering process are heterogeneous reactions.

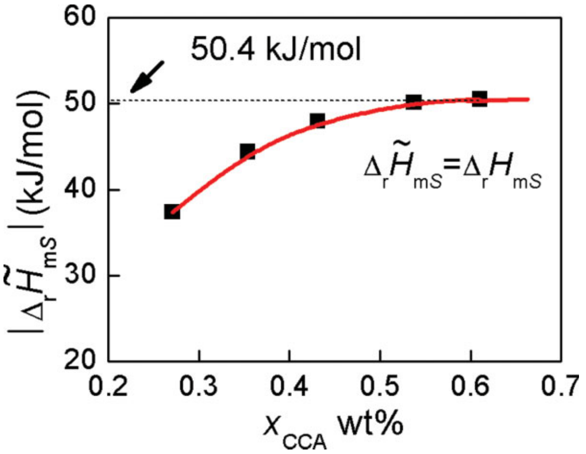

Figure 8. The apparent reaction enthalpy at different CCA concentrations.

x_{CCA} is the mass percent of CCA, the longitudinal coordinate is the absolute value of apparent reaction enthalpy. The flow rate of CCA solution is fixed at 78 ml/min and the flow rate of oleum is fixed at 6.2 ml/min in this experiment. The initial temperature was ranged from 25 to 35°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table 3. The Comparison of the Two Measuring Methods

Method	Volume	Running Time	Oleum Consumption
Micro-reactor	<1 ml	2–3 min	36–58 g/a measurement
Dripping calorimeter	2 l	1 h	250 g/a measurement

The reaction between CCA/n-hexane solution and oleum is a kind of heterogeneous reaction. Oleum was dispersed into CCA/n-hexane solution forming a liquid/liquid system. CCA is extracted from the oil phase to the oleum phase, and then the reaction takes place. The selectivity of this reaction is higher than 97% according to our previous results,[14] so only the main reactions are considered to have contributions on the enthalpy measurement. Like the homogenous reaction, the enthalpy of the reaction between CCA and oleum is still calculated from the temperature rise, since there is no phase transition in the system. For the reactions with phase transition, such as forming gases, the phase transition energy should also be considered. The molar reaction enthalpies of this system is -13.58 kJ/mol H_2SO_4 and -50.4 kJ/mol SO_3 ($H_2S_2O_7$) in literature.[22] Similar with the reaction between CCA and pure H_2SO_4, an apparent reaction enthalpy is defined too as shown in Eq. 10.

$$\begin{aligned} \Delta_r H_{mP} \cdot n_{H_2SO_4} + \Delta_r \widetilde{H}_{mS} \cdot n_{SO_3} &= -(Q_L + \Delta H) \\ \Delta_r \widetilde{H}_{mS} &= -\frac{Q_L + \Delta H + \Delta_r H_{mP} \cdot n_{H_2SO_4}}{n_{SO_3}} \end{aligned} \qquad (10)$$

where, n_{SO_3} is the molar feed rate of SO_3. The apparent reaction enthalpies with the variation of CCA concentrations are given in Figure 8. It shows that the absolute value of the apparent reaction enthalpy increases with the increase of CCA concentrations. When the concentration is higher than 55%, the apparent reaction enthalpy changes little with the variation of the CCA concentrations, which means oleum is consumed completely and the apparent reaction enthalpy is real reaction enthalpy ($\Delta_r H_{mS}$) at this time. From Figure 8, it can be seen that the reaction enthalpy measured by the micro-reactor-based capillary calorimeter fits well with the result from the literature. Besides, as a heterogeneous reaction, the mixing of the reactants is based on the mass transfer process between phases, which is much slower than the homogenous mixing process. With the nice heterogeneous mixing performance of the micro-reactor, this heterogeneous reaction is finished just with a residence time of 0.34 s. The stable time of this experiment is between 1.4 and 2.2 min for one measurement.

Comparing with the traditional dripping calorimeter used to measure the reaction enthalpy in literature,[22] the measurement proceeds quickly in micro-reactor-based calorimeters and the consumption of the reactants is low, as shown in Table 3. Additionally, due to the safety of micro-reactors, the safety of the measurement can also be accomplished for fast exothermal reactions with very reactive compounds like oleum in this work.

Conclusion

In summary, this work represented that the micro-reactor-based capillary calorimeter was an effective device to measure the enthalpy of fast exothermal reaction. The structure of this new calorimeter was simple and operated in the continuous way. By detaching the temperature sensors and the mixing channel with capillaries, the recorded temperatures only represented the fluids and the reaction enthalpy can be easily calculated with high accuracy. The reaction between NaOH and H_2SO_4 was chosen as a standard system to test the micro-reactor-based calorimeter, and the relative error between measuring result and literature result was lower than 3.5%. It was found that the temperatures could be stabled just in 5 min due to the nice mixing and plug flowing in the capillary. This fast temperature response benefits in reducing the consumption of reactants. To apply this new calorimeter in the industrial reaction system, the reaction between cyclohexanecarboxylic acid and oleum was chosen as another experimental system. By controlling the operating conditions, the reaction was taken to a homogeneous process and a heterogeneous process. Both measurements from the two systems were stabled quickly too, and the measuring results fit well with the results in literature. The repeatability of the experiment was good, and the relative error of the parallel trials was less than 2.4%. Although the mixing in the heterogeneous process was slower than the homogeneous process, the heterogeneous reaction still completed during the measurement with a residence time of 0.34 s, which showed the nice heterogeneous mixing performance of the capillary micro-reactor. Comparing with the traditional dripping calorimeter, the measurement proceeds quickly in this new calorimeter and the consumption of the reactants was low, which was benefit to the safety of the measurement.

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