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Short communication

Heat pipe controlled syntheses of ionic liquids in microstructured reactors

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ABSTRACT

The combination of a heat pipe and a microstructured reactor allows to perform highly exothermal reactions under safe conditions. First experiments for the synthesis of 1,3-dimethylimidazolium-triflate from 1-methylimidazol and methyl triflate showed that at high flow rates of more than 5 ml/min through a single 300 μm × 500 μm wide and 400 mm long channel quantitative conversion could be achieved. This chemical reaction, known for extreme heat release, can be retained under thermal control even at much higher flow rates.

1. Introduction

Ionic liquids (ILs) are versatile materials for several chemical applications, such as alternative solvents ('Green Solvents'), phase transfer catalysis or electrochemical deposition. They are defined as liquids at temperatures below 100 °C consisting entirely of ion pairs, so the most important chemical property is a negligible vapor pressure. Therefore, purification after synthesis by distillation or recrystallization is in most cases not possible.

At the first glance, ILs are usually synthesized in a simple manner by *N*-alkylation of suitable substrates, e.g., tert. amines, imidazoles, and pyridines, with alkylating agents like alkyl halides, alkyl sulfates, sulfonic acid esters, sultones, and others [1]. This type of chemical reaction suffers often from the huge heat release and therefore a lot of effort was devoted to the design of batch or continuous flow processing in macro- or micro-scale.

To investigate the usability of heat pipe cooling the alkylation of 1-methylimidazole (MIM (**1**)) with methyltriflate (MeOTf (**2**)) to 1,3-dimethylimidazolium trifluoromethanesulfonate ([DMIM][OTf] (**3**)) was chosen as a reference reaction (see Fig. 1) [2].

This reaction is extremely fast and highly exothermal. With regard to kinetics, a reaction order of two can be surely assumed and the reaction heat is released instantaneously [3,4]. It is known, that the chemical reaction is determined by the formula given above. Side products will not be detected, except discoloration due to overheating the reaction mixture [5]. Consequently, removal of the reaction heat is a crucial point for this continuous flow synthesis of (**3**) [6].

To solve this problem, a special designed microstructured reactor cooled by a heat pipe was used, which transfers thermal energy by evaporation and condensation of a thermal fluid. Thus, the difference between the vapor pressure over the hot end and the cooling end is the driving force for the mass transfer of the thermal fluid inside a heat pipe. Theoretically, the flow velocity of the vapor molecules can reach values close to the speed of sound. Therefore, heat pipes should be a very efficient tool for rapid cooling (and even heating) of microstructured reactors.

2. Experimental set-up and procedures

As a microstructured reactor a stainless steel (1.4435) plate with a simple single reaction channel was used (Fig. 2). The counterpart of the stainless steel plate, i.e. the cover of the microstructured channel, is made of polyetheretherketone (PEEK), a material with low heat conductivity, to ensure that the heat flux is mainly distributed through the stainless steel and the mounted heat pipe. In addition, a graphite gasket seals the two plates.

Reactants can be injected into three parallel channels which conflate in an integrated static mixer with a similar design of a so-called caterpillar mixer [7]. For the investigation of the IL (**3**) synthesis however, two of these inlets were used.

The length of the reaction channel, from the end of the static mixer to the product outlet is 400 mm, providing necessary residence time. With a cross section of 500 μm (wide) and 300 μm (depth), the channel provides a volume of 0.6 ml.

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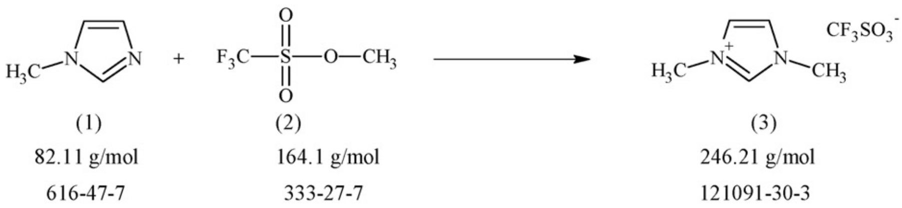

Fig. 1. Reaction scheme for the synthesis of 1,3-dimethylimidazolium-triflate.

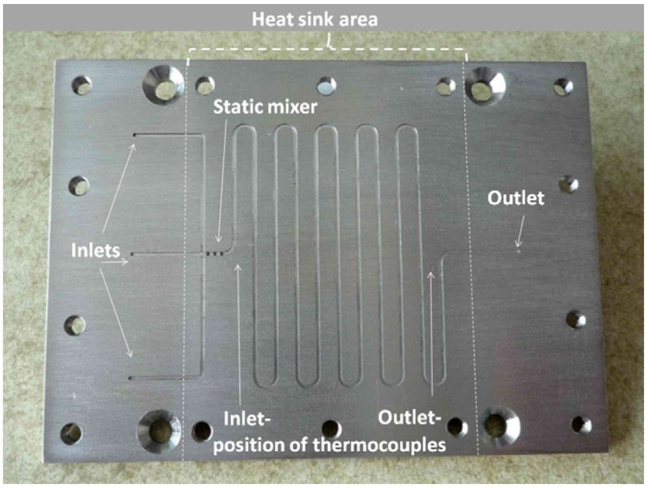

Fig. 2. Microstructured reactor plate with outer dimensions of 58 mm × 80 mm. The positions of the thermocouples and the heat sink of the heat pipe system are marked.

On the opposite site of the stainless steel part a heat pipe system of six separate heat pipes combined with an additional fan (Thermaltake^{TM} CL-P0369, Taiwan, http://www.tt-germany.com/) can be mounted as a heat sink to remove the released reaction heat (Fig. 3). This heat pipe system is originally used to for CPU cooling with thermal power losses above 120 W.

Temperatures were measured with NiCrNi thermocouples and logged into Voltkraft^{TM} K204 (Conrad Electronic, Hirschau, Germany) data logger.

1-Methylimidazole (**1**) and toluene were purchased from Fluka (Deisenhofen, Germany), methyl triflate (**2**) from ABCR GmbH, Karlsruhe, Germany. To ensure an equimolar continuous feed of the reactants, preparative HPLC pumps (Varian PrepStar^{TM}, SD-1, 50 ml Ti pump heads) were used. These pumps provide a very low deviation of the volume flow of 0.3% [8]. The volume flows rates ((**2**):(**1**)) were set to a 1:1 molar ratio, i.e. in milliliters per minute 0.356:0.250; 0.712:0.500; 1.42:1.00; 2.85:2.00; 5.70:4.00 and 11.4:8.00; or from 0.03 mol to 0.1 mol each.

Samples were collected directly from the outlet of the reactor. Quenching of the reaction was not possible due to the extremely high reactivity of (**2**). Incomplete conversion led to an instantaneous thermal overrun at the reactor outlet combined with an evaporation of (**2**). To characterize the obtained product, proton 300 MHz ^{1}H NMR spectra were measured either in deuterated chloroform or dimethyl sulfoxide (DMSO) on a Bruker^{TM} AC 300 spectrometer. To determine the conversion qualitatively the remaining amount of (**1**) was measured.

The microstructured reactor without the mounted heat pipe system was equipped with two thermocouples on the outer surface, one above the static mixer and the other one above the end of the reaction channel. The positions of the thermocouples mark the pad covered by the active surface of the heat transfer pad of the heat pipe. In addition, a thermocouple is placed into the outlet of the reactor to measure the fluid temperature directly. To avoid unspecific cooling by circumfluent air-flow, the reactor is placed into isolation material.

If the heat pipe system is mounted the thermocouples cannot be mounted on the reactor surface directly. Therefore, one thermocouple is placed at the side wall of the heat transfer plate and the other one directly on one of the heat pipes (Fig. 3). Again, a thermocouple is placed into the outlet of the reactor to measure the fluid temperature directly.

3. Results and discussion

To compare the effectiveness of the heat pipe system, the reaction was performed first without any cooling for two different flow rates, 0.35:0.25 and 0.7:0.5 (ml (**2**):(**1**)) (see Fig. 4).

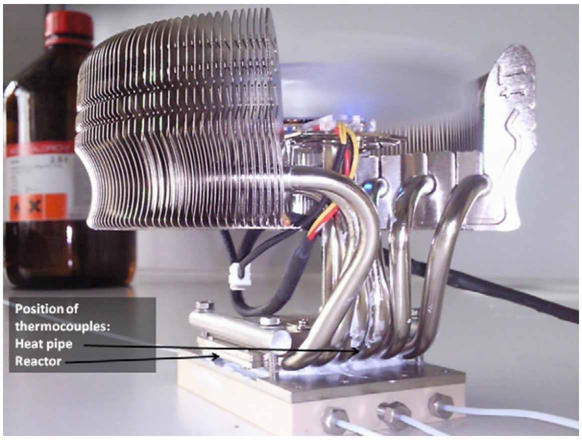

Fig. 3. Heat pipe system mounted on a microstructured reactor plate. The fan can be used as optional cooling.

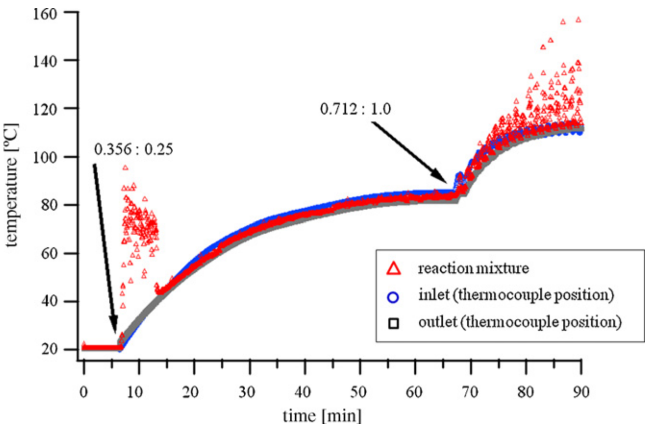

Fig. 4. Temperature curves without mounted heat pipe system. The flow rate unit is ml/min.

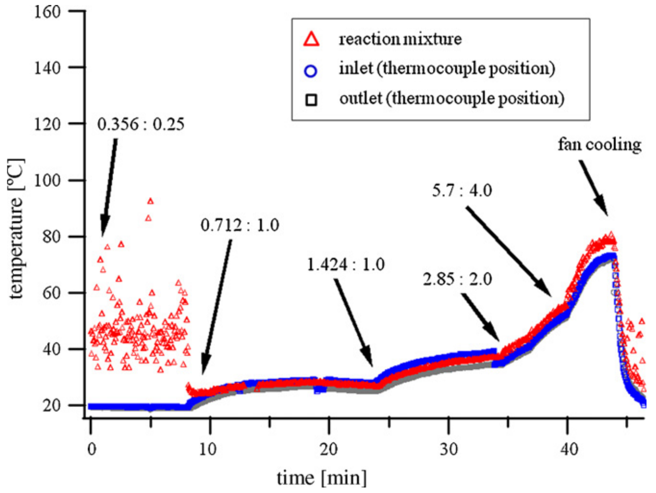

Fig. 5. Temperature curves with heat pipe and additional active cooling by an optional fan.

Starting with the lower flow rate, the reaction is already quenched inside the reactor due to an insufficient too low reaction temperature at the beginning. Even the residence time of about 1 min is not enough for the reaction to be completed. As a consequence, the most of the reaction takes place under undefined conditions at the reactor outlet. There, the temperature of the reaction mixture fluctuated up to 90 °C due to intermittent reaction. But the temperature rises slowly inside the reactor by the released heat until the inner reactor temperature reaches a value of approximately 45 °C. Then, suddenly the reaction proceed by self-acceleration inside the reactor (compare Fig. 4) and forms a stable thermal equilibrium at roughly 90 °C after 1 h.

After doubling the flow rate, i.e. shorten the residence time down to 30 s, the released reaction heat raised the reactor temperature by far the boiling point of (**2**). The formed vapor blows out the reaction mixture causing thermal runaways monitored by temperature fluctuations at the reactor outlet where the reaction is performed to completion.

Not surprisingly, this chemical reaction cannot be performed safely even in a microstructured reactor without a proper and efficient heat management.

By equipping the microstructured reactor with the heat pipe system a much better heat management and therefore higher throughputs were expected. However, using the same low flow rate as for the set-up without heat pipe cooling (0.356:0.25), no stable reaction conditions could not be achieved because the efficient heat removal quenches the reaction inside the reactor. By increasing the flow rates the heat pipe system allows a thermal control of the reaction, as shown in Fig. 5. Up to flow rates of (2.85:2.0) the residence time decreases down to 8 s. The respective ^{1}H NMR spectra of the raw products indicate a complete conversion (Fig. 6).

At a higher flow rate (5.70:4.0) the residence time is shortened to 4 s and the temperature rises immediately because of the limited heat removal capacity of the heat pipe system. This leads to an evaporation of (**2**) inside the microstructured reactor and a subsequent blow-out of the reaction mixture. As a consequence, the ^{1}H NMR spectrum shows an incomplete conversion.

The reaction can be retained under control by using an optional fan to cool the heat pipes by air-flow. As shown in Fig. 5, the temperature decreases immediately down to room temperature after turn-on the fan. It is obvious that a controlled cooling air-flow and a suitable residence time provided by bigger inner volume of the microstructured reactor can ensure safe and controlled reaction conditions even at higher flow rates.

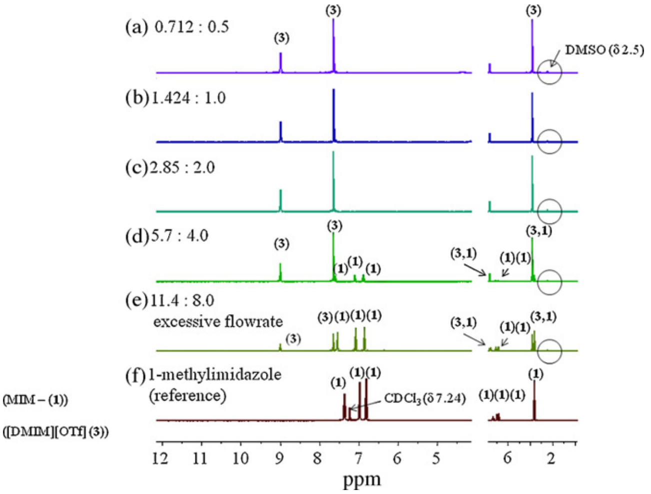

Fig. 6. ^{1}H NMR spectra for the runs with heat pipe. Chemical shifts for are given for (a–c) by ^{1}H NMR (300 Hz, DMSO) δ [ppm]: 3.83 (s, 6H), 7.65 (s, 2H), 9.00 (s, 1H), with traces of water ($\delta = 2.49$, 0.5). The reference spectrum of MIM (**1**) was measured in $CDCl_3$: δ: 3.63 (s, 3H), 6.82 (s, 1H), 6.99 (s, 1H), 7.24 ($CDCl_3$), 7.37 (s, 1H).

4. Conclusions

As shown above, the combination of a heat pipe and a microstructured reactor allows to perform highly exothermal reactions, not beyond IL syntheses, under safe conditions. First experiments showed that even unexpected high flow rates of 20 ml/min can be thermally controlled by the use of heat pipe systems with air-flow cooling, given that a sufficient residence time can be provided by the microstructured reactor.

In general, heat pipe systems can provide a very efficient passive cooling without using cooling liquids, e.g., water, thermostated baths or other materials which can have an impact on ecology and wasting energy. Especially for rapid growing application of microstructured reactors the implementation of heat pipes can contribute to a reduction of costs. Therefore, further investigations will be done with a redesigned reactor to increase the throughput remarkably. The aim will be to provide a suitable automated pilot-scaled system for small scale production of different ILs.

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