Contents lists available at ScienceDirect

Chemical Engineering Research and Design

journal homepage: www.elsevier.com/locate/cherd

Laser rapid-prototyping and modular packaging of chip-based microreactors for direct fluorination reactions

Dawid Cichowski[a,*], *Pengcheng Zhang*[b], *Peter Woias*[a], *Ingo Krossing*[b], *Keith Cobry*[a]

[a] *Department of Microsystems Engineering, Laboratory for Design of Microsystems, University of Freiburg, Germany*
[b] *Department of Chemistry, Laboratory for Inorganic Chemistry, University of Freiburg, Germany*

ARTICLE INFO

Article history:
Received 3 February 2017
Received in revised form 23 August 2017
Accepted 14 October 2017

Keywords:
Laser rapid prototyping
Packaging
Direct fluorination
Micromachining
Chip-based microreactors
Microfluidic

ABSTRACT

We have developed a laser rapid-prototyping method for the realization of microchannels and nozzles in silicon and nickel chips. A practical application of such microreactors, made by rapid prototyping, is the direct fluorination of organic substrates via microbubbles, a highly exothermic and chemically harsh reaction. By employing optimized laser raster ablation procedures, different channel cross-section shapes could be manufactured with adjustable channel wall angles. Modular compressive chip packaging allowed for safe reactor sealing without permanent chip-to-chip bonding. Fluorine gas was introduced into the microchannels, producing a monodisperse chain of bubbles (diameter ~200 μm) with the reaction taking place at the gas/liquid interfaces. Successful direct fluorinations of fluoroethylene carbonate were carried out over 107 h at room temperature without noticeable leakage or corrosion. High reaction efficiency and an excellent space–time yield for the four products (4,4-F_2EC: *trans*-F_2EC: *cis*-F_2EC: F_3EC) was demonstrated (65% F_2-usage, 1.41×10^6 mol m^{-3} h^{-1}). *cis*- and *trans*-F_2EC have shown great potential as electrolyte additives for increasing the lifetime of lithium ion batteries, and trifluorinated F_3EC, with eventually improved characteristics, was for the first time fully characterized, e.g. by NMR spectroscopy.

1. Introduction

Microstructured fluidic platforms provide great advantages in a wide range of thermal and chemical process engineering applications, including extractions, multiple emulsion droplet production, phase separations, synthesis of nanoparticles, organics, polymers, pharmaceuticals and other high-value chemicals (Yao et al., 2015; Polyzoidis et al., 2016; Nagaki et al., 2014; Wohlgemuth et al., 2015; Niu et al., 2015; Elvira et al., 2013). Depending on the chemical reactions involved, corrosive conditions, high pressures and highly exothermic processes are often present, which can be managed safely in the small reagent volumes in microchannels. Simultaneously, the high surface-to-volume ratios achieved in a microreactor serve to intensify processes by increasing heat and mass transfer (Razzaq et al., 2009). Such continuous flow reactors with channel dimensions in the sub-millimeter range thereby provide improvements in mixing and thermal management, and give access to a large variety of reaction conditions, which may otherwise not be feasible.

Laser ablation has been shown in prior literature to fabricate microchannels in microfluidic platforms (Gavriilidis et al., 2002; Chen et al., 2013a; De Marco et al., 2012). None of these studies, however, have investigated the realization of channels with arbitrary cross-sections or defined surface roughness in a systematic way. However, these design parameters would open a whole range of research opportunities on novel mixing geometries, tunable friction effects on a microfluidic scale, as well as bubble or droplet generation via manipulation of noz-

* *Corresponding author.*
E-mail address: cichowski@imtek.de (D. Cichowski).
https://doi.org/10.1016/j.cherd.2017.10.017

zle geometries. In addition, laser processing allows for a flexible choice of the reactor substrate material. Our development of a cheap and easy-to-manufacture chip-based microreactor system for the direct fluorination of organic substrates demonstrates the potential of such a design adaptation through laser rapid-prototyping with a versatile and reusable platform.

The use of conventional precision machining for the manufacture of fluidic channels for harsh conditions often involves high costs and long production times. Examples of such modular microreactors exist, for example the MikroReaktionsSystem/MMRS (Ehrfeld Mikrotechnik – Bayer Technology Services), the Lonza FlowPlate and the Corning Advanced Flow Systems. Integration into industrial production facilities, however, remains in a nascent phase due to economic risk factors related to manufacturing, maintenance and operation costs (Ehrfeld, 2012a, 2012b; Lonza, 2009; Corning, 2016; Hessel, 2015; Hessel et al., 2013; Nikačević et al., 2012; Bieringer et al., 2013). Alternatively, chip-based systems may be microfabricated with standard processes in a clean room. The disadvantage is that complex pre- and post-processing steps are required, being both time-consuming and expensive, as common microfabrication techniques like LIGA, DRIE or KOH etching require the deposition and patterning of multiple mask layers via photolithography (Kandlikar and Grande, 2003). In this paper, we present an alternative to these fabrication strategies. Laser rapid-prototyping avoids many of these costs and can save production time through a significant reduction in the number and complexity of the process steps.

Challenging, chemically harsh reactions are one area in which continuous-flow microreactors show great potential. This includes rapid direct fluorinations of organic substrates. Elemental fluorine (F_2) acts as an extremely strong oxidizing agent, resulting in highly exothermic or even explosive reactions (Navarrini et al., 2012; Lang et al., 2012; Elgue et al., 2012). Microreactors, with their low-volume but continuous flow, allow one to carry out direct fluorinations safely at a variety of temperatures, whereas a similar batch process might require cryogenic cooling (Newman and Jensen, 2013). Furthermore, reactions demonstrate improved thermal and mass transfer control, resulting in higher potential process efficiencies, both in terms of energy as well as atom usage. Targeted local heating and cooling schemes with large temperature gradients have been demonstrated as feasible in such systems (Mason et al., 2007; Hartman et al., 2011).

The design of reactors to date has remained long unchanged; they are based, for the most part, on individual straight channels manufactured with conventional machining techniques (exception: Jensen Group). Additionally, previous works have only demonstrated slug- or cylindrical bubble flow. Fluorine reactors with monodisperse microbubbles, as described in the current work, have not been reported. In light of the importance of highly fluorinated materials (Furuya et al., 2011; Kharitonov, 2008; Lee, 2007; Lindgren et al., 2016; Okamoto et al., 2016; Okazoe, 2010a, 2010b; Yang et al., 2011) for many technical applications, as well as the high volume used in pharmacy (20%) and agrochemistry (30%) (Furuya et al., 2011; Böhm et al., 2004; Hunter, 2010; Isanbor and O'Hagan, 2006; Manteau et al., 2010; Müller et al., 2007; Shibata et al., 2008; Wu et al., 2012), the lack of research into the application of microreactors for direct fluorinations is surprising. Direct fluorination with F2, rather than after reaction with HF, presents a much more economical method. Indeed, the robust and simple microreactor system presented in this work could overcome many of the technical and economic challenges to the implementation of direct fluorinations found at present.

From the view of process engineering, one of the decisive factors for an efficient direct fluorination of liquid solvents with a high space–time-yield is the size of the interfacial area between gas and liquid, where the reaction process occurs. Gas–liquid contactors using microchannels achieve the greatest such surface to volume ratios (Mallia and Baxendale, 2015). Several groups in the literature have demonstrated the feasibility of running a direct fluorination reaction in microchannel reactors by realizing reaction interfacial areas following different approaches in continuous flow, including slug (Jähnisch et al., 2000; De Mas et al., 2014; de Mas et al., 2005; , 2008), annular (Chambers et al., 2001; Chambers and Spink, 1999) or falling film flows (Jähnisch et al., 2000). Jähnisch et al. (2000) developed a channel array of 32 parallel straight channels (60.5 mm long, 200 μm wide, 70 μm deep) for the direct fluorination of toluene with slug flow. An active miniaturized heat exchanger cooled the microreactor down to temperatures of −15 °C. With a total gas–liquid flow of 19 mL/h in the reaction channels, direct fluorinations were carried out with maximum fluorine concentrations of 50%. The reactor was made of steel and electroformed nickel. Annular flow was used by Chambers et al. (2001) to fluorinate 1,3-dicarbonyl derivatives in a single straight reaction channel in a nickel block (500 μm wide, 500 μm deep, 60.5 mm long), which was sealed with a transparent polytrifluorochloroethylene (PTFCE) plate and a stainless steel cover. Cooling channels inside the nickel block held temperatures of 0 °C for direct fluorinations of aromatics and dicarbonyls with an annular flow at rates of 0.5 mL/h and fluorine concentrations lower than 10%. Another microreactor for direct fluorinations of toluene was a falling film reactor demonstrated by Jähnisch et al. (2000). Here, an open straight microchannel array in nickel (each channel 300 μm wide, 100 μm deep) was positioned vertically during operation, generating a thin liquid thin film of tens of microns by means of gravity forces. This film was exposed at its surface to a fluorine–nitrogen gas mixture, with a maximum fluorine concentration of 50% at temperatures from −15 °C to −40 °C. A review of fluorination reactors with a detailed overview of the functionality and the performed chemical reactions is given by Löb et al. (2004) and Mallia and Baxendale (2015). Considering that the groups performed different reactions under varying process conditions in reactors of differing design, a direct comparison of reactor performance is challenging. However, they all required cooling down to 0 °C or below for a successful direct fluorination process. In the current paper, we demonstrate an even greater gas–liquid surface-to-volume ratio by using monodisperse bubbly flow and were able to demonstrate successful reactions with fluoroethylene carbonate (FEC) at higher temperatures.

Considering these advantages, we have designed and fabricated fluorine- and HF-resistant microreactors using inexpensive laser ablation techniques with a common and relatively inexpensive pulsed Nd:YAG laser system, to form microchannels with a hydraulic diameter of 280 μm in silicon and nickel substrates. In recent years, laser ablation has become a major tool for high precision machining in laboratory as well as industrial settings. Heat conduction and thermal damage to the surrounding material may be minimized through efficient energy deposition, which may be controlled via laser pulse length, scan rate, spot-size and power, in order to allow tunable exposure of the material to the focused laser energy. Short pulses vaporize material directly with their high power density so that even hard materials such as diamond and tungsten can be patterned with high aspect ratios (i.e. 1:50 for holes with 10^{11} W/cm^2 as shown by Madou (2002). Continuous-wave and long-pulse laser ablation, on the other hand, heats up the target surface through the melting point to the vapor phase, producing ablated as well as discrete melted areas (Gavriilidis et al., 2002). Many different materials, such as PMMA, PEG-MA, silicon, nickel alloy, copper/brass and aluminum may be patterned by finding the appropriate processing strategy, as demonstrated by Chen et al. (2013a) and Brunne et al. (2013). Selection of the appropriate combination of substrate material, processing method (e.g. cut, ablate, engrave), laser type (e.g. wavelength, pulse length, intensity), optical setup (e.g. focal length, beam formation, scanner type) and processing parameters (e.g. pulse frequency, pulse overlap, beam guidance) is essential for achieving the desired result (Cichowski, 2013). Direct ablation of various substrates can be performed to manufacture fluidic devices with microchannels without additional processing steps, or for producing masters for polymer imprinting processes (De Marco et al., 2012; Chen et al., 2013b).

The first reactor type presented in the current work (Reactor A) was fabricated out of a silicon chip, which was laser structured and coated with a protective nickel layer via electroplating. Silicon has a higher thermal conductivity compared to nickel (Si: 148 W m^{-1} K^{-1}, Ni: 79 W m^{-1} K^{-1}), allowing for a high rate of heat dissipation from exothermic reactions, thus reducing the potential build-up of hot spots. Its well-studied mechanical and electronic properties offer the potential for an integration of thin film actuators (i.e. heaters) and sensors for direct in-situ process monitoring and control (De Mas et al., 2014). The second reactor type (Reactor B) was laser-ablated directly from