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Review

A review on microreactors: Reactor fabrication, design, and cutting-edge applications

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HIGHLIGHTS

- Materials for microreactor fabrication, fabrication methods, and design principles are presented.
- Challenges in microreactor commercialization and need for integrated process is highlighted.
- Applications of microreactors in the field of nanoparticles, polymers, organic chemicals, and medicines are presented.

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ABSTRACT

This review focuses on the latest trends and advancements in microstructured reactors. With the recent drive towards the production of miniaturized systems, microstructured reactors have gained significant prominence in the chemical and process industries. Herein, we describe the fabrication, commercial aspects, design principles, and cutting-edge applications of microreactors. An overview of the significant areas of application under broad categories such as biological and pharmaceutical applications, inorganic and noble metal nanoparticles, and organic chemicals and polymers is also included. Finally, the article discusses future research prospects and key issues on microstructured reactors.

Contents

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1. Introduction

Advancements in science and technology have resulted in significant developments in microreactors and microreactor-based devices. Microreactor applications have expanded rapidly over the last few decades, displaying the effectiveness of microreactors over batch processes and existing large-size continuous reactors. (Jorda and Vizza, 2012; Lavric and Cerato-noyerie, 2012; Phillips et al., 2014; Yoshida et al., 2013; Zhang et al., 2011) Besides being the "micro" form of a large-size reactor, a microreactor can also be employed to improve various unit operations and reactions in microspace. These miniaturized chemical reactors mainly offer controllable and high-throughput methods for the synthesis of chemicals with high yield, stability, selectivity, less energy consumption, improved sample consistency, low reaction volume, and homogeneity. (Capretto et al., 2013; Fanelli et al., 2017; Fitzpatrick and Ley, in press; Liu et al., 2015a,b; Martínez-cisneros et al., 2012; Movsisyan et al., 2016; Newman and Jensen, 2013; Phillips et al., 2014; Wegner et al., 2012; Yoshida et al., 2013) The simplest microreactors comprise a micrometer-sized capillary tube (diameter < 1 mm) or a network of channels fabricated into a substrate. In 1959, Professor Feynman brought micromachining into the limelight by proposing the concept of a micron-sized motor. Today, the field of microreactor technology has grown out of micromachining into a discipline with its own concepts. Hence, the keywords "MEMS," "BioMEMS," "Lab-On-Chip," "μTAS" (Micro Total Analysis Systems), and "microreactors" have become synonymous to advanced microfluidic devices used in a variety of cutting-edge applications. The work cited in this review illustrates that compared to counterpart bulk reactions, synthetic procedures carried out in microreactors invariably generate purer products in a much shorter time. The use of microreactors has seen significant enhancement from its roots in analytical systems to the high-throughput production of chemicals, efficient screening of cells and proteins, fabrication of portable devices, and the study of reaction kinetics. Thus, microreactors have gained attention from academics as well as the chemical and pharmaceutical industries. (Feng et al., 2015; Porta et al., 2016) To date, most of the research has highlighted on the use of individual microreactors; this has made it challenging to determine how best to utilize their key characteristics. These include the fabrication methods needed to achieve the desired resolution and size; determination of length-scale for commercial use; and the possible fields to which these microreactors can be applied. This work reviews recent works carried out to address these key characteristics. However, there is a need to develop microreactors with controlled surface features for which, fabrication technologies must go beyond conventional micromachining and MEMS techniques. To progress beyond the laboratory into commercial production, microreactors must be integrated with various types of sensors and actuators, specific to the type of industry. This integration can possibly be implemented on the same chip or via a hybrid integration scheme. The packaging of multiple reactors and processes poses various challenges in fluid handling and individual reactor control that are absent in the traditional design of chemical plants. Wohlgemuth et al. reported similar challenges for the biocatalytic processes and subsequent product recovery of microfluidic devices. (Wohlgemuth et al., 2015) Notably, research in this area has been increasing exponentially, reflecting the growing importance of this field. This review presents various aspects of microreactor technology ranging from fabrication to cutting-edge applications. Though we have described the basic design principles of microreactors, mathematical modeling and related issues are not discussed herein; these have already been described by Hardt (Hardt, 2006).

2. Fabrication of microreactors

In 2013, microfluidic-based devices were valued at $1.6 billion and the market is estimated to hit $5.7 billion by 2018. (Volpatti and Yetisen, 2014) Advancements include the miniaturization of reactors as well as enhancement in functionality. This milestone will be reached through the development of novel materials for microreactor fabrication, innovative and efficient designs, and integration of multiple unit operations into one device. To date, microreactors are fabricated using a variety of materials including polymers, silicon, metals, stainless steel, glass, and ceramics. Nowadays, advantages in microfluidics technology have simplified the fabrication of complex structures so that microreactors can be fabricated as microcapillaries and chips. Microcapillary reactors are fabricated from suitable tubing of desired length and material, while chip-based reactors employ glass, silicon, or plastics that are fabricated by micromachining, wet etching, and soft lithography techniques. (Krishna et al., 2013; Phillips et al., 2014) Fig. 1 illustrates both forms of microreactors.

Microcapillary reactors are mainly used for chemical reactions to attain high yields and conversions. (Jolliffe and Gerogiorgis, 2015; Rossetti and Compagnoni, 2016) Such microreactors offer better control on heat and mass transfer within the reaction. Yen et al. recently synthesized CdSe colloidal nanocrystals in a continuous flow microcapillary reactor comprising a convective mixer and a heated glass reaction channel in the form of a capillary. (Yen et al., 2003) Their results provided an insight into the kinetics of nanocrystal nucleation and growth. Fig. 1A presents the schematic of a microcapillary reactor for the synthesis of CdSe nanocrystals.

A microreactor can also be fabricated as a chip that offers easy control of microfluidics and integration of many processes into a single device. Such microreactors contain a series of miniature channels connected in a specific geometry to control the spatial and temporal alteration of a small volume of fluid. Multistep chemical syntheses have become possible due to miniaturized reaction networks fabricated onto a chip. (Fitzpatrick and Ley, 2016; Jensen et al., 2014) Kralj et al. fabricated a device capable of mixing and separating several organic-aqueous and fluorous-aqueous liquid-liquid systems. (Kralj et al., 2007) Fig. 1B presents the design schematic of a multiprocess microreactor capable of mixing, extraction, and phase separation; the extraction is reported to be equivalent to one equilibrium extraction stage.

The broad range of literature on microreactors may appear intimidating to chemical engineers and chemists more familiar with conventional batch and stirred continuous reactors. Additionally, techniques used for the fabrication of microreactors are frequently adopted from the well-established microelectronics and semiconductor industries. Herein, we systematically discuss the fabrication and flow behavior of customized reactors for specific applications.

2.1. Materials for fabrication

Microreactors can be fabricated using a broad range of materials such as glass, ceramics, perfluoroalkoxy (PFA), silicon, polymers,