Renewable and Sustainable Energy Reviews 47 (2015) 519–539

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

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

Review of the applications of microreactors

Xingjun Yao [a,*], Yan Zhang [a], Lingyun Du [a], Junhai Liu [a,*], Jianfeng Yao [b,**]

[a] Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252059, PR China
[b] Department of Chemical Engineering, Monash University, Clayton, VIC 3800, Australia

ARTICLE INFO

Article history:
Received 11 September 2013
Received in revised form
31 August 2014
Accepted 9 March 2015

Keywords:
Modify
Structured microreactors
Microchannel
Microfluidic
Catalytic film

ABSTRACT

Microreactors offer excellent mass and heat transfer performance for extraction and multiphase reactions. They provide a powerful tool for process intensification and micro scale processing. This paper reviews the structures of microreactors and units, and their applications on the synthesis of nanoparticles, organics, polymers and biosubstances. The structural evolution and properties of the commercialized and lab-made microreactors are introduced in detail. Recent developments of the fabrication, structures and applications of micro-structured reactors are highlighted. The promising direction in science and technology for future microreaction technology is also discussed.

Contents

1. Introduction

Micro-synthesis technique in both interdisciplinary engineering and sciences connects physics, chemistry, biology, and engineering arts for various applications. A microfluid segment in microreactor is defined as a minimum unit having microproperties that can be used to improve various unit operations and reactions in microspace. Chemist George Whitesides initially created inexpensive microfluidic devices using poly

* Correspondence to: No. 1 Hunan Road, Liaocheng University, Liaocheng City, Shandong Province, PR China. Tel./fax: +86 6358230056.
** Correspondence to: Room 212, Building 69, Clayton Campus, Monash University, Clayton, VIC 3800, Australia.
E-mail addresses: y_xingjun@163.com (X. Yao), jhliu_01@sina.com (J. Liu), yaojianf@gmail.com (J. Yao).

http://dx.doi.org/10.1016/j.rser.2015.03.078
1364-0321/

dimethylsiloxane (PDMS), and through the microreactor community led by the Institute for Molecular Manufacturing (IMM) in Germany and Yoshida's Microreactor Initiatives in Japan, considerable interest in the microreactor area has been built up. High throughput screening in microanalytical chemistry [1], biological analysis of cells and proteins [2], reaction kinetics and mechanisms studies [3] were the initial uses of microreactors. Microreactors have shown superior heat and mass transfer rates, and the contact time, shape and size of the interface between fluids can be easily and precisely controlled [4]. These attributes make microreactors ideal for fast reactions [5], highly exothermic reactions [6], and even explosive reactions [7,8]. The small volume capacity of microreactors has also allowed the efficient development of more sophisticated continuous flow reactions on increasingly complex molecular targets since they greatly reduce the quantities of materials needed to optimize reaction conditions.

Microreactors are fabricated in a range of materials, including ceramics, polymers, stainless steel, and silicon. The microreaction devices can be classified into two groups: chip-type microreactors and microcapillary devices. Chip-type microreactors offer several advantages including easy control of microfluidics, and integration of many processes into one reaction device. Manufacturing processes of such devices are mainly adaptations from the microelectronics industry. Dry- or wet-etching processes have been used for creating channels on a silicone or glass plates. Glass microreactors offer the benefit of visualizing the reaction progress, but are limited in reactor designs due to the difficulty of creating high aspect ratio structures. Polymer-based materials (e.g. Poly-dimethylsiloxane (PDMS), polymethylmarthacrylate (PMMA), polycarbonate, and Teflon) can be used for preparation of enzyme microreactors because most enzyme reactions have been performed in aqueous solution, especially for bio-analytical use. Stainless steel microreactor networks range from simple systems comprised of T-shape micromixers and narrow tubing to commercial systems with micro-fabricated components [9]. They can be operated at high pressure and temperature. These plates can be processed by photolithography, soft lithography, injection molding, embossing, and micromachining with laser or microdrilling. The LIGA (Lithographie Garbanoforming Abforming) process that combines lithography, electrochemical technology and molding, can also be used for the production of microreactors.

Many efforts have recently been made to prepare microreactors and microseparators, with the aim of achieving better control of the reaction parameters. Micromixers are usually designed to use active micromixing technique, and external energy inputs are acoustic, electrical, thermal, pressure disturbance or integrated microvalves, and pumps [10]. On the other hand, in passive mixing, there is an induced perturbation in the flow in order to enhance mixing, which is accomplished by interdigital multilamellae arrangements, eddy formation, nozzle injection in flows and collision of jets. The most common microstructures designs for passive mixing found are zig-zag microchannels, the incorporation of flow obstacle within the channels, T-, ψ- and Y-flow inlet structures and nozzles [11].

Micro process devices gained interests not only from academic investigations but also from chemical and pharmaceutical industry. Since then, many studies have been devoted to the understanding of the mixing mechanisms and characterizations of microstructured reactors. Five predominant flow regimes in small dimensions are bubbly, Taylar, Taylar-annular, annular, and churn flow [9]. The increasing practice can be deduced from the growing number of research documents, the larger number of participants at microreactor or microfluidic conferences, and the increasing commercialized products of the supplier companies in the field.

We report here the advancements made in the design and modification of microreactor structure over the last ten years and include the improvements in the synthesis of inorganic materials and organic reactions. Some excellent reviews have been published in the area that focused mainly on the reaction/process, the product properties, and the impact on downstream processing [12–18]. This review is organized into the following Section (1) Introduction, (2) Synthesis of Inorganic and metal nanoparticles, (3) Synthesis of organic microstructured reactors, (4) Conclusion.

2. Multiphase microstructured devices to synthesize inorganic and metal nanoparticles

2.1. Synthesis of inorganic nanoparticles

Fine particles are widely used as materials of many types of chemical industry products. Nagasawa and Mae [19] developed a microreactor with an axle dual pipe on the concepts of two immiscible liquids flowing in the inner and outer tubes, and maintained an annular and laminar flow of separated phases to create a micro space by the outer fluid wall as shown in Fig. 1(a). In this method, a nucleation section and a particle growth section are sequentially connected along the flow in the reactor. Mono-modal spherical particles of titania with narrow size distribution are successfully produced without precipitation of particles at the wall, as shown in Fig. 1(b), the particle size is precisely controlled by changing the diameter of the inner tube. The mean particle size is 45 nm for a tube of 307 μm i.d., 84 nm for a tube of 607 μm i.d., and 121 nm for a tube of 877 μm i.d. In this system, nuclei formation and particle growth proceed at the interface of the two fluids as shown in Fig. 1(c). This kind of axle dual pipe microreactor was verified that the arrangement of a middle layer between reactants is an attractive method for controlling particle properties and achieving stable continuous production. However, the microchannel has a risk of clogging by the precipitated particles, depending on such particle synthesis conditions as the microchannel dimensions and the type of processing. The stable continuous production does not cause clogging of a microchannel and gives high throughput as well, which is also important for industrial production. This was conducted by forming the zeolite synthesis hydrogel micro-droplets in a continuous paraffin phase through pumping a silica solution and an alumina solution respectively into two closely packed stainless steel capillaries positioned in the axis of a PTFE outer tube, followed by crystallization in the PTFE tube at 90 °C [20]. This one-step continuous synthesis method can not only avoid product variations from batch to batch, but also decrease the cost for large scale zeolite synthesis as well as versatile production of different types of zeolites. No clogging occurred during experiments conducted for 8 h.

Recently, semiconductor nanoparticles have drawn great attention due to their excellent characteristics. Yen and coworkers [21] reported a continuous-flow microcapillary reactor for the preparation of a series of CdSe nanocrystals. This reactor consists of a miniature convective mixer followed by a heated glass reaction channel (250 μm inside diameter) maintained at a constant temperature (180–320 °C).The Cd and Se precursor solutions are delivered in two separate flows and combine in the mixing chamber before they reach the heated reaction section. The presence of the chamber is necessary because once the Cd and Se precursor solutions meet at room temperature, they slowly forms small CdSe clusters. This cluster formation results in irreproducibility in the sizes of the final NCs (Nanocrystals) produced by the reactor so the Cd and Se precursors are not mixed until just prior to reaching the heated section. In this continuous-flow system, reactions are performed at steady state, making it possible to achieve better control and reproducibility. Further benefits can be realized by scaling down the reactor dimensions to micrometers, thereby reducing the consumption of reagents during the optimization process and improving the