Review

Advances in Microfluidic Synthesis of Solid Catalysts

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Abstract: Heterogeneous catalysis plays a central role in the chemical and energy fields, owing to the high and tunable activities of solid catalysts that are essential to achieve the favorable reaction process efficiency, and their ease of recycle and reuse. Numerous research efforts have been focused on the synthesis of solid catalysts towards obtaining the desired structure, property and catalytic performance. The emergence and development of microfluidic reactor technology provide a new and attractive platform for the controllable synthesis of solid catalysts, primarily because of its superior mixing performance and high heat/mass transfer efficiency. In this review, the recent research progress on the synthesis of solid catalysts based on microfluidic reactor technology is summarized. The first section deals with the synthesis strategies for solid catalysts, including conventional methods in batch reactors and microfluidic alternatives (based on single- and two-phase flow processing). Then, different kinds of solid catalysts synthesized in microflow are discussed, especially with regard to the catalyst type, synthetic process, structure and property, and catalytic performance. Finally, challenges in the microreactor operation and scale-up, as well as future perspectives in terms of the synthesis of more types of catalysts, catalyst performance improvement, and the combination of catalyst synthesis process and catalytic reaction in microreactors, are provided.

Keywords: microfluidic; microreactor; solid catalyst; catalyst synthesis; heterogeneous catalysis

1. Introduction

Solid catalysts have attracted a tremendous amount of research interest due to their wide range of applications in science and industry [1,2]. According to statistics, more than 80–90% of industrial chemical processes use catalysts to work effectively, and the vast majority of produced chemical products and commodities involve catalytic conversions [3,4]. Moreover, the research hotspots in recent decades, such as water purification, fuel cell, solar cell, hydrogen generation and storage, biodiesel production, drug delivery and release, are inseparable from the application of catalysts [5]. Nowadays, catalysts have become the core of the entire chemistry, chemical engineering, energy and environmental industries [6].

The emergence of nanotechnology has brought new opportunities to the research and evolution of solid catalysts [7]. Micro- and nanoscale catalysts have been found to possess better catalytic properties than their macroscale counterparts [8,9]. When the size of catalytic materials decreases to micrometer or even nanometer level, its specific surface area, surface steps, wrinkles and defects increase, resulting in the increase in catalyst active sites, which can greatly improve the catalytic activity and selectivity [10,11]. Accordingly, the preparation of micro- and nanoscale catalytic materials can improve the application efficiency of catalysts to a large extent. In addition, the preparation method significantly affects the crystal structures (e.g., shape, size, composition) and texture properties (e.g., porosity, specific surface area) of catalysts, which has a great impact on the catalytic performance. Therefore, the controllable synthesis of catalysts is crucial to enhance the efficiency and sustainability of catalytic processes [12].
Chemical precipitation method is one of the most commonly used methods for the preparation of catalytic materials (e.g., non-precious metal catalysts [13], metal oxide catalysts [14–17] or supports [18]). The precipitation process in laboratory or industrial production is usually carried out in batch stirred tanks. Due to the simple operation and low technical requirements of the precipitation process in batch, micro- and nanoscale solid catalysts with various morphologies and structures (e.g., nanospheres, nanorods, nanoplates, nanorings and microflowers) have been synthesized. However, because of the inherent process characteristics of batch operation mode, the mixing rate, mass and heat transfer efficiency are usually low, often resulting in a wide particle size distribution of the obtained catalytic materials and poor batch-to-batch repeatability [19]. In addition, the inability to precisely control the reaction time of batch reactors results in the overlapping of the reaction precipitation process with the subsequent structural rearrangement process. Namely, the nucleation, growth, and agglomeration processes may occur simultaneously [20]. This renders the inhomogeneous particle size, morphology and microstructure of catalysts obtained by the precipitation method in batch, which is not conducive to the well-controlled synthesis and large-scale production of catalytic materials [21].

The emergence and development of microfluidic reactor technology as a typical chemical process intensification method offer great opportunities to overcome the most pressing drawbacks of the precipitation method in batch as well as other conventional methods for the synthesis of solid catalysts [22]. This technology uses microchannels (with lateral dimensions typically from tens to hundreds of micrometers) to precisely manipulate and process fluids in a continuous flow manner [23–25]. In such confined microchannels, the specific surface area is significantly increased and the diffusion/conduction distance is much reduced. This, combined with the well-regulated laminar flow pattern under operation, renders an accelerated mixing speed and improved heat/mass transfer efficiency, which is beneficial to the reaction process control and regulation of the properties of the synthesized particles [26,27]. Microfluidic reactor technology thus offers great development opportunities in the field of synthetic chemistry in both academia and industry, including the controllable synthesis of solid catalysts as well [28,29]. Up to now, various solid catalyst particles have been successfully synthesized in microflow, such as noble metal nanoparticles (Au, Ag, Pd, Pt) [30–33], bimetallic nanoparticles [34,35], supported-metal nanoparticles [36], metal oxide nanoparticles (ZnO, CeO\textsubscript{2}, TiO\textsubscript{2}) [37–39], zeolites [40], metal-organic frameworks (MOFs) [41,42] and so on.

In this article, we briefly review the latest research progress on the utilization of microfluidic reactor technology for the preparation of solid catalysts. The review is divided into three sections. First, the synthesis principles of solid catalysts, including the underlying synthesis process, the commonly used conventional methods and microfluidic alternatives (based on single- and two-phase flow processing), are summarized. The following section addresses various types of solid catalysts synthesized by microfluidic methods, and the comparison of catalyst structure and performance prepared by different methods. Finally, we discuss the challenges in the microreactor operation for solid handling and scale-up, the integration with process analytic tools, as well as perspectives in the improvement of catalyst performance, the synthesis of new catalysts, the combination of synthesis process and catalytic reaction in microreactors. This review mainly focuses on the different microfluidic synthesis methods, and performance comparison between the obtained catalysts. For a more extensive overview on the in situ characterization or promising reaction application of solid catalysts using microfluidic reactors, and other application examples of solid catalysts synthesized in microflow, we refer the reader to other review articles [11,43–46].

2. Solid Catalyst Synthesis in Batch and Microflow
2.1. Synthesis Principle

The synthesis of (nanoscale) solid catalysts is largely based on wet chemical methods both in batch reactors and in microfluidic synthesis fields, which includes three stages: firstly, the reactant molecules are (uniformly) mixed (i.e., the micromixing process); sec-
ondly, a chemical reaction occurs to form a supersaturated solution; thirdly, the precipitate is formed in the crystallization process including nucleation, growth and agglomeration (Figure 1) [47]. The precipitate becomes the solid catalyst typically after filtering, washing, drying, and calcination/reduction process. When the concentration of the target product reaches supersaturation in the solution, it will be deposited by homogeneous or heterogeneous nucleation. During the precipitation process, the nucleation, growth and agglomeration of crystals have a great influence on the product particle size and morphology [49]. In order to generate non-agglomerated particles with a narrow particle size distribution, it is required that all nuclei are formed nearly simultaneously, and no secondary nucleation or particle agglomeration occurs during the subsequent crystal growth process. The particle size and its distribution and morphology of the target product depend on the relative rates of nucleation, crystal growth and agglomeration kinetics [49], which are therefore influenced by reaction conditions (temperature, concentration, solvent composition, pH, etc.) [50,51]. The morphology, size and structure have a significant impact on the physical and chemical properties of catalyst particles, which in turn affect their catalytic performance [15]. Therefore, it is of great significance to study the preparation method of catalysts to improve their catalytic activity and selectivity.

![M + N → MN](image)

**Figure 1.** The reaction process between M and N ions in the solution to form the solid catalyst MN. The red balls are for M ions, orange balls are for N ions, and small blue balls are for the MN insoluble. The reunited blue balls are for the MN crystal nuclei, and the finally obtained large blue balls are for the target product MN.

### 2.2. Batch Processes

The commonly used methods for solid catalyst synthesis in laboratory and industry mainly include chemical precipitation method, hydrothermal method, solvothermal method, sol-gel method and thermal decomposition method, etc. Generally, these methods are operated in batch mode, and Table 1 summarizes some solid catalysts obtained by these batch processes.

The precipitation method is the most frequently used one, which uses the chemical reaction between a salt solution and a precipitant solution to form a water-insoluble salt (Figure 2a) [52]. For example, ZnO nanoparticles were synthesized by the low temperature chemical co-precipitation between Zn(ac)₂·2H₂O and NaOH aqueous solution, which can be used as an effective catalyst for the degradation of Congo red dye [53]. Carbon nanotube (CNT)-Cu₂O nanocomposites were successfully prepared via a facile chemical precipitation method by adding ascorbic acid solid and NaOH solution to the mixed solution of carboxylated carbon nanotubes and CuCl. The nanocomposites exhibited excellent catalytic performance in the reduction of p-nitrophenol [54]. As a catalyst for NO oxidation, MnOₓ-CeO₂ could be obtained by the co-precipitation of the mixture of Ce(NO₃)₃·6H₂O and Mn(CH₃COO)₂·4H₂O with (NH₄)₂CO₃ solution [55], as summarized in Table 1.

In the hydrothermal method (Figure 2b) [56], a precipitant or chelating agent is added to the salt aqueous solution to prepare the precursor. Then, the mother liquor containing the precursor is poured into a closed vessel. Under the reaction conditions of high
temperature and high pressure in a closed system, the insoluble substances are dissolved and recrystallized by using air in the kettle or the added specific oxidant. Many inorganic functional materials, metal oxide and composite oxide nanomaterials have been successfully prepared by this method (Table 1). For instance, Ni-Ce-ZrO$_2$ catalysts were obtained via a one-pot hydrothermal method by mixing the Ni/Ce/Zr metal salt mixture solution and urea solution and keeping at 105 °C for 50 h. The catalyst exhibited a good catalytic activity and CH$_4$ selectivity for CO$_2$ methanation [57]. Mn-Ce oxides, which can be used as catalysts for the oxidation of toluene, were successfully synthesized via the combination of redox-precipitation and hydrothermal approach (i.e., by mixing KMnO$_4$ and Ce(NO$_3$)$_3$·6H$_2$O mixture solution with HCl solution and keeping at 100 °C for 12 h) [58]. FeS$_2$ microparticles were synthesized by mixing FeSO$_4$·7H$_2$O, Na$_2$S$_2$O$_3$·5H$_2$O and elemental sulfur and keeping at 200 °C for 12–36 h via a hydrothermal method. The microparticles can be used as a heterogeneous electro-Fenton catalyst to decompose H$_2$O$_2$ and thus degrade diclofenac sodium [59].

The solvothermal method utilizes the principle similar to the hydrothermal method to prepare materials that cannot grow in aqueous solution or are susceptible to oxidation, hydrolysis or water sensitivity (Figure 2b). Typical solvents used are alcohols, benzene, acids, and amines. As exemplified in Table 1, Co$_3$O$_4$/Co(OH)$_2$ hybrids were synthesized via a facile solvothermal method by heating the mixture of Co(NO$_3$)$_2$·6H$_2$O, sodium oleate, water, ethanol, n-hexane, and KOH at 200 °C for 12 h. The hybrids exhibited superior activity for photocatalytic water oxidation [60]. Near spherical-shaped TiO$_2$ nanoparticles with uniform size distribution were synthesized by the solvothermal method using titanium tetraisopropoxide as precursor, ethanol as solvent, and H$_2$SO$_4$ as hydrolyzing agent. The obtained TiO$_2$ nanoparticles can be used as a photocatalyst for the degradation of methyl orange and methylene blue dyes [61]. The monodisperse PtCu dendochedral nanoframes, as a promising catalyst in hydrogen evolution reaction, were obtained by a simple solvothermal method, where Pt(acac)$_2$ and CuCl$_2$ were used as precursors, cetyltrimethylammonium chloride as structure-director and dispersing agent, oleylamine as reductant, and allantoin as co-reductant and co-structure directing agent [62].

The sol-gel method uses metal alkoxides or inorganic compounds (e.g., nitrates, chlorides, acetates) as raw materials to carry out a series of hydrolysis and condensation reactions to form a stable sol (Figure 2c) [63]. The sol undergoes aging, colloidal particle aggregation, or polymerization to form a gel. Then, the gel is dried, sintered and solidified to obtain metal oxides or metals. As summarized in Table 1, when the solutions of Cu(NO$_3$)$_2$·3H$_2$O and CNTs (both in ethanol) were separately added to the mixture of tetrabutyl-orthotitanate, benzyl alcohol, ethanol and water, Cu doped TiO$_2$-10 wt.% CNT nanocomposite powder was successfully prepared by the sol-gel method. The nanocomposite can be used as a photocatalyst for the degradation of methylene blue [64]. The mixture of carbon spheres, MoCl$_5$, and diphenyl diselenide was ultrasonically dissolved in excessive ethanol to synthesize C@MoSe$_2$ core-shell nanocomposites by a simple sol-gel approach, and the nanocomposite can be used as an electrocatalyst for the hydrogen evolution reaction [65]. The mesoporous Ni-M/Al$_2$O$_3$ (M: Fe, Co, Zr, La and Cu) nanoparticles were prepared by a one-pot sol-gel method using Ni(NO$_3$)$_2$·6H$_2$O, Al(NO$_3$)$_3$·9H$_2$O and M(NO$_3$)$_3$·yH$_2$O as metal precursors, ethanol and propylene oxide as the solvent and gelling agent, respectively. The nanoparticles were shown as a promising catalyst in carbon dioxide methanation reaction [66].

In addition, the thermal decomposition method features the decomposition of the precursors (e.g., metal hydroxides, metal salts; usually obtained in a previous step from precipitation or crystallization in solution in batch) at a certain temperature to obtain metals or metal oxides (e.g., in the calcination stage) as catalysts. The obtained product generally maintains the morphology of the precursors. Co$_3$O$_4$ hexagonal nanoparticles were successfully fabricated through the simple thermal decomposition of β-Co(OH)$_2$ nanoparticles (previously obtained in the precipitation process by adding CoCl$_2$ and NaOH aqueous solutions into water), and exhibited a high catalytic activity in the reduction of
p-nitrophenol [67]. Mesoporous CeO₂ nanocrystals could be obtained by thermal decomposition of Ce-MOF (previously prepared via one-step hydrothermal synthesis), which had a superior catalyst activity for benzene combustion [68]. The magnetic porous Mn/Fe₃O₄ cubes were also synthesized by thermal decomposition of Fe-Mn-oxalate precipitant (previously obtained by adding FeSO₄·7H₂O and MnSO₄·H₂O to the oxalate solution), and this binary oxide showed a good catalytic activity and stability during the degradation of bisphenol A (Table 1) [69].

Figure 2. Typical steps involved in the commonly used solid catalyst synthesis methods in batch. (a) precipitation method; (b) hydrothermal/solvothermal method; (c) sol-gel method. (a–c) were reproduced/adapted with permission from references [52,56,63], respectively.
Table 1. The synthesis of solid catalysts by batch processes.

| Catalytic Material | Synthesis Method | Reagents | Synthesis Conditions | Size/Morphology | Tested Catalytic Reaction | Ref. |
|--------------------|------------------|----------|----------------------|-----------------|---------------------------|------|
| Ni/CeO₂            | Precipitation    | Ni(NO₃)₂·6H₂O, (NH₄)₂Ce(NO₃)₆, Na₂CO₃, NaOH | pH = 10 | CeO₂ (8–12 nm) | Methane oxidative reforming | [70] |
| ZnO                | Precipitation    | Zn(ac₂)·2H₂O, NaOH | 60 °C, 2 h | Nanoparticles (≈18 nm) | Congo red dye degradation | [53] |
| MnOₓ·CeO₂          | Precipitation    | Ce(NO₃)₃·6H₂O, Mn(CH₃COO)₂·4H₂O, (NH₄)₂CO₃ | 3 h aging at room temperature; 3 h calcination at 350/450 °C | Nanoparticles (8.8–12.1 nm) | NO oxidation | [55] |
| CNT-Cu₂O          | Precipitation    | Carboxylated carbon nanotubes, CuCl, ascorbic acid, NaOH | 1 h stirring at 30 °C | Nanoparticles | p-Nitrophenol reduction | [54] |
| Mn-Ce              | Hydrothermal     | KMnO₄, Ce(NO₃)₃·6H₂O, HCl, Ti-foil sodium citrate, HAuCl₄·4H₂O, Ti(OC₄H₉)₄ | 100 °C for 12 h; 4 h calcination at 350 °C | Microspheres (2–5 µm) | Toluene oxidation | [58] |
| Au-TiO₂            | Hydrothermal     | Urea, metal salt solutions | 50 h aging at 105 °C; 4 h calcination at 500 °C | Microspheres (≈1.2 µm) | Formaldehyde decomposition | [71] |
| FeS₂               | Hydrothermal     | FeSO₄·7H₂O, Na₂S₂O₃·5H₂O, sulfur AgNO₃ | 200 °C for 24 h | Framboids (2.61–3.9 µm) | Diclofenac sodium degradation | [59] |
| Au-SnO₂            | Solvothermal     | N,N-dimethylformamide, poly(vinylpyrrolidone) SnCl₄·5H₂O, gold chloride, hydrazine | 30 min stirring; 100 °C for 18 h | Nanoparticles | Rhodamine B degradation | [73] |
| TiO₂               | Solvothermal     | Titanium tetraisopropoxide, ethanol, H₂SO₄ | 90 °C for 12 h; calcination at 400/450/500 °C | Nanoparticles (near spherical; ≈5 nm) | Methyl orange degradation | [61] |
| Co₃O₄/Co(OH)₂      | Solvothermal     | Co(NO₃)₂·6H₂O, KOH, sodium oleate, ethanol, n-hexane | 200 °C for 12 h | Nanocubes (≈14 nm) | Photocatalytic water oxidation | [60] |
| Al-doped ZnO       | Sol-gel          | Zn(CH₃COO)₂·2H₂O, AlCl₃·6H₂O, ethanol, diethanol amine | 2 h stirring at room temperature; 1 h calcination at 400 °C | Nanoparticles | Methylene blue dye degradation | [74] |
| Catalytic Material                  | Synthesis Method | Reagents                                                                 | Synthesis Conditions                                                                 | Size/Morphology               | Tested Catalytic Reaction                       | Ref.  |
|-----------------------------------|------------------|--------------------------------------------------------------------------|--------------------------------------------------------------------------------------|-----------------------------|-----------------------------------------------|-------|
| Ni-M/Al₂O₃ (M: Fe, Co, Zr, La and Cu) | Sol-gel          | Ni(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, M(NO₃)ₓ·yH₂O, ethanol, propylene oxide    | 45 min aging at room temperature; 48 h drying at 85 °C; 3 h calcination at 700 °C; 1 h stirring at 0 °C; ultrasonication for 10 min; 1 h calcination at 400 °C | Nanocrystalline             | Carbon dioxide methanation                     | [66]  |
| Cu doped TiO₂-CNT                 | Sol-gel          | Tetrabutyl-orthotitanate, ethanol, benzyl alcohol, multi-walled carbon nanotubes, Cu(NO₃)₂·3H₂O | 1 h stirring at 0 °C; ultrasonication for 10 min; 1 h calcination at 400 °C | Nanocubes (≈25 nm)          | Methylene blue degradation                    | [64]  |
| C@MoSe₂                           | Sol-gel          | MoCl₅, diphenyl diselenide, ethanol                                       | 0.5 h ultrasonication; 2 h heating at 700 °C under Ar/H₂ | Core-shell nanoparticles (≈200 nm) | Hydrogen evolution reaction                   | [65]  |
| Mn/Fe₃O₄                          | Thermal decomposition | FeSO₄·7H₂O, oxalic acid, MnSO₄·H₂O                                       | 1 h calcination at 400 °C                                                          | 45.9 nm                     | Bisphenol A degradation                       | [69]  |
| Fe₃O₄-Cu                         | Thermal decomposition | Fe(acetylacetonate)₃, Cu(acetylacetonate)₂, oleylamine, benzyl ether     | 90 min reflux at 110 °C under stirring; 60 min heating at 225 °C                   | Nanocrystals                | 4-Nitrophenol degradation                     | [75]  |
| Co₃O₄                            | Thermal decomposition | CoCl₂·2H₂O, NaOH                                                        | 1 h aging at 50 °C under N₂; 2 h calcination at 300 °C                             | Hexagonal nanoplates (≈100 nm) | p-Nitrophenol reduction                       | [67]  |
| CeO₂                             | Thermal decomposition | 4,4′-bipyridine, dimethyl formamide, Ce(NO₃)₃·6H₂O                      | 24 h heating at 120 °C, 2 h calcination at 400/500 °C                            | Nanocrystals                | Benzene combustion                            | [68]  |
Although the above wet chemical methods performed in batch stirred tanks have the advantages of simple operation and low technical requirements, their inherent limitations tend to hinder their wide applications in both academia and industry. The conventional batch synthesis processes usually require bulky instruments or expensive autoclaves and complex stepwise operations, associated with non-optimized or low efficiency in the consumption of reagent, power and labor, and require long synthesis time. Moreover, because of its low heat transfer efficiency, for strongly exothermic reactions, the heat may not be dissipated in time especially when large amount of reagents are used in batch. This may cause an instantaneous increase in temperature and pressure, resulting in potential safety concerns. In addition, the low mixing rate and heat/mass transfer efficiency of batch reactors render temperature and concentration gradients during the synthesis process. Thus, the (nano)particle formation process cannot be precisely controlled, resulting in a large particle size, wide particle size distribution, inhomogeneous morphology and poor batch-to-batch repeatability.

2.3. Microfluidic Approaches
2.3.1. Advantages of Microfluidic Reactor Technology

For all the above-mentioned methods of solid catalyst synthesis, a good mixing between reagents in the solution and a fine control over other reaction parameters (e.g., concentration, temperature and reaction time) are important in determining the obtained catalyst structure, property and performance. Thus, there is an incentive to switch from batch to continuous flow processing in microreactors for process improvement. Numerous researches have reported the advantages of microfluidic reactor technology over conventional batch operation for the synthesis of nanoparticles using wet chemical methods [76,77]. When the precipitation process is conducted in a miniaturized microreactor, it is a facile, versatile and reproducible method due to the continuous operation mode, superior mixing efficiency and well-controlled residence time [78]. The precipitation process in microreactors can effectively differentiate the nucleation and growth processes, as well as mitigate the problem of nanoparticle agglomeration often encountered in a stirred tank, so that nanoparticles obtained in microreactors usually have a smaller particle size and more uniform particle size distribution than in batch [14]. It takes typically seconds to tens of minutes to synthesize solid catalyst nanoparticles by hydrothermal or solvothermal method in the microreactor, while it usually takes hours to days in a batch reactor [40,79]. Similarly, the synthesis of catalyst nanoparticles by the sol-gel method in a microreactor usually requires a short reaction time (e.g., 1 min), and the obtained nanoparticles have a small particle size, narrow and controllable particle size distribution [12,80].

From the discussion above, we can reasonably conclude that microfluidic reactor technology offers a series of advantages for the synthesis of solid catalysts. Firstly, the superior micromixing therein provides a (close to) uniform reaction environment for the precipitation process. Secondly, the efficient heat/mass transfer in microreactors renders a (nearly) uniform temperature/concentration distribution [81]. In addition, a fine control over the residence time is attainable in microreactors, which is conducive to the preparation of nanomaterials with a narrow particle size distribution and high repeatability between different flow operation sequences [82–85]. Moreover, nucleation, growth and agglomeration processes can be effectively controlled by accurately adjusting parameters during reactions in microflow. This unique characteristic enables microreactors to regulate the size, shape, and structure properties of solid catalysts. Finally, it is relatively easy to scale up compared with batch reactors. The scale-up of microreactors is primarily based on the numbering-up concept, that is, the superposition of microchannels. During this scale-up process, the synthesis parameters optimized previously in a single-channel microreactor are kept, so that the transport/reaction characteristics across a multitude of microchannels are identical in principle, which is beneficial to the fast, reliable and modular production of solid catalysts on a large scale [46].
2.3.2. Classification of Microfluidic Methods

According to the flow pattern manipulation during solid catalyst synthesis, microfluidic methods can be divided mainly into two types, namely single-phase flow (continuous flow, Figure 3a) and two-phase flow methods [84]. The two-phase flow method can be subdivided into gas-liquid/liquid-liquid segmented flow (Figure 3b) and liquid-liquid droplet flow (Figure 3c) methods. The length of droplets (if present) in segmented flow is larger than the microchannel diameter and there is usually a film present between the droplet and microchannel wall, while the droplet size is smaller than the microchannel diameter in the droplet flow mode and droplets are surrounded by the continuous liquid phase. In both biphasic flow modes, reactions can occur either in the dispersed phase (Figure 3bI, cI) or in the continuous phase (Figure 3bII, cII). In general, for reactions that are prone to blockage, reagents are usually confined in the dispersed phase, and the generated solid particles are prevented from contacting or interacting with the microchannel, thereby clogging can be prevented. Both single- and two-phase flow methods are characterized by low Reynolds numbers (and thus laminar flow conditions) due to small microchannel sizes, but the mixing behavior of reagents is largely different. The mixing of reagents in microreactors under single-phase flow operation is relatively slow and primarily driven by molecular interdiffusion, whereas reagents under two-phase flow operation can be more efficiently mixed (e.g., on sub-millisecond timescales) through the strong advection generated in droplets [86].

![Figure 3. Schematic illustration of microfluidic methods for solid catalyst synthesis: (a) single-phase flow (continuous flow) method, characterized by the presence of a laminar parabolic flow velocity; (b,c) two-phase flow method, which can be subdivided into segmented flow method (b) and droplet flow method (c). Adapted with permission from reference [19].](image-url)
2.3.3. Single-Phase Flow Method

The reagents involved in the single-phase flow method are all miscible (e.g., in commonly used solvents such as water, ethanol and ethylene glycol), and the process of synthesizing solid catalysts is to inject different reagents into microchannels to mix and react. Single-phase flow microfluidic systems for (catalytic) nanomaterial synthesis are considered to be very promising, because this method has the advantages of simple implementation, high flux, and easy control compared with two-phase flow method. However, there are two principal drawbacks that limit the application scope of single-phase flow method. One is that the products deposited on the microreactor wall may cause fouling or even blockage of the microchannel, posing difficulties for long-term operation. The other is that there is a wide distribution of residence time within the microchannel associated with the laminar parabolic velocity profile (Figure 3a), often resulting in a significant dispersion in the particle size and properties of the synthesized solid catalysts.

2.3.4. Two-Phase Flow Method

The two-phase flow method usually uses an inert gas or liquid that does not react or is immiscible with the reagent phase to divide the reagent phase into continuous slugs (i.e., when the wall is wetted by the liquid) or discrete droplets, which can greatly improve the mixing efficiency in the microchannel due to the recirculation of the liquid [87]. This method overcomes the main drawbacks of single-phase flow method, namely, the significant elimination of velocity dispersion and reduction of reactor contamination (due to the confinement of reactions in droplets) [27]. Moreover, the two-phase flow method has the advantages of a large phase boundary area, low axial backmixing degree, and narrow residence time distribution. Therefore, many studies have been focused on the controlled synthesis of nanoparticles using segmented flow and droplet flow methods [88,89].

3. Examples

Microfluidic reactor technology has been extensively used for the synthesis of various catalysts such as metals, metal oxides, and porous materials (zeolite, silica, MOFs). Most of the reports only deal with catalyst synthesis by microfluidic single- or two-phase flow method, and the performance study of catalysts (as listed in Tables 2 and 3). In addition, some studies adopted different methods to prepare catalysts, and compared the performance of catalysts obtained by different methods and the influence of preparation method on the catalyst properties in detail. In this section, some examples are provided for solid catalysts synthesized by microfluidic methods in recent years. The effects of different synthesis methods on the structural properties and catalytic performance of catalysts are also discussed.

3.1. Metal Catalyst

Metal nanoparticles are widely used in various technological fields, such as catalysis, fine chemicals, petrochemicals, pharmaceuticals, electronics, sensing, fuel cells, and environmental protection due to their excellent physical and chemical properties [90,91]. The size, shape, and structure of metal nanoparticles greatly influence their catalytic, optical, electronic and biomedical properties [92]. Researchers have explored a variety of synthetic strategies for the preparation of metal catalysts with a narrow particle size distribution [93].

3.1.1. Monometallic Catalyst

Among all metals, noble metals (e.g., gold, silver, palladium and platinum) are the most commonly used catalyst materials because of the easy adsorption of reactants on their surfaces, high catalyst activity and selectivity [94]. In the past two decades, the synthesis of gold nanoparticles by microfluidic reactor technology has become a major research hotspot and various gold nanoparticles with controlled sizes and morphologies have been successfully obtained.
As summarized in Table 2, ultrasmall Au nanoparticles with an average diameter of 1.0 nm and narrow size distribution were synthesized in a continuous single-phase flow microfluidic setup using HAuCl₄·3H₂O as precursor, NaBH₄ as reducing agent and PVP as stabilizer [76]. In comparison, the average diameter of Au nanoparticles produced in batch increased to 1.9 nm and the particle size distribution was also slightly broader. Depositing the obtained Au nanoparticles on TiO₂ could be used to prepare the catalyst for the oxidation of CO. Au nanoflowers with tunable sizes were synthesized by a rapid continuous single-phase microfluidic approach within 3 min using HAuCl₄·4H₂O as precursor and HEPES aqueous solution as reducing agent and size regulator (Table 2) [95]. The as-prepared Au nanoflowers exhibited a high catalytic activity for the reduction of 4-nitrophenol. A gas-liquid segmented flow microfluidic reactor was used to synthesize Au nanoparticles (Table 3) with diameters of 3–25 nm at room temperature (using HAuCl₄ as precursor and CO as gaseous reductant) [96]. The size and hydrophilicity of Au nanoparticles could be tuned by using different capping agents (Figure 4).

The synthesis of silver nanoparticles has also attracted great research interest because of their special chemical and optical properties [97]. Silver nanoshells with an average shell thickness of 11.6 ± 5.3 nm were successfully synthesized in a single-phase flow...
central collision-type microreactor using silver-ammonia complexes as precursor, AuNP-SiO₂ as core particles and formaldehyde as reducing agent (Table 2) [98]. Compared with the batch synthesis process, the microfluidic synthesis process was time-saving and the obtained shell structures were homogeneous due to the intensive mixing and large surface to volume ratio of the microreactor. Spherical silver nanoparticles with a mean diameter of 7.6 ± 1.8 nm were successfully obtained in a droplet flow microfluidic device using AgNO₃ as precursor, NaBH₄ as reducing agent, EDTA as complexant and PVP as dispersant (Table 3) [99]. The spherical-shaped Ag nanoparticles with an average size of 4 nm and Au nanoparticles with an average size of 14–17 nm could be obtained in a segmented flow capillary microreactor using AgNO₃ and AuHCl₃·3H₂O as the respective metal precursors, silicon oil as continuous phase, NaBH₄ and sodium citrate as reducing agent [100].

Much effort has been taken on the preparation of palladium and platinum nanoparticles with a controllable size and shape due to their wide application in the field of catalysis [101,102]. Pd nanoparticles, which can be used as an electrochemical catalyst, were synthesized in a flow microreactor (under single-phase flow) using PdCl₂ as precursor, NaBH₄ as reducing agent, and cetyltrimethylammonium bromide as stabilizing agent, and the size of the nanoparticles could be controlled within 5–200 nm by changing the solution flow rate [32]. Ultra-small Pt nanoparticles as well as alloyed nanoparticles including PtPd, PtRu and PtRh (Table 2), which can be used for the catalytic oxidation of volatile organic compounds, were prepared in microreactors (under single-phase flow) using H₂PtCl₆ (K₂PdClO₄, RuCl₃, RhCl₃) as precursor and tetrakis(hydroxymethyl)phosphonium chloride as reducing and stabilizing agent [36]. Compared with the traditional batch process for the synthesis of Pt nanoparticles, the microfluidic method had a short residence time, high yield and high productivity. Pd nanorods with a diameter of about 4 nm and an aspect ratio of up to 6 were prepared by a continuous segmented flow microfluidic method using air as the segmentation gas and Na₂PdCl₄ mixed in the mixture of water, KBr, ethylene glycol, and polyvinyl pyrrolidone as precursor (Table 3) [103]. This method only required 2 min to synthesize Pd nanorods, while it usually took hours in batch systems. Moreover, the obtained Pd nanorods showed an excellent activity for the catalytic hydrogenation of styrene.

3.1.2. Bimetallic Catalyst

By combining two metals, the properties of the resulting nanoparticles may differ from those of pure metals due to the interaction between metal particles. The bimetallic particles often form alloys or core-shell structures and usually exhibit an excellent catalytic performance because of the synergistic effect of metal atoms [104]. For example, Au@Ag core-shell nanoparticles were synthesized (using HAuCl₄ and sodium citrate for the synthesis of Au core, and AgNO₃ and ascorbic acid for the preparation of Ag shell) in a single-phase microreactor (Figure 5a) and a conventional batch reactor, respectively [105]. Compared with the batch results, the spherical Au@Ag core-shell nanoparticles synthesized in the microreactor exhibited a more uniform shell size (Figure 5b,c) due to the faster mixing of reagents and better control over the reaction time. Moreover, the microreactor could be used to produce various uniform core-shell nanoparticles, such as Au@Pd (Figure 5d), Au@Au, and Au@Au with an interior nanogap. Hybrid Au-Pd dumbbell-like nanostructures, which involved the synthesis of Pd nanorods using Na₂PdCl₄ as precursor and ethylene glycol as reducing agent and solvent, as well as the growth of Au on Pd nanorods using HAuCl₄ as precursor and ethylene glycol as reducing agent, were successfully synthesized (Table 2) [106]. In more detail, Pd nanorods were synthesized in a sequential-addition microfluidic reactor by segmented flow method, and the growth of Au was conducted in an ultrasonic integrated microfluidic reactor by single-phase flow method. Core@shell Au@Pd nanostructures with controlled shape and dimensions have been obtained in a continuous flow droplet microreactor, including the synthesis of Au core (using HAuCl₄·3H₂O as precursor, NaBH₄ or sodium citrate as reducing agent) and
the growth of Pd shell (using H$_2$PdCl$_4$ as precursor, L-ascorbic acid as reducing agent, and silicone oil as the carrier medium) (Table 3) [107]. The droplet-based microreactor further enabled the inline analysis and modification of process conditions compared with the batch method.

Figure 5. (a) Schematic diagram of the microfluidic device for the facile production of various uniform metal core-shell nanoparticles. The microreactor with built-in upper staggered herringbone microstructures had two inlets (fed with two aqueous solutions) and one outlet. The right image shows the upper herringbone structure of the microchannel from the top view and side view, and the mixing and flow of nanoparticles. TEM images of Au@Ag core-shell nanoparticles: (b) microfluidic synthesis; (c) batch synthesis. TEM images of Au@Pd core-shell nanoparticles: (d) microfluidic synthesis; (e) batch synthesis. Reproduced with permission from reference [105].

3.1.3. Supported Metal Catalyst

Metal nanoparticles used for catalytic reactions usually have a small particle size and high surface free energy, making them easy to agglomerate and difficult to recover and recycle. To overcome these shortcomings, they are usually anchored on solid supports (e.g., carbon materials, metal oxides). The specific surface area of solid supports is usually large, which greatly increases the dispersibility and stability of metal nanoparticles. Moreover, there may be interactions between particles and supports, which will further enhance the catalyst performance [108,109]. Therefore, the design and application of
supported metal catalysts is an important method to improve and ensure its catalytic activity and selectivity.

Highly dispersed PtFeCu/C ternary nanocatalysts (Table 2), which showed an excellent catalytic performance for methanol oxidation, were synthesized by single-phase flow method in a microfluidic setup with four parallel channels [112]. The aqueous solution of \( \text{FeCl}_3 \cdot 6\text{H}_2\text{O}, \text{CuCl}_2 \cdot 2\text{H}_2\text{O} \), and \( \text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O} \) containing suspended carbon black was used as metal precursor solution, and \( \text{NH}_3\text{BH}_3 \) as reducing agent. The high flow rate and multiple channels increased the throughput obviously. \( \text{M/TiO}_2 \) (M = Pd, Pt or Au) nanoparticles were continuously synthesized by a stabilizer-free method based on a segmented flow microfluidic system using \( \text{Pd(NO}_3)_2 \), \( \text{H}_2\text{PtCl}_6 \) or \( \text{HAuCl}_4 \) mixed with \( \text{TiO}_2 \) aqueous suspension as precursor, \( \text{NaBH}_4 \) with \( \text{NaOH} \) as reducing agent, and n-octane as continuous phase (Table 3) [77]. Compared with \( \text{M/TiO}_2 \) nanoparticles prepared by the batch method, the obtained nanoparticles in microflow had a smaller noble metal particle size (<5 nm), better dispersity, and thus showed a higher catalytic activity in the hydrolysis of ammonia borane. Ultafine Ag nanoparticles with a controllable particle size (1.5–5.6 nm) and narrow particle size distribution were uniformly deposited on rGO by segmented flow processing in the microreactor (Figure 6a,c,d), using \( \text{AgNO}_3 \) as precursor, trisodium citrate and \( \text{NaBH}_4 \) as reducing agent, sodium dodecyl sulfate (SDS) as stabilizing agent and octane as continuous phase [111]. The average particle size of Ag nanoparticles in Ag-rGO composites was smaller than those synthesized in batch (Figure 6b).

![Figure 6.](image-url)
Table 2. The synthesis parameters, characteristics and application of solid catalysts synthesized by single-phase flow methods in microreactors.

| Catalytic Material | Microreactor Material | Reagents | Synthesis Conditions | Size/Morphology | Advantages of Microfluidic Method | Tested Catalytic Reaction | Ref. |
|--------------------|-----------------------|----------|----------------------|----------------|----------------------------------|--------------------------|------|
| Au                 | Silicon/glass         | HAuCl₄·3H₂O, NaBH₄, PVP | 13 bar N₂ | NPs (1.0 ± 0.4 nm) | Efficient mixing; narrow size distribution | CO oxidation | [76] |
| Au                 | PTFE                  | HAuCl₄·3H₂O, trisodium citrate | 70–100 °C, back pressure at 275 kPa | NPs (1.9 ± 0.2 nm) | Enhanced nucleation rate; inhibited particle growth rate | - | [112] |
| Au                 | PDMS                  | HAuCl₄·4H₂O, HEPES, ammonia, AuNP-SiO₂, PVP | 80 µL/min, pH = 7.4 | NPs (88 ± 11 nm) | Precise control of reaction time | Reduction of 4-nitrophenol | [95] |
| Ag                 | PDMS                  | AgNO₃, HCHO, L-ascorbic acid, H₂PtCl₆·CTAB, H₂PtCl₆·H₂O | pH = 8 | Nanoshells (11.6 ± 5.3 nm) | Large surface to volume ratio; rapid mixing | | [98] |
| Pd                 | PEEK and PTFE         | H₂PtCl₆·NaOH, THPC | 96 °C water bath for 20 min under stirring | Nanocubes (≈14 nm) | Efficient mixing and heat transfer; narrow size distribution | NO₂ reduction | [113] |
| Pt                 | PTFE tube             | H₂PtCl₆·NaOH, THPC | 25–95 °C thermostatic bath, residence time at 1–5 min | NPs (<2 nm) | Short residence time; high yield and productivity | n-Hexane oxidation | [36] |
| Au-Pd              | Silicon/glass         | HAuCl₄·3H₂O, K₂PdCl₄, NaBH₄, PVP | 13 bar N₂, ice/water bath | NPs (≈1 nm) | Rapid mixing | CO oxidation | [114] |
| Au-Pd              | Silicon               | HAuCl₄, KBr, PVP, EG, Na₂PdCl₄·Bi(NO₃)₃·5H₂O, H₂PtCl₆·6H₂O, PVP, ethanol, EG, PEG, Na₂PdCl₄, K₂PtCl₄ | 8 bar, 160 °C, 120 s; 2 bar, 100 °C, 5 min | NPs (15.1 ± 2.3 nm) | Controlled heat/mass transfer | Ethanol oxidation | [106] |
| Pt-Bi              | Stainless steel       | HAuCl₄, L-ascorbic acid, PVP, KBr | Heat region 200–350 °C | Nanorods(17 nm) | Rapid heat transfer; precise control of temperature | Methanol fuel cells | [35] |
| Pd@AuPt            | PMMA and PSA          | HAuCl₄, L-ascorbic acid, PVP, KBr, AgNO₃, H₂O₂, CuSO₄·5H₂O, SDS, Na₃C₆H₆O₃·2H₂O, NaBH₄, NaOH, H₂PtCl₆·6H₂O, FeCl₃·6H₂O, FeCl₃·6H₂O | 60 °C shaking incubator at 200 rpm | NPs (10–12 nm) | High accuracy and reproducibility | H₂O₂ synthesis | [115] |
| Ag@Cu₂O           | PTFE                  | HAuCl₄, CuCl₂·2H₂O, EG, H₃N·BH₃, NaOH, H₂PtCl₆·6H₂O, FeCl₃·6H₂O, NaCl·6H₂O | Flow rate at 0.25 mL/min + 0.5 mL/min | Ag Cores (20–50 nm) | High efficiency | Methyl orange degradation | [116] |
| PtFeCu/C           | Stainless steel       | CuCl₂, H₂O₂, EG, H₃N·BH₃, NaOH, NaOH, H₂PtCl₆·6H₂O, FeCl₃·6H₂O | 60 min ultrasonication, 0.5 h stirring | NPs (1.8 ± 0.3 nm) | High throughput | Methanol oxidation | [110] |
Table 2. Cont.

| Catalytic Material | Microreactor Material a | Reagents b | Synthesis Conditions | Size/Morphology c | Advantages of Microfluidic Method | Tested Catalytic Reaction | Ref. |
|-------------------|-------------------------|------------|---------------------|------------------|-----------------------------------|--------------------------|------|
| Cu-CuO            | Stainless steel         | CuSO₄, NaBH₄, PVP, ammonium hydroxide, NaOH | pH = 10–12, flow rate at 20 mL/min | Nanocomposite (≈10 nm) | Small particle size; narrow size distribution | Methylene blue degradation | [117] |
| Ag₃PO₄            | PDMS and PMMA           | AgNO₃, disodium hydrogen phosphate | Flow rate at 130 µL/min, Heating oil 180 °C, back pressure at 2 MPa | NPs (20–30 nm) | Narrow size distribution; rapid synthesis | Rhodamine B degradation | [118] |
| TiO₂              | Stainless steel         | TiOSO₄, CO(NH₂)₂ | | NPs (≈5.0 nm) | Small particle size; even size distribution | Methylene blue decomposition | [119] |

a. PTFE: poly(tetrafluoroethylene); PDMS: polydimethylsiloxane; PEEK: polyether ether ketone; PSA: polysulfonamide; PMMA: polymethylmethacrylate. b. PVP: polyvinyl pyrrolidone; HEPES: 2-[4-(2-Hydroxyethyl)-1-piperazinyl]-ethanesulfonic acid; CTAB: cetyltrimethylammonium bromide; THPC: tetrakis(hydroxymethyl)phosphonium chloride; EG: ethylene glycol; PEG: polyethylene glycol; SDS: sodium dodecyl sulfate. c. NPs: nanoparticles.

Table 3. The synthesis parameters, characteristics and application of solid catalysts synthesized by two-phase flow methods in microreactors.

| Catalytic Material | Microreactor a | Reagents b | Synthesis Conditions c | Size/Morphology d | Advantages of Microfluidic Method | Tested Catalytic Reaction | Ref. |
|-------------------|---------------|------------|------------------------|------------------|-----------------------------------|--------------------------|------|
| Au                | Glass         | HAuCl₄, CO gas | Residence time at 3–5 min, room temperature, atmospheric pressure; SF | NPs (3–25 nm) | Large surface-to-volume ratio; high mass transfer | - | [96] |
| Au                | PTFE and PEEK | HAuCl₄·3H₂O, PVP, PP9 ascorbic acid, C₁₂H₁₆O₄ | Droplet length at 2.0 mm and distance at 1.33 mm; SF | NPs (2.5–4 nm) | Fast mixing; low concentration gradient | - | [120] |
| Ag                | PDMS and Silicon | AgNO₃, NaBH₄, N₂, PVP, NaOH, NH₄OH, EDTA, mineral oil | pH = 10–12, room temperature, flow rate at 10–30 mL/h; DF | NPs (7.6 ± 1.8 nm) | Rapid mixing | - | [99] |
| Pd                | PTFE and silica | Na₂PdCl₄, KBr, silicone oil, PVP, L-ascorbic acid | Oil phase flow rate at 180 µL/min, residence time at 6 min; DF | NPs (9.0 ± 1.5 nm) | Fast and efficient mixing; controlled reaction condition | - | [121] |
| Pd                | Silicon/Pyrex  | Na₂PdCl₄, PVP, DMF, EG, KBr, air | 0.8 MPa, 180 °C, residence time at 10–120 s; SF | Nanorods (≈4 nm) | Reduced synthesis time | Styrene hydrogenation | [103] |
| Catalytic Material | Microreactor \(^a\) | Reagents \(^b\) | Synthesis Conditions \(^c\) | Size/Morphology \(^d\) | Advantages of Microfluidic Method | Tested Catalytic Reaction | Ref. |
|--------------------|---------------------|----------------|------------------------|----------------|-------------------------------|----------------------|------|
| Ag, Au             | PTFE and silica     | AgNO\(_3\), NaBH\(_4\), H\(_3\)AuCl\(_3\), 3H\(_2\)O, trisodium citrate, silicon oil H\(_3\)AuCl\(_3\), 3H\(_2\)O, NaBH\(_4\), PdCl\(_2\), HCl, NaBr, CTAB, CTAC, L-ascorbic acid, sodium citrate, silicone oil | Ag: residence time 0.6 min; Au: oil bath at 105 ℃, residence time: 3–20 min; SF | NPs (Ag: ≈4 nm; Au: 16–17 nm) | Controlled residence time | - | [100] |
| Au@Pd             | PTFE and silica     | AgNO\(_3\), NaBH\(_4\), H\(_3\)AuCl\(_3\), 3H\(_2\)O, trisodium citrate, silicon oil H\(_3\)AuCl\(_3\), 3H\(_2\)O, NaBH\(_4\), PdCl\(_2\), HCl, NaBr, CTAB, CTAC, L-ascorbic acid, sodium citrate, silicone oil | Total flow rate at 0.7 mL/h, oil bath at 55 ℃; DF | Core-shell nanostructures (shell thickness: 2.8 nm) | Inline analysis for quick modification of process conditions | - | [107] |
| FePtSn/C           | Stainless steel     | FeCl\(_2\), 4H\(_2\)O, NaBH\(_4\), H\(_2\)PtCl\(_6\), 6H\(_2\)O, NMP, PVP SnCl\(_2\), 2H\(_2\)O Ti\(_2\), NH\(_3\), H\(_2\)PtCl\(_6\), NaBH\(_4\), NaOH | Reaction and nucleation at 120 ℃, Fe/Pt/Sn ratio at 1/1/0.3, particle growth at 30 ℃; DF | Alloy NPs (≈2–3 nm; on the carbon surface) | Uniform size distribution | Methanol oxidation | [34] |
| M/TiO\(_2\) (M = Pd, Pt or Au) | PTFE and PFA | Pd(NO\(_3\))\(_2\), 2H\(_2\)O, H\(_2\)PtCl\(_6\), 6H\(_2\)O, n-octane, H\(_3\)AuCl\(_3\), 4H\(_2\)O | Ultrasonication for 25 min, water bath at 25–80 ℃, residence time at 2 min; SF | Noble metal NPs (<5 nm; anchored on TiO\(_2\)) | Enhanced mixing; small particle size | Ammonia borane hydrolysis | [77] |
| Cu, CuO\(_x\)     | Glass               | CuSO\(_4\), 5H\(_2\)O, seignette salt, NaOH | pH = 12, 350 ℃, 2 h; DF | Microspheres (100–500 μm) | Controlled particle diameter | Hydrogenation; Fenton-like reactions | [122] |
| Ag-rGO            | PTFE and PFA        | AgNO\(_3\), SDS, octane, NaBH\(_4\), trisodium citrate | AgNO\(_3\):NaBH\(_4\) = 1.3 or 1.20; SF | Ag NPs (1.5–5.6 nm) | Precise control of reaction parameters | - | [111] |
| Co/rGO            | Stainless steel, FEP| CoCl\(_2\), 6H\(_2\)O, GO, NaBH\(_4\), octane Fe\(_3\)O\(_4\), 7H\(_2\)O | Water bath at 40 ℃; SF | NPs (2.0 ± 0.45 nm) | Improved micromixing | p-Nitrophenol reduction | [123] |
| Fe\(_3\)O\(_4\)    | PEEK and PTFE       | KNO\(_3\), NaOH, L-lysine, H\(_2\)SO\(_4\) | 70–110 ℃, 1.4 bar; SF | Nanoflakes (30 ± 8 nm) | Accelerated mixing; reduced processing time | - | [124] |
| mSiO\(_2\); SiO\(_2\)@mSiO\(_2\); Au@SiO\(_2\) | PTFE | NH\(_3\)(aq), ethanol, TEOS, OTMS | Gas pressure at 1.5 bar; SF | Mesoporous (core-shell) spheres (300–400 nm) | High yield; controlled particle features | - | [125] |
| Catalytic Material | Microreactor | Reagents | Synthesis Conditions | Size/Morphology | Advantages of Microfluidic Method | Tested Catalytic Reaction | Ref. |
|-------------------|-------------|----------|----------------------|-----------------|---------------------------------|--------------------------|-----|
| Zeolite A         | PTFE        | NaOH, sodium aluminate, sodium silicate | Oil bath at 90 °C; SF | 0.9–1.5 µm | High mixing efficiency; no clogging | -                         | [126] |
| MOF              | PDMS and PFA | Cu(NO$_3$)$_2$·H$_2$O, H$_3$BTC, DMF, ethanol, silicon oil MMA, EGDMA, DADMAC, AIBN, platinum seed | Silicon oil bath at 90 °C; DF | Octahedral crystals (5–15 µm) | Continuous fabrication; time-saving | -                         | [42] |
| PMMA-polyDADMAC/Pt | FEP        | MMA, EGDMA, DADMAC, AIBN, platinum seed | Water bath at 97 °C; DF | ≈0.7 µm | Fast mixing; short residence time | Azo-dye bleaching         | [127] |

a. PTFE: poly(tetrafluoroethylene); PDMS: polydimethylsiloxane; PEEK: polyether ether ketone; PFA: perfluoroalkoxy alkane; FEP: fluorinated ethylene propylene. b. PVP: polyvinyl pyrrolidone; EG: ethylene glycol; SDS: sodium dodecyl sulfate; PP9: perfluoromethyldecalin; EDTA: ethylene diamine tetraacetic acid; DMF: dimethyl formamide; CTAB: hexadecyltrimethylammonium bromide; CTAC: cetyltrimethylammonium chloride solution; NMP: N-methyl-2-pyrrolidone; GO: graphene oxide; TEOS: tetraethylorthosilicate; OTMS: trimethoxysilane; MMA: methyl methacrylate; EGDMA: ethylene glycodimethacrylate; DADMAC: diallyldimethyl ammonium chloride; AIBN: azobisisobutyronitrile; H$_3$BTC: 1,3,5-benzenetricarboxylic acid; C$_{12}$H$_{22}$O$_4$: 2-hydroxy-4-(2-hydroxyethoxy)-2-methylpropiophenone. c. SF: segmented flow; DF: droplet flow. d. NPs: nanoparticles.
3.2. Metal Oxide Catalyst

Although noble metal catalysts have an excellent catalytic performance, the shortage of resources and high price limit their application scale. Transition metal oxides (e.g., TiO$_2$, ZnO, CeO$_2$, CuO, Fe$_2$O$_3$) are inexpensive and abundant. They have excellent redox properties and can be used as catalysts for many reactions, though their catalytic activity is usually lower than that of noble metal catalysts [15,128]. For example, phosphated TiO$_2$ catalysts were prepared by a continuous sol-gel method in a microreactor (under single-phase flow), which is an eco-friendly catalyst for the selective synthesis of 5-hydroxymethylfurfural (a biobased platform chemical) [12]. Because of the great flexibility and precise control of chemical process, the yield and space-time yield of phosphated TiO$_2$ obtained in the microreactor process were higher than that of the conventional batch synthesis process and the phosphated TiO$_2$ exhibited a remarkably higher glucose conversion and slightly improved selectivity during the catalytic process compared with that obtained in the batch reactor. Benefiting from the high microscopic mixing rate of the membrane dispersion microreactor, the mesoporous $\gamma$-Al$_2$O$_3$ nanofibers were synthesized by a simple, template-free and single-phase microfluidic method using NaAlO$_2$ and Al(NO$_3$)$_3$·9H$_2$O as raw materials. And the obtained $\gamma$-Al$_2$O$_3$ nanofibers showed considerable pore volumes and uniform pore size distributions compared with those prepared by traditional batch stirring methods [129]. The morphology-controlled synthesis of ZnO nanostructures (spindles, sheets and spheres) was reported via the precipitation of Zn(NO$_3$)$_2$ and NaOH by a facile surfactant-free method in microreactors (under single-phase flow) [130]. These ZnO nanostructures were tested as photocatalysts for the degradation of dye and exhibited an excellent catalytic efficiency.

CeO$_2$ nanoparticles were synthesized through the precipitation of Ce(NO$_3$)$_3$·6H$_2$O and NH$_3$·H$_2$O using a single-phase flow microreactor and a batch stirred tank reactor under the same experimental conditions [39]. CeO$_2$ nanoparticles prepared in the microreactor were nearly 2 times smaller in size, had a better dispersion and narrower particle size distribution than those obtained in batch (Figure 7). When used as catalyst for the mineralization of acid orange 7, the degradation efficiency approached 84.1% for CeO$_2$ nanoparticles synthesized in the microreactor within 0.5 h, which was ~40.6% higher than those prepared in batch. CeO$_2$ nanorods and nanocubes were synthesized by hydrothermal method using Ce(NO$_3$)$_3$·6H$_2$O and NaOH as reagents in a self-made single-phase flow microfluidic system [131]. CeO$_2$ nanorods were transformed to nanocubes by introducing PVP as surfactant under hydrothermal conditions. For comparison, CeO$_2$ nanoparticles were prepared by precipitation method in a stirred tank reactor. The preparation of CeO$_2$ nanostructures by hydrothermal method took only 8 min in the microreactor, while several days were needed in the conventional batch system. The catalytic activity for the decomposition of hydrogen peroxide followed the sequence: CeO$_2$ nanocubes > CeO$_2$ nanorods > CeO$_2$ nanoparticles, which was explained by the microfluidic reaction system that generated nanostructures with a smaller particle size, thereby obtaining larger specific surface areas and better catalytic performance.

In addition, SnO$_2$ nanoparticles were synthesized in a single-phase flow microreactor and a batch reactor using SnCl$_4$·5H$_2$O and NaOH as raw materials to compare its structure and photocatalytic performance [132]. SnO$_2$ nanoparticles obtained in batch were characterized by agglomerated structures composed of extremely tiny nanoparticles with an average size of around 2–3 nm. In contrast, those synthesized in the microreactor had less agglomeration and consisted of extremely small SnO$_2$ nanoparticles with an average size of 3–5 nm. The SnO$_2$ nanoparticles prepared in the microreactor presented photocatalytic activity in the degradation of methylene blue dye because of the significant increase in surface defects. These results demonstrate that the change in synthetic techniques altered the surface properties (e.g., extent of oxygen vacancies and defects at the surface) and optical band gaps, and these changes in turn affected the photocatalytic properties of SnO$_2$ nanoparticles [132].
Figure 7. The membrane dispersion-based microreactor system for CeO$_2$ nanoparticle preparation, with the shown flow profile and inner structure of the microreactor (a); TEM images and primary particle size distribution of CeO$_2$ particles synthesized in the microreactor (b,c) and batch stirred tank reactor (d,e). Reproduced/adapted with permission from reference [39].

3.3. Porous Catalytic Material

Porous materials have attracted an extensive scientific research interest in the field of catalysis due to their uniform, abundant, and tunable porous structures, high specific surface area, large adsorption capacity, and excellent physicochemical properties. The most common porous materials that can be used as catalysts include among others zeolites, silica, and MOFs [133].

3.3.1. Silica

Silica is a kind of porous material and its synthesis has received a great deal of research attention due to its wide application in many fields, especially as catalysts and catalyst supports. Over the past decade, microfluidic reactor technology has been introduced to overcome some of the challenges faced in the synthesis of silica, such as precise regulation of its morphology, particle size, and porosity [134]. For instance, silica spheres (diame-
ter: 300–400 nm), core-shell spheres with the mesoporous silica shell (up to ca. 60 nm) and the dense silica core (SiO$_2$@mSiO$_2$) as well as gold-encapsulated spheres (Au@SiO$_2$) were efficiently produced in a microreactor under gas-liquid segmented flow (Table 2; Figure 8a) [125]. Typically, silica spheres were prepared using ammonia as catalyst in the ethanol-water mixture and TEOS in ethanol as precursor. For the silica shell deposition, the mixture of TEOS and OTMS in ethanol was employed as the second precursor. Au@SiO$_2$ particles were synthesized by further adding the aqueous gold colloids in the mixture of ammonia and ethanol. The segmentation of flow was found crucial to obtain the desirable monodispersity of silica spheres or core-shell particles, whereas a significant shell thickness was present under single-phase laminar flow operation.

Hollow silica nanoparticles with an average diameter of $\sim 30$ nm were prepared using tetraethylorthosilicate as precursor, poly (acrylic acid) as template by a micromixer (under single-phase flow) [135]. Compared with the batch reactor, the fast mixing efficiency in the microreactor dramatically reduced the aggregation of poly (acrylic acid) template, which was beneficial to obtain silica nanoparticles with a smaller diameter and narrower size distribution. Silica bearing different surface silanol groups was synthesized using sodium silicate aqueous solution and CO$_2$ as raw materials in a segmented flow microreactor and conventional batch reactor under similar reaction conditions [136]. The obtained silica samples were employed as supports for Pd-based catalysts for benzyl alcohol oxidation. Compared with conventional batch method, silica prepared in the microreactor had a higher specific surface area, more uniform distribution of surface silanol groups and better catalytic effect due to the high mass transfer efficiency of the microreactor.

3.3.2. Zeolite

Zeolite is a kind of crystalline aluminosilicate with regular and uniform pores that has a wide range of applications, especially in the field of catalysis, due to its nanoporosity and acidity [137]. The preparation process of zeolite generally consists of two steps: firstly the mixing of silica and alumina solutions to prepare the hydrogel, and then the hydrothermal crystallization process of the hydrogel. Zeolites with adjustable sizes were prepared in a segmented flow-based microreactor by the one-step hydrothermal synthesis, using silica and alumina solutions as dispersed phase and liquid paraffin as continuous phase (Figure 8b) [126]. The microreactor system had the advantages of no clogging as well as saving time and cost for zeolite synthesis, because of the in situ mixing of silica and alumina solutions (Table 3).

Porous zeolite A nanocrystals with a uniform particle size were efficiently synthesized by a hydrothermal method conducted in a droplet flow-based microreactor, using fluoro-carbon oil as continuous phase and the gel solution as dispersed phase (precursor), that is, obtained by the aging of an alumina precursor solution and tetraethylorthosilicate [40]. The aqueous droplets were surrounded by oil medium, preventing the contact of the formed nanocrystals with the microchannel wall, thereby preventing channel clogging. Moreover, it took only tens of minutes to synthesize nanocrystals in the microreactor, compared with hours to days in batch. The obtained zeolite A exhibited a superior catalytic performance and an improved stability in the synthesis of alkyl borate.

3.3.3. MOFs

MOFs, consisting of metal clusters and organic bridging ligands, are a promising class of porous-crystalline materials that can be used in many fields such as catalysis, adsorption, sensing and separation [138]. These materials usually have plenty of pores and high specific surface areas, different transition metals or functional groups, which are very suitable as catalysts. The continuous synthesis of MOFs by means of microreactors has become a research hotspot in recent years due to the ultra-high mixing efficiency and precise control of reaction parameters therein [42].

For example, MIL-88B type MOFs with average sizes of 90–900 nm and narrow particle size distributions were prepared under liquid-liquid segmented flow processing.
through microreactors, using FeCl₃·6H₂O solution and three different ligands solution (H₂BDC (benzene-1,4-dicarboxylic acid), NH₂-H₂BDC, Br-H₂BDC) as continuous phases and silicone oil as discrete droplets (Figure 8c) [139]. MOFs could be obtained at a residence time as short as 20 s in the microreactor and this method can effectively reduce microreactor clogging by preventing the obtained particles from interacting with the microchannel walls. The synthesis of uniform HKUST-1 microcubes, composed of Cu(II) dimers and 1,3,5-benzenetricarboxylate, was also reported in droplet flow-based microreactors, using silicon oil as continuous phase and the DMSO solution of the precursor of Cu(NO₃)₂ and 1,3,5-benzenetricarboxylate containing uniform polystyrene nanoparticles as dispersed phase [140].

Figure 8. (a) Schematic of the segmented flow capillary microreactor set-up employed for the synthesis of mSiO₂, SiO₂@mSiO₂, and Au@SiO₂ (left) and TEM image of the obtained Au@SiO₂ (right). The gas-liquid segmentation present in the microreactor, as well as the progressive SiO₂@mSiO₂ shell growth, is schematically highlighted in the magnified red rectangle. The inset in the TEM image shows the schematic diagram of the core-shell structure. (b) Schematics of the coaxial capillary assembly and formation of the segments in the PTFE capillary involved in the liquid-liquid segmented flow microfluidic system for one-step continuous synthesis of zeolite A, with the left, middle and right pictures on the bottom illustrating the mixing status of silica and aluminum solutions at the mixing inlet, 1 s and 5 s, respectively (left) and SEM pictures of the obtained zeolites (right). (c) Schematic of the microfluidic setup, segmented flow pattern, and synthesis details of MOFs (left) and the TEM image of Fe-MIL-88B-NH₂ synthesized at 95 °C after a residence time of 600 s (right). (a–c) were reproduced/adapted with permission from references [125,126,139], respectively.
3.4. Miscellaneous Catalysts

Other kinds of particles (e.g., semiconductors, quantum dots and metal salts) as potential catalyst candidates have also been prepared in microreactors [141]. For example, Ag$_2$S/ZnS core-shell quantum dots (QDs) with a different ZnS shell thickness could be prepared in a droplet microreactor, by interfacial reaction between Zn-oleylamine precursor (in the continuous oil phase) and Ag$_2$S QDs (in the dispersed aqueous phase) [142]. Spherical Ag$_3$PO$_4$ nanoparticles with a narrow size distribution were successfully synthesized in a T-shaped microreactor (via single-phase flow method) using silver nitrate and disodium hydrogen phosphate as raw materials [118]. The photocatalytic efficiency of these Ag$_3$PO$_4$ nanoparticles for the degradation of Rhodamine B dye could reach >97% within only 15 min.

4. Conclusions and Perspectives

The development of microfluidic reactor technology has opened a new and attractive platform for the controlled synthesis of solid catalysts, including among others monometallic and bimetallic catalysts, supported metal catalysts, metal oxides and porous catalytic materials. Compared with solid catalyst synthesis using wet chemical methods (e.g., precipitation, hydrothermal/solvothermal, sol-gel methods as well as thermal decomposition methods) performed in traditional batch reactors, continuous processing in microreactors based on the single-phase or two-phase flow mode could achieve a much better micromixing and heat/mass transfer efficiency. This allowed a (close to) uniform reaction environment, and a fine control over reaction parameters (e.g., concentration, temperature and reaction time), and thus the preparation of solid catalysts with a smaller particle size, more uniform particle size distribution and better morphology control in a significantly shorter reaction time (e.g., typically minutes or even seconds regarding the formation of nanoparticles or nanocrystals) in microreactors than in batch. As a result, solid catalysts prepared by microfluidic approach often exhibited a better catalytic performance in the target applications than their counterparts obtained via batch protocols.

Although a great research progress has been made in the microfluidic synthesis of solid catalysts in recent years, there are still considerable scopes for optimization in terms of the synthesis process, catalyst quality, functionality and yield. To advance this technology, some aspects need to be addressed carefully. Firstly, the fouling or even clogging of microchannels may happen by solid products formed in the reaction process because of the agglomeration of particles or the deposition of particles on the microchannel walls due to the gravity or particle-wall interaction. Such phenomena can occur especially during the single-phase flow mode and long-term operation, which might be mitigated via the introduction of strong cavitation effects by coupling ultrasonication with microreactors, the employment of mechanical vibration in continuous flow, the modification of the wettability of microchannel surface (e.g., to be superhydrophobic or superoleophobic), or the use of the two-phase flow method to confine the reaction in the dispersed phase that is not in contact with the wall [143,144]. Secondly, a better synthesis optimization and control can be assisted via coupling microreactors with some online analysis and measurement systems, which enables real-time monitoring and accurate analysis of the as-synthesized particles and immediate adjustment of synthesis conditions to obtain the desired products [19,145]. Thirdly, the majority of current research remains still on the laboratory scale. Effective scale-up strategies for large-scale fabrication of solid catalysts in microreactors with a multitude of microchannels need to be researched further, especially those addressing well the local particle-fluid hydrodynamics [46]. The up-to-date scale-up strategies include the internal numbering-up method (i.e., via arranging a number of identical microchannels in parallel within one microreactor module), the external numbering-up method (i.e., via providing an individual supply system to each microreactor), and the sizing up method (i.e., selective dimension enlarging) [146]. The numbering-up (both internal and external) method may require hundreds to thousands of reaction units to meet high throughput of industrial production. The question of how to achieve a uniform fluid distribution in each
microchannel in the microreactor system realized by the internal numbering-up method represents a somewhat significant challenge, especially when it comes to multiphase fluid flow, let alone the presence of particles [147,148]. In the external numbering-up method, each microreactor requires its own supply system (e.g., pump, buffer tank) and auxiliary equipment (e.g., mixing unit, pressure detector unit, temperature controller unit), resulting in excessive installation and operating costs. The size (e.g., length or diameter) of the microchannel can be increased to some extent to achieve a higher throughput while maintaining the mixing and transfer characteristics at the microscale (the sizing up method). Though this size increase can greatly reduce the occurrence of clogging, the hydrodynamic and transport properties might change dramatically if the channel size becomes too large. Thus, the throughput might be only increased to a somewhat limited extent by this method.

To date, a practical and feasible approach for the scale-up of microreactors to satisfy the industrial demand is to combine the strategies of internal numbering-up, external numbering-up, and sizing up, followed by the optimization of the microreactor structures. This approach would facilitate a fast and reliable reproduction of laboratory achievements on the industrial scale [146–149].

The future research interests are envisaged in the following areas. It is necessary to synthesize more catalytic materials that have not been investigated in microreactors so far, in order to explore the full potential of microfluidic synthesis approach. There exists a lot of room for improvement regarding the activity, selectivity and stability of solid catalysts obtained in microreactors, which necessitates an in-depth fundamental study. Last but not least, the integration of solid catalyst synthesis in microreactors and its further incorporation in microreactors (e.g., in the form of nanofluids, packed beds or catalyst slurries [43,46]) for more sustainable and efficient chemical synthesis represents an emerging area to develop.

To summarize, although microfluidic reactor technology is still in its development phase and faces some challenges, it has become an indispensable tool in the synthesis of solid catalysts. With the continuous and rapid development of this technology, these challenges will be gradually resolved, holding promises for breakthroughs in solid catalyst synthesis. In the near future, microfluidic reactor technology may open new research frontiers and provide unparalleled opportunities for the production of widely used catalysts that not only enable the precise tuning of catalyst particle size, morphology and microstructure, but also catalytic activity, selectivity and other desired functions to fully fulfill the target reaction performance requirements.

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