

Preparation of ceramic and metallic monolith reactors

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Abstract

Monolith reactors have several important benefits in chemical processing. High surface area to volume ratio, open structure, low pressure drop, excellent mass transfer characteristics are some of the advantages of these reactors. Commercially used monolith reactors/catalysts are mostly made of ceramic or metallic substances. This short review describes the different preparation methods of ceramic and metallic monolith reactors and the different variables that optimize the preparation methods.

Key words: Ceramic, metallic, monoliths, preparation, washcoating

Introduction

Monolith reactors are catalytic reactors that consist of a single, solid block with a network of small channels or passages running through it. These channels are coated with a catalytic material that helps to promote the desired chemical reaction [1,2]. Monolith reactors are typically made of ceramic or metallic materials and can be used in a wide variety of chemical and petrochemical applications. Monolithic reactors have gained significant use in various adiabatic gas-solid reactions, particularly in environmental applications such as catalytic converters for treating automotive exhaust gas such as nitrogen oxides, carbon monoxide, and hydrocarbons. They are used as catalysts for eliminating nitrogen oxides from flue gas emitted by coal-fired power plants through SCR. Other applications include gas-to-liquid conversion processes, where they are used to convert natural gas or other gases into liquid fuels such as diesel and gasoline and hydrogen production from natural gas and other hydrocarbons [3]. In the last few decades, there is an increasing interest in utilizing monolithic catalysts/reactors for gas-solid-liquid three-phase and gas-solid two-phase reactions in the chemical and process industries. The rationale for this is the multitude of advantages that monolithic catalysts offer over conventional random catalysts in powder and pellet forms.

Owing to their unique design, monolith reactors can provide several advantages over traditional packed-bed reactors. They have a honeycomb-like structure that provides a large surface area for reactants to contact each other and enhance reaction rates. The open structure of monolith reactors allows for low-pressure drops across the reactor, which means that less energy is required to push the reactants through the reactor. The large surface area of monolith reactors also provides for efficient heat transfer, which can be important in exothermic reactions where heat needs to be removed from the system. Monolith reactors can be designed to provide better selectivity for certain reactions. The fundamental importance of the monolithic reactors coated with a thin layer of catalytic material is its efficient mass transfer abilities. The thin catalyst coating ensures that reactants and products travel through very short distances during the reaction and face very small internal diffusional resistances. This results in a possibility of controlling the selectivity of many complex reactions. Monolith reactors are relatively easy to scale up, as they can be simply replicated to increase the reactor volume. This makes them an attractive option for commercial production of chemicals. They are also known for their compact design, ease of product separation, enhanced thermal stability, high mechanical strength, and resistance to fouling and corrosion, making them well-suited for harsh and high-temperature environments [4].

Ceramic and metallic monoliths are two common types of monolithic reactors used in chemical and catalytic processes. The main differences between these two types of monoliths lie in their material properties, performance, and applications.

Ceramic monoliths are extruded structures that have a honeycomb shape with thousands of parallel channels running axially. They are made of a ceramic material such as cordierite, aluminium oxide, or silicon carbide that have a low coefficient of thermal expansion. Ceramic monoliths are used as catalyst supports for various applications, such as vehicle emissions control, diesel particulate filters, catalytic incineration, and chemical processes. They have advantages such as high surface area, low pressure drop, and good thermal stability [4]. Ceramic monoliths are usually coated with a washcoat that contains oxides and catalysts

(such as platinum, palladium or rhodium) on the walls of the channels. Alternatively, they can be extruded from porous materials that provide high internal surface area without a washcoat. Metallic monoliths, on the other hand, are made of metals such as stainless steel, nickel, or titanium. They are typically used in high-pressure and high-temperature applications where their mechanical strength and durability are important. Metallic monoliths are also known for their excellent thermal conductivity and good electrical conductivity. These properties make them suitable for use in catalytic combustion, gas-to-liquid conversion, and fuel cell applications. Metallic monoliths are also coated with a washcoat that contains oxides and catalysts on the walls of the holes. Alternatively, they can be made of porous metal foams that provide high internal surface area without a washcoat [5].

Here, the basic features of monolith reactors/catalysts, various methods of monolith reactor/catalyst preparation and the variables which determine the optimum conditions for preparation of ceramic and metallic monoliths shall be discussed.

Basic Features of Monolith Reactors

Monolithic reactors, also referred to as monolith catalysts, consist of numerous thin, straight and parallel flow channels that are separated from each other by walls. These channels can have various shapes, including circular, square, triangular, or hexagonal, but square is the most common. Metal monoliths can also have channel geometries produced by wrapping up flat metal sheets with corrugated metal sheets in between. Typically, they are constructed from ceramic or metal materials, although some may also be composed of plastic [2]. Among the various substrates, ceramic monoliths made from cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) are the most used due to their minimal thermal expansion coefficient, adequate porosity for easy washcoating and adherence, and high mechanical strength.

Cell density is the most important feature of monoliths. This determines the size of the channels through which the reactants and products flow. The cell density N for a square cell is defined as the number of cells per unit cross-sectional area and is expressed as cells per square inch (cpsi).

$$N = \frac{1}{L^2} \quad \text{where } L \text{ is the cell spacing}$$

The open frontal area (OFA) resulting in low pressure drop is defined as a function of the cell density, wall thickness and cell spacing.

$$\text{OFA} = N(L - t)^2 \quad \text{where } t \text{ is the wall thickness}$$

The geometrical surface area (GSA) is defined as

$$\text{GSA} = 4N(L - t)$$

The hydraulic diameter (D_h) is defined as

$$D_h = \frac{(L - t)}{4}$$

From reaction engineering point of view, OFA relates to the void fraction in the packed bed, GSA is analogous to the external surface area per unit volume of bed, D_h refers to the open flow path in a packed bed while t parallels the pellet size in a packed bed [2,7]. For cordierite monoliths, the cell density typically varies between 100 to 1200 cpsi, the void fraction between 0.5 to 0.9 and wall thickness between 0.006 and 0.05 cm [6, 8]. A monolithic structure is generally characterized by the wall thickness and cell density, which are independent of each other. Nijhuis et al. [4] reported that higher cell density in a monolith result in higher geometrical surface area and thus, more effective use of the catalyst. However, manufacturing and washcoating of higher cell density monoliths more difficult, and leads to a higher pressure drop over the reactor (though it is still 10 times lower than in a packed bed). Also, at higher cell density, the wall thickness decreases resulting in a change in the porosity of the structure. Thus, the reaction rate and possible consequential side reactions are influenced by the choice of optimal cell density.

The specific requirements of a process dictate the selection of geometric and physical properties for the monolith, including its shape, channel size, wall thickness and porosity, as well as the thickness and microstructure of the catalytic layer.

Preparation methods for ceramic monolith reactors

Monolithic reactors made of ceramic can be prepared in different ways –

(i) Forming extrudates made of the ceramic material, binder, and solvent:

Ceramic monolith structures are typically obtained using extruders, which are specially designed devices, and less commonly through corrugation. The starting materials used in extrusion are usually clays, binders, and additives, depending on the desired type of ceramic. Cordierite and alumina are the most used materials for monolith extrusion, with cordierite accounting for over 90% of all monolith catalysts used for exhaust gas clean-up in cars. Other materials such as SiC, TiO₂, ZrO₂, ZrSiO₄, ZrB₂, Al titanate, Li-Al silicate, and others are less common and can be more expensive. For extrusion methods, specially designed dies have been developed so that the monolith structures can be produced as a continuous process. This is essential to ensure that the monoliths can be manufactured successfully at an industrial scale.

The preparation of ceramic monolith structures is mostly described in patent literature and a few scientific and technical publications. For instance, the preparation of cordierite monoliths, involves mixing a starting mixture of talc, clay, and other materials containing Al and Si, shaping the mixture by extrusion, drying it, and thermally treating it at 1473–1773 K through drying, calcination, and sintering. The characteristics of ceramic monolithic catalysts produced through extrusion depend on various factors such as the type and properties of the starting materials, the presence of additives, the pH of the mixture, the water content, and the pressure used during extrusion [9-10]. Additives such as celluloses, CaCl₂, ethylene, glycols, diethylene glycols, alcohols, paraffins, and heat-resistant inorganic fibers [9], are often utilized to improve properties such as resistance to temperature shocks, porosity, adsorbability [5], and mechanical strength. Aside from water, other solvents like ketones, alcohols, and ethers can also be utilized [5], [9]. Monolith can be also made of catalytically active zeolite materials. According to Avila et al. [6], the process for preparing high surface area zeolite extrudates involves dry mixing of the raw material and binder, followed by kneading and plasticizing with water until the mixture has the appropriate rheological properties. The paste is then extruded through special dies to form monoliths, which are finally dried and calcined to remove water and provide the necessary mechanical strength. Hammon et al. [11] provide a detailed account of the formation of ZSM5 monolith extrudates. Their approach involves using a dough consisting of 100 g H-ZSM5, 84 g water, 8 g hydroxyethylcellulose (to adjust viscosity), 15 g ammonium acetate (to modify the electrical double layer around zeolites), and 11 g lubricating oil (to prevent the mixture from adhering to the metal surface of the extruder).

(ii) Sol-gel method of preparing monoliths:

This method involves using a solution of metal alkoxides or other precursors to form a gel, which is then dried and sintered to form a ceramic monolith. This method is useful for preparing ceramic monoliths with high purity and controlled porosity. In addition to the method previously described for the preparation of cordierite ceramic involving calcination of a mixture of clay, talc, and other components containing Al and Si, there is also a sol-gel method [12-13]. This method offers several advantages over the previous one, such as the production of high-purity cordierite ceramic due to the use of purer starting materials, the ability to precisely control the microstructure, adjust the homogeneity on an atomic level, and the possibility of carrying out the process at lower temperatures (around 1273 K). Additionally, this method enables the addition of various components in a single step, among other benefits.

(iii) Hydrothermal synthesis of coating on the surface of the cordierite:

The hydrothermal synthesis process provides several advantages for coating the surface of cordierite. The high pressure and temperature conditions allow for the formation of coatings with high density and uniformity. The use of a liquid medium allows for the deposition of coatings with complex shapes and morphologies. Thirdly, the process is relatively simple and scalable, making it suitable for industrial applications.

There are several materials that can be deposited on the surface of cordierite using hydrothermal synthesis. These include metal oxides, such as alumina, titania, and zirconia, as well as zeolites and other porous materials. The choice of coating material depends on the specific application and the desired properties of the coated cordierite substrate.

For example, zeolites can be directly synthesized onto the monolith by impregnation with a solution of the precursor. This method has the advantage of stronger adhesion of the zeolite layer which is useful for monoliths used in automobiles subjected to road vibrations. Direct synthesis also makes it possible to obtain preferential orientations of the zeolite crystals on the cordierite surface that favour the diffusion of reactants inside the zeolite pores. Ulla et al. [14] reported the synthesis of ZSM5 layers (upto 30% by weight) on cordierite substrates by direct hydrothermal synthesis method or secondary growth method. The cordierite pieces were immersed in the precursor gel inside an autoclave placed in a convection oven at the desired temperature for 8-24 h. After this, the substrates were rinsed with water and dried. The steps were repeated for higher loadings. For secondary growth method the substrates were treated with seeding gel prior to the above step. Ulla et al. [15] also reported the synthesis of 50 wt% mordenite coating on cordierite substrates using the seeded synthesis method. The preparation of thin films of ZSM5 by solid state in situ crystallization method was described by Madhusoodana et al. [16]. In this method, the cordierite substrates were coated with zeolite precursor sol, then changed to gel and finally converted to ZSM5 by heated in an autoclave without any added solution. Basaldella et al. [17] prepared continuous, multilayered ZSM5 films by direct synthesis on cordierite modules using different H_2O/SiO_2 ratio in the synthesis mixture. They showed that dilution of the synthesis mixture prevents the films from becoming dense and modifies crystal morphology.

(iv) Washcoating of the cordierite walls with a catalyst suspension

When it comes to coating a secondary support, like γ -alumina, onto monoliths, the usual method involves immersing the monolith in a solution or slurry mixture, letting it soak for a few minutes, removing excess liquid from the channels with compressed air, and then calcining it. This process is repeated several times to create the necessary secondary support layer. Depending on preference, modifications to the coating technique can be made, such as constant rotation of the monolith during calcination, or drying after each dip. Repeating the process of dipping, rotating, drying, and calcination can result in a more uniform coating across the channels. The amount of coat layer on the monolith is typically expressed in weight percent and can vary depending on the application.

Zeolites may be incorporated in the low surface area ($\sim 0.7 \text{ m}^2/\text{s}$) cordierite substrates by the slurry washcoating method. The washcoating procedure as described by Nijhuis et al. [4] involves preparation of a stable slurry of the material, immersing the dry monolith in the slurry for a short period, removing the monolith from the suspension, blowing out the excess solution, drying and high temperature calcining for fixing the coating on the substrate. The procedure is often repeated several times to obtain the desired coating amount.

The macroporous structure of the cordierite monolith facilitates the anchoring of the washcoat layer. For sufficient adhesion of the coated layer, the particle size of the slurry should be smaller than the size of the macropores in the cordierite ($5 \mu\text{m}$). Agrafiotis and Tsetsekou [18] studied the effect of alumina powder characteristics on washcoat quality and concluded that reduction of the particle sizes to $2\text{-}5 \mu\text{m}$ ensured adhesion comparable to that of the commercial catalyst. Earlier studies on effect of particle size on adhesion of washcoats of alumina, zirconia, titania and ceria showed that adhesion of oxide washcoats was independent of the type of oxide and depended only on the size of particles with particle sizes less than $2 \mu\text{m}$ giving excellent adhesion [19].

The particle sizes of powders such as alumina, zeolites etc., are reduced by wet ballmilling technique. Blachou et al. [20] investigated the wet ball milling characteristics of alumina to prepare slurries for monolithic structure impregnation. They determined that the viscosities of the wet ball milled alumina slurries depended on pH with minimum viscosity at a pH of 3.5-3.8. Addition of HCl in the concentration range of 1-10% did not have any effect on the process. The pore volume distribution of the alumina coating was influenced by the particle size distribution of the alumina suspensions. In case of zeolites, reduction in particle size by ball milling may also result in collapse of the zeolite crystal structure causing loss in crystallinity and a decrease of surface area of the material. This may cause changes in the catalytic behaviour of the material in terms of both conversion and selectivity. Kharitonov et al. [21]

studied the mechanism of FeZSM5 milling and determined that the destruction of the lattice structure followed a first order process. Dry milling the zeolite for 40 min resulted in complete amorphization of the material and disappearance of catalytic activity in oxidation of benzene to phenol. Studies by Kosanovic et al. [22,23] show that high energy ball milling (at 3000 rpm) of ZSM5, Zeolite A and X result in severe loss in crystallinity. Xie and Kaliaguine [24] reported that vigorous dry ball milling of KNa zeolites results in collapse of the zeolite crystal structure, but positively affect the selectivity for base catalyzed reactions by reducing the density of the strong Bronsted acid sites and maintaining the Lewis base strength. However, Akcay et al. [25] indicated that wet ball milling can decrease the size of zeolite particles with minimum loss in crystallinity. The decrease in crystallinity for Zeolite Y was about 10% after 2 h and 45% after 14 h of wet milling at 600 rpm.

According to research conducted by Kolb et. al. [26, 27], the coating process for monolithic structures consists of two main steps: filling the capillary with slurry and then removing excess slurry from the capillary by forcing air through it. They observed that the thickness of the coating deposited on the capillary by a liquid was dependent on the non-dimensional capillary number (Ca), which is proportional to the ratio of viscosity to surface tension.

The characteristics of the washcoated layer are functions of slurry properties such as pH, zeta potential, viscosity, solid content etc. Agrafiotis and Tsetsekou [28] studied the effect of processing parameters on the properties of γ -alumina washcoats deposited on ceramic monoliths. They showed that the slurry stability was a strong function of pH; zeta potential measurements indicated that alumina slurries were stable at pH as low as 4.5 or above 10. Viscosity of alumina slurries depended on solid content, pH and particle size distribution of the powder used with a value of 50-150 mPas being optimum. Inorganic electrolytes or organic deflocculants could be used for viscosity adjustments. The solid content of the slurry should be high enough to get satisfactory loading per impregnation. The loading reproducibility and uniformity was also a function of the slurry viscosity. Similar results were observed by Agrafiotis et al. [29] for the washcoating of Ytria stabilized zirconia slurries. The preparation conditions to obtain optimum loading and quality of washcoats for mordenite, ferririte and ZSM5 were investigated by Zamaro et al. [30]. They observed that homogeneous washcoats were obtained by using dilute suspensions and multiple impregnations. Non linear increase in the zeolite load was observed with increasing slurry concentrations. The authors also remarked that as the zeolite is deposited in successive impregnations, the geometry of the channels become circular. The washcoat thickness is an important parameter as it was seen that the mass transfer coefficient varies with washcoat thickness in the case of monolithic reactors [31]. The washcoat stability was in the order ZSM5>mordenite>ferririte. They remarked that coating did not result in diffusive restrictions as the activity of the In-ZSM5 catalyst was as good as the powder catalyst. Zamaro et al. [32] also studied the effect of different solvents for washcoating and determined that water yielded zeolite washcoats with the best mechanical stability. The stability of washcoats was often improved by the use of binders. The report by Nijhuis et al. [4] stated that addition of nano-sized binder to the washcoat slurry helped to increase the contact surface between the larger particles themselves and also between the particles and the support. During the drying process, the binder particles accumulated at gaps between two large sized zeolite particles and this helped in the anchoring of the washcoat. They specified that the amount of binder used should be about 10 wt % of the total silica or alumina content. In case of zeolite washcoats, addition of binders like colloidal silica has enhanced the stability of the washcoat [30, 33, 34]. In some cases, as reported by Boix et al. [33, 34], addition of binders such as Cabot Silica and $\text{Al}(\text{NO}_3)_3$ modifies the catalytic behaviour of the zeolite.

Preparation methods for metallic monolith reactors

Metallic monoliths can be prepared using various methods depending on the desired properties and applications. Here are some commonly used preparation methods:

- (i) Metallic monoliths are typically constructed from stainless steel or the Fecralloy material (73% Fe, 15-20% Cr, 5% Al, and rare metals in traces) through the process of corrugation. The process of corrugation, which involves flexing flat and corrugated metal plates and/or bends, is nearly always used for the production of metallic monoliths. Typically,

thin metal plates or bends made of iron alloys with small amounts of aluminum are used. The oxidation of aluminum produces a layer of aluminum oxide that is crucial for good adhesion of the second oxide layer, applied later in the preparation process as the support for a catalytically active component. The corrugated sheets can be obtained in various ways and are subsequently cut into desired shapes, such as parallel or spiral structures. This has been documented in multiple sources [3,6,9].

(ii) Coating of metal monoliths - Colloidal coating is a process where nanoparticles are used to fill the pores. According to the report by Barbero and co-workers [35], they achieved a successful coating of their metallic monoliths by utilizing colloidal alumina as both a primer and stabilizer.

The metallic monoliths themselves have very low BET surface area. As a result, the primary support, which is the monolith, needs to be covered with a layer of porous metallic oxide (such as Al_2O_3 , TiO_2 , or a mixture of oxides) as a secondary support. The most common method for achieving this is through washcoating [4], although there are other techniques available. The coating process involves using a solution or colloid suspension containing precursor particles for one or more oxides. In some cases, the sol-gel method is utilized, where the liquid phase comprises precursors for the secondary support. The primary challenge in coating alumina on these monoliths is ensuring proper adhesion to the surface. Research suggests that increasing the concentration of aluminum during the preparation of the metallic structure may improve adhesion. However, it is possible to regulate the quality of adhesion through coating techniques.

For washcoating metallic substrates, it is essential to have stable slurries with moderate viscosities (ranging from 5 to 30 mPa·s). The properties of particle size (typically between 1 to 10 μm), solid content (as high as possible), and additives play a vital role in controlling the stability and viscosity of the slurry.

The protective layer covering the metallic substrate must be adherent, compatible with the catalytic coating, and have a surface roughness that allows the catalyst particles to fit inside the surface grooves, promoting mechanical anchoring of the catalyst to the layer.

The specific load obtained after washcoating depends on the viscosity, solid content, and the method used to remove excess slurry. To achieve the target load, it is generally necessary to apply repeated coatings to generate thin layers, resulting in more homogeneous coatings.

The adherence of the coating depends on the compatibility with the substrate surface, both chemically and physically, and the use of additives such as binders that remain after calcination or compounds that allow for a soft drying process to prevent cracking and detachment. Mechanical constraints increase with decreasing channel size, which improves the adherence of the coating.

Deposition of metallic component on coated monoliths

The incorporation of the metallic component in a monolithic catalyst can be carried out using the same techniques as the pellet and powder catalysts. However, due to the shape of the monolith there may be a problem of heterogeneity, especially for monoliths of high cell density where the surface tension of the impregnating solution can cause difficulties in the distribution of materials inside the monolith channels [6]. Xu and Moulijn et al. [9] described several methods such as impregnation, adsorption and ion exchange, precipitation or co precipitation, deposition-precipitation, sol-gel method, slurry dip coating, in situ crystallization and addition of catalytic species to the mixture of extrusion for active phase incorporation in monolithic catalysts.

For metal incorporation on zeolite powders and zeolite coated monoliths, the methods most commonly used are ion-exchange and impregnation (both wet and dry). In some studies, metals like Cu, Co, Pt, In etc were introduced by ion-exchanging the zeolite washcoated monolith with a solution of the metal precursor (0.025M) such as $\text{Cu}(\text{CH}_3\text{COO})_2$, $\text{Co}(\text{CH}_3\text{COO})_2$, $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ and $\text{In}(\text{NO}_3)_3$ respectively [29,32,34,35]. In most cases the exchange was done by dipping the coated monoliths in aqueous solution of the precursor (solid/liquid ratio = 10g/l) for 24 h at room temperature. The monoliths were then removed, dried and calcined. Nijhuis et al. [4] have commented on the problem of maldistribution of metal that occurs during the

drying of a wet-impregnated monolith and found microwave drying to be the best drying method.

Another widely used practice is to load the metal on powder zeolites by ion exchanging with the metal salt and then washcoating the monolith with this catalyst. Boix et al. [33,36], Tomasic and Gomzi [37], and Chatterjee et al.[38] prepared powders of PtCoferriite, CuZSM5 and CrY/Co-Y respectively and coated the monoliths with the slurries of these powders. The monoliths were then subjected to the usual drying and calcinations methods. Several studies in literature also describe active metal impregnations in zeolite powders using the impregnation method [49-41].

Conclusion

Different methods of preparing ceramic and metallic monolithic catalysts/reactors along with the important parameters that determine the preparation of a efficient catalytic system has been summarized. It was found that washcoating of the catalytically active material on the surface of monolith was the most common process of incorporating the active catalytic phase on the monolith.

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