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Monolith structures, materials, properties and uses[☆]

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Abstract

Extruded monolith substrates are widely used in automotive and stationary emission control reactors such as selective catalytic reduction (SCR) units. Monoliths are increasingly being used, developed, and evaluated as catalyst supports in many new reactor applications such as chemical and refining processes, catalytic combustion, ozone abatement, and others.

This paper gives a general overview of monolith fabrication, characteristics and typical use. Several commercial product applications and new developments for use of monolith reactors in automotive, stationary and chemical industry are discussed.

Keywords: Monoliths; Honeycomb; Monolith reactor; Automotive emissions; Stationary emissions; Chemical process; Carbon; Gamma alumina; Zeolites

1. Introduction

Extruded monolith substrates are widely used in automotive and stationary emission control reactors for the selective catalytic reduction (SCR) of nitrogen oxides. Monoliths are increasingly under development and evaluation for many new reactor applications, e.g. chemical process and refining industries, catalytic combustion, ozone abatement, etc. [1–9]. Table 1 lists various applications in which monoliths are used. In automotive applications, ceramic monoliths are made from synthetic cordierite, $2MgO\cdot 2Al_2O_3\cdot 5SiO_2$, a material having a low thermal coefficient of expansion [7]. Cordierite is a highly anisotropic crystalline phase with concomitant high thermal expansion anisotropy that leads to orientation during extrusion and low overall expansion.

Compositions based on cordierite possess a unique combination of several critical characteristics: (a) thermal shock resistance due to a low thermal expansion coefficient; (b) porosity and pore size distribution suitable for ease of washcoat application and good washcoat adherence; (c) sufficient refractoriness because the melting point exceeds 1450°C; (d) sufficient strength for survival in an automotive exhaust environment; and (e) compatibility with washcoat and catalysts [7].

The combination of high cell density, 31–186 cells/cm^2 (200–1200 cells/in.^{2}), with thin walls, 0.051–0.27 mm (0.002–0.0105 in.), give rise to low backpressure in automotive exhaust systems. This combination also yields high open frontal area (OFA), 72–87%, which is a necessary condition for low backpressure.

Physical and chemical properties of cordierite raw materials are controlled to a high degree necessary for sophisticated quality control. For example, the particle size of various commonly used raw materials, silica, clay, alumina and talc, are closely controlled to consistently yield the desired porosity and pore size distribution as well as hold parts to close tolerances.

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Table 1
Applications of cordierite cellular ceramic substrates

Automotive emission control
Diesel particulate filter
Stationary emission control
Woodstove combustor
Molten metal filter
Natural gas storage
Indoor air purification
Ozone abatement
Catalytic incineration
Industrial heat recovery
Ultrafiltration
Chemical process catalyst support
Water filtration

Examples of monolithic substrates are shown in Fig. 1. The monolith parts itself can be produced in a number of sizes and shapes, typically round or oval cross-sectional areas for automotive applications, or square for stationary emission uses. Cross-sectional part diameters for single pieces up to 35 cm have been produced commercially for heavy duty vehicle uses. Much larger cross-sectional areas are made by stacking blocks together for stationary emission reactor systems. In addition to the overall part dimension, the geometry of the monolith channels can be produced in many forms including square, round, hexagonal, and triangular.

Cell configurations and properties of monoliths are described in terms of geometric and hydraulic parameters [2,10]. These properties can be defined in terms of cell spacing L, the distance measured from the center of one cell wall of a square channel to the next wall, and wall thickness, t.

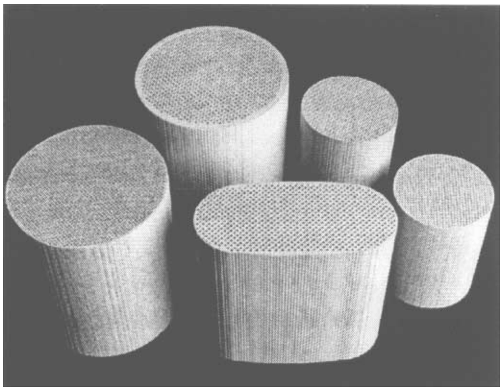

Fig. 1. Cellular ceramic monoliths.

The cell density N is defined as the number of cells per unit of cross-sectional area and is expressed in units of cells per square inch (cpsi) or per square centimeter.

$$N = \frac{1}{L^2} \tag{1}$$

The OFA is defined as a function of wall thickness, cell spacing and cell density, as shown in Eq. (2).

$$\mathrm{OFA} = N(L-t)^2 \tag{2}$$

The hydraulic diameter defined by Eq. (3) decreases as the cell density increases for a monolith. The

$$D_{\mathrm{h}} = L - t \tag{3}$$

hydraulic diameter is different for uncoated and washcoated monoliths since washcoating with catalyst or ceramic materials changes the wall thickness.

In designing monolithic catalysts, there is a balance between geometric surface area and pressure drop. The pressure drop across the monolith depends linearly on flow velocity and length.

$$\Delta P = \frac{2 f \ell \rho v^2}{G_{\mathrm{c}} D_{\mathrm{h}}} ch \tag{4}$$

where f is the friction factor, dimensionless; D_{h} the hydraulic diameter (cm); G_{c} the gravitational constant; ℓ the monolith length (cm); v the velocity in channel (cm/s); and ρ the gas density (g/cm^3).

These fundamental equations allow one to design monolith geometric parameters such as cell density or wall thickness to meet the constraints of external processing requirements such as space velocity, flow rates, pressure drop, etc. For a more detailed discussion see Refs. [1,2].

In the case of automotive catalytic converters, the design and durability of advanced ceramics must promote fast light-off, improved conversion efficiency, and reduced backpressure [1]. Current designs are focusing on thinner wall monoliths. Thermal shock resistance and a low coefficient of thermal expansion are important properties of automotive converter substrates, and are a major reason why cordierite is the ceramic material of choice for this application.

The success of cordierite monoliths as catalyst substrates in the treatment of automotive exhaust has given rise to interest in the chemical industry as substrates for catalytic reactors. For many of these applications, the use of other substrate materials and designs can be utilized since the thermal shock requirements are not as demanding as automotive. In general, many inorganic catalyst support materials used today in conventional chemical and refining application can be extruded into a monolith form. This has ignited interest in monolith reactors as potential replacements for fixed bed and slurry reactors. Monolith reactors offer the advantage of thinner walls, high geometric surface area, low-pressure drop, good mass transfer performance, and ease of product separation. There may also be advantages in kinetics and mass transfer in gas/liquid phase applications due to better catalyst wetting, higher effectiveness factors, and thin films that are conducive to high mass transfer rates. However, the hydrodynamics and flow distribution of multi-phase flow through a monolith reactor bed is still not fully understood [3,4,11–13].

This paper gives a general overview of monolith fabrication, characteristics and typical use. Several commercial product applications and new developments for use of monolith reactors in automotive, stationary and chemical industry are discussed.

2. Extrusion process

The extrusion of cordierite or other ceramic materials into monolith shape follow the basic steps outlined in Fig. 2 [7]. In the first step good mixing of raw materials is necessary to insure complete reaction or interaction of raw materials. Plasticizing with solvent, usually water, is required to bring the batch materials to a condition suitable for forming by extrusion. Extrusion is done with a series of unique dies developed for this process [14]. Uniform drying of monoliths is necessary to insure that enough moisture is driven off without cracking the monolith body. In the final step, the dry monolith part is calcined at elevated temperatures to complete solid state reactions and to obtain the desired physical properties. For cordierite, calcining is conducted at 1400°C to transform the mixture into a phase-oriented, low expansion sintered body.

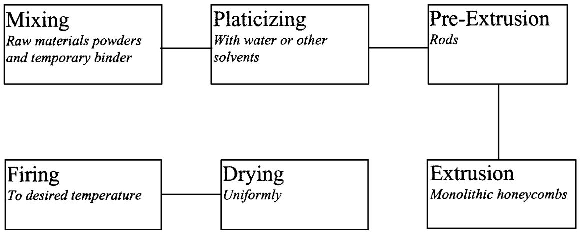

Fig. 2. Fabrication of monolithic honeycomb substrates.

Extruded carbon monoliths are fabricated in a similar process except for the use of phenolic resins and fillers in the extrusion step followed by curing, carbonizing, and activation steps [15].

3. Automotive

Future emission limits for gasoline- and diesel-fueled vehicle require more efficient exhaust gas after treatment devices. For gasoline engines, the catalytic converter is one essential part of a complex system design. As emission regulations become more stringent, new developments in engine control, fuel management, catalyst technology, and advanced substrate technology is needed.

The most widely used ceramic material for extruded monolithic substrates is cordierite, $2MgO\cdot 2Al_2O_3\cdot 5SiO_2$. For use as automotive catalytic converter, cordierite has a set of unique properties including high porosity, low thermal expansion, high thermal shock resistance, and a tailored microstructure [10].

Advances in ceramic substrate technology are made possible through judicious choice of cell shape and size, wall porosity and microstructure of cordierite. Table 2 lists some of the cell sizes and shapes of monoliths that are generally used in commercial substrates. Cell densities in the range 400–1200 cpsi are of interest for automotive catalytic converters. The trend is toward the use of ultra-thin-walled substrates for automotive catalytic converters for light-off performance. As part of the overall system design, more durable washcoat formulations and high temperature stable catalysts are needed to achieve longer lifetime of the converter [1].

4. Diesel particulate filter

The diesel particulate filter (DPF) is the most effective method to remove soot particles from diesel

Table 2
Monolith substrates of interest for automotive converters

Cell density (cpsi)	Web thickness, 1 mil = 0.001 in.	Geometric surface area (cm^2/ccm)	OFA
25	(35 mil) 0.889 mm	6.51	0.681
50	(25 mil) 0.635 mm	9.17	0.678
100	(15 mil) 0.381 mm	13.39	0.723
200	(10.5 mil) 0.267 mm	18.98	0.725
300	(8 mil) 0.203 mm	23.51	0.742
400	(4 mil) 0.102 mm	27.09	0.846
600	(4 mil) 0.102 mm	31.01	0.787
900	(2 mil) 0.051 mm	43.11	0.834

engine vehicle exhaust with filtration efficiencies up to 95% [10]. Regeneration of the filter is critical for continuous engine and vehicle operation at low backpressure. Controlled on-board regeneration of diesel filters is an area that continues to be explored. Both passive and active techniques are under investigation.

A DPF differs from automotive catalyst substrates in that alternate channels are plugged on the entrance face and the adjacent channels are plugged on the exit face of the filter, forming a checkerboard pattern. Filtration occurs when the particle laden exhaust gas is forced through the wall between adjacent channels. Soot particles are trapped in the entrance channel and clean exhaust passes out from the exit channel. Periodically the soot is burned off, thereby cleaning the channel and recovering backpressure. Cordierite and silicon carbide are two materials that are commercially available for diesel exhaust after treatment. Development of new materials for DPF type filters is in progress.

A high cell density cordierite DPF product, RC 200/19, was recently introduced at the 2001 SAE conference held in Detroit. The geometry is 200 cpsi with 0.019 in. (0.048 cm) wall thickness compared to a standard EX-80 product having 100 cpsi with 0.017 in. wall (0.048 cm). RC 200/19 has a higher thermal mass which leads to lower temperatures during regeneration [16,17].

5. NO_x adsorbers

The NO_x storage catalyst was developed to meet low emissions and fuel consumption targets for gasoline engine vehicles. The NO_x adsorber is a washcoat containing barium, potassium, or other alkali/alkaline earth metal oxides as adsorbents [18–20]. During adsorption, a nitrate is formed with the alkali oxide through conversion of NO to NO_2 with O_2 promoted by platinum. It is known that potassium is a better adsorbent than barium in high temperature conversion of NO_x, however, one problem with potassium is its migration from the washcoat into the substrate and subsequent loss of adsorption efficiency. Zeolites, titanias, and silicas are being developed as barriers to prevent potassium migration and sulfur poisoning of the NO_x adsorber [19].

6. Chemical process industry applications

Successful use of cordierite monolith catalysts in the treatment of automotive exhaust has given rise to their use in other catalytic applications. For many of these, the use of other substrate materials and designs can be utilized since the requirements are not as demanding as automotive. This has resulted in an increase in the potential use of monoliths in chemical and refining catalyst applications.

Monolith catalyst substrates can be either metal or ceramic. They can be washcoated with a high surface area catalyst support material and impregnated, or extruded directly into catalytic bodies using appropriate batch materials. The use of monoliths in multi-phase reactors is of interest as possible replacements for slurry and fixed bed reactors. Monolith reactors offer the advantage of thinner walls, high geometric surface area, low pressure drop, good mass transfer, and ease of product separation [4,8,11–13].

Hydrogen peroxide is presently the only large-scale industrial application of monolithic catalysts in a multi-phase process [21]. Anthraquinone is used to facilitate the selective oxidation of hydrogen to hydrogen peroxide indirectly using a chemical redox approach in a two-step process. The quinone reduction step utilizes a monolith catalyst containing palladium on a washcoat in a gas/liquid multi-phase reactor.

Schanke et al. [24] describe the use of a multi-phase monolith reactor system for Fischer–Tropsch synthesis in a recent US patent. The monolithic catalyst is comprised of γ-alumina, silica, zeolite, or titania and a conventional Fischer–Tropsch catalyst combined with a precious metal promoter. The strongly exothermic nature of Fischer–Tropsch synthesis requires effective heat transfer for successful reactor operation.

Vinyl acetate is synthesized by the vapor phase reaction of ethylene, oxygen, and acetic acid over a monolith catalyst. The monolith catalyst consists of Pd and Au deposited on silica-coated cordierite or mullite monoliths. Catalyst space–time yields for vinyl acetate production of 434 g/l h at 192°C have been reported [22,23].

Addiego et al. [25] have reported the extrusion of iron oxide honeycomb catalysts for the vapor phase dehydrogenation of ethyl benzene to styrene. They indicate styrene selectivity >90% and ethyl benzene conversion greater than 60%. The low pressure drop characteristic of monolith shapes for this equilibrium limited reaction is an important benefit.

Unreacted *o*-xylene and other intermediates are converted to phthalic anhydride (PA) in a post-reactor containing a monolith catalyst located downstream of the main PA reactor in the Wacker low energy phthalic anhydride process. The use of the proprietary catalyst in the post-reactor provides higher overall conversion to PA and increases operational flexibility around the main reactor [26].

7. Carbon

Carbon monoliths have potential for use in a wide variety of applications for which activated carbon bodies are suited. Examples include residential water purification, volatile organic compound emission control, natural gas fuel storage for gas-powered vehicles or equipment, indoor air purification, industrial respirators, automotive cabin air filters, ventless hoods, chemical separations, NO_x, and SO_x, control, and exhaust traps for automotive cold start emissions [15,19,27–30].

Preparation of carbon monoliths is either by full-body extrusion or as a coating on cordierite substrates. Activated carbon-coated monoliths are fabricated using high yield polymeric phenolic resins having low viscosity. A pore former polymer is added for mesopore formation (30–100 Å). The manufacturing process includes dipping a porous ceramic monolith in a resin, drying, curing, carbonizing in nitrogen, and activating in carbon dioxide or steam. Gadkaree and others have described more details of this process elsewhere [15].

Table 3 shows the physical properties of activated monoliths prepared by the above method [27]. At least 50% of the pores are in the mesopore range. Surface areas range from 700 to 1000 m^2/g.

Activated carbon monolith catalysts are prepared by the incipient wetness impregnation method or by inclusion of catalyst functionality in the polymeric resin during process steps [27].

Extrusion of full-body carbon monoliths is similar to that described in Fig. 2. The basic process involves forming a mixture of a thermosetting resin, which can be either a solid or liquid resin and a filler, which can be carbonizable or inorganic. The mixture is extruded into a monolith, dried, and the resin is

Table 3
Physical properties of coated carbon monoliths

Sample	Surface area (m^2/g)	Pore volume			Total pore volume (cm^3/g)	Fraction micro	Fraction meso	Fraction macro
		t-Micro	Meso	Macro				
1	698	0.27	0.32	0.02	0.61	0.45	0.52	0.04
2	1041	0.29	0.81	0.03	1.12	0.26	0.72	0.02
3	863	0.17	0.91	0.07	1.16	0.15	0.79	0.06
4	828	0.04	1.30	0.08	1.41	0.03	0.92	0.06

cured. The cured monolith is carbonized and activated [15,18].

8. Zeolites

Zeolites, both natural and synthetic, have found wide use for removal of NO_x from coal-fired utilities and gas turbine catalysts for SCR of NO_x using NH_3. Zeolites can be combined with vanadia/titania to produce a catalyst with a wide $DeNO_x$ operating window that is more resistant to deactivation [7].

Zeolite catalysts can be extruded or coated onto metal or ceramic substrates. Again, the extrusion process is the same as that outlined in Fig. 2. The coating process involves preparation of a zeolite slurry using a binder, usually colloidal silica or alumina, dipping the monolith, then drying and firing. Ion exchange of zeolite can be done before or after coating and/or extrusion. One potential disadvantage of coated and extruded zeolites is the use of binder that can block the zeolite pores and active metal sites. As such, the amount of binder should be kept to a minimum.

The in situ growth of a zeolite on a substrate is one way to prevent blockage of pores and active material. The substrate is covered by a thin layer of synthesis mixture or immersed in a liquid that contains the mixture inside an autoclave. Patil [31] discusses preparation of mixtures of mordenite and MFI type zeolites on cordierite support. The main disadvantages of in situ growth of zeolites are complexity compared to washcoating and growth of thin layer of zeolite on the substrate surface. The main advantage is complete accessibility of reactants inside the zeolite pores.

9. γ-Al_2O_3 monoliths

γ-Al_2O_3 is used in many applications (e.g. automotive catalytic converter) as a high surface area washcoat on the channel walls of monolith substrates [1]. However, for many applications, porous washcoats are inadequate and catalyst supports made up mostly or entirely of active high surface area γ-Al_2O_3 are used. Such applications include processes wherein the kinetics of the chemical reaction on the catalyst are slow relative to the diffusion and mass transfer steps involved in the overall process.

Extruded monoliths of γ-Al_2O_3 consists of a mixture of alumina powder, organic binder, and precursors such as colloidal alumina solution as a permanent binder. Narrow pore size distribution and high strength are attained by proper selection of starting oxides and processing variables. High strength and surface area are needed to maintain structural integrity of the support in a reactor. Low to moderate firing temperatures are required to preserve the high porosity and BET surface area of the starting materials [32,33].

Many potential monolith applications require a high BET surface area for effective catalyst function and have 50–300 m^2/g. Higher BET surface areas offer the possibility for a more compact reactor, which could lead to significant cost reductions for the overall reactor system [1].

10. Conclusions

Extruded monolith catalyst substrates for automotive catalytic converters will continue to use cordierite as the material of choice. Cordierite offers unique properties in porosity, strength, thermal shock, thermal expansion and robustness required for auto exhaust treatment. Advances in ceramic processing have led to the development of higher cell density materials with improved strength and thermal properties. With proper selection of raw materials and processing control of microstructure, pore size distribution, strength and other physical properties can be tailored for specific applications.

The success of cordierite as catalyst support for treatment of automotive exhaust emissions has given rise to considerable interest in the chemical industry. For many applications, the use of other materials and designs can be utilized, since the requirements are not as demanding as automotive. Hydrodynamics of multi-phase flows in monolith beds need to be better understood for wide use of monoliths in the chemical and refining industries. In particular, design will be a key parameter to control the fluid flow inside monolithic reactors and hydrodynamic knowledge is being generated. Monolith reactors have potential to replace fixed bed and slurry reactors for certain types of reactions.

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