

Monolithic ceramics and heterogeneous catalysts: honeycombs and foams

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Recent advances have been made in research on ceramic monolithic catalyst supports, particularly on honeycombs and ceramic foams. In the case of honeycombs, cordierite is the most commonly applied composition, but alternative materials, such as SiC, are beginning to be used for demanding conditions. Typical catalytic applications of honeycombs include use as catalyst supports for the removal of gaseous or particulate emissions from combustion engines (gasoline and diesel), and for reducing nitrogen oxide emissions from power plants. Ceramic foams are used commercially for the filtration of molten metals, and are attracting increasing attention as catalyst supports due to high thermal stability, high porosity and increased tortuosity with respect to honeycombs.

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Abbreviations

CTE coefficient of thermal expansion
SSA specific surface area

Introduction

Heterogeneous catalysis lies at the heart of most conversion processes in oil refining, and in petrochemicals manufacture, natural gas conversion, and environmental processes. The catalysts typically used are porous inorganic solids, with or without added metals. Catalyst shaping is an important issue, with a need to balance performance, strength, and pressure drop across the catalyst system. Many catalysts are used as randomly packed fixed beds of small particles (e.g. extrudates, granules or spheres), typically in the millimeter size range. Monolithic structures, which consist of large single catalytic entities, are attracting increasing attention, and recent progress is reviewed in this article. Two types of monolithic catalyst are discussed: honeycombs, which are made in very large numbers as carriers for automotive exhaust catalysts, and the much newer ceramic foams. Figure 1 illustrates both. The term monolith is sometimes regarded as being synonymous with honeycomb, but we suggest that monolith more appropriately refers to any catalyst bed which is a single entity.

The term ceramic is less well defined, particularly when discussing porous ceramics. Here it is taken to mean inorganic materials of high thermal stability, for example, those stable above 700°C, composed of oxides or non-oxides such as carbides. As the field of technical ceramics continues to expand, the use of ceramic materials as catalyst supports is opening several opportunities (see [1] for a review of applications, preparation, and stability of porous ceramic materials). In general, catalyst supports are characterized by high surface area to volume ratios (with a specific surface area [SSA] often exceeding 200 m² g⁻¹) but in most monolithic supports the SSA is approximately 1 m² g⁻¹, which is still considerably higher than that of most technical ceramic materials. The technology exists to coat monoliths with a porous layer, thereby substantially increasing the SSA.

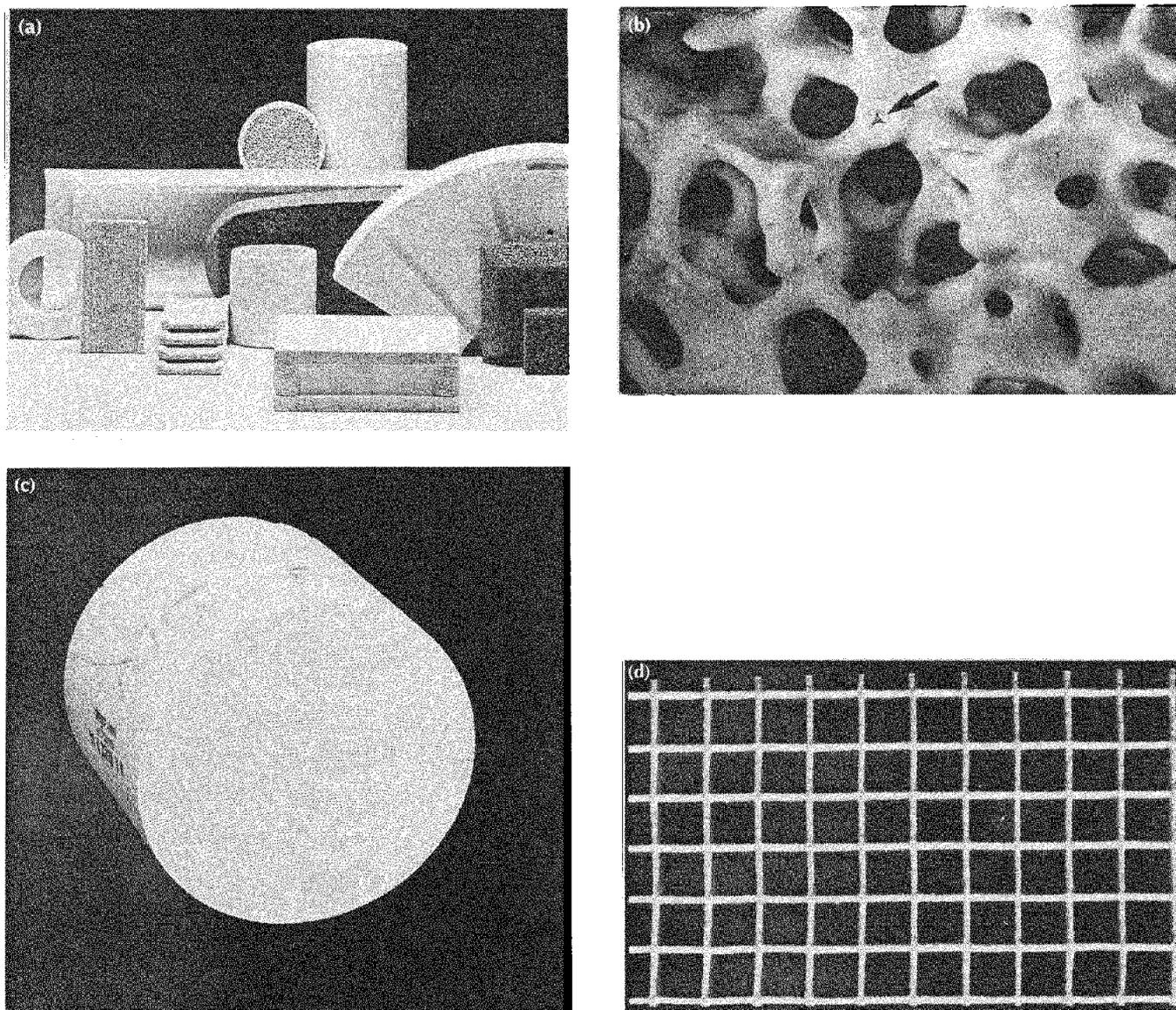
Supplementary material on catalysts can be obtained from several sources. Application of honeycomb monoliths in heterogeneous catalysis has been reviewed [2**]. An article on catalysts for environmental processes, from a materials perspective, includes information on both honeycombs and foams [3*]. The proceedings of a conference on advanced catalytic materials contains papers presented in a session on honeycombs and foams [4*] and another which dealt with advances in porous materials in general [5*].

In addition, the fabrication techniques used to produce honeycombs and reticulated ceramics are becoming progressively more complex and at the same time better controlled. This brief review will focus on recent advances in ceramic catalyst carriers and their advantages with respect to mechanical, thermal, and chemical stability. New candidate materials for catalyst supports will also be discussed.

Foams

Ceramic foams, sometimes referred to as reticulated ceramics, are three-dimensional cellular structures in which the cells are connected by open windows, giving high porosity of the order of 80–90% void space. These materials have been developed, mainly in the past decade, to filter out impurities from molten metals. In the past two years, interest in these materials as catalyst carriers has expanded considerably. Ceramic foams possess certain advantages compared with the honeycombs: a much wider range of shapes are available due to the method of preparation discussed below; the more tortuous nature of the porosity which improves reactant mixing and favors

Figure 1



Monolithic ceramic catalyst supports. (a) Examples of the range of shapes possible from ceramic foams; (b) $\sim 10\times$ magnification photograph of the ceramic foam structure illustrating the random structure and the triangular void artifact of the fabrication process (arrow); (c) cordierite honeycomb structure showing a typical example of a cylindrical monolith; and (d) a close-up of the honeycomb showing the square-channel architecture. Photographs (a) and (b) courtesy of Hi-Tech Ceramics, Alfred, NY; photographs (c) and (d) courtesy of Corning, Inc., Environmental Products Division, Corning, NY.)

surface reactions; and radial transport within the monolith is significantly improved.

Applications of ceramic foams as catalyst supports

Twigg and Richardson [6**] have summarized work on the use of foams as catalyst supports in the areas of ammonia oxidation, catalytic combustion, partial oxidation, steam reforming, exhaust catalysis, and solar-driven methane- CO_2 reforming. Further work has since appeared on foam supported catalysts for methane [7] or propane [8] combustions.

Schmidt and Diez [9**] have summarized their work on a variety of monolithic structures (gauzes, honeycombs, fiber mats and foams) as supports for metals in the catalytic partial oxidation of methane to synthesis gas (CO/H_2), of alkanes to alkenes, and of methane to HCN; a full paper has also appeared on aspects of this work [10]. It was found that conversions and selectivities were generally better using the foam-based catalysts. These reactions are typically operated adiabatically, at temperatures of about 1000°C or higher, and at very high space velocities, for example, $100\,000\text{ h}^{-1}$. Such reaction conditions clearly require materials of high thermal stability and high

porosity, and ceramic foams have the additional advantages of tortuosity and shapeability.

Preparation of foams

The preparation of ceramic foams is based on impregnating a piece of polymeric foam, typically polyurethane, with a slurry of inorganic particles. This composite material is then heat treated to burn out the polymeric substrate and sinter the inorganic particles together. The ceramic structure replicates the original organic polymer structure. It has been said that this technique has "revolutionized the field of highly porous ceramics" [11*].

The details of this polymeric foam infiltration process are frequently proprietary, or described in the patent literature, but a full description has now appeared in a journal article [12]. Control of slurry properties through use of a dispersant, a surfactant and a binder and pH adjustment is important, as well as the temperature program in the heat-treating step.

A significantly different procedure from the one described above is being developed: this relies on *in-situ* polymerization of an organic monomer in the presence of water, dispersants, initiator catalyst and ceramic powder of selected particle size, followed by use of a foaming

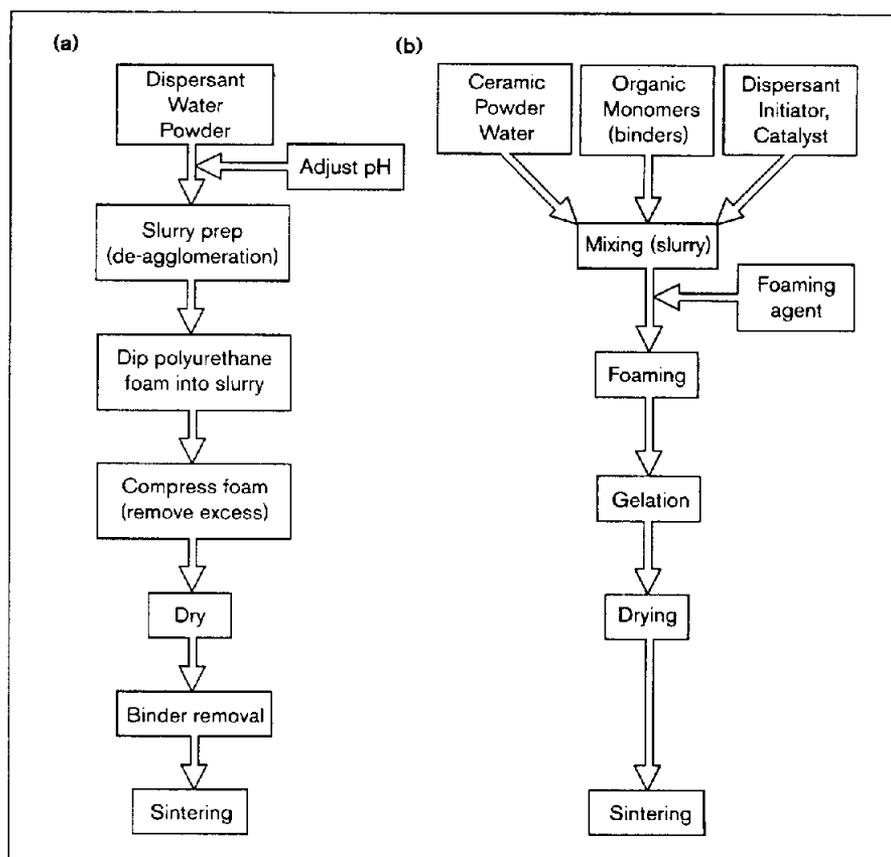
agent [11*]. The principal advantages of this technique appear to be the significant increase in green strength (i.e. the strength prior to calcination), allowing the foam to be machined before heat treatment and sintering, and the extension to finer pores than those obtainable with the replication technique. Figure 2 outlines the processing steps followed for the production of foams using the traditional approach and the new *in-situ* polymerization approach.

Modification of foams

Ceramic foams as prepared have low surface areas, of the order of $1\text{ m}^2\text{ g}^{-1}$. Coating of foams with oxide layers can be used to increase surface area or to alter surface composition. Work in this direction has been mentioned in several publications, but few details have been provided. Examples include alumina wash coating of a lithium aluminosilicate foam [13], wash coating of an α -alumina foam with a γ -alumina layer [9**], the use of alumina sols, with or without lanthanum nitrate additions, to modify foams [7], and a technique of coating ceramic foams with perovskites, through coating the foams firstly with epoxy resin, then by infiltration with perovskite powder [14]. When the foam is coated with γ -alumina, or any hydrated form of alumina, the practical maximum use temperature is limited to approximately 700°C before the

Figure 2

Flow charts depicting (a) the traditional, slurry infiltration as described in [12] and (b) the new *in-situ* polymerization processing routes used in the production of reticulated ceramics [11*].



SSA is significantly reduced due to the transformation to other crystalline forms of alumina [15].

Strength of foams

With respect to strength, it has been stated that the main disadvantage of foams is their weakness. Improvements to the strength have been achieved by using additives or negative image foams [6**]. Negative image foams are formed by completely filling the pores of an organic cellular polymer with a ceramic slurry, followed by calcination to leave a material in which the pore structure corresponds to the space originally occupied by the polymer; this provides a denser material than the cellular polymer, but at the cost of lower porosity. In addition to these two options for improving strength, knowledge on crack formation [12] and the use of new processing techniques [11*] may help in designing stronger foams.

Honeycomb structures

Honeycomb structures can be viewed as two-dimensional cellular structures in which flow through the honeycomb occurs through long parallel channels. In some applications the catalyst is a metal introduced to the support via a solution method, or a high surface area alumina coating applied to the support through a suspension technique, as mentioned previously for the coating of reticulated ceramics. As the processing of honeycomb structures becomes routine, more applications for honeycomb structures are being developed.

Applications of ceramic honeycombs as catalyst supports

There are three major applications of honeycomb-type ceramic catalyst supports: first, the use of honeycomb structures to serve as automotive exhaust catalyst supports for the removal of NO_x , CO, and hydrocarbons from the moving gas stream [3*,16**]; second, for diesel exhaust filters where, in addition to removing gaseous species, the honeycomb is also critical in removing particulates from the gas stream [17**,18*,19**]; and third, for controlling gaseous and particulate emissions in stationary applications, such as coal-burning power plants, primarily for the removal of NO_x [16**,20]. In all three cases, the catalyst supports have been designed for use in high-temperature gas streams to allow the minimum pressure drop across the support while maintaining thermal, mechanical, and chemical stability. Honeycomb structures for automotive exhaust catalyst supports were developed in the early 1970s and are considered the standard today. Filters are differentiated from catalytic supports in general in that filters are used to remove particulate matter from the gas stream, where catalytic monoliths support catalysts that remove species through catalytic reactions.

The diesel and coal plant applications differ from those of the automotive honeycomb structures in that they are also used as particulate filters, with alternate channels of the honeycomb blocked to force the exhaust stream to pass through the porous wall of the honeycomb, trapping

approximately 90% of the particles. These materials are also used as catalysts for the treatment of exhaust gases. The requirements for power plant applications, (i.e. fluidized bed combustion, coal gasification, and coal-fired turbine concept), dictate that the substrates be thermally stable up to 1350°C, chemically stable in oxidizing or reducing environments, and have a lifetime of >10000 hours [1].

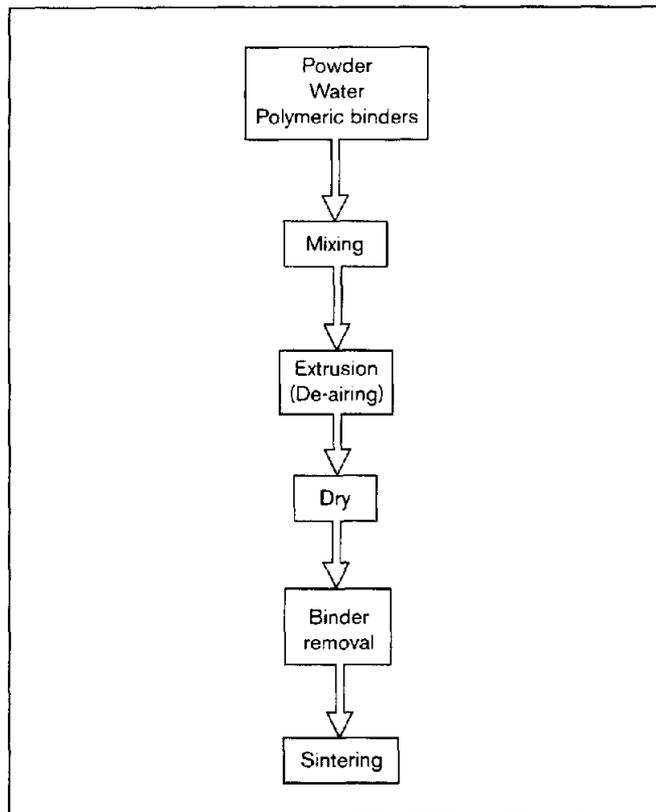
In the case of high surface area aluminas, such as those formed from pseudo-boehmite powders (heat treated to form γ -alumina in the catalyst support), temperatures between approximately 600°C and 900°C cause a significant reduction in specific surface area, and lead to the formation of δ -, θ -, and eventually α -alumina. The stability of α -alumina is one of the highest of the ceramic materials, but α -alumina is also susceptible to sintering at temperatures above 1100°C, further reducing the pore size and the surface area [15].

Preparation of honeycombs

Honeycomb structures are produced exclusively through the process of extrusion. The material to be extruded is usually a mixture of ceramic powders which has been plasticized to give favorable extrusion performance. Figure 3 outlines the approach used to fabricate honeycomb structures [16**]. Industrially, both auger-type (screw-driven, continuous) and piston-type (hydraulic-driven, discontinuous) methods are used, depending on the product. The key to the fabrication of high quality honeycombs lies in the quality of the extrusion dies and in the control of the plasticity of the extrusion mass before extrusion [16**,21]. Production of the sophisticated extrusion dies is proprietary expertise. After extrusion, the substrates are dried, then heat treated to sinter the ceramic in order to provide it with strength and the desired pore characteristics. During the heat treatment process, the cordierite crystals are aligned along the c-axis within the cell walls to provide the lowest thermal expansion along the axial direction [16**].

Assuming that the extrusion die is of high quality, the quality of the substrate is entirely dependent on the plasticity of the extrusion batch; however, the characterization of plasticity is currently a major obstacle in the preparation of extruded material, with the extruder itself serving as the characterization tool. The obvious limitation of characterizing samples with an extruder is that samples which are not extrudable cannot be tested. Recent work has focused on the development of a high pressure shear rheometer for the quantitative characterization of plasticity (W Carty, unpublished data). The use of the high pressure shear rheometer is a promising approach, and has been successfully applied to the area of clay-based systems such as those used in the manufacturing of porcelain dinnerware, which is similar in composition to those used for cordierite honeycomb supports [22*]. In systems that are not clay based (nearly all other ceramic honeycomb

Figure 3



Processing routes for the preparation of honeycombs [16**,21]. If the material to be extruded contains sufficient clay, it is not usually necessary to add the polymeric additives.

systems), polymeric additives are necessary to provide sufficient plasticity for the material to be extruded. The amount and type of plasticizers added is determined by empirical evaluation rather than by scientific approach and remains one of the most poorly understood areas of ceramic processing.

Material selection and thermal and chemical stability

Cordierite

For automotive supports, cordierite ($2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$) is by far the most commonly used material, and is usually produced from a mixture containing clay (usually in the form of kaolinite, $\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\cdot \text{H}_2\text{O}$). The use of clay in the extrusion batch inherently provides the plasticity necessary for the extrusion process. Significant advances in die design have reduced the honeycomb wall thickness, increasing the open cross-sectional area, thereby reducing the pressure drop across the honeycomb catalyst support [16**]. Cordierite has been the material of choice for automotive applications because of its low coefficient of thermal expansion (CTE) and relatively low cost of production compared with other ceramic materials [17**]. Recent work has focused on the production of cordierite containing aluminum-titanate (tialite), a

composite material with a reduced CTE, particularly in the low temperature range (20–300°C) as compared to pure cordierite [23].

In diesel engine applications, the substrate also serves as a particulate trap, removing carbon particles from the exhaust stream. The gasification of the trapped particles is accomplished by at least one of three processes: first, increasing the residence time of the particles to allow oxidation to occur (possible only in systems in which the exhaust gases are oxidizing); second, catalytic reaction at the walls of the substrate; or third, through a regeneration process using elevated temperatures, (to burn off or oxidise particulates which have been deposited from the gas stream), often in excess of 1000°C. Problems can arise with cordierite substrates in the presence of other oxides, which can react with cordierite at high temperatures to form other, less stable phases. For example, CaO, Fe_2O_3 , Na_2O , V_2O_5 , and ZnO, which are common impurities found in the combustion products of hydrocarbon fuels, and are sometimes found as a component of the active catalyst, break down cordierite to form other crystalline phases [24**,25**]. The most serious contaminants are Na_2O and V_2O_5 . Na_2O can completely destroy the cordierite structure at temperatures above 900°C [24**] and begins to form a feldspar-type mineral, carnegierite ($\text{Na}_2\text{O}\cdot \text{Al}_2\text{O}_3\cdot 4\text{SiO}_2$), at temperatures as low as 700°C [25**]. Carnegierite has a significantly higher CTE than cordierite, producing sufficient stresses on heating and cooling to cause cracking [24**]. V_2O_5 is similarly damaging, and as it has a melting point of 800°C, it is in the liquid phase at the regeneration temperatures, which enhances its reactivity and mobility. During the reaction with cordierite, it can form amorphous phases, which reduce the surface area of the support. In addition, the amorphous phases solidify on cooling, leading to large thermally induced stresses and, frequently, to cracking due to CTE mismatch. V_2O_5 can also form stable Mg- and Al-vanadates, releasing SiO_2 which crystallizes to cristobalite [25**]. If Na_2O and V_2O_5 are present during the regeneration process (which is almost always the case), stable NaVO_3 compounds can be formed. These reactions are apparently independent of time, being almost entirely dependent on temperature: this means that even short times at high temperature during the regeneration process can lead to significant degradation of the cordierite substrate.

Silicon carbide

Silicon carbide (SiC) has been investigated over the past several years as a material for diesel engine honeycomb support systems. It offers several advantages over cordierite in that it has better thermal stability and a higher thermal conductivity, leading to a reduction in thermal gradients [17,18*,19**]. Table 1 lists the properties of SiC and cordierite for comparison. Because these materials are also used as filters, they require substantially higher levels of controlled porosity to allow sufficient gas flow velocities

to be maintained. The sintering mechanisms active in SiC are via solid-state or gaseous transport (compared with liquid- or viscous-phase sintering mechanisms in oxides) which are basically inactive at temperatures below 1600°C, substantially enhancing the pore stability in SiC compared with oxide materials. That is, expanding further the note in parenthesis: most oxide ceramic materials are ionically bonded and therefore have a melting point, which means that the primary sintering mechanisms tend to be via liquid- or viscous-phase transport or via bulk diffusion. These mechanisms tend to be activated at lower temperatures and are generally rapid. SiC is a covalently bonded material and does not have a melting point, but instead it sublimes at extremely high temperatures. Thus, the viscous- and liquid-phase sintering mechanisms are not functional. Solid-state or gaseous diffusion mechanisms tend to be slower sintering mechanisms, only becoming rapid at extremely high temperatures. Above 1600°C oxidation becomes the dominant degradation mechanism in SiC; oxidation mechanisms and related problems have been thoroughly addressed by Stobbe *et al.* [17**]. In addition, a new method of closing alternate channels has been developed which produces a higher active surface area filter [19**].

Table 1

Comparison of the properties of silicon carbide and cordierite in the form of honeycomb catalyst supports [17].**

Property of filter substrate	Silicon carbide	Cordierite
Bulk density (g cm ⁻³)	1.8	1.0
Porosity (%)	50	46
Cells (cm ⁻²)	8	16
Cell size (mm)	2.5×2.5	2.1×2.1
Modulus of elasticity (GPa)	85	5
Poisson's ratio	0.16	0.26
Modulus of rupture (perpendicular to channels) (MPa)	19.5	3.5
Thermal conductivity at 25°C (W/m·°C)	11	<0.5
Thermal conductivity at 630°C (W/m·°C)	7	<0.5
Coefficient of thermal expansion (10 ⁻⁶ °C ⁻¹)	4.6	1.0
Decomposition/melting temperature (°C)	2300	-1200

Hexa-aluminates

As the structure of the ceramic material becomes more complex, its thermal stability is improved, due to the difficulty of the ions to easily rearrange within the crystalline lattice. Hexa-aluminates are an example of this, and two reports have been published on the stability of hexa-aluminates doped with Sr, La, and Mn (in which Mn substituted for Al³⁺ in the lattice and serves as

the 'catalytically active component') for use in elevated temperature catalytic applications [26*,27]. The first case investigated the stability of hexa-aluminate powder synthesized via the hydrolysis of alkoxide solutions, in which the SSA diminished (from 20 m² g⁻¹) over the first 5000 hours to become stable at 6 m² g⁻¹ over the second 5000 hours when held at 1300°C [26*]. In the second study, honeycombs were produced from powders prepared using a similar technique, and were successfully tested at temperatures up to 1200°C in a 160 kW gas turbine [27].

Perovskites

The preparation of mixed-oxide perovskite-based honeycombs has been reported. Powdered perovskites were obtained by plasmachemical or mechanochemical routes, and were extruded to form honeycombs with square or triangular cells [28,29]. These materials were tested for CO and NO_x catalytic oxidation and high temperature stability with promising results.

Future directions

The application of ceramic foams in catalysis is clearly expanding. It can be anticipated that further work will be carried out on improving the properties of foams (e.g. pore size distributions [13], and strength), on the modification of foams as described above, and on a wider range of applications, including liquid-phase catalytic reactions.

Honeycomb structures are well established as catalyst supports for automotive applications and for particulate filters. For automotive exhaust applications, cordierite will continue to be the primary material, but new applications are stimulating the development of alternative materials with improved catalytic properties. The use of SiC appears to have the greatest potential in the area of diesel exhaust filters and for power plant applications in which thermal and chemical stability is essential.

Conclusions

During the past two years significant advances have been made in the fabrication of monolithic ceramic catalyst supports, in particular honeycombs and ceramic foams. With respect to honeycombs, the continued development of processing techniques is leading to increased thermal, mechanical and chemical stability. Cordierite is the principal composition used but alternative materials such as SiC offer several advantages. Ceramic foams have been developed as filters for molten metals and are attracting increasing attention as catalyst supports. Foams possess high porosity, high thermal stability, and higher tortuosity than honeycombs. An exciting advance is the development of a new fabrication technique for foam ceramics, using *in-situ* polymerization. This allows the generation of finer pore structures than is possible with the traditional polymer replica technique.

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