Monolithic reactors for environmental applications
A review on preparation technologies

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Abstract

The main aspects of preparation technologies for the manufacture of environmental monolithic catalysts have been reviewed on the basis of the patent literature, the authors' own experience in their laboratories, and the current open literature. The main topics covered in this review are the preparation of massive monoliths by extrusion, the coating of ceramic monoliths, and metallic monoliths. Extrusion, one of the most extensively used processes for the production of ceramic monoliths, should fulfill a number of conditions as adequate plasticity of the pastes to allow their extrusion and their immediate conformation into rigid structures under monolithic shape. This is no trivial matter, since in developing monoliths with new materials a great effort should be devoted to finding appropriate conditions. With respect to coated monoliths, the convenient characteristics of a good monolithic catalyst should be met by managing preparation procedures. Thus, preparation technologies are composed of both materials science and engineering aspects. One emerging technology is the growth of zeolites on monolithic walls. Zeolites are among the most studied materials for environmental applications. Among metallic monoliths, those based on ferritic steel containing alumina are the most important, but those made of aluminum coated by alumina produced by anodisation are excellent materials to prepare metallic monoliths. The melting point of aluminum (660 °C) limits its use to medium–low temperature processes, but the especial characteristics of the anodisation alumina offer exciting prospects.
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1. Introduction

The catalytic system most widely used in environmental applications is the monolithic reactor. Monoliths are also called honeycombs because the first monoliths had a cross-section like a honeycomb structure. They offer great advantages over pellet catalysts, the most important one being the low-pressure drop associated with the high flow rates that are common in environmental applications.

The first success of the monolithic catalyst was in the automobile exhaust treatment. After that, other applications became available, the environmental ones being by far those most demanded. The following environmental applications have been reviewed by Heck et al. [1]: three-way catalysts; diesel catalysts for the abatement of liquid particulate (soluble organic fraction) and gaseous CO and hydrocarbons; ozone abatement in aircraft; natural gas engines; ozone destruction on automobile radiators; CO and hydrocarbon oxidation in small engines; selective reduction of NO_x; destruction of volatile organic compounds (VOC) from chemical plants, domestic sources and restaurants; catalytic

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combustion. As emerging applications: hydrogen generation for the fuel cell; steam reforming of hydrocarbons; water gas shift catalysts; preferential oxidation of CO at low temperatures (COPROX).

The present review focuses on preparation techniques for three main aspects: (I) ceramic monoliths, (II) washcoating of low-surface area ceramic monoliths and (III) metallic monoliths. Apart from being fundamental engineering issues, each of them is enriched with the experience generated at the authors' own laboratories.

2. Ceramic monoliths from extrusion

The historical development of this type of system has been described in several reviews in recent years. Although they have generally been based on the development of catalysts for automobiles [2,3], other possible applications have also been reviewed such as catalysts or filters in other processes of environmental protection in fixed sources, or catalysts for production processes. Among these, we should highlight the contribution by Irandoust and Andersson [4] on the analysis of different catalytic processes where the use of monolithic catalysts leads to appreciable advantages with respect to the conventional fixed bed catalysts (pellets), or the work of Voecks [5] on unconventional applications of this type of catalyst. Recently, Lucas and Claus [6] proposed the novel application of ceramic monoliths using their cells as microreactors in systems of combinatorial catalysis.

A detailed description of the characteristics and physical properties of these systems was carried out by Luca and Campbell [7], and more recently by Cibulsky and Moulijn [8], presenting an excellent comparison between the properties of the monoliths related with pressure drop, mass and heat transfer phenomena, and those of conventional particle catalysts.

Concerning the preparation of this type of structures, the first descriptions of manufacturing ceramic monoliths appeared almost at the same time as those for metallic ones, originally for such applications as heat exchangers [9], or for conducting and distributing a stream of hot gases [10]. However, the development of these systems was undoubtedly accelerated by the commercial implementation of the TWC in the USA and Japan during the 1970s.

The different preparation methods of ceramic monoliths were reviewed by Luca and Campbell [7], who exhaustively summarized all the production methods described up to 1977. Afterwards, Lachmann et al. [11–14] published a series of review papers about the preparation methods of ceramic monoliths, and more recently Nijhuis et al. [15] published a review article focused on how to convert a bare monolith body into a proper catalyst.

Briefly, it may be said that initially ceramic monoliths were prepared by corrugation [16] in an attempt to follow the methodology used for metallic monoliths. For their preparation, the powdered ceramic materials were deposited with a binder over a flexible support. Subsequently, alternating undulated and flat plates were used to produce a corrugated monolithic structure (Fig. 1). After the green body of the desired shape was obtained, the ceramic monolith was achieved by firing to sinter the ceramic particles and thus produced a unitary structure.

Although originally molding techniques were employed [17,18] for the production of ceramic monoliths, extrusion is undoubtedly the most widely used procedure for the preparation of this type of structure.

For extrusion methods, the development of specially designed dies to produce these structures in a continuous manner has been one of the keys to their successful manufacture at an industrial scale. The progressive perfection of dies [19–22] has permitted the preparation of monoliths with cell densities of up to 1600 cpsi [15]. In parallel, increased knowledge about the influence of different variables affecting the extrusion process [23,24] has allowed the optimization of the fluid dynamic properties of the monoliths not only from the point of view of the pressure drop but also from the design with different shapes that lead to an improved behavior of the catalysts with respect to phenomena such as the mass [25,26] or heat transfer [27].

Considering both the component distribution and the preparation method, there are two basic types of monolithic catalysts: coated and incorporated.

"Coated-type" catalysts are based on an inert ceramic substrate of low-surface area, which is coated with a thin film of porous material that permits the dispersion of the corresponding active phases or with a ready-made catalyst. By these means, the catalytically active elements are solely on the external walls of the monolith that is mainly constituted by an inert and non-porous material.

The "incorporated" catalysts are characterized by having their active phases distributed not only on the exterior walls of the monolith but also within them. Two types of catalysts may be distinguished depending on the method for active phase incorporation: (a) catalysts where the active phase is deposited by impregnation of a high surface area ceramic monolith that acts as a support of the precursor salt and (b) "integral" or "extruded" catalysts, in which the active phases or their precursors are mixed with the other components that constitute the catalyst before its extrusion in monolithic shape.

Fig. 2 presents a schematic diagram of the preparation methods of the various types of catalysts as a function of the type of monolith and the method for incorporation of the active phases. The selection of one preparation route or another depends on the type of catalyst desired. Similarly, the most adequate catalyst depends on the application for which it is destined and on the actual operating conditions to which it will be submitted. If the catalyst is to be exposed to conditions where erosion can take place (large gas volumes, presence of fly ash or particles in suspension, etc.) "incorporated" catalysts should be used because the active phases are within the whole of the monolithic structure, while for systems where the velocity of the process is negatively effected by diffusion

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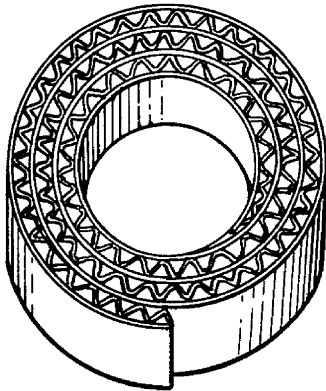**R. Z. HOLLENBACH**

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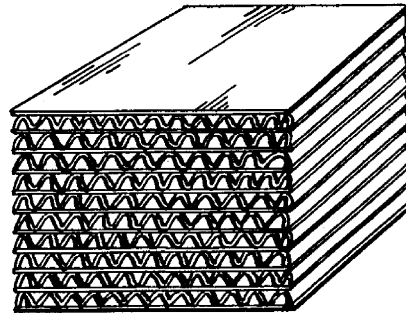METHOD OF MAKING CERAMIC ARTICLES
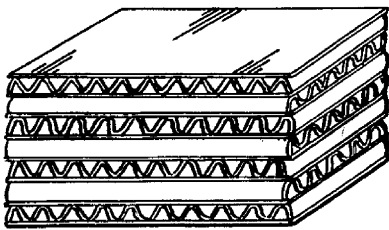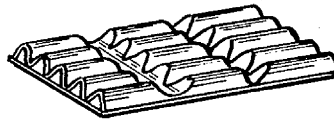Filed Sept. 8, 1958

Fig. 1

Fig. 2

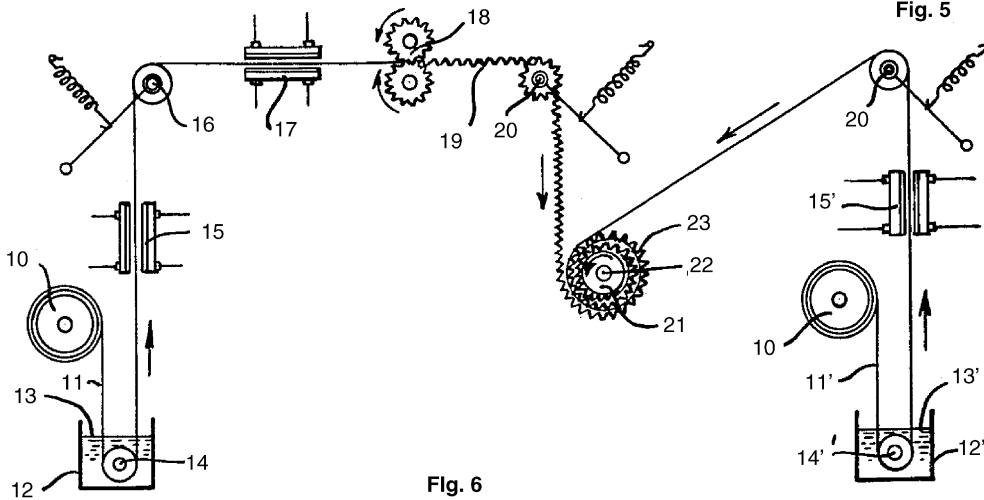Fig. 3

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Fig. 1. Diagram of manufacture of ceramic monoliths by corrugation (ref. [15]).
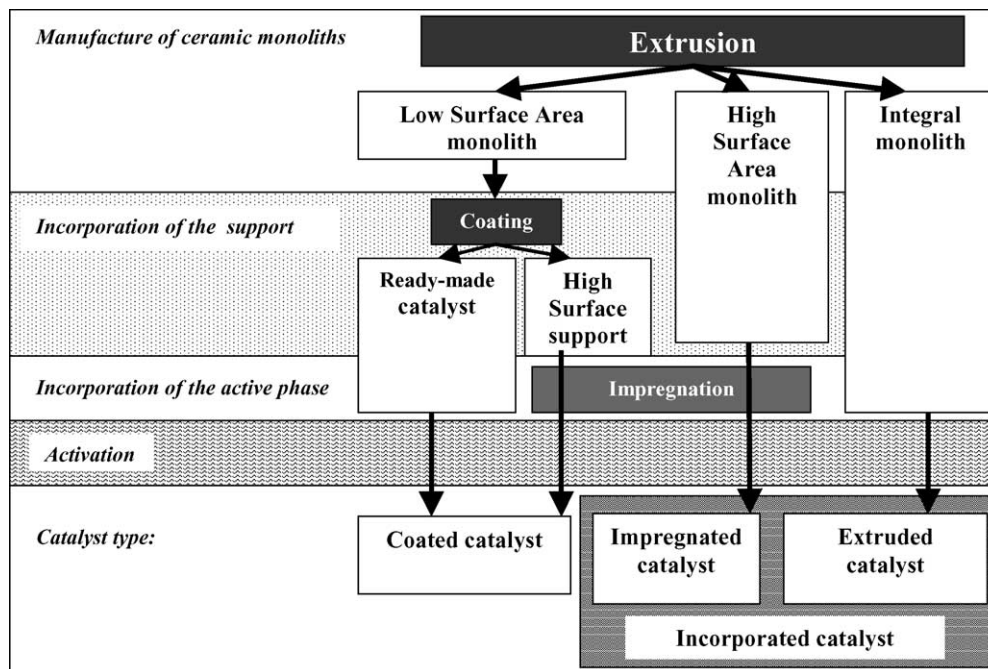
Fig. 2. Diagram of preparation paths for extruded monolithic catalysts.

limitations and the price of the active phases is high the wash-coated systems are preferred given that the accessibility to the active centers of the reaction gas is of major importance.

According to these considerations, three types of ceramic monoliths may be distinguished: (1) low-surface area monolithic carriers (Section 2.1), (2) high surface area monolithic supports (Section 2.2) and (3) integral monolithic catalysts (Section 2.3).

In addition to the description of the extrusion processes for the preparation of these three types of ceramic monoliths, in this section attention will also be drawn to both active phase incorporation methods and characteristics of the catalysts obtained in relation with the operating variables in the catalyst preparation process. In the following section, the preparation of washcoated catalysts will be described.

2.1. Monoliths as catalytic carriers: low-surface area monoliths

To be used as carriers, monoliths should have the following characteristics:

(a) Very low thermal expansion coefficient (TEC) ($\leq 5 \times 10^{-6}\,K^{-1}$) leading to a high thermal shock resistance and maintain stable washcoats.
(b) High melting point and thermal stability and adequate mechanical properties to support the operating conditions to which they will be submitted.
(c) An adequate plasticity to permit their extrusion and immediate conformation into rigid structures with monolithic shape.
(d) A certain roughness with porosity suitable for an effective washcoat application.

The most widely used material for the manufacture of extruded monolithic substrates or carriers for automotive exhaust emission control is cordierite, which has a very low TEC [28] and high refractoriness, good mechanical strength and an appropriate open porosity [29].

The fabrication of these ceramic monoliths can be carried out in one of the following two ways.

2.1.1. Preparation of the monolith using cordierite as the starting material

With regards to the procedures that utilise cordierite as a raw material, the simplest process consists in kneading together cordierite powder, water and an agglomerating agent, which could be polyethylene oxide, cellulose, methylcellulose or their mixtures [30–32]. The paste thus formed is extruded in the desired shape, dried and calcined at 1300–1400 °C for 3–4 h.

Sometimes, in the composition of the dough small quantities of carbonates, saw-dust or starch are added in order to improve the macroporosity of the final product [33,34]. Likewise, other additives have been used with higher thermal expansion coefficients, such as spinels, mullite or zirconia [35–37] to improve the mechanical properties of the monolith.

In other procedures, a mixture of cordierite and alumina in equal proportions are kneaded with small quantities of wax. After extrusion the monolith is hydrated at 90 °C and then calcined at 1200 °C [38,39].

Other treatments or procedures that appear to be of interest are the following:

- The dry addition of ammonium molybdate to the cordierite improves the subsequent extrusion of the paste [40].

- Before calcinations, the monolith can be treated with a surfactant agent to avoid cracking [41].
- Nitric acid treatment of the finished monolith increases its specific surface area and reduces its thermal expansion coefficient [42].

2.1.2. Preparation of the monolith from mixtures of precursors and their posterior cordierisation

As the cordierite mineral is not abundant, for industrial production usually it has to be synthesized. Thus, there are many raw materials that may be used for the preparation of cordierite monoliths where the employment of aluminum silicates, such as kaolin or clays, and the use of talc together with alumina is frequent. The simplest composition is a mixture of kaolin and talc that can be kneaded with the aid of a dispersant (sodium lignosulfate), an agglomerant (polyvinyl alcohol) and a lubricant (water). The paste is extruded, dried and subsequently calcined at 1300 °C for 2 h [43]. Nevertheless, in the majority of the procedures described in patents over the preparation of monoliths from mixtures of precursors and their posterior cordierisation, three or more components are utilised in proportions that are adequate to obtain a $SiO_2:Al_2O_3:MgO$ ratio equal to 51.4:34.9:13.7, that is close to that corresponding to cordierite, the most frequently used being mixtures of talc + kaolin or clay + aluminum hydroxide [44].

Talc is present in the composition described in most patents. The contribution of magnesium in some procedures is made by the addition of magnesium hydroxide [45,46]. The second component (kaolin or clay) contributes with the silica and some of the alumina. The same effect may be obtained with the addition of halloysite or saponite [47,48]. The third component (aluminum hydroxide) is used to provide the aluminum necessary to complete the cordierite composition, although the use of mixtures of this hydroxide with alumina is also frequent [49,50].

Generally, the multi-component mixtures are prepared for extrusion with the aid of an agglomerant and water. Once extruded, the monolith is dried and then calcined at 1200–1450 °C for 2–3 h.

Some aspects that could be of interest will now be mentioned:

- Extremely low values of thermal expansion coefficient can be obtained by preparing the monoliths with excess silica and alumina and subsequent extraction of some of these oxides by treatment with strong mineral acids [51].
- There is an increase in the porosity of cordierite monoliths by impregnation with lithium silicate solutions and subsequent calcination at 1200 °C for 2 h [52].
- Addition of 2–10% phosphorus pentoxide to the paste increases the thermal shock resistance of a cordierite monolith [53].

Sometimes, the overall composition is designed to obtain cordierite plus other materials such as spinel, mullite or similar, in order to improve the thermal shock resistance of the monolith [54]. It is also very important to control the particle size of the raw materials to achieve a good contact between the solids that take part in the reactions during this process.

To reduce the contraction that occurs during calcination the component mixture can be previously mixed with water, dried and calcined at 900–1400 °C. Subsequently, this material is pulverized to >10 μm and kneaded with agglomerants and water to form the monolith which is then treated at 1400 °C for 3–5 h [55]. The powder could likewise be mixed with 20% cordierite or with 10% aluminum titanate during the preparation of the paste employed for the conformation of the monolith [45,56].

It is also worth mentioning the patented procedures to avoid or repair the small fissures that can appear in the monolith during the calcination process, which are generally based on the incorporation of methylcellulose in the paste composition [57,58].

Finally, the preparation of cordierite by sol–gel methods should also be mentioned [59–61].

Taking into account what has previously been stated, the materials that can be considered adequate for use as ceramic supports in the fabrication of catalytic cartridges should have the following characteristics:

- The major component of the material should be cordierite >65%, although the presence of mullite, spinel or similar appear to improve the thermal shock resistance and the mechanical properties of the monolith.
- The thermal expansion coefficient of these materials along the extrusion axis can reach values as low as $(1–2) \times 10^{-6} K^{-1}$.
- The thermal shock resistance of the monolith should be not lower than 800 °C.

Taking into account these premises, Blanco et al. [62] proposed the preparation of monoliths, using alumina and sepiolites as raw materials which, depending on the proportions in which they are mixed and the treatment temperature, lead to solids with a high cordierite content. Fig. 3 shows the
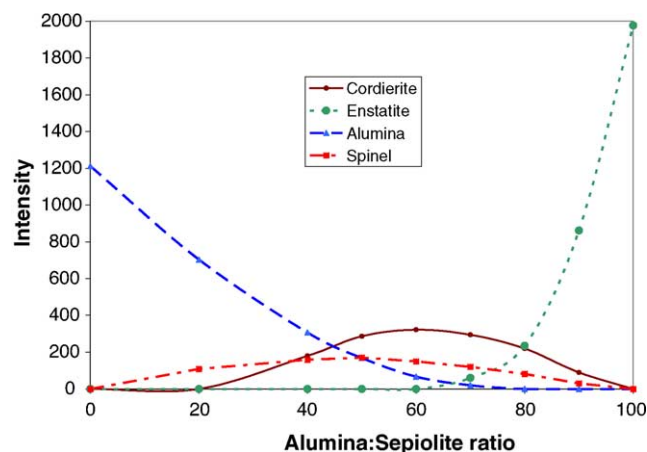

Fig. 3. XRD analysis of alumina:sepiolite monoliths treated at 1473 K (adapted from ref. [61]).
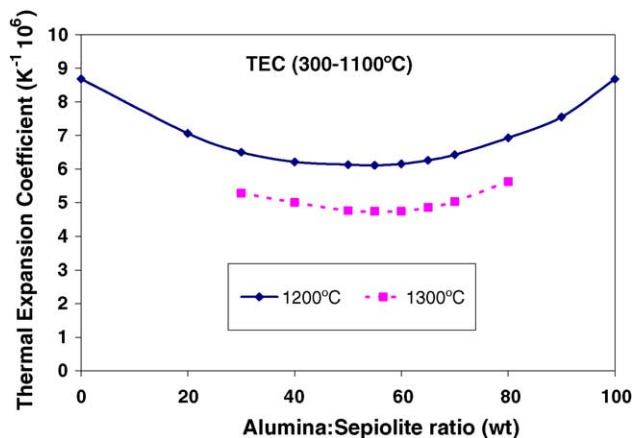
Fig. 4. TECs of Alumina:sepiolite monoliths treated at (—)1200 °C and (- - -) 1300 °C. Range: 300–1100 °C (adapted from ref. [61]).

variation of the crystalline species as a function of the weight ratio of both materials. Fig. 4 presents the variation in the TEC of the corresponding mixtures.

In order to adjust the mixture composition to values close to the $SiO_2:Al_2O_3:MgO$ ratio corresponding to cordierite, the magnesium silicate raw material was subjected to a magnesium extraction process with nitric acid. Thus, the resulting material fulfilled the proposed objectives using starting materials of low cost [63].

2.2. Monoliths as catalytic supports: high surface area monoliths

The excellent properties of monolithic catalysts demonstrated in systems for the decontamination of automobile exhaust gases has led to attempts to apply this type of catalyst to other processes such as hydrotreatment, methanation, fuel cells and biochemical reactions [4], those for stationary source emission control [64] being the ones most extensively developed. In this type of process, thermal shock resistance or thermal stability is less important but high surface area and high amounts of support material per unit volume of monolith are necessary.

The increasing number of applications in which these structured systems can contribute significant advantages call for monoliths in which the major components are those materials that have historically been used in the fabrication of catalyst supports: alumina, silica, titania, zirconia, zeolites [8,13,65] and more recently activated carbon [66,67]. In this way, depending on the particular needs, monoliths with tailor-made composition and porous structure can be produced [68].

These monolithic catalysts are manufactured following the same steps outlined for cordierite extrusion, but using the corresponding raw materials. The basic steps are:

- dry mixing of the solid raw materials (oxides or salts and binders);
- wet mixing and kneading (water and additives organic and/or inorganic);
- extrusion of the paste through special dies to form the monolithic honeycomb shape;
- drying uniformly at 30–100 °C;
- firing and removal of temporary binders (400–800 °C).

For these materials high values of surface areas, 200–400 $m^2 g^{-1}$, are achievable, but the mechanical strength is significantly lower than that of low-surface area monoliths. Generally, it is necessary to adopt a compromise solution in the heat treatment temperature to achieve an elevated mechanical stability without losing specific surface area. In order to obtain this, it is usually necessary to include permanent agglomerants in the composition, such as siliceous materials for zeolite monoliths [69,70] or titania [71] or transition aluminas [14] or colloidal alumina solutions [29,65] for γ-alumina monoliths.

Among these, probably the ones most widely used in industry are those based on titania, which are extensively employed in the SCR processes for NO_x removal from the 1970s [72,73] and more recently in photocatalytic processes for volatile organic compound mineralization [74,75].

In the case of titania monoliths for these applications, in the first step, the titania raw material is mixed with inorganic additives such as: glass fibres, natural silicates [76,77] and organic additives such as polyvinyl alcohol, polyethylene oxide [78] or methylhydroxyethyl cellulose [79]. The inorganic binders give the needed mechanical strength to the monolith and the organic plasticizers the rheological properties to the paste in order to achieve good extrusion characteristics. In this step, it is important not only to take into account the nature and proportion of the materials used but also to control the particle size of each given that this will have important consequences during subsequent stages [80].

In the second stage, water is added and the mixture kneaded in order to achieve a homogenous dough with good plasticity. In this stage, the control of parameters such as water content and rheological properties such as plastic strength, P_m, plastic viscosity, η_m and the dynamic limit of catalyst paste fluidity P_{k2} [78] are necessary, because these extrusion parameters have a significant influence on both the extrusion process and the physical and textural characteristics of the resulting solid [80,81].

During the kneading process, it is essential to also take into account the electrical characteristics of the particle surfaces that are being compacted, that is the isoelectric point (IEP) of the raw materials and the zero point charge ZPC of the resulting material and to control the pH of the medium in which the dough is homogenized. The viscosity of the paste has a direct dependence on the pH during kneading, since the repulsion forces of the particles are minimal at pH around the ZPC of the material [82,83]. Thus, control of this parameter and the ionic strength of the medium can regulate the viscosity of the paste in order to achieve the necessary properties for its successful extrusion. Fig. 5 depicts a map of the stability for a concentrated suspension of alumina as a function of the pH and the ionic strength of the medium.
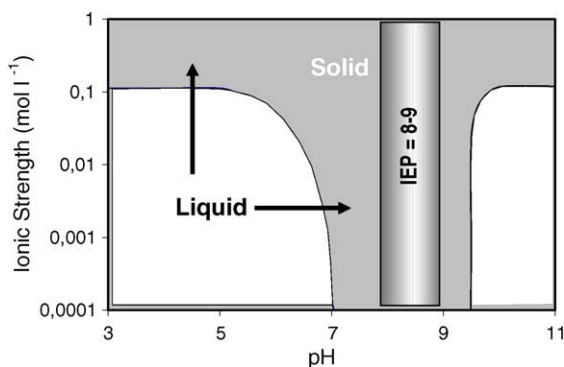
Fig. 5. Stability map of a concentrated aqueous alumina suspension as a function of pH and salt concentration (adapted from refs. [81] and [82]).

Taking into account that the IEP of alumina is between 8 and 9, this map reflects how close to the IEP, where the repulsions between particles are minimal, the aggregation effects that lead to compaction of the solid appear. On the contrary, an increase or decrease in the pH, significantly reduces the viscosity, due to the corresponding repulsive forces generated between the positive or negative charges, respectively.

It can also be appreciated in Fig. 5 how an increase or reduction in the viscosity also depends on the ionic strength of the medium. Thus, to achieve a satisfactory extrusion the need for controlling both parameters should not be neglected.

The pH during kneading can also affect the relative distribution of the various components in the mixture. Knapp et al. [84] have shown that in samples prepared mixing titania and sepiolite, higher titania coverage could be obtained when mixtures of both components were kneaded in a concentrated acid medium.

One of the most important steps in the preparation process of this type of monolith is the drying where the liquid phase is eliminated and the extruded material shrinks, and cracks of more or less importance can be easily formed that may lead to the breakage of the monolith. Thus, in this stage a careful control of the temperature and humidity is necessary [85], so that the drying process of the green body is as slow and uniform as possible in order to achieve a high compaction of the particles avoiding the appearance of cracks and breakages in the monolith [79,80].

In the final stage, the monoliths are calcined at temperatures between 500 and 700 °C depending on, amongst other things, the additives used in the preparation of the monolith and the application for which it is destined. In this stage, two objectives are pursued: on the one hand, the calcination of the precursors of the used raw materials, in this case TiO_2, generally with an anatase structure, and on the other, the burnout of the organic materials introduced, that leave as CO_2 and H_2O, producing an additional porosity in the final monolith that favors the processes of mass transfer in the interior of the catalyst [86]. Thus, the inclusion of these additives can be motivated by purely rheological necessities or by the need to control the final porosity of the monolith [68].
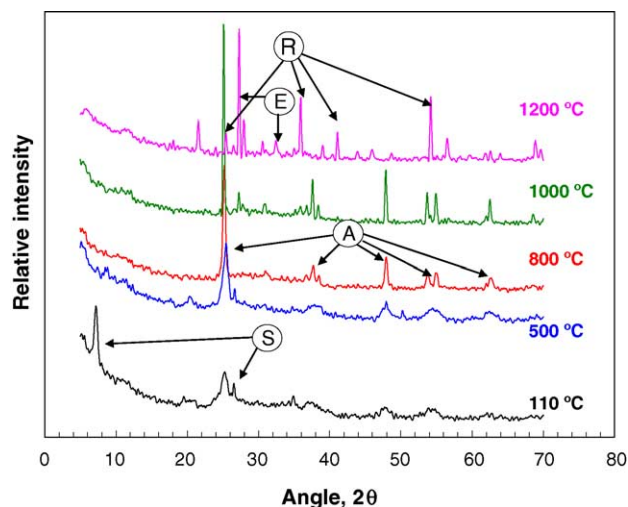

Fig. 6. XRD patterns for monoliths of TiO_2:sepiolite 50:50 wt.%, treated at various temperatures, showing the principal peaks for anatase (A), rutile (R), sepiolite (S) and enstatite (E) (adapted from ref. [73]).

There is no doubt that the final treatment temperature to which the monolith is exposed is a decisive parameter given that it greatly affects the mechanical, textural and chemical properties of the catalyst. In the case of TiO_2, in the previously mentioned applications, it is necessary to maintain the anatase structure. Thus, a moderate heat treatment temperature is required to avoid the rutilation of the TiO_2. This transformation, depending on the nature and amount of other compounds that are present with this oxide can take place at temperatures close to 600 °C [87] or be avoided even at temperatures higher than 800 °C as can be seen in the Fig. 6, where the XRD patterns for monoliths of TiO_2:sepiolite 50:50 (w/w), treated at various temperatures are shown [77].

In this type of catalyst, a principal handicap is the low mechanical strength. Generally, heat treatment at high temperatures leads to a considerable increase in this property, although this is normally accompanied by a significant reduction in the porosity. This effect may be appreciated in
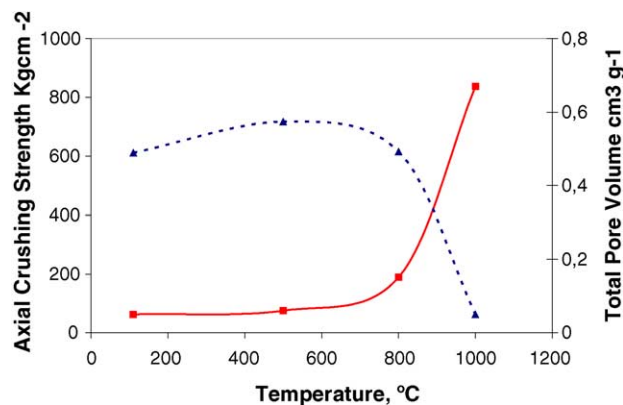

Fig. 7. Axial crushing strengths (full lines) and total pore volumes (dotted lines) as a function of treatment temperature. Monoliths of TiO_2:sepiolite 50:50 wt.% (adapted from ref. [73]).

the results shown in Fig. 7, where the values of mechanical strength and total pore volume in monoliths prepared with TiO_2 and sepiolite [77] treated at temperatures between 110 and 1000 °C are presented. The variation of these parameters together with the progressive reduction in the surface area on raising the heat treatment temperature requires the adoption of a compromise between both properties. Thus, a detailed analysis of the effect produced by the calcination conditions in each system should be carried out in order to adequately define the temperature and duration of the treatment.

The monolith thus obtained can in some cases be used directly, especially if used as an adsorbent [88] or if the material used is the active phase of the catalyst, as in the case of TiO_2 in photocatalytic oxidation processes [89]. If, on the contrary, it is used as a porous support, for the preparation of the final catalyst the addition of the active phase is necessary. The active phase can be incorporated by the conventional methods employed for catalysts, whose application in the case of monoliths is described in Section 2.4.

2.3. Extruded monolithic catalysts: integral monoliths

An alternative method to introduce the active phase in a monolith is to include the corresponding compound or precursor in the composition of the dough to be extruded. In this way, the active phase is distributed throughout the monolith and also significantly reduces the number of steps necessary for the preparation. However, this also leads to special complications, not only during extrusion, given that the presence of additional salts could significantly alter the rheological properties of the paste, but also in the necessary control of the thermal treatments, drying and firing, since during these steps the following processes must be carried out:

(a) Elimination of the solvent (generally water), with the precautions indicated in Section 2.1.2.
(b) Decomposition of the organic additives included as plastifiers, which could cause local temperature rises and significant transformations in the porous structure of the solid.
(c) Possible transformations in the material used as support, especially related to changes in the crystalline phases and porous structure.
(d) Transformation of the precursors into the catalytic active phases, which normally involve decomposition of their salts with the subsequent formation of gases (NO_x, SO_x, CO_2, etc.) whose effect could be very different if carried out over an established support, as in the case of the impregnated catalysts or carried out while the support is forming its structure.

In summary, it may be said that although the preparation of this type of catalyst involves fewer steps it needs a greater control of the process variables in order to avoid undesired transformations of the active elements and the support.

In spite of the previously mentioned difficulties, this type of monolith is employed for important applications, such as the SCR process [14]. In this system, many different catalysts have been developed, that operate in different conditions, depending on the possible configuration (high-dust, low-dust or tail-gas). In power plant effluent gas purification, the most common system is high-dust, which uses monolithic catalysts based on vanadium and titanium oxides, also including oxides of tungsten and molybdenum in their composition [72,90].

Forzatti el al. [91] have described the preparation of a catalyst based on tungsta/titania (90%, w/w), bentonite (6.5%, w/w) and glass fibres (3.5%, w/w) and water with small amounts of methyl-hydroxy-ethyl cellulose and polyethyleneglycol, analysing the influence on the extrusion process of variables, such as water content, organic and inorganic additives and particle size distribution, placing special emphasis on the importance of the drying steps and calcination on the resulting final product.

Among the principal advantages that this type of monolith present for these applications are their resistance to deactivation by erosion or abrasion, especially important when in the gases to be treated there exist solids in suspension that pass through the catalyst at high speed, as in the high-dust systems of coal fired power plants. Under these circumstances, Blanco et al. [92] have shown the behavior of a catalyst of Ti, V and W oxides prepared using sepiolite as a permanent agglomerating agent, which presented excellent catalytic properties and a high mechanical strength over the whole operation time in an industrial plant [93]. In this catalyst, the vanadium oxide, which is the active phase, is deposited selectively on the titanium dioxide particles, which themselves are dispersed among the fibers of the silicate binder distributed uniformly throughout the monolith wall. In this type of catalyst, it is of utmost importance to optimize the porous structure in order to avoid, as much as possible, limitations in the speed of the process due to diffusion phenomena [94]. Likewise, it is also important to optimize the preparation procedures in order to obtain an active phase distribution that maximizes the accessibility of the reaction gases to the reactive centers. This can be achieved by controlling the manner in which the various components of the catalyst are incorporated and their possible interactions.

2.4. Incorporation of active phase into the monoliths

The incorporation of the active phase in a monolithic support, if it is an extruded catalyst, a high surface support or a low-surface area monolith coated with the support, can be carried out using the same techniques used with catalysts in pelleted form. However, the unique distribution of material in the monolith demands that special precautions must be taken to avoid problems of heterogeneity, especially important when dealing with monoliths of high cell density where the surface tension of the impregnating solution can cause difficulties in the distribution of the materials within the channels of the monolith.

Xu and Moulijn [95] in their review of different active phase incorporation procedures for monolithic catalysts
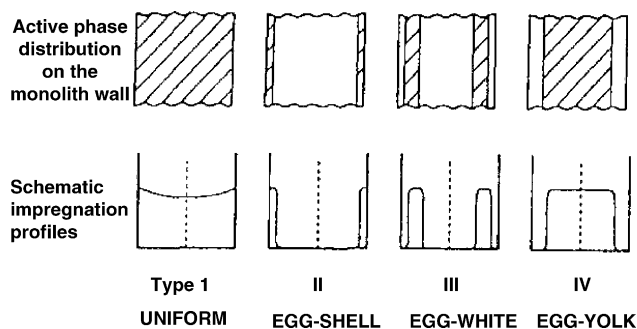
Fig. 8. Models of profiles for the incorporation of active phases to the wall of a monolith (adapted from refs. [95] and [96]).

described more than nine methods: (A) impregnation, (B) adsorption and ion exchange, (C) precipitation or coprecipitation, (D) deposition precipitation, (E) sol–gel method, (F) slurry-dip coating, (G) in situ crystallization, (H) addition of catalytic species to the mixture of extrusion and (I) others such as chemical vapor deposition, spray-coating, etc.

The selection of a method is a function of both the nature and concentration of the active phase that is to be incorporated, the type of active phase precursor used, and of the process in which it is to be used, namely the operating conditions to which the catalyst will be submitted and the possibilities of deactivation by chemical or physical agents to which it will be exposed. Depending on the method used and the incorporation conditions (time, temperature, pH, concentration of reactives, etc.) the active phase incorporation can be directed towards more "exposed" zones or more "protected" within the wall, leading to four active phase distribution models within the monolith wall. These models, designated by Lee and Aris [96] as type I, "uniform"; II, "egg-shell"; III, "egg-white" and IV, "egg-yolk", are presented in Fig. 8. In this way, a large number of possibilities in the design of the catalyst became possible, especially for multi-component systems. Thus, it is not difficult to understand that for many years catalysis had been thought of as an art.

Both these authors and Komiyama, in 1985 [97], established the basis for the standardization of impregnation processes so that the active phase deposition within porous solids lead to that considered as the most adequate for the desired process.

These bases were established from the landmark postulation of Brunelle that the adsorption of noble metal complexes onto common oxides supports was essentially coulombic in nature [98]. This postulation was related by Komiyama [97] with the distribution profiles obtained on varying the pH of impregnation. More recently, Perego and Villa, in their revision of catalyst preparation methods [99], have taken these principles and shown how during the impregnation process the IEP of the support along with the pH of the solution and the nature and concentration of the ionic species of the precursor play an important role. Thus, Spieker and Regalbuto developed the bases for a model to simulate the behavior of

noble metal adsorption over metal oxide supports such as alumina [100] or silica [101].

The consideration of these principles is an excellent tool to explain the influence of different preparation variables such as the pH of the medium, concentration of the impregnating salt and of other possible ions present in the medium and even the relationship between the volume of impregnating liquid and the amount of catalyst and the different impregnation methods over the distribution of different phases in the monolith wall. On the contrary, as Perego and Villa indicated "much of the irreproducibility which is frequently reported in the literature for supported catalysts must also be ascribed to the fact that these principles are not taken in consideration".

The importance of the drying protocol on the distribution of Ni and Rh active phases within alumina monoliths has been shown by Vergunst et al. [102] and Hepburn et al. [103]. According to these authors, during drying of the monolithic structure after impregnation, a macroscopic redistribution of the active phase precursor can occur due to the capillary suction that causes an accumulation of the active phase in the outer shell of the monolithic structure.

Hepburn, studying the effects of drying on the preparation of HF Co-impregnated rhodium/Al_2O_3 catalysts, showed that in order to preserve the egg-white catalyst character, which exists immediately after impregnation, the total drying time must be less than the time required for diffusion to the center of the support. Thus, controlling the regime in which drying takes place uniform rhodium distribution, inner bands (egg-whites) of Rh or inner cores (egg-yolks) of Rh in the wall of the monolith could be achieved. In order to prepare monolithic catalysts of Ni/Al_2O_3 with a uniform active phase distribution Vergunst et al. recommended the methods such as freeze-drying, microwave drying and deposition–precipitation.

A special case to take into account when carrying out selective impregnation within a zone of the monolith is that when the porous support is a composite in which the active phase should selectively impregnate on only one of the components. This is a characteristic of monoliths for whose extrusion permanent additives have been employed which present a significant adsorption capacity even after calcination, as in the case of several materials that employ clays as binders [77]. These materials normally have little activity in the studied reaction, so that there is a necessity of directing the impregnation selectively to the desired component. To do so, it is necessary to know the IEP of the various components in the support. It is convenient to determine these values for each of the raw materials used. Even though excellent reviews report this parameter for most of the oxides used as catalyst supports [104], there are marked discrepancies in the values reported by different authors [105]. These differences are due to either the method used for the determination or to structural changes.

Once the IEP values of the components are known the impregnation should be carried out considering that a particle at a pH value below its IEP is charged positively and thus has
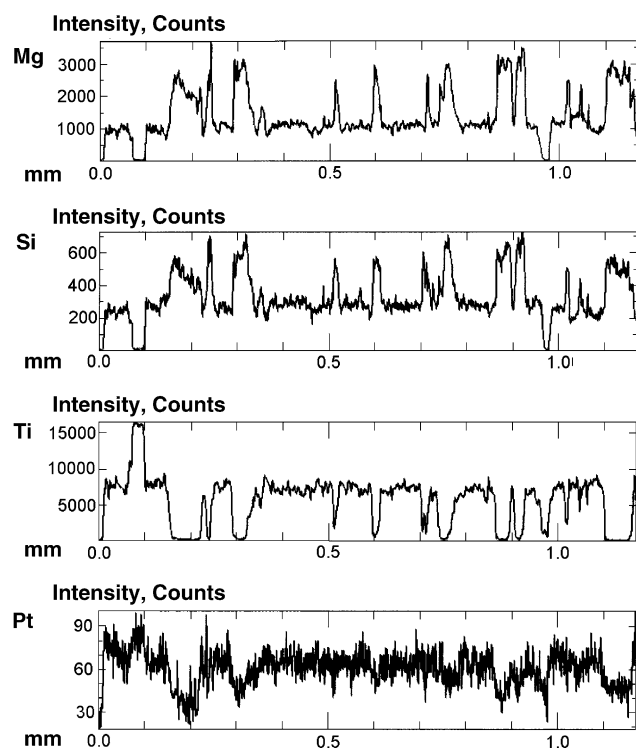
Fig. 9. EPMA-WDS line profiles of Pt, Ti, Mg and Si across a wall section of a Pt(0.1)/TiO$_2$:sepiolite 50:50% (w/w) catalyst.

a tendency to adsorb anionic species over its surface, while a particle at pH higher than its ZPC tends to adsorb cationic species. Thus, by determining the ZPC of the resulting material and the nature of the ionic species of the precursor salt in the media in the conditions in which the impregnation will be carried out the selective impregnation of the active components may be achieved.

Avila et al. [106] have described Pt incorporation over a monolithic support formed by a mixture of TiO$_2$:sepiolite 50:50% (w/w) employing an impregnation method from an aqueous chloroplatinic acid solution to obtain a catalyst in which the Pt was deposited preferentially on the TiO$_2$ particles, as may be appreciated in Fig. 9, where the concentration profiles through a monolith wall are shown.

In this figure, the relatively uniform distribution of TiO$_2$ and magnesium silicate (sepiolite) particles may be seen. Thus, the Si and Mg profiles are parallel and their shape is opposite to that of Ti. The Pt, only present in a very small fraction (0.1 wt.%), presents a profile that can be considered as parallel to that of Ti, which reflexes the selective impregnation of this species over the TiO$_2$ and not over the sepiolite.

Taking as a reference the model of Regalbuto et al. [101] it can be considered that the PtCl$_5$(H$_2$O)$^-$ species present in the solution at a pH 5 have a tendency to unite with the TiO$_2$ surface whose IEP = 6.3 and is thus positively charged [84]. Sepiolite has an IEP = 2.2; consequently, it would be negatively charged at this pH and thus its ability to adsorb the anionic Pt species would be very low.

3. Deposition of a catalytic layer onto low-surface area ceramic monoliths

This section of the review focuses on the preparation of ceramic monoliths coated with environmental catalysts. It is well known that the most widely used catalyst for environmental applications is the three-way catalyst, which consists of a complex mixture of oxides and noble metals deposited onto an alumina carrier which is washcoated on a honeycomb monolith. Since there are so many good papers and reviews on this subject [107–110], here we will mainly refer to less conventional systems which are applied as a slurry coating or by in situ synthesis. Examples of continuously developing materials are zeolites, which are among the most promising materials for the abatement of atmospheric pollutants, e.g. the oxidation of volatile organic compounds and the selective reduction of NO$_x$.

Different procedures can be performed from coating the monolith walls with a support material such as alumina or silica, followed by the impregnation of the active phase, to the coating of a ready-made catalyst. In Nijhuis et al.'s excellent review [15], a thorough description of the methods obtained in their laboratory is presented since not much open literature was available at the date of that publication. Whereas at present, the number of publications has increased considerably.

Ceramic catalytic monoliths can be obtained under the form of extrudates (see Section 2) in which the catalytically active material is used to manufacture the monolith. Another possibility consists in the deposition of the powder as a coating onto a ceramic honeycomb substrate. It is well known that the most widely used material for monolithic structures is cordierite (a ceramic material consisting of magnesia, silica and alumina in the ratio of 2:3:2) because of its high mechanical strength and its low thermal expansion coefficient. The macropores of the cordierite structure allow the anchoring of a powder layer.

In the case of zeolites, the coating layer can be made in two different ways: by hydrothermal synthesis (direct synthesis, seeded growth or vapor phase synthesis) [111,112], and by the deposition from a slurry of zeolite particles followed by a stabilizing thermal treatment. Both methods will be discussed in this section. The first method has the advantage of a stronger adhesion of the coating to the support. The main disadvantages of this method, however, are that it is considerably more complex than slurry-coating and that a dense layer can be formed with small intercrystalline pores in which diffusion limitations can occur.

The coating from a slurry, commonly called "washcoating", is usually carried out with a slurry of particles of a comparable size to that of the macropores of the support [15]. The main advantages of this method are a shorter diffusion distance to the active catalyst species for the reactants flowing through the channels and the fact that ready-made catalysts can be directly deposited from the slurry. The preparation of the finished catalysts always involves dipping the

monolith into the slurry, blowing air to remove the excess liquid, drying and calcination. The last step is very important since the calcination binds the washcoat to the monolith walls, and is usually done at temperatures of 550 °C or higher [113]. Besides, a binder can be used in order to improve the binding strength. However, for the washcoating of a powder with small particle size, which is the case of zeolite, it has been reported that the use of a binder is not essential [114].

3.1. Washcoating of a ceramic monolith by dipping it in a slurry: key preparation procedures

In pioneering articles, Kolb et al. [115–117] described the fundamental principles of the coating of monolithic structures. The monoliths used in their work were made of extruded cordierite with a square-channeled shape of 400 channels in.$^{-2}$. The rheological behavior of the slurries was governed by the solids content, pH, zeta-potential and shear rate, the two first being the most important variables for viscosity control [116].

A fundamental process during the filling of the monolith channels is the absorption of part of the water contained in the slurry by the porous monolith walls. A cake develops, whose thickness is dependent on the substrate porosity and dimensions, slurry properties, and rate at which the channels are filled [117]. After blowing the excess slurry out with air, a remaining coating load results, which strongly depends on the air velocity.

As it can be seen, the characteristics of the final coated monoliths are a complex function of monolith characteristics, slurry properties and preparation conditions. We will focus on the effect of the slurry properties and preparation conditions since standard cordierite monoliths are the most widely used as ceramic substrates thus fixing the monolith characteristics.

3.2. Effect of the slurry properties on washcoat quality

The properties of a slurry can be governed by selecting three main variables:

(a) properties of the solid particles;
(b) properties of the solvent;
(c) solids wt.% in the slurry.

Other variables like pH, viscosity, zeta-potential, are considered to derive from those variables. This is just a simplified picture used for the sake of clarity during the analysis.

3.2.1. Properties of the solid particles

Both chemical and textural properties are relevant in this analysis. It has been shown from results of different laboratories that the adhesion of the coating depends primarily on the particle size of the deposited powders. The severe conditions of operation in environmental applications (i.e. car exhaust system) can lead to the detachment of the washcoat layer. Therefore, the adhesion of the substrate is a very important
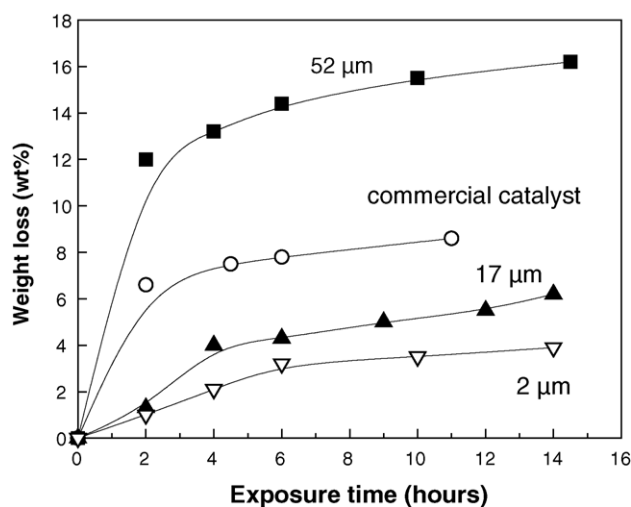

Fig. 10. Weight loss of γ-alumina washcoats as a function of time and particle size of the deposited powder during treatment in a stream of hot air (800 °C) and high GHSV (80,000 h^{-1}) simulating severe car exhaust conditions. Adapted from ref. [114].

requirement. However, very few studies have addressed the problem of adhesion quality between the washcoat film and the monolithic support [114].

Agrafiotis et al. [114,118–121] studied the effect of powder characteristics and processing parameters on the properties of alumina, zirconia and titania washcoats deposited on ceramic honeycombs. They studied the adhesion of the washcoat layers upon the monolith walls by exposing the loaded monoliths in a stream of hot air in a small laboratory reactor simulating the car exhaust system (free volume velocity: 10^6 h^{-1} at 800 °C) and measuring their weight loss as a function of time [114].

Fig. 10 shows the weight loss of γ-alumina washcoats as a function of time and particle size of the deposited powder. It is concluded in [114] that adhesion of the washcoat layer on the support takes place primarily by a mechanical mechanism such as "anchoraging" and interlocking of the washcoat particles with the surface irregularities of the support, and to a much lesser extent via chemical or affinity mechanisms. They also suggest that this dependence on particle size is general, irrespective of the kind of powder employed [118]. Apart from the effect of particle size on the washcoat properties, it is known that it can affect catalytic behavior, giving place to changes either on activity and/or selectivity. In the case of zeolites, this issue has been the object of recent publications [122–125]. The wet treatment of powders in a ball mill is one of the more widely used ways to get a uniform slurry suspension. Thus, this treatment can reduce the size of crystals. Xie and Kaliaguine [122] reported that a vigorous dry ball milling of KNazeolites results in the collapse of the zeolite crystal structure, but positively affects the selectivity for base catalyzed reactions. Kosanovic et al. [125] and Kharitonov et al. [124] also studied the amorphization of zeolites during dry milling. On the other hand, Ackay et al. [123] indicated

that wet ball milling can decrease the particle size of zeolite HY with minimal loss of crystallinity.

Zamaro et al. [126] reported results on zeolites ZSM5, mordenite and ferrierite washcoated on a cordierite honeycomb monolith. The zeolites were selected in view of their activity for the SCR of NO_x when exchanged with cations like Co, Cu and In. In this work, an accelerated ultrasonic test reported in the patent literature [127] was performed in order to evaluate the washcoat adherence. The degree of erosion was measured by weighing the sample before and after the ultrasonic treatment under an atmosphere with controlled humidity. It was found that the mechanical stability is a function of the zeolite type, the order being ZSM5 > mordenite > ferrierite.

As it can be seen in Fig. 11, the zeolite crystals are aggregated in particles of different size and geometry, depending on the zeolite type. The stability order correlates well with the size of aggregates; higher adhesion is obtained with lower sizes. Bigger aggregates cannot enter inside the cordierite pores; thus a poor adhesion is obtained. This result is in line with that reported in [114]. Ferrierite aggregates have 60 μm of average size, while mordenite and ZSM5 have aggregates of 3 μm. Cordierite pores have 5 μm of average size, thus both ZSM5 and mordenite can yield an effective anchorage with the monolithic substrate, which is not the case of the ferrierite powder. Beers et al. [128,129] obtained cordierite monoliths washcoated with BEA zeolite under the form of clusters of 4–20 μm, which seems to be somehow bigger than cordierite macropores. However, they reported good adhesion results, probably because they used a binder and optional extra components such as surfactants [129].

The basic principle of the effect of a binder during slurry coating is described in [15]. Relatively large particles to be coated are present in the slurry together with binder particles, typically two orders of magnitude smaller in size. As the liquid evaporates during the drying step, the small particles are drawn by capillary forces at the location where they are most effective, the points where the larger particles touch each other. The preferential accumulation of binder particles in these points increase the surface of contact, thus favoring the anchorage process.

Obuchi et al. [130] also used a binder material (15 wt.% of alumina-sol, Sumitomo Chemicals, A-11) to increase the stability of a washcoat of Na-ZSM5. They used this system, exchanged with In for the selective reduction of NO_x with organic substances in diesel engines.

However, it should be pointed out here that in some cases the use of a binder can modify the behavior of the catalytic system, moreover in selective reactions. For example, the selective reduction of NO_x with hydrocarbons consists in two parallel main reactions: the oxidation of the hydrocarbon with NO_x and the oxidation of the same hydrocarbon with O_2. If the second reaction is preferred, the system is not effective for NO_x abatement because the reductant is consumed by the oxygen, which is usually in excess. In this vein, Boix et al. [131] reported that alumina, added under the form of

(A)

(B)

(C)
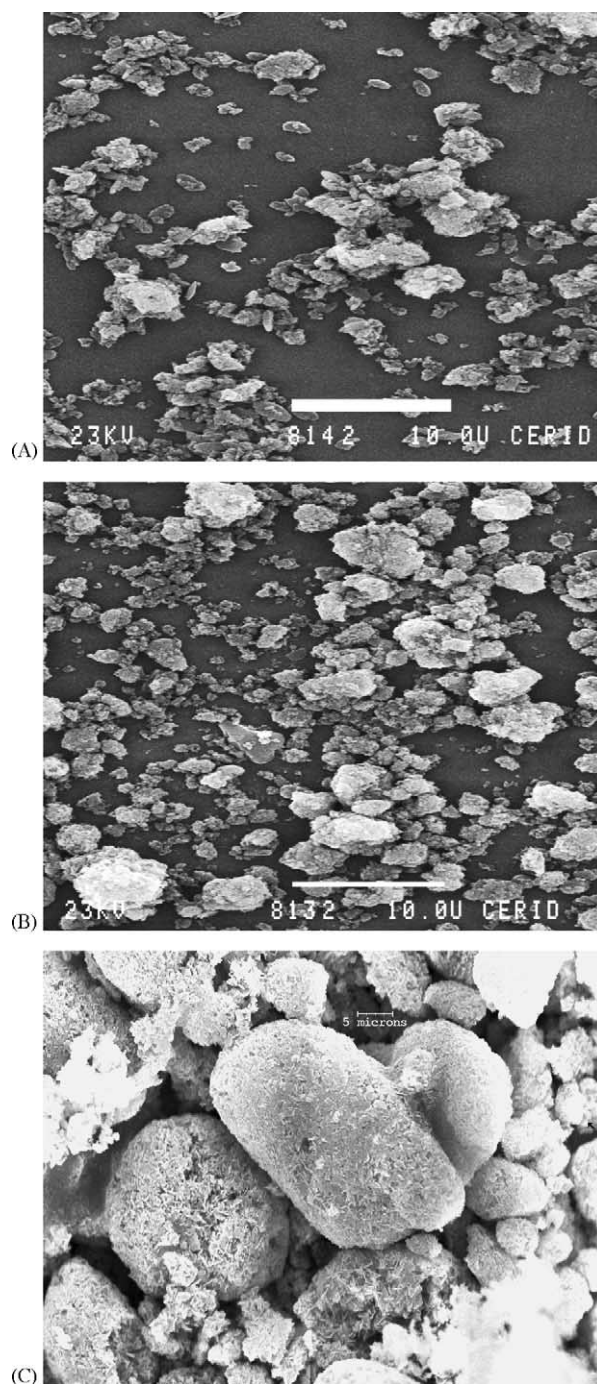
Fig. 11. SEM pictures of zeolites (as received). (A) NH_4-ZSM5; (B) NH_4-mordenite; (C) K-ferrierite. Adapted from ref. [126].

a precursor $Al(NO_3)_3$ to washcoats of Co-ZSM5, inhibits the activity for the NO_x selective reduction with CH_4 under the presence of oxygen excess, due to the formation of a non-stoichiometric spinel which expulses active Co ions from exchange positions.

On the other hand, the use of silica as a binder was reported to have a beneficial effect in the same reaction, increasing the selectivity towards NO_x reduction when Co-ferrierite is

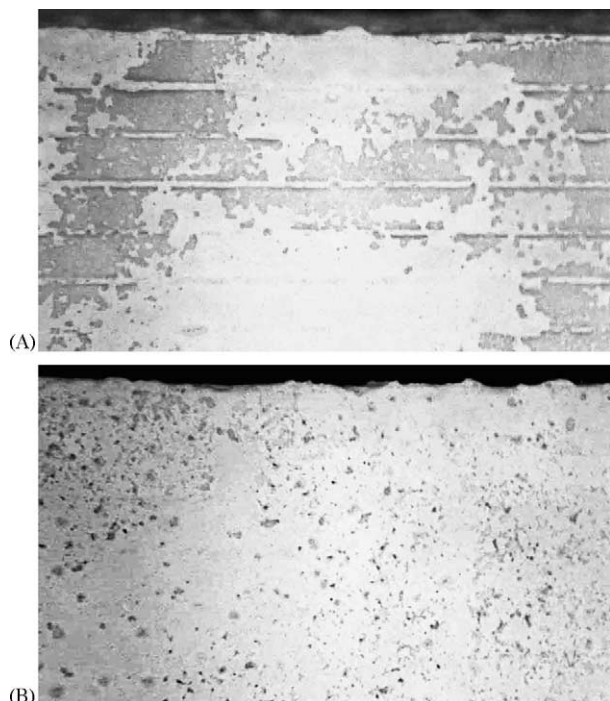Fig. 12. Stability of a NH_4-mordenite washcoated on a ceramic monolith. Stereomicroscopic observation of the zeolite film after ultrasound treatment: (A) washcoat without binder and (B) washcoat with silica as a binder. Adapted from ref. [126].

washcoated onto a ceramic monolith [113]. It was found that the contact between the small fumed-silica particles interacts with zeolite crystals avoiding the Pt segregation and the cobalt oxide formation during the calcination and reduction treatments. In this case, silica has a beneficial effect also on the mechanical stability, as seen in Fig. 12, in which pictures of the monolith walls before and after ultrasonic treatment are shown.

3.2.2. Properties of the solvent

The most widely used solvent for the preparation of the slurry is water. Fundamental properties of the slurry, like viscosity and the dispersion of the particles, can be modified by using different solvents. Solvent viscosity and surface tension affect the flow originated when the suspension excess is eliminated from the channels during the blowing stage. However, as far as we know, there is no systematic study on the effect of the use of different solvents in the open literature. The only explored way to change the solvent properties is the addition of a surfactant agent. For example, Beers et al. reported the use of 1.8% of Tepol to disperse BEA zeolite crystals in water [128].

Although specific works on the influence of liquid media upon washcoat properties are rarely found, interesting results on dispersion of particles in different liquid media were published by Ren et al. [132] who studied the characteristics of dispersion behavior of fine particles in different liquid media. They used calcium carbonate and talcum dispersed in water, ethanol and kerosene, and conducted their work using sedimentation analysis. It was found that the dispersion behavior of fine particles complies with the principle of polarity compatibility. The dispersion effect can be improved when the surface polarity of particles approaches that of liquid media. The better the wettability of particles in liquid media, the bigger the dispersion extent. They found that the dispersion extent of calcium carbonate and talcum particles ranks in the order ethanol > water > kerosene and ethanol > kerosene > water, respectively. Dispersion behaviors of other mineral particles in water or organic dyes in polar or non-polar media have been also reported in the literature [133–135]. Unfortunately, these materials are not relevant for catalytic use, but these results can help in improving slurry quality by changing the solvent. Not only can the particles dispersion and the viscosity be altered, but also the characteristics of the blowing process can be modified by the volatility of the solvent [127].

A fundamental property of aqueous solvents is the pH. The acidity of the slurry directly affects the viscosity and stability of the particles dispersion. Valentini et al. [136] studied the effect of HNO_3 concentration on alumina slurries. They found that the load of deposited coating in γ-Al_2O_3 tubes versus the acid concentration goes through a maximum at $4.33\,mmol\,g^{-1}$ of HNO_3/alumina powder. The deposited layers with an acid/alumina ratio greater than or equal to $3.6\,mmol\,g^{-1}$ were poorly adhered. A similar trend was observed for a variety of supports. They interpreted these results in the light of rheologic measurements. They observed that for HNO_3/alumina ratios less or equal to $2.16\,mmol\,g^{-1}$ the slurries exhibited a pseudo-Newtonian behavior, the viscosity remaining constant with increasing shear rate. For greater ratios, the slurries became non-Newtonian, their viscosities decreasing with increasing shear rate. A plot of the viscosity at constant shear rate exhibited the same trend shown by the coating load, concluding that the slurry flow behavior determines the coating thickness, and that the slurry viscosity is controlled by a gelation process. The acid concentration has a complex influence on the gelation process, which was unclear at the moment of reporting these interesting results.

Agrafiotis and Tsetsekou [121] studied the effect of processing parameters on the properties of γ-alumina washcoats deposited on ceramic honeycombs. In this work, they reported results on the slurry stability studied with the aid of zeta-potential measurements. Since the natural pH of γ-alumina slurries lay in the pH 0–9.2 range, and at this pH the slurries were unstable and settled fast, they combined the effect of a defflocculant and the pH to increase slurry stability. They measured the defflocculant and HCl concentrations upon stability and zeta-potential. They found that in the absence of defflocculant high zeta-potentials and therefore good dispersion were achieved at pH values lower than 5 or greater than 9, the isoelectric point being around 7.7. With the addition of 1% of defflocculant (NH_4-PMA) the whole zeta-potential–pH curve is shifted towards a lower pH region, and the isoelectric point of the slurry to 5.5. They concluded that, since a strongly
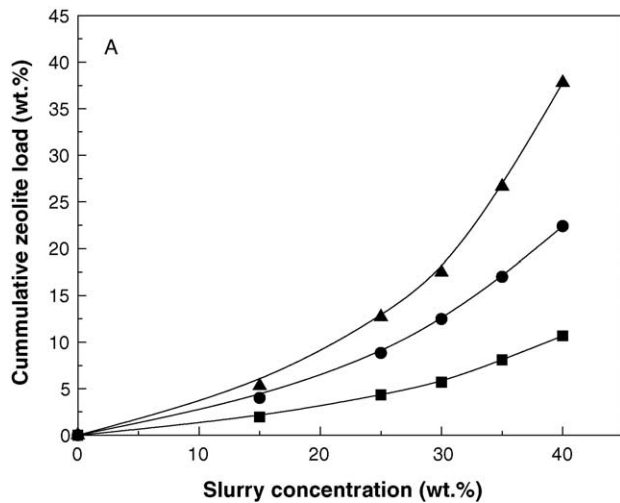
Fig. 13. Effect of slurry concentration upon zeolite loading in the washcoat. (A) Cumulative loadings and (B) zeolite loaded in each immersion. (■) One immersion; (●) two immersions; (▲) three immersions. Adapted from ref. [126].

acidic environment required for good dispersion (the case of HCl) can cause corrosion problems, the use of deflocculant is advised in order to have much milder conditions. Moreover, the same authors report that the addition of deflocculant has a beneficial effect in reducing the slurry viscosity.

3.2.3. Solids wt.% in the slurry

Regulating the load of the material deposited on monoliths is one of the most important preparation aspects. The main characteristic dimensions of the coating are two: the minimum thickness and the maximum thickness at the corners. The amount of material loaded during the washcoating procedure and the characteristic dimensions strongly depend on the powder concentration in the slurry and the number of immersions. By varying these conditions, the desired washcoat loading and thickness can be adjusted.

Zamaro et al. [126] studied the influence of the above mentioned washcoating conditions upon the washcoat characteristics. Monoliths with different ZSM5 zeolite content, between 4 and 27 wt.%, were prepared by combining different suspension concentrations and a number of immersions. Within this range, a non-linear increase of the load with the suspension concentration was observed (Fig. 13). A similar trend was observed for the loads achieved at each immersion stage for different concentrations, which explains the different slopes of the curves in Fig. 13. This load was calculated as the increase in weight after each immersion. It is worth noticing that the increase in weight is not a function of the number of previous immersion stages, suggesting that once the first layer of zeolite crystals is formed, the surface rugosity remains invariant and very similar to the bare monolith rugosity.

A fundamental property of a powder slurry is its viscosity (η), which can be simply related to the solids concentration

through equation [137]:

$$\frac{\eta(\gamma)}{\eta^\circ} = \frac{1}{(1 - \gamma)^{2.5}}$$

where γ is the volume fraction of solids and η° is the viscosity of pure water. The volume fraction of solids can be easily calculated from the density of particles and the concentration of the slurry. A plot (not shown) of the relative viscosity versus the slurry concentration gives a curve, which is qualitatively similar to the curves shown in Fig. 13, which indicates that the characteristics of washcoats are strongly related to this property.

The combination of high solids contents and fine particles can lead to slurries with very high viscosity. Agrafiotis and Tsetsekou [121] obtained optimum loading conditions for γ-alumina washcoats on ceramic honeycombs when the slurry viscosity lay between 50 and 150 mPa s. Therefore, for high solid contents and low particle size they adjusted the viscosity with the use of either HCL or polymetacrylate, an organic polyelectrolite.

During the preparation of a slurry, the adhesion and aggregation of fine particles can occur, depending on adhesive forces between particles [138]. In the same vein, Starov et al. [137] reported that colloidal and hydrodynamic forces cause cluster formation in disperse particles even at low concentration. Thus, it should be taken into account that small particles can be under the form of aggregates in liquid media thus decreasing the viscosity of the slurry.

Another important property of washcoat layers is the geometry. It is interesting to note that even though a very good homogeneous distribution of coatings can be obtained, a local non-homogeneity in each channel would continue to exist in the monolith. This effect is inevitable when the immersion method is used and is a negative factor since for its use under reaction conditions, the limitations in mass transfer will be critical at the channel corners. This effect was investigated for different zeolite washcoats in [126]. The authors observed through microscopy that as the material is being deposited in successive immersions, the geometry of the channel becomes progressively more circular. This fact is known, and the film shape correlates with the flow lines of a viscous fluid displaced by an air bubble moving inside a square-section capillary [116]. The rate of blowing air and the viscosity of the suspension affects the load, thickness and shape of the films. Since a relatively low air-flow was used, the suspension–air interface on the transverse plane of the channels generated during the suspension excess blowing is asymmetrical. Accumulation at the vertices is due to higher viscous strengths in this zone. When this sector is filled with the first material deposition, the channel adopts a more circular geometry. In subsequent depositions, it can be observed that the accumulation at the vertices gets smaller and smaller until the transverse symmetry of the channel becomes circular. In this vein, Hayes et al. [139] carried out a numerical investigation of the diffusion and reaction in the washcoat of a catalytic monolith reactor. They found that three factors significantly affect the

rate and the role of mass transfer: the washcoat thickness, the channel radius including its non-uniformity around the channel, and the angular diffusion caused by variable thickness. In an experimental study, Sassi et al. [140] studied the geometry and thickness on NO_x trap desulfation, concluding that the decrease of washcoat thickness leads to an increase of the NO_x trapping capacity. However, the increase of uniformity in the washcoat geometry obtained with the use of hexagonal cells has no effect on NO_x storage, but they showed a better global resistance to sulfur poisoning. Matsumoto [141] in a recent article describes the recent advances developed by Toyota in automobile exhaust catalyst. For use in low emission vehicles, a CeO_2–ZrO_2 support was designed for high performance three-way catalysts. A novel NO_x storage-reduction catalyst (NSR) was developed for automotive lean-burn engines, which can store NO_x in an oxidizing atmosphere and then reduce stored NO_x at stoichiometric or reducing conditions. To enhance the removal of sulfate, which poisons the catalytic trap, a hexagonal cell monolithic substrate was used, which results in a uniform catalytic washcoat thickness.

However, this uniformity is not the best choice for all of the applications. Kruse et al. [142] demonstrated that for automotive catalytic converters rectangular channels offer the best relationship between the heat/mass and pressure drop factors. The authors compared channel shapes, regular polygons, isosceles triangles and sine ducts.

3.3. In situ synthesis onto a ceramic monolith

Instead of dipping from a slurry, catalysts or catalytic supports can be directly synthesized onto the monolith by impregnation with a solution of the precursor. This procedure is not too different if compared with the conventional impregnation of pellets, and it has been addressed in Section 2 of this review. However, there is a field that is rapidly growing in importance, that is the direct synthesis of zeolites in different types of supports. As said above, this method has the advantage of a stronger adhesion of the coating to the support, but it is considerably more complex than slurry-coating and a dense layer can be formed with small intercrystalline pores in which diffusion limitations can occur.

However, not only intercrystallyne diffusion is important in catalytic environmental applications. The accessibility of the active sites within the zeolite framework could also strongly pose a limit in reaction velocity. Direct synthesis methods can help in obtaining preferential orientations, in order to favor the diffusion of reactants inside zeolite pores [112]. For example, MFI zeolite crystals have straight, nearly circular (0.53 nm × 0.56 nm) channels running along the *b*-direction, and zig-zag elliptic (0.51 nm × 0.55 nm) channels along the *a*-axis, while there are no channels along the *c*-direction. Therefore, zeolite films consisting of intergrown crystals with either *a*- or *b*-axes perpendicular to the support, or films with a random orientation of the constituent crystals would have a greater accessibility, compared to *c*-oriented films. Preferential orientation is often found during the prepa-

ration of zeolite films and membranes and the orientation of the crystals seems to depend not only on the characteristics of the support but also on the conditions of crystal growth (seeding, temperature and gel composition) [112].

A thorough and critical review was published by Tavolaro and Drioli [143] in which zeolite membrane structures obtained by different preparation methods and their applications were addressed. They concluded that new strategies are necessary for the synthesis of zeolite phases in membrane configurations, different from the traditional hydrothermal methods, and that a common problem in zeolite membrane synthesis is that, despite the use of a pre-defined methodology, it is difficult to obtain membranes with consistent and predictable properties.

A variety of supports have been used for the direct synthesis of zeolites, among them ceramic foams, metallic monoliths and gauzes, but only a few articles using ceramic monoliths have been reported in the open literature. Among the first papers published in this area, Aiello et al. [144] reports a technique for the in situ crystallization of a MFI-type zeolite over a commercial cordierite honeycomb to be used for withholding hydrocarbons from the automotive engine exhaust until catalyst light-off occurs. The reported technique consists in imbibing the substrate with a $100SiO_2 \cdot xAl_sO_s$–$16TPAOH − 6TPABr \cdot 1500H_2O$ followed by hydrothermal treatment at $170\,°C$. They found that with low Al content the crystallization is completed within a few hours but by increasing the Al content ($x = 1.4$) crystallization takes place after 48 h, and with $x = 1.5$ no crystallization is observed after 7 days. They concluded that the addition of aluminum to the solution accelerates gel layer formation but retards the nucleation and zeolitization processes within it, which is in agreement with what was reported before for powders [145,146]. The authors also indicated that they were able to obtain about 90 g of MFI crystals per liter of honeycomb, forming a continuous monocrystal film on the ceramic surface. In the same vein, the preparation of a ZSM-5 thin films on cordierite honeycomb by solid state in situ crystallization was reported by Madhusoodana et al. [147].

Basaldella et al. [148,149] prepared continuous, multilayered ZSM-5 zeolite films by direct synthesis on cordierite modules. The influence of the H_2O/SiO_2 ratio used in the synthesis mixture on the film properties was studied by inspecting the film formed in the external module surface at several water contents. They showed that dilution prevents the film from becoming dense, modifies zeolite crystal morphology and markedly reduces the crystallization of zeolite into a non-adhered powder form. They also tested the performance of a Cu/ZSM-5-coated monolithic catalyst in the lean NO_x reduction reaction, which proved to be an active, stable catalytic system.

Ulla et al. [112] synthesized Zeolite ZSM-5 layers (up to ca. 30% by weight) on cordierite substrates, following either a direct hydrothermal synthesis procedure or a secondary growth method, in this case after seeding of the support with a colloidal suspension of silicalite. The Si/Al ratio in the syn-

thesis gel ranged from 14 to 100, but layers with a high Al content (i.e. a low Si/Al ratio) could not be prepared directly on the cordierite support. However, MFI layers with a low Si/Al ratio were readily grown after depositing an intermediate Si-rich layer. They also reported that the Si/Al ratio of the synthesis gel has a direct effect on the morphology, crystallinity and orientation of the MFI layer formed. Ohrman et al. [150] also used the seed film method, controlling the film thickness with an ultrasound treatment. Their catalysts were useful for *p*-xylene isomerization, the films being less deactivated than the conventional ones prepared on alumina beads.

As said before, a problem of the in situ synthesis of zeolites is the lack in the accessibility of molecules during the catalytic reactions. However, this aspect was recently overcome by Ulla et al. [151] in the case of a mordenite structure by preserving the individuality of the synthesized crystals. The better accessibility of the mordenite material on the monolith was proven in kinetic diffusion experiments where water adsorption was continuously monitored. They compared mordenite crystals, a mordenite membrane and the system under study. The higher accessibility corresponded to the mordenite crystals on the monolith, followed by the mordenite membrane, and finally by the powder ($3\,\mu m$ in size, 86 mg of mordenite powder supported as a bed on a non-porous plate), which showed the highest diffusion resistance.

4. Metallic monoliths

One of the first references in the literature about catalysts on metallic substrate specifically deals with environmental use [152]. In 1950, Suter and Ruff reported the use of a kind of filter made of stainless steel wires, Chromel or Nichrome, coated with a noble metal and electrically heated, to eliminate obnoxious odours from ovens used for the drying of enamels and other coatings. Some years later, another of the pioneering works about catalysts on metallic substrate was also proposed for environmental use: the elimination of nitrogen oxides from exhaust gas streams [153]. In 1975, UOP proposed an all metal, high temperature resistant, catalyst element of Pt and/or Pd on a base alloy comprising primarily Fe, Cr and Al, active in the catalytic incineration of noxious fumes from industrial ovens [154]. But at that time, the 1970 US Clean Air Act was the kick-off for a huge research effort on the purification of automotive exhaust gases. Beside the initial pellet beds and cordierite monoliths, metallic monoliths were soon proposed [155–161] due to their higher mechanical resistance and thermal conductivity, the possibility of thinner walls allowing higher cell density and lower pressure drop. But additional advantages of the metallic substrate were soon discovered, in particular, the easy way to produce different and complicated forms adapted to a wide variety of problems and uses. Perforated Lessing rings [162], beds packed with perforated metal ribbon strands having different crimped configurations [163], heat exchangers [164] and

other forms were proposed as alternatives to the most popular rolling or piling up alternate corrugated and flat thin sheets. In this case, the flat sheet was used to prevent the nesting or intermeshing of the corrugated ones producing small parallel channels with laminar flow.

The performance of these classic monoliths with sinusoidal straight channels has been improved by introducing local turbulence within the channels. Different strategies were proposed and will be discussed later, but all of them are possible due to the metallic nature of the substrate (maleable and easy to perforate and cut).

Many different metals and alloys have been proposed for the manufacture of monoliths in search for mechanical, chemical and thermal stability, availability in thin foils and good surface adherence of the catalytic coating. In addition to some Ni and Cr alloys, steel is the most widely used alloy, in particular ferritic alloys containing Al that can produce alumina protecting coatings with excellent properties for anchoring the catalytic coating. Another interesting material to prepare metallic monoliths when the working temperature is not so high as in automotive exhausts is aluminum. It has excellent mechanical and thermal properties, and can be anodised producing very adherent alumina layers with adequate textural properties to be used as catalytic support [165–167].

The new stricter emission limits for car exhausts all around the world demand more effective catalytic solutions. Metal catalyst substrates offer a variety of solutions for all combustion engine applications [168]:

- Significant reductions of all emissions (HC, CO, NO_x and PM) can be achieved for both spark ignition and diesel engines.
- New developments like cone-shaped catalysts and open particulate traps help to meet future emission legislation.
- New, high cell density, ultra-thin foil substrates further increase catalyst efficiency.

4.1. Metallic substrates

The choice of a metal alloy to be used as catalytic substrate depends on three main groups of characteristics:

(1) The properties related to the use of the catalyst: mechanical, thermal and chemical resistance under operation conditions.
(2) The properties related to the catalytic coating adhesion.
(3) The properties related to the fabrication process: capability of rolling to thin foils, weldability, etc.

Usually, the first group of characteristics is the most important one, especially for automotive use, which presents the most stringent conditions of temperature, atmosphere, durability and mechanical stress. Therefore, steel and other iron alloys are the ones most frequently used.

Downs in a patent from 1927 was the first to propose iron as a metallic substrate for catalysts in his "calorizing" process [169]. Iron particles of the desired size were dipped in

melted aluminum producing a coating of iron aluminum alloy presenting a rough surface to which the catalyst can be adhered. In this pioneering work, the two main roles played by aluminum were implicit: protection of the base metal against high temperature oxidation and promotion of the adhesion between the base metal and the catalyst coating. Later on, the same idea was again proposed for different alloys (stainless steel, nichrome, nickel and other alloys resistant to oxidation), forming the alumina coating by applying finely divided aluminum powder dispersed in an organic vehicle, treating the coated substrate with steam at elevated temperature and pressure, and calcining the resulting alumina [170–172]. Retallick and Dumbar proposed a composition for a catalyst support, consisting in a hot-dip coating process for coating aluminum on ferritic steel strip, which is subsequently rolled to foil [173]. An improvement of this technique by Kilbane et al. [174] proposed a hydrogen pre-treatment at high temperature that enhanced the wetting of the ferritic chromium steel to substantially eliminate uncoated or pin hole defects in the aluminum coating layer. Inaba et al. proposed a similar method but included a chemical attack of the formed Al alloy before the final calcination to partially dissolve the aluminum, thus increasing the surface porosity [175,176]. In this particular case, the coating was directly used as support for the active phase, platinum. Davies [177] reported a different method to produce the alumina coating of carbon steel foils by immersion of the foil into a hot lead bath containing alloying ingredients (Cr and Al), which displaced the iron atoms in the said foil to allow the diffusion of these alloying ingredients throughout the entire thickness of the said foil. Lead was used in the bath because it is incompatible with the iron matrix but dissolves Cr and Al. The alloyed matrix was then calcined to produce the alumina coating. The advantage claimed by this method is the possibility to use the easy-to-produce thin foils of carbon steel avoiding the difficult rolling of ferritic steels. An alternative to hot-dip methods is the aluminum coating by a vapor deposition technique, proposed by Cornelison and Retallick [178]. It produces thin and uniform coatings on any base material even on those difficult to wet by molten aluminum.

Taking into account the important role, played by aluminum in the use of steel as a catalytic substrate, the interest of using alloys containing this element is evident. High temperature oxidation resistant alloys were developed in the 1960s, based on Fe, Cr, Al and Y [179,180]. But it was in the 1970s, thanks to the work of the United Kingdom Atomic Energy Authority, when these ferritic steels became available and could be made into thin foils, corrugated and then piled up to form honeycomb structures [165,181–183].

The main components of these alloys are Fe, Cr, Al and Y. The formation of a self-healing protective "skin" of alumina allows the ultra-thin steel to withstand the high temperatures and corrosive conditions in auto exhaust and other environmental uses. These materials also have high thermal shock resistance and high melting and softening points and facilitate the development of high cell densities with very low-pressure losses [184].

In addition to the main components of these ferritic steels, chromium (17–22%) and aluminum (5–8%), other reactive elements (RE) are present in small quantities because they are fundamental to improve the oxidation resistance of the alloy and to aid oxide adhesion. Table 1 lists a number of commercial alloys all of them having from 5 to 6% Al. Increasing this content above 6% would be an advantage because this would increase the available aluminum reservoir and hence the component life [185]. It is important to note that during the high temperature use of the alloy, the alumina protective layer continues growing until the aluminum is consumed. Breakdown of this thermally grown alumina would lead to breakaway oxidation conditions and rapid component failure. This is especially important for the new ultra-thin foils (20 μm) available for the high cell density monoliths (1600 cpsi). Reducing the thickness from 70 to 20 μm means that the component life will be reduced by a factor 12 [185]. However, it is quite difficult and usually uneconomical to increase the Al concentration to a value more than 5 mass%, because such an alloy is brittle, hence inducing difficulty during production or lowering productivity. It is generally easier to produce the thin foil or even the monolith from an alloy having low Al content and hence good mechanical and manufacturing properties, and subsequently to treat it to increase the Al content by one of the strategies previously discussed.

Fukuda et al. [186] studied the growing mechanism of the alumina scale in Fe–Cr–Al alloys with reactive elements (La, Zr and Hf). When a clean untreated foil is heated in air, oxygen is in contact with the metal surface and a first

Table 1
Materials for metal foil catalytic monoliths (ref. [185])

Alloy	Fe	Cr	Al	Ti	La	Zr	Y	Ce	Hf
Aluchrom	Bal.	20.6	5.4	0.010		0.170	0.006		
Aluchrom YHf	Bal.	20.3	5.6	0.010		0.054	0.046		0.31
FeCrAlloy	Bal.	20.3	5.4	0.084		0.080	0.045		
FeCrAlloy JA13	Bal.	16.3	5.0	0.010		0.050	0.320		
Kanthal AF	Bal.	21.1	5.2	0.094		0.058	0.034		
Kanthal APM	Bal.	21.1	5.9	0.026		0.110			
Nisshin steel	Bal.	19.9	5.0		0.120				
Ugine Saoie 12178	Bal.	19.9	5.0		0.009			0.019	
Ugine Saoie 12179	Bal.	20.0	5.0		0.014			0.030	

layer of alumina ($\approx 0.5\,\mu$m) is formed, containing some Fe and Cr. Equiaxed grains form this layer and the grain boundary allows some oxygen diffusion to the metal surface, where the oxidation continues. Nevertheless, the oxygen partial pressure at the metal-oxide interface is much lower and the oxidation slows down and no more Fe and Cr is oxidized under these conditions. Alumina grows according to sub-parabolic time dependence kinetics [187] with columnar grain morphology as long as aluminum remains in the alloy. When the starting alloy contains reactive elements, the oxidation process is slower and the alumina scale more adherent. Fukuda et al. showed that reactive elements are concentrated in the grain boundary of the alumina, proposing that they act as glue between grains, reducing the oxygen permeability and increasing the layer stability [186].

But the role played by the minor elements in Fe–Cr–Al alloys is more complex. In this way, Quadakkers et al. showed that in yttria-containing alloys titanium addition appears to be of vital importance for maintaining optimum scale adhesion during cyclic oxidation [187]. At the same time, the impurity elements, such as carbon and nitrogen, should be kept at minimum levels in order to prevent enhanced oxidation due to the incorporation of matrix carbo-nitride precipitates into the alumina scale [187].

The stability of the metallic monoliths made on Fe–Cr–Al alloys submitted to cyclic heating and cooling treatments depends on a complex balance between different phenomena. A "perfect" adhesion between scales and foils increases the oxidation resistance but induces thermal stress between them. The aluminum consumption in the base alloy produces a density increase (from 7.15 g cm^{-3} for Fe–20Cr–6Al to 7.5 g cm^{-3} for Fe–20Cr) that is in opposition to the thermal expansion mismatch between the scale and the alloy substrate that induces a thermal stress on the alloy during cooling which is in the tensile state [188]. A growth stress is also presented due to the combined effects of the oxide growth as well as the structure change that might take place in either the scale or alloy itself. Schutze and Przybilla suggested that there can be a "relaxation" mechanism, which relieves the foil from the compressive or tensile stress cited below [188]. Therefore, this material has to strike a balance between the perfectly adherent scales for the maximum protection and somewhat reduced oxidation resistance needed for the relaxation of adhesion [189].

4.2. Monolith design and manufacturing aspects

The most frequent design in metallic monoliths is based on rolling (Fig. 14) or piling up (Fig. 15) alternate corrugated and flat strips. Multiple parallel channels are generated in-between the corrugated strip. Crimping a metal foil on a pair of rollers having sinusoidal or triangular teeth produces corrugation. Variation in the number of cells per unit area is achieved by varying the pitch and width of the profile on the crimping rolls [190].
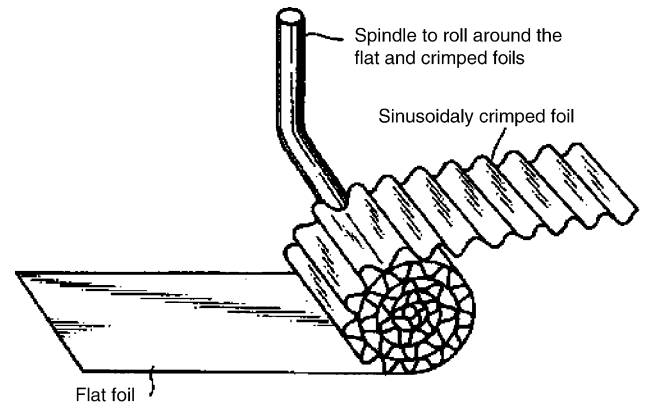

Fig. 14. Monolith construction by rolling around a spindle alternate flat and crimped foils (adapted from ref. [190]).

Pulsate flow and vibrations produce the deformation of the center of the cylindrical rolled monoliths that are pushed out during use (telescoping) [191]. This phenomenon can be prevented by forcing pins through the layers perpendicular to the channels, or using various forms of welding [192] and brazing between layers or across one or both end faces [193]. An interesting alternative to the classical brazing methods is proposed by EMITEC [194], which propounds the use of sandwich metal foils having the external layer of aluminum and the internal one of Fe–Cr alloy. Monoliths prepared from this material are heated and the aluminum melts, one part migrating to the inner layer and another part flowing by capillarity to contact points between the flat and corrugated foils where a kind of welding is produced.

An elegant solution to prevent telescoping, but at the same time keeping a high amount of elasticity to avoid creep fa-
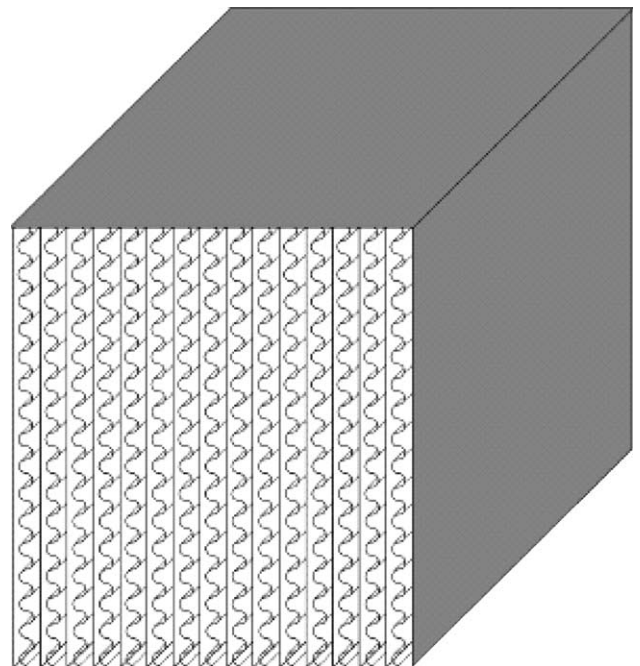

Fig. 15. Monolith construction by piling up alternates flat and crimped foils.
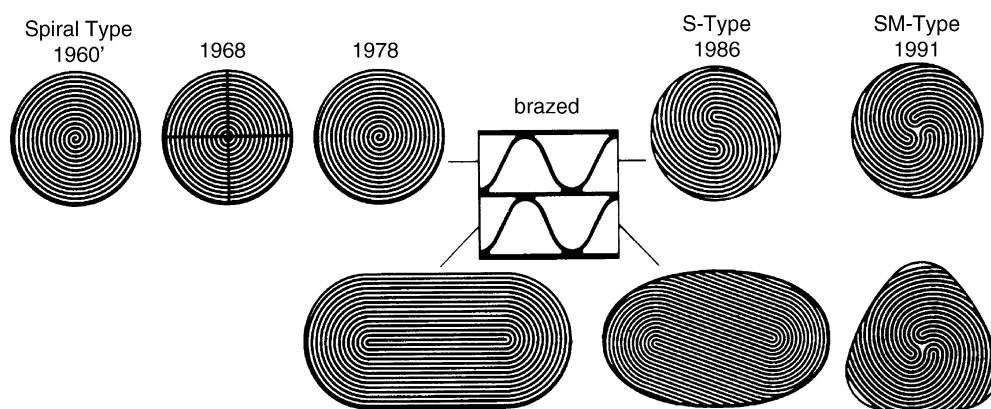
Fig. 16. History of metallic substrates by EMITEC (adapted from ref. [192]).

tigue defects was proposed by EMITEC in 1986: the "S-type" design (Fig. 16). Two stacks of alternating corrugated and flat foils are wound around two mandrels in opposite directions before the assembly is inserted into a tubular mantle. The ends of the foils are brazed to the mantle. The layers are at an angle to the mantle and curve toward the center, carrying expansion forces in that direction and causing the structure to undergo torsional deformation [195]. The "SM-type" design (Fig. 16) introduced some years later [196], uses three mandrels allowing the adaptation to markedly irregular cross-sectional shapes.

All the design modifications previously cited are related to mechanical and thermal resistance but there is another family of modifications oriented to the improvement of flow patterns. Indeed, the flow pattern through monoliths of multiple parallel channels has two main characteristics:

- The flow inside the channels is basically laminar. Therefore, the transfer coefficients from the bulk fluid phase to the catalyst in the wall surface are low.
- Channels are independent from one another and therefore there is no radial flow in the whole monolith and the eventual maldistribution at the monolith entry cannot be compensated along its path.

Maus and Wieres proposed some cuttings and depletions in the crimped foils to interconnect channels [197]. In this way, not only the radial flow is improved but also the initial flow maldistribution can be partially compensated. The turbulence is also increased and hence the transference to the wall is also improved [198–200]. Another improvement aimed to increase the turbulence inside the channels is to produce microstructures both in the flat and in the crimped foil perpendicular to the macrostructures forming the channels (Fig. 17) [199–201]. Both microstructures and channel interconnections not only increase the pressure drop but also increase the monolith efficiency. This higher efficiency allows length reductions that compensate the increased pressure drop per unit length. The final balance is that more compact and lighter converters can be used.

A different approach to interconnect channels and increase turbulence is to eliminate the flat foil. It can be done by rolling a pair of foils having corrugations which are disposed obliquely relative to each other, thus preventing them from nesting [202]. Whittenberger proposed metal foils corrugated in a chevron pattern and folded in a coinciding fashion or zig-zag manner to form a stack useful as catalytic converter [203]. On the other hand, Cornelison, for parallelepipedic monoliths, proposed to substitute the flat foil with a thin wire mesh or frame allowing inter-channel connection [204].

Related to the eventual flow maldistribution at the monolith entry due to the sudden diameter increase, EMITEC has developed conical honeycombs with channels of increasing size producing at the entry of the subsequent main monolith the same flat profile of the previous pipe [205]. The efficiency of the monolith is thus increased in addition to the hot spots prevention. These improvements have been fundamental for the development of the new close-coupled converter design necessary to meet future car emission legislations [206]. Also related to these new stringent emission limits for automobiles is the problem of the cold start. This point is especially important in Europe where very short displacements are frequent.
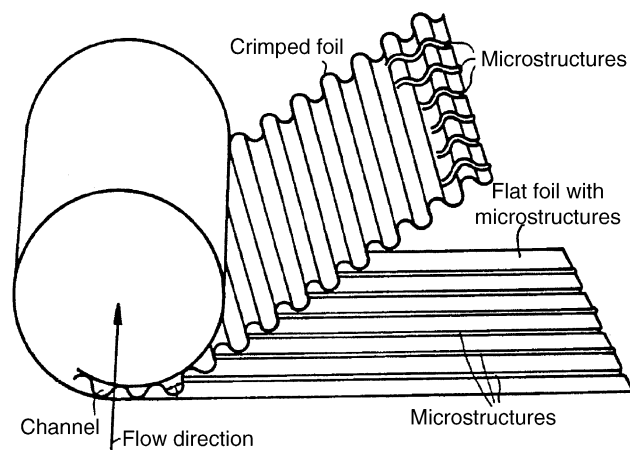

Fig. 17. Monolith presenting microstructures transversal to flow direction (adapted from ref. [201]).

One of the proposed solutions to overcome the problem is to heat up the converter electrically throughout the ohmic resistance of the base material [190,207,208].

4.3. Surface treatments and catalytic coating

Some of the preliminary references in the literature suggested the direct deposition of the active phase (usually noble metals) onto the base metal [152–154]. Nevertheless, it was soon discovered that an intermediate layer of a true catalytic support would help to obtain a higher and more stable dispersion of the active phase. The first approach was to use the alumina scale generated to protect the base metal as catalytic support. Downs already suggested this idea in his pioneering work [169]. In general, aluminum was added to the base alloy and then it was oxidized in air at high temperature. But some singularities were proposed to improve the textural properties of the alumina layer. Thus, Keith used a treatment with steam at elevated temperature and pressure and subsequent calcining in air [170]. Another technique consists in attacking the aluminum coating with an alkali or an acid to dissolve it partially, creating a porous surface layer. Subsequently, the oxidation in air produced alumina [176,209].

The excellent properties of the Fe–Cr–Al alloys previously discussed make this material the standard for preparing metallic monoliths. The alumina scale protects the base alloy against oxidation but does not present adequate properties as catalytic support. Consequently, an additional layer of alumina or other oxide must be deposited on the surface. Usually, this is done by dipping the metal in a slurry containing the support or the final catalyst (washcoating) and therefore also the roughness of the surface is important. Indeed, a rough surface retains a thicker slurry film and facilitates the interaction that ensures the new coating anchoring.

Several studies can be found in the patent literature about the pre-treatment conditions to prepare a protective alumina scale with adequate roughness for slurry washcoating [210–214]. It is generally accepted that the best morphology corresponds to long randomly oriented whiskers. The pre-treatment conditions to obtain such morphology depend on the exact alloy composition, and in particular on the reactive elements [211]. Nevertheless, a good general view is presented in Fig. 18 adapted from ref. [209]. At low temperatures and short treatment times the oxide scale formed is flat and therefore not convenient for washcoating. At very high temperatures, the amount of oxide produced is high but a significant sintering of the alumina produces a soft relief. The central region corresponds to the formation of long and randomly oriented whiskers that allow good slurry retention during washcoating and an excellent interaction after calcination that ensures a good adherence. Examples of this morphology can be seen in Figs. 19 and 20. The central region is surrounded by a region with smaller whiskers [211] not optimal as washcoating substrate.

Finally, it must be pointed out that in contrast with the abundant information available in the patent literature, studies
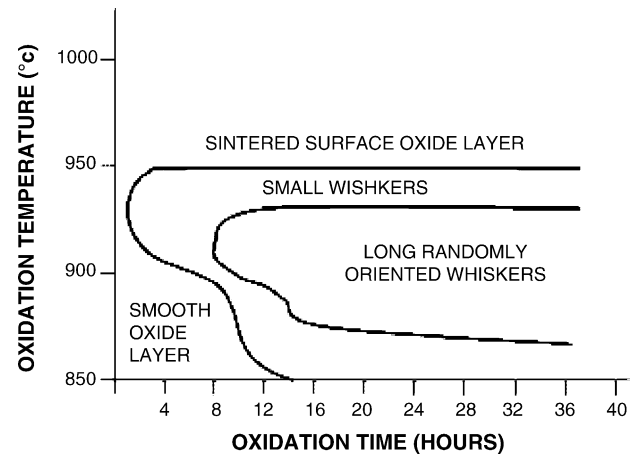

Fig. 18. Oxidation regions as a function of time and temperature for a Fe–Cr–Al–Y alloy in air (adapted from ref. [211]).
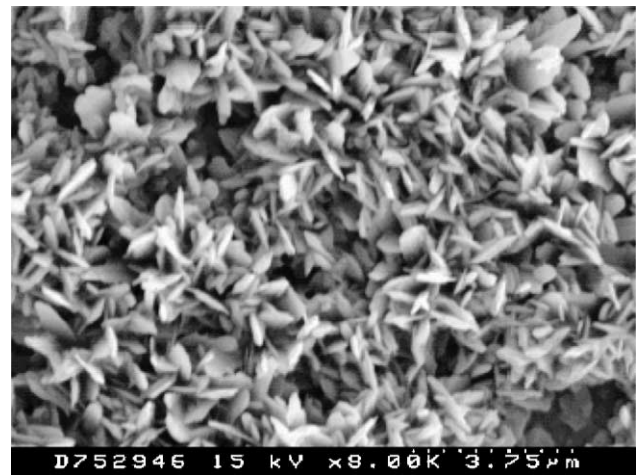

Fig. 19. SEM micrographs of alumina whiskers produced by heating in air a 50 μm foil of Fecralloy® for 22 h at 900 °C (top view).
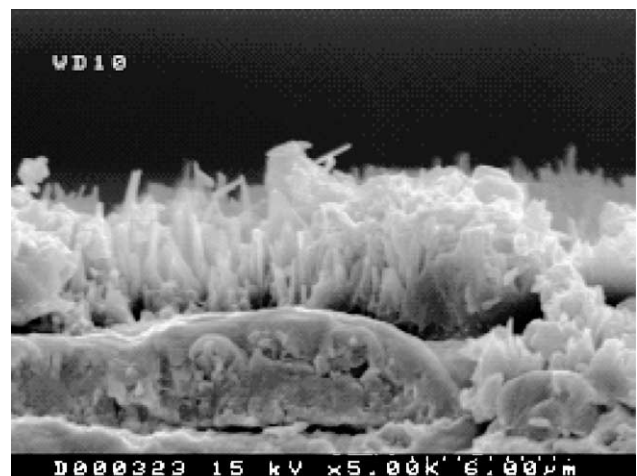

Fig. 20. SEM micrographs of alumina whiskers produced by heating in air a 50 μm foil of Fecralloy® for 22 h at 900 °C (lateral view).

about this subject in articles and books are scarce. Only some recent works give details about the metal foil pre-treatment [136,216,217]. One of them [136] agrees with the general view proposed in Fig. 18, but the other two suggest new pre-treatments. Zhao et al. [215] indicate that by oxidizing the foil at 1050 °C for only 30 min, it could reach almost the same coating adhesion level as at 900 °C for 10 h. Unfortunately, the origin of the alloy and the content of minor components are not indicated. Cerri et al. [216] concluded that the best pre-treatment condition was 5 min in oxygen (with 0.5% nitrogen) at 1200 °C [216]. In this case the material source is indicated but not the content of the minor components.

4.4. Coating adherence on metallic substrates

Differences between coating metals or ceramics with a catalyst arise both from chemical composition and surface roughness. It is generally accepted that it is more difficult to adhere inorganic coatings to a metal than to a ceramic material. It is therefore very important to test the coating adherence when metal substrates are used.

Liu et al. [217] studied the influence of different coating variables on the adhesion measured with a normalized method proposed by ASTM (D 3359-02). This test method covers procedures for assessing the adhesion of coating films to metallic substrates by applying and removing pressure-sensitive tape over cuts made in the film. Adhesion is evaluated by comparison with descriptions and illustrations presented in the ASTM document. Details of the method are well described but the limiting aspects are the availability and variability of the pressure-sensitive tape proposed: Permacel 99, manufactured by Permacel, New Brunswick, NJ 08903. Yasaki et al. [218] proposed to assess adhesion by calculating the amount of coating lost after dipping samples in a bath of a supersonic cleaner for 30 min. Additional details of the same method were given by Valentini et al. [136] who used petroleum ether in a sealed beaker placed in an ultrasonic bath. Zhao et al. [215] used the same method together with a thermal shock test. This one was carried out by heating the coated foils to 950 °C for 20 min, and then quenching them in water at 25 °C. This thermal shock process was repeated 10 times for each sample, after which the weight loss was measured. Both methods showed the same trends as a function of the preparation variables, but surprisingly, the ultrasonic adhesion test showed in general higher weight losses than the thermal shock test. Especially interesting in this paper is the comparison of the adhesion tests results with the measurement of the interface shear strength. An excellent reverse relationship between weight loss and interface shear strength was obtained. But unfortunately, no details about this measurement were provided. These authors only indicated that the interface shear strength was measured using a tensile testing machine, model 1-5-1, with constant speed of 10 mm min^{-1} [215].

4.5. Alumina on aluminum monoliths prepared by anodisation

Aluminum coated by alumina produced by anodisation is an excellent material to prepare metallic monoliths. The melting point of aluminum (660 °C) limits its use to medium–low temperature processes, but the special characteristics of the anodisation alumina offer exciting perspectives:

- Alumina produced by anodisation is an excellent catalytic support.
- Texture of the alumina can be adapted by tuning up the anodisation parameters.
- Alumina coating is extremely adherent and stable, resistant to thermal mechanical shocks.
- Anodisation is a well-known process easy and inexpensive for industrial use.

Extensive work has been done to study anodisation as a protective treatment of aluminum for buildings, decoration or household materials. The final properties of the alumina layer obtained by the electrochemical method will depend on different variables of the anodisation process. The choice of the electrolyte will influence the formation of more or less porous alumina [219–227]. The use or not of agitation during the anodisation process can also affect the final properties of the Al_2O_3 [228–240]. The anodisation time [227–238], the electrolyte concentration [228–242], temperature [229-244] and the electrolytic current density [219,227–245] will also affect the final structural properties of the formed alumina such as the surface pore density, the pore diameter and shape, the alumina amount and surface area, etc.

The alumina layer formed on the metallic aluminum substrate possesses unbranched and regular pores with a length controlled by the alumina layer thickness, which has resulted very advantageous for some catalytic reactions. Thus, Hönicke and co-workers [246–249] use aluminum anodisation as a base material to construct microreactors, which is a research area of increasing interest [250,251]. On the other hand, the metallic nature of the substrate has led to use this kind of anodised catalyst with high thermal conductivity in very exothermic reactions, producing lower temperature gradients and hot spots [252,253]. Furthermore, noble metals deposited on anodised aluminum catalysts have also been used in complete oxidation reactions for pollution control [252–255].

Burgos et al. [167] have recently published a wide study about the anodisation of aluminum to prepare metallic monoliths. They studied the influence of anodisation time, current density, electrolyte nature, its temperature and concentration, and the effect of agitation, on the final alumina textural properties. The conclusion is that two main processes control the formation of the alumina layer: the generation of alumina and its redissolution inside the pores. Higher anodisation times and current densities will generate more alumina, and higher electrolyte concentration, temperature and the same alumina layer growth will favor the alumina redissolution. Consider-

Table 2
Selected conditions for the monolith anodisation (from ref. [167])

Variable	Selected condition
Electrolyte	H_2SO_4
Electrolyte concentration (M)	1.6
Current density (A dm^{-2})	2
Temperature (°C)	30
Time (min)	50
Agitation	Bubbling air

Table 3
Geometric properties of the anodised monoliths prepared in ref. [167]

Cylinders (length × diameter) (cm)	3 × 1.6
Geometric volume (cm^3)	6
Total surface exposed (m^2)	40
Cell number (cells in.$^{-2}$)	355
Specific surface per cell (m^2 cell^{-1})	0.36
Cell area (m^2 cell^{-1})	1.9×10^{-4}
Surface/volume ratio (m^{-1})	1900
Empty fraction (%)	81
Wall thickness (mm)	0.1

ing the study carried out, a certain value for each process variable has been proposed to obtain reproducible monoliths with adequate specific surface and pore diameter to be used as catalysts (Table 2). The monoliths prepared in this way present the geometric and textural parameters presented in Table 3.

A remarkable work difficult to classify has been recently published by Balomenou et al. [256]. These authors proposed a mixed monolithic reactor made of ceramic plates in a metallic housing to implement the non-Faradaic electrochemical modification of catalytic activity (NEMCA effect), deeply studied by Vayenas and co-workers (see literature cited in Ref. [256]). They reported the development of a novel Y_2O_3–ZrO_2 monolithic, electrochemically-promoted catalyst, which was tested for hydrocarbon oxidation and NO reduction by C_2H_4 in the presence of O_2, and were successful in the electropromotion of thin Rh and Pt elements with metal dispersions of at least 10%. With this novel technology they claimed economic advantages for the practical utilisation of electrochemical promotion.

5. Conclusions

The different possibilities in formulating catalysts for a given process are potentiated by the combination with a monolithic support. The deposition of an active phase in a monolith allows the introduction of engineering concepts in catalysts design and, although the general basis for preparation of catalytic monoliths are well established, there are so many aspects that are continuously developing giving place to an exciting field of research.

Especially for the use in environmental catalysts, the use of monoliths is usually mandatory and ceramic monoliths are the most widely employed. The extrusion process, the one most used for making ceramic monoliths, should meet several conditions as an adequate plasticity of the pastes to permit

their extrusion and immediate conformation in rigid structures in monolithic shape. This is no trivial matter, since in developing monoliths with new materials a great effort should be devoted in finding the adequate conditions for extrusion.

Once an environmental powder catalyst has been developed at laboratory level, i.e. it has the adequate activity and selectivity for the abatement of a contaminant, the following step is the coating of a ceramic monolith with it. The objective is to obtain a monolithic system with at least the same performance of the powder. Usually this is not an easy task, since there are several problems to be solved. The coated catalyst should be thermally and mechanically stable, and this property can be met with the help of a binder. But, the binder can chemically interact with the active phase decreasing the activity and/or the selectivity. Another aspect that can negatively affect the performance is the geometry of the washcoat. This should be adequate for convenient mass and heat transfer phenomena. Those convenient characteristics of a good monolithic catalyst should be met by managing preparation procedures. Thus, preparation technologies are composed of both materials science and engineering aspects. One emerging technology is the growth of zeolites on monolithic walls. Zeolites are among the most widely studied materials for environmental applications.

The development of new metallic monoliths strongly enriched the field of monolithic environmental catalysts. Their higher mechanical resistance and thermal conductivity, the possibility of thinner walls allowing higher cell density and lower pressure drop, are strong advantages of metallic monoliths. An additional advantage of metallic substrates is the easy way to produce different and complicated forms adapted to a wide variety of problems and uses. Among metallic monoliths, those made of aluminum coated by alumina produced by anodisation are excellent materials to prepare metallic monoliths. The melting point of aluminum (660 °C) limits its use to medium–low temperature processes, but the especial characteristics of the anodisation alumina offer exciting perspectives.

Acknowledgments

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