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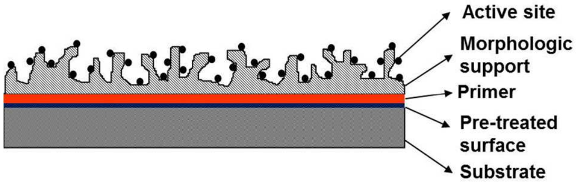

# Methods for the catalytic activation of metallic structured substrates

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## Abstract

Coating is the most widely used technique for the preparation of structured catalysts. This paper reviews the main methods reported in the open literature for depositing catalytic layers onto metallic substrates, specifically focusing on the coating of metallic honeycomb monoliths and open-cell foams. All the relevant steps, including substrate pre-treatments, means for catalytic activation and thermal treatments, are discussed.

**Keywords:** metallic structured catalysts, coating methods, open-cell foam, honeycomb monolith, washcoating.

## Contents

## 1. Introduction: metallic structured catalysts in heterogeneous catalysis

Several methods are available in the literature for the preparation of structured catalysts, intended as ceramic ($Al_2O_3$, cordierite, SiC, etc.) or metallic (e.g. stainless steel, aluminum, copper, etc.) substrates, usually in the form of a monolithic matrix (i.e. a continuous structure including many small - in the order of millimeters – more or less regular channels), on which catalytic active sites are properly dispersed. In principle, two main ways exist for catalytically activating a structured substrate: *i) incorporation* of the catalyst directly inside the substrate, and *ii) coating* of the substrate.

*Incorporation* of catalytic components into the monolith structure is performed by adding them to the ingredient mixture from which the monolith is to be subsequently formed (e.g. by extrusion) and calcined. Although the preparation of this class of catalysts involves fewer steps, it usually needs an excellent control of the process variables in order to avoid undesired transformation of the active elements and of the substrate [1]. For this reason, this option is limited to a few applications [2].

*Coating*, instead, is by far the most used technique because of its simplicity and versatility [3, 4] and consists in depositing a layer of high-surface-area ( > 10 $m^2/g$) oxide(s) onto the surface of a low-surface-area (often coinciding with the geometric surface area) monolithic substrate (Fig. 1). Active elements may be incorporated into the coating layer either during the coating step or afterwards, by using any well-known technique (e.g. impregnation, deposition-precipitation, ion exchange) [4]. The selection of the method to be employed is a function of both nature and concentration of the active phase to be incorporated, the chemical nature of active phase precursor 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 any present chemical or physical agent.

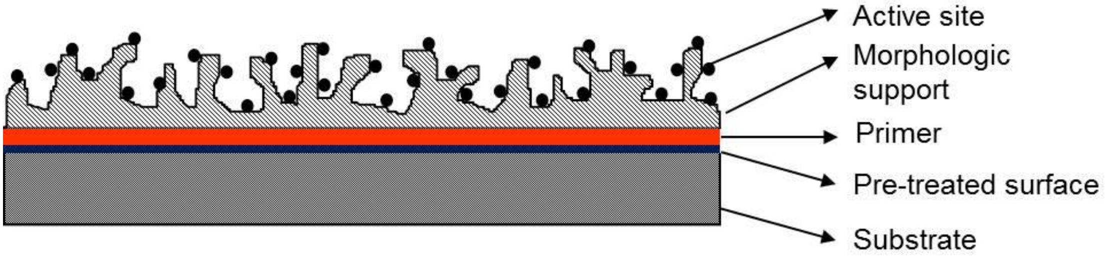

Figure 1 – Sketch of structured catalyst prepared by coating

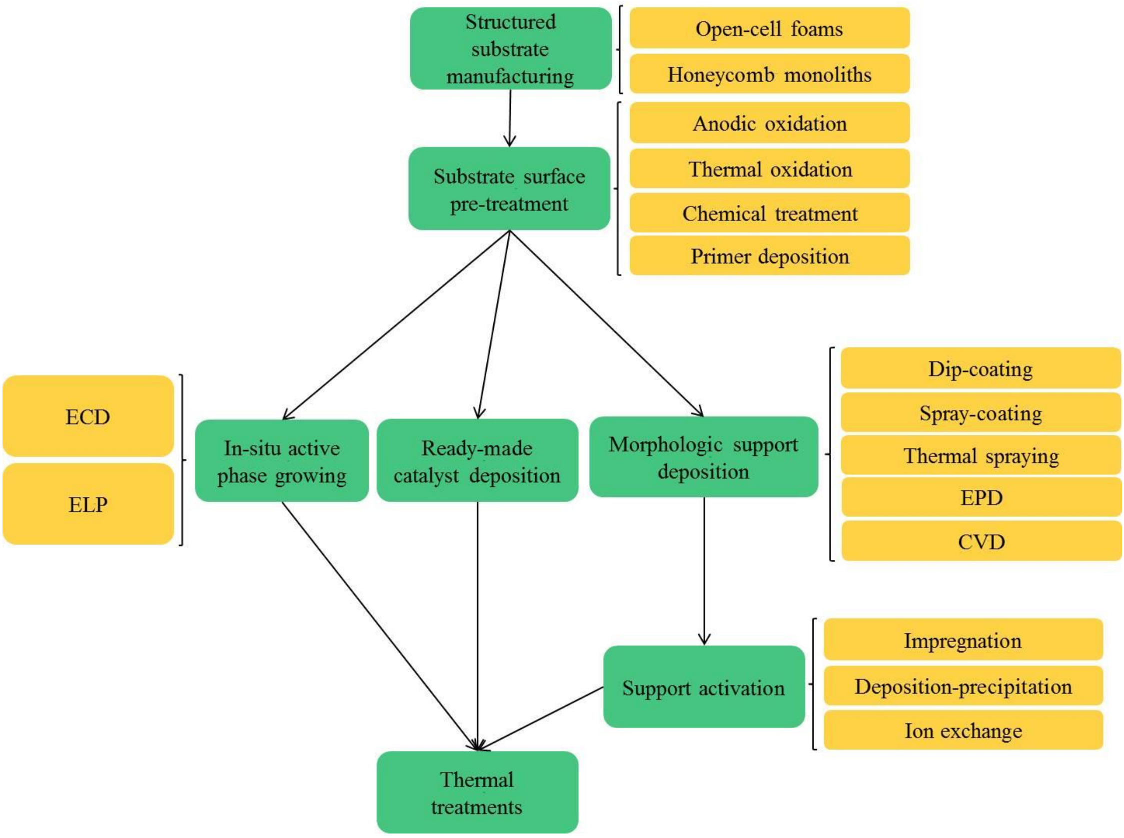

Figure 2 – Main steps involved in the preparation of a metallic structured catalyst by coating

Due to their importance in environmental catalysis, dedicated reviews are available on how to coat ceramic monoliths [1, 3, 5], but they are not comprehensive as they do not consider at all or pay little attention on how to coat structured substrates made of metallic materials. Accordingly, the present work is devoted to fill that gap and is aimed to review and critically analyze the most relevant contributions of the research community to the catalytic activation of metallic structured substrates. In particular, the most widely used techniques for pretreating their surface, depositing the catalytic material and thermally treating the coating layer are discussed (Fig. 2).

The adoption of metallic structured catalysts dates back to the 50's of the last century, when prototypes of Stainless Steel, Chromel, Nikrothal and Nichrome wires, grids, mats and crimped ribbons (Fig. 3a-b) were coated with noble metal catalysts (i.e. Pt or Pd) and used in the field of environmental catalysis due to their good resistance to the high electrical currents employed to heat up the catalytic systems by Joule effect [6] (See Table 1). The high operating temperatures typical of such catalytic processes also require good thermal resistance, which still finds a good match with the properties of metallic materials.

Later on, ceramic (i.e. cordierite) honeycomb monoliths have been proposed, studied for many years and extensively adopted, especially for adiabatic applications [7, 8]. With respect to the previous structured catalyst configurations, ceramic honeycombs provide better bonding of the catalyst to the support material thanks to their intrinsic porosity, while still keeping the pressure drop to a minimum thanks to their high void fraction and to the laminar gas flow regime inside the monolith channels. Furthermore their cost is relatively low [5].

In the 90's, the use of monolithic catalysts, in particular honeycombs and open-cell foams, made of highly conductive materials (Fig. 3c-d) was proposed also for strongly exo-/endothermic gas-solid chemical reactions (e.g. steam reforming, selective oxidations, Fischer-Tropsch synthesis, methanol synthesis) in order to minimise the hot/cold spots in conventional multitubular reactors with external cooling/heating media and to prevent mechanical-strength and thermal-shock limitations [9-13].

Recently, metallic microfibrous substrates (Fig. 3e) have been proposed as alternative conductive substrates to be coated with a catalyst layer [14] or loaded with catalytic powders [15] (MFEC, MicroFibrous Entrapped Catalysts).

A special word is worth to be spent concerning microreactors (Fig. 3f), as a valuable alternative to conventional reactors on the small (micro) scale [16]. Such reactors are still based on the same concept of multitubular reactors, where very effective heat transfer is achieved by increasing the heat transfer surface to reactor volume ratio. In microreactors, this feature is maximized through the adoption of microchannels (characteristic dimension < 1mm) coated with thin catalyst layers [17-19], which results in extremely high surface-to-volume ratios (i.e. ~$10^3$-$10^5$ $m^2/m^3$, [20]). Accordingly, very efficient heat transfer is obtained, therefore offering a compact and modular solution for easy scale-up and control of a variety of heat transfer limited industrial processes.

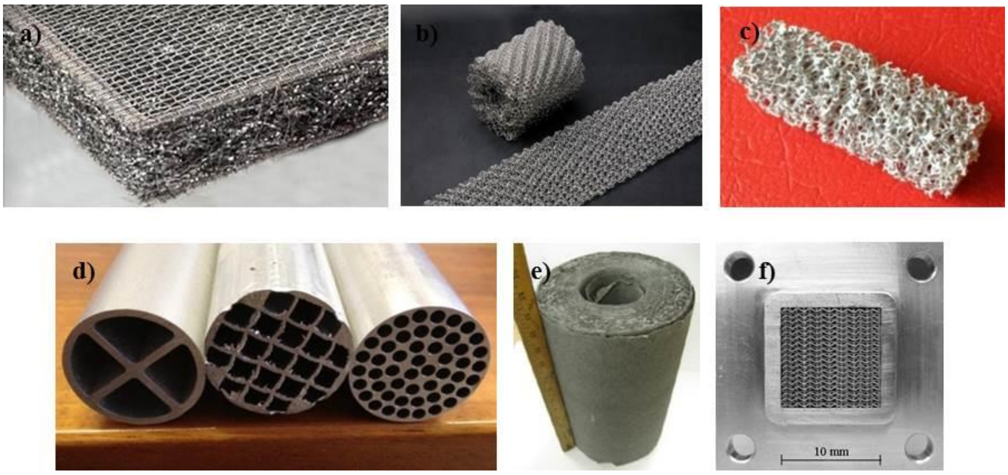

Figure 3 – Examples of *a)* metallic ribbon [21], *b)* wire mesh [22], *c)* open-cell foam, *d)* honeycomb monolith, *e)* MFEC roll (reprinted from [15] with permission from RSC), *f)* microchannel reactor (reprinted from [23] with permission from RSC)

Due to the particular attention of the research community in the field, the present review is focused only on metallic honeycomb monoliths and open-cell foams as structured substrates for gas/solid or gas/solid/liquid reactions and, specifically, on how to effectively deposit a catalyst layer onto such structures. It is worth noticing that some of the techniques applied to coat flat surfaces may be applied to coat microchannel plates as well before being assembled. However, particular attention has to be paid in this case to assure proper sealing during plates assembling and welding.

## 2. Metallic substrates

### *2.1 Honeycomb monoliths*

Honeycomb monoliths are structures composed of parallel repeating channels wherein the flowing reacting mixture is segregated. The most important physical characteristic when used as catalyst substrates is the size of the channel (commonly named *channel opening*) through which the gaseous reactants and products flow (Fig. 4a). Alternatively, the number of cells per square inch (abbreviated CPSI) can be used.

Metallic honeycombs may be usually manufactured by following two main routes: *i)* extrusion or *ii)* rolling of alternate corrugated and flat foils. Extrusion brings to the formation of monolithic materials with thermally-connected structures (Fig. 4a). Such a technique, well consolidated for ceramic honeycombs [1], is still very challenging for metallic ones, at the point that very few commercial solutions are available at present [24-26] and only some prototypes made of Al, Fe, Cu were manufactured with cell densities ranging from 50 to 600 CPSI [24, 26, 27] and void fractions in the order of 70-90%. Corrugation, instead, has been extensively studied in the literature (Table 1) and may yield more complex geometries such as spiral rolls (Fig. 4b) or alternate crimped and flat strips packed in the form of columnars (Fig. 4c). However, such a method has the drawback of losing the cross-sectional continuity of the solid matrix, even when the rolled/packed layers are welded together. As a result, corrugated honeycombs exhibit markedly much worse effective radial thermal conductivities with respect to thermally connected matrices obtained by extrusion. This becomes a key issue when applied to heat transfer limited catalytic processes.

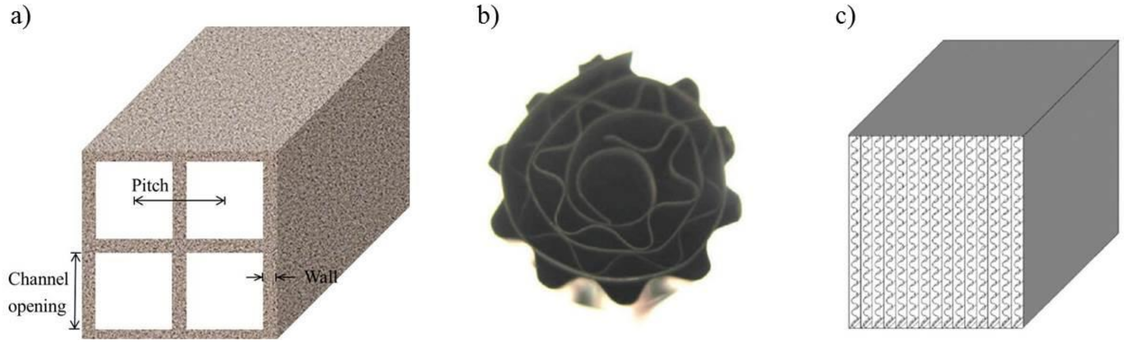

Figure 4 – Sketch of a) extruded honeycomb monolith with squared channels, b) honeycomb from corrugated flat FeCrAlloy foils (reprinted from [28] with permission from RSC) and c) honeycomb from alternate crimped and flat strips (reprinted from [1] with permission from RSC)

Use of ceramic honeycomb monoliths is well established in environmental catalysis. Indeed, higher surface-to-volume ratios are obtained with respect to conventional packed-bed of pellets thanks to the high void fraction of the substrate. Greatly reduced pressure drop (up to two orders of magnitude) may be reached as well, thanks also to the laminar flow in the straight monolith channels. Moreover, thin catalyst layers may be deposited, limiting the impact of internal mass transfer resistances in fast chemical processes.

Applications of monolith catalysts to gas/solid or gas/liquid/solid processes for chemicals production have been instead scarcely investigated and long discouraged so far mainly for two reasons [7]: *i)* conventional parallel channel monoliths are practically adiabatic, severely limiting the temperature control in many endothermic and exothermic chemical processes; *ii)* the overall load of catalytically active phase in a monolith catalyst is less than the amount of catalyst in a bed of pellets of comparable volume: this would be a clear disadvantage for the reactions under kinetic control usually met in chemical syntheses.

Nevertheless, honeycombs made of conductive materials have been found very appealing when applied to highly exo-/endothermic catalytic processes (Table 1) (e.g. partial oxidation of methanol [29], methane steam reforming [30], methanol synthesis [28], Fischer-Tropsch synthesis [31]). Indeed, effective radial thermal conductivities are one order of magnitude greater than in packed beds and near-isothermal reactor operation is possible even under very high thermal loads [32]. As a consequence, there is potential for a better control of the process selectivity and for slower catalyst deactivation rates by thermal effects (e.g. sintering), as well as for enhanced productivities and/or intensification of chemical processes.

Last but not least, metallic honeycomb monoliths can be manufactured with thinner walls, with open frontal areas (OFAs) approaching 90%, offering even lower pressure drops than ceramic monoliths at comparable or greater specific surface areas [7, 33].

For this reason, specific honeycomb designs should be developed in order to take full advantage of heat conduction within the monolithic matrices as well as to assure high catalyst loads [10].

However, it is also worth noticing that such structured catalysts are intrinsically more expensive than pelletized ones. In the case of chemicals production, therefore, replacement of the conventional catalyst technology with honeycomb monolith catalysts requires very significant and well proven benefits [34].

## *2.2 Open-cell foams*

Open-cell foams, also named sponges, are monolithic blocks with a cellular structure and more or less isotropic mechanical properties in which space is filled by filaments (*struts*) forming a continuous network which encloses cavities (*cells*), interconnected by open-windows (*pores*). The unit cell (Fig. 5) is usually a polyhedron whose average characteristic size is called *cell diameter* and in which the faces have their own average characteristic dimension, i.e. the *pore diameter*. Struts, whose dimension is typically in the order of hundreds of microns, may be solid or hollow, depending on the forming method, and may have different cross section geometry: circular (most common), triangular, etc. Struts are interconnected by means of nodes.

Metallic open-cell foams are manufactured as monolithic pieces by using different techniques that can be found in [35, 36]. The pore density, i.e. the number of pores per linear inch (abbreviated PPI), is commonly considered as the main geometrical parameter and, for typical fabrication materials like e.g. Al, FeCrAlloy or Cu, can range from 5 to 40 PPI, with void fractions in the order of 90-95% [11, 37].

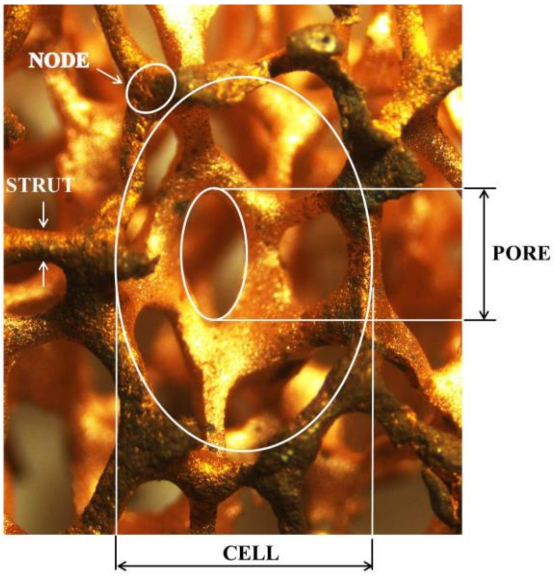

Figure 5 - Open-cell foam geometrical characterization

Even though less applications to catalytic processes (e.g. methane steam reforming [38, 39], CO oxidation [40], VOC abatement [41], soot and $NO_x$ abatement [42], Fischer-Tropsch synthesis [43], methanol synthesis [44]) have been proposed in the literature (Table 1), metallic open-cell foams offer similar advantages to honeycomb monoliths, including *i)* high porosity, *ii)* high surface-to-volume ratios therefore leading to high activity per unit reactor volume [45], *iii)* reduced pressure drop [46], *iv)* high mechanical strength which allows the design of light and stiff components [47], *v)* limited impact of internal mass transfer resistances and *vi)* high radial heat transfer rates when adopting conductive substrate materials, due to the enhanced heat conduction within the thermally connected solid matrix, therefore limiting temperature gradients and hot/cold spots in highly exo-/endothermic processes [13, 45, 47]. With respect to honeycomb monoliths, sponges also exhibit greater gas/solid heat and mass transfer rates (but greater pressure drops) thanks to the tortuous fluid flow paths within the foam structure [45].

Foams are commercially available in a variety of types (i.e. different material, pore density and void fraction [48, 49]), but the knowledge of the catalysis related-properties of these structures is still incomplete and detailed simulation studies and experimental investigations are required to conclusively assess their potential as effective catalyst supports.

Table 1 – Known applications of metallic structured catalysts in heterogeneous catalysis.

| **Process/application** | **Substrate geometry*** | **Substrate manufacturing** | **Substrate material** | **Active phase** | **Reference** |
|---|---|---|---|---|---|
| Catalytic combustion of methane | Foam | Replicated+Electrolysis | Ni, Ni-Cr | $LaCoO_3$ perovskite | [50] |
| | Honeycomb | Corrugated and rolled foils | FeCrAl | Mn-Co-Pd | [51] |
| | Honeycomb | Stack of corrugated foils | FeCrAl | Pd | [52] |
| | Honeycomb | Corrugated and rolled foils | FeCrAl | Ce-Cu | [53] |
| | Honeycomb | Corrugated and rolled foils | FeCrAl | Ce-La | [54] |
| | Honeycomb | Corrugated and rolled foils | FeCrAl | La-Fe-Mg | [55] |
| | Honeycomb | Corrugated and rolled foils | FeCrAl | $LaMnO_3$ | [56] |
| | Honeycomb | Corrugated foils | Al | $LaMnO_3$ | [57] |
| | Honeycomb | Corrugated and rolled foils | FeCrAl | Pd | [58] |
| | Honeycomb | Corrugated foils | Al | Pd/Fe-Al oxide | [59] |
| | Honeycombs | Corrugated and rolled foils | FeCrAl | Pt | [60] |
| | Honeycombs | Corrugated and rolled foils | Aluminum-containing SS | Pd | [61] |
| 1) Catalytic combustion of methane coupled with 2) methane reforming with $CO_2$ | Honeycomb | Corrugated and rolled foils | FeCrAl | 1) La-Fe-Mg;<br>2) Ni/SBA-15 | [62] |
| Catalytic combustion of naphthalene, CO and $CH_4$ | Honeycomb | Extruded | FeCrAl | MgO-Pt | [63] |

| | | | | | |
|---|---|---|---|---|---|
| | Slabs | - | Al | Pd | [64] |
| | Slabs | - | Al and FeCrAl | Pd | [65] |
| Catalytic combustion of ethanol, ethyl acetate and toluene | Honeycomb | Corrugated and rolled foils | 1) Al; 2) FeCrAl | $MnO_x$ | [66] |
| | Honeycomb | Corrugated and rolled foils | 1) FeCrAl; 2) Al | Mn-Cu | [67] |
| | Honeycomb | Corrugated and rolled foils | FeCrAl | $MnO_x$ | [68] |
| Catalytic fume incineration | Wire, screen | - | SS, Chromel, Nichrome, | Pd, Pt | [6] |
| | Ribbon, wire | - | Chromel, Nikrothal, Nickrome | Pd, Pt | [69] |
| Chlorination/oxychlorination of alkenes and alkanes | Honeycomb | Extruded | FeCrAl, Ni, Al, Cu | $CuCl_2$ | [70] |
| CO oxidation | Plates | - | Al | Au | [71] |
| | Honeycomb | Extruded | Cu | Pd | [72] |
| | Foam | Replicated | FeCrAl | Pt | [40] |
| | Foam | Replicated | FeCrAl | Pd | [73] |
| | Foam | Replicated | FeCrAl | Pt | [74] |
| | Honeycomb | Corrugated foils | AISI 304 SS | Au-Ce | [75] |
| | Honeycomb | Corrugated and rolled foils | Al | Au-Ce | [76] |
| | Honeycomb | Corrugated and rolled foils | FeCrAl | Au/B-AlFe(10) | [77] |
| | Honeycomb | Corrugated and rolled foils | AISI 304 SS | Au-Ce | [78] |
| | Fiber mats | Sintered | FeCrAl | Pd | [14] |
| Controlled hydrogen oxidation | Honeycomb | Packed plates | SS | Pt | [79] |
| Deep oxidation of n-butane | Foam | Replicated | Cu, Ni, Cr, Fe | $CuCr_2O_4$ | [12] |
| Dehydration of isopropanol to propene | Plates | Stacked | SS | $\gamma$-$Al_2O_3$ | [80] |
| Ethyl acetate and toluene oxidation | Honeycomb | Rolled corrugated sheets | FeCrAl and AISI 304 SS | Mn | [81] |
| | Honeycomb | Corrugated foils | FeCrAl | MnCu | [82] |
| Ethylene oxidation to ethylene oxide | Honeycomb | Packed foils | Aluchrom (FeCrAl) | Ag | [83] |
| Exhaust gas aftertreatment | Screen | - | SS 304, 316, chromium steel 410 and 420 | Ru, Ir | [84] |
| | 1) Honeycomb; 2) Screen | 1) Rolled sheets; 2) - | Nichrome, Inconel, Type 310 SS | Ni-Cu | [85] |

| | | | | | |
|---|---|---|---|---|---|
| | Spiral, wire | - | FeCrAlY | Pt, Pd, Ir, Rh | [86] |
| | Wire gauze | - | FeAl | Pt, Pd | [87] |
| | Honeycomb | Corrugated and rolled up sheets | Fe-Ni. Cr-Ni, Co-Cr, Co-Ni-Cr | Pt | [88] |
| | Honeycomb | Corrugated foils | FeCrAl | Pt, Pd, Rh | [89] |
| | Honeycomb | Corrugated foils | Aluminum-containing SS (18Cr-3Al) | Pt, Ru | [90] |
| | Foam | Replicated | Nickrome, Steel | Pt, Pd | [91] |
| | Honeycombs | Corrugated foils | Metallic | Pt, Rh | [92] |
| | Wire | - | FeCrAl | $Al_2O_3$-$TiO_2$ | [93] |
| | Honeycomb | Corrugated foils | Metallic | Pd | [94] |
| | Foil | - | FeCrAl | Cu-Co | [95] |
| Fischer-Tropsch synthesis | Honeycomb | Corrugated and rolled up foils | Steel | Co | [96] |
| | Foam | Sintering | SS | Co-Ru | [97] |
| | 1) Honeycomb; 2) Foam | 1) Corrugated; 2) Replicated | 1) FeCrAl; 2) Aluminum | Co | [98] |
| | 1) Honeycomb; 2) Honeycomb monolith | 1) Corrugated and rolled foils; 2) Extruded | Al | Co | [31] |
| | 1) Honeycomb; 2) Foam | 1) Corrugated and rolled foils; 2) Replicated | 1) FeCrAl; 2) Al | Co-Re | [43] |
| | Foam | - | Metal | Co | [99] |
| | Microfibers | Sintered | Cu, Ni, SS | Co | [15] |
| Glucose dehydration | Foam | Bubbling | Al | ZrPO | [100] |
| Hydrogenation of acetophenone ($C_8H_8O$) | Grids | - | 316L SS | Pd, Ru | [101] |
| Hydrogenation of 3-methyl-1-pentyin-3-ol | Foam | Replicated | Al | Pd | [102] |
| Methanation | Honeycomb | Extruded | FeCrAl | Ru | [103] |
| Methane partial oxidation | Honeycomb | Corrugated plates | FeCrAl | Pd | [104] |
| | Foam | Replicated | FeCrAl | Ni-MgO | [105] |
| | Foam | Replicated | Ni | Ni or Ce-Zr/Ni | [106] |
| | Honeycomb | Corrugated foils | FeCrAl | Pd | [107] |
| | Foam | Replicated | Ni | Ni/$MgAl_2O_4$ | [108] |
| Methane dry reforming | Foam | Replicated | Ni-Cr-Al | Ru, Rh, or Ni | [109] |
| | Honeycombs | Corrugated and rolled foils | FeCrAl | Ni | [110] |
| | Foam | Replicated | Ni-Cr-Al | Ru | [111] |
| | Foam | Replicated | Ni | Ce-Zr-Ni | [112] |

| | | | | | |
|---|---|---|---|---|---|
| Methane steam reforming | Honeycomb | Corrugated foils | Steel | Noble metals | [113] |
| | Foam | Replicated | Ni and Ni-Cr | La-Co | [114] |
| | Plate | - | Al/Cr-Alloy/Al | Ni | [115] |
| | Honeycomb | Corrugated plates | FeCrAl | Ni | [116] |
| | Plate | - | Al/Cr-Ni/Al | Ni | [117] |
| | Foam | Replicated | FeCrAl | Ni | [118] |
| | Honeycomb | Corrugated and rolled foils | FeCrAl | Ni | [30] |
| | Foam | Replicated | FeCrAl | Ni | [119] |
| | Foam | Replicated | FeCrAl | Ni | [39] |
| | Foam | Replicated | FeCrAl | 1) Ni; 2) Rh | [120] |
| | Foil | - | FeCrAl | Ni-Rh | [121] |
| Methanol steam reforming | 1) Foam, 2) foils | 1) Replicated, 2) corrugated | Al | Cu | [122] |
| | Plates | - | CrNiMo and CrNiMoTi SS | Cu-Cr | [123] |
| | Foam | Replicated + electrolysis | Cu | Cu-Zn | [38] |
| | Plate | - | Al | Cu | [124] |
| | Honeycomb | Packed plates | SS | 1) Cu/ZnO; 2) Pt | [125] |
| | Foam | Replicated | Ni, FeCrAl, Cu and CuZn | Zr-doped Cu/Zn/Al and Ni-doped Cu/Zn/Al | [126] |
| Methanol synthesis | Honeycomb | Corrugated and rolled foils | FeCrAl | Cu-Zn | [28] |
| Methanol-To-Olefin process | Honeycomb and foam | Not specified | Metal | Mg-ZSM-5 | [127] |
| $NH_3$ high-T decomposition | Honeycomb | Extruded | $TiO_2$ | $MnO_2$-CuO-$Fe_2O_3$ | [128] |
| Oxidative decomposition of o-DCB | Honeycomb | Packed sheets | Carbon steel | $V_2O_5/TiO_2$ | [129] |
| | Honeycomb | Packed sheets | SUS 316L | $V_2O_5/TiO_2$ | [130] |
| POX and OSR of propane | Honeycomb | Stacked and electron beam welded foils | 1) FeCrAl; 2) Rh | 1) Ni or Rh; 2) Rh | [131] |
| POX of n-hexadecane | Honeycomb | Corrugated and rolled foils | FeCrAl | Pd | [132] |
| SCR of $NO_x$ | Wire gauze | - | AISI 316 SS | Cu-ZSM-5 | [133] |
| | Plates | - | AISI 316 SS | ZSM-5 | [134] |
| | Plate | - | Al | Cu-Mn-$CeO_x$ or Pt | [135] |
| Soot combustion | Foam | Replicated | AISI 314 SS | Co,Ba,K/$ZrO_2$ | [42] |
| SR and POX of hydrocarbons | Sheet | Corrugated | Metal | Rh | [136] |
| Steam reforming of n- | Honeycomb | Corrugated and rolled | Kanthal | Ni | [137] |

| | | | | | |
|---|---|---|---|---|---|
| hexane | | foils | (FeCrAl) | | |
| Steam reforming of i-octane | Honeycomb | Packed platelets | Aluchrom (FeCrAl) | Ni | [138] |
| Toluene oxidation | Foam | Bubbling | Al | Pt-ZSM5 | [139] |
| VOCs oxidation | Foam | Bubbling | Al | Pt | [140] |
| WGS | Honeycomb | Packed platelets | ASTM 316Ti SS | Cu-Zn | [141] |
| Xylose dehydration | Foam | Bubbling | Al | MOR | [142] |

*Substrate geometry has been named as in the original cited manuscript.

## 3. Surface pre-treatment methods for metallic substrates

It is generally accepted that it is more difficult to adhere inorganic coatings to a metal than to a ceramic material. This is mainly due to both the different chemical composition and surface roughness of the two types of substrate [1]. Whereas ceramic substrates often possess a porous superficial structure ready to be coated as such, metallic ones need to be treated to increase superficial roughness, thus surface area, favouring better adhesion of the catalytic layer and extending the structured catalyst life time [33, 143]. The need of a proper surface pre-treatment before the deposition step to improve the coating adhesion is further justified by the higher probability of detaching and losing the catalytic layer due to the large expansion coefficient of metals, especially in high temperature operations [114, 118].

Several surface pretreatment procedures have been developed, mainly including *i)* anodic oxidation, *ii)* thermal oxidation, *iii)* chemical treatment and *iv)* primer deposition.

### *3.1 Anodic oxidation*

This method, usually applied to aluminum substrates [144, 145], is based on a well-known electrochemical process: the application of an electric field to an electrolyte in contact with an aluminum surface generates a porous oxide layer at the surface [144, 146]. The electrolyte is usually an acid, typically sulfuric acid. Burgos *et al.* [147] report that two main processes control the formation of the alumina layer, namely the generation of alumina and its redissolution. Higher anodisation times and current densities will generate more alumina, while higher electrolyte concentration, temperature and the same alumina layer growth will favour redissolution of the alumina.

A more sophisticated technique is the pulse current anodic oxidation, which consists in pulsing from high to lower voltage (e.g. 22 to 15 V) instead of using constant voltage as in typical anodic oxidation process. This method provides increased corrosion resistance and abrasion resistance, improved thickness uniformity and reduced total time required to produce a given thickness [148, 149].

Anodic oxidation may be used either as a pretreatment before another coating method [57, 76, 150], or as a way to obtain a thin porous layer that can be directly impregnated afterwards [71, 84, 151].

### 3.2 Thermal oxidation

Like anodic oxidation, thermal oxidation is not really a deposition method but a surface modification technique. This procedure mainly consists in modifying the metal surface by calcination in order to promote the segregation of a metal oxide layer on the surface of the substrate. Such a layer increases the specific surface of the structured substrate and avoids loss of coating material at high temperature, due to the different thermal expansion coefficients of the coating layer, mainly ceramic, and of the metal substrate. In some cases, the segregated oxide layer is resistant to oxygen diffusion and protects the underlying matrix against further degradation [152]. This is extremely important, for example, at the high temperature and humid conditions typical of catalytic combustions [153].

Thermal oxidation is usually applied to FeCrAl substrates. It may be used either as a pretreatment step to increase catalyst adhesion [49, 65, 89, 154-157] or to generate a catalyst support to be impregnated [131].

Typical thermal oxidation procedures on FeCrAl foams to be coated with a layer of Pd/$\gamma$-$Al_2O_3$ [65] involve calcination at 900°C for 10 h, to promote the migration of $\alpha$-$Al_2O_3$ to the surface with the consequent formation of a dense oxide layer. This results in a stronger affinity between the metal surface and the coating layer as well.

Catillon *et al*. [38] also adopted this technique for pretreating copper foams: they calcined their samples in air at 400°C for 3 min. However, it is worth mentioning that, contrary to bare aluminum or aluminum contained in FeCrAl alloy, the oxidation rate of Cu is too fast and no self-protective oxide layer forms to prevent further oxidation. Therefore, when heated up in air, metallic copper samples readily undergo bulk oxidation, thus degrading their thermo-electrical and mechanical properties [158].

### 3.3 Chemical treatment

It is usually applied to aluminum substrates, and it consists in dipping the substrates into an acidic solutions to increase the surface roughness and to favour the formation of an $Al_2O_3$ layer [69]. Visconti *et al*. [31] first immersed aluminum slabs in HCl solutions (37 wt.%) for 2 min at r.t. to increase the surface roughness and then in $HNO_3$ (65 wt.%) for 10 min at 80°C to favour the formation of a superficial $Al_2O_3$ layer. The HCl treatment was also used by Suknev *et al.* [159] to form a pseudo-layer accessible to chemisorption of small charged particles. At the end, the substrates are usually washed with acetone to remove the superficial impurities due to manipulation. However, chemical treatment of aluminum structured substrates with more complex geometries (e.g. honeycombs) may lead to the complete dissolution of the substrate, so that in some cases this treatment has been skipped [31].

Concerning other materials, Reymond [101] claims the use of HCl 12 wt.% for 20 min at 60°C to pre-treat AISI 316L SS grids, whereas Cui *et al.* [160] succeeded in etching and/or oxidating the surface of their titanium-based substrate by an alkali treatment. Substrates made of copper are instead not suitable for chemical etching, since copper violently reacts with $NH_3$, $HNO_3$ and HCl, giving the respective salts [161]. Nevertheless, Catillon *et al*. [38] claim a chemical pre-treatment step of their copper foam samples, but no detailed information concerning the procedure are available.

### *3.4 Primer deposition*

Even when the surface of the structured substrate is pretreated, according to the techniques described in previous sections, the chemical affinity between the substrate and the catalytic active phase may be still insufficient. In this case, typical coating procedures would result in scarce adhesion. This disadvantage may be overcome for instance by coating the substrate with an intermediate layer, commonly named *primer*, and depositing the catalytic material onto it [65, 72, 90, 143, 154, 162-164]. The primer layer, often made of silica or alumina, is usually prepared by dip-coating of the substrate in a colloidal dispersion of the precursor to be used as primer followed by a proper drying process [165].

Zhao *et al*. [154] deposited a boehmite (γ-AlOOH) primer to improve the adhesion between the coating layer and oxidized FeCrAl foils used as substrates. The boehmite sol was obtained by direct reaction between aluminum foils and 10 % hydrochloric acid. The sol was deposited on the FeCrAl foils by dip-coating (see section *4.1.1.2*), at constant withdrawal velocity of 3 cm/min. Coated samples were dried at room temperature for 30 min and calcined at 500°C for 3 h. The primer-coated foils were used as substrate for γ-$Al_2O_3$-based coated sample.

Valentini *et al.* [65] adopted instead a boehmite primer prepared by dispersing 10 wt.% of a commercial aluminum hydroxide powder in a 0.4 wt.% $HNO_3$ aqueous solution. After mixing for 10 min, a stable dispersion of boehmite was obtained. Afterwards, they dipped Al and FeCrAl slabs using that boehmite dispersion and a withdrawal speed of 3 cm/min. Dipped samples were dried at room temperature for 30 min. They reported the formation of a well adherent and uniform layer on the surface of all substrates. Tronconi *et al.* [72] and Visconti *et al.* [31] adopted the same recipe to deposit a boehmite primer layer onto their extruded copper and aluminum honeycomb monolith substrates, respectively.

## **4. Substrate catalytic activation techniques**

This section is focused on the most widely used techniques for activating metallic substrates by coating. For simplicity, we herein classify three main processes by which a pre-treated structured substrate may be catalytically activated: *i)* deposition of the morphologic support first and subsequent deposition of the active phase onto it; *ii)* direct deposition of a ready-made catalyst without any preliminary support deposition; *iii)* in-situ growing of the active phase. More attention will be paid to the first method, whereas only few indications will be given concerning the other two, since not many significant applications have been reported in the literature so far.

### *4.1 Morphologic support deposition and activation*

All the methods consisting in the combination of two distinct subsequent steps, i.e. one to deposit the morphologic support and the other to provide the coating layer with a catalytic functionality, are discussed in the following paragraphs. The former stage includes dip-coating, spray-coating, electrophoretic deposition and chemical vapour deposition. For the latter, impregnation, deposition-precipitation, ion exchange are possible.

#### *4.1.1 Support deposition*

##### *4.1.1.1 Wet coating techniques: dip-coating and spray-coating*

Wet coating techniques are the most versatile and easiest ones for producing coatings by depositing a liquid-like precursor onto a substrate that is converted to the desired coating material by subsequent post-treatment steps [166]. Amongst the variety of wet coating techniques, dip-coating is one of the most widely adopted for coating metallic structured substrates (see Table 3). The first step consists in filling the voids of the structured substrate with a liquid-like material (commonly a powder suspension or a sol-gel dispersion) by dipping. In a second step, the excess of fluid is typically eliminated by withdrawing the substrate from the liquid-like material at controlled speed (Fig. 6a). During this process, different opposite forces act on the fluid film during the extraction step: the gravitational force, attracting the film downward, and the viscous force which hinders its sliding [167, 168]. The thickness of the film deposited depends on the balance between the fluid viscosity and the withdrawal speed of the substrate [65]. In the case of a vertical flat slab, the Landau-Levich law [169] states that the resulting coating thickness is proportional to the product of the suspension viscosity and the withdrawal velocity, raised to the two thirds power [170, 171]. Therefore, the control of the fluid rheological behavior and of the withdrawal velocity reveals crucial in determing the final coating layer properties.

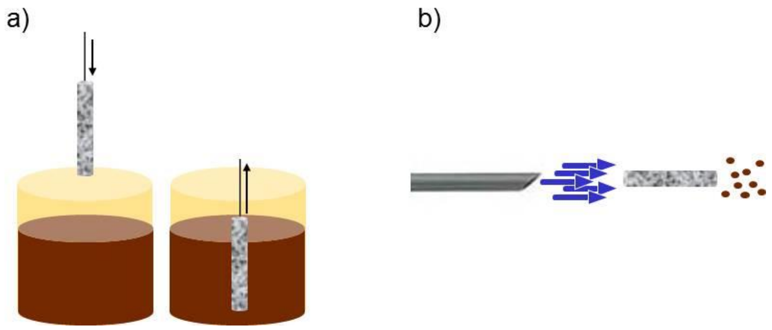

Figure 6 – The dip-coating (a) and blowing (b) procedure

The withdrawal technique, however, is suitable for simple substrate geometries (e.g. slabs), in which the viscous forces are the only ones opposing to the relative fluid movement. Indeed, more complicated geometries like e.g. spirals, honeycomb monoliths and open-cell foam, especially those having high relative densities, may induce capillary forces which prevent the excess fluid to flow out of the substrate channels/cells under the simple effect of the gravitational force. Blowing (also known as flow-coating) (Fig. 6b) is thereby used to drain the excess fluid off (the term “dip-blowing” comes from here) [61, 63, 73, 172] and is typically performed by applying an air jet (e.g. at 5 bar for 10 seconds [39]). In this case, the thickness of the deposited layer depends on the balance between the viscous force within the fluid (i.e. the rheological behaviour) and the shear stress applied by the gas flow. In turn, the shear stress depends on the specific (per unit surface) air flow adopted: this parameter can be modulated by the dimension of the nozzle of the spray gun and the upstream pressure of the compressed air. If blowing is performed, the use of fluids with lower viscosity than those used for simple dip-coating applications are required. The modulation of the viscosity can be obtained by proper tuning of the fluid composition [173].

Alternatively, centrifugation of the “wet” sample at 400 rpm for 10 min may be used to remove the excess fluid trapped in the structured substrate [75].

Starting from suspensions or sol-gel dispersions, an alternative method to dip-coating is spray-coating [174], intended as in its original version of spray painting, invented in 1892 but widely spread only after the 1920s with the automobile mass production line [175-178]. The basic principle of spray coating is to atomize the precursor contained in a suspension/dispersion into a fine spray by means of a jet of compressed air and subsequently direct the spray onto the surface to be coated [179]. The porous structure of sprayed coatings depends significantly on the jet outflow regime, which is strongly related to the rheology, the flow rate of the sprayed suspension/dispersion and the spraying distance. Spray-coating is fast, flexible and suitable for coating large surfaces [180]. Moreover, contrary to conventional dip-coating methods, the spraying technique allows one-side coatings. The rheological properties of the sprayed material greatly differ from those typical of conventional dip-coating methods, namely viscosity since the shear rate is many times larger during spraying than immersing [3]. Accordingly, *ad-hoc* suspension/dispersion recipes have to be developed and optimized.

The adoption of the spray-coating technique for coating metallic substrates is well established in the industrial practice, in the field of exhaust gas aftertreatment [181-183] and for other catalytic applications [127, 184, 185]. Other examples are reported by Chapman and Watton [89], who sprayed alumina sol onto FeCrAlY foils further impregnated with a noble metal catalyst to be used as catalytic converter for treating automotive exhaust gases, and by Schuessler *et al.* [186], who sprayed a suspension of alumina supported Pt over copper plates to be used in a fuel cell. Moreover, Gallo Stampino *et al.* [187] studied the effect of both the rheological behavior and the aerograph nozzle dimensions on the performaces of PEM fuel cells assembled with GDEs prepared by spraying a catalyst (30% Pt/C) suspension.

Screen printing technique can also be adopted. However, such a technique is suitable only for flat surfaces and is commonly applied in the case of microchannel rectors with complex channel geometry, for which coating of microchannel plates has been proposed before welding them to create the final device [188].

As stated above, the preparation of a precursor of the support (or catalyst) layer consisting of a liquid-like material with appropriate rheological behavior is a key step in all the wet deposition techniques. Two main methods are typically adopted for this purpose: *i*) the slurry route and *ii*) the sol-gel route.

#### *4.1.1.1.1 Slurry method*

The use of a suspension, commonly named *slurry*, is quite common in structured catalysts preparation and it can be applied on the preformed powders of both the morphologic support or the finished catalyst itself.

A properly sized powder, binder, dispersant that can be acid (usually nitric acid, but also citric or acetic acid) or surfactant, and a solvent are the typical ingredients, whose concentrations may largely vary, primarily depending on the nature of the solid to be suspended and the required rheological behavior.

The selected solvent depends on the material to be coated. For most materials, deionied water is preferred due to its availability, low price and easy handling. Alternatively, organic solvents like ethanol, higher alchools, diethylether, ethylacetate or butylacetate may be preferred to achieve good slurry stability.

The recipe of the suspension (e.g. water/powder ratio, acid/powder ratio, dispersant content), and thereby its rheological behavior, particularly in terms of slurry viscosity, strongly affects the coating performances [65, 189, 190]. Indeed, low viscosity values promote good adhesion but low loadings are obtained, whereas high viscosity induces high catalyst loading but poor adhesion [65]. Rheological measurements have shown that typical slurries for dip-coating exhibit a non-Newtonian (shear-thinning) behavior, being the viscosity decreasing on increasing the shear rate. Examples of slurry viscosities are 10-0.01 Pa·s at 10-500 $s^{-1}$ of shear rate [31, 65].

Acids are typically employed as dispersant to stabilize slurries and properly tune their rheology via powder surface charging. In this case, the operating pH directly influences the rheological behavior and stability of the suspension. A similar effect is found for the solid concentration. Generally, once the $H_2O$/powder ratio is fixed, more acidic suspensions result in higher viscosity due to a higher concentration of suspended powders [31, 65]. However, a threshold value, corresponding to the maximum surface charging of that particle, exists beyond which no further improvement in the solid dispersion may be achieved. Accordingly, an increase in the viscosity, observed upon further acid addition, has been related to acid-catalyzed cross-linking reactions inside the slurry [173]. Typical values of $H_2O$/powder ratio range between 1.5 and 4 g/g [31, 65, 141], whereas acid/powder ratios usually stay between 1 and 4 mmol/g [31, 65].

In some cases, however, acidic additions to the slurry are not suitable. Indeed, acidic attacks may cause significant chemical transformations of the catalyst powder. For instance, $Cu/ZnO/Al_2O_3$-based catalysts readily react with nitric acid, causing a loss of active metals in the form of dissolved nitrates [161]. To estimate the amount of dissolved ions, chemical analysis of mother liquors is commonly done after slurry ultracentrifugation and ultrafiltration. In other cases the addition of acid is responsible for structural changes in the catalyst. In this regard, Germani *et al.* [141] found that a small addition of acetic acid (0.01 g acid/g $H_2O$) to the slurry of a Cu/Zn/Al catalyst causes loss of copper dispersion due to the reaction between the acid and the smaller copper crystallites, removing part of the copper from the catalyst surface and redepositing it as larger particles upon drying. Therefore, alternative routes to promote slurry stability and to obtain suitable rheologies for deposition have to be found.

For example, small amounts (typically 2% of the total solids weight) of additives may be added to promote slurry stability. For instance, long-chain surfactants containing hydrophilic and hydrophobic groups, like polyethylene glycol, polyethylene imine, Triton X-100 [191], adsorb on the catalyst surface leading to steric stabilization of the slurry. Some of them are also used as rheology modifiers like e.g. isopropyl alcohol, polyvinyl alcohol, polyvinylpyrrolidone, ammonium methacrylate, methylhydroxyethyl cellulose [28, 125, 141]. As an alternative to organic compounds, inorganic colloids (e.g. alumina, silica) may also be used as thickeners. The thickening effect depends not only on the molecular weight, but also on the additive chemical structure. Furthermore, it has to be considered that surfactants, thickeners and other additives may present competitive and synergic mechanisms, making difficult the prediction of the behavior of such complex mixtures. For instance, it is well known in the literature that small additions of PVA [192] or methylhydroxyethyl cellulose [161] in an aqueous slurry cause significant air bubble entrapment, which may affect the slurry rheology.

After being selected, the slurry ingredients are usually milled for some hours in a rotating jar at constant velocity (e.g. 50 rpm [173]) and ambient temperature (ball-milling procedure). Zirconium oxide spheres are typically added to the mixture as grinding bodies, with a $ZrO_2$/powder ratio usually between 4 and 8 g/g [31, 173, 193]. The process is aimed at reducing the powder particle size from several tens (i.e. typical average size of commercial powdered catalysts or catalyst morphologic supports [141]) to few (i.e. 2-10) microns [3], usually passing through a change in the form of the distribution (i.e. bimodal/monomodal) [173]. This typically leads to satisfactory adhesion and endurance of the coating material [189]. On the other hand, it should be noted that smaller particles lead to more viscous slurries: after deposition, they may form a dense layer with small pores in which diffusional limitations may become noticeable [5].

The ball-milling process lasts for about 24 hours [31, 193], after which no more changes in the particle size distribution take place [161]. It is worth mentioning that this technique involves a strong mechanical action and therefore, when applied to catalytic materials, it may result detrimental for the catalyst activity, due to changes in the surface area or porosity, that have to be verified [141]. Alternatively, the catalytic powder may be added to the slurry, the ingredients being mixed together using a mild agitation without grinding bodies. Since in these cases the coating is carried out using relatively large particles, the contact surface between these particles and the substrate is usually small. Therefore, a binder, preferably colloidal silica/alumina, pseudo-boehmite or waterglass ($Na_2SiO_3$), is often added to increase the contact surface. Alumina has the advantage that it is more thermostable than silica, which may be attacked by steaming in high-temperature applications. On the other hand, alumina may introduce acidity into the system, making the use of a silica binder more favorable for some applications. For instance, Zwinkels *et al.* [194] coated FeCrAl foils with colloidal silica sol containing the catalyst precursor (i.e. ZSM-5 powder). Catillon *et al.* [38], instead, immersed copper foams in a colloidal solution containing acidified alumina sol and alumina powder.

Colloidal solutions may be added before milling, but in the case of pseudo-boehmite or waterglass it is recommended to add them after the milling process because these binders increase the slurry viscosity [5]. Furthermore, the size of the binder particles has to be carefully controlled: if they are similar or smaller than the micropores of the catalyst to be coated, the catalyst pores might be blocked by the binder particles and the catalyst would lose efficiency. This poses a strict limit on the minimum usable size for the binder particles.

Since only small amounts of permanent binder are generally used, the interaction between particles and substrate is relatively weak until the binder particles are “melted” in between the larger particles during the calcination step [5]. Therefore, a temporary thickener/surfactant may be added to suitably tune the suspension rheology and promote the adhesion of the coating layer to the monolith after deposition and before calcination. During calcination, this compound is then burned off.

Several instruments and analytical techniques come into help during the optimization of the slurry recipe. For instance, the slurries rheological behavior may be analyzed by means of a rotational rheometer [65]. The granulometry of catalyst particles dispersed in the slurry may be accurately measured by a laser particle size analyzer [31, 173]. The evaluation of the surface charging to optimize the amount of acid to be added to the slurry may be done via acid titration [173] or zeta-potential measurements [195].

When the dispersion is ready for deposition, the substrate (pre-coated with a primer, if required – see section *3.4*) is dipped into the slurry for some seconds and then withdrawn. If required, a blowing step may also be performed. Drying and calcination then follow (see section *5*).

Typical average thicknesses obtained by using the slurry method range from few to several tens of microns, which correspond to specific loads (i.e. loading/exposed substrate surface) in the order of 1-100 $g/m^2$ [3, 28]. Noteworthy, in the existing literature, loadings expressed as wt.% are usually preferred due to the simplicity associated with their measurement. However, these values are misleading when comparing the loadings deposited onto different substrate materials. Indeed, in this case, identical coating layers deposited onto substrate materials with the same geometry but different densities would result in different wt.% loadings, which are meaningless form the catalytic point of view.

If higher catalyst loadings are required (e.g. in the case of slow reactions), the coating procedure may be repeated, so to obtain multiple coating layers. The number of multiple depositions is however limited by the adhesion quality of the coated materials [65, 76, 100, 143].

#### *4.1.1.1.2 Sol-gel method*

In the “sol-gel method” the starting point is a colloidal dispersion (hence the alternative name of colloidal coating) of a chemical precursor of the coating material (e.g. pseudo-boehmite, usually diluted in nitric acid, as precursor of $\gamma$-$Al_2O_3$).

A typical procedure for coating a monolith in this manner is to prepare the dispersion (i.e. the sol) starting from inorganic or metal-organic precursors of the solid to be coated (e.g. hydrated aluminum oxides, like pseudo-boehmite or boehmite, aluminum alkoxides or aluminum chloride + aluminum). Depending on the precursor, deionized water is added as solvent or reactant. Some chemicals are sometimes added to adjust stability and/or viscosity. For example, nitric acid is added by Chapman and Watton to stabilize an aqueous sol made of colloidal alfa alumina monohydrate [89]. The addition of polyvinyl alcohol (PVA) as thickener is also possible [38, 86].

The peptization of the sol can be controlled by tuning its composition (e.g. acid content) or ageing time. This step is crucial because it influences the final viscosity of the dispersion. Indeed, high viscosities enable the deposition of thicker layers, but they are prone to cracks. Gel formation process, which may last from a few minutes to several weeks, depending on the particles concentrations and size in the sol, has to be avoided in view of the solid nature of the gel. Accordingly, a trade-off has to be found for each case.

When the colloid is ready for deposition (i.e. the right rehelogical behavior has been obtained), the monolith is then submerged in it for a few seconds and, analogously to the slurry method, withdrawn at controlled speed [73, 86, 194]. If required, the excess material deposited on the coated monolith may be blown out by an air jet [73] or by centrifugation [76]. The coated substrates are eventually dried and calcined (see section *5*).

Similar, or even thinner, layer thicknesses to those found in structured substrates coated by using the slurry method are obtained. Furthermore, more uniform coating deposition and better adhesion are typically found [73].

One of the most common drawback of the use of both slurries and sol-gel dispersions is related to adhesion performances of the coated layer, that depends on many parameters such as nature and geometry of the substrates, nature of the coated material, solid concentration, thickness of the layer and, last but not least, thermal treatment. Cracks may form, which may bring to possible coating layer detachment upon use. This is, for instance, the case of the application of structured reactors in liquid phase reactions where the liquid flowing in the channels/pores of the structured catalyst may erode the coating layer or react with it [101].

Besides, the use of slurries, and in some case even dispersions, does not allow the achievement of thin or dense layers that are required in particular applications. For these reasons, alternative techniques such as thermal spraying, EPD or CVD have been developed (see sections *4.1.1.2-.3-.4*). Electrochemical deposition (ECD) is also possible. In this regard, Stefanov *et al.* [196] adopted such a technique to obtain a layer of porous $ZrO_2$ onto FeCrNi foils. Details on such technique, which is usually adopted for in situ active phase growing onto metallic substrates, are given in section *4.3.1*.

### *4.1.1.2 Thermal spraying*

Amongst the more sophisticated spraying techniques which include cold-spraying, warm spraying, plasma spraying, high velocity oxy-fuel (HVOF) spraying, one of the most promising in the field of metallic structured catalysts preparation is plasma spraying [93, 197, 198]. Developed in the 1970s, plasma spraying is an evolution of the conventional spray-coating technique and makes use of a high-temperature plasma jet generated by arc discharge with typical temperatures higher than 15000K (Fig. 7), which melts the sprayed particles and makes it possible to prepare solid surface coatings (made of alumina, titania, zirconia, etc.) on metals with high mechanical and thermal stabilities [197].

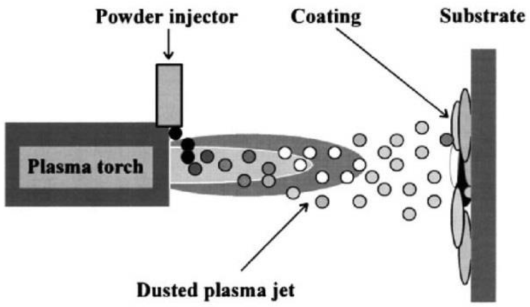

Figure 7 – Plasma spray coating technique (reprinted from [197] with permission from RSC)

The plasma spray method allows the design composite materials consisting of different combinations of plasma-sprayed catalytic and protective layers. Moreover, there are minor limitations on the complexity of the monolithic substrate geometry [197]. In addition to the variables already involved in conventional spray-coating technique, the plasma torch power, typically ranging between 200-250 A and 180-270 V [197], plays an important role in determining the coating performances as well.

Wu *et al.* [93] used both plasma spraying and dip-coating methods to coat FeCrAl mesh. The same thickness was obtained with both methods, but starting from different suspensions: suspended alumina with polyvinyl alcohol and water for plasma-spray coating, suspended alumina in a boehmite sol (hybrid method) for dip-coating. The spray-coated layer had thicknesses in the 10-50 microns range and was found more adherent. Another example of plasma spraying is provided by Ismagilov *et al.* [197], who adopted this technique for spraying alumina layers onto titanium plates and nickel foams finding a strong and uniform coating adhesion to the metal surface. The coated foams were subsequently impregnated with lanthanum and cobalt and tested in the methane oxidation reaction.

### *4.1.1.3 Electrophoretic deposition (EPD)*

Electrophoretic deposition (EPD) is a process wherein a DC electric field is applied across a stable colloidal solution or suspension of charged particles attracting them to an oppositely charged electrode [199]. One electrode (cathode) consists of the substrate to coat, the anode being either an aluminum [150] or stainless steel [130] foil. The set-up used in such process is depicted in Fig. 8 in the case of a structured substrate consisting of a wire mesh.

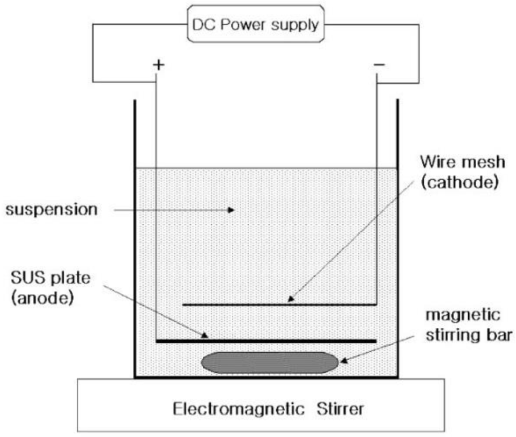

Figure 8 - Electrophoretic deposition (reprinted from [130] with permission from RSC)

The thickness of the coating depends on the distance between the two electrodes, on the DC voltage, on the properties of the suspension (e.g. pH) and on the duration of the deposition. EPD is an inexpensive and simple method, characterized by short times for the coating formation [150]. This technique may be used to obtain a highly porous coating layer. Vorob'eva *et al.* [150], for example, used alumina sol (from hydrolysis of aluminum isopropoxide) for particle suspension during electrophoretic deposition. After drying and calcination, they obtained a very regular layer of aluminum oxide on their stainless steel gauze, with a high BET surface area.

EPD may be also used to deposit a pre-coating layer to favour the adhesion of a catalytic layer deposited in a second time by a conventional dip-coating method [130, 200]. For example, Yang *et al.* [130] used an aluminum powder composed by particles of 5 μm average diameter as starting material for preparing the suspension. Polyacrylic acid and aluminum isopropoxide were used as additives both to improve the adhesion of aluminum particles and to control the suspension conductivity. They claimed to have deposited 100–120 μm thick aluminum layers onto stainless steel wire mesh by EPD, further oxidized to form a porous $Al_2O_3$ layer. The wire mesh sheets were then alternately packed in a honeycomb-type module and coated with $V_2O_5/TiO_2$ catalyst by the conventional slurry-coating procedure.

EPD was also used by Slovetskaya and Kustov [51] for the direct deposition of a suspension containing activated zeolites (Pd, Mn, Co/ZSM-5) and aluminum hydroxide sol as binder on FeCrAl foil.

### *4.1.1.4 Chemical vapour deposition (CVD)*

In the chemical vapour deposition (CVD) process, the substrate is placed inside a reactor chamber to which a number of gases - including the catalyst precursor, an inert gas (usually $N_2$) and, in some cases, $O_2$ - are supplied [3] (Fig. 9). The chemical precursor may be the same one used in sol–gel methods (e.g. metal alkoxides), but no solvent is required. The fundamental principle of the process is that a chemical reaction takes place between the source gases. The product of that reaction is a solid material which deposits as a very thin layer on all surfaces inside the reactor chamber. To enhance the deposition rate, the use of low pressures (in the order of mbar) and high temperatures (several hundreds degrees) may be required.

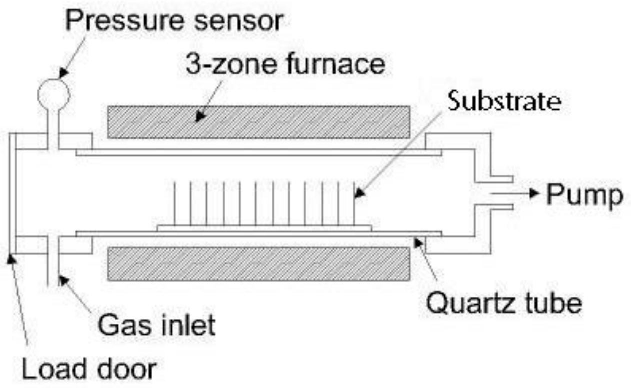

Figure 9 - Typical CVD apparatus [201]

CVD may be used to deposit a porous layer (i.e. the morphologic support) before its activation [41, 79]. For example, aluminum isopropoxide was used by Janicke *et al.* [79] for the production of aluminum oxide coatings in stainless steel micro-channels, before the impregnation with a platinum precursor.

For completion, it is worth mentioning that ALD (atomic layer deposition) is a modification to the CVD process consisting in feeding the precursors as alternate pulses separated by inert gas purging. The thickness of the deposited layer linearly depends on the number of cycles. This modern method grants more uniform films than conventional CVD techniques. For example, such a technique was adopted by Mies *et al.* [202] to deposit an intermediate oxide film before zeolite deposition on Molybdenum foils and by Yang *et al.* [99] to deposit an $Al_2O_3$ thin film on a metal foam prior to dip-coating in a Co-based slurry.

It is worth noticing that the most suitable support deposition technique has to be chosen in function of the substrate geometry. Specifically, techniques such as thermal spraying or EPD are mostly applicable to flat or corrugated surfaces, whereas dip-coating and CVD are capable to provide homogeneous coatings even in the case of complex 3D structures such as honeycomb monoliths or open-cell foams (Table 2).

Table 2 – Critical aspects related to the most widely adopted support deposition techniques onto metallic substrates characterized by different geometries

| | **Flat or corrugated surfaces** | **Pre-formed (e.g. extruded) honeycomb monoliths** | **Open-cell foams, wire meshes or similar** |
|---|---|---|---|
| Dip-coating | Applicable | Accumulation at channels corners | Risk of pore blocking |
| Thermal spraying | Applicable | Not applicable in the case of very small channels | Risk of disomogeneities |
| EPD | Applicable | Risk of disomogeneities | Risk of disomogeneities |
| CVD | Applicable | Require a careful optimization of process conditions | Require a careful optimization of process conditions |

### *4.1.2 Support activation*

To this category belong all the techniques for depositing the active phase precursor onto the substrate (usually pre-coated with a layer of ceramic support, e.g. alumina), thus activating it. Impregnation, deposition-precipitation, ion exchange, electrochemical deposition (ECD) and electroless plating (ELP) techniques are usually adopted when dealing with metallic substrates. Amongst these techniques, impregnation is the most widely used for both metallic honeycomb monoliths and open-cell foams (see Table 4) due to its simplicity and effectiveness.

#### *4.1.2.1 Impregnation*

The term *impregnation* refers to that process in which a physical contact between the support to be impregnated and a liquid solution containing the catalytically active phase is promoted to favor the migration of the liquid phase onto the support thanks to chemico-physical interactions. Most of the time, the impregnation follows either an anodisation step, an oxide deposition or other methods to obtain a porous support onto metallic structured substrates [203].

Two methods of contacting may be distinguished, depending on the solution volume: wet impregnation and incipient wetness impregnation.

Wet impregnation, usually adopted at the industrial scale to activate pelletized catalysts, is the procedure generally implemented at the lab scale to catalytically activate a structured support as well. It consists in immersing the substrate – generally for 3-4 hours - in a diluted solution in which the active phase precursor (often a salt of the active metal) is dissolved [45, 50, 79, 89, 90, 128].

After withdrawal, excess liquid is blown out by using pressurized air. When the substrate is still wet, it should be kept in a horizontal position while continuously being rotated to prevent gravity from causing maldistribution. Drying and calcination usually follow to remove the imbibed solvent and impurities and to form the catalytically active species.

The amount of active phase precursor to be added to the impregnating solution is calculated to achieve a desired active phase loading, assuming that the precursor in the solution is entirely transferred to the support at the end of the process. The actual amount of active phase deposited is usually determined *a posteriori* by means of elemental chemical analysis of the residual impregnating solution.

Incipient wetness impregnation, or dry impregnation, consists in preparing an amount of solution containing the active phase to be deposited equal to the pore volume of the support to be impregnated and in impregnating it drop by drop until the whole pore volume is filled [71, 129, 197].

As a result, dry impregnation allows the deposition of all the active phase contained in the solution without any loss. The operation must be accurately controlled and, since the maximum active phase loading is limited by the solubility of the precursor in the solution, repeated applications of the solution may be necessary.

Such a technique is easily feasible if the support to be activated is in the form of powder or pellets, since it may be kept under stirring during impregnation, letting the active phase being uniformly deposited on it. However, some works have been published concerning dry impregnation over structured substrates as well [71, 123, 197]. Like for wet impregnation, drying and calcination usually follow.

For both impregnation methods, temperature is the main operating variable, influencing both the precursor solubility and the solution viscosity and, as a consequence, the wetting time. The concentration profile of the impregnated compound along the penetration coordinate depends on the mass transfer rates within the pores during impregnation and drying. The faster the rate, the flatter the concentration profile. In case of very slow mass transfer rates, on the contrary, egg-shell profiles with the active phase concentrated only near the outer surface of the impregnated support are obtained.

#### *4.1.2.2 Deposition-precipitation*

Instead of impregnating the support with a solution of the catalyst precursor and inducing the decomposition of this latter species during the final thermal treatments, the catalyst precursor may be transferred from the solution to the support by means of a controlled precipitation. This method, named deposition-precipitation, has the advantage that an insoluble salt of the catalyst precursor is deposited as a result of the precipitation step, which can no longer move during following thermal treatments [5].

Two consecutive processes are mainly involved in the deposition-precipitation method [38, 204-207]: *i)* precipitation from the bulk solution or from the fluid inside pores; *ii)* interaction with the support. In the first step, solutions are formed using the precursor salt in sufficient amounts to give the desired active phase loading (under the hypothesis that the active phase dissolved in the solution is entirely transferred to the support), then a precipitating agent (often an alkali solution) is added to the solution causing the salt precipitation. It is crucial that precipitation in the bulk solution is avoided, since it would give rise to deposition of big particles outside the pores of the support, thus resulting in a poorly active catalytic material. Accordingly, the nucleation rate must be higher at the support surface than in the bulk solution and the homogeneity of the solution must be preserved. A possible method to obtain uniform precipitation is to use the hydrolysis of urea as a source of OH− instead of conventional alkali [5, 38]. Urea dissolves in water and decomposes slowly at ca. 90°C, giving a uniform concentration of OH− in both the bulk and pore solutions. Thus the precipitation occurs evenly over the support surface, making the use of urea the preferred method for active phase loadings in excess of 10–20 wt.%.

#### *4.1.2.3 Ion exchange*

It consists in replacing an ion of the support with another ion species contained in a contacting solution via electrostatic interaction. To obtain the ion exchange, the support containing ions A is plunged into an excess volume (compared to its pore volume) of a solution containing ions B. Ions B gradually penetrate into the pores of the support, while ions A pass into the solution until equilibrium is established corresponding to a given distribution of the two ions between the solid and the solution [4, 133, 208].

In general, all ion-exchange procedures successfully adopted for pelletized catalysts may also be used to prepare structured catalysts. For these preparations, the circulation of liquid through the monolith, necessary if the amount of liquid exceeds the monolith empty volume, grants homogeneous distributions [5, 102]. The advantage of the ion-exchange deposition procedure for metal catalysts is that the metal interacts with the support thus ruling out maldistribution problems. Indeed, when such ion-support interactions are not sufficiently strong, movement of the exchanged ion may occur during thermal treatments, thus influencing the active phase distribution.

### *4.2 Ready-made catalyst deposition*

Although the active phase and the morphologic support are usually deposited separately on a monolithic body, these two steps may be combined. This is the case when, for example, an optimized supported catalyst formulation is available and a proper technique to deposit it on a metallic structured substrate has to be developed [31, 141, 209]. For such cases, the slurry method is usually adopted, but the slurry recipe and the deposition technique should be optimized as a function of the catalyst properties (see section *4.1.1.1.1*).

### *4.3 In-situ active phase growing and other coating techniques*

In-situ growing groups all those methods in which the catalyst, or its precursor, is let growing directly onto the carrier. The main advantage is the possibility to support the catalyst directly onto the substrate without the presence of any binder that may hinder the accessibility of reactants to the active phase [5]. Furthermore, a stronger coating adhesion is usually obtained [1]. However, such techniques are considerably more complex to be carried out than the most common coating procedures [5].

These methods find a particular application in the case of zeolites, whose direct synthesis onto different types of substrates [5, 133, 134, 210-212] is gaining importance, especially for membrane applications (Table 5). Indeed, applying the zeolite crystals by dip-coating would result indeed in a coating consisting of randomly oriented zeolite crystal layers, whereas the in-situ growing allows complete coverage of an oriented zeolite crystal layer, thus enabling a well-defined morphological structure of the zeolite itself [133, 213]. For example, Mintova *et al.* [214] reported the synthesis of SAPO-5, Sil-1 and Zeolite Y on copper and steel substrates. Mies *et al.* [202] coated instead molybdenum-containing plates with ZSM-5. Jansen *et al.* well reviewed this technique: we refer to their work for further details [133].

Amongst the in-situ growing techniques, electrochemical deposition (ECD) and electroless plating (ELP) are the most relevant. In some cases, EPD and CVD, already presented in sections *4.1.1.3-.4* as support deposition techniques, can be also applied. More details on these specific techniques can be found in [3].

Alternative coating techniques have been also proposed for metallic substrates. They include: *i)* carbon nanotubes deposition [215, 216] and *ii)* sputtering [83]. However, limited applications still exist in the literature concerning these methods. Accordingly, they will not be further discussed within this review paper.

### *4.3.1 Electrochemical deposition (ECD) and electroless plating (ELP)*

Both electrochemical deposition (ECD) and electroless plating (ELP) use ionic solutions. The first method, also called ‘‘electroplating’’ or simply ‘‘electrodeposition’’, usually produces metallic coatings by the action of electric current (typical voltages are in the order of 3-9V) [6, 69, 83, 84, 95, 118]. The deposition of a metallic coating onto an object is achieved by letting moving the positively charged metal ions present in the medium solution to the negatively charged electrode (cathode) that consists in the substrate to be coated (Fig. 10). When this occurs, the negatively charged cathode provides electrons to reduce the positively charged ions to their metallic form.

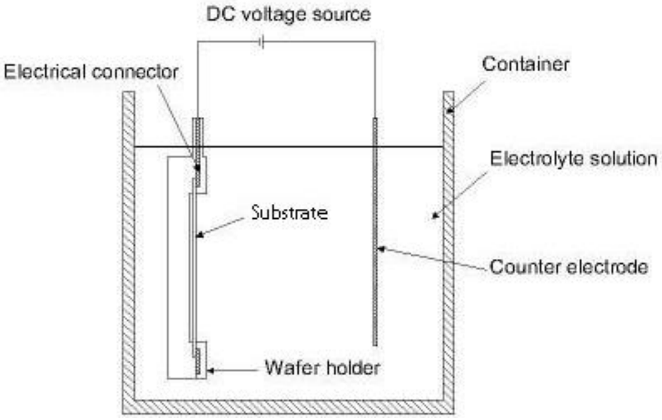

Figure 10 - Electrochemical deposition apparatus [201]

Similarly to ECD, electroless plating (ELP) uses instead a redox reaction to deposit a metal onto a substrate without the passage of an electric current [124, 217]. The deposition of the metal is accomplished by the chemical reduction of metallic ions in an aqueous solution containing a reducing agent [101]. The metal to be deposited has to be more electropositive than the substrate. This redox process is similar to a galvanic process (anodic and cathodic reactions take place in the mechanism), the electron supply being the chemical reducing agent.

According to this method, Reymond [101] deposited layers of Pd an Ru over 316L SS grids using $PdCl_2$ and $RuCl_2$ as metal precursors and sodium hypophosphite or sodium borohydride as reducing agents, respectively. Fukuhara *et al.* [124] prepared instead a copper-based catalyst on an aluminum plate. The plate was first immersed in a zinc oxide plating bath to displace surface aluminum with zinc. Subsequently, the plate was immersed in plating baths of iron. Finally, it was immersed in a copper plating bath based on $Cu(NO_3)_2$. The bath contained a formaldehyde solution as reducing agent. These successive plating steps provided a better adhesion of the coated layers to the substrate because of small differences between standard potential electrodes.

Table 3 – Support deposition techniques onto metallic substrates

| **Support deposition method** | **Substrate geometry and material** | **Support material** | **Reference** |
|---|---|---|---|
| Dip-coating by slurry method | Pre-oxidized FeCrAl plate | $Al_2O_3$ | [90] |
| | Metallic honeycomb | $BaO-Al_2O_3$ or $SrO-Al_2O_3$ | [218] |
| | Pre-oxidized metallic monolith | $\gamma$- $Al_2O_3$/La/ $Mn(NO_3)_2$/urea/ $Pt((NO)_3)_4$ | [63] |
| | Aluminum foam | Commercial Cu-based methanol reforming catalyst | [122] |
| | Pre-oxidized FeCrAl wire | $Al_2O_3$ mixed powders | [93] |
| | Pre-oxidized FeCrAl and Al slabs | $Al_2O_3$ | [65] |
| | Corrugated and rolled up steel foils | Co-Re/$Al_2O_3$ | [96] |
| | Pre-oxidized carbon steel wire-mesh honeycomb | $TiO_2$ | [129] |
| | Alumina-coated SS foam | Co/$Al_2O_3$ | [97] |
| | Pre-oxidized SS plates | $Al_2O_3$ | [123] |
| | Al/$Al_2O_3$-coated SS | Pd/$TiO_2$ | [200] |

| | | |
|---|---|---|
| wire mesh | | |
| Ni-Cr-Al foam | $\gamma$-$Al_2O_3$ | [109] |
| Pre-oxidized corrugated rolled up FeCrAl plate | Pd-Ru/Ce-$Al_2O_3$ | [104] |
| Pre-oxidized FeCrAl foils | $Al_2O_3$ | [154] |
| Pre-oxidized $Al_2O_3$-coated SUS 316L wire mesh honeycomb | $V_2O_5/TiO_2$ | [130] |
| Pre-oxidized FeCrAl foils | Ce-Cu-O-$\gamma$-$Al_2O_3$ | [53] |
| Pre-oxidized FeCrAl foam | Pt/$\gamma$-$Al_2O_3$ | [40] |
| $Al_2O_3$-coated $TiO_2$/SS 316L plates | $TiO_2$ | [219] |
| $ZrO_2$-coated SS packed plates | 1) Cu/ZnO/$Al_2O_3$/$ZrO_2$;<br>2) Pt/$ZrO_2$ | [125] |
| $Al_2O_3/TiO_2/La_2O_3$-coated corrugated FeCrAl foils | $LaMnO_3$ or $LaCoO_3$ | [56] |
| $Al_2O_3$-coated FeCrAl foils | $Al_2O_3$ | [220] |
| Pre-oxidized corrugated FeCrAl sheets and Al foam | Co/$\gamma$-$Al_2O_3$ | [98] |
| Pre-oxidized FeCrAl plates | Ni/MgO/$Al_2O_3$ | [116] |
| Pre-oxidized FeCrAl foils | Alumina-$Ce_{0.68}Zr_{0.32}O_2$ | [221] |
| Pre-oxidized Aluchrom (FeCrAl) packed platelets | $Al_2O_3$ | [222] |
| Pre-oxidized ASTM 316Ti SS packed platelets | CuO/ZnO/$Al_2O_3$ | [141] |
| Alumina-coated Ni, FeCrAl, Cu and CuZn foams | Zr-doped Cu/Zn/Al and Ni-doped Cu/Zn/Al | [126] |
| Pre-oxidized FeCrAl plate | Pd/$\gamma$-$Al_2O_3$ | [107] |
| Pre-oxidized corrugated and rolled up Al sheets | $LaMnO_3$ | [57] |
| Pre-oxidized Al foam | Pt-ZSM5 | [139] |
| Pre-oxidized corrugated and rolled up FeCrAl | MnCu | [82] |

| | | | |
|---|---|---|---|
| | foils | | |
| | Pre-oxidized corrugated and rolled up FeCrAl foils | Au/B-AlFe(10) | [77] |
| | $SiO_2$/SS foam | $TiO_2$ | [41] |
| | Pre-oxidized corrugated and rolled up FeCrAl plates | Pd/$\gamma$-$Al_2O_3$ | [132] |
| | Corrugated and rolled up FeCrAl sheets | $CuO/ZnO/Al_2O_3$ | [28] |
| | Pre-oxidized corrugated and rolled up FeCrAl foils and Al foam | Co-Re/$\gamma$-$Al_2O_3$ | [43] |
| | Pre-oxidized Al foam | $\gamma$-$Al_2O_3$ | [102] |
| | Alumina-coated metal foam | $Co/Al_2O_3$ | [99] |
| | Pre-oxidized Al foam | ZrPO | [100] |
| | Pre-oxidized Al foam | MOR | [142] |
| Dip-coating by sol-gel method | FeCrAlY spiral or wire | $Al_2O_3$ | [86] |
| | Pre-oxidized FeCrAl foil | $\gamma$-$Al_2O_3$ | [89] |
| | Pre-oxidized Fe-Al honeycomb | Colloidal alumina, rare earth oxide, silica and zirconia | [223] |
| | Pre-oxidized alumina-coated FeCrAl foil | ZSM-5 | [194] |
| | Pre-oxidized corrugated FeCrAl foils | $Al_2O_3$ | [52] |
| | Pre-oxidized copper foam | $Al_2O_3$ | [38] |
| | Pre-oxidized FeCrAl foam | $Al_2O_3$ | [73] |
| | Pre-oxidized SS 316L plates | $TiO_2$ | [219] |
| | $TiO_2/TiO_2$/SS 316L plates | $VO_x$ | [219] |
| | SS packed plates | $ZrO_2$ | [125] |
| | Pre-oxidized corrugated FeCrAl and AISI 304 SS foils | $Mn/Al_2O_3$ | [81] |
| | corrugated FeCrAl foils | $Al_2O_3$-$TiO_2$-$La_2O_3$ | [56] |
| | Pre-oxidized FeCrAl foils | $Al_2O_3$ | [220] |
| | Ni, pre-oxidized | $Al_2O_3$ | [126] |

| | | | |
|---|---|---|---|
| | FeCrAl, Cu and CuZn foams | | |
| | Pre-oxidized AISI 304 SS | $Au/Ce/Al_2O_3$ | [75] |
| | Pre-oxidized corrugated and rolled up Al foils | Au/Ce | [76] |
| | Pre-oxidized AISI 314 SS foam | $ZrO_2$ | [42] |
| | Pre-oxidized corrugated and rolled FeCrAl and Al up foils | $Al_2O_3$ | [66] |
| | $TiO_2/SiO_2$/SS foam | $VO_x$ | [41] |
| Spray-coating | FeCrAl, SS monoliths | Base metal catalyst | [182] |
| | Extruded/corrugated metallic monoliths | Co | [184] |
| | Metallic monoliths | Pd,Rh,Ce,La/ $Al_2O_3$ | [185] |
| | Metallic mesh/screen | $V_2O_5$-$WO_3$/$TiO_2$ | [183] |
| | Mg, Ni, Co, Fe, Ag, Cu, Al honeycomb monolith | $Pt/Al_2O_3$ | [181] |
| | Metallic honeycomb or foam monoliths | Mg-ZSM-5 | [127] |
| | Pre-oxidized FeCrAl foil | $\gamma$-$Al_2O_3$ | [89] |
| | Cu plates | $Pt/Al_2O_3$ | [186] |
| Thermal spraying | Pre-oxidized FeCrAl wire | $Al_2O_3$-$TiO_2$ and $Al_2O_3$ mixed powders | [93] |
| | Pre-oxidized Fe-Cr foil | Ni-Rh/$Al_2O_3$ | [121] |
| | Ti plates and Ni foam | $Al_2O_3$ powder | [197] |
| EPD | Pre-oxidized SS wire | $Al_2O_3$ | [150] |
| | Corrugated SS wire-mesh sheets | $Al/Al_2O_3$ | [200] |
| | Pre-oxidized SUS 316L wire mesh honeycomb | $Al_2O_3$ | [130] |
| ECD | Pre-oxidized FeCrNi foil | $ZrO_2$ | [196] |
| CVD | SS honeycomb | $Al_2O_3$ | [79] |
| | Aluchrom (FeCrAl) | $Al_2O_3$ | [83] |
| | Pre-oxidized SS foam | $Al_2O_3$ | [97] |
| | AISI 316L SS foam | $SiO_2$ | [41] |
| ALD | Pre-oxidized Mo plates | $Al_2O_3$ and $TiO_2$ | [202] |
| | Metal foam | $Al_2O_3$ | [99] |

Table 4 – Support activation techniques for metallic substrates

| **Support activation method** | **Substrate geometry and material** | **Active phase** | **Reference** |
|---|---|---|---|
| Wet impregnation | $Al_2O_3$-coated FeCrAl spiral or wire | Pt, Pd, Ir, Rh | [86] |
| | $Al_2O_3$-coated FeCrAl foil | Pd, Pt | [89] |
| | $Al_2O_3$-coated FeCrAl plate | Pt, Rh | [90] |
| | $Al_2O_3$-coated Ni and Ni-Cr foams | $LaCoO_3$ | [50] |
| | $Al_2O_3$-coated SS honeycomb | Pt | [79] |
| | Pre-oxidized $TiO_2$ extruded honeycomb monolith | Mn, Cu, Fe | [128] |
| | Pre-oxidized Al plate | Cu-Mn-$CeO_x$ or Pt | [135] |
| | Pre-oxidized FeCrAl honeycomb | Rh, Ni | [131] |
| | Pre-oxidized Ni foam | Ce-Zr/Ni | [106] |
| | $Al_2O_3$-coated FeCrAl foam | Pd | [73] |
| | $Al_2O_3$-coated Aluchrom (FeCrAl) packed platelets | Ni | [138] |
| | Alumina-coated Ni, FeCrAl, Cu and CuZn foams | Zr-doped Cu/Zn/Al and Ni-doped Cu/Zn/Al | [126] |
| | Pre-oxidized Al/Cr-Ni/Al plate | Ni | [117] |
| | $ZrO_2$-coated AISI 314 foam | Ba, Co, K | [42] |
| | $Al_2O_3$-coated corrugated and rolled up FeCrAl and Al foils | Mn | [66] |
| | Pre-oxidized corrugated and rolled up FeCrAl and Al foils | MnCu | [67] |
| Incipient wetness | $Al_2O_3$ plasma sprayed coating over Ti plate and Ni foam | La and Co cations | [197] |
| | Pre-oxidized Al plates | Au | [71] |
| | $TiO_2$-coated carbon steel wire-mesh honeycomb | $V_2O_5$ | [129] |
| | $Al_2O_3$-coated SS plates | Cu-Cr | [123] |
| | NiCrAl and $Al_2O_3$-coated NiCrAl foams | Ru, Rh, Ni | [109] |
| | $Al_2O_3$-coated corrugated FeCrAl foils | Pd | [52] |
| Deposition-precipitation | Cu-Ni, Fe-Ni, Ni foam | Cu,Co,Mn,Ce, Ni oxides | [206] |
| | $Al_2O_3$-coated copper foam | Cu, Zn | [38] |
| Ion-exchange | ZSM-5-coated AISI 316 SS wire gauze | Cu | [133] |
| | $Al_2O_3$-coated FeCrAl panels | Pt, Pt-Pd | [208] |
| | $Al_2O_3$-coated Al foam | Pd | [102] |

Table 5 – In-situ active phase growing

| In-situ growing method | Substrate geometry and material | Active phase | Reference |
|---|---|---|---|
| Zeolite in-situ growing | AISI 316 SS wire gauze | ZSM-5 | [133] |
| | AISI 316 SS plates | ZSM-5 | [134] |
| | $Al_2O_3$/$TiO_2$-coated Mo plates | ZSM-5 | [202] |
| | Pre-oxidized FeCrAl foil | ZSM-5 | [210] |
| | Cu foam | Zeolite 4A | [211] |
| EPD | Ni, Ni-Cr foam | Cu, Cr, Co, Mn, Fe, Ni oxides | [206] |
| | FeCrAl foil | Pd, Mn, Co/ZSM-5 | [51] |
| ECD | Pre-oxidized SS, Chromel, Nichrome wire or screen | Pd, Pt | [6] |
| | Pre-oxidized crimped SS 304 and 316 or Cr steel 410 and 420 sheets or wire screens | Ru-Ir-Ni | [84] |
| | Pre-oxidized Chromel, Nikrothal, Nickrome wire, screen, ribbon | Pd, Pt | [69] |
| | Aluchrom (FeCrAl) packed foils | Ag | [83] |
| | FeCrAl foam | Ni/Al-$NO_3$ | [118] |
| | SS foil | $La_2O_3$/$ZrO_2$ | [95] |
| ELP | Pre-oxidized AISI 316L SS grids | Pd, Ru | [101] |
| | Pre-oxidized Al plate | Cu | [124] |
| | Cu foam | Pt | [217] |

## 5. Thermal treatments

Post-deposition procedures generally involve thermal treatments to consolidate and to anchor the coating layer. They usually include *drying* and *calcination* [207, 224, 225].

### 5.1 Drying

*Drying* is the elimination of the solvent (usually water) from the pores of a solid [207]. This task is critical because it basically determines the textural properties and the final porosity of the coating layer. Different types of drying have been reported in the literature, being static air drying overnight at around 100-120°C the most commonly adopted technique [28, 45, 102, 211, 226].

Strong capillary forces are generated during drying, which contract the solid coating. This can produce cracks, whose amount and size can influence the coating adhesion [227]. Cracks can be hardly eliminated, but they can be limited by adopting two different strategies, aiming at reducing/eliminating the capillary forces. The first one is the use of additives (like polyvinyl alcohol or surfactants) to reduce surface tension. The second approach is to limit the effect of the capillary forces by using a more sophisticated thermal treatment. For example, flash-drying, which basically consists in a very fast drying of the coated substrates by their introduction in a pre-heated ventilated oven for a few minutes (for example 280°C for 5 minutes), is sometimes preferred in view of reduced shrinkage effect. Indeed, this procedure is capable to provide good coating adhesion and avoids textural changes during solvent evaporation [65, 70].

Even better results are obtained by freeze-drying process, in which any liquid movement is completely ruled out and both a homogeneous distribution [5, 75, 228] and good coating adhesion [227] are obtained. Freeze-drying consists in freezing the material and then reducing the surrounding pressure to allow the frozen solvent to sublimate directly from the solid phase to the gas phase. To do that, the material should be cooled below its triple point. In case of water as solvent, this is usually done at −50/−80°C and few Pa. Freeze-drying usually causes less damage to the coating structure than other thermal treatments using higher temperatures, since no shrinkage or toughening of the material being dried occur. However, the time employed to freeze the material is critical: short times are required to avoid the formation of pores or gaps inside the coating layer due to the crystallization and next sublimation of the solvent molecules. In addition, the formation of large solvent crystals may break the coating texture. Such a technique is also more expensive than the other drying methods [5].

### *5.2 Calcination*

*Calcination* is a further thermal treatment in addition to drying [207]. It is commonly carried out in air, but also in $N_2$ or under vacuum, at temperatures higher than those used in the catalytic reaction or catalyst activation and regeneration to make sure that any possible structural transformation of the catalytic material due to high temperature occurs before the structured catalyst is loaded into the reactor.

In the case of deposition of metallic active phases (for example via impregnation), the calcination step converts partially hydrolyzed metal oxides and metal nitrates into metal oxides through thermal decomposition, dehydrolysis and phase transition processes. The metal oxide formed after calcination is mechanically and chemically more stable and cannot be re-dissolved into water.

During this step, possible residues of high molecular weight binders are usually removed by thermal decomposition as well [141], thus avoiding any possible interaction with the catalytic active phase in reacting conditions.

The calcination process lasts for several hours depending on the desired final temperature and the heating/cooling ramp used, with holding times of about 2-4 hours [65, 84, 89, 90, 141, 143, 150, 218]. Heating and cooling rates should be carefully controlled to avoid thermal shocks to the coating layer: commonly, few degrees per minute are employed [222].

Changing the calcination temperature, even when phase transitions are ruled out, can affect the pore size distribution: increasing temperature can result in a collapse of micropores and in the increase of the mean pore size. Ismagilov *et al.* [197], for example, found that an increase of the calcination temperature from 600°C to 1000°C caused a decrease in the BET area of their $LaAlO_3/\gamma\text{-}Al_2O_3$ plasma sprayed nickel foams samples from 20 to 8 $m^2/g$. Moreover, a difference in the catalyst activity appeared when the duration of the calcination step at 1000°C was increased from 3 to 9 h. The calcination temperature apparently affected the adhesion of the coating layer as well, which improved when increasing this parameter [65].

## 6. Chemico-physical characterization of coatings

Once deposited and consolidated, the quality of the coating layers may be assessed with specific tests devoted to the evaluation of: *i)* adhesion, *ii)* thickness, *iii)* loading, *iv)* superficial morphology (e.g. thickness homogeneity, presence of cracks, pore volume, surface area).

Adhesion is perhaps the most important coating property, to which several authors devote particular attention, especially when metallic substrates are employed. Indeed, this feature mainly depends on the interaction between the ceramic coating layer and the metallic substrate, which is typically low due to the limited surface roughness of metals, the poor chemical affinity between metals and ceramics and the marked difference between the differential thermal expansion coefficient of the two materials. Accordingly, suitable surface pre-treatment techniques have to be identified to provide a high-surface-area material, able to properly anchor the coating layer. Complementarily, the deposition of a primer layer is a strategy often implemented to further improve the coating adhesion properties.

As for ceramic coatings, the coating thickness is also critical, being responsible of the presence of coating cracks, whose amount and dimension may affect the adhesion performances. In this regard, as discussed in section 5, a careful selection of drying and calcination methods may help in limiting the shrinkage extent.

Different procedures are found in the open literature to evaluate the mechanical stability of the coated substrates. Valentini *et al.* [65], for instance, assessed the adhesion by evaluating the coating loss after immersing the structured catalyst sample within a sealed beaker containing petroleum ether and exposed to ultrasounds for 30 min. Meille *et al.* performed a similar test, but lasting only 1 min in a beaker containing heptane or water [191]. Basile *et al.* [119] and Almeida *et al.* [98] used the same method as well as Zhao *et al.* [154], who performed an additional thermal shock test. This was carried out by heating the coated foils to 950°C for 20 min, followed by quenching in water at 25°C. This thermal shock process was repeated 10 times for each sample, after which the weight loss was measured.

It is worth noticing that ultrasound bath and thermal shock tests are severe methods of adhesion testing and they are commonly employed for properly adhering systems. Alternatively, milder adhesion tests by blowing a gas stream through the monolith [190] or by tapping the monolith on a surface may be employed (drop test) [5, 141, 229].

Concerning the determination of the coating thickness, the most common way is using microscopy techniques, e.g. optic microscope or SEM [31, 79, 146]. Alternatively, X-ray tomography can be used. For simple substrate geometries, e.g. slabs, the direct measure by means of a micrometer is usually performed [31]. In this case, the average thickness of the layer is calculated as the arithmetic mean of three to five values taken in different points of the structured catalyst. Alternatively [31], if the coating density is available and the geometric surface area can be easily measured or estimated, the average thickness may be evaluated starting from these latter data and the coating loading.

The coating loading is usually evaluated as difference between the total weight of the coated substrate and that of the bare one, as done e.g. by Rouge *et al.* [80].

Thickness homogeneity and cracks may be assessed either by visual inspection or, more accurately, by optical and electron microscopy [31, 65, 79, 114, 146].

Eventually, FT-IR [173] and XRD spectra [63, 65, 114], TPR/O, TG-DTA, CO chemisorption [92], $N_2$ adsorption isotherms [63, 134], mercury porosimetry [141] and SEM analysis [93] may be performed if more detailed data concerning surface characterization of the coating layer like e.g. pore volume determination, phase identification, surface area modification should be gathered.

The ultimate way to characterize the quality of the coating layers consists in testing the intrisic activity of the structured catalyst at representative reacting conditions. The results obtained are indeed a direct index of key properties of the structured catalytic material, such as the presence of mass transfer limitations, the active phase dispersion and the mechanical and chemical stability of the coating.

## 7. Conclusions

The main methods for preparing a metallic structured catalyst by coating have been reviewed.

Contrary to ceramic substrates, metallic substrates often need surface pre-treatments to enhance surface roughness and coating adhesion. Except for copper-based substrates, for which it is still controversial, this is usually done by pre-oxidising the surface of the substrate by anodic oxidation, thermal or chemical treatment, depending on the substrate nature. Sometimes, a primer is also deposited onto the bare substrate as an alternative of or in addition to surface pre-treatment to improve the coating feasibility.

At this point the substrate can be coated either with a layer of a morphological support, which can be catalytically activated in a subsequent step, or with a ready-made catalyst.

Amongst coating procedures, the slurry method is the most widely used, both to deposit support materials and for coating ready-made catalysts, due to its simplicity and versatility.

Concerning instead support activation procedures, impregnation is the most widely used technique, even though ion-exchange technique also leads to homogeneous active phase distributions.

Freeze-drying gives the best results amongst the final thermal treatments, leading to homogeneous coating distributions. Indeed, it usually causes less damage to the structure of the coating layer than other thermal treatments using higher temperatures, since neither shrinkage nor toughening of the material being dried occur. However, flash-drying is often preferred due to its simplicity and the common availability of the required equipment, as well as due to its ability to provide good coating adhesion and avoid textural changes during solvent evaporation.

Calcination is usually done in air, in $N_2$ or under vacuum to consolidate the coating layer morphology, remove residues of high molecular weight binders and convert partially hydrolyzed metal oxides and metal nitrates coming from e.g. an impregnation step into metal oxides which are also mechanically and chemically more stable. The calcination process lasts several hours and slow heating/cooling rates are commonly employed to avoid thermal shocks to the coating layer.

For all these techniques, recipes and operating procedures should be optimized depending on the substrate geometry and material and on the nature of the catalyst to be deposited.

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