Structured catalysts for non-adiabatic applications
Enrico Tronconi, Gianpiero Groppi and Carlo Giorgio Visconti

Introduction

Structured catalysts consist in ceramic (e.g. Al_2O_3, cordierite, SiC) or metallic (e.g. stainless steel, Al, Cu) substrates, pre-shaped in the form of a single continuous structure with stable geometry (often a monolithic honeycomb matrix including many small parallel channels with openings in the order of one to few millimeters), over which the catalytically active sites are properly dispersed. It is well recognized that the high void fractions of such substrates, combined with the laminar flow prevailing in the channels, enable substantial reduction of pressure drop with respect to conventional packed beds of catalyst pellets. Also, the large geometrical surface areas and the thin catalyst layers in coated monoliths may diminish mass transfer limitations [1••]. Finally, the well-defined regular geometry, as well as the laminar flow conditions, enable accurate theoretical predictive modeling of mass, heat and momentum transport in honeycomb monolith catalysts, at least for fluid-solid systems [2•].

After their extremely successful commercial application to the control of automotive emissions and to the reduction of nitrogen oxides from power stations in the 1980s, honeycomb monoliths have become the standard catalyst shape in most applications of environmental catalysis [1••]. This motivated the study of the adoption of structured catalysts in other areas of heterogeneous catalysis. Particularly attractive were the expectedly lower pressure drop and the potentially smaller size of the reactor as compared to conventional pelletized catalysts in many gas-phase chemical processes. Early studies in this field, using methanation and hydrogenation as model reactions, pointed out however additional prospective benefits. In a pioneering piece of work, for example, Tucci and Thomson [3] carried out a comparative study of methanation over ruthenium catalysts both in pellet and in honeycomb form: in addition to pressure drops lower by two orders of magnitude they found also significantly higher selectivities over the monolith catalyst, likely resulting from lower internal diffusional resistances. Parmaliana and coworkers [4–7] investigated the hydrogenation of benzene and dehydrogenation of cyclohexane in ceramic monoliths washcoated with alumina impregnated with either Ni or Pt: again, the low diffusional resistances in monolith catalysts enabled the authors to determine intrinsic Eley-Rideal rate expressions.

In spite of the initial promising indications, however, over three decades later the use of monoliths as catalysts or catalyst supports in the processes of the chemical industry is still very limited. Two statements have so far mostly discouraged the extensive use of monolithic catalysts outside the well-known environmental applications [8•]:

a) the overall load of catalytically active phase in a washcoated monolith catalyst is less than the amount of catalyst in a bed of bulk pellets of comparable volume: this is not important for the fast, diffusion-limited reactions of environmental catalysis, but represents a clear disadvantage for the reactions under kinetic control usually met in the chemical process industry;

b) conventional parallel channel monoliths are virtually adiabatic: this is compatible with the processes for the abatement of pollutants (e.g. NOx, VOCs) in diluted streams, but would severely limit the control of temperature in many endothermic and exothermic chemical processes, wherein heat exchange is often a crucial issue.

In reality, both such concerns can be overcome by dedicated designs of structured catalysts, addressing the specific requirements of chemical applications. Washcoat catalyst loadings in excess of 25% (v/v) are within

Corresponding author: Tronconi, Enrico (enrico.tronconi@polimi.it)

the range of what is feasible with monoliths nowadays: in combination with the enhanced effectiveness factors in the washcoat layers, this can be enough for several industrial processes. As presented in the following, conductive heat exchange in monolith structures can be even more effective than convective heat transfer in packed beds. Furthermore, new structured supports, like open-cell foams, are now being considered, which also show promising heat transfer properties.

There remain, however, several more practical reasons which hinder the application of structured catalysts and supports to chemical syntheses, as well summarized in [9]:

a) the many different pelletized catalysts operating in the many processes of the chemical industry are often the result of long and costly development work, their properties are well tailored to the specific process needs and their performances are typically quite satisfactory: accordingly, replacement of the conventional catalyst technology with monolith catalysts requires very significant and proved benefits;
b) the production volumes of industrial catalysts are lower by orders of magnitude as compared to the volumes of catalysts for the environment: thus, it is difficult to justify dedicated research efforts as well as capital investment to develop monolithic systems with intrinsic catalytic properties similar to those of conventional systems;
c) the methods for loading, packaging, sealing and unloading structured catalysts in the synthesis reactors are different from those well established for pellet catalysts, and cannot be directly derived from the experience made in stationary environmental installations: additional developments in this area are required, too;
d) structured catalysts are intrinsically more expensive than pellet catalysts.

In essence, it appears that substantial improvements are required in order to motivate such a significant change of the catalyst technology. Notwithstanding such difficulties, however, there is a steadily increasing number of research activities concerning the use of monolithic and other structured catalysts/reactors in chemicals production [10•]. In fact, after the early phase when only sparse attempts were reported, multiple application areas have been now identified and rationalized in which monolithic catalysts may have intrinsically superior performance characteristics.

One topic receiving great attention nowadays in view of its large industrial potential is the development of novel catalytic oxidation processes using structured reactors with extremely short contact times, whose large flow rates would generate unacceptable pressure drops in packed-bed reactors. Manufacture of olefins via catalytic oxidative

dehydrogenation of light paraffins and catalytic partial oxidation of hydrocarbons for syngas production are two important examples of processes in this area for which applications of monolithic catalysts have been envisaged, being facilitated by low pressure drops at high flow rates [11]. Again in view of their reduced pressure drop, it has been recognized that monolith structures hold also a good potential for applications as pre-reactors and post-reactors of selective oxidation processes [8]. Such applications still involve adiabatic operation of the structured reactors.

A novel, innovative area of development is represented by the use of structured catalysts in chemical processes under non-adiabatic conditions. As mentioned above, the global heat transfer properties of honeycomb monoliths have been traditionally regarded as very poor, but recently monolithic structures and configurations have appeared with interesting characteristics for heat exchange: a new promising area is, for example, the use of honeycomb catalysts with high thermal conductivity in exothermal selective oxidation processes where multitubular reactors are employed; along similar lines, there is growing interest in the potential of open-celled foam (or sponges) as novel structured catalyst supports with enhanced heat exchange properties. Such an emerging application of structured catalysts/reactors is the focus of the present contribution: it is reviewed and discussed in the following (Figure 1).

Figure 1
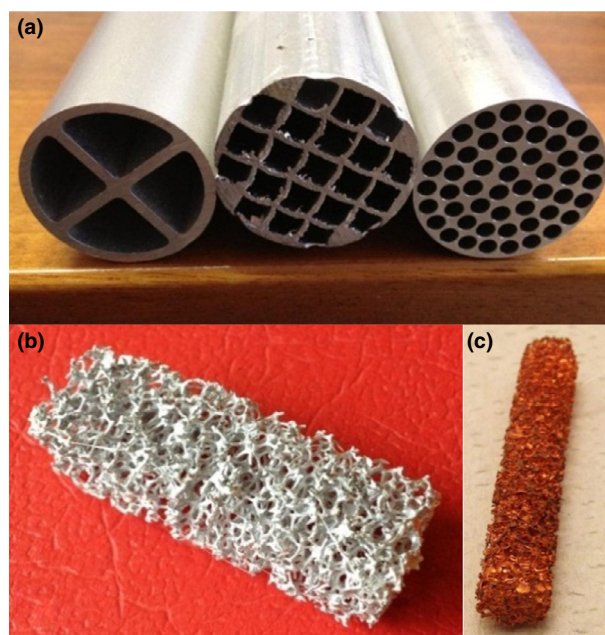
Examples of conductive structured substrates for exothermic or endothermic applications: **(a)** aluminum honeycomb monoliths, **(b)** aluminum open-cell foam, **(c)** copper open-cell foam.

Honeycomb monoliths as non-adiabatic catalysts

For quite some time the use of monolithic catalysts in non-adiabatic reactors has been regarded as unfeasible due to poor radial heat transfer: indeed, ceramic honeycombs are made of essentially insulating materials; a pioneering theoretical analysis of Cybulski and Moulijn [12*] evidenced that commercial monolith structures consisting of corrugated metal sheets exhibit modest heat transfer performances, too.

Nonetheless, the thermally connected nature of the monolith supports provides in principle for an alternative mechanism of radial and axial heat transport, namely heat conduction, which is essentially not available for random packings of catalyst pellets. The conduction within the solid phase of the pellets in fact is almost negligible, since only point contacts exist between the pellets, and convection in the gas phase dominates as the primary mechanism for heat exchange. Accordingly, the only practical way of enhancing heat transfer is to increase the flow velocity, but this is limited by the pressure drop, which grows more than linearly with flow rate. By using monolith honeycomb structures with parallel channels as catalyst elements no radial transfer of gas may exist, but the contribution of thermal conduction through the solid phase (i.e. the monolith matrix) can become quite significant if suitable materials and geometries are adopted.

The effective axial heat conductivity of monolith substrates $k_{e,a}$ is readily estimated as

$$k_{e,a} = k_s(1 - \epsilon) \tag{1}$$

with k_s is the intrinsic thermal conductivity of the support material and ϵ is the monolith void fraction (or open frontal area, OFA).

Early attempts to model radial heat conduction in monoliths, also including comparison with experimental data, were published in [13–15]. Based on a simple analysis of heat conduction in the unit cell of a honeycomb monolith with square channels according to an electrical network analogy, Groppi and Tronconi [16*,17] derived approximate predictive equations for the effective radial thermal conductivity in washcoated monoliths, with square and equilateral triangular channels. Hayes and coworkers [18] validated such equations against numerical solutions of the temperature field in honeycomb structures, finding maximum deviations of less than 20% for a typical monolith void fraction of 75%. They derived also an alternative equation, based on a different (parallel) arrangement of the resistance network, which improved somewhat the prediction accuracy. Recently, Visconti et al. [19**] have published a simple 'symmetric' model, which provides the best match with the exact T-field: neglecting the contribution of the catalytic washcoat, as well as the minor contribution of heat conduction in the gas phase, the symmetric model yields.

$$k_{e,r} = k_s \frac{1 - \epsilon}{1 + \epsilon} \tag{2}$$

As Eq. (2) shows, the effective radial conductivity $k_{e,r}$ is directly proportional to the intrinsic thermal conductivity of the support material, k_s: thus, the adoption of highly conductive materials is expectedly very beneficial for the enhancement of radial heat transfer in monoliths. In Figure 2 estimates of $k_{e,r}$ according to Eq. (2) are plotted versus the monolith open frontal area ϵ for honeycomb structures made of metallic and non-metallic materials with different intrinsic thermal conductivity. It should be emphasized that when highly conductive materials (Cu, Al, SiC) are used the estimates of $k_{e,r}$ in Figure 2 become one order of magnitude greater than the effective radial thermal conductivities in packed beds of catalyst pellets, which under typical conditions of selective oxidations in externally cooled multitubular reactors are typically in the range 2–5 W/m/K [20,21]. The plot shows also that the radial effective conductivity is adversely affected by large monolith void fractions ϵ.

These evaluations point out that heat exchange in monolithic structures can be made more efficient than in pellets, but monolith supports with specific designs must be adopted, based on a dedicated selection both of the monolith geometry and of the fabrication material aimed at minimizing resistances to conductive heat transfer. Notably, the existing commercial monolith substrates, developed for the adiabatic applications of environmental

Figure 2
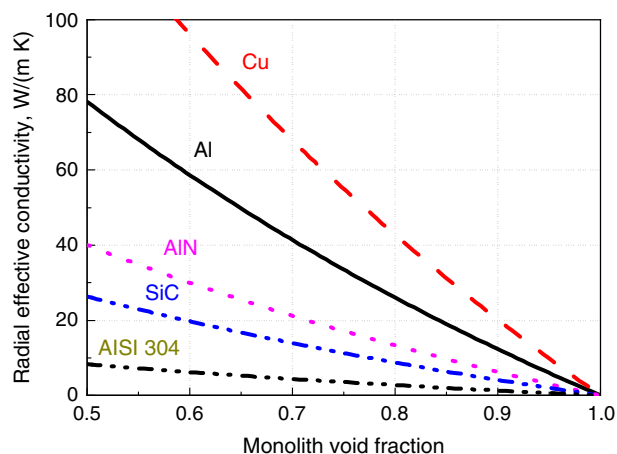
Effect of material properties and monolith void fraction on the radial effective thermal conductivity of honeycomb monoliths with square channels. Based on Eq. (2).

catalysis, were not originally designed for that purpose: neither the construction material nor the geometry of such supports is optimized for heat conduction. In fact, the intrinsic conductivity of ceramic honeycombs is very low, whereas the available metallic monolith structures are made of poorly conductive alloys (e.g. FeCrAlloy) and are assembled by piling up and rolling corrugated sheets which result in poor thermal contact. Finally, in commercial monoliths the open frontal area is kept as high as possible, typically 0.7–0.8 for ceramic monoliths and 0.85–0.95 for metallic ones, so as to match the severe pressure drop constraints of environmental processes: this is also negative for radial heat transfer.

Based on the above considerations, heat conduction in the walls of monolith structures can be exploited in principle as an effective heat transfer mechanism for exothermic or endothermic catalytic processes: published studies concerning such applications are summarized in the following.

Groppi and Tronconi have systematically investigated the potential of novel monolithic catalyst supports with high thermal conductivity in view of replacing conventional packed beds of catalyst pellets in multitubular reactors for gas/solid selective oxidations [16•,17,22–25]. Starting from the evaluation of effective radial thermal conductivities in monolith structures (Figure 2), they predicted that in principle the radial heat transfer in fixed-bed gas/solid reactors could be substantially enhanced when changing the dominating heat transfer mechanism from convection to conduction. This would be a very important result, since both the design and the operation of technical packed-bed reactors are limited at present by the removal of the reaction heat, which occurs by convective transport from the randomly packed catalyst pellets to the reactor tube walls: therefore limits on the reactor tube diameter of 1–1.5 inches as well as very high gas flow rates are typically required to prevent unacceptable hot spots. Significantly improved radial heat transfer, on the other hand, would bring about reduced risks of thermal runaway, better thermal stability of the catalyst, improved selectivity, as well as potential for novel designs of industrial reactors with incremented throughputs and/or enlarged tube diameters, corresponding to reduced investment costs.

In order to assess such prospective advantages, the thermal behavior of 'high conductivity' monolith catalysts in exothermic reactions was investigated both by simulations and by experiments. This early work, focused on selective oxidation processes, is reviewed in [26•]. As an important result, it was recognized that, while the early models assumed no heat transfer resistance between the monolith catalyst and the coolant, actually a thermal contact resistance can be expected at the interface between the monolith and the inner reactor tube wall ('gap' resistance), as detected also in the experimental

investigations [25,27]. Calculations predict that such a resistance becomes crucial for the onset of hot spots in the ethylene oxide reactor whenever the corresponding 'wall' heat transfer coefficient is less than about 500 W/(m^2 K) [17]. Accordingly, solutions aimed at achieving effective thermal contact between the honeycombs and the reactor tubes ('packaging' methods) represent an important development goal, which must be necessarily pursued in connection both with the manufacturing technologies of monolithic catalysts and with the specific features of the individual catalytic processes.

The 'gap' resistance was further rationalized in subsequent work [26•,28•]. It was shown that the associated heat transfer mechanism relies primarily on heat conduction across the stagnant gas film trapped in the gap between the monolith and the reactor tube. In fact, the gap resistance was inversely proportional to the gap size δ evaluated at the reaction conditions (so differential thermal expansion of the monolith and tube materials should be considered) [28•], and directly proportional to the gas-phase conductivity k_g, as evidenced by heat transfer measurements over Cu monoliths using N$_2$–He mixtures of different compositions [26•]:

$$h_w \approx \frac{k_g}{\delta} \qquad (3)$$

h_w estimates in excess of 700 W/(m^2 K) were obtained when using pure He [26•].

Although the experimental results reported above were all collected at the laboratory scale, a first proof-of-concept at an industrial scale has been recently reported in the open literature [29••], involving a campaign of o-xylene oxidation runs in a tubular pilot reactor loaded with washcoated conductive (aluminium) honeycomb catalysts and operated under representative conditions for the industrial production of phthalic anhydride (PA). In a preliminary exploratory phase structured supports (Al slabs and honeycombs) were washcoated first with a primer (dispersible boehmite) and then with a V$_2$O$_5$/TiO$_2$-based precursor powder for industrial o-xylene oxidation catalysts (Polynt). The coating procedure was first validated by isothermal kinetic runs in a lab-scale microreactor (i.d. = 12.6 mm) loaded with a washcoated Al slab shaped in the form of a spiral (3 cm × 15 cm, total active catalyst mass = 400 mg), covering a range of representative temperatures (320–400 °C) and o-xylene feed contents (1–3%, v/v). For the pilot reactor runs, sixteen Al honeycombs supplied by Corning Inc. (26 cpsi, o.d. = 24.4 mm, length = 10 cm) washcoated with a total catalyst mass of 46 g were loaded in the upper part of an industrial pilot reactor (Polynt) consisting of a single jacketed tube (length = 3 m, i.d. = 24.6 mm) cooled with molten salts. The tube loading was completed with inert rings. Axial T-profiles were recorded by a thermocouple sliding in a 2 mm o.d. thermowell inserted in the central

channel of the honeycombs. The pilot reactor was operated continuously for over 1600 hours. After startup, the air flow rate was kept at 4 Nm^3/h and the o-xylene feed load was progressively increased from 120 to 400 g/h while adjusting the salt bath temperature to keep the measured hot spot temperature around 440 °C. Figure 3a compares the axial T-profile from one of such runs at reference industrial conditions for PA production (o-xylene feed concentration = 80 g/Nm^3) with a T-profile measured in the same pilot reactor loaded with conventional catalyst pellets (rings) and operated at the same conditions with a similar hot spot temperature. The Al honeycomb supports afforded substantially reduced axial T-gradients, and enabled operation of the reactor with a much higher salt bath temperature (392 °C vs. 359 °C in the case of rings): the maximum T-difference with the salt bath was halved (Figure 3b) and the average bed temperature was therefore about 20 °C higher. T-gradients were still moderate at o-xylene loads close to 100 g/Nm^3, an upper limit for the current industrial PA packed-bed reactors technology. The Al honeycombs were successfully unloaded at the end of the pilot reactor runs.

A strong enhancement of radial heat transfer rates ($\approx 2x$) associated with the use of novel monolithic catalysts with high thermal conductivity has been thus demonstrated at an industrial scale for the first time. Such a unique improvement can be exploited for intensification of the PA process in a number of ways, for example, to increase the o-xylene feed load > 100 g/Nm^3 (and the PA productivity accordingly) in existing technical reactors, or to design new reactors with larger tube diameters. In more general terms, the results herein presented, being obtained with substrates and under conditions representative of real applications, appear quite encouraging in view of practical implementations of 'high conductivity' monolith catalysts in selective oxidation processes.

Another area of growing interest for conductive monolith catalysts is represented by exothermic CO hydrogenation processes (syngas chemistry).

In the well known low-T, low-P exothermic methanol synthesis over Cu-based catalysts, temperature control is a crucial aspect in order to optimize selectivity and catalyst lifetime. Work from Holmen and coworkers [30•,31] showed improved performances over coated metallic structured substrates, and ascribed them to the better thermal properties of the structured systems, resulting in a more uniform temperature distribution. The application of conductive (copper) monolith (and also open-cell foam) catalysts to the methanol synthesis has been recently investigated in our labs in collaboration with Total Petrochemicals [32–34]. Specifically, simulation results have pointed out that radial heat transfer in technical Lurgi-type multitubular packed-bed converters is very efficient due to high flow velocities, which require however long tubes (e.g. 8 m). Reduction of the tube length in view of compact methanol synthesis units for exploitation of small natural gas reservoirs or biomass would be therefore unfeasible because of the dramatic loss of convective heat transfer performance. On the other hand the conductive heat transfer mechanism of structured systems is essentially

Figure 3
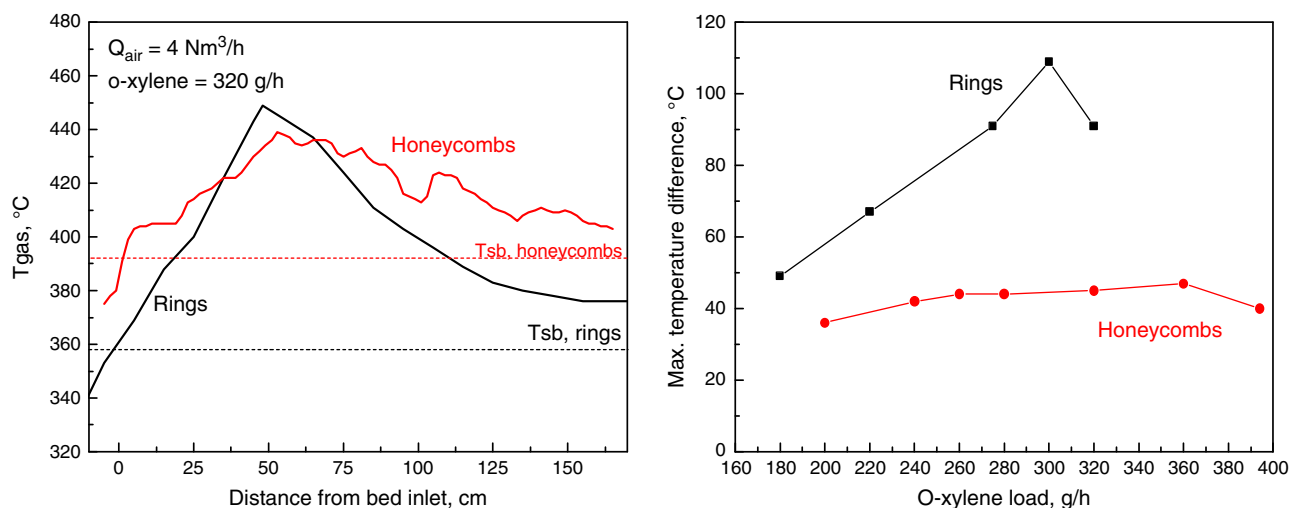
Temperature profiles of the gas phase (left) and maximum temperature difference (right) in o-xylene oxidation pilot runs with ring pellets or Al honeycombs. The maximum temperature difference is defined as the difference between the hot-spot temperature and the temperature of the cooling salt bath.
Source: Reprinted with permission from [29••]. Copyright 2014 American Chemical Society.

flow independent, so that shortening of the tube length would bring about in this case no significant loss in radial heat transfer efficiency.

The low-temperature Fischer–Tropsch (FT) synthesis for the production of synthetic fuels is a strongly exothermic process of growing strategic importance, wherein temperature control is a crucial issue. The adoption of honeycomb monoliths as supports for cobalt based FT catalysts was proposed at the beginning of this century by the research groups of Holmen at NTNU Trondehim [35•] and of Moulijn at TU Delft [36], and considered a few years later also by the group of Turek at Clausthal University of Technology [37,38]. Their works refer however to conventional ceramic monoliths, similar to those widely adopted for environmental applications, which are essentially made of thermally insulating materials. FT Reactors are therefore operated adiabatically and the heat removal issue is solved by recycling to the reactor a fraction of the liquid products pre-cooled in an external heat exchanger. For this reason such units are referred to as monolith loop reactors (MLR). Co-feed of a liquid phase is managed so as to operate the reactor in the slug flow or Taylor flow regime (i.e. the liquid phase is recirculated at high liquid flow rates), where high mass transfer coefficients can be achieved [38]. Such reactors have been successfully used in experimental studies at the lab scale [35•,37,39–41] and their performances at the industrial scale have been simulated by mathematical models [38,40], but this solution has received scarce attention by the industrial world so far. Upon attempting the development of a mass-transfer and heat-transfer enhanced catalytic systems, the use of home-made or commercial monolith structures consisting of corrugated metal sheets has been also proposed [42–44] as an alternative to ceramic honeycomb monoliths for the FTS. However such structures exhibit modest heat transfer performances even assuming an infinitely high wall heat transfer coefficient, as evidenced by the theoretical analysis of Cybulski and Moulijn [12•] and by the experimental work of Boger and Heibel [28]. A related technology, named monolith loop catalytic membrane reactor (ML-CMR), was proposed in 2005 by the US company CeraMem [45] mainly to overcome the limitations related to the segregated flow typical of classical honeycomb monoliths.

The potential of conductive honeycomb catalysts for the FTS in multitubular reactors is actively investigated in our group at Politecnico di Milano. Preliminary results concerning both washcoating of aluminum structured supports with increasing geometrical complexity and lab scale FT tests over such catalysts were published in [46]. Aluminum was selected as the material for the structured supports because of (i) the excellent intrinsic thermal conductivity (200 W m^{-1} K^{-1} [47]), (ii) the chemical inertia at the actual FTS process conditions,

(iii) the low density, (iv) the chemical affinity with the morphological support of the adopted catalyst and (v) the reasonable volumetric cost. Well-adherent washcoat layers with thickness less than 45 μm were obtained by dip-blowing aqueous slurries of a representative Co/γ-Al$_2$O$_3$ catalyst onto a 27 cpsi extruded aluminum honeycomb monolith supplied by Corning Inc. The thickness of the washcoat layer was chosen considering both the need of maximizing the catalyst loading in the reactor and the threshold limit of 40–50 μm reported in the literature for the onset of intraporous mass-transfer restrictions [48]. Comparative tests with the original powdered catalyst and the washcoated monoliths, carried out in a lab-scale tubular reactor at industrial process conditions, confirmed the adequacy for the FTS of such structured catalysts, which resulted stable with time on stream while showing activities and selectivities similar to those of the original catalyst powders [46].

In a subsequent paper [49] the adoption of conductive honeycomb catalysts in tubular reactors for the FT was investigated by means of a pseudo-continuous, heterogeneous, two-dimensional mathematical model of a single reactor tube. Simulation results indicate that extruded aluminum honeycomb monoliths, washcoated with a Co/γ-Al$_2$O$_3$ catalyst, are promising for the application at the industrial scale, in particular when adopting supports with high cell densities and catalysts with high activity. Limited temperature gradients are in fact predicted even at extreme process conditions, thus leading to interesting volumetric reactor yields with negligible pressure drop. Flat axial and radial temperature profiles have been simulated along the catalytic bed, showing the unique ability of the adopted structured catalysts to manage the heat removal issue and to guarantee an excellent temperature control, that is crucial in FTS (see Figure 4). Notably, this result can be achieved without recycling to the reactor large amounts of liquid hydrocarbon products in order to remove the reaction heat, as opposite to existing industrial Fischer–Tropsch packed-bed tubular reactors.

At the present stage of development the crucially T-sensitive Fischer Tropsch synthesis appears as one of the most promising areas of application of conductive structured catalysts. Further developments are therefore expected in the near future. In the same field, a competing solution, though based on somewhat similar principles, is represented by the so called microchannel reactor technology [44,50–57], whose distinguishing feature is also the very high efficiency of reaction heat removal. A major difference with the conductive structured catalysts concept is that microchannel systems introduce a totally new reactor technology, which is intrinsically more complex and expensive and still needs to be fully proven at the industrial scale.

Figure 4
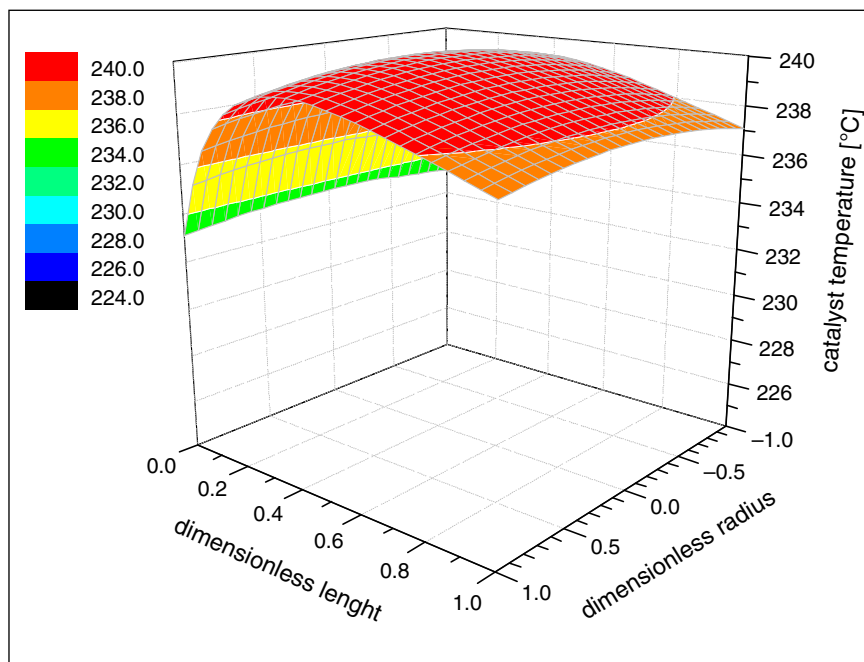
Simulated temperature profile in FTS tubular reactor in the case of 1 in. o.d. monolith, 100 cpsi.
Source: Reprinted from [49], Copyright 2014, with permission from Elsevier.

Open-cell foams as non-adiabatic catalysts

The word foam usually refers to a dispersion of gas bubbles in a liquid, but can be used also to describe a uniform dispersion of a gaseous phase in a solid matrix. Open-celled foams (also known as sponges) are made of interconnected solid struts which enclose cavities (the cells) communicating through windows (or pores) [58,59**,60,61]. They are commercially available in a variety of metallic and ceramic materials, and have found several industrial applications due to their cellular structure with special geometry, mechanical strength, low relative density (i.e. high porosity) and high surface area. Reported applications include: thermal insulation, energy absorption, silencers, filtration of molten metals, purification of hot gases. In particular, metallic foams, manufactured from different metals like stainless steel, Cu, Al and Ni have been used in heat exchangers, and as fuel cell electrodes, high temperature filters, electron emitters, among others [62–66].

The application of open-cell foams to heterogeneous catalytic processes was proposed already several years ago [67,68,69•,70••]. In fact foams have interesting structural properties which make them potentially attractive as enhanced catalyst carriers, replacing random packed beds of pellets for tubular reactors. Their very high porosities (from 70 to 95%) result in low pressure drop, while their high surface areas per unit volume can enhance the interaction between the reactants and a catalyst coated onto the foam struts. For these reasons, the use of foam catalysts has been primarily considered so far for fast, diffusion-limited adiabatic processes (like e.g. catalytic partial oxidation of hydrocarbons for hydrogen or syngas generation, catalytic combustion of natural gas, SCR-DeNOx catalytic converters for power stations or for the aftertreatment of vehicle exhausts), where enhanced heat and mass transfer rates would result in more compact, efficient and lightweight reactors. Significant (though not conclusive) progress made in the last few years in the engineering prediction of interphase (gas–solid) transport properties of open-cell foams [71,72•,73–75,76•] has shown that, in fact, interphase mass and heat transfer rates are typically much greater in catalytic foams than in packed-beds due to continuous boundary layer redevelopments. Ref. [72] presents a comparative analysis of pellets, honeycombs and foams as catalyst carriers for adiabatic, mass transfer limited processes: the analysis is based on a trade-off index representing quantitatively the compromise between mass transfer and pressure drop. It is also worth noticing that radial mixing is not possible in honeycomb monoliths due to the segregated flow in parallel channels, but is of course quite possible in open-celled foam structures. This may be beneficial to prevent non-uniform distributions of reactants over the reactor cross section.

A less commonly appreciated aspect is that open-celled metal foams can be made of highly thermal conductive metals: for example, sponges made of Al or Cu are commercially available. Combined with their continuous, thermally connected structure, this offers in principle good potential for the enhancement of radial heat transfer in non-adiabatic reactors loaded with catalytic foams in comparison with traditional packed bed reactors for highly endothermic and exothermic heterogeneous catalytic processes: enhanced global heat transfer rates in conductive foams can decrease axial and radial temperature gradients, minimizing hot (or cold) spots. The potential of open-cell foams for intensification of non-adiabatic processes in fixed-bed catalytic reactors therefore relies on the same conductive heat transfer mechanism discussed in the previous section for monolithic substrates. A major difficulty here, however, is that reliable engineering correlations for the prediction of global heat transfer rates in foams, validated at a representative scale, are still lacking. Recent efforts in the characterization of heat transport in catalytic foams are reported in [77–83].

Bianchi *et al.* [81,82] performed single-phase heat transfer measurements, using both N_2 and He as process gas, over a number of Al and FeCrAlloy foams with different pore sizes and void fractions, whose morphology had been characterized by X-ray micro-computed tomography techniques. They fitted their experimental T-distributions with a classical 2D pseudo-homogeneous heat transfer model in order to obtain estimates of the effective radial conductivity $k_{e,r}$ and of the wall heat transfer coefficient h_w. The results clearly showed that conduction within the solid matrix is the dominant contribution to $k_{e,r}$ and h_w became the controlling parameter [81]. In the case of foams made of Al, $k_{e,r}$ was well predicted by the purely conductive theory of Lemlich [84]:

$$k_{e,r} = k_s \frac{1 - \epsilon}{3} \qquad (4)$$

Both the heat transfer experiments and a numerical study in a 3D geometry of a foam sample reconstructed from the X-ray scan pointed out that the wall heat transfer coefficient depends only weakly on the flow velocity, but is strongly promoted by high cell densities (i.e. by small foam cells) and by high gas thermal conductivities [82]. This suggested a dimensionless correlation of the wall heat transfer coefficient using the cell size d_c as the characteristic length, as represented in Figure 5.

Although the physical interpretation of such results is still open, they suggest however that, at least in the investigated range of process conditions ($4 < Re_{dc} < 255$), the main contribution to the heat transfer in the near-wall region originates from a static mechanism associated with heat conduction across the thin layer of gas at the interface between the foam periphery and the inner tube wall.

Figure 5
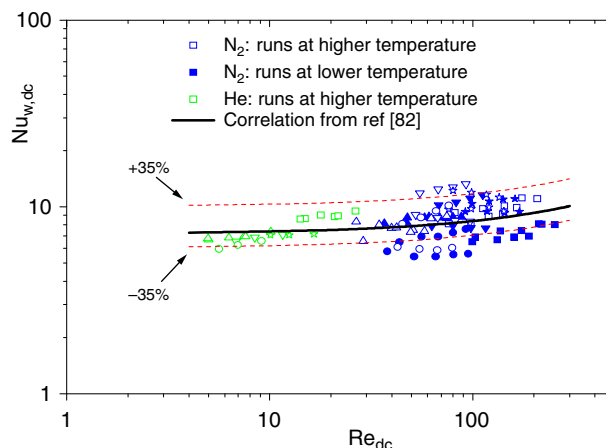
Dimensionless wall heat transfer coefficient $Nu_{w,dc} = (h_w\, d_c)/k_g$ versus Reynolds number. Reprinted from [82], Copyright 2014, with permission from Elsevier. Correlation: $Nu_{w,dc} = 7.18 + 0.029\, Re_{dc}^{0.8}$ $4 < Re_{dc} < 255$.

A recent experimental comparative study of heat transport in catalytic sponges and in spherical pellets, tested in the exothermal hydrogenation of benzene in a tubular cooled reactor [83], confirms that foam packings exhibit better heat transport properties than packed beds of particles; furthermore, in line with [81] it was found that the intrinsic thermal conductivity of the solid material has the strongest impact on the heat transfer performance, that was enhanced as well by increasing the foam relative density.

The good heat transfer performance of aluminium foams has been demonstrated also for the case of gas–liquid co-current down flow in a comparative study with other structured packings covering all important flow regimes [85••].

To conclude the discussion of the heat transfer properties of open-cell foams, it is worth mentioning that also the contribution of radiative heat transfer can be more important in the case of the relatively open foam structures than in packed beds of pellets (it is essentially negligible in honeycomb catalysts). This makes foam substrates quite attractive for intensification of high-temperature catalytic processes, like for example, methane steam and dry reforming [86•].

Examples of exothermic and endothermic industrial processes for which adoption of foam catalysts has been explicitly discussed in the open literature include so far methane steam and dry reforming [70••,86•], Fischer–Tropsch synthesis [87,88], methanol synthesis [32–34], o-xylene oxidation to phthalic anhydride [89,90•]. In these papers, the emphasis is often put on the potential

granted by the structured packing for the design of compact reactor configurations, as required, for example, for GTL-FPSO (Gas To Liquid-Floating Production Storage and Offloading) units [86].

Conductive micro-fibrous entrapped catalysts

The Tatarchuk group at Auburn University has developed an alternative concept of conductive catalyst structures with enhanced heat transfer characteristics: they consist of sintered micron-sized metal fibers with small catalyst particles entrapped inside [91•,92–94]. Flow heat transfer experiments over such micro-fibrous entrapped catalysts (MFEC) made of conductive metals provided much greater effective thermal conductivities and wall heat transfer coefficients than comparative runs over conventional packed beds of particles [91•]. The MFEC structure is packed with pre-manufactured catalyst particles, so it does not require catalytic activation by washcoating, and can be associated with significantly higher catalyst volume fractions than coated monoliths or foams.

The enhanced heat transfer properties of MFEC structures have been recently demonstrated in the low temperature Fischer–Tropsch synthesis at 225–255 °C, 20 bar, H_2/CO = 2.0, selected as the probe reaction due to its exothermicity and temperature dependent selectivity. 15 wt% Co/Al_2O_3 catalyst particles (149–177 µm) were studied in both a packed bed configuration and after being entrapped within a 7.4 vol.% network of sintered Cu fibers (12 µm). In a 41 mm i.d. reactor, the maximum temperature deviation from the centerline to the reactor wall was only 6.4 °C for the copper MFEC, while in contrast, the packed bed diluted to the same catalyst density and operated at an equivalent condition had a centerline temperature deviation of 460 °C [92]. A CFD study shows that the MFEC is able to perform well in flowing gas because of its ability to radially conduct large amounts of heat along its copper fiber cylinders [93]. Recent efforts in this area address the development of a modified resistance network model in order to predict the effective thermal conductivity of sintered microfibrous materials made of conductive metals [94]. Results emphasize the importance of minimizing the contact resistance among the fibers, improving their connection quality, in order to optimize conductive heat transfer.

State of development: gaps and needs

An intrinsic difficulty associated with the adoption of washcoated conductive honeycomb monoliths and foams as catalyst supports is the limited volume fraction of catalytically active material (catalyst inventory) as compared to packed beds of catalyst pellets. In simple terms, the catalyst volume fraction results from the product of the specific surface area of the substrate by the catalytic washcoat thickness. The latter is usually constrained by adhesion issues. Accordingly, conductive structured catalyst configurations with high geometric areas, or with

high cell densities (i.e. small honeycomb pitch or small foam pore size), are of great interest. An alternative approach relies on packing the structured supports with small catalyst particles, similar to the micro-fibrous entrapped catalysts discussed above [95,96••]. For example, this approach has been claimed by Eni S.p.A and Politecnico di Milano to increase the catalyst inventory in tubular reactors for the Fischer–Tropsch synthesis loaded with conductive honeycomb monoliths [95]. A similar concept has been proposed by Kapteijn and co-workers [96••] in the case of cross-flow structures for gas/liquid systems (and in particular for the Fischer–Tropsch synthesis): their packed structures had a slightly lower catalyst hold-up than a randomly packed bed (50 vs. 65%), but the smaller catalyst particles could be used more efficiently due to greater effectiveness factors. Besides, for comparable pressure drop the structured flow paths of the fluids through the packing roughly doubled the overall heat transfer coefficient. This seems quite promising in view of overcoming the other main objection (low catalyst inventory) originally raised against the adoption of structured catalysts for chemical processes.

In general terms, the design and preparation of structured catalysts involves a number of additional technological hurdles: at the moment a thorough, fundamental understanding of washcoating methods is still lacking, and washcoating procedures need to be developed empirically for each specific application [97–99,100•]. Notably, in the case of large-scale applications conductive structured catalysts should be manufactured to meet the high standards of reproducibility of the process industry.

Protocols for loading and unloading monolith-based or foam-based reactors need also to be developed and assessed. In multitubular reactors there could be a problem with charging and discharging the reactor tubes, which are never perfectly straight; also, methods are needed to control the thermal contact between the substrates and the tube walls, which is crucial for the overall heat transfer performances [27,28]. All of these practical aspects need to be investigated further at a representative scale.

Specifically for open-cell foams and MFEC, well established, generally accepted engineering correlations for the estimation of gas/solid mass and heat transfer, and particularly for global radial and axial heat transfer are still lacking. Simpler methods/models for characterization of the complex foam geometry are also urgently needed.

Summary and perspectives

Conductive structured catalysts promise remarkable advantages over conventional catalyst structures in terms of reduced pressure drop and optimal interphase mass and heat transfer, but also offer unparalleled potential for engineering the heat management in catalytic reactors for non-adiabatic processes. Nevertheless, a still

incomplete understanding of the transport phenomena in such structures, difficulties with their catalytic activation via washcoating, and limitations on the feasible overall catalyst inventory have hindered so far the commercial application of the technology.

In the last decade progress in the fundamental understanding of the transport phenomena in structured catalysts, generating engineering correlations and data, as well as improved manufacturing technologies leading to new substrates with enhanced geometries and made of a wide range of structural and functional materials, have clarified and emphasized the advantages of structured catalysts over conventional pellet catalysts. As illustrated above, a good number of exploratory studies has been performed by now on several catalytic processes. At this stage, demonstrative realizations are needed to address practical aspects associated with, for example, loading, sealing and unloading of the monoliths or foams in the reactors, and particularly the economic value of their operational advantages in respect to higher catalyst manufacturing and development costs.

The challenge is therefore to setup an integrated project demonstrating all the fundamental and practical aspects of the technology. Such a demonstration project should target an application where the technical/economic benefits would be substantial: likely candidates are syngas production processes (NG steam reformers), and/or GTL processes (Fischer–Tropsch synthesis). If successful, such a first demonstration could pave the way to the rapid development of other applications, also in less rewarding sectors.

In comparison to monoliths, applications of open-cell foam structures and MFEC to the process industry are still at an earlier developmental stage. Indeed, foams and filamentous materials do not benefit from the extensive experience of the last three decades in the use of monolith catalysts for environmental processes, and thus may require additional research work for the evaluation of their full potential.

Acknowledgments

References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:

- • of special interest
- •• of outstanding interest

Honeycomb monoliths

1. Cybulski A, Moulijn JA: **Monoliths in heterogeneous catalysis**. *Catal Rev Sci Eng* 1994, **36**:179-270.
•• Still a reference in the field: written by the pioneers in the topic.

2. Gundlapally SR, Balakotaiah V: **Heat and mass transfer correlations and bifurcation analysis of catalytic monoliths with developing flows**. *Chem Eng Sci* 2011, **66**:1879-1892.
• The most updated source of theoretically-based estimates for gas-solid mass transfer coefficients in honeycomb monoliths.

3. Tucci ER, Thomson WJ: **Monolith catalyst favored for methanation**. *Hydroc Proc* 1979, **58(2)**:123-126.

4. Parmaliana A, Crisafulli C, Maggiore R, Bart JCJ, Giordano N: **Catalytic activity of honeycomb catalysts. I. The benzene-cyclohexane (de)hydrogenation reaction**. *React Kinet Catal Lett* 1981, **18**:295-299.

5. Parmaliana A, Mezzapica A, Crisafulli C, Galvagno S, Maggiore R, Giordano N: **Benzene hydrogenation on nickel/honeycomb catalysts**. *React Kinet Catal Lett* 1982, **19**:155-160.

6. Parmaliana A, El Sawi M, Mento G, Fedele U, Giordano N: **A kinetic study of the hydrogenation of benzene over monolithic-supported platinum catalyst**. *Appl Catal* 1983, **7**:221-232.

7. Parmaliana A, El Sawi M, Fedele U, Giordano G, Frusteri F, Mento G, Giordano N: **A kinetic study of low temperature hydrogenation of benzene over monolithic-supported platinum catalyst**. *Appl Catal* 1984, **12**:49-57.

8. Boger T, Heibel AK, Sorensen CM: **Monolithic catalysts for the chemical industry**. *Ind Eng Chem Res* 2004, **43**:4602-4611.
• Interesting overview of non-environmental applications of monolithic catalysts, written from an industrial perspective.

9. Heck RM, Gulati S, Farrauto RJ: **The application of monoliths for gas phase catalytic reactions**. *Chem Eng J* 2001, **82**:149-156.

10. Groppi G, Beretta A, Tronconi E: **Monolithic catalysts for gas-phase syntheses of chemicals**. In *Structured Catalysts and Reactors,* 2nd edition. Edited by Cybulski A, Moulijn JA. CRC Press; 2006:243-310.
• A survey of the applications of monolith catalysts in the Chemical Process Industry.

11. Beretta A, Donazzi A, Livio D, Maestri M, Groppi G, Tronconi E, Forzatti P: **Optimal design of a CH$_4$ CPO-reformer with honeycomb catalyst: combined effect of catalyst load and channels size on the surface temperature profile**. *Catal Today* 2011, **171**:79-83.

12. Cybulski A, Moulijn JA: **Modeling of heat transfer in metallic monoliths consisting of sinusoidal cells**. *Chem Eng Sci* 1994, **49**:19-27.
• Pioneering analysis of heat transport in metallic monolith structures.

13. Flytzani-Stephanopoulos M, Voecks GE, Charng T: **Modelling of heat transfer in non-adiabatic monolith reactors and experimental comparison of metal monoliths with packed beds**. *Chem Eng Sci* 1986, **41**:1203-1212.

14. Kolaczkowski ST, Crumpton P, Spence A: **Modelling of heat transfer in non-adiabatic monolithic reactors**. *Chem Eng Sci* 1988, **43**:227-231.

15. Kolaczkowski ST, Crumpton P, Spence A: **Channel interaction in a non-adiabatic monolithic reactor**. *Chem Eng J* 1989, **42**:167-173.

16. Groppi G, Tronconi E: **Continuous versus discrete models of nonadiabatic monolith catalysts**. *AIChE J* 1996, **42**:2382-2387.
• Provided the first engineering equation to estimate the effective radial thermal conductivity of honeycomb monoliths.

17. Tronconi E, Groppi G: **"High conductivity" monolith catalysts for gas/solid exothermic reactions**. *Chem Eng Technol* 2002, **25**:743-750.

18. Hayes RE, Rojas A, Mmbaga J: **The effective thermal conductivity of honeycomb monolith structures**. *Catal Today* 2009, **147**:S113-S119.

19. Visconti CG, Groppi G, Tronconi E: **Accurate prediction of the effective radial conductivity of highly conductive honeycomb monoliths with square channels**. *Chem Eng J* 2013, **223**:224-230.
•• Recommended reference for the estimation of the effective radial thermal conductivity in honeycomb monoliths.

20. Doraiswamy LK, Sharma MM (Eds): *Heterogeneous Reactions: Analysis, Examples and Reactor Design, Vol. 1. Gas Solid and Solid–Solid Reactions*. John Wiley; 1984.

21. Eigenberger G: **Reaction engineering**. In *Handbook of Heterogeneous Catalysis*, Vol. 3. Edited by Ertl G, Knozinger H, Weitkamp J. John Wiley-VCH; 1997:1399-1425.

22. Groppi G, Tronconi E: **Design of novel monolith honeycomb catalyst supports for gas/solid reactions with heat exchange**. *Chem Eng Sci* 2000, **55**:2161-2171.

23. Groppi G, Tronconi E: **Simulation of structured catalytic reactors with enhanced thermal conductivity for selective oxidation reactions**. *Catal Today* 2001, **69**:63-73.

24. Groppi G, Airoldi G, Cristiani C, Tronconi E: **Characteristics of metallic structured catalysts with high thermal conductivity**. *Catal Today* 2000, **60**:57-62.

25. Tronconi E, Groppi G: **A study on the thermal behavior of structured plate-type catalysts with metallic supports for gas/ solid exothermic reactions**. *Chem Eng Sci* 2000, **55**:6021-6036.

26. Groppi G, Tronconi E: **Honeycomb supports with high thermal**
 • **conductivity for gas/solid chemical processes**. *Catal Today* 2005, **105**:297-304.
Reviews the early work in the area of conductive monolithic substrates.

27. Tronconi E, Groppi G, Boger T, Heibel A: **Monolithic catalysts with 'high conductivity' honeycomb supports for gas/solid exothermic reactions: characterization of the heat-transfer properties**. *Chem Eng Sci* 2004, **59**:4941-4949.

28. Boger T, Heibel AK: **Heat transfer in conductive monolith**
 • **structures**. *Chem Eng Sci* 2005, **60**:1823-1835.
Experimental study and rationalization of the 'gap' heat transfer resistance at the interface between monolith and tube wall in tubular reactors.

29. Groppi G, Tronconi E, Cortelli C, Leanza R: **Conductive**
 •• **monolithic catalysts: development and industrial pilot tests for the oxidation of o-xylene to phthalic anhydride**. *Ind Eng Chem Res* 2012, **51**:7590-7596.
To our knowledge the only report available so far in the open literature of a pilot-scale proof of concept in the area of conductive monolith catalysts.

30. Phan XK, Bakhtiary HD, Myrstad R, Thormann J, Pfeifer P,
 • Venvik HJ, Holmen A: **Preparation and performance of a catalyst-coated stacked foil microreactor for the methanol synthesis**. *Ind Eng Chem Res* 2010, **49**:10934-10941.
First proposal of metallic structured reactors for the methanol synthesis.

31. Phan XK, Bakhtiary HD, Myrstad R, Pfeifer P, Venvik HJ, Holmen A: **Preparation and performance of Cu-based monoliths for methanol synthesis**. *Appl Catal A: Gen* 2011, **405**:1-7.

32. Montebelli A, Visconti CG, Groppi G, Tronconi E, Ferreira C, Kohler S: **Enabling small-scale methanol synthesis reactors through the adoption of highly conductive structured catalysts**. *Catal Today* 2013, **215**:175-186.

33. Montebelli A, Visconti CG, Groppi G, Tronconi E, Kohler S: **Optimization of compact multitubular fixed-bed reactors for the methanol synthesis loaded with highly conductive structured catalysts**. *Chem Eng J* 2014. underreview.

34. Montebelli A, Visconti CG, Groppi G, Kohler S, Venvik HJ, Myrstad R: **Washcoating and chemical testing of a commercial Cu/ZnO/Al$_2$O$_3$ catalyst for the methanol synthesis over copper open-cell foams**. *Appl Catal A: Gen* 2014 http://dx.doi.org/ 10.1016/j.apcata.2014.05.005. submitted.

35. Hilmen AM, Bergene E, Lindvag A, Schanke D, Eri S, Holmen S:
 • **Fischer–Tropsch synthesis on monolithic catalysts of different materials**. *Catal Today* 2001, **69**:227-232.
First proposal of monolithic reactors for the Fischer–Tropsch synthesis, including metallic monoliths.

36. de Deugd RM, Kapteijn F, Moulijn JA: **Trends in Fischer–Tropsch reactor technology-opportunities for structured reactors**. *Topics Catal* 2003, **26**:29-39.

37. Guettel R, Knochen J, Kunz U, Kassing M, Turek T: **Preparation and catalytic evaluation of cobalt-based monolithic and powder catalysts for Fischer–Tropsch synthesis**. *Ind Eng Chem Res* 2008, **47**:6589-6597.

38. Guettel R, Turek T: **Comparison of different reactor types for low temperature Fischer–Tropsch synthesis: a simulation study**. *Chem Eng Sci* 2009, **64**:955-964.

39. Hilmen AM, Bergene E, Lindvag A, Schanke D, Eri S, Holmen A: **Fischer–Tropsch synthesis on monolithic catalysts with oil circulation**. *Catal Today* 2005, **105**:357-361.

40. de Deugd RM, Chougule RB, Kreutzer MT, Meeuse FM, Grievink J, Kapteijn F, Moulijn JA: **Is a monolithic loop reactor a viable option for Fischer–Tropsch synthesis?** *Chem Eng Sci* 2003, **58**:583-591.

41. de Deugd RM, Kapteijn F, Moulijn JA: **Using monolithic catalysts for high selective Fischer–Tropsch synthesis**. *Catal Today* 2003, **79–80**:495-501.

42. Almeida LC, Gonzales O, Sanz O, Paul A, Centeno MA, Odriozola JA, Montes M: **Fischer–Tropsch catalyst deposition on metallic structured supports**. *Stud Surf Sci Catal* 2007, **167**:79-84.

43. Kim H, Ryu J, Joo H, Yoon J, Jung H, Yang J: **Mass- and heat-transfer-enhanced catalysts system for Fischer–Tropsch synthesis in fixed-bed reactors**. *Res Chem Interm* 2008, **34**:811-816.

44. Almeida LC, Echave FJ, Sanz O, Centeno MA, Arzamendi G, Gandìa LM, Sousa-Aguiar EF, Odriozola JA, Montes M: **Fischer–Tropsch synthesis in microchannels**. *Chem Eng J* 2011, **167**:536-544.

45. Bradford MCJ, Te M, Pollack A: **Monolith loop catalytic membrane reactor for Fischer–Tropsch synthesis**. *Appl Catal A: Gen* 2005, **283**:39-46.

46. Visconti CG, Tronconi E, Lietti L, Groppi G, Forzatti P, Cristiani C, Zennaro R, Rossini S: **An experimental investigation of Fischer– Tropsch synthesis over washcoated metallic structured supports**. *Appl Catal A: Gen* 2009, **370**:93-101.

47. Incropera FP, De Witt DP (Eds): *Introduction to Heat Transfer*. Wiley; 1996.

48. Kapteijn F, de Deugd RM, Moulijn JA: **Fischer–Tropsch synthesis using monolithic catalysts**. *Catal Today* 2005, **105**:350-356.

49. Visconti CG, Tronconi E, Groppi G, Lietti L, Iovane M, Rossini S, Zennaro R: **Monolithic catalysts with high thermal conductivity for the Fischer–Tropsch synthesis in tubular reactors**. *Chem Eng J* 2011, **171**:1294-1307.

50. Gumuslu G, Avci AK: **Parametric analysis of Fischer–Tropsch synthesis in a catalytic microchannel reactor**. *AIChE J* 2012, **58**:227-235.

51. Chin Y, Hu J, Cao C, Gao Y, Wang Y: **Preparation of a novel structured catalyst based on aligned carbon nanotube arrays for a microchannel Fischer–Tropsch synthesis reactor**. *Catal Today* 2005, **110**:47-52.

52. Cao C, Hu J, Li S, Wilcox W, Wang Y: **Intensified Fischer–Tropsch synthesis process with microchannel catalytic reactors**. *Catal Today* 2009, **140**:146-156.

53. Myrstad R, Eri S, Pfeifer P, Rytter E, Holmen A: **Fischer–Tropsch synthesis in a microstructured reactor**. *Catal Today* 2009, **147**:S301-S304;
Knochen J, Guttel R, Knobloch C, Turek T: **Fischer–Tropsch synthesis in millistructured fixed-bed reactors: experimental study and scale-up considerations**. *Chem Eng Proc* 2010, **45**:958-964.

54. Wang Y, Tonkovich L, Mazanec T, Daly FD, VanderWiel D, Hu J, Cao C, Kibby C, Li XS, Briscoe MD, *et al.*: Fischer–Tropsch synthesis using microchannel technology and novel catalyst and microchannel reactor. US 7,084,180, 2006.

55. Almeida LC, Echave FJ, Sanz O, Centeno MA, Arzamendi G, Gandia LM, Sousa-Aguiar EF, Odriozola JA, Montes M: **Fischer– Tropsch synthesis in microchannels**. *Chem Eng J* 2011, **167**:536-544.

56. Kolb G: **Review: microstructured reactors for distributed and renewable production of fuels and electrical energy**. *Chem Eng Proc* 2013, **65**:1-44.

57. Holmen A, Venvik HJ, Myrstad R, Zhu J, Chen D: **Monolithic, microchannel and carbonnanofibers/carbonfelt reactors for syngas conversion by Fischer–Tropsch synthesis**. *Catal Today* 2013, **216**:150-157.

Open-cell Foams

58. Gibson LJ, Ashby MF (Eds): *Cellular Solids: Structure and Properties*. Pergamon Press; 1988.

59. Gibson LJ, Ashby MF (Eds): *Cellular Solids: Structure and*
•• *Properties*, Second Edition. Cambridge University Press; 1999.
A bible on foams, written by pioneers in the field.

60. Ashby MF (Ed): *Metal Foams: A Design Guide*. Elsevier; 2000.

61. Dukhan N (Ed): *Metal Foams: Fundamentals and Applications*. DEStech Publications; 2013.

62. Chin P, Sun X, Roberts GW, Spivey JJ: **Preferential oxidation of carbon monoxide with iron-promoted platinum catalysts supported on metal foams**. *Appl Catal A: Gen* 2006, **302**:22-31.

63. Sirijaruphan A, Goodwin JG Jr, Rice RW, Wei D, Butcher KR, Roberts GW, Spivey JJ: **Metal foam supported Pt catalysts for the selective oxidation of CO in hydrogen**. *Appl Catal A: Gen* 2005, **281**:1-9.

64. Cookson EJ, Floyd DE, Shih AJ: **Design, manufacture, and analysis of metal foam electrical resistance heater**. *Int J Mech Sci* 2006, **48**:1314-1322.

65. Scheffler F, Herrmann R, Schwieger W, Scheffler M: **Preparation and properties of an electrically heatable aluminium foam/zeolite composite**. *Microp Mesop Mater* 2004, **67**:53-59.

66. Bidault F, Brett DJL, Middleton PH, Abson N, Brandon NP: **A new application for nickel foam in alkaline fuel cells**. *Int J Hydrog En* 2009, **34**:6799-6808.

67. Twigg MV, Richardson JT: **Preparation and properties of ceramic foam catalyst supports**. *Stud Surf Sci Catal* 1994, **91**:345-359.

68. Richardson JT, Peng Y, Remue D: **Properties of ceramic foam catalyst supports: pressure drop**. *Appl Catal A: Gen* 2000, **204**:19-32.

69. Peng Y, Richardson JT: **Properties of ceramic foam catalyst**
• **supports: one-dimensional and two-dimensional heat transfer correlations**. *Appl Catal A: Gen* 2004, **266**:235-244.
Early paper on heat transport properties of foams: the proposed correlations refer however to one ceramic foam only.

70. Twigg MV, Richardson JT: **Fundamentals and applications of**
•• **structured ceramic foam catalysts**. *Ind Eng Chem Res* 2007, **46**:4166-4177.
Extensive review paper covering the uses of ceramic open-cell foams as structured catalyst supports. The part on fundamentals is however outdated.

71. Buciuman FC, Kraushaar-Czarnetzki B: **Ceramic foam monoliths as catalyst carriers. 1. Adjustment and description of the morphology**. *Ind Eng Chem Res* 2003, **42**:1863-1869.

72. Giani L, Groppi G, Tronconi E: **Mass transfer characterization of**
• **metallic foams as supports for structured catalysts**. *Ind Eng Chem Res* 2005, **44**:4993-5002.
Provides a comparative analysis of gas-solid mass transfer in packed pellets, honeycombs and open-cell foams, based on a dimensionless ratio between mass transfer rate and pressure drop.

73. Giani L, Groppi G, Tronconi E: **Heat transfer characterization of metallic foams as supports for structured catalysts**. *Ind Eng Chem Res* 2005, **44**:9078-9085.

74. Große J, Dietrich B, Martin H, Kind M, Vicente J, Hardy EH: **Volume image analysis of ceramic sponges**. *Chem Eng Technol* 2008, **31**:307-314.

75. Große J, Dietrich B, Incera Garrido G, Habisreuther P, Zarzalis N, Martin H, Kind M, Kraushaar-Czarnetzki B: **Morphological characterization of ceramic sponges for applications in chemical engineering**. *Ind Eng Chem Res* 2009, **48**:10395-10401.

76. Incera Garrido G, Patcas FC, Lang S, Kraushaar-Czarnetzki B:
• **Mass transfer and pressure drop in ceramic foams: a description for different pore sizes and porosities**. *Chem Eng Sci* 2008, **63**:5202-5217.
Reports possibly the most accurate correlation for gas-solid mass transfer in open-cell foams.

77. Grosse J, Dietrich B, Incera Garrido G, Habisreuther P, Zarzalis N, Martin H, Kind M, Kraushaar-Czarnetzki B: **Morphological characterization of ceramic sponges for applications in chemical engineering**. *Ind Eng Chem Res* 2009, **48**:10395-10401.

78. Edouard D, Huu TT, Huu CP, Luck F, Schweich D: **The effective thermal properties of solid foam beds: experimental and estimated temperature profiles**. *Int J Heat Mass Transfer* 2010, **53**:3807-3816.

79. Dietrich B, Schell G, Bucharsky EC, Oberacker R, Hoffmann MJ, Schabel W, Kind M, Martin H: **Determination of the thermal properties of ceramic sponges**. *Int J Heat Mass Transfer* 2010, **53**:198-205.

80. Dietrich B, Kind M, Martin H: **Axial two-phase thermal conductivity of ceramic sponges – experimental results and correlation**. *Int J Heat Mass Transfer* 2011, **54**:2276-2282.

81. Bianchi E, Heidig T, Visconti CG, Groppi G, Freund H, Tronconi E: **An appraisal of the heat transfer properties of metallic open-cell foams for strongly exo-/endo-thermic catalytic processes in tubular reactors**. *Chem Eng J* 2012, **198–199**:512-528.

82. Bianchi E, Heidig T, Visconti CG, Groppi G, Freund H, Tronconi E: **Heat transfer properties of metal foams supports for structured catalysts: Wall heat transfer coefficient**. *Catal Today* 2013, **216**:121-134.

83. Gräfl, Rühl AK, Kraushaar-Czarnetzki B: **Experimental study of heat transport in catalytic sponge packings by monitoring spatial temperature profiles in a cooled-wall reactor**. *Chem Eng J* 2014, **244**:234-242.

84. Lemlich R: **A theory for the limiting conductivity of polyhedral foam at low density**. *J Colloid Interface Sci* 1978, **64**:107-110. Schildhauer

85. TJ, Pangarkar K, van Ommen JR, Nijenhuis J, Moulijn JA, Kapteijn F:
•• **Heat transport in structured packings with two-phase co-current downflow**. *Chem Eng J* 2012, **185**:250-266.

Very nice comparative study of heat transport in cross-flow structures, knitted wire packings and open-cell Al foams: the focus is on gas-liquid systems, but single-phase data are also presented.

86. Park D, Moon DJ, Kim T: **Steam-CO₂ reforming of methane on**
• **Ni-γ-Al₂O₃-deposited metallic foam catalyst for GTL-FPSO process**. *Fuel Proc Tech* 2013, **12**:28-34.
An important application example of foams to the development of reformers for compact GTL processes.

87. Liu Y, Edouard D, Nguyen LD, Begin D, Nguyen P, Pham C, Pham-Huu C: **High performance structured platelet milli-reactor filled with supported cobalt open cell SiC foam catalyst for the Fischer–Tropsch synthesis**. *Chem Eng J* 2013, **222**:265-273.

88. Lacroix M, Dreibine L, de Tymowski B, Vigneron F, Edouard D, Bégin D, Nguyen P, Pham C, Savin-Poncet S, Luck F, Ledoux MJ, Pham-Huu C: **Silicon carbide foam composite containing cobalt as a highly selective and re-usable Fischer–Tropsch synthesis catalyst**. *Appl Catal A: Gen* 2011, **397**:62-72.

89. Reitzmann A, Bareiss A, Kraushaar-Czarnetzki B: **Simulation of a reactor for the partial oxidation of o-xylene to phthalic anhydride packed with ceramic foam monoliths**. *Oil Gas Eur Mag* 2006, **32**:94-98.

90. Muelheims P, Kraushaar-Czarnetzki B: **Temperature profiles and**
• **process performances of sponge packings as compared to spherical catalysts in the oxidation of o-xylene to phthalic anhydride**. *Ind Eng Chem Res* 2011, **50**:9925-9935.
Comparative study of heat transport in open-cell foams and pellets under reactive conditions.

Microfibrous Structures

91. Sheng M, Yang H, Cahela DR, Tatarchuk BJ: **Novel catalyst**
• **structures with enhanced heat transfer characteristics**. *J Catal* 2011, **281**:254-262.
Introduces the interesting concept of micro-fibrous entrapped catalysts.

92. Sheng M, Yang H, Cahela DR, Yantz WR Jr, Gonzalez CF, Tatarchuk BJ: **High conductivity catalyst structures for applications in exothermic reactions**. *Appl Catal A: Gen* 2012, **445–446**:143-152.

93. Sheng M, Cahela DR, Yang H, Gonzalez CF, Yantz WR Jr, Harris DK, Tatarchuk BJ: **Effective thermal conductivity and junction factor for sintered microfibrous materials**. *Int J Heat Mass Transf* 2013, **56**:10-19.

94. Sheng M, Cahela DR, Yang H, Gonzalez CF, Yantz WR Jr, Harris DK, Tatarchuk BJ: **Microscale heat transfer comparison between packed beds and microfibrous entrapped catalysts**. *Eng Appl Comput Fluid Mech* 2013, **7**:471-485.

95. Iovane M, Zennaro R, Forzatti P, Groppi G., Lietti L, Tronconi E, Visconti CG, Rossini E, Mignone E: Reactor for exothermic or endothermic catalytic reactions. WO/2010/130399.

96. Vervloet D, Kapteijn F, Nijenhuis J, Ruud van Ommen J: **Process intensification of tubular reactors: considerations on catalyst hold-up of structured packings**. *Catal Today* 2013, **216**:111-116.
    ●● Elegant, inspiring paper analyzing the concept of packed structured catalysts, a possible solution for the low catalyst inventory problem in structured catalysts.

Washcoating methods

97. Meille V: **Review on methods to deposit catalysts on structured surfaces**. *Appl Catal A: Gen* 2006, **315**:1-17.

98. Giani L, Cristiani C, Groppi G, Tronconi E: **Washcoating method for Pd/γ-Al$_2$O$_3$ deposition on metallic foams**. *Appl Catal B: Environ* 2006, **62**:121-131.

99. Zhang H, Suszynski WJ, Agrawal KV, Tsapatsis M, Hashimi SA, Francis LF: **Coating of open cell foams**. *Ind Eng Chem Res* 2012, **51**:9250-9259.

100 Montebelli A, Visconti CG, Groppi G, Tronconi E, Cristiani C,
● Ferreira C, Kohler S: **Methods for the catalytic activation of metallic structures**. *Appl Catal A: Gen* 2014. accepted. DOI: 10.1039/C4CY00179F.
Review paper focused specifically on the deposition of catalytic layers onto metallic open-cell foams.