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Review

Honeycomb supports with high thermal conductivity for gas/solid chemical processes

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Abstract

The scope of this review article is to address the use of novel monolithic catalysts with high thermal conductivity in externally cooled tubular reactors for gas/solid exothermic chemical processes in place of conventional packed beds of catalyst pellets.

After discussing the analysis and the implications of heat conduction in honeycomb monolith structures, we review herein simulation studies and experimental investigations showing that near-isothermal reactor operation can be achieved even under very high thermal loads by adopting specific materials and designs of the honeycomb supports associated with high effective radial thermal conductivities. For such monoliths, the limiting thermal resistance is located at the interface between the monolith and the inner tube wall ("gap resistance"). Recent measurements of the "gap" heat transfer coefficient point to very large values (>400 W/(m^2 K)), which are controlled both by the tube–monolith clearance at the actual operating conditions and by the thermal conductivity of the process gas.

Contents

1. Introduction

Honeycomb monoliths have become since many years the standard catalyst shape in most applications of environmental catalysis [1]. On the other hand, the adoption of monolithic catalysts in other areas of heterogeneous catalysis has started being explored only at the beginning of the 1980s, after their successful commercial application to the control of automotive exhausts and to the reduction of nitrogen oxides. Particularly attractive were the expectedly lower pressure drop and the potentially smaller size of the reactor as compared to conventional pelletized catalysts in gas-phase processes, but early studies in this field, using methanation [2] and hydrogenation [3] as model reactions, pointed out additional prospective benefits. In spite of the initial promising indications, however, more than two 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 long discouraged the extensive use of monolithic catalysts outside the well known environmental applications [4]:

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(a) Conventional parallel channel monoliths are virtually adiabatic: this is compatible with the processes for the abatement of pollutants in diluted streams, but would severely limit the control of temperature in many endo- and exothermic chemical processes.
(b) 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: again, this is not important for the fast, diffusion-limited reactions of environmental catalysis, but would be a clear disadvantage for the reactions under kinetic control usually met in chemical syntheses.

In reality, both such concerns can be overcome by dedicated monolith designs, addressing the specific requirements of chemical applications: as presented in the following, conductive heat exchange in monolith structures can be even more effective then convective heat transfer in packed beds, whereas washcoat catalyst loadings in excess of 25% (v/v) are well within the range of what is practiced with monoliths nowadays.

There remain, however, several more practical reasons which hinder the application of monolithic catalysts and supports to chemical syntheses [5]:

(c) 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.
(d) 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.
(e) The methods for loading, packaging, sealing and unloading monolithic 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.
(f) Monolithic 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 catalysts/reactors in chemicals production. An innovative area of development is represented by the use of monolithic catalysts in gas/solid endo-exothermal processes where multitubular packed-bed reactors are employed. Early studies by Flytzany-Stephanopoulos and Voecks investigated steam reforming of *n*-hexane over Ni-based catalysts supported by cordierite and metallic structures made of Kanthal [6]. The use of extruded honeycomb monolith catalysts in strongly exothermic selective chlorination and oxychlorination reactions was reported also in an industrial patent assigned to Wacker and Degussa [7]. Although superior performances were claimed with respect to conventional packed bed reactors, no rationale was provided to explain such results.

In the last decade, efforts have been devoted to investigate advantages associated with the use of monolithic catalysts with high thermal conductivity and to gain insight for the rational design of novel multitubular reactors. Such efforts are described in this paper. We will first review the phenomena and the implications associated with heat conduction in the solid matrix of honeycomb monolithic structures; then we will discuss theoretical as well as experimental investigations of this concept, in part originating from our group, including recent novel results.

2. Heat conduction in honeycomb monoliths

The use of monolithic catalysts in non-adiabatic fixed-bed reactors has been often regarded as unfeasible due to poor radial heat transfer properties: indeed, ceramic honeycomb monoliths are made essentially of insulating materials; a theoretical analysis of Cybulski and Moulijn [8] evidenced that commercial monolith structures consisting of corrugated metal sheets exhibit modest heat transfer performances, too.

Nevertheless, 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 not available for random packings of catalyst pellets. The conduction within the solid phase of the pellets in fact is practically negligible, since only point contacts exist between the pellets, and convection in the gas phase dominates as the primary mechanism for heat exchange. By using monolith honeycomb structures with parallel channels as catalyst elements no radial transfer of gas may exist, but the 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 structures $k_{e,a}$ is readily estimated as:

$$k_{e,a} = k_s(1-\varepsilon) \qquad (1)$$

where k_s is the intrinsic thermal conductivity of the support material and ε is the monolith open frontal area. Based on a simple analysis of heat conduction in the unit cell of a honeycomb monolith with square channels, Groppi and Tronconi [9,10] have derived the following predictive equation for the effective radial thermal conductivity in washcoated monoliths, $k_{e,r}$:

$$k_{e,r} = k_s \left((1 - \sqrt{\varepsilon + \xi}) + \frac{\sqrt{\varepsilon + \xi} - \sqrt{\varepsilon}}{(1 - \sqrt{\varepsilon + \xi}) + \frac{k_w}{k_s}\sqrt{\varepsilon + \xi}} + \frac{\sqrt{\varepsilon}}{(1 - \sqrt{\varepsilon + \xi}) + \frac{k_w}{k_s}(\sqrt{\varepsilon + \xi} - \sqrt{\varepsilon}) + \frac{k_w}{k_s}\sqrt{\varepsilon}} \right)^{-1} \tag{2}$$

where ε and ξ are the monolith volume fractions of voids and washcoat, whereas k_s, k_g, k_w are the intrinsic thermal conductivities of support, gas phase and washcoat, respectively. A similar equation was derived also for monoliths with equilateral triangular channels [9].

Eq. (2) indicates that the effective 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 of course very beneficial for the enhancement of radial heat transfer in monoliths. In Fig. 1 estimates of $k_{e,r}$ according to Eq. (2) are plotted versus the monolith open frontal area ε for honeycomb structures made of various metallic and non-metallic materials with different intrinsic thermal conductivity; for the sake of simplicity, the volume fraction of active washcoat, ξ, as well as the minor contribution of heat conduction in the gas phase have been neglected in this case. It should be emphasized that when highly conductive materials are used the values of $k_{e,r}$ in Fig. 1 are greater by one order of magnitude than the effective radial thermal conductivities in packed beds, which are typically in the range 2–5 W/(m K) [11]. The plot also shows that the radial effective conductivity is adversely affected by large monolith void fractions. Accordingly, heat exchange in monolithic structures can be made efficient (even more efficient than in pellets), but monolith supports with specific designs must be adopted, based on a discerning selection of the monolith geometry and material aimed at minimizing resistances to conductive heat transfer. In fact, the existing commercial monoliths were not originally designed for such purposes: neither their construction material nor their geometry is optimized for heat conduction. The intrinsic conductivity of ceramic honeycombs is very low, whereas the available metallic monolith structures are made of poorly conductive alloys (e.g. FeCr alloy) and are assembled by piling up and rolling corrugated sheets which are in poor thermal contact with one another, thus increasing the overall resistance to heat transfer. Furthermore, 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 applications.

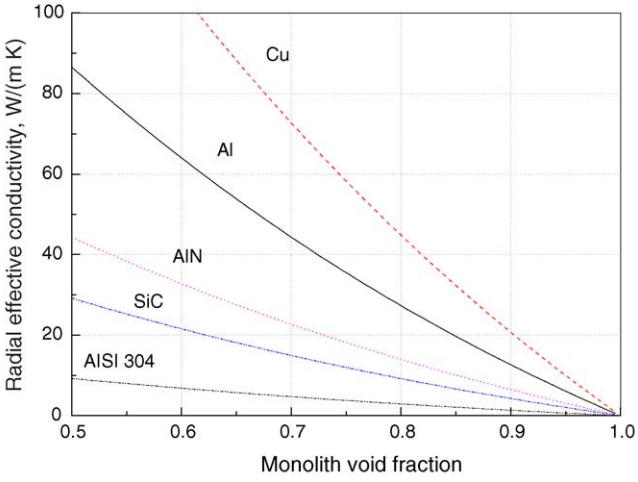

Fig. 1. Effect of material properties and monolith void fraction on estimated radial effective thermal conductivity of honeycomb monoliths with square channels (from Ref. [10]).

3. Exothermic reactions in honeycomb monolith catalysts

The evaluations summarized by Fig. 1 predict that in principle the radial heat transfer in fixed-bed gas/solid reactors could be substantially enhanced by 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 currently limited 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 in. as well as 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, possibly higher selectivity, as well as potential for novel designs of industrial reactors with incremented throughputs and/or enlarged tube diameters, corresponding to reduced investment costs. As an example, an EP application to EVC [12] describes the use of catalysts with various metallic honeycomb supports in chlorination/oxychlorination reactions, claiming greater yields and selectivities, avoidance of hot spots, greater catalyst life and flexibility in use as compared to conventional catalysts in pellet form.

In order to assess such prospective advantages, the thermal behavior of ‘‘high conductivity’’ monolith catalysts in exothermic reactions has been investigated both theoretically and experimentally in the last few years [9,10,13–19].

3.1. Simulation studies

A preliminary modeling analysis [13], focused on catalyst design aspects, involved the parametric study of a multitubular externally-cooled fixed bed reactor for a generic selective oxidation process, where the catalyst load consisted of cylindrical honeycomb monoliths with washcoated square channels and highly conductive supports. Simulation results were generated by a steady-state pseudo-continuous 2D monolithic reactor model, where the catalyst is regarded as a continuum consisting of a static, thermally connected solid phase and of a segregated gas phase in laminar flow inside the channels [9]. It was shown that metallic honeycombs are indeed promising for limiting temperature gradients as compared to pellets, to the extent that near-isothermal operation of the catalytic bed can be approached even for strong exothermal duties. In order to take full advantage of heat conduction in monoliths, however, specific honeycomb designs must be developed which include relatively large volume fractions of support made of materials with a high intrinsic conductivity (e.g. copper or aluminum), as well as large loads of active catalytic components: it is worth emphasizing that such designs are structurally different from those of the existing commercial monolithic supports used in environmental catalysis, which carry a relatively small load of active washcoat since the related reactions are very fast, and exhibit very large open frontal areas, the main goal in these applications being the cutback of pressure drops.

In a subsequent study, two important industrial selective oxidation processes were addressed in details, namely the partial oxidation of methanol to formaldehyde and the epoxidation of ethylene to ethylene oxide [14]. In both cases, secondary undesired reactions play a significant role, i.e. the combustion of the primary product in the formaldehyde process and the combustion of the ethylene reactant in the ethylene oxide process, so that the study provided also information on how the adoption of "high conductivity" monolith catalysts would affect the selectivity of industrial partial oxidation processes for either a consecutive or a parallel reaction scheme.

With reference to the Formaldehyde reactor, the simulations showed that the HCHO molar yield could be incremented from the 93.6%, reported for an optimized packed-bed reactor process [20] up to over 97% if aluminum washcoated honeycombs with suitable design were loaded in the original reactor tubes. The optimal performance of the monolith catalysts originates from: (i) a thin catalyst layer, which prevents diffusional limitations from adversely affecting the selectivity; (ii) a thickness of the highly conductive monolith walls adequate enough to grant near-isothermal operation, preventing hot spot formation; (iii) a high level of the coolant temperature, which increments the average reactor temperature and hence the overall CH_3OH conversion, thus compensating for a smaller volume fraction of active catalyst than in packed beds, without adversely affecting the selectivity: in fact the process is operated essentially under kinetic control, due to the thin washcoat layers deposited onto the monolith catalysts, and the activation energy of the undesired reaction (combustion of formaldehyde) is lower than that of the primary reaction.

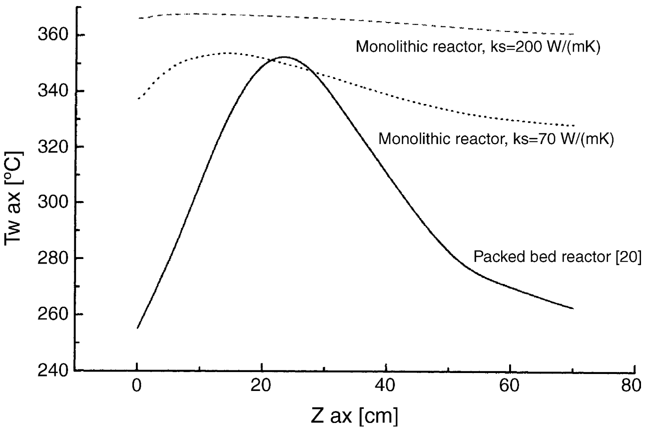

Fig. 2. Oxidation of methanol to formaldehyde. Axial catalyst temperature profiles for: (a) packed bed reactor, $T_{cool} = 250$ °C (from Ref. [20]); (b) monolithic reactor, $k_s = 70$ W/(m K), $T_{cool} = 327$ °C; (c) monolithic reactor, $k_s = 200$ W/(m K), $T_{cool} = 361$ °C. From Ref. [14].

In its optimized configuration the monolithic reactor would be virtually isothermal, as illustrated in Fig. 2. Although the optimization of the monolithic reactor was carried out without any constraint on the catalyst temperature, alternative sub-optimal configurations with lower levels of the coolant temperature were investigated, too, in view of possible problems with the thermal stability of the catalyst: even with largely reduced temperature levels, it was still possible to achieve HCHO yields significantly superior to the performance of the industrial packed-bed reactor.

Further simulations predicted a high (>95%) HCHO yield even in the case of reactor tubes with diameter incremented from 1 in., the current industrial standard, to 3 in., which would afford important savings in the reactor investment costs. However, the volume fraction of the conductive monolith support needs to be incremented up to 0.4 to compensate for the greater heat transfer resistances. For all the simulated conditions, the estimated pressure drop was less than 1% of the inlet pressure, versus over 10% in the industrial packed-bed reactor.

In the case of the ethylene oxide reactor, on the other hand, in order to optimize the selectivity it is crucial to prevent hot spots, being the activation energy of the parallel parasitic ethylene combustion greater than the activation energy of the primary epoxidation reaction. The simulation results [14] confirmed that isothermal operation is feasible also for the ethylene oxide reactor due to the excellent effective thermal conductivity of the metallic monoliths. For a monolith pitch $m = 2$ mm, and for monolith volume fractions of support and catalyst both equal to 0.2, the reactor behavior was found identical to that of an ideal isothermal reactor under a variety of conditions, provided that k_s, the intrinsic thermal conductivity of the monolith support, was ≥ 50 W/(m K), which can be provided, e.g. by aluminum or copper. Notably, thick catalytic washcoats would increment the conversion without adversely affecting

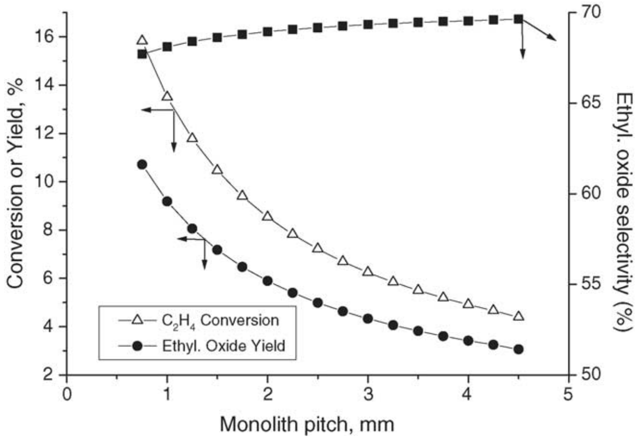

Fig. 3. Epoxidation of ethylene: calculated effect of the monolith pitch on C_2H_4 conversion, C_2H_4O selectivity and molar yield. Washcoat thickness = 120 μm, support volume fraction = 0.2, k_s = 200 W/(m K), T_{cool} = 250 °C. Tube diameter = 39.2 mm. From Ref. [14].

the selectivity. On the other hand, increments of the coolant temperature, as adopted for the formaldehyde reactor, are not compatible with the present kinetic scheme, since they would lower the selectivity in this case. For a fixed washcoat thickness (e.g. the greatest one compatible with adhesion requirements), however, the overall catalyst load can still be incremented by incrementing the monolith cell density. Calculations for a 120 μm thick catalytic washcoat shown in Fig. 3 suggest that high conductivity honeycombs with small pitch would indeed bring about significant improvements of C_2H_4 conversion with only a slight loss of selectivity.

While the results presented so far were generated assuming 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, as detected also in the experimental investigations reported below [15,16,18]. Calculations predict that such a resistance may become critical 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) [10]. Accordingly, solutions aimed at achieving effective thermal contact between the honeycombs and the reactor tubes (‘packaging’ methods) represent an important development goal.

Along similar lines, the application of highly conductive monolithic catalysts in the production of phthalic anhydride by selective oxidation of *o*-xylene has been also simulated in a recent publication [17]. In this study, the characteristics of new prototype honeycomb copper substrates produced at Corning Inc. [20] were assumed, and account of the monolith–reactor contact resistance was included according to the experimental results described in Ref. [16]. The simulation results confirm that significant incentives can be expected from the excellent conductive heat transfer properties of these novel substrates. In general, due to a better control of the hot spot the operating window is enlarged with respect to the conventional packed-bed reactor: for example, it is possible to operate with lower hot spot temperatures, allowing for extended catalyst lifetimes. Guidelines are also given for the rational design of the monolithic catalysts with respect to requirements on catalyst inventory and intraporous diffusional limitations, as summarized in Fig. 4. Note that using a 200/10 cpsi honeycomb, only 28 μm thickness of coating are required to obtain the same loading of active phase, 70 kg/m^3, of a conventional packed bed reactor loaded with 8 mm × 5 mm × 5 mm rings coated with an active layer about 100 μm thick. Besides, using a 400/7 cpsi honeycomb with active layer thickness of 100 μm an active phase loading of almost 300 kg/m^3 can be achieved, which corresponds to over 25% of the reactor volume. Such a value, obtained with commercially feasible monolith geometry and washcoat thickness, is able to match the catalyst loading requirements of most of the existing selective oxidation processes. The authors complemented their study with an economic analysis of three different possible strategies for exploiting the advantages of high conductivity monolith supports: (a) operation at equal feed conditions but at a higher coolant temperature to maintain the same hot spot temperature, resulting in a higher yield; (b) operation at equal air flow but with a higher feed concentration of *o*-xylene, resulting in a higher throughput; (c) operation at equal *o*-xylene throughput but with a reduced air flow, which requires less energy. Economic evaluations designate solution (b) as by far the most rewarding one: however, the related increase in capacity would usually require some investment in the downstream equipment, while solutions (a and c) appear already very attractive, leading to annual cost reductions in the order of 1 million US$ for a 45 kt/a unit.

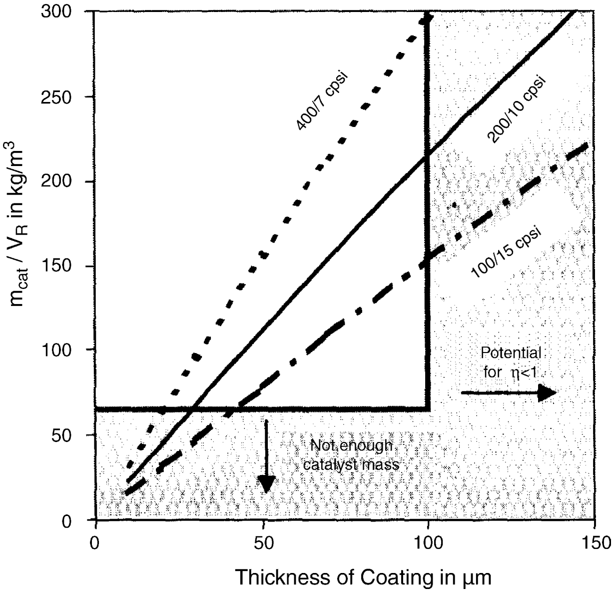

Fig. 4. Oxidation of *o*-xylene: monolith catalyst design. Calculated relationship between active mass per unit volume and washcoat thickness for three monolith support structures. The blank area represents the desired range. From Ref. [17].

3.2. *Experimental studies*

In parallel with the modeling analyses discussed above, the heat exchange characteristics of "high conductivity" monolith catalysts have been also addressed experimentally [10,15,16,18,19], the goal being to investigate the thermal behavior of structured metallic catalysts in the presence of a strongly exothermic reaction, focusing specifically on the influence of such catalyst design parameters as material, configuration and geometry of the structured support, and formulation and load of the catalytic washcoat. Since commercially available monolithic supports for environmental catalysts are not suitable for this class of applications, as explained above, in the early studies home-made "high conductivity" structured catalysts were prepared by assembling washcoated slabs of aluminium or stainless steel to form plate-type catalytic cartridges, which were also equipped with thermowells for sliding thermocouples in order to monitor the temperature distributions. The washcoat consisted of Pd (3%, w/w) on γ-Al_2O_3, and the catalysts were tested in the oxidation of CO, selected as a model exothermic reaction [15]. Samples with different characteristics were prepared and tested to address the effects of: the support material (Al versus stainless steel); the thickness of the metal slabs; the washcoat load; the contact thermal resistance at the reactor wall. Major results are summarized in the following.

(a) Over all the samples with Al support, temperature gradients were negligible in the direction transverse to flow, and were only moderate along the axial coordinate even at the most severe reaction conditions. Representative measured temperature distributions are displayed in Fig. 5A: due to the high intrinsic heat conductivity of the Al support, virtually all of the overall heat transfer resistance was confined at the interface between the catalyst slabs and the inner reactor wall.
(b) When tested under the same reaction conditions the sample with a stainless steel support exhibited much more marked temperature gradients, also along the transverse coordinate (Fig. 5B). This is evidently related to the difference in the intrinsic thermal conductivity of aluminium and of steel, which are approximately 200 and 20 W/(m K), respectively. Temperature gradients further increased when using thinner steel slabs ($s = 0.2$ mm versus 0.5 mm) as a result of the decreased effective support thermal conductivity.
(c) Different washcoat compositions and washcoat loads altered the catalytic activity but not the thermal behavior of the structured systems.
(d) The addition of small fins along the contour of the slabs improved the thermal contact at the catalyst–reactor interface significantly decreasing the overall heat transfer resistance.

The experimental results were adequately represented by a 1D heterogeneous non-isothermal model of the plate-type structured catalysts, accounting for heat generation by CO oxidation over the catalyst slabs, heat conduction along the slabs, and heat exchange to the surrounding heat sink across the catalyst–reactor interface [10,15]. Notice that the assumption of negligible T-gradients in the direction transverse to gas flow (1D approximation) is experimentally verified in the case of highly conductive supports (see e.g. Fig. 5). In the model equations, h_w (wall heat transfer coefficient) and h_{in} (inlet heat transfer coefficient) were regarded as adaptive parameters, and were estimated by fitting the calculated axial temperature distributions to a set of experimental catalyst temperature profiles, whereas the rate parameters were estimated from independent regression analysis of CO conversion data in isothermal runs [15]. Good fit of temperature profiles measured in CO oxidation runs under a wide range of different operating conditions were obtained for the samples with Al support: in all cases the estimated wall heat transfer coefficients h_w were of the order of 100 W/(m^2 K), the highest value (119 W/(m^2 K)) corresponding to the catalyst with fins [15].

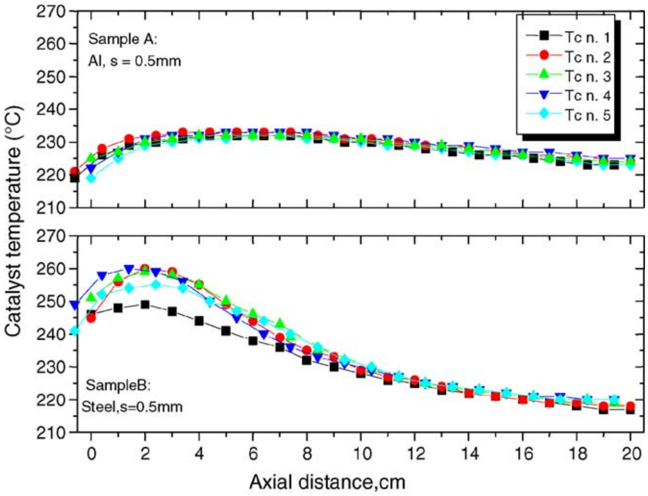

Fig. 5. Comparison of temperature distributions measured over catalyst samples A (Al support) and B (steel support) under the same reaction conditions: CO feed concentration = 5% (v/v), feed flow rate = 1000 cm^3/min (STP), oven temperature = 216 °C. CO conversion = 100%. From Ref. [10].

Honeycomb substrates with high thermal conductivity have been recently produced at Corning Inc. from extrusion of Cu powder, followed by drying and firing [21]. Differently from conventional manufacturing processes of metallic monoliths based on piling up and rolling of corrugated sheets, extrusion provides in fact the required continuous and thermally connected matrix which is optimal for conductive heat transfer. Tronconi et al. [16] have reported an experimental study of the heat transfer properties of such prototype systems. The supports were Ni-plated to prevent oxidation of copper, washcoated with Pd/γ-Al_2O_3, loaded in a 1 in. i.d. tube inserted in an oven and tested in both pure heat transfer and reactive experiments,

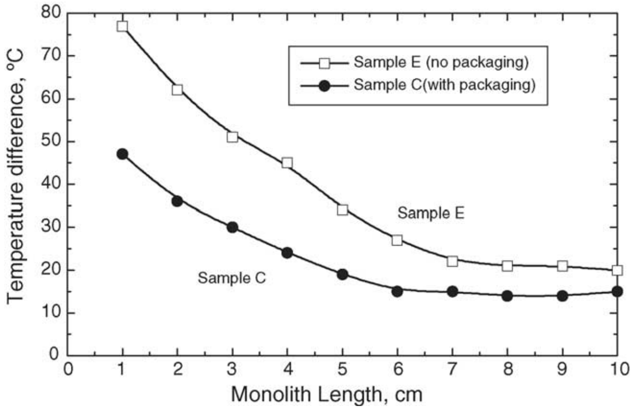

Fig. 6. CO oxidation runs over copper monoliths: effect of packaging on the T-difference between monolith axis and tube wall. Flow rate = 7000 cm^3/min (STP), CO feed = 5% (v/v). T_{oven} = 215 °C (sample C), 200 °C (sample E). From Ref. [16].

again using CO oxidation as a strongly exothermic model reaction. The axial T-profiles measured by three sliding thermocouples directly inserted into the monolith channels at different radial positions showed that even under the most severe conditions investigated in reactive runs, corresponding to a radial heat flux exceeding 23 kW/m^2, radial temperature gradients were still negligible with respect to the T-differences prevailing between the monolith and the reactor wall, where the controlling heat transfer resistance is confined.

In addition to the characterization of extruded monolithic supports with high intrinsic conductivity suitable for industrial applications, the purpose of this work was also to test packaging systems aimed at reducing the heat transfer resistance at the monolith–wall interface (‘gap’ issue). Fig. 6 compares the temperature differences measured between the monolith centerline and the reactor tube wall in reactive runs at comparable conditions over copper monolith catalysts packaged differently: sample C represents the data for an ‘advanced’ packaging method, whereas sample E was loaded without special measures to ensure good heat transfer across the gap. It is apparent that the advanced packaging results in a significant reduction of the temperature gradient across the monolith–tube interface, and hence of the associated thermal resistance, along the entire monolith length. These data confirm that it is critical but also feasible to enhance the wall heat transfer coefficient h_w by a suitable packaging method.

Estimates of the ‘‘gap’’ heat transfer coefficient (h_w) were obtained by regression of temperature profiles in both heat transfer and CO oxidation experiments, based on a heterogeneous 1D monolith reactor model similar to that reported in Ref. [15]. The estimated heat transfer coefficient from the monolith to the tube wall was 220 W/(m^2 K) when no special packaging concept was used. With one of several advanced packaging concepts tested, heat transfer coefficients in the target range of 400–500 W/(m^2 K) were achieved. For comparison, the overall heat transfer coefficients of standard catalyst packings, such as rings, would be well below 100 W/(m^2 K) under the flow rates used in the experiments, and would also be at best in the range of 200–250 W/(m^2 K) under typical industrial conditions. Hence, these results appear very encouraging in view of a practical implementation of ‘‘high conductivity’’ monoliths.

Recently the ‘gap’ issue has been systematically investigated by Boger and Heibel [18]. They performed pure heat transfer experiments using extruded metallic monoliths inserted with controlled clearance into a stainless tube externally cooled by water at 20 °C. An integral heat transfer coefficient h_{int} was evaluated from measurements of inlet and outlet temperatures of the gas (N_2 or air) flowing through the monolith. Values of h_{int} in excess of 1000 W/(m^2 K) were obtained. The results clearly pointed out a role of the nominal size of the gap between the monolith and the stainless tube on the overall heat transfer properties but also evidenced a marked effect of operating parameters, such as gas flow rate and inlet temperature. The experimental results were analyzed by means of a mathematical model accounting for the role of radial and axial solid heat conduction and of gas/solid heat transfer resistance in the monolith channels, so as to isolate the contribution of the ‘gap’ resistance to heat transfer. Such analysis reconciled the effects of the operating variables and monolith material and geometry and pointed out that the heat transfer coefficient between the monolith skin and the internal tube wall can be simply calculated as:

$$h_{gap} = \frac{k_g}{\delta_{gap}} \qquad (3)$$

where the size of the gap, δ_{gap}, must be evaluated locally as a function of the initial clearance between monoliths and tube during loading at room temperature and of the different thermal expansion of monoliths and tube at their actual operating temperature. The authors emphasize the practical role of the latter phenomenon, particularly when using monoliths made of materials with high thermal expansion coefficients, such as aluminum. Indeed due to differential thermal expansion very good heat transfer coefficients can be obtained even with loose tolerances at room temperature, which facilitate loading the monolith in the reactor tube. Furthermore, the heat transfer performances improve in the reactor zone with maximum reaction and heat release rates, where the occurrence of hot spots results in a self-regulating effect.

According to Eq. (3) also a higher thermal conductivity of the gas, k_g, can be beneficial, as e.g. when switching from exothermic oxidation to exothermic hydrogenation reactions. The effect of gas conductivity on the wall heat transfer coefficients has been recently investigated by Tronconi and co-workers [19] by performing experiments with N_2, He and their mixtures as flowing heat transfer medium in a copper monolith with a fixed gap size. The results reported in

Table 1
Wall heat transfer coefficients for different flowing gases

Gas	k_g at 200 °C (W/(m K))	h_w (W/(m^2 K))
N_2	0.037	349
N_2/He = 1.38/1	0.082	463
N_2/He = 1/3	0.139	600
He	0.206	767

Table 1 confirm that the wall heat transfer coefficient, h_W, increases with the thermal conductivity of the flowing gas, although the effect is less pronounced than predicted by Eq. (3): in fact, when switching from N_2 to He k_g increases by a 5.5 factor, but this only results in a two-fold increment of h_w.

4. Conclusions

A good number of exploratory studies has been performed by now addressing the use of novel monolithic catalysts with high thermal conductivity in externally cooled tubular reactors for gas/solid exothermic chemical processes in place of conventional packed beds of catalyst pellets. In addition to well recognized advantages of negligible pressure drop and fine control of diffusional intraporous limitations, it has been established both by simulation and by experimental investigations that, even under very high thermal loads, near-isothermal reactor operation can be achieved, provided that specific designs of the honeycomb supports with high effective radial thermal conductivities are adopted. For such monoliths, the limiting radial thermal resistance is located at the interface between the monolith and the inner tube wall (“gap resistance”). Recent measurements of the “gap” heat transfer coefficient point to very large values (>400 W/(m^2 K)), which are controlled both by the tube–monolith clearance at the actual operating conditions and by the thermal conductivity of the process gas. The feasibility of loading, sealing, unloading of the monoliths in the reactor tubes has been also preliminarily explored.

At the present stage, further efforts in this area should be primarily focused on realizations of the concept at the demonstrative scale as well as on the economic evaluation of its operational advantages versus its higher catalyst manufacturing and development costs as compared to conventional packed beds.

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