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Structuring Catalyst and Reactor - An inviting avenue to Process Intensification

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Multiphase catalytic processes involve the combination of scale-dependent and scale-independent phenomena, often resulting in a compromised, sub-optimal performance. The classical approach of randomly packed catalyst beds using unstructured catalyst particles may be outperformed by the careful design of the catalyst at the nano-scale and by the judicious choice and design of reactor. Application of structured catalysts and reactor internals and the combination of advanced reactor and catalyst systems with in situ separation allow decoupling the various phenomena involved, opening the way to intensified processes on a large scale. The integral approach of Catalysis and Reaction Engineering discussed here will play a pivotal role in the development of novel, future-proof processes.

A Introduction

In the art of heterogeneous catalysis, the use of porous particles that provide large interfacial reaction areas per unit volume is common practice. Indeed, large surface areas infer high active site dispersion, while the use of porous particles can add extra functionalities, such as shape selectivity, to a given catalyst. At the same time, heterogeneous catalysis cannot be understood without taking diffusion into account. Already in 1939, Ernst W. Thiele, one of the fathers of Chemical Engineering, wrote *“In general, it appears to be tacitly assumed by workers in this field that the reacting fluid penetrates to the pores in the interior of the grains and maintains substantially a constant composition throughout all the pores of a single grain, which is the same as the composition of the bulk of the fluid bathing the grain at the time.”*¹

The importance of diffusion in catalysts arises from the fact that the catalytically active site needs to be reached by the reactants, and products need to move away from this site. When a scientist discovers in the laboratory a catalytic material with excellent performance, an innovation is born but not yet such a thing as a practical process. In a scale up program a technically satisfactory performing catalyst has to be developed, preferably in concert with the reactor application.² Often a particulate form

will be developed that can be directly used in a commercial reactor, for instance in a fixed bed, a slurry or a fluid bed reactor. In these reactors, reactants need to move from the bulk fluid to the active site. As commonly applied in industrial catalysis, macro-porous ($d_{pore} > 50$ nm) particles at the bed level consist of pelleted smaller particles with meso (2 nm $< d_{pore} < 50$ nm) or even micro-pores ($d_{pore} < 2$ nm). External resistances, which can stand in the way of optimal catalysis, are stagnant film layers around the particles that can introduce external heat and mass transfer limitations. These are controlled by the reactor hydrodynamics. Additionally, macro-pores in the pelleted particles and meso and micro-pores in the small particles or crystals can induce internal (diffusional) mass transport limitations. Internal temperature gradients are generally absent due to the good thermal conduction in the solid (pelleted) particles.

Most transport limitations and associated catalyst effectiveness are based on solving the reaction-diffusion problem at two different levels: (i) the microlevel, focusing on molecules and catalytic sites and (ii) the mesolevel[†], focusing on the catalyst particle and the catalytic reactor. Following from this simple concept, in an ideal catalytic system we would like to: (i) minimize diffusion pathways at all scales in order to maximize utilization of the intrinsic properties of the catalytic sites and

(ii) eliminate external mass and heat transport resistances. The overall performance is a result of the interplay of kinetics, thermodynamics, transport phenomena and hydrodynamics. These intrinsic and extrinsic processes are strongly coupled, and optimizing one aspect goes at the expense of another, resulting in a trade-off. Dudukovic et al.³ formulated this dilemma as *"The unresolved problems in massive adiabatic packed beds are the issues of flow distribution and optimal catalyst shape for low-pressure drop and high mass and heat transfer. The last requirement defies the Chilton–Colburn analogy in a quest for a holy grail, i.e., excellent mass and heat transfer rates at low-pressure drop!"*

Probably the most elegant way of addressing these challenges consists of structuring the catalytic system at both micro- and meso-levels. In such a way, this coupling is alleviated and it should be possible to optimize the reactor operation and utilize the potential of catalytic functions and to simplify fluid mechanics. This is the main purpose of Catalysis Engineering and the topic of this article.

Structuring of the catalyst and reactor is one of the successful approaches in Process Intensification. It will be shown that structuring indeed is an avenue to higher rates and selectivities by reducing mass and heat transport limitations. In addition, 'unusual' conditions can be selected, for instance operation within the explosion limits can be feasible. Scaling up and scaling down can be done relatively easily.⁴ At the small size, an option is to carry out production on-site instead of in big centralized plants. The advantage can be reduction in transportation costs and increased safety (for instance no dangerous transport of chlorine, ammonia). Safety is also improved by the low materials hold-up.

In this perspective, we summarize the main advantages and challenges of catalyst and reactor optimization via structuring, with structured being defined as opposite to random. Different examples from the literature are used to illustrate the benefits that structuring offers to process intensification and catalyst performance rationalization.

B Structuring at the particle level: from hierarchical materials to multifunctional catalysis

Limitations due to restricted access, slow transport and diffusion boundaries provoke low catalyst utilization. In many cases, synthetic porous materials such as zeolites or metal organic frameworks are victims and executioners of such limitations. Following the classical Thiele approach, when considering slab geometry like, i.e. in the case of ZSM-5⁵ and a first order irreversible reaction, under isothermal conditions:

Thiele Modulus

$$\phi = \sqrt{\left(\frac{r_{\text{intrinsic}}}{r_{\text{diffusion}}}\right)} = L \sqrt{\frac{k_v}{D_{\text{eff}}}} \quad [\text{eq. 1}]$$

Concentration profile along the crystal:

$$c = c_s \frac{\cosh(\phi X / L)}{\cosh(\phi)} \quad [\text{eq. 2}]$$

Effectiveness factor

$$\eta = \frac{r_{\text{observed}}}{r_{\text{intrinsic}}} = \frac{\tanh(\phi)}{\phi} \quad [\text{eq. 3}]$$

Figure 1 shows how the concentration profile across a zeolite crystal at different values of the Thiele modulus varies and the dependence of the effectiveness factor on the Thiele modulus for the specific case of equations 1-3. Full utilization of the catalyst particle ($\eta \rightarrow 1$) only takes place at very low values of the Thiele modulus ($\phi \rightarrow 0$). Contrarily, $\phi = 10$ renders $\eta = 0.1$, meaning that only 10% of the catalyst volume is effectively used in the reaction. Transport limitations negatively impact not only activity, but occasionally also selectivity and stability.⁶

If a small Thiele modulus is desired, two different strategies can be followed: shortening the diffusion length L and/or enhancing the effective diffusivity D_{eff} in the zeolite pores. The latter strategy has led to the development of Ordered Mesoporous Materials (OMMs),⁷ where diffusion is governed by Knudsen or bulk diffusion.⁷⁻⁹

Parallel to the development of OMMs, much effort has been devoted to enhance diffusional transport in zeolites, while maintaining intact the other properties of the material. The synthesis of new structures with large and ultra-large pores,¹⁰⁻¹⁴ the modification of the textural properties of known frameworks by creating mesopores via synthetic^{15, 16} or post-synthetic approaches¹⁷⁻²², the synthesis of small zeolite crystals with a more convenient external to internal surface ratio,²³ the synthesis of micro-mesoporous composites²⁴ by using mixed template^{25, 26} or by recrystallization²⁷⁻³⁰ approaches, the delamination³¹⁻³⁷ of crystalline-layered and the direct synthesis of lamellar structures are the most often followed approaches.

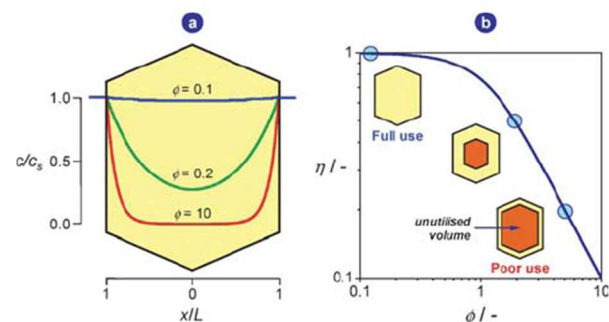


Figure 1. Concentration profiles across a zeolite crystal (slab geometry) at different values of the Thiele modulus, ϕ (a). The reactant concentration across a zeolite crystal is extinguished ($c/c_s = 0$) near the surface at $\phi = 10$, while being practically uniform and very similar to the surface concentration ($c/c_s = 1$) at $\phi = 0.1$. The dependence of the effectiveness factor on the Thiele modulus is shown in (b). Low Thiele moduli lead to full catalyst utilisation ($\phi \rightarrow 0, \eta \rightarrow 1$) while high Thiele moduli render a poorly utilised catalyst ($\phi \rightarrow \infty, \eta \rightarrow 1/\phi$). Reproduced with permission from Royal Society of Chemistry.⁵

Ultra large pore zeolites such as SSZ-53¹³ and delaminated zeolites such as ITQ-2³⁴ have been successfully applied to hydrocracking of bulky molecules under mild conditions, showing an outstanding performance due to an improved transport of molecules and a higher acidity. The partial conversion of a mesoporous material TUD-1 into BEA or Y-type zeolite and application in alkylation or hydrocracking indicated an effective diffusion improvement by up to 15 times. Demetallation methods such as acid leaching and steaming (dealumination) have been shown to be less efficient ways to improve transport than expected. In the case of dealuminated USY pellets (FCC catalyst), the rate of molecular exchange between catalyst particles and their surroundings is primarily determined by intraparticle diffusion, i.e. at the reaction temperature, diffusion is controlled by the macropores and not by the micro- or mesopores.³⁸ Moreover, when dealuminated crystals are used instead of catalyst pellets, the mesopores do not form a connected network, and the diffusion of guest molecules through the crystals via only mesopores is not possible.³⁹ On the other hand, desilication⁴⁰ seems to be much more effective, yielding to a greatly improved physical transport in the zeolite crystals, as revealed by transient uptake experiments of neopentane in ZSM-5,¹⁹ diffusion studies of *n*-heptane, 1,3-dimethylcyclohexane, *n*-undecane in mesoporous ZSM-12⁴¹ and diffusion and adsorption studies of cumene in mesopore structured ZSM-5.⁴² Up to three orders of magnitude enhanced rates of diffusion were found in the hierarchical systems as compared to their purely microporous precursors due to improved accessibility and a distinct shortening of the diffusion pathway in micropores.¹⁹ Catalytic testing of various mesoporous zeolites has proven the effectiveness of the desilication approach in the liquid-phase degradation of HDPE, cumene cracking and methanol to gasoline on desilicated ZSM-5.⁵ The superior catalytic performance of templated mesoporous zeolites and zeolite nanoparticles deposited on different supports have been widely demonstrated. The activation energy of the vapour-phase benzene alkylation with ethylene to ethylbenzene was found to be higher for a carbon templated ZSM-5 than that of the purely microporous zeolite (77 vs 59 kJ/mol), this fact was attributed to the alleviated diffusion limitation in the case of the mesoporous crystals. Hierarchical mesoporous BEA zeolite templated with a mixture of organic ammonium salts and cationic polymers shows a higher activity in the alkylation of benzene with propan-2-ol than a microporous BEA sample with the same Si/Al ratio.⁴³ Catalytic test reactions on the oxidation of 1-naphthol over titanium silicalite-1 (TS-1), Ti-coated MCF and MCF materials coated with (TS-1) nanoparticles, revealed increased 1-naphthol conversion and activity for the TS-1 coated MCF materials compared to the TS-1 zeolite due to the presence of mesopores.⁴⁴ Catalytic tests on MAS-7 and MTS-9 (mesoporous materials build up from zeolite beta and titanium silicalite-1 precursor particles, respectively) in the cracking and hydroxylation (with H₂O₂) of different small and bulky molecules (cumene, phenol, TMP...) showed high activity. The

acylation of different amino derivatives with fatty acids is carried out smoothly and under green conditions when using UL-MFI-type (mesoporous ZSM-5) as catalyst.⁴⁵ Last but not least, the applicability of 2D zeolites recently discovered by Ryoo's group has been demonstrated for a wide range of reactions, from MTO⁴⁶ to the gas phase Beckmann rearrangement⁴⁷ and toluene disproportionation.⁴⁸

In all above examples, shortening diffusion pathlength and a proper connectivity between mesopores results in a more efficient use of the zeolite crystals and therefore in higher activity per gram (and volume) of catalyst without losing the main zeolitic properties (i.e. high acidity and shape selectivity). On the totally opposite case, under certain circumstances diffusion can play in favour of selectivity. The most outstanding example is the methylation of toluene on ZSM-5.⁴⁹ As demonstrated by Nishiyama et al. when applied to the alkylation of toluene with methanol, H-ZSM-5 crystals with a polycrystalline epitaxial silicalite-1 coating significantly enhances *para*-selectivity up to 99.9%. The enhanced *para*-selectivity is attributed to the selective diffusion through the inactive silicalite coating on the H-ZSM-5.⁴⁹ The use of larger crystals also increased the diffusional length and selectivity but at the expense of a reduced catalyst effectiveness.⁵⁰ The inert coating further prevented isomerization of the *p*-xylene and high reactor yields could be obtained. This example nicely illustrates that diffusion limitations can advantageously be used to increase catalytic selectivity (obviously at the price of a decreased catalytic activity). Similar examples on the use of selective diffusive layers either to protect active sites^{51,52} or to promote secondary reactions have been published during the last few years⁵³ and open the scope to a new definition of membrane reactors, where the membrane is either at the particle or at the active site level (*vide infra*).

These last examples make a perfect link to the relation between catalyst structure and multifunctional catalysis. One of the key factors affecting multifunctional catalysts is the proximity between active sites. A classical example of such multifunctional catalysis is the hydroisomerization of *n*-paraffins. This reaction globally proceeds on Pt containing zeolites through the dehydrogenation of an alkane at the platinum sites to an alkene that reacts on the acid site of the zeolite. Here it either undergoes isomerization or is cracked via β -scission. The alkenes then get hydrogenated to the corresponding alkane on a platinum site.⁵⁴ In this case, it has been thoroughly demonstrated that site proximity and Pt dispersion are key factors affecting catalyst life-time.

Very recently, we have demonstrated the importance of structure and site proximity in the performance of bi-functional catalysts consisting of Co nanoparticles and a zeolite component for the direct synthesis of gasoline range hydrocarbons from syngas. By comparing the performance of 'core-shell' Fischer-Tropsch particles consisting of a Co supported on silica core and a zeolite outer "membrane"^{55, 56} with catalysts making direct use of the zeolite as support for cobalt nanoparticles. In the latter case, we used both purely microporous ZSM-5 and micro-mesoporous ZSM-5 supports

obtained via desilication and acid treatment.⁵⁷⁻⁶¹ The superior activity and selectivity to liquid hydrocarbons obtained over the mesoporous zeolite supported catalysts demonstrates that the interplay between diffusion and active site proximity can be optimized.⁶²

Also on the particle level application of layered⁶³ catalysts can be advantageous, as demonstrated in exhaust catalysis with highly fluctuating operating conditions and complex interplay of reaction kinetics, diffusion and temporary storage of intermediates and products.⁶⁴

When it comes to multifunctionality and structure in catalysis, Metal Organic Frameworks (MOFs) deserve special attention. Due to their intrinsic nature, MOFs offer unprecedented possibilities for the careful design of structured multifunctional solids. Although still at their infancy and with some issues to be unravelled, already outstanding examples of such multifunctional modular design of catalysts using MOFs as platforms have been reported in the literature.⁶⁵ From bifunctional acid-metal⁶⁶⁻⁶⁹ to acid-base⁷⁰⁻⁷² and metal-metal systems.⁷³⁻⁷⁶

C Structuring at the reactor level

In the chemical industry fixed bed reactors are commonly used. Their popularity is based on the simplicity of construction and the high catalyst loading. However, as a rule the bed consists of a random packing of catalyst particles and, as a consequence, the spatial structure is not optimal with respect to the position of the active sites and the hard to predict hydrodynamics with a more or less turbulent, chaotic character. A completely different approach is to build reactors with a regular structure.⁷⁷ A structuring approach can also be applied to reactors with a mobile catalyst, such as fluidized beds and slurry bubble columns,^{78, 79} but we limit ourselves here to fixed structured packings. Typical examples are given in Figure 2.

Monoliths consist of parallel channels. They are the reactor of choice in most environmental applications in the gas phase, including the huge automotive market. The reasons for their popularity are the low pressure drop at high flow rates, the dust tolerance, the high mechanical strength and the easiness of positioning (horizontal, vertical, tilted). In addition, the mass production has resulted in affordable prices. For conventional fixed-bed reactors a clear distinction exists between catalyst particle and reactor. In many respects a monolith can be referred to both as a reactor and a packing. Catalyst bales consist of packets of conventional catalyst particles located in the reactor volume in a structured way. Static mixers are similar to monoliths channels but they contain twisted (zig-zag or skewed) channels (vide infra). Foams are 3D-cellular materials containing interconnected pores. Such a network can be thought to some degree as the negative image of a packed bed. Strictly speaking they do not qualify as structured reactors (i.e., they are not regular) but they exhibit typical features of structured reactors, namely, low pressure drop, good and uniform access

to the catalyst sites. We categorize them in the family of structured reactors.

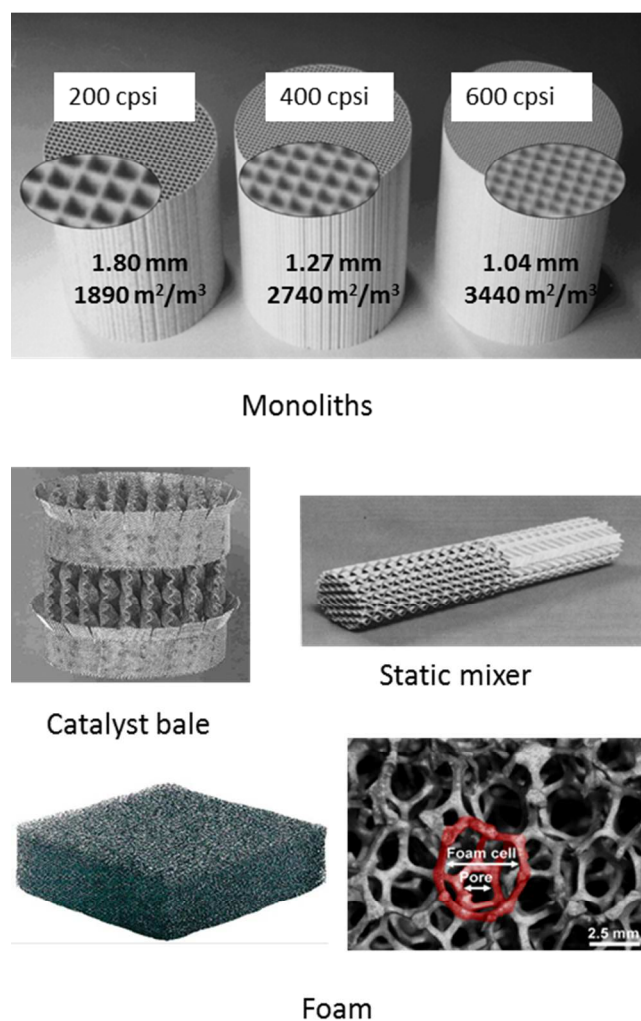


Figure 2. Examples of structured packings. For the monoliths common cell densities (cps: cells per square inch) are indicated together with their channel diameter and geometric surface area.

Usually the catalyst material is introduced as a porous coating, mainly because the geometric surface area of a commercially available structured reactor body is too small (typically less than $4 \text{ m}^2/\text{g}$) to accommodate sufficient numbers of active sites. Several procedures can be used. For a detailed overview on manufacture of monolith supported catalysts we would like to refer the reader to more extensive reviews on this topic.⁸⁰⁻⁸² Monolithic structures can be coated by (partly) filling the pores of the macroporous walls or by depositing a layer on top of the walls (referred to as ‘slip casting’ or ‘filter cake formation’). Usually the catalyst layer is very thin, but compared to the bare monolith the specific surface area is several orders of magnitude higher. Analogously to the above discussion of the Thiele approach it can be estimated that the characteristic dimension for liquid phase systems is in the 10-100 μm range, in good harmony with normal washcoating recipes. For gas

phase applications the characteristic dimension is larger and often a thicker coating is optimal. At the same time, the maximum possible catalyst inventory by applying washcoating techniques will always be smaller than in traditional packed bed reactors. However, the utilization of very active catalysts and their full utilization more than compensates for the lower inventory, especially when expensive noble metals are used as active sites.

A wealth of articles have been published on catalyst synthesis on structured supports. A review has appeared recently⁴ A fascinating example is work of de Lathouder⁸³ who synthesised Carbon Nanofiber coatings on monoliths, resulting in a carpet of CNF covering the monoliths walls with a mesoporous texture (layer thickness 10 μm , pore diameter 8 nm). Because of its favourable open texture without microporosity this system allows high diffusion rates for relatively large molecules and it is an excellent support for biocatalysts such as lipase (diameter ~ 5 nm).

In many respects, structuring at the level of the reactor is analogous to structuring at the level of the catalyst particles: shape, dimensions, pore texture should be optimized for high density of the active sites and a high accessibility. In general, commercial monoliths have a square channel geometry. In most coating procedures, because of the relatively high capillary forces in the corners, an undesired, uneven distribution of the coating with relatively thick layers in the corners is the result. Homogeneous support layers can be prepared by carrying out successive dip coatings with small inert, non-porous particles (a circular channel shape is created), followed by coating with the desired support. Examples have been reported of perfect layers with a well-defined diameter of 10-15 nm all over the monolith.⁸⁴ In such a “High-performance monolith” for commonly encountered kinetic networks the conditions for high activity and selectivity are optimal.

Catalytic coatings are not the only way of positioning active sites in the monolith reactor. The channels can be packed with (commercially available) catalyst particles. In fact monoliths are favourable geometries for hosting catalyst particles.⁸⁵ Monoliths can be scaled up or down by increasing or decreasing the diameter of the monolith, keeping the dimension of the individual channels constant. When we scale down to one single channel, we enter the realm of microreactors. The main parameter of the packing is the ratio of the particle and the channel diameter.⁸⁶ When the channels are filled with particles with a diameter close to the channel diameter ($d_{\text{reactor}}/d_{\text{particle}}$ ratio typically 1-2) a so-called single-pellet-string or composite structured packing reactor is the result.⁸⁷ When the particle diameter is much smaller than the channel diameter (typically $d_{\text{reactor}}/d_{\text{particle}} > 10$) we prefer the term micropacked bed reactor. Thus, assuming a mm-scale channel diameter, micropacked beds contain particles in the range up to 200 μm and the single-pellet string reactor particles in the mm range. The total family of packed beds containing channel reactors might best be referred to as “structured packed beds”. Systems such as static

mixers packed with catalyst particles (see *infra*) also belong to this category.

Structured catalysts and reactors do not suffer from the random or chaotic behaviour encountered in classical reactors. The hydrodynamics is relatively simple and as a rule the laminar flow regime prevails. One might wonder about possible radial mass transfer limitations in the channels because of the absence of turbulent flow conditions. First, we focus on monoliths with the catalyst present as a coating.^{4,88} For gas phase processes for most common designs (channel diameter 1-3 mm) there is not any problem regarding a significant radial concentration profile. Due to the fast diffusion, in general significant radial profiles cannot exist. In contrast, liquid phase systems can be problematic. Remarkably, gas/liquid systems do not pose such problems because of their special hydrodynamic regime. The practically important flow regimes are film flow (large diameter, large gas flow rate) and segmented flow (small diameter, moderate gas flow rate). At most practical conditions, in 1-2 mm channels segmented flow is encountered, often referred to as Taylor flow. In this flow regime the radial mass transport is an order of magnitude faster than for single phase liquid systems. It is enlightening to compare the Taylor flow regime with the usual turbulent regimes. Although for Taylor flow the exchange rates are relatively high, the pressure drop and energy consumption are an order of magnitude lower, a clear contribution to Process Intensification!

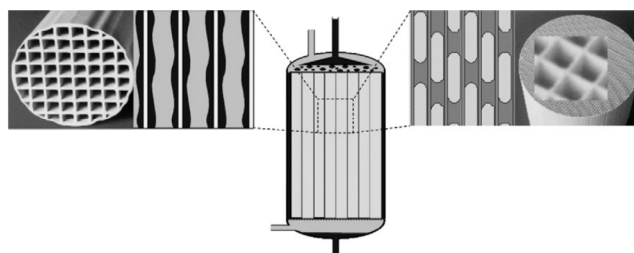


Figure 3. Film flow (left) versus Taylor flow (right). Film flow occurs at high flow rate; it is suited for catalytic distillation and stripping. Taylor flow is associated with a minimal pressure drop, plug flow behaviour and fast mass transport from gas phase to catalyst surface.

Structured packed beds need a separate discussion. Micropacked bed reactors show specific behaviour. The inherent small particle size in the small channels causes the hydrodynamics to be dramatically different compared to the industrially applied trickle-bed reactors. For particles smaller than typically 200 μm the capillary forces predominate over the viscous and gravitational forces, in sharp contrast with large-scale industrial reactors. The gas flow follows preferential pathways (a kind of snake flow) through beds consisting of small particles.⁸⁹ This flow behavior might not have been expected because from the widely reported hydrodynamic plots for trickle bed reactors⁹⁰ the operation of these micro-packed bed reactors is in the trickle flow regime. Compared to conventional trickle bed reactors these micropacked bed

reactors have the big advantage of much more favourable dimensions (minimal internal diffusion limitations) and due to the high capillary forces, as a rule, wetting will be no problem. However, remarkably, the reactor shows a *poor* radial mass transport.⁹¹

For single-pellet string reactors the flow regime is similar to that of empty tubes: at conditions where in the empty tube the Taylor flow regime prevails, in single-pellet string reactors also a type of Taylor flow is observed.⁹² In addition, for these packed channels the mass transfer is enhanced, again similar to Taylor flow in empty channels. Although their pressure drop is higher than for empty tubes, these structured packings still show relative low pressure drops compared with conventional packed bed.^{93, 94} Thus, both single-pellet string and micropacked bed reactors have pro and cons. Single-pellet string reactors exhibit low pressure drop and, for multiphase applications, a relatively high external rate of external mass transfer, but the internal diffusion is slow (similar to conventional trickle bed reactors). For micropacked bed reactors the opposite is the case. Due to the capillary forces the gas flow follows preferential pathways resulting in a large liquid film thickness. However, the particle size is very low and internal diffusion limitations will be minimal.

So far, we mostly discussed mass transport at the mesolevel: how can reactants and products quickly transfer between bulk and catalytic sites. Convective mass transport normally ensures supply of reactants to and removal of products from the bulk: a feed stream to the reactor inlet and a product stream from the reactor outlet are sufficient. For heat transport this is different. Many relevant reactions have a reaction enthalpy significantly different from zero, potentially leading to large temperature differences. When reactant concentrations are low – typically in environmental applications such as exhaust gas or water cleaning – the heat production or consumption will be limited. However, when considering the intensified production of a certain chemical, this will often involve large heat flows. In that case, controlled heat supply or removal is required to keep the reaction environment at a temperature that is optimal concerning conversion, selectivity, and catalyst deactivation. Typically, fluid-particle heat transport and intraparticle heat transport resistances are of minor importance; the largest temperature gradients are found at the reactor scale. In many cases, (close to) adiabatic operation is undesirable: the large temperature gradient between reactor inlet and outlet would seriously harm productivity. To keep the temperature reasonably constant, it will be needed to remove heat in the radial direction, either by conduction through the support or via the fluid. We will discuss both cases.

Geometrically, a structured packing is much better suited for conductive heat transport than a randomly packed bed, since in the latter particles only have point contacts, which diminishes heat transfer.⁹⁵ However, a second requirement is that the support material has a sufficiently high conductivity. Standard monoliths made from ceramic material via extrusion have a

poor conductivity. Metallic monoliths were already investigated in the 1980's by Flytzani-Stephanopoulos and coworkers⁹⁶; in the past decade, an extensive oeuvre on this topic has been published by Tronconi and co-workers.^{95, 97-99} They showed that constructing monoliths of high-conductivity materials such as copper, aluminium or silicon can lead to reactors with an excellent heat transfer, provided that the monolith walls are not too thin. An alternative in the use of metallic foams as well-conducting catalyst support structures.¹⁰⁰ Sheng et al.¹⁰¹ have developed yet another concept: they propose a structure consisting of sintered micron-sized metal fibers with small catalyst particles entrapped inside, giving a high conductivity. As said, randomly packed bed reactors show poor conductivity, confined to the particles' contact points. Furthermore, their radial heat transport by fluid flow is also limited: fluid mixing is restricted, and the fluid motion is usually characterized by the presence of stagnant zones, channelling effects and preferred pathways. The heat transport behaviour of these reactors could be improved by operating at higher flow rates so that channelling effects are minimized and radial mixing is increased. But this is mostly achieved at the expense of high pressure drop, resulting in less favourable economics¹⁰².

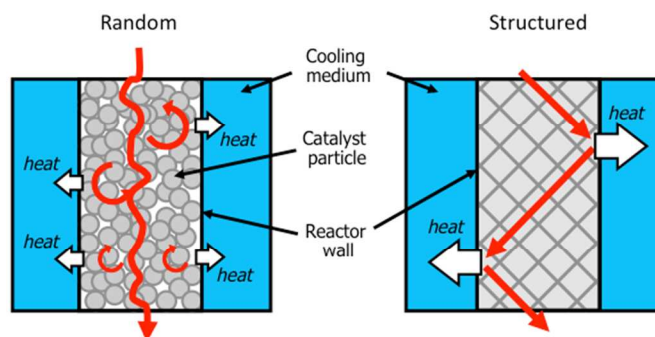


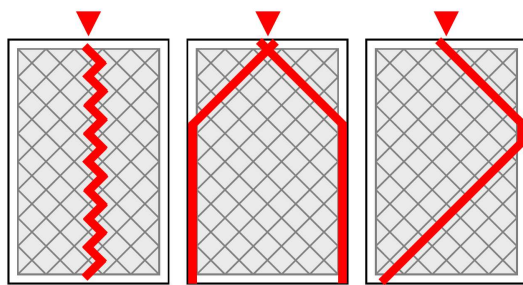
Figure 4. Possible flowpaths of reactants (co-current, top-down) through an axial cross-section of a randomly packed bed (left) and a cross flow structured geometry (right).

Alternative packings such as foams and knitted wire packings with their highly porous structure and therefore a much lower pressure drop allow higher gas and liquid throughputs.¹⁰³ For example, the more open structure of foams leads to greater turbulence, which increases convective heat transport.¹⁰⁴ In addition, in packings such as foam the catalyst support has a continuous nature (as opposed to particle point contacts in a packed bed), making that conduction by the support can also give a significant contribution to the heat transport, depending on the material and volume fraction, as discussed before.

A way to further increase radial heat transport in structured packings is to enforce convective flow in the radial direction. This can be realized by choosing a geometry that forces the fluid flow to have both an axial and a radial component, for example by introducing diagonal flow channels. Figure 4 gives a schematic view of a possible flow path in an axial cross-section of a randomly packed bed and a cross flow structure

(CFS). Examples of these types of structures are Katapak-MK and Mellapak, developed and manufactured by Sulzer.

Two different types of CFS can be distinguished: the open CFS (OCFS) and the closed CFS (CCFS). An OCFS packing consists of a stack of corrugated plates with alternating angle configuration (e.g. 45° and -45°). The channels are formed by the corrugations in the plates. In this case the fluid streams in the channels of one plate can mix with those of the channels from a neighbouring plate at cross sections. In a CCFS geometry, alternately corrugated and flat plates are stacked. This makes that mixing between the channels of neighbouring plates is prevented; mixing can only take place at the end of the channels, as they reach the wall. The different flow paths that are possible are depicted in Fig. 4.¹⁰⁵ The actual flow through the packings is a combination of all possible flows.



(a) OCFS (b) OCFS, CCFS (c) OCFS, CCFS

Figure 5. Types of flow through an axial cross section of the cross-flow packing: (a) flow through the center of the packing moving to the neighboring layer at each cross section, (b) flow through the gap between the packing and the reactor wall, and (c) flow through the channels of the packing exiting the channel at the reactor wall and entering a new channel.

Flow path (b) and (c) in Figure 5 suggest that the spacing between the packing and the reactor wall is of great importance. We indeed found experimentally an influence of this spacing on the overall heat transfer.¹⁰⁵ CFSs offer a great advantage from the point of view of heat transfer. CFS packings perform much better than randomly packed beds concerning heat transport, but they have a lower catalyst hold-up. Usually, their walls will have a catalytic coating with a limited thickness to avoid mass transfer limitation; typical catalyst hold-ups are ~ 20 vol%, compared to ~ 65 vol% for a packed bed. An attractive alternative for coating the walls is to fill the channels with catalyst particles, which will enable catalyst loadings up to 50 vol%.¹⁰⁶

Von Scala *et al.*⁹⁴ already showed for gas flow through CFS structures that their heat transfer is very efficient. In recent years, we have carried out extensive comparisons of the heat transport performance for gas-liquid flows between packed beds, CFS structures, and some other alternatives such as metallic foams and knitted wire packings.^{102, 103, 105, 107} These comparisons showed a superior performance for the CFS structures. Between the CCFS and OCFS structures little difference in heat transport performance was found, but for

both structures a proper distribution of gas and liquid (as, e.g. in Taylor flow) is required to get the best performance. It should be noted that for the CFS packing, it is questionable whether describing the heat transport with an effective radial conductivity and a wall heat transfer coefficient is the most appropriate approach. Recently, we proposed a single-parameter model that better describes the heat transport by convection in these packings.¹⁰⁸ Up to date, a thorough comparison between highly conductive structured packings (e.g., metallic monoliths) and structured packings with a forced radial flow component (e.g., CFS) has not yet been published, in spite of important conceptual differences such as the anticipated stronger effect of flow properties on the heat transfer performance of CFSs than on that of conductive structures. Good heat transfer in structured reactors will need increasing attention: the drive to make reactors smaller as well the development of increasingly active catalysts, will lead to a further increase of the heat production per unit of volume in future reactors.

Recently, small-scale flow reactors have received a lot of attention, first as laboratory reactors and later also for industrial-scale production of fine chemicals, pharmaceuticals, specialty chemicals, and even bulk chemicals.¹⁰⁹ These so-called microreactors consist of single or multiple small-diameter channels (typically 10-2000 μm) that allow reactions to be carried out on a (sub)millimetre scale. Capillary microreactors where the catalyst is present as coating are a good example.¹¹⁰ Although belonging to the family of structured reactors they form a separate category, in particular, with respect to heat transport: since their channels are not embedded into a single matrix, as it is generally the case for monoliths, ample opportunity for heat transport via the walls exists.

D Membrane reactors redefined

Reaction-separation combinations in catalytic membrane reactors,^{111, 112} a much studied topic in structured reactors,⁴ is generally limited to systems on a reactor scale, where a catalytic bed or layer is enclosed by a catalytic or non-catalytic membrane housing. This requires a balancing of the production rate in the catalyst volume and the permeation rate through the membrane.¹¹³⁻¹¹⁵ The tuning parameter is the area to volume (A/V) ratio, which is limited on a reactor scale. Applying a membrane coating on a catalyst particle increases this A/V ratio tremendously,^{116, 117} and coating the active site or zeolite crystal with a membrane layer even further (Figure 6).¹¹⁸ Several orders of magnitude in A/V ratio are feasible, extending the applicability of membrane reactors beyond the classical concept. The coated catalyst can be considered as a small reactor fed by diffusive transport ('capsule catalyst', 'nanoreactor'). A penalty has to be paid, however, since both reactants and desired products should be able to permeate, although at the same time the membrane might protect against

unidentified poisons present in the feed. Furthermore, the sensitivity for defects on the overall reactor performance is lower.

Recent decade an increasing interest is observed in the development of so-called core-shell catalysts,¹¹⁹⁻¹²³ an active phase surrounded by a porous shell. Next to the abovementioned selective conversions,¹¹⁸ major identified advantages are an extremely high thermostability of sintering-sensitive metal (oxide)particles and a high protection against poisons.¹¹⁹⁻¹²³ Also in electrocatalysis evident improvements in activity and stability are shown.¹²⁰ In these applications both engineering and catalytic advantages come together, and although the catalyst synthesis maybe more expensive, this may be outweighed by the gain in feedstock and energy savings in pre- and post-separation.

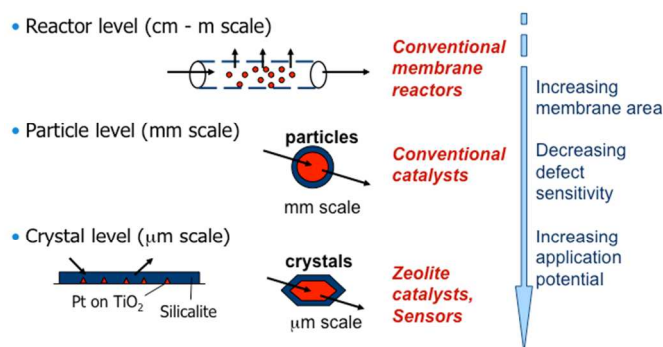


Figure 6. Levels of integration in membrane reactors

Concluding remarks

Structuring of catalysts and reactor internals leads to apparent improvements in both catalyst and reactor performance. On the catalyst level this comprises higher activity, selectivity, and stability against poisoning and sintering. Especially promising are combinations of catalyst functionalities in one particle, and membrane-catalyst particles. On the reactor level the decoupling of hydrodynamics, transport phenomena and reaction kinetics allow easier optimization of catalytic reactor operation. Salient results can be obtained in multiphase operations improving mass and heat transport, often the determining or limiting processes. Structuring of catalytic reactors paves the way to the holy grail in reactor engineering, as formulated by Dudukovic et al.³

Last but not least, we would like to emphasize the pivotal role of chemical reaction engineering. Indeed, despite much scepticism in the past years, chemical engineering is turning out to be unavoidable in the future: the pressing need for cleaner methods of chemical production due to stricter environmental legislation along with sustainable development with fuel cells, hydrogen technology, electro- and photo-catalysis are some examples that illustrate the increasing necessity for reaction engineering approaches able to turn very exciting discoveries into innovative new processes. We are confident that

approaches like the ones discussed in this perspective will be essential to achieve these objectives.

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† The macrolevel, the process as a whole, is not considered here, although the implementation of a catalytic reactor has implications for the process design.

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