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Structured catalysts and reactors – Perspectives for demanding applications

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ABSTRACT

In this perspective paper a brief overview is given of the past developments in the field of structured catalysts and reactors, the potential for process intensification, energy and materials efficiency. Current exciting new developments for demanding processes are highlighted and directions indicated that contribute to a future sustainable chemical industry.

1. Introduction

The topic of structured reactors and catalysts found its basis as a subdiscipline in Chemical Engineering after the pioneering seminar on monolithic catalysts in St. Petersburg [1] and its follow up the series of ICOSCAR conferences, the ‘International Conference On Structured Catalysts And Reactors’ established by the authors, a topic to which the scientists honored with this special issue contributed appreciably [2,3]. This successful development was accompanied by several authoritative works in the scientific literature [4–9] that paved the way for the current status in this field after 6 successful ICOSCAR meetings (Delft (2x), Ischia, Beijing, San Sebastian, Bad Herrenalb) [10–13]. This special issue provides an ideal opportunity to provide a personal outlook on further developments in the field of structured catalysts and reactors through examples with emphasis on fixed bed catalytic reactors.

2. Basics

The motivation to introduce structure in catalytic reactors is best understood by considering the design relations of these systems, *i.e.* the momentum, materials and energy balances, and following the principles of systematic reactor selection of Krishna and Sie (K&S) [14].

As example, Fig. 1 shows the 2D-energy and 1D-material balances for a cooled Gas-Liquid plug flow reactor in which an exothermal reaction takes place over a porous catalyst. Axial and radial dispersion are not considered here for simplicity. Heat and mass transfer to/from the catalyst and the effective diffusion inside the catalyst determine the

effectiveness and selectivity. Besides kinetics and thermodynamics, hydrodynamics, GL-interface, particle size, and effective diffusivity control the productivity and heat generation. Heat removal occurs through radial convective and conductive transport and transfer through the reactor wall, and in axial direction by convection of the fluid mixture through its heat capacity. The momentum balance describes the pressure drop over the reactor (*e.g.* an Ergun-type relation), where the hydrodynamic flow diameter and porosity of the packing are essential.

This illustrates the various elements that determine in concert the overall performance of the reactor system.

In their strategy for multiphase reactor selection (including single phase), Krishna and Sie distinguished three tier decision levels, (I) Catalyst design, (II) Injection strategies of reactants and energy, and (III) Hydrodynamic flow regimes (Fig. 2). Based on the desired requirements for the system under consideration (the ‘wish list’) for each level optimal choices are made independently, and the challenge is to combine these into an optimal reactor configuration. At this point often conflicting requirements have to be faced. As example a limited pressure drop over a packed bed may require large particles, while for full catalyst utilization small particles are desired. This coupling reduces the design freedom in finding an optimum. Introduction of monolithic (‘honeycomb’) catalysts releases this coupling. The channel size (= the hydrodynamic diameter controlling the pressure drop), and the catalyst layer thickness (the diffusion length controlling the utilization) can now independently be chosen to optimize the monolithic catalyst [15,16]. So, structuring allows decoupling of at first sight conflicting requirements and allows more degrees of design freedom [8,17]. As

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example in SCR the desired, fast NO_x reduction over V₂O₅/TiO₂ in monolith channels is gas-solid transfer limited, while the undesired, much slower SO₂ oxidation is kinetically controlled [18]. The desired reaction being proportional to the geometric gas-solid area, the undesired one to the catalyst volume. Reducing the thickness of the catalyst layer will strongly affect only the undesired SO₂ oxidation, leaving the desired reaction untouched. So by simple engineering of the monolithic catalyst the process selectivity can be tuned.

The favorable properties of monolithic structures had already been recognized in the development of automotive three-way catalysts (TWC) [19] and selective catalytic reduction (SCR) systems [20]. As additional advantages they are not subjected to attrition by engine vibrations and are not sensitive to dust laden gas flows, unlike packed beds.

Therefore, it is not surprising that in the early phases in the topic of Structured Catalysts and Reactors the main focus was on monoliths [4, 17,21,22], although soon foams, corrugated metal sheet packings, knitted wires, micro-fibrous entrapped catalysts, and other structures were considered [23–27], each with their specific advantages and disadvantages. In a monolith radial mass transport between channels is not possible, while in foams this is excellent; radial concentration differences are easily evened out by mixing. In the early days of monolith R&D Flytzani-Stephanopoulos already emphasized the need to overcome this issue: “a novel monolith geometry allowing for radial gas mixing may combine the best heat transfer features of both the honeycomb monolith and the pellet bed geometries and result in still higher savings in an industrial application” [28].

Next to the advantage of low pressure drop, mentioned earlier, the high structure voidage results in a relatively low catalyst inventory

(max. ~25 vol.%), even after special coating techniques [3,29–31], and in a poor or limited heat conduction. Ceramic monoliths should be considered as adiabatic reactors, and, although better, even metallic structures have a moderate heat conduction due to the low metal content [32–34] but still better than packed beds [28]. The catalyst inventory can be increased up to ~55 vol.% by filling the structures with catalyst particles instead of coating the structured support [35,36]. This is not only cheaper, but also smaller catalyst particles can be used than in a full packed bed due to the still higher voidage by the higher particle-wall contact area, so without a large negative impact on the pressure drop [37]. A higher catalyst utilization can be expected for operations affected by diffusion limitations.

After this brief overview of consideration to utilize Structured Catalysts, the Krishna & Sie approach will be applied to illustrate the attractiveness/advantages and opportunities of Structured Catalytic Reactors in this R&D field by three examples of demanding fixed bed catalytic processes with a large heat effect operated in an adapted process design or under non-adiabatic conditions.

3. Current status and developments

The three catalytic processes are two gas-solid (GS) reactions, the exothermal selective oxidation of *o*-xylene to phthalic anhydride (SOXPA), and the endothermal methane steam reforming (MSR, in literature also denoted by SMR), and a gas-liquid-solid (GLS) reaction, the low-temperature Fischer-Tropsch Synthesis (LT-FTS) to heavy paraffins. In all cases the reaction enthalpy is such that it can have a strong impact on the reactor performance, including productivity and

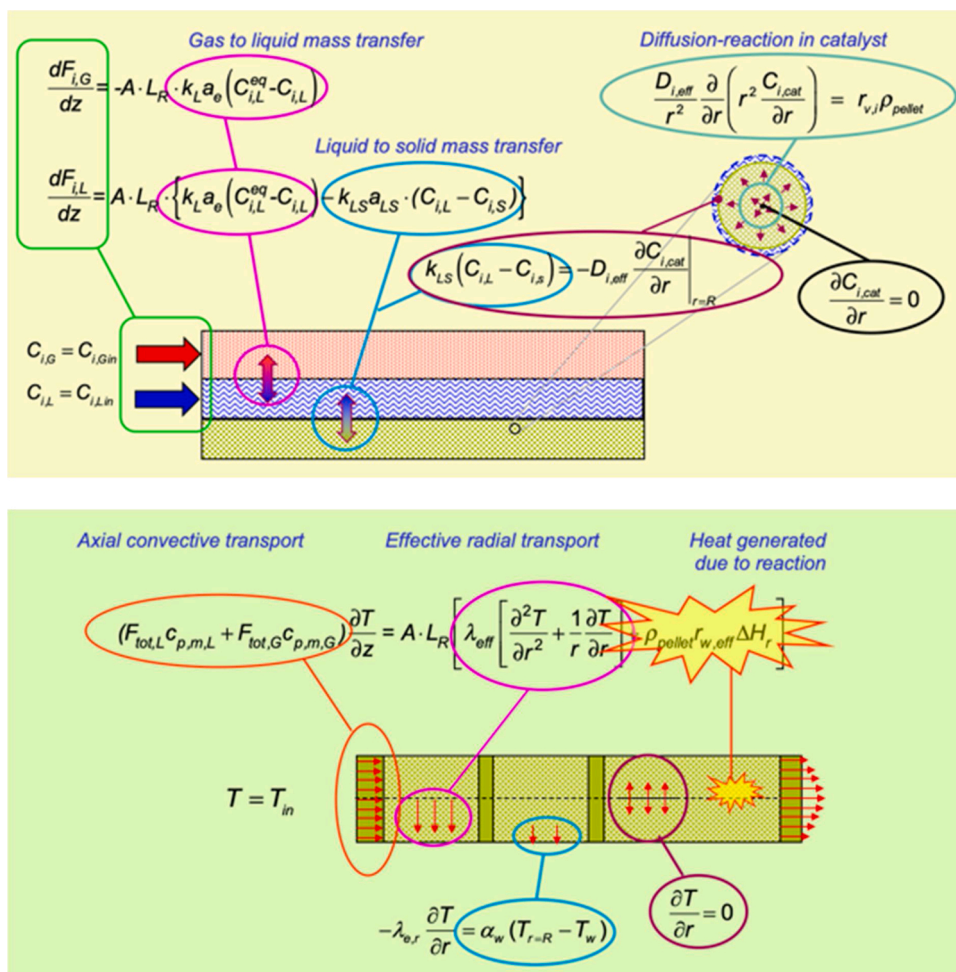


Fig. 1. Illustration of materials (top) and energy (bottom) balances for a multiphase catalytic packed bed reactor. Axial diffusion not considered.

selectivity of the desired product(s).

The 'wish list' for all these processes is maximization of productivity and selectivity in the reactor operation.

Following K&S in these cases the catalyst should have such dimensions that diffusion limitations are absent. These are detrimental for consecutive reactions to maximize the desired intermediate product yield, for equilibrium limited reactions to maximize the catalyst utilization, and in FTS to maximize the heavy paraffin yield [38]. So, in general short diffusion distances are optimal on the tier decision level I of Catalyst design.

On level II, Injection and dispersion strategies of mass and heat, a continuous flow operation and energy supply or removal through heat exchange surfaces was fixed. Regarding the 'state of mixedness' for similar reasons as for Catalyst design, plug flow operation is desired. Any degree of axial mixing will lower the product yield and should be minimized. Regarding the energy in- or output, complete 'mixing of temperature' is desired to approach isothermal reactor operation. Any temperature increase may lower the reaction selectivity, cause hot-spot formation or even a reactor runaway, while a temperature decrease lowers the product yield due to slower kinetics and shifting the equilibrium conversion.

Since all catalysts are assumed to be fixed, level III Hydrodynamics mainly concerns the mass and heat transfer between the fluids and catalyst and with the reactor wall. The convective fluid velocities, particle size and packing geometries are essential parameters in the transfer coefficient correlations. Higher flow rates, smaller particles and larger bed tortuosities and packing densities generally improve these coefficients.

In view of the wish list and the consequent operation at high flow rates and conversion to obtain high space time yields and selectivity of the desired product, the obvious challenge is to combine the requirements of short diffusion distances, plug flow, isothermicity, and high catalyst inventory in one reactor system. This is the topic where structuring of catalysts and reactor can give improvements over the classical solutions. Below this is outlined how this is approached for the three chosen model cases.

Classically, various approaches are used [14]. Egg-shell catalysts combine a short diffusion distance with a large particle size. However, a

large part of the reactor volume is filled with inert material. Cooled multitubular fixed bed reactors with thousands of tubes maximize the heat exchange area and reactor volume ratio (minimizes the radial heat transport distance in a packed bed), but become heavy and expensive. Fluidized or entrained bed operation may improve the energy exchange, but materials and operational issues may arise.

3.1. Selective oxidation of *o*-xylene SOXPA

Groppi, Tronconi et al. [9,39] elegantly compared on a pilot scale level in a 1500 h campaign under industrial operating conditions the SOXPA, performed with commercial eggshell ring-shaped catalysts ($9 \times 5 \times 1.5$ mm) and washcoated (85 μm) aluminium monoliths in a 1 inch 3 m long fixed bed reactor in a molten salt bath to remove the heat of reaction. The local reaction temperature should not exceed 440 °C. Half of the reactor length contained catalyst. The $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst load slightly differed, 70 kg/m^3 vs. 62 kg/m^3 for the monolith, but in both cases the short diffusion distances are satisfied, with the monolith having a low pressure drop. The heat of reaction is removed via radial heat transport through the reactor wall. In a packed bed this is generally rather poor [40] while the thermal conduction through the aluminium monolith resulted in a twice higher overall heat transfer coefficient than for the packed bed (500 vs. 250 $\text{W m}^{-2} \text{K}^{-1}$). The largest heat transport resistance in the monolith reactor was still found in a gap between the monolith and the reactor tube wall. One could conclude from that that the radial temperature gradient in the monolith is smaller than in the packed bed. In axial direction the temperature rise from the reactor inlet to the hot spot was much lower and the salt bath could be operated at a higher temperature. The temperature difference between the hot spot and the salt bath was much lower (Fig. 3). The overall result is that the monolith reactor can be operated at an at least 20 °C higher average temperature (Fig. 3) than the packed bed without exceeding the maximum allowed temperature in the reactor. Consequently, a higher space time PA yield at high selectivity could be reached due to the faster kinetics and effective catalyst utilization in spite of a 12 % lower catalyst inventory. Alternatively, larger reactor diameters, more active catalysts [41] or higher feed concentrations could be used to intensify the PA productivity.

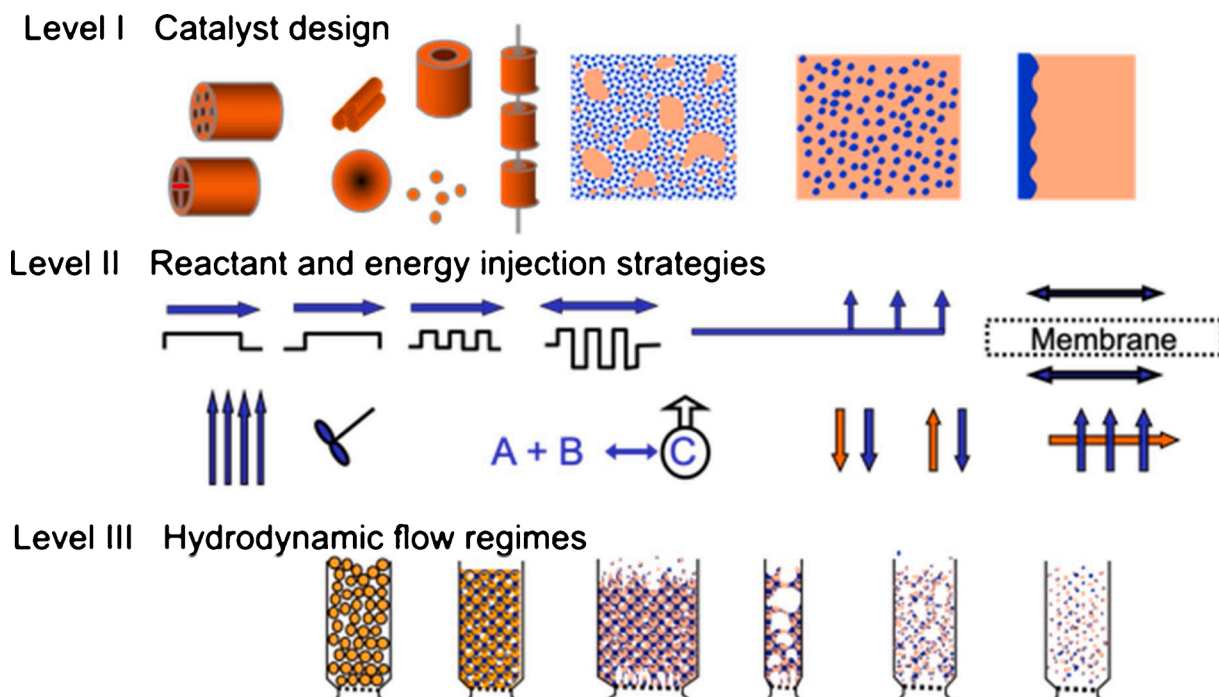


Fig. 2. Strategies for multiphase reactor selection, after [14].

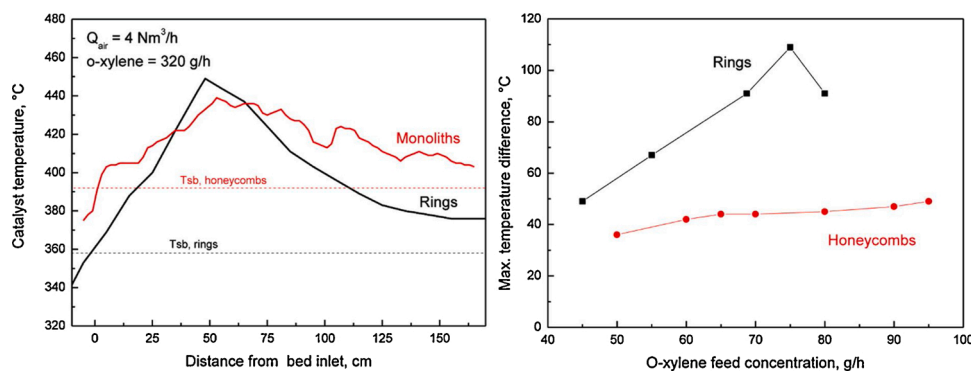


Fig. 3. *o*-Xylene oxidation runs in an industrial tubular pilot reactor, comparison of washcoated Al honeycomb monoliths versus eggshell ring catalyst pellets at reference industrial conditions. (left) Axial temperature profiles. Conditions: Air flow rate = 4 Nm³/h, *o*-xylene feed = 320 g/h. Salt bath temperature = 391 °C (honeycombs), = 358 °C (pellets). (right) Effect of the *o*-xylene feed load on the maximum temperature difference ($T_{\text{hotspot}} - T_{\text{saltbath}}$). Reprinted with permission from [39]. Copyright 2014 American Chemical Society.

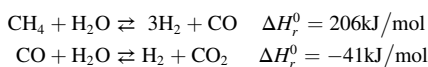
As alternative to the thermally conductive monolith, ceramic open cell foams have been considered. A foam can be considered as a negative image of a packed bed, so the relatively large open space results in low pressure drop and by washcoating an efficient catalyst utilization is obtained. Foams allow for radial mixing, and concentration and temperature differences can be alleviated through convective transport. A modeling study [42] indicated that the space-time-yield of PA could be more than doubled, if conventional fixed beds of catalyst particles would be replaced by washcoated ceramic foam packings. Experimental work confirmed these simulations and showed the importance of the thermal conductivity of the foam. A SiC based foam catalyst showed the lowest hot spot temperature and highest space time yields in comparison with mullite foams and packed beds of eggshell particles [43], in line with the work of Groppi and Tronconi.

Having approached an approximate isothermal operation in such a cooled reactor for a related reaction (*o*-xylene oxidation to phthalic acid), Eberle et al. proposed a combination with a finishing reactor based on a ceramic monolith coated with titania as catalyst. By intermediate cooling the inlet temperature can be tuned resulting in an increased conversion and yield of PA [44].

These examples demonstrate that improved (radial) heat transfer properties in thermally conductive foams and monoliths, allow for a stretching of the operational window to more severe process conditions while reducing the danger of thermal catalyst deactivation and reactor runaways. Ceramic structures are nevertheless still useful under less exothermal adiabatic operating conditions.

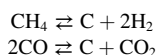
3.2. Methane steam reforming MSR

The classical production of hydrogen and syngas through the energy demanding steam reforming of methane is still performed on a large scale [45]. Two main reactions occur:



Methane-steam mixtures are passed over a catalyst bed in ~2 inch reactors, heated by radiation and convection from the outside in a furnace, often fired with methane as well. The Ni-based catalyst particles are often so-called miniliths (1–2 cm) of various shapes, of low porosity and able to withstand the high operating temperatures (700–800 °C) [46]. The high endothermicity of this reversible process favors operation at high temperatures. The process is strongly heat transfer limited, causing steep radial and axial temperature profiles. The intrinsic catalytic activity is not limiting, *i.e.* catalyst utilization is low.

At these high temperatures next to the main reactions carbon formation may occur by methane decomposition and the Boudouard reaction.



This may cause catalyst deactivation [47] and blocking of the reactor. Careful catalyst packing is essential to approach an even distribution of heat transport through the reactor wall and consumption by the catalyst's action. Carbon formation and hot spot (no catalytic action) development bear the danger of reactor deterioration due to local thermal stresses. Excess steam is used to avoid this while also favoring higher conversion levels, although at the cost of a higher steam energy demand.

In this process the challenge lies in the good and even distribution of the heat supply and consumption, with a catalyst less prone to carbon formation. Avoiding local overheating is essential.

In a pioneering study Balzarotti et al. approached this by using washcoated metal open cell foams (copper and FeCrAlloy) or foams packed with eggshell Rh/Al₂O₃ particles (600 μm diameter, shell thickness 40 μm) and comparing these with a packed bed operation of the MSR in a reactor of 29 mm diameter, a catalyst bed height of 25 mm and a SiC bed preheating section. Rh is used as it is less sensitive to carbon formation. The amount of catalyst was kept equal in all cases by diluting with inert solid (SiC for the packed bed or Al₂O₃ for the packed foam) [48,49].

Fig. 4 shows the superior heat supply of the foam reactors. The cold spot, the maximum difference between the wall and centerline temperature is 50 vs. 130 °C for the foam vs. packed bed configurations at 800 °C. Hardly any difference exists between the temperature profiles of the washcoated and packed foam reactor, the latter having the advantage to avoid special washcoating procedures and the convenience of using standard catalyst particles. The nearly equal center and half radius temperature profiles indicate the good conductive heat transport by the foam, that the radiative contribution is not significant and the major resistance to heat transport is between the wall and foam. Due to the operation conditions the reactors approach equilibrium conversions at 800 °C, but at lower temperatures the foams yield the higher conversion levels.

In a recent study [48] with packed foams the high heat conductivity clearly showed the superiority of copper over FeCrAlloy foam. Also a higher cell density of copper foam (40 versus 10 PPI) improved the performance. A heat transport modeling analysis indicated the superior conductance in the packed foam due to the matrix conductivity and the good foam to particles transfer (Fig. 5). The major resistance is in the transfer from wall to foam and to particles, but still yielding an overall heat transfer coefficient U_{overall} of 750 W m⁻² K⁻¹ for the packed copper foam (40 PPI). Pilot studies should demonstrate the feasibility for large scale application by longer-term operation with copper foams, and the use of larger reactor diameters.

Johnson Matthey patented the CATACEL stackable structured reactor for steam reforming [46,50,51]. Folded metal foil 'fans' coated with a thin catalyst layer are stacked in a reactor tube such that the gas is forced to flow radially in- and outwards in consecutive layers (Fig. 6). Heat transfer is mainly through convection, similar as in other corrugate packings [52]. Claimed improvements are a reduced steam/carbon

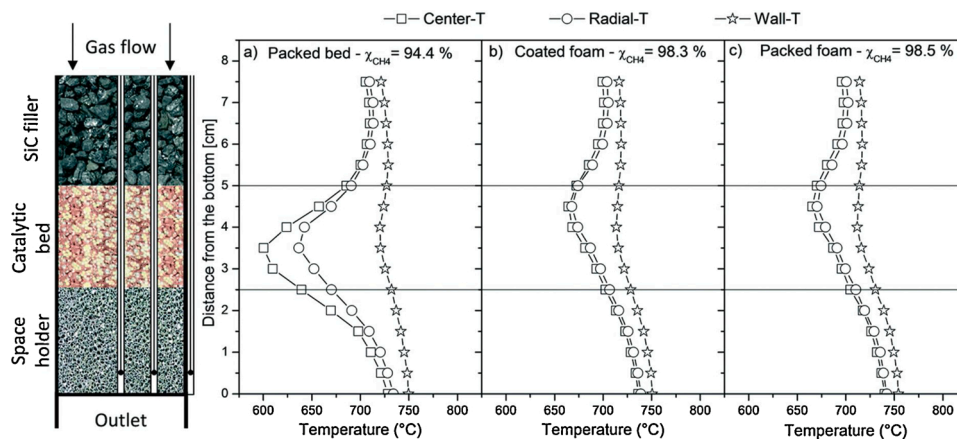


Fig. 4. Axial temperature profiles in the MSR measured at the three radial positions (i.e. reactor centerline (square), half radius (circle) and external reactor wall (star)) for the packed bed (a), washcoated Cu foam (40 PPI) (b) and packed Cu foam 40 PPI (c) configurations. $T_{\text{oven}} = 800\text{ }^{\circ}\text{C}$ and $\text{GHSV} = 10,000\text{ h}^{-1}$. Reprinted with permission from [49] ©The Royal Society of Chemistry 2019.

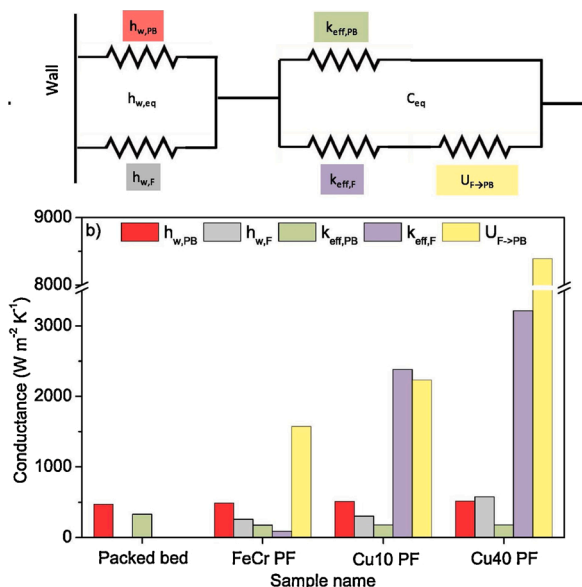


Fig. 5. Graphical representation of the radial thermal conductance contributions to the overall heat transfer for different reactor configurations in the MSR. Oven temperature and GHSV equal to $800\text{ }^{\circ}\text{C}$ and $10,000\text{ h}^{-1}$, respectively. Key: Transfer at the wall through the packed bed $h_{w,PB}$ and the foam $h_{w,F}$, and in the packed foam by conductivity of the foam $k_{eff,F}$ and the packed bed $k_{eff,PB}$, and exchange between packed bed and foam $U_{F \rightarrow PB}$. Reprinted with permission from [48]. ©Elsevier 2019.

ratio, 20–30 % better heat transfer, 20 % reduction in pressure drop and 1.5–2 times larger geometrical gas-solid area, determining the mass and heat transfer which are the limiting processes in the catalysis. This system is already operational on a commercial scale [53,54].

These examples show that heat transfer can be improved both by conductive and convective mechanisms. So, promising alternatives exist for the operation of MSR and allows for retrofitting existing large-scale units, demonstrated for the convective approach. The excellent heat supply could allow lower oven temperatures and reducing steam-to-methane ratio, or alternative heating (solar, electrical) lowering the danger of material failure and catalyst deactivation.

3.3. Low temperature Fischer-Tropsch Synthesis LT-FTS [55–57]

In the low temperature Fischer-Tropsch Synthesis (LT-FTS) supported cobalt catalysts are used to convert syngas (H_2/CO mixtures) to heavy paraffins (wax) at temperatures of $200\text{--}250\text{ }^{\circ}\text{C}$ and pressures up to $30\text{--}40\text{ bar}$ in multitubular fixed bed reactor or slurry bubble column operation.



The product composition is generally expressed by the chain growth probability α (0–1 range), related to a polymeric growth mechanism at the catalyst surface. The closer α to 1 the higher the fraction of longer paraffins produced. The chain growth probability increases with decreasing H_2/CO ratio and decreasing temperature (Fig. 7).

Here the wall-cooled three-phase GLS fixed bed reactor is taken as reference, and all aspects outlined in Fig. 1 play a role. The porous catalyst is usually assumed to be filled with product liquid. The physical properties solubility and diffusivity of the main reactants CO and H_2 are

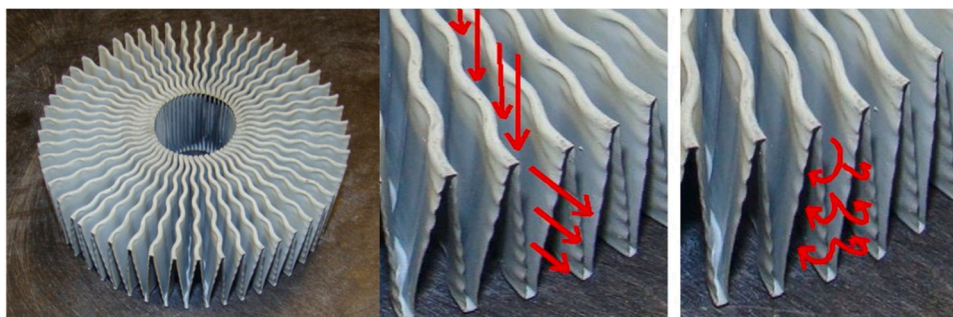


Fig. 6. CATACEL SSR™ metal foil 'fan' coated with reforming catalyst. Gas is forced to flow radially in- and outwards, impinging on the reactor wall, picking up heat and flowing inwards. Stacks of fans are used to retrofit reactor tubes. Reprinted with permission from [46]. © Springer 2016.

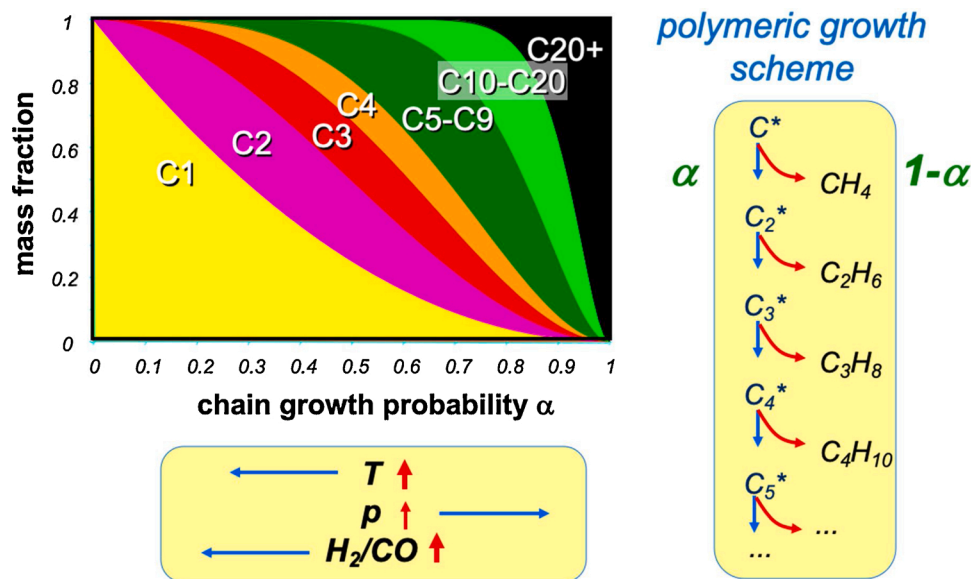


Fig. 7. Low temperature Fischer-Tropsch synthesis product distribution dependency on the chain growth probability α and operating conditions.

different, causing a difference in their liquid phase ratio with respect to the gas phase and strong variation in the intraparticle composition. This has a strong impact on the chain growth probability and catalyst utilization [38], next to the influence of the radial and axial temperature profiles in the reactor [58]. Sub-stoichiometric H_2/CO feed ratios can eliminate changing intraparticle H_2/CO ratios in larger particles [38].

So, there is a complex interplay between mass and heat transport in the reactor and catalyst resulting in the overall performance, generally expressed by the space-time yield STY to C_5+ products (STY_{C_5+}) that is aimed to be maximized.

Especially the heat management is challenging, while transport limitations can be alleviated by using catalysts with short diffusion distances in the active phase ($< \sim 50 \mu m$), like eggshell catalysts, washcoated monoliths or ceramic foams [59,60].

Although liquid is present in the reactor the radial heat transport in the packed bed is moderate and does not prevent steep temperature profiles. This transport has convective and static contributions and both can be improved by introducing structured elements [61].

Convective transport can be improved by corrugated sheet packings (Sulzer-type or CATACEL). These cause a zig-zag flow through the reactor whereby the produced reaction heat is transported by the heat capacity of the fluid from the reactor core to the wall, considerably improving the radial transport compared to a packed bed [52,62]. For a Sulzer type packing the overall heat transfer coefficient for a GL reactor with diameter of 5 cm is improved to $500\text{--}1000 \text{ W m}^{-2} \text{ K}^{-1}$, depending on the gas and liquid flow rates. Simulations for washcoated corrugated sheet packings show an STY_{C_5+} advantage over packed beds only for catalyst activities higher than 5 times the Yates and Satterfield (YS) reference [61,63], due to the low catalyst inventory. Filling the structures with catalyst particles the catalyst hold-up can be increased up to $\sim 50\%$ without compromising on the heat transport properties [35]. An extensive model optimization study compared a 2.5 cm diameter packed bed reactor with a packed closed corrugated flow structure (PCCFS) for different catalyst activities, operational parameters and boundary conditions [55,56]. Above 5YS catalyst activities the performance of the packed CCFS was superior in STY_{C_5+} with $\alpha > 0.9$. Reactor lengths of only 2.5 m, instead of commercial lengths of 10–15 m, were sufficient to reach acceptable H_2 and CO conversions. Also two or three times larger diameters could still keep similar performances as the packed bed reactor, potentially reducing the number of reactor tubes in a multi-tubular reactor ($20\text{--}30 \cdot 10^3$) enormously.

The alternative approach is to improve the thermal conductive

transport. This can be achieved by using thermally conductive metal monoliths or foams, washcoated or packed with catalyst particles to maximize the catalyst inventory [57,60,64], similarly as for the examples above. The best operational results were obtained with the aluminium open cell foam (40 PPI, 4 cm dia \times 4 cm length) packed with $300 \mu m$ Co/alumina catalyst particles, resulting in a packing fraction of 48 vol.% in the foam and 38 vol.% in the reactor. LT-FTS operation was compared with a conventional packed bed reactor with the same amount of catalyst diluted with α -alumina to the same bed volume [57]. The packed foam could be operated up to $240^\circ C$ with CO conversions of 67.5 % with only $6^\circ C$ temperature increase due to the excellent heat removal. The thermal heat duty at this condition amounted 1360 kW/m^3 , unknown levels in lab-scale operation. The packed bed reactor had to be operated at much lower temperatures, and already at $195^\circ C$ showed signs of runaway tendencies. The foam-catalyst system was operated for 800 h without change in activity.

To improve radial thermal conduction Tatarchuk et al. used beds of stacked disks of micro-fibrous entrapped catalysts (MFEC, Fig. 8) [27, 65].

They consist of sintered micron-sized conductive metal fibers with

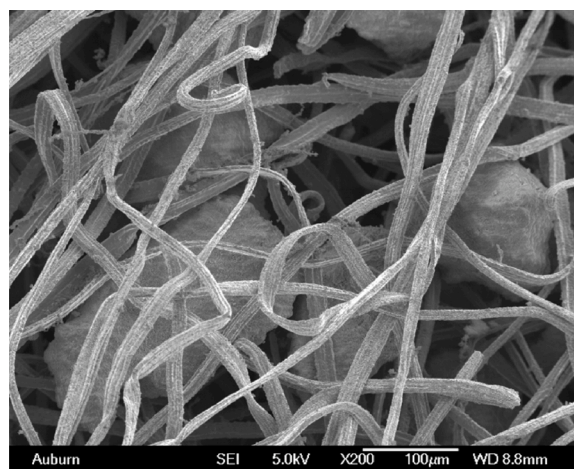


Fig. 8. SEM of a copper micro-fibrous entrapped catalyst MFEC with Co/Al_2O_3 particles; copper fiber $12 \mu m$, Co/Al_2O_3 particles $149\text{--}177 \mu m$. Reprinted with permission from [65]. © Elsevier 2012.

small catalyst particles (149–177 μm) entrapped inside [27]. The volume loading of the particles ranged from 18 to 30%. When using copper fibers the static radial conductivity of the packing is ~ 50 times improved and the overall heat transfer 15–22-fold (for 15 and 41 mm I. D. reactor, respectively) compared to a conventional packed bed. Due to the stacking the axial conductivity is only 1/10 of the radial conductivity. In LT-FTS a 41 mm diameter reactor with such a packing could be operated under fairly isothermal conditions (max. deviation 6.4 $^{\circ}\text{C}$) where a comparable conventional packed bed showed runaways [65]. The more uniform temperature distribution also improved the chain growth probability of the MFEC reactor operation at higher temperature levels (Fig. 9).

The examples above illustrate the opportunities to improve the radial heat transport in LT-FTS to remove the heat of reaction and approach more isothermal operation. This allows higher inlet temperatures of the feed, operation at a nearly constant axial and radial temperature, resulting in a higher volumetric productivity at desired chain growth probability. Not only more active catalysts of smaller size can be used at full utilization, also shorter reactors and larger tube diameters are becoming an option. A simple scaling analysis learns that heat production Q_{prod} and heat removal Q_{removal} should then be in balance, the former being proportional to the reactor (\sim catalyst) volume V_r , the latter to the wall area A_r . So larger diameters are feasible if the improved overall heat transfer coefficient U_{overall} scales with the reactor diameter D_r for a constant catalyst activity and temperature difference:

$$Q_{\text{prod}} = V_r \cdot \eta \cdot r_v \cdot (-\Delta H_r)$$

$$Q_{\text{removed}} = A_r \cdot U_{\text{overall}} \cdot \Delta T \Rightarrow U_{\text{overall}} \frac{V_r}{A_r} = D_r$$

4. Process examples conclusions

The presented process examples demonstrate the opportunity of clear amelioration in reactor operation and process intensification by structuring catalyst and/or reactor. The observed most salient improvements are summarized as:

- Heat supply and removal is enormously improved by thermally conductive structures
- Use of catalyst particles as packing of these structures overcomes laborious washcoating, eliminates danger of catalyst loss and reactor plugging by flaking off
- Smaller particles and more active catalyst can be used at nearly isothermal conditions and full catalyst utilization, resulting in higher volumetric productivity.
- Dimensions may change: shorter reactors and larger diameters, reducing material cost and weight.
- Increased safety, reduced danger of hot spots, runaways in exothermal operations and of materials failure due to thermal stress by local overheating in endothermal operation.

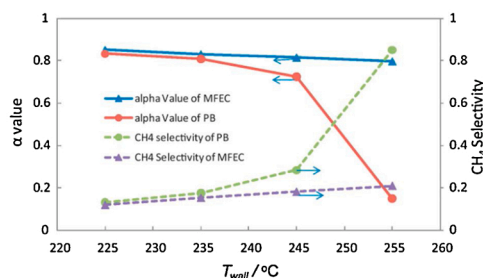
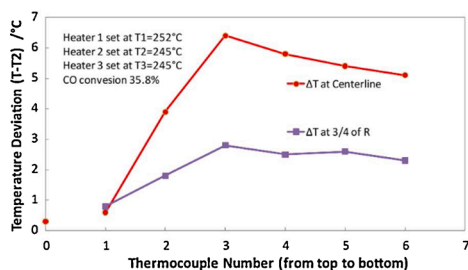


Fig. 9. Left: Temperature profiles inside the catalyst bed of copper MFEC (copper fibers 7.4 vol.%, $\text{Co}/\text{Al}_2\text{O}_3$ 30 vol.%) in the 41 mm ID reactor, 20 bar, $\text{H}_2/\text{CO} = 2$ and 2750 h^{-1} GHSV. Right: The chain growth probability and methane selectivity for the diluted packed bed ($\text{Co}/\text{Al}_2\text{O}_3$ 30 vol.%, neat Al_2O_3 34 vol.%) and the copper MFEC in the 15 mm ID reactor as a function of the wall temperature. Reprinted with permission from [65]. © Elsevier 2012.

- Longer catalyst lifetime, reduced chance of catalyst deactivation by thermal sintering and coking by undesired side reactions [47].

It is obvious that the solutions presented in the foregoing examples are applicable to all catalytic processes with large heat effects, such as selective oxidations, reforming, syngas conversion, methanol synthesis, methanation, hydrogenations, oxidative dehydrogenation, ammonia synthesis, etc. [45].

Based on the current information preference goes for packed thermally conductive foam reactor operation for the considered demanding GS and GLS processes. This has an excellent radial heat transport which is independent of the operating conditions as most contribution is by conduction. Also, the foam allows for radial mass transport, evening out concentration differences, something a monolith lacks [28]. It is simple to apply, as standard optimized catalyst particles can be used and no other specific technologies have to be applied for retrofitting. Only foam production and reactor loading are the practical challenges. For GS processes in the mass transfer limited regime the washcoated corrugated metal foil catalyst has been demonstrated as commercial viable option. Unknown is the behavior with catalyst packing for applications where catalyst inventory is important.

5. Emerging opportunities

In the foregoing a preference was indicated for thermally conductive metallic foams as structured internal for a catalytic reactor. The best conductive materials that can stand reaction conditions of the above examples are copper and aluminium [9]. The structure of these foams, however, is very irregular, and so is the local conductivity.

As emerged from the various heat transport studies the major heat transport resistance resides in the transfer from the bed or structure to the wall (cf. Fig. 5) [66,67]. In a packed bed this is due to a lower packing density at the wall and the particles only have point contact. With structured internals the small slit or space between wall and structure is the cause, especially in gas phase operations. Special techniques are considered to improve the fitting, like utilizing differences in thermal expansion of monoliths into tubes or sintering foam to the wall [68], but introduce a new manufacturing element. A packed foam will have contributions from both the foam-wall contact and the turbulent mixing. The latter can be improved by internals directing the flow with a radial component.

The irregularity of the foam and hence the packing distribution [37] asks for an optimization of the structure on a local level. Also this irregularity may result in some degree of axial mixing [69,70], reducing reactor performance, although the positive effect on heat transport is dominant.

The classical manufacturing of structured bodies like monoliths, foams, corrugated sheets bodies [25,71], does not leave much freedom to apply structural variations or increase control. This limits the range of structures that are available.

Additive manufacturing, also called 3D printing, extends the range of

available structures nearly infinitely, structures that were impossible to achieve before. This applies to reactors, reactor internals and even catalysts with a high control of uniformity. Metals and ceramics, including catalysts, can be shaped in any regular structure one can envisage by various techniques [72]. An impressive application in bulk catalysis is the enormous process intensification of the NO oxidation for nitric acid manufacturing by applying a washcoated structured isoreticular Al-foam designed to improve the mass transfer, heat exchange rate and keeping a low pressure drop [73].

Applying 3D printing removes the non-uniformity issue and other structures can be envisaged, e.g. by introducing anisotropy to induce directional transport of mass or heat, to improve the heat transfer to the reactor wall, and to secure well-distributed gas-liquid flow. The pioneering work of Schwieger and Freund [74–77] with periodic Open Cell Structures (POCS) built from elementary cells (Kelvin, cubic, diamond, hybrids etc.) are starting to become an important research topic in structured catalytic reactors (Figs. Fig. 1010, Fig. 1111).

As mentioned earlier, a practical aspect of structured reactors is the loading and unloading of reactor tubes. As a tight structure-wall contact is important narrow fitting of the inserted structure is preferred. Direct printing of the tube wall is an option. Here, it would be interesting to explore the feasibility of (structured) materials with a negative Poisson's ratio, called auxetic [78–81]. Upon exerting force they contract in more directions, so structures with that property will easily slide into a tube when pushed and expand upon removing the force, achieving a good wall contact.

The POCS-based reactors can be applied to both exo- and endothermic processes. In the latter case the energy input could in principle be realized in other ways than external heating, providing a new degree of design freedom. Resistive heating of an electrical conductive internal structure [82–84] or by inductive heating of magnetic nanocatalysts [85–88] have been proposed. A washcoated Ni-foam could be quickly heated up for the (exothermal) CO₂ methanation in a lab-scale reactor and further gently heated to compensate for heat losses of the reactor tube [82]. Interestingly, the electric current is claimed to enhance catalyst activity and the sulphur poisoning resistance. Inductive heating of catalyst particles was also shown to rapidly start up the process [85]. Rapid resistive (Joule) heating of the FeCrAlloy reactor tube washcoated with a catalyst for the endothermic methane steam reforming (MSR) removed the external heating of the reactor by combustion of fuel, heat recovery and reduced CO₂ emissions [83,84]. Alternatively, rapid start-up was also achieved with inductive heating of a packed bed of magnetic catalyst particles [86,88].

In both ways of operation the energy transport is no longer limiting and material diffusion becomes determining. Washcoated reactor channel diameters of 0.5 mm are suggested [84], which correspond well with monolithic structures, or packed POCS with very homogeneous structural features.

Electrification of the chemical industry opens a complete new arena

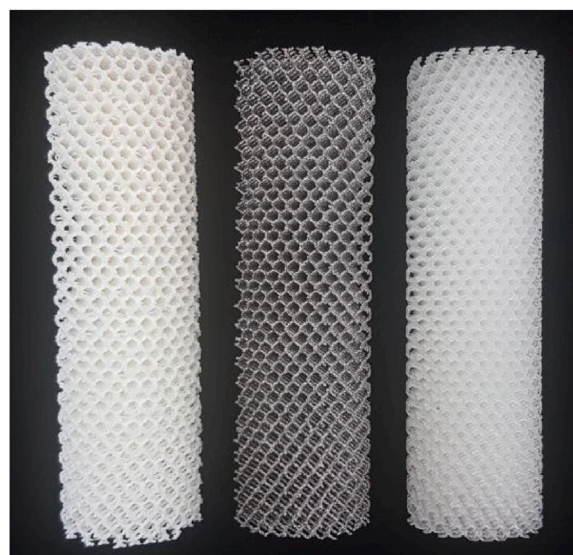


Fig. 11. Additively manufactured POCS packings (with diamond unit cells) made of ABS, Ti6Al/4 V and resin (from left to right). Reprinted with permission from [75]. © Elsevier 2018.

for structured reactors R&D with large potential for process intensification, especially in regions where large quantities of electrical energy are produced. The intermittent character of this source seems easily be coped with by the rapid start-up feature of this type of reactor operation.

6. Concluding remarks

Structured catalysts and reactors are still an innovative and lively topic. For demanding applications, crucial issues are how to handle exo- and endothermic reactions and how to create high catalyst loadings in the reactor. Parallel channel ceramic monolith reactors (honeycombs) behave as virtually adiabatic reactors.

For gas phase emission control, heat effects are small because of the low concentrations of the relevant compounds that have to be converted. As a consequence, in this case honeycombs are excellent designs. For reactions with large heat effects in chemicals production a tailored process design can be attractive. An early example is the hydrogenation of nitrobenzene in a monolith loop reactor. Here heat production and heat removal are carried out in two separate pieces of equipment. The post-reactor described above (selective oxidation of *o*-xylene) is another early example of heat effect management by a specific process design. A more drastic solution is to produce reactors with improved radial heat transport, either by conduction or by convection. Conductive heat transport can be improved by selecting the right material, metal rather

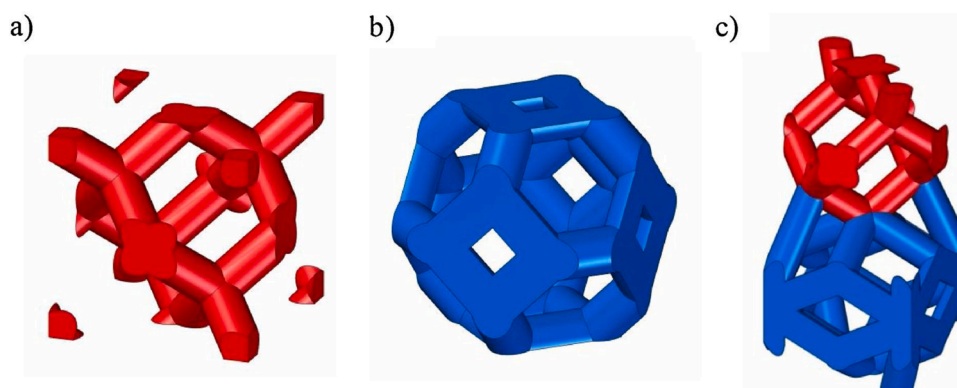


Fig. 10. Unit cells of the POCS a) Kelvin, b) Diamond, and c) hybrid DiaKel. Reprinted with permission from [75]. © Elsevier 2018.

than ceramics. In all three cases described above the potential of metallic honeycombs is obvious. The other way to increase radial heat transport 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. These 'cross-flow channels' result in improved heat transport. Also foams exhibit relatively fast radial heat transport and can be applied.

Solving the issue of low catalyst loading can be based on combination of structured bodies with catalyst particles. An obvious example is packing a honeycomb with catalyst particles [8], but there is a practically unlimited number of options. The structured body can be composed of conducting material (Cu and Al are excellent), resulting in a combination of increased radial conductive heat transport with high catalyst loading. Of course, in case the reaction is mass transfer limited the catalyst geometrical surface area should be maximized instead of inventory.

The energy supply in endothermal processes still relies on external heating by fuel combustion, but excess production of renewable electricity can provide an alternative by resistive or inductive heating of reactor internals.

Choosing the right morphology, structured bodies (foams, cross-flow structures, bird-nests geometry, novel 3D printing products) can be designed for optimal radial convection and the combination with catalyst particles solves both issues (heat management and catalyst inventory). The great variety of potential structures will enable finding breakthroughs in chemical engineering.

In reactor design, materials choice is of high importance, for instance, stability is needed at the reaction conditions and in the specific reaction medium. For the morphologies considered in this article, additional criteria for materials' selection hold. Focus has been on examples where improved radial heat transport is beneficial. In this case metals suggest themselves (copper and aluminum work well), but also silicon carbide and even carbon are feasible candidates. In the latter case the required high-temperature carbonization of polymeric structures introduces manufacturing challenges due to the associated shrinkage [89].

The time has come to develop dedicated reactor designs instead of 'one-fits-all' designs.

Credit authors statement

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Declaration of Competing Interest

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