

The Potential of Structured Reactors in Process Intensification

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Abstract

Structured catalytic reactors have a large potential in Process Intensification. In many respects they outperform conventional reactors such as packed-bed and slurry reactors, both for gas and for gas – liquid systems. The most important structured reactors are based on gauzes, foams, and monoliths. In general, monoliths are the most satisfactory structured reactors. In gas-phase applications they are often preferred due to their favourable properties with respect to selectivity, pressure drop, and robustness. Their millisecond characteristics have potential in syngas production and selective conversions into valuable products. In gas-liquid applications they exhibit high rates, high selectivity (for serial kinetics), and they operate close to plug-flow behaviour. They are compact reactors with excellent performance in activity and selectivity. They allow co- as well as counter-current operation at common industrial conditions and can be used in multifunctional reactors, *e. g.* catalytic distillation. The use of a structured reactor allows the decoupling of intrinsic reaction kinetics, transport phenomena, and hydrodynamics. In this way these processes in a catalytic reactor can be optimised independently, giving rise to an excellent reactor performance. Structured catalysts and reactors will play a major role in Process Intensification.

INTRODUCTION

Chemical reactors form the heart of a (petro-)chemicals production plant. Given the large variety of plants it is no surprise that many different chemical reactors are used. Catalytic reactors roughly can be divided in random and structured reactors. It is useful to start with a summary of the major basic concerns (apart from high activity, selectivity, *etc.*) for catalytic reactors:

- catalyst quality on a microscopic length scale (quality, number of active sites);
- catalyst quality on a mesoscopic length scale (diffusion length, loading, profiles);
- ease of catalyst separation and handling;
- heat supply and removal;
- hydrodynamics (regimes, controllability, predictability);
- transport resistance (rate and selectivity);

- safety and environmental aspects (run-aways, hazardous materials, selectivity);
- costs.

With regard to these aspects random and structured reactors behave quite differently. In terms of costs and catalyst loading randomly packed-bed reactors usually are most favourable. So, why would one use structured reactors? It will become clear that in many of the concerns listed structured reactors are to be preferred. Precision in catalytic processes is the basis for process improvement. It does not make sense to develop the best possible catalyst and then use it in an unsatisfactory reactor. Both the catalyst and the reactor should be close to perfect. Randomly packed beds do not fulfil this requirement. They are not homogeneous because mal-distributions always occur; at the reactor wall these are unavoidable, originating from the looser packing there. These mal-

distributions lead to non-uniform flow and concentration profiles and even hot spots may arise [1]. A similar analysis holds for slurry reactors. For instance, in a mechanically stirred-tank reactor the mixing intensity is highly non-uniform and conditions exist where only a relatively small annulus around the tip of the stirrer is an effective reaction space.

Catalytic conversion and separation are conventionally carried out in separate pieces of equipment. A combination of functions in single units is an elegant form of Process Intensification. When one of the functions is a chemical reaction, such a unit is referred to as a *multifunctional reactor*. A good example is catalytic distillation [2]. Structured reactors will play a key role in the design of novel processes based on multifunctional reactors [3]. A monolith is a good example.

STRUCTURED REACTORS

Structured reactors and catalysts are encountered in a large variety [3, 4]. Structured catalytic reactors can be divided in two categories. The first category contains a structured catalyst, whereas the second one contains ‘normal’ catalyst particles arranged in a non-random way. In the first category the catalyst and reactor are essential identical entities.

Because of their low pressure-drop, structured reactors in practice dominate the field of treating tail gases. Figure 1 gives an impression of the major types of reactors. The monolithic reactor represents the class of ‘real’ structured catalytic reactors, whereas the parallel-passage and the lateral-flow reactor are based on a structured arrangement of packings with ‘normal’ catalyst particles.

Monoliths usually are made from ceramics, but metals are also used. Monoliths can be produced by extrusion of support material (often cordierite is used, but various types of clays or typical catalyst carrier materials such as alumina, titania, *etc.* are also used), a paste containing catalyst particles (*e. g.* zeolites, V-based catalysts), or a precursor for the final product (*e. g.* polymers for carbon monoliths). Alternatively, catalysts, supports, or their precursors can be coated onto a monolithic support structure (‘washcoating’). Zeolites have been coated by growing them directly on the support during the synthesis [5]. Coating literature and patents is a large field and, in principle, a variety of preparation procedures are available. All major catalyst support materials, ceramic and polymeric, have been extruded as monolith [4, 6]. Metallic support structures are used for automotive applications [7].

Monoliths are the dominant catalyst structures for three-way catalysts in cars [8–11],

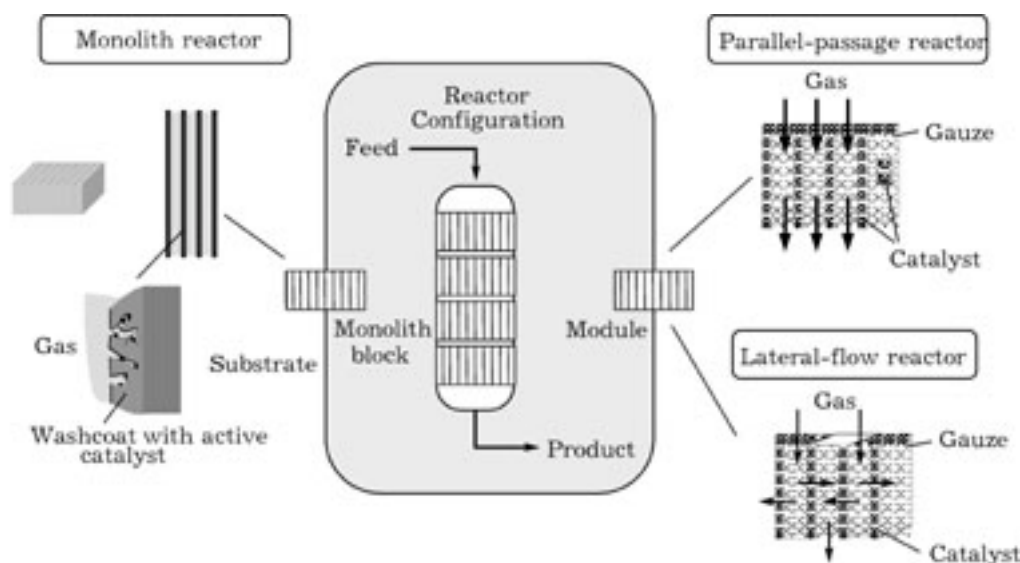


Fig. 1. Low pressure-drop reactors used for tail gas treating.

TABLE 1

Diffusion time scales in catalytic reactors ($l_D^2/2D$) for three diffusion lengths (l_D)

D (m ² /s)	$l_D = 1$ mm	$l_D = 0.1$ mm	$l_D = 1$ mm	$l_D = 1$ mm
Gas	10^{-5}	50 ms	0.5 ms	50 ns
Liquid	10^{-9}	500 s	5 s	500 ns
Liquid in cat pore	10^{-10}	5000 s	50 s	5 ms
Liquid in zeolite pore	10^{-11}	50 000 s	500 s	50 ms

selective catalytic reduction catalysts in power stations [12–15], and for ozone destruction in aeroplanes. What causes this popularity? The catalyst consists of one piece, so no attrition due to moving particles in a vibrating case occurs. The large open frontal area and straight channels result in an extremely low pressure-drop essential for end-of-pipe solutions like exhaust pipes and stack gases. The straight channels prevent the accumulation of dust.

Of course, monolithic catalysts have disadvantages. They share with packed-bed catalysts the requirement of a sufficient stability or in any case a good regenerability. With respect to mass- and heat-transfer characteristics, the major limitations are the laminar flow through the channels, no interconnectivity between the channels, and a poor radial heat conductivity. The latter two properties are much better for the foam-type monoliths, but with a trade-off in a higher pressure-drop and/or lower catalyst loading (sites/m³). In principle, a laminar flow velocity profile is associated with low mass-transfer rates and a large residence time distribution. Fortunately, due to the small channel size and high diffusivity (D), for gases this radial transport in the channels is sufficiently fast. Typical time scales for diffusion ($l_D^2/2D$) are given in Table 1. In liquid phases the diffusivity is three orders of magnitude smaller and this is one of the reasons that monoliths do not enjoy a high popularity in liquid-phase operations. It will be shown that this is based on a misconception.

The honeycomb type monoliths are characterised by a very high geometric surface area. Dependent on the cell density this can exceed $3000 \text{ m}^2/\text{m}^3_{\text{reactor}}$! Figure 2 shows square-channel cordierite monoliths with cell densities of 200, 400, and 600 cpsi (cells per square inch). These examples are quite realistic. At present the monolith commonly used for cars is a 400

cpsi monolith. The value for the geometrical surface amounts to $3440 \text{ m}^2/\text{m}^3_{\text{reactor}}$. In packed beds this value is much lower in order to avoid unrealistic pressure-drops. It is to be expected that future monoliths will exhibit even larger geometric surface areas. That alone makes them highly useful for Process Intensification programs.

GAS-PHASE REACTIONS

It is fair to state that the most important application of structured reactors by large is in environmental catalysis. The major applications are in automotive emission reduction. For diesel exhaust gases a complication is that it is overall oxidising and it contains soot. New ideas have emerged, all of them involving structured reactors. The truck market is dominated by diesel engines. In that application space requirement is a major issue and Process Intensification is badly needed. Space velocities exceeding $100\,000 \text{ h}^{-1}$ are demanded. Other important areas are reduction of NO_x from power plants and the oxidation of Volatile Organic Compounds (VOCs). In synthesis gas production also structured reactors suggest themselves, for instance in catalytic partial oxidation (CPO) of methane.

MULTIPHASE REACTION SYSTEMS

Various types of reactors are being used commercially for multiphase applications, the

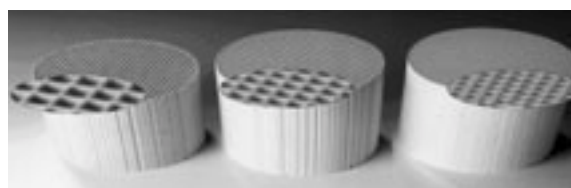


Fig. 2. Square-channel cordierite monoliths with cell densities of 200, 400, and 600 cpsi.

major ones being the slurry reactor, bubble-column reactor, and the trickle-bed reactor [16]. Each reactor has its own advantages and disadvantages. Slurry catalysts are small (typically 50 μm), while trickle-bed particles are larger (millimetre scale) in view of the allowable pressure-drop over the bed. The particle size is a crucial parameter. In general it can be stated that larger particles are less efficient and, even more important, are less selective in those reactions where the desired product is subject to an undesired following reaction ($A \rightarrow B \rightarrow C$ with B the desired product). In that often-encountered case the slurry reactor is more selective than the trickle-bed reactor. In terms of Process Intensification a mechanically stirred-tank reactor often is not a good choice. In practice it is no exception that gas-liquid mass transfer is rate determining. That implies that only the part of the space close to the tip of the stirrer(s) is well used. A large part of the reactor does not contribute much to the productivity and dependent on the kinetics will lead to low selectivity. Moreover, major disadvantages of the slurry reactor are the often difficult separation of product and catalyst and catalyst attrition. The trickle-bed reactor is much more convenient but large particle sizes are unavoidable. An important limitation of trickle-bed reactors is that in practice they are nearly always operated co-currently to avoid liquid entrainment by the gas ('flooding'). Some important commercial applications, however, would benefit from counter-current operation, especially equilibrium-limited reactions and reactions with strong product inhibition [17].

Hydrodynamics and mass transfer in monoliths

Hydrodynamics for co-current operation. For co-current gas-liquid flow, several flow regimes can occur. The preferred one usually is the so-called Taylor or slug flow [18, 19]. This type consists of gas bubbles and liquid slugs flowing consecutively through the small monolith channels. The gas bubble fills up the whole space of the channel and only a thin liquid film separates the gas from the catalyst. The rate of mass transfer is large as a result of two effects. Firstly, the liquid layer between bubble and catalyst coating is thin, increasing mass

transfer. Secondly, the liquid slugs show an internal recirculation during their travel through a channel. Because of this, radial mass transfer is increased. Moreover, the gas bubbles push the liquid slugs forward as a piston and a type of plug flow is created. Compare this with single-phase liquid flow through the channels. Because of the low channel diameter the flow will be laminar and, as a consequence, the radial transport will be extremely slow, leading to a very poor reactor performance: rates are slow and the reactor exhibits strong non-plug-flow behaviour. For multiphase operation at slug flow conditions the increase in the mass-transfer rate is an order of magnitude larger than for single-phase liquid flow, whereas the increase in friction, that is pressure-drop, is much less. A fortunate finding is that Taylor flow conditions are easily realised under practical conditions.

Ideally, in contrast to packed beds, scale-up of monolithic reactors is very simple. When we know the behaviour of one channel, we should be able to predict the whole reactor. Is this really true? Compared to a packed bed, a monolithic reactor differs in radial transport. When the initial distribution of liquid in the radial direction is non-ideal, going down through the reactor, this unfavourable distribution does not change. In contrast, in a packed-bed reactor some redistribution occurs. Therefore, in scale-up the reactor inlet system has to be designed well so that the distribution of the liquid in the top of the reactor is ideal. We found that if a bubble emulsion on top of the monolith is present a satisfactory distribution seems to be guaranteed, similar as found for trickle-bed reactor operation. It appeared that the flow rate has to be above a specified minimum value (linear velocities > 0.1 m/s) in order to guarantee a good distribution of liquid over the cross-section of the reactor. It might be worthwhile to investigate whether systems can be developed or conditions established that allow low flow rates. Combinations of monolithic-catalyst packages with Sulzer-type contactors are being conceptually investigated in our group. They might increase the window of operability towards lower flow rates. Moreover, they might lead to flexibility allowing more compact reactor systems. The first results are promising.

TABLE 2

Comparison of mass-transfer rates for three common reactor types

Reactor type	$k_t a$, s^{-1}
Trickle bed	0.05–0.2
Slurry	0.1–0.3
Monolith	> 1

Note. The corresponding production rate in the monolith at 373 K and a hydrogen pressure of 10 bar amounted to 40 mol/(m³_{reactor} s).

Mass transfer for co-current operation. Mass transfer was studied experimentally in various ways. As an example of the performance, a monolith was compared with a trickle-bed reactor under identical reaction conditions in co-current mode for the hydrogenation of α -methylstyrene. The washcoated 400 cpsi monolith yielded a ten times higher hydrogenation rate per unit volume of reactor. This stresses the high mass-transfer rate in the monolith [16, 20]. Mass transfer is usually expressed as the factor $k_t a$, the mass-transfer coefficient times the exposed surface area per unit volume. In Table 2 the three common reactor types are compared. Obviously, operation of the monolithic reactor in the Taylor flow regime leads to a high degree of Process Intensification [1].

Counter-current operation. Under practical conditions counter-current operation in a packed-bed reactor is not feasible because flooding occurs [21, 22]. The reason is that in the small interstitial space extended momentum transfer takes place between the liquid flowing down and the gas flowing up. At velocities used in industry this would imply that the particle size has to be increased by an order of magnitude. This leads to unacceptable internal-diffusion limitations. Clearly, momentum transfer has to be decreased while maintaining high rates. This can be done by structuring the catalyst or by clever arrangement of the catalyst particles in the reactor. From an extensive study, it appeared that also in structured reactors, counter-current operation is possible at industrially relevant conditions. The breakthrough was the design of optimal monolithic structures and dedicated inlet and outlet systems. See [23] for details.

Potential of monolith reactors

The catalyst to be used in a reactor operation can be coated as a thin layer on the channel walls, and, hence, the reactor can be described as a ‘frozen slurry reactor’. The diffusion length is small and well controllable. The high cell density of the monoliths creates a high geometric surface area. Using a packed bed, unrealistically small particles would be needed to achieve this. Catalyst separation and handling are as convenient as in a common packed bed.

Monolith reactors are intrinsically safe. The monolith channels have no radial communication in terms of mass transport and the development of runaway by local hot spots in a trickle bed reactor cannot occur. Moreover, when the feed of liquid or gas is stopped, the channels are quickly emptied.

From the above, it should be evident that monolithic reactors (and other structured reactors) in many respects are superior to conventional reactors. Indeed, for several reactions, monolithic catalysts have been reported, although only at the bench or pilot scale except for one case. The interesting points are to demonstrate that the ‘theoretically’ outlined advantages are indeed present. They in fact boil down to larger reactor productivity, better selectivity control, and higher efficiency compared to conventional reactors. The first also implies better catalyst utilisation. Obvious is the fact that the catalyst is fixed in a reactor and pressure-drops are low.

The hydrogenation step in the anthraquinone process of AKZO-Nobel is an industrial realisation of a monolithic reactor and includes a lot of pioneering work by the Anderson group [24–28]. More examples of the use of monoliths can be found in [27, 29].

In our own group in co-operation with a chemical company, we have studied the selective hydrogenation of pyrolysis gasoline. This study [30] demonstrated the plug-flow behaviour needed for such a selective conversion and the efficient use of the active phase, which was at least a factor three to four better than in trickle-bed operation. The hydrogenation of α -methylstyrene mentioned above, is an even more appealing example of better active-phase

utilisation and confirms the good mass-transfer properties.

The co-current monolith reactor, with its plug-flow characteristics, can in principle be used in downflow, upflow and horizontal-flow mode, provided a good gas-liquid distribution is secured [31]. The latter mode might solve a major problem in practical applications of monoliths: because for hydrodynamic reasons high flow rates are needed, the reactor length tends to be very large. Research with respect to this type of reactor is in progress. An important outcome of the research might be that coupling of monolithic elements, mixing units and heat exchangers leads to flexible cascade-reactor systems enabling multistep synthesis in one pass.

The best-studied mode is co-current downflow. A monolith reactor operating in this mode is an alternative to the bubble-column reactor often used in biotechnological applications. Since bubble-column reactors have a large height and large gas flow rates are required, the energy input to introduce and compress the gas for injection at the bottom is relatively high. In the down-flow monolith reactor, this gas injection is automatically achieved. The co-current reactor type can easily be used as a stirred reactor type by a large recirculation flow without extremely large energy input due to the low pressure-drop. An external heat exchanger can be scaled independently of the reactor to deliver the required heat duty [1, 16].

Of course, monoliths have disadvantages. Currently, they are more expensive than particle catalysts. In fixed-bed operation, they will have to exhibit a sufficiently long lifetime. In quickly (irreversibly) deactivating reactions, they cannot be used. It is of extreme importance that the inlet distribution should be secured. In co-current flow, both gas and liquid have to be contacted evenly with the catalyst at the monolith walls.

In the evaluation of the properties of catalytic reactors there are three important aspects that strongly determine the overall performance: the amount of catalyst and intrinsic kinetics, the transport phenomena (diffusion in and outside the catalyst), and the hydrodynamics in the reactor. In classical reactors these are strongly interrelated and cannot be de-

finied and designed independently. As an example, for fast reactions small catalyst particles are desired from the point of view of catalyst effectiveness, but a packed bed with small particles will result in an unacceptable pressure drop. Therefore, an optimum has to be sought for the particle size. The elegance of structured reactors is that these three aspects can be designed and optimised fairly independently, resulting in an optimised reactor performance.

In slow reactions the intrinsic reaction kinetics control the process, so the catalyst inventory should be as high as possible. Increasing the wall thickness of a monolith can have the desired effect. In fast reactions mass transfer or intraparticle diffusion becomes controlling. Thinner catalyst coatings, Taylor flow, *etc.* can be applied to optimise these requirements. If mass transfer is controlling the productivity is proportional to the geometric surface area of the monolithic structure. Increasing the cell densities is recommended, of course not to the point where unacceptable pressure-drops arise.

CONCLUSIONS

Monolithic and other structured catalysts exhibit favourable properties with respect to practical convenience, high rates, high selectivity, and low energy consumption. From an engineering point of view, also the easy scale-up and the potential of high safety are appealing. Monoliths are not limited to single-phase processes but they are also well placed for multiphase processing.

Monoliths exhibit a large flexibility in operation. They are suited well for optimal semi-batch, batch, continuous, and transient processing. Catalytic conversion can be combined with *in situ* separation, catalytic reactions can be combined, heat integration is possible, and all lead to Process Intensification. Monoliths allow the efficient use of small catalyst particles, *e.g.* zeolites, and have a substantial flexibility with respect to catalyst inventory in a reactor. Multifunctional reactor operations like reactive stripping or distillation are challenging applications that are not too far away.

The essence of the use of a structured reactor is that it allows the decoupling of intrinsic reaction kinetics, transport phenomena, and hydrodynamics. In this way these phenomena, which control the overall behaviour of a catalytic reactor, can be optimised independently, giving rise to an excellent reactor performance.

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