

Process Development and Scale Up:

II. Catalyst Design Strategy

by

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Summary

The possibility to influence the performance of a heterogeneous catalyst by tailoring the size and shape of catalyst particles, their porous texture and the distribution of active sites within them should be exploited when developing a catalyst for a given process. This should be done within the context of the total process requirements, giving consideration to kinetic and mass transport as well as hydrodynamic requirements of the selected reactor configuration. The present paper discusses catalyst particle design in the above context and provides some guidelines on the choice of the important factors for heterogeneous catalyst particles. Rather than viewing a heterogeneous catalyst as some form of “catalytic substance”, a heterogeneous catalyst should be considered as a part of a catalytic system of which the design involves catalytic site engineering, catalyst particle engineering and reactor engineering.

Introduction

In the design of a catalytic process in principle different levels of design can be distinguished, viz.,

- at an atomic or molecular level
- at the level of a catalyst particle in the case of a heterogeneous catalytic process
- at the level of the catalytic reactor, and
- at the level of the integrated complete process.

The first three levels are visualized in Figure 1.

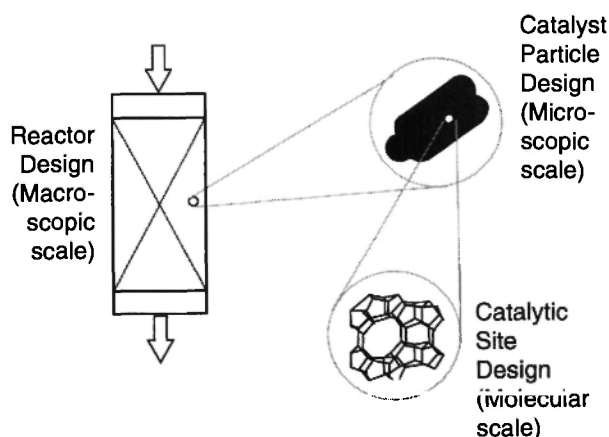


Figure 1. Levels of design of a catalytic reaction system involving a heterogeneous catalyst.

At the first level the main discipline involved is that of chemistry and catalysis. The chemistry and catalysis involved is specific to the particular reactions that form the basis of the process. This type of study is generally most prominent in the initial exploratory phases of process R & D and features less in the development stage. For these reasons design of catalysts, whether homogeneous or heterogeneous ones, on an atomic level will not be treated here in detail since this belongs to the discipline of catalysis as commonly defined. This design of catalysts at an atomic level can be termed catalytic site engineering.

Most studies in heterogeneous catalysis are concerned with characterizing or improving the catalytic site or active phase for a given reaction. In these respects heterogeneous catalysis is usually considered as a surface phenomenon or as a molecular

phenomenon in a similar way as homogeneous catalysis. Compared with the latter type of catalysis, heterogeneous catalysis is generally at a disadvantage as the catalytic site is usually less well known and less amenable to rational chemical tailoring. However, apart from the obvious advantages of easy separation of catalyst from product and in many cases easy regenerability, heterogeneous catalysts also offer distinct advantages from a reaction engineering point of view: a variety of reactor types including fluidized bed, slurry, fixed bed, ebulliating bed, and fixed bed can be applied to effect contact between reactants and catalyst.

Catalyst design strategy at the microscopic level of the catalyst particle cannot be isolated from the type of reactor chosen and is therefore a part of reaction selection strategy; Krishna and Sie (1994) consider catalyst design as the first in a three-level strategy for reactor selection as shown in Figure 2. Both are in turn dependent upon the characteristics of the conversion reactions and the desired performance of the process.

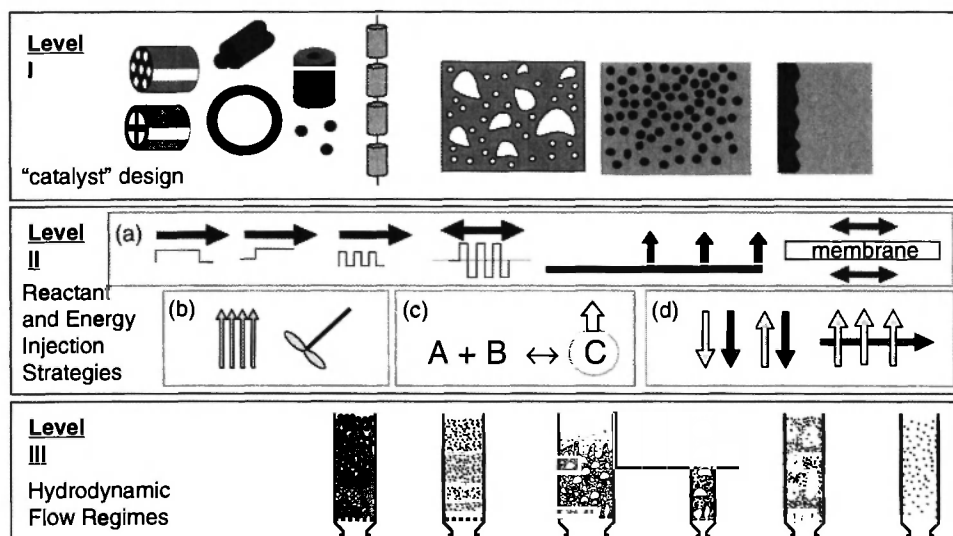


Figure 2. Three-level strategy for multiphase reactor selection. Adapted from Krishna and Sie (1994).

Whilst the choice of reactor type sets limits to suitable sizes and shapes of catalyst particles via demands on fluidizability, suspensibility, pressure drop, flowability, etc., there is the possibility to vary catalyst morphology within these constraints so as to meet process demands dictated by reaction and diffusion in an optimal way. Particularly with larger

particles as used in fixed or moving bed reactors the interplay between chemical kinetics and rates of diffusion of reactant or product molecules can be influenced by variation of catalyst size, shape and porous texture. The distribution of active material inside the catalyst particles can be an additional variable in designing optimal catalysts, in particular when diffusion limited poisoning reactions occur. Figure 3 shows the main variables involved in the relationship between catalyst particle design and process characteristics and need.

Catalyst Particle Design

Aspects

- Particle size
- Particle shape
- Porous texture
- Activity distribution

Process Needs and Characteristics

- Reactor Type
 - Hydrodynamics
 - Pressure drop
 - Mass and Heat Transfer
 - Fluidizability
 - Slurry viscosity
 - Suspensibility
 - Mechanics
 - Strength and Flowability
- Kinetics and Diffusion
 - Activity
 - Selectivity
 - Stability

Figure 3. Design of catalyst particles tailored to process needs.

In this paper we will discuss the relation between desired process performance and catalyst particle parameters, i.e., catalyst design on the second of the four levels in the above classification. Main attention will be given to catalyst particles for fixed bed reactors. Subjects to be discussed are the possibility to vary the geometry of the catalyst particles and the topology of the active phase inside them, taking into account diffusion and kinetics of the reactions involved, including poisoning reactions.

Although fixed bed reactors belong to the most widely applied reactors because of their relative simplicity, special process features may demand other types of reactors, as discussed by Krishna and Sie (1994). The implications of other reactor types than fixed bed ones on catalyst particle design will form a subject of discussion in the last part of this paper.

Intraparticle diffusion

The finite rate of diffusion of reactants or products inside catalyst particles can affect the rate or selectivity of the conversion to desired products, i.e., the apparent activity or selectivity of the catalyst. It can also have consequences for the deactivation behaviour of the catalyst. These effects will be discussed below.

Effect of intraparticle diffusion on catalyst activity

Effect of particle size

Intraparticle diffusion limitation occurring with relatively fast reactions and slowly diffusing reactant molecules may result in incomplete utilization of the catalyst as the interior is not reached by the reactant molecules. This effect has been the subject of many chemical engineering studies and is relatively well understood; see e.g. Weisz and Prater (1954) and Satterfield and Sherwood (1963). Utilization is expressed as the effectiveness factor η , which for a given particle geometry is a function of the generalized Thiele modulus

$\phi_{gen} \equiv \frac{V}{SA} \sqrt{\frac{k_m \rho_v}{D_{eff}}}$, in which (V/SA) is the volume/external surface area ratio of the catalyst.

For a given conversion rate, the external surface determines the flux density for diffusion of reactants to the catalytic surface inside the catalyst volume. The ratio (V/SA) , which has the dimension of length, can be considered to be a measure of the average diffusion distance necessary to penetrate the particle. The relation between η and ϕ_{gen} is shown in Figure 4. As

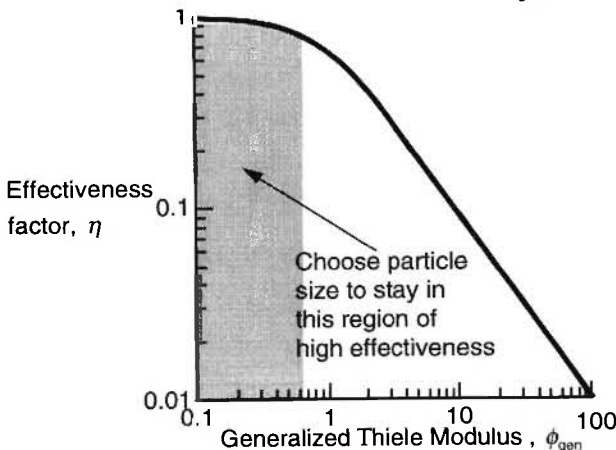


Figure 4. Effectiveness factor as a function of the generalized Thiele modulus for a first-order reaction.

a general rule, the particle size choice should aim at high effectiveness, so as to make good use of catalyst materials and reactor volume, and for improved activity. There are exceptions to this general rule, however, as will be discussed later.

Pore diffusion limitation is not uncommon in industrial fixed-bed catalytic processes, particularly in classical processes which use relatively large catalyst particles (pellets of 5 - 15 mm diameter). Simple calculations comparing the time needed for diffusion over a given distance inside the particle with the maximum time available for the reaction show, that for practical reaction rates as apply to most processes and typical diffusivities in gas or liquid-filled pores of catalysts, diffusion limitation will generally occur with particles having a diameter of a few millimetres. In the case of very fast reactions or very slow diffusion, as in the case of so-called conformational-type diffusion inside zeolite pores, pore diffusion limitation will occur with particles of even much smaller dimensions.

Figure 5 shows effectiveness factors of some catalysts in gas phase reactions as a function of catalyst size. It can be seen that in these processes catalyst utilization is far from complete for fixed-bed catalysts of practical sizes, i.e., above 3 mm. In such gas phase reactions the diffusivity inside the catalyst particles is usually a Knudsen-type diffusion or a surface diffusion, and hence depends on the gas pressure and the pore texture.

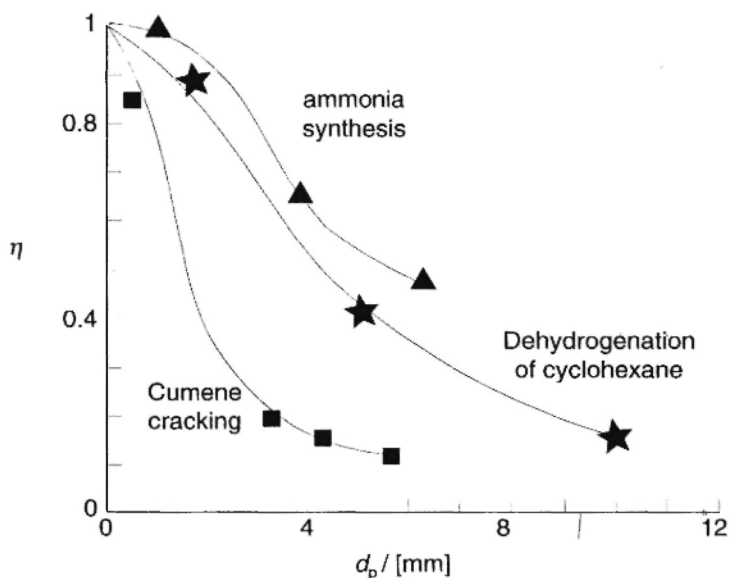


Figure 5. Effectiveness factors in some gas-phase fixed-bed processes. Data from: Corrigan et al., (1953), Weisz and Schwegler (1955) and Bokhoven and Van Raayen (1954).

In catalytic processes where liquid is present, the catalyst pores are likely to be filled with liquid and the low diffusivity in the liquid phase may increase the likelihood of diffusion limitation. Figure 6 (a) shows the effect of particle size on the performance of a Co/Mo/Alumina catalyst for hydrodesulfurization of a gasoil in trickle flow, demonstrating the occurrence of diffusion limitation. Figure 6 (b) shows effectiveness factors of a series of catalysts of different particle sizes having the same composition. It can be seen that utilization of the catalyst is reasonably complete only with particles having a diameter of less than 1 mm. Catalyst utilization is far from complete for catalysts of relatively large size (pellets of 5 -15 mm diameter and length) as used in classical hydrogenation processes before and shortly after World War II. Currently, extrudates of about 1.5 mm size are used for hydroprocessing, achieving effectiveness factor values close to unity.

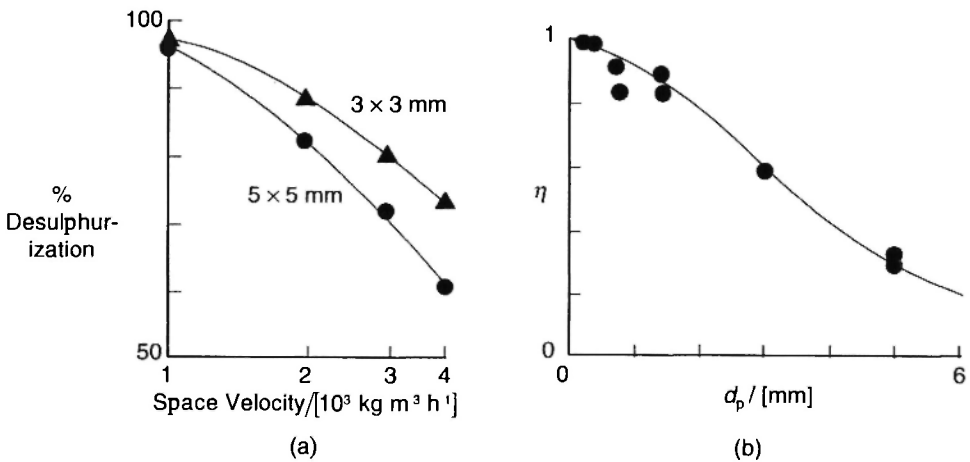


Fig. 6. (a) Effect of catalyst particle size in trickle-flow hydrodesulfurization of Kuwait straight run gasoil over a Co/Mo/Alumina catalyst (b). Utilization of catalyst as a function of particle size in hydrodesulfurization of Kuwait straight run gasoil over a Co/Mo/Alumina catalyst. Adapted from Le Nobel and Choufour (1959).

Another example of the occurrence of diffusion limitation caused by the presence of liquid in the catalyst pores is depicted in Figure 7. This figure shows the effectiveness factor as a function of the Thiele modulus for a number of Fischer-Tropsch catalysts operated under different conditions. The experimental results are in very good agreement with the theoretical

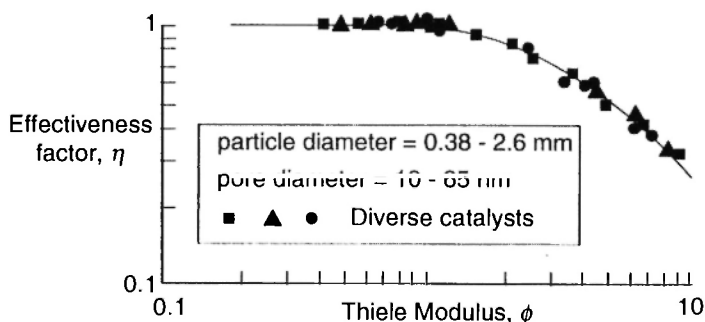


Figure 7. Effectiveness factors as a function of the Thiele modulus for Co-type Fischer-Tropsch Catalysts. Adapted from Post et al. (1989).

curve calculated for the case that the reaction rate obeys first-order kinetics in hydrogen (as has been verified experimentally) while the limiting factor is the rate of diffusion of hydrogen as reactant in the liquid hydrocarbon product which fills the pores. The excellent fit demonstrates that as far as catalyst effectiveness is concerned its dependence on catalyst morphology may be established on the basis of first principles if the reaction kinetics and the mechanism of diffusion are known.

Geometry of catalyst particles

The geometric factor which governs the utilization of catalyst particles from a given catalytic material is in first approximation the ratio between external surface area and volume of the particle, (SA/V) , c.f. expression of the generalized Thiele modulus). For geometrically similar shapes the (SA/V) is inversely proportional to a characteristic dimension, e.g., the diameter d_p . Hence, for such similar shapes the (SA/V) multiplied with the diameter d_p is a dimensionless constant which is characteristic for the shape. Figure 8 compares the (SA/V) of some catalyst shapes currently used in fixed-bed reactors in a plot of the above dimensionless constant against the length over diameter ratio (L/d_p) . The cross sections of some of the less common shapes considered in this figure are shown in more detail in Figure 9.

It can be seen that rings, hollow extrudates and more sophisticated shapes such as "wagon wheels" and "miniliths" offer a greater surface to volume ratio than the more common cylindrical tablets and cylindrical extrudates of the same outside diameter and length. Since

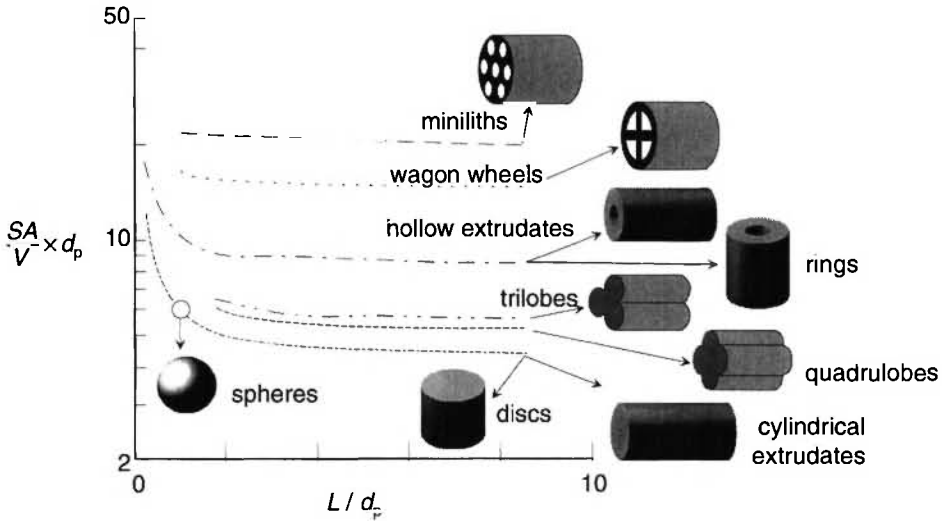


Figure 8. Surface area over volume ratio of catalyst particles.

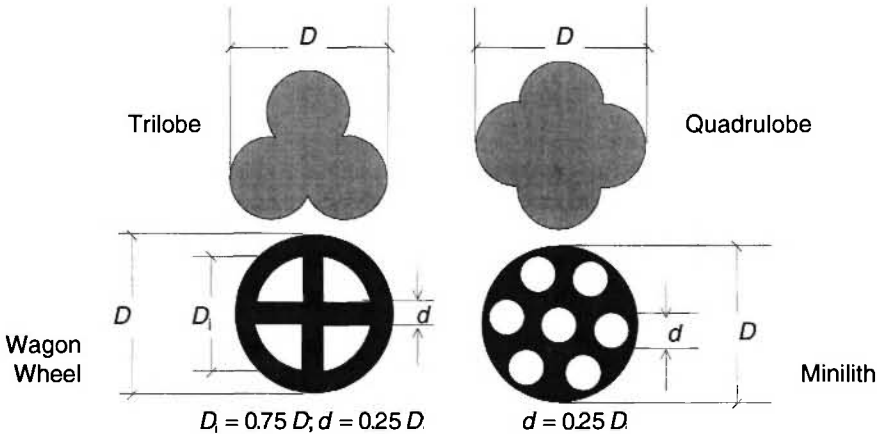


Figure 9. Cross sections of Trilobe, Quadrulobe, Wagon wheel and Minilith extrudates.

pressure drop and effective radial heat conductivity in packings are mainly determined by the outside diameter of the particles, these shapes are advantageously used in gas-phase operated adiabatic fixed-bed reactors or non-adiabatic tubular reactors. For liquid-phase processes they are less advantageous since the hollow space is likely to be filled with relatively stagnant liquid. Extrudates with a clover leaf cross section, viz., trilobe or quadrulobe extrudates, offer a greater

surface to volume ratio than cylindrical extrudates of the same maximal outside diameter and retain their advantage also in liquid phase operation. It can be seen that round, disk-shaped tablets of a length to diameter ratio below one, have a greater surface area than cylindrical extrudates with a ratio above one of the same diameter. Notwithstanding this extrudates have largely superseded tablets in most fixed bed processes. This is because reduction of the diameter of pressed tablets to values much lower than 5 - 15 mm, as used in classical fixed-bed processes, results in rapidly escalating manufacturing costs (the number of particles for a given weight of catalyst increases with the third power of the linear dimension). Extrudates, however, can be produced at little extra costs at diameters below 1 mm.

Size and shape of catalyst particles in relation to productivity and other factors in fixed bed processes.

As discussed above, the problem of diffusion limitation can be alleviated by choosing smaller catalyst particles of a shape that has a high surface-to-volume ratio. However, there are factors which limit the increase of the surface to volume ratio by adaptation of particle size and shape, viz., pressure drop, catalyst cost and particle strength (Worstell, 1992). The main limiting factor for reduction of particle size in a fixed bed reactor is generally the pressure drop over the bed. Figure 10 shows the general relation between pressure drop and

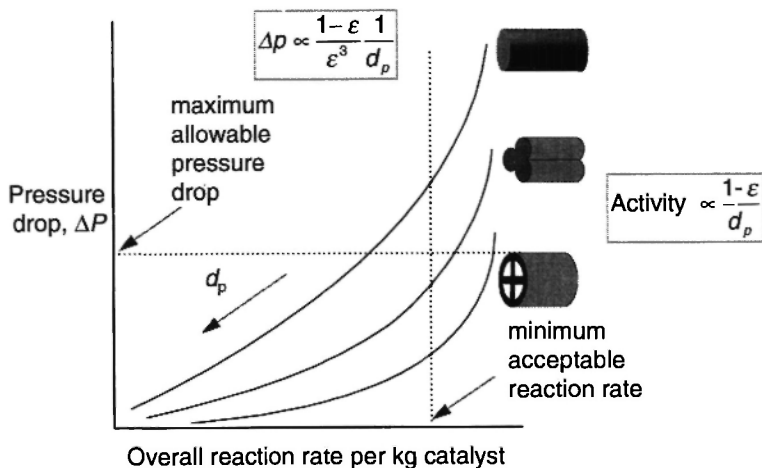


Figure 10. Relation between reactor productivity and pressure drop for some types of fixed-bed catalysts.

reactor productivity for extrudates of different shape and size. This figure shows trends rather than quantitative data, since the latter depends on several factors such as properties of reactant fluids, aspect ratio of the bed, axial versus radial flow, etc. The demand for a minimum desired reaction rate within a maximum allowable pressure drop determines suitable sizes and shape of catalyst particles for a given case. For instance, for the case depicted it can be seen that cylindrical extrudates need not be considered, but that wagon wheels in a certain range of sizes can be used. Trilobe extrudates of a specific size are marginally applicable for this case.

The superiority of wagon wheel and trilobe extrudates over cylindrical extrudates with respect to the reaction rate - pressure drop relation is caused by the higher surface area to volume ratio of the former types of extrudates. However, these types of extrudates also have their drawbacks so that they may not be the preferred type under all circumstances.

Figure 11 shows the relationship between manufacturing costs and surface-to-volume ratio for the different types of extrudates. It can be seen that in general the simple cylindrical extrudates are the cheapest to manufacture. The figure shows that to satisfy the specifications on minimum SA/V ratio and maximum allowable costs, as indicated in this figure for a hypothetical case, both trilobe and cylindrical extrudates may be considered. Of these two, cylindrical extrudates present the more economic solution.

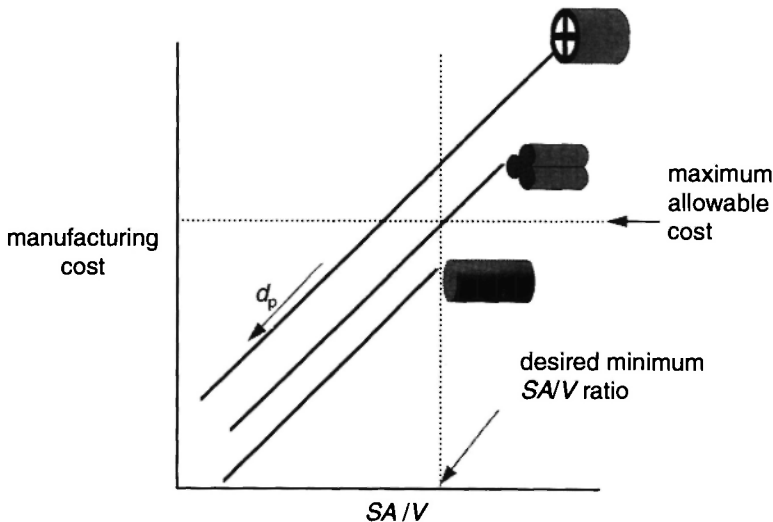


Figure 11. Relation between reactor manufacturing cost and surface/volume ratio of some fixed-bed catalysts.

Strength of catalyst particles is in most cases an important factor in fixed bed processes. Particles should be able to withstand the forces exerted on them by the weight of the bed above, and by the pressure drop. This strength is generally measured either on a single catalyst particle, giving the so called side crushing strength (SCS), or measured by exerting a pressure on a small bed of particles, giving the so called bulk crushing strength (BCS). Figure 12 shows the relationship between catalyst strength (either SCS or BCS) and SA/V ratio for extrudates of some different shapes and different sizes. It can be seen that extrudates of the more sophisticated shapes are in general less strong. Minimum requirements on strength and SA/V ratio as indicated in this figure for a hypothetical case, can be satisfied by all three types of extrudates. Whereas the requirements are amply fulfilled by trilobes and cylinders, this is only marginally so in the case of wagon wheels.

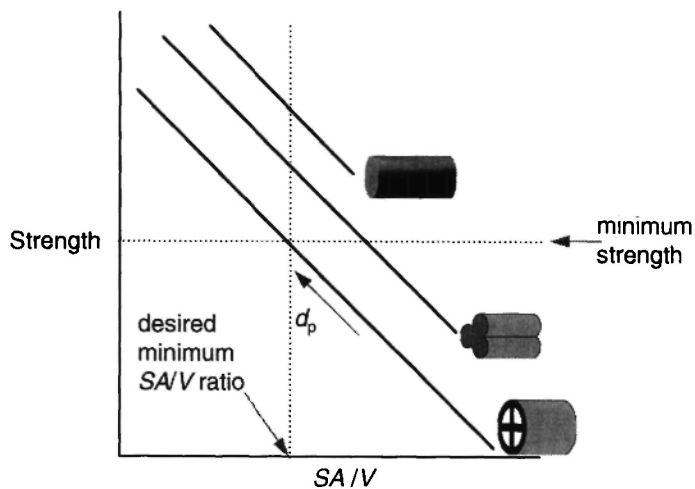


Figure 12. Strength versus surface/volume ratio of some fixed-bed catalysts.

Effect of diffusion limitation on selectivity.

Diffusion limitation not only affects the apparent activity of a catalyst, but can also affect selectivity. The best known effect of diffusion limitation is a negative one. This applies to a case of consecutive reactions $A_1 \rightarrow A_2 \rightarrow A_3$, where A_2 is the desired product. Diffusion limitation reduces the chances of the intermediate product A_2 escaping from the catalyst particle so

that the selectivity of its production will be lowered due to increased chances of A_2 being further converted to unwanted product A_3 .

A good example of the influence of intraparticle diffusion on selectivity is the partial hydrogenation of edible oils to modify their melting behaviour and their taste stability. Edible oils consists of esters of mainly unsaturated acids and glycerol. Hydrogenation of oils is the reaction of hydrogen with unsaturated triacylglycerol molecules over a nickel based catalyst. For example, the hydrogenation of trioleoylglycerol (Ol_3) to tristearoylglycerol (St_3) occurs according to the following consecutive steps: $Ol_3 \rightarrow StOl_2 \rightarrow St_2Ol \rightarrow St_3$ where $StOl_2$ and St_2Ol represent the partially hydrogenated products. With respect to product properties like melting behaviour, selective hydrogenation giving the maximum concentration of intermediates $StOl_2$ and St_2Ol is required. The selectivity can be influenced by proper choice of the pore size and particle size of the catalyst; see Figure 13 (Colen et al., 1988).

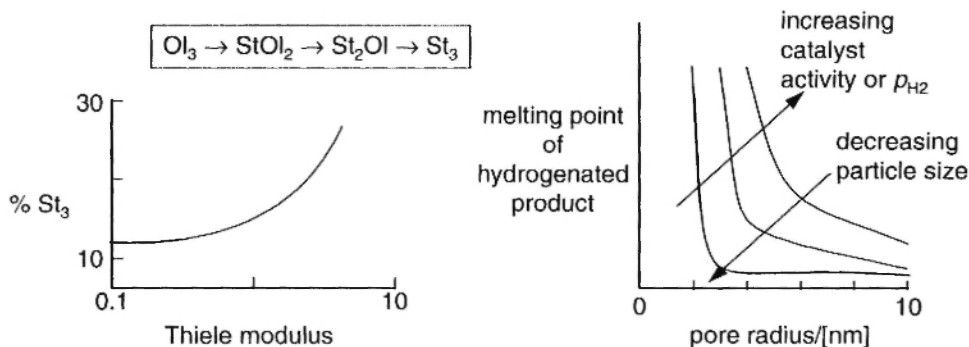


Figure 13. Influence of intraparticle diffusion on selectivity of intermediate product in a consecutive reaction sequence. The reaction considered is the hydrogenation of trioleoylglycerol (Ol_3) to tristearoylglycerol (St_3), which proceeds through the partially hydrogenated intermediates St_2Ol and $StOl_2$. By tailoring the catalyst with respect to particle size and pore size the diffusional influence can be altered to obtain a product with the desired property such as melting point. Adapted from Colen et al. (1988).

In contrast to the above case, diffusion limitation can also have positive consequences, as will be illustrated below. An example of the use of diffusion limitation as a means to steer the formation of products towards a desired molecule is the selective production of p-xylene by disproportionation of toluene (Weisz, 1980; Haag et al., 1981). The principle is

schematically shown in Figure 14. The selective formation of *p*-xylene from toluene depends on the differences in diffusion rates between the isomeric xylenes in ZSM-5 zeolite. *p*-xylene diffuses much faster than the two other xylenes, while the feed molecule toluene and the byproduct benzene diffuse even faster. Without diffusional control the relative proportions of the xylene isomers will correspond to the thermodynamic equilibrium between the xylene isomers. As the diffusion of the xylene molecules becomes more limiting the differences in diffusivity of the isomeric xylenes gain importance, resulting in increased selectivity to the para isomer.

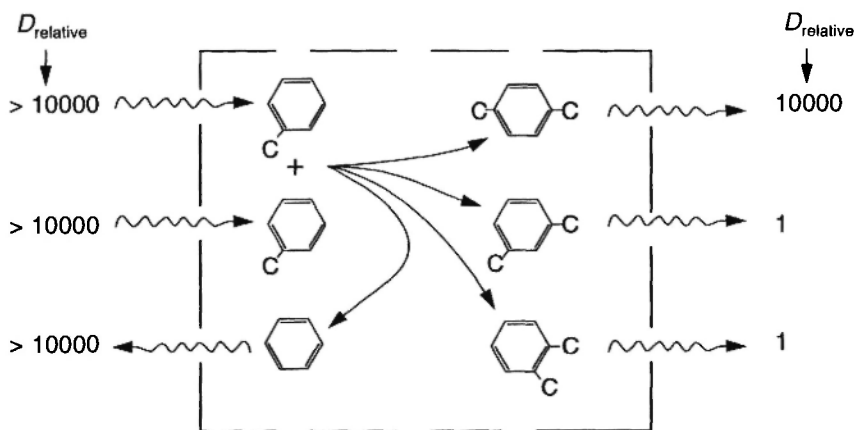


Fig. 14. Schematic representation of the role of diffusion in production of *p*-xylene by disproportionation of toluene. Adapted from Weisz (1983).

Figure 15 shows that the selectivity to *p*-xylene is a unique function of the diffusion time of *o*-xylene in the crystallites of ZSM-5, which can be varied by variation of crystallite size, by modification with different cations, or by coke deposition (Olsen and Haag, 1984). The time needed to reach 30% of the sorption capacity has been taken as a measure of the effective accessibility. It can be seen that under conditions of pronounced diffusional control and with the elimination of activity of the external surface of the zeolite crystals quite high selectivities to the para isomer can be attained, far exceeding the value of about 20% dictated by bulk thermodynamic equilibrium. The latter selectivity is obtained in the absence of diffusion limitation.

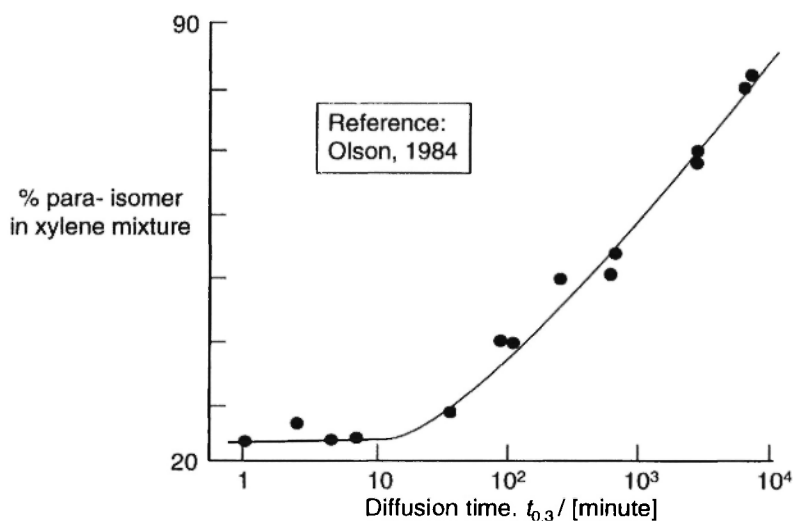


Figure 15. Relation between diffusion parameter and p-xylene selectivity in disproportionation of toluene over ZSM-5 catalysts.

Effect of diffusion limitation on catalyst deactivation.

If the catalyst deactivates as a consequence of the occurrence of a reaction which is subject to diffusion limitation, regulated access of the catalyst particle to the poison generating molecules by tailoring catalyst morphology offers a means to control catalyst life. This principle forms the basis for catalyst design for hydroconversion of metal-containing residual oils (Sie, 1980). In this process, the deposition of contaminant metals (Ni, V) as sulfides on the catalyst surface deactivates it for the main reactions, the hydrodesulfurization and hydrocracking of the oil molecules. The metals originate from large molecular complexes (asphaltenes) which because of their size diffuse very slowly into the catalyst particles. Since the breakdown of these molecules which releases the metals is pore diffusion limited, deposition of the metal sulfides occurs in an outer zone of the particle, leaving the inner core unpoisoned. This is evidenced by visual examination of used catalyst particles (after burning off carbon deposits), as can be seen in Figure 16. The presence of deposited contaminant metals in an outer zone of the particles can be proven by electron microprobe analysis of used catalysts as shown in Figure 17.

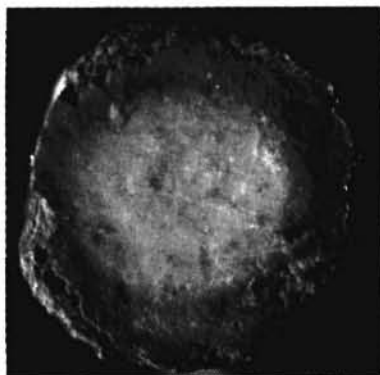


Figure 16. Photomicrographs of calcined and broken catalyst particles that have been used in hydroprocessing of residual oils.

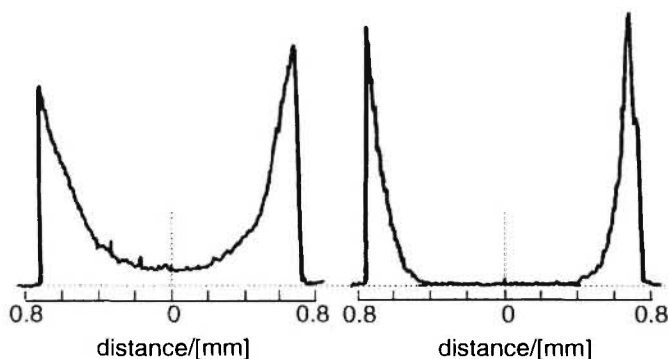


Figure 17. Electron microprobe scans for vanadium in catalyst particles used in the hydroprocessing of residual oil, showing the K- α signal of vanadium across the particle diameter. The accessibility of the catalyst at the right is less than that at the left.

The penetration depth of metal-containing asphaltenic species into the catalyst particle determines the size of the unpoisoned inner core of the catalyst particle and thereby its residual activity for the desired reactions, hydrodesulfurization and hydrocracking of the non-asphaltenic oil molecules. Equally important is the effect of penetration depth on catalyst life; in the course of time metal sulphides continue to be deposited in the peripheral zone and eventually fill the pore volume in this area completely, which means the end of catalyst life. As the zone is broader and involves a larger proportion of the particle, it takes more time to

completely deactivate the catalyst. Figure 18 shows that for different catalysts used in hydrodesulphurization of a given residual oil feed the maximum metal uptake capacity is proportional to the effectively used pore volume for metal deposition (Sie, 1992; 1993).

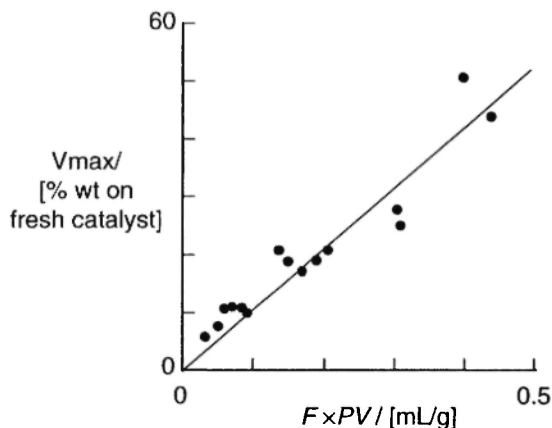


Figure 18. Correlation between vanadium uptake capacity with effective pore volume in residue hydroprocessing. F is the effectiveness factor for storage of metals deposits in the pore volume of the catalyst particle, which can be determined from electronmicroprobe scans as shown in Figure 17. Adapted from Sie (1993).

By variation of catalyst morphology, i.e., changing catalyst size and shape or the porous texture, one can precisely regulate the relative depth of metals penetration and thereby control the life of the catalyst and its activity for the main reactions. This is illustrated in Figure 19 which shows the effect of average pore diameter on the performance of a series of similarly shaped catalysts for hydrodesulphurization of a Middle East atmospheric residue. Catalyst activity in this plot has been defined as the 2nd order rate constant for sulphur removal at half of the useful catalyst life. It can be seen that activity decreases as accessibility for asphaltenes increases with larger pore diameters. This is because the active inner core of the catalyst becomes smaller. Catalyst life, which is also shown in this plot, becomes longer as accessibility increases because a larger proportion of the catalyst pore volume becomes available for storage of metal deposits.

From Figure 19 it can be seen that even relatively small changes in average pore diameter (1 nm) can have significant effects. Control of average pore size of the catalyst

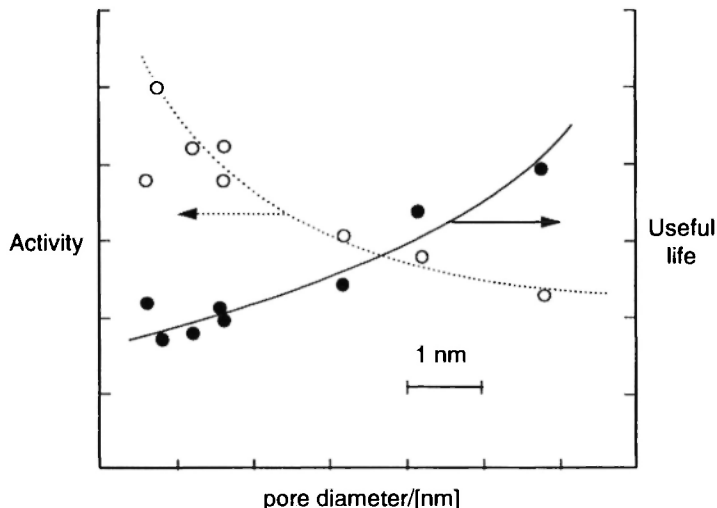


Figure 19. Effect of average pore diameter on the performance of catalysts for the hydrodesulfurization of atmospheric residue of a Middle East crude oil. Catalysts studied belong to a series of Co/Mo/Alumina catalysts of identical shape and size having sharp unimodal pore size distributions. Adapted from Sie (1993).

support (which can be done, for instance, by hydrothermal treatment) thus offers a means to adjust catalyst performance for a given duty.

In a fixed bed process for hydroprocessing of residues the removal of metals from the oil stream will cause a decrease in their concentration in the direction of the stream. Therefore, the balance between activity and tolerance for metals deposition will not be the same in different parts of the reactor or reactor train. Thus, it is advantageous to use a combination of different catalysts rather than just one: a highly metals tolerant catalyst upstream which can cope with the relatively high concentration of metal contaminants in the feed, and a highly active catalyst in the downstream part. The latter catalyst will have a low tolerance for metals deposition, but this tolerance suffices since the metals concentration in the oil has already been lowered. Ideally, a large number of catalysts designed for a gradually sliding balance between activity and metals tolerance should be placed in series.

With such a multi-catalyst combination, definition of an optimal catalyst is not straightforward since the desired activity and life of a catalyst depend on its position in the reactor train, on feedstock characteristics, on target conversion level and desired onstream

time, etc., as is shown in Figure 20. However, when a process model is available which has been validated with sufficient practical data, it becomes possible to predefine catalyst parameters for a desired duty (Oelderik, et al., 1989).

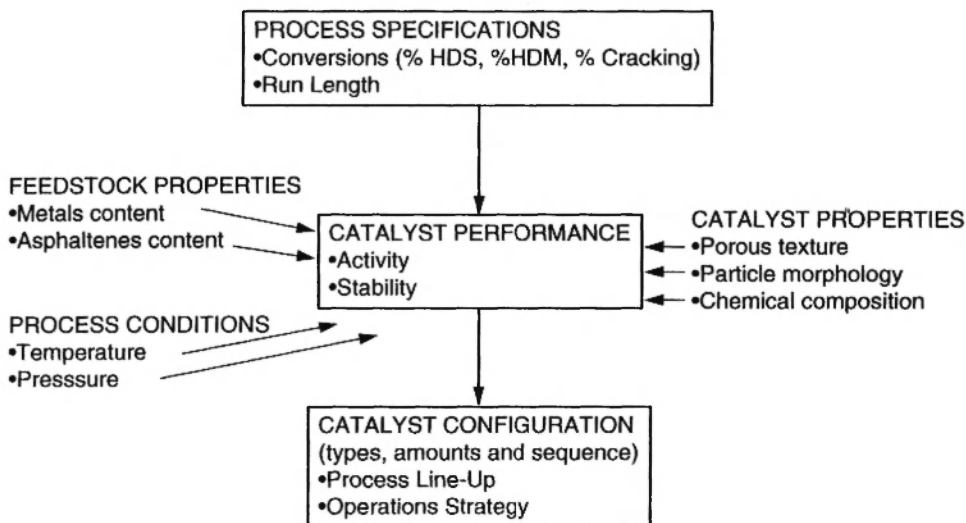


Figure 20. Relationships between process, feedstock and catalyst parameters determining the choice of hydroprocessing catalysts. Adapted from Oelderik et al. (1989).

An example of catalyst design assisted by a computerized process model is shown in Figure 21. It can be seen that catalyst life passes through a maximum at a certain value of the average pore diameter. At smaller diameters, the catalyst deactivates faster because the relatively shallow outer layer available for deposition of metal sulphides becomes more rapidly filled. At larger diameters, the activity of the catalyst is relatively low (as a consequence of the relatively small unpoisoned inner core) so that higher temperatures have to be applied to reach the process specifications. The smaller span of operating temperatures thus shortens the operating cycle.

It can be seen that in this example the experimentally tested base case is not far from the calculated optimum situation, but this is of course not always true. This possibility of designing catalysts is especially important in residue hydroprocessing since actual life tests require runs of several thousands of hours, so that catalyst optimization by way of empirical

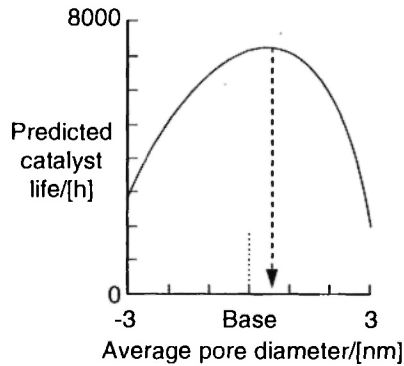


Figure 21. "Computer-aided design" of catalyst porous texture. Predicted life as a function of the average pore diameter of a tail-end catalyst in the hydroconversion of an Arabian Heavy vacuum residue at 60 % conversion. Adapted from Oelderik et al. (1989).

testing is not likely to achieve an optimum result within a reasonable amount of time and effort.

Spatial distribution of activity within catalyst pellets.

Effect of non-uniform distributions

In the absence of diffusion limitation, it is a common policy to uniformly load the support pellet with catalytically active species, in order to maximize the catalytic activity per unit volume of catalyst bed. If the effectiveness factor is below one, it is obvious that catalytic agent may be saved by leaving the inner core free from it without losing overall activity. However, non-uniform distributions of activity within a catalyst pellet can have additional advantages besides savings in active material. Different activity distributions possible are shown in Figure 22.

In the case of a bimolecular reaction following Langmuir kinetics where one reactant is strongly and rapidly adsorbed, a diffusion resistance can enhance the rate of chemical reaction. An example of such a case is the oxidation of CO over noble metal catalysts. Becker and Wei (1977) have theoretically analyzed this situation and concluded that a catalyst with the active ingredient in the interior (egg yolk-type catalyst) is more advantageous than alternative

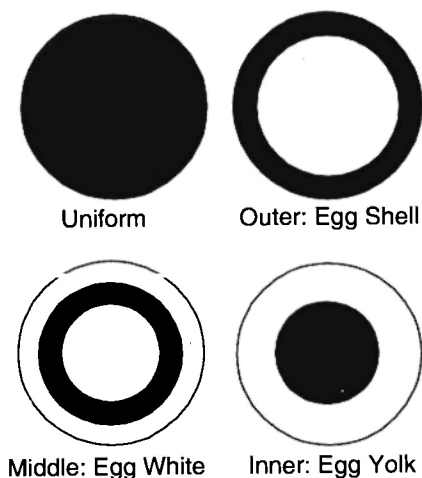


Figure 22. Different activity distributions in a catalyst pellet.

catalysts in which the active material is in an exterior layer (egg shell-type catalyst), in a middle layer (egg white-type catalyst), or uniformly distributed. The problem of optimal activity distributions has been studied theoretically by several authors for various cases of single, parallel and consecutive reactions, in the presence or absence of extraparticle mass transfer limitation and for non-isothermal cases (Morbidelli and Servida, 1982; Morbidelli et al., 1985; Morbidella and Varma, 1982; Vayenas and Pavlou, 1987a, 1987b; Corbett and Luss, 1974, Shadman-Yazi and Peterson, 1972). Reviews on the optimal distributions of catalytic material in catalyst pellets have been presented by Dougherty and Verykios (1987) and more recently by Gavriilidis and Varma (1993).

The recent work of Lin and Chou (1994) demonstrates the benefits of a non-uniform activity distribution in the case of selective hydrogenation of isopentenes over an alumina-supported Pd catalyst. The unwanted product, isopentane is formed by further hydrogenation of the isopentenes (methyl butenes: $3M1B + 2M1B + 2M2B$); see the reaction scheme in Figure 23. Figure 24 (a) compares the activity of a homogeneously loaded catalyst with that of an egg-shell catalyst of the same metal loading. It can be seen that the egg-shell catalyst has a higher activity; less residual isoprene is found in the product. Figure 24 (b) compares the selectivities of the two catalysts for production of methyl butenes; the superior selectivity of the egg-shell catalyst is clearly demonstrated.

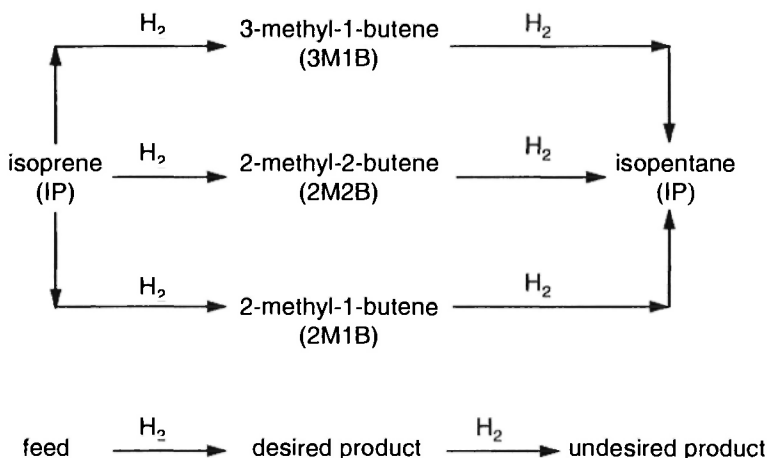


Figure 23. Reaction network for isoprene hydrogenation.

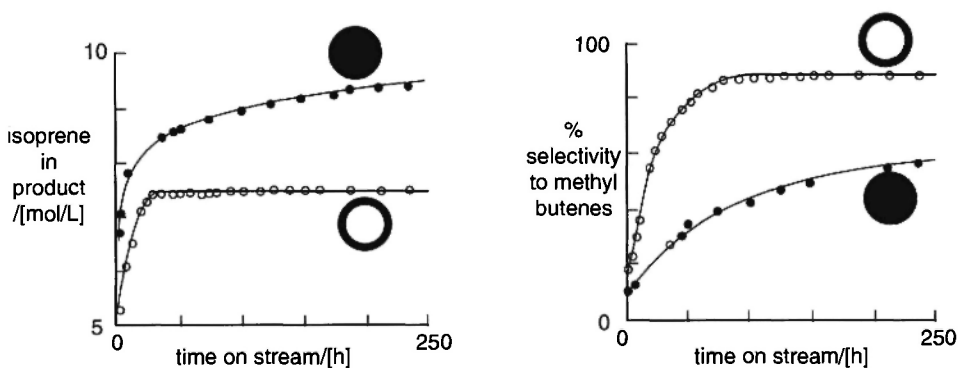


Figure 24. Effect of activity distribution on (a) activity and (b) selectivity in isoprene hydrogenation. The catalyst used is 2 % w PdAlumina. Adapted from Chou et al. (1994).

Figure 24 also shows that the egg-shell catalyst is also superior with respect to stability; after a rapid initial change of catalyst performance both activity-maintenance and selectivity-maintenance are better for the egg-shell catalyst. The higher activity of the egg-shell catalyst can be explained by the better utilization of the Pd metal. Since the desired product of the selective hydrogenation, isopentenes, can diffuse more easily out of the catalyst particle there is less opportunity for further hydrogenation to isopentane; this leads to higher selectivity to the desired product. Catalyst deactivation is ascribed to the occurrence

of a side reaction, viz., isoprene polymerization, ultimately leading to "coke" on the catalyst. As isoprene is more rapidly converted and initial products of conjugated dienes oligomerization leave the catalyst particle more readily, there will be a lower tendency for coke formation.

The above benefits derived from more easy access of the feed molecules to the catalytic phase and the more ready escape of product molecules from it can also be realized by employing much smaller catalyst particles instead of an egg-shell catalyst. However, such smaller particles may give rise to unacceptably high pressure drops over a fixed bed; fluidized bed operation is then required.

Other non-uniform activity distributions than of the egg-shell type can have particular advantages when the main reaction is accompanied by an irreversible poisoning reaction (DeLancey, 1973; Becker and Wei, 1977; Bacaros et al., 1987).

In the case of a diffusion-limited poisoning reaction, where the poisoning occurs in an outer shell (pore-mouth poisoning) it can be advantageous to concentrate the active component in a layer inside the pellet. When the bare support is capable of adsorbing the poison the active components inside are thus protected from it. The main factors determining the best type of activity distribution are the Thiele moduli for the main reaction and the poisoning reaction. Figure 25 presents a catalyst selection chart on this basis.

The definition of the "best" catalyst for a given case is not necessarily straightforward and will depend on the relative weights attached to different performance aspects. This may be illustrated by the work of Becker and Wei (1977a), who computed results for four different types of activity distributions in automotive exhaust catalysts. The predicted performances of fresh and aged catalysts in Figure 26 clearly show differences in behaviour between the four catalyst types. Which catalyst is best depends on whether emphasis is placed on fresh or on aged catalyst performance and whether low temperature activity (light-off) or high temperature activity is considered more important.

The above principles have been applied in the design of actual pellet-type automotive catalysts by Hegedus and Summers (1977). By modifying the pore structure and surface area of the support, as well as the noble metal penetration depth, Pt/Pd/Alumina catalysts with improved activity and resistance to poisons (P, Pb) have been obtained. With more than one catalytic metal present, the concentration profiles of the metals need not be identical. In further studies by Hegedus and Summers (1978) sizeable improvements in both steady-state

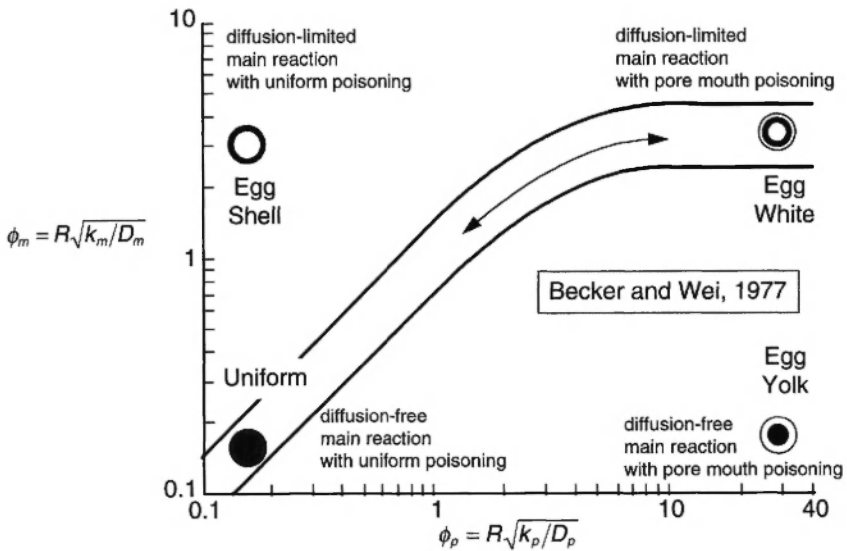


Figure 25. Catalyst selection chart for four catalyst designs for a catalytic reaction accompanied by a poisoning reaction. Criterion: longest catalyst life with effectiveness of 0.4 or higher. Adapted from Becker and Wei (1977).

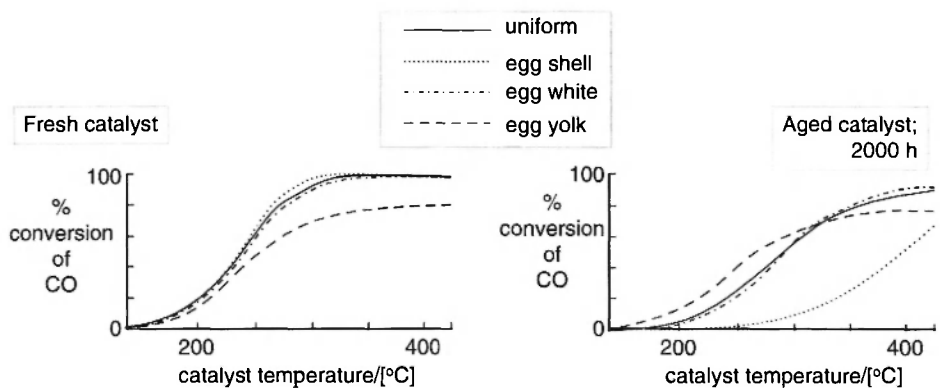


Figure 26. Comparison of predicted performances of base metal oxide catalysts with different activity distributions as automotive exhaust catalysts. Adapted from Becker and Wei (1977).

and light-off performance were obtained when the catalyst had an outer shell of Pt and an inner shell of Pd. These authors even studied catalysts containing three different noble metals and demonstrated improved poison resistance and light-off characteristics for a configuration

with an external shell of Pt and internal rings of Rh and Pd (1979) The design concept underlying such a catalyst is illustrated in Figure 27.

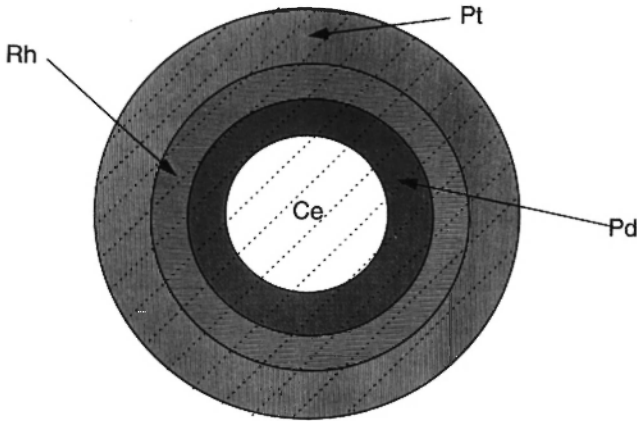


Figure 27. Design concept for a low-Rh automotive exhaust catalyst. After Hegedus and Summer (1978).

In recently published work, Brunovská et al. (1994) demonstrated that the location of a layer of Pt inside an alumina pellet can have a significant effect on the performance of egg-white type of catalysts for hydrogenation of ethene in the presence of thiophene as an impurity. Figure 28, which presents some results from their work, demonstrate that a catalyst with the active layer close to the outer surface of the pellet is initially the most active (lowest

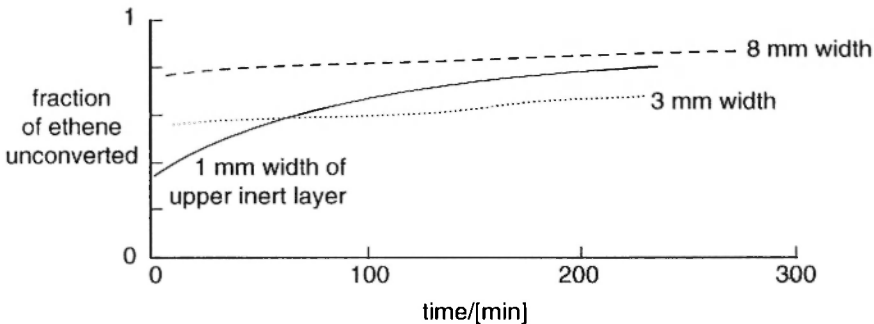


Figure 28. Effect of active layer location on the performance of egg-white type Pt/alumina catalysts in the hydrogenation of ethene in the presence of thiophene as contaminant. After Brunovská et al. (1994).

amount of unconverted ethene), but deactivates most rapidly due to easy access of the poisoning thiophene molecules. A very deep location of the active layer gives a relatively stable catalyst, but the activity for ethene conversion is relatively low. As can be seen from Figure 28, an intermediate location of the active Pt layer gives the best results for the case considered.

Preparation of catalysts with activity profiles

Catalyst particles with inhomogeneous distributions of active ingredients may in principle be prepared in a variety of ways. The desired activity profile may either be obtained in the process of shaping the catalyst, or the distribution of active material may be established in particles of preshaped carrier.

An example of establishing an activity profile during shaping is to use a nodulizing technique to prepare pellets from powders, with varying concentration of active ingredient in the powder during various stages of pellet building. Similarly, preparation of pellets from active powdered catalyst diluted with varying proportions of inert powder is possible (Ruckenstein, 1970; Varghese and Wolf, 1980).

Egg-shell type distributions of active metal in preshaped carrier material can be obtained by partial imbibition of a metal salt solution into dry catalyst support particles. If migration of metal species during subsequent drying is avoided, the active metal will be present in an outer layer in the catalyst. Partial penetration can be realized by limiting the time of contact between catalyst support and metal salt solution.

Zhang and Schwarz (1992) studied the effect of imbibition variables on penetration depth. The time dependence of the penetration depth of salt solution into the catalyst particles is a function of support characteristics and physical properties of the solution, as is illustrated by Figure 29. Thus it is possible to regulate the penetration depth of metals into the catalyst particles by judicious choice of imbibition conditions.

Impregnation of supports with active metals can also lead to non-uniform distributions, e.g., diffusion limitation of particle penetration by ions in solution may easily lead to egg-shell type catalysts. Strong interactions of metal ions with chemical groups at the surface can also result in higher peripheral concentrations due to chromatographic effects. Heise and Schwarz (1985, 1986, 1988) studied the effects of solution pH on the adsorption of

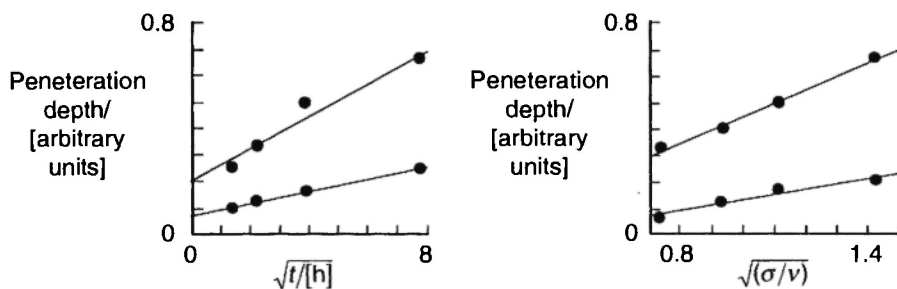


Figure 29. Effect of experimental parameters on the imbibition of silica with solutions of nickel nitrate in ethylene glycol-water. Left: penetration depth vs. square root of immersion time (Ni in glycol). Right penetration depth vs. square root of the ratio of surface tension and viscosity (Ni in aqueous glycol, $t = 5$ s). Open points: high SA silica; filled points: low SA silica. Adapted from Zhang and Schwartz (1992).

hexachloroplatinic acid on alumina. Lowering the pH reduced the adsorption strength and increased the depth of penetration of metal into the support. Ionic strength and concentration effects also influence penetration depth and these effects can be described by a model.

By adding additional components to the impregnation solution the adsorption process may be influenced, e.g., by the effect of competitive adsorption (Heise and Schwarz., 1987; Schwarz and Heise, 1990).

Instead of coimpregnation of a support with a compound containing the catalytic metal and an adsorption modifying additive, one may also employ a sequential impregnation procedure. If the support is first impregnated with a salt solution of the metal followed by a solution containing a displacing agent, the location of the metal zone may be moved in a controllable way. Thus Brunovská et al. (1994) succeeded in preparing Pt/alumina catalysts of the egg-white type in which the location of the Pt band inside the pellets could be controlled by varying the time of post-impregnation with citric acid, see Figure 30. Figure 31 shows microphotographs of cross sections of catalyst pellets prepared in this way.

Using various chemical additives which function as site blocking agents, chasers, etc., a variety of Pt profiles have been obtained by Shyr and Ernst (1980) as is illustrated by Figure 32. Photomicrographs of similarly prepared egg shell-, egg yolk- and egg white- type copper on magnesia-alumina catalysts are shown in Figure 33.

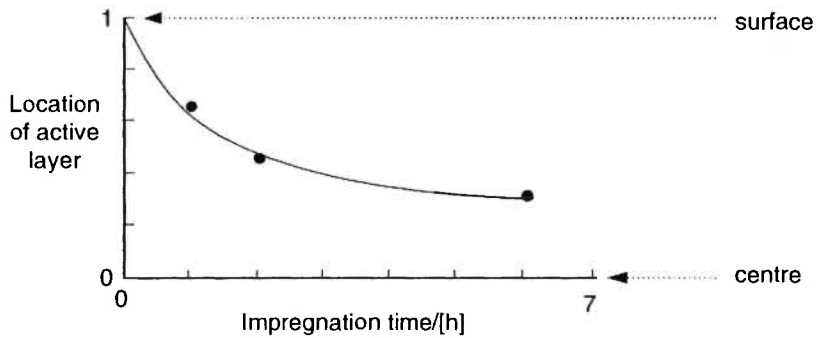


Figure 30. Effect of citric acid post-impregnation time on the location of the platinum layer in Pt/alumina catalysts. Adapted from Brunovská et al. (1994).

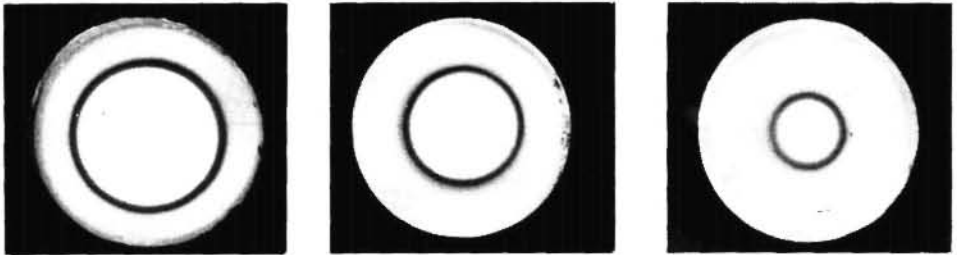


Figure 31. Photomicrographs of cross-sections of catalyst pellets prepared by sequential impregnation of alumina carrier with platonic acid and citric acid. Photo courtesy of A. Brunovská, Slovak Technical University, 1994.

Deposition-precipitation of catalytic material onto the surface within shaped catalyst particles can also lead to inhomogeneous distributions. The rates of the reactions responsible for deposition (generation of H^+ or OH^- ions, reactions with surface groups) can be varied so that the combined effects of reaction and diffusion determines the resulting concentration profiles. Thus, an egg shell-type distribution may be obtained as shown in Figure 34.

Transient pH gradients within a particle obtained after inhibition of a carrier with a liquid solution can be utilized to control the local rate of deposition of catalytic material by a pH-dependent precipitation reaction (De Jong, 1991). In this way also egg yolk-type distributions may be obtained.

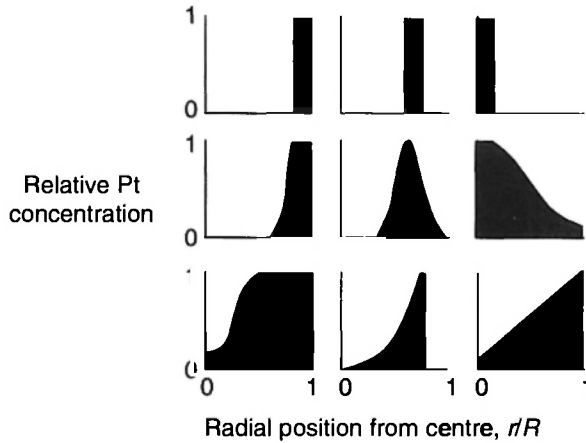


Figure 32. Types of Pt profiles in alumina particles obtained by co-impregnation. Upper row from left to right: sharp profiles corresponding to egg shell-, egg white- and egg yolk-type catalysts. Middle and bottom row: different profiles with more gradual variation of concentration. Adapted from Shyr and Ernst (1980).

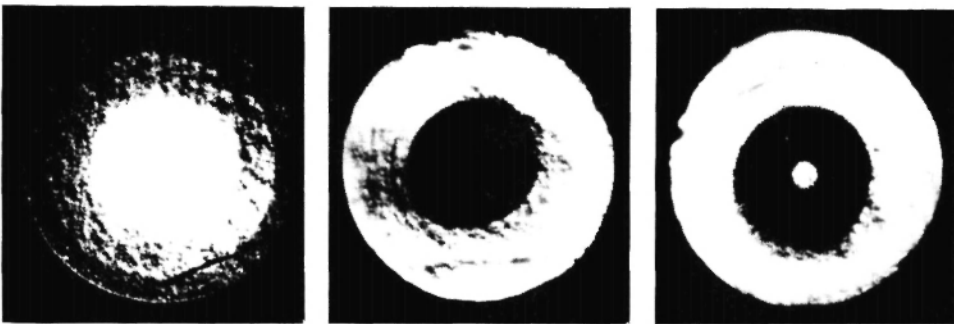


Figure 33. Photomicrographs of egg shell-, egg yolk- and egg white- type copper on magnesia-alumina catalysts. Courtesy of C.M.M. Mesters, Koninklijke/Shell-Laboratorium, Amsterdam, 1985.

Intraparticle heat effects

In the foregoing parts of this paper the effects of particle size, shape and distribution of active catalytic material have been discussed in relation to diffusion of molecules. These aspects of catalyst morphology can also be important in relation with heat transport inside the

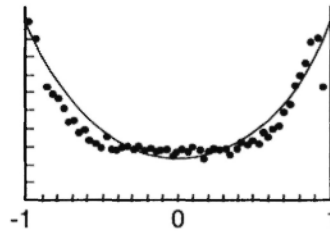


Figure 34. Egg shell-type metal distribution of Mn on silica obtained by deposition-precipitation. Profile determined experimentally from electron microprobe analysis with model based on Thiele modulus. After De Jong (1991).

catalyst particles when dealing with highly exothermic reactions.

When intraparticle heat transfer rate is low (poorly conducting catalyst carrier) and rate of heat generation is very high, instabilities can occur. Pore diffusion limitation of the reaction can in such a case be desirable since heat generation will be less intense and more located in the outer part of the particles, from which the heat can be removed more easily. In addition, the apparent activation energy will be lowered, which imply that the reaction rate will depends less strongly on temperature so that run-away is less likely to develop. Figure 35 indicates the region where instabilities may develop with strongly exothermic reactions.

Intraparticle heat transport can also have an effect on selectivity when the selectivity of the desired reaction is strongly dependent upon temperature and when significant amounts of heat are generated by the reaction itself or by accompanying reactions. A temperature

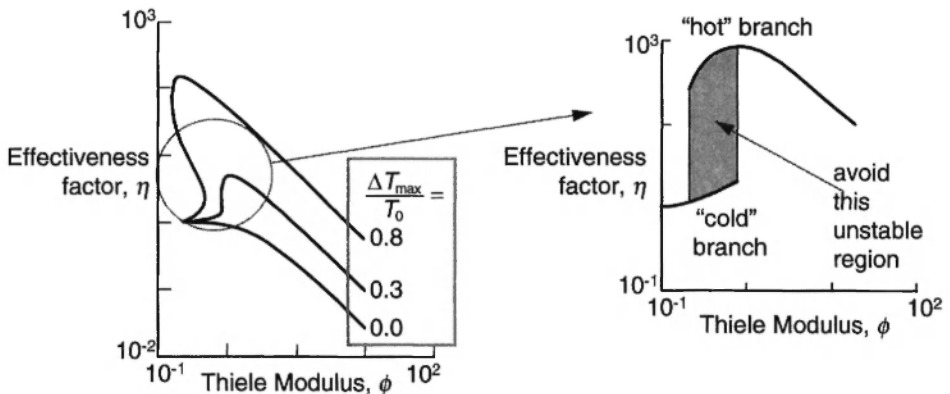


Figure 35. Intraparticle heat transfer effects as a factor in catalyst particle size selection.

profile over the catalyst particle with a peak at the interior as a result of reaction occurring in this region generating heat which has difficulty in being transferred towards the outside may give rise to deterioration of selectivity. In this case one could opt for shortening the path of intraparticle heat conduction by choosing small particles or shapes such as rings, miniliths, etc., depending upon allowable pressure drop. Another solution is to locate the catalytic active material at the outside of the particles. i.e., apply an egg shell-type catalyst.

The latter approach is illustrated in Figure 36 for the oxidation of ethene to ethene oxide; a strongly exothermic reaction which is accompanied by an even more exothermic unwanted reaction, viz., total combustion to carbon dioxide and water. The latter reaction, which lowers the selectivity to desired ethene oxide, has a higher activation energy than the desired one. Therefore intraparticle temperature gradients are detrimental to selectivity.

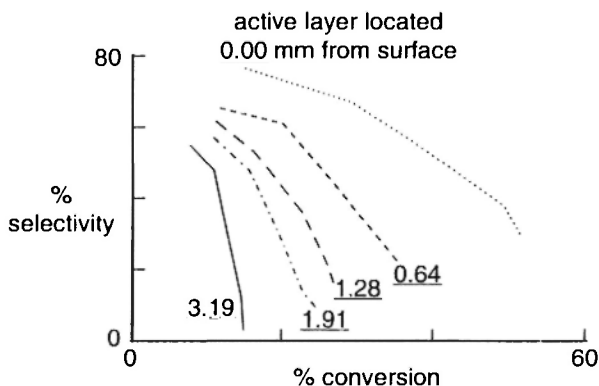


Figure 36. Selectivity to ethene oxide in partial oxidation of ethene as a function of the location of active active layer. Adapted from Gavrilidis and Varma (1992).

Mechanical transport properties of catalyst particles

Aside from intraparticle mass and heat transport effects as discussed above, the mechanical transport properties desired for a chosen reactor type are factors in catalyst particle design.

In fluidized-bed processes the maximum particle size is dictated by the requirement to operate above the minimum fluidization velocity. For typical velocities in many gas phase

processes this implies relatively small catalyst particles, i.e., diameters below a few tenths of a millimetre. For good fluidization behaviour in a bubbling fluidized bed catalyst particles in the form of microspheres with a certain size distribution, e.g., in the range between 30 and 150 μm , are preferred. Microspheroidal catalyst particles in this size range can be prepared by spray drying of a hydrogel or slurry containing the catalytic material. A typical size distribution of a fluid catalytic cracking catalyst produced in this way is shown in Figure 37.

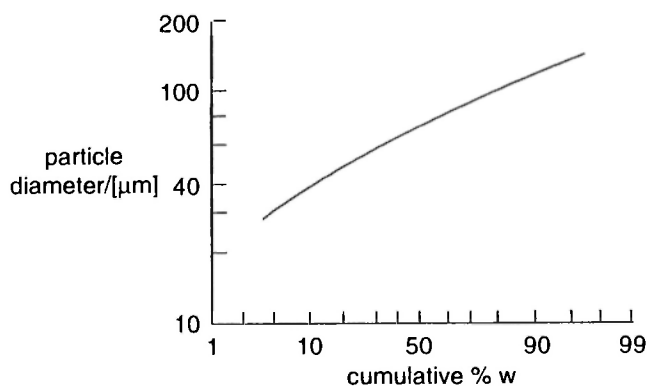


Figure 37. Typical size distribution of a commercial Fluid Catalytic Cracking catalyst.

Fluidized reactors are very often applied when there is a need to cycle catalyst particles between the reactor and a regenerator (in case of fast catalyst deactivation of the catalyst during the reaction) or a heater (in case heat has to be supplied). Rapid transport of catalyst between vessels imply subjecting the particles to strong attrition forces and the attrition resistance is therefore an important criterion. The microspheroidal form as already mentioned is a favourable shape to reduce mechanical attrition.

However, when the catalytic material is inherently weak, special means are required to bring attrition resistance to the required level for a practical process. A way in which this can be achieved is illustrated by the development of the catalyst for the recently commercialized fluid bed butane oxidation process of Du Pont to produce maleic anhydride. The vanadium phosphate (VPO) used as catalyst is too weak to withstand the forces associated with the cycling between the fluidized bed regenerator and the riser reactor where gas velocities up to 10 m/s prevail. Attrition resistance is imparted to the VPO catalyst by spray drying this material together with a polysilicic acid (PSA) hydrogel under conditions

which allow silica to migrate to the outer regions, thus encapsulating the active VPO catalyst into a porous silica shell whose pore openings allow reactant and product molecules to diffuse in and out the particle; see Figure 38.

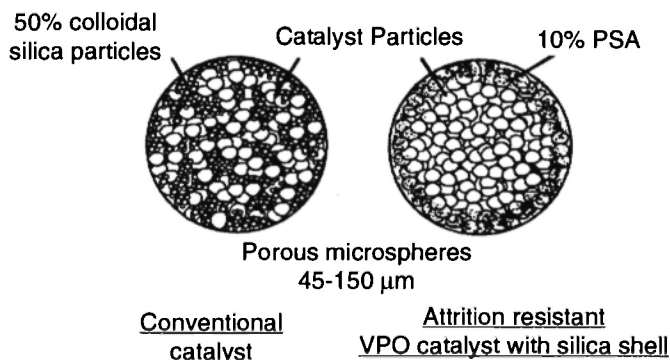


Figure 38. Attrition resistant VPO catalyst with silica shell as used in the Du Pont butane oxidation process. After Contractor et al. (1987).

In slurry processes the particle size is often determined by the desired catalyst concentration to obtain acceptable reaction rates on the one hand, and maximum allowable slurry viscosity on the other. At the same solids concentration, finer particles give rise to higher slurry viscosities. Other factors which have an impact on the choice of particle size are the settling velocity (one may either want to avoid settling at the velocities applied or to have rapid settling for slurry thickening), filterability of the slurry, or separation possibility by hydrocyclones, sieve bends, or other separating equipment.

Separation of solid catalysts from liquid by the separation methods mentioned above is difficult or impossible for very fine catalyst particles. Such catalyst particles, e.g., smaller than 1 micron may be desirable for reasons of catalyst effectiveness with fast reactions. Another advantage of such fine particles is that due to the fast reaction and their presence in or near the diffusion film they may enhance the gas/liquid mass transfer significantly. A possible way to use ultrafine particles in a slurry bubble column and yet avoid the solid/liquid separation problem is to make the particles magnetizable, so that they can be removed from the liquid with an electromagnetic separator, see Figure 39.

Another conceptual way of improving the separation possibilities between catalyst

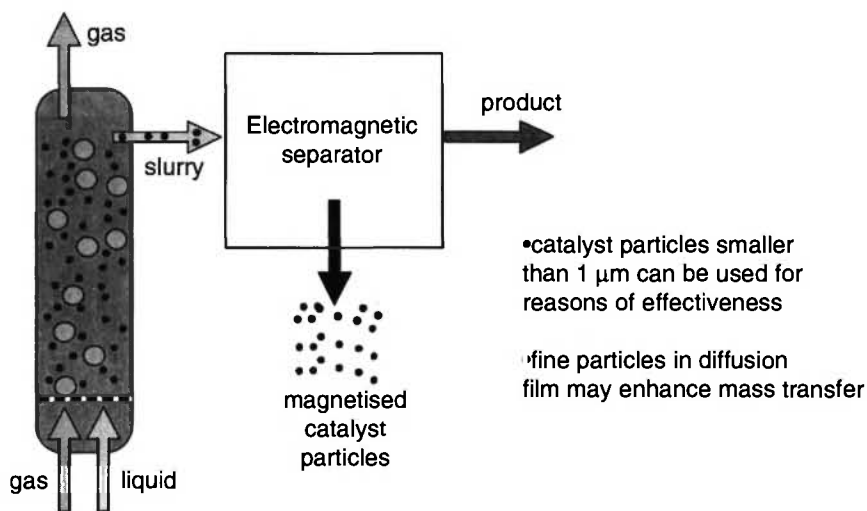


Figure 39. Conceptual reactor system using extremely fine particles for fast reactions.

and liquid is to encapsulate the catalyst by a porous shell rather similar to the butane oxidation catalyst discussed above; see Figure 40. This technique may even be applicable to homogeneous catalysts: if the metal organic complex synthesized from components small

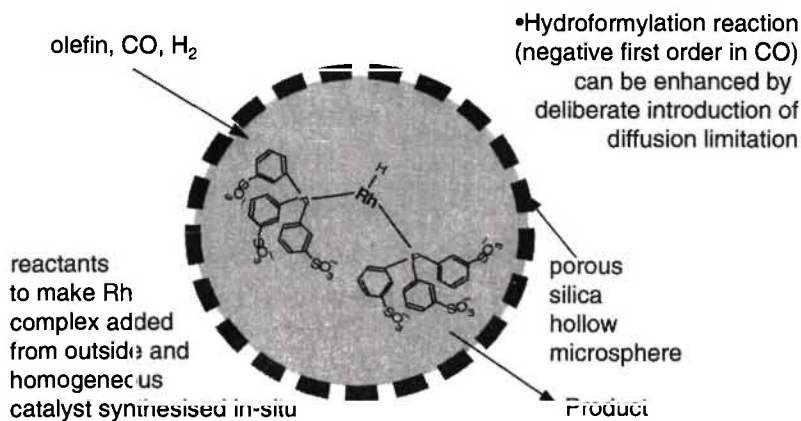


Figure 40. Concept of an encapsulated (homogeneous) catalyst. The homogeneous catalyst is encapsulated inside a porous hollow microsphere. The complex is synthesized in-situ and cannot diffuse out due to the small pore size say of the order of 1 nm. These spheres are dispersed inside the reactor. Deliberate introduction of diffusional limitation for CO to the ligand has potential beneficial effects.

enough to pass through the pores of the shell is too bulky to diffuse out of the shell, a situation is obtained akin to the well-known ship-in-bottle. In this concept, there is not only a diffusion barrier for the active catalyst, but there may also be a diffusion limitation for the reaction. In the case of a hydroformylation reaction which is of a negative order in CO such a diffusion barrier may be beneficial.

In moving-bed processes, smooth movement of the catalyst poses demands on flowability and additional requirements have to be met on attrition resistance and crush strength. Even flow is particularly important if a narrow residence time distribution of the particles is desired. The requirements are best met by spherical particles of a glassy material, which can be produced by a sol-gel technique: droplets of a sol or soft hydrogel are allowed to further gelate and harden while they sink in an oil bath. After drying and calcining, hard spheres of a xerogel are obtained, for instance alumina, silica-alumina or silica xerogel.

Uniformity of size may also be important for moving bed catalysts. Since the particles are free to move, undesired segregation may occur when particles appreciably differing in size are present (Note that the mass of a particle is proportional to the third power of its diameter). As a result of movement, smaller particles may tend to occupy the space left by the larger ones, thus decreasing the permeability of the packing. Figure 41 shows the narrow size distribution of silica spheres suitable as carrier for a moving bed catalyst (De Jongste, 1984).

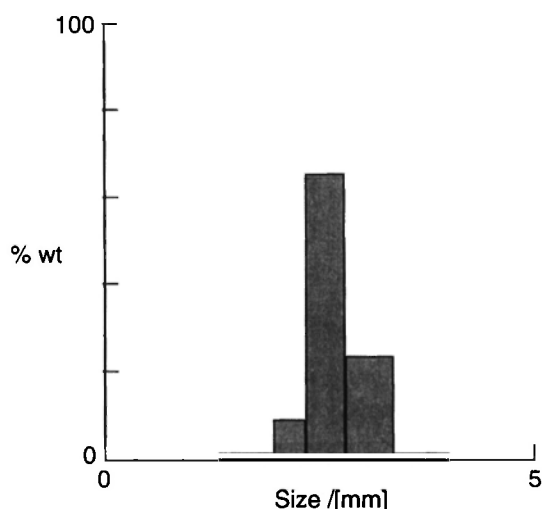


Figure 41. Particle size distribution of Shell silica spheres suitable for moving-bed applications. Adapted from De Jongste (1984).

Structured packings and monoliths

The design of catalyst particles with intraparticle diffusion and kinetics of the main, poisoning or other accompanying reactions as design factors is a departure from the classical view which considers a catalyst particle just as a mass of catalytic substance. In the above design, the catalyst particle is in fact treated as a tiny reactor, and the actual reactor is thus an assembly of such microscopic reactors.

The distinction between "catalyst particle" and "normal reactor" as visualized in Figure 1 becomes vague and may even disappear with less common reactor types featuring catalyst in the form of structured packings, monoliths or membranes. These types of reactor can be the preferred ones if special process requirements have to be met.

In the treatment of flue gases, e.g., in NO_x removal by selective reduction to N_2 with ammonia, monoliths are being applied because of their low pressure drop and tolerance to plugging by dust. These features are due to the presence of straight parallel channels through which gas flows in the laminar regime. Because the diameter of the channels is rather small, mass transfer by radial diffusion in the gas to the gas/solid interface can be sufficiently fast. These monoliths form the elements of a commercial reactor, which consists of a stacking of monolith blocks.

The features of low pressure drop and dust tolerance are also of importance in the application of monoliths in automotive exhaust catalysis. For this application, monoliths offer the additional advantages of minimal volume for the required catalytic conversion (which gives flexibility in mounting a catalytic exhaust converter in a car) and minimal mass. The latter is important since it minimizes the heating up time and thus the extra emissions during the cold start period when the temperature is still too low for the catalyst to be active.

Figure 42 shows a picture of a monolith as now widely used for cars with emission control. Figure 43 presents a drawing of a so-called three-way catalytic converter, which is now generally applied to effectively reduce exhaust emission of gasoline powered cars.

The monolith-type catalyst as used in an automotive exhaust converter is an example of a sophisticated piece of catalyst design. The monolith structure is made of a non-catalytic, thermally resistant ceramic material such as cordierite, and the surface of the channels in this structure are covered by a catalytic layer. This layer, the so-called wash coat, consists of

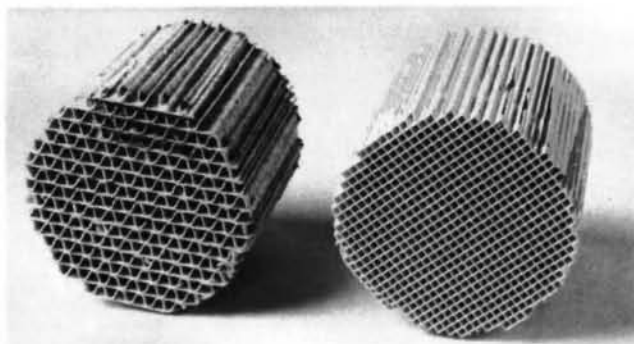


Figure 42. Picture of monolith as used for car emission control.

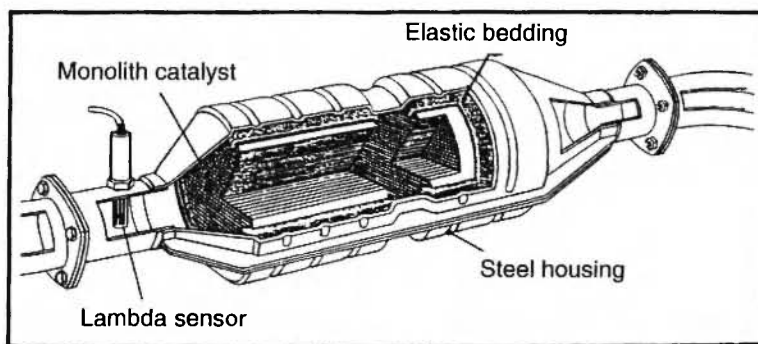


Figure 43. Drawing of a three-way catalytic converter for control of emission of gasoline powered cars.

porous alumina which supports highly dispersed metals such as platinum and rhodium. This catalyst architecture is schematically shown in Figure 44. It can be seen that this architecture encompasses all levels of design shown in Figure 1. Indeed, in the automotive exhaust converter the distinction between "catalyst particle" and "reactor" has vanished.

Concluding remarks

The possibility to affect catalyst performance by tailoring the size and shape of catalyst particles, their porous texture, and the distribution of active material within them is a feature which distinguishes heterogeneous from homogeneous catalysis. Although this

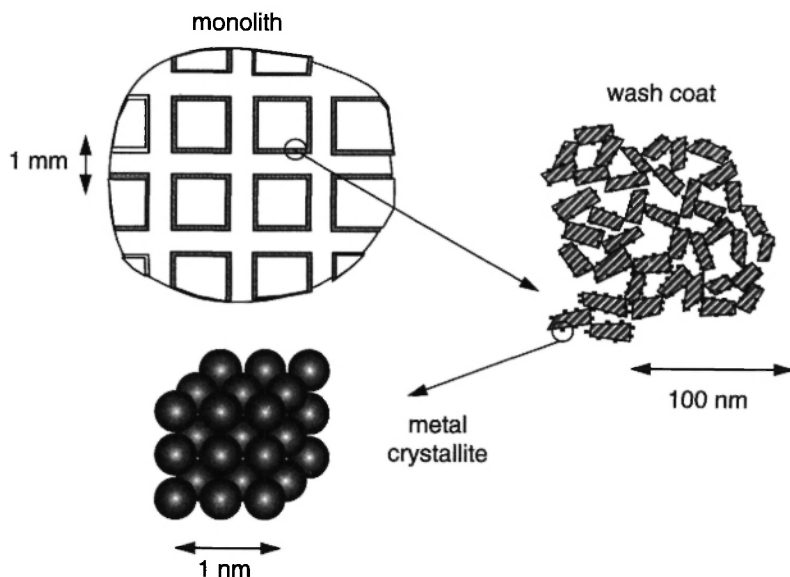


Figure 44. Schematic drawing of the architecture of a monolith exhaust catalyst.

possibility has perhaps not always been sufficiently recognized and exploited, one can discern a clear trend of increasing sophistication in catalyst design in time. Compared with classical catalytic processes, where catalysts were often used in the form of granules from broken filtercake or pressed tablets of relatively large size with no or hardly any control over porous texture or activity distributions, current heterogeneous catalysts are much more adapted to the specific processes, giving regard not only to specific hydrodynamic and mechanical requirements of the selected reactor configuration but also to the kinetic and mass transport characteristics of the reactions involved.

Rather than viewing a heterogeneous catalyst particle as a form of catalytic substance (still a rather common view in catalysis) one should regard the particle as a microscopic reactor for which the principles of reactor engineering are applicable. Fortunately, there is a trend towards increased attention for catalyst morphology design as is exemplified by the advent of extrudates of special, non-cylindrical cross sections, catalysts with tailored porous texture and with specific activity distributions.

An example of a modern sophisticated design of a catalyst "particle" is the monolith-type catalyst as used in flue gas treatment (NO_x removal by selective catalytic reduction) and

in automotive exhaust treatment. In these cases the distinction between catalyst "particle" and "reactor" has even vanished. The latter examples of sophisticated catalyst morphology may perhaps be looked upon as trend setters for future heterogeneous catalytic processes in which hydrodynamics, kinetics, and diffusion are elements in an integrated design of catalytic systems which involves catalytic site engineering, catalyst particle engineering, and reactor engineering.

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