Alternative Reaction Engineering Concepts in Partial Oxidations on Oxidic Catalysts

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Alternative Reaction Engineering Concepts in Partial Oxidations on Oxidic Catalysts

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The production of organic oxygenates by partial oxidation on oxidic catalysts is of considerable industrial importance. Excellent selectivities and yields are often obtained in multitubular reactors due to high performance catalysts. However, there are several processes, e.g., the production of maleic anhydride and phthalic anhydride, where the product yield could be enhanced and improvements are desirable. Various reaction engineering concepts are proposed for that purpose, from reactor structuring to electrochemical promotion. In this article, the actual state of these efforts, which are often at the very beginning, is reviewed.

Keywords   Selective oxidation, Reactor structuring, Fluidized bed, Membrane reactor, Electrochemical promotion

1.   INTRODUCTION

The partial oxidation of hydrocarbons to oxygenates is of high economic importance. It is claimed that selective heterogeneous oxidation catalysis produces about 25% of the most important industrial intermediates (1) and that such processes comprise approximately one quarter of the value produced by all catalytic processes worldwide (2).

In general, transition metal oxides are used as catalysts. Intensive investigations of those systems and advanced catalyst development have made tremendous progress over the years. This is exemplified schematically in Fig. 1 for the case of the partial oxidation of propene to acrolein. The selectivity
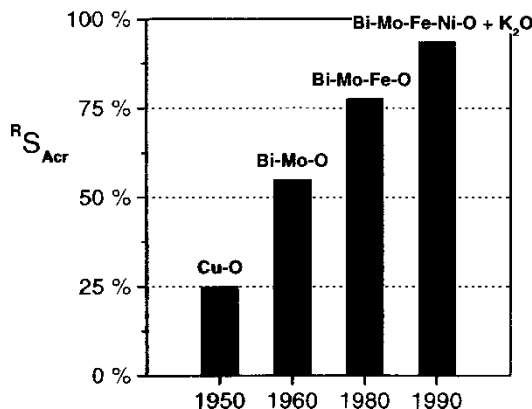
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Figure 1: Evolution of the catalyst for the partial oxidation of propene to acrolein ($^{R}S_{Acr}$: Reactor selectivity to acrolein).

to the desired intermediate is increased by the use of increasingly complex catalyst systems.

Selective catalytic oxidations are of equally high theoretical interest and much effort has been applied to determine why and how advanced catalysts work selectively. Based on experimental investigations and theoretical considerations, detailed mechanisms have been proposed, leading to guidelines for further development. Those aspects have been treated widely in reviews (3), conference proceedings (4), and books (5), cited as examples among others.

However, it is not the catalyst alone that determines the efficiency of a process. Reactor configuration and operation play an equally important role. In most cases, the reaction is performed with fixed beds of catalyst in multitubular reactors cooled by molten salt. Due to the high exothermicity of partial oxidations, the efficiency of the heat transfer leads to operational constraints. Even so, very high selectivities and yields can be achieved in some cases, for example in the formation of acrylic acid as reported in the patent (6), as well as in the open literature (7). Under such circumstances, there seems to be no need to alter the proven process.

Alternative reactor concepts are, therefore, proposed and tested in cases, where selectivities and yields are more modest, such as the partial oxidation of n-butane to maleic anhydride (8) or of o-xylene to phthalic anhydride (9).

In addition, one should not forget the environmental impact of improvement. Every small increase in selectivity is beneficial to the environment (10) because resources are saved and green house gas emissions, namely CO_x, are reduced.

In the following survey, mechanistic details and the physico-chemical function of the catalyst are not the main subject but rather the question is discussed if alternative reactor concepts are imaginable and realizable. It is

focused on the partial oxidation of hydrocarbons and of related oxygenates on oxidic catalysts. However, the reported concepts may be applied, mutatis mutandis, to other reactions, as well. Due to the multitude of ideas expressed especially in academia, the selection can by no means be comprehensive. As mentioned in another recent article on the subject (11), the selection is rather influenced by the interests and experience of the authors.

2. KINETIC CONSIDERATIONS

The influence of reactor configuration and operation can not be quantified and simulated without knowledge of the reaction network and its kinetic coefficients. In the case of partial oxidation, a desired intermediate is formed among other stoichiometrically independent products generated from a reactant, e.g., the hydrocarbon. Therefore, selectivity is an essential parameter. The relationship between experimental data, the network of individual reactions, and derived quantities like conversion, selectivity to, and stability of the desired intermediate has been discussed in detail by Riekert (12). In order to achieve this, the simplest network, a triangular scheme of three irreversible reactions [Eq. (1)], has been considered:

$$\begin{array}{ccc} & B & \\ {}^{1}\nearrow & & \searrow{}^{2} \\ A & \xrightarrow[\ \ 3\ \ ]{} & C \end{array} \qquad (1)$$

This scheme is valid, for example, in the description of the partial oxidation of methanol to formaldehyde (12, 13) and of acrolein to acrylic acid (7, 14). In (12), it has been shown how the product selectivities depend on the different control volumes to be considered—reactor, catalyst grain, surface element of the active compound. Therefore, one has to differentiate between reactor selectivity, catalyst or grain selectivity, and intrinsic selectivity of the active compound.

In the reactor, the selective formation of B is a function of the conversion of the reactant A. The reactor selectivity, $^{R}S_{B}$, is obtained with a mass balance around the open system in steady state. Its variation with the conversion, X_{A}, is shown schematically in Fig. 2a together with the yield, Y_{B}. Starting from a value of 0.8, arbitrarily chosen in the figure, it decreases monotonically and reaches 0 at complete conversion of A. The starting value at $X_{A} = 0$ represents the upper limit obtainable in the reactor, the so-called grain selectivity $^{K}S_{B}$. It is given by Eq. (2):

$$^{K}S_{B} = \lim_{X_{A} \to 0} {}^{R}S_{B} \qquad (2)$$

where, $^{K}S_{B}$ is a characteristic parameter of the catalyst grain and does not depend on reactor configuration and flow pattern. For a given reactor, the shape of the curvature $^{R}S_{B}$ vs X_{A} is a function of the stability of the

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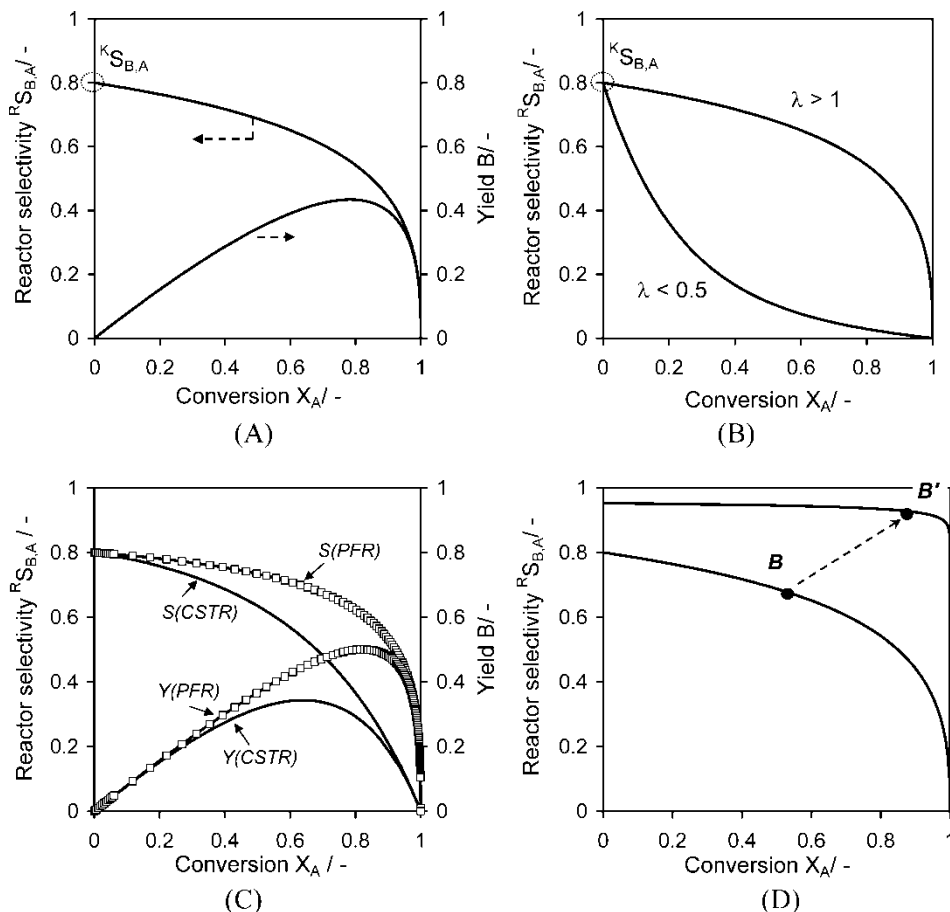
Figure 2: Theoretical considerations about the selectivity and yield of an intermediate product B as function of the conversion of a reactant A for a triangular reaction network: (A) plug flow reactor, grain selectivity $^{K}S_{B,A} = 0.8$, stability $\lambda = 2$; (B) influence of the stability λ; (C) influence of the reactor operation ($^{K}S_{B,A} = 0.8$, $\lambda = 2$): CSTR versus PFR; and, (D) improvement via catalyst developement and reaction engineering concepts.

intermediate, which can be shown schematically in Fig. 2b starting at the same value of the grain selectivity.

The stability of the intermediate B can also be quantified by a dimensionless parameter, λ. It is shown in (12) how the quantities $^{K}S_{B}$ and λ can be derived from the kinetic coefficients k_i in the case of three individual reactions of 1st order with respect to the reactants A and B. Under such conditions, the stability of B is given by $\lambda = k_1/k_2$, which is simply the ratio of the kinetic coefficients of its formation and further reaction. The approach is illustrated by a case study, namely the partial oxidation of methanol (12, 13).

In addition, it has to be pointed out that the residence time distribution in the reactor affects reactor selectivity and yield at given values of grain selectivity and stability. This is shown in Fig. 2c, where both quantities are shown in the case of a plug flow reactor (PFR) and a gradientless system (CSTR), starting at a grain selectivity of 0.8. It is clearly seen that back-mixing has a negative effect on the yield obtainable under otherwise identical conditions, where $\lambda = 2$.

Thus, it is the joined effort of catalyst development and reaction engineering to improve the selective formation of an intermediate, as shown schematically in Fig. 2d.

Mechanistic interpretations are often used as a guideline in chemical reaction engineering concepts. In this context, it is important to note that it is commonly agreed that the kinetics of partial oxidations on oxidic catalysts follow a redox mechanism. The organic reactant is partially oxidized by lattice oxygen and the reduced catalyst is reoxidized by oxygen from the gas phase. This mechanism, first proposed by Wagner und Hauffe (15), is generally named after Mars and van Krevelen (16). The direct interaction of the organic compound with oxygen weakly adsorbed from the gas phase is thought to be detrimental, leading to deep oxidation and formation of CO_x.

3. REACTION ENGINEERING: ALTERNATIVE CONCEPTS

It is the objective of the alternatives tested to further increase the yield or space time yield by reaction engineering using catalysts, which show already a high performance. The different concepts start from the knowledge of the reaction network or are simply based on the hypothesis of the Mars-van Krevelen mechanism.

A first approach intends to act upon the relative rates of distinct reaction paths by carefully adjusting different catalysts and/or by adjusting different temperature zones. This approach also contains special geometric arrangements of the catalyst (e.g., specially shaped catalyst bodies, monolithic structures, and micro-structured reactors) to intensify mass and heat transfer processes. These concepts may be called structuring.

Another way is the use of the catalyst as a mobile phase. This leads to an improvement of the isothermicity or the enlargement of the domain of safe reactor operation by the increase of transport coefficients. It equally enables the more global approach of separating oxidation and reduction of the catalyst, the two steps of the Mars-van Krevelen mechanism.

A third approach tries to act upon the rate of single steps in the net by modifying the local concentration of the reactants through distributed feeding. This concept stands for the efforts on membrane reactors.

Finally, the nature of the oxidizing species may be altered by use of electrochemical transport of oxygen towards the catalyst.

Until now, most of the preliminary works have merely shown the principle feasibility of the concepts. Their success and real perspectives should be evaluated by comparison with the results from classical fixed bed reactors.

3.1 Structuring

Composition and possibly temperature ("hot spot") change along the length of a fixed bed. Consequently, the rates of the individual reactions of the network are not constant, and their relative importance with respect to selectivity and yield vary locally. Therefore, it is not possible to operate a process with optimum efficiency with just one catalyst at a given temperature. Often a two or more step process is preferred to increase the yield of the desired product. This is illustrated by the synthesis of acrylic acid by partial oxidation of propene, realized in two steps with two different catalysts at two different temperatures. Figure 3 (17) represents the variation of the dimensionless concentrations of the different carbon containing species involved under typical industrial conditions (T = 380°C 1 stage 1, T = 280°C stage 2). It is clearly seen that catalyst and temperature are adapted in each step to realize the selective formation of the desired product.

Even in a one step process, an increase of the yield in the fixed bed is possible if the catalyst characteristics and the local distribution of other parameters (composition and temperature) are mutually adjusted. Roughly speaking, a
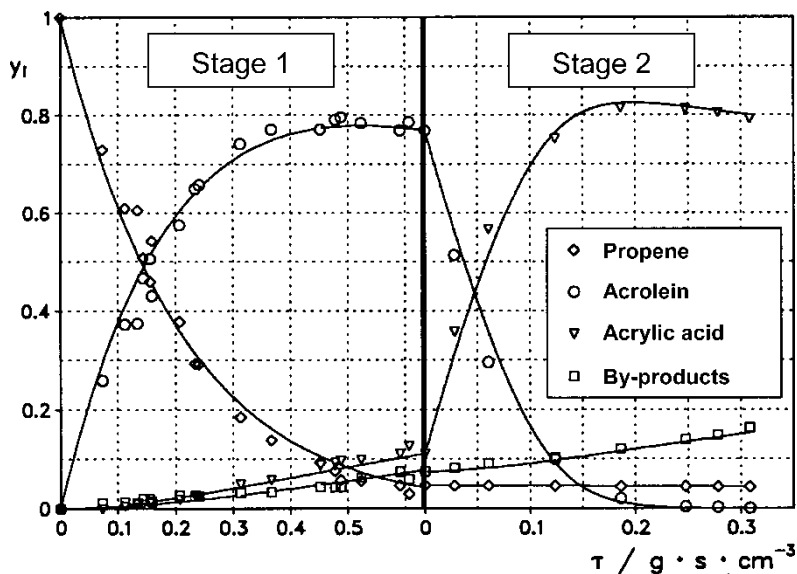

Figure 3: Kinetics of the two step synthesis of acrylic acid adapted from (17): stage 1: inlet molar fraction $x_{0,\,propene} = 0.05$, $x_{0,\,oxygen} = 0.11$, rest: Nitrogen, T = 380°C, stage 2: T = 280°C (y_i: dimensionless concentration of component i ($=x_i/x_{0,\,propene}$), τ: modified residence time).

highly selective transformation of the reactant is needed at the reactor inlet whereas a high stability of the partially oxidized product has to prevail near the exit. The exact solution depends on the complexity of the network.

The partial oxidation of i-butene may be chosen as a typical example. Based on the network shown on Fig. 4a, the positive effect of a temperature structuring in two zones (420 and 380°C) can be predicted. This is also represented in Fig. 5 by the full lines. It was confirmed a posteriori by experiments (points) and leads to an increase of 5% in the combined yield of methacrolein and methacrylic acid in comparison to an isothermal operation at 420°C. Using 2 catalysts and 3 temperature zones, an additional 4% could be added to obtain a maximum value of 76% (18). In this context, the structured bed may be considered as the reduction of a multiple step process to one.

In the case of phthalic anhydride formation, the reaction network is more complicated and is shown in its simplified form in Fig. 4b (9). Once more, the influence of different reactions on reactor selectivity depends on the local composition of the gas phase. For example, it is necessary to avoid reaction $1 \rightarrow 4$ near the inlet, where the concentration of o-xylene is high, whereas reaction $3 \rightarrow 4$ is not of much concern as almost no phthalic anhydride is present. The opposite must be true towards the exit. This can be achieved through the use of different catalysts. The search for an optimal catalyst sequence was based on the strategy of biological evolution resulting in layers containing two to four different catalysts. Typical results, summarized from (9), are shown in Table 1. The analysis
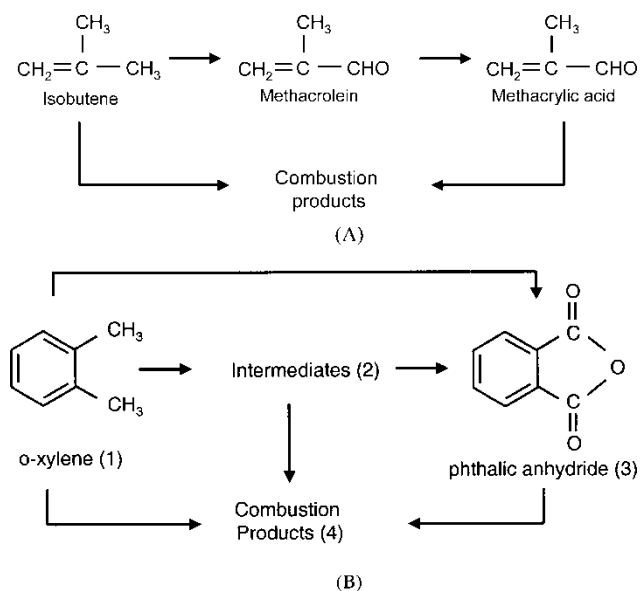

Figure 4: Reaction network of the partial oxidation of (A) isobutene to methacrylic acid (18) and (B) o-xylene to phthalic anhydride adapted from (9).
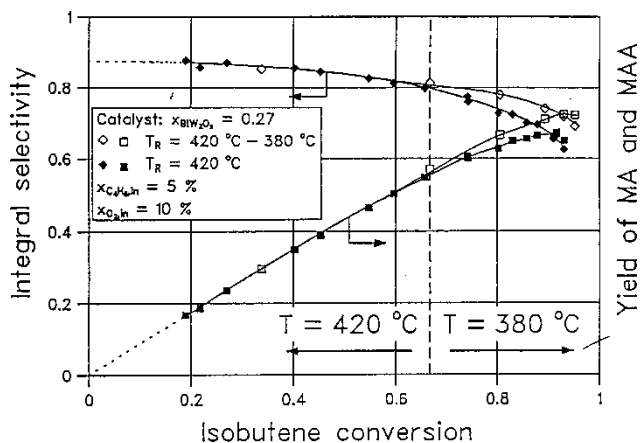
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Figure 5: Selectivity and yield of methacrolein and methacrylic acid in an ideal fixed bed reactor (PFR) with different temperature zones adapted from (18).

demonstrates that in the most frequent case of three different zones the 1st catalyst led to high formation of phthalic anhydride, the function of the 2nd catalyst was the production of the different precursors (intermediates) of phthalic anhydride from o-xylene, and that at the 3rd catalyst the remaining precursors are transformed to phthalic anhydride, while simultaneously avoiding the deep oxidation of the latter (19).

The computed maximum yields were verified experimentally. Two different concepts were considered: an isothermally operated fixed bed composed of three different catalysts (cf. Table 1), and a fixed bed of three catalysts operated at three different temperature zones. In the latter case, a decreasing sequence of temperatures from inlet to exit gives the best result. As in the practical case, the "hot spot" is located near the reactor entrance; this result indicates the possibility to make profit out of an unavoidable fact.

Table 1: Optimisation of a fixed bed reactor for the phthalic anhydride production structured with catalysts of different activities operating at different temperatures (SFBR: structured fixed bed reactor, PAA: phthalic anhydride) (9).

Catalyst set	1	2	3
Number of catalysts			
Available	9	9	9
Selected	2	4	3
Temperature/K	683	643	663
Attainable maximum yield of PAA			
With 1 cat	0.643	0.692	0.780
SFBR, cal	0.709	0.724	0.794
SFBR, exp	—	0.73	0.79

The literature survey of Li (19) contains much more theoretical studies than experimental investigations. Among the latter, the patent literature prevails. This situation has not changed within the years in the domain of partial oxidations. Thus, if we take the partial oxidation of propane to acrylic acid as an example, we find two recent mentions of a structured catalyst bed (20, 21) among various patents concerned with both catalyst and temperature structuring (22–25), or the use of a co-catalyst (26). The list is far from being exhaustive.

Regardless, it has been shown both theoretically and experimentally that structuring improves the efficiency of the process in different partial oxidations. It is difficult to know if and to what extent structured fixed bed reactors are used in industrial practice in partial oxidations of hydrocarbons.

In phthalic anhydride synthesis, the reactor tubes contain two layers of catalyst with different activity (27). The catalyst at reactor inlet exhibits lower activity to reduce the temperature and avoid excessive hot spots. The higher activity of the second layer ensures conversions near 100%. It has been examined in a study of Papageorgiou and Froment (28) how further structuring could improve the performance of the reactor using the same catalyst. Figure 6 represents the different configurations considered: the multitubular reactor (MTR); the three bed multitubular reactor (TBMTR); and a multitubular adiabatic reactor (MBAR). A kinetic model and adjusted parameters, determined by Papageorgiou, Abello, and Froment (29), were used in the simulation. It is shown that at a conversion of o-xylene of 99% an increase in selectivity to phthalic anhydride of 4.6% in the TBMTR and 3.9% in the MBAR is obtained as compared to the MTR.

In the patents of different companies, even a higher level of structuring is suggested. For example in (30, 31), multiple layers of different catalysts of eggshell type are proposed. They are arranged in distinct sequences and lengths. The catalysts in each layer differ in the chemical composition (30), in the BET surface area (30, 31) and in the content of the catalytic material on the inert carrier resulting in a different shell thickness (31). Phthalic anhydride yields of more than 80% can be achieved. Besides an improved reduction of the temperature gradients in the catalyst bed, the formation of intermediate products, like phthalide, which is detrimental even in traces for the phthalic anhydride quality, can be efficiently diminished.

Other ordering principles may equally be considered as structuring and are briefly discussed in the following. In order to avoid heat transfer limitations in fixed beds and to achieve isothermal operation of highly exothermal reactions, the so-called catalytic wall reactor has been proposed for kinetic measurements. In partial oxidations it had been used first by Chandrasekharan and Calderbank in 1980 (32) in the oxidation of o-xylene on vanadia-titania. In the case of the oxidation of propene to acrolein, a very detailed kinetic study has been published recently by Redlingshöfer et al. (33). The investigation includes data on important side reactions, particularly where the rate
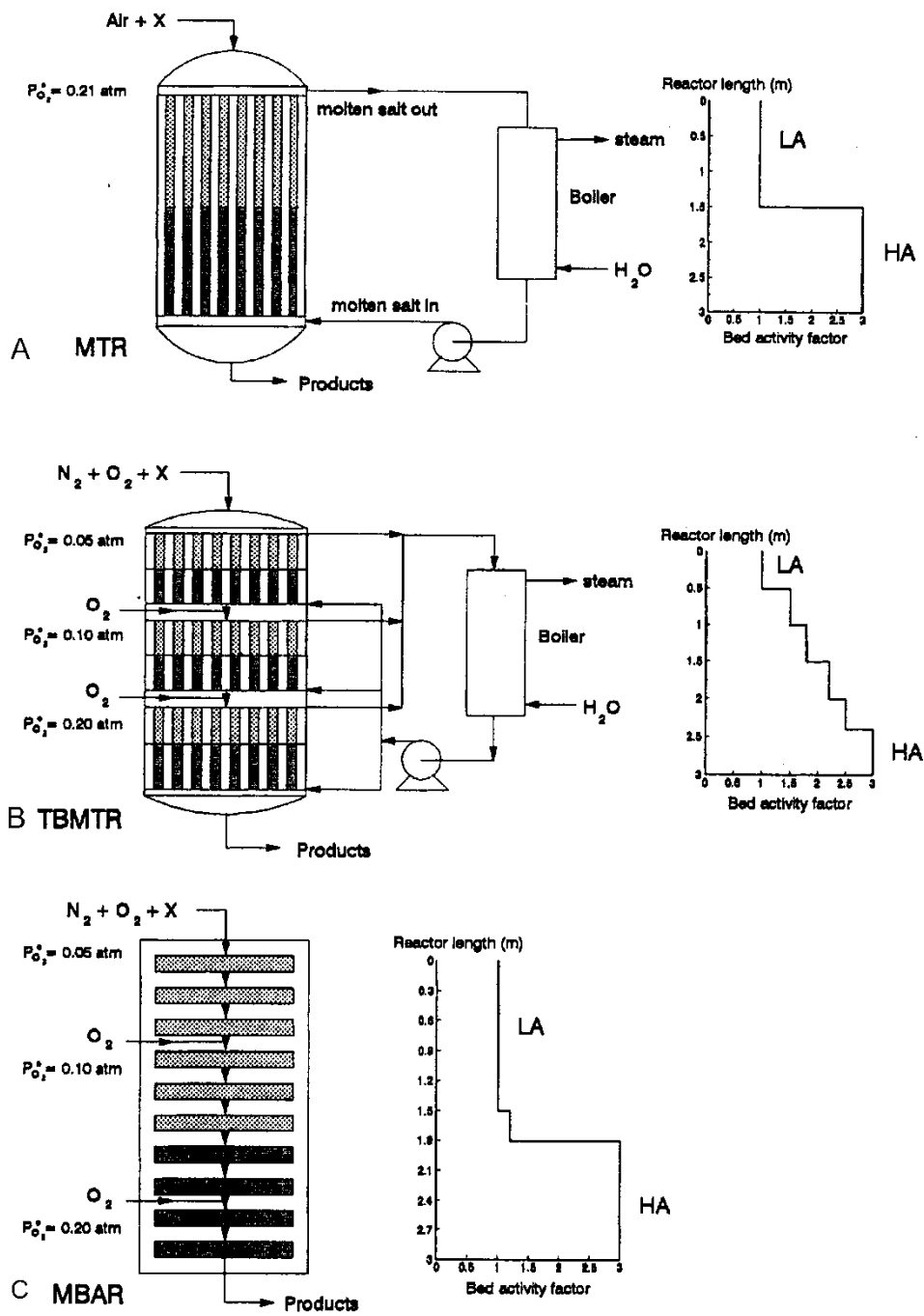
Figure 6: Different concepts of fixed bed reactors for phthalic anhydride production: (A) multitubular reactor (MTR); (B) three bed multitubular reactor (TBMTR); and (C) multibed adiabatic reactor (MBAR). (HA: High activity catalyst, LA: Low activity catalyst) adapted from (28).

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determining steps are altered in different temperature domains. The absence of a hot spot in the wall reactor is experimentally demonstrated in the n-butane oxidation in contrast to the classical fixed bed (34). The catalytic wall reactor showed a 50% higher selectivity to the partially oxidized product at the same conversion.

In the investigations cited so far, the inside tube wall was coated with the catalyst. A recent model study (35) proposed the concept of multitubular reactors, where the catalyst is deposited on the external surface of the reactor tubes, the heat being removed by a coolant flowing inside. The study claims several advantages of this arrangement but admits that experimental verification is still lacking.

Many microreactors or micro-structured reactors may also be considered catalytically active wall reactors. They consist of miniaturized systems, the characteristic dimensions of their internal structures, e.g., the channel diameter, lying in the domain between 1 mm and 1 μm. Microreactors combine high surface to volume ratios with considerable increase of transport intensities, like the heat transfer to the walls. They are inherently safe since radical chain reactions are quenched at the wall and heat explosions are also unlikely.

A detailed review on the application of micro-structured reactors for heterogeneously catalysed gas phase reactions is given by Kolb and Hessel (36). Up to now, only few partial oxidations have been studied in such devices. They have model character but results comparable to industrial performance in classical fixed beds have not been obtained so far. However, efforts are made to evaluate the economic feasibility of a process containing micro-structured reactors and the possibility of scale-up of laboratory results (37).

A last point to be mentioned are special geometric structures of the catalyst itself. These structures may concern both the packing of catalyst bodies with particular shapes (e.g., hollow cylinders, rings), and the structured catalyst carriers (e.g., honeycombs, sponges, packings). In both cases, a reduction of the pressure drop in the reactor and an intensification of the radial heat transfer are current goals. Specially shaped, oxidic catalyst bodies are often used in industrial fixed bed reactors for partial oxidations [e.g. (27, 30, 38)]. The application of honeycomb monoliths is currently limited to catalytic exhaust gas cleaning, although some applications for the chemical industry, even for partial oxidations, were also evaluated (39, 40). However, an intensification of the heat transfer is only possible if honeycombs made of material with high heat conductivity (e.g., Al, Cu, SiC) are available, since a radial gas dispersion is not possible in these kind of monoliths. Sponge monoliths (commonly called "foams"), made of ceramics or metal, might be more promising, because their three dimensional structure with high porosities (75–95%) and high surface areas related to the bed volume (up to 20,000 m^{-1}) can combine properties of packed beds and honeycombs in a beneficial way

(41, 42). Simulations for industrial reactors used in the partial oxidation of o-xylene to phthalic anhydride have been published recently (43). Therein, it was shown that reactors packed with sponge monoliths provide lower pressure drops and significant lower axial and radial temperature gradients as compared to reactors packed with catalyst bodies. The results of several case studies demonstrate that more severe operational conditions, e.g., higher wall temperatures, higher flow rates, higher catalyst loadings, can be applied. Under these conditions space time yields of phthalic anhydride are more than twice as high compared to conventional reactors. In addition, tubes with higher diameters could be installed in industrial multitubular reactor. Experimental investigations must show if these expectations can be met.

In general, the distribution of the active material in a catalyst pellet could also affect activity and selectivity. This depends now on the interplay between the internal mass and heat transfer processes and the reaction rates. Morbidelli et al. (44) have theoretically investigated several cases by simulations and developed a strategy to optimize the distribution of the active material in a catalyst pellet dependent on the rate of reaction and of the transport processes. Their findings are supported by the results of experimental studies for different reactions which they comprehensively reviewed (44). In the case of partial oxidations on oxidic catalysts, only one important application is found in the open literature and patents. Therein, the active catalytic material is coated on inert shaped bodies ("egg-shell") (7, 9, 17, 19, 21, 27, 29– 31, 44, 45). This configuration suppresses overheating of the catalyst pellet, selectivity loss through undesired side reactions in the catalyst, and deactivation of the active material.

3.2   Fluidized Beds and Instationary Operation

Heat transfer is much more efficient and the constraints of explosion limits are less critical in fluidised beds than in fixed beds. Due to this, attempts have been made to use fluidised bed reactors in partial oxidations in order to reduce the temperature of hot spots. Thus, fluidised bed reactors figure on the list of modern processes for producing maleic anhydride from n-butane (46). It is reported that the so-called ALMA process (47) is currently the most technically advanced process (48) using this concept.

Besides special requirements on the catalyst like resistance to abrasion, fluidised beds have the disadvantage that selectivity can be lowered due to back-mixing of the porous catalyst, where the reaction takes place, even if plug flow is prevailing in the gas phase. This effect could be similar to that shown schematically in Fig. 2c. In addition, the formation of gas bubbles leads to by-pass effects that reduce the conversion of the reactant. In the process of scaling up, back-mixing is further modified and the bubble velocities

are increased. Therefore, selectivities and conversions obtained are of the same order of magnitude in both fluidised and fixed beds and the mean value of the yield in both reactor types lies around 55% relative to n-butane. However, lower investment costs and increased productivity, due to higher butane concentrations and enlarged dimensions may give economic advantages to fluidised beds.

Higher productivity can be obtained with higher reactant concentrations, limited in fixed bed reactors to 1.8 Vol.% butane due to safety concerns. Thus, reactor technology is moving towards increasing butane partial pressures in order to increase productivity. However, to minimize hazards the oxygen content has to be reduced, leading to more by-products (49). The approach is then limited due to separation problems despite higher production rates.

Back-mixing of the solid in the fluidised bed is used by Rubio et al. (50) to provide separate zones for catalyst oxidation and for butane reaction/catalyst reduction. The recirculating solid catalyst is charged with oxygen near the entrance of the fluidised bed reactor. In the upper part of the bed the catalyst comes into contact with butane, which reacts with the "stored" lattice oxygen. This concept allows for higher butane concentrations outside the explosion limits of the industrially operated fixed bed reactor. The efficiency of the device is higher than a fluidised bed with co-feeding of reactants. The performance of the two-zone fluidised bed reactor has been compared with other reactors under conditions of higher butane concentrations. Better yields to maleic anhydride than those reported in the literature for fixed bed reactors with co-feeding of reactants or membrane reactors have been obtained. However, in the upper part of the device the oxygen concentration should not fall short of a minimum value. A too strong reduction of the catalyst decreases the selectivity to maleic anhydride dramatically; this fact is certainly due to the different time constants of catalyst reduction and oxidation. The reoxidation is considerably slower than the reduction of the solid (51, 52).

Obviously, a system that keeps the oxidation and reduction zones separated could be advantageous. This is, at least partially, realized in the so-called "interconnected fluidised bed reactor" (53), which had been explored in the oxidative dehydrogenation of butane. The results have been encouraging and it is claimed that the existence of an easily controlled flow of solids between different zones is suitable for large-scale applications.

A step further in avoiding the disadvantages of catalyst back-mixing, is the use of circulating fluidised beds. The main idea behind this choice is based on the complete separation of catalyst reduction and oxidation, the two steps of the Mars-van Krevelen mechanism (16), which is generally accepted even if there are still some doubts concerning its validity in the oxidation of n-butane (54). Therefore, 2 distinct reactors with characteristic residence times are used in order to take into account the different time constants of reduction and reoxidation of the catalyst mentioned above. The reduction

takes place in a riser reactor with short residence times to avoid overreduction and the reoxidation proceeds in a fluidised bed regenerator (Fig. 7). An alternative to the riser-regenerator-system is the downer-regenerator-device, as the downer reactor has the advantage of a narrower residence time distribution. The different aspects of both systems have been intensively studied by laboratory experiments as well as by computer simulation in the group in Erlangen [e.g., (55, 56)]. Circulating fluidised beds had already been realized industrially in a series of processes. Their use has been proposed as a potential heterogeneous catalytic application, as well (57).

The most advanced project has been Dupont's CFB technology for maleic anhydride (8), a process included in a production unit of tetrahydrofuran. Its riser-regenerator system is represented schematically on Fig. 7. The advances of this process have been reported over the years (58, 59), leading to the use of a demonstration plant with a 27 m tall riser zone. The residence time in this riser is up to 10 seconds, which is small compared to the residence time of several minutes in the regenerator. The first commercial plant based on this technology started up in late 1996 in Asturias, Spain. In the last publication on this subject (8), it was hopefully expected "that the design rates
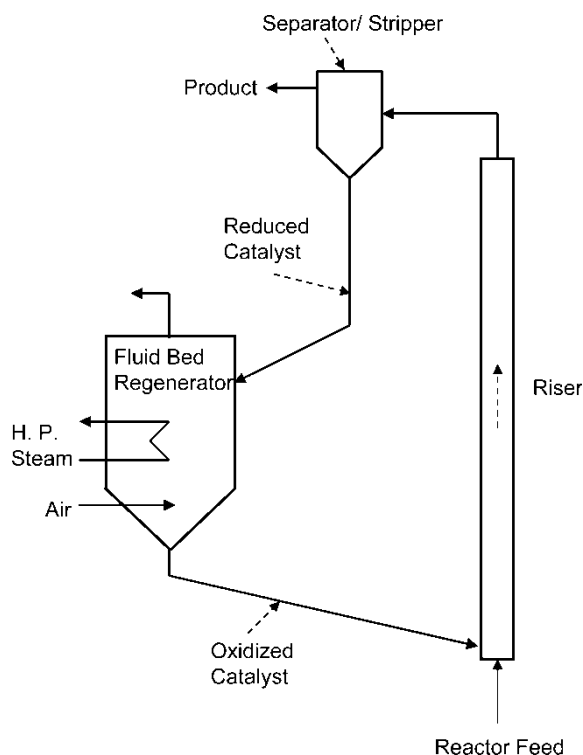

Figure 7: Circulating fluidised bed reactor for butane oxidation adapted from (8).

projected could be achieved in a three years true frame." At the same time, it had been reported (60) that the riser-regenerator approach was equally developed in the partial oxidation of propene to acrolein. In 2001, patents had been obtained on the same process (e.g. (61)). Other patents concern the partial oxidation of propane to acrylic acid and acrylonitrile (62, 63).

However, to our knowledge, those patents are the last publications on the subject of circulating fluidised beds in partial oxidations. Furthermore, it seems that the hopes expressed in (8) could not be fulfilled. This is certainly due to difficulties with this innovative and sophisticated yet complicated technology. The announcement in 2004, that the equipment of the Dupont plant was on sale, was considered as "very disappointing" (64) for the alkane oxidation community. Nevertheless, this fact also shows that certain difficulties ony reveal after the operation of a plant in industrial scale.

In principle, the separation of reduction and reoxidation of the catalyst can also be achieved through instationary reactor operation like the reverse-flow reactor (65), or the Rotocat (66), which is based on the rotating Ljungstrom heat exchanger. Both devices are applicable in flue gas cleaning (66, 67) and an industrial SCR unit had been built in a 215 MW power station (68). In those applications, the reactants are co-fed but separate feed is principally possible. It is the difference between the time constants of reduction and re-oxidation of the catalyst (8), mentioned previously, that prevents this alternative in partial oxidation.

Nevertheless, the reverse-flow operation could be beneficial to decrease the hot-spot temperature and to obtain a more favourable temperature distribution along the catalyst bed. This has been studied by simulation in the case of partial oxidation of o-xylene to phthalic anhydride using a triangular reaction scheme (69). In fact, the hot spot was about 20 K less during instationary operation but it turned out that the final conversion, as well as selectivity and yield of phthalic anhydride, are not significantly affected.

3.3 Membrane Reactors

Membrane reactors belong to the so-called multifunctional reactors and have been the subject of intense investigation, shown by the regular international conferences in recent years [e.g., (70–72)]. Generally, membranes can be classified into two major groups: porous and dense membranes. The permeability on porous membranes is rather high compared to dense membranes, whereas the permselectivity is only moderate. Dense membranes rely on the transfer of ionic species, e.g., O^{2-}. Reactors with dense membranes have been reviewed very recently (73). Due to the low values of permeability, the oxygen flux is normally increased by electrochemical pumping. The applications of dense membranes in partial oxidations will, therefore, be discussed in the next paragraph.

When membrane reactors contain porous membranes, we distinguish between inert membrane reactors (IMR) and catalytic membrane reactors (CMR). The former may be further subdivided into distributors of reactants and extractors or product separators (74), schematically shown on Fig. 8.

In fact, there are 2 important domains where membrane reactors might be applied in order to improve the performance compared to conventional reactor concepts:

- an adapted dosing of a certain reactant into the reactor to enhance the selective formation of a desired product; and,

- the selective extraction of a limiting reaction product in a reversible reaction out of the reactor.

Both possibilities are illustrated by case studies in a recent review (75).

In the latter case, the dehydrogenation of cyclohexane to benzene was studied in the laboratory scale both in a membrane reactor and a classical fixed bed. It was concluded that a careful analysis should be performed prior to substituting a fixed bed reactor with a membrane reactor in order to perform reversible reactions since there might be simpler improvements.

In the former case, optimised dosing concepts had been investigated theoretically and experimentally in the oxidative dehydrogenation of ethane (76). The theoretical results, based on a simplified triangular reaction network, revealed the potential of an increase of selectivity. However, the experimental part emphasized the need for more realistic models, concerning both the selected reaction network and the individual rate equations. The reaction order plays a decisive influence on the dosing of a particular reactant.

In the formation of oxygenates by partial oxidations, the use of a catalytically active membrane has been proposed in order to increase the selective formation of the oxygenated intermediate (77). The gas mixture containing propane and oxygen was fed to the axis of a porous cylinder supporting the catalyst layer, and the products were collected on the outside of the device. Compared to the classical fixed bed, the yield of acrolein increased six fold when the catalytically active membrane was sufficiently small. This result is due to the reduction of the residence time in the reaction zone, which interrupts the reaction network at an earlier stage preventing further oxidation. However, the yield among other oxygenates remained poor.

There is an alternative possibility to increase the selective formation of acrolein from propane on the same catalyst by use of a membrane reactor. As the order of reaction with respect to oxygen is more positive in the complete oxidation to CO_x than in the partial oxidation, working at low oxygen partial pressure should be advantageous. Therefore, an inert membrane has been used to dose the oxygen into the fixed bed of catalyst through the porous reactor wall acting as an oxygen distributor (78). The device is schematically
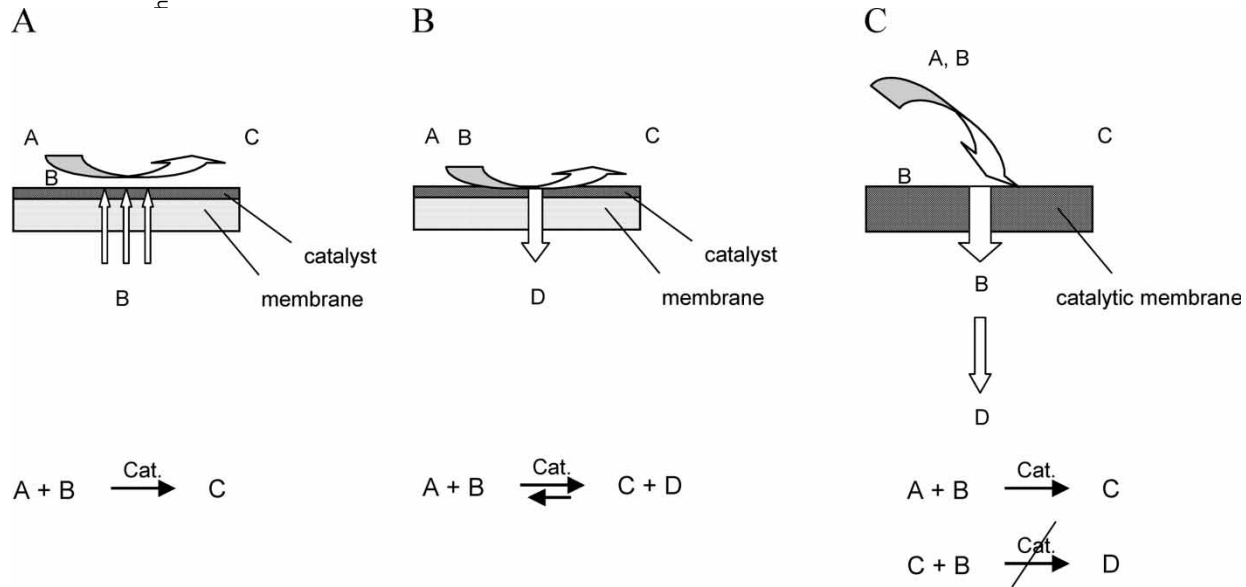
Figure 8: Different concepts of catalyst and membrane in a membrane reactor: (A) distributor, (B) extractor (both inert membrane concepts (IMR)); and (C) catalytic membrane adapted from (74).

represented on Fig. 9. It resulted in acrolein selectivities 2–4 times higher than in the reference experiment in the classical fixed-bed.

Catalytic membranes have also been studied in the partial oxidation of toluene as an alternative to the main production route, the liquid phase oxidation, in order to reduce the formation of by-products (79). The reported values of the reactor selectivity to benzaldehyde are still very low. However, the selectivity versus conversion curves show a significant increase in the membrane reactor by comparison with a classical fixed bed.

In contrast to the investigations described above, the application of membrane reactors in the partial oxidation of butane aims at the improvement of a process already realized industrially that gives unsatisfactory yields. The use of inert membranes is proposed to realize a locally distributed feed of one reactant, especially the oxidant. If the oxygen is distributed through an inert membrane to a fixed bed of a typical VPO catalyst (80), the butane/ oxygen ratio can be up to seven times higher than in industrial practice where 1 to 2% butane in air is co-fed. This is possible because the device is inherently safer due to the hydrocarbon and oxygen mixing in the presence of solids, which are efficient flame arrestors. However, the yields remain poor even if the inert membrane reactor may be considered as "a promising contactor." It is mentioned in (80) that the unsatisfactory results could result from the fact that the catalyst had been tailored to a far higher oxygen excess. Therefore, two different configurations of the membrane reactor had been compared experimentally by the same group (81) as shown on Fig. 10. In fact, the outward flow inert membrane reactor led to higher yields due to different
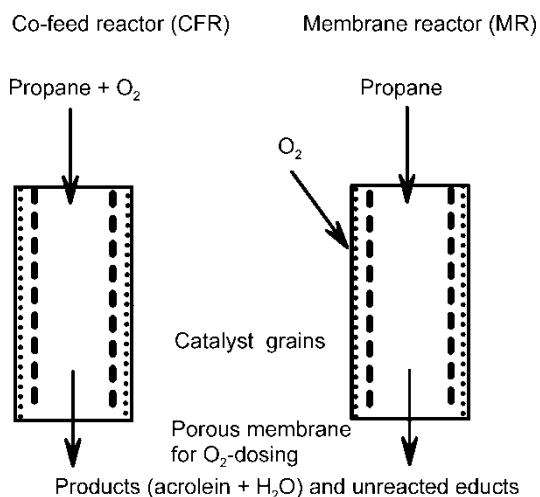

Figure 9: Partial oxidation of propane to acrolein, co-feed and membrane reactor, adapted from (78), courtesy of P. Kölsch.
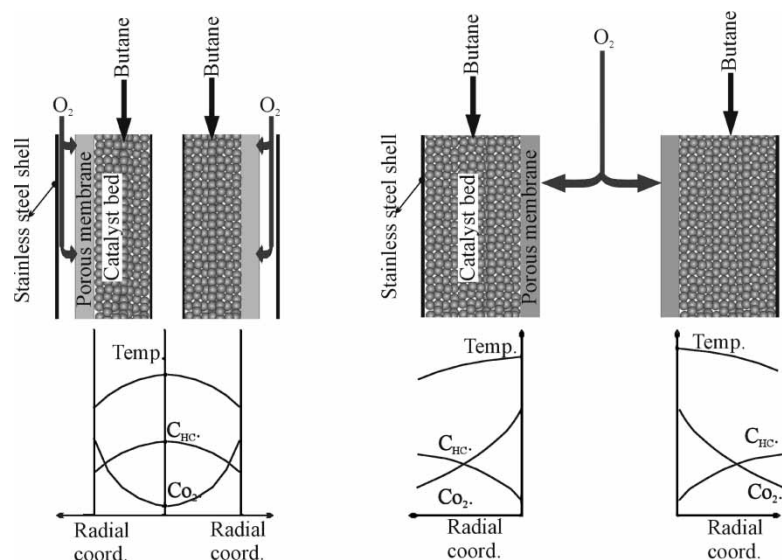
Figure 10: Different configurations of membrane reactors for the partial oxidation of butane to maleic anhydride adapted from (81), courtesy of J. Santamaria.

concentration and temperature profiles schematically indicated on the figure. Once more, the oxidation state of the catalyst, the ratio V^{5+}/V^{4+}, is believed to be responsible for such differences and the low yields in both cases. This suggestion is confirmed by Mota et al. (82) in the comparison of a conventional microreactor and a membrane reactor. The results indicate different oxidation states at different locations in the reactor, leading to a poor performance at the inlet. Therefore, the yield is improved by a reversed flow operation. The addition of some oxygen in the hydrocarbon feed is suggested as it had been proposed in the fluidised bed device of Rubio et al. (50).

Finally, Alonso et al. (83) investigated the combination of a membrane reactor with an externally fluidised bed. The butane is fed to a fixed bed inside a porous membrane tube, while an oxygen rich gas is fluidised by an inert powder on the shell side. This concept should combine the advantages of fixed and fluidised bed through maintaining isothermal conditions in the reactor and through providing an efficient mean to generate steam. In order to evaluate the potential of the concept, the authors compared published data from a full-scale pilot project (84), where a simple triangular reaction network is considered and calculations of the performance of the device were made using a detailed reaction engineering model. The results indicate that the hot spots are minimized, and the reactor is inherently safe due the presence of solids. The higher butane concentration and the controlled addition of oxygen along the reactor by means of the membrane lead to

higher product rates. It is claimed that the maleic anhydride yields are potentially 50% higher compared to a conventional fixed bed.

The same device has been studied by simulation in the oxidative dehydrogenation of propane to propene (85). Once more, the oxygen transport through the membrane wall is determined by the pressure drop. The controlled addition of the oxidant along the reactor axis improves the selectivity to propene and broadens the operating range with respect to hydrocarbon and oxygen feed rates. The authors claim an economic potential because the operation is not limited by hot spot temperatures to the same extent as commercial fixed-bed reactors.

The alternative device, a distributive feeding of oxygen into a fluidised bed via inert membranes, has recently been investigated in the partial oxidation of methanol (86). The experimental results are interpreted with the aid of a two-phase model accounting for permeation through the membranes. The reactor is equipped with horizontal porous ceramic membranes and cooling tubes. High methanol conversions and high selectivities to formaldehyde were achieved at very high methanol inlet concentrations, much higher than employed in industrial processes. The high formaldehyde yield, together with an inherently safe isothermal reactor operation, is due to decreased axial gas back-mixing. However, no comparison with the conventional fixed bed is given so far.

3.4 Electrochemical Promotion

It is a problem in partial oxidations of hydrocarbons and oxygenates to avoid the further oxidation of the desired intermediate because such intermediates are normally more reactive than the initial reactant. Therefore, the supply of the "right" oxygen species is a key parameter to limit the extent of simultaneous and/or successive formation of total oxidation products within the network of individual reactions. Partial oxidations usually proceed by a Mars-von Krevelen mechanism in which the surface of the oxidic catalyst is continually reduced and re-oxidized, the immediate source of oxygen being the lattice oxygen. This lattice oxygen can be exclusive, or at least its supply can be enhanced, by the use of oxygen ion conducting solids, like yttrium stabilized zirconia, which may be considered as a non-porous membrane.

The application of such materials is part of the electrochemical activation in catalysis [e.g., (87)], where solid-electrolye membrane reactors have been reviewed recently (88). If solid electrolyte potentiometry is a means to characterise oxidic catalysts in-situ (89), oxygen-ion conducting solids can also be used to electrochemically pump oxygen to or from the electrode-catalyst. The operation uses an external power source to impose an electric current through the solid electrolyte membranes, causing pumping of O^{2-} ions toward or from the catalyst.

1   solid electrolyte
2, 3 anodic and cathodic electrode
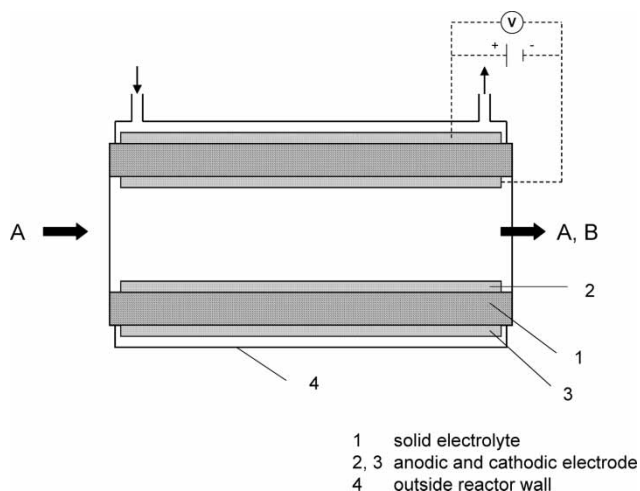4   outside reactor wall

Figure 11: Solid electrolyte membrane reactor (SEMR) adapted from (88).

Figure 11 shows schematically a tubular solid electrolyte membrane reactor (SEMR) in its simplest form. A tube, open at both ends and made of solid electrolyte, is enclosed in another coaxial tube. The two electrodes are deposited on the peripheral inside and outside walls of the solid electrolyte. Other possible geometries are described in (88).

Besides oxidative methane coupling (90), there are only a few investigations of electrochemical promotion in partial oxidations. Among the references reported by Stoukides (88), the oxidation of alkanes and alkenes has mostly been studied on metals, motivated by the interest in the NEMCA effect (87, 91). It may be partially due to the fact that the preparation of oxidic catalyst electrodes is complicated (89).

Most investigations on oxidic catalysts have been done by Takehira et al. (92–98) and were initially motivated by mechanistic considerations. They reported the role of lattice oxygen in the bismuth molybdate catalysts for the alkene oxidation using Au (92), Mo-Bi mixed oxide on Au (93) and (Pb, Bi)MoO_4 on Au (94) catalyst electrodes. The rate of formation of oxygenated compounds from alkenes on both oxides was enhanced by accelerating the oxygen pumping through the solid electrolyte. Moreover, use of MoO_3-Au resulted in a significant enhancement in the formation of acrolein from propene with increasing oxygen pumping (95). As for alkane oxidation, C_2-C_4 were partially oxidized to the corresponding oxygenated compounds over Au under oxygen pumping (96), among which ethane was oxidized to acetaldehyde with a high selectivity of 45% (97).

The electrochemical cell is shown on Fig. 12. The device is similar to that used in potentiometric measurements (89) but no characterization of the flow pattern (r.t.d.) is reported. In addition, the reactor selectivities to oxygenated
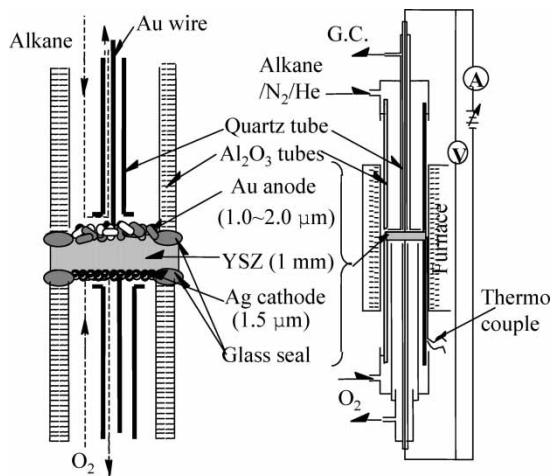
Figure 12: Electrochemical cell for the partial oxidation of ethane to oxygenates, courtesy of K. Takehira.

products are given without the corresponding conversions. Therefore it is not possible to compare such results, e.g., 40% selectivity to acetaldehyde from ethane (92), to those obtained in chemical reactors.

In the last paper of the series (98), the electrochemically promoted oxidative dehydrogenation of ethane and propane is compared to results measured in a conventional fixed-bed reactor. A drastic enhancement on the MoV_2O_8 catalyst film through electrochemical oxygen pumping is reported. The oxygen dehydrogenation of ethane has also been studied on a different non-porous solid electrolyte membrane (99). A selectivity to ethylene of 80% was achieved at an ethane conversion of 84%, whereas 53.7% ethylene selectivity was obtained using a conventional fixed-bed reactor under the same reaction conditions and the same conversion. A 100-hour continuous operation of this process was carried out, and the results indicate the feasibility of practical applications.

In the partial oxidation of n-butane to maleic anhydride, the potential of an electrochemical membrane reactor has been investigated recently (100). A vanadium phosphorous oxide catalyst on gold has been used as a catalytically active anode, and the oxygen flux was controlled by the external applied current. It had been verified that the gold layer alone did not catalyse the partial oxidation in the temperature range of 730 to 773 K. At 750 K, the selectivity to maleic anhydride was about 39%, the conversion of n-butane and pumped oxygen being $15-16$ and $47-50$%, respectively. Though the experimental results presented in the paper demonstrated the feasibility of the partial oxidation to maleic anhydride in an electrochemical membrane reactor, the authors concede that "the industrial application of an electrochemical

membrane reactor for butane oxidation is not foreseeable in the immediate future."

The investigation of electrochemical promotion in partial oxidations is at a very early stage and is still concerned with the principle feasibility. One of the reasons may be that "heterogeneous catalysis and electrochemistry have been traditionally thought to be different scientific domains" (91). Further studies should concentrate on the kinetics and enable the comparison of the results with conventional reactors in order to quantify a possible enhancement of the performance. Additionally, possible applications are linked to the development of fuel cells (SOFC), and the availability of solid electrolyte membranes and stacks on a larger scale in order to gain an economic perspective.

4. CONCLUSIONS AND OUTLOOK

Due to the originative imagination of chemical engineers, quite a variety of alternative concepts have been proposed to improve the performance in partial oxidations of small hydrocarbons and oxygenates. There are different degrees of realisation, ranging from common practice like structuring to first attempts like electro-chemical promotion.

However, it is difficult to discern if and to what extent the new concepts lead to improvement, particularly in exploratory investigations. Even if an enhancement is indicated by comparison with the classical fixed-bed reactor as a standard, the catalysts investigated often give poor results relative to industrial application, as can be seen in the case of membrane reactors. In addition, reported values of selectivity or yield are frequently obtained at different conversion in the control volume considered or the conversion is not indicated at all. It has been emphasized in Section 2 why this situation does not allow for accurate conclusions. Erroneous statements are possible, since the relationship between selectivity and conversion is simultaneously dependent on intrinsic catalyst characteristics and the flow pattern in the reactor itself.

We do not believe that there are unique criteria to evaluate new technologies or to compare different processes. Each case must be analyzed separately. Such a case study has recently been published by Vitry et al. (101), where the design of a new process based on propane instead of propene selective oxidation to acrolein and acrylic acid has been analyzed. The authors discuss successively:

- raw material cost and competing processes;

- location of the plant;

- product quality and by-products;

- process selection including market size and production foreseen; and,

- investment and operating cost.

The change in raw material from propene to propane is motivated by the fact that the average propane price has been half of the propene price over the last 10 years. Since acrolein and acrylic acid belong to the class of commodity chemicals, the price of the raw materials mainly determines the product price. However, as propane is more difficult to react, and its reaction will generate more heat, the capital investment will be higher.

Investment and operating cost estimates are normally considered as confidential and are hardly available in the open literature. In the present case, capital investment is estimated about 50% higher in the propane case. The variable cost could be slightly more favorable for propane (-10%) than for the propene-based process. Therefore, the authors highlight the need for further research to improve the propane catalyst disclosed so far. According to Ballarini et al. (64), all these economic considerations are also valid if the feedstock is changed from alkenes to alkanes in other partial oxidation processes. However, these authors also pointed out that the cost difference between different raw materials are often not as high and fluctuating. Thus, even if a feedstock change may be an incentive nowadays, its realization requires many investment and risk assumptions because of the future price development, independent of the catalyst performance.

A further point is the reactor technology, which does not necessarily depend on the question about feedstock of the process. Fixed, fluidized, and circulating fluidized beds are looked at as alternative processes, and the advantages and disadvantages are also widely discussed in (101) for the example of acrylic acid production. A lot of data have been collected, which are normally not easy to obtain from the open literature. However, although the case study clearly illustrates the interest of an alternative process, instead of a definite conclusion, it is merely suggested at the end that the oxidation process should be assisted by a reaction engineering specific for the propane oxidation. Although this proposition does not sound very satisfying, it displays how difficult an evaluation of a new technology is, due to the numerous and various aspects that have to be regarded.

Another interesting aspect has been recently addressed by Dubois (10) concerning the environmental impact of different processes due to the CO_2 emissions associated with the production of chemicals. All research groups working in the field of partial hydrocarbon oxidation are usually confronted with the loss of product selectivity due to complete oxidation. However, CO_2 formation will probably need to be regarded under new constraints in the future, since a CO_2 taxation has been or will be introduced in some countries. Therefore, Dubois emphasizes the importance of the location of the new plant mentioned above. Moreover, a re-evaluation of alternative reactor concepts might be worthwhile. Since, for example, the CO_2 formation is intrinsically reduced in the riser regenerator technology due to the absence of gas phase oxygen, this concept might be interesting again. However, a life cycle analysis of

chemicals must be done as detailed as possible. This could call attention to the thermodynamically based concept of the efficiency of energy-utilization in chemical processes, discussed some 30 years ago (102).

One bottleneck in the development of alternative reactor-concepts is the lack of detailed knowledge of the kinetics at the catalyst under consideration. If the truism that "the availability of a kinetic model is unavoidable for the optimization of a (membrane) reactor (78)" is not denied, then it is frequently not taken into account. Even if one with less ambition is satisfied by the mere improvement of a process without looking for the optimum—if there is one—the reaction kinetics have to be known in sufficient detail to evaluate the modifications.

It is recommended to compare the results obtained in alternative devices to a common standard, the classical fixed-bed, using the same catalyst in both cases in a form suitable to exclude internal transport resistances ["egg-shell" (44, 45)]. High performance catalysts should be compared if possible for proprietary reasons. It is interesting, but not convincing, if an alternative concept improves the application of a catalyst much below industrial standards.

The relations in Section 2 have to be taken into account. At least, the comparison of measured quantities, selectivity, yield, and productivity, obtained in different control volumes at the same conversion. Even better would be the comparison of the complete selectivity or yield versus conversion curve because this relationship represents the simultaneous influence of catalyst and flow pattern.

If the experimental results are encouraging, a further step should consists of simulating the different reactors with the aid of sufficiently detailed kinetics (reaction network and kinetic coefficients) and reactor modeling, the latter being the typical task of a reaction engineer. Depending on the reactor concept under consideration, additional terms for sources and sinks have to be added to material and energy balances.

As many alternative concepts are based on innovative materials, it is clear that further improvements in reaction engineering equally depend on parallel developments in material science. An example is to obtain selective permeability in inert membranes or high oxygen fluxes in solid electrolytes at reasonable temperatures. Such key compounds should be available at a large scale and at a reasonable price.

One major obstacle to the realization and operation of innovative concepts is the time lag between the basic idea and the construction together with rapid economic evolutions. It is said that the failure of the riser-regenerator approach of Dupont (8) is less due to technical problems than to a rapidly changing market situation for different raw materials and intermediates.

Conversely, an economic change may also be considered an incentive to try alternative concepts. It cannot be excluded that the market situation is favorable when a new process is ready to be realized. Therefore, every new idea is welcome and should be investigated in the context described previously.

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