Chapter 5

REACTION KINETICS/REACTOR DESIGN Jens Rostrup-Nielsen

5.1 INTRODUCTION

Reaction kinetics is an important tool for industrial catalysis. It provides the basis for reactor design and it may contribute to the understanding of reaction mechanisms and thereby supply ideas to formulate new catalysts and to explore new reaction paths.

Reactor and reaction engineering was added to catalysis during the 1950s and, with the introduction of computers, it developed to perfection, "the noble art of modelling", although most of it was still based on Langmuir assumptions and Hougen-Watson kinetics.

From the late 1960s, surface science made its substantial input to the understanding of catalysis, which almost transferred catalysis into "the noble art of characterization".

Industrial catalysis needs both elements. Research and development in catalysis requires a multidisciplinary effort concerning the manufacture of the catalysts, the study of the catalyst's impact on the chemical process, and the scale-up of results to industrial reactor design. It is important that there is a close interaction between fundamental catalysis and reaction engineering (see Figure 1).

The traditional scheme has been to start doing basic research to create ideas for applied research, and to complete the applied research before beginning development and engineering. A more effective approach is to work with overlapping phases, meaning that the applied research is supplemented by fundamental studies.

As an example (Rostrup-Nielsen, 1993a), the testing at semi-industrial scale, at industrial mass velocities, and heat transfer rates may well provide results that are relevant for engineering of industrial units. But in addition, practice has shown that it is often at this scale that the secondary phenomena such as unforeseen deactivation phenomena are best recognized. On the other hand, the progress in surface science has provided a basis for a detailed understanding of poisoning phenomena. This knowledge can be used in characterizing the spent catalysts from pilot plants and forming the basis for a new approach in catalyst development, and thereby the cycle is closed. The interaction between the two fields may help in focusing the fundamental studies on the relevant problems.

5.1





5.2 **REACTION KINETICS**

5.2.1 Paradox of Heterogeneous Catalysis

With the introduction of the chemical reactor, engineering procedures were developed to establish rate expressions from experimental work by using the Langmuir/Hinsheiwood approach for formulating possible mechanisms and their equivalent rate equations (Hougen et al., 1959; Froment et al., 1979).

$$r = \frac{(\text{kinetic factor}) \cdot (\text{driving force})}{(\text{adsorption group})}$$
(1)

The rate equation showing the best fit or the minimum residual squares of conversion was chosen and often this was taken as proof for the mechanism behind the expression. This could easily be misleading because even if it made the mechanism plausible, the fit by itself could be no proof of its assumptions.

Also, it was shown that many of the rate data could be expressed by simple power rate expressions (Weller, 1956).

$$\mathbf{r} = \mathbf{k} \cdot \mathbf{p}_{\mathbf{A}}^{\alpha} \cdot \mathbf{p}_{\mathbf{B}}^{\beta} \cdot \mathbf{p}_{\mathbf{c}}^{\gamma} \tag{2}$$

which could reflect the simpler Freundlich isotherm. This isotherm is related to the Langmuir isotherm³ by the approximation:

$$\frac{Ap}{1+Ap} \sim B \cdot p^{n}, \quad 0 < n < 1 \tag{3}$$

Therefore, one should be careful in describing conclusions about reaction sequences from the form of the kinetic expression only (see Figure 2).



Figure 2. Ki sides Alone Cannot Explain Mechanism.

In principle, the different isotherms represent different distributions of adsorption sites, reflected by different variations of the heat of adsorption with coverage. Nevertheless, it was shown that even when assuming a wide distribution of heat of adsorptions, the resulting kinetics would be close to that obtained when assuming that the reaction took place only on the most active site (Boudart *et al.*, 1984). This is the background for what was termed the "paradox of heterogeneous catalysis" (Boudart, 1956), stating that irrespective of the complexity of the catalytic su face, very often kinetic data can be represented by the Langmuir isotherm even though assumptions are far from reality.

It was shown that many reactions can be represented by simplified re equences when it is possible to assume or identify a most abundant surface intermediate (MASI) and either a rate determining step (rds) or two irreversible steps (Boudart *et al.*, 1984). On this basis, simplified kinetic expressions can easily be derived.

Many early kinetic studies were influenced by uncontrolled mass and heat transfer restrictions. Such kinetic information was of little use for scale-up to industrial conditions or for determining reaction mechanisms. The interaction between catalytic reaction and diffusion was analyzed in depth (Froment *et al.*, 1979; Satterfield, 1970), including the complex impact on the selectivity of catalysts. Today, most kinetic studies are carried out on catalyst powder in reactor systems, resulting in gradientless conditions. If experiments are to be carried out on catalyst pellets, it is essential to use full size pellets and that the conditions reflect industrial mass velocities and heat transfer rates.

The reaction engineering methods resulted in computer models capable of describing the complex interaction between intrinsic kinetics and mass and heat transfer inside the pellet and in the film surrounding the catalyst pellet. These models were included at an early stage in reactor engineering models for design (Kjær, 1972; Froment *et al.*, 1979).

In conclusion, kinetics and reaction engineering was developed almost to perfection 25 years ago, and reaction engineering was considered a mature field of science.

5.2.2 Breakdown of the Simplified Approach

The simplified approach has proven powerful for many industrial reactions. Nevertheless, irrespective of high sophistication of the mathematical modelling of chemical reactors, most work was still based on semi-empirical Langmuir-Hinshelwood kinetics. However, the simplified Langmuir-Hinshelwood approach breaks down in a number of situations. The "rds" as well as the "masi" may change through the reactor as a function of conversion or temperature. If it changes with conversion, it will also change inside the catalyst pellet, if the effectiveness factor is low.

Also, one may speculate about the meaning of * in the kinetic sequence. Surface science has provided information on the atomic scale, which may justify a more detailed approach to kinetics.

The size of the ensemble required may change with conversion and temperature. Also, the surface may be reconstructed under reaction conditions (Somorjai, 1991; Ruan *et al.*, 1992), depending on the composition of the gas at various positions in the reactor. The supported liquid phase catalyst for SO₂ oxidation for sulphuric acid may be considered as an extreme. The composition of the vanadium-potassium salt melt changes not only through the reactor, but also inside the catalyst pellet (Villadsen *et al.*, 1978).

Surface science (LEED, STM, etc.) has demonstrated that the structure of the adsorbed layer does not reflect random adsorption. On the contrary, the typical picture is the formation of island structures. Hence, the "mean field" assumption behind rate equations stating that the rate of a surface reaction between two adsorbed species is proportional with their surface coverages.

$$\mathbf{r} = \mathbf{k} \, \theta_{\mathbf{A}} \, \theta_{\mathbf{B}} \tag{4}$$

may reflect a simplified picture of the real situation. It may be more likely that reactions take place at the edges of surface islands (Ruan et al., 1992; Lang et al., 1992).

The reaction may also show oscillations on the surface as observed recently for CO oxidation on palladium (Ehsasi et al., 1992). In conclusion, there are several reasons that the simplified Langmuir-Hinshelwood approach may break down (see Figure 3).

- rds/masi
- Required "ensemble" may change with conversion, temperature
- Catalyst structure
- "Mean tield" assumption may not reflect situation

Figure 3. Breakdown of Simple Approach.

5.2.3 Kinetics and Surface Science — Micro-Kinetics.

The classical way of overcoming the situation described above is to use steady state kinetics with no assumption of a rate determining step. This approach easily leads to complicated equations with a number of constants difficult to determine in catalytic reactions. However, progress in surface science has provided strong tools for estimating the kinetic constants of the various reaction steps.

Work on ammonia synthesis (Stoltze et al., 1985) is one example of bridging the gap between surface science at ultra-high vacuum and industrial conditions, which is based on a well-known process with a well-established rate determining step. For reactions with a less established basis, it may be helpful to use "in situ" techniques where the catalyst structure or the surface intermediates are studied under reaction conditions by exposing the catalytic reactor to radiation such as X-rays from Synchrotron radiation (for EXAFS), gamma-rays (from Mössbauer spectroscopy) and infra-red (for FTIR), etc. Recent work has shown examples of "direct" observation of surface reactions by STM and AFM.

The "in situ" approach is illustrated by the selective catalytic reduction over a vanadium/titania catalyst:

$$NO + NH_3 + \frac{1}{4}O_2 = N_2 + \frac{1}{2}H_2O$$
 (5)

This reaction was studied in a FTIR cell (Topsoe *et al.*, 1991) working as a catalytic reactor. The FTIR-spectra indicated that the same adsorbed ammonia species are present on the surface, but no adsorbed NO-species. These observations were used at first to formulate a simple kinetic model for the SCR-reaction involving a rate-determining step of gaseous NO reacting with adsorbed ammonia being in equilibrium with the gas phase.

$$NH_3 + * \neq NH_3 *$$
 (1) fast (6)
NO + NH_3 + product + * (2) slow

The model results in the rate expression (Topsøe et al., 1991; Dumesic et al., 1993a).

$$\mathbf{r} - \mathbf{k}_2 \cdot \mathbf{p}_{\mathbf{N}0} \cdot \frac{\mathbf{K}_1 \cdot \mathbf{p}_{\mathbf{N}H_1}}{1 + \mathbf{K}_1 \cdot \mathbf{p}_{\mathbf{N}H_2}}$$
(7)

However, more detailed studies (Dumesic *et al.*, 1993a) involving a variety of experimental techniques (TPD, TPR and *in situ* FTIR) lead to a more complex mechanism involving a change of the active site during the reaction sequence:

$$\begin{array}{ll} NH_3 + \ast & \rightleftarrows NH_3 \ast & (1) \\ NH_3 \ast + \neq & \rightleftarrows NH_3 \neq + \ast & (2) \text{ slow} & (8) \\ NH_3 \neq + NO \rightleftharpoons \text{ products} + \neq & (3) \text{ slow} & \end{array}$$

resulting in the following rate equation;

$$r = k_2 \cdot p_{H0} \frac{(k_2/k_3) K_1 \cdot p_{HH_2}/p_{H0}}{1 + (k_2/k_3) K_1 \cdot p_{HH_2}/p_{H0} + (k_2/k_3) \cdot k_{-2}/k_3 p_{H0} + K_1 \cdot p_{HH_2}}$$
(7)

which approaches first order kinetics at low concentrations. The nature of the two sites $(* \text{ and } \neq)$ and their transformations during the reaction cycle were identified by spectroscopic studies (N. Topsøc, to be published).

The input from surface science to micro-kinetics has made it meaningful to solve the steady state rate equations, which is possible with modern computer techniques (Dumesic *et al.*, 1987; Stewart *et al.*, 1993). Micro-kinetics analysis (Dumesic *et al.*, 1993b) of various reaction sequences is a useful tool to combine the kinetic data with information from related kinetic studies (TPD, tracet studies, *etc.*) with data from surface science (sticking coefficiencies, surface bond energies, *etc.*).

The pre-exponential factors for the elementary steps in the reaction sequence may be estimated by using transition state and collision theory, and thermodynamic consistency may be achieved by statistical mechanics for estimating equilibrium constants (Dumesic *et al.*, 1993b).

There is a need to assess the effects of surface nonuniformity directly by measurements of heats of adsorption versus coverage (micro-calorimetry). It would be beneficial to measure surface coverages and collect kinetic data simultaneously (Dumesic, 1995) to obtain information on the surface chemistry at steady state. It may help to identify the slow steps and it may also give an input to assess whether the "new field assumption", e.g. whether Equation (4) is applicable. It is also required to carry out isotopic tracer studies over a wider range of reaction conditions to allow a more quantitative analysis of data. This would provide a powerful tool to extract reliable rate constants (Dumesic 1993).

The micro-kinetic analysis should be considered a tool for providing a consistent description which may then form the basis for formulating more predictive rate equations for reformulation of the catalyst or for exploration of new reaction paths. The consolidation of spectroscopic kinetic and surface chemical data may provide a basis to study new catalytic cycles and new catalyst systems. This "micro-kinetic synthesis" (Dumesic *et al.*, 1993b) requires a multi-disciplinary effort and it may also serve to bridge the work in catalysis research groups with the work of highly specialized groups in surface science.



Figure 4. Micro-Kinetic Analysis.

5.2.4 Kinetics of "ppm Reactions"

The breakdown of the simplified approach is evident in particular for processes in which one component should be completely removed down to a ppm-level. These types of reactions are becoming more important in environmental processes such as selective catalytic reduction for removal of NO_x , catalytic combustion of carbon monoxide, hydrocarbons and other organic compounds in waste gas streams.

The oxidation of carbon monoxide on noble metals has been studied in detail on well-defined surfaces of platinum (Ertl, 1983). The reaction order changes from minus one at high CO coverages to first order at very low partial pressures of carbon monoxide, which reflects a change in reaction mechanism. The availability of oxygen was critical at high CO coverages, meaning that the inhibited adsorption of oxygen was the rds. At low CO coverages, the rate took place between adsorbed carbon monoxide and oxygen at the periphery of islands of adsorbed oxygen atems with the surface reaction becoming the rds. The simplified kinetics may well assist in establishing rate equations for the extreme conditions, but it may hardly lead to a description of the wide transition zone. Also, Langmuir kinetics cannot explain the oscillations observed recently (Ehsasi *et al.*, 1992) at very low pressures.

The interaction between diffusion restrictions and intrinsic kinetics becomes complex as the concentration of the reactants approaches zero (Rostrup-Nielsen, 1993b, in press). Table 1 shows how the impact on the effectiveness factor depends on the reaction order of the intrinsic reaction. A zero order reaction becomes diffusion limited, whereas a second order reaction of stoichiometric mixtures is determined by intrinsic kinetics. The relative rates have been estimated in Table 1 for a high conversion process assuming identical intrinsic rates at the reactor inlet (Rostrup-Nielsen, 1993b, in press). The actual rates were estimated assuming as an example $\emptyset = 0.3$ for the first order reaction. It is demonstrated that wrong kinetics can lead to estimated rates at high conversion being more than one size of order wrong.

Table 1.Relative Rates in High Conversion Processes (Rostrup-Nielsen, 1993b in press),Same Intrinsic Rate at Reactor Inlet. $\eta = 0.3$ for first order reac. .n.

Intrinsic Reaction Order	-1	0	1	2
Thiele modulus Φ_L *	1/C	1.′√C	-	√C
Effectiveness factor, $\eta < 0.3$	a-C√k_1	a√k₀C	a√k ₁	$a\sqrt{k_2/C}$
$\operatorname{Lim} \eta \to \text{for } \mathbb{C} \to \mathbb{O}$	0	0	const.	1.
Reactor Inlet X=0% — Intrinsic rate — Actual rate	1.0 1.5	1.0 1	1.0 0.3	1.0 0.1
Reactor Exit X=99% — Intrinsic rate — Actual rate	100 0.02	1 0.01	0.01 0.003	10 ⁻⁴ 10 ⁻⁴

*
$$\Phi_{L} = d_{p,a} \sqrt{k_{i}/D_{eff}} \cdot C^{(m-1)/2} = a \cdot \sqrt{k_{i}/C^{1-n}}$$

The change of reaction order with conversion can have substantial impact on the estimated catalyst volume as illustrated in Figure 5. The tentative conversion profiles are based on identical intrinsic rates at the reactor inlet. The first order reaction remains first order irrespective of diffusion restrictions, whereas the effective reaction order of the second order reaction will start at less than two (ca. 1.5) and increase to two as intrinsic kinetics take over.

Figure 5 also shows the effective rate for the SCk-reaction using the simplified mechanism (Eq. 7). The SCR-reaction with stoichiometric concentrations of reactants starts with a reaction order close to one and approaches second order, according to Equation (7). As mentioned above, the simplified model s not sufficient and kinetics should rather be expressed by Equation (9).



Figure 5. Tentative Concentration Profiles Assuming Different Reaction Orders. (Rostrup-Nielsen, 1993a, in press) (dotted lines; no diffusion restrictions)

This emphasizes the need for reaction expressions covering a much wider range of gas compositions, in particular, with only traces of reactants being present. Steady state kinetics as shown in Equation (9) may be required to describe the complex transitions described in Figure 4.

5.2.5 Complex Reaction Schemes

Although very complex reaction schemes can be described by the state-of-art methods in reaction kinetics (Froment *et al.*, 1979), this is true mainly for reaction systems for which the intrinsic kinetics of the individual reactions are linear. In the case of nonlinear kinetics, there are still problems to be solved for reactions involving multi-component mixtures (Sapre and Krambeck, 1991). Nonlinear kinetics reflects the situation where the probability of reaction of any molecule depends on the other type of molecules in its surroundings. It means that lumped kinetics as applied in many hydrocarbon reactions may be misleading (Astarita *et al.*, 1992). In particular, this creates a problem for reactors not showing uniform behavior (*i.e.* other than plug flow, batch type). A better understanding of the kinetics of the conversion of multi-component mixtures is also required in view of legislation focusing on the control of the molecular composition of fuels.

5.2.6 Research Needs

The breakdown of the simplified approach in reaction kinetics may not be critical to conventional reactor design, but it may well become important for future industrial practice because of high demands to complete conversion and maximum selectivity caused by environmental requirements.

Micro-kinetic analysis may provide a useful tool for a more detailed kinetic description. It may also solve the problem of the rds/masi changing with conversion by giving meaningful input to steady-state kinetics.

However, there is a need for more research into the methods and underlying theories. Collision and transition state theories may not be sufficiently advanced to estimate kinetic parameters for all the chemical processes on the catalyst surface (Dumesic *et al.*, 1992). There is a need to apply the micro-kinetic approach to important reactions in the energy conversion processes and to the "ppm" reaction in environmental catalysis to provide a better design basis and to explore new reaction path. ere is a need to study reactions rather than characterize sites,

So far, micro-kinetic analysis has been based mainly on the assumptions of a "mean field" and a well-defined reaction site. Some attempts have been made to include ordered lattice structures in a classical adsorption model, but more work is required (Alstrup *et al.*, 1987). As an alternative, Monte Carlo simulations of surface reactions (Alstrup *et al.*, 1987; Deem *et al.*, 1992) may include the complexity of surface chemistry and the violation of the "mean field" assumption. Much more work is needed.

Also, the micro-kinetic methods should be refined to include the information that the active site (ensemble) may change with the temperature and the conversion (and composition of the gas phase). Work in this field is almost "nonexistent".

Surely, these improvements would lead to complex computer algorithms rather than simple rate expressions, but they may result in more predictive methods for reactor design.

There is a need to provide a better description of reaction schemes showing nonlinear intrinsic kinetics work to eliminate the risks involved in using "lumped kinetics".

5.3 **REACTOR DESIGN**

5.3. State-of-the-Art

The introduction of computer methods has allowed more precise designs of chemical reactors by using models to solve the heat and mass balances to various degrees of sophistication (Froment *et al.*, 1979). The one-dimensional pseudo-homogeneous models consider only plugflow in the axial direction and do not account for gradients around and inside the catalyst pellets. The two-dimensional models include the radial gradients in the reactor as well, which is important when heat transfer to the reactor tube is decisive for the reactor design. At an early stage, it was possible to include the gradients inside and around the catalyst pellets in first order heterogeneous models (Kjaer, 1972). Two-dimensional heterogeneous models still require long computer time, but there are recent examples (Wagner *et al.*, 1992).

The mathematical modelling of the ammonia synthesis reactor (Jarvan, 1970; Dybkjær, 1986) is one example of how it was possible with a first order heterogeneous model to analyze the feedback from industry. With this input and the precise knowledge of the reaction kinetics, pore structure, *etc.* it was possible to model a new radial flow converter having a very comple. Flow pattern, and to scale up directly to industry. Another example is the use of a two-dimensional pseudo-homogeneous model to analyze full-size monotube pilot runs on steam reforming and CO_2 -reforming to provide a design basis for tubular reformers operating much closer to carbon limits, resulting in more economic manufacture of syngas (Rostrup-Nielsen *et al.*, 1993). A two-dimensional model was also applied to simulate thermocracking reactors with their very complex kinetics (Froment, 1992). This was coupled to modelling of the furnace taking into account the position of each burner and the flue gas flow pattern.

Although much more complex than fixed bed reactors, the knowledge of fluidized bed reactors has improved significantly over the last decade (Kunii *et al.*, 1991). "Fluidization is not such a black art and if we keep careful tab of our uncertainties and get the needed information for scale-up, we should be able to design fluidized bed successfully". The scale-up of the Mobil MTG-process to fluidized bed (Grimmer *et al.*, 1988) and the development of a fluidized bed isobutane dehydrogenation process (Sanfilippo *et al.*, 1992) are more recent examples.

It might then be concluded that chemical reactor engineering has become a mature field of science. This is not true. As an example, there are big problems related to the reactor engineering of reactions in complex multi-component mixtures. A lumped kinetic function is not a true kinetic equation, and therefore it cannot be used directly to analyze reactors other than plug flow and batch reactors (Astarita *et al.*, 1992).

Moreover, the challenges to chemical reactor technology have changed. The chemical process industry is faced with environmental requirements which will necessitate the design of reactors for much higher conversions and much better selectivities. This is necessary to minimize the release or removal of products to a degree which would not be economic without considering the environmental requirements. First, this situation opens room for new reactor concepts such as catalysis combined with separation or reactors utilizing transient operation. Secondly, the use of catalysis to clean flue gases and other waste streams requires catalyst shapes and reactor configurations which are not typical for the process industry. Safety concerns require better models to predict how reactors will operate in run-away or rapid shut-down mode.

The challenges to reactor engineering are summarized in Figure 6.

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- Safety concerns require better models to predict how reactors will operate in run-away or rapid shut-down mode
- New reactor concepts to push conversion and selectivity
- Environmental catalysis to clean waste streams
- Reactor modeling of transient operation

, Figure 6. New Challenges to Reactor Engineering

5.3.2 Separation Catalysis

By combining catalysis with separation, it is possible to push a thermodynamic equilibrium by removing one of the products. Also, it is possible to add one of the reactants at controlled primes.

Catalytic reactive distillation is practiced at large scale in the manufacture of MTBE (Dokerty et al., 1992). Pure MTBE leaves the bottom of the reaction distillation column and a methanol/ C_4 azeotrope is leaving the top. The heat of reaction is used in the distillation. This principle might be used for other processes, where the temperatures for the distillation of the reaction can be made to coincide by adjusting the pressure. Reactive distillation may be attractive whenever a liquid phase reaction must be carried out with a larger excess of one of the reactants (e.g. alkylation). With reactive distillation, it may be possible to operate closer to stoichiot. Dr kerty et al., 1992).

Condensation of a reaction product was utilized in a gas phase reactor for methanol synthesis (Boegiid-Hansen et al., 1991) to push the equilibrium, and it was possible to achieve almost complete conversion of the stoichiometric syngas into methanol.

Combining catalytic reactors with membranes has the potential to greatly improve several important processes (Westertorp, 1992; Hsieh, 1991), such as dehydrogenation of alkanes, the manufacture of styrene, and steam reforming of hydrocarbons. These endothermic reactions require high temperatures to push the chemical equilibrium. When using membrane catalysis, it would be possible to carry out the reactions at lower temperatures, withdrawing the hydrogen product through the membrane. So far, the dense (monolithic) palladium membranes appear too costly, although it has been claimed (Gryaznov, 1992) that the thickness can be reduced from the conventional 50 microns to 2.5 microns in a composite membrane with a corresponding high hydrogen flux of 10 $m^3/m^2/h$. Still, it is a challenge to materials science to make these thin membranes tight and stable.

The use of porous ceramic membranes (Westertorp, 1992; Hsieh, 1991) results in lower selectivity but larger permeabilities. Both reactants may diffuse through the membrane and there appears to be a relatively narrow window of operation, because the permeation rate of the component to be removed should be larger than reaction rate, whereas the permeation rate of the other reactants should be lower than the reaction rate.

This situation might be improved by zeolite membranes, introducing shape selectivity as a separation parameter (Geus *et al.*, 1991; Haag *et al.*, 1991). The ceramic membranes may also be used to control addition of, for instance, oxygen in partial oxidation reactions (Westertorp, 1992).

Other principles for separation catalysis (Westertorp, 1992) are chromatographic reactors, product selective adsorbents, and high temperature fuel cells (Vayenas et al., 1991).

5.3.3 Transient Reactors

The use of periodic flow reversal in adiabatic fixed bed reactors for an exothermic reaction has the potential to eliminate complex heat transfer equipment inside the reactor at the same time as the reaction is equilibrated at low temperature (Westertorp, 1992; Matros, 1989).

For large-scale high pressure syntheses, such as ammonia and methanol syntheses, the transient principle results in too expensive equipment, because the required reactor volume is higher than in the conventional layout. Also, the principle means that the catalyst is poisoned from both ends. The principle appears advantageous for low pressure applications, such as catalytic combustion of waste gas, streams containing organics (Matros, 1989; Jensen *et al.*, 1991), and in some cases for sulphuric acid manufacture (Matros, 1989). The increased reactor volume may be compensated for by the elimination of an expensive feed effluent heat exchanger.

The application of pulse reactors utilizing higher selectivities in a transient region of the reaction is still a field to be explored.

5.3.4 New Catalyst Shapes

Traditionally, catalysts are supplied as pellets in the shape of spheres, cylinders, or rings. The catalyst shape is related to effective activity, pressure drop, and heat transfer as well, all parameters that are essential for reactor optimization. Small pellets result in high activity but high pressure drop as well. Monoliths have been introduced to solve this problem, in particular for low pressure processes, with auto exhaust catalysts as the classical example. For large scale applications, such as catalytic reduction of NO_x in power plants, square cross-section monolithic catalysts are usually installed. The flow pattern in monolithic catalyst beds results in a complex pattern for film diffusion control of the catalytic reactor (Ullah *et al.*, 1992). This is particularly true when monoliths have noncylindrical channels.

Development in materials science has made it possible to place the catalyst on construction materials forming "catalyzed hardware". It is tempting to place the catalyst on a heat transfer surface, thus eliminating the heat transport over the gas film at the internal tube wall in the conventional design. Catalyzed hardware for internal reforming in a high temperature fuel cell is one example (Rosump-Nielsen *et al.*, 1991), but the principle has potential for many other applications, such as methanation (Pennline *et al.*, 1979) and methanol synthesis (Curry-Hyde *et al.*, 1986). For selective partial oxidations, catalyzed hardware would mean a better temperature control and reduced "particle" size, both leading to higher selectivities at the same time as pressure drop will be low.

5.3.5 Complex Reactor Systems. Fluid Mechanics

The flow pattern in these reactors with new catalyst shapes can be very complex and far from the plug flow usually assumed in the reactor design models (Balling *et al.*, 1989). More input from fluid mechanics should be included in the design models as, for instance, applied in the Harwell program, FLOW 3D (CFDS, 1992). This is true also for trickle bed reactors. More knowledge is required to model these reactors, in particular on the "physics at the particle level". A list of research topics (Ng *et al.*, 1987) include studies using the method of Computer Aided Tomography to verify the simulated flow features at the particle level.

5.3.6 Heat Input to Endothermic Reactions

Heat transfer surfaces are expensive; hence, process economy can be improved by new means of heat transport. Also, hot reactor walls may contribute to reducing catalyst selectivity. In syngas manufacture, attempts have been made to replace the expensive fired tubular reformer with heat exchange reformers where flue gas or hot gas from an oxygen tired secondary reformer exchanges heat in an endother ': steam reforming process (Rostrup-Nielsen, 1993c, in press). This results in an increase of heat exchange efficiency from 50 to 80% of the fired duty (Stahl et al., 1985). In dehydrogenation of isobutane, the heat transfer may take place by heating up the catalyst by the circulating fluidized bed (Sanfilippo et al., 1992). More advanced ideas involve the circulation of an inert fluidized powder, blown through a stationary catalyst bed (Westertorp, 1992). Other ideas involve coupled reactions, for instance, combustion of hydrogen in a membrane dehydrogenation reactor supplying the heat for the dehydrogenation (Gryaznov, 1992).

5.3.7 Simultaneous Gas Phase and Catalytic Reactions

A number of reactions of potential interest involve simultaneous reactions in the gas phase and on the catalyst. Examples are catalytic combustion (Ahn *et al.*, 1986) for gas turbines, oxidative coupling of methane (Lunsford, 1993), and catalytic steam cracking (Albright *et al.*, 1983). Better modelling (Ahn *et al.*, 1986) is required of these complex reactions. Two-dimensional models are required to include the impact of radial temperature gradients on the kinetic severity function (Albright *et al.*, 1983) of the homogeneous reactions in steam crackers. This function describes the residence time temperature history of the reactants in a way that is consistent with reaction kinetics.

5.3.8 The Need for Explorative Process Engineering

It is important at an early stage to establish a preliminary flowsheet for a new catalytic process and to identify the constraints and the room for improvements and breakthrough. As an example, a future methanol synthesis (Rostrup-Nielsen, 1993a, in press) may only present a breakthrough if it is able to accept the normal CO_2 -content (ca. 5% in the synthesis gas). Otherwise, the savings in the synthesis may easily be compensated for by the more expensive syngas manufacture, which at present amounts to ca. 70% of plant costs. Another example is the direct conversion of methane into a methanol or by oxidative coupling to ethylene. A preliminary flowsheet analysis shows that a minimum requirement to selectivity can easily be identified (Rostrup-Nielsen *et al.*, 1992). In simple terms, the direct methane conversion processes should have a CO_2 -yield substantially below 20 C-atom% to represent a breakthrough compared to the indirect route.

There are several constraints in the reactor design for oxidative coupling (Dautzenberg et al., 1992). A fluidized bed appears feasible to control heat transfer, whereas a multi-tube reactor would have impractical dimensions.

For oxidative coupling, it is also important to identify how to incorporate product separation and use of product ethane. As an example, one interesting approach has been the use of a fluidized bed reactor using the endothermic pyrolysis of recycle ethane as a cooling agent for the reaction (Edwards *et al.*, 1991).

5.3.9 Research Needs

The new challenges to reactor engineering require more research in a field which had been developed almost to maturity.

There appear to be several opportunities in coupling catalysis with separation and, in particular, for membrane catalysis there is an obvious need for more experimental work (Westerterp, 1992; Hsieh, 1991).

The low permeation rate should be improved by several sizes of order. Fouling problems must be overcome, and there is a need for better design to supply or withdraw heat to and from largescale membrane reactors as well as a need to solve the difficulty of keeping pressure difference across the membrane to almost zero in large-scale industrial reactors.

The large-scale monolithic reactors, as well as trickle bed reactors, require a much better understanding of the fluid mechanics to provide better design models. This is true also for nonconventional applications of catalysis in connection with catalytic combustion for gas turbines, internal reforming in fuel cells, the application of catalyst inside engines, *etc.* In general, one would see the shape of the catalyst and the reactor approach each other, for instance, by the use of "catalyzed hardware". This calls for new reactor modelling. Many important large-scale reactions in energy conversion involve syngas or coal gas with high partial pressures of carbon monoxide. These gases involve the risk of serious corrosion attack by metal dusting (Grabke *et al.*, 1987). This is a phenomenon which is only partly understood. More research is required into the mechanism to predict design criteria for various construction materials.

Reactor studies and innovative flow sheeting need to be included in the planning of fundamental studies on new processes in order to better identify constraints and room for breakthroughs.

5.4 RESEARCH RECOMMENDATIONS

(see also 5.2 and 5.3.9)

5.4.1 Reaction Kinetics

Micro-kinetic studies

 Further development of methods to transfer information from a variety of surface science techniques into computer models of advanced reaction sequences.

Nonlinear kinetics

 Development of better basis for describing the reaction of multi-component mixtures.

5.4.2 Reactor Design

Separation catalysis

- Materials development
- (stable Pd-membranes, ceramic membranes, zeolite membranes) — New reactor concepts
- (low temp. steam reforming, dehydrogenation of alkanes and ethylbenzene)
- Reactor systems for better temperature control

Modelling

- Fluid mechanics and catalytic reactors
- Simultaneous gas phase and catalytic reactions
- Complex reaction networks in complex reactor systems
- Reactor performance at transient conditions

Construction materials

- Metal dusting corrosion in CO-rich gases

Innovative flowsheet analysis

- Encouragement to collaboration between science and engineering groups in order that constraints and room for improvements are identified at an early stage.

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