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Development of technical catalysts

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Abstract

Heterogeneous catalysis is the backbone of the modern chemical industry. The successful development of technical catalysts requires a highly interdisciplinary approach and a permanent close interaction between catalyst and process development. Although many modern methods are available for the characterisation of catalytic materials, still no substitute for a pilot plant test is available. Therefore the application of representative testing conditions in the laboratory or pilot plant reactor is of crucial importance. In order to identify the relationships between the often complicated solid state synthesis process during catalyst manufacture, the structural properties of the catalyst and its performance, correlation analysis are used.

Keywords: Heterogenous catalysis; Pilot plant test; Catalyst

1. Introduction

Technical catalysts are one of the most effective value-generating products of our modern world that itself to a large extent is based on chemical processes. This becomes evident if the value invested into the catalyst itself is compared to the value of chemicals that are produced by catalytic processes. The global catalyst market in 1995 was estimated to about 8.6 thousand million US$, with a significant growth predicted until 2001 (Table 1).

The world chemicals production in 1995 was estimated to be about 1200 thousand million US$ [1]. The ratio of both numbers is less than 1/100. Since the invention of the catalytic sulphuric acid process in 1888 by Rudolph Knietsch, about 25 million tons of acid have been manufactured at BASF. The total amount of catalyst needed during this time was about 1800 tons. Thus, the specific catalyst consumption in this process has been only about 70 ppm.

Catalysts, at the same time, are also very important to achieve environmentally benign processing, including the large segment of automotive exhaust gas treatment. Improved process selectivity through improved catalysts is one of the most effective means of environmental benign processing and also coincident with improved process economy. A well-known example [2] is the introduction of zeolites into catalytic cracking since the early sixties that resulted in annual savings of petroleum of about 400 million barrels per year for the same amount of gasoline produced. Depending upon the price of oil, this corresponds to annual savings between 7 and 10 billions $ raw material.

Therefore, it seems very worth looking at the methods by which these products are developed on an industrial scale. In doing so, it may also become clearer what the meaning of the word 'technical' in the

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Table 1
Global catalyst markets (billion US$)

Sector	1995	2001
Refining	1.9	2.4
Chemical	2.2	2.5
Polymerisation	1.4	1.8
Environmental	3.1	4.0
Total	8.6	10.7

title is about, e.g. what makes the difference between a ‘technical’ catalyst and an ‘ordinary’ one. There is much open literature on the scientific aspects of catalyst preparation, including the conference series initiated by Delmon in 1975 [3]. On the other hand, however, quite a bit of secrecy is spread over technical catalysts, their composition, their performance, and especially the methods by which they are produced which is understandable if one keeps in mind the big leverage they have on process economics.

The great majority of all industrial catalytic processes use heterogeneous catalysts which is why this paper will be restricted to this part of the field. Nonetheless it needs to be mentioned that there are also important homogeneously catalysed processes, one of the most prominent ones probably being the hydroformylation of olefins with CO/H_2 using cobalt or rhodium complexes as catalysts. Some 6 million tons of aldehydes are produced in this way annually. It is interesting to watch current efforts to heterogenise these molecularly catalysed processes by means of liquid/liquid two-phase systems. Recent examples include the Hoechst/Rhone-Poulenc oxo-process or the attempts of IFP to transform their DIMERSOL-process into a two-phase system.

Historically, the development of catalysts was strictly empirical, more resembling the attempts of the alchemists to make gold than a science. The beginning of systematic research may be traced back to the beginning of the 19th century, and an interesting review by Mittasch [4] on the history of ammonia synthesis gives a lively picture of how in these days the field gradually grew into a science in which mechanistic ideas were used as guidelines to a systematic ordering of many experimental observations. During the development of the ammonia catalyst, at the beginning of 1919 already more than 10 000 catalytic tests with about 4000 catalysts had been performed in the BASF laboratories. The key to success at that time was interdisciplinarity of fundamental physical chemistry, empirical trial and error lead by chemical intuition, highly developed engineering facilities, and last but not the least, people with endurance in spite of many setbacks during the project. In essence, the same mixture, although with a shift from empirism towards rational catalyst design, is still needed today for a successful technical catalyst development.

2. Properties of technical catalysts

It is the purpose of every chemical process to transform inexpensive raw materials into more valuable products. The whole chemical industry is based upon such transformations. In more than 80% of the cases, catalytic processes are used. In these cases, it is of extreme importance that catalyst and process cannot be seen independently of each other. Rather, the chemical synthesis can only be optimised by optimising the combined system, process and catalyst. For this reason it is essential that catalyst development is started at an early stage when a new industrial synthesis is developed. This requires close co-operation between synthetic chemist, process engineer and catalyst researcher which is best achieved when the research organisation also provides an appropriate structure.

Technical heterogeneous catalysts, along with activity and selectivity which are also important for laboratory samples, have to fulfil a number of additional conditions:

1. They are applied in large-scale technical reactors with reactor volumes from 1 up to several 100 m^3. This has consequences for the mass and heat transfer and the mechanical properties of the catalyst. It also requires a reasonable lifetime of the catalyst, including the rather trivial but nonetheless sometimes difficult demand to survive the chemical conditions, for example hot and strongly acidic liquid phases in the reactor.
2. The catalyst itself has to be manufactured in large-scale equipment, that is, there has to be a reliable solids’ production process for the catalyst, with all the challenges that are involved when it comes to

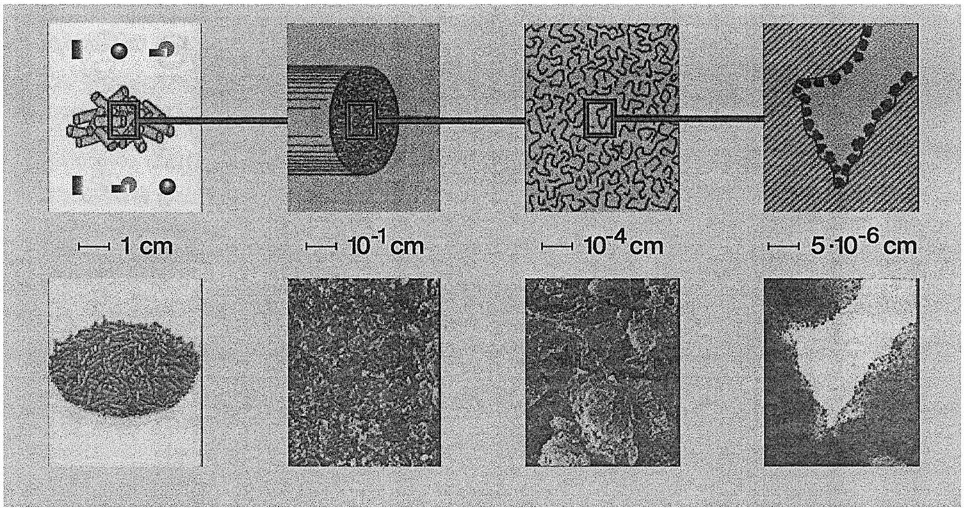

Fig. 1. Structural features of a supported catalyst.

solids' process technology. The challenge is especially high when speciality catalysts are involved; these are only produced in small volumes and sometimes, due to long catalyst lifetimes, with quite a bit of time elapsing between catalyst production campaigns.

3. Beyond that, however, there is also for technical catalysts the goal to improve the understanding of the elementary steps of the catalysed reaction at the catalyst surface. In doing so, further improvements of the catalyst itself, and probably even more importantly, the combined system of catalyst and process can be expected. A close co-operation between academia and industry has proven to be extremely fruitful for this task.

Heterogeneous catalysts come in many different shapes to best fulfil the different conditions met in chemical plants as described below, and there are different possibilities to arrange them into groups.

First, they can be described by the distribution of the active component in the catalyst: carrier-free, supported and coated catalysts.

Carrier-free catalysts consist entirely of catalytic material. They may be made up of oxide or mixtures of oxides as well as of metals and alloys. Porous structures are often generated during the catalyst manufacturing process, but there are also non-porous systems, especially when metals or alloys are used.

Supported catalysts are characterised by a composite structure using a porous support which may or may not be catalytically active itself but upon which the active species is deposited in a highly dispersed form. There are a number of advantages in this concept: the synthesis of the catalyst is relatively easy and reliable; it is possible independently to adjust the pore structure of the material as required by the reaction; and last but not the least, they allow a very effective use of expensive materials like noble metals. Fig. 1 illustrates the structural details of a supported metal catalyst. The magnification increases from left to right by six orders of magnitude. The electron micrographs in the lower row are schematically repeated in the upper row. The structure of the extrudates contains an open network of pores, and in the lower right corner, one can recognise the catalytically active platinum crystallites on the walls of the pore.

Coated catalysts are characterised by the fact that only a thin outer layer of the support is loaded with the active component. The carrier may be porous or an inert material with no pores. In both cases, the motivation is to suppress consecutive reactions which would occur if the reactants had a longer residence time inside the catalyst material. If the kinetics and the mass transport properties of the reaction system are known, it is possible to calculate the optimum thickness of the active layer and to prepare the respective optimised catalysts. Selective hydrogenation processes are examples where this type of catalyst is frequently applied. Depending upon the specific reaction and upon whether the process is run in the gas or liquid phase, the thickness of the active layer may range from below 100 µm to several hundred microns.

Second, the outer shape of the catalyst, which in a crucial way has to meet the process conditions, can be used as an ordering principle.

In the laboratory, and in a number of technical processes, especially in the fine chemicals area, suspended catalysts are widespread. For this application, the catalyst is manufactured as a powder of specific size distribution. One of the major advantages of suspended catalysts is the fact that there are often no mass transfer limitations between the liquid and the solid phase. The upscaling from laboratory results to a technical reactor is also relatively straightforward. A disadvantage is that the separation of the suspended catalyst can become tedious, especially when it has to be done in a continuous process.

The second large area where this type of catalyst is applied is in fluidised bed systems. The global value of FCC catalysts alone in 1995 was 900 million US$, 10% of the total catalyst market [1]. Here, even more than with liquid–solid systems, the shape and size distribution of the powder are important, and in addition to that, a very high level of mechanical strength of the powders has to be reached. The mechanical stress in a fluidised bed is in fact very much the same as in a jet mill, an instrument that is usually used for the communition of particles.

The majority of the large catalytic processes, however, are operated in the fixed bed configuration. The main advantage of this concept is the ease with which catalyst and products can be separated from each other. In order to operate a fixed bed system, a number of properties have to be met by the catalyst. Mechanical strength is required when the reactor is charged with the catalyst – some reactors reach heights of up to 10 m – and moreover to withstand the hydrostatic pressure in the reactor. The pressure drop across the reactor must be as low as possible, which requirement has to be compromised with the other one that as much active mass per unit volume as possible should be in the reactor in order to keep the reactor volume small. Mechanically weak catalysts may break during operation, leading to an inhomogeneous pressure drop and therefore to inhomogenous product flow across the bed. In the end, this can even lead to hot spots in the bed but in any case it leads to increased compression cost during the operation of the reactor.

Special forms of fixed bed catalysts are the honeycomb extrudates which are widely applied in automobile exhaust systems and in offgas cleaning devices. Their main advantage is an especially low pressure drop if high gas velocities are applied. On the other hand, the production of these honeycomb extrudates and their subsequent coating with a thin porous layer of active material is relatively difficult. So far, monolithic catalysts have not yet found wide application in chemical synthetic processes.

It should be evident from this short listing that the mechanical and hydrodynamic properties of a catalyst are of equal importance for the performance to the usually tested parameters activity and selectivity in laboratory experiments. A summary of the various shapes and application forms of heterogeneous catalysts is given in Fig. 2.

Still the most difficult to achieve but at the same time the most important property of a technical catalyst is its lifetime under process conditions. The importance of this topic is underlined by the fact that for a number of years there has been a special series of conferences on catalyst deactivation [5]. It is relatively easy to determine the catalyst poisons which have to be avoided either in the feed or in the materials which are used to synthesise the catalyst. It is in this context noteworthy that it was one of the major breakthroughs during the development of the ammonia catalyst by Mittasch [4] when he realised that the iron oxides used for the catalyst must not contain any sulphur as this had turned out to be a catalyst poison!

Much more difficult is the task to predict the ageing of the catalyst due to processes such as sintering, agglomeration of finely dispersed active components, recrystallisation of amorphous structure elements or gradual coking. This difficulty will probably never be completely solved because a good catalyst under reaction conditions is always characterised by a dynamic surface. Therefore stabilisation and activity seem to work in opposition. Nonetheless good technical catalysts reach lifetimes of several years if they are regenerated periodically under appropriate conditions.

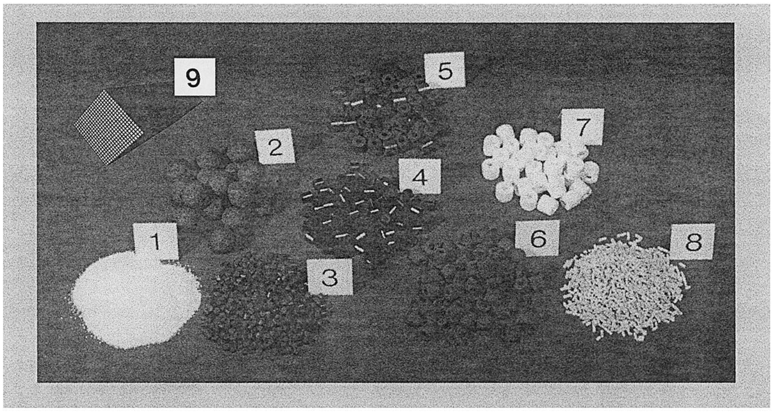

Fig. 2. Shape variety of technical catalysts.

3. Characterisation of technical catalysts

Given the long list of demands that have to be fulfilled simultaneously by modern high performance catalysts, it is obvious that there is an equally long list of methods that are used for their characterisation. All methods are used as well to characterise fresh catalysts as to investigate the changes that have occurred after some time of operation under reaction conditions. In some cases even the in situ observation of the catalyst sample is possible.

It starts with the determination of the bulk chemical composition where techniques as AAS,[1] ICP[2] and XRF[3] are used. One should not forget the importance of using only specified raw materials with minimum levels of impurities for the manufacturing of catalysts to avoid contamination with catalyst poisons. Quite frequently the composition of the bulk differs from the composition of the catalytically active surfaces. Today, there are numerous surface sensitive techniques, for example photoelectron spectroscopy (XPS or ESCA, UPS), electron microprobe and various kinds of electron microscopy. The same techniques can also be used to determine the elemental distribution of different crystallographic phases which in many catalysts are intimately mixed on a submicron scale. High resolution transmission electron microscopy (HRTEM) is able to resolve locally the crystallographic structure of the catalyst, as does X-ray diffraction for the bulk structure of the material. AFM[4] techniques also increasingly enter research laboratories to reveal details of the catalyst surface structure on an atomic scale. In X-ray amorphous materials, EXAFS[5] spectroscopy may give information about the local environment of catalytically active species. The same is possible with the various vibrational spectroscopic techniques like IR- or Raman-spectroscopy. The latter methods, as well as X-ray diffraction, can also be applied in situ to observe the working catalyst or its surface and to identify adsorbed species at the catalyst surface and bulk changes, respectively, under reaction conditions. Chemisorption of molecules that are presumed to exist on the catalyst surface during the reaction can be used to support a hypothesis on the reaction mechanism. These techniques, although already fairly old, are still irreplaceable for the determination of the dispersion of active metals in supported catalysts. Another rather old technique, the measurement of the specific surface area according to the BET-theory, completes this first group of methods.

Like the chemical, the mechanical properties of catalysts are also subject to a large arsenal of measurements. Stability against fracture, abrasion and other forms of wear is determined in many different tests that all try to simulate the situation which the catalyst will experience in the reactor under synthesis

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[1] Atomic absorption spectroscopy.

[2] Inductive coupled plasma.

[3] X-ray fluorescence spectroscopy.

[4] Atomic force microscopy.

[5] Extended X-ray absorption fine structure.

conditions. These tests have often been created empirically and therefore, for the sake of comparison between different labs, needed to be standardised.[6] The pore structure of the catalyst also has to be counted among the mechanical properties. Essentially two methods are applied here: mercury porosimetry and nitrogen isotherms are the most frequently used. Quite often there is a conflict between mechanical strength and large pore volumes, both of which are valuable properties.

Last but not the least, there is still no way to avoid the activity test in a laboratory reactor or a pilot plant before a newly developed catalyst will be charged into a technical reactor. Even at the stage of screening tests, one should never underestimate the importance of proper testing conditions if reliable data on the performance of a newly developed catalyst are to be obtained. This is of high importance because newly developed catalysts are frequently designed for large volume processes where even modest differences in performance are of great economic importance. Laboratory testing of catalysts for these processes must therefore give accurate results which can discriminate between catalysts with relatively small, yet commercially significant, performance differences. Consequently, significant numbers of publications about the proper design of labscale or pilot plant testing equipment have appeared in which the problems of downscaling are discussed [6].

In the case of fixed bed systems, industrial laboratories frequently use integral reactors for testing. A safe way to represent an industrial fixed-bed reactor on a laboratory scale is to reduce the diameter while keeping the length the same. The reason for that is that in a well-designed technical reactor the cross-sectional differences in the bed are normally negligible. A tall, slender test reactor can therefore be a very good representation of the commercial one. As a rule of thumb, the reactor diameter should be at least 3–5 times the diameter of the tested catalyst pellet if the results are not to be falsified by wall effects. The second question then is how long the reactor should be: reducing the length while keeping the space velocity the same will reduce the fluid velocity proportionally and thus affect the fluid dynamics. This in turn may have significant effects on the inter-phase mass transfer situation in the catalyst bed. For gas-phase processes, the situation is comparatively simple and it can be expected that reliable results can be obtained even from small lab-scale reactors. Much more difficult are liquid single-phase and especially two-phase trickle bed configurations which are, for example, applied largely in large volume oil refining processes. The major obstacle for downscaling in this case is that a minimum bed length is required before an acceptably low degree of residence time dispersion of the liquid is obtained. If original catalyst pellets with a few millimetres diameter are used, the minimum bed length easily reaches several metres. On the other hand, with particles below 0.1 mm diameter, this length can be reduced to less than one metre, which is the basis for the catalyst dilution technique. Even in trickle bed set-ups, it is possible to obtain reliable performance data if the original catalyst pellets are diluted with very fine inert powder [7,8]. The effect of the fine powder is that the fluid dynamics are largely governed by the fines whereas the catalytic behaviour is governed by the catalyst particles of the same shape, size and form as in the industrial unit. Clearly, this approach has the desired advantage that only small amounts of catalyst are needed for the test and that the consumption of feed is also kept within an acceptable range but care has to be taken to achieve a homogeneous packing of the fixed bed.

Finally, one also has to consider whether the fixed bed should be run in the upflow or downflow mode. As shown above, especially in the case of three phase trickle beds which are often used in hydrogenation processes, it is often quite difficult to simulate the reactor performance appropriately in lab-scale equipment. In the laboratory up-flow configurations may therefore be preferred but one has to keep in mind that this may be the reason for deviations from the lab results during scale up [9].

The ultimate goal of every new catalyst development is the passing of the lifetime test. This test is usually done in a pilot plant with catalyst volumes of at least several hundred cm^3. The pilot plant has to provide all relevant returns of product streams to observe the effect of traces of by-products on the catalyst life. Fully automated experimental laboratory plants are widely used today for this purpose [10], and it is again of great importance that the mass and heat transfer conditions in the catalytic reactors of these

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[6] See for example, UOP Laboratory Test Methods, ©UOP 1996.

units are as close as possible to those of the anticipated production plant. Of equal importance of course is the proper selection of reliable pieces of equipment in the pilot plant if one aims at continuous operating times of 8000 h or more.

The last step in the catalyst development cycle is the correlation of performance data obtained in the test units with all available structural information and the conditions during the manufacturing of the catalyst in order to obtain a product with reliable and reproducible properties. It is not only the process where the catalyst is used in that has to be developed, but also the process by which the catalyst itself will be produced on a technical scale. This last point probably is the most important difference between technical catalysts and the 'ordinary' ones which have already been mentioned in Section 1. Even though numerous analytical techniques today have accelerated the development time, years are therefore still needed before a newly developed catalyst can be introduced into technical processes on a commercial scale.

4. Molecular modelling

Molecular modelling methods have become very efficient tools in the industrial research for new drugs and agricultural chemicals. Similarly they are about to enter the field of homogeneous catalysis where they are already quite helpful in the design of new structures and the investigation of possible transition states on a reaction path.

For solid-state applications, the development has been a lot slower, and there are only a few examples where the interaction of surfactants with the surface of solids has been successfully modelled. In some cases these surfactants could be optimised to their function as growth regulators during the crystallisation of solids [11]. In heterogeneous catalysis, the tool of molecular modelling still is even more in its infancy although it is also on its way to develop into a tool for experimentalists [12]. In part this is because, compared to the modelling of molecular species for the mathematical description of a solid surface, a lot more atoms have to be put into the model, thereby requiring much higher calculating power. Secondly, especially in the case of heterogeneous catalysis, a successful model should include the dynamics of the catalyst surface under reaction conditions and this makes the situation even more complicated. Catalyst dynamics also include the well-known effect in the industrial practice: that there is often an activation period before a fresh catalyst reaches its full performance.

Quite successfully used in industrial research, however, are computer graphics for the visualisation of crystal structures, especially in the case of porous structures like zeolites, they are used to decide whether a given reactant would fit into a given space or not. This can, for example, be quite helpful in the selection of structures for shape-selective catalysts.

5. Examples

The following section will highlight the importance of the specific parameters of a catalyst for its overall performance. In all cases, it is not the active phase itself which has been optimised but rather the structure of the solid. The approach resembles what is known as galenic in the pharmaceutical industry where also often the method of administration of the drug decides whether the desired effect of the treatment is obtained in the optimum way.

5.1. Effect of pore structure

Fig. 3 shows the measured pore size distributions of two otherwise identical styrene catalysts. The different pore size distributions have been obtained by the addition of a pore-forming additive. The effect of the additive is that the formerly rather wide spectrum of pores with relatively small diameters has shifted towards larger pores. Accordingly, the total pore volume also increases from 0.09 to 0.14 cm^3/g. Both catalysts have been tested in a pilot plant unit, and for comparison purposes the temperatures for a set degree of conversion and the selectivities at these temperatures have been measured. Evidently the introduction of macropores leads to a significantly improved catalyst with nearly 1% higher selectivity, in this case equal to a 1% gain in yield. The macropores obviously act as transport pores through which the reactants reach the active surface within the catalyst particle in a more effective way. Evidently a 1% yield gain represents a big incentive in the production of styrene with its current world production capacity of more

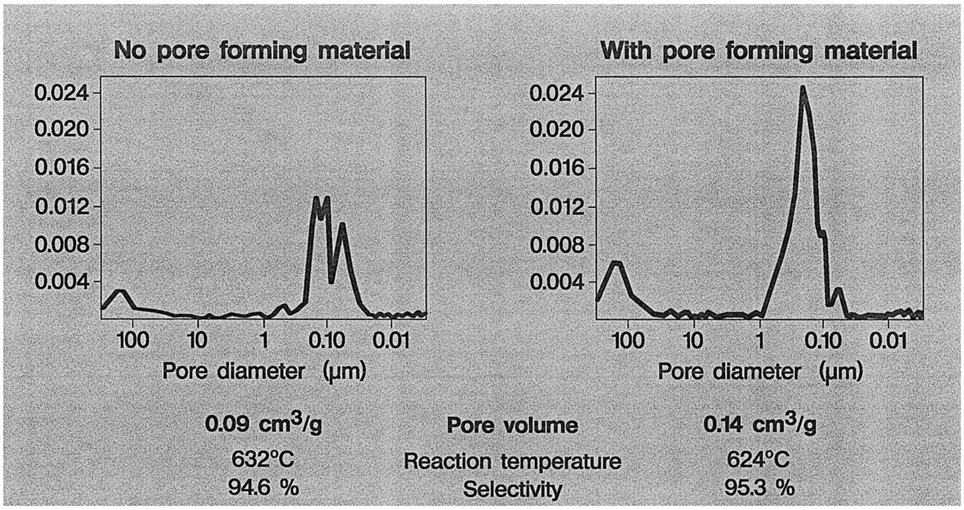

Fig. 3. Pore structure of the styrene catalyst: influence on catalyst performance.

than 20 million tons per year, corresponding at current prices to a market value of some 12 billion US$. The styrene catalyst market alone in 1995 was some 100 million US$.

5.2. *Effect of coating thickness*

Another large volume process is the production of acrylic acid, with a current world capacity of about 2.8 million tons, that largely uses the two-step catalytic oxidation of propene. In a first step, propene is oxidised to acrolein, this being carried out technically at very high conversions using a coated catalyst in which the active mass is deposited on a catalytically inert support. If the thickness of the catalytic coating has not been optimised, the catalyst is not operating under optimised conditions of heat and mass transport and this leads to the undesired occurrence of unselective consecutive reactions, namely combustion. Fig. 4 shows for two catalysts the measured selectivities to acrolein and acrylic acid as a function of conversion. The catalysts are identical except for the thickness of the catalytically active coating. The diagram shows that under the industrial relevant conditions of high conversion, the selectivities of the catalysts drift dramatically apart. We, together with a group at the

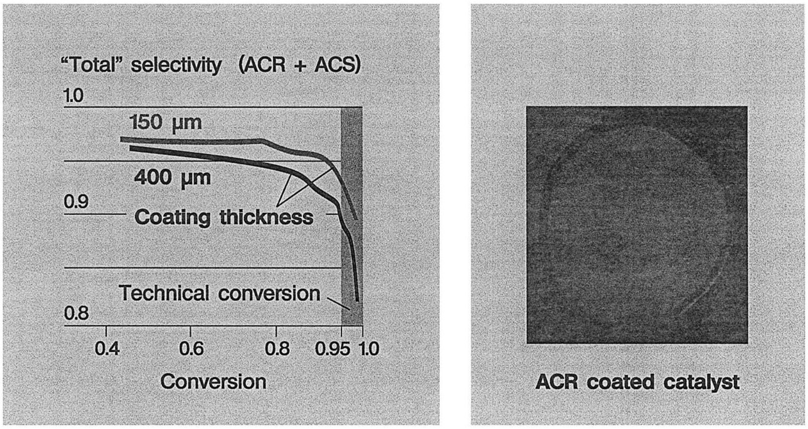

Fig. 4. Effect of coating thickness on mass and heat transfer in the acrolein catalyst.

Table 2
Effect of coating thickness on the performance of acrolein catalysts

	Catalyst A	Catalyst B	Catalyst C
Content of active component (wt %)	22.5	37	47
Coating thickness (μm)	150	285	400
Characteristic length (μm)	135	240	315
Maximum yield (%)	89	88	85
Rate constant (cm^3/g s)			
At 400°C	6.0	6.43	4.63
At 420°C	7.75	7.83	5.91
Thiele modulus φ (first order)			
At 400°C	0	0.3	0.7
At 420°C	0	0.6	0.8
Effectiveness factor η			
At 400°C	1	0.99	0.87
At 420°C	1	0.9	0.83

university of Karlsruhe [13,14], have studied the influence of mass transport effects for this type of catalyst in some more detail to examine further optimisation potential. Table 2 shows the data of a set of catalysts prepared with different coating thickness

The rate constants of catalyst C with the thickest coating differ markedly from the two other catalysts A and B for which the figures are approximately equal. Above a certain thickness of coating the conversion of propene is influenced by mass transfer effects. This is also reflected in the different maximum attainable yields. Since the two catalysts A and B with coating thickness of 150 and 285 μm scarcely differ from one another for both activity and selectivity, the results for the catalyst A can be regarded as free of mass transfer effects and to represent the intrinsic kinetic data. It is then possible to calculate the Thiele modulus and the effectiveness factor for the catalysts with thicker coatings. These data are also listed in Table 2.

For the industrial process these data are of high value because they enable an estimate of what loss of yield one should expect on increasing the coating thickness of the catalyst in order to increase the productivity of the reactor. In a given reactor volume, it is thus possible to calculate the best compromise between productivity and acrolein yield.

5.3. *Egg-shell catalysts for selective hydrogenation reactions*

In the selective hydrogenation of hydrocarbon streams, the transformation of dienes into olefins or of acetylenes into olefins is often required without the formation of alkanes. For the frequently applied palladium-based systems, the adsorption strength follows the order acetylenes>dienes>olefins. Therefore, as long as the active component in the catalyst is covered with dienes or acetylenes, very high selectivities can be reached. The catalyst design has to consider the balance between diffusion rate of the educts and their reaction rate with hydrogen inside the catalyst pellet in a way that the above mentioned condition is always met. If the rates are known quantitatively, the optimum thickness of the Pd-loaded catalyst shell can be calculated [15]. It is then necessary that catalyst preparation methods are at one's disposal that allow the reproducible manufacturing of catalysts with exactly the optimum shell thickness. Impregnation techniques are usually used for this purpose, and it has been shown that the stronger the interaction is between the molecular Pd-precursors in the impregnation solution with the oxidic surface of the support material, the thinner will be the resulting Pd-containing shell in the catalyst [16]. Fig. 5 shows as an example a series of Pd/Al_2O_3 catalysts that has been prepared for the selective tail end hydrogenation of acetylene traces in the ethylene stream coming from a steam cracker and the effect of the proper adjustment of the Pd-profile in the catalyst on the performance of the catalyst. All catalysts contain the same amount of Pd but different solutions have been used to impregnate the support material. The selectivity of the catalysts was measured with a 1% acetylene, 1% hydrogen in 98% ethylene mixture at 70% conversion.

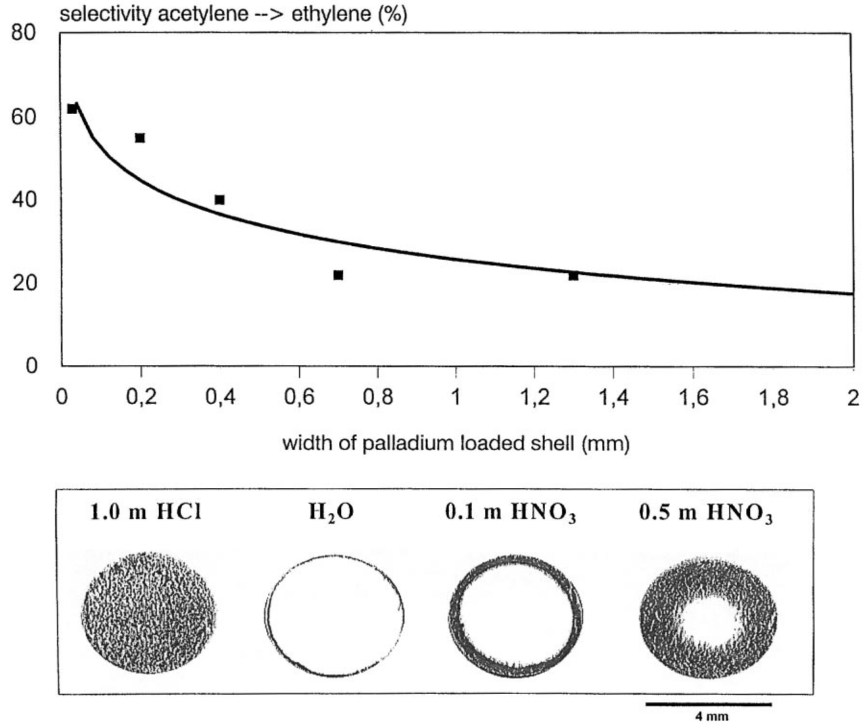

Fig. 5. Adjustment of Pd-profiles in selective hydrogenation catalysts and effect on catalyst performance.

Again the economic effect of improved catalysts is very significant. The worldwide capacity of ethylene plants was 70 million tons in 1996; if in all plants the selectivity for ethylene could be increased by only 0.1%, this would, at current prices, represent an additional ethylene value of about 40 million US$.

5.4. *Effect of precursor selection during catalyst manufacture*

The next example shows how the preparation of well-defined inorganic precursor phases can affect the performance of catalysts. The investigated catalyst system is the one used for the low temperature shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2$$

The catalysts used for this reaction are based upon copper, zinc and aluminium and are produced by the precipitation of the corresponding hydroxycarbonates. Depending upon the conditions of pH and temperature during the precipitation, various solid phases are produced which differ in their copper, zinc and aluminium content. Extensive X-ray diffraction studies revealed that crystals of layered hydroxycarbonates of the hydrotalcite type lead to the most active catalysts. Precursors containing appreciable amounts of other carbonate or hydroxide phases along with the hydrotalcite yielded markedly less active catalysts. Fig. 6 shows the X-ray pattern recorded for a precursor with the desired structure. The diffraction pattern also contains traces of the copper-zinc spinel phase which may occur if the next manufacturing step is not properly controlled. Good catalysts are characterised by the fact that they are X-ray amorphous after calcination. It is difficult under these circumstances to predict the catalyst performance reliably unless the parameters of the production process are kept under extremely tight control.

5.5. *Formation under reaction conditions*

Finally, the topic of catalyst stability under reaction conditions will also be addressed (Fig. 7). In the case

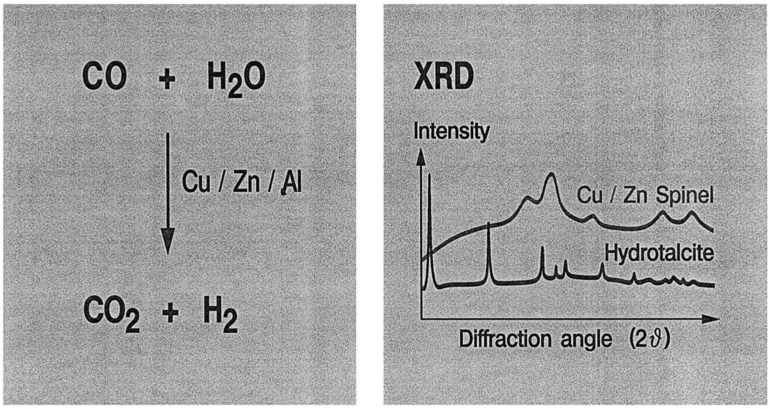

Fig. 6. X-ray diffraction as a means of process control during catalyst manufacturing catalyst precursor and unwanted spinel phase in low temperature conversion catalyst.

of the ethylene oxide catalyst, for instance, one recognises an initial ageing period during which a sintering of the active component, silver takes place. After about three weeks under operation conditions, this sintering process slows down and gives the catalyst its desired long term stability. Even today, with a worldwide installed production capacity of about 12.5 million ethylene oxide, our understanding of this sintering process is largely empirical. At first, the catalyst is very active, but not particularly selective. During the maturing period, the decrease in activity is compensated for by raising the temperature; at the same time the selectivity increases. The parameters that influence the sintering process are defined as closely as possible by using the above mentioned physical and chemical investigation methods, and the results are incorporated into the proprietary technical procedure for the catalyst manufacturing process.

6. Summary and future trends in catalysis

The development of technical catalysts is a markedly interdisciplinary task involving knowledge

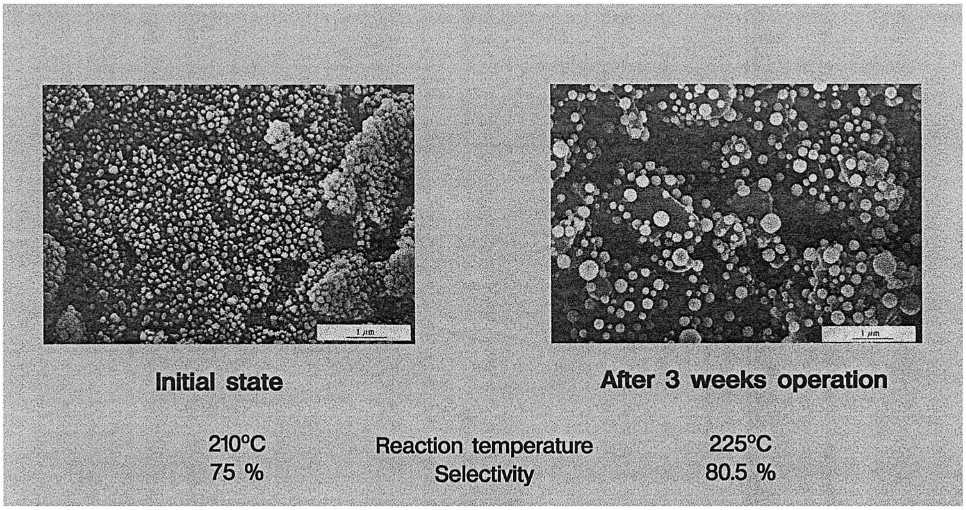

Fig. 7. Catalyst formation followed by electron microscopy for the ethylene oxide silver catalyst.

gained from numerous areas of chemistry, chemical engineering and process engineering. Catalysts are always constituents of a process. Over a period of barely 200 years, catalysis has developed from the first alchemistic experiments into a field of knowledge with a wide industrial basis. Catalysts find application in almost every process of the chemical and petrochemical industries as well as in the field of environmental protection. They are also to be encountered in many different aspects of our daily life.

Two major areas for future catalyst development can be anticipated. Firstly, there will continue to be a need for improving existing catalytic processes in terms of savings of energy and raw materials. This may either be the development of new processes based on new raw materials or the development of processes for new chemicals. Increasingly strict environmental protection requirements will gain importance globally in this connection.

Secondly, one can expect increased industrial exploitation of biochemical reactions, these being characterised by high selectivity and low energy requirements as compared to conventional processes. Attempts will also be made to mimic biocatalysts, if possible as heterogeneous catalysts – surface organometallic chemistry could be one approach on this road. On the whole, empirical trial and error methods will be increasingly substituted by rational catalyst design methods.

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