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The Yin and Yang in the Development of Catalytic Processes: Catalysis Research and Reaction Engineering

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catalyst design · heterogeneous catalysis · industrial chemistry · reaction engineering

1. Introduction

BASF, over the entire 150 years of its existence which are celebrated in this issue of Angewandte Chemie, has been a chemical company which relied heavily on novel developments in catalysis. The catalyst business of BASF is a centerpiece of the company, both with respect to sales to the market and to internal use of proprietary catalytic systems. While BASF has historically been very strong in chemical catalysis, the acquisition of Engelhard Corporation in 2006 expanded the catalysis portfolio appreciably in the fields of automotive exhaust catalysis and refinery catalysis.

Catalysis is also a key research field within BASF, and many new catalysts have been the result of these research efforts, as will be discussed in the following. The ammonia laboratory—named after the biggest and probably most important process developed there in the early 1900s, the ammonia synthesis—hosts the major catalysis research activities.

Crucial to the success of BASF and many other large chemical companies is not a single entity, such as the ammonia lab, but the highly integrated structure of both research and development and the production itself. In homogeneous catalysis, particularly for small-scale batch processes, the reactors are often universally useful, and similar reaction systems can be used for different molecular catalysts in a generic manner. In heterogeneous catalysis, on the other hand, the need for close interaction between the catalyst specialists and the reaction engineers is obvious. If a highly active catalyst mass has been discovered for a reaction with a pronounced thermal signature, this discovery is of little value when no reaction engineering solution can be found to supply or remove the heat. Moreover, if the shape and the pore system of the catalyst pellet cannot be adjusted in a way to optimize mass transfer, high activities of the active mass may not be fully exploited. For catalytic reaction systems requiring high pressures for high conversion and acceptable space-time-yields, suitable high-pressure reactors are needed to carry out the reactions in a commercially viable fashion. And—looking at the integration of a single reaction step in a bigger process scheme—catalysts with excellent selectivity can substantially reduce separation efforts and costs in downstream processing. It is thus mandatory not to develop the catalyst alone, without consideration of the overall process, but to work on the co-development of the catalyst, reactor, reaction conditions, and integration into the overall production scheme.

Figure 1 shows schematically the major interdependencies between catalysis and reaction engineering. Primarily, these mutual relationships are rooted in fundamental kinetic laws such as the reaction kinetics, but also the kinetics of physical phenomena such as mass, heat, and momentum transport. Although inherently catalyst independent, thermodynamics might also set important boundary conditions to process design, for example, the set of reaction conditions, which in some cases may reflect back on catalyst selection. In addition, operational and economic factors can also influence the way in which catalyst design and reactor/process engineering are interrelated. As an example, a catalyst with a higher working temperature window might be preferred to an alternative catalyst, capable of performing the same reaction at lower temperatures, if in the latter case heat integration and thereby the overall economics of the process is compromised by the impossibility to use the reaction heat to generate steam of the "thermal quality" required to be employed at a "heat sink", somewhere else in the process.

On these grounds, several links between intrinsic properties of the catalysts and reactor/process design considerations are established, some of which are indicated in Figure 1. How active a catalyst is determines, for instance, the temperature and pressure conditions at which the reaction should be carried out, and the contact time required to achieve a given pass conversion. The selectivity achieved with a given catalyst has direct implications for the design of separation and purification steps. Selectivity issues can also advise a limited conversion level per pass, which is in turn determinant for reactor engineering aspects such as the recycle ratio. Moreover, catalyst stability is an additional key attribute with profound implications for reactor selection and process conception. On the one hand, simply the nature of the catalyst deactivation alone can be decisive. For instance, if severe carbon build-up takes place in the course of the reaction, this might bring along a significant volume change in the solid catalyst, which cannot be handled in fixed-bed reactor configurations. On the other hand, the deactivation

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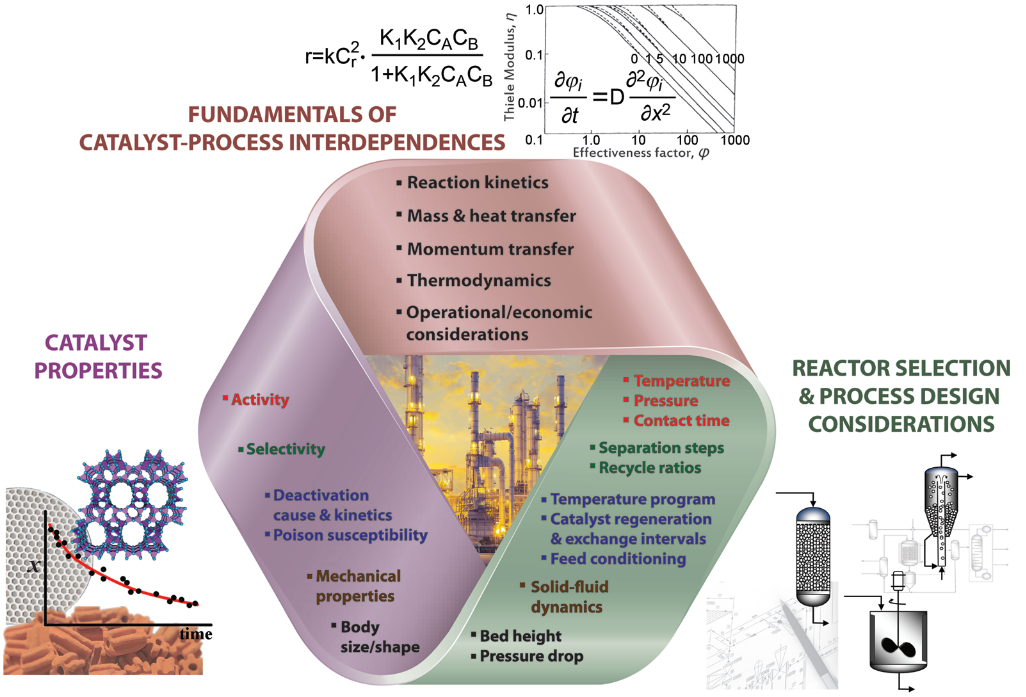

Figure 1. The three-in-one faces of catalytic process development. The figure summarizes some major interdependencies between catalyst development and reactor/process engineering as well as the underlying fundamental phenomena.

kinetics and its reversible or irreversible character determine how often catalyst regeneration or exchange is needed, with certain reactor configurations such as fluidized beds allowing much more frequent catalyst renovation than, for instance, fixed-bed configurations. In addition, the mechanical properties and shaping of the catalyst need to be aligned to the specific fluid–solid hydrodynamics encountered in the reactor. In fixed-bed configurations, the size and shape of the catalyst bodies are determinant not only for mass transport phenomena, but also for the pressure drop through the catalyst bed. In fluidized-bed, trickle-bed or stirred reactors, on the contrary, attrition resistance is a dominant factor, while catalyst particle size needs to be reduced to achieve adequate solid suspensibility.

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Both engineers and catalysis researchers have to be fully aware of these considerations, and especially students in both disciplines should be acquainted with these correlations and interdependencies already at an early stage in their studies. Catalyst and reactor design are complex, multi-variable tasks which encompass both scale-dependent and scale-independent fundamental processes, a challenge of particular relevance when devising process intensification strategies.[1] Much can be learned concerning the intimate relationship between catalyst development and reaction engineering by looking at the development of large technical processes. Interestingly, the demands and impulses between the fields are not unidirectional, that is, it is not always an innovation in the field of catalysis which triggers novel engineering solutions, but it goes both ways, and often multiple times for the same process over its development. It could be the new catalyst which induces new developments in reaction technology, but it may also be new process options which eventually allow use of previously rejected catalyst development lines or trigger the search for new catalysts.

Activity, selectivity, and stability can be considered the most prominent performance traits of any given catalyst.

However, their relative importance depends on several different considerations and might differ significantly among different processes. If the target reaction product is also the thermodynamically most favorable one, catalysts might be used simply to increase reaction rates or lower reaction onset temperatures, the catalyst intrinsic activity becoming the most relevant performance parameter. Processes such as SO_2 oxidation (sulfuric acid synthesis) and ammonia synthesis might serve as good examples. Often, however, catalysis is needed to direct the reaction towards a product which is not the most favored from a thermodynamic standpoint. In these cases, exemplified by the epoxidation of propylene with H_2O_2, selectivity becomes the most relevant performance parameter for catalyst development, especially since other reaction pathways may even lead to a less desirable situation than no reaction at all, that is, full combustion. Stability is always a central catalyst feature when a large-scale process is under consideration. In specific situations, for example, when a highly active and selective catalyst has been developed, stability becomes the major performance target for catalyst optimization. Current methanol synthesis processes based on highly optimized copper-based catalysts might serve as a relevant showcase.

In the following, the interplay between catalysis and reaction engineering will be discussed for the example of several large-scale catalytic processes, predominantly for those in which the contributions from BASF played a major role.

2. Sulfuric Acid Production

The production of sulfuric acid is one of the oldest chemical production processes.[2] Although the first patent had been filed already in 1831,[2] the advent of the heterogeneously catalyzed processes came with the introduction of dyestuff production in the 1870s, when the demand for oleum increased strongly. Up to that time the production capacities that could be reached with the old lead chamber process were sufficient. The first catalysts for sulfuric acid production were based on platinum, mostly supported on pumice or asbestos; one of the earliest technical solid catalysts employed in large-scale chemical production. Platinum catalysts, however, were very susceptible to poisoning, and thus extensive gas purification was required before gases could enter the catalyst bed. The demands placed on the purification section were highly dependent on the source of the sulfur dioxide. If the SO_2 was generated by combustion of sulfur, impurity levels were relatively low. Much more problematic was when SO_2 was generated by roasting of sulfide ores, where the dust contains metals, such as arsenic, which would poison the platinum surfaces. Thus, the advent of catalysts based on vanadium oxide in the 1930s was a major step forward.

In the early days of the development of the contact process, the fundamental thermodynamics were not well understood.[3] Clemens Winkler was one of the pioneers in producing sulfuric acid by the contact process, and he contributed largely to the development of this technology. However, he was also at the root of a misconception. Due to his early publication,[4] the sulfuric acid process was thought to proceed to highest conversion of sulfur dioxide in concentrated, stoichiometric gas mixtures which contradicted the laws of mass action formulated by Guldberg and Waage eight years earlier, but which was not recognized at that time.[3] In addition, it was believed that high reaction temperatures were needed for good conversion, based on the observation that the catalysts became most active when they were heated to high temperatures. The interplay between the exothermicity of the reaction and the temperature dependence of the equilibrium constant was not fully clear until the extensive studies and the report of Knietsch and colleagues at BASF who realized, amongst other important factors, that the contact vessels required cooling rather than heating.[5] This was a breakthrough in the process development, and from that time on, heat management became one of the crucial issues in sulfuric acid plants, in addition to the gas purification stage.

Still, the conversion levels reached in a single-bed reactor were insufficient, and thus, an intermediate SO_3 absorption which was reintroduced decades later as “double absorption process”—was implemented already at the turn of the century. By converting the reaction gas mixture almost to equilibrium in a first bed, conversion could be increased in a second bed, after the formed SO_3 had been removed from the product gas mixture by absorption in concentrated sulfuric acid. Moreover, this intermediate absorption also cooled down the gases so that the full temperature rise could be used, from onset of the reaction at low temperatures to the temperature at which equilibrium was reached.

Nevertheless, although these process innovations, that is, cooling the reactors and intermediate adsorption, made large-scale industrial synthesis of sulfuric acid possible, the stringent requirements for inlet gas purification remained to be a serious problem. This could only be solved with a novel generation of catalysts, which were based on vanadium oxide. Early vanadium-based catalysts were already described around the turn of the 19th century, and a patent on a supported alkali metal-containing vanadia catalyst was issued to BASF in 1913.[6] Due to its reduced sensitivity against poisoning and the substantially reduced costs, this catalyst replaced the old platinum-based system over the next 10–20 years. Concomitantly, heat management of the process was improved, and additional intermittent cooling stages were introduced in order to bring overall conversion close to the 100 % level. The effect of using several beds (in addition to an intermediate absorption stage) is illustrated in Figure 2.

The supported, alkali-promoted vanadia catalyst is an interesting and highly unusual catalyst system in that the active phase is liquid under reaction conditions.[7] Key for the catalyst activity and insensitivity against poisoning is the presence of molten phases, owing to which catalysis is not a surface process anymore, but in this case proceeds in the liquid phase, where molten vanadium(V) oxo-sulfate complexes form under reaction conditions.[8] The reaction sets in at the temperature at which the active phase becomes liquid, and this pointed to possibilities for improvement of the catalyst, that is, using additives to lower the melting point. This was achieved by the replacement of potassium by cesium,

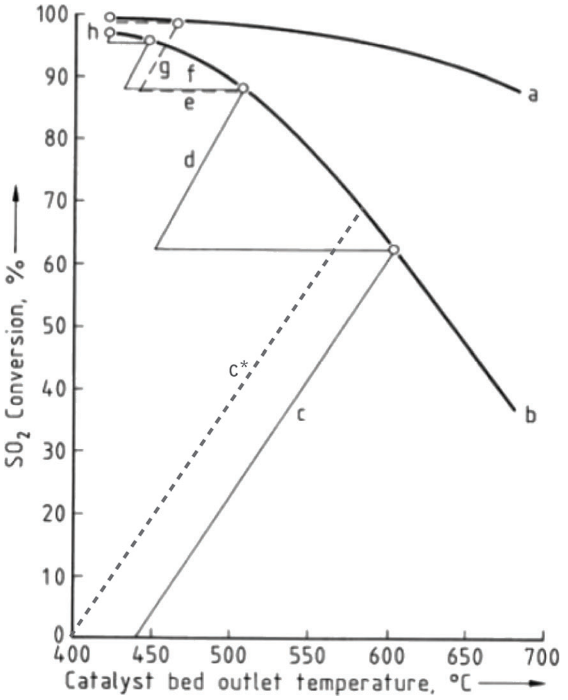


Figure 2. Reaction profiles and SO_2 conversion versus temperature for 4-bed normal contact (single-absorption) and (2 + 2) double-absorption sulfur dioxide oxidation processes (feed containing 8.5 vol% SO_2). a) Double-absorption process equilibrium curve after intermediate absorption. b) equilibrium curve for normal contact process. c) Adiabatic reaction in the first bed. c*) Adiabatic reaction in the first bed, if a catalyst with 30 °C lower onset temperature of activity is used. d) Adiabatic reaction in the second bed. e) Cooling and intermediate absorption. f) Cooling. g) Third bed. h) fourth bed. Adapted with permission from Ref. [2].

which reduces the melting point from approximately 410 °C to about 380 °C. Inspection of Figure 2 reveals that decreasing the onset of reaction by 30 °C increases the conversion in the first bed by approximately 5%, eventually allowing overall substantially lower tail SO_2 emissions. Reducing the working temperature of vanadium-based catalysts further is cumbersome, since at lower temperatures the activity and stability of the catalyst become seriously compromised. Whilst a number of reaction mechanisms have been proposed, involving either a vanadium redox cycle[9] or only vanadium (V) species,[8] the deleterious effect of low reaction temperatures is rather consensually ascribed to the massive reduction of vanadium species, followed by precipitation of low-valence vanadium compounds from the melt.[10] If lower temperatures, especially for the last bed, are targeted at, other active phases need to be used, such as ruthenium oxide.[11] In modern plants, a well-balanced interplay between the most advanced catalysts, heat management and absorption is used. Details of the catalysts can differ between the different beds. There are installations in which the first bed is based on the conventional potassium vanadium catalyst which is topped by a layer of cesium-promoted catalyst to reduce ignition temperature, while the fourth and fifth beds in five-stage reactors may consist completely of the cesium-promoted system to maximize conversion.[3] In double-absorption units with five beds (intermediate absorption after the third bed) overall SO_2 conversions exceeding 99.8% can be achieved.

An often underestimated engineering aspect in catalysis is the shape of the catalyst bodies, and this is also the case in sulfuric acid production. Initially, various shapes had been used for sulfuric acid catalysts. Mostly simple cylindrical extrudates were used. However, nowadays energy savings, especially of electrical energy for the blowers, have high priority, so catalyst shapes with reduced pressure drop had been developed, such as ring-shaped bodies or ribbed rings, and marketed under different names, for example, "Star Rings" (BASF)[12] or "Daisy" (Topsoe).[13] In addition to being beneficial to counter intraparticle mass transport limitations, these advanced shapes reduce the pressure drop over the catalyst bed and display a higher tolerance against dust, slowing down the rate of pressure drop during operation.

In situations where heat management is difficult due to the high exothermicity of the reaction, the use of fluidized beds with their excellent heat transfer properties could be highly advantageous. However, so far catalyst development could not meet the requirements of the conditions in a fluidized bed.[14] Abrasion is the crucial factor in fluidized-bed operation, and this problem could not be solved at that time if other important factors, such as pore volume, pore size, and particle size were to be kept within acceptable ranges. Two pilot plants were in operation in the 1970s, but they were both shut down due to the technical problems encountered.[14] Since then, no bigger project seems to have been started on fluidized-bed operation for sulfuric acid production.

Vanadium-based catalysts pose limitations on the process conditions, primarily the admissible SO_2 inlet concentration. If inlet concentrations are too high, the catalyst loses activity; moreover, with high inlet concentrations of SO_2, the adiabatic temperature rise in the first bed might lead to temperatures at the bed exit at which the catalyst deteriorates. However, there is increasing interest in higher SO_2 concentrations. A large fraction of the SO_2 converted to SO_3 is so-called "metallurgical SO_2", that is, it stems from roasting of sulfidic ores. The smelters increasingly use oxygen for the roasting process instead of air[15] and this can lead to SO_2 concentrations exceeding 50%. This does not allow to adjust the O_2/SO_2 ratio to the optimum value of approximately 1.1 required by the vanadium oxide-based SO_2 oxidation catalysts.[16] The current technical solution is the dilution of the gas to reduce inlet SO_2 concentrations to about 8%, which means bigger plant size and higher energy consumption by blowers and other aggregates.

If the desirable high SO_2 concentrations should be managed, advances in the catalyst are required. Vanadium-based systems do not have sufficiently high thermal stability, platinum is too expensive, and the required gas-cleanup also entails increased costs. An alternative could be iron-oxide-based catalysts, which are known for decades to be active for SO_2 oxidation.[2] Since iron oxides are generally stable up to high temperatures, their used as active phases has been explored with some success in SO_2-rich feeds up to pilot plant level.[17] However, production scale units have not been built, yet, since not all properties of the catalyst could be optimized to a satisfactory level. There is still research on novel catalyst materials and compositions, including studies using high-throughput methods,[18] but for the time being, variants of the long-known vanadium-based catalysts remain to be the workhorses of the industry. If, however, novel catalysts are found for SO_2 oxidation, this could allow completely new process options in the sulfuric acid industry.

3. Ammonia Synthesis

Ammonia synthesis from the elements is arguably the most important technical catalytic process ever invented, since the food production of the global population relies on nitrogen fertilizers. Ammonia synthesis is a prototypical case study for the intimate interplay between catalyst development and reaction engineering, and this could not be better shown than by the two Nobel Prizes given to the key scientists in this development, Fritz Haber in 1918 for the Synthesis of Ammonia from the Elements and Carl Bosch of BASF in 1931 (together with Friedrich Bergius) for their merits in the discovery and development of chemical high-pressure processes (of which the ammonia process was a prominent example). The technical ammonia process recently celebrated its 100th birthday (Figure 3), as only a few years after the initial discoveries by Fritz Haber was the first plant started up in 1913.

Figure 3. Fully edible "Ammonia molecule on a surface" served at BASF's 100 year celebration of ammonia synthesis. The blue ball represents the nitrogen atom, the bottom three white balls are the hydrogen atoms and the top white ball is the lone pair.

The early development in the synthesis of ammonia profited heavily from the lessons learned in the oxidation of sulfur dioxide. Knietsch, who pioneered the development of sulfuric acid production in BASF, provided the blueprint for the first ammonia reactors, and was mentioned in Bosch's Nobel Prize lecture.[19] Whereas the development of the sulfuric acid process was to some extent delayed by misconceptions of the thermodynamic basis for the reaction, for ammonia synthesis, the analysis of the thermodynamics of the system was at the root of the development and key to Haber's groundbreaking work. The seminal publication of Haber and Le Rossignol[20]—only published three and a half years after completion of the work due to the commercial implementation; and one of the most impressive scientific publications the authors know, covering thermodynamics, newly developed high-pressure technology, recycle, and the kinetics of the ammonia synthesis over different catalysts, studied with the limited experimental tools available around 1910—thus rightfully first discusses the equilibrium of the ammonia synthesis under different conditions. Based on earlier measurements of Haber and van Oordt,[21] the authors came to the conclusion that low temperatures and high pressures would be favorable, and the separation of the ammonia formed and recycle of the unreacted gases would be necessary in a technical process.

It was thus clear that an efficient catalyst would be needed to design a technical process, since a purely thermal process or one based on a low-activity catalyst would need to proceed at temperatures where the equilibrium was so unfavorable that the yield would be unsatisfactory. Haber and especially Mittasch at BASF then started a very extensive catalyst screening program in order to provide a catalyst with sufficient activity to be the basis of the technical process. Initially, osmium was high on the list for a catalyst material and used in the early experiments. However, it suffered from obvious problems, which—in addition to possible formation of OsO_4—are best expressed in a quote from Bosch's Nobel Prize lecture: "The two tubes drawn by Mannesmann had each done service for 80 h, then they burst. If we had charged them with osmium instead of with our new catalyst, the world's supply of this rare metal which we had already bought up would have vanished".[19] Such a catalyst material was clearly not the basis for a globally used technology, which ammonia synthesis proved to become.

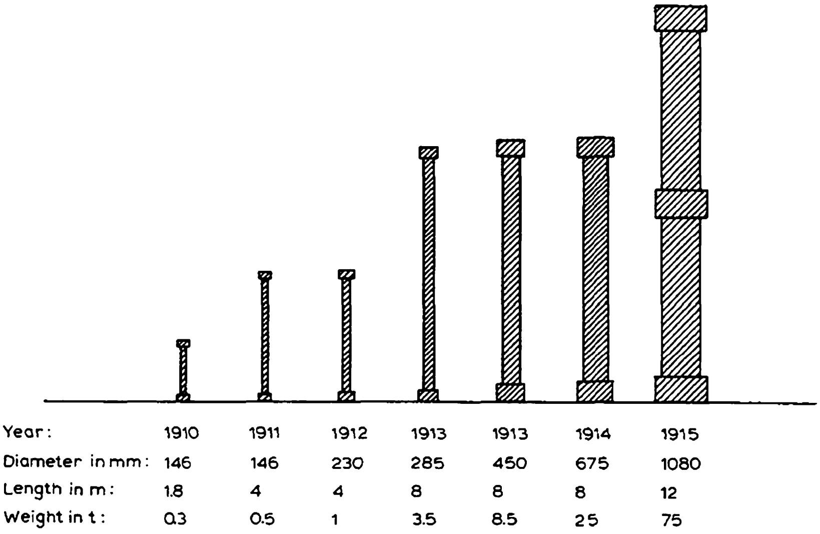
This realization was the reason for the catalyst discovery program—one may actually call it a high-throughput-program—initiated both in Haber's lab and in BASF by Mittasch, in whose lab overall around 20000 experiments were carried out.[19] In his 1913 publication, Haber described experiments with catalysts based on cerium, manganese, tungsten, uranium, ruthenium and osmium.[20] The crucial discovery of the iron-based catalyst obtained from the Gallivare magnetite sample was made by Mittasch, though, who had homed in actually rapidly on iron compounds after an initial broader screening. This Gallivare iron oxide already had most of the crucial features which characterize today's ammonia catalysts: in addition to iron, it contained potassium, deemed to be an efficient "electronic promoter", as well as alkaline earth elements (Ca) or aluminum compounds in the role of "structural promoters". Nowadays the catalyst precursor is fused from iron oxide, with addition of potassium oxide and aluminum and/or magnesium oxide, then crushed and reduced under synthesis conditions. The exact nature of the ammonia catalyst and the function of the different components, the pretreatment, and the activation process have been the subject of thousands of publications and review articles[22–25] and hence do not need to be discussed in detail here. The relevant result for the process development was the availability of a catalyst which was based on abundant raw materials and principally allowed the synthesis of ammonia under conditions which appeared at least feasible around 1910, even if they had never before been employed industrially.

This moved the major hurdles to the process development and the engineering challenges. The first concerned the quality of the feed gas. In order to protect the catalyst, all oxygenates, specifically carbon oxides and water, have to be removed down to a low parts-per-million level, since they act as inhibitors for the ammonia catalyst,[26,27] and might, after prolonged exposure, lead to irreversible catalyst deactivation.[28] For a short time, the hydrogen had been purified by low temperature distillation,[19] but soon a catalytic process was developed in which the synthesis gas obtained by steam reforming was exposed to a series of treatments, including water-gas-shift stages and a final methanation step. Procurement of sufficiently pure hydrogen is still a major factor in an ammonia plant.

The second set of reaction engineering challenges concerned the high-pressure/high-temperature equipment. Here, many solutions for the details had to be found, such as sealings, valves, and recycle system. The biggest single challenge, however, was the right choice of construction materials for the converter itself, and in searching for the cause of failures, a whole research field of materials science was opened up, that is, the phenomenon of hydrogen embrittlement, which was the reason why the early tubes burst. These tubes were made from a high-strength steel, the carbon in which was hydrogenated to methane by high-pressure hydrogen which led to the embrittlement. The solution was a thin lining of the pressure-bearing steel tubes by soft steel. This soft steel did let some of the hydrogen pass through by diffusion, but it was released through holes in the pressure bearing tubes. While this solved the problem initially, the work on hydrogen embrittlement led also to the development of novel steel qualities, and as a result, alloys became available relatively soon which can withstand the conditions in an ammonia plant, so that the lining is not required anymore.[29]

In hindsight highly surprisingly, both the challenges with respect to the catalyst and to the process engineering could be solved within a matter of only a few years and the first production plant was commissioned in 1913. Reactors rapidly increased in size (Figure 4), and already after a decade the reactors had truly impressive dimensions (Figure 5). Although there has been substantial progress in plant layout and individual components since the early development, the overall concept scheme and the catalyst are essentially still modelled after the first plants in which catalysts and process were well adapted to each other, and the majority of current plants use the iron-based catalyst system. Nevertheless, already in the early days an alternative catalyst material was identified which performed well, that is, ruthenium-based systems, for instance Ru/MgO.[20,22] Ruthenium has key advantages: it is less susceptible against poisoning, and it allows synthesis at appreciably lower pressures, below 100 bar, as compared to the iron system, which requires pressures around 150–200 bar.

Work on ruthenium catalysts, however, was dormant for decades due to the high price of the base metal. It was rejuvenated in the 1970s by the pioneering work of Aika and colleagues (covered comprehensively in Refs. [30ab]). The ruthenium is supported on carbon and promoted with alkali or alkaline earth-metal oxides. Such catalysts form the basis of a new ammonia process, the Kellog Advanced Ammonia Process (KAAP).[31,32] This process operates at pressures around 90 bar, leading to lower capital costs.[33] The ruthenium catalyst is claimed to be 20 times as active as conventional, iron-based ammonia catalysts, and the lower process pressure allows use of only a single-stage synthesis gas compressor. Moreover, pipe and wall thicknesses are lower. However, this comes at the expense of higher catalyst costs, with the strongly fluctuating ruthenium price as an additional uncertainty. Besides, methanation of the carbon support is an



Year:	1910	1911	1912	1913	1913	1914	1915
Diameter in mm:	146	146	230	285	450	675	1080
Length in m:	1.8	4	4	8	8	8	12
Weight in t:	0.3	0.5	1	3.5	8.5	25	75

Figure 4. Size development of ammonia synthesis reactors in the early days of the process (from Bosch Nobel Lecture). Reproduced with permission from Ref. [19].

Figure 5. Photograph of an ammonia synthesis reactor from 1925, now exhibited in front of the BASF Gesellschaftshaus.

issue under the operation conditions of the ammonia synthesis.[34] KAAP ammonia converters consist of four radial flow beds, with intermediate coolers. The first bed uses a conventional iron catalyst, while the three other beds are filled with the ruthenium-based catalyst.[35] The first plants with ruthenium catalysts began operation in 1998, and by now seven plants are operating. Research on ruthenium-based catalysts is continuing, so that further improvements in the process can be realized. Muhler and colleagues[36] reported a barium-promoted Ru/MgO catalyst, which—due to the fact that it does not contain carbon—does not suffer from the methanation problem. The barium-promotion was suggested to increase the number of B5 sites which were described as the active sites for ammonia synthesis.[37] Recently, a highly interesting ruthenium-based catalyst was reported in which the ruthenium was supported on an electride (Figure 6).[38] The electride is a compound which contains electrons trapped in the cages of the crystal structure. It is a stable compound with the empirical formula $[Ca_{24}Al_{28}O_{64}]_4^+[e^-]_4$.[39] This support is an excellent electron donor, and can also reversibly encapsulate hydrogen in the cavities, which reduces the susceptibility of the ruthenium catalyst against hydrogen poisoning. As a result, a high-activity ammonia synthesis catalyst was obtained with a turn-over-frequency a factor of ten higher than those of catalysts described so far.

Whether such catalysts will be stable and useful under the conditions of the technical ammonia synthesis remains to be seen—the discovery of this class of catalysts may trigger new developments in reaction technology. On the other hand, challenges for catalyst development can be derived from the conditions under which an improved overall process could operate: substantial energy savings (about 1 GJ per ton of ammonia) could be realized, if the operation pressure could be reduced to the pressure of the synthesis gas stage. This, however, would require lower temperatures as well, in order to achieve sufficiently high conversion.[27] A catalyst enabling this would need to have an activity about two orders of magnitude higher than the magnetite-based systems, which places a significant challenge on catalyst development. Novel catalyst generations, such as the electride-based system, may reach this activity. Also theoretical approaches to predict catalysts with high activity could support such a development, and first steps have been taken.[40] However, beyond activity, as outlined in the introduction, many other factors would decide whether such laboratory results could be transferred to industrial practice.

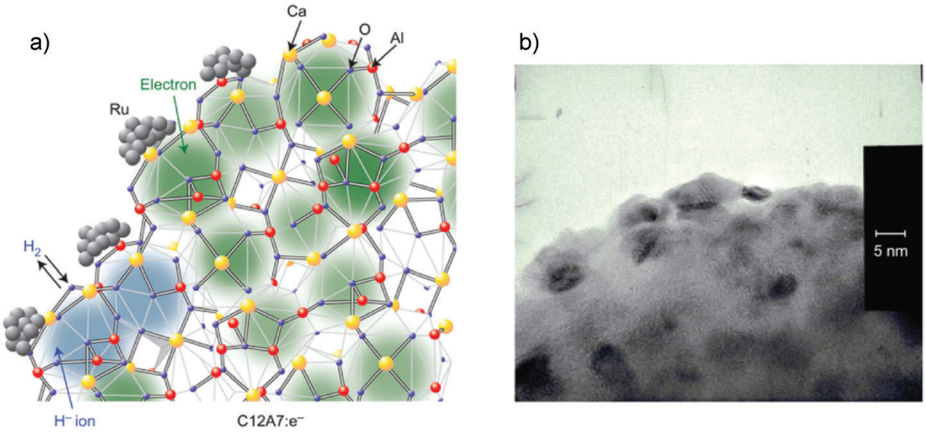


Figure 6. Electride-supported ruthenium catalyst for ammonia synthesis. a) Schematic model of Ru nanoclusters supported on the surface of a C12A7:e⁻ electride. b) TEM micrograph of a catalyst with 0.3 wt% ruthenium loading. Reproduced with permission from Ref. [38].

The ammonia synthesis process allows an interesting comparison: At the beginning of the 20th century, the development of the ammonia process from laboratory to industrial implementation was surprisingly short. The decisive work of Haber on the ammonia synthesis started around 1906, he approached BASF in 1908, in 1913 the first plant was commissioned and started operation. This is an extremely short time, considering, that initially the thermodynamics were not known, no catalyst was available, and also the reaction technology for the process basically had to be developed from scratch. Nowadays, the implementation of a completely new process proceeds on time scales easily exceeding substantially ten years, in spite of all the advances we have made in understanding of the basic principles of catalysis, engineering, in-situ spectroscopies, fluid dynamics simulations, high-throughput experimentation, and other modern tools. It is interesting to briefly analyze why nowadays times from discovery to implementation are substantially longer. Firstly, it is always easier to innovate in an early phase of the development of a field, when technological advances can be leveraged to result in high commercial gains. Nowadays, many processes in the chemical industries have reached a high level of maturity, and even if small improvements may make a big difference due to the high volumes involved, the competition a new process has to face is much more severe than in the early days. For many production routes several alternative technologies are available. Secondly, for the chemical product slate produced today there are plants already running, many of which are fully depreciated, and thus a new process needs to be much superior to compete with already established and well-optimized existing routes. Thirdly, economic differences between different processes are often relatively small and may crucially depend on feedstock costs. These become increasingly difficult to forecast; one can just consider the strongly fluctuating crude oil prices of the last years. In such an uncertain environment, there is an adversity against high investments in novel technology—unless the technology addresses exactly this point—, and this prolongs the decision making process for investing in new technology. Fourthly, the legal framework governing chemical production has become much more complex, and thus the red tape before starting up a new process has become much longer than in the early days of the chemical industry. It is this interplay of different factors which makes the implementation of completely new processes difficult. In catalysis, often the most interesting innovations are "drop-in" solutions, where an improved catalyst can be used in existing plants with just minor modification of the rest of the plant. Although also this entails a risk—the catalysts may not function as expected on the commercial scale—the overall investment and thus the associated financial risk is much smaller than for the implementation of a completely new process. Implementation of new processes can typically be expected if new technology is vastly superior to existing processes. It is also extremely helpful, if the market is actually expanding so that the new technology does not need to push older processes out, but increasing production capacities for certain products are required which entails investment in new plants in any case.

4. Methanol Synthesis

Methanol synthesis is another prototype example how catalyst discovery and reaction engineering went side-by-side to improve overall process performance. In the case of methanol synthesis, the drivers were new developments in process engineering, since the essential active catalyst materials were already known in the 1920s. Industrial catalytic methanol synthesis started with the work of Mittasch and Pier at BASF.[41] Pier used the experimental setup for the ammonia synthesis, and instead of the ammonia synthesis gas he used a feed stream consisting of carbon monoxide and hydrogen. In the original patent, already a number of different possible catalysts are mentioned, including those based on chromium oxide and on copper, even a CuZn alloy is described as active. Again, the reaction is exothermic, proceeds under volume reduction, and is equilibrium limited. Thus, as it concerns to thermodynamics, there are many similarities to ammonia synthesis.

The key for the process development was handling gases under high pressure, and for methanol synthesis the reaction engineering preceded the catalyst development. With the available equipment, different "contact masses" were tested, and a number of active compounds were identified. As in the development of the ammonia catalyst, Alwin Mittasch was a key player.[42] He had already observed methanol synthesis activity for some compositions in the experiments to develop the ammonia catalyst. In the case of methanol synthesis, they were essentially the reaction conditions which eventually determined the choice of the catalyst for the early methanol process. The biggest challenge with respect to the catalyst at that time was the resistance to catalyst poisons. The synthesis gas was produced from coal or lignite, and thus contained chlorine and sulfur, which were detrimental to most of the active masses explored.[43] The best compromise between activity and poison susceptibility was found with a ZnO/Cr_2O_3 system which, however, required operation pressures of 250-350 bar and temperatures of 320–450 °C. Nevertheless, due to the previous work on high-pressure synthesis by Carl Bosch and his team at BASF, technology to handle such conditions was available, and thus processes employing the ZnO/Cr_2O_3 catalyst were the standard technology for more than 40 years.

This changed, when in the 1960s ICI introduced a new process which was based on a $Cu/ZnO/Al_2O_3$ catalyst.[44] These catalysts still form the backbone of the methanol industry today. Numerous studies have been published in which the different factors contributing to activity and stability have been elucidated, although there is still controversy with respect to many aspects of the system. It appears now clear that metallic copper, which typically makes up more than 50 wt % in technical catalyst formulations, is the predominant catalytically active species. One function of the ZnO is to provide good dispersion of the copper. However, the role of ZnO goes beyond that of a conventional support. The ZnO is reported to induce strain in the copper particles, making them more active.[45] Moreover, for high activity, steps seem to be required on the copper surface, ideally in close proximity to positively polarized ZnO_x species.[46] Al_2O_3, present in the commercial catalysts in contents typically

< 15 wt%, is considered a structural promoter which adds to catalyst stability under reaction conditions, likely by hampering the sintering of copper nanoparticles which is considered to be a primary cause of catalyst deactivation.[47] In addition, various further additives can influence the activity or stability of the methanol synthesis catalysts.[48]

The state of the catalyst under reaction conditions may change in response to changes in the gas-phase composition, and both by EXAFS[49] and by in situ TEM[50] could this dynamic catalyst reorganization be observed. Reducing atmospheres favor mutual wetting phenomena between Cu and ZnO phases, whereas at highly reducing conditions, brass is formed. Many protocols have been put forward to prepare methanol synthesis catalysts, the most generally used being the co-precipitation of Cu-Zn-Al hydroxycarbonates, the catalyst precursor, from metal nitrate solutions. The parameters during the precipitation of the hydroxycarbonates, as well as the subsequent aging, calcination and reduction treatments are all highly influential on the properties of the final catalysts, and the exact procedures are a well-guarded trade secret of catalyst manufacturers. Albeit well-optimized and established, a major shortcoming of this synthesis route is the generation of significant volumes of nitrate-contaminated wastewater, and the associated costs of treatment prior to its disposal, which motivates current research and development (R&D) efforts to devise alternative synthesis routes aimed at reducing or eliminating the generation of wastewater while preserving the nano- and microstructures required in high-performance catalysts.[51]

In spite of their delayed industrial application, copper-based catalysts had long been known to be active for methanol synthesis since the 1920s, as mentioned above. The major factors leading to their introduction to industrial practice were not so much the novel catalyst formulations—although the addition of the alumina or other refractory oxides contributed to retard deactivation and therefore extend catalysts lifetime—but the change of the feedstock to natural gas and advances in the purification technology, which reduced sulfur and chlorine concentrations in the synthesis gas feed to very low levels ($H_2S < 100$ ppb).[52] Sulfur compounds are removed from natural gas typically via the Claus process. The sulfur concentration is further reduced in the water-gas-shift step or via scrubbing operations, such as the Rectisol wash which uses methanol washing to reduce sulfur concentrations to the 100 parts-per-billion level. Nowadays many different synthesis gas purifications processes are available, each of them tuned towards specific application fields.[53] In addition, the ZnO component of the catalyst itself has some self-protecting properties, since it reacts with sulfur impurities to form ZnS. Chlorine compounds lead to accelerated catalysts deactivation, since both zinc and copper form chlorides with low melting points and enhanced mobility, which lead to an accelerated copper sintering and thereby loss of active surface area.[54] However, in modern gas purification units, also chlorine levels are reduced to acceptable concentrations, so that nowadays copper–zinc-based methanol catalysts—both due to improvements in the catalyst manufacturing and the process conditions—have a lifetime between two and four years.[43]

Since the formation of methanol is an equilibrium-limited reaction, many process designs use multiple catalyst beds just as in sulfur dioxide oxidation, either with external cooling between beds or internal cooling by injection of cold syngas.[53] However, there are also liquid-phase processes, such as the LPMEOH developed by Air Products.[43] Here, the conventional copper-based catalyst is suspended in powdered form in a high-boiling-point liquid, so that no new catalyst development was required. The advantage of the liquid-phase process is the improved heat transfer, which enables higher pass conversions and allows the recycle ratio to be kept lower than in conventional gas-phase processes. Moreover, liquid-phase processing is compatible with the use of copper nanoparticles as catalysts, which would not be suitable for gas-phase operations. For suspended copper nanoparticles, methanol synthesis activity has been reported at temperatures as low as 170 °C.[55,56] Currently the stability of such colloidal catalysts is certainly insufficient. However, due to the favorable equilibrium at lower temperatures, liquid-phase processes may become more interesting in the future, if catalysts with higher activity at temperatures lower than those used in the gas phase processes (around 240 °C) can be developed.

4.1. Excursion: Catalysts and Reaction Engineering in High-Throughput Experimentation[57]

Methanol synthesis catalysts are one example, in which high-throughput experimentation (HTE) has been used in heterogeneous catalysis.[58] A high-pressure/high-throughput channel reactor was used in that study to explore the synthesis field for $Cu/ZnO/Al_2O_3$ catalysts. Figure 7 illustrates the correlations between precipitation conditions of the catalyst precursors and activity, BET surface area and copper surface area. The reactor used to evaluate the catalyst performance closely resembled conventional plug-flow reactors, it basically consisted of a common feed tube, a passive gas distribution system, 49 parallel channels, and a multiport valve for fast sequential analysis.

Similarly to industrial practice, in high-throughput lab-scale experimentation,[59] catalyst synthesis and conformation are intimately linked to the reactor design. Initially, in HTE two different concepts were pursued. One line of development relied on the use of highly parallelized synthesis and evaluation systems, where the synthesis format was determined by the requirements of the catalytic testing. Following this approach, catalysts are typically prepared in minute amounts on flat substrates, as demanded for a massively parallelized readout of catalytic activity. Examples for it are the thermographic imaging techniques, where small solid samples were typically prepared by sol–gel techniques on slate plates,[60] or scanning mass spectrometry techniques, where the inlet gas was fed through moveable capillaries to the catalyst spot on the substrate, and the product gases were passed to a mass spectrometer.[61] Alternatively, also the substrate plate with the catalysts could be moved in front of a fixed capillary.[62] Such techniques allowed very rapid assessment of the catalytic properties of the solids on the

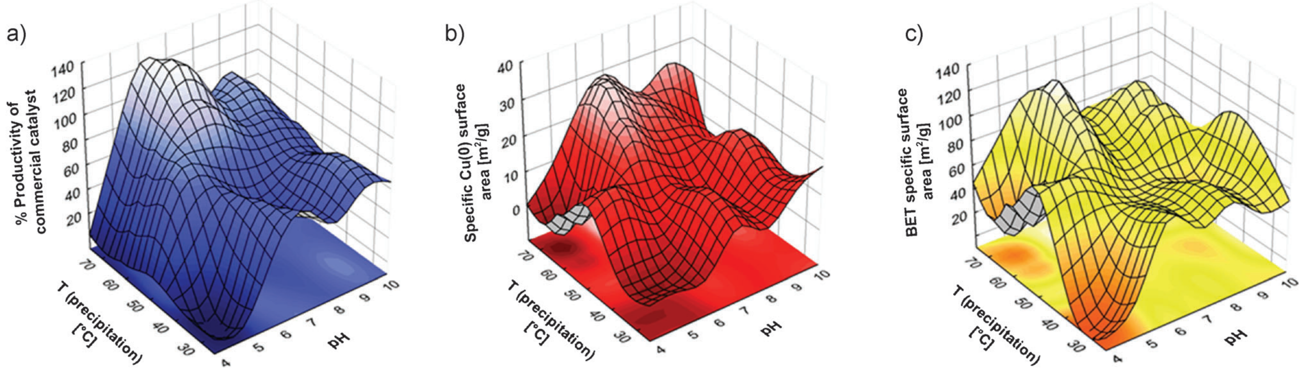


Figure 7. a) Activity, b) copper surface area, and c) BET surface area of a set of $Cu/ZnO/Al_2O_3$ methanol synthesis catalysts for which the precursors were synthesized by co-precipitation at different pH and temperature. The catalytic activity is normalized to a commercial methanol synthesis catalyst as benchmark. Adapted with permission from Ref. [58].

substrate. However, problems such as mass transfer limitations, deviations from isothermicity or scalability of the catalyst synthesis hampered the transfer of the results to technical catalysis.

Thus, almost simultaneously, a second development line of catalysis HTE was followed, where the requirements of technical processes were reflected in the synthesis of the catalyst material and the technologies applied for catalytic performance screening.[58,63–65] The reactors were parallel tubular reactors with approximately the dimensions of laboratory reactors, that is, inner diameters of several millimeters and bed length of several centimeters. Several tens of such channels could be integrated in a common reactor block, with common gas inlets (Figure 8). The outlet streams coming from the parallel reactors were typically fed in a sequential fashion, via multiport valves, into fast analytical instruments. In some cases, parallel analytics was used, such as IR focal-plane array detectors with multi-channel cuvettes[66] or photoacoustic detection devices.[67] However, conventional analytical techniques are more versatile, and thus nowadays IR-spectroscopic methods or (micro) gas chromatography techniques are customarily employed in industrial labs.[68,69] In order to maximize the reliability of the results, great care has to be taken, for instance, during catalyst loading to the miniaturized reactors. Catalysts are normally pressed and ground to a sieve fraction to achieve proper fluid dynamics, and homogeneity of the packing of the catalyst both within one bed and between different beds is of utmost importance. The same holds true for the integration of catalyst and inert dilutants in reactions with a strong thermal signature. Compared to the massively parallelized approaches described above, these methods have the disadvantage of a lower throughput, but the results are more immediately relevant for industrial catalysis. In industrial projects, data quality corresponding to that obtained in pilot plant reactors has been achieved.

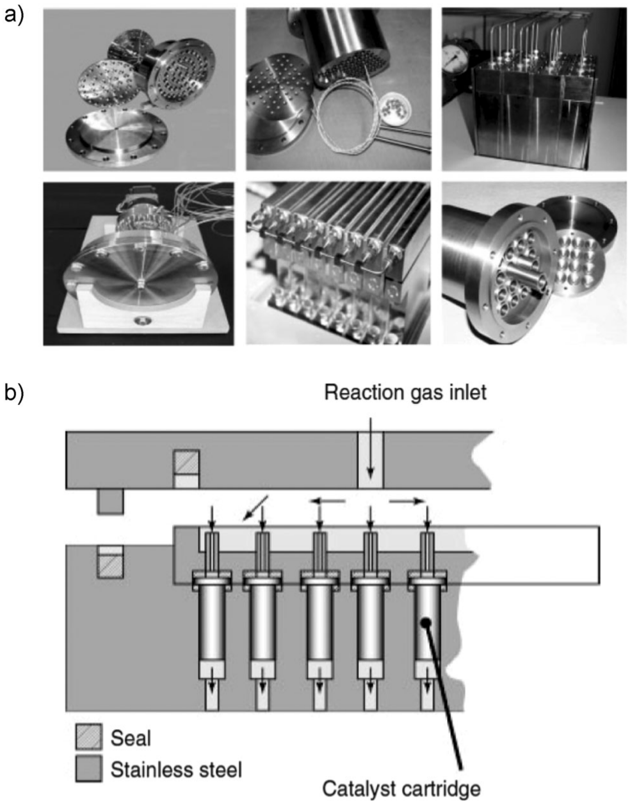


Figure 8. High-throughput experimentation (HTE) reactors. a) Photographs of different HTE reactors developed at the Max-Planck-Institut für Kohlenforschung and hte AG. b) Schematic drawing of a HTE reactor for high-pressure reactions corresponding to the lower left photograph in panel (a). Reproduced with permission from Ref. [59].

The preceding discussion demonstrates that in HTE, reactor technology, analytical systems, and catalyst are intimately connected. If a maximum degree of parallelization is desired, one has to adapt the reactor technology to the needs of the massively parallelized analytical system, and consequently, also the synthesis format of the catalyst is typically far away from conventional catalyst preparation. If, on the other hand, one would like to stay close to industrial-type reactors and their engineering solutions, conventional catalyst types can be employed, but the degree of parallelization is limited—although several ten parallel reactors are routine in industrial laboratories. About 15 years after the first publications on the use of HTE technologies in heterogeneous catalysis, it seems that the market has decided on the second approach, which was first employed commercially by hte Aktiengesellschaft, Heidelberg. Hence, currently most industrial HTE projects rely on the use of catalyst morphologies and reactor configurations (e.g. fixed-bed reactors) which resemble more closely what is customary in industrial practice. This way, transferability and upscaling of HTE results are facilitated, though at the expenses of parallelization. BASF was one of the early supporters of and investors in hte Aktiengesellschaft, and since 2012, hte—now as a limited company—was fully acquired by BASF and is now a 100 % BASF subsidiary, serving the needs of BASF with respect to HTE technology, but also running projects with external partners.

5. Fluid Catalytic Cracking

The process of catalytic cracking is at the core of the refinery industry, where it has been playing a central role as the primary conversion process for 80 years.[70] Modern fluidized catalytic cracking (FCC) processes are operated in over 400 refinery sites worldwide and process millions of cubic meters of hydrocarbon feedstocks daily. In addition, the historical evolution of this process represents both the prime example of the impact of heterogeneous catalysis in the oil industry as well as a seminal lesson in chemical reactor engineering, being the origin of several reactor concepts which remain in use in various catalytic processes.

In the early 1910s the introduction of the Burton oil thermal cracking process signified a notable advancement with respect to previous technologies adapted from coal tar cracking. It enabled improving the yields to gasoline products, which started to be increasingly demanded as transportation fuels. Despite earlier attempts to apply $AlCl_3$ homogeneous catalysts in petroleum cracking, oil catalytic cracking is considered to commence with the introduction of the Houdry process in the 1930s. Testing commercial samples supplied by Filtrol, a company at that time dedicated to the decolorization of lubricant oils, Eugene Houdry first discovered the outstanding properties of acid-leached clays as solid cracking catalysts to increase the yield and quality of the gasoline product fraction obtained from oil processing. In 1936, Socony-Vacuum revamped a thermal cracking unit in Paulsboro (New Jersey, US) to apply the Houdry process, in what can be considered the first commercial catalytic cracking unit. Ever since, the process has been the niche for noteworthy innovations in the fields of heterogeneous catalysis and reactor engineering, which have had implications also for the development of a number of other catalytic processes.

Cracking catalysts have evolved dramatically since the first implementation of the Houdry process. Shortly after the first application of acid-treated clays as solid catalysts, synthetic amorphous silica-alumina catalysts were developed as a means to gain additional control over structural and catalytic features.[71] Initially, silica-alumina materials were developed with alumina contents up to about 15 wt %. Later on, in the mid-1950s, American Cyanamid introduced materials with a higher alumina content, up to 25 %, which displayed wider pores and higher mass-specific catalytic activity than their low-Al counterparts. The advent of fluidized-bed reactors, in the early 1950s, required the catalysts to be shaped as attrition-resistant microspheres. This introduced spray-drying technologies, which were applied to conform catalysts based on an amorphous silica-alumina material as the main active component, along with a clay (typically kaolin) matrix and binder additives.

The most revolutionary advancement in catalytic cracking, and one of the key milestones in the history of catalysis, was the introduction by Mobil of the first zeolite-based catalysts in the early 1960s. The initially selected zeolite X was shortly after replaced by zeolite Y, which has hitherto remained unrivaled as the main active component in cracking catalysts. Work of Rosinski and Plank at Mobil[72] led to the introduction of rare-earth-exchanged zeolites, which improved the catalytic activity and stability of the zeolite component under the steaming conditions encountered during catalyst regeneration. Only four years after the first zeolite-based FCC catalysts came to market, they were already used in about 85 % of the existing units, a remarkably fast adaptation for a traditionally prudent industry.

By the early 1980s the FCC technology was widespread and catalyst market amounted to over $130 million per year, dominated by suppliers such as Grace, Filtrol, and Engelhard. Catalyst manufacturing methodologies operated at Grace and Filtrol involved the spray-drying of a suspension containing the rare-earth-exchanged zeolite that was crystallized in advance, treated clay, and binder components. The resulting microspheres were subjected to "finishing" thermal treatments to improve their mechanical properties. (Figure 9). The synthesis strategy developed by Engelhard was fundamentally different. In this case, kaolin clay was first spray-dried followed by calcination treatments to obtain mechanically robust and porous kaolin microspheres. In a subsequent step, silicon and aluminum nutrients were introduced and the zeolite was hydrothermally crystallized in situ on the pore walls of the clay particles (Figure 9). Ion exchange and thermal treatments led to the final FCC catalyst. These remain the two main synthesis approaches for commercial FCC catalysts.

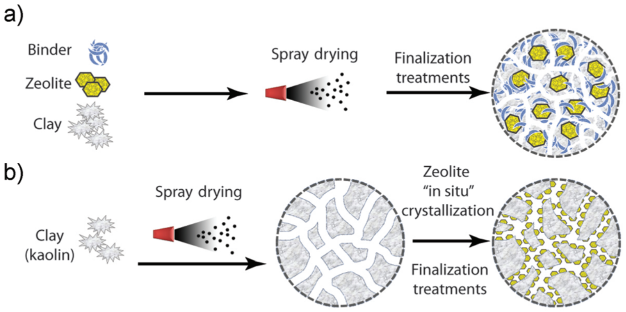


Figure 9. Illustrative schemes of common synthesis routes to manufacture industrial FCC catalysts. a) Spray-drying conformation of multicomponent FCC particles. b) The Engelhard in situ zeolite crystallization approach.

The development of solid catalysts displaying increasingly higher activities and different selectivities to various product slates has mandated a synergetic evolution of cracking reactor designs over time. Owing to the particularly fast catalyst deactivation encountered in cracking operations, reactor conception has been largely determined by the competition between the cracking and coking reactions and the heat integration between these endo- and exothermic reactions. The original Houdry process operated a fixed-bed multitubular reactor, filled with millimeter-sized catalyst pellets. A molten-salt heat-exchange system provided heat integration, whilst a swing reactor unit allowed switches between operation and catalyst regeneration within minutes, a time frame which was compatible with the deactivation rate of clay catalysts. However, major concerns of this design included variations in the effective contact time as catalyst deactivation proceeded and a non-uniform distribution of the temperature during the regenerative combustion cycle. In response to these issues, moving-bed reactors were implemented in the so-called Thermofor catalytic cracking (TCC) process. With this technology, a rather constant reactant-catalyst residence time could be achieved. Nonetheless, as for the previous fixed-bed configuration, catalyst particles were in the millimeter size range, which continued to introduce heat and mass transfer limitations during coke burning, setting limits to the regeneration temperature, increasing the size of the regenerator, and thereby the catalyst holdup.[73] Albeit not so important at that time as it is nowadays, a large catalyst inventory reduced notably the flexibility of the TCC process to respond to fluctuations in the nature of the feedstock or the product market scenarios.

In part as a means to develop a process that would neither pay royalties nor infringe the patents on the fixed-bed and moving-bed Houdry processes, a consortium of American companies came up with the idea of devising a reactor technology using a powdered catalyst.[71] As a result, the first fluidized-bed reactors were introduced in the mid-1940s, giving name to the FCC process as we know it today (Figure 10). This reactor design employs spherical catalyst microparticles, typically in the 10–150 μm range, which are fluidized in contact with the hydrocarbon feed. Solid catalyst circulation rates can be improved with respect to the moving-bed predecessor design, whereas the micrometer-sized catalyst particles allow faster regeneration due to enhanced mass and heat transfer kinetics. Moreover, the excellent heat transfer properties of fluidized solid beds enable a closer-to-isothermal operation, at higher reaction temperatures—and shorter contact times—while ensuring efficient heating of the feed by the catalyst particles leaving the regenerator. As a result, the FCC technology soon started to replace the previous technologies. An additional thrust was the substitution of amorphous silica-alumina-based catalysts by zeolite-based catalysts. The superior activity of zeolites and their faster deactivation rate made it desirable to operate with shorter residence times and fast reaction-regeneration cycling, the features offered by the fluidized-bed reactors. Further, continuous improvements in the catalyst activity resulted in the cracking reaction being eventually completed in the riser transfer line which connected the regenerator and the reactor vessels. Again, this brought about reactor engineering solutions, with the design of riser-cracker fluidized-bed reactors, in which the riser is elongated and the original reactor chamber simply houses cyclones and stripper subunits through which the spent catalyst circulates towards the regenerator (Figure 10). With this new design, which is widely operated in modern FCC facilities, contact times smaller than 5 seconds are customary, that is, orders of magnitude shorter than with the initial fixed-bed reactor configurations. This provides yet another example for the catalyst–reactor co-evolution necessary to develop and optimize industrial catalytic processes.

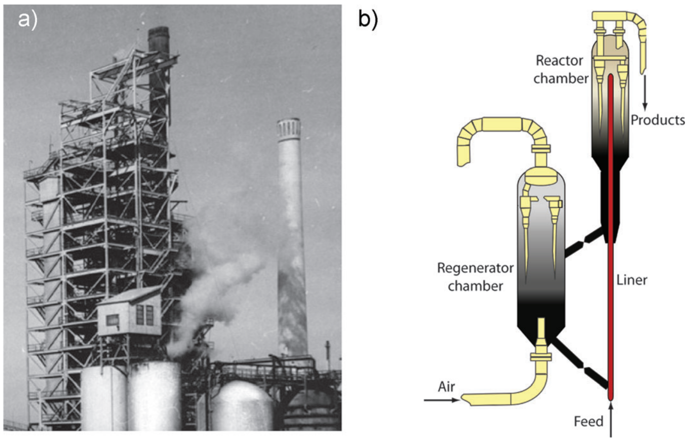


Figure 10. a) Photograph of one of the first FCC units installed in US in the 1940s. b) Schematic representation of a modern, riser-reactor FCC unit.

At present, the FCC process is a mature technology, although continuous innovations in various engineering aspects still continue, primarily driven by advancements in modeling and simulation capabilities. Besides, adaptations to the evolution of feedstocks and product demands require reactor engineering activities to accompany catalyst innovations. As a prime example, light olefins, most notably propylene, are increasingly demanded nowadays as petrochemical feedstocks. This has translated into a growing number of refiners which target higher short-olefin products from their FCC units to maximize revenues. While catalyst manufacturers offer new high-propylene-yield formulations, for example, incorporating higher contents of olefination co-catalysts such as ZSM-5 zeolite, higher yields to the C_4 hydrocarbon cut require also new designs (or alterations) for several subunits of the FCC reactor to capture the incremental propylene yield.[74] In addition to reactor re-designs, downstream units might also require adaptations to cope with increased flow rates of light olefin products and thereby debottleneck the overall process.

The adaptations of the FCC process driven by changes in feedstock availability and product markets are also motivating activities in the field of catalyst development. In 2011, the market volume of FCC catalysts amounted to about 32 % of the refinery sector and circa 10 % of the entire catalysts market, with annual revenues of around $2 billion and a projected growth rate of about 3 % in the present decade.[75] After acquisition of Engelhard Corporation in 2006, BASF entered the list of the top three suppliers of FCC catalysts in the world. Presently, the company continues to strengthen its position in the strategic FCC sector and to introduce new catalyst technologies. Illustrative of these activities are the start-up of a FCC testing and research laboratory at the facilities of hte Aktiengessellschaft in Heidelberg (Germany) and the strategic alliance signed with Shell in 2013 to supply FCC catalysts for the global refining activities of the Anglo-Dutch oil company.[76]

Important lines of catalyst development target the design of novel catalysts able to maximize the yield to propylene or having lower lanthanide contents, in response to the instability of the rare-earth markets.[77] In addition, research efforts are also devoted to develop new strategies to improve control over secondary mesoporosity in the zeolitic active phases, which allows more efficient processing of heavier feedstocks. These approaches are not limited to steaming and demetallation strategies, which are intuitively more suitable for large-scale production. Recently, researchers at Rive Technology, a spin-off company of the Massachussets Institute of Technology (US), reported the successful up-scaling, in cooperation with Grace, of a catalyst production procedure based on mesoporous zeolite Y obtained by a surfactant-templating route.[78] Another important goal of current R&D activities is to gain improved control over the spatial distribution of different components within the catalyst microspheres. Albemarle, another prime FCC catalyst supplier, in partnership with the Weckhuysen group at Utrecht University are currently actively developing strategies based on (correlative) microspectroscopic methods to visualize the spatial distribution of the various catalyst components as well as to identify preferential poison deposition sites within FCC particles.[79] Along similar lines, one of the latest innovations incorporated to the BASF's FCC catalyst portfolio includes the so-called multi-stage reaction catalysts (MSRC). This manufacturing technology is claimed to enable the incorporation of several functionalities in a spatially controlled manner within the catalyst particles. Such catalyst engineering can offer control over the order in which consecutive cracking reactions take place or result in a more effective protection of active components from metal poisons.[80]

6. Direct Epoxidation of Propylene with Hydrogen Peroxide

Essentially all the propylene produced for chemical purposes is consumed as an intermediate in other chemical manufacturing processes. Propylene oxide (PO), which is produced by propylene epoxidation, is among the most demanded organic chemicals, with a current worldwide market capacity exceeding 7 Mt per year. PO is a reactive and versatile compound which serves as feedstock for the production of polyether polyols for urethanes, propylene glycols, and glycol ethers, subsequently used as starting building blocks for the production of a wide array of chemicals and polymers.

Processes of propylene epoxidation to propylene oxide have been operated at an industrial scale for more than a century and their historical evolution represents another prototypical case of how advancements in heterogeneous catalysis have contributed to improve the efficiency and reduce the environmental footprint of the chemical industry.[81] The earliest propylene epoxidation industrial process, which remains operated today, is based on the non-catalytic dehydrochlorination of chlorohydrines in the liquid phase. A major concern of this route is the co-production of a large amount of chlorine salts brine, the disposal of which requires extensive treatments. In the early 1970s, new chemical processes based on the use of oxygen as oxidant and organic hydroperoxides as intermediate oxygen "couriers" came into commercial operation. In these processes, organic hydroperoxides are synthesized in a first stage, by partial oxidation of, for example, isobutene or ethylbenzene, and subsequently employed as propylene epoxidation reagents on either soluble metal complexes or solid catalysts. Despite the catalytic nature of the second stage, overall, stoichiometric amounts of either *tert*-butanol or 1-phenylethanol, which can be subsequently dehydrated to styrene, are obtained as side-products. To eliminate by-products, Sumitomo developed a process in the early 2000s, based on the same concept, although applying cumene hydroperoxide as intermediate. In this process, the by-product of the propylene epoxidation step is cumyl alcohol, which can be conveniently dehydrated and hydrogenated back to cumene and recycled to the process inlet. PO is the only product overall, whereas only small cumene losses need to be compensated with a makeup feed stream.

Solid catalysts employed at the propylene epoxidation step in processes based on organic hydroperoxides typically consist of amorphous, mesoporous titanosilicates.[82] These catalysts are generally passivated by surface silylation treatments in order to create a hydrophobic environment in the vicinity of the active titanium sites, which improves the selectivity to PO by favoring its rapid desorption and preventing secondary reactions, particularly ring-opening to propylene glycol, which can be catalyzed by surface acidic groups.

Despite the successful operation of organic hydroperoxide technologies for decades, the direct use of hydrogen peroxide (H_2O_2) as epoxidation reagent is highly desired from both economic and environmental standpoints. In recent years, commercial-scale processes for the direct epoxidation of propylene with H_2O_2, generally referred to as HPPO processes, have become a reality thanks to quantum-leap innovations in heterogeneous catalysis accompanied by reactor engineering and process conception efforts.

In the early 1980s researchers at Eni first reported the synthesis of titanium silicalite-1 (TS-1),[83] a crystalline titanosilicate with MFI-type zeolitic structure. TS-1 was found to be an efficient solid catalyst for the epoxidation of propylene with H_2O_2, allowing the reaction to proceed in liquid media at mild temperatures ($< 60\,°C$) with, in principle, water as the only by-product (Figure 11). This discovery supposed an important incentive to develop a commercial HPPO process. However, owing to the peculiarities introduced by both the novel zeolitic catalyst and the use of H_2O_2 as oxidation reagent with respect to existing epoxidation technologies, significant and parallel catalyst, reactor, and process engineering efforts have been necessary to translate the break-

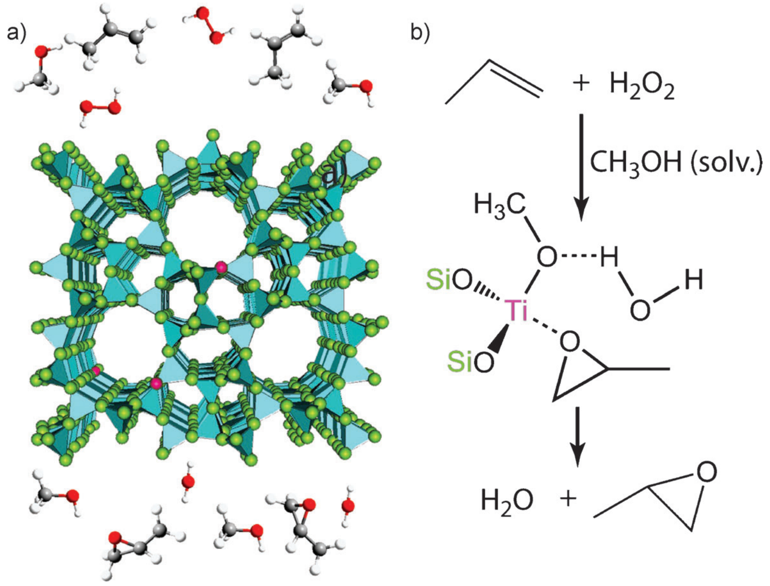


Figure 11. a) Structural model of the TS-1 propylene epoxidation catalyst, adapted with permission from Geoffrey Price.[84] b) Schematic representation of a proposed reaction mechanism on framework Ti atoms, adapted with permission from Ref. [97].

through discovery by Eni researchers into a large-scale chemical process.

The structure of TS-1 is built from SiO_4 and TiO_4 tetrahedra, which define a three-dimensional microporous system with straight channels (0.53 Å × 0.56 Å) intersecting sinusoidal channels (0.51 Å × 0.55 Å).[85] Even though the actual reaction mechanism remains debated, a general consensus exists that the epoxidation functionality is owed to tetrahedrally coordinated Ti^{IV} atoms incorporated into the zeolite framework (Figure 11). Under standard synthesis conditions, the maximum content of such framework Ti species is typically limited to about two to three Ti atoms per unit cell, whereas any surplus of Ti tends to segregate as extra-framework TiO_x species and TiO_2 precipitates, species which were deemed detrimental for the catalytic performance. In addition, the fully coordinated silicate framework of the zeolite creates a confined, hydrophobic environment in the neighborhood of the active sites which, in analogy to surface silylation in the amorphous, mesoporous solid catalysts used in conventional epoxidation processes, plays a central role in enhancing the selectivity to PO.[85] On the contrary, zeolite framework defects are unwanted, as their slightly acidic character promotes secondary reactions which lower the PO yield and contribute to catalyst deactivation. Moreover, owing to the likelihood of encountering diffusional constraints in liquid-phase catalysis, the zeolite crystallite size and/or the presence of secondary mesoporosity have been long considered catalytically relevant structural features. Such a multivariable landscape prompted extensive R&D efforts to optimize the structure of TS-1 catalysts for propylene epoxidation, alongside developing synthesis procedures compatible with industrial-scale production.

The standard synthesis procedure for TS-1 involves the hydrothermal treatment of pre-hydrolyzed Ti and Si precursors in the presence of tetrapropyl ammonium hydroxide (TPAOH) as structure-directing agent. Despite Si and Ti alkoxides represent ideal precursors in such a sol–gel synthesis route, research has been focused towards their substitution by alternative, less costly compounds such as $TiOCl_3$ or even rutile (for Ti) and fumed or colloidal SiO_2 (for Si).[86] On the same grounds, researchers at Evonik developed a synthesis route based on spray pyrolysis of volatile $TiCl_4$ and $SiCl_4$ precusors, followed by a hydrothermal treatment of the resulting mixed oxide in the presence of TPAOH.[87] As for the crystallization of other zeolites incorporating heteroatoms in lattice positions, the absence of alkali cations in the synthesis gel was reported essential.[86] This also poses a challenge for the industrial-scale production of TS-1, due to the high costs of alkali-free TPAOH solutions. An alternative approach was developed by the group of Ullrich Müller at BASF,[88] which employed tetrapropyl ammonium bromide (TPABr), less expensive to be obtained as an alkali-free reagent than TPAOH, as structure-directing agent. In this case, the synthesis gel requires significant amounts of NH_4OH as alkalinizing agent.

As a means to improve accessibility to the framework Ti sites, synthesis methodologies have been developed to reduce the zeolite crystal size, down to the submicron range. For example, the group of Tatsumi (Tokio) achieved TS-1 nanocrystals through control over the crystallization kinetics;[89] Serrano et al.[90] used silanization of zeolitic seeds to limit crystal growth; researchers at BASF have patented the application of spheroidal dispersions of polyacrylates to achieve uniform TS-1 nanocrystals;[91] while Ryoo and coworkers[92] synthesized TS-1 nanosheets using a modulated structure directing agent with long alkyl chains. Routes to introduce mesoporosity through either templating or demetallizing strategies have also been put forward.[86] The ultimate catalytic performance in propylene epoxidation was, nonetheless, deemed to result from an interplay between accessibility of the active Ti framework sites and the hydrophobicity of the zeolite, which is undesirably decreased upon decreasing the crystal size or introducing mesoporosity as these approaches usually result in a higher density of lattice defects and surface silanol groups. For industrial application, the TS-1 active component must be conformed into macroscopic bodies incorporating also a binder material. Acidity needs to be also avoided in the binder material to prevent secondary acid-catalyzed reactions which lower the selectivity to PO.[93]

In the course towards industrial operation, catalyst development has gone hand-in-hand with reactor and process engineering. In 2002, EniChem, today Polimeri Europa, set up a prototype plant in Italy to explore the application of TS-1 catalysts in a prospective commercial process. Soon thereafter, Evonik (formerly Degussa) in partnership with the engineering company Uhde, as well as Dow Chemicals and BASF, first independently and in joint venture after 2003, initiated R&D programs towards the conception and implementation of an industrial HPPO process. The new process introduces significant variations with respect to the existing technologies, which extend from catalyst structure and functionality to the nature of the oxidation reactant, and which needed to be thoroughly addressed during process conception. Solvent selection and optimization of solvent-to-reactants ratio in the feed stream have been claimed essential to achieve single-liquid-phase operation and prevent segregation of the hydrophobic propylene and the hydrophilic H_2O_2 reactants.[94]

Propylene epoxidation is a remarkably exothermic reaction ($\Delta H_r^0 \approx -213\ \text{kJ mol}^{-1}$). Hence, heat-transfer considerations are of utmost importance for reactor design. While this is a common characteristic of all epoxidation processes, it becomes accentuated in the HPPO process. Unlike organic hydroperoxides employed as oxidants in classical PO manufacturing processes, which are relatively stable thermally—they are synthesized through partial oxidation reactions at temperatures up to 150–200 °C[81]—H_2O_2 decomposition occurs readily at moderate temperatures. The apparent activation energy for H_2O_2 decomposition on (Ti)SiO_2 oxides (about 40 kJ mol^{-1} [95]) is higher than that for the propylene epoxidation reaction (about 26 kJ mol^{-1} [96]), indicating that an increase in the reaction temperature benefits the undesired reactant decomposition. Additionally, higher temperatures promote ring-opening side-reactions which have a negative impact on the selectivity to PO. The reaction is therefore performed at mild temperatures (reportedly lower than 60–80 °C), while it is critical to prevent higher temperatures in the reactor and particularly the creation of hot-spots.[97]

These considerations have required dedicated reactor conception and engineering for the HPPO process. While stirred-tank reactors were applied in the stages of catalyst development and optimization of reaction conditions, packed-bed, trickle-bed or heat-exchanger reactor configurations are preferred for large-scale, continuous operation. Using jacketed multi-tubular reactors, like those often described for propylene epoxidation processes based on organic hydroperoxides, researchers at Degussa reported on the need for adequate dilution of the TS-1 catalyst with inert material to prevent hot-spots during operation.[98] Along similar guidelines, Dow and BASF developed jointly several reactor configurations, based on integration of reaction with plate-type heat exchangers, designed to achieve isothermal operation in the HPPO process.[99] With the same goal of improved heat transfer, researchers at BASF have patented procedures for the direct crystallization of the TS-1 zeolite catalyst on the surface of thermally conductive, metallic gauzes.[100] Applying a two-step reactor concept with intermediate heat-exchange and PO separation stages (Figure 12), the HPPO process jointly developed by Dow and BASF has been claimed to reach nearly quantitative H_2O_2 conversion with $>94\,\%$ selectivity to PO.[94] Moreover, the microporus structure of TS-1 catalysts is expected to be more prone to deactivation than mesoporous TiO_x/SiO_2 catalysts used in conventional processes of PO production.[101] Secondary reactions such as the hydrolysis of PO may result in the formation of (poly)glycols or 2-methoxypropanol. Side-reactions of the methanol solvent might also produce methylformate. Some of these products are likely to remain retained within the narrow zeolite channels, leading to pore blockage and catalyst deactivation. Consequently, in connection to reactor conception, suitable regeneration processes have been developed. In this respect, Evonik claimed reflux with

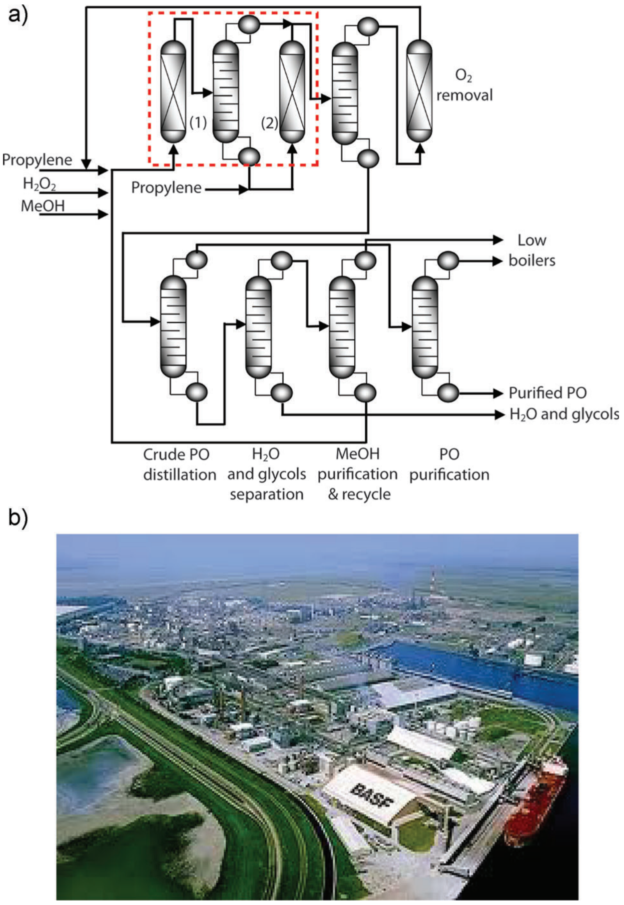


Figure 12. a) Flow chart of the HPPO process developed by Dow and BASF, adapted from.[94] The two-reactor core of the process is framed in red. b) Overview photograph of the BASF complex in Antwerp (Belgium).

H_2O_2 to allow full recovery of the original catalytic activity.[102] Alternatively, patents filed by BASF disclose methods involving controlled oxidation of organic residues in a stream of diluted O_2 or alternative oxidants such as O_3 or nitrogen oxides.[103] It should be noted that the above discussions on catalyst and reactor design are based on published scientific and patent literature, whilst the final commercialized process and proprietary catalysts might differ from what is in public domain.

Several years of advancements in catalyst, reactor, and process engineering have taken the HPPO process to a fully commercial scale. Since 2008, the Korean company SKC has produced more than 100 Mt per year PO in Ulsan (South Korea) using the HPPO technology developed by Degussa-Evonik and Uhde. Shortly after, Dow and BASF inaugurated a HPPO facility in Antwerp (Belgium). The site includes a world-scale unit which produces 230 kt per year of H_2O_2 using the Solvay anthraquinone process and has a nominal PO capacity of 300 Mt per year.[94] In 2011, an even larger facility operating the same technology was commissioned in Map Ta Phut (Thailand), whereas an additional HPPO plant is currently under construction in the Jubail industrial city (Saudi Arabia).

With respect to classical PO processes, modern HPPO technologies avoid the need to co-process a side-product and simplify separation and product purification stages owing to the high selectivity of the reaction step, which lowers equipment requirements and represents savings in capital investments. Reductions of 70–80% in the production of wastewater have also been claimed,[94] which further contribute to reduce installation footprint and capital costs. Besides, the production of water as the only side-product eliminates the need for additional, stable markets to commercialize other by-products. Currently, over 1 million tons per year propylene oxide is produced using the HPPO technology, and this process is expected to constitute an increasingly higher share of the worldwide PO production in the coming years, at the expense of technologies leading to by-products and particularly the classical chlorohydrines-based process (Figure 13).

Beyond the HPPO technology, a highly sought-after target remains the development of efficient propylene epoxidation processes based on either the (in situ) synthesis of H_2O_2 from H_2 and O_2 followed by propylene epoxidation, or the direct epoxidation of propylene with O_2, in analogy to the existing process for ethylene. Significant R&D efforts are currently committed to this goal, and innovations in the field of solid catalysts, for example, based on advanced control over sub-nanometer metallic clusters[105] or nanoscale spatial compartmentalization of different catalytic functionalities,[106] continuously provide moderate steps forward which, nevertheless, have not yet sufficed to justify commercial interest. In the event that a future breakthrough in heterogeneous catalysis would bring such processes within reach, reactor engineering will undoubtedly play a pivotal role towards commercial realization, which includes providing safe approaches for reactions such as the direct oxidation of H_2 or propylene with O_2.

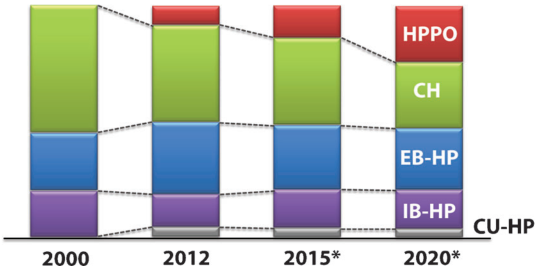


Figure 13. Predicted evolution of the relative worldwide capacity of existing propylene epoxidation processes. *:estimated data. HPPO: Direct epoxidation of propylene with hydrogen peroxide; CH: Chlorohydrines-based process; EB-HP: ethylbenzene hydroperoxide process; IB-HP: isobutene hydroperoxide process; CU-HP: cumene hydroperoxide process. Adapted from Ref. [104].

7. Concluding Remarks

Large-scale industrial processes never have a single root. They can be realized because different disciplines join forces to achieve success. In the development of catalytic processes, catalysis research and reaction engineering are two indispensable elements which have to come together before an industrial process is implemented. Often a new catalyst opens new process options, such as TS-1 which started the development of the HPPO processes, but the situation can also be reversed. The high-pressure catalytic processes implemented in the early decades of the 20th century all relied on the high-pressure technology developed for the ammonia synthesis, and only due to the availability of the tools and techniques to handle these conditions could novel catalysts enter commercial exploitation. This Yin and Yang of catalytic process development is an integral and integrating element of the chemical industries, where science and engineering join hands, and the earlier the interaction between the disciplines starts, the easier will the process development be in the later stages. Research and development at BASF is a prime example for the fruitfulness of this approach, and what has been beneficial to the company for 150 years will not lose its value also in the decades to come.

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[1] a) *Re-Engineering the Chemical Processing Plant: Process Intensification* (Eds.: A. Stankiewicz, J. A. Moulijn), Marcel Dekker, New York, **2004**; b) J. Gascon, J. R. van Ommen, J. A. Moulijn, F. Kapteijn, *Catal. Sci. Technol.* **2014**, DOI: 10.1039/C4CY01406E.

[2] H. Müller in *Sulfuric Acid and Sulfur Trioxide. Ullmann's Encyclopedia of Industrial Chemistry* (Eds.: G. Bellussi), Wiley-VCH, Weinheim, **2000**, pp. 141–211.

[3] L. J. Friedmann, S. J. Friedmann, *AIChE Clearwater Convention*, Paper 8.2.7, AIChE Boca Raton, Florida, **2008.** http://www.aiche-cf.org/Clearwater/2008/Paper2/8.2.7.pdf.

[4] C. Winkler, *Dinglers Polytech. J.* **1875**, *218*, 128.

[5] R. Knietsch, *Ber. Dtsch. Chem. Ges.* **1901**, *34*, 4069 – 4115.

[6] German patent (BAS AG), DE 291 792, **1913**.

[7] N. Neth, G. Kautz, H.-J. Huster, U. Wagner, *Chem. Ing. Tech.* **1979**, *51*, 825.

[8] A. Christodoulakis, S. Boghosian, *J. Catal.* **2003**, *215*, 139 – 150.

[9] P. Mars, J. G. H. Maessen, *J. Catal.* **1968**, *10*, 1 – 12.

[10] S. G. Masters, A. Chrissanthopoulos, K. M. Eriksen, S. Boghosian, R. Fehrmann, *J. Catal.* **1997**, *166*, 16 – 24.

[11] T. R. Felthouse, A. Bino (Mscs. Inc.), WO 2007/035949A2, **2007**.

[12] http://www.sulphuric-acid.com/techmanual/contact/contact_catalysts_basf.htm, accessed on October 1st, 2014.

[13] http://www.topsoe.com/products/vk-38-daisy, accessed on October 1st, 2014.

[14] F. Näumann, M. Schulz in *Handbook of Heterogeneous Catalysis* (Eds.: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp), Wiley-VCH, Weinheim, **2008**, pp. 2623 – 2635.

[15] P. E. Queneau, *Metall. Trans.* **1977**, *8*, 357 – 369.

[16] J. Adlkofer, E. Diekmann, E. Winkler, *Sulphur* **1993**, *229*, 50 – 52.

[17] A. Wingen, N. Anastasievic, A. Hollnagel, D. Werner, F. Schüth, *J. Catal.* **2000**, *193*, 248 – 254.

[18] a) J. Loskyll, K. Stöwe, W. F. Maier, *Sci. Technol. Adv. Mater.* **2011**, *12*, 054101 – 054109; b) J. Loskyll, K. Stöwe, W. F. Maier, *ACS Comb. Sci.* **2013**, *15*, 464 – 474.

[19] C. Bosch, *Nobel Lecture, May 21st, 1932, Nobel Lectures, Chemistry 1922 – 1941*, Elsevier Publishing Company, Amsterdam, **1966**, pp. 197 – 241.

[20] F. Haber, R. Le Rossignol, *Z. Elektrochem.* **1913**, *19*, 53 – 108.

[21] F. Haber, G. van Oordt, *Z. Allg. Anorg. Chem.* **1905**, *44*, 341 – 378.

[22] R. Schlögl in *Handbook of Heterogeneous Catalysis* (Eds.: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp), Wiley-VCH, Weinheim, **2008**, pp. 2501 – 2575.

[23] R. Schlögl, *Angew. Chem. Int. Ed.* **2003**, *42*, 2004 – 2008; *Angew. Chem.* **2003**, *115*, 2050 – 2055.

[24] G. Ertl, *Angew. Chem. Int. Ed.* **2008**, *47*, 3524 – 3535; *Angew. Chem.* **2008**, *120*, 3578 – 3590.

[25] T. Kandemir, M. E. Schuster, A. Senyshyn, M. Behrens, R. Schlögl, *Angew. Chem. Int. Ed.* **2013**, *52*, 12723 – 12726; *Angew. Chem.* **2013**, *125*, 12955 – 12959.

[26] D. W. Allen, W. H. Yen, *Ammonia Plant Saf.* **1973**, *15*, 96.

[27] M. Appl, *Ammonia, 2. Ullmann's Encyclopedia of Industrial Chemistry* (Ed.: G. Bellussi), Wiley-VCH, Weinheim, **2011**, pp. 139 – 225.

[28] "Poisoning of ammonia synthesis catalysts": P. E. H. Nielsen in *Ammonia: Catalysis and Manufacture* (Ed.: A. Nielsen), Springer, Berlin, **1995**, pp. 191 – 198.

[29] M. Appl, *Ammonia, 3. Ullmann's Encyclopedia of Industrial Chemistry* (Ed.: G. Bellussi), Wiley-VCH, Weinheim, **2011**, pp. 227 – 261.

[30] a) K.-I. Aika, K. Tamaru in *Ammonia: Catalysis and Manufacture* (Ed.: A. Nielsen), Springer, Berlin, **1995**, pp. 103 – 148; b) O. Hinrichsen, *Catal. Today* **1999**, *53*, 177 – 188.

[31] P. J. Shires, J. R. Cassata, B. G. Mandelik, C. P. van Dijk, US 4479925A, **1984**.

[32] G. S. Benner, J. R. Le Blanc, J. M. Lee, H. P. Leftin, P. J. Shires, C. P. van Dijk, US 4568532A, **1986**.

[33] http://www.kbr.com/Technologies/Process-Technologies/KBR-Advanced-Ammonia-Process/, accessed October 3rd 2014.

[34] Z. Kowalczyk, J. Sentek, S. Jodzis, R. Diduszko, A. Presz, A. Terzyk, Z. Kucharski, J. Suwalski, *Carbon* **1996**, *34*, 403 – 409.

[35] A. K. Rhodes, *Oil Gas J.* **1996**, *94*, 37 – 41.

[36] H. Bielawa, O. Hinrichsen, A. Birkner, M. Muhler, *Angew. Chem. Int. Ed.* **2001**, *40*, 1061 – 1063; *Angew. Chem.* **2001**, *113*, 1093 – 1096.

[37] S. Dahl, E. Törnqvist, I. Chorkendorff, *J. Catal.* **2000**, *192*, 381 – 390.

[38] M. Kitano, Y. Inoue, Y. Yamazaki, F. Hayashi, S. Kanbara, S. Matsuishi, T. Yokoyama, S. W. Kim, M. Hara, H. Hosono, *Nat. Chem.* **2012**, *4*, 934 – 940.

[39] S. Matsuishi, Y. Toda, M. Miyakawa, H. Hayashi, T. Kamida, M. Hirano, I. Tanaka, H. Hosono, *Science* **2003**, *301*, 626 – 629.

[40] J. K. Nørskov, T. Bligaard, J. Rossmeisl, C. H. Christensen, *Nat. Chem.* **2009**, *1*, 37 – 46.

[41] A. Mittasch, M. Pier (IG Farben), DE 565 309, **1923**.

[42] K. Becker, *Chem. Ing. Tech.* **2013**, *85*, 1824 – 1834.

[43] P. J. A. Tijm, F. J. Waller, D. M. Brown, *Appl. Catal. A* **2001**, *221*, 275 – 282.

[44] J. M. Kidd, J. T. Gallagher (ICI), UK 1 159 035, **1969**.

[45] I. Kasatkin, P. Kurr, B. Kniep, A. Trunschke, R. Schlögl, *Angew. Chem. Int. Ed.* **2007**, *46*, 7324 – 7327; *Angew. Chem.* **2007**, *119*, 7465 – 7468.

[46] M. Behrens, F. Studt, I. Kasatkin, S. Kühl, M. Hävecker, F. Abild-Pedersen, S. Zander, F. Girgsdies, P. Kurr, B. L. Kniep, M. Tovar, R. W. Fischer, J. K. Norskov, R. Schlögl, *Science* **2012**, *336*, 893 – 897.

[47] a) J. B. Hansen, P. E. Højlund Nielsen, *Methanol Synthesis. Handbook of Heterogeneous Catalysis* (Eds.: G. Ertl, H. Knozinger, F. Schuth, J. Weitkamp), Wiley-VCH, Weinheim, **2008**, pp. 2920 – 2949; b) G. Prieto, J. Zečević, H. Friedrich, K. P. de Jong, P. E. de Jongh, *Nat. Mater.* **2013**, *12*, 34 – 39.

[48] G. C. Chinchen, P. J. Denney, J. R. Jennings, M. S. Spencer, K. C. Waugh, *Appl. Catal.* **1988**, *36*, 1 – 65.

[49] J. D. Grunwaldt, A. M. Molenbroek, N. Y. Topsøe, H. Topsøe, B. S. Clausen, *J. Catal.* **2000**, *194*, 452 – 460.

[50] P. L. Hansen, J. B. Wagner, S. Helveg, J. R. Rostrup-Nielsen, B. Clausen, *Science* **2002**, *295*, 2053 – 2055.

[51] a) M. Behrens, S. Kißner, F. Girsgdies, I. Kasatkin, F. Hermerschmidt, K. Mette, H. Ruland, M. Muhler, R. Schlögl, *Chem. Commun.* **2011**, *47*, 1701 – 1703; b) G. Prieto, K. P. de Jong, P. E. de Jongh, *Catal. Today* **2013**, *215*, 142 – 151.

[52] J. Ott, V. Gronemann, F. Pontzen, E. Fielder, G. Grossmann, D. B. Kersebohm, G. Weiss, C. Witte, *Methanol. Ullmann's Encyclopedia of Industrial Chemistry* (Ed.: G. Bellussi), Wiley-VCH, Weinheim, **2012**, pp. 1 – 27.

[53] W. Boll, G. Hochgesand, C. Higman, E. Supp, P. Kalteier, W. D. Müller, M. Kriebel, H. Schlichting, H. Tanz, *Gas Production, 3. Gas Treating. Ullmann's Encyclopedia of Industrial Chemistry* (Ed.: G. Bellussi), Wiley-VCH, Weinheim, **2011**, pp. 483 – 539.

[54] J. A. Moulijn, A. E. van Diepen, F. Kapteijn, *Appl. Catal. A* **2001**, *212*, 3 – 16.

[55] S. Vukojević, O. Trapp, J. D. Grunwaldt, C. Kiener, F. Schüth, *Angew. Chem. Int. Ed.* **2005**, *44*, 7978 – 7981; *Angew. Chem.* **2005**, *117*, 8192 – 8195.

[56] S. Schimpf, A. Rittermeier, X. N. Zhang, Z. A. Li, M. Spasova, M. W. E. van den Berg, M. Farle, Y. M. Wang, R. A. Fischer, M. Muhler, *ChemCatChem* **2010**, *2*, 214 – 222.

[57] One of the authors, F. Schüth, was cofounder of hte AG, a company active in high throughput experimentation in heterogeneous catalysis. Currently, however, there is no formal association to hte anymore, since the company was fully acquired by BASF in 2013.

[58] C. Baltes, S. Vukojevic, F. Schüth, *J. Catal.* **2008**, *258*, 334 – 344.

[59] F. Schüth in *Handbook of Heterogeneous Catalysis* (Eds.: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp), Wiley-VCH, Weinheim, **2008**, pp. 2053 – 2074.

[60] A. Holzwarth, H. W. Schmidt, W. F. Maier, *Angew. Chem. Int. Ed.* **1998**, *37*, 2644 – 2647; *Angew. Chem.* **1998**, *110*, 2788 – 2792.

[61] M. Orschel, J. Klein, H. W. Schmidt, W. F. Maier, *Angew. Chem. Int. Ed.* **1999**, *38*, 2791–2794; *Angew. Chem.* **1999**, *111*, 2961–2965.

[62] P. Cong, R. D. Doolen, Q. Fan, D. M. Giaquinta, S. Guan, E. W. McFarland, D. M. Poojary, K. Self, H. W. Turner, W. H. Weinberg, *Angew. Chem. Int. Ed.* **1999**, *38*, 483–488; *Angew. Chem.* **1999**, *111*, 507–512.

[63] C. Hoffmann, A. Wolf, F. Schüth, *Angew. Chem. Int. Ed.* **1999**, *38*, 2800–2803; *Angew. Chem.* **1999**, *111*, 2971–2975.

[64] C. Hoffmann, H. W. Schmidt, F. Schüth, *J. Catal.* **2001**, *198*, 348–354.

[65] C. Kiener, M. Kurtz, H. Wilmer, C. Hoffmann, H.-W. Schmidt, J. D. Grunwaldt, M. Muhler, F. Schüth, *J. Catal.* **2003**, *216*, 110–119.

[66] P. Kubanek, O. Busch, S. Thompson, H. W. Schmidt, F. Schüth, *J. Comb. Chem.* **2004**, *6*, 420–425.

[67] T. Johann, A. Brenner, O. Busch, F. Marlow, S. Schunk, F. Schüth, *Angew. Chem. Int. Ed.* **2002**, *41*, 2966–2968; *Angew. Chem.* **2002**, *114*, 3096–3100.

[68] S. A. Schunk, D. Demuth, A. Cross, O. Gerlach, A. Haas, J. Klein, J. M. Newsam, A. Sundermann, W. Stichert, W. Strehlau, U. Vietze, T. Zech in *High-Throughput Screening in Heterogeneous Catalysis* (Eds.: A. Hagemeyer, P. Strasser, A. F. Volpe), Wiley-VCH, Weinheim, **2004**, pp. 19–61.

[69] O. Trapp, *Angew. Chem. Int. Ed.* **2007**, *46*, 5609–5612; *Angew. Chem.* **2007**, *119*, 5706–5710.

[70] R. Sadeghbeigi, *Catalytic Cracking Handbook*, Butterworth-Heinemann, Woburn, MA, **2000**.

[71] A. W. Peters, W. H. Flank, B. H. Davis, *Innovations in Industrial and Engineering Chemistry* (Eds.: W. H. Flank, M. A. Abraham, M. A. Matthews), American Chemical Society, Washington, DC, **2008**, pp. 103–187.

[72] C. J. Plank in *Heterogeneous Catalysis*; (Eds.: B. H. Davis, W. P. Hettinger), ACS Symposium Series; American Chemical Society, Washington, DC, **1983**, pp. 253–271.

[73] A. A. Avidan, *Ind. Eng. Chem. Res.* **1990**, *29*, 931–942.

[74] S. W. Golden, R. Pulley, C. F. Dean, *Oil and Gas Journal* **2004**, Catalyst Report-Edition.

[75] Amy Motto, Goldman Sachs 2013 Chemical Intensity Day, Global Catalyst Outlook & Trends, http://phx.corporate-ir.net/External.File?item=UGFyZW50SUQ9MTc2MjgyfENoaWxkSUQ9LTF8VHlwZT0z&t=1, accessed October 8th, 2014.

[76] BASF's news release, http://www.basf.com/group/pressrelease/P-13-167. Accessed October 8th, 2014.

[77] BASF's technical note, http://www.catalysts.basf.com/p02/USWebInternet/catalysts/en/function/conversions:/publish/content/microsites/catalysts/prods-inds/process-catalysts/BF-9626_US_REAL_Technical_Note.pdf. Accessed October 8th, 2014.

[78] J. García-Martínez, K. Li, G. Krishnaiah, *Chem. Commun.* **2012**, *48*, 11841–11843.

[79] a) I. L. C. Buurmans, J. Ruiz-Martínez, W. V. Knowles, D. van der Beek, J. A. Bergwerff, E. T. C. Vogt, B. M. Weckhuysen, *Nat. Chem.* **2011**, *3*, 862–867; b) J. Ruiz-Martínez, A. M. Beale, U. Deka, M. G. O'Brien, P. D. Quinn, J. F. W. Mosselmans, B. M. Weckhuysen, *Angew. Chem. Int. Ed.* **2013**, *52*, 5983–5987; *Angew. Chem.* **2013**, *125*, 6099–6103.

[80] BASF news release, http://www.catalysts.basf.com/p02/USWeb-Internet/en_GB/content/microsites/catalysts/news/news101. Accessed October 8th, 2014.

[81] A. Forlin, M. Bergamo, J. Lingner in *Liquid Phase Oxidation via Heterogeneous Catalysis: Organic Synthesis and Industrial Applications* (Eds.: M. G. Clerici, O. A. Kholdeeva), Wiley, Hoboken, **2013**, pp. 474–496.

[82] J. K. F. Buijink, J. J. M. van Vlaanderen, M. Crocker, F. G. M. Niele, *Catal. Today* **2004**, *93–95*, 199–204.

[83] M. Taramasso, C. Perego, B. Notari (Snamprogetti S.P.A.), US 4410501, **1983**.

[84] http://www.personal.utulsa.edu/~geoffrey-price/zeolite, accessed October 1st, **2014**.

[85] M. C. Clerici in *Metal Oxide Catalysis*, (Eds.: S. D. Jackson, J. S. J. Hargreaves), Wiley-VCH, Weinheim, **2009**, pp. 705–754.

[86] M. G. Clerici, M. E. Domine in *Liquid Phase Oxidation via Heterogeneous Catalysis: Organic Synthesis and Industrial Applications* (Eds.: M. G. Clerici, O. A. Kholdeeva), Wiley, Hoboken, **2013**, pp. 21–94.

[87] K. Schumacher, M. Moerters, H. Mangold, S. Hasenzahl (Evonik-Degussa), US 2010/0209339A1, **2010**.

[88] U. Müller, W. Steck, *Stud. Surf. Sci. Catal.* **1994**, *84*, 203–210.

[89] R. Watanabe, T. Yokoi, T. Tatsumi, *J. Colloid Interface Sci.* **2011**, *356*, 434–441.

[90] D. Serrano, R. Sanz, P. Pizarro, I. Moreno, *Chem. Commun.* **2009**, 1407–1409.

[91] U. Müller, L. Ma, F.-S. Xiao, X. Yang (BAS AG), WO 2006/111584, **2006**.

[92] K. Na, C. Changbum Jo, J. Kim, W.-S. Ahn, R. Ryoo, *ACS Catal.* **2011**, *1*, 901–907.

[93] G. Li, X. Wang, H. Yan, Y. Liu, X. Liu, *Appl. Catal. A* **2002**, *236*, 1–7.

[94] P. Bassler, H.-G. Göbbel, M. Weidenbach, *Chem. Eng. Trans.* **2010**, *21*, 571–576.

[95] A. Hiroki, J. A. LaVerne, *J. Phys. Chem. B* **2005**, *109*, 3364–3370.

[96] S. B. Shin, D. Chadwick, *Ind. Eng. Chem. Res.* **2010**, *49*, 8125–8134.

[97] V. Russo, R. Tesser, E. Santacesaria, M. Di Serio, *Ind. Eng. Chem. Res.* **2013**, *52*, 1168–1178.

[98] T. Haas, W. Hofen, S. Pilz, G. Thiele, W. Woell (BASF AG, Dow Chemical Co), WO 02/085874A1, **2002**.

[99] a) G.-P. Schindler, C. Walsdorff, R. Korner, H.-G. Gobbel (BASF AG, Dow Chemical Co), US 2007/004926, **2007**; b) P. P. Kampe, P. Resch, S. Y. Chin, P. Bassler, U. Mueller, G.-P. Schindler, H.-G. Goebbel, J. H. Teles, K. Gumlich, T. Grassler, C. Bartosch, R. Jacubinas, M. Weidenbach (BASF AG, Dow Chemical Co), US 2012/0065413A1, **2012**.

[100] U. Müller, F. J. Bröcker, G. H. Grosch, H. Pütter, M. Schulz, N. Rieber, W. Harder (BASF AG), US 6106797, **2000**.

[101] Q. Wang, L. Wang, J. Chen, Y. Wu, Z. Mi, *J. Mol. Catal. A* **2007**, *273*, 73–80.

[102] G. Thiele (Degussa AG), US 5675026, **1997**.

[103] a) G. H. Grosch, U. Müller, A. Walch, N. Rieber, W. Harder (BASF AG), US 2004/0152583A1, **2004**; b) J. H. Teles, A. Rehfinger, P. Bassler, A. Wenzel, N. Rieber, U. Müller, P. Rudolf (BASF AG), US 6958304 B, **2005**.

[104] F. Schmidt, M. Bernhard, H. Morell, M. Pascaly, *Chim. Oggi* **2014**, *32*, 31–35.

[105] a) J. Huang, T. Akita, J. Faye, T. Fujitani, T. Takei, T. M. Haruta, *Angew. Chem. Int. Ed.* **2009**, *48*, 7862–7866; *Angew. Chem.* **2009**, *121*, 8002–8006; b) S. Lee, L. M. Molina, M. J. López, J. A. Alonso, B. Hammer, B. Lee, S. Seifert, R. E. Winans, J. W. Elam, M. J. Pellin, S. Vajda, *Angew. Chem. Int. Ed.* **2009**, *48*, 1467–1471; *Angew. Chem.* **2009**, *121*, 1495–1499; c) Y. Lei, F. Mehmood, S. Lee, J. Greeley, B. Lee, S. Seifert, R. E. Winans, J. W. Elam, R. J. Meyer, P. C. Redfern, D. Teschner, R. Schlögl, M. J. Pellin, L. A. Curtiss, S. Vajda, *Science* **2010**, *328*, 224–228.

[106] a) Q. Jin, J. Bao, H. Sakiyama, N. Tsubaki, *Res. Chem. Intermed.* **2011**, *37*, 177–184; b) L. Xu, Y. Ren, H. Wu, Y. Liu, Z. Wang, Y. Zhang, J. Xu, H. Peng, P. Wu, *J. Mater. Chem.* **2011**, *21*, 10852–10858.