

Future trends

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Chapter 13

Future trends

The large scale continuous processes that lie at the core of the modern chemical and petrochemical industries have their roots in scientific innovations that started nearly one hundred years ago. As Chapter 1 has described, the prime driving force for process innovation was the availability of new feedstocks and the need for new conversion processes and products. This force will remain an important one in industry. Today, for example, improved catalytic processes will be necessary to exploit natural gas resources or to produce hydrogen as an energy carrier.

While half of the large scale chemical processes currently in use are based on homogeneous catalysts, the early processes were mainly based on heterogeneous catalysts. The study of heterogeneous catalysis has led to the generation of new scientific subdisciplines, most of which are directed towards the improvement or adaptation of existing processes. This knowledge was mainly developed in industrial laboratories committed to the improvement of catalytic processes, an activity which has produced significant economic benefits. Catalysis has become established as a research discipline whose aim is an understanding of catalysis as a phenomenon.

For a long time practical catalysis remained an empirical art rather than a scientific discipline, mainly because the complexity of the catalytic systems obscured the molecular insights needed for their control in a predictive manner. The modern spectroscopic techniques available to the analytical laboratory enable detailed catalyst analysis and *in-situ* studies. Advanced inorganic and organometallic chemistry and catalyst synthesis (e.g. zeolite synthesis) are also significant. This has changed catalytic practice and has resulted in a considerable reduction of catalyst development times. Nonetheless, in catalysis, accidental discovery and high risk exploratory research are still important factors in innovation.

13.1 ENVIRONMENTAL DEMANDS

There is a long list of desirable reactions that are thermodynamically possible, but for which no direct catalytic reactions exist as yet. Examples are the direct oxidation of methane to methanol, or benzene to phenol. Environmental requirements, in particular, are giving a new direction to catalytic applications. The concentration of environmentally damaging compounds — sometimes present in minute quantities in the emission of engines, electricity plants or chemical plants — has to be further reduced. Examples are NO_x and SO_2 as well as chlorinated hydrocarbons. The removal of lead from gasoline, which was required to enable the use of automotive exhaust catalysts, led to the placing of completely new demands on refinery catalysts. There is a need for new chemicals as substitutes for such environmentally damaging products as phosgene, dimethylsulphide, hydrogen fluoride and especially compounds containing chlorine or bromine. Catalysts for the production of organic chemicals are required that replace classical organic syntheses and reduce acid consumption and the resulting salt waste products. Such processes will result in improved atom utilization.

New, preferentially stereoselective, catalytic reagents will produce enantiomerically pure products, the specific chemical activity of which reduces adverse effects when applied in agriculture or medicine. Biocatalysis will continue to play an important role here.

13.2 AUTONOMOUS DEVELOPMENTS: CHEMISTRY

At present we are beginning to understand the reaction mechanisms of many heterogeneous catalytic reactions at the molecular level. A major breakthrough came with the design of catalytic model systems, such as single crystal surfaces, enabling exhaustive structural characterization and model catalytic experiments. The surface science approach forms the basis of current developments of surface chemical reaction rate theory.

A recent trend in organometallic chemistry is the exploration of metallic clusters of increasing size, approaching the size of clusters used in heterogeneous catalysis. The two fields, with their very different historical background, have reached a stage where an appreciation of the correspondence and difference between molecular events on heterogeneous catalysts and organometallic complexes will soon become possible, leading to the exploitation of a common molecular understanding.

There is a significant difference in the ways homogeneous and heterogeneous catalysts are tuned towards higher activity or improved selectivity. The organometallic complexes used in homogeneous catalysis are optimized by choice of ligand or metal components. The main function of the ligand systems is often the

control of the geometric arrangement of the reactive complexed intermediates, thus determining the selectivity of the reaction. The predictive power of this approach is already impressive. The knowledge and means to steer the catalytic reaction will undoubtedly continue to grow.

In heterogeneous catalysis both morphology and catalyst composition can be varied. Usually small particles of a catalytically active material are dispersed on the surface of a supporting material having a high surface area. The particle size and morphology of catalyst pellets are important parameters in reactions that are diffusion limited. Zeolitic materials are unique, because they can be manufactured with micropores of molecular size, thus enabling stereoselective catalysis. Essentially, the preparation of heterogeneous catalysts is very much related to the materials science aspects of the solid-liquid interphase. Synthetic inorganic chemistry and organometallic chemistry are changing catalyst preparation by giving us the possibility to prepare active catalyst precursors under molecular control.

The continuing expansion in the possibilities afforded by computational modelling has enhanced its potential impact on catalyst improvement and design. The application of statistical mechanical techniques will enhance the predictive power of computational techniques when calculating thermodynamic or kinetic constants. An important step is the integration of molecular kinetic information with macroscopic, practical reaction conditions. The success of theoretical approaches based on transition state theories has been recently demonstrated by a prediction of the rate of the heterogeneously catalyzed ammonia synthesis reaction based on computed elementary reaction rate constants. This provides the essential bridge between molecular catalysis and process engineering.

Polymers and polymer based materials have become indispensable to our modern society. Many catalytic processes have been developed to produce the necessary intermediates. Improvements will result in significant benefits. New catalytic systems have recently been developed — initially as homogeneous catalysts but subsequently also in an immobilized form — which have led to a variety of new polymers. The choice of ligand in homogeneous catalytic systems enables high regio-, stereo- and enantiomeric control, leading to the production of new types of polymers with old monomers. Furthermore, catalysts have been found that catalyze the polymerization of otherwise unreactive monomers, such as cyclopentenes. New types of polymers with interesting properties can be produced based on ethylene and CO. The structures that can be 'designed' and made have increased dramatically recently, e.g. block copolymers, graft polymers, organic polymers incorporating organometallic complexes and inorganic materials, polymers with special optical properties, materials with desired molecular weight distributions, etc. With this extensive and exciting toolbox available it will be necessary to be able to predict polymer properties even more accurately because of the tremendous number of possibilities available from a catalysis point of view.

The use of antibody catalysis is attracting attention, especially because antibody catalysis is as yet the only approach available which uses an '*ab initio*' method for the development of new catalysts; for example, the antibody mimics the shape of a transition state of the substrates, thus enhancing catalytic reaction rates. Economic application may lie far in the future, however. There is no such approach available in classical metal (complex) catalysis, however, and we have to rely on the development of known catalytic reactions and the development of accidentally discovered leads.

13.3 AUTONOMOUS DEVELOPMENTS: CATALYTIC REACTION ENGINEERING

In the development of new catalytic processes it is essential to integrate catalyst preparation, catalytic testing and catalytic reactor design. Developments in catalytic reaction engineering often involve the combination of several functions in one reactor concept. Catalytically active membranes are being investigated for application at higher temperatures based on ceramic microporous materials as well as zeolites. As mentioned earlier, multifunctional catalysts, combining catalytic components of different functionality, have become very important. An example is the hydrocracking catalyst combining a hydrogenative and an acidic component. The shape and strength of catalyst particles is crucial to catalytic process applications and is an essential component of practical catalyst manufacture. In fascinating novel applications the difference between particle and reactor vanishes, e.g. in exhaust gas cleaning using monolithic converters.

In homogeneous catalysis ligand systems may define the medium for the reaction. Water-soluble ligands have been developed, but in other instances two phases have to be used. Ultrafiltration may become a useful technique for catalyst removal if one uses encapsulated homogeneous catalysts or larger oligomeric catalysts. New catalytic systems involve the use of easily functionalizable dendrimers. In all these systems a combination of catalysis and separation can be envisaged that also enhances rates and selectivity.

In the polymer field simultaneous catalytic formation and shaping of the end product or intermediate product is gaining attention, e.g. approaches have been developed which allow polymerization in extruders.

Non-stationary operations have found large scale industrial application. An important classical example is catalytic cracking, where oil is exposed with a short residence time to a rapidly deactivating zeolitic catalyst, which is regenerated in a second step by removal of deposited coke. A novel non-stationary process is selective butane oxidation over a regenerable oxidation catalyst (see Chapter 2). Undoubtedly we will see more examples of this type of process, in which the proper catalytic step and the regeneration of the catalytic sites occur in different compartments under different conditions. A nice application involves

the conversion of very inert molecules such as methane. Dissociative adsorption usually requires high temperature and pressure, but associative reactions are most selective at a lower temperature. Rapid deactivation by non-selective site reactions may also occur in catalytic systems, requiring frequent regeneration. The beauty is that catalysis and regeneration can be performed under different conditions.

The use of regenerable inorganic reagent intermediates is also very elegantly exploited in the production of organic chemicals. The generation of undesired, environmentally damaging coproducts is prevented. Alternative approaches to overcome the difficult dissociative step have also been developed. At high temperature conductive oxides can be applied as electrodes for electrocatalytic oxidation. Plasma catalytic processes have been proposed to replace high temperature thermal activation with low temperature electrical discharge activation.

Catalytic reaction engineering forms a link between chemistry and chemical engineering and is the key to catalytic process improvement and innovation. Catalysis is a branch of the chemical sciences that strongly affects frontier research in physical chemistry, organometallic chemistry and reaction engineering. The rapid development of modern chemistry and physics promises an interesting and rewarding future.