

History of catalysis

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Chapter 1

History of catalysis

1.1 INTRODUCTION

The name 'catalysis' was coined by Berzelius in 1836. He concluded that besides 'Affinity' a new force is operative, the 'Catalytic Force'. Reaction occurred by catalytic contact. The word 'catalysis' stems from the Greek: it has the sense of 'down' and 'loosen'. At that time affinity was known as a chemically driving force, but no understanding existed, on a molecular level, of reaction rates. Catalysis — as a tool for carrying out reactions — had already been exploited much earlier. It has been applied for thousands of years in processes such as fermentation. An interesting example is the production of sulphuric acid. In the Middle Ages this was synthesized in small quantities in glass equipment by burning sulphur with nitric acid in humid air. In 1746 lead was used as a construction material for the reaction chambers and larger production volumes became possible. In 1793 Clement and Desormes showed that the quantity of nitre could be much reduced by admitting additional air to the reactor. They were aware of the fact that the nitrous vapours are only intermediates and that the oxidising agent is air. Their conclusion was correct, and nitre is what we would nowadays call a catalyst.

At the end of the eighteenth and the beginning of the nineteenth century the influence of metals and oxides on the decomposition of several substances was studied by many scientists. It was noticed that contact with different substances gives very different products. An example is the decomposition of alcohol: in the presence of copper or iron, carbon and an inflammable gas is produced. In the presence of pumice stone decomposition into ethene and water was observed. In other words, selectivity was demonstrated. Many other important milestones can be mentioned: we limit ourselves to a few. Thenard investigated the dissociation of ammonia in contact with metals. In 1813 he found that the dissociation occurs over various metals, provided they are hot. Later he systematically studied the dissociation of hydrogen peroxide. He concluded that some of the solids studied

changed and others did not. Humphry Davy performed systematic investigations with the objective of developing a miner's safety lamp. He discovered that the oxidation of coal gas is catalyzed by platinum. He found that palladium was also active whereas copper, silver and gold did not show any catalytic activity. Davy found that the platinum wires he used had to be hot and, as a consequence, he concluded that the action of platinum was to heat the reacting mixture. The fact that only platinum and palladium were active was explained on the basis of their low heat capacity and low thermal conductivity. Later it was found that finely dispersed platinum is active even at room temperature and Davy's explanation was thus not correct. Platinum catalyzes the combustion of the components of coal gas, in particular CO and CH₄, which in the absence of a catalyst can lead to an explosion. Copper and silver are also active in the oxidation of CO, but they are not sufficiently active in CH₄ oxidation. Of course, depending on the construction, a wire can function as a flame arrester in which radical terminations take place and, as a consequence, explosions are avoided.

In 1834 Faraday proposed that the reactants have to adsorb simultaneously at the surface, but he did not really explain the catalytic action. Of course, neither did Berzelius give an explanation, but he nicely generalized many results in a simple description. Later, Ostwald gave the definition that a catalyst does not influence the thermodynamic equilibrium of reactants and products but affects the rates of the chemical reactions. The conclusions of Berzelius and Faraday proved to be correct.

1.2 INDUSTRIAL CATALYSIS

Industrial catalysis is an old practice. Catalysts have always been used in the production of wine and beer. Among the first industrial catalytic processes are a few inorganic oxidation processes, viz. the Deacon process (oxidation of HCl into Cl₂) and the production of sulphuric acid. These processes were developed before a scientific basis of chemical reactivity was established. Only after the formulation of the theory of chemical equilibria by van 't Hoff did a framework for catalyst development become available. This had a major impact on the development of a process for the synthesis of ammonia at the beginning of the twentieth century, allowing a systematic, scientifically based search for a good catalyst to be performed. It also initiated the development of chemical process engineering as we know it today.

1.2.1 Sulphuric Acid

The production of sulphuric acid was commercialized in the mid-18th century. In the so-called lead chamber process the oxidation of SO₂ into SO₃ was catalyzed by NO. The acid produced is not very concentrated. The raw material used was elemental sulphur from Sicily. Later pyrite was used because of its lower price.

One of the consequences was a much higher impurity level in the feed to the reactor. As early as 1831 a process was patented in which SO_2 was oxidized in the presence of finely divided platinum. The commercial application, however, was strongly delayed due to technical difficulties, the major one being catalyst poisoning.

In the First World War the explosives industry demanded highly concentrated sulphuric acid, which required a different technology. A logical way to go was to use the heterogeneous metal catalysts which had just been developed at that time. Initially, platinum supported on silica or asbestos was used as a catalyst. Subsequently, platinum was substituted by V_2O_5 -based catalysts because of the high price of the precious metal and the fact that it is easily poisoned by the pollutants present in the raw material, such as arsenic. The raw material has also changed. Nowadays it is once again mainly elemental sulphur, which, to a considerable degree, is a product from the hydrotreatment of oil.

1.2.2 Ammonia Synthesis

Initially, the source of ammonia was coke oven gas and Chile saltpetre. In Germany, in particular, it was recognized as early as the turn of the 20th century that insufficient ammonia was available for agricultural needs. Moreover, the use of ammonia for the manufacture of explosives increased dramatically due to the beginning of the First World War. Extensive efforts were made by teams in many countries, but particularly in Germany, to synthesise NH_3 directly from N_2 . Non-catalyzed routes were discovered and were commercialised; but they were very inefficient. The breakthrough was the development of a catalytic process.

In 1905 Haber reported a successful experiment in which he succeeded in producing NH_3 catalytically. However, under the conditions he used (1293 K) he only found minor amounts of NH_3 . He extrapolated his value to lower temperatures (at 1 bar) and concluded that a temperature of 520 K was the maximum temperature for a commercial process. This was the first application of chemical thermodynamics to catalysis, and precise thermodynamic data were not then known. At that time Haber regarded the development of a commercial process for ammonia synthesis as hopeless and he stopped his work. Meanwhile, Nernst had also investigated the ammonia synthesis reaction and concluded that the thermodynamic data Haber used were not correct. He arrived at different values and this led Haber to continue his work at higher pressures. Haber tried many catalysts and found that a particular sample of osmium was the most active one. This osmium was a very fine amorphous powder. He approached BASF and they decided to start a large program in which Bosch also became involved.

The process development studies were carried out in a systematic way. A good catalyst had to be formulated; the reactor was to be scaled up; and an integrated process had to be designed, including the production of sufficiently pure synthesis gas. Haber envisaged the process scheme given in Fig. 1.1.

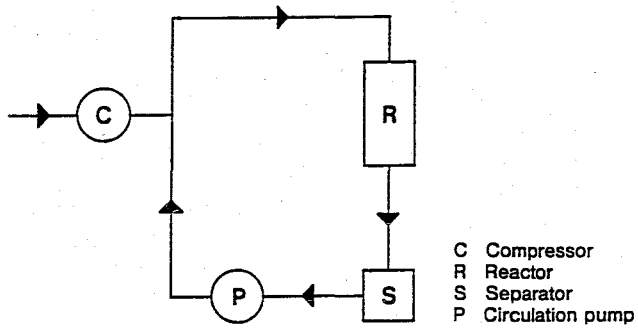


Fig. 1.1. Process scheme for the production of ammonia according to Haber.

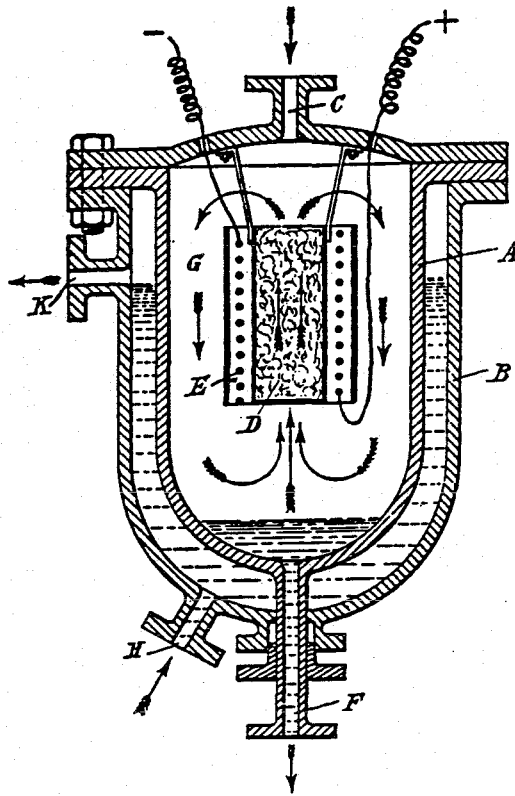


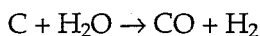
Fig. 1.2. Reactor for the synthesis of ammonia (BASF 1910).

Systematic studies were carried out in order to discover a suitable catalyst. Iron catalysts were especially tried, because it was known that iron catalyzes the decomposition of ammonia, which is the reverse of the reaction being studied. It

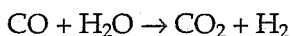
was discovered that iron alone was only slightly active but its activity could be improved (promoted) or worsened (poisoned) by additives. In their studies over 10 000 catalysts were prepared and over 4000 were tested.

When the laboratory studies gave promising results, scale-up studies commenced. The major problem was the construction of a reactor which was able to withstand the reaction conditions. Due to the high pressure, high-strength carbon steel was used; however, this steel is corroded by H_2 under the severe reaction conditions used, and consequently loses its strength. Bosch designed a reactor which contained an outer wall of high carbon steel, lined internally with soft, low carbon steel (Fig. 1.2). The catalyst was also heated internally, so that the external wall was continuously kept at a low temperature.

Very pure, electrically generated H_2 was available for the pilot studies, but for a commercial plant, this was of course not practical. The solution was found in coal gasification:



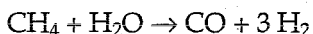
followed by the water-gas shift reaction:



Haber received the Nobel prize in 1919 for his work on ammonia synthesis. Bosch was awarded the 1931 Nobel prize for his achievements in high-pressure technology.

Up to the 1950s the technology for ammonia synthesis did not change very much. Fundamental changes became possible in the '60s. These changes were of both a chemical and a technological nature.

Technically, the most attractive hydrocarbons for the production of H_2 are methane and, to a lesser extent, oil (' CH_2 ')



These reactions are carried out catalytically using nickel catalysts. However, a side reaction is carbon deposition. Since the rate of this side reaction increases with pressure, the production of synthesis gas at high pressure was not feasible. The addition of promoters, which catalyze the carbon steam reaction, suppresses carbon deposition, thus allowing higher pressures. This made a revolution possible in the ammonia synthesis industry. At the same time progress in the development of centrifugal compressors enabled large, single-train plants to be constructed. These developments have led to much more efficient ammonia plants. Figure 1.3 illustrates the process development since the beginning of commercial ammonia production by nitrogen fixation.

Still further process improvements may be possible, but potential improvements should be analyzed by considering the whole process integrally.

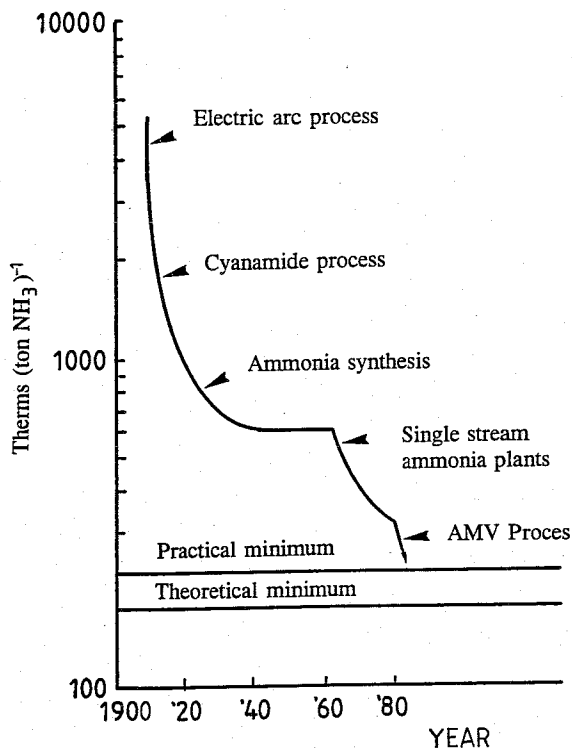


Fig. 1.3. Efficiency of nitrogen fixation [5].

1.2.3 Coal, Oil, Natural Gas

Industrial catalysis has always been closely connected with changes in society. If we confine ourselves to the last 100 years, it is appropriate to highlight the fuel market. In this period a transition is observed from coal to oil and, more recently, to natural gas.

1.2.3.1 Coal

Essentially, in all coal utilization processes the first step is a heating step and a variety of pyrolysis products are formed, depending on the technology. This is illustrated in Fig. 1.4 [7].

A major application of coal was the production of coke. This process is a mild pyrolysis process and, besides coke, large quantities of coke oven gas are also produced containing many of the base materials for the chemical industry, e.g., ammonia, acetylenes and aromatics.

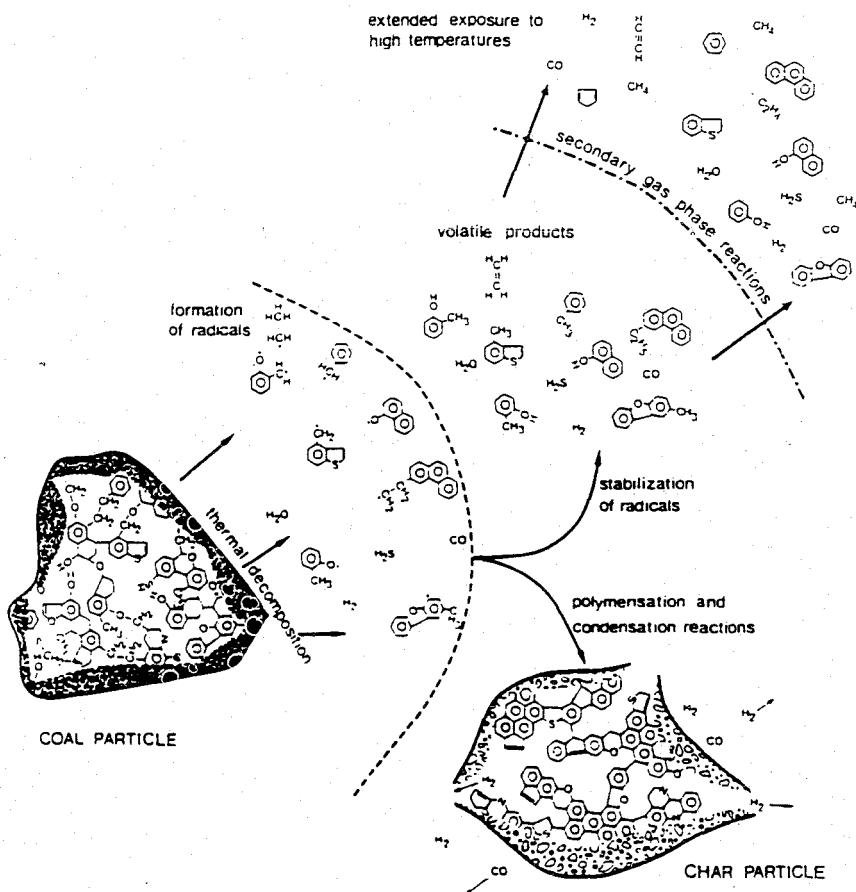


Fig. 1.4. Reactions occurring during the pyrolysis of coal.

In Germany, before and during the Second World War, a large amount of ethylene was produced from acetylene derived from coke oven gas. Coke ovens also provided essentially all the aromatics in Germany. Coal was also gasified, giving synthesis gas, a mixture of CO and H_2 . Products such as ammonia and methanol were catalytically produced from this synthesis gas. Fischer-Tropsch technology was also developed to convert synthesis gas to motor fuels.

Coal was also directly hydrogenated into liquids which could be used as feedstocks in the chemical industry. The first catalytic hydrogenation of coal was reported by Berthelot in 1869, using HI as a catalyst. The success in developing catalytic high pressure processes for ammonia and methanol also stimulated process development in catalytic coal hydrogenation. Catalyst deactivation appeared to be a major problem. The solution was found in carrying out the process in two steps: first a liquid phase hydrogenation was carried out in a slurry of coal particles, oil produced from coal and highly dispersed catalyst. Many catalysts

were tried, e.g. iron oxide and sulphide. In the second stage the oils from the first stage were hydrogenated in a fixed bed reactor. As early as 1924 it was known that sulphides of Mo, W, Co and Fe were suitable hydrogenation catalysts which were not poisoned by the heteroatoms (S, N, O) in the feedstock. Later, in the development of hydrotreating processes for the oil refinery industry, the same catalysts were applied, but now in the treatment of oils.

The extensive activity in Germany in the '40s is well illustrated by Table 1.1.

TABLE 1.1

German hydrogenation plants 1943/44

Start-up date	Location	Raw material	Pressure (bar)		Product capacity 1943/44 (t per year)
			Liquid phase	Vapour phase	
1927	Leuna	Brown coal Brown coal tar	200	200	650 000
1936	Boehlen	Brown coal tar	300	300	250 000
1936	Magdeburg	Brown coal tar	300	300	220 000
1936	Scholven	Bituminous coal	300	300	230 000
1937	Welheim	Coal tar pitch	700	700	130 000
1939	Gelsenberg	Bituminous coal	700	300	400 000
1939	Zeitz	Brown coal tar	300	300	280 000
1940	Luetzkendorf	Tar oils	500	500	50 000
1940	Poelitz	Bituminous coal oils	700	300	700 000
1941	Wesseling	Brown coal	700	300	250,000
1942	Bruex	Brown coal tar	300	300	600 000
1943	Blechhammer	Bituminous coal and tar	700	300	420 000
12 Plants					about 4 million

1.2.3.2 Oil and Natural Gas

In the U.S. oil and natural gas were playing a significant role, together with coal, as early as the 1920s. It was obvious that, compared with coal, oil was a superior chemical feedstock since the hydrocarbons are present in a gaseous or liquid form. The problem was that crude oil is very unreactive; this applies particularly to the paraffins which are main constituents of crude oil. The situation changed when thermal and, later, catalytic cracking processes were developed.

Distillation of crude oil does not result in large amounts of gasoline of a satisfactory octane number. Cracking of larger molecules, isomerization and

aromatization have to be carried out in order to produce sufficient amounts of high quality gasoline.

As early as 1915 $AlCl_3$ was used in a batch process. It is not surprising that there was a severe problem in the disposal of the sludges consisting of spent catalyst dissolved in hydrocarbons. At the same time activated clays were found to exhibit catalytic activity. A major breakthrough was the work of Houdry — a mechanical engineer and an automobile racing driver. He concluded that the limitations on the engine performance were not of a mechanical nature; the constraints were due to the performance of the gasoline. He developed a fixed bed process in which activated clay was the catalyst. Activated clays had been used before to produce kerosine for lamp oil. The cracking unit consisted of parallel reactors which were operated cyclically. A scheme of an early design is given in Fig. 1.5.

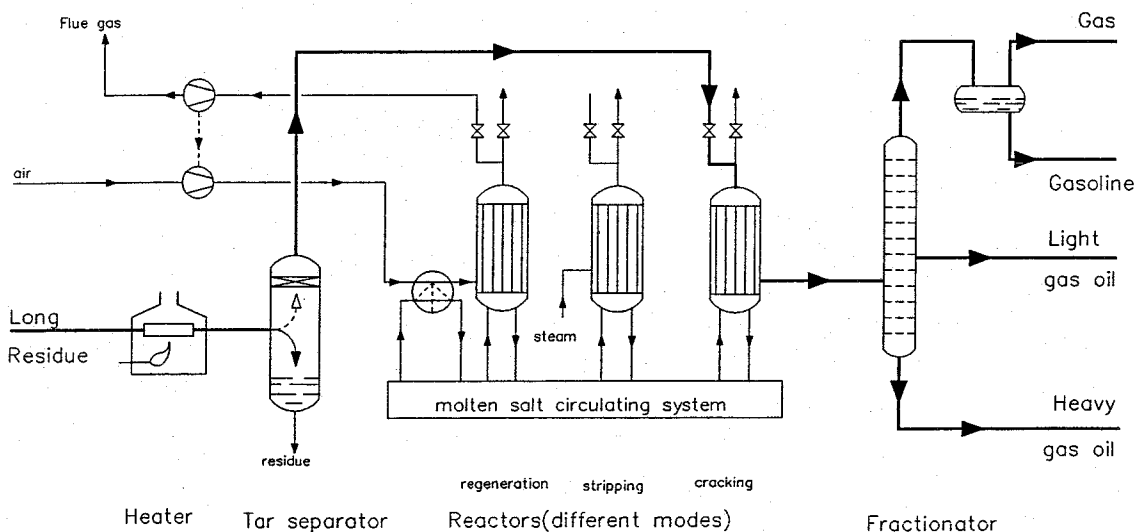


Fig. 1.5. Houdry catalytic cracking process.

Three catalytic converters are present in order to enable the process to operate continuously. Under typical conditions a reactor was on stream for 10 min. Subsequently, it was purged for 10 min and regenerated for 10 min. In regeneration the coke deposited on the catalyst was removed by burning, so continuous operation was possible. Heat was supplied by a molten salt system. In a next generation an adiabatic process was implemented, thus eliminating the molten salt heat transfer system. The heat produced during the regeneration was stored in the bed and provided the heat needed for heating the feedstock to the reaction temperature and providing the heat of reaction. Most of the aviation gasoline used in the Battle of Britain was produced in Houdry units. The next generation

of catalytic crackers was developed immediately after the commercialization of the Houdry units. These were based on the principle that the catalyst particles move between a cracking zone and a regeneration zone. Conveyor type reactors have been used and commercialized. A particularly successful approach, developed mainly by the Standard Oil Company of New Jersey, has been the Fluid Catalytic Cracking (FCC) technology. This technology was introduced at the beginning of the '40s. The reactor and the regenerator were fluidized beds and silica-alumina catalysts were used. The FCC process has been continuously improved both with respect to the catalyst and to the design of the reactor and the process. The acid treated clays were gradually replaced by synthetic silica-alumina catalysts. In the early '60s these were replaced by zeolite-based catalysts. The fluid cracking reactor was replaced by a riser reactor after the mechanical strength and the activity of the catalyst particles had been sufficiently improved.

Catalytic cracking was not the only technology being developed for gasoline needs. iso-Octane was produced as early as 1930 by oligomerization of lower olefins followed by hydrogenation. Ipatieff discovered paraffin alkylation in 1935, in which isobutane was alkylated with butenes or propene, the catalysts being sulphuric acid and hydrofluoric acid. This is an example of homogeneous catalysis. Alkylation was the basis of large volumes of aviation gasoline in World War II. While sufficient amounts of alkenes were available, there was a shortage of isobutane. Isomerization processes were commercially applied to convert n-butane into isobutane with a catalyst consisting of a mixture of AlCl_3 and HCl .

1.2.4 Catalytic Reforming

During the Second World War methylcyclohexane was transformed into toluene over molybdena/alumina catalysts. An attempt was made to use the same process for the 'catalytic reforming' of naphtha in order to increase the octane number by carrying out isomerization, cyclization and dehydrogenation of paraffins into aromatics. The stability of the catalyst was unsatisfactory because a large amount of coke was deposited. The breakthrough came with a catalyst developed at Universal Oil Products (about 1950). This catalyst was Pt supported on an acidic support. The process was called 'Platforming'. This catalyst could be used over a period of 6–12 months and could be regenerated by careful oxidation. It was observed that small amounts of sulphur did not poison the catalyst but even enhanced the reaction rate. Although a scientific success, further catalyst development was needed because the catalyst contained 3% Pt and this was considered far too expensive. Catalysts with satisfactory activity were developed with Pt concentrations between 0.2 and 0.7%. A major improvement was the application of bimetallic catalysts. The first commercially successful one, developed by Chevron, contained Re besides Pt, and was much more stable. The process based on this catalyst is called 'Rheniforming'. Catalytic reforming has

had a great impact: in 1950 about 2% of the U.S. gasoline pool was from catalytic reforming; by the late '50s this figure had risen to 30%.

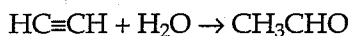
1.2.5 Hydrorefining

Hydrorefining is directly related to the technology developed in coal liquefaction. In this process heteroatoms, in particular S and N, are removed by catalytic hydrogenation. This is done in order to abate pollution and to prevent extensive catalyst deactivation in further catalytic processing. The most common catalysts are CoS-MoS₂/Al₂O₃ and NiS-MoS₂/Al₂O₃. This technology has seen widespread application only since the late '50s. A recent development is the processing of residual oils. Catalyst poisoning is more severe, here, in particular because these feedstocks contain large amounts of metals which deposit on the catalysts. The most abundantly occurring metals are Ni and V. A typical feature of these feedstocks is the presence of large hydrocarbon molecules. The answer has been found in the production of catalysts supported on wide-pore carriers.

It was not only gasoline production that was fundamental in the late '30s; synthetic rubber was just as important. In 1934 BASF and Bayer had developed Buna-S rubber, which was a copolymer containing styrene. Processes were also developed in the U.S. to produce styrene.

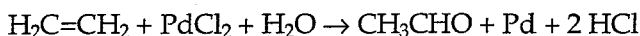
1.2.6 Acetaldehyde

Acetaldehyde is an intermediate in acetic acid and vinyl acetate production. Since 1916 it has been produced from the addition of water to acetylene, a reaction catalyzed by divalent mercury in sulphuric acid (20%)/water. Acetylene was made from coal. In Germany in particular, a lot of research was carried out on the use of acetylene as a chemical feedstock.

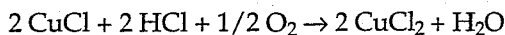
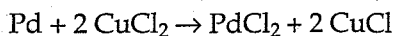


Coal was also the feedstock for synthesis gas (*vide infra*). Many contributions to acetylene chemistry are due to Reppe. His work on new homogeneous metal (mainly nickel) catalysts for acetylene conversion, carried out in the period from 1928 to 1945, was not published until 1948. Under the influence of nickel iodide catalysts, acetylene, water and CO were found to give acrylic acid. A process based on this chemistry was commercialized in 1955.

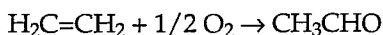
When the oil era started ethene became a much cheaper C₂ feedstock than acetylene and a search was started for new catalytic conversion routes for ethene. In their attempts to epoxidize ethene over a palladium catalyst Smidt and co-workers at Wacker-chemie discovered that ethene and water produced acetaldehyde. They rediscovered a stoichiometric reaction that had been known since 1894 (Phillips):



Smidt combined this reaction with a redox system, which led to a catalytic process ('Wacker process'):



The overall reaction reads:



1.2.7 Butanol

Since the twenties and thirties butanol together with acetone was produced by fermentation of carbohydrates (corn). In the sixties the process was replaced by the hydroformylation of propene. In the OXO process alkenes react with synthesis gas in the presence of a homogeneous catalyst to give a mixture of branched and linear aldehydes:



In formal terms, the addition of formaldehyde across the double bond has taken place. The reaction was discovered by Roelen while working on the conversion of synthesis gas to hydrocarbons. The process was first patented in 1938 and a commercial plant was briefly operated at the end of the war after which it was dismantled. In 1948 a commercial plant was put on stream by Exxon in the U.S.

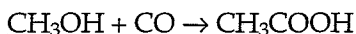
The primary aldehyde product is reduced to the desired butanol, or it is subjected to a base-catalyzed aldol condensation and then hydrogenated to give 2-ethylhexanol. The phthalic ester of the latter is used as a plasticiser in PVC. The first process was based on a $\text{Co}_2(\text{CO})_8$ catalyst, a precursor of $\text{HCo}(\text{CO})_4$. The pressure is high, ca. 200–300 bar, in order to maintain the catalyst's stability. In the '60s Shell developed a process using phosphine ligands which allowed the use of lower pressures. The catalyst is less active but it directly produces alcohols with a somewhat higher linearity.

A breakthrough occurred in the mid-seventies when Union Carbide and Celanese introduced Rh/phosphine catalysts in commercial processes. This catalyst is based on the work by Wilkinson's group; he received the Nobel prize for his work in 1973. Rhodium-based catalysts are much more active than cobalt catalysts and, under certain conditions, at least for 1-alkenes, they are also more selective. The processes for the hydroformylation of higher alkenes (detergent alcohols) still rely on cobalt catalysis. A new development is the use of water-soluble complexes obtained through sulphonation of the ligands (Ruhrchemie).

The new hydroformylation plants for the production of butylaldehyde from propene are all based on rhodium catalysts.

1.2.8 Acetic Acid

Originally, acetic acid was produced by fermentation; this is still the major process for the production of vinegar. Modern production is by acetaldehyde oxidation, liquid phase hydrocarbon oxidation and preferentially by methanol carbonylation. The latter process is to be preferred because of the low raw material and energy costs. As early as 1913 BASF described the carbonylation of methanol at high temperature and pressure:



Due to the extreme conditions commercialization was not successful. Corrosion was very important; only gold and graphite appeared to be resistant enough. Even gold-lined autoclaves were used. In the early '30s the process was abandoned for economic reasons.

Carbonylation with homogeneous nickel catalysts was very extensively studied by Reppe in the thirties and forties. This work was not published until 1953. Based on these results, an acetic acid manufacturing process was commercialized in 1955.

In 1941 Reppe demonstrated the potential of many metal carbonyls in several reactions including hydroformylation. This work resulted in 1960 in a process based on CoI_2 operating at 700 bar and 250°C. Corrosion problems were overcome by applying Hastelloy C.

In 1968 Monsanto reported a chemically related process based on rhodium iodide complexes. Due to its high reaction rates, high selectivity and different kinetics, the process differs substantially from the cobalt process. Commercialization was achieved in 1970. Operating conditions are remarkably mild: 30 bar, 180°C.

1.2.9 Polymerization

The first polymerizations were free radical reactions. In 1933 researchers at ICI discovered that ethene polymerizes into a branched structure that is now known as low density polyethene (LDPE). In the mid-'50s a series of patents were issued for new processes in which solid catalysts were used to produce polyethene at relatively low pressures. The first was granted to scientists at Standard Oil (Indiana) who applied nickel oxide on activated carbon and molybdenum oxide on alumina. Their research did not lead to commercial processes. In the late '40s Hogan and Banks of Phillips were assigned to study the di- and trimerization of lower olefins. The objective was to produce high octane motor fuels. When they tried a chromium salt as promoter of a certain catalyst (Cr was a known reforming

catalyst) they found solid white material which appeared to be polyethene. It is worth mentioning that the same scientists discovered the metathesis of alkenes! The Phillips catalyst has been improved and is used in many commercial plants. About a year later Ziegler's group patented a catalyst based on TiCl_4 and aluminium alkyls.

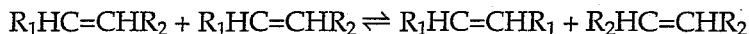
Initially, the activity of these catalysts was poor and, as a result, a high concentration of catalytic material was present in the product. An expensive catalyst removal step was necessary. Catalysts were later improved and a process became feasible in which the polymer formed precipitates and catalyst removal is no longer needed.

In 1956 Natta discovered that propene can be polymerized with a titanium catalyst and that a highly regular polymer is formed.

Ziegler and Natta shared the Nobel prize in 1963.

1.2.10 Metathesis

A novel catalytic reaction was discovered independently by scientists of Phillips Petroleum Company, du Pont and Standard Oil in Indiana. They found that alkenes can react according to the following stoichiometry:



The mechanism has been subject to much debate. The research in this field has had a large impact on transition metal catalysis. It is also interesting that in this field the usually large gap between heterogeneous and homogeneous catalysis does not exist. There was never much doubt that the reaction mechanisms were not the same in both cases.

The first large-scale application was the Phillips Triolefin Process (1966) in which propene was converted into ethene and 2-butene. Due to market changes the reverse process, in which propene is produced, became more attractive later. This process has been in operation since 1985. Another process is the Shell Higher Olefin Process (SHOP) in which ethene is oligomerized and the products are metathesized into detergent range olefins. The same company developed a process in speciality chemicals in which alpha-, omega-dienes are formed from cyclic alkenes.

Metathesis is not limited to acyclic alkenes. Cyclic alkenes also undergo metathesis with the formation of polymers. Homogeneous catalysts are used in most cases. New polymers are produced in this way by Huls, CdF Chimie and Hercules.

1.2.11 Motor Vehicle Emission Control

The development of catalytic reactors for cleaning the exhaust gases of motor vehicles has been stimulated enormously by Californian legislation. In 1959 and

1960 laws on motor vehicle emission standards were enacted which would become operative when at least two different devices were developed which could measure these standards. This gave a large impetus for the research. However, in the mid-'60s, the car industry announced that engine modifications were successful and that the standards could be met without catalytic converters. This delayed further research in the development of catalytic converters. In the late '60s a further tightening of the standards was announced and catalytic research increased considerably. The Clean Air Act of 1970 set standards that went well beyond existing technology and it was clear that catalytic mufflers would be essential.

The initial objective was to reduce the emission of CO and hydrocarbons. The mixture in the engine was fuel-rich and under those conditions the concentrations of CO and hydrocarbons are relatively high, whereas the NO_x concentration is low. The exhaust gases were oxidized in a converter to which air was supplied. Somewhat later the NO_x standards tightened and also the amount of NO had to be reduced. So both oxidation and reduction reactions were required. In the beginning, a so-called dual bed system with separate reduction and oxidation catalysts was envisaged. The engine would be operated under fuel-rich conditions in the first bed; reduction would take place. After air injection into the second bed, CO and the hydrocarbons would be oxidized. The next generation of catalysts could catalyze all reactions simultaneously, provided the fuel-air ratio in the gas mixture was stoichiometric. A typical example of the influence of the fuel-air ratio (lambda) is given in Fig. 1.6.

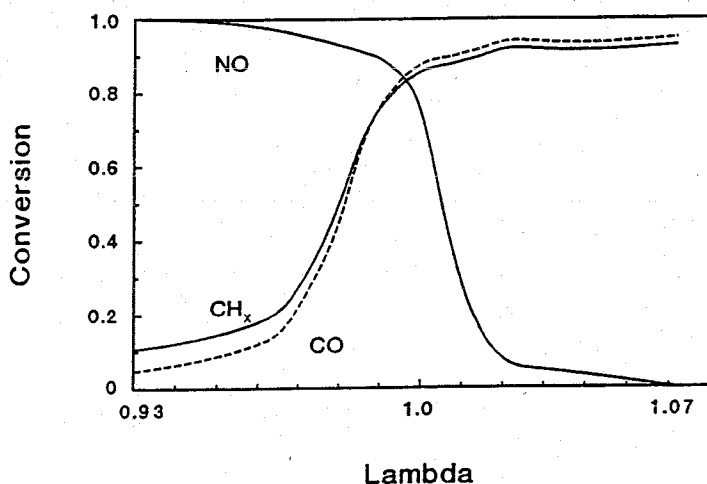


Fig. 1.6. The concentration of CO, NO, CH_x, and O₂ emitted by a gasoline engine as a function of λ , the fuel-air ratio.

At $\lambda < 1$ the activity for NO reduction is high, but not for the oxidation of CO and hydrocarbons. At $\lambda > 1$ the reverse is the case. A special control system had to be developed to guarantee the desired exhaust gas composition. The control system appears to be more critical than the catalyst itself.

The catalysts in use contain Pt and Rh as major constituents. A converter typically contains 1–2 g Pt and 0.2–0.3 g Rh. The design of the reactor has received a lot of attention. Beads were also applied initially, but nowadays monolithic honeycombs are used almost exclusively.

The introduction of catalytic converters has had a tremendous impact on the composition of gasoline. The catalysts used became poisoned by small amounts of impurities; in particular the lead compounds present in high octane gasoline were detrimental. Processes which produce high octane number compounds were therefore stimulated. First, cracking and reforming increased in importance. More recently, the aromatics content is also expected to have to decrease and alternative processes are in use or under way, e.g. MTBE (methyl tertiary-butyl ether) is already produced on a large scale (see 2.12).

1.3 SUMMARY

The discussion of the history of catalysis in this chapter has been limited to the major events, so many interesting developments could not be mentioned. Moreover, the selection of topics has been subject to a personal bias. A more comprehensive overview is given in Table 1.2 of the development of industrial catalytic processes. The list is impressive and it is also clear that catalysis remains a very fascinating area.

Many reasons underlie the development of the science and technology of catalysis. One of the driving forces that should not be overlooked is the availability of the raw materials. Originally, biomass was predominant. Later coal became the most important industrial feedstock. Coke oven gas components played the role of base chemicals. Subsequently, oil took over the place of coal and the technological scene changed profoundly. More recently, natural gas resources appear to have become much more important than had been expected. Therefore it is not surprising that a lot of research in catalysis is aimed at processes based on natural gas. It is also clear that biomass is experiencing a revival. Figure 1.7 illustrates this point: it shows that for a number of important chemicals, the development of processes is linked to the availability of different raw materials. In recent years environmental considerations have been the major driving force for novel processes, often catalytic processes.

TABLE 1.2

Historical summary of the development of industrial processes

Year	Process	Catalyst
1750	H ₂ SO ₄ lead chamber process*	NO/NO ₂
1870	SO ₂ oxidation	Pt
1880	Deacon process (Cl ₂ from HCl)	ZnCl ₂ /CuCl ₂
1885	Claus process (H ₂ S and SO ₂ to S)	Bauxite
1900	Fat hydrogenation	Ni
	Methane from syngas	Ni
1910	Coal liquefaction	Fe
	Upgrading coal liquids	WS ₂
	Ammonia synthesis (Haber-Bosch)	Fe/K
	NH ₃ oxidation to nitric acid	Pt
1920	Methanol synthesis (high pressure process)	Zn, Cr oxide
	Fischer-Tropsch synthesis	Promoted Fe,Co
	SO ₂ oxidation	V ₂ O ₅
	Acetaldehyde from acetylene*	Hg ²⁺ /H ₂ SO ₄
1930	Catalytic cracking (fixed bed, Houdry)	Clays
	Ethene epoxidation	Ag
	Polyvinyl chloride*	Peroxide
	Polyethylene (low density, ICI)*	Peroxide
	Oxidation of benzene to maleic anhydride	V
	Alkylation*	HF/H ₂ SO ₄
1940	Hydroformylation, alkene to aldehyde*	Co
	Catalytic reforming (gasoline)	Pt
	Cyclohexane oxidation (nylon 66 production)*	Co
	Benzene hydrogenation to cyclohexane	Ni, Pt
	Synthetic rubber, SBR*	Li, peroxide
	BNR*	Peroxide
	Butylrubber*	Al
1950	Polyethylene (high density), Ziegler-Natta	Ti
	Phillips	Cr
	Polypropene, Ziegler-Natta	Ti
	Polybutadiene, Ziegler-Natta	Ti
	Hydrodesulphiding (HDS)	Co, Mo sulphides
	Naphthalene oxidation to phthalic anhydride	V, Mo oxides
	Ethylene oxidation to acetaldehyde*	Pd, Cu
	<i>p</i> -Xylene oxidation to terephthalic acid*	Co, Mn
	Ethylene oligomerization*	Co
	Hydrotreating of naphtha	Co-Mo/Al ₂ O ₃
1960	Butene oxidation to maleic anhydride	V, P oxides

Continued

TABLE 1.2 (Continuation)

Year	Process	Catalyst
	Acrylonitrile via ammoxidation of propene (Sohio)	Bi, Mo oxides
	Propene oxidation to acrolein/acrylic acid	Bi, Mo oxides
	Xylene hydroisomerization	Pt
	Propene metathesis	W, Mo, Re
	Adiponitrile via butadiene hydrocyanation*	Ni
	Improved reforming catalysts	Pt, Re/Al ₂ O ₃
	Improved cracking catalysts	Zeolites
	Acetic acid from MeOH (carbonylation)*	Co
	Vinyl chloride via ethene oxychlorination	Cu chloride
	Ethene oxidation to vinyl acetate	Pd/Cu
	<i>o</i> -Xylene oxidation to phthalic anhydride	V, Ti oxides
	Propene oxidation to propene oxide*	Mo
	Hydrocracking	Ni-W/Al ₂ O ₃
	HT water-gas shift process	Fe ₂ O ₃ /Cr ₂ O ₃ /MgO
	LT water-gas shift process	CuO/ZnO/Al ₂ O ₃
1970	Methanol synthesis (low pressure, ICI)	Cu-Zn-Al oxide
	Acetic acid from MeOH (carbonylation, low pressure process, Monsanto)*	Rh
	Improved process for xylene isomerization	Zeolite
	α -Alkenes via ethene oligomerization*/isomerization/metathesis (SHOP)	Ni, Mo
	Improved hydroformylation*	Rh
	Auto exhaust gas catalysts	Pt/Rh
	L-DOPA (Monsanto)*	Rh
	Cyclooctenamer (metathesis)*	W
	Hydroisomerization	Pt/zeolite
	Selective reduction of NO (with NH ₃)	V ₂ O ₅ /TiO ₂
1980	Gasoline from methanol process (Mobil)	Zeolite
	Vinyl acetate from ethene and acetic acid	Pd
	Methylacetate (carbonylation)*	Rh
	Methylacrylate via <i>t</i> -butanol oxidation	Mo oxides
	Improved coal liquefaction	Co, Mo sulphides
	Diesel fuel from syngas	Co
1990	Polyketone (from CO and ethene)*	Pd

The data refer to activities of a pilot plant scale at least.

*Homogeneous catalyst system.

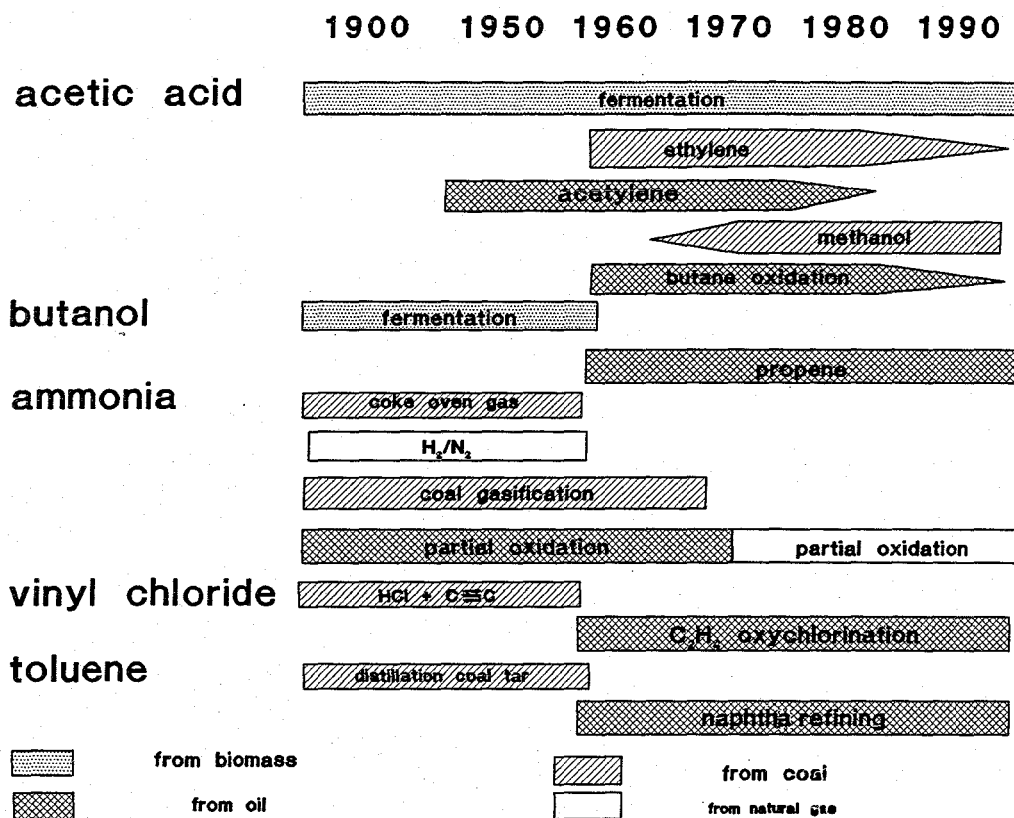


Fig. 1.7. Raw materials for some important chemicals.

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