A brief history of catalysis

Bård Lindström[a] and Lars J. Pettersson[b]

a Volvo Technology Corporation, Alternative Drivetrains, Dept 06120 CTP, Sven Hultins gata 9D, SE-412 88 Göteborg, Sweden, e-mail bard.lindstrom@volvo.com

b KTH-Royal Institute of Technology, Department of Chemical Engineering and Technology, Teknikringen 42, SE-100 44 Stockholm, Sweden, email bardl@ket.kth.se

Historical studies are usually divided into segments of time that were marked by intellectual progress or specific achievements. Some periods are clearly identified by great events or an individual accomplishment that revolutionizes the entire concept. However, in most cases the advancement from one period to another is not marked by distinct accomplishments, but rather the result of a series of advances. This paper follows this conventional style and we have divided our subject of catalysis into five distinct periods.

The first period of catalysis dates back to the dawn of civilization, at a date lost in time when mankind began to produce alcohol by fermentation. The work done during the first period of catalysis consists mainly of isolated observations that were sporadically documented without any effort made to explain these phenomena. The first period of catalysis ended stridently when Jöns Jacob Berzelius systematically investigated the recorded observations and classified them as catalysis in 1835[1,2]. The conclusions drawn by Berzelius were based upon discussions and experimental work with contemporary scientists in Europe[3].

If the first period of catalysis was chaotic then the second period was characterized by systematic research and the discovery of new catalytic processes. During this period it became quite clear that catalysis was applicable in most chemical processes and that by implementing catalysis in an industrial process there could be significant financial gains. This new perception of catalysis was clearly formulated by Wilhelm Ostwald, who once wrote that "there is probably no chemical reaction which can not be influenced catalytically"[1,4].

The point in time when the shift from the second to the third period occurs is not as clear as between the first and the second. The third period of catalysis begins sometime during the end of the nineteenth century, when the growth of academic knowledge translated into industrial applications. At this point the number of catalytic processes that had been developed had grown into hundreds and the economic potential of some of these processes were highly feasible. There was also a general growth in the demand for bulk chemicals and therefore minimization of by-products, by catalysis, had evident economic advantages. The industrial production of bulk chemicals of this period was at an all time high during World War 1[1], when the demands on explosives based upon nitric acid reached preposterous proportions.

The fourth period of catalysis began at the end of the First World War, when the demand for explosives diminished, and the industrial production shifted towards the manufacturing of synthetic fuels and new innovative processes such as Fischer-Tropsch. The most significant new process innovation of this period was the FCC (Fluid Catalytic Cracking) process,

Libavius

D. O. M. A.

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Figure 1 Front cover of Alchemia (1597) by Andreas Libavius[5] which enabled the Allied forces to provide fuel to its fighters during World War Two. When the war ended there was a notable change in the trend of the catalytic industry and thus the end of the fourth period of catalysis.

The fifth period, which lasted to some undefined point at the beginning of the 1970s, was strongly characterized by the petrochemical industry and various catalytic processes for the manufacturing of synthetic polymers. The dominating role of the petrochemical industry was the result of the explosive automotive market that had developed in Europe and North America after World War Two.

At some point during the early 70s the world started to become aware of the impacts that industry had on the environment, partially sparked off by Rachel Carson's "Silent Spring".

This new trend of thought gave birth to the discipline of environmental catalysis. Environmental catalysis was the first step towards the modern chemical industry where catalysis is applied to almost every process, including the production of fine chemicals for pharmaceutical applications to the production of bulk chemicals and exhaust gas catalysts. The sixth period, which started in the seventies, and that can only be characterized by continuous invention of new catalytic processes, has not yet clearly passed into a seventh stage. The use of enzymatic bio-catalysis could possibly be the start of a new catalytic era; however it is too early yet to tell.

From alchemy to chemistry (Ø–1834)

The art of producing alcohol from sugar, by fermentation, has ancient roots and the origins of this process are too remote to trace[1]. However, it was during the alchemic era that the process was first clearly formulated. The first known reference to the use of inorganic catalysis is from 1552, when Valerius Cordus used sulfuric acid to catalyze the conversion of alcohol to ether [1,5].

The alchemical period[1,5] was dominated by the search for a "magical catalyst" that could convert base metals into noble metals. The knowledge of chemical reactions during this period was mainly empirical. The discoveries made during this period were often isolated and collaboration between the scientists of the period was sparse. It was when, in 1957, Andreas Libavius wrote his masterpiece "Alchemia" (see Figure 1)[6], which is often referred to as the first textbook of chemistry, that it was first possible for the scientists to compare their work with others. The work is particularly interesting for us as it is the first historical reference to catalysis as a chemical phenomenon. Libavius (see quotation below), however, uses the term catalysis to describe the decomposition of base metals into silver and gold rather than the catalytic phenomena described by Berzelius[2].

> *De magisteriis substantiae, ubi primum det metallorum transformatione, magisterium substantiae fit vel genesi vel catalysi*

The formulation of the laws for the conservation of matter made it possible to distinguish between chemical and catalytic reactions[1]. The conservation of matter was based upon the ideas of Lavoisier, Cavendish, Priestley, Berthollet, Proust, Gay-Lussac and Dalton[1,7–9].

Figure 2 Humphry Davy (1778–1829)

The principle features of catalysis were first presented by Fulhame in 1794[1,10] when she suggested that the presence of small quantities of water was required for the oxidation of carbon monoxide and that the water was unaffected by the chemical reaction. Similar observations were made by Kirchhoff who hydrolyzed starch to sugars by using dilute acids in 1812. Kirchhoff observed that the acids were not altered by the chemical reaction[1,9,11].

Sir Humphry Davy (see Figure 2) suggested in 1817 that combustible gases, when mixed with oxygen, could explode if they were exposed to heated platinum at temperatures below the ignition temperature[11]. From his own words it is quite clear that Davy was uncertain of what caused this peculiar phenomenon:

> *I have shown, that the temperature of the flame is infinitely higher than necessary for the ignition of solid bodies. It appeared to me, therefore, probable, that in certain combinations of gaseous bodies, for instance, those above referred to, when increase of temperatures was not sufficient to render the gaseous matters themselves luminous; yet it might be adequate to ignite solid matters exposed to them.*

From this passage it appears that Davy believed that the catalyst itself was ignited rather than the combustible gases.

The work of Davy was followed up in 1818 by Erman, who showed that it was possible to perform the combustion at 50 °C[1,9].

Thenard[13,14] showed in 1818 that it was possible to stabilize hydrogen peroxide in acidic solutions while it decomposed in the presence of water. (Thenard is also accredited with the discovery of hydrogen peroxide[14].) He was also able to show that it was possible to decrease the rate of decomposition by adding noble metals and that the rate of decomposition was dependent on the metal used. The influence of noble metals on decomposition was investigated further by Edmund Davy who demonstrated in 1820 that it was possible to rapidly oxidize alcohol to acetic acid over platinum when exposed to air[15]. This was later verified by Döbereiner in 1822[16]. Döbereiner also showed it was possible to combust hydrogen and oxygen at room temperature over platinum. This discovery led to the construction of the hydrogen lamp.[17].

Inspired by Döbereiner's discoveries, Dulong and Thenard began investigating a series of materials to examine whether it was possible to promote the reaction of hydrogen and oxygen with materials other than platinum. In the course of their study they discovered that several substances (e.g. gold, silver and even glass) were able to promote the combustion of hydrogen and that the activity was dependent on the material used[9,18,19].

The deactivation of platinum-based catalysts was first studied by Henry in 1825[20]. Henry discovered that certain substances (for example hydrogen sulfide and carbon disulphide) inhibited the combustion of hydrogen. Henry also noted that platinum catalysts were less active for the combustion of methane and ethylene than for hydrogen and carbon monoxide. With this new discovery Henry developed models for separating and analyzing combustible gases based upon their reactivity in the presence of platinum-based catalysts.

Turner[21] showed that it was possible to combine hydrogen with chlorine by using a platinum-based catalyst. Prompted by this discovery, Phillips developed the first commercial catalytic process, the oxidation of sulfur dioxide over platinum-based catalysts[22].

Figure 3 Michael Faraday (1791–1867)

The work of Faraday[7–9,23] was not mentioned by Berzelius in his summary of the catalytic phenomena; however it is an excellent study of the catalytic properties of platinum for the oxidation of hydrogen. When describing the required properties of platinum for ignition, Faraday came to the following conclusion:

> *The only essential condition appears to be a perfectly clean and metallic surface, for whenever that is provided, the platina acts, whatever form and condition in other respects may be.*

In his study Faraday (see Figure 3) also investigated both the effects of pretreatment and poisoning. He made a clear distinction between permanent and temporary poisons that could be removed by regeneration.

Mitscherlich performed detailed studies on the effects of sulfuric acid on the conversion of ethanol to ether. Mitscherlich concluded that only small quantities of acid were required to convert large amounts of ethanol[1,24]. In 1835 Berzelius analyzed Mitscherlich's work and came to the conclusion that the promotional effects of sulfuric acid did not simply depend on the affinity of sulfuric acid for water, as it was possible to control the product composition by varying the conditions. Berzelius continued to draw analogies between the effect of sulfuric acid on ethanol to the decomposition of hydrogen peroxide and the conversion of starch into sugar. Based upon these analyses, Berzelius presented the following analogy in 1835[1,2,7–9,25].

> *It is then shown that several simple and compound bodies, soluble and insoluble, have the property of exercising on other bodies and action very different from chemical affinity. The body effecting the changes does not take part in the reaction and remains unaltered through the reaction. This unknown body acts by means of an internal force, whose nature is unknown to us. This new force, up till now unknown, is common to organic and inorganic nature. I do not believe that this force is independent of the electrochemical affinities of matter; I believe on the contrary, that it is a new manifestation of the same, but, since we cannot see their connection and independence, it will be more convenient to designate the force by a new name. I will therefore call it the "Catalytic Force" and I will call "Catalysis" the decomposition of bodies by this force, in the same way that we call by "Analysis" the decomposition of bodies by chemical affinity.*

With these famous words Berzelius (see Figure 4) started a new era of catalysis.

From empirics to science (1835–1887)

The second period of catalysis was marked not only by systematic research and the discovery of new catalytic processes but also by an enhanced perception of chemical reactions. We have therefore tried to show how an increase in the understanding of chemical reactions influenced the

Figure 4 Jöns Jacob Berzelius (1779–1848)

development of catalysis, rather than only listing the new processes chronologically.

Wilhelmy proved in 1850 that the rates of chemical reactions were dependent on the concentration of the reactants. In his experiments Wilhelmy showed that the rate at which sugar cane was reversed was dependent on the concentration of sugar used[1,26]. The establishment of a rate dependency of chemical reactions led to the recognition of reversibility of chemical reactions. Williamson showed in 1851 that esters could easily be reversed back to alcohol. Berthelot and Pean de St. Gilles, inspired by the discoveries of Williamson, began investigations of the etherification of alcohol. In 1862 they were able to prove that the etherification of ethanol was a simple reversible reaction. The investigations of Berthelot and Pean de St. Gilles also showed that the rate of etherification was directly proportional to the concentration of the acid[1].

Guldberg and Waage continued the work of Berthelot and were able to derive a more precise interpretation of the experimental results, and subsequently formulated the first quantitative law. In a paper presented in 1864[1,9,27], Guldberg and Waage proposed that there was a relationship between the tendency of a chemical reaction and the "active masses" of the reactants. The term "active mass" referred to the relationship between the number of molecules and the volume, which is synonymous with the concentration of the species. The degree of a chemical reaction was, according to Guldberg and Waage, dependent on the concentration of the reactants and a constant which could only be determined experimentally.

The results of Guldberg and Waage were not accepted until Van't Hoff pointed out in 1877 that the constant was in reality a rate constant, which could be used to measure the chemical change. Van't Hoff's definition was much clearer than Guldberg and Waage's and as a result of his definition the concept of affinity was immediately accepted[1,9].

The dependency of a chemical reaction on the temperature and pressure were originally presented by Le Chatelier in 1884. By combining the results of Le Chatelier with that of Guldberg and Waage, it was possible to deduce a mathematical expression that quantitatively described the relationship between the rate of reaction and the temperature and pressure of the reaction. The developments achieved in this field are the result of several prominent researchers including Van't Hoff, Horstmann, Gibbs and Nernst (see Figure 5).

The results presented so far in this section can be applied to all chemical reactions, not only catalytic reactions, and we will now present these discoveries from a catalytic perspective.

In 1877 Lemoine[28] showed that by applying a catalyst to a chemical reaction the rate at which equilibrium was reached could be increased, but the position of the equilibrium was not altered. During the same period the same conclusion was reached from a thermodynamic perspective:

> *A catalyst which contributes no energy to a chemical system cannot change the position of the equilibrium, it can only alter the rate at which it is reached*[9,28].

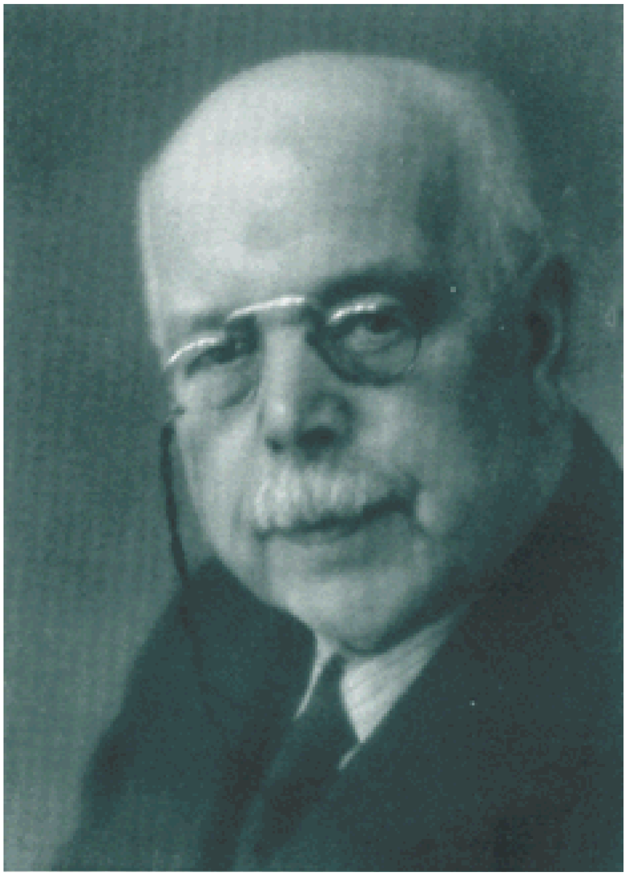


Figure 5 Walther Nernst (1864–1941)

This view was modified by Ostwald (see Figure 6) who claimed that a catalyst cannot initiate a chemical change, it can only accelerate or retard[1,5,9]. This definition received strong reservation from several researchers as many investigators had noted that several reactions could only take place in the presence of a catalyst. The difference between the two definitions is however merely hypothetical, as, for practical reasons, there is no difference between a reaction with an infinitely small rate and one not taking place at all.

In this section we have tried to present the change of ideas rather than listing the hundreds of new catalytic processes that were developed during the second period of catalysis. This is to recognise that the change of thought of chemical reaction engineering was the main driving force of the second period. We begin the third period of catalysis in 1898, as this was the year that saw the birth of one of the most important industrial processes of the twentieth century.

The birth of industrial catalysis (1898–1918)

The industrial catalytic production of bulk chemicals in Europe and America did not begin at the end of the nineteenth century, as one might suspect when reading our motivation for setting this time as the start of the third period of catalysis. The production of sulfuric acid was, for instance, above 50 tons per year in the UK alone. However it was not until 1898 that the production problems with "contact" sulphuric acid were solved by Knietsch[1]. The work of Knietsch enabled a remarkable expansion in the worldwide production of sulfuric acid, which was near one million tons per year at the end of the period.

The third period was marked by the discovery and implementation of new catalytic processes. We have therefore tried to show how these new processes were linked with the events of the period and how the catalytic industry changed as Europe entered the Great War.

The ammonia process, which was without a doubt the most significant process of the period, was originally developed to provide Europe with a fertilizer to prevent a famine. However most of the ammonia produced ended up as a major bulk chemical in the production of nitrogen-based explosives. The possibility of using ammonia in the production of explosives can in large part be accredited to Ostwald, who developed a process for the oxidation of ammonia to nitric acid in 1902[1,9,29].

The first important advancement in the development of the ammonia process came in 1903 when Haber and Nernst discovered that in order to obtain significant activity the process had to be operated at high pressure. During the course of their work Haber and Nernst also realized that high activity and equilibrium concentration could be achieved by operating the process at both elevated temperature and pressure. The first small scale catalytic production of ammonia began in 1905, when Haber used an iron-based catalyst[29–32].

The development of an industrial process for synthesizing ammonia can mainly be accredited to the work of Haber, Bosch and Mittasch. Carl Bosch began working for BASF in 1908 and was immediately assigned to the development of the ammonia process. In 1909 Mittasch developed the first industrial catalyst for the production of ammonia from hydrogen and nitrogen, and one year later the first large scale production of ammonia based upon the Haber process was constructed at the BASF plant in Ludwigshafen. By the end of 1913 most of the ammonia produced in Europe was designated for the production of explosives, and by this time BASF had constructed two new ammonia plants. BASF were by now also producing nitric acid on an industrial scale, using the Ostwald process, solely for military applications. By 1914, when war had broken out in Europe, all of BASF's production of ammonia was designated for the production of explosives[29,33–36].

Figure 6 Wilhelm Ostwald (1853–1932)

The progress of catalysis during the war was slow, but there are a few developments worth mentioning. In 1915 Irving Langmuir presented his theories on the adsorption isotherm based upon early work done by Haber[37]. Langmuir is also accredited with the developing Temperature Programmed Desorption the following year[38].

In 1918, at the end of the third period, Haber received the Nobel Prize in chemistry for the synthesis of ammonia. The decision to give Haber the award sparked off protests all over Europe due to his role in the development of chemical weapons (chlorine gas), which was used against the Allied troops during the war. The third period of catalysis ended somewhat in shame as the catalytic developments were dominated by the production of weapons of destruction.

The increase in global mobility by developing catalytic fuel processes (1918–1945)

The catalytic developments of the fourth period were dominated by the petroleum industry. In this section we will try to follow the catalytic evolution chronologically as there are a large number of significant events that need to be highlighted. Special attention will however be paid to the petroleum industry as it defined the catalytic progress of the period.

The first significant development came in 1920 when the Standard Oil Company began large scale industrial production of isopropanol from petroleum. The production of isopropanol is significant as it was the first large scale process which used petroleum in the feed.

In 1922 Franz Fischer and Hans Tropsch managed to synthesize hydrocarbons from carbon monoxide and hydrogen (from coal gasification) at room temperature. This discovery is without a doubt one of the most important chemical achievements of the period. Fischer and Tropsch continued development of their process and in 1925 were able to obtain high yields by operating the process at high pressure. The process was particularly important during World War Two when the demands for hydrocarbons rapidly increased. The process is as relevant today as it was 80 years ago, and is employed by several companies, including Shell and SASOL[39–41].

Methanol has been one of the most important bulk chemicals of the twentieth century with a vast amount of applications, ranging from functioning as a base chemical in the production of formaldehyde and MTBE, to being used as a fuel in fuel cell vehicles. The first large scale industrial production of methanol started in 1926 when DuPont began producing synthetic methanol[42,43].

In 1927 the knowledge of catalysis took a gigantic step when Hinshelwood presented his kinetic theory based upon earlier findings by Langmuir. The principles of Langmuir-Hinshelwood kinetics are still being applied in catalytic modeling today and gave Irving Langmuir the Noble Prize in 1932. The discoveries of Langmuir and Hinshelwood was popularized by Olaf Hougen and Kenneth Watson who applied Langmuir and Hinshelwood's theories to reactor design and chemical engineering principles[44].

1921 was the year that, after investigating over 2,000 different substances, Thomas Midgley at General Motors Chemical Company discovered that tetraethyl lead could be added to gasoline as an antiknocking agent. The discovery of tetraethyl lead was extremely significant as it both increased the performance of the automobile engine as well as prevented destruction of the engine by knocking[45].

Steam reforming has been vital for the production of hydrogen in the modern petroleum industry. The first commercial steam reforming plant was constructed in 1930 by the Standard Oil Company in New Jersey.

The knowledge of surface chemistry developed at a significant rate during the 1930s. Special attention should be paid to Igor Tamm, who performed ground breaking work on electron states on metallic surfaces, and to John Barden for his investigations on the structure of electrons on metallic surfaces[5].

The catalytic cracking of petroleum was developed by Eugène Houdry in 1936 and is certainly one of the most important chemical processes ever developed. Houdry originally developed the process for the Sun Oil Company, who did not want to resort to tetraethyl lead as an additive in petroleum. The process became incredibly relevant during World War Two when there developed a sudden demand for aviation gasoline. Between 1938 and 1950 construction was completed on several cracking units all over the world and several improvements were made to the process. The most important modification came in 1941 when fluid catalytic cracking (FCC) technology was introduced. The FCC technology was developed by Lewis and Gilliland, at MIT, for the Standard Oil Company. The modification made by Lewis and Gilliland solved most of the problems associated with the fixed-bed Houdry process and played a very important part in providing the vast quantities of gasoline that was needed during World War Two[39,46,47].

The ammonia process, which was incredibly important during the third period of catalysis, was investigated further during the fourth period of catalysis. The most significant development came in 1940 when Temkin published a detailed description of the kinetics of the ammonia process. Hendrik Kramer published the same year a detailed study on the kinetics of catalytic reactions[5,48].

The fourth period of catalysis ended with that of World War Two in 1945. The most important catalytic event at the end of the period is the Allies' decision to split I. G. Farben into BASF, Bayer and Hoechst as a result of their role during the war.

From war to peace (1946–1970)

As the world moved away from a war-based economy there was a natural shift in the demands of chemicals. In Europe there was an explosion in the market for automobiles, which in turn caused a swift increase in the demand for petroleum. The catalytic production of polymers from petrochemicals also played a vital role. The petroleum industry that forged the fourth period of catalysis therefore played an equally important part in the fifth period, with the only real difference being the commodities produced. In order to avoid missing any of the significant events of this period we will present the events of this period chronologically.

In 1949 the first organized catalysis meeting took place at the University of Pennsylvania. The meeting was organized by Prof. Farkas, who was later elected chairman of the Catalysis Club which held its first meeting in December of the same year. 1949 was also important from a commercial viewpoint as it was the year that the first commercial naphtha reforming plant became operational. The plant was constructed and operated by Universal Oil Products (UOP)[47].

1950 is undoubtedly one of the most important years in the history of catalysis. It was this year that the Faraday Society organized the first conference ever devoted to heterogeneous catalysis. The meeting was attended by most of the dignitaries of catalysis, and some of the topics presented at the meeting were[49]:

- D. D. Eley, The heat of adsorption of hydrogen on metals.
- G. M. Schwab, Alloy catalysts for dehydrogenation
- D. D. Dowden and P. W. Reynolds, Electronic effects in catalysis by metal alloys
- W. Selwood and L. Lyon, Magnetic susceptibility and catalyst structure
- M. W. Tamele, Surface chemistry and catalytic activity of silica-aluminum catalysts
- John Turkevich, H. H. Hubbell and James Hillier, Electron microscopy and small angle X-ray scattering

During the same year a linear relationship between quinoline chemisorption and catalytic activity for gasoline cracking was developed by Oblad's group[47,50].

In 1951 Wheeler discovered that diffusion had a significant impact on the activity and selectivity of a catalytic system. Wheeler's work has played a crucial role in the design of industrial catalytic systems[51].

In 1953 there were two major catalytic discoveries, those of Karl Ziegler and Oblad's group. The first and most important was Karl Ziegler's discovery of a catalytic system for polymerizing ethylene at low temperatures and pressures to form linear crystalline polyethylene[52]. One year later in 1954 Giulio Natta invented stereo-specific polymerization of propylene to form crystalline propylene. Ziegler and Natta's discovery gave birth to a new industry, and new products based upon their original ideas are continuously being developed today[53]. Karl Ziegler and Giulio Natta were awarded the Nobel Prize in 1963 for their work on polymerization.

1953 was also the year that Oblad's group discovered that naphtha reforming takes place by dual functional catalysis which enabled increased activity and selectivity in industrial naphtha reforming[47].

A significant development in catalysis came in 1954 when the first method for characterization of catalysts was developed by Eischen and co-workers. Eischen's group developed a method for studying carbon monoxide adsorption on copper catalysts, with IR-spectroscopy. Eischen's group also developed methods for the characterization of active sites on metal and metal oxide surfaces by adsorption, as well as a method for distinguishing between Brønsted and Lewis acid sites[54].

Other advances in 1954 worth mentioning are the introduction of chromium-based catalysts for the production of polyethylene by Phillips Petroleum and the announcement of the Gulf Oil company to use Ziegler-Natta catalysts in the production of synthetic rubber[47].

The Phillips process developed in 1954 became in 1956 the world's largest source for polyethylene. The process appeared at the time to be superior to the Ziegler-Natta Process; however the key to Phillips' success was a result of clever engineering and large scale manufacturing[55]. 1956 was also the year that the first International Congress on Catalysis (ICC) was held in Philadelphia. There were more than 500 delegates present at the conference and the forum still exists today as an independent organization.

In 1960 there were three industrially important processes introduced on the commercial market[47]:

- Ethylene to acetaldehyde — Wacker Chemistry[56]
- Benzene to Cyclohexene (Hydrar process) — UOP
- World's first Acrylonitrile Plant — SOHIO

1962 was an important year for catalysis both academically and commercially. It was the year that saw the birth of Journal of Catalysis, the first journal devoted solely to catalysis, and the Nickel-based steam reforming catalyst was introduced. The $NiK_2Al_2O_3$ catalyst had higher activity and selectivity than all other previous steam reforming catalysts, increasing the economic gains of the process[57].

In 1964 there was an extraordinary number of new catalysts and processes developed. The most important was Mobil Oil's development of the rare earth metal stabilized X-zeolite for catalytic cracking. The development of this zeolite revolutionized the petroleum industry and is today one of the most important catalytic materials available[58].

Other developments worth mentioning are:

- The metathesis of olefins by Banks et al.[59]
- The development of the mechanism for hydro-cracking by Coonradt and Garwood[60]
- The mechanism for CO adsorption on transition metals explained by Blyholder[61]

When Wilkinson developed a homogeneous catalyst for hydrogenation in 1965, he started a new branch of catalysis[62]. Today, homogeneous catalysis plays an important role in the production of pharmaceuticals and fine chemicals. The discovery gave Wilkinson the Nobel Prize in 1973.

In 1966 ICI developed a copper-based methanol synthesis catalyst that enabled the process to operate at low temperature and moderate pressure. The modification of the methanol process played an important part when an alternative for tetraethyl lead was to be developed, as vast quantities of the substitute were required[63].

Other developments of 1966 that are worth mentioning are:

- The introduction of the concept of hard and soft acid sites by Pearson[64]
- The development of a method for calculating the coordination number of surface atoms in the stable form of small metal particles by van Hardeveld and Montfoort[65]

We have decided to end the fifth period of catalysis at the end of the sixties as there is no clear transition into the sixth period and therefore the beginning of a new decade seems as good a starting point as any.

Environmental catalysis (1970–20??)

The sixth and current period of catalysis has been characterized and influenced by environmental driving forces and the Science's integration with new technologies, such as super computers. The development of rapid inexpensive computational systems has in fact created a new branch of catalysis, namely mathematical modeling, which has had a significant impact on the methods used today for developing new catalytic systems.

The amount of new processes, catalysts and discoveries during the sixth period are countless and listing them all chronologically would be implausible for this paper. We have therefore indentified the most significant developments and how they influenced the progress of catalysis and affected the world.

The negative impact of the exhaust gas from automobiles was debated heavily during the late sixties and early seventies. The first commercial exhaust after-treatment system was developed by Engelhard in the mid sixties[66]. The development of exhaust gas catalysts has led to incredibly large reductions in emissions and has also governed the evolution of the combustion engine. The exhaust gas catalyst system is now the most common catalytic reactor in the world.

The role of the zeolite increased steadily during the sixth period as research groups all over the world attempted to find new areas of application for zeolites. The most notable new processes using zeolites during the sixth period are Mobil Oil's methanol-to-gasoline process which operates with a ZSM-5-zeolite catalyst (1976)[67] and the oxidation of benzene to phenol over a Fe-ZSM-5 zeolite catalyst (1990).

During the eighties there were several new catalytic processes introduced to the market. One of the most important process developments was the introduction of Selective Catalytic Reduction (SCR) for controlling the NO_x emitted from nitric acid and stationary power plants[68]. SCR technology is today implemented in several mobile applications ranging from large ships to heavy-duty trucks.

There were also several developments in catalytic processes for the production of synthetic polymers during the eighties. In 1980 Shell and Union Carbide developed a process for producing linear low-density polyethylene. The process was revolutionary as it gave the producers total control over the material properties of the product. The process was later extended to the production of polypropylene. The advantages of using homogeneous catalysts in the production polymers were clearly demonstrated[69].

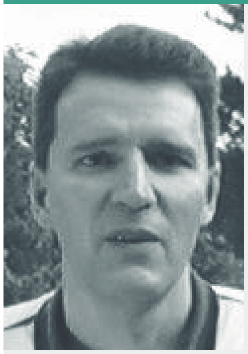
The ammonia process is today as relevant as it was during the second period of catalysis and improvements and investigations into the nature of the process are constantly being carried out. In 1982 Ertl's group defined the energy profile of the synthesis of ammonia and in 1992 the first commercial use of a catalyst without iron was presented[70].

Other process developments of the period worth mentioning are the introduction of Reduced Crude Cracking (RCC) by Ashland Petroleum., the use of Fischer-Tropsch as a source for producing alpha-olefins and UOP's Cyclar process for the production of aromatics from Liquefied Petroleum Gas (LPG).

Epilogue

The point in time when the transition into a new area of catalysis will take place is today impossible to predict. What we can however say with certainty is that the future of catalysis all will be as exciting tomorrow as it was during the early years. Without a doubt there will be scientific contributions from the catalytic scientists of tomorrow that will be remembered by future generations in the same manner that we remember the accomplishments of Berzelius and Davy.

Curricula vitae



Lars J. Pettersson is an associate professor in chemical engineering at the Department of Chemical Engineering and Technology, Royal Institute of Technology in Stockholm. He received his Master of Science and PhD at the same university. Lars has more than 20 years of experience in using heterogeneous catalysis for improving efficiency and lowering emissions in the transportation sector. Exhaust gas catalysts for alternative-fuelled vehicles and onboard hydrogen generation for vehicles with fuel cells or international combustion engines as power sources are some examples of his work. Lars has a particular interest in the history of science and technology with a special focus on Berzelius activities and the early years of the petroleum industry. He teaches Reaction and Separation Engineering, Environmental Catalysis, Material and Energy Balances, and Chemical Reaction Engineering, as well as various courses on a postgraduate level.

Bård Lindström obtained his Master's degree in Chemical Engineering from the Royal Institute of Technology-KTH in Stockholm and stayed on for doctoral work in the group of Ass. Prof. Lars J. Pettersson. His PhD thesis focused on the development of a compact methanol reformer for generating hydrogen for fuel cell vehicles. The result of his PhD studies resulted in several publications in international journals.

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