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A history of industrial catalysis

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ABSTRACT

Histories of catalysis have been told by others from different perspectives. This manuscript highlights key catalytic discoveries that led to commercialized, industrial processes. The intent to show how catalysis evolved over the last 250 years into major industries focused not only at catalyst production, but also significantly impacting the production of commodity, specialty and fine chemicals, as well as petrochemical, petroleum, emissions control, and polymerization. For centuries before 1750, catalysts were used to make beverages and foods. One sees that the Lead Chamber process for the production of sulfuric acid is among the earliest of catalytic processes and reaches back to 1750. Pursuit of a sound fundamental understanding of catalysis in the 19th century, led to the application of these materials to a variety of basic chemicals. The development of petroleum fuels led to a vast petrochemicals business which in turn fed a growth in specialty and performance chemicals. New drivers in the 20th century from the transportation and the environmental business sectors provided market pull to bring about more catalytic solutions for more industries. The often novel, catalytic properties of zeolites created new commercial applications, while environmental legislation created market pull to use catalysis to meet the new regulatory standards. As we move forward into the new century, we continue to see market pull from growing interests in biomass, sustainability, emissions control, and energy.

1. Scope of the assessment

The impact of catalysis and catalysts is substantial. Today over 90% of all industrial chemicals are produced with the aid of catalysts [1]. Industrial chemicals and petroleum refining are interconnected with industrial catalysis. Catalysts impact a sizable fraction of *any* nation's gross domestic product. These materials achieve very high turnovers, such as those in olefin polymerization with some catalysts producing over a million pounds of polymer per pound of metal (in the catalyst) per hour! In 1991 it was estimated that the total value of fuels and chemicals derived from catalysts exceeded $900 billion/year [2]. World catalyst demand is forecast to grow to $16.3 billion through 2012 [3] according to the Freedonia Group. In 2003 global sales of catalysts exceeded 12 billion dollars which was up from 9.3 billion dollars in 1998. [4]. Sales are often divided into chemicals, petrochemicals and petroleum refining products, polymerization, and environmental/emissions.

The story of catalysis has been told in the past by practitioners with different perspectives [5–10]. Lindstrom and Pettersson [11] chose to look at the development of catalysis over periods of time back to the dawn on civilization. Hans Heinemann began his summary following WWII [8]; Kieboom et al. provided a more detailed review which ended in the late 1990s; and Neidleman focused on biocatalysis only [12]. In 1996, Professor Burtron Davis (University of Kentucky) prepared a very nice pictorial poster presentation on 50 years of catalysis (from 1949) which is available on the WWW [13] and at the NACS web site [14]. This was originally prepared to commemorate the advances in catalysis during the formative years of the development of catalysis in America and displayed for the 50th anniversary of the International Catalysis Conferences (Baltimore, MD USA, 1996). It steps one through the science of catalysis marking key events in catalysis over that exciting, 50 years period. B.H. Davis, W.P. Hettinger Jr. also prepared a special symposium series book on an American History of Heterogeneous Catalysis in 1982. This contains a lot of specific chapters on the history around many valuable, catalyzed processes [15] in the US.

This manuscript seeks to provide, on a global basis, brief examples of the development of catalysts into commercial processes. Catalysts are often discovered by more than individuals, rather it is often a team effort. What I would like to do here is describe the history of industrial catalysis on a global perspective and how the work of individuals as well as large teams ultimately led to many of our current commercial, catalytic processes. This assessment will focus primarily on the birth and renaissance of catalysis for more than 250 years from the 18th into the 21st century and focus on the role of industry in discovering,

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developing, and commercializing catalysis. Also, the intent is to focus on the driving forces behind much of industrial catalysis and how those efforts were often initiated, inspired and supported by the scientists focusing on explaining the fundamentals of the science. Early sketches of key catalytic discoveries and how they led to commercial processes will be provided. The purpose, in this limited number of pages, is to provide some of the key, historical events, but not in a comprehensive or detailed treatise nor to summarize the many more commercialized processes [16,17]. Rather it is my intent to show how catalysis evolved over the last 250 years into major industries focused not only at catalyst production, but the production of commodity, specialty and fine chemicals, as well as petrochemical, petroleum, emissions control, and polymerization.

2. Catalysis for commodity chemicals

Catalysis was practiced by many early societies without realizing its impact as demonstrated by the production of wine and beer (fermentation), soap, cheese, sulfuric acid (oil of vitriol), and ether. Catalysis emerged from scientists seeking to understand the chemistry and the origin of the promotion by catalytic materials. Sir Humphrey Davy (in 1817) [*throughout this manuscript, specified years are intended to reflect the approximate year*(*s*) *of impact of the person's work*] observed the accelerated combustion of coal gas with oxygen using a glowing Pt wire (heterogeneous, catalytic oxidation). Ultimately, society used chemicals to improve the way we produce materials in our environment. This led to the growth in applications of catalysis (often driven by the scientific knowledge generated within the academic community and industry) which began to translate into hundreds of economically attractive, industrial applications. Huge industries emerged around making chemicals, fuels and pharmaceuticals in sufficient quality so that materials and products could be produced in sufficient quantities and at a reasonable cost. Thus, catalysts were discovered and developed as a means to enhance the production of these materials. Much of the very early history of catalysis before 1934 is nicely summarized by Burwell [18] and Robertson [19].

Jöns J. Berzelius, a Swedish chemist, recognized a common “force” governing various chemistries reported by others and provided an early definition (1836) [20,21] of catalysis: reactions that are accelerated by substances that remain unchanged after the reaction. Scientists like Berzelius, Sir Humphrey Davy [22], and Wilhelm Ostwald, working in the 1800s, discovered and pursued many of the early fundamental concepts of catalysis. Others like Louis Jacques Thenard (1813 studying the decomposition of NH_3), Joseph Priestley, Johann Wolfgang Döbereiner (in 1810: Pt black oxidation of alcohols), Ambrogio Fusinieri (1824, catalytic oxidation over Pt) [23], Michael Faraday [24] and Pierre Dulong appreciated the use of various materials as catalysts without defining them as such or defining the fundamental underpinnings [25].

As early as 1746, John Roebuck, an English inventor, began producing somewhat (~35%) concentrated sulfuric acid in large lead-lined chambers [26]. Here SO_2 (produced by burning sulfur or roasting of sulfur containing metal ores) is oxidized by NO_2 in large, lead-lined chambers (easier to scale-up than using glass). In 1831, Peregrine Phillips Jr. a Bristol manufacturer of vinegar, developed the more economical Contact process for the manufacture of much more concentrated sulfuric acid using a Pt or later a V_2O_5 catalyst.

In 1838, Frékéderic Kuhlmann [8] filed for a patent on the aerial oxidation of ammonia over platinum to nitric acid. He, and others, appreciated the strategic need for nitrates for explosives production in the event of war without a dependence on distant imports of Chilean saltpeter. Many fundamental issues of science, process chemistry, and global events delayed commercialization of this invention until 1906.

Although catalysis is practiced on a large scale by Nature in the form of digestion, fermentation, and many other forms of enzymatic processes, the first man-made commercially catalyzed processes did not emerge until about 1750 and then there was a gap until the late 1800s. Here, catalysts first emerged for the production of large volumes of key chemicals, including:

- Sulfuric acid in 1746 [10] Lead Chamber process.
- SO_2 oxidation by the Contact Process in 1831.
- Chlorine production in 1875 over $CuCl_2$ (Deacon process) by $HCl + O_2$ (now outdated) [27].
- Sulfuric acid production enhanced by use of V_2O_5 in 1875.
- Nitric acid production enhanced by the use of Pt gauzes in 1904.
- NH_3 synthesis from N_2 and H_2 in 1905; at large scale at BASF in 1910.
- Methanol synthesis developed by BASF (1923) at high pressure over a ZnO-chromia catalyst.
  - ◦ This marked the emergence of synthesis of large volume organic chemicals.
- Fischer–Tropsch synthesis of synthetic fuels commercialized in 1930 as an alternative to processing heavy oil, although discovery of the process goes back to 1913 patents by Mittasch and Schneider [28].

The very first commercial applications of catalysis occurred without a firm grasp of the science and principles like equilibrium; equipment for running reactions at high pressures did not exist. Applications of these early inventors led the way for industrial production of basic chemicals such as the synthetic production of indigo, sulfuric acid, hydrolysis of starches, and the hydrogenation of fats. Studying the oxidation of ammonia, Wilhelm Ostwald and his assistant, Eberhard Brauer, built a pilot plant in 1904 to confirm their laboratory studies and theories on ammonia oxidation. In May 1906, a 300 kg/day HNO_3 plant using corrugated Pt strips was brought on stream; in 1908 production was 3000 kg HNO_3/day. Details for most of above examples of early, commercial catalytic processes (largely for the production of commodity chemicals and feedstocks) are provided in Eric Rideal and Hugh Taylor's excellent early book (in 1919) on catalysis [21] and the book on selected histories by Davis and Hettinger [15]. (The former book is no longer under copyright and can be downloaded directly from the World Wide Web [29].)

At first, we see catalysis as a science being pursued by creative individuals largely in academia seeking to understand how catalysts influenced chemistry. In time as the demand for the production of substantial volumes of these catalyzed chemicals emerged, small industrial companies emerged to make these value-added chemicals. In addition an industry developed for preparing these iron, vanadium, cerium, chromium, copper, and manganese oxides as well as clay catalysts. These companies often employed and/or were founded by those from academia; thus, creating a profession using students trained in academia to add value to the chemicals based on the understanding created in the academic labs. Later, the Kaiser–Wilhelm–Gesellschaft research institutes in Germany created a home for those pursuing technical applications of catalysis and teamed with those in industry. Some industrial companies eventually generated their own fundamental research labs in the 1940s through the 1970s to focus on a huge growth in new chemical products (Dow, GE, DuPont, BASF, ICI, Monsanto, and others). So too, governments worldwide provided early funding of academic labs and then also started to build their own federally funded labs to use and to create new catalytic science. These included the US National Labs at Oak Ridge, Sandia, and Hanford (the latter is now PNNL National Labs); the Max

Planck Institutes in Germany; the Boreskov Institute of Catalysis in Russia, NIOK (Netherlands Institute of Catalysis Research); as well as other government funding of individuals and centers within universities around the globe. From the 1970s to present, these national labs have served to bring together academic, industrial and government participants in catalysis research. In addition, catalysis underpins many of the different institutes within the Max Plank Society as supported by German federal and state funding.

3. Individuals establish fundamentals; teams emerge

At the turn of the 20th century, we saw individual scientists pursuing a fundamental understanding of catalysis, eventually teaming with others to undertake the enormous efforts needed to develop industrial catalysts:

- Nicolas Clément (Lead Chamber process for H_2SO_4) was a professor at Conservatoire des Arts et Metiers in Paris.
- Wilhelm Ostwald was a chemistry professor (in Latvia and Germany) famous for his pioneering work in electrochemistry and catalysis.
- Paul Sabatier was a chemistry professor in France whose fundamental studies included the role of finely divided metals for hydrogenating organic compounds.
- Vladimir Ipatieff, a Russian nobleman working at the Mikhail Artillery Academy and later Professor of chemistry and explosives at University of St. Petersburg. He later fled to the USA and had a dual appointment at UOP and Northwestern University. He led the discovery of the promoter effect (1909) and paraffin alkylation by olefins (1935) with acid catalysts (solid phosphoric acid) [10,30,31]. He played a leading role in the development of UOP's polymerization, alkylation, and isomerization processes, and thus made a major contribution to the development of the high-octane aviation fuel.
- Carl Bosch was a chemist working for BASF with his assistant, Alwin Mittasch; they scaled up the NH_3 synthesis process developed by Fritz Haber from Technische Hochschule of Karlsruhe (later the Director of the Kaiser Wilhelm Institute for Physical Chemistry). This work on the NH_3 synthesis catalyst and process is a major milestone of catalysis.
- Irving Langmuir began at Stevens Tech (USA) then joined GE in 1909 working on light bulb problems while contributing to the fundamentals of catalysis especially with respect to surface chemistry. In 1915, he first described heterogeneous catalysis as something that occurred in a single layer of gas molecules (although an oversimplification) held on a solid surface [32].
- Sir Hugh Taylor (a chemistry professor at Princeton) and Sir Eric Rideal (a Professor of Physical Chemistry at Kings College) together authored the first notable book on catalysis (1919) [21].
- Franz Fischer was director of the Kaiser Wilhelm Institute for coal research working with Hans Tropsch in the 1920s.
- Murray Raney (1926) is noted for the unique type of metal hydrogenation (particularly of vegetable oils) catalysts which bear his name [33].
- Herman Pines of UOP and Northwestern University (while working with Vladimir Ipatieff) was very active [34] for over 50 years (beginning in $\sim$1930) in developing acid and base catalysis, aluminas, aromatization, alkylation, dehydrogenation catalysts and metal hydrogenation catalysts, all of which were very instrumental in a number of commercial petrochemical processes (high-octane gasoline (in collaboration with Ipatieff), biodegradable detergents, and dehydrogenation of paraffins).
- Paul Emmett's work provided additional fundamental understanding of NH_3 synthesis and he contributed to the BET method for measuring surface area [35].
- Heinz Heinemann had an impressive career in both industry and academia. While at Berkeley, the research team he led invented the process of oxydehydrogenation; over his long career, he was associated with more than 14 commercial processes.
- Frank G. Ciapetta (1950) was another pioneer in catalysis who is noted for his work on a new, general class of paraffin isomerization catalysts (consisting of a hydrogenation-dehydrogenation agent such as Ni or Pt in combination with an acidic cracking catalyst (such as silica–alumina)) [36].

4. Basic chemicals industry emerges

During the building of fundamentals of catalysis, a chemicals industry emerged largely based upon the use of catalysts. First with the efficient production of basic, inorganic chemicals such as sulfuric acid, ammonia, and nitric acid. These were driven by the need for NH_3 as a component of agricultural fertilizer, and later by the need for bulk chemicals, especially for explosives in World War I. Other food processing needs emerged such as the hardening of fats over Ni based catalysts in 1907.

Early in the 20th century, coal was a primary feedstock for basic organic chemicals, largely based on coal liquefaction, distillation of coal tar, acetylene (from coke) or coal gas (CO/H_2). Although the first oil well was drilled in 1859 and thermal cracking of petroleum was available, it was not until the accelerated demand for gasoline and the development of the Houdry catalytic cracking process that the modern petrochemicals industry really emerged. Petroleum, being a liquid, Houdry's catalytic cracking (1930) played a major role in this shift away from coal feedstocks. Later, the FCC (Fluid Catalytic Cracking) process proved invaluable for high-octane aviation fuel for jet fighters in WW II. With the development of a petrochemicals industry, catalysis played a crucial role in producing products to enhance our quality of life through plastics, pharmaceuticals, and specialty chemicals. The many, major applications of catalysis to the petroleum industry did not begin after the 1920s with rapid growth after the 1940s. Occasionally, industrial teams developed new catalyst technology, but in many cases specific individuals are credited with the key discovery.

- Oxidation of benzene and aromatics to anhydrides in 1920 over V_2O_5.
- Isopropanol, the first bulk chemical produced from petroleum (from refinery propylene over an acid catalyst) in 1920 by Standard Oil of New Jersey.
- Production of H_2 by steam reforming in 1930 for use in refineries.
- Ethylene oxide with Ag/alumina in 1937.
- In 1938 Otto Roelen discovered oxo synthesis while working at Fisher's Kaiser Wilhelm Institute for coal research.
  - This marked the emergence of a major, homogeneously catalyzed processes.
- Eugene Houdry was a mechanical engineer in France, who came to the USA lured by Vacuum Oil Co. and formed his own historic catalyst company; he is credited with the extremely important discovery and development of catalytic cracking [37]. He pioneered the use of clay catalysts and the engineering of continuous unit operations. The first commercial cracker went on stream in Marcus Hook, PA in 1937.
- In 1938 Standard Oil Eger Murphree, H. Martin, D. Campbell, and C. Tyson teamed with MIT's Warren Lewis and Ed Gilliland to develop the Fluid Catalytic Cracking (FCC) process [38].
- In the 1960s the approach of hydrocracking (cracking of molecules in the presence of H_2) (originally used in Germany (from 1915 to 1945) to crack coal based feeds) was revived beginning with Chevron using metal promoted silica–aluminas, aluminas, and later zeolites [39].

The work of Fisher and Tropsch in producing chemicals from synthesis gas led to huge commercial plants using coal or later natural gas as feedstocks to produce liquid fuels. This work of several groups of scientists is nicely summarized in the recent reviews by Casci et al. [28] and with a different focus by Stranges [40].

5. Transportation as a driver

As the transportation industry emerged in the 20th century, catalysts were there to refine petroleum products into fuel feedstocks via:

- Alkylation of olefins and isomerization of paraffins with $AlCl_3$ in 1932.
- Catalytic cracking in 1936.
- Naphtha reforming in 1950.
- Friedel-Crafts for cumene production and later zeolites [41].
- Oxychlorination in 1964.
- Zeolitic cracking and hydrocracking in 1964 (more details in Section 9.0, below).
- Multi-metallic reforming in 1967.
- Hydrodesulfurization in 1960s.
- Dewaxing and hydroprocessing [42].

6. Polymers contribute to growth of petrochemicals

Refining petroleum produced other products that could be used to generate petrochemicals used to enhance our quality of life. Again catalysts were discovered to improve the production of chemicals. At first bulk chemicals were produced and led to other commodity chemicals such as polyethylene, acetic acid, and propylene oxide, many enabled by catalysts, including:

- 1930s and 1940s DuPont developed nylon intermediates via adipic acid.
- Vladimir Haensel, a student of Ipatieff's, joined UOP and developed Platforming^{TM} [43] in the 1950s which used very small amounts of Pt as a catalyst for the high yield of high-octane gasoline from petroleum based feeds.
- Robert Banks and J. Paul Hogan discovered a Cr/silica catalyst for ethylene polymerization at Phillips Petroleum in the early 1951; prior to this, such polymerizations were free-radical initiated at very high pressures. This was commercialized in 1956.
- Karl Ziegler in 1953 at Max Planck Institute for Coal Research discovered use of Ni and Al-alkyls for ethylene polymerization and Giulio Natta at Milan Polytechnic Institute discovered stereoregular polymers.
- Late 1950s, Chevron scientists had discovered Pt–Re bimetallics for reforming of petroleum.
- James Idol of Sohio led the discovery (1957) of bismuth molybdate catalysts for the ammoxidation of C_3H_6 to acrylonitrile acrylonitrile. [Idol is the inventor listed on the key Sohio patents, but others involved in the early work included James Callahan, Ernest Millberger, Art Miller, Robert Grasselli, and Robert Foreman].
- ICI (1960s) developed a Cu/ZnO catalyst for methanol synthesis operating at much lower temperatures and pressures tied to a more efficient synthesis gas purification.
- Hoechst-Wacker process using an organopalladium catalyst for acetaldehyde synthesis from ethylene and water in 1960s.
- Both UOP and Monsanto commercialized (1960s) processes for the production of biodegradable detergents (LAB, Linear Alkyl Benzene Sulfonates) [44,45].
- Halcon (Scientific Design) team in 1962 discovered direct, selective O_2 oxidation of propylene to propylene oxide with t-BuOH co-product and commercialized this in partnership with ARCO.
- Scientists at Phillips Petroleum, DuPont, and Standard Oil of Indiana independently discovered olefin metathesis in 1964 [46]. The Phillips Triolefin process was commercialized in 1966 and later Shell commercialized the Shell Higher Olefins process (SHOP) in 1977 [10].
- John Sinfelt's development of bimetallic catalysts (1969) (in particular Pt–Ir) at Exxon led to improved commercial reforming of petroleum naphtha fractions for producing high-octane components for gasoline; his work provided scientific basis for several practical applications in petroleum refining.
- Numerous industrial teams discovered and developed emission control catalysts for transportation vehicles in the 1970s (see Section 5).
- Union Carbide and Celanese commercialized the selective oxidation of propylene to acrylic acid in 1970s; this was an important shift away from the use of acetylene as a feedstock.
- Also in the 1970s, Union Carbide and Celanese introduced improved Rh phosphine catalysts for making aldehydes (hydroformylation).
- William Knowles at Monsanto in 1974, discovered a catalytic route to L-dopa [44] using Rh-chiral phosphines; his was the first direct, commercial synthesis of an optically active material over a synthetic catalyst.
- Metallocenes for olefin polymerization were discovered by W. Kaminsky in 1976.
- Low pressure, homogeneous, Rh catalyzed acetic acid production from methanol in 1980 at Monsanto: five months from the first lab experiment to scale-up [44] led by James Roth.
- Eastman Chemicals opens the first coal to acetyl chemicals in 1983.
- MeOH to gasoline or olefins (Mobil Oil) in mid 1980s.
- Shape selective reactions (such as of ethylbenzene) in 1980–1995 (see Section 9).
- UNIPOL^{TM} polypropylene process by Union Carbide in 1985.
- James Stevens at Dow Chemical developed high yield polymerization catalysts including the INSITE^{TM} process using single-site, constrained geometry catalysts (late 1980s).
- Propylene oxide from H_2O_2 and propylene in 2008 with the TS-1 catalyst.

During this growth of new chemicals, the first organized meeting in catalysis (organized by B. Farkas) occurred in 1949. The first issue of Advances in Catalysis emerged in 1948, and the first conference in heterogeneous catalysis was sponsored by the Faraday Society in 1950. The first International Congress on Catalysis was held in Philadelphia, PA, USA in 1956. The birth of the Journal of Catalysis occurred 6 years later in 1962, and Catalysis Reviews in 1967. In 1965, the North American Catalysis Society (originally as the Catalysis Society of North America) was created by the association of several local catalysis clubs within the USA.

Additional details behind some commercialized processes above can be found in articles by Zoeller (Eastman's Chemicals from coal) [47]; M. Twigg (auto exhaust catalysts) [48] and G. Lester [49]; E. Flanigan (zeolite discovery and applications) [50]; J. Hart and R. Syvert (Selectfluor – a specialty fluorinating agent) [51]; R. Farrauto and R. Heck (monoliths for environmental applications) [52]; W. Kaminsky (metallocenes) [53]; J. Roth (acetic acid and detergents) [44]; H. Eleuterio (methathesis) [54]; W. Reichle (catalytic cracking) [55]; A. Bisio (UNIPOL polymerization process) [56]; G. Kauffman (Nylon) [57]; alkylation [41]; M. Kerby, T. Degnan, D. Marler, and J. Beck (petroleum lubricants) [42]; V. Haensel (Platforming) [43] and by T. Degnan, G. Chitnis, and P. Schipper (ZSM-5 at Mobil) [58].

7. Fine and specialty chemicals grow

While a commodity chemicals industry was maturing in the 1950s and 1960s, a specialty chemicals industry was building and growing, resulting in new families of chemicals:

- Production of agricultural pesticides.
- Production of pharmaceuticals.
- Water treatment chemicals.
- DABCO® urethane catalysts at Houdry Process Corp.
- Selective hydrogenations; hydroformylations in 1964 (G. Wilkinson and others).
- Asymmetric hydrogenation in 1974.
- Numerous elective oxidations with H_2O_2 or O_2.
- Production of new fibers.
- Production of dyes, pigments, etc.
- Flavor and fragrance chemicals.

Many of these specialty chemicals were being driven by the discovery of very selective (regio and optically active) catalysts with high product selectivity using optimal feedstocks.

8. Environmental emissions business

The growth of the transportation industry, industrial activity, and a severe increase in air-born pollutants drove the implementation of new laws and the creation a new industry using catalysts to control vehicle and stationary engine emissions [6,59]. From the 1960s and driven by vehicle and stationary emissions regulation, environmental catalysis grew to become a huge segment of the current global catalyst business. Today, sales of environmental catalysts comprise almost one third of the $16 billion catalyst business. These commercialized events included:

- Hydrodesulfurization in 1960s, a extremely important method for removal of sulfur from fuels, resulting in considerable reduction in global emissions of sulfur oxides.
    - Created stepped-up demand for SMR for H_2 production.
- Auto emission control catalysts in 1974 (oxidation), 1978 (three-way) [48,49], 1990s (Pd three-way) [60].
    - Developed by Johnson Matthey, Houdry Catalyst, UOP, W. R. Grace, and American Cyanamid, Engelhard (now BASF), Degussa, and Corning (for catalyst supports) (refer to [60]).
    - By 1990 emissions of hydrocarbons, NOx, and CO from vehicles were reduced by 90% over levels in 1965 while allowing better fuel economy once optimised.
- Selective catalytic reduction of NOx by NH_3 (SCR) for power plants in 1980 using V, W, and Ti oxides extruded into monolith forms.
- Ozone emission control catalysts developed by Engelhard (now BASF).
- Reduction of ozone generating CFCs [61].
- Catalytic destruction of volatile organic compounds (often with precious metal supported on extruded honeycomb monoliths) is extremely important to the consumer products industry, as well as to foods and chemicals production [62].
- Diesel oxidation exhaust catalysts in 1990 using cerium only.
- Variety of solutions using metal oxides for catalytic decomposition of N_2O [63] which resulted in an 81% reduction of all N_2O emissions from the world's adipic acid plants.
- Pt–Rh-alkali NOx storage catalysts, Toyota Motor, 1994.
- Diesel particulate catalysts in 2003.
- Urea SCR for NOx emissions control in mobile vehicles, 2004.
- NOx removal in FCC regenerator units, 2007 [64].

More details can be found in the classic book by Heck et al. [60].

9. Zeolites – a materials driver

Not only did needs like transportation and emissions control generate new catalysts and entirely new businesses, but the discovery and development of zeolite molecular sieves [50,58,65] stimulated the discovery of many novel and selective catalytic processes. The discovery of shape selective zeolites in the 1960s [66] led to many novel, new petrochemical and chemical processes providing high selectivity to a wide variety of reactants and products, strong acid sites, and using materials with novel cation exchange or promotion effects. (Once again, my intent here is not to review the history of zeolites, but only their application to catalysis.) Major discoveries in the use of zeolites for hydrocarbon conversion were developed by a number of industrial laboratories including Union Carbide, Exxon, Mobil Oil (now ExxonMobil), Shell, and others. Some of these processes were already captured above during the discussion about petroleum refining:

- Robert Milton (Union Carbide in 1950s), Donald Breck, Richard Barrer, and Edith Flanigen developed commercially viable routes to various zeolites which enabled their widespread application.
- Jules Rabo working at Union Carbide applied the use of zeolites to petroleum refining (isomerization, 1959), while Charles Plank and Ed Rosinski of Mobil Oil applied zeolites to catalytic cracking (1962) of heavy oil fractions [65].
- Paul Weisz and V. Frilette of Mobil Oil developed the concept (1960) of shape selective catalysts and Werner Haag applied shape selectivity to the production of aromatics.
- George Kerr of Mobil Oil discovered high silica zeolites (ZSM-5 in 1967) and the first, large scale, commercial cracking trial was run in 1983 [50].
- W.R. Grace in 1969 discovered the steaming of Y zeolite to produce ultra-stable Y zeolite.
- Marco Taramasso, Giovanni Perego, and Bruno Notari in 1983 discovered TS-1 (titanium silicalite-1), a selective oxidation catalyst for the epoxidation of olefins, at ENI-SNAM Progetti S.p.A.
- UOP/HYDRO (1995) discovered and developed SAPO-34, a non-zeolitic, phosphate molecular sieve that has strong application to methanol to olefins.

In general, zeolites were used in large volumes to further enhance the catalytic cracking and hydrocracking of petroleum feedstocks and the

- Production of chemicals and fuels.
- Dewaxing of distillates and lubebase feeds.
- Oligomerization of olefins.
- Xylene synthesis and isomerization.
- Ethyl benzene and PET, and
- Gasoline and light olefins from methanol (Mobil Oil, 1976).

10. Emergence of biomass feedstocks

Just as we saw zeolites create new products and processes, we see the concern about renewables, CO_2 levels, and sustainability creating a new chemicals business oriented at biomass feedstocks dependent upon new catalysts to make them competitive with petroleum based feedstocks. These include:

- Trans-estherification of triglycerides with alcohols to biodiesel(fatty acid methyl esters) + glycerin.
- Bioethanol to ethyl acetate.
- Starch to ethanol.
- Glycerin to propylene glycol, propanediol, and other C3s.
- Corn to 1,3-propanediol (Dupont's Bio-PDO) [67].

11. Catalysts driving new technologies

In addition to technology needs driving the development of new catalysts for new products and processes, we have seen catalysts evolve into more exotic materials now driving new technological approaches and new industries, such as

- Electrocatalysis,
- Fuel cells,
- Photocatalysis,
- Phase transfer catalysis.

12. New times bring changes to R&D

In the 1990s we saw the decline of the once popular long term industrial research labs critical to the discovery and development of catalysts. Contract research, often in concert with academic based centers, emerged as a popular way to pursue longer term research.

In this new century, it is clear that, for the most part, chemical companies have abandoned the need to create large catalysis centers within industrial labs; some large catalysis departments remain in some of the major petroleum companies, but increasingly, chemical and petrochemical companies rely now on catalyst producers, institutes, and/or academic groups to discover new catalysts or technology. Each of the major catalyst vendors (such as Johnson Matthey, Süd-Chemie, W.R. Grace, UOP/Honeywell, Albemarle, Royal Dutch Shell, BASF Catalysts, Umicore, Nippon Shokubai, Mitsui Chemicals, and Haldor-Topsøe) maintain sizable research centers in catalysis. In any event, industry must still invest years of effort and sizable capital to develop new technology by scale-up and process design optimization around new catalyst formulations.

The locus of activity in catalysis continues to move. Certainly in the 18th and 19th centuries most of the discovery and growth was in Europe. With the advent of petroleum as a fuel in the 20th century, we saw tremendous growth of catalysis research in the US. Now in the latter decades of the 20th and into the new century we see considerable new growth of catalysis first in Japan and Korea, and now in China with the formation of a major, regional catalysis society (APACS, Asia Pacific Association of Catalysis Societies). Catalysis is associated with the growth of nations, but it also is directly responsible for feeding that new growth through new products and processes to meet societal demands.

13. Summary

Finally, I apologize for topics and discoveries that I have not mentioned; my intent was not to be comprehensive, but to lay out step-out advances in the applications of catalysis to commercial endeavors. There are often many different perspectives behind the history of anything; this is just one history of (industrial) catalysis that should be viewed with the others mentioned at the start of this article [5–15].

Thus, we see the history of industrial catalysis in the last 250 years is still evolving. Beginning as catalysts for bulk basic, industrial, inorganic chemicals, and transitioning to the creation of huge investments and volumes based on petroleum and the need for transportation fuels. Fuels production provided added value with the production of petrochemicals (benzene, adipic acid, acetic acid, etc.) and both business segments required the discovery of novel environmental catalysts. Independently, there emerged novel polymers, specialty chemical, pharma and enzymatic processes also reliant on catalysts. Today, we see a new evolution of alternative fuels largely based on biomass and once again critically dependent on new catalysts. We also see that the locus of intense activity has moved, first from Europe to the USA, and now into the Asia-Pacific region. While the science and production of catalysts continues in Europe and the USA, new growth and aggressive expansion is occurring in Asia. In any event, catalysts will continue to evolve and contribute to supporting new energy resources, attaining tougher emission standards, and adapting to changing feedstocks.

14. What may yet emerge

Looking back on the history of industrial catalysis one is led to speculate on what lies ahead. It is clear that environmental catalysis will have a big impact, and catalysis will be needed to address increased sulfur and NOx emissions, lower CO_2 levels, and alternative fuels. Alternative fuels will rely on catalysts to support new sources of energy as well as a transition to a more energy efficient society in the decades to come. Catalysts will play a crucial role in improved process efficiencies driven by feedstock, energy and the environment. Catalysts will contribute to water purification and recycle, the photodecomposition of water, and perhaps even solar conversion of CO_2 into CHO_x. These will all employ an increased use of theory and modeling to improve our understanding, predictability, testing, and development of catalysts.

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Assembling the history behind any topic is dependent on the views and information available to the author. For that reason, after the bulk of the manuscript was completed, I did reach out to other established experts and sought their input for capturing missed events or improving the manuscript. In this regard, I would like to especially thank, George Lester, Leo Manzer, Ron Heck, Kathy Taylor, and Burt Davis for providing a quick review of the manuscript and offering useful minor changes which I've tried to incorporate.

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