CATALYTIC INDUSTRIAL PROCESSES

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Summary

The success of the chemical industry is in large part merit of the discovery and development of catalysts, and industrial catalysis is essential for most modern, cost and energy efficient means for the production of a broad range of petroleum refining, chemical products, pharmaceuticals and for environmental protection. The global market for catalyst manufacture exceeds $14 billion and it can be estimated that catalysts induce a business of end user goods of over $7,500 billion yearly. The major sectors of catalysts sales are for the oil refining, chemical processing, and emission control markets.

In petroleum refining catalytic processes provide almost entirely the high quality fuels required by the market facing successfully the more and more stringent mandated fuel specifications, and the deteriorating characteristics of crude oils in terms of sulfur and gravity. The bottom-of-the barrel is upgraded through catalysis from low grade and less marketable fuel oil to desulfurized distillates. Industrial catalysis makes also real and economic the exploitation of unconventional heavy crudes and the use of renewable raw materials with the production of biofuels.

Fossil resources, mainly Oil & Gas, additionally do represent the raw materials of choice for all synthetic materials surrounding us. Industrial application of catalytic processes concerns the large fields of the hydrocarbons transformation into intermediates and final products. New catalytic technologies are under development for methane conversion and pose the basis for a new gas-based chemistry. Good hopes for the environment preservation rely firmly on catalytic processes in the production phase and in the emission control.

In the industrial applications catalysis has reached in the last decades a noteworthy

degree of maturity and continues to produce innovation that is reflected in the significant contribution to the development of the modern society. This goal is achieved thanks to the closest synergy of the scientific understanding of catalytic phenomena and the scale-up of the gained knowledge into commercial application.

1. Introduction: Drivers for Development

Catalysts are substances which modify the rate of a chemical reaction without themselves being changed or consumed in the process and without affecting the overall thermodynamics of the system.

The word *catalysis* (from the old Greek $\kappa\alpha\tau\alpha$ -, “down,” and $\lambda\upsilon\epsilon\iota\nu$, “loosen”) was first employed by the Swedish chemist Jöns J. Berzelius in 1835 to correlate observations on the promotion of some reactions made by other chemists in the late 18th and early 19th centuries. The substances promoting various reactions, like the conversion of starch to sugar by Kirchhoff or the combustion of gases by Sir Humphry Davy, were defined *catalysts*, and Berzelius postulated the action of an unknown catalytic force. Other chemists involved in early catalytic studies mentioned *contact processes* (Mitscherlich) or *contact action* (Döbereiner).

The term "catalyst" has also migrated from the world of science to everyday spoken language. It is noteworthy that this term is always used with a positive meaning. "Catalyst" from the Thesaurus of The American Heritage Dictionary is something that *incites or rouses to action: stimulus, fillip, goad, incitement, instigation, motivation, prod, push, spur, stimulant, provocation, activator, energizer, excitant*. This positive perception of a widely used tool in Chemistry is quite astonishing in these days when the societal concerns towards the chemical industry are prominent.

Since ancient times, catalytic processes were applied in order to improve humankind lifestyle. Fermentation (and therefore bio-catalysis) allowed Noah to produce his wine [Bible] or the Sumerian husbandmen to brew their beer [Arnold 2005]. Primordial catalysts were used for preparing pigments, inks, soaps that have allowed the civilization progress and the human culture growth.

The societal benefits of chemical transformations are related indeed to their technological implementation. The studies finalized to develop and scale-up catalytic processes are, by definition, application oriented: as a consequence the target of industrial catalysis is to make concrete innovations in better processes resulting in better economics, better utilization of raw materials and energy as well in improving the environmental impact.

Catalysis and catalysts play a primary role in today technology: a great part of the fertilizers, pharmaceuticals, energetic vectors and of the materials used by human beings are produced via catalytic processes. Chemical Catalysis is an essential tool for chemicals and materials production, for fuel and other energy conversion systems, for combustion devices, for fuel cells, and for pollution control systems. Often it is the key to making an entirely new technology or transmitting new life into obsolete or mature technologies. Additionally to the traditional need for productivity improvements, environmental drivers, energy saving, and industrial safety bring new aspects to the importance of catalytic innovation [Dautzenberg 2004].

Table 1 [Stoltze 2006, Sanfilippo 1997] shows a historical summary of the development of industrial processes and how catalysis has a tremendous impact on the human activities as concerns economic development, environment preservation and, more broadly, societal progress. Since the middle of the 20th century, catalysis has undergone remarkable development both from the point of view of fundamental knowledge and from that of its applications. Between 1930 and the early 1980s, the chemical process and petroleum refining industries introduced 63 major products and 34 major process innovations. More than 60% of those products and 90% of the processes relied on catalysis for synthesis reactions [SRI 1996].

Year	**Process**	**Catalyst**
1750	H_2SO_4 lead chamber process	NO/NO_2
1796	von Marum: dehydrogenation of alcohols	Metals.
1817	H. Davy: oxidation of methane	Pt wires
1824	W. Henry: oxidations	Pt on clay
1825-1833	Michael Faraday: ignition of H_2 in air	Pt
1831	Philip: patent on oxidation of sulfur dioxide	Pt
1836	Berzelius defines catalysis (J.Berzelius: Ann Chim Phys 61 (1936) 146	
1870	SO_2 oxidation	Pt
1875	Squire and Messel: industrial oxidation of SO_2	Pt
1879	Clemens Winkler: contact process for sulfuric acid synthesis	
1880	Deacon process (Cl_2 from HCl)	$ZnCl_2$ /$CuCl_2$
1885	Karl Benz and Gottlieb Daimler: automobile gasoline	
1885	Claus process (H_2S and SO_2 to S)	Bauxite
1889	L. Mond and C. Langer: Methane steam reforming	Ni
	BASF: Industrial synthesis of sulfuric acid	Pt
1895	Fritz Haber: production of small amounts of NH3 from N2+3H2	Fe
1900	Fat hydrogenation	Ni
	Methane from syngas	Ni
1902	Sabatier, Sanderens: Hydrogenation of alkenes	Ni
	Ostwald Nitric acid synthesis by oxidation of ammonia	Pt
1903	Fritz Haber and Walther: high pressures key to ammonia synthesis.	
1908	Carl Bosch: development of the industrial synthesis of ammonia at BASF	
1909	Mittasch develops industrial catalyst for	

	NH3 synthesis at BASF.	
	O. Dieffenbach and W. Moldenhauer: Steam reforming patent	
1910	BASF plant in Ludwigshafen for NH_3 by the Haber process.	Fe
	Coal liquefaction	Fe
	Upgrading coal liquids	WS_2
1913	Nitric acid industrial production by BASF (Ostwald process).	
	Cl_2 is used as poison gas at Ypres. Haber (leading role in the development of chemical warfare) wife commits suicide when he refused to abandon this work.	
1917	The Chemical Constr. Co. builds an ind. nitric acid plant (Ostwald process)	
1920	Methanol synthesis (high pressure)	Zn, Cr oxide
	Fischer-Tropsch synthesis	Promoted Fe, Co
	At General Motors tetraethyl lead as an anti-knock additive to gasoline.	
	SO_2 oxidation	V_2O_5
	The Standard Oil Co (New Jersey) starts industrial production of isopropanol from petroleum	
	Acetaldehyde from acetylene	Hg_2+/H_2SO_4
1930	Standard Oil of New Jersey: First industrial steam reformer installed at Baton Rouge	
	Catalytic cracking (fixed bed, Houdry)	Clays
	Ethylene epoxidation	Ag
	Polyvinyl chloride	Peroxide
	Polyethylene (low density, ICI)	Peroxide
	Oxidation of benzene to maleic anhydride	V
	Alkylation	HF/H_2SO_4
1940	Hydroformylation, olefin to aldehyde	Co
	Catalytic reforming (gasoline)	Pt
	Cyclohexane oxidation (nylon 66)	Co
	Benzene hydrogenation to cyclohexane	Ni, Pt
	Synthetic rubber, SBR	Li, peroxide
	BNR	Peroxide
	Butylrubber	Al
1950	Polyethylene (high density), Ziegler-Natta	Ti
	Polypropylene, Ziegler-Natta	Ti
	Polybutadiene, Ziegler-Natta	Ti
	Hydrodesulfiding (HDS)	Co, Mo sulphides
	Naphthalene oxidation to phthalic anhydride	V, Mo oxides
	Ethylene oxidation to acetaldehyde	Pd, Cu

	p-Xylene oxidation to terephthalic acid	Co, Mn
	Ethylene oligomerization	Co
	Hydrotreating of naphtha	Co-Mo/Al_2O_3
1960	Butene oxidation to maleic anhydride	V, P oxides
	ICI: First steam reformer operating at high pressure (15 atm)	Ni
	ACN (ammoxidation of propylene - Sohio)	Bi, Mo oxides
	Propylene oxidation to acrolein/acrylic acid	Bi, Mo oxides
	Xylene hydroisomerization	Pt
	Propylene metathesis	W, Mo, Re
	Adiponitrile (butadiene hydrocyanation)	Ni
	Improved reforming catalysts	Pt, Re/Al_2O_3
	Improved cracking catalysts	Zeolites
	Acetic acid from MeOH (carbonylation)	Co
	Vinyl chloride via ethylene oxychlorination	Cu chloride
	Ethylene oxidation to vinyl acetate	Pd/Cu
	o-Xylene oxidation to phthalic anhydride	V, Ti oxides
	Propylene oxidation to propylene oxide	Mo
	Hydrocracking	Ni-W/Al_2O_3
	HT water-gas shift process	Fe_2O_3/Cr_2O_3 /MgO
	LT water-gas shift process	CuO/ZnO/Al_2O_3
1970	Methanol synthesis (low pressure, ICI)	Cu-Zn-Al oxide
	Acetic acid (MeOH carbonylation, low pressure process, Monsanto)	Rh
	Improved process for xylene isomerization	Zeolite
	-Alkenes via ethylene oligomerization/ isomerization/metathesis (SHOP)	Ni, Mo
	Improved hydroformylation	Rh
	Auto exhaust gas catalysts	Pt/Rh
	L-DOPA (Monsanto)	Rh
	Hydroisomerization	Pt/zeolite
	Selective reduction of NOx (with NH3)	V_2O_5/TiO_2
1980	Gasoline from MeOH process (Mobil)	Zeolite
	Vinyl acetate (ethylene - acetic acid)	Pd
	Methylacetate (carbonylation)	Rh
	Methylacrylate via t-butanol oxidation	Mo oxides
	Improved coal liquefaction	Co, Mo sulphides
	Diesel fuel from syngas	Co
1990	Polyketone (from CO and ethylene)	Pd

Table 1. Historical summary of the development of industrial catalytic processes

The use of catalytic reaction technology is essential for the economic viability of the chemical manufacturing industry. In addition, catalysts are critical keys in controlling emissions of gaseous pollutants to the atmosphere, most notably from automobiles and electric power plants. More than 90% of all molecules of current transportation fuels at some point during their manufacture have passed over at least one catalyst, some 80% of all chemical products are manufactured with the aid of catalysis and more than 20% of all industrial products rely on catalytic reaction technology [Marcilly 2003, SRI 1996].

Catalytic processes require the existence of a very particular industry for catalyst manufacture. This sector is a highly specialized and diversified business. About 100 companies worldwide, less than 20 are the major ones, have some degree of capability in the production of catalysts on their own technologies or as toll manufacturers. The worldwide market value for catalysts was reported to be over $14 billion in 2006. Table 2 shows the value of the global catalyst market and the relevant Average Growth Rate (AGR) in the main fields and processes of current catalyst applications [TCGR 2004]. Since the cost of catalyst ranges typically from 0.1% (petroleum refining) to 0.22% (petrochemicals) of the product value [Rabo 1993], it can be estimated that catalysts induce a market of manufactured goods exceeding $7,500 billion yearly.

	2003	**2006**	**2009**	**AGR 2003- 09**
Refining	2,464	2,682	2,946	3.3%
Petrochemicals	2,195	2,340	2,491	2.2%
Polymers	2,568	2,999	3,425	5.6%
Fine Chem. & Interm. and Others	1,276	1,621	1,965	9.0%
Environmental	3,581	5,028	5,704	9.9%
Total	12,084	14,670	16,531	6.1%

Table 2. Global Catalyst Market Value 2003-2009 (Mil $)

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Biographical Sketch

Domenico Sanfilippo was born in Catania (Italy) in 1945 and got the Doctorate in Industrial Chemistry from the University of Catania in 1969.
He joined Snamprogetti S.p.A., Milan (Italy) in 1970. Currently he is Manager of Onshore Technologies. The position covers the management of proprietary technologies, including Urea, High Quality fuels Components, Styrene Monomer, Dehydrogenation, etc. used for the company activities of licensing out and EPC contracting. He is responsible of the R&D of new technologies. Previously he has been Manager of the Research Laboratories and of the Catalysis Center.
He is Contract Professor of Industrial Chemistry at the University of Messina and of Scale-up of Chemical Plants at the University of Genoa.
In his career he has actively contributed to the development of several commercial technologies with respect to the aspects involving catalysis, reactor engineering and process development, as well the management of the projects. Some examples are the dehydrogenation of paraffins, new styrene synthesis, high-octane gasoline components, new hydrogen technologies, methanol and higher alcohol synthesis, ethylene oxide and glycol processes. Main fields of interest include the technical, economical & environmental aspects of fuels, Natural Gas, Refinery and Petrochemical Processes.

Dr. Sanfilippo is author of more than 40 patents, 50 papers/book chapters and 80 Communications and Editor of 3 books.

His memberships include the Board of Directors of Haldor Topsoe Inc. (2006-2007), the Board of Directors of the Federation of Scientific and Technological Associations (Milan), the Board of the Int. Association of Catalysis Societies, and several International Committees. He is member of the Editorial Board of Catalysis Letters, Topics in Catalysis, Japanese Survey of Catalysis, Chimica e Industria, Catalysis Today (1994-2002).

Dr. Sanfilippo is also Past-President of Industrial Chemistry Division and Lombardy Branch of the Italian Chemical Society. He received in 2000 the Gold Medal “Piero Pino” for Industrial Chemical Processes Development.