ELSEVIER

Catalysis Today 34 (1997) 261–267

CATALYSIS TODAY

Chapter 1

Catalysis: through cultural synergism to the target

Domenico Sanfilippo

Research Department, Snamprogetti S.p.A., Via Maritano, 26, 20097 S. Donato Milanese, Italy

'No organ of the human body can claim the right to consider itself more important than the other ones and refuse to cooperate with them, otherwise the entire body will die'.

Menenius Agrippa (494 b.c.) to the Roman plebs on the Sacred Mount, striking and refusing to further contribute to the previous social duties.

1. Impact of catalytic processes

Since ancient times, fermentation (and therefore catalytic) processes allowed Noah to produce his wine [1] or the Sumerian husbandmen their beer [2]; in the last century Berzelius, Davy and Faraday among others, laid the bases of modern catalysis, but it has been during the twentieth century, as shown in Table 1 [3], that catalysis has become one of the most powerful tools of the current manufacturing industry. Indeed, catalysis has a tremendous impact on the human activities as concerns economic development, environment preservation and, more broadly, societal progress.

Catalysis and catalysts play a primary role in present day technology: a great part of the fertilizers, pharmaceuticals, energetic vectors and of the materials used by human beings are produced via catalytic processes. More than 90% of all molecules of current transportation fuels have passed over at least one catalyst and some 80% of all chemical products are manufactured with the aid of catalysis [4].

About 100 companies worldwide (40 are the major ones) have some degree of capability in the production of catalysts. The worldwide market for catalysts was reported to be over 450 000 tons for 1989, with a trend of increasing to over 580 000 tons for the year 2000. Table 2 shows the main fields and processes of current catalyst applications [5].

Since the cost of catalyst (worldwide market $5 billion in 1989) ranges typically from 0.1% (petroleum refining) to 0.22% (petrochemicals) of the product value, it has been estimated that Catalysts induce a market of manufactured goods exceeding $2400 billion yearly [5–7].

The society benefits of catalysis are therefore related to its technological implementation. The development and scaleup of catalytic processes are, by definition, application oriented: the target of industrial catalysis is indeed to make concrete innovations in better processes resulting in better economics.

2. The long journey of an idea

I do not know of any systematic methodology for generating new ideas. It was the need for a more powerful gasoline that pushed the race driver and mechanical engineer Eugene Houdry to develop the cracking process; the

PII S0920-5861(96)00053-3

Table 1
Historical summary of the development of industrial processes [3] [a]

Year	Process	Catalyst
1750	H_2SO_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_2S 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)	Zn, Cr oxide
	Fischer–Tropsch synthesis	Promoted Fe, Co
	SO_2 oxidation	V_2O_5
	Acetaldehyde from acetylene	Hg^{2+}/H_2SO_4
1930	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
	Phillips	Cr
	Polypropylene, Ziegler–Natta	Ti
	Polybutadiene, Ziegler–Natta	Ti
	Hydrodesulfiding (HDS)	Co, Mo sulfides
	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
	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

Table 1 (continued)

Year	Process	Catalyst
1960	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
	α-Alkenes via ethylene 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_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

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

Chilean nitrates embargo to Germany boosted the Haber and Bosch studies for the fixation of atmospheric nitrogen in ammonia synthesis; catalytic reforming and alkylation allowed the RAF pilots to have available a powerful fuel to win the battle of Britain.

Table 2
Main end uses of catalysts in ton/year [5]

	Year	
	1989	2000
Automotive	66000	94000
Petroleum processes	309000	381000
Catalytic cracking	241000	288000
Hydrotreating	24900	34800
Catalytic reforming	5000	7000
Hydrocracking	5700	7300
Isomerization	800	1000
Other petroleum processes	31600	42900
Chemical catalysts	67000	94000
Condensation	6600	8900
Oxidation	17200	23200
Hydrogenation	26600	35300
Polymerization	1500	2600
Synthesis Gas	5000	6600
Other chemical syntheses	10000	17400
Miscellaneous	11000	17000
Total catalyst production	453000	586000

More closely to the present, several driving forces lead to innovation in the development of catalytic processes. The strategic lines (typically market driven) and the cultural background of research teams and of companies, the attention paid to worldwide scientific advancement, including to the 'weak signals', represent the lenses which give an insight into the way of producing a completely new material, or a simpler and less capital-intensive route of producing an existing product, or of converting lower cost feedstocks (or waste by-products) to valuable products. Societal concerns and evolving legislation are additional springs pushing efforts for improved technologies.

It is my opinion that the achievement of a technological success, even involving innovative catalysts, is more probable when the initial idea is already process 'pulled' (e.g. the possibility of transforming 'A to B', and I do not know what catalyst could work), in respect to the catalyst 'pushed' research (e.g. the availability of a 'wonderful catalyst', and I do not know for what reaction).

Every researcher in an industrial environment should have the possibility of devoting some percent of her/his time to innovations in not yet structured projects (of course along the corporate strategic main lines), and likewise every researcher in an academic environment should pay attention to the strategic indications of the industrial world.

The development of a commercially successful process is in any case a scientific as well a technical triumph. The journey of an idea, from its birth at the level of innovative discovery up to the start-up of a commercial prototype, is a sequence of steps of increasing difficulty to be overcome, that can assume different names, like discovery, exploratory phase, intensive phase, pre-development, development and, eventually, venture and commercial application.

Even in a continuum, the R&D activities, can be grouped into two basic periods, the 'exploratory and definition phase' and the 'intensive and development phase', being the former already oriented, but still looking for a general definition of the process, and the latter strictly finalized to achievement of the complete technology know-how.

3. The exploratory and definition phase

Beyond the role of basic research of providing the tools for any knowledge advancement, all finalized projects face the 'exploratory and definition phase', that includes all actions aimed at assessing the technical feasibility of the innovation: thermodynamic constraints control, potential catalyst hypothesizing, preparing, characterizing and screening, process conditions exploration, level of novelty evaluation are the most typical activities.

The key step at this phase is always the identification/availability of an effective catalyst. This aspect has been losing over the years the halo of a 'black art' for few initiates and has evolved towards a more scientific approach of catalyst design through investigations at micro and macro level. New very effective physico-chemical inspections of the catalyst characteristics, theoretical and quantum chemistry, catalyst modeling, microkinetics and mechanistic simulations, new computational methods implemented in new powerful software and hardware all help the researcher to bring under control the three vertexes of the triangle: how the catalyst has been prepared (material science); how it actually 'looks' (physico-chemical characterization and surface science); how it performs (catalyst testing).

As concerns equipment, the exploratory phase is certainly carried out at 'laboratory level' in bench scale units. In the case of heterogeneous catalysis, typically reactor size ranges from milligrams to a few grams of catalyst, generally in powder and granulates, not in the final shape.

Once a catalyst with sufficient performances is available, and before entering the following expensive phase of intensive research and process development, it is necessary to assess the economic feasibility of the innovation. On the basis of the results of the exploratory activity, it is possible to have a schematic design of the process, to size approximately all equipment, and then to have a rough plant cost estimate and some economical indexes. If the new process does not appear attracting at this point (not even using the target catalyst performances!), only a very strong strategic decision of the organization or some expected important fall out could let the project live, otherwise it will be killed. This check-point of the process economic evaluation should be anticipated as much as possible and repeated at any time in case of important 'bad or good news' from the research.

4. The intensive and development phase

The development of an industrial catalytic process is a complex multidisciplinary activity aimed at translating the innovative idea into an applied innovation, through providing and assembling all theoretical and experimental information concerning the catalyst, reaction and reactor engineering and the whole process design. The password of the intensive research and process development is 'optimization' of the catalyst formulation, performances, and operating conditions, of the best reactor configuration, and eventually of the process flowsheet including energy and raw materials consumption, investment costs, safety, environmental constraints, and controllability among other aspects.

The industrial development of a catalytic process is based on experimental studies. Haber and Bosch received the Nobel prize for their basic studies on the ammonia synthesis, but the contribute of the experimental work was essential: in few years over 20000 catalysts were tested [8]. Indeed the basis of intensive research is the collection of absolutely reliable experimental data. As concerns equipment, the intensive/development phase is carried out on bench scale plants at laboratory level, on pilot plants, on process demonstration units; typically reactor size increases from grams to tons of catalyst.

Process development involves the scaleup, which means the translation to a commercial scale of the experience gained since the lab experiments. Scaleup, therefore, beyond the technical approach, covers several aspects of the coming commercial activity, including product development and market impact studies. The reported literature [9,11–13] gives an overview on the subject.

In the intensive research phase, even at laboratory level, experiments and equipment must be designed bearing already in mind the full scale plant: the first step for scale up studies is therefore 'scale down' the hypothesized problems of commercial unit, bringing them to a small scale, where all information needed has to be collected and modeled effectively. Scaleup from small scale studies based on making 'the toy bigger', could be a very misleading concept, as in Fig. 1.

The breakdown into simpler subsystems has some limits, since it increases the risk of missing some key factor in the investigation or of

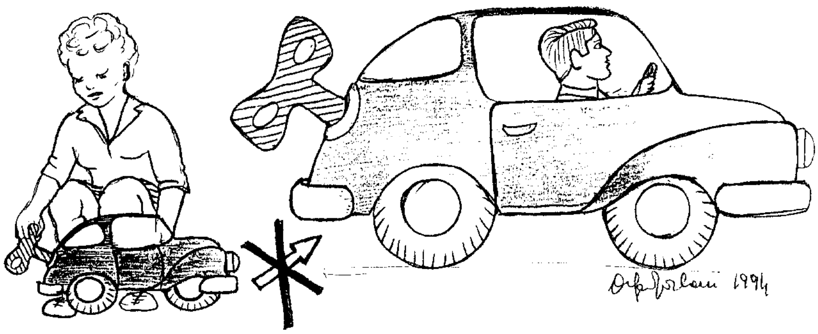

Fig. 1. Misleading concepts in scaleup!

attributing to the system some effects due to the small scale. Scaleup from laboratory scale to industrial scale in one step is rarely feasible. Generally, additional steps are necessary.

Oversimplifying, three experimental approaches are possible: laboratory, where the mechanisms that are independent of size (thermodynamics, kinetics) are studied, mock-up (cold models), in order to analyze separately the physical mechanisms sensitive to size (hydrodynamics), pilot plants or even demonstration units which permit a simultaneous analysis of physical and chemical mechanisms, and of their possible interaction.

The accepted calculated risk determines the extent of homology and then the scaleup ratio (the relationship between the size of the foreseen next scale unit and the size of the current experimental one) that is required in the intermediate step. Due to the high cost of pilot plants, there is great interest in moving in one step from bench scale to, at least, a process demonstration unit (PDU) to be used as a reference for larger future installations. There are no general rules for scaleup ratios. Typical values based on experience are reported in Table 3 [9].

Higher scaleup ratios, at an acceptable level of risk, can be achieved only when marginal modifications to an existing technology (incremental research) are planned or extensive experience exists on similar systems or when a fundamental approach is possible to both chemical and engineering problems. Personally I can bear witness to successful scaleup ratios from bench scale to PDU exceeding 100000 or even 500000.

Table 3
Typical scaleup ratios of various systems [9]

System	Lab to pilot	Pilot to commercial
Substantially gaseous	$5\times10^2-10^3$	$2\times10^2-10^3$
Gas reactants, liq/sol products	$2-5\times10^2$	$1-5\times10^2$
Liq/gas reactants, liq products	$1-5\times10^2$	$1-5\times10^2$

A very important aspect of the development of catalytic processes is the scaleup of the catalyst production from the few grams typical of lab preparation to the tons needed by commercial units. Catalyst production is a real, complex chemical process that requires at least the same attention as that paid to the reaction.

5. Projects survival and success rate

The idyllic picture appearing up to now in this Chapter is not always or entirely true. Experience indicates that only a small number of innovative ideas complete their journey up to commercial implementation.

First of all, it is not an easy task to overcome all the technical difficulties and achieve superior products/processes. But even in the case of technical success, other hurdles make a selection among R and D projects: during the several years required by the process development, the economic scenario can change substantially (in the last 20 years the oil price has been subjected to sudden ups and downs) or the company strategy can change, the results can arrive too

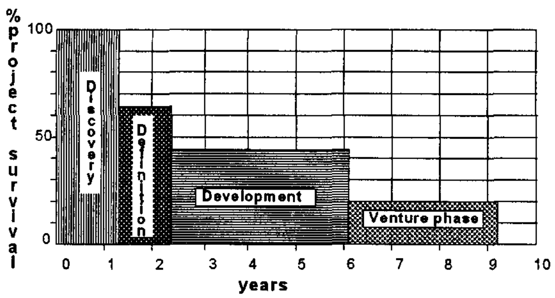

Fig. 2. R&D project attrition rate.

early (market not yet mature) or too late (someone else has arrived first) and, in any case, how big should the contemplated advantage of the new technology be to prevail over a referenced competing product/process? 10% or 20% or 30% or even higher? What is the breakeven between potential benefits and risk? One of the key factors will be the attitude of the companies regard to innovation.

Projects undergo very considerable 'attrition'. According to some industrial experience [10], about 80% of the projects at the discovery phase reach the definition phase, less than 50% attain the development phase, and only 20% survive up to the venture phase as shown in Fig. 2.

A different picture is given by another source [11] according to which 1 to 3% of ideas for a new process at the early research stage reaches commercialization. Projects at the development stage have a probability of about 10 to 25%, and at the pilot plant stage of 40 to 60%. Of course, the success rate for process modification will be higher than that of completely new processes.

6. Multidisciplinarity mandates integration

The handling of the complexity of the phenomena involved in catalysis, in catalyst and catalytic processes development, involves skills coming from many complementary disciplines in the field of chemistry, physics and engineering, each one developing independently its own progress and advancing towards a very sophisticated level of specialization. R&D in catalysis groups in a common culture disciplines such as for instance materials and surface science, solid state physics and chemistry, organometallic chemistry, chemical kinetics, chemical reaction and reactor engineering as well as more powerful tools and emerging methodologies such as synchrotron light, computational chemistry and ab initio calculations.

Successful catalytic processes development is then achieved by large multidisciplinary teams of experts, bearing in mind that the development activity is not a relay race and the project has not to pass from one competence to the next like the baton from one racer to the other, but all skills have to work together synergistically from the lab level up to the start-up of the commercial unit, with a continuous feedback of information.

No single discipline is more important than any other one. There is a real need for mutual understanding and integration. Integration is an unavoidable necessity, that should not be felt by the individuals as an ethical duty or a management imposition, but as an intrinsic cultural attitude.

Management has the responsibility of the correct involvement of the broad spectrum of specialistic skills and of making available the complete view of the total problem under study.

7. Perspectives in catalytic process development

Catalysis and the related disciplines are continuously evolving from the point of view of both the proposition of new technological topics and the availability of new scientific methodologies that, through a deeper understanding of elementary steps, allow a conceptual design of the catalyst and its engineering environment.

Several authors have recently reported their opinions on future challenges for Catalysis [4,6,7,14]. Major advances rather than incremental improvements are expected as the environmentally driven needs and opportunities (primary or secondary prevention), the utilization of alternative feedstocks (methane, LPG) or the worsening of the existing ones (heavier feed, higher sulfur and metals content): NG to petrochemicals as well as liquid fuels via methane direct conversion or via Syngas chemistry are examples of challenges to face the changing fuel product slate (more motor fuels, less fuel oil) and the changing fuel specifications.

As to individuals, a major challenge is to smooth the barrier between science and technology.

References

[1] Bible, Genesis 9, 20.

[2] P. Wührer, Origini e storia della birra, Unione Ital. Fabbricanti Birra e Malto, 1958.

[3] J.A. Moulijn, P.W. van Leeuwen and R.A. van Santen, Catalysis, Vol. 79, Elsevier, Amsterdam, 1993.

[4] J. Haggin, Chem. Eng. News, 15 July (1991) 30.

[5] Interpipe Services, Heterogeneous Catalysts, Market Study, 1989.

[6] J.F. Roth, Chemtech, June (1991) 357.

[7] J.A. Rabo, in Guczi, et al., Editors, Proc. 10th Int. Cong. Catalysis, Budapest, 19–24 July 1992, New Frontiers in Catalysis. Elsevier, Amsterdam, 1993.

[8] J.R. Anderson and M. Boudart, Catalysis. Science and Technology, Vol. 7, Springer Verlag, Berlin, 1985.

[9] A. Bisio and R.L. Kabel, Scale-up of Chemical Processes, Wiley, New York, 1985.

[10] E.E. Paschke, Amoco Chemical Company, Private Communication, 1993.

[11] J.M. Douglas, Conceptual design of Chemical Processes, McGraw-Hill, 1988.

[12] J.P. Euzen, P. Trambouze and J.P. Wauquier, Scale-up Methodology for Chemical Processes, Editions Technip, Paris, 1993.

[13] R.P. Palluzzi, Pilot Plant Design, Construction, and Operation, McGraw-Hill, New York, 1992.

[14] J.M. Thomas and K.I. Zamaraev, Perspectives in Catalysis, Blackwells, London, 1992.