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Catalysis Today 36 (1997) 367–374

CATALYSIS TODAY

Catalytic process development: A process designer's point of view

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Process designers are not members of the catalyst community; few have ever developed or even tested a catalyst. However, in an important way, they are the first customers for new or improved catalysts. Their interest is limited to data that will enable them to make a series of complex decisions about commercial catalytic reactor systems in a manufacturing environment. Understanding their needs (and prejudices) should enable the catalyst community to deliver 'new' catalysts more effectively.

Most, if not all of the catalysts used commercially today for manufacturing chemicals and petroleum refining were largely developed by tedious trial and error. Hundreds of man-hours have been spent in the laboratories of users and catalyst vendors to develop and evolve a commercially viable catalyst. Not surprisingly, there is a growing interest in utilizing more rational approaches toward the development of catalysts, particularly if one is trying to achieve desirable environmental goals.

A review of recent literature on catalysis will uncover two interwoven strands:

- A belief that catalysts can be designed; and
- A strong feeling, almost messianic, that new catalysts can lead to reduction of the pollution burden on the environment.

Indeed, a most elementary literature search covering the past 10 years will uncover over 350 articles and one patent using the phrases, designing catalysts or designer catalysts, in the title and probably several thousand that use these words (or similar ones) in the text.

'Benign by design' is a concept (although it was not originated by him) that has been popularized in recent years by Professor Mark Davis of the California Institute of Technology. Let us first consider briefly from a process designer's viewpoint, the implications of the concept 'benign by design' or a 'clean technology'.

To arrive at a level of performance implied by the concept of a 'clean technology' requires more than just an improvement in the performance of a catalyst, such as a higher yield or improved selectivity. At a minimum, we must accept that the area of interest is always a manufacturing site (cradle-to-grave or life-cycle thinking, while important, are not part of our considerations at this juncture). If the pollution burden on the environment is to be reduced, then we must recognize that everything that happens or may happen within a plant site is linked. A change in the mode of operation of a process unit can quickly cascade through the operation of the emissions and waste-management systems, the energy systems, and may even have an impact on raw material, product storage and transportation. Gaining an understanding of these linkages and their consequences is of prime concern to a process designer.

Synthetic routes that use highly toxic and volatile raw materials, such as phosgene, must be avoided if possible. When not possible and if the raw materials cannot be generated as needed, the designer will have

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PII S0920-5861(96)00231-3

to have a sophisticated understanding of what is involved in transporting and storing them. Procedures that protect personnel against exposure to them and handle accidental releases in a responsible manner are also absolutely vital.

Whether used as a reaction media or to facilitate separations, the magnitude of the solvent inventories and the circulation rates are important. Small relative losses (e.g., <1/2% of circulation) will result in a significant consumption of solvents in a commercial-size unit. Solvent stability and spent solvent recovery and regeneration (if required) will be found to have a significant impact on both storage requirements, waste-management systems and possibly the economic attractiveness of the proposed catalyst.

The performance of a catalyst in a laboratory reactor is only an indicator of its potential applicability in a commercial process and its environmental impact. For example, catalysts are not per se benign. In case you do not believe this, you may speak to the operator of an FCC unit who has just had a rain of catalyst fall down on a community because a multistage cyclone system failed. Moreover, catalyst emissions (particularly of trace metals) and disposal of spent catalysts are areas of increasing concern and attention by designers.

Catalysts, in the commercial world, cannot be divorced from the reactors that contain them and the process technology utilized. Catalyst design may, in practice, be some judicious blend of organometallic chemistry, surface science, material science, computational chemistry, chemical kinetics, and reactor engineering. The process designer, however, will largely focus his attention on the kinetics and reactor engineering (ignoring the other elements) since his goal is a reactor system that permits the recovery of a product with minimum dilution by reactants and solvents.

The focus of this paper is on the production of organic chemicals using heterogeneous catalysts. There are several reasons for this limitation; heterogeneous catalysts are the focus of the Blechner Center for Industrial Catalysts and Process Development. They comprise roughly 70–80% of the worldwide $10 billion catalyst market for chemical and petroleum-refining processes. Moreover, catalysts are not significant for the production of inorganic chemicals; there are about 10 catalytic inorganic reactions of which the most important are NH_3, synthetic gas production, and in the future NO_x reduction. Finally, my background and interests are in the production of organic chemicals, the overwhelming majority of which are produced with heterogeneous catalysts.

The focus of many laboratory studies is limited to understanding how the activity and selectivity of a family of catalysts can be altered. Stability is also studied (although for a variety of practical reasons) to a lesser degree. In my experience, industrial and academic laboratories often develop inappropriate and sometimes misleading data on heterogeneous catalytic reactions. What is important for the designer is not how the catalyst performs in a laboratory reactor, but rather what its performance in a commercial reactor is projected to be. The projections depend critically on the data collected from experiments in laboratory reactors. Inaccuracies in the early stages of a catalyst development program often result in a multitude of difficulties, the most important being the failure to commercialize a process that could have been beneficial from an environmental point of view and, most importantly, profitable.

The potential and relevance of alternative techniques for the development of catalysts can be appreciated only when the commercial motivations for the development are clearly understood. From a process designer's point of view, whether a development is primarily market-driven or science-driven is critical in his decision-making process.

In a market-driven development, improving the performance of an existing, well-established process through modification of a catalyst, is the goal (but not always). Use of the new catalyst will require only minimal changes in an existing process unit and its supporting systems. Ideally (a process designer's dream), the improved catalyst need only be substituted for the current one in the existing reactor; this possibility makes a plant test the sole arbiter of success.

The major tasks involved in a market-driven development are shown in Fig. 1. Since the modifications in the catalyst are often only minor perturbations from a previous composition, the processes used to prepare the catalyst are similar, if not identical, to those currently in use. Moreover, a significant data-base of information is usually available to the process designer on the performance of a previous commercial

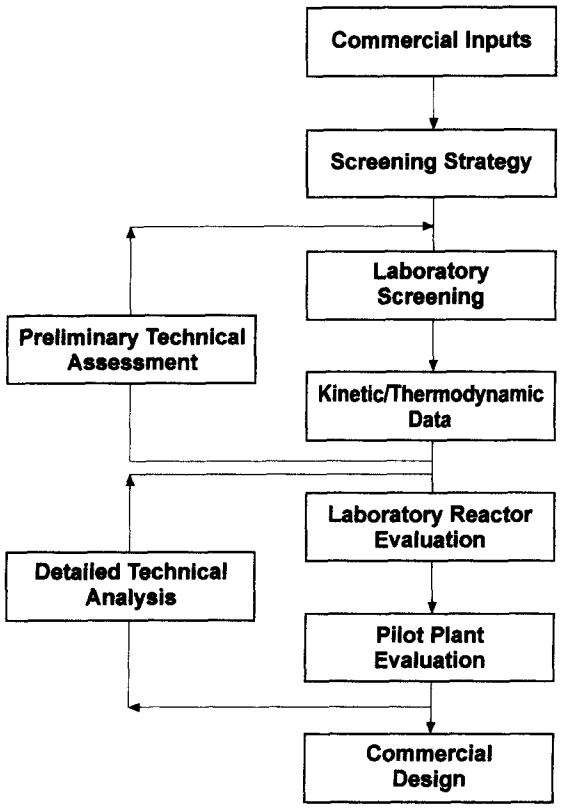

Fig. 1. Major tasks in a market-driven catalytic process development program. Adopted from Ref. [2].

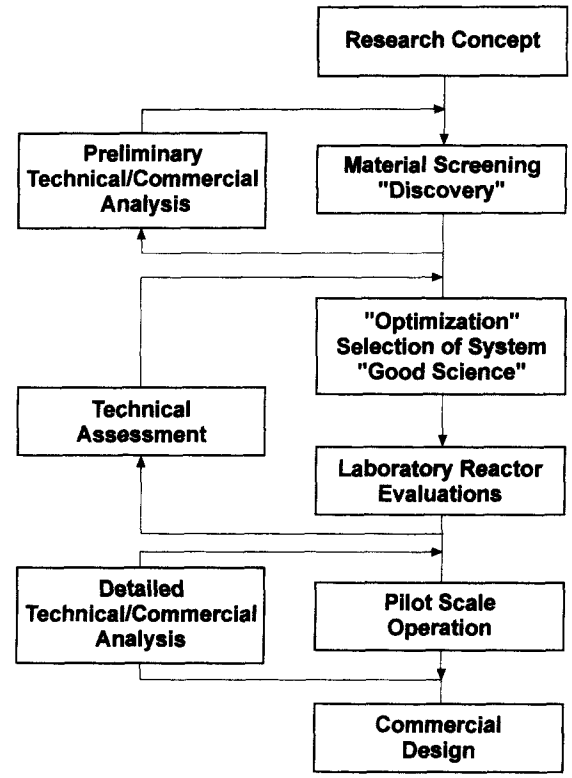

Fig. 2. Major tasks in a science-driven catalytic process development program. Adopted from Ref. [2].

version. Therefore, his projections will be forthcoming if not generous and his concerns minimal.

A science-driven development involves inventing a novel (or new) catalyst that may (or may not) form the basis for a profitable commercial plant, unlike a market-driven development in which case a significant portion of the work will be exploratory in nature, broad in its scope, and uncertain in outcome. Only a limited data-base may exist to guide the selection of initial catalyst compositions, associated preparation procedures, and 'test' reaction conditions; this can result in the process designer being quite reluctant to make projections, even conservative ones.

The major tasks that must be conducted before a catalyst and the associated process (e.g., reactor and support systems) are projected to be commercially viable, are shown in Fig. 2. The key technical hurdles will include (at a minimum):

- An initial discovery that results from a highly exploratory laboratory research program;
- Extensive laboratory reactor testing; and
- Demonstrations on a pilot-plant scale.

The scope and intensity of the pilot-plant demonstrations will be greatly influenced by the perceived uncertainties of the process designer. If answers are not forthcoming (or better yet, anticipated and volunteered), the development will stall.

Regardless of whether a program is perceived to be market driven or science driven, some experimental data at each stage of a program will be viewed by a process designer as particularly critical. In my experience, understanding the implications of the:

- characteristics of the catalyst,
- protocol for manufacture of the catalyst, and
- contemplated (projected) commercial reactor, are critical to the success of the program.

Table 1
Characteristics of industrial heterogeneous catalysts [a]

Activity	Reactor productivity/operating conditions
Selectivity	Undesirable/competitive reactions
Stability	Poisoning, fouling, sintering, phase transformation
Morphology	Form, grain size, filling density
Mechanical	Strength/crushing/attrition abrasion/erosion
Thermal	Thermal conductivity, specific heat
Regenerability	Activity, selectivity, mechanical strength
Manufacturability	Reproducibility

[a] Adopted from Ref. [9].

The apparent similarity of Figs. 1 and 2 may be misleading to some. The engineering analyses done between each of the indicated stages and the commercial design are, in my experience, quite different, for market-driven and science-driven programs. A commercial design not only addresses equipment, systems, and physical layout, but also catalyst preparation on a commercial scale, safe operating procedures, analytical methods, product specifications, etc. In a science-driven program, many of these will be done for the 'first time' on a commercial scale.

When in a series of studies one ignores or minimizes the importance of studying some characteristics of the catalyst (Table 1) by either assuming the answer or reasoning by analogy, one is asking for future difficulties. For example, the morphology of a catalyst is often critical to the selection of the commercial reactor system. The physical form of a catalyst and its grain size must be suited to the projected reactor. Unfortunately, the form, grain size, and filling density of a catalyst are all related to its pore volume; therefore, changes in what appear to be unimportant physical properties may have a complex interaction on catalyst activity and, particularly, selectivity.

For a process designer the reproducibility of the catalyst manufacturing protocol is critical in his evaluation of the laboratory and pilot-plant data. We are all aware that the performance of a catalyst depends on how it has been manufactured; seemingly, small differences in the procedure can have a marked impact on the performance of a catalyst. However, I have been involved in several development programs where significant effort and time had to be devoted to reproducing 'the batch' of the catalyst that performed very well months before. When this happens, a program can be seriously disrupted; if it occurs more than once, particularly when studies are being conducted in pilot units, the program is in jeopardy of being terminated.

The life of a catalyst (number of regenerations and hours on-line) will determine many important factors in the process design, manufacturing operability, and project economics. Unfortunately, laboratory programs and pilot-plant tests will not (at least for a process designer) yield unequivocal information about the catalyst life, which only a commercial experience will. Therefore, the development program should generate information about each of the pathways, e.g., poisoning, fouling, sintering, etc. that can specifically impact the life of the catalyst under study and how one goes about to recover activity [3,4]. Projections about the catalyst life are more reliable in a market-driven program.

A large number of diverse reactor types are used commercially. In text books, there is a tendency to discuss these in idealized terms such as PFRA and CSTRS. A feeling for the richness and variety of

Table 2
There is a complex interaction between the catalyst and the reactor [a]

Reactor type	Residence time distribution		Catalyst	
	Fluid(s)	Solid	Activity	Temperature
Fixed bed	PF	Batch	f(t)	f(Z,R)
Fluid bed	PF	CST, STR	f(t)	'Uniform'
Slurry	CST or PF	CST, STR	f(t)	'Uniform'
Gauze	'PF/CST'	Batch	f(t)	'Uniform'
Trickle bed	'PF'	Batch	f(t)	f(ZvR)
Moving bed	PF	PF	Constant	f(Z,R)
Transport line	PF	PF	Constant	f(Z)

[a] Adopted from Ref. [1].

commercial reactors is essential; this can be obtained from a study of the patent literature or a careful reading of Ref. [5].

What is important for the process designer and ultimately the operator of the plant is the complex interaction between the catalyst, the reactants and products, and the reactor (Table 2). The phase relations in the reaction space, e.g., solid–liquid, are critical to both the selection and the design of a reactor. They are particularly important when, to optimize conversion and yield, a number of reactors are combined (interconnected) into a reactor system. While many textbooks discuss given specific flow and thermal conditions, certain reactors as 'ideal', nevertheless a robust reactor design must, at a minimum, address:

- Formation of flow patterns in the reactor, e.g., dead zones, short-circuit flows, and channeling;
- Transport processes in the individual phases in the reactor, e.g., axial backmixing;
- Temperature and concentration profiles that are a result of transport resistance in, and between phases;
- Segregation processes;
- Incomplete mixing of reactants;
- Accommodation of catalyst activity; and
- Deactivation.

In my judgment, the best discussion of the complex interactions that a process designer must cope with can be found in [1]. Those who can obtain a reasonable mastery over the material in this text (particularly, since it was not well proofread) are prepared to address the challenge of the current literature.

In thinking about catalyst process development, it is useful to consider what meaningful information can be derived from experiments in laboratory-scale and pilot-plant reactors (Table 3). In practice, the scope of the listed studies often overlap, sometimes significantly; the degree of overlap and the time spent for each study will depend significantly on the level of experience an organization has with the nature of the catalyst–reactor combination under study. For example, Lurgi (a well-established licensor of methanol catalysts and process technology) would, in my judgment, approach the development of an FCC catalyst very differently from how Exxon (a pioneer in FCC technology) would. The converse would be true, in my judgement, if Exxon were to undertake the development of a methanol process and catalyst.

Table 3
Applicability of laboratory-scale reactors to the development of catalytic processes

Objective of study	Understanding information sought
Catalyst screening	Development of catalyst candidates
Parameter screening	Identification of reaction variables
Reaction network	Characterization of reaction pathways (in a lumped sense)
Kinetic parameters	Development of a 'kinetic model'
Catalyst life	Impact of operating conditions
Process 'optimization'	Define 'best combination' of catalyst and conditions
Scaleup [a]	Validation of critical reactor design issues

[a] Scaleup studies can be conducted in a variety of units, e.g., pilot plants, commercial units and hydraulic mockups; the issues being studied will determine what unit is used. Adopted from Ref. [6].

Design of a reactor is facilitated by the availability of a mathematical model that combines information on reaction thermodynamics, kinetics, and transport–kinetic interactions, e.g., heat and mass transfer effects. The experimental inputs needed to support the development of the model can be obtained from studies in laboratory-scale reactor systems. The traditional approach (which is the only approach understood by an overwhelming majority of process designers, including the writer) involves interpretation of steady-state or quasi-steady-state reactor performance data from which kinetic rate equation constants are eventually extracted by parameter estimation techniques. While it is known that such data can be interpreted by more than one reaction mechanism, a process designer will be satisfied if the kinetic expressions are based on an understanding of the principal chemical pathways (in a lumped sense). Fortunately, the extensive studies of Mobil and related academic studies published in [7], summarize in a useable form, how to go about obtaining a reaction network for mixtures of reactants.

Continuous-flow laboratory reactors can be broadly classified by the flow pattern of the gas, liquid, and solid phases (Fig. 3); quantitative interpretation of experimental data from reactors that have a non-ideal flow, is much more complex and not as straightforward compared to that obtained from reactors whose flow pattern is either perfectly backmixed or in plug flow

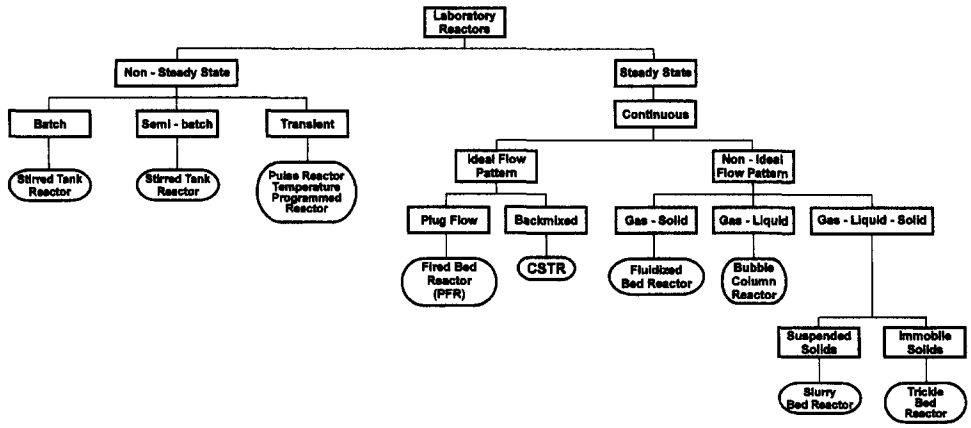

Fig. 3. Classification of multiphase laboratory reactors. Adopted from Ref. [6].

[8]. Making a projection of the performance of a commercial reactor from studies in a laboratory requires, at a minimum, calculation of

- mass balances,
- one energy balance, and
- force balances for each fluid in the reactor.

In addition, one must decouple the kinetics for the reaction network from the deactivation of catalyst activity.

Meaningful and useful data (useful to a process designer) can best be obtained in continuous isothermal reactors that have a well-defined flow pattern and low pressure drop. Continuous microreactors meeting these criteria are available today at a reasonable cost; modern microreactor systems incorporate:

- Reliable mass flowmeters with a 1/2–1% accuracy up to 50 atm;
- PC-based control systems; and
- Continuous analytical capability for streams containing gases, liquids, and semisolids, e.g., waxes.

Fortunately, the capability of the equipment needed for continuous studies in small-scale reactors continues to improve.

The nature of the small-scale reactor (Table 4) to be used depends both on the objectives of the study (Table 3) and the number of phases involved in the reaction system. The recommendations given in Table 4 were developed from practical and theoretical reasonings that are too lengthy to be given here (unfortunately, the only thorough discussion, known to the writer, of the reasoning supporting these recommendations is in a proprietary report [10]). The guidance given in Table 4 should only be regarded as a 'majority opinion'; situations often exist where laboratory reactors other than those recommended in Table 4 are a better alternative. For example, many fine chemical manufacturing processes utilize batch or

Table 4
A laboratory reactor is not a commercial reactor

Objective of study	Solid–gas	Solid–liquid	Solid–gas–liquid
Catalyst screening	PFR	PFR STR (batch)	STR (semi-batch)
Parameter screening	CSTR	CSTR STR (batch)	STR (semi-batch)
Reaction network	CSTR	CSTR	Trickle bed CSTR
Kinetic parameters	CSTR	CSTR	Trickle bed CSTR
Catalyst life	CSTR PFR	CSTR PFK	Trickle bed CSTR
Process 'optimization'	CSTR PFR	CSTR PFR	Trickle bed CSTR
Scaleup	PFR fluidized bed	PFR slurry	Trickle bed slurry

semi-batch agitated reactors. In these cases, the objectives of a study may be achieved more efficiently through the use of similar laboratory reactors.

One must always remember that the small-scale experimental studies envisioned in Table 4 generate data; they do not demonstrate a commercial reactor. For example, a CSTR is rarely used in a commercial process, simply because for a given production rate a CSTR will have larger volume than a plug-flow reactor (often costing more). However, for many small-scale studies, CSTRs are optimal since:

- Rates can be derived directly from simple material balances;
- The temperature and pressure are uniform;
- Parameters for reactive kinetics and catalyst decay can be separated; and
- Conditions in the reactor do not vary by position; therefore, the transport resistances at phase boundaries and within a catalyst can be estimated.

The merits and demerits of the Carberry Spinning Basket, Berty internal recycle reactor or external recycle CSTR have been extensively discussed in the literature; experience and personal prejudice often are the basis for making a choice in a specific situation. For example, I do not like data from a Berty reactor since one cannot be certain that gas and liquid are recycled in known (calculated) proportions.

The development of catalysts and process systems based on them involves manipulation of a large number of variables; the most important of these being the following:

- Composition of the catalyst;
- Procedure used to manufacture the catalyst; and
- Nature of the environment the catalyst is exposed to (e.g., reactants, poison, operating conditions).

Similarly, catalyst performance is a composite of reaction rate, yields and selectivity, catalyst life, and the purity of the desired product(s).

One might believe, in view of this complexity, that catalyst development programs would benefit from the use of carefully planned experimental designs that permit conclusions to be drawn through a rigorous statistical analysis of the data. In recent years, dozens of 'cookbooks' on how to use experimental designs have been published; 'cook software' that facilitates the design and analysis of experiments is also available. However, far too few studies, in my experience, utilize even a semblance of an experimental design. For example, I recently studied over 2000 patents on a commercial reaction of interest to a client. In only about 50 of the patents do the reported conclusions about the responses expected from changes in the process factors have any statistical basis.

While heterogeneous catalysts cannot yet be designed, an understanding of their behavior sufficient for the design and operation of commercial processes that are environmentally 'acceptable', is in our grasp today. However, developing and conducting experimental studies that generate useful data requires answering the question (before starting a study): why is the study being done? The nature of the phenomena to be studied and the projection of commercial performance that will be made from the experimental data, is of critical importance. Only when this has been clearly established can the best method for an experimental study be chosen. Otherwise, the study may result in data which is of little value and, unfortunately, may be misleading; as many studies do!

A reading list may be more appropriate for many than a set of references; in my judgment the following are particularly relevant to the issues reviewed in this article.

Acknowledgements

I would like to express my gratitude to many experts and friends (process designers) who helped me in the preparation of this article by providing key information or reviewing the test. I would especially like to thank Gianni Astarita, Mordechai Herskowitz and Reuel Shinnar; however, the passion with which some of the views are expressed is solely the responsibility of the author.

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