

## TESTING OF CATALYTIC PROPERTIES

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### Summary

Catalysis enhances the sustainability of our society. Raw material utilization, energy efficiency, elimination of hazardous synthesis routes are issues typically addressed by catalysis contributing to safer, more reliable and more economical chemical processes. Catalyst development and improvement require an elaborate testing of candidate catalytic materials, not only the physical properties, such as porosity, crystallinity, surface composition,... but also, and even more importantly, the functional properties. The latter are defined in Section 1 of this contribution. Having defined ‘*what*’ is to be tested, Sections 2 and 3 address ‘*how*’ this testing is to be performed. In Section 2, the various, generally available reactor types are listed and discussed, whereas Section 3 deals with the intrinsic character of the observed catalytic kinetics. So-called ‘*intrinsic*

*kinetics*' are obtained when the observations are only affected by the chemical kinetics at the catalyst's active sites and not by any kind of transport phenomena at the pellet scale, nor by flow pattern non idealities at the reactor scale. The last two sections are devoted to particular applications. Specific reactor types have been developed, vide Section 4, for measuring phenomena such as deactivation or for obtaining more detailed insight in catalytic reaction mechanisms. During the last decade, important efforts have been spent on enhancing the rate of catalyst discovery. Not only catalyst synthesis has been automated by parallelization and robotization, also adapted testing facilities have been developed in order to keep up with the vast catalyst libraries that have become available. These 'high-throughput technologies' are discussed in Section 5.

## 1. Definition of Catalytic Properties

Catalytic performance is related to an amount of reactant that is transformed into product, desired or unwanted. Depending on the reaction of interest, the user is interested in (i) the total amount of reactant transformed, i.e., the conversion, (ii) the amount of a specific product formed per reactant converted, i.e., the selectivity, or (iii) the amount of product formed per reactant fed, i.e., the yield. As important as these properties, is the extent to which they are maintained with the time on stream, i.e., the extent of catalyst deactivation.

### 1.1. Conversion

The overall catalyst activity is assessed through the conversion. This conversion is defined as the number of moles reactant converted per number of moles reactant fed, i.e.,

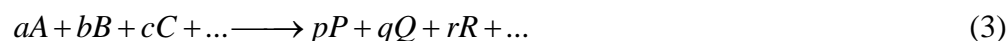
$$X_A = \frac{F_{A0} - F_A}{F_{A0}} \quad (1)$$

for continuous flow reactors and

$$X_A = \frac{N_{A0} - N_A}{N_{A0}} \quad (2)$$

for batch reactors.

When two or more reactants are fed, a conversion can be obtained for each of the reactants. For the reaction stoichiometry:



the following relation between the individual reactant conversions is obtained:

$$X_A = \frac{a}{b} \frac{F_{B0}}{F_{A0}} X_B = \frac{a}{c} \frac{F_{C0}}{F_{A0}} X_C = \dots \quad (4)$$

for continuous flow reactors and

$$X_A = \frac{a N_{B0}}{b N_{A0}} X_B = \frac{a N_{C0}}{c N_{A0}} X_C = \dots \quad (5)$$

for batch reactors.

Typically, the conversion is the first property investigated in the development of new and improved catalysts. For more complex reactions, however, the catalyst activity is not sufficient for characterizing the catalyst's behavior and other properties, such as selectivity and yields are required.

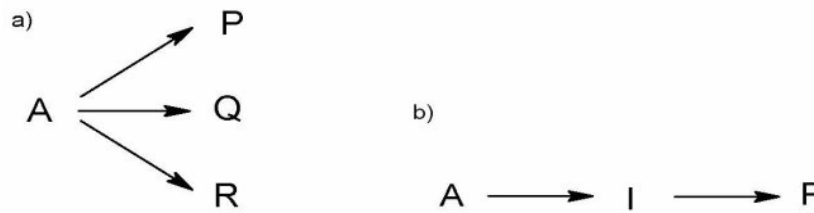


Figure 1. Examples of ‘complex’ reaction networks. a) parallel reaction, b) consecutive reaction.

## 1.2. Selectivity

In the case of complex reactions consisting of parallel and/or consecutive reaction pathways that contain intermediate, desired and/or by-products, vide Figure 1, a quantity such as the selectivity can be defined as an indication of the amount of a specific product formed in the reaction. Various definitions of selectivity are used in the literature and, hence, when reviewing results in terms of selectivity, one should always verify the exact definition of the selectivity used. In general, the selectivity expresses the number of moles transformed into a certain product compared to the total number of moles converted, i.e.,

$$S_P = \frac{F_P}{F_{A0} - F_A} \quad (6)$$

for continuous flow reactors and

$$S_P = \frac{N_P}{N_{A0} - N_A} \quad (7)$$

for batch reactors.

For given operating conditions, the selectivity depends on the conversion. Although high selectivities of desired products are preferred, the total number of moles converted into this desired product should be sufficiently large. This aspect indicates the necessity of an additional characteristic property, which is discussed in the next section.

### 1.3. Yield

In contrast to the definition of the selectivity, the definition of a yield is not related to the number of moles converted but to the number of moles fed, i.e.,:

$$Y_P = \frac{F_P}{F_{A0}} \quad (8)$$

for continuous flow reactors and

$$Y_P = \frac{N_P}{N_{A0}} \quad (9)$$

for batch reactors.

It can be easily observed from Eqs. (1), (2) and (6-9) that the following relationship holds between the conversion, the selectivity and the yield:

$$Y_P = S_P X_P \quad (10)$$

It might be tempting in catalyst design and development to maximize the yield of a desired product. As evident from Eq. (10) catalyst optimization solely based on product yields might lead to highly active catalysts exhibiting high conversions with a relatively poor selectivity. The ultimate targets defined in catalyst development will depend on the process economics, i.e., the minimization of losses through reactant conversion into undesired products compared to limiting the higher operating costs induced by larger recycle streams.

### 1.4. Catalyst Deactivation and Sustainability

The catalyst properties as defined in the above sections are subject to deterioration during the use of the catalyst, i.e., so-called catalyst deactivation occurs. Generally, deactivation phenomena occur on a much longer time scale than that of the desired reaction, however, large variations in time scales for deactivation are reported. The shortest are of the order of seconds or even shorter such as in fluid catalytic cracking, while the longest are of the order of a few years such as in hydrocracking. There are three main causes of catalyst deactivation: solid state transformations, poisoning and coking. Solid state transformations cover a wide variety of phenomena that range from modification of the carrier, e.g.,  $\gamma$ -alumina transformation into  $\alpha$ -alumina as a result of a prolonged exposure to higher temperatures, to migration of promoter atoms. Catalyst poisoning is the result of the chemisorption of impurities in the feed and is generally considered to be irreversible. Coking consists of the irreversible deposition of carbonaceous residues from reactants, products or intermediates and is to be considered as a side reaction.

## 2. Reactor Types

Catalyst properties such as conversion, selectivity, yield and deactivation are tested in a reactor where the catalyst is brought into contact with the reactants at the selected operating conditions. Various ideal reactor types exist, each with their advantages and disadvantages.

## 2.1. Batch Reactor

A batch reactor is a discontinuous reactor which is agitated in order to realize a uniform temperature and composition through the reactor, vide Figure 2. A batch reactor is typically used for liquid phase reactions in which the catalyst is suspended, leading to a so-called slurry phase. The reaction mixture composition is followed as a function of the batch time which means that at regular times a sample has to be withdrawn from the reactor for analysis.

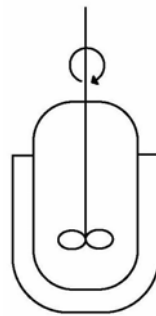


Figure 2. Schematic representation of a batch reactor

The continuity equation for the main reactant in a batch reactor is written for the entire reactor volume:

$$\frac{dN_A}{dt} = VC_{\text{cat}}R_A \quad (11)$$

For a first order reaction this equation is transformed into

$$\frac{dC_A}{C_A} = C_{\text{cat}}k_A dt \quad (12)$$

Assuming that the catalyst concentration is constant throughout the experimentation, this equation can be integrated from time 0 to the actual batch time:

$$C_A = C_{A0} \exp(-C_{\text{cat}}k_A t) \quad (13)$$

resulting in an exponential decay of the concentration of  $A$  with the batch time.

A batch reactor has its simple implementation as its main advantage. An ordinary flask in which reactants are poured, mixed using a magnetic stirring plate and brought to the testing temperature is sufficient to realize a batch reactor if the operating conditions allow such a construction and type of material to be used. The start of the reaction is then determined by dropping the catalyst into the reaction mixture. Of course, when

higher pressures and temperatures are required, autoclave type of vessels are required. The catalyst then has to be in place prior to reaching the testing temperature and pressure and, hence, the start of the reaction is much less well-defined than in the first case. Also devices made for allowing sampling may lead to non idealities and disturb the ideal batch reactor characteristics. To overcome these limitations imposed by batch reactors two continuous reactor types are available. More importantly, batch reactors do not allow to assess the occurrence of catalyst deactivation. Finally their application is limited to reactions that occur on a time scale which is compatible with the time scale required for sampling.

## 2.2. Perfectly Mixed Flow Reactor

The answer of the perfectly mixed flow reactor, also denoted as Continuous Stirred Tank Reactor (CSTR), to the issues met with a batch reactor is to change the discontinuous character of the batch reactor into a continuous character, vide Figure 3. The uniformity of temperature, pressure and composition inside the reactor is preserved. This implies that upon the entry of the reactant mixture in the reactor, the outlet composition is achieved.

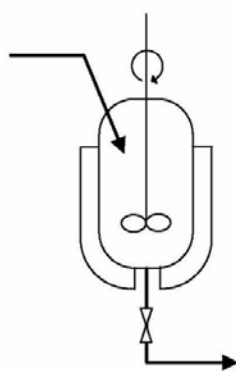


Figure 3. Schematic representation of a perfectly mixed flow reactor

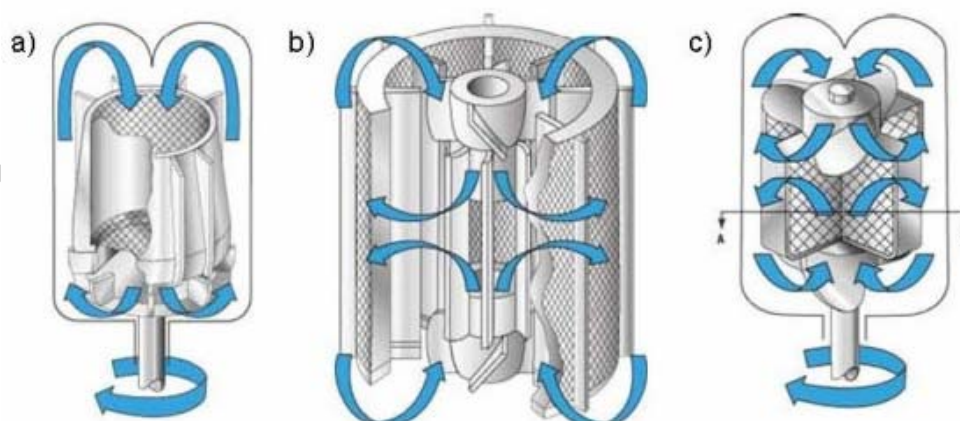


Figure 4. Representation of the internal construction and flow pattern of commonly encountered perfectly mixed flow reactors. The aggregation state of the reaction mixture is indicated between brackets a) Bertly reactor (gas) b) Robinson Mahoney reactor (gas and liquid) and c) Carberry reactor also denoted as spinning basket reactor (gas)

The perfectly mixed flow reactor is operated till a steady state is reached prior to analyzing the reactor effluent. In commonly encountered perfectly mixed flow reactors,

vide Figure 4, the catalyst is not suspended in a liquid but contained in a catalyst basket. This basket can be stationary such as in the Berty reactor used for gas phase conditions, vide Figure 4a or in the Robinson-Mahoney reactor used for gas-liquid conditions, vide Figure 4b. In a perfectly mixed flow reactor of the Carberry type, Figure 4c, the catalyst basket is mounted on the agitator and, hence, is continuously spinning around. The continuity equation for the main reactant in a perfectly mixed flow reactor at steady state conditions can be written as:

$$F_{A0} - F_A = -VC_{\text{cat}}R_A \quad (14)$$

Assuming a constant, total volumetric flow rate  $F_{Vt}$  this continuity equation can be transformed into

$$F_{Vt}C_{A0} - F_{Vt}C_A = -VC_{\text{cat}}k_A C_A \quad (15)$$

for a first order reaction. Rearranging the above equation into

$$C_A = \frac{C_{A0}}{1 + \frac{V}{F_{Vt}}C_{\text{cat}}k_A} \quad (16)$$

leads to monotonic decrease of the concentration of A with the space time,  $\frac{V}{F_{Vt}}$ .

A perfectly mixed flow reactor has as main advantage that net production rates can be directly observed, see Eq. (14), with a relatively small experimental error. Disadvantages of a perfectly mixed flow reactor are the moving parts necessary for establishing the uniformity throughout the reactor. It makes the design and construction of a perfectly mixed flow reactor relatively complex. Moreover, moving parts inevitably suffer from wear and tear, which imposes constraints on the operation.

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### Biographical Sketches

**Joris W. Thybaut** (°1975, Ghent Belgium) is assistant professor at Ghent University since October 2005. He obtained his master's degree in chemical engineering in 1998 at the Laboratorium voor Petrochemische Techniek (LPT) at the same university. He continued at the LPT for a PhD on single-event microkinetic (SEMK) modeling of hydrocracking and hydrogenation.

After obtaining his doctoral degree in 2002 he extended his area of research to other important processes such as catalytic cracking, hydrotreating, methane oxidative coupling and Fischer Tropsch synthesis, with SEMK as the common point of interest. In 2003 he went to the 'Institut des Recherches sur la Catalyse' in Lyon, France, for a postdoc on high throughput experimentation. Today he's setting up a platform for high-throughput kinetics at the Laboratory for Chemical Technology at Ghent University.

**Guy B. Marin** (°1954, Oostende, Belgium) is chair of the department "Chemical engineering and technical chemistry" at Ghent University (Belgium). He received his degree from Ghent University in 1976 where he also obtained his Ph.D. in 1980.

After a post-doctoral stay in 1981 at Catalytica Associates and Stanford University he obtained tenure at the Ghent University in 1986. He took a position of full professor in 1988 at the Eindhoven University of Technology (The Netherlands) where he taught chemical reactors. In 1997 he returned to Ghent as director of the Laboratory of Chemical Technology. Chemical reaction engineering and catalysis in general and reaction kinetics in particular are the main leads in his research program. He co-authored more than 200 papers in international journals.

He is editor-in-chief of "Advances in Chemical Engineering" and co-editor of the Chemical Engineering Journal. He is a member of several Scientific Committees advising companies and governmental organizations.