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Catalysis Today 52 (1999) 133–145

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Experimental methods in catalytic kinetics

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Abstract

Selecting an appropriate experimental procedure and a suitable laboratory reactor is crucial for evaluating the kinetics of a catalytic process. In this paper, practical guidelines are suggested for carrying out a kinetic study for a given reaction system. Comparison of various laboratory reactors is presented and some of the pitfalls and limitations are discussed. The influence of transport phenomena due to the flow, the catalyst and the reactor geometry is analyzed and the criteria for their absence are given in a convenient form. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic kinetics; Transport resistance; Effective diffusivity; Fixed-bed reactors

1. Introduction

The successful design of a catalytic industrial reactor lies primarily on the reliability of the experimentally determined parameters used in the scale-up [1]. As a consequence, it is very important to collect accurate and meaningful laboratory data, with proper experimental set-ups, and according to carefully planned kinetic experiments. *The planning of the experiments and the kinetic analysis* is the subject of another paper of this special issue.

In this paper we will discuss *how to experimentally approach a catalytic study* for a given reaction system. A ‘‘modus operandi’’ will be given in order to select the appropriate experimental procedure and to choose suitable experimental set-ups, among a wide variety of potential laboratory ones. The focus will be the selection process rather than a comprehensive review of all laboratory reactors and devices. For the latter purpose we suggest several interesting papers, appeared in the literature, to which refer as supplementary reading [2–5].

2. Preliminary considerations

All catalytic processes, regardless of type, involve various phenomena in addition to the desired catalytic reactions. These include:

- side or interfering chemical reactions,
- thermodynamic, physical and chemical equilibrium,
- heat transfer,
- mass transfer between phases or even within a given phase,
- flows of fluids (free convection or forced convection) or of granular solids.

These phenomena are differently affected by the operating variables and by reactor size and geometry, as reported by Trambouze [6].

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PII: S0920-5861(99)00071-1

To analyze the behavior of a catalytic reactor it is necessary to build a mathematical model (*reactor model*) describing these various aspects. Therefore, it is important to collect accurate and reliable data for *mass, energy and momentum transport* as well as *chemical kinetics*. Then the data must be analyzed to find adequate model equations and to estimate reliable *parameters* dependent only on the macroscopic variables of the reactor (i.e., pressure, temperature, space velocity). For the data collection, specially designed laboratory or pilot experiments are needed, as only in few cases a theoretical evaluation is possible [7]. Though data analysis procedure has been developed in order to estimate simultaneously *chemical kinetic parameters* and *transport parameters* from data obtained under non-isothermal integral experiments (see [8]), an approach is advisable in order to break down the problem into its different components. In this way, the experimentation necessary to develop the reactor model is split into complementary parts.

First we will concentrate on *the criteria for performing kinetic experiments under conditions where transport resistances are negligible* (Section 4). When this is possible, *intrinsic kinetic equations* will be obtained and the reaction kinetic parameters (*rate constant k, activation energies E*, and *adsorption constants K*) will be estimated.

The following step will be the evaluation of the *catalyst pellet efficiency* in kinetic experiments carried out in the absence of *external mass and heat transfer effects* (Section 5). Then we will consider measures performed to determine the *catalyst particle parameters* (e.g. *effective diffusivity and effective thermal conductivity*). All the parameters estimated by this approach will allow to formulate a *kinetic model of the catalyst pellet* which is the "core" of the catalytic reactor model.

The kinetic model of the catalyst pellet can be embedded in the model of any type of reactor (e.g., fixed-bed, fluidized-bed, trickle-bed and slurry). The latter will also account for all the transport phenomena outside the catalyst particle. So it is necessary to build up a mathematical model of the *intrareactor regime*, including the mass, energy and momentum continuity equations for axial and radial transport through the catalyst interstices. These equations depend on the type of reactor under development and the transport parameters can be estimated from available correlations [9] or measured by means of experiments performed under non-reacting conditions. As belonging to the *scale-up* stage of the catalytic process, these experiments are outside the purpose of this paper. This subject is discussed in literature [6,10–12].

2.1. Reactor classification

An useful classification of laboratory reactors is reported in Fig. 1, as suggested by Anderson et al. [13]. The distinctions among the reactors are based upon time dependencies (*steady state* vs. *non-steady state*), conversion level (*integral* vs. *differential*) and flow pattern.

2.1.1. Steady state operation

The first distinction among laboratory operations is whether the temperature and the concentrations at any chosen point in the reactor is invariant with time. If so, the operation is classified as *steady state*. Steady state operations are performed in *continuous reactors*. A continuous flow of reactants (sometimes including products and/or diluent) is supplied to the reactor. The same mass flow rate of product stream is withdrawn. Continuous reactors are commonly distinguished by the nature of their *flow pattern* and of *catalyst handling* (Table 1). The catalyst amount inside a continuous reactor is constant with time. This is obtained either by a *batch overall* or a *continuous overall* of the catalyst. Furthermore, the catalyst can be either *mobile* or *immobile* in the reactor. All of them exhibit a flow pattern that lies between the ideal extremes of *plug flow* and *perfect mixing*.

These two flow patterns are called "ideal" as they enable a simple mathematical description and an easier data treatment. As we will discuss later, *any continuous reactor with other than ideal flow behavior should be discarded as unsuitable for kinetic study.* According to Table 1, it is inadvisable to determine the kinetics for catalytic reaction in *fluidized bed* or *bubble column*. These reactors may occasionally be acceptable for testing catalysts but are not recommended for obtaining *intrinsic kinetic* data.

2.1.1.1. Continuous fixed-bed reactors with plug flow. This reactor is a tube packed with a solid catalyst. When the reacting fluid moves through the

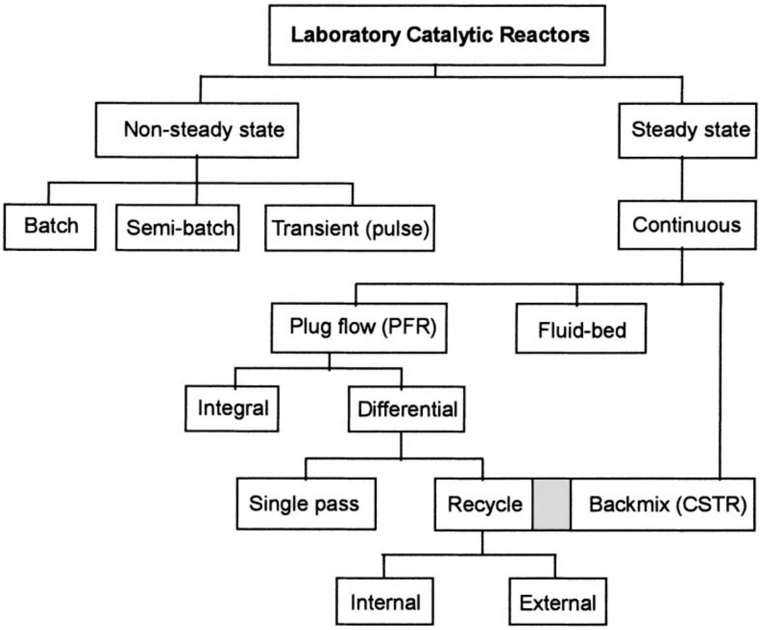

Fig. 1. A suggested classification of laboratory reactors [13].

Table 1
Continuous laboratory reactors

Characteristic flow pattern				
Catalyst handling		Plug flow	Intermediate	Perfect mixing
Batch overall	Immobile in reactor	Fixed-bed, trickle-bed		Recycle reactors
Batch overall	Mobile in reactor (with mixing)		Fluidized-bed, bubble column	Stirred tank
Continuous overall	Mobile in reactor (the catalyst moves as a compact packed-bed)	Moving-bed		
Continuous overall	Mobile in reactor (with mixing)		Fluidized-bed, bubble column	Stirred tank

reactor tube in turbulent flow, the fluid moves like a plug or piston. This reactor is commonly called *plug flow reactor* (PFR). The condition of turbulent flow generally ensures the absence of temperature, velocity and concentration gradients in the radial direction. The PFR is well-mixed radially and zero-mixed axially.

A distinction commonly made among these reactors is based on the magnitude of *conversion per pass* over the catalyst. A reactor is generally termed *differential* when the conversion of reactant through the catalyst bed is less than 5% per pass. In this condition the rate becomes approximately linearly proportional to the change in conversion. So the reaction rate can be calculated directly from the incremental change in conversion. If the conversion per pass exceeds 5%, the reactor is called *integral* and the reaction rate is obtained by a more complex analysis of the experimental data.

A typical fixed-bed laboratory reactor is the so called *microreactor* [2,14] for *single-pass* operations. A microreactor can be *either differential or integral.*

Recycle reactors are *multi pass* reactors where a major portion of the effluent is recycled to the reactor inlet. When the recycle ratio is high (e.g. >25) the reactor can be regarded as *a continuously stirred tank reactor* (CSTR). There are two classes of recycle reactors: *external recycle* (*or loop*) reactors and *internal recycle* reactors. External recycle is usually achieved using an external pump that must be able to operate at the required temperature without chemically contaminating the recycle stream. This is a quite difficult task. Furthermore, the high ratio between wall surface and volume, typical of external loops, may be detrimental when the wall material shows any kind of catalytic activity. Another problem concerns the high *dead volume* (reactor volume other than catalyst volume) if homogeneous reactions take place. For this reasons external recycle is not often used. In contrast, *internal recycle* is usually achieved through an internal impeller and is well suited for high pressure operation [3]. A variety of internal recycle designs have been proposed in literature [5] and some are commercially available.

2.1.1.2. Continuous reactors with perfect mixing. This class includes *recycle reactors with high recycle ratio* and *continuously stirred tank reactor* (CSTR). Both of types are termed gradientless because of the absence of *intrareactor concentration* and *temperature gradients*. According to the ideal behavior the reaction rate may be obtained directly from a simple algebraic equation expressed in terms of effluent concentration.

From a practical point of view problems arise in order to obtain uniform catalyst dispersion. The possibility to suspend the solid particles uniformly in the fluid is strongly dependent on the density difference between solid and fluid and on the efficiency of the stirring device. The substantial difference in density between gas and solid makes virtually impossible to suspend catalyst solid particles in a gas. Liquid suspensions (*slurries*) can overcome the problem of solid particle dispersion and favor temperature uniformity. In all cases vigorous and efficient stirring is essential.

An alternative for solid catalyst particles with size suitable to be retained by a wire mesh (>1 mm) are *basket reactors*. With assorted impellers and baffles, these devices are adaptable to gas–solid, liquid–solid and gas–liquid–solid reactions.

When the impeller includes the basket itself, the reactor is called *spinning basket reactor.* A reactor of this type was first proposed and used by Carberry [15]. On the contrary, in *stationary basket reactors* the stirred tank performances are obtained by rotating special impellers inside a pot holding a fixed basket inside [2,5].

2.1.2. Non-steady state operation

Contrary to the steady state reactors, the conditions in *non-steady state systems* vary with time. If so, the reactor are classified as a *non-steady state*. This class includes *batch reactors, semibatch reactors and transient reactors*.

In *batch reactors* [2], the catalyst and all the chemical species are charged into a vessel and brought to react as a function of real time, under specified conditions of temperature and pressure. The progress of the reaction is monitored by periodically analyzing the vessel content. The simplest form is the *stirred batch reactor* which is a STR operated *batchwise*. Therefore, stirred batch reactors can be either slurry reactors or spinning basket reactors, depending on the particle size and fluid density. Also external recycle reactors have been used for batch experiments [16].

In *semibatch reactors* [2], one (or more) of the reactants are charged batchwise, while a coreactant is fed continuously. Gas–liquid–solid reactions are frequently carried out in this semibatch mode, with the catalyst and liquids charged initially and gases fed as they are consumed by the reaction. The coreactant can be fed at a rate suitable for the desired control of the overall reaction rate and heat generation or abstraction. The data obtained consist of species concentrations vs. real time, as in the case of batch reactors.

Transient reactors are continuous reactors operating under non-steady state conditions. A perturbation is made in the reaction conditions and the time-dependent response is used to obtain the kinetic information. *Pulse reactors* [4] are common examples of this type. A given amount of reactants is injected into a gas stream that passes through a small bed of catalyst at a fixed temperature. The conversion is quantified via on-line analysis of the exiting pulse. Transient reactors are also used in the *Temperature programmed reaction* (TPR) [17] technique. In TPR, a fixed-bed reactor containing the catalyst is fed continuously with the reactants. The feed composition and the feed rate are fixed, while the catalyst temperature is changed according to a predetermined program. The composition of reaction products is determined via on-line analysis of the exiting stream. The conversion is so recorded as a function of time on stream and on temperature.

In Fig. 2 the laboratory reactors discussed above are summarized according to the operation mode.

3. Nature of reacting system

Building a mathematical model of the catalyst and reactor is usually required in view of two different objectives: *development* of a newly discovered catalyst or catalytic process and *optimization* of an existing catalytic process. In both cases the *reacting system* is well known. Sometimes, even in the case of a new catalytic process, the industrial reactor type is already defined. The selection of the experimental set-up however, is related to the reacting system more than to the kind of industrial reactor. In fact the laboratory reactor does not necessarily be a reduced scale replica of the industrial reactor.

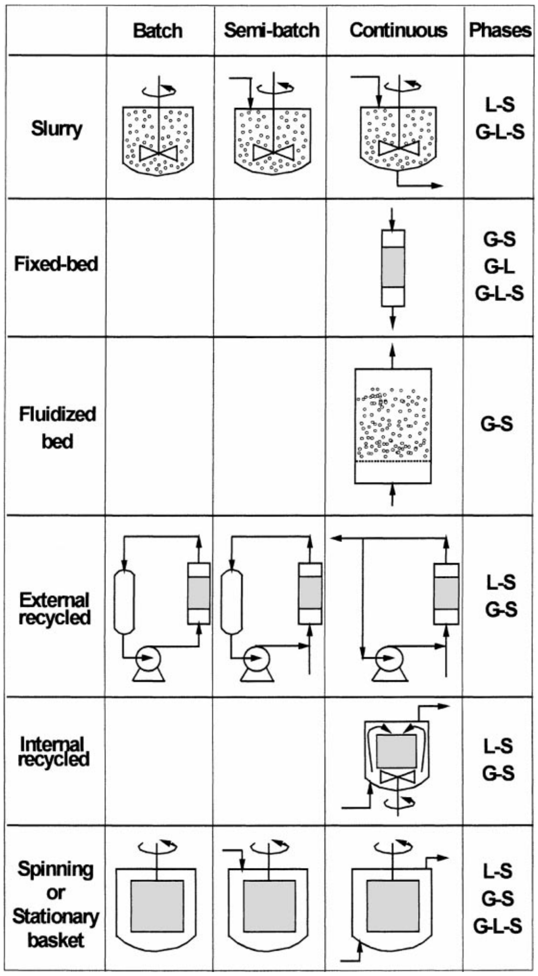

Fig. 2. Common laboratory reactors: operation modes and reacting system (L:liquid, G: gas, S: solid).

So we assume that before to select the suitable set-up and to start up any experimental program, a clear understanding of the nature of the reacting system is available. This includes the matters concerning *thermodynamics* and *physical data* of the reacting system. Some particularly prominent areas are highlighted below.

3.1. *Thermodynamics*

Any reaction kinetic study should begin with a thorough analysis of the thermodynamics of the system. Thermodynamics impacts on chemical reaction engineering in two major ways. It may be used to quantify *heat effects* in reacting systems and it enables the calculation of the *equilibrium conversion* (i.e., *maximum conversion* which may be obtained in a chemical reaction) and the effects of feed composition, temperature and pressure on that maximum conversion.

3.1.1. *Heat effects*

A dominant issue in performing experimental kinetic studies is the management of heat transfer. Therefore it is necessary to know if we are dealing with *exothermic* or *endothermic* reactions and to know how much heat must be exchanged in order to maintain *isothermality*. The matter of calculation of *heats of reaction* (ΔH_r^0) is covered in all texts on chemical engineering thermodynamics [18].

3.1.2. *Equilibrium conversion*

First of all one should determine whether or not the reaction thermodynamics is favorable and, in particular, be aware of any limitation of conversion because of *equilibrium*. Regardless of the reactor type, size, or catalyst used, you can never do better than equilibrium. Thermodynamics gives a limit on what can be achieved. It also gives an important clue toward optimal experimental conditions.

Standard free-energy (ΔG^0) value is obtained from thermal data as well as ΔH_r^0. From ΔG^0, the equilibrium constant, hence the maximum conversion to which a chemical reaction can proceed, may be calculated [18]. It applies to the conversion of reactants in their standard states to products in their standard state. ΔG^0 may be a function of temperature but it will not be a function of total pressure. Therefore, the equilibrium constant (K_a) defined on the basis of thermodynamic activities, will also be independent of total pressure. On the contrary K_p, defined on the basis of partial pressures, can become a function of pressure due to the non-ideality of gases. In order to account for non-ideality, fugacity coefficients must be introduced. The fugacity coefficients can be obtained from generalized coefficient charts available in many thermodynamic texts [18].

However, the calculation of chemical reaction equilibrium is an area of chemical reaction thermodynamics in which errors are most likely to arise. Therefore, the previous calculations must be performed with care. An interesting example showing the criticisms of these analysis has been reported by Kabel [19].

3.2. *Physical data*

Heterogeneous catalyzed reactions are two-phase systems at least, solid (the catalyst) and liquid and/or gaseous (the reactants and the products). Preliminary evaluations of the liquid–vapor equilibrium of the reacting system should be performed to know the physical state of reactants and products under the reaction conditions. This information is useful for the correct reactor choice. As it will be described below, reactors more suitable for liquid–solids, gas–solid or liquid–gas–solid phases can be choosen [20,21], as roughly reported in Fig. 2.

4. Intrinsic kinetics

Once we have a clear understanding of the nature of the reaction system we must consider what attributes of the laboratory reactor will be important to perform kinetic experiments under conditions where transport resistances are negligible. If this is possible the *intrinsic reaction rate* will be determined.

Few general characteristics are considered crucial for the correct carrying out of a kinetic experiment in order to obtain *intrinsic reaction rates*:

- *isothermality*;
- *ideality of flow pattern* for continuous operations or *ideality of mixing* for batch and semibatch operations;
- absence of *interphase* and *intraphase* concentration and temperature gradients.

Isothermality. Isothermality means absence of *temperature gradients* inside the reactor. For complex reacting system, with multiple reactions paths having different activation energies, it may make very difficult to unscramble the rate constant from non-isothermal data [22].

Ideality of flow pattern or ideality of mixing. As discussed above for continuous reactors, flow patterns lie between the ideal extremes of *plug flow* (PFR) and *perfect mixing* (CSTR). Adopting laboratory reactors having ideal flow pattern ensures an easy data treatment because of the simple mathematical description. Ideal flow pattern for continuous reactors corresponds to ideal mixing for *batch stirred reactors* (BSTR). Deviation from ideality occurs because of the presence of macrogradients of concentration or temperature in the reactor. These macrogradients may result, for instance, from incomplete mixing in STR or from axial dispersion, wall effects or catalyst bypassing in PFR. These *intrareactor* gradients affect the evolution of the chemical reaction and unless accounted for, will falsify the interpretation of the results obtained.

Absence of interphase and intraphase gradients. Gradients of concentration and temperature can also occur at the boundary between different phases in the reactor. With solid catalysts such gradients may occur between the internal solid surface and the bulk fluid (*interphase*) and within the catalyst particles themselves (*intraphase*). Such gradients are also known as *external* or *internal*, respectively. The presence of gradients severely complicate the analysis of the rate data.

In the subsequent discussion we will show how to select and operate laboratory reactors in order to ensure the existence of the previous attributes and to measure *intrinsic kinetic rates*. We will concentrate on simple practical rules and on experimental diagnostic tests, while referring to the literature for mathematical criteria [21,23]. According to Fig. 2 the following reactor types will discussed:

- fixed (two-phase or trickle)-bed reactors;
- stirred reactors;
- recycled reactors.

4.1. Fixed-bed reactors (two-phase)

According to Fig. 2, fixed-bed laboratory reactors can be used for two-phase system (gas–solid or liquid–solid) and for three-phase systems (gas–liquid–solid). The latter, called *trickle-bed* reactors, will be treated separately.

Plug flow operation. In order to ensure a plug flow pattern the following conditions must be fulfilled:

- The reactor diameter (D) must be at least 10 catalyst particle diameter (d_p) ($D/d_p>10$) [21].
- For gas–solid systems the catalyst bed length (L) should be at least 50 particle diameter ($L/d_p>50$) [24].
- For liquid–solid systems, at the low flow common in laboratory reactors, the catalyst bed length should be several hundred particle diameter [21].

The flow of fluids through a packed bed generally results in a decreasing gradient of total pressure. This can produce an axial change of reactant partial pressure. In order to ensure *isobaric operation* the particle diameter d_p should be selected carefully. If d_p is so small that a significant pressure drop is obtained, an additional equation must be coupled to the reactor model (e.g. Ergun equation [25]). This will complicate the interpretation of experimental data.

Isothermality. Intrareactor temperature gradients can be largely eliminated by using the *differential operation*. In this case a small amount of catalyst is used in order to reach low conversion level. This operation method allows to assume that through the thin catalyst bed layer both temperature, pressure and concentrations are constants [1,21,22]. In this sense the differential reactor is the simplest *gradientless reactor*. The main problems with this kind of operation is the analysis of the product composition. By its nature, the differential reactor gives a small incremental conversion, which can be difficult to measure for a complex multicomponent mixture. Moreover, by-passing in a differential reactor will be fatal in terms of measuring accurate contact time and, as a consequence, in terms of results obtained.

In practice, very often *integral operations* are used. The main difficulty with the integral reactors is to achieve uniform temperature along the catalytic bed. This problem is particularly important with severely *exothermic* (or *endothermic*) reactions.

The experimental methods for reducing temperature gradients are mainly the *dilution* of both feed and catalyst and *decreasing of reactor diameter*. The feeding of an inert substance together with reactants allows to increase the heat removal from the reaction zone. The catalysts dilution with inert solid particles (generally quartz), having the same size of the catalytic particles, reduces the local hot-spot and improves the temperature distribution along the catalytic bed. The decreasing of reactor diameter should necessarily be accompanied by the reduction of particle diameter, in order to fulfill the PFR condition. Otherwise by-passing problems (uneven distribution of the different phases through the catalytic bed) will arise. However, the need to reduce catalyst particles produces high pressure drops. In this case the problems are resolved by mixing catalyst particles with inert particles of suitable size, in order to guarantee a good fluid distribution and a low pressure drop. A reproducible procedure for packing small-diameter packed beds with a mixture of fines and catalyst was proposed by Dudukovic et al. [26].

Absence of interphase (external) gradients. In gas–solid systems temperature gradients between gas and solid surface is quite common. The extent of these gradients can be reduced by properly reducing the particle diameter and/or by increasing the *flow rate*. On the contrary, temperature gradients are rarely a controlling factor in liquid–solid systems [21].

Interphase concentration gradients are very common for both gas–solid and liquid–solid systems. As in the case of temperature gradients, concentration gradients can be reduced by increasing the flow rate of reactants.

Two diagnostic tests (a and b) are applicable in order to check the presence of *interphase limitations* [24]. Both are based on the principle that in the absence of interphase transport limitations, the conversion at any space velocity must be independent of the linear velocity through the bed. Space velocity can be defined as the volume of reactant fed per volume of catalyst per unit time (liquid hourly space velocity, LHSV), which is the inverse of the contact time (τ).

Test a. In a given reactor section, consecutive tests are carried out by increasing both reactant flow rate (volume of reactant per unit time, *F*) and catalyst volume (*V*), while keeping constant their ratio (LHSV). The conversion of reactant will change until interphase limitations (external diffusion) are present (Fig. 3).

Test b. In a given reactor section two series of tests are run, first on a catalyst volume *V*, and second on catalysts volume 5 *V*. In each series τ is varied and two curves are traced for conversion vs. τ. If the two curves overlap there are no interphase limitations (Fig. 4).

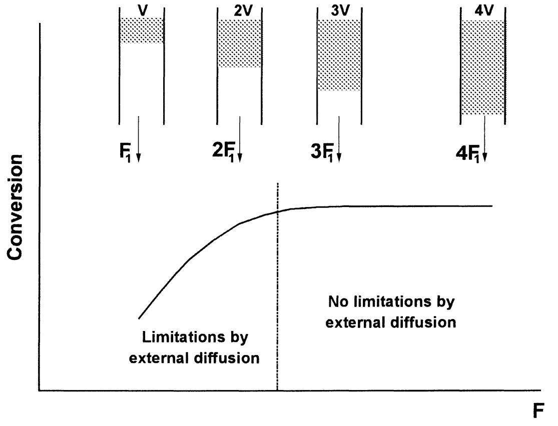

Fig. 3. Flow rate test (a): influence of flow rate on conversion at a constant space velocity [24].

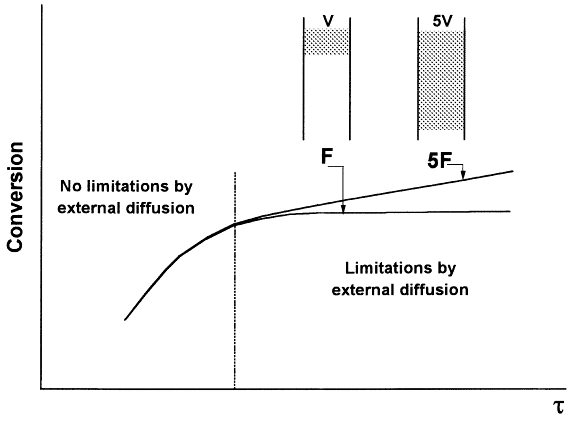

Fig. 4. Flow rate test (b): influence of flow rate on conversion at the same contact time (*t*) [24].

The presence of interphase concentration gradients can also be evidenced by experimentally determining the *apparent activation energy.* In the case of a gas–solid reaction, if the apparent activation energy is less than 20 kJ/mol, interphase diffusion limitations are suspected [24].

Absence of intraphase (internal) gradients. In terms of isothermal operation, *interphase temperature gradients* are usually more difficult to overcome than *intraphase gradients*. The fundamental reason for this is the relatively low thermal conductivity of the reaction fluid layer surrounding the catalyst particles, with respect to the relatively higher thermal conductivity of the catalyst itself.

The most effective procedure for avoiding inter- and intra-particle temperature gradients is to reduce the catalyst particle size as much as possible, unless pressure drop problems can arise.

In *intraparticle domain*, concentration gradients are usually more important than temperature gradients [9,21]. Again the particle size should be reduced as an experimental verification, and the smallest feasible particle used.

An useful diagnostic test to check for the presence of intraphase concentration gradient consists of determining the isothermal conversion for particles of different size at constant space velocity [24]. If the conversion varies by decreasing the particle size, *intraphase mass transfer is limiting*, whereas a constant conversion indicates that the system is under *chemical kinetic control* (Fig. 5).

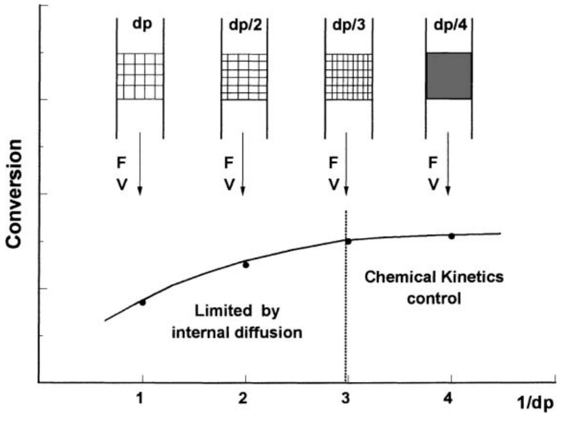

Fig. 5. Experimental test to evaluate the influence of catalyst particle diameter (d_p) on the conversion [24].

4.2. Trickle-bed reactors

A laboratory-scale trickle-bed reactor is not a good tool for quantifying catalytic reaction kinetics [21]. This is because in trickle-bed reactors fluid dynamics and reaction kinetics are so closely interlinked that their effects on conversion are practically inseparable [27].

At any rate, when an integral trickle-bed reactor is used to measure the reaction rate, in addition to what already discussed for fixed-bed, the following care must be taken.

- Complete wetting of the catalyst is mandatory. For this reason *upflow liquid arrangement* is advisable.
- *Axial dispersion* is far more significant in the liquid-phase than in gas-phase. In order to avoid back-mixing, the catalyst bed length (L) should be at least 100 times the catalyst particle size (d_p) [21,27].
- The ratio between reactor diameter (D) and d_p should be not smaller than 25, otherwise by passing (e.g. wall effects) become significant [27].

A good practice is to dilute the catalyst with smaller inert particles (e.g. the diluent used can be as small as $d_p/10$). In this case the fluidodynamics are largely dictated by the packing of the small inert particles [27].

4.3. Stirred reactors

According to Fig. 2, stirred reactors include *slurry* and *basket* reactors. Both types can be operated continuously or batchwise in the presence of two or three phases. To simple derive intrinsic kinetic information from stirred reactors, all the attributes previously discussed (*perfect mixing*, absence of *interphase* and *intraphase* concentration and temperature gradients) should be verified. The approach is very close to that already discussed for fixed-bed reactors. Some differences can arise depending on the phases involved.

A *perfectly mixed reactor* is *gradientless* at the reactor scale, i.e., a global uniformity of concentrations and temperature throughout the reaction volume is realized. Thus in a *perfectly mixed reactor* there are no *intrareactor* gradients. A simple procedure to assess the perfect mixing at the reactor scale is the so called *agitation test* [21,28]. The aim of the test is to evaluate the *minimum stirring rate* needed to avoid segregation of both fluid and solid catalyst and to obtain perfect mixing. So the conversion is measured while increasing the stirring rate and keeping constant any other variable. Perfect mixing is obtained when the conversion is independent on any further increase in stirring speed. Kinetic data obtained at this stirring conditions will be analyzed assuming a CSTR (or BSTR) model.

The *agitation test* is also useful to check for the presence of *interphase gradients*. In fact increasing the stirring rate corresponds to the increase of the flow rates in the *flow tests*, previously discussed for fixed-bed reactors (Section 4.1). So in the case of *gas–solid* and *liquid–solid* systems, an operating regime practically free form interphase limitations is the one in which the reactant conversion does not vary with further increase in the stirring speed.

As for the *intraphase gradients*, also in the case of stirred reactor the common test is to divide the catalyst into progressively *smaller particles* until further subdivision has no effect on the reactant conversion.

The case of *three-phase* systems is more complicated, in particular with slurry reactors. In fact the overall reaction involves transport phenomena acting at both gas–liquid and liquid–solid interfaces. The basic approach to eliminate transport limitations is the same as in two-phase operation, i.e., to provide effective stirring [29]. However, as stirring affects gas–liquid transport more than liquid–solid transport [30], the agitation test could be inadequate to evidence liquid–solid transport limitations. In order to evaluate which transport limitation is determining, an additional test can be performed by *varying the amount of catalyst*. At the steady state, the rate of mass transfer of the gaseous reactant A across of the phase boundaries should be equal the rate at which A is consumed in the catalyst particle [1]. Under this assumption, for a single reaction that is first order in A the following equation can be drawn: $C_i/R_A = r_b + \frac{1}{m}(r_c + r_r)$ where C_i is the concentration of A in the liquid-phase at the gas–liquid interface; R_A the observed consumption rate of A (mol cm^{-3} s^{-1}); m is the catalyst loading in the slurry (kg m^{-3}).

The different *resistances* are so defined: r_b – resistance to gas absorption through liquid film at gas–

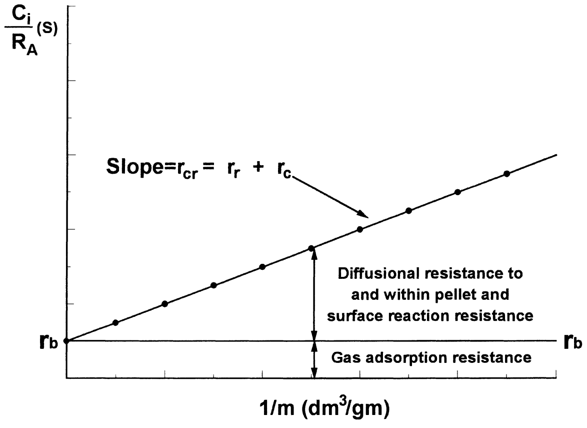

Fig. 6. Effects of catalyst amount on controlling resistance in a slurry reactors [1].

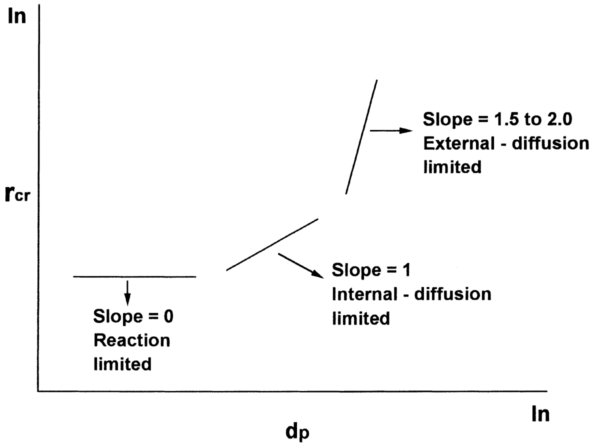

Fig. 7. Effect of particle size on controlling resistance in a slurry reactors [1].

liquid interface (s), r_c – resistance to mass transfer through liquid film at liquid–solid interface (kg m^{-3} s), and r_r – resistance to diffusion and reaction within catalyst particle (kg m^{-3} s).

Measuring the reaction rate under a fixed set of conditions with different catalyst loading will allow to obtain a plot like that reported in Fig. 6 [1]. Such a plot reveals the comparative effects of the absorption resistance r_b (*intercept*) and the combined resistance $(r_c + r_r)$ (*slope*) on the measured rate. The objective of the kinetic study of course is to operate in a regime where r_r is dominant.

If the gas adsorption r_b is a significant portion of the total resistance, it is advisable to improve gas–liquid contacting in order to lower the intercept. This can be done by reducing the gas bubbles dimension, for instance by both improving the *sparger* or increasing the *stirring rate*. Once the contribution of r_b has been satisfactorily reduced, the roles of r_c and r_r must be separated. This is done by *varying the catalyst particle size*. The interactions between mass transport and reaction kinetics are such that the influence of particle size reveals which resistance (external diffusion, internal diffusion and chemical reaction kinetics) is controlling. The experimental strategy [1] is to draw a plot like that of Fig. 6 for each of the several particle sizes. Then the $(r_c + r_r)$ values obtained are plotted as a function of particle diameter on a log–log graph (Fig. 7). The slope of the line indicates which resistance is dominant. So, in order to operate under *chemical reaction kinetic control* it is advisable to use small particles and small gas bubbles.

4.4. Recycle reactors

Recycle reactors (*external* and *internal*) can be regarded as stirred reactors having different devices to provide efficient phase contacting. In addition to what already reported for stirred reactors, only few points will be discussed in the following.

Perfect mixing in recycle reactor is achieved by increasing the recycle-to-feed flow ratio. For instance, in the case of gas-phase fixed-bed recycle reactors a ratio exceeding 25 is required to allow the assumption of the CSTR model. Higher ratios may be required if the reactor is operated at very high conversion [21]. In addition, as recycling results in higher mass velocities through the catalyst bed, *interphase gradients* are easily eliminated.

4.5. Kinetics affected by catalyst deactivation

Attention so far has been restricted to experimental methods for measuring of intrinsic kinetic rates in the absence of catalyst deactivation. Unfortunately, most heterogeneous catalytic reactions are affected by deactivation, that can be due to [31]: irreversible chemisorption of impurities of the feed stream (poisoning); irreversible modification of the catalytic surface under reaction conditions (textural modification);

deposition of carbonaceous residues from reactants, products or intermediates (coking).

In many cases, the deactivation is so rapid that an independent determination of intrinsic kinetic constants is not feasible. An alternative approach is to determine the kinetic parameters simultaneously for both reaction and deactivation in a single experimental program. In this section we will briefly discuss few guidelines on the subject. A more detailed description of the kinetic data collection and analysis in the presence of catalyst deactivation is given in [23].

- Batch operations are unuseful for kinetic study in the presence of deactivation. The coincidence of time for reaction and for deactivation does not allow decoupling and unambiguous determination of the parameters for the two processes.
- To put in evidence and to determine the kinetic parameters of reaction and deactivation, it is necessary to operate in a continuous mode.
- The simplicity of analyzing CSTR data in comparison to PFR data is especially evident in the presence of deactivation [21]. For such reasons CSTR is preferred for quantifying simultaneously reaction and deactivation kinetics.
- Catalyst deactivation kinetics may also be studied in a PFR, but mathematical resolution of the process involved is more complicated. Differently from CSTR, differential rather than algebraic equations are to be treated. Moreover, the deactivation process in a PFR is related not only to time on stream (t.o.s) but also to the position within the reactor. The latter effect is due to a change in the catalyst environment as the reactants decrease and because products are formed as the feedstream flows through the reactor. Thus the PFR presents severe difficulties in terms of uncoupling and modeling kinetic and deactivation phenomena [21].

5. Kinetic modeling of the catalyst pellet

Once the *intrinsic kinetics* has been determined on catalyst particle of proper size (i.e., as smaller as possible), just the first step has been brought to completion. The following step will be the modeling of the performances of the *full-size catalyst* (*catalyst pellet*), i.e., the catalyst used in the industrial reactor. This step will be obviously avoided when the catalyst pellet performance is not affected by intrapellet limitations as assessed by the test described in Section 4.1.

As discussed in the previous section, the performance of the catalyst pellet may be affected by *intraphase* (*intraparticle*) *transport limitations* (i.e., *internal mass and heat transfer limitations*) causing a variation of the *overall reaction rate*. This means that a new kinetic study must be performed in order to determine the reaction rate on the pellet (*global reaction rate*). *Intrinsic reaction rate* (r_i) and *overall reaction rate* (r_o) are related by the following equation:

$$r_\mathrm{o} = \eta r_i,$$

where η is the *effectiveness factor* [1,14,31]. Such a parameter indicates the importance of internal physical phenomena (mass and heat transfer) with respect to the chemical phenomena. Its value could be smaller, equal or larger than 1 depending on several factors [31]. The effectiveness factor is related, in fact, to the Thiele modulus (ϕ) [1,31] which, in turn, is connected with geometrical and physical factors such as pellet radius and effective diffusivity. Furthermore reaction characteristics can influence the effectiveness factor value. Depending if *eo* or *endothermic* reaction is involved, there will be an increment, or a reduction, respectively, of temperature moving from external surface toward the center of the pellet. For an exothermic reaction the temperature rises going into the pellet, then the reaction rate will be improved with respect to the intrinsic reaction rate. The opposite behavior will be obtained in case of endothermic reaction.

To model the performance of the catalyst pellet it is necessary to know: *pellet geometry, intrinsic kinetics, effective thermal conductivity (λ) and effective diffusivity* (D_eff). Therefore, in the following we will describe how to determine experimentally the overall rate and the catalyst pellet parameters (λ and D_eff).

5.1. Overall reaction rate

In order to measure the *overall reaction rate*, the kinetic experiments on the catalytic pellets have to be performed according to the rules and suggestions discussed in Section 4.

Again it will be advisable to operate in a laboratory reactor with an *ideal flow pattern* or *perfectly mixed*, under *isothermal* conditions and in the *absence of interphase gradients*.

Accordingly, the preferred options are basket (spinning or stationary) and recycle reactors [14]. Proper experimental conditions will be selected assessing a perfect mixing and the absence of external transport limitations, by performing the *agitation test* previously discussed (Section 4.3). The use of fixed-bed reactor for kinetic experiments with catalyst pellets is to be considered with care. In fact, in order to ensure a plug flow character with large particle diameter (d_p), large reactor sizes are necessary (see Sections 4.1 and 4.2). Therefore, the heat transfer becomes very difficult. Hence, unless quite low reaction heats are involved, the isothermality is almost impossible. At any rate, the suggestion of diluting the catalyst pellets with smaller particles of inert material (Section 4.2) is to be considered.

5.2. Catalyst pellet parameters

Effective thermal conductivity λ can be measured experimentally on a single pellet by transient experiments under non-reacting conditions [32].

The *effective diffusivity* can be evaluated experimentally or through mathematical models supported by porosimetric measurements [29]. This models should be used with care, especially when extrapolation of experimental data or prediction of the diffusion coefficient are required [32].

Experimental measurements under non-reacting conditions can be made at the steady or unsteady state [23]. However, the measure of the effective diffusion coefficient developed under reaction conditions is advisable since it leads to a more direct evaluation of this parameter. These measurements can be performed in the so called single pellet reactor [7]. The procedure consists in measuring the intraphase temperature gradients in a single catalyst pellet, that is contained in a reactor continuously fed with the reactants [32]. Under steady state conditions, the temperature difference between the surface and the center of the pellet (ΔT) is related to the concentration difference (ΔC) by the Prater equation [29]:$\Delta T = ((-\Delta H_r)D_{\rm eff}/\lambda)\Delta C$ where $\Delta H_{\rm r}$ is the reaction heat. $D_{\rm eff}$ is evaluated by measuring ΔT at different reactant concentrations [32].

6. Conclusion

The experimental evaluation of the kinetics of heterogeneous catalytic reactions is a complex procedure, involving the determination of the *intrinsic kinetics* and the *overall kinetics* of the catalyst pellet. Several important requirements must be fulfilled in order to obtain reliable and meaningful experimental data, that can be summarized as follows:

- Isothermal operation is very important for generating quantitative kinetic data in a laboratory reactor.
- Ideal flow patterns (perfectly mixed of plug flow) are essential for straightforward interpretation of kinetic data.
- Inter and intraphase transport limitations must be avoided to measure intrinsic kinetic rates.
- Interphase transport limitations must be avoided to measure the effectiveness factor of the catalyst pellet.

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