

Reaction kinetics and scale-up of catalytic processes

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Abstract

Kinetic studies typically deal with initial rates whereas most of the catalyst volume in industrial reactors work close to equilibrium. The challenge for scale-up of catalytic processes is illustrated with examples from steam reforming and a few ppm reactions. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

1.1. Is reaction kinetics required for scale-up of catalytic processes?

Simulation is a strong tool for scale-up of catalytic processes saving expensive pilot work. The advanced computer models are, however, no better than the predictive power of the reaction kinetics. More emphasis should be made on reaction kinetics close to equilibrium. Better reaction kinetics is also required to describe the complexity of ppm-reactions. Still, the scale-up requires integral tests to verify the rate equation at full conversion and to identify secondary phenomena. It is important to apply microkinetic analysis based on fundamental studies of surface reactions and structures to provide a basis for more reliable rate equations.

1.2. Any need for kinetics?

The development of the radial flow converter for ammonia synthesis in the mid-sixties is a clear example of the importance of reaction kinetics [1,2]. Well-defined laboratory measurements and the analysis of industrial data formed the basis for adjusting the kinetic parameters in a modified Temkin rate equation [3]. The industrial data were analyzed [4] by means of a one-dimensional heterogeneous reactor model [5]. As it was not possible to test the complex reactor system at small scale, the jump to full industrial scale was made relying on the kinetics and the computer model.

With the later correlation between surface science data for the individual elementary steps and industrial rates [6], it might be claimed that the scale-up could have been done, in principle, on basis of the kinetic data for the elementary steps obtained in high vacuum studies. However, the detailed mechanism of the ammonia synthesis is still being discussed [7] and as expressed by Boudart [8]: “Many of the general concepts in heterogeneous catalysis have originated and are still tested in the study of ammonia synthesis . . . the trustworthy bellwether of heterogeneous catalysis”.

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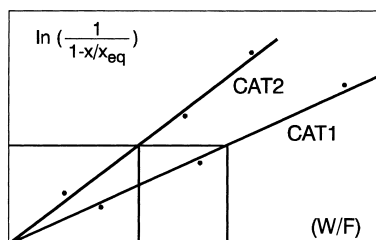


Fig. 1. Activity plot: $r = k(1 - x/x_{eq})$.

On the other hand, it is noteworthy that the scale-up of fluid bed catalytic cracking [9] being one of the largest, but also most complex catalytic processes, was done within two years with little knowledge of the reaction kinetics.

In general, reaction data can be generated empirically from pilot tests. Even complex catalytic systems may follow a pseudo first order relationship [10] when only space velocity is varied at otherwise constant conditions. If so, linear plots of conversion versus reciprocal space velocity (W/F) can be established (Fig. 1). Also comparison of the activity of different catalysts can be made by comparing space velocities giving the same conversion:

$$\frac{(W/F)_2}{(W/F)_1} = \frac{k_1 \int f(x) dx}{k_2 \int f(x) dx} = \frac{k_1}{k_2} \quad (1)$$

In this way, the kinetic expression has no impact and need not to be known.

A process engineer may just require that the catalyst fulfills a certain space time yield (0.1–1.0 kg product/kg cat/h) [11] depending on catalyst life and costs. Otherwise, the catalyst is just a material resulting in a pressure drop. Add to this that it is rather the exception than the rule that catalyst activity turns out to be the decisive factor for sizing the industrial reactor [1,12]. The catalyst volume is often determined by heat transfer restrictions or aging, poisoning, carbon formation, etc. and the reactor concept may be chosen by considering the catalyst life and the method of regeneration [1,13]. Hence, it may be relevant to question the importance of reaction kinetics for the scale-up of catalytic processes.

There are, however, at least two reasons that kinetics are required for scale-up:

1. The increased use of simulation.
2. The ppm reactions.

2. Rate equations — different approaches

With the strong computer methods available, simulation is a strong tool in scaling up saving expensive pilot plant work. It is possible to simulate the complex interaction of heat transfer and catalytic reaction by homogeneous or heterogeneous two dimensional models [14]. One example is steam reforming [15,16]. It will also be possible to link these calculations with fluid dynamic simulation (CFD) [17] and to do transient analysis [18] of the reactor behavior. Transients are not the least important in the use of catalysts in automotive systems. Kinetic simulation may also be applied to analyze local situations — for instance potential for carbon formation [15], catalyst over temperature, selectivity and pore diffusion, etc.

The simulation methods require good kinetic models.

The Langmuir Hinshelwood approach [10,14] in establishing rate equations has proven to be useful and flexible.

$$r = \frac{\text{Kinetic factor} \times \text{driving force}}{\text{Adsorption group}} \quad (2)$$

The rate equation showing the best fit or the minimum residual of squares is chosen without being a proof of the postulated reaction sequence behind it.

Many reactions can be represented by simplified reaction sequences when it is possible to assume or identify the most abundant reactive intermediate (mari) and either a rate determining step (rds) or two irreversible steps [19]. On this basis, simplified rate expression can be derived. Boudart [20] used the term “the paradox of heterogeneous catalysis”. The paradox was explained by assuming that the majority of the reaction takes place on the most active sites or that the catalyst is covered by the most active sites [8].

Many rate data can be easily fitted to simple power law expressions [21,22]:

$$r = k p_A^\alpha p_B^\beta p_C^\gamma \quad (3)$$

which reflects the Freundlich isotherm. This expression has less constants and may require fewer experiments, but they are less friendly in computer modeling — for instance, if some of the components are not present in the feed.

Simplified rate equations as Eqs. (2) and (3) are often valid in only a narrow range of process parameters.

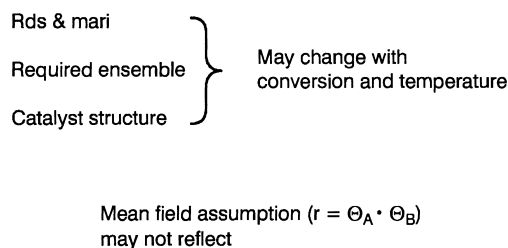


Fig. 2. Break-down of simple Langmuir Hinshelwood approach [23].

The assumptions behind the simplified Langmuir Hinshelwood approach breaks down in a number of situations [23] as summarized in Fig. 2. The rds and mari may change throughout the reactor as temperature and gas composition changes. If they change with conversion, the rds and mari will also change inside the catalyst pellet if the effectiveness factor is low. In general, one may speculate about the meaning of the * in the kinetic sequence. The size of the ensemble required by the reaction may also change with conversion and temperature and the catalyst may be subject to surface reconstruction or even structural changes of the bulk phase as the gas composition and temperature changes.

As expressed by Boudart [24], “a catalyst is a resistant self-assembly in space and time . . . to treat an active site or a catalyst as a *dead* object in time with a *fixed* structure in space is a wrong model of the catalytic cycle”.

Our present knowledge of surface layers and reactions not the least from recent observations by scanning tunneling microscopy [25] indicates that reactions most likely take place at edges of surface islands of chemisorbed species, at corners, steps, etc. Hence, there are good reasons to question the mean field assumption behind the Langmuir Hinshelwood approach [23].

The problem related to changing rds and mari can be solved by using steady-state kinetics. The present computer methods make it possible to solve complex set of equations. One solution is to apply the Temkin identity [19].

Microkinetic analysis [26] gives a meaningful input to the many constants of the expanded reaction sequence. Still, microkinetic methods should be refined to include the information that the active site (ensemble) may change with conversion and temperature.

Table 1
 Different approaches for intrinsic kinetics for steam reforming of hydrocarbons

Bodrov et al. [27]	Langmuir Hinshelwood
Khomenko et al. [28]	Temkin identity
Rostrup-Nielsen [29,30]	Two-step kinetics power law
Tøttrup [31]	Pellet kinetics
Xu and Froment [32]	Langmuir Hinshelwood
Aparicio [33]	Microkinetic analysis

Table 1 illustrates how different approaches have been applied for establishing intrinsic kinetics for steam reforming of hydrocarbons.

Most kinetic studies deal with initial rates far from equilibrium which may reflect the situation in only a small part of the industrial reactor. Most of the catalyst volume will work close to equilibrium. This is illustrated in Fig. 3 for a tubular reformer.

The rate of reversible reactions is usually expressed by

$$r = r_1(1 - \beta)^{1/\gamma} \quad (4)$$

Although this expression satisfies the thermodynamic requirements, it is in principle not clear that an expression such as Eq. (4) should adequately account for the observed rates close to equilibrium [34]. However, as shown by Boudart [34] that close to equilibrium “the rate of reaction is first order with respect to

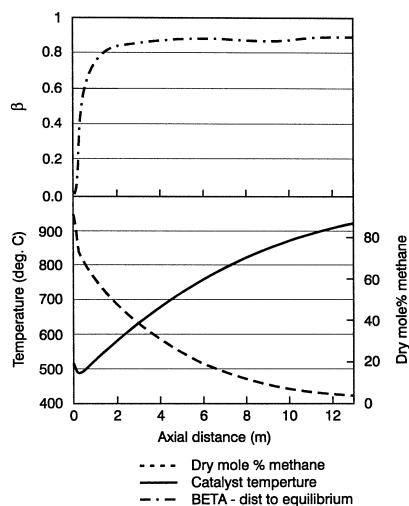


Fig. 3. β -factor: tubular reformer ($\text{H}_2\text{O}/\text{CH}_4 = 2.5$, $P = 30$ bar).

any parameter that expresses the distance away from equilibrium”.

As illustrated for tubular reforming in Fig. 3, the β -value is almost constant (0.88) from 1 m from the inlet. The methane content decreases with increasing temperature. The driving force is the change of methane concentration at equilibrium with temperature. It can be shown [29] that $d(C_{\text{CH}_4})/dZ$ is close to $d(\text{CH}_4(\text{eq}))/dZ$. Hence

$$\begin{aligned} r &= k(C_{\text{CH}_4} - C_{\text{CH}_4}(\text{eq})) = F \frac{d(C_{\text{CH}_4}(\text{eq}))}{dZ} \\ &= F \frac{d(C_{\text{CH}_4}(\text{eq}))}{dT} \frac{dT}{dZ} \end{aligned} \quad (5)$$

meaning that the rate becomes proportional with the slope (dT/dZ) of the imposed temperature profile [29].

In an adiabatic reactor, dT/dZ approaches zero as the reaction approaches equilibrium. This is reflected by a falling β -value throughout the reactor as illustrated in Fig. 4. The β -value comes close to 1 meaning very low reaction rate in a large fraction of the reactor.

3. The ppm reactions

The problems discussed above are aggravated for the so-called “ppm reactions” aiming at complete conversion to the ppm level [30,35]. It involves large conversion in single reactors as illustrated in Table 2. This may change some of the usual assumptions, when establishing rate equations. Apart from the assumptions listed in Fig. 2, it includes the steady-state assumption and the assumption of quasi-equilibrated steps [35].

The interaction between diffusion restrictions and intrinsic kinetics may become complex as the concentration of reactants approaches zero. It was demonstrated [30] for selective reduction of NO with NH_3 (SCR-reaction) with both reactants approaching ppm

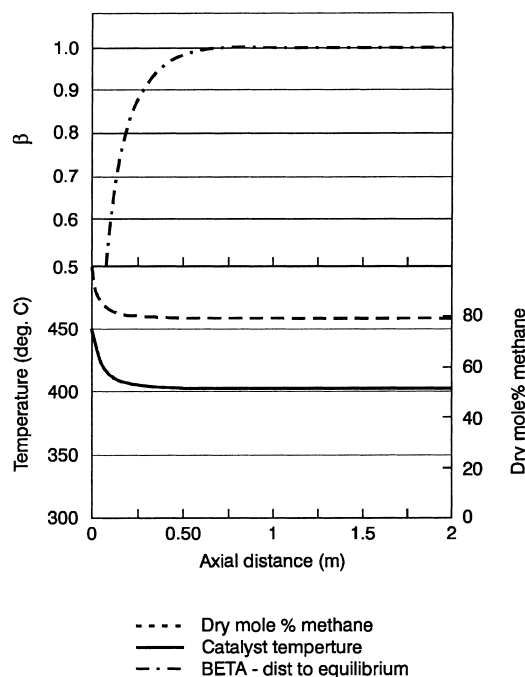


Fig. 4. β -factor: adiabatic reformer ($\text{H}_2\text{O}/\text{CH}_4 = 2.5$, $P = 30$ bar).

levels that incorrect kinetics can lead to estimated rates at high conversion being more than one order of magnitude wrong. Hence, it is important that the kinetics is based on a solid micro-kinetic analysis to cover a wide range of conversion [36].

In practice, poor mixing and possible by-pass effects [37] may have a more important impact on reactor performance. It is essential to have even flow distribution at the ammonia injection and good mixing before any maldistribution is frozen in the monolith catalyst. A similar situation exists for the deep desulphurisation of diesel. Even a small maldistribution of flow may result in poor reactor performance [37].

Table 2
Examples of ppm-reactions

Reaction	Concentration			Conversion (X%)
	Component	Inlet (%)	Outlet (ppm)	
DeNO _x (SCR), power plant	NO _x	0.04	40	90
HDS/diesel	S	0.3	30	99.0
Methanation	CO	0.3	1–2	99.95
NH ₃ -plants	CO ₂	0.2	3–4	99.8

Table 3
Guidelines for reliable catalyst testing [39]

Select appropriate laboratory reactor
Establish ideal flow pattern
Ensure isothermal operation
Diagnose and minimize transport disguises
Access catalyst stability early

Hydrotreating of oil is an example of complex reaction schemes [23] involving non-linear kinetics. The reaction path may depend on the structure of the individual sulfur components. The differences become more pronounced at high conversion [38]. The individual reactions may also be interlinked, meaning that lumping of kinetics for individual components can be misleading.

4. The scale-up problem

Reaction kinetics is important for the scale-up of catalytic processes not the least for making reliable computer simulations. This requires careful experimental work at well-controlled conditions as listed in Table 3 [39].

Reliable laboratory data require that heat and mass transfer effects are under full control. The most important criteria are ideal plug flow and isothermal operation.

However, gradientless tests are not sufficient. There is a need for integral tests [1] to verify the rate expression at full conversion to check the impact of the phenomena listed in Table 4. The conditions must be selected carefully (Table 5). It is important that the integral test can be carried out at industrial pellet size and pressure to avoid severe errors due to the complex relation between the pore volume distribution of the catalyst and the effective diffusion coefficient. It is also

Table 4
Phenomena to be checked in integral tests

Product inhibition at high conversion
Validity of rate equation (Fig. 2)
Mass and heat transfer restrictions
Gas film related deactivation phenomena
Other secondary phenomena
Feedstock characteristics and reactor performance

Table 5
Requirements of integral tests [1]

Full conversion
Industrial pellet size
Industrial pressure
Real — feedstock
Industrial mass velocity
Pseudo-adiabatic conditions

important that scale-up is carried out with real feedstock to check non-linear effects and to identify possible impact of impurities. The integral test should be carried out at a scale to identify important secondary deactivation phenomena which may be related to film diffusion effects [1]. The scale-up can lead to surprises for new processes because it may not be possible to observe the deactivation problem before approaching industrial mass velocities. Also, it may be important to ensure pseudo-adiabatic conditions (or realistic heat transfer rates). The challenge is to identify the smallest scale required to fulfill these requirements [1].

This empirical approach to develop and check rate data is not sufficient [1]. It is important to take advantage of the input from fundamental surface studies and, in particular of knowledge gained by in-situ studies of the catalyst [23,40] at process conditions and by characterization of spent catalyst samples [23]. This provides a basis for microkinetic analysis and a more realistic reaction sequence. It means that development of reaction kinetics becomes a learning process and not just a statistic exercise. It is important to put more effort in studying the catalytic reaction rather than characterizing the solid material used as catalyst.

The coupling between empirical reaction kinetics and reaction mechanism remains a scientific challenge. It may be, it is not essential for the scale-up of the process, but it provides deeper insight into catalysis.

Boudart likes to quote Cyrano de Bergerac talking about his literary efforts during his last moments. “*C’est bien plus beau lorsque c’est inutile*”. It is more beautiful because it is not useful.

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