Analysis of heat and mass transfer in transient experiments over heterogeneous catalysts
Dekker, F.H.M.; Bliek, A.; Kapteijn, F.; Moulijn, J.A.

Published in:
Chemical Engineering Science

DOI:
10.1016/0009-2509(95)00210-V

Citation for published version (APA):
ANALYSIS OF MASS AND HEAT TRANSFER IN TRANSIENT EXPERIMENTS OVER HETEROGENEOUS CATALYSTS

F. H. M. DEKKER and A. BLIEK
Department of Chemical Engineering, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

and

F. KAPTEIJN† and J. A. MOULIJN
Department of Chemical Engineering, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

(First received 5 January 1995; revised manuscript received and accepted 20 June 1995)

Abstract—This article discusses the effects of extra- and intraparticle mass and heat transfer in transient experiments over heterogeneous catalysts. To this purpose, the time-dependent transport in a catalyst particle when introducing a reactant in an inert gas phase has been analyzed. The analysis has led to one criterion assuring the absence of both extra- and intraparticle mass transfer limitations during steady-state experiments. Furthermore, criteria for the absence of mass and heat transport limitations during transient experiments have been developed by extending the criteria for the absence of mass and heat transport limitations during steady-state experiments. As will be shown, transient kinetics are not affected by heat transfer as long as the steady-state criteria for the absence of mass and heat transport limitations are fulfilled.

INTRODUCTION

In heterogeneous catalysis much effort is put into the determination of the reaction kinetics. The primary goal of the kinetic research is either to be able to optimize the design of a reactor or to gain more insight on the fundamentals of a reaction. Since heterogeneous catalysis involves, by definition, at least two phases, exchange of heat and mass between the phases is required for the reaction to take place. Due to these transport phenomena, the observed rate at which the reaction takes place is not necessarily the same as its intrinsic rate, i.e. the unique rate for a given catalyst at given conditions. Thus, when investigating the reaction kinetics in a laboratory-scale catalytic reactor, one has to account for the factors that may generate a resistance to the reaction and that disguise the intrinsic kinetics.

Various criteria have been developed to assure the absence of mass and heat transfer limitations in steady-state kinetic research (Carberry, 1987; Fro-ment and Bischoff, 1990; Lee, 1985; Moulijn et al., 1991). They evolve when assuming that only a certain maximum deviation of the observed rate from the intrinsic rate is allowed. Usually, the deviation is permitted to be 5% at maximum. These criteria can be used for the specification of reaction conditions leading to intrinsic kinetic data and are summarized in Table 1. The criteria are easily applicable, since they consist of both observable and procurable parameters.

The criteria are unfortunately not directly applicable to transient experiments. In a transient experiment in which, for example, a reactant is introduced into an inert gas phase, the reaction is always mass transport limited at the moment that the transient is imposed. The capacity of the particle and the rate of the transport processes determine to what extent this influences the response curves. Although transient techniques are increasingly being used in heterogeneous catalysis (Bennett, 1976; Biloen, 1983; Gleaves et al., 1988; Kobayashi and Kobayashi, 1974; Kobayashi, 1982; Mirodatos, 1991; Tamaru, 1991), no evaluation of mass and heat transport during a transient experiment has been reported to date. The present study was started in order to reveal this information and therefore discusses the transient behavior of extra- and intraparticle mass and heat transport. Since steady-state transport criteria are easily examined and transient kinetic research often follows steady-state kinetic research, the transient criteria are developed by extending the steady-state criteria. The programs PDECOL (Madsen and Sinovac, 1979) and DSS2 (Schiesser, 1991) have been used to solve the partial differential equations.

MASS TRANSFER COMBINED WITH REACTION

Extraparticle mass transfer combined with reaction

The transfer of mass from the bulk of the gas phase to the external surface of the catalyst is most conve-
Table 1. Criteria for negligible transport effects in steady-state kinetic research

<table>
<thead>
<tr>
<th>Transport process</th>
<th>Criterion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extraparticle mass transport</td>
<td>( Ca = \frac{r_{\text{obs}}}{k_aa'c_b} &lt; 0.05 )</td>
</tr>
<tr>
<td>Intraparticle mass transport ( (\text{Wheeler-Weisz criterion}) )</td>
<td>( \eta_{\text{ns}}\phi_{\text{obs}}^2 = \frac{r_{\text{obs}}L^2 n + 1}{D_c c_i} &lt; 0.1 )</td>
</tr>
<tr>
<td>Extraparticle heat transport</td>
<td>(</td>
</tr>
<tr>
<td>Intraparticle heat transport</td>
<td>(</td>
</tr>
</tbody>
</table>

The unsteady-state mass balance, eq. (5), describes the change of the concentration at the external surface of the catalyst as a function of time. The Damköhler number, \( Da \), is the parameter in eq. (5) that controls the solution, but it is not an observable. \( Da \) can be calculated, however, via the Carberry number, \( Ca \), and the external effectiveness factor, \( \eta_{\text{ns}} \): 

\[
Da = \frac{Ca}{\eta_{\text{ns}}} = \frac{r_{\text{obs}}}{r_{\text{intr}}\eta_{\text{ns}} N_{s,\text{max}} r_{\text{obs}}}.
\]  

The Carberry number gives the ratio between the observed reaction rate and maximum external mass transfer. Since the observed reaction rate equals the mass transfer rate through the gas film, the Carberry number also symbolizes the dimensionless concentration difference over the gas film: 

\[
Ca = \frac{r_{\text{obs}}}{k_ya'c_b} = \frac{c_b - c_i}{c_b}.
\]  

The external effectiveness factor, \( \eta_{\text{ns}} \), represents the ratio between the observed reaction rate and the reaction rate without external mass transport limitations, i.e. the intrinsic rate. For an isothermal reaction with order \( n \) one obtains

\[
\eta_{\text{ns}} = \frac{k_ya'c_b^n}{k_sc_b^n} = \frac{c_b^n}{(1-Ca)^n}.
\]  

Hence, the expression for \( Da \) in terms of the observable \( Ca \) becomes

\[
Da = \frac{Ca}{(1-Ca)^n}.
\]  

The following initial condition applies for a step-response experiment in which a reactant is introduced in an inert feed at \( t = 0 \):

\[
\begin{aligned}
\xi &= \begin{cases} 
\xi_0 & \text{for } \tau_{\text{ext}} < 0 \\
1 & \text{for } \tau_{\text{ext}} \geq 0
\end{cases}
\end{aligned}
\]  

Figure 1 gives the dimensionless concentration at the surface of the catalyst particle, \( \xi_{\text{ext}} \), as a function of the dimensionless time, \( \tau_{\text{ext}} \), for three values of \( Ca \) after imposing this step change. The results are found to be independent of the reaction order. The figure shows...
that a smaller $Ca$ gives a larger $\xi_s$ at a certain $t_{es}$. This is caused by the decreasing reaction rate compared to mass transfer rate at decreasing $Ca$.

The criterion used for negligible extraparticle mass transport limitations under steady-state conditions (Table 1) states that the Carberry number (or the dimensionless concentration difference over the gas film) must be smaller than 0.05 which is equivalent to $\xi_s$ larger than 0.95. This criterion is represented by the horizontal line in Fig. 1 and must also be fulfilled when the steady-state is reached after a transient has been imposed. Figure 2 gives the time $t_{es}$ needed to reach a certain $\xi_s$ as a function of $Ca$. Again the solution was independent of the reaction order. The time needed to reach a certain $\xi_s$ increases with increasing $Ca$. Furthermore, the higher the chosen critical value for $\xi_s$ the longer it takes to reach it. When $Ca$ is 0.05, the $\xi_s = 0.95$ is approached asymptotically (Fig. 1), resulting in a sharp increase in the value of $t_{es}$ at $Ca = 0.05$ and $\xi_s = 0.95$ (Fig. 2).

As a criterion for the absence of an external concentration difference in a transient experiment over a nonporous catalyst, we state that the deviation from the steady-state criterion must not be more than 5%.

The value for $\xi_s$ at the steady-state criterion, i.e. $\xi_s^{st}$, is 0.95. This gives for the value of $\xi_s$ at the transient criterion, $\xi_s^{tr}$.

$$\xi_s^{tr} \geq 0.95 \xi_s^{st} \approx 0.9.$$  \hspace{1cm} (14)

The dimensionless time $t_{es}$ needed to fulfil this criterion, $t_{es}^{tr}$ depends on the value for $Ca$ (Fig. 2), but the most critical value ($Ca = 0.05$) gives

$$t_{es}^{tr} \geq 2.9.$$  \hspace{1cm} (15)

Only after this time the reaction rate data are not disguised by mass transfer. Before this time the effects of mass transfer cannot be neglected.

**Extra- and intraparticle mass transfer combined with reaction**

In case of porous catalysts, we need to account for intraparticle diffusion. Now, following the transport through the gas film surrounding the catalyst particle, the reactant has to be transported through the pores inside the particle to reach the active sites. The rate of the transport can be described by Ficks law:

$$N_i = - D_e \frac{\partial c_i}{\partial r}.$$  \hspace{1cm} (16)

The diffusion does not occur in a homogeneous medium but through the pores of the pellet only. Therefore, the above equation holds for the effective diffusion coefficient, $D_e$. $D_e$ includes corrections for the particle porosity, $\varepsilon_p$, and for the orientation of the pores with respect to the diffusional direction.

The reaction at the pore wall occurs simultaneously with diffusion through the pores; thus, the diffusion process is not a strictly consecutive one and must be considered together with reaction. For a spherical particle the unsteady-state mass balance can be formulated as

$$\frac{\partial c_i}{\partial t} = D_e \frac{\partial}{\partial r} r^2 \frac{\partial c_i}{\partial r} + r_0.$$  \hspace{1cm} (17)

The reaction rate, $r_0$, is now given by

$$r_0 = - k_i c_i^s.$$  \hspace{1cm} (18)

Only the isothermal transport is considered, thus $k_i = k_s = k_p$. The following boundary conditions apply:

$$\frac{\partial c_i}{\partial r} = 0 \text{ for } r = 0$$  \hspace{1cm} (19)

$$k_p (c - c_i) = D_e \frac{\partial c_i}{\partial r} \text{ for } r = R.$$  \hspace{1cm} (20)

The mass balance in dimensionless form becomes

$$\frac{\partial \xi_i}{\partial \tau_{in}} = \frac{1}{z^2} \frac{\partial}{\partial z} \left( z^2 \frac{\partial \xi_i}{\partial z} \right) + 9 \phi_b^2 \frac{2}{n + 1} \xi_i^n.$$  \hspace{1cm} (21)

where $\xi$ is again defined as in eq. (6) and

$$\tau_{in} = \frac{D_e}{\varepsilon_p R^2 R} t.$$  \hspace{1cm} (22)

$$z = \frac{r}{R}.$$  \hspace{1cm} (23)
The squared overall Thiele modulus based on the concentration in the bulk, \( \phi_\beta^2 \), gives the ratio between the rate of reaction and rate of diffusion in a catalyst particle:

\[
\phi_\beta^2 = L^2 \frac{k_b n + 1}{D_e} \frac{c_s^{-1}}{2}
\]  

(24)

where \( L \) represents the characteristic catalyst dimension

\[
L = \frac{V_p}{S_p} = \frac{1}{a}. 
\]  

(25)

The squared overall Thiele modulus is related to the squared Thiele modulus for internal mass transport, \( \phi_{in}^2 \):

\[
\phi_\beta^2 = \frac{1}{\xi_s^{-1}} L^2 \frac{k_b n + 1}{D_e} \frac{c_s^{-1}}{2} = \frac{1}{\xi_s^{-1}} \phi_{in}^2. 
\]  

(26)

The boundary conditions in dimensionless form are

\[
\frac{\partial \xi}{\partial z} = 0 \quad \text{for} \quad z = 0 
\]  

(27)

\[
\xi - \xi_s = \frac{1}{Bim} \frac{\partial \xi_s}{\partial z} \quad \text{for} \quad z = 1. 
\]  

(28)

The Biot number for mass transport, \( Bim \), gives the ratio between the extra- and intraparticle mass transfer rates and represents the ratio of the internal and external concentration gradient at the external surface and is defined as

\[
Bim = \frac{k_b R}{D_e}. 
\]  

(29)

A parameter in the dimensionless unsteady-state mass balance is the squared overall Thiele modulus, \( \phi_\beta^2 \), which is, just as the Damköhler number for extraparticle mass transport, not an observable. However, when multiplied by the overall effectiveness factor, \( \eta_o \), it is:

\[
\eta_o \phi_\beta = \frac{r_{obs} L^2 n + 1}{D_e c_s^2}. 
\]  

(30)

Here the overall effectiveness factor is the product of the internal and extraparticle effectiveness factors:

\[
\eta_o = \eta_{in} \eta_{ex} = \frac{r_{obs} k_s c_s^2}{k_b c_s^2} = \frac{r_{obs}}{k_b c_s^2} = \eta_{in} \xi_s. 
\]  

(31)

and gives via eq. (26),

\[
\eta_o \phi_\beta = \eta_{in} \phi_{in} ^2 \xi_s. 
\]  

(32)

The observed reaction rate is equal to the flux through the external surface of the particle, which leads [via eq. (28)] to

\[
\eta_o \phi_\beta = \left(1 - \xi_s\right) \frac{Bim n + 1}{3} \frac{1}{2}. 
\]  

(33)

This gives for \( \xi_s \):

\[
\xi_s = \left[ \frac{\eta_{in} \phi_{in} ^2}{Bim n + 1} + 1 \right]^{-1}. 
\]  

(34)

Then via eq. (26) the following expression for \( \phi_\beta^2 \) is found:

\[
\phi_\beta^2 = \frac{\phi_{in}^2}{n + 1} \left[ \frac{\eta_{in} \phi_{in}}{Bim} + 1 \right]^{-1}. 
\]  

(35)

An analytical expression for \( \eta_{in} \phi_{in}^2 \) can be derived for a first-order irreversible reaction in a spherical particle:

\[
\eta_{in} \phi_{in}^2 = \phi_{in} \left( \frac{1}{\tanh 3 \phi_{in}} - \frac{1}{3 \phi_{in}} \right). 
\]  

(36)

Figure 3(a) gives the relation between the observable \( \eta_o \phi_\beta \) and \( \eta_o \) for several values of \( Bim \) under steady-state conditions. The curves in the figure hold for a first-order reaction (using the analytical expression for \( \eta_{in} \phi_{in}^2 \)) but they can hardly be distinguished from those for a second-order and third-order reaction (numerically calculated). The curve obtained when using \( Bim = 100 \) equals that obtained when excluding the extraparticle mass transfer and considering only the intraparticle mass transfer. In this case the concentration at the particle surface is identical to that in the bulk (the value for \( \xi_s \) is 1). Figure 3(a) shows that a higher \( \eta_o \) is reached for smaller values of \( \eta_{in} \phi_{in}^2 \) (at constant \( Bim \)). This is caused by a decrease of the relative importance of reaction compared to diffusion at decreasing \( \eta_o \phi_\beta \). Furthermore, the figure shows that when \( Bim \) decreases also \( \eta_o \phi_\beta \) decreases (constant \( \eta_{in} \phi_{in}^2 \)). This is caused by a decrease of the relative importance of the internal concentration gradient compared to the external concentration gradient at the external particle surface at decreasing \( Bim \). In other words, the ability of the external mass transfer to keep up with the reaction and diffusion decreases when \( Bim \) decreases.

The criterion used for the absence of concentration gradients under steady-state conditions states that \( \eta_o \) must be larger than 0.95. Therefore, \( \eta_o \phi_\beta \) for which \( \eta_o = 0.95 \) is given in Fig. 3(b) as a function of \( Bim \). In fact, this figure connects the intersection points of the

Fig. 3(a). Relation between \( \eta_{in} \phi_{in}^2 \) and \( \eta_o \) at steady state for several values of \( Bim \) (n = 1). The horizontal dashed line represents the steady-state criterion, i.e. \( \eta_o = 0.95 \).
Analysis of mass and heat transfer in transient experiments

Fig. 3(b). Relation between $B_i_n$ and $\eta_0 \phi_0^2$ where $\eta_0 = 0.95$

horizontal line ($\eta_0 = 0.95$) with the curves at several $B_i_n$ out of Fig. 3(a). Figure 3(b) can be used to determine the maximum tolerated value for $\eta_0 \phi_0^2$ at a certain $B_i_n$ to assure the absence of concentration gradients under steady-state conditions. The figure shows that $\eta_0 \phi_0^2$ at which $\eta_0 = 0.95$ hardly changes anymore when $B_i_n$ is larger than 20. Here, the concentration at the particle surface is only 1% less than in the bulk and the external gradient can be disregarded. In this region it is sufficient to check the Wheeler–Weisz criterion as given in Table 1 for steady-state conditions.

Doraiswamy and Sharma (1984) have given an effectiveness factor plot similar to Fig. 3(a). Here, the effect of extraparticle mass transfer is also included through the mass Biot number. However, they have plotted the effectiveness factor as a function of the Thiele modulus which is not an observable. An analogous analysis of the diffusion-reaction problem taking into account the resistance to external mass transport was made by Mehta and Aris (1971). Their charts simplify the iterative calculation of the overall effectiveness factor, but an expression in terms of an observable was not given. Similar to Fig. 3(a), Carberry (1976, 1987) has plotted the effectiveness factor as a function of the observable $\eta_0 \phi_0^2$ for various values of $B_i_n$ for a first-order reaction. Carberry, however, has not extended the analysis to a criterion assuring the absence of both extra- and intraparticle mass transfer limitations, as given in Fig. 3(b).

Next, we consider a transient experiment in which a reactant is introduced in an inert feed at $t = 0$. This leads to the following initial conditions:

$$\xi = \begin{cases} 
\zeta_i = 0 & \text{for } t_{in} < 0 \text{ and } \forall \tau \\
1 & \text{for } t_{in} \geq 0.
\end{cases}$$  \hspace{1cm} (37)

Figures 4(a) and (b) give the concentration profiles in the catalyst particle after the step change has been imposed. Figure 4(a) shows that the smaller $B_i_n$ the slower the increase of the concentration at the particle surface, $\zeta_i$, and the smaller the value for $\zeta_i$ at the steady state. This is caused by a smaller ratio between the extra- and intraparticle mass transfer coefficients for a smaller $B_i_n$. A change of $B_i_n$ also results in a change of the concentration profile in the catalyst particle. The influence of $n$ and $\phi_0^2$ on the concentration profile are illustrated in Fig. 4(b). Here, $B_i_n$ is larger than 20 which means that the concentration at the particle surface equals the bulk concentration (in other words $\phi_0^2$ equals $\phi_0^2$). The figure shows that the smaller $\phi_0^2$, the faster the concentration in the catalyst particle increases. This is caused by a decreased reaction rate compared to diffusion rate for lower values of $\phi_0^2$. Furthermore, the figure shows that the concentration in the catalyst particle increases faster for a third-order reaction than for a first-order reaction. The latter is caused by the term $(n + 1)/2$ in the squared overall Thiele modulus. The consequence of this term is that the ratio between the reaction rate and diffusion rate [given by the term $(L^2 k_b \epsilon_c^{-1})/D_r$ in $\phi_0^2$] changes when the reaction order changes at a constant value of $\phi_0^2$.

The steady-state criterion for negligible extra- and intraparticle mass transport states that $\eta_0 > 0.95$, which corresponds to a maximum allowable value for the observable $\eta_0 \phi_0^2$ [Fig. 3(b)]. This criterion must also be fulfilled when the steady state is reached after a transient has been imposed. Figure 5(a) gives the time $\tau_{in}$ needed to reach a volume-averaged dimensionless concentration in the catalyst particle, $\zeta_{asp}$, of...
which gives for \( \frac{\tau}{\tau_{\text{Avg}}} \),
\[
\frac{\tau}{\tau_{\text{Avg}}} \geq 0.95 \frac{\tau}{\tau_{\text{Avg}}} = 0.9. \tag{38}
\]

The dimensionless time \( \tau_{\text{in}} \) needed to fulfill this transient criterion, \( \tau_{\text{in}} \), depends on \( n, B_{i\text{m}} \) and \( \eta_0 \phi_B^2 \). The most critical values for \( \tau_{\text{in}} \) are obtained when using \( n = 1 \) and \( \eta_0 \phi_B^2 \) for which \( \eta_0 = 0.95 \) at each \( B_{i\text{m}} \) [Fig. 3(b)]. The dashed curve in Fig. 5(a) gives the most critical values for \( \tau_{\text{in}} \) as a function of \( B_{i\text{m}} \). For \( B_{i\text{m}} \) larger than 20 (no extraparticle gradient), \( \tau_{\text{in}} \) approaches 0.25.

Comparing the extraparticle criterion for a nonporous catalyst with the intraparticle criterion shows that \( \tau_{\text{in}} \) is 3 times more severe than \( \tau_{\text{ex}} \) in case \( B_{i\text{m}} \) is larger than about 20.

### MASS AND HEAT TRANSFER COMBINED WITH REACTION

**Extra- and intraparticle mass and heat transfer combined with reaction**

Thus far, only concentration gradients were considered. However, also temperature gradients might be important, since heat transport may not be fast enough to keep the catalyst particle isothermal when a large amount of heat is consumed or produced. The external mass transport could be discussed independently of the internal mass transport by considering a nonporous catalyst. The external heat transport, however, must always be examined in combination with internal heat transport, since catalyst support materials generally transport heat rather easily. Mostly heat transfer resistances are located in the film rather than in the particle. Furthermore, heat transfer must be considered simultaneously with mass transfer, caused by the coupling of mass and heat transfer via the rate term.

We have solved numerically the combined unsteady-state mass and energy balances for a step change from an inert to a reactive gas feed [eq. (37)]. The temperature of the bulk was held at a certain (dimensionless) temperature. Initially, the catalyst particle has the same temperature as the bulk. When heat is produced (exothermic reaction) or consumed (endothermic reaction) during the reaction, the temperature in the catalyst particle, respectively, increases or decreases. Due to the exponential relation between the temperature and the rate of reaction, this might influence the concentration of the reactant in the particle. However, it is found that the heat production/consumption in the particle is small as long as the steady-state criteria for the absence of extra- and intraparticle mass and heat transfer are satisfied. In this case the heat production/consumption does not influence the solution of the mass balance and the results are identical to those given in the previous section. The concentration in the catalyst particle differs from that for a thermoneutral reaction, only when the heat production/consumption is very large, but in this case the steady-state criteria are not satisfied anymore. This outcome means that the catalyst...
Table 2. Criteria for negligible transport effects in transient kinetic research over spherical catalyst particles, to be used in addition to the steady-state criteria given in Table 1 and Fig. 3(b)

<table>
<thead>
<tr>
<th>Transport process</th>
<th>Criterion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extrtraparticle mass transport (nonporous particle)</td>
<td>( \tau_{et} = \frac{k_{et}^D}{D} \geq 2.9 )</td>
</tr>
<tr>
<td>Extra- and intraparticle mass transport</td>
<td>( \tau_{im} = \frac{D_e}{c_{en} R_i^2} \geq 0.25 )</td>
</tr>
<tr>
<td>( Bi_m \geq 20 )</td>
<td>( \tau_{im} \geq \text{dashed line in Fig. 5(a)} )</td>
</tr>
<tr>
<td>( Bi_m &lt; 20 )</td>
<td></td>
</tr>
</tbody>
</table>

can be considered as isothermal under transient conditions provided that the steady-state criteria are fulfilled.

**DISCUSSION**

The criteria for the absence of mass and heat transfer limitations have been developed via simulation of an instantaneous step-response experiment. However, they are also valid for transient experiments in which the concentration is changed in any other form, e.g. pulse or noninstantaneous step change, as each change within an input function can be considered as step change itself. Only if the concentration changes very rapidly in the input function, the concentration in the bulk phase might have altered considerably within the time period needed to fulfill the transient criterion. In this case the diffusion process is too slow for the center of the catalyst particle to follow the complete input function. Whether the latter situation exists can be checked by comparing the time period necessary to fulfill the transient criterion with the specific time constants for the input function.

The presented analysis of mass and heat transfer in transient experiments has been limited to a single particle, whereas the system used for a great many transient kinetic experiments is a packed bed. Performance of a step change in the concentration of a non-reactive component over both an empty reactor and a reactor filled with catalyst can reveal information on the behavior of the transient in the packed bed. If both responses have the same shape, then diffusion and radial/axial dispersion can be neglected. This was found in a previous study in which we modelled the CO and CO\(_2\) responses obtained after a step change in the gas-phase concentration of CO over oxidized Cu and Cr (Dekker et al., 1994). A changing curve shape indicates that diffusion or radial/axial dispersion influences the responses. The influence of diffusion can be calculated and the dispersion can be included in the overall mass balance. When additionally the area under the response curves changes, then some of the inert component is stored in the catalyst particles. This situation might exist when large catalyst particles are used.

**CONCLUSIONS**

The mass and heat transfer in a catalyst particle after introduction of a reactant into an inert gas phase were analyzed in this study. The analysis has led to one criterion for the absence of both extra- and intraparticle mass transport limitations under steady-state conditions [Fig. 3(b)]. Additionally, criteria have been developed assuring the absence of mass and heat transfer limitations in transient kinetic research using step changes in the feed concentration. The transient criteria have been related to criteria for steady-state kinetic research, since steady-state transport criteria are easily examined and transient kinetic research often follows steady-state kinetic research. The average concentration in the catalyst at the transient criterion (Table 2) was allowed to deviate 5% at most from that at the steady-state criterion (Table 1). During the time period needed to reach a deviation less than 5%, the obtained responses may represent the dynamic mass transport rather than the true kinetics. Heat effects can be neglected during the transient period after a step change as long as the steady-state criteria for the absence of temperature gradients are satisfied.

**NOTATION**

- \( a \) particle surface area per unit volume of packed bed, \( \text{m}^{-1} \)
- \( a' \) specific particle surface area, \( \text{m}^{-1} \)
- \( c \) concentration in bulk phase, \( \text{mol} \text{ m}^{-3} \)
- \( c_n \) concentration in bulk phase at steady-state conditions, \( \text{mol} \text{ m}^{-3} \)
- \( c_i \) concentration at a position the catalyst particle, \( \text{mol} \text{ m}^{-3} \)
- \( c_s \) concentration at the surface of the catalyst particle, \( \text{mol} \text{ m}^{-3} \)
- \( C_p \) heat capacity, \( \text{J} \text{ mol}^{-1} \text{ K}^{-1} \)
- \( D_e \) effective diffusion coefficient, \( \text{m}^2 \text{ s}^{-1} \)
- \( k \) reaction rate coefficient, \( \text{s}^{-1} \)
- \( k_{et}^D \) extraparticle mass transfer coefficient, \( \text{m} \text{ s}^{-1} \)
- \( L \) characteristic catalyst particle size, \( \text{m} \)
- \( n \) reaction order, dimensionless
- \( N \) molar flux, \( \text{mol} \text{ m}^{-2} \text{ s}^{-1} \)
- \( r \) radial distance from center of catalyst particle, \( \text{m} \)
observed volumetric reaction rate,
\[ r_{\text{obs}} = \text{mol m}^{-3} \text{s}^{-1} \]

volumetric reaction rate, \( r_v \), \( \text{mol m}^{-3} \text{s}^{-1} \)

particle radius, \( R \), m

total external surface area of catalyst particle, \( S_p \), m²

total external surface area of catalyst particle in packed bed, \( S_t \), m²

time, s

volume of packed bed, m³

volume of catalyst particle, m³

dimensionless radial distance in catalyst particle

void fraction of catalyst bed, dimensionless, \( \varepsilon_b \)

void fraction of catalyst particle, dimensionless, \( \varepsilon_p \)

effectiveness factor, dimensionless, \( \eta \)

dimensionless concentration in bulk phase, \( \xi \)

dimensionless concentration at a position in catalyst particle, \( \xi_i \)

dimensionless concentration at surface of catalyst particle, \( \xi_s \)

dimensionless time for extraparticle mass transfer, \( \tau_{\text{ex}} \)

dimensionless time for intraparticle mass transfer, \( \tau_{\text{in}} \)

Thiele modulus, dimensionless, \( \phi \)

Biot number for mass transport, \( B_i \)

Carberry number, \( C_a \)

Damköhler number, \( D_a \)

average, \( \text{avg} \)

in the bulk phase, \( b \)

external, \( \text{ex} \)

global, \( G \)

at a position in the catalyst particle, \( i \)

internal, \( \text{in} \)

intrinsic, \( \text{intr} \)

maximum, \( \text{max} \)

observed, \( \text{obs} \)

at the surface of catalyst particle, \( s \)

REFERENCES


