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Dekker, F.H.M.; Blik, A.; Kapteijn, F.; Moulijn, J.A.

DOI

[10.1016/0009-2509\(95\)00210-V](https://doi.org/10.1016/0009-2509(95)00210-V)

Publication date

1995

Document Version

Final published version

Published in

Chemical Engineering Science

[Link to publication](#)

Citation for published version (APA):

Dekker, F. H. M., Blik, A., Kapteijn, F., & Moulijn, J. A. (1995). Analysis of heat and mass transfer in transient experiments over heterogeneous catalysts. *Chemical Engineering Science*, 50(22), 3573-3580. [https://doi.org/10.1016/0009-2509\(95\)00210-V](https://doi.org/10.1016/0009-2509(95)00210-V)

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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; Froment 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 Sinovec, 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-

†Corresponding author.

Table 1. Criteria for negligible transport effects in steady-state kinetic research

Transport process	Criterion
Extraparticle mass transport	$Ca = \frac{r_{\text{obs}}}{k_g a' c_b} < 0.05$
Intraparticle mass transport (Wheeler-Weisz criterion)	$\eta_{\text{in}} \phi_{\text{in}}^2 = \frac{r_{\text{obs}} L^2}{D_e c_s} \frac{n+1}{2} < 0.1$
Extraparticle heat transport	$ \beta_{\text{ex}} Ca = \left \frac{k_g (-\Delta H) c_b}{h T_b} \right \frac{E_a}{R T_b} Ca < 0.05$
Intraparticle heat transport	$ \beta_{\text{in}} \gamma_s (\eta_{\text{in}} \phi_{\text{in}}^2) = \left \frac{D_e (-\Delta H) c_s}{\lambda_e T_s} \right \frac{E_a}{R T_s} (\eta_{\text{in}} \phi_{\text{in}}^2) < 0.05$

niently described by the so-called film model. The film model assumes the existence of a stagnant layer of thickness δ along the external surface of the catalyst. The rate of the transfer is proportional to the driving force, i.e. the concentration gradient over the gas film:

$$N_s = k_g(c - c_s). \quad (1)$$

When using the film model, the unsteady-state mass balance for the concentration at the external surface of a *nonporous* catalyst can be expressed as:

$$\frac{\partial c_s}{\partial t} = k_g \frac{a}{\varepsilon_b} (c - c_s) + r_v \frac{1 - \varepsilon_b}{\varepsilon_b} \quad (2)$$

where a represents the particle surface area per unit volume of packed bed and can be expressed as the specific particle area a' :

$$a = \frac{S_t}{V_l} = \frac{S_p}{V_p} (1 - \varepsilon_b) = a' (1 - \varepsilon_b). \quad (3)$$

The reaction rate per unit volume of catalyst for a reaction of order n gives for a reactant,

$$r_v = -k_s c_s^n. \quad (4)$$

Since a thermoneutral reaction is considered, the bulk gas-phase temperature equals the surface temperature; thus $k_s = k_b$.

The unsteady-state mass balance in dimensionless form gives

$$\frac{\partial \xi_s}{\partial \tau_{\text{ex}}} = (\xi - \xi_s) - Da \xi_s^n \quad (5)$$

where

$$\xi = \frac{c}{c_b} \quad (6)$$

$$\tau_{\text{ex}} = \frac{k_g a}{\varepsilon_b} t. \quad (7)$$

The Damköhler number, Da , gives the ratio between the reaction rate without external transport limitations and the maximum external mass transfer rate:

$$Da = \frac{k_b c_b^n}{k_g a' c_b}. \quad (8)$$

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, η_{ex} :

$$Da = \frac{Ca}{\eta_{\text{ex}}} = \frac{r_{\text{obs}}}{N_{s, \text{max}}} \frac{r_{\text{intr}}}{r_{\text{obs}}}. \quad (9)$$

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:

$$Ca = \frac{r_{\text{obs}}}{k_g a' c_b} = \frac{c_b - c_s}{c_b}. \quad (10)$$

The external effectiveness factor, η_{ex} , 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

$$\eta_{\text{ex}} = \frac{k_s c_s^n}{k_b c_b^n} = \frac{c_s^n}{c_b^n} = (1 - Ca)^n. \quad (11)$$

Hence, the expression for Da in terms of the *observable* Ca becomes

$$Da = \frac{Ca}{(1 - Ca)^n}. \quad (12)$$

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

$$\xi = \begin{cases} \xi_s = 0 & \text{for } \tau_{\text{ex}} < 0 \\ 1 & \text{for } \tau_{\text{ex}} \geq 0. \end{cases} \quad (13)$$

Figure 1 gives the dimensionless concentration at the surface of the catalyst particle, ξ_s , as a function of the dimensionless time, τ_{ex} , 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 ξ_s at a certain τ_{ex} . 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 ξ_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 τ_{ex} needed to reach a certain ξ_s as a function of Ca . Again the solution was independent of the reaction order. The time needed to reach a certain ξ_s increases with increasing Ca . Furthermore, the higher the chosen critical value for ξ_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 τ_{ex} 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%.

Fig. 1. Dimensionless surface concentration, ξ_s , as a function of dimensionless time, τ_{ex} , for several values of Ca , after a step change from an inert to a reactive gas phase at $t = 0$. The horizontal dashed line represents the steady-state criterion, i.e. $\xi_s = 0.95$.

Fig. 2. Dimensionless time, τ_{ex} , needed to reach a certain dimensionless surface concentration, ξ_s , as a function of Ca , after a step change from an inert to a reactive gas phase at $t = 0$.

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

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

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

$$\tau_{ex}^{tr} \geq 2.9. \quad (15)$$

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:

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

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, ε_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

$$\frac{\partial c_i}{\partial t} = \frac{D_e}{\varepsilon_p r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_i}{\partial r} \right) + \frac{r_v}{\varepsilon_p}. \quad (17)$$

The reaction rate, r_v , is now given by

$$r_v = -k_i c_i^n. \quad (18)$$

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

$$\frac{\partial c_i}{\partial r} = 0 \quad \text{for } r = 0 \quad (19)$$

$$k_g(c - c_s) = D_e \frac{\partial c_i}{\partial r} \quad \text{for } r = R. \quad (20)$$

The mass balance in dimensionless form becomes

$$\frac{\partial \xi_i}{\partial \tau_{in}} = \frac{1}{z^2} \frac{\partial}{\partial z} \left(z^2 \frac{\partial \xi_i}{\partial z} \right) - 9\phi_G^2 \frac{2}{n+1} \xi_i^n \quad (21)$$

where ξ is again defined as in eq. (6) and

$$\tau_{in} = \frac{D_e}{\varepsilon_p R^2} t \quad (22)$$

$$z = \frac{r}{R}. \quad (23)$$

The squared overall Thiele modulus based on the concentration in the bulk, ϕ_G^2 , gives the ratio between the rate of reaction and rate of diffusion in a catalyst particle:

$$\phi_G^2 = L^2 \frac{k_b}{D_e} \frac{n+1}{2} c_b^{n-1} \quad (24)$$

where L represents the characteristic catalyst dimension

$$L = \frac{V_p}{S_p} = \frac{1}{a'}. \quad (25)$$

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

$$\phi_G^2 = \frac{1}{\xi_s^{n-1}} L^2 \frac{k_s}{D_e} \frac{n+1}{2} c_s^{n-1} = \frac{1}{\xi_s^{n-1}} \phi_{in}^2. \quad (26)$$

The boundary conditions in dimensionless form are

$$\frac{\partial \xi_i}{\partial z} = 0 \quad \text{for } z = 0 \quad (27)$$

$$\xi - \xi_s = \frac{1}{Bi_m} \frac{\partial \xi_i}{\partial z} \quad \text{for } z = 1. \quad (28)$$

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

$$Bi_m = \frac{k_g R}{D_e}. \quad (29)$$

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

$$\eta_G \phi_G^2 = \frac{r_{obs} L^2}{D_e c_b} \frac{n+1}{2}. \quad (30)$$

Here the overall effectiveness factor is the product of the internal and external effectiveness factor

$$\eta_G = \eta_{in} \eta_{ex} = \frac{r_{obs}}{k_s c_s^n} \frac{k_s c_s^n}{k_b c_b^n} = \frac{r_{obs}}{k_b c_b^n} = \eta_{in} \xi_s^n \quad (31)$$

and gives via eq. (26),

$$\eta_G \phi_G^2 = \eta_{in} \phi_{in}^2 \xi_s. \quad (32)$$

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

$$\eta_G \phi_G^2 = (1 - \xi_s) \frac{Bi_m}{3} \frac{n+1}{2}. \quad (33)$$

This gives for ξ_s ,

$$\xi_s = \left[\frac{\eta_{in} \phi_{in}^2}{Bi_m \frac{n+1}{6}} + 1 \right]^{-1}. \quad (34)$$

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

$$\phi_G^2 = \phi_{in}^2 \left[\frac{\eta_{in} \phi_{in}^2}{Bi_m \frac{n+1}{6}} + 1 \right]^{n-1}. \quad (35)$$

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

$$\eta_{in} \phi_{in}^2 = \phi_{in} \left(\frac{1}{\tanh 3\phi_{in}} - \frac{1}{3\phi_{in}} \right). \quad (36)$$

Figure 3(a) gives the relation between the *observable* $\eta_G \phi_G^2$ and η_G for several values of Bi_m 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 $Bi_m = 100$ 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 ξ_s is 1). Figure 3(a) shows that a higher η_G is reached for smaller values of $\eta_G \phi_G^2$ (at constant Bi_m). This is caused by a decrease of the relative importance of reaction compared to diffusion at decreasing $\eta_G \phi_G^2$. Furthermore, the figure shows that when Bi_m decreases also η_G decreases (constant $\eta_G \phi_G^2$). 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 Bi_m . In other words, the ability of the external mass transfer to keep up with the reaction and diffusion decreases when Bi_m decreases.

The criterion used for the absence of concentration gradients under steady-state conditions states that η_G must be larger than 0.95. Therefore, $\eta_G \phi_G^2$ for which η_G is 0.95 is given in Fig. 3(b) as a function of Bi_m . In fact, this figure connects the intersection points of the

Fig. 3(a). Relation between $\eta_G \phi_G^2$ and η_G at steady state for several values of Bi_m ($n = 1$). The horizontal dashed line represents the steady-state criterion, i.e. $\eta_G = 0.95$.

Fig. 3(b). Relation between Bi_m and $\eta_G \phi_G^2$ where $\eta_G = 0.95$ ($n = 1$).

horizontal line ($\eta_G = 0.95$) with the curves at several Bi_m out of Fig. 3(a). Figure 3(b) can be used to determine the maximum tolerated value for $\eta_G \phi_G^2$ at a certain Bi_m to assure the absence of concentration gradients under steady-state conditions. The figure shows that $\eta_G \phi_G^2$ at which $\eta_G = 0.95$ hardly changes anymore when Bi_m 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 $\eta_G \phi_G^2$ for various values of Bi_m 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:

$$\xi = \begin{cases} \xi_i = 0 & \text{for } \tau_{in} < 0 \text{ and } \forall z \\ 1 & \text{for } \tau_{in} \geq 0. \end{cases} \quad (37)$$

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 Bi_m the slower the increase of the concentration at the particle surface, ξ_s , and the smaller the value for ξ_s at the steady state. This is caused by a smaller ratio between the extra- and intraparticle mass transfer coefficients

Fig. 4. Dimensionless concentration, ξ , in a spherical catalyst particle as a function of z at several dimensionless times, τ_{in} , after a step change from an inert to a reactive gas phase at $t = 0$. (a) $n = 1$, $\phi_G^2 = 0.1$, (---) $Bi_m = 1$, (—) $Bi_m = 10$; (b) $Bi_m > 20$, (---) $n = 1$, $\phi_G^2 = 0.01$, (---) $n = 1$, $\phi_G^2 = 0.1$, (—) $n = 3$, $\phi_G^2 = 0.1$.

for a smaller Bi_m . A change of Bi_m also results in a change of the concentration profile in the catalyst particle. The influence of n and ϕ_G^2 on the concentration profile are illustrated in Fig. 4(b). Here, Bi_m is larger than 20 which means that the concentration at the particle surface equals the bulk concentration (in other words ϕ_G^2 equals ϕ_{in}^2). The figure shows that the smaller ϕ_G^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 ϕ_G^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 $(L^2 k_b c_b^{n-1})/D_e$ in ϕ_G^2] changes when the reaction order changes at a constant value of ϕ_G^2 .

The steady-state criterion for negligible extra- and intraparticle mass transport states that $\eta_G > 0.95$, which corresponds to a maximum allowable value for the observable $\eta_G \phi_G^2$ [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 τ_{in} needed to reach a volume-averaged dimensionless concentration in the catalyst particle, ξ_{avg} , of

Fig. 5(a). Dimensionless time τ_{in} , needed to reach an average dimensionless concentration, ξ_{avg} , of 0.9 as a function of $\eta_G \phi_G^2$ for several Bi_m , after a step change from an inert to a reactive gas phase at $t = 0$ ($n = 1$). The dashed line gives the criterion for the dimensionless time at transient conditions, τ_{in}^{tr} , as a function of the maximum allowable $\eta_G \phi_G^2$ at several Bi_m .

Fig. 5(b). Dimensionless time, τ_{in} , needed to reach a certain average dimensionless concentration, ξ_{avg} , as a function of $\eta_G \phi_G^2$, after a step change from an inert to a reactive gas phase at $t = 0$ ($n = 1$, $Bi_m > 20$).

0.9 as a function of $\eta_G \phi_G^2$ for several Bi_m . It is found that the time needed to attain a given value of ξ_{avg} increases with increasing $\eta_G \phi_G^2$ (and with decreasing n). The figure shows that the smaller Bi_m the longer it takes to reach $\xi_{avg} = 0.9$ at a certain $\eta_G \phi_G^2$. As under steady-state conditions the mass transfer process may limit the maximum achievable particle-averaged concentrations, no ξ_{avg} can be reached (not even for $\tau_{in} \rightarrow \infty$). This is demonstrated by the sharp increase of τ_{in} at the maximum $\eta_G \phi_G^2$. Figure 5(b), in which Bi_m is larger than 20 (i.e. $\eta_G \phi_G^2 = \eta_{in} \phi_{in}^2$), shows that the higher ξ_{avg} the longer it takes to reach it.

During a transient experiment the degree of mass transfer limitation changes over time, ultimately to arrive at the steady-state value. It is found that the volume-averaged dimensionless concentration is 0.95 when the Wheeler–Weisz criterion applies under steady-state conditions, ξ_{avg}^{st} . The deviation from the steady-state criterion is allowed to be 5% at most,

which gives for ξ_{avg}^{tr} ,

$$\xi_{avg}^{tr} \geq 0.95 \xi_{avg}^{st} \approx 0.9. \quad (38)$$

The dimensionless time τ_{in} needed to fulfil this transient criterion, τ_{in}^{tr} , depends on n , Bi_m and $\eta_G \phi_G^2$. The most critical values for τ_{in} are obtained when using $n = 1$ and $\eta_G \phi_G^2$ for which $\eta_G = 0.95$ at each Bi_m [Fig. 3(b)]. The dashed curve in Fig. 5(a) gives the most critical values for τ_{in}^{tr} as a function of Bi_m . For Bi_m larger than 20 (no extraparticle gradient), τ_{in} approaches 0.25.

Comparing the extraparticle criterion for a nonporous catalyst with the intraparticle criterion shows that τ_{in} is 3 times more severe than τ_{ex} in case Bi_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)

Transport process	Criterion
Extraparticle mass transport (nonporous particle)	$\tau_{\text{ex}} = \frac{k_g a}{\varepsilon_b} t \geq 2.9$
Extra- and intraparticle mass transport	
$Bi_m \geq 20$	$\tau_{\text{in}} = \frac{D_e}{\varepsilon_p R^2} t \geq 0.25$
$Bi_m < 20$	$\tau_{\text{in}} \geq$ dashed line in Fig. 5(a)

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 fulfil 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 fulfil 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 CO₂ 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, m^{-1}
a'	specific particle surface area, m^{-1}
c	concentration in bulk phase, mol m^{-3}
c_b	concentration in bulk phase at steady-state conditions, mol m^{-3}
c_i	concentration at a position the catalyst particle, mol m^{-3}
c_s	concentration at the surface of the catalyst particle, mol m^{-3}
C_p	heat capacity, $\text{J mol}^{-1} \text{K}^{-1}$
D_e	effective diffusion coefficient, $\text{m}^2 \text{s}^{-1}$
k	reaction rate coefficient, s^{-1} , $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$, ...
k_g	extraparticle mass transfer coefficient, m s^{-1}
L	characteristic catalyst particle size, m
n	reaction order, dimensionless
N	molar flux, $\text{mol m}^{-2} \text{s}^{-1}$
r	radial distance from center of catalyst particle, m

r_{obs}	observed volumetric reaction rate, $\text{mol m}_{\text{cat}}^{-3} \text{s}^{-1}$
r_v	volumetric reaction rate, $\text{mol m}_{\text{cat}}^{-3} \text{s}^{-1}$
R	particle radius, m
S_p	external surface area of catalyst particle, m^2
S_t	total external surface area of catalyst particle in packed bed, m^2
t	time, s
V_l	volume of packed bed, m^3
V_p	volume of catalyst particle, m^3
z	dimensionless radial distance in catalyst particle

Greek letters

ε_b	void fraction of catalyst bed, dimensionless
ε_p	void fraction of catalyst particle, dimensionless
η	effectiveness factor, dimensionless
ξ	dimensionless concentration in bulk phase
ξ_i	dimensionless concentration at a position in catalyst particle
ξ_s	dimensionless concentration at surface of catalyst particle
τ_{ex}	dimensionless time for extraparticle mass transfer
τ_{in}	dimensionless time for intraparticle mass transfer
ϕ	Thiele modulus, dimensionless

Dimensionless numbers

Bi_m	Biot number for mass transport
Ca	Carberry number
Da	Damköhler number

Subscripts

avg	average
b	in the bulk phase
ex	external
G	global
i	at a position in the catalyst particle
in	internal
intr	intrinsic
max	maximum
obs	observed
s	at the surface of catalyst particle

Superscripts

st	at steady-state criterion
tr	at transient criterion

REFERENCES

- Bennett, C. O., 1976, The transient method and elementary steps in heterogeneous catalysis. *Catal. Rev.- Sci. Engng* **13**, 121–148.
- Biloen, P., 1983, Transient kinetic methods, *J. Mol. Catal.* **21**, 17–24.
- Carberry, J. J., 1976, *Chemical and Catalytic Reaction Engineering*, pp. 194–243. McGraw-Hill, New York.
- Carberry, J. J., 1987, in *Catalysis, Science and Technology*, Vol. 8 (Edited by J.R. Anderson and M. Boudart), pp. 131–172. Springer, Berlin.
- Dekker, F. H. M., Kloppe, G., Blik, A., Kapteijn, F. and Moulijn, J. A., 1994, Modelling the transient kinetics of heterogeneous catalysts. CO oxidation over supported Cr and Cu. *Chem. Engng. Sci.* **49**, 4375–4390.
- Doraiswamy, L. K. and Sharma, M. M., 1984, *Heterogeneous Reactions: Analysis, Examples, and Reactor Design*, Vol. 1: *Gas-Solid and Solid-Solid Reactions*, p. 128. Wiley, New York.
- Froment, G. F. and Bischoff K. B., 1990, *Chemical Reactor Analysis and Design*, 2nd Edition, pp. 61–197. Wiley, New York.
- Gleaves, J. T., Ebner, J. R. and Kuechler, T. C., 1988, Temporal Analysis of Products (TAP)—A unique catalyst evaluation system with submillisecond time resolution. *Catal. Rev. - Sci. Engng* **30**, 49–116.
- Kobayashi, H. and Kobayashi, M., 1974, The transient response method in heterogeneous catalysis. *Catal. Rev.- Sci. Engng* **10**, 139–176.
- Kobayashi, M., 1982, Characterization of transient response curves in heterogeneous catalysis. I. Classification of the curves. *Chem. Engng. Sci.* **37**, 393–401.
- Lee, H. H., 1985, *Heterogeneous Reactor Design*, pp. 71–150. Butterworth Publishers, Boston.
- Madsen, N. K. and Sinovec, R. F., 1979, ALGORITHM 540 PDECOL, General collocation software for partial differential equations [D3]. *ACM Trans. Math. Software* **5**, 326–351.
- Mehta, B.N. and Aris, R., 1971, Communications on the theory of diffusion and reaction—VII The isothermal p th order reaction. *Chem. Engng. Sci.* **26**, 1699–1712.
- Mirodatos, C., 1991, Use of isotopic transient kinetics in heterogeneous catalysis. *Catal. Today* **9**, 83–95.
- Moulijn, J. A., Tarfaoui, A. and Kapteijn, F., 1991, General aspects of catalyst testing. *Catal. Today* **11**, 1–12.
- Schiesser, W. E., 1991, *The Numerical Method of Lines. Integration of Partial Differential Equations*. Academic Press, San Diego.
- Tamaru, K., 1991, in *Catalysis Science and Technology*, Vol. 9 (Edited by J. R. Anderson and M. Boudart), pp. 87–129. Springer, Berlin.