

THE EFFECT OF EXTERNAL MASS TRANSFER ON THE SELECTIVITY OF HETEROGENEOUSLY CATALYZED CONSECUTIVE COMPETITIVE REACTIONS

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The effect of mass transfer between the external surface of a non-porous catalyst particle and the stream of reaction mixture on the selectivity in a system with two consecutive competitive reactions without heat effect was studied on a mathematical model. It was found that unless the effect of imperfect external mass transfer is eliminated, the yield of intermediate product is always lower than in the kinetic region. However, even in the cases when the effect of external diffusion cannot be completely eliminated it is possible to attain high yield of the required intermediate product provided that a smaller amount of the substance, common to both reactions, than the stoichiometric one is used. Examples of the effect of external mass transfer on the yield of intermediate product in a flow stirred reactor are presented.

This study follows the foregoing papers which dealt with the description of the effect of external mass transfer¹ and/or of mass and heat transfer² on the selectivity of consecutive reactions of the $A \rightarrow R \rightarrow S$ type. This work aims at finding the effect of external mass transfer on a reaction system in which two consecutive competitive reactions take place which mutually compete for one of reaction components, for the case that the required substance is the intermediate product.

THEORETICAL

Let the chemical reactions



take place on one particle of non-porous catalyst. On the assumption of validity of rate equation of the power form, the rate of the reactions can be expressed by the relations:

$$r_1 = k_1 c_A^a c_B^b, \quad (I)$$

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$$r_2 = k_2 c_{R_s}^r c_{B_s}^m . \quad (2)$$

The rate of transfer of single substances to the external surface of catalyst or from the external surface of catalyst is given by the relations

$$r_{DA} = k_{gA} a_m (c_A - c_{As}) , \quad (3)$$

$$r_{DB} = k_{gB} a_m (c_B - c_{Bs}) , \quad (4)$$

$$r_{DR} = k_{gR} a_m (c_R - c_{Rs}) . \quad (5)$$

If the assumption of steady state holds, the accumulation of substances on the catalyst surface does not occur and the rate of substance supply is equal to the rate of their consumption in chemical reaction. In this case it is possible to write formally:

$$r_{DA} = r_1 , \quad (6)$$

$$r_{DB} = r_1 + r_2 , \quad (7)$$

$$r_{DR} = r_2 - r_1 . \quad (8)$$

The condition of steady state in combination with the rate equations and the equations describing the rate of mass transfer leads to the relations

$$r_1 = k_1 \left(c_A - \frac{r_1}{k_{gA} a_m} \right)^n \left(c_B - \frac{r_1 + r_2}{k_{gB} a_m} \right)^n , \quad (9)$$

$$r_2 = k_2 \left(c_B - \frac{r_1 + r_2}{k_{gB} a_m} \right)^m \left(c_R - \frac{r_2 - r_1}{k_{gR} a_m} \right)^r . \quad (10)$$

With the aim of converting the equations to the dimensionless form, a standard reaction rate was chosen and the rates of the first and second reaction were related to this rate. As the standard rate, the rate was chosen at which the first reaction would take place at the standard concentration of substance A and at the concentration of substance B equal to the standard one under the conditions when the influence of the external mass transfer does not appear (*i.e.* the concentration of substances on the surface of catalyst particle and in the bulk of reaction mixture are identical). In this way defined standard rate is expressed by the relation: $r_{10m} = k_1 c_{A_m}^{(a+n)}$. The dimensionless rate equations implying the effect of external diffusion can be written in the form

$$R_1 = (C_A - \Phi_{Am}R_1)^a [C_B - \Phi_{Am}(k_{gA}/k_{gB})(R_1 + R_2)]^n, \quad (11)$$

$$R_2 = (k_2/k_1) c_{Am}^d [C_B - \Phi_{Am}(k_{gA}/k_{gB})(R_1 + R_2)]^m \cdot \\ \cdot [C_R - \Phi_{Am}(k_{gA}/k_{gR})(R_2 - R_1)]^r, \quad (12)$$

$$d = r + m - n - a. \quad (13)$$

The dimensionless quantities C_A , C_B , C_R , R_1 , R_2 , and Φ_{Am} are defined by the expressions:

$$C_A = c_A/c_{Am}, \quad C_B = c_B/c_{Am}, \quad C_R = c_R/c_{Am}, \quad (14)$$

$$R_1 = r_1/r_{10m}, \quad R_2 = r_2/r_{10m}, \quad (15)$$

$$\Phi_{Am} = r_{10m}/k_{gA}a_m c_{Am}. \quad (16)$$

The parameter Φ_{Am} defined by the relation (13) gives the ratio between the rate of the first reaction under standard conditions and the maximum possible rate of external transfer of substance A under the given conditions. This parameter is a suitable coordinate for describing the extent of the influence of external mass transfer. In the kinetic region its value is zero and towards the region controlled by external mass transfer its value increases. Its physical meaning was discussed more fully in one of foregoing papers³. To compare the influence of external mass transfer on the selectivity of reaction under different conditions it is possible to define the selectivity factor

$$S = (r_1 - r_2)/r_1 = (R_1 - R_2)/R_1. \quad (17)$$

The selectivity factor defined in this way gives the instantaneous rate at which the intermediate product is formed related to the rate of decrease of starting substance A.

By choosing the volume concentrations of reacting substances, it is possible to find in this manner, on substituting into Eqs (11), (12) and (17), the instantaneous selectivity of reaction on only particle of catalyst. For different values of the parameters it is possible then to test their relative importance as to the extent of influencing the selectivity of the process by the external mass transfer¹.

It is very important to find for practical purposes how the influence of external diffusion upon a reaction appears in the yield of required product in some of fundamental types of reactor. As an example, a flow stirred reactor is chosen. For the reaction scheme consisting of Eqs (A) and (B), it is possible to derive the relations from the balance of the reactor:

$$C_{A0}(1 - X_A) = C_{A0} - C_A = DaR_1, \quad (18)$$

$$C_R = Da(R_1 - R_2), \quad (19)$$

$$C_{B0} - C_B = Da(R_1 + R_2). \quad (20)$$

(It is assumed that at the inlet of reactor there is the zero concentration of substance R). Da is the modified Damkohler number representing the dimensionless time and defined by the relation

$$Da = Wr_{10m}/Fc_{Am}. \quad (21)$$

By combining Eqs (18), (19) and (20) with Eqs (11) and (12), the complete description of reaction system is given. On the basis of this description it is possible to determine the outlet concentrations of all substances, the rate of the first and second reaction and the time needed for reaching the required conversion degree for the given inlet concentrations of substances A and B, and on the basis of the knowledge of outlet concentrations it is possible to determine the yield of intermediate product defined by the relation

$$V_R = C_R/(C_{A0} - C_A). \quad (22)$$

RESULTS AND DISCUSSION

In comparison with simple consecutive reactions (of the type $A \rightarrow R \rightarrow S$), a new aspect in case of the consecutive competitive reactions is the presence of common reactant which both reactions compete for. It is, however, evident that as far as the common substance is in large excess, it is possible to neglect its concentration gradient between the bulk of reaction mixture and the surface of catalyst particle and, in the reactor, it is possible to neglect the decrease of common substance in the course of reaction. The effect of concentration of the substance in excess can be included into the rate constants and the reaction system behaves analogously as if simple consecutive reactions took place here. It is necessary to emphasize, however, that from the point of view of quantitative effect of diffusion, there is a difference as for the case. An increase in the concentration of substance B causes an increase in the reaction rate at constant rate of diffusion, which in its consequence means the shift of the reaction regime deeper into the region of the influence of external diffusion. The behaviour of consecutive competitive reactions influenced by the external mass transfer is illustrated on the case of a flow stirred reactor. It is evident from Fig. 1 that the yield of intermediate product for fivefold excess of common substance (curve 3) with regard to the stoichiometric amount (curve 1) and for the same hydro-

dynamic conditions is influenced substantially more strongly by the external mass transfer. This and all further calculations were carried out for reactions which are of the first order with respect to the concentrations of reacting components and on the assumption that the mutual ratio of mass transfer coefficients of all reacting substances is unit and depends neither on the composition of reaction mixture, nor on the rate of mass transfer, nor on temperature. It is not to be assumed that the results for other orders or for different ratios of the mass transfer coefficients would be in principle disparate. The discussion of results aims at the case when the substance, it is competed for, is in the stoichiometric amount or the amount is smaller, for only in this case the rate of mass transfer of this substance has the decisive effect on the rate and selectivity of reaction. The results obtained may be applied as well to the reactions with heat effect as far as they take place in the liquid phase or in strongly diluted gaseous solutions.

Now let us consider the consecutive competitive reactions taking place on a catalyst particle in a hypothetical flow stirred reactor in which it is possible to change hydrodynamic conditions at constant concentration of reacting substances. The coefficients of mass transfer are functions of hydrodynamic conditions. Their value increases with increasing flow velocity of gases about a catalyst. On the contrary, a decrease in flow velocity brings about a decrease of values of transfer coefficients and con-

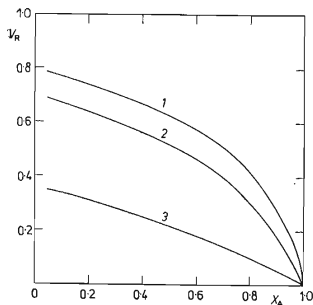


FIG. 1

Dependence of the Yield of Intermediate Product on the Conversion Degree of Initial Substance for Various Concentrations of Common Reactant

$C_{A0} = 1$, $C_{R0} = 0$, $k_1/k_2 = 5$, $\Phi_{Am} = 1$;
 1 $C_{B0} = 2$, 2 $C_{B0} = 3$, 3 $C_{B0} = 10$.

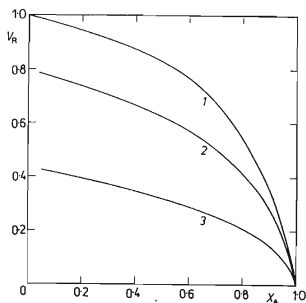


FIG. 2

Dependence of the Yield of Intermediate Product on the Conversion Degree of Initial Substance for Various Values of Parameter Φ_{Am}

$C_{A0} = 1$, $C_{R0} = 0$, $C_{B0} = 2$, $k_1/k_2 = 5$;
 1 $\Phi_{Am} = 0$, 2 $\Phi_{Am} = 1$, 3 $\Phi_{Am} = 10$.

sequently a decrease of rate of mass transfer. Owing to the decrease in flow velocity, then the surface concentration of starting substances A, B decreases and, on the contrary, the surface concentration of intermediate product R increases, which consequently leads to a decrease in the rate of the first reaction and to the preference of the second one in which the required intermediate product disappears. Thus, by having the effect of external mass transfer, the selectivity of reaction necessarily decreases. This fact is demonstrated in Fig. 2 in which the dependence is represented of the yield (or selectivity, for in a flow stirred reactor both the terms are identical) on the conversion degree of initial substance without the influence of diffusion and with different degree of extent of the effect of external mass transfer. An analogous dependence for another ratio of values of rate constants of the first and second reaction is illustrated in Fig. 3. On comparing both figures it is evident that the selectivity of reaction will be influenced by diffusion the less the larger the ratio of rate constants of the first and second reaction is.

It is interesting to find the effect of external mass transfer on the yield of intermediate product for the reaction scheme:

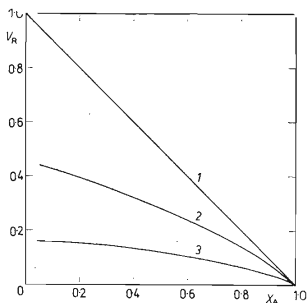


FIG. 3

Dependence of the Yield of Intermediate Product on the Conversion Degree of Initial Substance for Various Values of Parameter Φ_{Am}

$C_{A0} = 1, C_{R0} = 0, C_{B0} = 2, k_1/k_2 = 1;$
 1 $\Phi_{Am} = 0, 2 \Phi_{Am} = 1, 3 \Phi_{Am} = 10.$

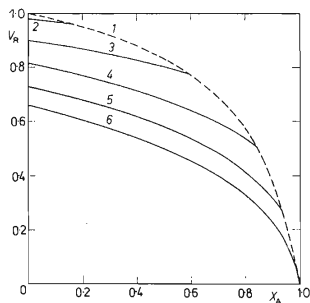


FIG. 4

Dependence of the Yield of Intermediate Product on the Conversion Degree of Initial Substance for Various Values of Starting Concentration of Common Substance B

$C_{A0} = 1, C_{R0} = 0, k_1/k_2 = 5; 1 \Phi_{Am} = 0, C_{B0} = 4$ (kinetic region), 2 $\Phi_{Am} = 1, C_{B0} = 0.2, 3 \Phi_{Am} = 1, C_{B0} = 1, 4 \Phi_{Am} = 1, C_{B0} = 2, 5 \Phi_{Am} = 1, C_{B0} = 3, 6 \Phi_{Am} = 1, C_{B0} = 4.$



when the substance B is in so small amount that it is theoretically sufficient for the 100 per cent conversion of substance A by the first reaction but does not suffice any more for the total conversion of intermediate product. Illustration of this situation is given in Figs 4 and 5. It is evident from them that the selectivity is the higher the smaller amount of common substance is present in the reaction system. This fact can be explained in this way: With decreasing content of substance B in the bulky phase of reaction mixture, the rate of its transport to the surface of catalyst decreases at the same time, too. Consequently, the surface concentration decreases as well. The rate of diffusion of substance B becomes the controlling process, which in its consequence means the same influencing of the rates of both reactions (both are of the first order with respect to the substance B) and therefore the shift of selectivity to the kinetic relations. It is shown graphically in Fig. 4 — in the region close to exhausting the substance B (concentration on the surface approaches zero), the curves

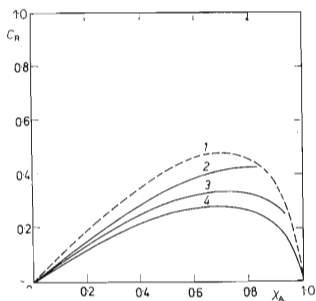


FIG. 5

Dependence of Concentration of Intermediate Product on the Conversion Degree of Initial Substance for Various Values of Concentration of Common Substance B

$C_{A0} = 1$, $C_{R0} = 0$, $k_1/k_2 = 5$; 1 $\Phi_{Am} = 0$, $C_{B0} = 4$ (kinetic region), 2 $\Phi_{Am} = 1$, $C_{B0} = 2$, 3 $\Phi_{Am} = 1$, $C_{B0} = 3$, 4 $\Phi_{Am} = 1$, $C_{B0} = 4$.

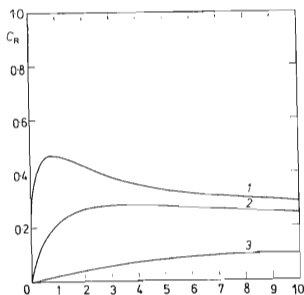


FIG. 6

Dependence of Concentration of Intermediate Product on Retention Period for Various Values of Parameter Φ_{Am}

$C_{A0} = 1$, $C_{R0} = 0$, $C_{B0} = 4$, $k_1/k_2 = 5$; 1 $\Phi_{Am} = 0$, 2 $\Phi_{Am} = 1$, 3 $\Phi_{Am} = 10$.

join the curve of kinetic region. Thus, even in the cases when it is not possible to eliminate successfully the influence of external mass transfer, it is possible to reach a high yield of required intermediate product provided that a smaller amount of common substance than the stoichiometric one is used. But on the other hand, this procedure brings along a substantial increase in reaction time needed to attain the required conversion. This "time factor" of the external mass transfer is illustrated graphically in Fig. 6 in which the dependence of the intermediate product concentration on the reaction time for different values of the parameter Φ_{Am} is presented.

In practice the case often occurs that the common substance B has a constant concentration in the course of reaction. It can be like this *e.g.* when hydrogenating in the liquid phase, when the hydrogen concentration is maintained on constant level. As far as the concentration of the substance is all the time unchanging and much smaller than the concentration of other substances, then it is possible to assume that for the substances A and R, the concentration on the surface is the same as in the bulk of reaction mixture. Thus only the effect of external mass transfer of substance B comes into operation. If the dependence of rate of the first and second reaction on the parameter Φ_{Am} is investigated (for only particle of catalyst) at constant concentrations of substances A and B, then this reaction system behaves as if the partial pressure or the concentration of substance B were changed without taking the effect of external mass transfer. The dependence of surface concentration of the substance B on the parameter Φ_{Am} for this arrangement is represented in Fig. 7. With the actual course of reaction this case is rather more complicated because, even at constant concentration of substance B in solution, the surface concentration changes during the experiment or with the change of concentrations of substances A and R, *i.e.* the decrease of concentration on the surface is dependent on the reaction rate.

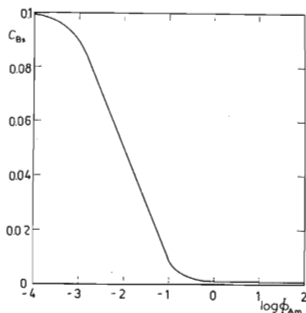


FIG. 7

Dependence of Surface Concentration of Common Substance B on Parameter Φ_{Am} for Eqs (A) and (B)

$$C_A = 100, C_B = 0.1, C_R = 10, k_1/k_2 = 5.$$

As it has been stated, if the effect of external mass transfer comes into operation, the found selectivity is always lower than in the kinetic region. This involves a danger of testing an industrial catalyst in laboratory reactors in one pass of reaction mixture, where, as a rule, the effect of external mass transfer is not eliminated. In that case a catalyst may be excepted from further study as a non-selective one though it would show a satisfactory selectivity at higher flow velocities under the conditions of industrial operation.

LIST OF SYMBOLS

a	reaction order
a_m	specific external surface of catalyst particle related to weight unit of catalyst (m^2/g)
c_A, c_B, c_R	concentration of substance A, B, and R in volume of mixture (mol/m^3)
c_{As}, c_{Bs}, c_{Rs}	concentration of substance A, B, and R on surface of catalyst particle (mol/m^3)
c_{Am}	standard concentration of substance A (mol/m^3)
C_A, C_B, C_R	dimensionless concentration of substance A, B, and R in volume of mixture
C_{A0}, C_{B0}, C_{R0}	dimensionless concentration of substance A, B, and R at inlet of reactor
d	parameter defined by Eq. (13)
Da	modified Damkoehler's number defined by Eq. (21)
F	feed of substances (m^3/h)
k_1, k_2	rate constants of first and second reaction ($\text{m}^{3b}/\text{h g}_{\text{KAT}} \text{mol}^{b-1}$), where b is order of corresponding reaction
k_{gA}, k_{gB}, k_{gR}	mass transfer coefficient of substance A, B, and R (m/h)
m, n, r	reaction order with respect to single component
r_1, r_2	reaction rate of first and second reaction ($\text{mol}/\text{g}_{\text{KAT}} \text{h}$)
r_{10m}	standard reaction rate of first reaction ($\text{mol}/\text{g}_{\text{KAT}} \text{h}$)
R_1, R_2	relative reaction rate of first and second reaction
S	selectivity factor defined by Eq. (17)
V_R	yield of substance R defined by Eq. (22)
W	catalyst weight (g)
X_A, x_A	conversion degree of initial substance A
Φ_{Am}	parameter defined by Eq. (16)

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