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HEAT AND MASS TRANSFER IN HETEROGENEOUS CATALYSIS. XXV.* THE EFFECT OF MASS TRANSFER BETWEEN EXTERNAL SURFACE OF A NON-POROUS CATALYST PELLET AND A STREAMING REACTION MIXTURE ON THE SELECTIVITY OF TWO CONSECUTIVE REACTIONS WITHOUT THERMAL EFFECT

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The effect of mass transfer between the external surface of a non-porous catalyst pellet and a streaming reaction mixture on the selectivity in a system of consecutive reactions without thermal effect in the steady state was studied on a mathematical model. It has been established that the external heat transfer significantly suppresses production of the intermediate products and gives preference to the final product. Examples are shown of the effect of the external mass transfer on the yield of intermediate product in basic types of isothermal reactors.

This paper opens a series of communications dealing with the effect of the external heat and mass transfer on the selectivity in systems of chemical reactions. The presented problem is quite complex and will therefore be solved beginning from the simplest systems and additional factors will gradually be incorporated. In this communication we examine the effect of the external mass transfer on the selectivity in a system of two consecutive reactions without thermal effect taking place on the surface of a non-porous catalyst. Reactions without thermal effect were chosen in order that the problem is not complicated by the non-isothermality of the system. The results can, of course, be applied to the reactions in the liquid phase or in very dilute gas mixtures as well. A non-porous catalyst was chosen in order that the effect of the external mass transfer could be studied separately. The selectivity in a porous catalyst is affected both by the external and internal mass transfer.

MODEL OF A CATALYST PELLET

The calculations were performed for a system of consecutive reactions of the type

$$A \xrightarrow[k_1]{r_1} R \xrightarrow[k_2]{r_2} S. \qquad (1)$$

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It is assumed that the reaction rate of both reactions is a function of concentration at the surface of the catalyst pellet. Then for both reactions following relations are valid:

$$r_1 = k_1 c_{\rm As}^{\rm n} , \qquad (2)$$

$$r_2 = k_2 c_{\text{Rs}}^{\text{m}} \,. \tag{3}$$

The rate of the transport of the species A to the surface of the catalyst pellet is given by the relation:

$$r_{\rm DA} = k_{\rm gA} a_{\rm m} (c_{\rm A} - c_{\rm As}) \tag{4}$$

and the rate of the transport of the species R from the surface of the pellet into the volume of the reaction mixture is given by the relation:

$$r_{\rm DR} = k_{\rm gR} a_{\rm m} (c_{\rm Rs} - c_{\rm R}) \,. \tag{5}$$

In the steady state the rate of transport of the species A to the surface of the pellet must be equal to the rate of reaction of the species A, and the rate of formation of the species R by chemical reaction from the species A must be equal to the sum of the rate of transport of the species R into the volume of the reaction mixture and its rate of conversion into S. The steady state condition leads to the relations:

$$r_1 = k_1 c_{\rm As}^{\rm n} = k_{\rm gA} a_{\rm m} (c_{\rm A} - c_{\rm As}) , \qquad (6)$$

$$r_2 = k_2 c_{\rm Rs}^{\rm m} + k_{\rm gR} a_{\rm m} (c_{\rm Rs} - c_{\rm R}) \,. \tag{7}$$

Solution of the set of Eqs (6) and (7) determines the rate of both reactions. For computational purposes the equations were put into dimensionless form by the following procedure. One initial concentration of starting substance in the volume of the reaction mixture was selected as standard c_{Am} . It is advantageous to select concentration of the starting substance in the stream at the inlet of the reactor. The dimensionless concentrations of the species in the volume of the reaction mixture and at the surface of the pellet are then defined as a ratio of a given concentration and the standard one:

$$C_{\rm A} = c_{\rm A}/c_{\rm Am}; \quad C_{\rm R} = c_{\rm R}/c_{\rm Am}; \quad C_{\rm As} = c_{\rm As}/c_{\rm Am}; \quad C_{\rm Rs} = c_{\rm Rs}/c_{\rm Am}.$$
 (8)

The dimensionless reaction rates of the first and the second reaction were defined as a ratio of a given reaction rate to the rate of the first reaction at the standard concentration of the starting substance and with absence of the external mass transfer:

$$R_1 = r_1/r_{\text{lom}}; \quad R_2 = r_2/r_{\text{lom}}.$$
 (9)

Eqs (6) and (7) can thus be put into dimensionless form:

$$R_{1} = C_{As}^{n} = \frac{1}{\phi_{Am}} \left(C_{A} - C_{As} \right), \qquad (10)$$

$$R_1 - R_2 = C_{As}^n - \frac{k_2}{k_1 c_{Am}^{-m}} C_{Rs}^m = \frac{1}{\Phi_{Am}} \frac{k_{gR}}{k_{gA}} (C_{Rs} - C_R).$$
(11)

On solving the set of Eqs (10) and (11) the values of the dimensionless concentration at the surface of the pellet and the values of the relative reaction rates were determined. A review of the relationships obtained for different values of the reaction orders n and m is given in Table I. Parameter Φ_{Am} appearing in these equations is defined by the relationship:

$$\Phi_{\rm Am} = r_{\rm lom}/k_{\rm gA}a_{\rm m}c_{\rm Am} \,. \tag{12}$$

This parameter controls the effect of the external diffusion on the course of the first reaction (analogous to the Thiele modulus in internal diffusion). Its physical meaning has already been discussed in one of the preceding communications¹. For evaluation of the results and comparison of the selectivity under different conditions a factor of selectivity was defined by the relationship:

$$S = (r_1 - r_2)/r_1 = (R_1 - R_2)/R_1.$$
(13)

The factor of selectivity gives the ratio of the observed instantaneous rate of formation of the intermediate product to the total rate of disappearance of the starting substance. A relationship for the selectivity in a system of consecutive reactions of the first order is given below for ilustration:

$$S = 1 - {\binom{k_2}{k_1}} \left(\frac{C_{\rm R}}{C_{\rm A}} \frac{1 + \Phi_{\rm Am}}{\Phi_{\rm Am}} \frac{k_{\rm gR}}{k_{\rm gA}} + 1 \right) / \left(\frac{k_2}{k_1} + \frac{1}{\Phi_{\rm Am}} \frac{k_{\rm gR}}{k_{\rm gA}} \right). \tag{14}$$

For comparison of the effect of external mass transfer on the yield of the intermediate product in principal types of reactors, the yield was defined as a ratio of the amount of the starting substance converted into the intermediate product to the amount of the starting substance converted into both products. On taking the inlet concentration for standard and if the feed contains no species R, the yield can be determined from the following relation:

$$V_{\rm R} = C_{\rm R} / (1 - C_{\rm A}) \,. \tag{15}$$

The following relationships were used to calculate the reactor yield:

- for a continuous perfectly mixed reactor

$$1 - C_{\mathsf{A}} = \mathsf{Da}R_{\mathsf{1}}, \tag{16}$$

$$C_{\mathbf{R}} = \mathrm{Da}(R_1 - R_2). \tag{17}$$

- for a mixed batch reactor or a continuous plug flow reactor

$$Da = \int_{C_{A}=1}^{C_{A}} - dC_{A}/R_{1}$$
 (18)

$$Da = \int_{C_R=0}^{C_R} dC_R / (R_1 - R_2).$$
 (19)

The integration was performed assuming that the mass transfer coefficients are independent of the reaction time. Da is a modified Damköhler group defined for continuous reactors as

$$Da = \frac{W}{F} \frac{r_{\rm om}}{c_{\rm Am}}, \qquad (20)$$

and for batch reactors as

$$Da = \frac{W}{V} \frac{r_{0m} t}{c_{Am}}.$$
 (21)

RESULTS AND DISCUSSION

The effect of the external mass transfer on the selectivity of the reaction depends on several parameters: The value of Φ_{Am} , the ratio of the reaction rate constants k_1/k_2 , the ratio of mass transfer coefficients k_{gA}/k_{gR} and on the reaction orders n and m. The parameter Φ_{Am} controls the remoteness of the regime of the first reaction from the kinetic region; in the kinetic region its value is zero and increases toward the region of external diffusion. As has been pointed out in the preceding paper, the value of this parameter can be varied by the change of the velocity of gas flow

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in the vicinity of the catalyst pellet (its value is approximately proportional to the inverse of the square root of the gas velocity) and by the change of the size of the catalyst pellet (its value is approximately proportional to the square root of the pellet diameter). The value of the parameter Φ_{Am} depends on the value of the reaction rate constant and therefore increases with increasing activity of the catalyst and with

TABLE I

Review of Calculated Dimensionless Concentrations on the Surface of Pellet and Relative Reaction Rates for Different Orders

Reaction order	$\Phi_{\rm Am}$	Concentration	Reaction rate
		First reaction	
n = 0	$\Phi_{\rm Am} > C_{\rm A}$	$C_{\rm As} = 0$	$R_1 = C_A / \Phi_{Am}$
n = 0	$\Phi_{\rm Am} < C_{\rm A}$	$C_{\rm As} = C_{\rm A} - \Phi_{\rm Am}$	$R_1 = 1$
n = 0.5		$C_{\rm As} = [(\Phi_{\rm Am}^2 + 2C_{\rm A}) - \Phi_{\rm Am}(\Phi_{\rm Am}^2 + 4C_{\rm A})^{1/2}]/2$	$R_1 = (C_{As})^{1/2}$
n = 1		$C_{\rm As} = C_{\rm A}/(1+\varPhi_{\rm Am})$	$R_1 = C_{As}$
<i>n</i> == 2	-	$C_{\rm As} = [(1 + 4\phi_{\rm Am}C_{\rm A})^{1/2} - 1]/2\phi_{\rm Am}$	$R_1 = C_{As}^2$
		Second reaction	
<i>m</i> = 0	$\begin{array}{l} \mathbf{R_2}\boldsymbol{\Phi_{Am}} > \\ > \mathbf{R_1}\boldsymbol{\Phi_{Am}} + \\ + \ \mathbf{C_R}(k_{gR}/k_{gA}) \end{array}$	$C_{\rm Rs}=0$	$R_2 = R_1 + (C_R/\Phi_{Am})$ (k_{gR}/k_{gA})
<i>m</i> = 0	$\begin{array}{l} \mathbf{R_2}\boldsymbol{\Phi_{Am}} < \\ < \mathbf{R_1}\boldsymbol{\Phi_{Am}} + \\ + \ \mathbf{C_R}(k_{gR}/k_{gA}) \end{array}$	$C_{\text{Rs}} = C_{\text{R}} + \Phi_{\text{Am}}(k_{\text{gA}}/k_{\text{gR}}) (C_{\text{As}}^{\text{n}} - k_2/k_1 c_{\text{Am}}^{\text{n}})$	$\mathbf{R}_2 = k_2 / k_1 c_{\mathrm{Am}}^{\mathrm{n}}$
m = 0.5	_	$\begin{split} C_{\text{Rs}} &= \text{B} - [\text{B}^2 - 4\text{A}^2(1/\Phi_{\text{Am}}^2).\\ \cdot (k_{\text{gR}}/k_{\text{gA}})^2]^{1/2} / (2/\Phi_{\text{Am}}^2)(k_{\text{gR}}/k_{\text{gA}})^2\\ \text{A} &= \text{R}_1 \Phi_{\text{Am}} + C_{\text{g}} (k_{\text{gR}}/k_{\text{gA}})/\Phi_{\text{Am}}\\ \text{B} &= (k_2/k_1 c_{\text{Am}}^{n-0.5})^2 + (2\text{A}/\Phi_{\text{Am}})\\ (k_{\text{gR}}/k_{\text{gA}}) \end{split}$	$R_2 = C_{Rs}^{1/2} (k_2 / k_1 c_{Am}^{n-0.5})$
<i>m</i> = 1	-	$\begin{split} C_{\rm Rs} &= \left[(C_{\rm R}/\Phi_{\rm Am}) (k_{\rm gR}/k_{\rm gA}) + {\rm R_1} \right] / \\ / \left[(k_2/k_1 c_{\rm Am}^{\rm n-1}) + (1/\Phi_{\rm Am}) (k_{\rm gR}/k_{\rm gA}) \right] \end{split}$	$R_2 = (k_2/c_{Am}^{n-1}k_1) C_{Rs}$
<i>m</i> = 2	_	$\begin{split} C_{\rm Rs} &= (\{(1/\phi_{\rm Am}^2) (k_{\rm gR}/k_{\rm gA})^2 + \\ &+ 4(k_2/k_1c_{\rm Am}^{2-2}) ({\rm R}_1 \phi_{\rm Am} + \\ &+ C_{\rm R}(k_{\rm gR}/k_{\rm gA}))/\phi_{\rm Am} \}^{1/2} - \\ &- (1/\phi_{\rm Am}) (k_{\rm gR}/k_{\rm gA}))/(2k_2/k_1c_{\rm Am}^{-2}) \end{split}$	$R_2 = (k_2/k_1 c_{Am}^{n-2}) C_{Rs}^2$

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Dependence of Surface Concentrations on the Parameter $\Phi_{Am}(k_1/k_2 = 5)$

1 $C_{\rm R} = 1$, $C_{\rm A} = 1$; 2 $C_{\rm R} = 0.5$, $C_{\rm A} = 1$; 3 $C_{\rm R} = 0.1$, $C_{\rm A} = 1$; 4 $C_{\rm A} = 1$.





Dependence of the Relative Reaction Rate of the Second Reaction on the Parameter $\Phi_{Am}(k_1/k_2 = 5)$

1 $C_{\rm R} = 1$, $C_{\rm A} = 1$; 2 $C_{\rm R} = 0.5$, $C_{\rm A} = 1$; 3 $C_{\rm R} = 0.1$, $C_{\rm A} = 1$.



FIG. 3

Dependence of the Selectivity Factor on the Parameter $\Phi_{Am}(k_1/k_2 = 5)$

¹ $C_{\rm R} = 0.1, C_{\rm A} = 1; 2 C_{\rm R} = 0.5, C_{\rm A} = 1; 3 C_{\rm R} = 1, C_{\rm A} = 1.$





Dependence of the Maximum Attainable Concentration of Intermediate Product on the Parameter Φ_{Am}

1 Batch reactor, $k_1/k_2 = 5$; 2 Continuous mixed reactor, $k_1/k_2 = 5$; 3 Batch reactor, $k_1/k_2 = 1$; 4 Continuous mixed reactor, $k_1/k_2 = 1$. increasing temperature. The ratio of the reaction rate constants k_1/k_2 depends on the properties of the reaction and the catalyst. The value of this ratio was chosen so as to make the rate of the first reaction in the kinetic region higher or comparable with the second reaction (which is the case where a satisfactory yield of the intermediate product in the kinetic region is possible). Assuming a highly diluted solution, the ratio of the mass transfer coefficients depends only on the ratio of the diffusion coefficients and therefore on the ratio of molecular weights. Approximately we can write:

$$k_{\rm gA}/k_{\rm gR} = D_{\rm A}/D_{\rm R} = (M_{\rm R}/M_{\rm A})^{1/2} \,. \tag{22}$$

The calculations were performed for a single value of this ratio equal unity and assuming further that the ratio of the mass transfer coefficients is independent of composition of the reaction mixture, of the rate of mass transfer and temperature. The discussion is directed to the case where the desirable product is the intermediate product R, since this is the case where the question of selectivity is of fundamental importance for reactor design. Table I comprises the calculated relationships for the concentrations at the surface and the reaction rates (for reaction order 0; 0.5; 1; 2). The calculations itself were performed for a set of reactions of the first order. It is unlikely that the results for other order would be fundamentally different.

The Change of the Selectivity of Reaction in Transition from the Kinetic Region into the Region of External Diffusion

In the course of reaction concentration differences appear between the surface of the pellet and the stream of gas. The concentration of the starting substance A is atways lower at the surface than in the bulk of the gas. The concentration of the intermediate product R is higher at the surface of the pellet than in the gas for all times in a continuous mixed reactor. In a batch reactor and in a continuous plug flow reactor it is higher than the concentration in the gas before the maximum concentration of the intermediate product is attained and lower afterwards.

The variations of the course of the reaction in transition from the kinetic region into region of external diffusion can be illustrated by the dependence of the surface concentrations, reaction rates and the factor of selectivity on the parameter Φ_{Am} . An example of the dependence of these quantities on the parameter Φ_{Am} for different values of the ratio C_R/C_A is shown in Figs 1–3. From the results it can be concluded that on transition from the kinetic region into the region of external diffusion the factor of selectivity markedly decreases and, for example, for a system of consecutive reactions of the first order approximates to a negative limit given by the relation:

$$S_{\rm dif} = -k_{\rm gR} C_{\rm R} / k_{\rm gA} C_{\rm A} \,. \tag{23}$$

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With the increasing effect of the external diffusion the maximum attainable concentration of the intermediate product decreases as well. An example of the dependence of the maximum attainable concentration of the intermediate product on the parameter Φ_{Am} is given in Fig. 4.

The course of the selectivity in transition from the kinetic region into the region of the external mass transfer is somewhat different depending on whether the first reaction is much faster in the kinetic region than the second reaction, or whether their rates are comparable. In the first case (very selective catalyst) three regions can be distinguished. The kinetic region on one hand where both the first and the second reaction take place in the kinetic region. Here the mass transfer plays no role and the selectivity is determined solely by the kinetics. Further the region where the first reaction is influenced by external mass transfer, while the second reaction remains in the kinetic region. The decrease of the selectivity in this region is almost exclusively due to the decrease of the rate of the first reaction, while the rate of the second reaction remains practically unchanged. In the third region both the first and the selectivity is reduced by the decrease of the rate of the external mass transfer and the selectivity is reduced by the decrease of the rate of the first reaction and by the



FIG. 5

Dependence of the Selectivity Factor on k_1/k_2 Ratio at Different Values of the Parameter $\Phi_{Am}(C_R/C_A = 0.1)$

 $1 \ \Phi_{Am} = 0.1; \ 2 \ \Phi_{Am} = 0.5; \ 3 \ \Phi_{Am} = 1;$ $4 \ \Phi_{Am} = 5.$





Comparison of Temperature Dependence of Reaction Rates With and Without the Effect of External Mass Transfer (equal activation energies E = 10 kcal/mol)

1 Rate of the first reaction, no mass transfer effect; 2 rate of the first reaction with the effect of external diffusion 3 rate of the second reaction with the effect of external diffusion 4 rate of the second reaction in the kinetic region.

increase of the rate of the second reaction. If the reaction rates of both reactions are comparable in the kinetic region (less selective catalyst), then both reactions pass practically simultaneously into the region of the external diffusion. The case of the second reaction being faster in the kinetic region than the first one is of no practical significance since a satisfactory yield of the intermediate product cannot be achieved even in the kinetic region. It is of interest to examine the question of misinterpretation of the relationship between true kinetic properties of a catalyst and the properties which would have been determined if the effect of the external diffusion had been neglected. Examples of the dependence of the factor of selectivity on the ratio k_1/k_2 for a system of first order reactions and for different values of the parameter

 Φ_{Am} are shown in Fig. 5. It is apparent that the effect of the external mass transfer seemingly impairs the selectivity of the catalyst.





Temperature Dependence of the Selectivity Factor

1 Reactions with equal activation energies affected by external diffusion; 2 reactions with difference in activation energies $\Delta E =$ = 5 kcal/mol in the kinetic region.





Effect of Concentration on the Selectivity (constant ratio $C_{\rm R}/C_{\rm A} = 0.1$)

a) Order of the first reaction n = 0.5, $\Phi_{Am} = 1$, $k_1/k_2 = 1$; a_1 Same conditions for the kinetic region (*i.e.* $\Phi_{Am} = 0$); b n = 1, $k_1/k_2 = 1$, $\Phi_{Am} = 1$; $b_1 n = 1$, $k_1/k_2 = 1$, $\Phi_{Am} = 0$; c n = 2, $k_1/k_2 = 1$, $\Phi_{Am} = 1$; $c_1 n = 2$, $k_1/k_2 = 1$, $\Phi_{Am} = 0$. The Effect of Temperature on the Selectivity of Reaction (under Constant Hydrodynamic Conditions)

The value of the parameter Φ_{Am} depends on temperature because the reaction rate increases with temperature exponentially, while the value of the mass transfer coefficient changes with temperature only slightly. In the following it will be assumed that the coefficients of mass transfer do not change with temperature. The temperature increase will therefore result in transition of the pellet's regime from the kinetic region into the region of the external diffusion and accordingly in deterioration of the selectivity factor. Fig. 6 plots the dependence of the reaction rate of the first and the second reaction on temperature provided that the activation energies of both reactions are the same. In view of the equality of activation energies of both reactions, the effect of temperature on the selectivity is induced only by the action of external mass transfer. Fig. 7 shows the dependence of the factor of selectivity on temperature for the same situation. An example of the dependence of the selectivity factor on temperature for a reaction with the absence of the external mass transfer and the difference in activation energies 5 kcal/mol is shown for comparison. It is obvious that the effect of the external mass transfer will play an extraordinarily important role in affecting the reaction selectivity. Its influence is in some regions comparable with the temperature dependence of the selectivity of reactions with considerably different activation energies.

The Effect of Concentration on the Selectivity (under Constant Hydrodynamic Conditions)

In order to examine the change of the external mass transfer effect on the selectivity due to the change of concentration of the starting substance, we studied the effect of the change of concentration of the starting substance on the selectivity at a constant ratio of the concentration of intermediate product and that of the starting substance. The conclusions can serve for estimation of the suitability of working with higher or lower concentrations of starting substance. It is advantageous to analyse two cases separately: A case when both reactions are of the same order, and, on the other hand, when they differ. In the former case the change of concentration has no effect on the selectivity in the kinetic region, provided that the value of the ratio $C_{\rm R}/C_{\rm A}$ remains constant. The change of the selectivity in the diffusion region can be anticipated from the following reasoning. The external mass transfer is of the first order with respect to concentration, and the reactions are of the order n = m. The decrease of concentration will slow down more that step having higher order. Therefore, if the order of the reaction is higher than unity, the decrease of concentration will shift the regime toward the kinetic region. If the reaction order is less than unity, the concentration decrease will, on the contrary, shift the regime of the pellet toward the region of the external mass transfer. The analysis is more complex for reaction systems with different reaction orders as the selectivity is also affected by the change of concentration in the kinetic region; namely the concentration increase decreases the selectivity, provided that the order of the second reaction is higher. A review of possible combinations is summarized in Table II. Fig. 8 illustrates some of them.

Examples of Influenced Yield in the Reactor

In the foregoing paragraphs we have qualitatively clarified the problem of the effect of the external mass transfer on the selectivity of a reaction. To discuss the yield, one has to solve an accurately defined type of reactor, since the yield of consecutive reactions is affected (isothermal reactors) by the type of the reactor (residence time distribution). Examples were calculated for a continuous plug flow reactor and a batch reactor. The last two types of reactors do not differ from the kinetic point of view and the results will therefore be presented together. A comparison of the performance of a batch reactor and a continuous mixed reactor in the dependence on the degree of conversion for different values of the parameter $\Phi_{\rm Am}$ is shown in Fig. 9. Fig. 10 plots the dependence for different values of the parameter $\Phi_{\rm Am}$ and the ratio k_1/k_2 .

These results prove that the effect of the external mass transfer may significantly deteriorate the selectivity of the process involving consecutive reactions. In the region



FIG. 9

Dependence of the Yield of Reactor on Conversion $(k_1/k_2 = 5)$

1 Batch reactor, $\Phi_{Am} = 0$; 2 batch reactor, $\Phi_{Am} = 0$; 3 continuous mixed reactor, $\Phi_{Am} = 0$; 4 continuous mixed reactor, $\Phi_{Am} = 0$; 5 batch reactor, $\Phi_{Am} = 1$; 6 continuous mixed reactor, $\Phi_{Am} = 1$.





Dependence of Concentration of Intermediate Product in Batch Reactor on Conversion of Starting Substance

 $\begin{array}{ll} 1 & \varPhi_{\rm Am} = 0, \ k_1/k_2 = 5; \ 2 & \varPhi_{\rm Am} = 1, \\ k_1/k_2 = 5; \ 3 & \varPhi_{\rm Am} = 0, \\ k_1/k_2 = 1; \ 4 & \varPhi_{\rm Am} = \\ = 1, \ k_1/k_2 = 1. \end{array}$

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TABLE II

	т	n/m	Effect of increased concentration on selectivity at constant ratio $C_R/C_A = 0.1$	
			kinetic region	diffusion effect
>1	>1	1	no influence	decreases
< 1	< 1	1	no influence	increases
1	1	1	no influence	no influence
>1	≥ 1	> 1	increases	increases or decreases
≥1	< 1	< 1	decreases	decreases
≦1	< 1	>1	increases	increases
< 1	< 1	< 1	decreases	increases or decreases
<1	> 1	< 1	decreases	decreases
>1	< 1	>1	increases	increases

Effect of Concentration (constant hydrodynamic conditions) on Selectivity

of strong influence of the external mass transfer (diffusion region) it is impossible to achieve a high yield of the intermediate product even if the catalyst is very selective. These conclusions may have a very significant practical importance. On their basis it can be concluded for example, that if the properties of catalysts are studied in laboratories under conditions when the external mass transfer is not eliminated, then inevitably, more active catalysts will appear less selective and the selectivity of the process will decrease with increasing temperature. The hydrodynamic conditions in laboratory reactors used for the study of the properties of catalysts are, as a rule, considerably different from those in industrial reactors. It is then quite possible that a catalysts which proved unselective in the laboratory would provide a good yield of the intermediate product in industrial reactors.

LIST OF SYMBOLS

a _m	specific external surface of catalyst pellet related to unit of weight of catalyst (m^2/g)
c_A, c_R	concentration of species A and R in volume of mixture (mol/m^3)
C_A, C_R	dimensionless concentrations of species A and R in volume of mixture defined by
	Eq. (8)
c_{As}, c_{Rs}	concentration of species A and R on surface of catalyst pellet (mol/m ³)
C_{As}, C_{Rs}	dimensionless concentration of species A and R on surface of catalyst defined by
	Eq. (8)
Da	modified Damköhler group defined by Eq. (20) and (21)
$D_{\rm A}, D_{\rm R}$	diffusion coefficient of species A and R (m^2/h)
F	feed of species A and R (m^3/h)
k_{1}, k_{2}	reaction rate constants of first and second reaction $(m^3/h g_{Kat} mol^{m-1})$
Kan, Kap	mass transfer coefficients of species A and R (m/h)

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$M_{\rm A}, M_{\rm R}$	molecular weight of A and R (g/mol)
n, m	reaction order of first and second reaction
rlom	reaction rate of first reaction at standard concentration and with absence of external mass transfer $~(mol/h~g_{KAT})$
r ₁ , r ₂	reaction rate of first and second reaction (mol/h g _{KAT})
R_{1}, R_{2}	relative reaction rates defined by Eq. (9)
$r_{\rm DA}, r_{\rm DR}$	transfer rates of A and R (mol/h g _{KAT})
S	selectivity factor defined by Eq. (13)
t	time of reaction in batch reactor (h)
VR	yield of R defined by Eq. (15)
ν	reactor volume (m ³)
W	weight of catalyst (g)
x	degree of conversion of starting substance A
ϕ_{Am}	parameter defined by Eq. (12)

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