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DETERMINATION OF THE VIRTUAL RATE CONSTANT OF A CATALYTIC ISOMERIZATION PROCESS

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In connection with catalytic reactions, it is the overall reaction rate that is defined in practice. However, the processes proceed through a number of steps and accordingly it is more preferable to consider each individual partial process. An equation has been derived for the determination of the virtual rate constant of the reaction occurring at the internal surface of the catalyst particles which also contains the figures of mass transfer (external and pore-diffusion). A possibility is hereby given to interact at the most advantageous point, in order to speed up the overall reaction. The overall reaction rate is, at best, equal to that of the surface reaction (if the diffusion hindrance is eliminated) and consequently the latter is preferably determined.

A mathematical estimation has also been derived for the determination of the mass transfer occurring in the boundary layer around the catalyst particles.

INTRODUCTION

Catalytic reactions occurring by the action of a porous catalyst proceed through a number of consecutive partial processes:

1. Diffusion of the reactants onto, and of the products away from the external surface of the catalyst (termed external diffusion).

2. Diffusion of reactants and products within the pores of the catalyst (termed pore diffusion).
3. Adsorption of reactants at the internal surface and desorption of products from the external surface of the catalyst.
4. Reaction at the internal surface of the catalyst.

The above-mentioned partial processes have been given a detailed analysis in the literature [1, 2].

The overall reaction rate is determined by one or more steps.

The reaction rate is defined in the literature - in accordance with industrial practice - by the following equation:

$$r_A = B \frac{dx_A}{dw} \tag{1}$$

It is apparent from Equation (1) that the overall reaction rate refers to the unit mass of the catalyst.

This approach undoubtedly very simple and accordingly it simplified the industrial application; however, it is burdened by a number of drawbacks:

- the effect of the individual partial processes upon the overall reaction rate is not taken into consideration;
- it is valid only for a given catalyst bed, and in the case of a change in any of the parameters of the catalyst bed, the results of the measurement are no longer valid;
- no information is provided on the temperature dependence of the reaction.

It seems more preferable to apply an approach in which the partial processes are, one by one, taken into consideration. By this way, it is possible to speed up the rate-determining step and thereby to modify the overall reaction rate in an advantageous direction. For this purpose it is, however, necessary to know the rate-determining step or steps.

From among the four partial processes described in the foregoing it is only the rate of the surface reaction which is independent of the geometric parameters of the catalyst bed and accordingly its determination seems to be of paramount importance. It is the rate of the surface reaction that determines the process, if the diffusion hindrance [3] has no role to play in the process. Adsorption cannot be separated from the surface reaction, and consequently an apparent rate constant is used,which also includes the rate constant of the adsorption process.

It can be mentioned as a further advantage of the approach that the empyrical formula of Arrhenius [4] holds for the surface reaction and consequently it is possible to calculate the rate constants of a whole temperature range, if the rate constants for two different temperatures have been determined.

The method is preferably demonstrated on a catalytic isomerization reaction, where a gaseous component is transformed into another similar one, without any change in mole numbers.

DESCRIPTION OF THE MODEL

Let us consider the following process:

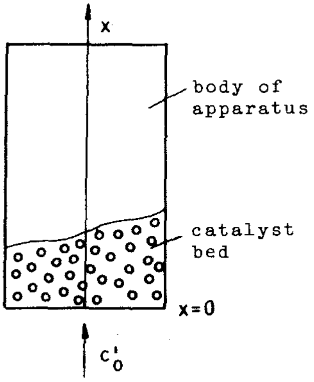

Fig. 1

The reactant $c'(o)$ concentration enters the apparatus at a point $x = 0$. The molecules of the reactant diffuse into the interior of the catalyst particles, are transformed there and return into the streaming gas mixture of the apparatus, containing the reagent and the product gases.

The gas mixture continuously becomes poorer in the reagent component along the "X" height co-ordinate, and simultaneously the concentration of the product increases in the bulk of the gas.

The sum of the concentration of the product and the reagent is constant, and consequently it is sufficient to follow only the changes in the concentration of the reagent.

THE MATHEMATICAL MODEL

The mathematical model is given by the mass balances, as formulated for the unit volume of the interior of the particle or for the unit volume of the catalyst bed. A detailed description of these will be omitted for the sake of brevity. The following simplifications have been adopted in establishing the mathematical model:

1. The mathematical model holds only for a stationary state, when the concentration in a given cross section of the catalyst bed does not change in time.
2. The concentration of the gas in a given cross section is constant.
3. Radial diffusion in the gas is negligible compared to the convective stream.
4. The catalyst particles are spheres of equal radii and they contact each other only in a point-like manner.
5. The reaction within the pores is of the first order.
6. The process is isothermal.
7. The adsorption process is instantaneous, that is to say, its rate constant may be incorporated into the apparent rate constant of the surface reaction (in this case adsorption and surface reaction have been regarded a single partial process).
8. The particles are homogenous.
9. Any transformation on the outer surface of the particles is negligible. (The internal surface of the particles is larger by several orders of magnitude than the external spherical surface.)

With the above-described simplification in view, the system of differential equations describing the process can be written by means of the differential balance as formulated for the catalyst particle and for the gas.

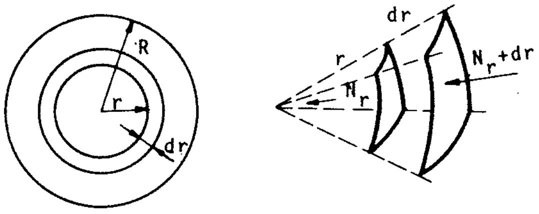

Fig. 2

Fig. 2 shows a section of a spherical catalyst particle, in which diffusion and reaction of the reagent takes place.

The material balance for a unit volume of the particle is the following:

$$4(r + dr)^2 \pi \vartheta D \frac{\partial}{\partial r} \left[c(x,r) + \frac{\partial c(x,r)}{\partial r} dr\right] =$$

$$= 4\ r^2 \pi \vartheta D \frac{\partial c(x,r)}{\partial r} + 4\ r^2 \pi dr a k c(x,r) \qquad (2)$$

Equation (2), after simplifications and carrying out the operations, can be written in the following form:

$$\vartheta D \left[\frac{\partial^2 c(x,r)}{\partial r^2} + \frac{2}{r} \frac{\partial c(x,r)}{\partial r}\right] = akc(x,r) \qquad (3)$$

After rearrangement:

$$\frac{\partial^2 c(x,r)}{\partial r^2} + \frac{2}{r} \frac{\partial c(x,r)}{\partial r} = \frac{ak}{D^*} c(x,r) \qquad (4)$$

where

$$D^* = \vartheta D \qquad (5)$$

The mass balance of the reacting gas is written for a unit volume of the catalyst bed.

The number of particles present in the unit volume: n [pieces/L^3] depends on the dimensions and order of the particles; this value is constant for the whole bed.

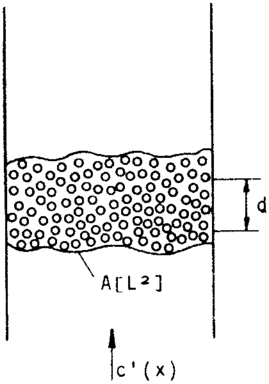

Fig. 3

$$v'A\varepsilon c'(x) = 4\ R^2\pi A dx n \vartheta D\left[\frac{\partial c(x,r)}{\partial r}\right]_{r=R} +$$

$$+\ A\varepsilon v'\left[c'(x) + \frac{dc'(x)}{dx}\,dx\right] \qquad (6)$$

Equation (6) expresses that the decrease in concentration in the bulk of the gas is brought about by diffusion oriented against the surface of the particles.

Having carried out the operations and simplifications, Equation (6) becomes.

$$\frac{dc'}{dx} = -\ b\ \left[\frac{\partial c(x,r)}{\partial r}\right]_{r=R} \qquad (7)$$

where

$$b = \frac{4\ R^2\pi n D^*}{\varepsilon v'} \qquad (8)$$

is a factor including the geometrical parameters of the catalyst bed and the linear gas velocity.

Accordingly, the system of differential equations to be solved is the following:

$$\frac{\partial^2 c(x,r)}{\partial r^2} + \frac{2}{r}\,\frac{\partial c(x,r)}{\partial r} = \frac{ak}{D^*}\,c(x,r) \qquad (9)$$

$$\frac{dc'(x)}{dx} = -\ b\ \left[\frac{\partial c(x,r)}{\partial r}\right]_{r=R} \qquad (10)$$

Equations (8) and (9) are in connection through the value of the concentration gradient arising at the external surface of the catalyst particles.

Equation (2) is partial; but having a construction that it can directly be integrated with respect to "r".

The general solution is the following:

$$c(x,r) = \frac{1}{r}\,[A\ \mathrm{ch}(\sqrt{\alpha}\ r) + B\ \mathrm{sh}(\sqrt{\alpha}\ r)] \tag{11}$$

where

$$\alpha = \frac{ak}{D^*} \tag{12}$$

A and B are integration constants.

The values of A and B can be calculated by the boundary conditions written for a particle.The boundary conditions are written with reference ot the centre of the particles and to their external surface:

$$\left[\frac{\partial c(x,r)}{\partial r}\right]_{r=0} = 0 \tag{13}$$

However, condition (13) cannot be applied, since in the expression $\frac{\partial c}{\partial r}$, "r" is in the denominator and the expression is meaningless if $r = 0$ is substituted. Instead, the following may be written, as follows from the diffusion process [5]:

$$\lim_{r\to 0} r^2\left(\frac{\partial c}{\partial r}\right) = 0 \tag{14}$$

It is apparent that after multiplication by "r^2", the denominator does not contain "r".

The second condition is determined by the circumstances prevailing at the external surface of the particle.

It may be assumed that the concentration of the bulk of the gas is present at the orifice of the pores. (The value of the mass transfer coefficient, k_c, is assumed to be infinite.)

In this case,

$$c'(x) = c(x,R) \tag{15}$$

However, if $k_c \neq \infty$, the Newtonian boundary may be written:

$$D^*\left[\frac{\partial c(x,r)}{\partial r}\right]_{r=R} = k_c[c'(x) - c(x,R)] \tag{16}$$

In the case of $k_c = \infty$, Equation (16) becomes Equation (15). The selection of the boundary condition to be applied may be done on the basis of information given by the measurements described in [6]. In some cases, the following calculation may be applied instead of measurements:

k_c may be regarded as infinite, if its value is greater by two orders of magnitude than the value of $D^*\left[\frac{\partial c(x,r)}{\partial r}\right]_{r=R}$ that is to say

$$k_c >> D^*\left[\frac{\partial c(x,r)}{\partial r}\right]_{r=R} \tag{17}$$

Boundary condition (15) may be applied in this case.

The order of magnitude of the value of k_c can be estimated on the basis of [7] while that of D^* on the basis of [8].

No information whatever is available on the value of $\left[\frac{\partial c(x,r)}{\partial r}\right]_{r=R}$ but it can be proved that even the greatest concentration gradient developed along the axis of the catalyst bed is smaller than the concentration gradient of the particle of $c'(o)$ concentration calculated with the assumption $k_c = \infty$ and placed into an infinite environment. Accordingly, the gradient calculated on the basis of this assumption approximates the real value of $\left[\frac{\partial c(x,r)}{\partial r}\right]_{r=R}$ from above.

If this value is substituted into Equation (17) and the relation is true, it is also possible to calculate with the boundary condition (15) in the case of the really prevailing concentration gradient.

With application of boundary condition (14),

$$A = 0 \tag{18}$$

By application of boundary conditions (15) or (16) and Equation (11), the following equation is obtained for the change in concentration along the axis:

$$c'(x) = c'(0)\, e^{-\frac{b}{R}[R\sqrt{\alpha}\,\mathrm{cth}(\sqrt{\alpha}\,R) - 1]x} \tag{19}$$

and

$$c'(x) = c'(0)\, e^{-bk_c \frac{R\sqrt{\alpha}\,\mathrm{cth}(\sqrt{\alpha}\,R) - 1}{D^*[R\sqrt{\alpha}\,\mathrm{cth}(\sqrt{\alpha}\,R) - 1] + k_c R} x} \tag{20}$$

Equations (19) and (20) contain the value of the virtual rate constant, "k", in an implicit manner.

DETERMINATION OF THE APPARENT RATE CONSTANT "k"

Equations (19) and (20) describe the changes in the concentration of the bulk of the gas as a function of the height co-ordinate. The parameters used (geometrical data of the catalyst bed, diffusion coefficient and mass transfer coefficient of the external diffusion) are such that are either at our disposal or can easily be determined [7, 8].

If the concentration of the bulk of the gas, c'(x) is determined along the axis of the catalyst bed in a point of known co-ordinates (it is most preferable to choose the height of the catalyst bed and the concentration of the gas leaving the system), the value of "k" can be calculated with the following transcendent equation:

$$L = \sqrt{\alpha}\,\mathrm{cth}\,(\sqrt{\alpha}\,R) \tag{21}$$

where

$$L = \frac{v'\varepsilon[\ln c'(0) - \ln c'(x)]}{4\,R^2\pi n\,D^* x} + \frac{1}{R} \tag{22}$$

if boundary condition (15) is applied, and

$$L = \frac{v'\varepsilon k_c[\ln c'(0) - \ln c'(x)]}{k_c\ 4\ R^2\pi n D^* x - D^*\varepsilon v'[\ln c'(0) - \ln c'(x)]} + \frac{1}{R} \qquad (23)$$

if boundary condition (16) is used in the calculations.

Equation (15) is solved for "α" and we have

$$ak = \alpha D^* \qquad (24)$$

Equation (24) gives the product of the virtual rate constant and the specific surface of the catalyst particle.

A similar consideration can also be applied for the case of non-spherical catalyst particles. The only difference is that the differential equations are not written in spherical co-ordinates, and the factor "b" in Equation (7), describing the geometrical paramaters, has to be modified.

Fig. 4 shows particles of cylinder and "flake" shape.

The differential equation for cylindrical particles is the following:

$$\frac{\partial^2 c(x,r)}{\partial r^2} + \frac{1}{r}\frac{\partial(x,r)}{\partial r} = \frac{ak}{D^*}\, c(x,r) \qquad (25)$$

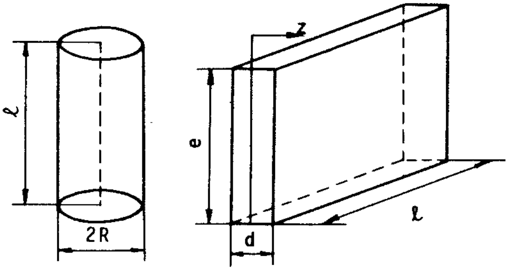

Fig. 4

whereas for "flake"-shaped particles it is:

$$\frac{\partial^2 c(x,z)}{\partial z^2} = \frac{ak}{D^*}\, c(x,z) \qquad (26)$$

In the case of cylinders, the mass balance of the bulk of the gas is the following:

$$\frac{dc'(x)}{dx} = -\, b_{\text{cylinder}} \left[\frac{\partial(x,r)}{\partial r}\right]_{r=R} \qquad (27)$$

where

$$b_{cylinder} = \frac{2\ R\pi\ell\ nD^*}{\varepsilon v'} \qquad (28)$$

and in the case of "flakes"

$$\frac{\partial c'(x)}{\partial x} = -\ b_{flake}\ \left[\frac{\partial(x,z)}{\partial z}\right]_{z=\frac{d}{2}} \qquad (29)$$

$$b_{flake} = \frac{2\ e\ell nD^*}{\varepsilon v'} \qquad (30)$$

Mass transport - occurring only at the superficies of the cylinder and at the e.ℓ plate of the "flake" - was taken into consideration when deriving the equations. This omission causes the values of "b" to be taken into account at a value lower than the real one. On the other hand, when describing the model it was assumed that the particles touch in one point only, that is to say, touching of the particles does not decrease the surface area available for diffusion. The errors arising on account of these two omissions influence the value of "b" in an opposite sense, and consequently it is not likely that it causes any considerable deviation in the calculated values.

SUMMARY

The virtual rate constant of catalytic isomerization was determined, with certain suppositions and with the application of the geometric properties of the particles.

In cases where the influence of the external diffusion resistance and that of pore diffusion does not manifest itself, the rate of the surface reaction is equal to the overall reaction rate.

The rates of external diffusion and pore diffusion were also taken into account, and consequently it is possible to select the

rate-determining process. A possibility is given hereby to interact at the most advantageous point in order to attain a more favourable overall reaction rate.

The empyrical formula of Arrhenius holds for the virtual rate constant calculated in accordance with the above, and consequently it is possible to determine the temperature dependence of the reaction from two measurements.

SYMBOLS USED

α	specific surface of catalyst particle, L^{-1}
$c(x,r)$	concentration in the interior of the particle, mole/mole
$c'(x)$	concentration in the bulk of the gas, mole/mole
k	virtual rate constant of the surface reaction, t^{-1}
k_c	mass transfer coefficient of the external diffusion, mole/L^2t
n	number of particles present in the unit volume of the catalyst bed, L^{-3}
r	radial co-ordinate, L
r_A	overall reaction rate, mole/Mt
v'	linear gas velocity, L/t
w	mass of catalyst, M
z	linear co-ordinate in case of "flake"-type particle, L
x	height co-ordinate, L
x_A	conversion, mole/mole
B	feeding rate, mole/t
$D^{*}=\vartheta D$	effective diffusion coefficient, L^2/t
R	radius of catalyst particles, L

ε free surface fraction of catalyst bed, L^2/L^2

ϑ porosity, L^3/L^3

In the signs, the internationally accepted dimension symbols were used:

L length

M mass

t time

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РЕЗЮМЕ

При контактных каталитических реакций на практике определяется валовая скорость реакции. Имея в виду то, что процесс происходит в нескольких ступенях, оказывается целесообразным отдельно учитывать частичные процессы. Выведена формула для определения константа виртуальной скорости реакции, происходящей на поверхности гранул катализатора, содержащего характерные данные массопередачи поровой диффузии. Таким образом, дается возможность вмешиваться с целью ускорения валового процесса на самом подходящем месте. Определение скорости поверхностной реакции является целесообразным, ведь скорость валовой реакции и в оптимальном случае (при прекращении диффузионного торможения) может достигать значения последней.

Автором была выведена расценка для определения массопередачи происходящей в граничной пленке вокруг гранул катализатора.