

SEMI-LINKED PORE MODEL FOR POROUS CATALYSTS

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A model of porous medium has been developed in which one part of cylindrical pores is mutually completely separated whereas the other part is interlinked so that an intermixing of pore contents may occur. For this model structure, relations were derived for determining the effectiveness factor of a catalytic reaction proceeding on the inner surface of pores. Simulation calculations for the *p*-, *o*-hydrogen conversion with the bidisperse structure of the catalyst reveal the effect of the size and number of pores. Effectiveness factors obtained by an experimental study of the catalytic *p*-, *o*-hydrogen conversion in the region of internal diffusion were correlated by using a simplified variant of this model and satisfactory agreement between the calculations and experiment was found.

For modelling of the diffusion of gases through porous catalysts and adsorbents, models based on the idea that the porous structure may be replaced by a bundle of straight parallel cylindrical capillaries with circular cross-section have recently proved useful. Different versions of this basic idea consider either that all pores (capillaries) have identical radii (Rothfeld model¹) or that there are several groups of pores with different radii (Feng, Kostrov and Stewart²). A more general case is represented by the model due to Johnson and Stewart³ or Satterfield and Cadle⁴ in which all pores whose radii are between r_{\min} and r_{\max} are considered (r_{\min} and r_{\max} are radii of narrowest and widest pores in the porous substance). It is further assumed in these models that the average angle between the direction of the diffusion flux and capillary axes is smaller than 90° so that the diffusion path is longer than the diffused distance measured in the direction of diffusion. This elongation of the diffusion path is characterized by the tortuosity factor, q , whose value must be determined experimentally. Thus, the tortuosity becomes an adjustable parameter, which includes inherently also other factors not considered in the model. Such are *e.g.* crookedness of pores, variability of their radii along the pore axis, roughness of the inner surface, *etc.*

The success of the outlined models of porous medium for diffusion of gases raises the hopes that the idea of the bundle of parallel cylindrical pores could prove useful even for the description of the effect of diffusion in a porous catalyst structure on the course of a heterogeneous catalytic reaction proceeding on inner walls of the capillaries. Any solution of this problem, however, must take into account the following requirement imposed on models of porous medium in catalytic reactions: at equal distances from the outer surface of a catalyst particle (which is surrounded by the reaction mixture of constant composition), an identical composition of the

reaction mixture can be expected regardless of the fact which pore radius is actually considered. Were all the pores along their axes perfectly separated, concentration profiles of reaction components along pore axes would be different in pores with different radii and the assumption of equal composition at equal distances from the outer surface would be violated. However, this condition would be satisfied if all the pores had identical radii or if pores of different radii were mutually interlinked in such a manner that would enable intermixing of their contents at all distances from the outer surface of the catalyst particle.

Limiting alternatives (existence of either completely separated or perfectly interlinked pores) may be used for construction of a more general model: the porous structure will be created by straight cylindrical capillaries with circular cross-sections of different radii r . The number of pores whose radii are between r and $r + dr$ is determined in accordance with the requirement that the distribution curves of pores in the model medium and in the substituted real porous medium be identical. Pores from the group with radii $r - (r + dr)$ and the normal to the outer surface of the porous particle form on the average a certain angle, which causes the tortuosity of these pores to be equal to $q(q = q(r))$. Of pores from this group, a certain fraction $\Delta(\Delta = \Delta(r))$ is mutually perfectly separated; the fraction of perfectly interlinked pores in this group is then $[1 - \Delta(r)]$. This model is schematically depicted on Fig. 1.

Our model of porous medium is thus characterized by three functions: frequency function of the distribution of pore volumes with respect to their radii, $f(r)$, tortuosity function, $q(r)$, and distributivity function, $\Delta(r)$. This general method of description allows us to make an easy transition to several more simple (and probably more real) cases: thus, for example, the porous medium can contain only pores of one or several certain radii or the tortuosity can have a constant value for pores of all different radii ($q = \text{const.}$) or pores from a certain range of radii can display a constant tortuosity which differs from that displayed by pores from another range of radii. In the same manner, the distributivity Δ may be considered either as entirely independent of the radius ($\Delta = \text{const.}$) or as constant in certain intervals of pore radii.

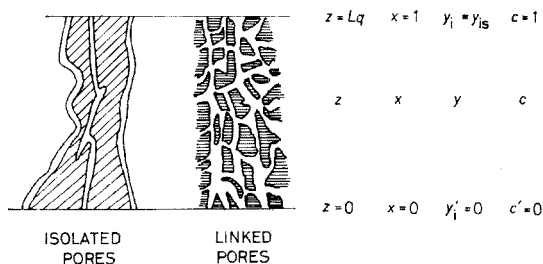


FIG. 1

Scheme of the Semi-Linked Pore Model

The frequency function of the pore volume distribution will be introduced so that the product $f(r) dr$ may represent the fraction of the volume of pores with radii $r - (r + dr)$ from the total pore volume. Then it must hold

$$\int_{r_{\min}}^{r_{\max}} f(r) dr = 1 \quad (1)$$

(from now on the lower and upper limits of the pore radii will be simplified to $r_{\min} = 0$, $r_{\max} = \infty$). The terms $\Delta(r) f(r) dr$ and $[1 - \Delta(r)] f(r) dr$ then obviously represent volume fractions of mutually separated and perfectly interlinked pores with radii $r - (r + dr)$ from the total pore volume, resp.

By using functions $f(r)$, $q(r)$ and $\Delta(r)$ we can determine the numbers of isolated, $dn_{\text{isol}}(r)$, and interlinked, $dn_{\text{link}}(r)$, pores with radii $r - (r + dr)$ which open into a unit of the outer surface of the porous particle. If the total pore volume related to volume unit of the porous particle is equal to ε (porosity), the following relations might be easily obtained

$$dn_{\text{isol}}(r) = \varepsilon \Delta(r) f(r) dr / \pi r^2 q(r), \quad (2)$$

$$dn_{\text{link}}(r) = \varepsilon [1 - \Delta(r)] f(r) dr / \pi r^2 q(r) \quad (3)$$

taking into account that the volume of isolated or interlinked pores (with radii $r - (r + dr)$) related to volume unit of the porous substance is $\varepsilon \Delta(r) f(r) dr$ or $\varepsilon [1 - \Delta(r)] f(r) dr$, resp., and the volume of one pore is $\pi r^2 q(r)$.

In the following we will consider a porous catalyst in the form of an infinite slab with half-width L , with the dimensionless length coordinate x perpendicular to the outer surface ($x = 0$ in the centre of the particle, $x = 1$ at the outer surface) and with unit cross-section parallel with the outer surface. The length coordinate is measured in the direction of the axis of cylindrical pores ($z = 0$ in the centre, $z = Lq$ at the outer surface of the particle). An isothermal catalytic reaction among p reaction components proceeds on pore walls in an m -component reaction mixture ($p \leq m$)

$$\sum_{i=1}^p a_i A_i = 0, \quad (i = 1, \dots, p; p \leq m), \quad (4)$$

where a_i is the stoichiometric coefficient of reaction component A_i ($i = 1, \dots, p$) ($a_i < 0$ for reactants and $a_i > 0$ for reaction products). The total molar concentration of the gaseous mixture is c_T (mol/cm³), the mole fraction of component A_i is y_i ; the composition of the reaction mixture at the outer surface of the particle is $y_{i,s}$.

The rate of reaction of key component A_1 related to surface unit of pores, R , is generally equal to $R = R(c_T, y_i)$ (mol/cm²s). It may be shown easily that the rate

of reaction related to volume unit of the porous particle ($\text{mol}/\text{cm}^3\text{s}$) is equal to $2\varepsilon\langle 1/r \rangle R$, where the integral mean value $\langle 1/r \rangle$ is defined by

$$\langle 1/r \rangle = \int_0^\infty [f(r)/r] dr. \quad (5)$$

In the case of diffusion of a multicomponent gaseous mixture through a pore in the transition region, the molar flux density of the key component (A_1) towards the interior of the particle, \mathcal{N} , (related to unit cross-section of the pore with radius r) may be expressed by

$$\mathcal{N} = \mathcal{D}(r) c_T [dy_1(r, z)/dz], \quad (6)$$

where $\mathcal{D}(r)$ is the diffusion coefficient of the key component in the multicomponent mixture; in the presence of reaction (4) this coefficient is defined by⁵

$$\mathcal{D}(r)^{-1} = (1/\mathcal{D}_{k1}) + \sum_{j=1}^p [(y_{js} - (a_j/a_1) y_{1s})/\mathcal{D}_{1j}] + \sum_{j=p+1}^m y_{js}/\mathcal{D}_{1j}. \quad (7)$$

$\mathcal{D}(r)$ is related to the radius through the Knudsen diffusion coefficient \mathcal{D}_{k1} of component A_1 :

$$\mathcal{D}_{k1} = (2/3) r w_1, \quad (8)$$

where w_1 is the thermal velocity of molecules A_1 [$w_1 = (8RT/\pi M_1)^{1/2}$]. It follows from Eq. (7) that $\mathcal{D}(r)$ depends also on the composition of the reaction mixture which surrounds the particle, y_{js} . Eq. (6) may be written also for other components of the reaction mixture; this allows us to express mole fractions of non-key components ($i = 2, \dots, m$) as linear functions⁵ of y_1 :

$$y_i - y_{is} = \delta_i (y_1 - y_{1s}), \quad (9)$$

with

$$\delta_i = \begin{cases} (a_i/a_1) (\mathcal{D}/\mathcal{D}_{is}) & (i = 2, \dots, p) \\ (\mathcal{D}_1/\mathcal{D}_{is}) & (i = p + 1, \dots, m). \end{cases} \quad (10)$$

The diffusion coefficients \mathcal{D}_i are defined by

$$\mathcal{D}_{is}^{-1} = \begin{cases} [(a_i/\mathcal{D}_{ki}) + \sum_{j=1}^p (a_j y_{js} - a_j y_{is})/\mathcal{D}_{ij} + a_i \sum_{j=p+1}^n y_{js}/\mathcal{D}_{ij}]/a_i; & (i = 2, \dots, p) \\ y_{is} \sum_{j=1}^p a_j/\mathcal{D}_{ij} & (i = p + 1, \dots, m) \end{cases} \quad (11)$$

Using relation (9), the rate of reaction of the key component, R , can be expressed as a function of y_1 only, i.e. $R = R(y_1)$.

Reaction in an Isolated Pore

Mass balance of the key component in an elementary part of a pore with radius r and length dz may be expressed as

$$d^2c/dx^2 = M^2\varrho(c), \quad (12)$$

in which the reduced mole fraction of the key component ($c = c(r, x)$) and the dimensionless length coordinate x are defined by

$$c = y_1/y_{1s}, \quad x = z/Lq. \quad (13)$$

In the case of a reversible reaction it is advantageous to define c by the relation $c = (y_1 - y_1^{eq})/(y_{1s} - y_1^{eq})$, where y_1^{eq} is the mole fraction of the key component in the equilibrium mixture which arises from the mixture surrounding the particle at isobaric conditions⁶, because then it holds $c \in (0,1)$ similarly as in the irreversible case. The dimensionless reaction rate ϱ is related to the rate at the outer surface of the particle R_s ($R_s = R(y_{1s})$) by

$$\varrho = R(y_1)/R_s \quad (14)$$

and M is the dimensionless Thiele modulus for isolated pores ($M = M(r)$), which can be written as

$$M = \Phi/F(r) \quad (15)$$

and Φ is the dimensional part of the Thiele modulus:

$$\Phi^2 = L^2 R_s / c_T y_{1s}. \quad (16)$$

[In the case of reversible reaction, y_{1s} in the denominator must be replaced by $(y_{1s} - y_1^{eq})$]. As the rate of reaction of the key component at the outer surface of the particle, R_s , is related to unit catalyst surface, the quantity Φ depends only on the reaction kinetics and on the magnitude of the catalyst particle. All texture and diffusional characteristics of the porous substance are included in the dimensional function $F(r)$

$$F^2(r) = (r/2) \mathcal{D}(r)/q^2(r). \quad (17)$$

The differential balance equation (12) is supplemented by the boundary conditions

outer surface of the particle: $x = 1 \quad c = 1$,

symmetry condition (particle centre): $x = 0 \quad dc/dx = 0$. (18)

The solution of balance (12) with boundary conditions (18) yields the profile of the dimensionless concentration along the pore length $c = c(r, x)$. It is remarkable that the pore radius affects the solution only through the Thiele modulus M , in which the function F contains r explicitly but also implicitly as $q(r)$ and $\mathcal{D}(r)$.

For determining the amount of the key component which has reacted in a pore with radius r , it is sufficient to know the concentration gradient at the outer surface of the particle ($x = 1$), i.e. $c'(r, 1)$ (the dash denotes the derivative with respect to x); with the help of this quantity, the molar flux of the key component through the opening of one pore towards the interior of the particle may be expressed as $\pi r^2 \mathcal{D}(r) c_{T} y_{1s} c'(r, 1) / L q(r)$. There are $dn_{\text{isol}}(r)$ pore openings with radii $r - (r + dr)$ on unit surface of the outer particle surface, through which the key component flows into the particle (and reacts there subsequently due to the existing steady state) in the amount of

$$(\varepsilon c_{T} y_{1s} c'(r, 1) \mathcal{D}(r) \Delta(r) f(r) / L q^2(r)) dr. \quad (19)$$

The amount of the key component which enters isolated pores of all possible radii is then obviously equal to

$$(\varepsilon c_{T} y_{1s} / L) \int_0^{\infty} [c'(r, 1) \mathcal{D}(r) \Delta(r) f(r) / q^2(r)] dr. \quad (20)$$

Reaction in Interlinked Pores

The assumption of perfect interlinking of pores means that the concentration profiles in all pores from this group are identical and equal to $\bar{c}(x)$ although the radii may be different. In constructing the mass balance equation for the key component, which on solving yields the concentration profile $\bar{c}(x)$, the following method may be adopted: the molar flux of the key component in a pore with radius r , located in the porous substance at coordinate z , is equal to $\pi r^2 \mathcal{N}(r, z)$; the number of interlinked pores with radii $r - (r + dr)$ which belong to unit cross-section of the porous substance perpendicular to the direction of the diffusion x is dn_{link} (Eq. (3)). By expressing the density of the diffusion flux $\mathcal{N}(r, z)$ from Eq. (6) and using the dimensionless variables from relation (13), the following expression is obtained for the molar flux through all interlinked pores in unit cross-section of the porous substance, N_{link}

$$N_{\text{link}} = (d\bar{c}/dx) (c_{T} y_{1s} \varepsilon / L) \int_0^{\infty} \{ \mathcal{D}(r) [1 - \Delta(r)] f(r) / q^2(r) \} dr, \quad (21)$$

in which the gradient $d\bar{c}/dx$ could be factored out of the integral as it is assumed that the concentration profile $\bar{c}(x)$ is identical in all interlinked pores.

The inner surface of interlinked pores with radii $r - (r + dr)$ and length dz is equal to $2\pi r dz dn_{\text{link}}$; because R moles of the key component will react on a unit of this surface, the number of mol of the key component which will react in the differential segment dz of all interlinked pores which pass through unit cross-section of the porous substance will be equal to

$$2RL\varepsilon \left\{ \int_0^{\infty} [1 - \Delta(r)] f(r) dr/r \right\} dx. \quad (22)$$

In steady state, this amount must be equal to the difference $N_{\text{link}}(z + dz) - N_{\text{link}}(z)$, *i.e.* dN_{link} (Eq. (21)). The mass balance of the key component in interlinked pores can be therefore written as

$$d^2\bar{c}/dx^2 = \bar{M}^2 \varrho(\bar{c}), \quad (23)$$

where the dimensionless reaction rate ϱ is defined in Eq. (14) and the Thiele modulus \bar{M} is equal to

$$\bar{M} = \Phi/\bar{F}. \quad (24)$$

The quantity Φ is determined by Eq. (16) and the quantity \bar{F} is given by

$$\bar{F}^2 = \frac{\int_0^{\infty} \mathcal{Q}(r) [1 - \Delta(r)] [f(r)/q^2(r)] dr}{2 \int_0^{\infty} [1 - \Delta(r)] [f(r)/r] dr}. \quad (25)$$

The differential balance of interlinked pores (23) is supplemented by analogous boundary conditions as in the case of the balance of isolated pores (12), *i.e.*

$$\begin{aligned} x = 1 \quad \bar{c} &= 1 \\ x = 0 \quad \bar{c}' &= 0. \end{aligned} \quad (26)$$

The concentration profile in interlinked pores $\bar{c}(x)$, which is obtained by solution of Eq. (23), depends only on the value of \bar{M} ; quantities depending on the pore radius r ($q, \Delta, f, \mathcal{Q}$) appear only in \bar{F} as integral mean values.

For determination of the amount of the key component which reacts in all interlinked pores opening into unit cross-section of the outer particle surface, a knowledge of the gradient of the dimensionless concentration at the outer surface $\bar{c}'(1)$ obtained by solution of balance differential equation (23) is sufficient. Similarly as in the case

of isolated pores it may be easily proved that this amount is equal to

$$(\varepsilon c_{T_{1s}}/L) \bar{c}'(1) \int_0^{\infty} \{ \mathcal{D}(r) [1 - \Delta(r)] f(r)/q^2(r) \} dr. \quad (27)$$

Effectiveness Factor

The effectiveness factor is defined as the ratio of the amount of the key component which will react in a particle of the given magnitude and the amount which would react if the inner surface of the particle were in contact with the reaction mixture of the composition equal to that at the outer surface of this particle. From expressions (20) and (27) for the amounts of the key component which enter a particle (and will react inside it) through isolated and interlinked pores which start in the unit of the outer surface, the following general expression form may be obtained

$$\eta = \eta_{\text{link}} w_{\text{link}} + \int_0^{\infty} \eta_{\text{isol}}(r) w_{\text{isol}}(r) dr. \quad (28)$$

The symbol η_{link} denotes the constant effectiveness factor of the interlinked pores

$$\eta_{\text{link}} = \bar{c}'(1)/\bar{M}^2 \quad (29)$$

and $\eta_{\text{isol}}(r)$ is the radius-dependent effectiveness factor of the isolated pores

$$\eta_{\text{isol}}(r) = c'(r, 1)/M^2(r). \quad (30)$$

The terms w_{link} and w_{isol} are weights of contributions due to interlinked and isolated pores

$$w_{\text{link}} = 1 - (\langle \Delta/r \rangle / \langle 1/r \rangle) \quad (31)$$

$$w_{\text{isol}}(r) = \Delta(r) f(r) / (r \langle 1/r \rangle) \quad (32)$$

in which the integral mean value $\langle \Delta/r \rangle$ is defined by

$$\langle \Delta/r \rangle = \int_0^{\infty} [\Delta(r) f(r) / r] dr. \quad (33)$$

If all pores are perfectly interlinked, *i.e.* for $\Delta = 0$, relation (28) reduces to the equality $\eta = \eta_{\text{link}}$, which describes one of the limiting forms of the semi-linked pore model – the average pore model. Taking into account interlinking of pores with arbitrary radii, the effect of internal diffusion on the rate of catalytic reaction is the same as if the porous medium were represented by a bundle of cylindrical capillaries

with a constant (average) radius and constant (average) tortuosity. This idea has been employed by Rothfeld¹ for the diffusion of binary mixtures of gases through a porous medium.

If pores with different radii are not interlinked at all (*i.e.* $\Delta = 1$), the first term on the RHS of Eq. (28) disappears and the resulting relation describes the second limiting form of the semi-linked pore model — the isolated pore model.

From the general expression (28), useful relations for the effectiveness factor in more simple texture cases might be obtained easily. Thus, one can for example assume that the distributivity and/or tortuosity is constant in the whole range of pore radii or, possibly, that they exhibit different (but constant) values in mesopores and macropores. Cases when the porous substance contains pores of certain sizes only can be handled in the same manner (*e.g.* a strictly bidisperse porous substance contains pores with radii r_1 and r_2 only; the frequency function $f(r)$ is then given by: $f(r) dr = \varepsilon_1/\varepsilon$ for $r = r_1$, $f(r) dr = \varepsilon_2/\varepsilon$ for $r = r_2$, $f(r) dr = 0$ for $r \neq r_1, r_2$; ε_1 and ε_2 are porosities of pores with radii r_1 and r_2 , the total porosity is $\varepsilon = \varepsilon_1 + \varepsilon_2$). Relations for several typical simplified situations are summarized in Appendix. Naturally, for each of these situations limiting forms for the average pore and isolated pore models may be found, too; it is sufficient to set $\Delta = 0$, or $\Delta = 1$, resp.

The Region of Strong Internal Diffusion

If the effect of internal diffusion is such strong that the concentration of the key component (reactant) drops to almost zero (in the case of a reversible reaction to its equilibrium value), the boundary conditions of the differential mass balances (12) and (23) in the centre of the particle ($x = 0$, $dc/dx = 0$, and $d\bar{c}/dx = 0$) may be replaced by

$$x = 0 \quad c = 0 \quad (34)$$

in the case of balance (12) and by

$$x = 0 \quad \bar{c} = 0 \quad (35)$$

for balance (23). The boundary condition at the outer surface of the catalyst particle remains unchanged (*i.e.* $c = 1$ and $\bar{c} = 1$ for $x = 1$). These boundary conditions allow one to integrate balances (12) and (23) analytically and to express gradients $c'(1)$ and $\bar{c}(1)$ which are necessary for determination of effectiveness factors (Eqs (29), (30)). If an asterisk denotes the region of validity of boundary conditions (34) and (35), the following relation results for the effectiveness factor η^*

$$\eta^* = \eta_{link}^* w_{link} + \int_0^\infty \eta_{isol}^*(r) w_{isol}(r) dr, \quad (36)$$

where

$$\eta_{\text{link}}^* = \varrho/\bar{M} = \varrho\bar{F}/\Phi, \quad (37)$$

$$\eta_{\text{isol}}^*(r) = \varphi/M(r) = \varphi F(r)/\Phi, \quad (38)$$

weights w_{isol} and w_{link} are given by Eqs (31) and (32); the dimensionless function φ is defined by

$$\varphi = \left[2 \int_0^1 \varrho(c) dc \right]^{1/2} \quad (39)$$

and depends only on parameters which appear in the kinetic equation of the reaction, $\varrho(c)$, or possibly on the composition of the reaction mixture at the outer surface of the catalyst particle (y_{js} ; $j = 1, \dots, m$). For a simple n -th order power-law kinetics, $\varphi = 2/(n + 1)$. In the special case of a first-order reaction ($n = 1$) we obtain $\varphi = 1$. Expressions for some cases of the Langmuir–Hinshelwood kinetics may be found in the literature (e.g. for example⁷).

By combining Eqs (31), (32), (36)–(39), the expression for η^* may be rearranged to read

$$\eta^* = 1/\mathcal{M} \quad (40)$$

where the generalized dimensionless modulus \mathcal{M} is given by

$$\mathcal{M} = \frac{\Phi}{\varphi \left\{ \left(1 - \frac{\langle \Delta/r \rangle}{\langle 1/r \rangle} \right) \bar{F} + \int_0^\infty \frac{\Delta(r) f(r) F(r)}{r \langle 1/r \rangle} dr \right\}}. \quad (41)$$

Quantities Φ , \bar{F} , $F(r)$ were defined in Eqs (16), (25) and (17).

If, in graphical representation of computed effectiveness factors, $\log \Phi$ and $\log \eta$ are considered as independent and dependent variables, respectively, then in the region of strong internal diffusion parallel straight lines with the slope of -1 are obtained. If $\log \mathcal{M}$ is employed as the independent variable, these straight lines merge into a single line which forms the asymptotic solution.

The Effect of the Catalyst Texture

For modelling the effect of the catalyst texture on effectiveness factors, simulation computations according to the semi-linked pore model were performed for a simple model catalytic reaction – the *para-ortho* hydrogen conversion at atmospheric pressure and 25°C. At constant pressure of hydrogen this reversible reaction is of first order with respect to the concentration of *p*-hydrogen⁸ (index 1):



(The diffusion coefficient $\mathcal{D}(r)$ in this system at 25°C and atmospheric pressure may be written as $\mathcal{D}^{-1}(r) = \mathcal{D}_{11}^{-1} + \mathcal{D}_{k1}^{-1}(r)$, where the self-diffusion coefficient of hydrogen is $\mathcal{D}_{11} = 1.647 \text{ cm}^2/\text{s}$ and the Knudsen diffusion coefficient $\mathcal{D}_{k1} = 118.4 \cdot 10^4 r$ for r in cm.). Differential mass balances of isolated and interlinked pores (12), (23) with boundary conditions (18), (26) may be then integrated analytically to yield

$$\eta_{\text{link}} = \tanh(\bar{M})/\bar{M} = \tanh(\Phi)/\bar{F}/(\Phi/\bar{F}), \tag{43}$$

$$\eta_{\text{isol}}(r) = \tanh[M(r)]/M(r) = \tanh[\Phi/F(r)]/[\Phi/F(r)]. \tag{44}$$

For the effect of the number and size of pores present in the catalyst to become clearly visible, a strictly bidisperse structure was selected which contained pores of two sizes only – r_1 and r_2 – and identical distributivities Δ and tortuosities q . (Case 4 in Appendix). Pore sizes (r_1, r_2) and their volume fractions ($\varepsilon_1/\varepsilon$ and $\varepsilon_2/\varepsilon$) were chosen

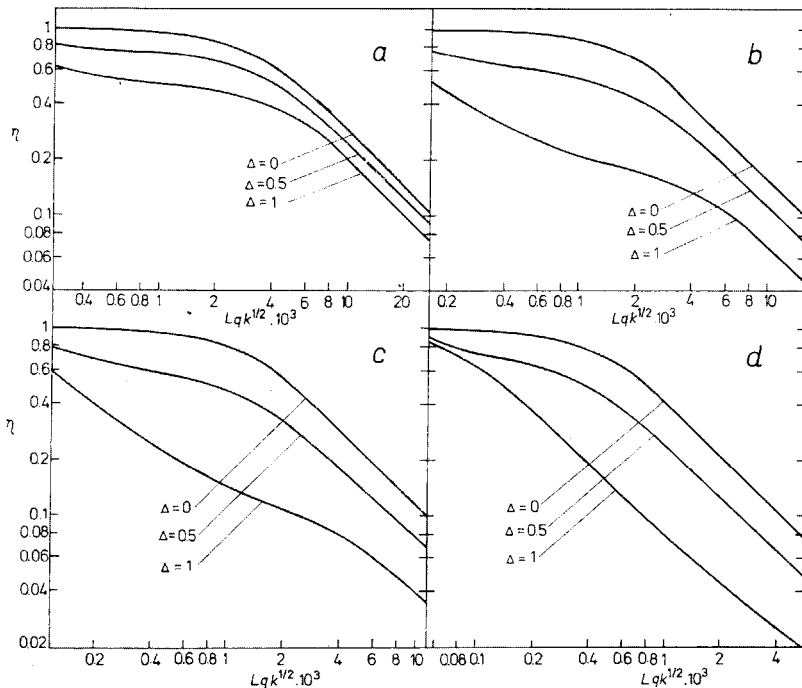


Fig. 2.

The Effect of the Relative Amount of Pores of the Same Size on the Effectiveness Factor

$r_1 = 3 \text{ nm}, r_2 = 300 \text{ nm}; a \varepsilon_1/r = 0.01, \varepsilon_2/\varepsilon = 0.99; b \varepsilon_1/\varepsilon = 0.05, \varepsilon_2/\varepsilon = 0.95; c \varepsilon_1/\varepsilon = 0.1, \varepsilon_2/\varepsilon = 0.9; d \varepsilon_1/\varepsilon = 0.5, \varepsilon_2/\varepsilon = 0.5;$ (L in cm, k in cm/s).

as independent variables. The effectiveness factor is then given by Eq. (A-13) in Appendix in which η_{link} and $\eta_{\text{isol}}(r)$ are given by Eqs (43), (44). The final results are in Figs 2 and 3 in logarithmic coordinates η versus (Φq) (for a first-order reaction, the structure of Φ is simple : $\Phi = Lk^{1/2}$). Fig. 4 shows the advantage of use of the generalized modulus \mathcal{M} as the independent variable.

It follows from the given results that at otherwise equal conditions, the effectiveness factor is always higher in the case of perfect interlinking of pores ($\Delta = 0$) than in the case when a part of pores is isolated ($\Delta > 0$). Lowest effectiveness factors were observed in the case of perfect isolation of all pores ($\Delta = 1$). This is due to the fact that the effectiveness factor is extremely low in narrow pores which, on the other hand, contain most of the catalytically active surface; the effectiveness factor increases in wider pores, but the contribution of such pores to the total catalyst surface is not as a rule too significant. If all pores are perfectly interlinked ($\Delta = 0$), we have a porous structure in which the entire catalytically active surface is concentrated in pores with one (mean) radius; as this radius is higher than that of narrowest pores, the effectiveness factor is also higher. Simultaneously, the difference between effectiveness fac-

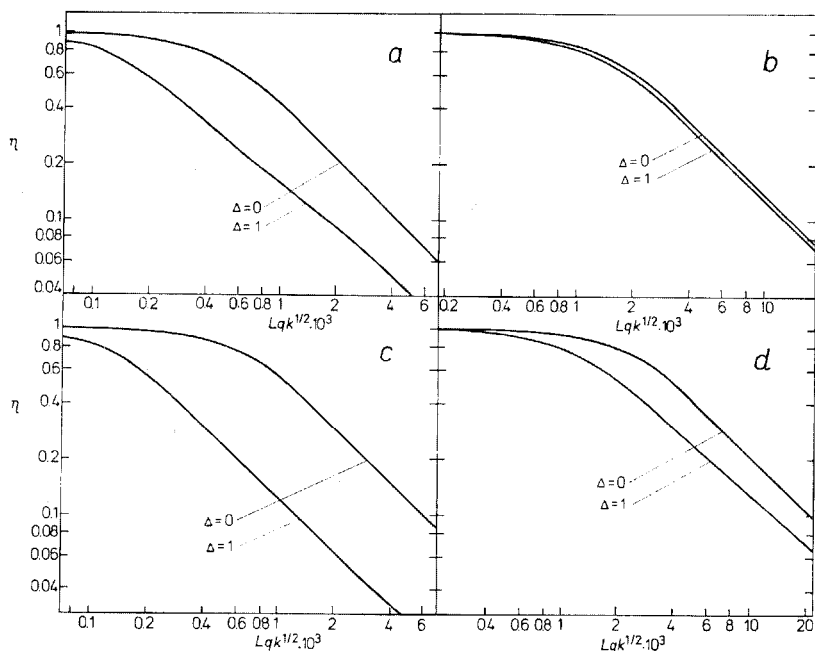


FIG. 3

The Effect of the Pore Size on the Effectiveness Factor

$\epsilon_1/\epsilon = \epsilon_2/\epsilon = 0.5$; a $r_1 = 5$ nm, $r_2 = 100$ nm; b $r_1 = 50$ nm, $r_2 = 100$ nm; c $r_1 = 5$ nm, $r_2 = 1000$ nm; d $r_1 = 50$ nm, $r_2 = 1000$ nm; (L in cm, k in cm/s).

tors for $\Delta = 0$ and $\Delta = 1$ can be considerable (Figs 3c, 2b-2d). Thus, the degree of interlinking of pores Δ plays an important role.

If a part of pores is isolated ($\Delta > 0$), the reaction in wide pores is affected by the internal diffusion only little. The transition into the region of strong internal diffusion appears therefore in these pores later than in more narrow ones. Consequently, the dependence $\eta - \Phi$ approaches its descending linear asymptote (the transition into the region of strong internal diffusion) more slowly in structures with isolated pores than in those containing perfectly interlinked pores (Figs 2b and 2c).

Some curves on Figs 2-4, especially when almost all pores are isolated, exhibit an inflection point. This situation occurs when η_{isol1} decreases sharply with increasing Φ in narrow isolated pores, whereas the effectiveness of isolated wide pores, η_{isol2} , decreases rather slowly. Should this inflection point appear in the vicinity of $\Phi \approx 1$, the weights of effectiveness factors of narrow and wide isolated pores ($\epsilon_1/[er_1\langle 1/r \rangle]$ and $\epsilon_2/[er_2\langle 1/r \rangle]$, resp. - see Eq. (A-10)) must have appropriate values (the weights represent fractions of surface in narrow and wide pores, resp.).

If narrow and wide pores are present in the same amount, then the diminishing of differences in their sizes brings corresponding $\eta-\Phi$ dependences closer to one another and *vice versa* (see Figs 3a and b and 3c and d). This is only natural as the distributivity loses its meaning if both kinds of pores become indistinguishable: the porous medium will contain pores of one size only and an unique $\eta-\Phi$ dependence will therefore remain.

If both isolated and interlinked pores exist in a porous substance, we must be careful in applying criteria which guarantee the absence of internal diffusion. Such criteria stem usually from the assumption that the reaction is not too much affected by internal diffusion if the value of the Thiele modulus is less than unity. However, in the analyzed bidisperse structure there are three Thiele moduli (\bar{M} , M_1 , M_2) which can exhibit rather diverse values: for conditions on Fig. 3c and $Lq k^{1/2} = 1.4 \cdot 10^{-3}$ we obtain e.g. $\bar{M} = 1.15$, $M_1 = 5.9$, $M_2 = 0.08$ which means that the

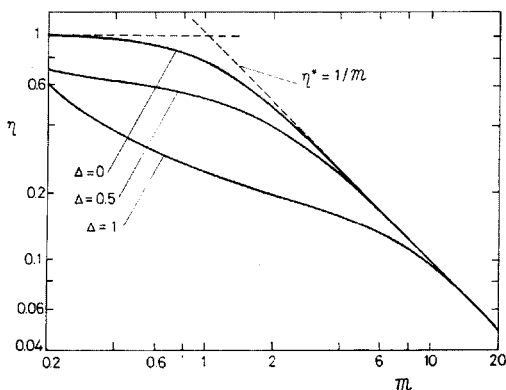


FIG. 4
 The Use of the Generalized Modulus \bar{M}
 for the Correlation of Effectiveness Factors
 $\epsilon_1/\epsilon = 0.05$, $\epsilon_2/\epsilon = 0.95$, $r_1 = 3$ nm, $r_2 =$
 $= 300$ nm.

reaction is affected by internal diffusion negligibly only in isolated wide pores ($M_2 < 1$) whereas the internal diffusion cannot be neglected in narrow isolated ($M_1 > 1$) and interlinked ($\bar{M} > 1$) pores. This is illustrated by the effectiveness factor which grows from 0.17 ($\Delta = 1$) to 0.71 ($\Delta = 0$).

p-o-Hydrogen Conversion

The variant of the semi-linked pore model with a constant distributivity and tortuosity (Eqs (A-1), (43), (44)) was applied to experimental data obtained in a study of *p-o* hydrogen conversion in the region of internal diffusion on a Girdler G-13 catalyst ($\text{CuO} \cdot \text{Cr}_2\text{O}_3$)^{8,9} at 25°C and hydrogen pressures between 200 and 760 Torr. The reaction was studied on five catalyst pellets in the form of an infinite slab with the half-width $L = 1-4.5$ cm and apparent density of 2.26 g/cm³. Two pellets with $L = 1.5$ cm and apparent densities of 1.95 and 2.0 g/cm³ were also used. The reaction kinetics studied in absence of internal diffusion (catalyst size 0.4 mm) confirmed the validity of rate equation (42), in which the rate constant k depends on the total pressure of hydrogen. In a manner outlined elsewhere^{8,9}, effectiveness factors were computed and an optimization technique (grid search method) was used to find such optimal values of distributivity Δ^{opt} and tortuosity q^{opt} which would satisfy the following criterion

$$Q(\Delta^{\text{opt}}, q^{\text{opt}}) = \min Q(\Delta, q), \quad (45)$$

where Q is the sum of squared deviations between experimental values of effectiveness factors and those calculated according to Eq. (A-9):

$$Q = \sum [\eta_{\text{calc}}(\Delta, q) - \eta_{\text{exp}}(\Delta, q)]^2. \quad (46)$$

TABLE I

Optimum ($\Delta^{\text{opt}}, q^{\text{opt}}$) and Remotest Pairs of q and Δ Corresponding to the 95% Significance Level ($\Delta^{\text{rem}}, q^{\text{rem}}$)

Pellet density, g/cm ³	Pellet length, cm	q^{opt}	Δ^{opt}	q^{rem}	Δ^{rem}
2.26	1.0-4.5	1.96	0.0	1.66	0.26
2.26	1.5	2.02	0.0	1.42	0.50
2.00	1.5	1.81	0.0	1.00	0.67
1.95	1.5	1.38	0.4	1.94-0.99	0.00-0.68

The sum in Eq. (46) is to be taken over all experiments on pellets with the same density. In the optimization, the values of distributivity were confined to the range $\langle 0, 1 \rangle$ and those of tortuosity to $q < 0$. Final optimum pairs of parameters Δ^{opt} and q^{opt} are summarized in Table I. Due to an existing correlation between parameters Δ and q , there is a region in the Δ - q plane where all combinations of Δ and q lead to a value of the objective function Q which, on a 95% probability level, is indistinguishable from the minimum value (valid for q^{opt} , Δ^{opt}). These regions are characterized in Table I by remotest pairs Δ^{rem} , q^{rem} , which lie farthest from the optimum pairs but still inside the 95% probability region.

It is obvious from this table that the tortuosity is in all cases higher than unity including the remotest pairs q and Δ . The optimum distributivity of more dense pellets (2.0, 2.26 g/cm³) equals zero; this corresponds to one of the limits of the semi-linked pore model – to a parallel pore model in which all pores are interlinked so that their contents can intermix. Only for the least dense pellet (1.95 g/cm³) it holds $\Delta = 0.4$; this means that a part of the pores (40%) is mutually isolated. A certain fraction of isolated pores can of course appear even in more dense pellets; this is documented by nonzero values of Δ^{rem} . If the parameter Δ possessed only the simple physical meaning suggested by the construction of our model (*i.e.* the fraction of the volume of mutually isolated pores) one would rather expect an increase of Δ with increasing pellet density (increase in the pressure of pressing would probably lead to blocking of connections among pores). It is therefore obvious that the distributivity as well as tortuosity must be regarded as adjustable parameters of a more complex and less easily definable physical meaning.

By using the optimum parameters q and Δ from Table I, effectiveness factors η_{calc} were calculated for conditions of all experiments. These values are compared with experimental ones, η_{exp} , on Fig. 5; good agreement between both effectiveness

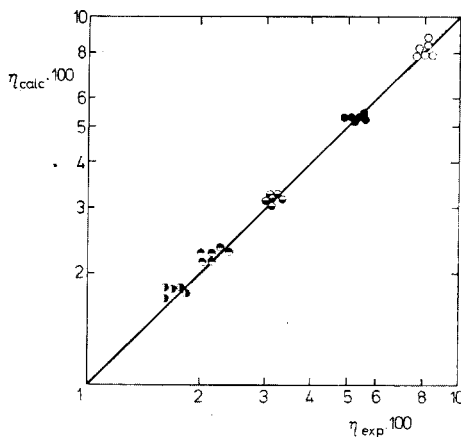


FIG. 5

The Comparison of Experimental and Calculated Effectiveness Factors for the Catalytic *p-o*-Hydrogen Conversion

Pellet: density 2.26 g/cm³, length ○ L 1 cm, ● L 1.5 cm, ◐ L 2.5 cm, ◑ L 3.5 cm, ◒ L 4.5 cm. Identically marked points correspond to different total pressures of hydrogen.

factors is obvious from this Figure. Simultaneously, the relative deviation $|\eta_{\text{calc}} - \eta_{\text{exp}}|/\eta_{\text{exp}}$ averaged over all experiments is equal to 6%.

APPENDIX

1) Constant Distributivity Δ

The effectiveness factor is equal to

$$\eta = (1 - \Delta) \eta_{\text{link}} + \Delta \int_0^{\infty} \eta_{\text{isol}}(r) f(r) dr / (r \langle 1/r \rangle), \quad (A-1)$$

where η_{link} is given by Eq. (29) and modulus \bar{M} by relation (24) in which \bar{F} is simplified to

$$\bar{F}^2 = \langle \mathcal{D}/q^2 \rangle / 2 \langle 1/r \rangle \quad (A-2)$$

$\eta_{\text{isol}}(r)$ is determined by Eq. (30) and modulus $M(r)$ by Eq. (15). The integral mean value $\langle \mathcal{D}/q^2 \rangle$ is defined by

$$\langle \mathcal{D}/q^2 \rangle = \int_0^{\infty} \mathcal{D}(r) f(r) dr / q^2(r). \quad (A-3)$$

2) Constant Δ and q

The effectiveness factor is given by Eq. (A-1), η_{link} and $\eta_{\text{isol}}(r)$ by Eqs (29), (30). Moduli \bar{M} and $M(r)$ are determined from Eqs (24), (15) in which \bar{F} and $F(r)$ are simplified to

$$\bar{F}^2 = \langle \mathcal{D} \rangle / 2q^2 \langle 1/r \rangle, \quad (A-4)$$

$$F^2(r) = (1/2q^2) r \mathcal{D}(r). \quad (A-5)$$

The integral mean value of the diffusion coefficient is equal to

$$\langle \mathcal{D} \rangle = \int_0^{\infty} \mathcal{D}(r) f(r) dr. \quad (A-6)$$

3) Bidisperse Porous Material

Denoting $\Delta(r_1) \equiv \Delta_1$, $\Delta(r_2) \equiv \Delta_2$, we obtain

$$\eta = [1 - \Delta_1 \varepsilon_1 / \varepsilon r_1 \langle 1/r \rangle] - (\Delta_2 \varepsilon_2 / \varepsilon r_2 \langle 1/r \rangle) \eta_{\text{link}} + \eta_{\text{isol1}} (\Delta_1 \varepsilon_1 / \varepsilon r_1 \langle 1/r \rangle) + \eta_{\text{isol2}} (\Delta_2 \varepsilon_2 / \varepsilon r_2 \langle 1/r \rangle). \quad (A-7)$$

η_{link} is determined from Eq. (29), $\eta_{\text{isol1}} \equiv \eta_{\text{isol}}(r_1)$, $\eta_{\text{isol2}} \equiv \eta_{\text{isol}}(r_2)$ from Eq. (30). Moduli \bar{M} , $M_1 = M(r_1)$ and $M_2 = M(r_2)$ are given by

$$\begin{aligned} \bar{M} &= \Phi / \bar{F}, \\ M_1 &= \Phi / F_1, \\ M_2 &= \Phi / F_2, \end{aligned} \quad (A-8)$$

in which $F_1 \equiv F(r_1)$, $F_2 \equiv F(r_2)$. A simplified meaning of \bar{F} , F_1 , F_2 follows from

$$\bar{F}^2 = \frac{[(1 - A_1) (\mathcal{D}_1 \varepsilon_1 / q_1^2) + (1 - A_2) (\mathcal{D}_2 \varepsilon_2 / q_2^2)]}{2[(1 - A_1) (\varepsilon_1 / r_1) + (1 - A_2) (\varepsilon_2 / r_2)]} \quad (A-9)$$

$$F_1^2 = (r_1/2) \mathcal{D}_1 / q_1^2, \quad (A-10)$$

$$F_2^2 = (r_2/2) \mathcal{D}_2 / q_2^2, \quad (A-11)$$

where $q_1 \equiv q(r_1)$, $q_2 \equiv q(r_2)$, $\mathcal{D}_1 \equiv \mathcal{D}(r_1)$, $\mathcal{D}_2 \equiv \mathcal{D}(r_2)$ and the mean value $\langle 1/r \rangle$ may be expressed as

$$\langle 1/r \rangle = (\varepsilon_1 / r_1 \varepsilon) + (\varepsilon_2 / r_2 \varepsilon). \quad (A-12)$$

ε_1 and ε_2 are porosities of pores with radii r_1 and r_2 ($\varepsilon = \varepsilon_1 + \varepsilon_2$).

4) Bidisperse Substance with Constant q and A

$$\eta = (1 - A) \eta_{\text{link}} + A[\eta_{\text{isol1}} \varepsilon_1 / (\varepsilon r_1 \langle 1/r \rangle) + \eta_{\text{isol2}} \varepsilon_2 / (\varepsilon r_2 \langle 1/r \rangle)]. \quad (A-13)$$

η_{link} is given by Eq. (29), η_{isol1} and η_{isol2} are defined in paragraph 3 of this appendix. Moduli \bar{M} , M_1 and M_2 are obtained from Eq. (A-5) with \bar{F} , F_1 and F_2 equal to

$$\bar{F}^2 = (\mathcal{D}_1 \varepsilon_1 + \mathcal{D}_2 \varepsilon_2) / \{2q^2[(\varepsilon_1 / r_1) + (\varepsilon_2 / r_2)]\}, \quad (A-14)$$

$$F_1^2 = r_1 \mathcal{D}_1 / 2q^2, \quad (A-15)$$

$$F_2^2 = r_2 \mathcal{D}_2 / 2q^2. \quad (A-16)$$

The meaning of quantities ε_1 , ε_2 , \mathcal{D}_1 , \mathcal{D}_2 is the same as in the preceding paragraph. Because the integral mean value $\langle 1/r \rangle$ is given by Eq. (A-9), the sum of terms $\varepsilon_1 / \varepsilon r_1 \langle 1/r \rangle$ and $\varepsilon_2 / \varepsilon r_2 \langle 1/r \rangle$ on the RHS of Eq. (A-10) equals unity; these terms represent weights of effectiveness factors of isolated pores with radii r_1 and r_2 .

Relations for effectiveness factors in the region of strong internal diffusion (η^*) are determined easily for simplified texture situations 1–4 from Eqs (37), (38); one must only employ corresponding expressions for \bar{F} , F_1 , and F_2 (Eqs (A-2), (A-4), (A-5), (A-9)–(A-11), (A-14)–(A-16)).

LIST OF SYMBOLS

a_i	stoichiometric coefficient
A_i	reaction component
c	dimensionless concentration
c_T	total molar concentration
\mathcal{D}_{ij} , \mathcal{D}_{ki}	binary diffusion coefficient of pair $i-j$ and Knudsen diffusion coefficient of component i in a circular capillary
\mathcal{D}	diffusion coefficient of the key component in the multicomponent reaction mixture in the transition diffusion region
f	frequency function of the pore volume distribution
F	function
\bar{F}	parameter
k	rate constant

L	half-width of the infinite catalyst slab
$\bar{M}, M(r)$	Thiele moduli
\mathcal{M}	generalized modulus
m	number of components of the reaction mixture
n	number of pores per unit of the outer surface
\mathcal{N}	diffusion flux per unit capillary cross-section
p	number of components which take part in reaction (4): $p \leq m$
q	tortuosity
r	pore radius
R	reaction rate of the key component
w	weight
x	dimensionless length coordinate in a porous particle
w_1	thermal velocity of molecules 1
y_i	mole fraction of component i
z	axial length coordinate in a pore
Δ	distributivity
ε	porosity
δ_i	parameter
Φ	parameter
η, η^*	effectiveness factor, effectiveness factor in the region of strong internal diffusion
φ	parameter

Indices

s	outer surface of a catalyst particle
eq	equilibrium mixture
isol	isolated pores
link	interlinked pores
opt	optimal value
rem	remotest value on the 95% significance level
$\langle \rangle$	integral mean value
'	derivative with respect to x

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