Determination of Transport Parameters of Porous Catalysts Using Unsteady Permeation of Gases*

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The new experimental way was proposed and verified in this study to get the associated transport parameters $\langle r \rangle \psi$, $\langle r^2 \rangle \psi$ from permeation measurements on the three industrial catalysts under non-stationary conditions in the modified Wicke—Kallenbach cell. These parameters were determined by the fitting to the theoretical model response curves by the Marquardt—Levenberg optimization method. The confidence intervals of the associated transport parameters were evaluated on the basis of the Beale criterion. The width of confidence intervals was discussed in terms of different mechanisms of mass transport. The advantages of the new experimental setup and calculation method were compared with the latter approach, too.

The prediction of mass transport of reaction components through porous material (catalyst) is necessary to include into description for the rational simulation and optimal management of chemical processes. Several models of mass transport were designed for this purpose – Mean Transport Pore Model (MTPM) [1], Dusty Gas Model (DGM) [2], Binary Friction Model (BFM) [3]. These can describe mass transport by the transport parameters sufficiently. Another useful role of transport parameters consists in the structural characterization of porous materials (adsorbents, membranes) for their planned preparation.

The transport parameters of porous catalyst are material constants that cannot be measured by direct way. The best method to get them is the experimental observation of the easy transport process in pores under well defined conditions (laboratory temperature and pressure, pure gases or binary gaseous mixtures). The transport parameters of porous material may be evaluated by comparison of the experimental results with calculated ones from the theoretical model. The whole spectrum of the physical processes has been proposed and validated: stationary [4] and nonstationary [5] diffusion of binary gas mixtures, forced flow of pure single gases under pressure gradient [6, 7], and combination of both here mentioned processes [8, 9]. In this respect, the transport experiments with inert gases have been preferred because the adsorption [10] of the gas components or their surface diffusion are not fully understood so far. Thus, the transport model

construction is then very complicated.

The main goal of this study was the proposition and validation of the new experimental way to get the set of the associated transport parameters from permeation measurements provided under nonstationary conditions in the modified Wicke—Kallenbach cell, to characterize three selected porous materials with different texture by the associated transport parameters and to determine their precision. The discussion and comparison of information gain of both the associated transport parameters and textural ones (from standard methods) was the last task of this work.

Gas Transport in Porous Body

The porous structure of real materials used in industrial plant operations is very complex. For that reason, the simplified transport models were designed. These are based on the concept of existence of easy structure units where the description of mass transport is well known. The most of transport models operate on the idea of cylindrical pores.

Character of gas transport can be classified after the value of Knudsen number Kn (the ratio of free gas molecule path λ to the pore size expressed as the radius of the transport pore $\langle r \rangle$) in the form

$$\text{Kn} = \frac{\lambda}{2\langle r \rangle} \qquad (1)$$

For Kn $\rightarrow \infty$, the movement of gas molecules is trans-

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*Presented at the 26th International Conference of the Slovak Society of Chemical Engineering, Jasná – Demänovská dolina, 24—28 May 1999.

Table 1. Textural Parameters of Tested Porous Materials

Quantity	ICI 52/1	Cherox 42-00	Alumina A5
Pellet height/mm	4.27	4.90	3.45
Pellet diameter/mm	4.86	5.00	3.45
Pellets volume/cm^3	3.327	4.041	0.032
Helium density/(g cm^{-3})	3.833	3.472	3.953
Apparent density/(g cm^{-3})	1.518	2.234	2.548
Pore volume/(cm^3 g^{-1})	0.377	0.167	0.134
Porosity	0.604	0.357	0.355
Surface BET/(m^2 g^{-1})	73.0	3.97	0.46
Mean pore size/nm	8.2	70	290 and 2070

ferred by collision with pore wall and then the gas transport takes place in Knudsen region. In the opposite case (Kn → 0), the mutual interactions of gas molecules with each other occur (collisions between gas molecule and pore wall are negligible) and the gas transport plays out in continuum (bulk region). Both the aforementioned transport mechanisms contribute to the overall gas transport in the transition region ($\lambda \approx \langle r \rangle$).

Gas permeation (forced flow) is defined as a process where gas transport in porous material performs by the pressure gradient. D'Arcy constitutive equation (2) is valid for the molar flux density N under isothermal conditions

$$N = -B\frac{\partial c}{\partial x} \qquad (2)$$

where c is gas concentration, x is geometric coordinate, and finally B denotes the effective permeability coefficient generally dependent on pressure p. This dependence is written by the Weber equation in the form

$$B = \frac{2}{3}\langle r \rangle \psi \sqrt{\frac{8R_g T}{\pi M}}\left(\frac{\omega + \mathrm{Kn}}{1 + \mathrm{Kn}}\right) + \langle r^2 \rangle \psi \frac{p}{8\mu} \qquad (3)$$

where $\langle r \rangle \psi$, $\langle r^2 \rangle \psi$ design the associated transport parameters of porous material, R_g denotes the universal gas constant, M is molar mass of gas, and μ is gas viscosity. Parameter ω characterizes the gas molecule slip on the pore wall. Because the majority of literature sources consider the slip parameter equal to 1, eqn (3) can be simplified in the following manner that was used for the purpose of this work, too

$$B = \frac{2}{3}\langle r \rangle \psi \sqrt{\frac{8R_g T}{\pi M}} + \langle r^2 \rangle \psi \frac{p}{8\mu} \qquad (4)$$

It must be underlined that the first right-hand term of eqn (4) describes the gas transport in the Knudsen region (associated transport parameter $\langle r \rangle \psi$), while the second one reflects viscous flow contribution ($\langle r^2 \rangle \psi$).

EXPERIMENTAL

In this work, the commercial porous catalysts were studied that are widely used in chemical industry for methanol synthesis and hydrogenation (ICI 52/1, ICI Ltd., Great Britain; Cherox 42-00, Chemopetrol Litvínov, Czech Republic), respectively. The third type of the porous solid was checked on the catalytic support α-alumina A5 (home prepared from boehmite Pural SB, Condea Chemie, Germany). All porous materials were shaped as cylindrical pellets. Their textural characterization was provided with the aid of the standard methods of textural analysis (helium pycnometry, mercury porosimetry, and BET isotherm method) on apparatus Micromeritics, USA. Textural properties of all tested porous materials are presented in Table 1. The catalysts ICI 52/1 and Cherox 42-00 are monodispersed (one maximum on pore size distribution curve) differing by the mean pore size (pore radius). Alumina is the bidispersed material where mesopores dominate over macropores.

Permeation cell (Fig. 1) consists of the input and measuring parts. The holder of porous material is inserted between these parts. The cylindrical porous pellets are sealed in the holder to expose their front part to the pressure of the gas input only. The input part of the cell serves for gas filling and it is supplied by the electromagnetic valve. This valve is connected to the input part of the cell by the capillary of the defined length and cross-section that regulates the velocity of the gas flow to fill this part quickly but without pressure shocks. The measuring part of the cell is equipped by the absolute pressure gauge (0 to 101 kPa, Omega Engineering, USA) that enables to record the pressure in this part of the cell as the response to the pressure change in the input part. The permeation cell is the main part of the apparatus where all technical operations (evacuation, pressure change, recording and storing of experimental data) are managed with the aid of computer.

All permeation experiments were made under laboratory temperature. The same value of initial pressure was adjusted in both parts of the cell at first. Then the input part of the cell was filled by the inert gas through the input valve (pressure change approx-
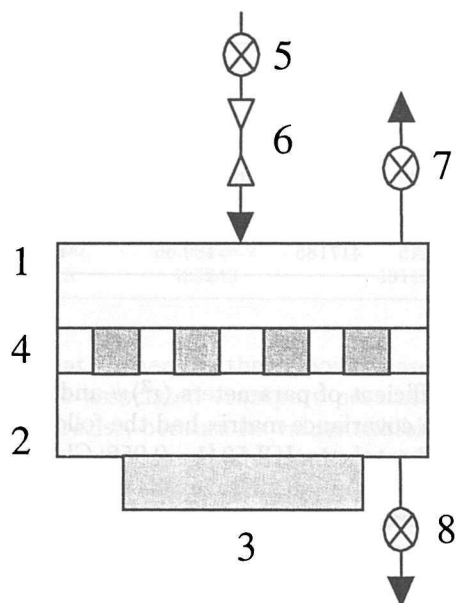
Fig. 1. Scheme of the new permeation cell. *1.* Input part of the cell; *2.* measuring part of the cell; *3.* pressure gauge; *4.* metal holder of porous pellets; *5.* input valve, *6.* capillary, *7, 8.* vacuum.

imately 101 kPa). From this moment ($t = 0$ s) the pressure response in the measuring part of the cell was recorded (the pressure increase as a function of time). Duration of gas filling (time until the input pressure p_{in} is equalized with pressure in the input part of the cell) was negligible in comparison with the duration of the observed pressure response. The pairs time—pressure were sampled with the frequency of 1 Hz. The inert gases – hydrogen, helium, nitrogen, and argon – of standard purity (99.5 %) delivered by Linde, Prague, Czech Republic were used in permeation experiments.

Balance of the Permeation Cell

Permeation of inert gases was observed in the modified version of the Wicke—Kallenbach cell, where the following mass balance inside porous material (continuity equation) is valid

$$-\frac{\partial N(t,x)}{\partial x} = \varepsilon \frac{\partial c(t,x)}{\partial t} \qquad (5)$$

where ε denotes porosity of catalyst (pore volume related to the volume unit of pellets) and c is the concentration of inert gas that is transported through porous material by permeation.

On assumption of ideal mixing the boundary condition is derived for the measuring part of the cell (coordinate $x = 0$ specifies the bottom around porous pellets, see Fig. 1)

$$V_0 \frac{\partial c(t,0)}{\partial t} = -\frac{V_p}{L} N(t,0) \qquad (6)$$

where V_0 is the volume of the measuring part of the cell, V_p denotes volume of all used porous pellets, and L is the pellet length. The similar boundary condition is defined for input part of the cell (volume V_L)

$$V_L \frac{\partial c(t,L)}{\partial t} = \frac{V_p}{L} N(t,L) +$$
$$+ \frac{\pi}{16 R_g T \mu} \xi \{ p_{in}^2 - [R_g T c(t,L)]^2 \} \quad (7)$$

where p_{in} specifies outer gas pressure and ξ is the capillary constant determined experimentally. Eqn (7) includes into model of the permeation cell the way of pressure change initialization in its input part, too.

Balance of the permeation cell must be supplemented by information about the state of the cell in time on beginning of permeation experiment – an initial condition (8). The gas concentration in pores at time $t = 0$ s is

$$c(0,x) = c_0 \qquad (8)$$

RESULTS AND DISCUSSION

Experimental pressure response reflects the gas transport in porous material and holds information on the associated transport parameters $\langle r^2 \rangle \psi$ and $\langle r \rangle \psi$. The transport parameters are not influenced by outer conditions, *i.e.* they do not depend on the temperature, pressure, and any kind of used gas. Thus, they can be used for comparison of porous materials to each other. The associated transport parameters were obtained with the aid of minimization of the object function χ^2 defined as the sum of squared deviations between experimental and theoretical pressure response after the following equation

$$\chi^2(\langle r \rangle \psi, \langle r^2 \rangle \psi) = \sum_{j=1}^{m} \sum_{i=1}^{n} [p_{ij} - R_g T c(t_{ij}, 0)]^2 \quad (9)$$

Four inert gases of different molecular mass (H_2, He, N_2, Ar) were used to get the experimental pressure responses. These responses were recorded for six various pressure levels p_{in} for every inert gas in the input part of the cell (*i.e.* for each porous material altogether $m = 24$ pressure responses, each of them has approximately 1000 points). Theoretical pressure responses were modeled by solution of the differential equations system (eqns (1, 3—8) integrated by the method of lines [8]. The minimization of the objective function (9) was made by the Marquardt—Levenberg method [11].

Fig. 2 depicts the excellent agreement of experimental data with those calculated after theoretical permeation model for the helium permeation in the catalyst Cherox 42-00. The theoretical model (full lines) fits the experimental data (symbols) very well.
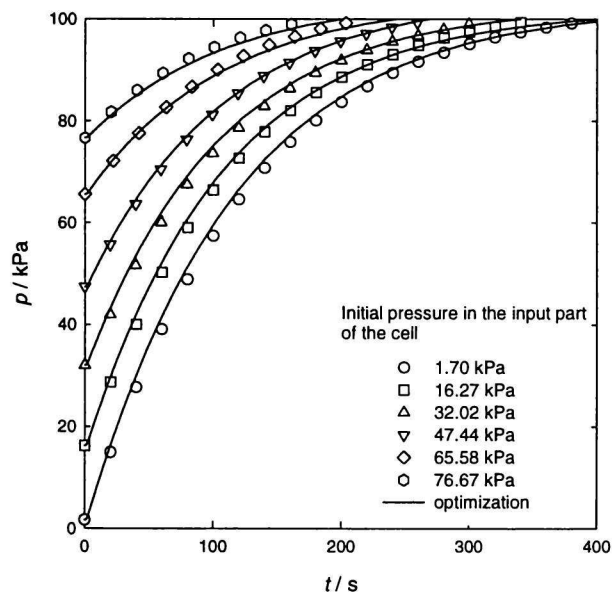
Fig. 2. Modeling of helium permeation in catalyst Cherox 42-00.

Table 2. Associated Transport Parameters of Porous Materials Tested

Catalyst	$\langle r^2 \rangle \psi$	$\langle r \rangle \psi$	$\chi^2 \cdot 10^{10}$
	nm^2	nm	Pa^2
ICI 52/1	20.57	1.107	1.210
Cherox 42-00	697.4	5.223	1.484
Alumina A5	417185	189.66	47.360

The associated transport parameters $\langle r^2 \rangle \psi$ and $\langle r \rangle \psi$ for three porous materials studied in this work are collected in Table 2.

The associated transport parameter $\langle r^2 \rangle \psi$ characterizes the viscous gas flow in catalyst and its values correspond to the increased pore size in the order ICI 52/1 (small pores) to bidispersed alumina (macropores). The inert gases are transported in the porous catalysts that have higher pores, predominantly in the bulk region. The opposite statement can be expressed for catalysts with narrower pores: the gas transport takes place in the Knudsen region. This observation agrees well with calculated results. The associated transport parameter $\langle r \rangle \psi$ includes information on permeation in the narrow pores. Volume of gas transported through the smaller pores of catalyst increases from bidispersed alumina A5 towards monodispersed ICI 52/1, relatively.

The obtained values of the associated transport parameters are comparable with those calculated from the pressure responses measured in the Wicke—Kallenbach cell when combined multicomponent non-stationary diffusion and permeation were studied, for example: the same porous catalyst Cherox 42-00 ($\langle r^2 \rangle \psi = 895.4$ nm^2, $\langle r \rangle \psi = 5.129$ nm, $\psi = 0.267$) [12].

The accuracy of the calculated values of the associated transport parameters is declared by their confidence intervals. The permeation model represented by eqns (1) and (3—8) is nonlinear in the transport parameters. The linearized model that is an essential part of iterative minimum found by the Marquardt—Levenberg method cannot be used for the confidence interval estimate. In addition, covariance matrix calculated on the basis of the linearized model was nondiagonal. Model parameters exhibit correlation (corre-

lation coefficient of parameters $\langle r^2 \rangle \psi$ and $\langle r \rangle \psi$ calculated from covariance matrix had the following values for studied catalysts: ICI 52/1 – 0.956; Cherox 42-00 – 0.944; alumina A5 – 0.897). In this respect, the correlation matrix can be used formally as the correlation parameter scale only.

The dependence of the object function χ^2 on both transport parameters for determination of maximal likelihood confidence intervals must be constructed. The confidence interval on the significance level α is then calculated from the discrete critical value of the object function χ^2_{crit}. *Beale* [13] proposed the following criterion χ^2_{crit} in this form

$$\chi^2_{\text{crit}} = \chi^2_{\min} \left[1 + \frac{p}{N-p} F(p, N-p, \alpha) \right] \qquad (10)$$

where p is the number of parameters and N is the constant denoting the number of experimental points or of pressure responses. $F(p, N-p, \alpha)$ describes $100(1-\alpha)$ % quantil of the Fisher distribution with two degrees of freedom, p and $(N-p)$.

Each pressure response contains finite number of pairs (time, pressure) the required density of which is unknown before mathematical calculation. It is necessary to consider only limited number of experimental points for the statistical treatment and calculation of confidence intervals for associated transport parameters; the discrete points in which the most sensitivity of pressure response to the small parameters change is exhibited. These sensitivity functions [14], *i.e.* partial derivation of $c(t, 0)$ with respect to the parameters, have two global extremes (it can be possible to find two places on the pressure responses) very sensitive to the changes of the individual transport parameters. For this reason, the number N was considered as number of experimental pressure responses $m = 24$ multiplied by the factor two.

The confidence intervals of the associated transport parameters $\langle r^2 \rangle \psi$, $\langle r \rangle \psi$ and values of the Beale criterion (significance level $\alpha = 0.05$) are introduced in Table 3. It is perspicuous that the value of associated transport parameter $\langle r^2 \rangle \psi$ for the monodispersed ICI 52/1 has relatively wider confidence interval than for the macroporous alumina A5. This is a typical case of porous catalyst with very narrow pores. However, uncertainty of this associated transport parameter will

Table 3. Confidence Intervals of Associated Transport Parameters (see Table 2)

Catalyst	$\langle r^2 \rangle \psi$ nm^2		$\langle r \rangle \psi$ nm		$\chi^2 \cdot 10^{10}$ Pa^2
	minimum	maximum	minimum	maximum	
ICI 52/1	1.75	39.15	1.077	1.138	1.378
Cherox 42-00	528.2	863.7	4.961	5.494	1.690
Alumina A5	403243	431151	173.71	205.97	53.950

be somewhat higher. In the opposite case, the estimate of the associated transport parameter $\langle r \rangle \psi$ is relatively precise, because its values exhibit very narrow span for all porous materials here tested.

In this place, the advantages are summarized to compare the proposed way of dynamic permeation measurement and the evaluation of the associated transport parameters of porous materials with the original method used in the last time. The original quasistationary method of measurement [6] implicates way of evaluation of transport parameters $\langle r^2 \rangle \psi$ and $\langle r \rangle \psi$. The complex construction of apparatus is then needed. The input and measuring parts of cell must have the same volume. Additionally, the input pressure changes must be realized as little pressure differences to keep condition of constant permeability coefficient (this one is pressure-dependent, see eqn (2)). In this respect, to gain the sufficient number of experimental points is laborious and time-consuming. If these assumptions are fulfilled, the partial differential equation can be overwritten to the ordinary one to find the analytical solution. The measured permeation data are then treated quickly and in an easy way and the transport parameters can be evaluated.

The new proposed way of permeation measurement offers to get a number of sufficient experimental data containing substantial information more effectively. The evaluation algorithm enables to differentiate and select the relevant information from experimental data. Thus, the possibility of correction of the experimental conditions with respect to the information gain of obtained data is ensured. Undoubtedly, the confidence of the evaluated associated transport parameters is increased. The calculation of the confidence intervals of transport parameters is the main goal of this study. On the other hand, permeation experiments done by the described way hold together some problems during application of very complex and sophisticated mathematical algorithm in the phase of experimental data analysis.

CONCLUSION

The optimization method of the associated transport parameters obtained from experimental pressure responses of the modified Wicke—Kallenbach cell was applied on the inert gas permeation through the three selected porous materials. The values of the associated transport parameters $\langle r^2 \rangle \psi$ and $\langle r \rangle \psi$ were calculated to describe the porous structure of industrial catalysts on the basis of dynamic gas transport and their appropriate confidence intervals. On comparison of results obtained with the aid of other methods (stationary diffusion, combination of stationary diffusion and permeation), it may be claimed that this new adapted way of stationary permeation measurement could be supplement to the classical methods of textural analysis.

SYMBOLS

B	effective permeability coefficient
c	molar concentration of a gas
Kn	Knudsen number
L	pellet length
M	molar mass
N	molar flux density
p	pressure
p_{in}	input pressure
R_g	universal gas constant
$\langle r \rangle$	mean transport pore radius
$\langle r^2 \rangle$	mean of squared transport pore radii
T	temperature
t	time
V_0	volume of measuring cell compartment
V_L	volume of input cell compartment
V_p	pellets volume
x	pellet length coordinate

Greek Letters

α	significance level
ε	material porosity
λ	free gas molecule path
μ	gas viscosity
ψ	geometric model parameter
ξ	capillary constant
χ^2	objective function
χ^2_{crit}	critical value of objective function
ω	gas molecule slip

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