

The intention of the new management of the Institute is to create conditions for more flexible structure of control, which would help to reach the top level of research. The following measures are planned for achievement of this ambitious aim: regular open competition for position of department heads; to strengthen the position of young scientific workers by introduction of junior research teams, and last but not least to stress a reliable process for evaluation of quality of scientists.

Further development depends on the manner of research funding in the Czech Republic. If we consider the lack of institutional funds, it would be necessary to take part in different projects of applied research without the possibility of choosing perspective problems. Our Institute is relatively well prepared for collaboration with industry, but we need cooperative partners ready for funding of ambitious research and development, e.g. research toward utilization of carbo- and heterohelices as chiral selectors for applications in chiral HPLC and membrane processes. For

example, one natural partner of the Institute in this research is an innovative company owned by our former colleague. One of our priorities for the future seems to be a search for such strategic partners.

A significant success in this effort represents the status of the recipient of “Competence Centre – BIORAF”, which the Institute has obtained recently. The Competence Centres program is focused on support of creation and operation of research, development and innovation for progressive fields with strong application potential and a prospective for important contributions to the growth of the competitiveness of the Czech Republic. The BIORAF Centre is concentrated on complex utilization of biomass by the methods of “green chemistry”.

Website: [www.icpf.cas.cz](http://www.icpf.cas.cz);

YouTube presentation:

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## Chemical Engineering Application of Transport Characteristics

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### Introduction

The industrial application of porous solids is quite widespread. Porous heterogeneous catalysts, adsorbents and membranes are used in the chemical industry and biotechnology, porous materials are common in building engineering, porous catalysts form the basis of mufflers in cars, etc. The rates of processes taking place in the pore structure of these materials are affected or determined by the transport resistance of the pore structure. Inclusion of transport processes into the description of the whole process is essential when reliable simulations/predictions have to be made. Trends, in modern chemical/biochemical reaction engineering, point to utilization of more sophisticated and therefore more reliable models of processes. The basic idea is that the better the description of individual steps of the whole process the better its description and, perhaps, even extrapolation. Dependable process description forms the basis of process control and process optimization. For example, optimum pore structure of adsorbents, membranes, enzyme/cell supports or heterogeneous catalysts can be suggested which will guarantee best activity or selectivity. Similarly, optimum operating conditions can be found when the process description is based on as full as possible knowledge of the process steps.

Because of the unique nature of pore structure of various materials, the pore structure characteristics relevant to transport in pores have to be determined experimentally. One of the possibilities is the evaluation of simple transport processes taking place in the porous solid in question. The relevance of evaluation of transport parameters from simple transport processes which take place in the porous solid in question stems from the possibility to use the same pore-structure model both for evaluation of transport parameters and for description of the process in question. It is a good idea to use a mass transfer process, which is similar to the

gas transport process under consideration. It is of advantage to choose for determination of transport parameters a (simple) process that can be followed easily at near-laboratory conditions and does not require sophisticated instrumentation.

Various choices can be made:

- pure counter-current diffusion of gas mixtures under steady-state conditions;
- binary diffusion under dynamic conditions;
- dynamic or steady-state permeation of individual gases;
- combined diffusion and permeation gas transport.

At the same time it is a good choice to use inert (*i.e.* nonadsorbable) gases; this eliminates transport of adsorbed gas along the surface of pores (surface diffusion) the nature of which is not very well understood.

The best way for experimental evaluation of transport parameters (material constants that are independent on pressure, temperature as well as the composition of used gases) are the mentioned simple transport processes. Thus, at least four combinations of transport processes can be used.<sup>1</sup>

The practical utilization of described methods and their wide practical impact are presented as examples from different areas of chemical engineering.

### Determination of effective diffusion coefficients of exhaust gases in automotive catalyst

Structured catalyst supports are widely used in automotive exhaust-gas converters.<sup>2</sup> Small sized channels are contained in monoliths to provide large surface area of the car catalytic converters. Typically, both metal and ceramic monoliths are used.<sup>3,4</sup> Ceramic monoliths made from cordierite with square cross-section channels are employed quite extensively because of relatively low production costs.<sup>5,6</sup> The active catalyst is supported

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(washcoated) onto the monolith by dipping it into slurry containing the catalyst precursors. A commonly used washcoat material is  $\gamma\text{-Al}_2\text{O}_3$  with a typical surface area of  $100\text{--}200\text{ m}^2\text{ g}^{-1}$ . The excess of the deposited material (washcoat) is then blown out with hot air and the monolith is calcined to obtain the finished catalyst.<sup>4,6,7</sup> This process gives a thin washcoat layer; however, it also results in a variation in thickness around the channel perimeter. Although the washcoat layer is thin, pore diffusion can affect monolith performance,<sup>8-12</sup> and thus need to be included in any realistic mathematical model. Therefore, it is necessary to have reliable information on the mass transport rate in the porous medium as well as the effective diffusivities of exhaust gases in the washcoat layer.

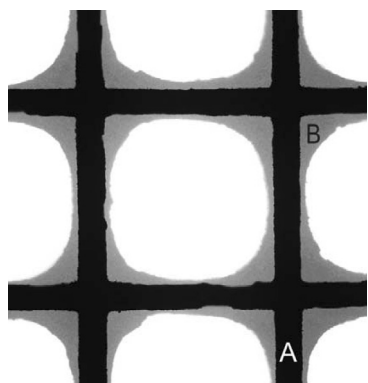


Fig. 1 – Washcoat monolith channels; A – Ceramic support, B – Washcoat layer on the ceramic support

Slika 1 – Kanali monolitnog katalizatora; A – keramička podloga, B – sekundarni nosač katalizatora

The square shape of the cells for the blank ceramic support monolith and the variation of the washcoat thickness around the perimeter after the monolith is coated by the washcoat procedure can be recognized in Fig. 1. To obtain the effective diffusion coefficients with relatively high accuracy, the inverse gas chromatography method was employed. True densities of washcoat samples (which were cut from different positions around the monolith perimeter) vary more than 10 %. The chromatographic technique suppressed this problem since the results were averaged over many pellets (more than two hundred pellets were packed into the columns). The obtained transport characteristics<sup>2</sup> were used for estimation of effective diffusion coefficients for  $\text{CO-N}_2$ ,  $\text{CH}_4\text{-N}_2$  and  $\text{C}_3\text{H}_6\text{-N}_2$  pairs, which are of interest world-wide. Such coefficients are found only rarely in the literature.

## Description of gas transport in strata during underground coal gasification

Underground coal gasification (UCG) is a method for in-situ coal conversion into a combustible gas with a high-energy value.<sup>13</sup> UCG minimizes the environmental damages in comparison with the traditional coal mining techniques.<sup>14</sup> Several modifications of UCG<sup>15-17</sup> were suggested and tested for *in situ* production of hydrogen through gasification of the unmineable coal seams not feasible for modern classic mining technologies. Especially for the deep coal seams, this method seems to be very promising.

During UCG the injected gas-oxidizing mixture (oxygen, air, steam/oxygen or steam/air) reacts with coal to form a product gas which is subsequently brought to the surface, then cleaned and used as a syngas both for power and fuel production (e.g. hydrogen, synthetic natural gas or liquid fuels).<sup>14</sup> In any case, the gases produced in the reaction zones could leak through overburden

strata. Therefore, the knowledge of the gas transport rates through porous layers is essential for project applicability to a wide range of geological conditions. Moreover, the coal seams are often situated near densely populated areas which could cause a serious problem during UCG without precise appraisal of the gas transport front in time.

Based on the knowledge of the real structure characteristics (determined by the classic textural analysis) of stratum and coal seam samples, the transport processes were modeled in order to evaluate the significance of the individual processes and their possible consequences. The influence of the kind of transported gases, temperature, and pressure together with transport-pore size were evaluated. It was found that the pressure increase influences the speed of the gas front movement more significantly than the temperature increase that is almost negligible.

The direct proportionality of the effective permeability coefficient to the effective squared mean pore radius was confirmed. At the same time, the effect of evaluated pore sizes on the rate of gas front movement was lower than the effect of the pressure increase. It was also found that the movement of the gas front for individual gases corresponds to gas viscosities; the higher the gas viscosity the lower the gas transport rate. The front of individual gases will move in the order hydrogen > ammonia > methane > hydrogen sulphide > carbon dioxide > carbon monoxide. The rate of the hydrogen front movement is approximately only twice higher than the movement of  $\text{CO}_2$  front; nevertheless,  $\text{H}_2$  front appears at the distance lower than one kilometre for the highest evaluated pressure after some years.

## Evaluation of gas transport through nanofibre membranes prepared by electrospinning

In recent years, the practical application (e.g. catalysis, filtration, tissue engineering and wound care) of nanofibre membranes has increased tremendously.<sup>18</sup> By the electrospinning process, which is the most common technology used for nanofibre preparation,<sup>19-23</sup> the prepared nonwoven mats include the submicron fibres with large surface area per unit mass and also very high macroporosity. Density of these materials is usually very low (commonly  $0.01\text{--}0.1\text{ g cm}^{-3}$ ). Especially, in heterogeneous catalysis nanofibre systems (membranes) promising seem to be porous carriers for immobilization of homogeneous catalysts based on the biopolymer compounds.<sup>19,24,25</sup> Immobilization on the nonwoven supports allows an accurate controlling of the catalytic activity and accessibility of the catalyst as well as its recovery from the reaction mixture. Sufficiently high specific surface area (ranging from  $5\text{--}35\text{ m}^2\text{ g}^{-1}$  in dependence on the fibres diameter) together with generally low transport resistance of nanofibrous membranes competes with the traditionally supported porous catalysts. Nanofibrous membranes seem to be promising supports owing to their fine porous structure, good pore interconnectivity, high specific surface area and appropriate transport properties (generally low diffusion resistance). It must be noted that membranes prepared from the layered nanofibres reveal enhanced transport properties useful for catalytic processes as well as various separation systems. These parameters depend on the fibre diameter, thickness of membrane, weight per unit area, etc.

The study was focused on optimization of preparation of polystyrene (PS) (shown in Fig. 2), polyurethane (PU) as well sandwich PU-PS-PU nanofibre membranes based on knowledge of their structural description and diffusion characteristics. Thus, the properties of prepared individual membranes can be optimized with respect to requirements for individual practical utilization. It was found that the diffusion resistance of the polyurethane membrane was much higher than that of the polystyrene membranes

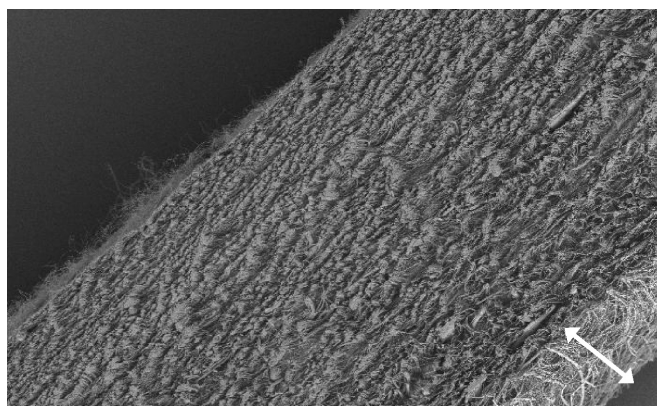


Fig. 2 – Nanofibre polystyrene membrane; the thickness is defined by the arrow

Slika 2 – Membrana izrađena od polistirenskih nanovlakana; strelica označava debljinu membrane

of the same thickness. The diffusion flow resistance increased with membrane thickness in the whole range of areal weights (usually expressed in  $\text{kg m}^{-2}$ ) for the polyurethane membranes. On the other hand, it remained nearly unchanged for the polystyrene membranes with a three times lower area weight. The diffusion resistance of the sandwich membrane correlates well with the diffusion resistance of the pure PU membrane and the diffusion transport through the PU membrane is the rate determining step. Thus, alternation of PU, PS membrane components together with the PU membrane thicknesses can control adjustment of the PS–PU sandwich membrane permeability.

### Preparation and microstructure optimization of iron oxide pellets for hydrogen storage

There exists a long known approach for hydrogen storage based on the steam iron process. By this method, hydrogen storage can be described as a reduction of iron oxides to metallic iron by

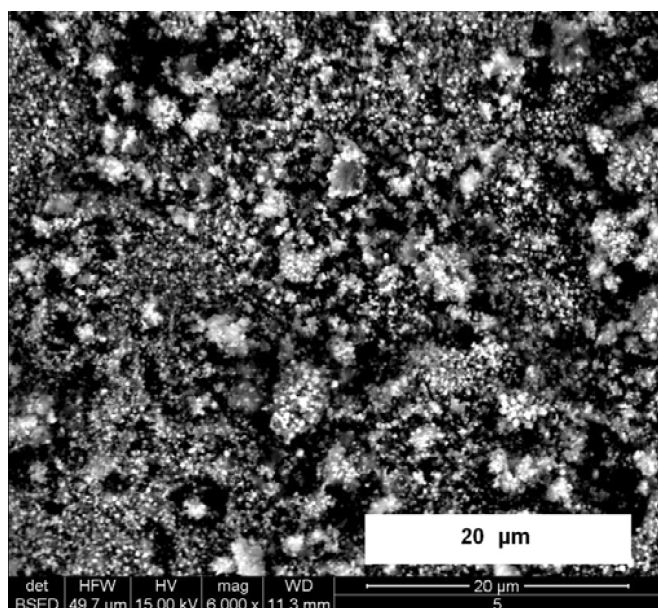


Fig. 3 – Scanning electron microscopy image of prepared  $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$  powders

Slika 3 – Skenirajuća elektronska mikrofografija pripravljenog praha  $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$

hydrogen<sup>26–29</sup> ( $\text{Fe}_3\text{O}_4 + 4\text{H}_2 \rightarrow 3\text{Fe} + 4\text{H}_2\text{O}$ ) and hydrogen production is achieved through the oxidation of iron by steam water ( $3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2$ ). The redox cycle of iron oxides can be applied as a new method of storage and supply of hydrogen. In this method, hydrogen is not stored directly, because redox cycle of iron/iron oxides works apparently as a medium for hydrogen storage. Theoretical amount of hydrogen stored as Fe metal is 4.8 wt. %. At high temperature and pressure, the reaction equilibrium is shifted to the right (i.e. hydrogen storage), at lower temperature and pressure the equilibrium is shifted to the left (i.e. hydrogen recovery). High repeatability of these cycles can be achieved by addition of various additives (e.g.  $\text{Al}_2\text{O}_3$ ) to iron.

The iron oxides were prepared by precipitation of aqueous ferric nitrate. The addition of aluminium oxide into iron oxides (see Fig. 3) prevents the sintering of metal iron and/or iron oxides during repeated redox cycles. Inverse gas chromatography technique together with classic texture analyses were employed to find the optimal porous structure based on the amounts of alumina additive together with the optimal calcination temperature for pellets preparation. It was found that pellet stability, which is essential for repetition of redox reaction and thus, process successfulness, depends on the material sintering during the process (and thus on its texture properties) and can be crucially affected by initial calcination temperature.

### Conclusions

The wide practical impact of the pore structure characteristics (transport parameters) relevant to transport in pores evaluated by the diffusion and/or permeation transport processes was demonstrated. Thus were determined the effective diffusion coefficients for  $\text{CO}-\text{N}_2$ ,  $\text{CH}_4-\text{N}_2$  and  $\text{C}_3\text{H}_6-\text{N}_2$  pairs (exhaust gases in automotive catalyst), which are of worldwide interest but rarely found in the literature. Similarly, the transport of process gases that form in surrounding strata during underground coal gasification was intimately described. The application of this method was also shown for the detail characterization of nanofibre membranes prepared by the electrospinning technique. The practical impact for the microstructure optimization of iron oxide pellets used for hydrogen storage was thoroughly discussed and explained.

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