EVALUATION OF LOCAL DIFFUSION COEFFICIENTS IN POROUS CATALYST

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Abstract
Local transport properties of porous medium are investigated by the means of 3D reconstruction and computer simulations on micro and nano scale. A new method for evaluation of local pore radii – maximum sphere inscriptions method (MSI) is proposed. The pore size distribution is compared with the results obtained by virtual capillary condensation method and experimentally measured pore size distribution. The obtained local pore radii are then employed in calculation of local Knudsen diffusivities. Relationship between mass transport and local Knudsen diffusivities is confronted with the results of molecular dynamics simulations.

Computer reconstruction
The information about catalyst structure (obtained from the SEM & TEM images and combined with the data from mercury porosimetry and adsorption/desorption isotherms) is then employed in the computer reconstruction of 3D porous catalyst. The reconstructed section of porous catalyst is represented by discrete phase function in the form of 3D model. The porous medium is generated by the particle-packing method. The method is based on random packing of primary particles (defined shape, size, mixing ratio) followed by partial ordering (defined fractional overlap between the particles), which approximates actual catalyst formation processes.

Porosity medium analysis
Virtual capillary condensation (VCC) can be used for evaluati- on of pore size distribution. The method is based on the fact that the equilibrium vapour pressure above a curved liquid-vapor in- terface is reduced, as expressed by the Kelvin equation:

\[ p^* = p_0 e^{-\frac{2\gamma L}{RT}} \]

The maximum sphere inscriptions method (MSI) is designed for the evaluation of local pore radius. Stereometric criteria are used: a sphere is gradually expanded in each spatial node of the pore until it collides with the wall. Local pore radius in each node is equal to the radius of the biggest sphere that covered it.

The local pore radii evaluation in this simple way tend to under- estimate, particularly in small pores with poor discretisation. To overcome this systematic underestimation, the penetration factor \( \sigma \), ratio of the penetrated volume and total volume of the inscribed sphere, needs to be introduced.

The penetration factor \( \sigma \) was obtained from the comparative simulations with simple cylindrical pores of defined diameter, where the evaluated mean radius have to be equal to the defined pore radius \( r \).

Continuum model vs. molecular dynamics
The local pore radii have then been used for the calculation of effective diffusion across the porous medium, whereby local Knudsen diffusion coefficients were employed depending on the local pore radius. This continuum-based approach was then compared with the results of diffusion through the same porous media simulated by the molecular dynamics.

Simulations of catalytic washcoat on nano-scale

Conclusions
The agreement of \( D_r \) and \( D_m \) is relatively good, but is not perfect – which it was not expected to be given that the MSI in combination with continuum model of diffusion is an approximation. We conclude that for the purpose of further reaction-diffusion type modelling of phenomena in porous catalyst at the smallest length-scale the use of the MSI method is satisfactory.

Our further work will include a detailed investigation of the effect or pore space morphology on the validity of the MSI method and its subsequent use for the solution of an inverse problem, i.e. porous medium design.

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