ISCRE25
FLORENCE 2018
BRIDGING
SCIENCE & TECHNOLOGY
The 25th International Symposium
on Chemical Reaction Engineering
20-23 May 2018
Florence, Italy
www.aidic.it/iscre25

Modeling gamma-alumina catalyst supports as networks of randomly connected pores

Sonia Ferreira[1,2], Jan Verstraete[1,*], Elsa Jolimaitre[1], Damian Leinekugel-Le Cocq[1], Christian Jallut[2]

[1] *IFP Energies nouvelles, Rond-point de l'échangeur de Solaize, 69360 Solaize, France*

[2] *Univ Lyon, Université Claude Bernard Lyon 1, CNRS, LAGEP UMR 5007, 43 boulevard du 11 novembre 1918, 69100, Villeurbanne, France*

**Corresponding author: jan.verstraete@ifpen.fr*

Highlights

- Microscopic pore network model based on interconnected cylinders
- Transient mass transfer simulations inside the network to calculate the tortuosity
- At least two levels of porosity are needed to obtain typical experimental tortuosities

1. Introduction

As active phases of modern catalysts are more and more efficient, diffusion within catalyst supports frequently becomes a limiting step. Hence, there is an increasing demand for comprehensive models to represent porous catalysts in order to optimize catalyst design and increase catalyst performance. Mass transfer through such porous media is classically represented on a macroscopic level based on the concept of an effective diffusion coefficient. To get a more realistic representation accounting for the structure and connectivity in porous media, microscopic models based on a pore network model are needed.

In the open literature, the available microscopic models are generally directly applied to diffusion-reaction systems without separately analyzing the mass transfer behavior and confronting it to experimental data. In this work, we represent the catalyst support by a network of interconnected cylinders of different sizes. In a second step, diffusion within the network is simulated by solving the transient material balance in each pore. To validate the approach, the effective mass transfer is estimated for the generated pore networks and compared to experimentally obtained effective diffusion coefficients from fixed-bed tracer experiments.

2. Methods

To generate porous networks constituted by randomly interconnected pores, a connectivity pattern, a pore size distribution and a pore existence probability are used as inputs. The initial condition of the network is a pre-defined grid of nodes positioned in 2D or 3D with N_x, N_y and N_z nodes along each axis, resulting in a maximum number of nodes in the network of $N_x \times N_y \times N_z$. A Monte Carlo algorithm walks through the grid and randomly creates pores based on the connectivity pattern. By changing the connectivity pattern, different types of networks can by generated in 2D (square, triangular, hexagonal) or in 3D (simple cubic, body-centered cubic, diamond, tetrahedral), each having a different maximum connectivity. Networks can also be created with a periodicity along the x, y, and/or z axis. At the end of the procedure, the textural properties of the support are calculated. The resulting network is then exported under the form of a connectivity matrix.

The transient mass transfer behavior in the pore network can be simulated by solving the diffusion equation, using either the Fick model or the Maxwell-Stefan model, for each pore. For nodes at the surface of the particle, the concentrations of the species are known, while Kirchhoff's laws are used as boundary conditions for the internal nodes. To simulate transient 1D mass transfer by diffusion in each pore, orthogonal collocation is used for the spatial discretization, while the time discretization uses the DAPSK routine.

3. Results and discussion

One of the outstanding features of the developed network generation algorithm is its capacity and highly efficient data storage. Indeed, it was possible to create extremely large networks (15000×15000 nodes in 2D and 600×600×600 nodes in 3D), containing up to 340 million pores connecting 225 million nodes. On a Dell desktop computer with a 3.5 GHz Intel Xeon E5 CPU and 16GB of RAM, it takes about 4 s to build a square

pore network with 200×200 nodes, and about 13 min to build a cubic network with 600×600×600 nodes. Regarding the mass transfer model, the memory requirements of the numerical solvers limit the network sizes that can be simulated, but 200×200 networks with over 100,000 pores have been simulated.

When comparing to actual aluminas (Figure 1a), the pore network generation algorithm is able to create pore networks that correctly describe the textural properties (ε, S_{BET}, V_p, PSD) of various aluminas within their experimental errors. A second validation for the generated pore network concerned the intra-particle diffusion. Hence, mass transfer in a periodic 2D network of 100×100 nodes was simulated to estimate the effective diffusion coefficient, and hence the tortuosity. The resulting values were compared with experimental data obtained for different gamma-aluminas pellets by using fixed-bed tracer experiments [1]. Surprisingly, none of the random porous networks generated with different connectivities and pore size distributions were able to correctly represent the intra-particle mass transfer. Indeed, plotting the calculated tortuosities against the catalyst porosity shows that tortuosity decreases with increasing catalyst porosity, as expected, and that our values are in line with those obtained by Tomadakis and Sotirchos [2]. However, for aluminas with an overall porosity of 0.7, the simulated tortuosities are therefore typically around 1.3, while the experimentally measured tortuosities obtained via Inverse Chromatography are much higher, typically between 2 and 3 [1], suggesting that only part of the porosity of the alumina support actively contributes to the mass transfer. It is therefore concluded that the porous networks of actual aluminas are not completely random, as our pore network model, but organized into two different levels of porosity. The first level of porosity would result from the stacking of the elementary nanocrystals of alumina and are called aggregates, while the second level is created by the porosity around the aggregates, thereby constituting a second pore network with slightly larger pores [1]. Our pore network algorithm was therefore modified to generate this type of network organization (Figure 1b) and intra-particle mass transfer was simulated in such networks. Figure 1c compares the calculated tortuosities from various two-level porosity networks with the correct textural properties to the experimental tortuosity of alumina C.

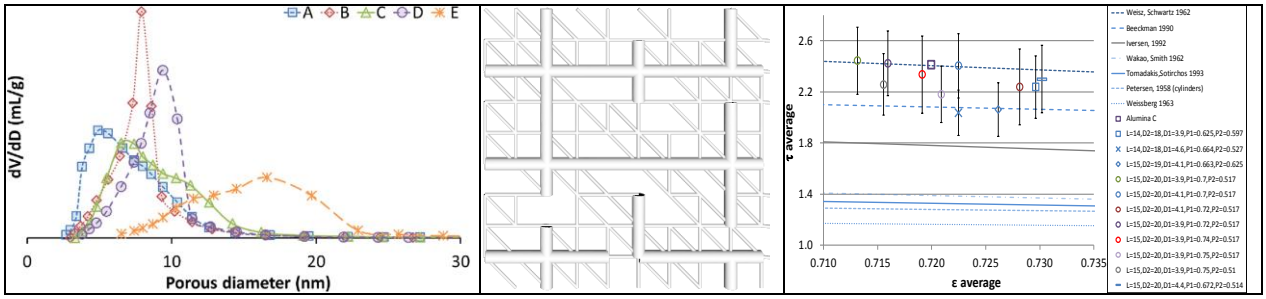

Figure 1. Diffusion in reconstructed gamma-alumina pore networks: (a) experimental BJH pore distribution for 5 alumina supports, (b) reconstructed pore network model with two levels of porosity, (c) calculated vs. experimentally measured tortuosity for pore networks with two level of porosity.

4. Conclusions

In this work, an efficient pore network generation tool was developed to represent gamma-alumina catalyst supports. To validate this representation, the textural and diffusional properties of these pore networks were compared to experimental values for actual aluminas. Using one-level porous networks, the textural properties are in good agreement, but a large discrepancy is observed when confronting the simulated tortuosities (<1.5) with experimental values (2 to 3). This implies that actual aluminas are organized differently, as already suggested in the literature [1]. Using pore networks with two porosity levels, both the textural and diffusional properties of actual aluminas were correctly represented.

References

[1] S. Kolitcheff, E. Jolimaitre, A. Hugon, J.J. Verstraete, P-L. Carrette M. Tayakout-Fayolle, Microporous and Mesoporous Materials (2017), 248, 91–98.
[2] M.M. Tomadakis, S.V. Sotirchos, Journal of Chemical Physics (1993) 98(1), 616–626.

Keywords: tortuosity, pore network models, diffusion, gamma-alumina supports.