Modeling Alumina Supports by Means of 3D Pore Network Models

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Highlights

- A fast algorithm to characterize digital pore networks was developed.
- Nitrogen sorption, mercury porosimetry, and cryoporometry were encoded and simulated.
- Pore blocking and thermodynamic or mechanical equilibrium were considered.
- Simulations for pore networks reproduce the trends of typical experimental curves.

1. Introduction

Porous materials are widely used as catalyst supports in the chemical industry. Amongst these are γ-aluminas, which are and relatively inexpensive and easy to fabricate. Various characteristics of the support have a direct impact on the final performance of the catalyst, amongst which are the chemistry, the surface area, the mass transfer properties, and the mechanical strength. Through optimization of the catalyst active phase, increasing catalyst activity may lead to internal mass transfer limitations, as the particle size of industrial catalysts is generally chosen to be large to limit the bed pressure drop. Since the architecture of the porous material can also induce internal mass-transfer limitations, understanding both the textural properties and the topology of the solid is key to further improve the catalyst performance.

Modeling the phenomena that occur in the interior of the pore network can allow to assess the catalyst support's architecture and tortuosity and orient its design. To assess the phenomena that occur inside the porous structure, it is possible to use either mimetic models or reconstruction models. Mimetic methods aim at creating the final material by simulating its synthesis, starting from the genesis all the way to the final structure of the solid. On the other hand, reconstruction methods directly model the material in its final state. Among the reconstruction methods, pore network models are common representations. They are widely used because of their ease of construction, flexibility, and reasonable computer processing unit (CPU) intensity. In this work, a methodology to create a γ-alumina digital twin capable of reproducing experimental nitrogen isotherms and scanning curves is described and validated against five different catalyst samples. Tracer diffusion simulations on these digital twins also allow to correctly estimate the tortuosity of each sample.

2. Methods

Five boehmite γ-alumina supports were studied in this work. These were obtained by precipitation of aluminum salts in an aqueous solution. The boehmite precipitate was filtered and washed. Shaping involved the passage from a boehmite powder to support pellets. Textural properties measured were physical nitrogen adsorption on an ASAP 2420 instrument and helium pycnometry on an Accupyc 1340 instrument [1].

The pore network model is created through a discrete reconstruction method that is based on a stochastic algorithm. In the model, the pores are represented by hollow cylinders that connect two nodes. These nodes are initially distributed on a lattice, which defines the maximum connectivity of the network. Different features provide heterogeneity to the digital structures and allow to get a good representation of both the textural properties and the topology of the network. The pore network generation algorithm is described in more detail elsewhere [2].

Nitrogen sorption is a classic characterization technique that is used to obtain information about the textural properties of porous solids. To model nitrogen porosimetry, the Kelvin equation was used to represent the thermodynamics of the vapor−liquid equilibrium in a confined medium. As the Kelvin equation models the core condensation, the Harkins−Jura statistical thickness equation was used to model the thickness of the adsorbed nitrogen layer on the pore walls prior to the core condensation. Further details of the algorithm can be found in [3].

3. Results and discussion

The textural properties of the digital pore network were calculated both geometrically and by processing the network through computer-equivalent characterization techniques. Compared to the direct calculation of the textural properties by simply assembling the properties of the individual pores, the direct simulation of the entire characterization profiles provides a better interpretation of the experimental results by analyzing the validity of the assumptions made by theoretical and/or empirical models used for the calculation of the material's textural properties from the experimental data. For the characterization techniques, the use of a dynamic priority list to handle the exploration of the network is valid for all characterization techniques, as the phase change and/or percolation phenomena occurring in every technique are constrained by the topology of the network. The algorithms correctly reproduce typical hysteresis behavior observed in the experimental results for alumina catalyst supports. To match the textural properties of the digital pore network with that of an actual alumina support, the input variables of the network model are modified until the differences between the output textural properties and actual values are minimized. A good agreement was observed between the properties of the digital twins and the actual aluminas.

Using the pore network model representation, the intraparticle diffusion of a tracer was simulated by a Fickian approach. The back-calculated tortuosity factor showed a good agreement with the experimentally measured values. The approach allowed to estimate the tortuosity factor of each catalyst within 20%.

Finally, diffusion-reaction was simulated in the case of selective hydrogenation of butadiene. By varying the pore network properties, their effect on the effectiveness factor was investigated.

4. Conclusions

In this work, a pore network generation algorithm was used to represent gamma-alumina supports. To obtain the textural properties of such a digital pore network, an Invasion Percolation algorithm was adapted in order to characterize this structure by means of the computer-equivalent of nitrogen porosimetry, mercury porosimetry, NMR cryo-porometry, and thermo-porometry. Using the developed algorithms, it was possible to generate digital pore networks whose properties are in good agreement with the properties experimentally measured by different characterization techniques on actual gamma-alumina supports. Finally, the pore network model representation of a gamma alumina has been used for simulating intraparticle diffusion in the case of tracer diffusion and of selective hydrogenation of butadiene.

References

[1] S. Kolitcheff, E. Jolimaitre, A. Hugon, J.J Verstraete, P-L. Carrette, M. Tayakout-Fayolle, Microporous and Mesoporous Materials 248 (2017) 91.

[2] G.A. Ledezma Lopez, J.J. Verstraete, L. Sorbier, A. Glowska, D. Leinekugel-Le-Cocq, E. Jolimaitre, C. Jallut Ind. Eng. Chem. Res. 60 (2021) 16728.

[3] G.A. Ledezma Lopez, J.J. Verstraete, L. Sorbier, A. Glowska, D. Leinekugel-Le-Cocq, E. Jolimaitre, C. Jallut, Chem. Eng. Sci. 260 (2022) 117812.

Keywords

Nitrogen sorption ; Mercury porosimetry ; Pore network models ; Gamma alumina supports.