# IMPREGNATION AND DRYING OF SUPPORTED METAL CATALYSTS: MODELLING IN PORE-SCALE

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#### Summary

Influence of the drying step on the final properties of a porous supported catalyst is investigated by mathematical modeling and experiments. The system under consideration is a mesoporous silicaalumina impregnated with a metal catalyst (Ni, Pt). The distribution and size of the metal nanocrystallites are strongly influenced by the drying conditions. In the model the porous support structure is digitally reconstructed in 3D, and computer simulation of the impregnation and drying is carried, using the generalized volume-of-fluid method. Local mass balances involve diffusion of the dissolved species, nucleation and crystal growth (including Ostwald ripening), and evaporation of the solvent coupled with propagation of liquid menisci (Kelvin equation).

#### Keywords

Rational design of catalysts, Computational catalysis, Multiphase and particulate reactors

### Introduction

The microstructure of the support determines transport properties of porous catalysts such as effective diffusivity<sup>1</sup> and thermal conductivity<sup>2</sup>. Spatial distribution and sizes of catalytic metal particles then influence local reaction rates.<sup>3</sup> Both reaction and transport properties affect conversions of input compounds in steady-state and under transient operating conditions.<sup>3</sup> In order to optimise the catalyst properties for the most efficient utilisation of the active metal, which is often an expensive element such as Pt, Pd, Au, etc., it is necessary to understand the processes that take place during the catalyst preparation. Experiments as well as mathematical modelling can be used to study the influence of preparation conditions on the resulting properties of supported metal catalysts.

In this contribution the influence of the drying step on the final catalyst properties is investigated. The system under consideration is a mesoporous support (silica and silicaalumina) impregnated with a metal catalyst (Ni, Pt). Impregnation of the support with a solution of the metal precursor is followed by drying whereby micro-crystals of the precursor are deposited in the pores of the support. The final steps include calcination in a reducing atmosphere thereby forming the catalytically active metal species. The catalytic activity depends on parameters such as total quantity, surface area and size distribution of the metal nano-crystallites, but also on their position within the pore space. All of these parameters are strongly influenced by the drying conditions.



**Figure 1**. a) SEM picture of meso-porous structure of  $Pt/\gamma$ -Al<sub>2</sub>O<sub>3</sub> (white: pores, grey:  $\gamma$ -alumina, black: Pt); b) 3D reconstructed structure with dispersed Pt particles.

### **Model and Results**

Porous medium can be experimentally characterised, e.g., by mercury porosimetry, adsorption-desorption isotherms and SEM/TEM microscopy.<sup>2</sup> The porous catalyst support is digitally reconstructed to re-create computationally its realistic structure in the form of a discrete 3D phase function.<sup>1-4</sup> A simulation of the impregnation and drying steps is then carried out in the reconstructed catalyst support, using generalised volume-of-fluid method<sup>2</sup>, to obtain catalyst structure with deposited metal crystallites.

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The mathematical model is based on local mass balances and includes diffusion of the dissolved species, nucleation and crystal growth in the pore space (including sizedependent effects such as Ostwald ripening, cf. Figure 2), and evaporation of the solvent coupled with propagation of liquid menisci in the pore space (governed by the Kelvin equation, cf. Figure 3). All the equations are solved within a spatially 3D domain of the computerreconstructed porous support.

The output of the simulation is a spatial distribution of crystallites in the pore space (cf. Figure 1) as a function of drying kinetics, initial concentration, and pore space morphology. The trends obtained from the model will be compared with experimental data for Ni impregnation on silica and used for model validation as well as for the identification of a priori unknown model parameters, related e.g. to the nucleation kinetics. Simulations of reaction and transport can be then done within the resulting reconstructed porous catalyst to evaluate important macroscopic characteristics like effective diffusivity. volume-averaged reaction rates, and effectiveness factor.<sup>3,5</sup>







**Figure 3**. Example of liquid meniscus in a 3D reconstructed cylindrical pore, and height of meniscus in dependence on contact angle  $\theta$ .

## Conclusions

The studied processes are strongly relevant to practical application during the preparation of porous supported catalysts (impregnation of active metals dissolved in a liquid, followed by drying of the solvent).

The methodology presented here follows from our previous work which dealt with the characterization and prediction of porous structure and modeling of reaction and transport inside the porous medium<sup>1-6</sup> and thus forms a new segment to the virtual platform for porous media simulations.

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