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High Throughput Nano-Tomography of DeNOx Catalysts for Diffusion Modeling

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Abstract

A high throughput nanotomography study of 78 DeNOx catalyst samples at a resolution of ~100nm was conducted in order to investigate long-term changes in their pore structure and thereby in the diffusive transport properties. We succeeded in deducing an effective diffusion constant for a scanned volume by using a finite element method (FEM) solution of the reaction diffusion equation directly on a mesh generated from the tomogram.

Keywords: Catalysis, Material Science, Nanotomography, Gas Transport in Porous Media, Diffusion Modeling, Finite Element Method.

Background and Objective

Nitrogen oxides (NOx) are toxic byproducts of the combustion of fossil fuels. With the use of a catalyst, NOx can be efficiently reduced by ammonia in the presence of oxygen yielding the non-toxic products N2 and H2O [1,2,3]. This process is called selective catalytic reduction (SCR) since ammonia is unique in its selectivity towards reduction of NOx to form N2. Commercial SCR catalysts are based on vanadia supported fiber re-enforced ceramic monoliths. Monoliths allow large flow rates with low pressure drop. The support material is designed to be highly porous in order in increase the reactive surface area, here it is TiO2 in its highly porous form of anatase. The system used for this study is a commercial catalyst commonly applied in industry to clean exhausts gases in trucks. While in use, those catalysts "age"; they loose reactivity over time. Structural changes in the support material are suspected to be a major contributor to this process, since they alter diffusivity of reactants and products as well as the chemically reactive surface area. Since those processes are interlinked, we do not want to rely on heuristic methods, which treat each effect separately, but instead aim for a full simulation of the reaction-diffusion dynamics on the structure of the sample. We therefore chose to use the finite element method (FEM) to solve the governing equations [4][5] directly on a tetrahedral mesh extracted from the tomograms. The first project goals are therefore to develop suitable methods to segment the gray scale tomograms into air and material. Thereafter, the FEM model has to be set up, together with a suitable meshing code. Once it is possible to model single subvolumes, we need to fully automatize the entire pipeline, in order to make full use of the many samples we were able to measure. This will produce statistically relevant data about the ageing process even though the samples themselves are expected to be highly inhomogeneous.

The project will allow for both, a better fundamental understanding of the diffusion processes in this type of porous system, as well as deep insights in the ageing process from a material science point of view. This will eventually lead to the development of more efficient and longer lasting catalysts.

Experiments

Using the experimental setup for nanotomography at the beamline BL47XU enabled us to acquire tomograms from various positions and aging steps of 2 different types of catalyst. For each type and aging step we typically managed to scan three samples. The samples were industrially produced DeNOx monoliths. The ageing has been done in a test oven at 550 degree C. We had a fresh sample and the ageing steps 500h, 1000h and 2000h We took each three samples from three positions from the monolith. The samples for the experiment were elongated pieces of ~50 - 100 microns in diameter, mounted directly on a brass sample holder with vacuum grease. We used a X-ray energy of 8keV. A full tomogram consist of 1800 projections.

We analyze the reconstructed data, by first generating a binary image through a suitable segmentation method. We then generate a triangular unstructured volume mesh of the pore space. We use the mesh to analyze the volume and extract relevant statistical parameters, such as surface area, pore size distribution and porosity. We then solve the reaction diffusion equation for the concentration of NO directly on the mesh, via the finite element method. This tells us exactly how diffusion limits the catalytic efficiency of the

catalyst. In order to compare to experimental data, we use the extracted microscopic parameters as an input for an analytic model [6] predicting the efficiency of a sample large enough for a catalytic test unit, which is typically of the order of several centimeters. We are using Otsu's method for segmentation. The mesh is generated with an algorithm based on the CGAL library [7]. The FEM uses a custom code implemented in MATLAB.

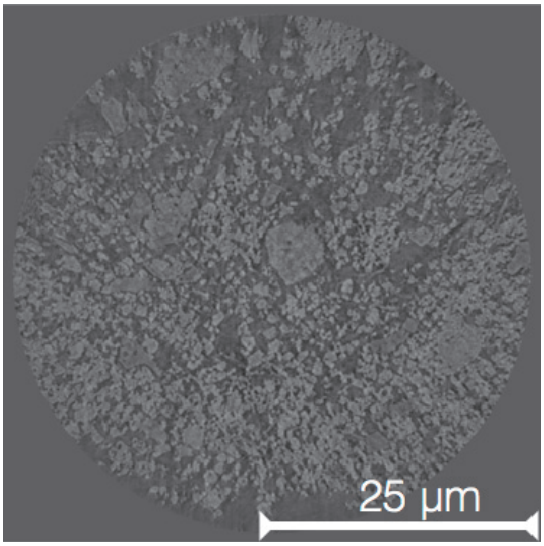

Figure 1 : Slice through a typical tomogram obtained at the experiment. The resolution was ~100 nm.

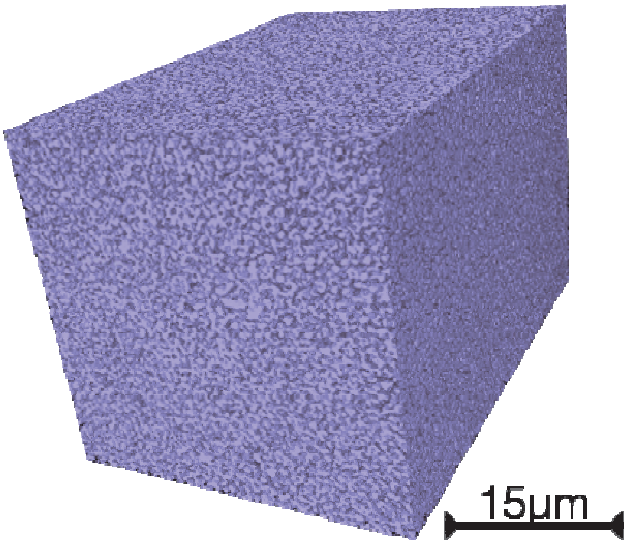

Figure 2: 3D rendering of a segmented tomogram.

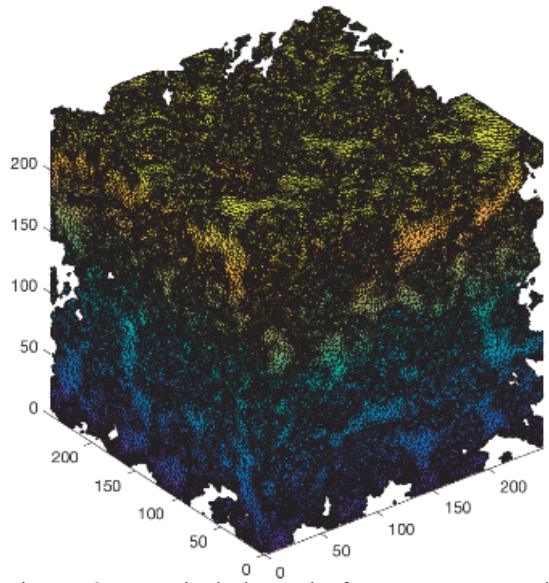

Figure 3: Tetrahedral mesh from a segmented sub-volume of a tomogram, which is used as an input for a FEM simulation of the reaction-diffusion dynamics in the system.

Parameter	Value
Prosity [%]	0.4
Effective Diffusion Constant [cm^2 / s]	0.032
Effective Volume Rate [1/s]	290
Tortuosity	2.1

Table 1:Bulk parameters directly extracted from the local information in the tomogram.

Results and Discussion

The image quality is high enough to easily segment (Fig. 2) and mesh (Fig. 3) the volumes. We were able to calculate porosity, an effective diffusion constant, an effective catalytic reaction rate and the tortuosity for the scanned volume.

Next Steps

At the point of writing this report, we are working on a cluster implementation of the analysis code, which will be capable of performing all steps without user input on all of the scanned volumes. Once this is done, we can proceed to analyze the full dataset of 78 tomograms and get information about the homogeneity of the sample across a monolith and the influence of ageing on the structure and how it affects the catalytic efficiency.

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