Diffusion Engineering of an Ammonia Slip Catalyst Through X-ray Tomography

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Abstract

A high throughput nano-tomography study of over 30 Ammonis Slip Catalyst (ASC) samples at a resolution of ~100 nm was conducted in order to investigate the structural changes due to different preparation methods and in a further step, calculate the effective diffusion through the layer.

Keywords :   Catalysis, Material Science, Nanotomography, Gas Transport in Porous Media,
Diffusion Modeling

Background and Objective

The current technology for removal of harmful NOx gases from diesel exhaust is based on the selective catalytic reduction by ammonia (NH3-SCR), in which NOx is selectively reduced to N2, according to 4 NO + 4 NH3 + O2 → 4 N2 + 6 H2O. In practical applications, this reaction is done with a 5-10% of excess ammonia, which is removed afterwards in the ammonia slip catalyst by oxidation of ammonia with oxygen to N2. Typical operation conditions for these catalysts are 200-500 °C, with NO and NH3 inlet concentrations on the order of 100-1000 ppm, and 5-10% O2 and water. Standard catalysts for SCR are V2O5/TiO2 and Cu- or Fe-zeolites [1], which are typically applied on the walls of a monolithic support, with channels on the order of 1-2 mm in size.

Ammonia slip catalysts (ASC) are also monolithic catalysts, containing an ammonia oxidation catalyst, which usually is Pt, combined with an SCR catalyst. The function of the SCR catalyst is to enhance the selectivity to N2, since the majority of ammonia is oxidized to NOx over the Pt catalyst. The latest designs of the ASC contain a layered structure, in which the oxidation catalyst is covered with a thin SCR layer. It has been shown that such a layered design results in a significantly better selectivity to N2 [2].

As a consequence of the layered catalyst design, the diffusion of NH3 and NO through the SCR layer has a direct impact on the performance of the final product. If the diffusion through the SCR layer is difficult, the ammonia will not reach the oxidation catalyst, resulting in a low conversion of ammonia. Making a thinner SCR layer will improve the ammonia conversion, but then the selectivity to N2 decreases, which is not desirable. A faster diffusion through the SCR layer will allow for a sufficient ammonia conversion without compromising the selectivity towards N2.

One cause for a slow diffusion of NH3 and NO is the pore structure of the SCR layer. The effective diffusion through the SCR layer is determined by the contributions of the bulk diffusion of these components and the Knudsen diffusion with decreases with the pore size in the SCR layer, for pore sizes diameter well below 1μm. The best diffusion properties are thus obtained by creating an SCR layer with sufficient pores of about 1 μm in diameter.

To produce an SCR layer with the desired pore size, organic pore modifiers can be used. These modifiers are deposited together with the catalyst particles in the SCR layer. Then these are burnt off, leaving free space between the particles, and in this way extra pores are created in the SCR layer. The aim of the project is to relate the differences in performance to the pore structure in the SCR layer. By using different amounts and types of organic pore modifiers, SCR layers with different pore structures can be made. Without advanced characterization methods, it is difficult to relate the effect of the pore modification to the performance, since many of the relevant parameters of the pore space, such as connectivity and tortuosity are inherently 3D.

Experiments

Using the experimental setup for nano-tomography at the beamline BL37XU enabled us to acquire tomograms from 6 different preparation types (Figure1). For each type we managed to image up to 5 samples. The setup worked mostly without any problems. Over all, we recorded and reconstructed 30 high quality tomograms with a voxel size of 40.5 nm within 24 hours. At the moment of the writing of this report, we are working on advanced algorithms for pore structure analysis.
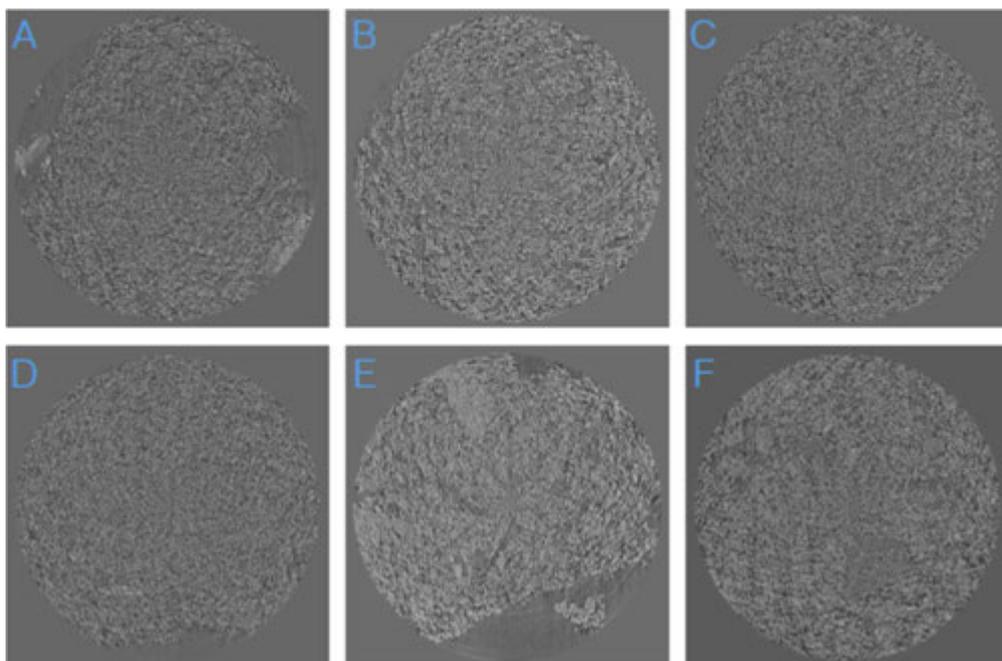
Figure 1: Slices from six different samples which have been prepared with different pore modifications. The changes in pore structure are clearly visible. Note for example the larger particles in B, or the large agglomerates in F.

Results and Discussion

The high image quality at BL37XU gave important qualitative insight into the effect of different preparation methods of the ASC monolith (Figure 1). Since we are only interested in the diffusion trough one thin layer which is part of a multilayer catalyst, established laboratory techniques such as mercury intrusion porosimetry are not applicable here, since they rely on a powder made form the entire monolith and are thus insensitive to specific areas of the sample. In contrast, as demonstrated, using high resolution X-ray tomography can give local information, since we were able to extract a single layer by hand from the monolith and image it at BL37XU. However, the image quality is not good enough to use the established workflow for X-ray based analysis of the pore size distribution, which is to segment the image and then use a shrinking ball algorithm to measure the distance of each pore-voxel to the next wall. It will therefore be necessary to develop segmentation free methods to estimate the pore size distribution.

Next Steps

We are currently involved in a research effort together with Computer Scientists from the Danish Technical University (DTU) to develop an appropriate segmentation free method to calculate the pore size distribution from the tomograms. Once successfully, we can use this to calculate the diffusivity through the layer [4][5] and compare those results to experimental performance measurements.

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