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Multi-Dimensional Multi-Functional Catalytic Architecture: A Selectively Functionalized Three-Dimensional Hierarchically Ordered Macro/Mesoporous Network for Cascade Reactions Analyzed by Electron Tomography

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The controlled placement of chemical functionalities on solid supports is a central tenet that underpins catalytic engineering. Control of the spatial distribution of individual functions in particular can enable choreographing and enhancement of reaction processes, including multi-functional behavior. Advancing this design strategy, the selective harboring of catalytic functions in compartmentalized porous networks, with interconnected routes for transport of reactants and products, is an attractive concept that could achieve fine control of catalytic cascade reactions. Inherently this implies sophisticated multi-dimensional architectures, requiring both innovative synthesis protocols and methods capable of characterizing the structures. Here we report the three-dimensional pore structure and selective functionalization of a hierarchical macro/mesoporous silica framework for Pd/Pt catalyzed cascade reactions, achieved by electron tomography in the scanning transmission electron microscope (STEM).

A hierarchically ordered macro/mesoporous SBA-15 silica framework was synthesized through stepwise template removal [1]. Decoupling of the individual template extractions allowed independent functionalization of macropore and mesopore networks on the basis of chemical and/or size specificity, wherein Pt nanoparticles ~2 nm diameter were directed selectively into 3.5 nm mesopores, while larger ~6 nm Pd nanoparticles would be confined to the macropores. Electron tomography was performed using high-angle annular dark-field imaging in STEM, along with total variation minimization based 3D reconstruction. Macro/mesopore structure and Pd/Pt particles were segmented from the tomogram by a series of image processing steps including denoising, unsharp masking, histogram intensity thresholding, binarization, and morphological and logical operations.

To reveal the 3D structure requires several modes of visualization, summarized in Figures 1 and 2, which verify the key aspects of the catalyst design. The tomogram encompasses approximately one third of a macropore (viewed face on in Figure 1) and the beginnings of several others. Between macropores, a complex multi-directional mesopore structure is disclosed, comprising regions with linear ordered hexagonal arrangement of mesopores as well as regions with significant pore curvature. Packing faults in the mesopore structure are also seen, and the three-dimensional interrogation enables comprehension of the macro/mesopore connectivity. The location of the larger Pd and smaller Pt nanoparticles is revealed directly, which reside dominantly in the macropores and mesopores, respectively.

The tomographic analysis offers a 'reactant's view' through the structure, quantitative analysis of the morphology and catalyst loading, and permits a direct relation to the efficacy for guided catalytic cascades. Providing feedback for development of synthetic strategies, tomographic analysis should play a significant role in the advancement of multi-dimensional multi-functional materials embracing spatially compartmentalization of functions, which could be deployed to achieve a variety of chemical conversions in a more efficient and ‘green’ manner [2].

References:
[1] CMA Parlett *et al*, Nature Materials **15** (2016) p. 178-182.
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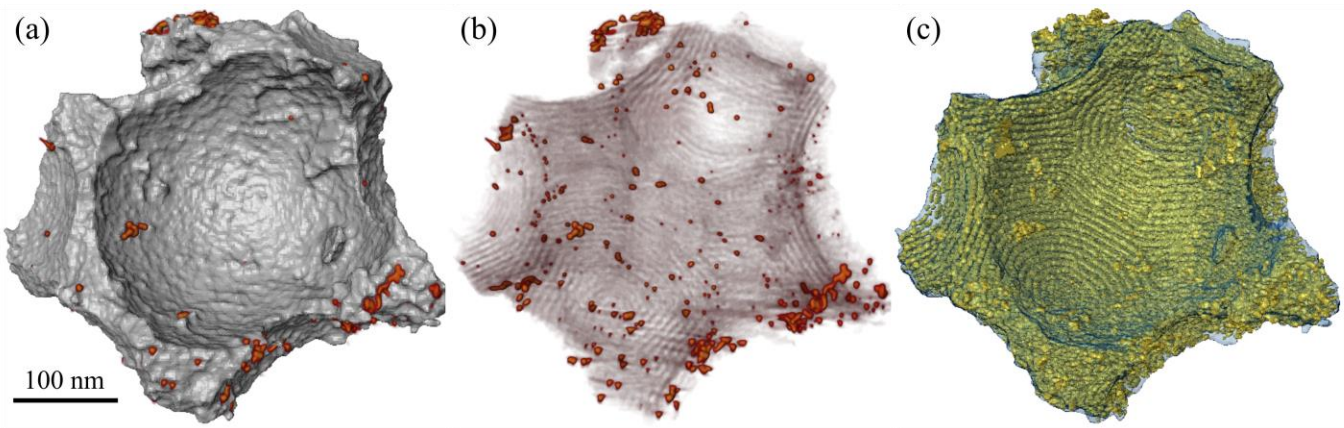

Figure 1. Visualizations of an electron tomography reconstruction of a hierarchical macro/mesoporous SBA-15 silica selectively loaded with small (~2 nm) Pt nanoparticles in the mesopores and larger (~6 nm) Pd nanoparticles in the macropores. (a) volume rendering combined with surface rendering of the outer morphology of the SBA-15 (note that only the larger Pd nanoparticles in the macropores are visible), (b) volume rendering alone (showing both Pd nanoparticles and the smaller Pt nanoparticles located within the internal mesopores), (c) semi-transparent rendering of the surface in (a) along with surface rendering of the internal mesopore structure.

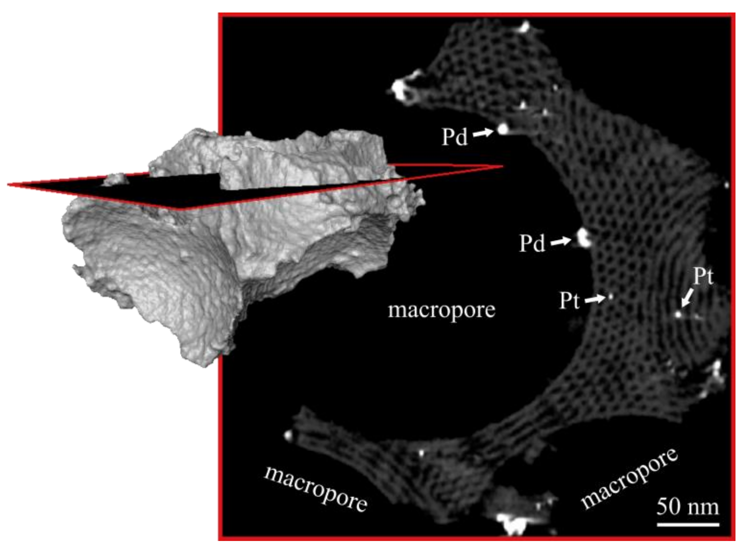

Figure 2. Taking slices through the tomographic reconstruction, exemplified here for a slice at the position shown on the inset surface rendering, provides clear identification of the Pd and Pt particle locations, which are seen to reside in the macropores and mesopores, respectively.