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Rapid Screening of Nanoporous Structures in SiO_2 Catalyst Particles via Helium Ion Microscopy

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Porous materials are some of the most important materials in a vast number of applications including biomaterials, medical delivery systems, solar cells and catalysts [1]. However, the number of techniques available to quantify pore size and pore structure in these material systems is limited. The most common technique to quantify porosity is gas absorption; gas absorption produces a global pore size average, and does not reveal any local microscopic or nanoscale information on pore size, distribution, or shape [2]. Electron microscopy is also challenging in imaging these materials, due to charging; and typically necessitates additional sample preparation steps, such as metal coating, or cryogenic preparations – potentially significantly altering the imaged surface.

In this work, we demonstrate helium ion microscopy (HIM) as an alternative to gas absorption and electron microscopy to quantify nanopore size, shape and distributions. HIM offers high-resolution surface imaging of non-conductive materials without a conductive coating. Since helium ions are positive, charging can be ameliorated by using electrons emitted from a low energy electron flood gun. Furthermore, using modern data analytics on the HIM images we quantify the pore size and distribution at the surface of SiO_2 catalyst particles provided by ExxonMobil. In this work, we compare our approach to the industry standard gas absorption technique, and simulate ion-beam material interaction to understand how pores evolve as a function of beam irradiation.

To extract the pore locations from the HIM images, we utilized a watershed based image processing technique, and the results are shown in Figure 1a, with the red outlines of the detected pores overlaid on top of the original HIM image of the SiO_2 particle. We can then extract pore sizes of the detected pores and this is demonstrated in the colormap in Figure 1b. Further we can overlay the pore size distribution calculated with the gas absorption data obtained from the same SiO_2 sample, Figure 1c. The average calculated pore radius for HIM is 6.87 nm extracted from figure 1c, and 6.62 nm for gas absorption.

To understand the effect of the helium beam on the pore structure, we utilized EnvizION simulations of 3.5 nm radius pores under He-ion irradiation and the simulations are shown in Figure 3 [3]. The simulated dose of 62,500 ions is approximately the imaging dose per frame in the HIM. The simulated results for frames 4 and 32 in both x-y projection Figure 2(a, b), and the x-z projection Figure 2(c, d) are shown. As can be seen, the pore structure at the surface does begin to degrade with higher dosage, but at lower doses the pore structure remains mostly intact.

In conclusion, we have developed a new method to visualize pore distributions and quantitatively determine average pore size using HIM imaging. This is complementary to gas absorption that give average pore sizes across a bulk sample and gives the ability for visualization of size, shape, and distribution of the pores at SiO_2 surfaces [4].

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[4] This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility. The authors acknowledge the ExxonMobil Chemical company for financial support and providing the samples for this work.

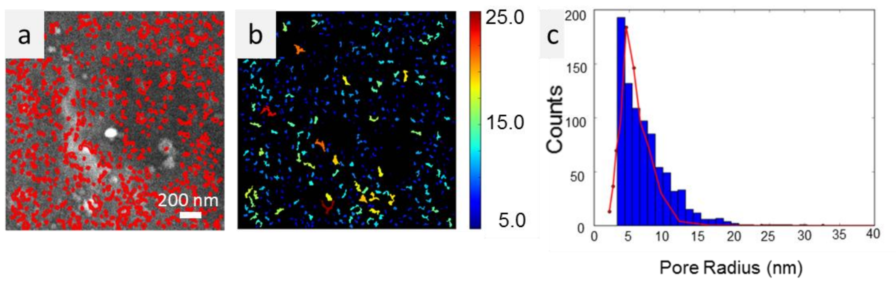

Figure 1. (a) The helium ion micrograph of the surface of a SiO_2 particle with the red outlines highlighting the detected pores. (b) Pore size colormap, with the colorbar as the pore radius. (c) The histogram of the overall pore size distribution for HIM image (panel a, b) and gas absorption data shown as a red line.

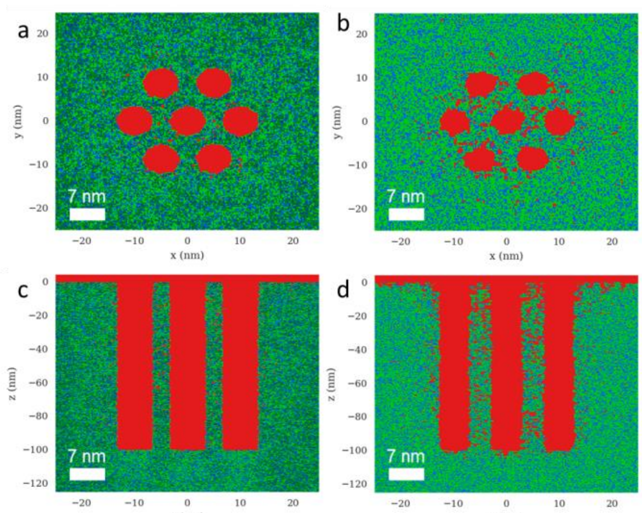

Figure 2. EnvizION simulation of the interaction between the helium ion beam and the SiO_2 surface for 3.5 nm radius pores. (a) X-Y projection after 4 frames. (b) X-Y projection after 32 frames. (c) X-Z projection after 4 frames. (d) X-Z projection after 32 frames.

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