P-32

Study Of In-situ And Ex-situ Porosity Of Mesoporous Silica Gel

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Abstract

This study adopts a direct experimental approach for determining ex-situ irregular shaped pore distribution analysis of adsorbent material using Atomic Force Microscopy (AFM) operated in Phase mode. In-situ Porosity is estimated from N2 adsorption/desorption isotherm data using Non Local Density Function Theory (NLDFT). AFM is used to obtain the surface topographic information of RD and B type silica gel which are then undergone by image processing to acquire information related to the pore size and its distribution. A comparative study then performed to cognize the trend of in-situ and ex-situ porosity.

1. Introduction

This adsorption-desorption is a surface based phenomenon and it is considered that the monolayer and multilayer adsorption of gas molecules take place on the surface of the material. One of the surface characteristic is porosity which have significant influence in adsorption-desorption[1] . For determining the porosity and the surface area there are multifarious methods are available, among them imaging techniques are more straight-forward and allows direct visualization of the surface and even inside of the material[2]. Atomic Force Microscopy is a probe based microscopy technique that can be used to visualize the surface in Nano-scale and it can be operated in ambient condition. In this work, we have introduced a novel technique for taking surface images of spherical silica gel. which were visualized and analyzed with different tips and modes to find the optimized mode for imaging. Additionally, we have developed a method for quantitative analysis of surface porosity based on depth based pore detection technique.

2. Experimental

AFM (SMP-9700, Shimadzu Corp.) was operated in phase mode which outputs height images along with phase change related information. In this experiment, only the height image was considered. The reason behind avoiding phase data was to focus the detection based only height images. Estimation of the surface energies was beyond the scope of this experiment. Operating frequency of the cantilever (NCHR, Nanoworld) was set to a slight lower than it's resonant frequency where the gradient of the waveform of frequency vs amplitude graph is the steepest. The operating point was optimized after taking several images. A scanning area was set to 5 μm × 5 μm with 512×512 resolution and 1 Hz scanning frequency.

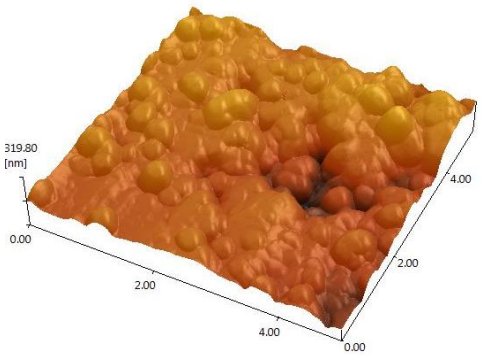

Figure. 1. 3D topographic image of RD type silica gel taken by AFM

3. Result and Discussion

3.1 Qualitative study

This imaging part focused on taking the 3D images of the surface of silica gel to understand the surface morphology visually. Figure 1 shows the 3D image of the surface of the silica gel of 25μm^2 scan area. Before

taking the images sample was treated by a standard procedure to elude the vapor and contamination. For example, silica gel was degassed at 85℃ for 2 hours and preserved in a sealed container and during the scan the humidity of the chamber was reduced to minimum. Later the surface was scanned with three different tips setting the Operating point to 0.4 V (Figure 1 (b)) to confirm the reproducibility. Image flattening, filtering, drift correction was performed to get clear visualization.

3.2 Quantitative Analysis

3.2.1 Image filtering:

The scanned image having height information was post-processed to eliminate the tilt and drift problem. To eliminate these unwanted topographic disorders 2D-FFT was used.

3.2.2 Ex-situ pore detection:

Ex-situ irregular shaped pores were detected using watershed method, where first grain location was identified then location was confirmed with segmentation method[3]. The identification of grain location is different than conventional methods. At first the local minima of the pores are identified. Then the repetitive steps took place to compare with the other local minima in close contact. Then the pore boundaries are marked by identifying the overlapping points. The image was cropped to 600 nm×600 nm for identifying the pores conveniently. The identified pores are counted using inverse grain detection method. The pore count information is shown in Figure 2, where pore count of two different silica gel are presented.

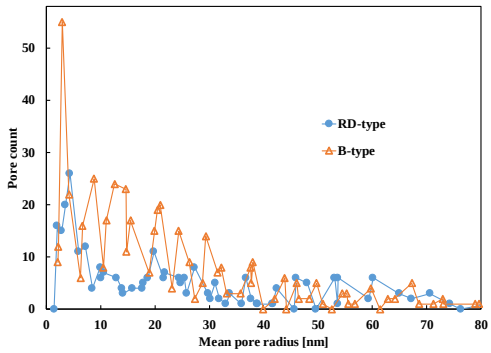

Figure 2. Pore counting by direct visualization

3.2.3 In-situ Pore Size Distribution

The 3Flex™ Surface Characterization Analyzer has been used to investigate the N2 adsorption/desorption isotherms. The surface area of each composite adsorbent has been investigated using Brunaure-Emmett-Teller (BET) method whilst the Non-Local Density Functional Theory (NLDFT) has been used to estimate the In-situ pore volume. Cumulative representation of the NLDFT pore size distribution shows that for both the silica gel sample follows the similar trend (Figure 3). However, the rise of the curve for RD type silica gel has begun early indicating it consist of comparatively small pores of similar width.

On the other hand, cumulative count of surface porosity by AFM shows different trend. Lower slope of the curve indicates the pore width of larger range of dimensions. However, both of the silica gels show similar trend in surface porosity.

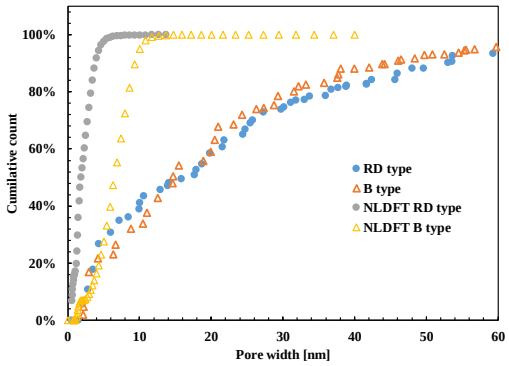

Figure 3. Comparative representation of in-situ and ex-situ pore size distribution

4. Conclusions:

AFM images were used to determine the pore distribution using depth based analysis. Surface textures which do not constitute the pores were removed by 2D-FFT filtration before pore detection and counting. Direct identification of ex-situ pores by AFM indicates the different trend of pore distribution compare to indirect estimation of in-situ pores.

Reference

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P-32

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