A fractal description of pore structure in the SBA family of mesoporous silicates

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Introduction

The accurate description of a material's surface properties is necessary to describe molecular processes in catalysis. SBA-15 is a template-synthesized mesoporous silicate that has found extensive use as a model support for studies in supported catalysis. Thorough structural analyses [1,2] clearly describe the dual micropore-mesopore structure with a broad distribution of micropore sizes; however, most artistic renditions of SBA-15 show the micropores as relatively unidimensional, [3-5] as illustrated in Figures 1a, 1b, and 1c. Here we show that the microporosity may alternatively be understood as a manifestation of the fractal nature of the mesopore surface (Figure 1d). A second objective is to utilize the well-defined pore geometry of SBA-15 to compare alternative approaches to calculating fractal dimension from nitrogen adsorption data.

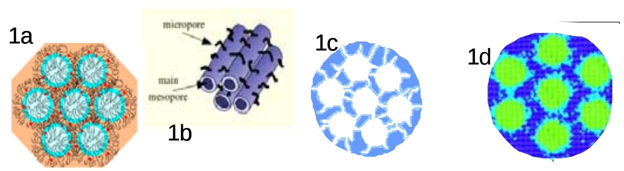

Figure 1: Images of SBA-15 from the literature: **1a** from D. Goldfarb, image from www.bgu.ac.il/.../images/research/sba-15.gif, [4] **1b**, from S. Bhattacharya, image from http://supriyo.net/research1.htm,[3]; **1c** from Smith and Lobo[5]. Figure **1d**: fractal recreation of 2D projection of pore surface D ~ 2.36.

Methods

SBA-15, SBA-16 and SBA-11 were prepared following a protocol adapted from Zhao et al. [6] We use calcination temperature from 300–1000 ºC to adjust the degree of microporosity or fractal character in the SBA materials. Nitrogen sorption isotherms were collected on a Micrometrics ASAP 2010 instrument, and we employ Pfeifer et al's fractal interpretation to multilayer adsorption based upon the Frenkel-Halsey-Hill (FHH) theory for adsorbent - adsorbate interactions in multilayer coverage.

Results and Discussion

We compare the average fractal dimension calculated using 3 different approaches; only Pfeifer's fractal-FFH approach yields results that are consistent with observations for the range of fractal character in all samples. This fractal dimension obtained from a fractal-FHH analysis of multilayer adsorption accurately predicts the ratio of BET surface area to the BJH mesopore surface area. This is plotted versus micropore volume in Figure 2 for samples of SBA-15 and SBA-16. SBA-16 shows greater microporosity and a much more significant fractal character, an expected result attributed to the much longer ethylene-oxide fragments in the block co-polymer template. Samples where microporosity has been annealed out by calcination suggests both the cylindrical mesopore surface of SBA-15, and the spherical pore surface of SBA-16 have no irregularities and their dimensionality is close to 2. These results are consistent with the observation that polymer interfaces formed by diffusion of one species (silica) into another (PEO) results in complex interfaces with fractal characteristics.

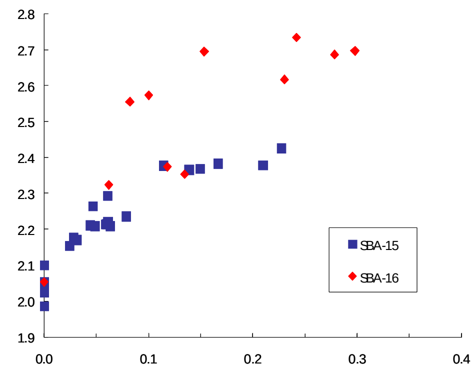

Figure 3: Plot of fractal dimension versus micropositY for SBA-15 and SBA-16 materials

Significance

The fractal-FHH analysis presented here offers an important perspective on the pore structure of block-copolymer templated mesoporous silicates; moreover, the fractal dimension of the surface provides a quantifiable descriptor of mesopore surface character. We believe this quantifiable descriptor of surface character can provide the basis for understanding support effects in a broad array of supported catalyst studies. Ongoing studies test the hypothesis that catalyst performance should be a function of fractal surface dimension.

References

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