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Fractal structure of porous silica studied by SAXS

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Introduction

Fractal is always used to explain self-similarity observed in coastlines, clouds, etc. However, it is not only a mathematical concept, but also a useful one in material design. From the viewpoint of material design, the uniqueness of fractal patterns and objects is that they theoretically posses infinite length, infinite surface area and zero volume as found in Koch curve, Sierpinsky gasket and Menger sponge because of hierarchical structures.

Relation to this, we have succeeded to create porous materials with fractal geometries by a novel template method. Using particles of alkylketene dimer (AKD) and a sol-gel synthesis of tetramethyl orthosilicate (TMOS), Menger sponge-like fractal porous silicas with fractal dimension D = 2.5 ~ 2.7 were created in the range over three decade in 50 nm ~ 30 μm [1, 2, 3]. In further studies, we have attempted to create fractal porous silicas in which more developed hierarchical structures exist.

Experiments

Samples were prepared as follows. First, AKD was dissolved in to n-hexane and sprayed by nitrogen gas to prepare the AKD particles. The particles were stood at room temperature for several days to induce “fat blooming” [4]. In this process, flower-like particles (sub-μm ~ tens μm in diameter) were prepared. After that, the particles were stacked into a vessel with suitable packing. The TMOS solution containing poly(ethylene glycol) (PEG) and calf thymus DNA filled the spacing between the particles, where PEG and DNA were utilized to design nm-scale pores as discussed later. After the sol-gel reaction, the products were stood for three days at ambient temperature. The samples were systematically prepared at different conditions (polymerization and concentration) of PEG and DNA. Next, the products were calcined at 500 °C for 2 hours to remove the wax particles. Finally, SAXS experiments using the samples were performed at BL-15A by IP in camera length 1~2 m.

Results and discussion

Here, we present overview of a series of the experimental results although we skip the detail. Fig. 1 shows a typical example of Menger sponge-like porous silicas in which it is found in 50 nm ~ 30 μm and the structures below 50 nm and above 30 μm were approximated as usual three-dimensional structure. The aim in our experiments is to find the experimental strategy how to create small pores in nm ~ several tens nm. In this experiment, we adopted the PEG and DNA molecular chains for the design because the molecular chains may be aggregated under suitable solvent conditions. In particular, we noticed that DNA chains are aggregated in organic solvents such as methanol and TMOS and the aggregated DNAs form the small pores after the calcinations, where the aggregated DNAs are bundles, network structures, etc. As a result, we found that this strategy was not succeeded because 4 nm pores which is arising from the network structure of SiO_2 formed in the sol-gel synthesis, mainly occupy the porous structures in several~ several tens nm scale.

To solve this problem, there are two approaches. One is to add PEG and DNA at higher concentrations. This is reasonable in fractal objects in which smaller pores occupy. However, the preparation conditions become quite severe. Other is to utilize another template objects such as nm-silica particles with different size.

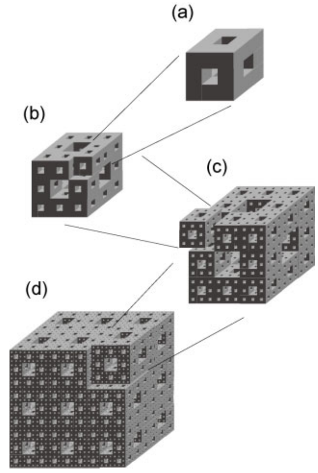

Fig. 1 A schematic representation of Menger sponge.

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