

論文の内容の要旨

論文題目 Synthesis of Inorganic-Organic Hybrids from Functionalized Cubic
 Siloxane-Based Molecular Units
(官能基を有するかご型シロキサン系分子単位からの無機-有機ハイブリッドの創製)

氏 名 チャイキッテイスイン ワッチャロップ

Interactions of atoms, ions, molecules and clusters both at outer surface and inside pores of porous materials are of scientific and technological interests. Besides the well established applications of porous materials, i.e. ion exchange, adsorption and catalysis, emerging areas of application, for example, low-k dielectric films for use as electrical insulators, molecular recognition and separation membranes, chemical sensors, and optoelectronic devices, show great promise. Zeolite, which possesses hydrated, crystalline, microporous tectoaluminosilicate, is a representative class of the nanoporous materials. Progress in synthesis of zeolite has been made through experimentally trial-and-error routine; hence, the products crystallized in a particular system are hardly predicted. Moreover, designed synthesis of zeolites with tailored porosity has been impossible because of a lack of understanding in their crystallization mechanisms.

In the chapter 1, brief introduction of porous and cluster-built materials, and scope and structure of the present doctoral dissertation are presented. Bottom-up approach has been focused as a potential strategy to innovate a priori materials with desired structures and properties. Strategic building blocks can be designed to structure-direct the formation of objective materials, which leads to a wide spectrum of desired functions. In this doctoral dissertation, the bottom-up concept has been applied to synthesize inorganic-organic hybrid materials from well designed molecular building units. Cubic siloxane-based cages, which resemble to the double four-ring (D4R) unit recognized as a secondary building unit of many zeolite frameworks, have been chosen as the starting units due to their rigidity, high symmetry, and functionalization capability.

Considering intermolecular interactions as a primary parameter affecting the final structures of the hybrid materials, D4R cages with different organic moieties that can form relatively weak π - π interaction and hydrogen bond, moderately strong coordination bond, and strong covalent bond have been designed and

synthesized mainly by Pt-catalyzed hydrosilylation and cross-metathesis reactions as described in the chapter 2. Mono-addition of organic groups that are able to provide weak intermolecular interaction (i.e., aromatic rings and urea group) and octa-addition of organic groups that can form stronger coordination (i.e., carboxy group) and covalent bonds (i.e., aryl bromide) into the terminal groups of D4R cages have been studied. D4R cages with Si–H or vinyl groups as terminal groups have been synthesized, and subsequently functionalized into desired organic moieties. The products with high regio- and stereoselectivity have been obtained under the investigated conditions. Such functionalized D4R cages have been used for the construction of inorganic-organic hybrid materials described in the chapter 3–5.

Siloxane D4R cages with the partially substituted end-groups has been considered as one of the suitable units for the formation of crystalline silica-based inorganic-organic hybrid materials because the unsubstituted end-groups (i.e., Si–H) can further be condensed to form siloxane bonds (Si–O–Si). In the chapter 3, monosubstituted D4R cages with aromatic rings can be crystallized into molecular crystals with the assistance of π – π interaction. The crystals have been modeled as the lamellar structures based on the X-ray diffraction patterns and computational structural minimization. The unsubstituted end-groups have been converted into alkoxy (Si–OR) or silanol (Si–OH) groups by Ir-catalyzed hydrolytic oxidation or alcoholysis. Subsequently, siloxane-based hybrid materials have been synthesized from the molecular crystals of the D4R cages via solid-state hydrolysis-polycondensation.

As order and crystallinity are not prerequisites for fine control over porosity of materials, porous poly(organosiloxane)s with relatively high surface area have been synthesized by connection of D4R cages via strong covalent as presented in the chapter 4 and 5. Synthesis of poly(organosiloxane) networks by Sonogashira cross-coupling reaction of bromophenylethenyl-terminated D4R cages and ethynyl compounds is reported in the chapter 4. The resulting carbon–carbon triple bonds can act as suitable linkers because of their rigidity. In the synthesis viewpoint, one of the advantages of polymer-based materials is that they can be synthesized in a modular manner; hence, their properties can be tuned or tailored by careful design and selection of monomers. Consequently, pore characteristics of the porous poly(organosiloxane) networks would be tailored by simply varying the length (e.g., phenyl and biphenyl) and the connectivity (e.g., di- and triethynyl) of the organic linkers. In comparison with other porous organic polymers reported previously, the poly(organosiloxane) networks synthesized in this work show relatively high surface area (apparent specific BET surface area of 850–1050 m² g⁻¹) and comparably high thermal stability. Moreover, the obtained porous poly(organosiloxane) networks can adsorb hydrogen molecules with relatively high isosteric heats of adsorption, raising the opportunity to utilize this porous hybrid materials as hydrogen storage materials. As very small ions such as fluoride can be encapsulated in the cubic D4R cages, the presence of such cages in the polymer networks can provide for the possibility to attain ionic porous polymers by post-synthetic modification.

In contrast to the co-polymerization (or cross-coupling) presented in the chapter 4, homo-polymerization (or homo-coupling) of functionalized D4R cages has been studied in the chapter 5. In other words, the D4R cages can serve as a single monomer for construction of the porous poly(organosiloxane) networks. In particular, microporous inorganic–organic hybrid material has simply been synthesized by homo-coupling of the bromophenylethynyl-terminated cubic siloxane cages as only building units via nickel-mediated Yamamoto reaction. The present work demonstrates that interpenetration or interweaving of the polymer network can be prevented by decreasing the linker distances, as evidenced as the sharp pore size distribution of the resulting hybrid. In comparison with the porous poly(organosiloxane) networks reported in the chapter 4, the present hybrid materials exhibit slightly high thermal stability with comparably high surface areas. Most of the D4R cages has retained in the resulting network, which is very useful for further post-synthetic modifications. As another alternative way, micro- and mesoporous inorganic–organic hybrid material has been synthesized by Friedel–Crafts alkylation of the benzylchloride-terminated cubic siloxane-based monomers. Although the D4R cages have been collapsed gradually occurring as the polymerization reaction proceeds, the resulting hybrid exhibits extremely high surface area ($1860 \text{ m}^2 \text{ g}^{-1}$) and pore volume ($1.94 \text{ cm}^3 \text{ g}^{-1}$), which are among the highest values reported for the siloxane-based porous solids thus far. A series of porous poly(organosiloxane) networks has been achieved by combination of structural, synthetic organic, and materials chemistry, which can expand to synthesize other porous hybrid materials.

Finally, the chapter 6 presents general conclusions and future perspectives of this doctoral research. Overall, the present research has been devoted to develop the new synthesis route leading to designed framework materials from the strategic molecular building units. Considering secondary building units existing in zeolite frameworks, the cubic siloxane cage has been selected as a starting precursor. Utilization of intermolecular interaction ranging from weak interactions, i.e., hydrogen bond, π – π stacking, and van der Waals force, through coordination bond, to strong carbon-carbon covalent bond, siloxane-based inorganic–organic hybrid materials have been synthesized with partially targeted manners. By employing diversified interactions, carefully designed and synthesized cubic siloxane cages would shed a new light as molecular building units leading to functional materials; thus, the concept of this doctoral dissertation can be extended to other framework hybrid materials with “truly” designed structure and function.