

J. Heyrovský Institute of Physical Chemistry, v.v.i.

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10⁰⁰ - 11⁰⁰ Dongyuan Zhao
11⁰⁰ - 11²⁰ Coffee
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Hydrothermal Synthesis of Ordered
Mesoporous Carbon Materials
for Applications

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Overcoming Diffusion Restrictions
in Porous Solids - Optimizing Pores
and Interfaces

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Hydrothermal Synthesis of Ordered Mesoporous Carbon Materials for Applications

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Ordered mesoporous carbon materials have attracted a lot of attention because of their unique structures and chemical properties, wide applications for super-capacitor, hydrogen storage, adsorption and separation. Normally the hard-templating method is utilized to fabricate ordered mesoporous carbons, but it is fuss, high-cost, and difficult to realize industrial production. Here, we demonstrate a surfactant-templating approach to synthesize ordered mesoporous phenolic resin polymers and a direct transformation to homologous carbon frameworks [1]. A family of ordered mesoporous organic polymers and carbons are simply achieved by using commercial available cheap phenol and formaldehyde as precursors, triblock followed with a carbonization process. The mesoporous carbons have a large uniform mesopore (2 ~ 20 nm), high surface areas (800 ~ 2400 m²/g) and large pore volume (0.8 ~ 2.4 cm³/g). The mesostructures can be easily tuned from hexagonal (space group *p6mm*) and cubic (*Im3m*, *Ia3d*, *Fd3m*, *Fm3m*). It is interesting that by using this hydrothermal method, single crystals, nanospheres, vesicles and monoliths can be easily synthesized. For example, mesoporous carbon nanospheres with uniform diameter of 20 ~ 140 nm are fabricated through a low-concentration route (Fig. 1). All the mesopores (~ 2.6 nm) are open and accessible. It shows no cytotoxicity and easily penetrates into living cells. The derived carbons with thick walls are first example of molecular sieves which have ultra high stability. We also show here large-scale synthesis approach based on the hydrothermal cooperative assembly. Kilogrammes of ordered mesoporous carbons are easily obtained for applications in catalysis, electrochemical supercapacitors and water-treatment.

[1] F. Q. Zhang, Y. Meng, D. Gu, Y. Yan, C. Z. Yu, B. Tu, D. Y. Zhao, *J. Am. Chem. Soc.*, **127**, 13508 (2005); *J. Am. Chem. Soc.*, **129**, 7746 (2007); *Chem. Mater.*, **18**, 5279 (2006);

[2] Y. Huang, *et al*; *Chem. Commun.*, 2641 (2008);

[3] Y. Wan, Y. F. Shi, D. Y. Zhao, *Chem. Mater.*, **20**, 933 (2008); D. Gu, *et al*, *Adv. Mater.*, **22**, 833 (2010); Y. Fang, *et al*, *Angew. Chem. Int. Ed.*, 49(43), 7987–7991 (2010).

Overcoming Diffusion Restrictions in Porous Solids – Optimizing Pores and Interfaces

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Diffusion of molecules into and out of porous solids is a key factor in processes, such as heterogeneous catalysis, adsorption, and separation. Fast diffusion enhances catalytic conversion and efficient adsorption in porous solids. Therefore, it is important to understand the transport processes that are taking place in pores and on the surfaces of solids. Pore sizes, pore topologies, and surface properties of a given solid are important factors that significantly affect transport of molecules.

Recently, we could show that specific transport barriers can exist on the surfaces of zeolites. On the other hand, large MFI crystals could be synthesized without any apparent surface barrier as well as zeolites on which surface barriers had been generated on purpose via post synthetic modification. We could also show that specific barriers may exist at interfaces of crystal segments in large MFI zeolite crystals. Fragmentation of such crystals into individual single crystals resulted again in crystallites without any apparent surface barrier.

Another option to reduce transport limitations in catalysis is creation a hierarchical pore systems, consisting of larger transport pores that are connected to smaller micropores in which the catalytic conversion may take place. Materials with such pore systems can be generated from nanoscopic zeolite crystallites. The zeolite nanoparticles possess rather high external surface areas. Systematic aggregation of such zeolite nanoparticles with linker species into larger aggregates preserved the accessibility of the external surface area of the zeolites as well as the textural mesopores in between the particles. The mesopores act as transport pores, in which molecules can migrate faster than in the smaller micropores of the zeolite. Alternatively, hierarchical pore systems can be generated via post-synthesis modifications of larger zeolite particles, e.g., via controlled dissolution of a part of the zeolite crystallites. In this manner, again hierarchical pore systems can be generated that allow fast diffusion of molecules within larger transport pores (mesopores) that extend into the zeolite particles.