Structural Studies of Mesoporous Crystals Using Electron Microscopy

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メソ多孔結晶は，無機物質（シリカ）の前駆体と界面活性剤が自己組織的に集合し，周期配列したハイブリッド構造である．焼成によって界面活性剤を取り除いたメソ多孔結晶は，一様な大きさのメソ細孔（2nm＜細孔径＜50nm）を持ち，大きな表面積と細孔体積を持つと同時に非常に狭い細孔径分布を示す．また，熱的，化学的に安定であることから触媒や吸着剤などとしての利用が期待され，さらに毒性が無く生体適合性を有することから薬剤伝達システムの担体としても研究が進められている．

その一方で，その構造的な特徴から通常のX線を用いた三次元構造の評価が難しく，透過型電子顕微鏡（TEM）を用いた構造評価は非常に強力な手法である．本研究ではTEMを用い電子線結晶学をもとにメソ多孔結晶の三次元構造を評価した．

Silica mesoporous crystals have attracted a lot of attention in different fields ranging from chemistry, to engineering or even pharmacy since the first mesoporous crystals were reported in early 1990's. [1, 2] Mesoporous crystals are nowadays one of the most frequently mentioned nano-structured materials, where the inorganic precursors and amphiphilic molecules self-assemble and give well-ordered nano-structures. Mesoporous crystals contain ordered mesopores (2 nm < pore diameter < 50 nm) characterized by a very narrow pore size distribution as well as a large specific surface area and pore volume.

On the other hand, they show excellent structural diversity as a result of well ordered mesophase of silica and water-surfactant system. After removal of surfactant under the calcination, the amorphous silica framework keeps the mesophase structure. There have been several structures found in silica mesoporous crystals, using cationic or anionic surfactant, or block copolymer. Some of the structures have been well known in liquid crystal system.

The silica mesoporous crystals have two main structural characteristics: disorder on atomic scale (short-range), but well-defined order on mesoscopic scale (long-range). There features rise in poor resolved X-ray diffraction patterns with little structural information. On the other hand, transmission electron microscopy (TEM) has been a very powerful tool to characterize the structure with mesoscale order. We have developed a method based on electron crystallography that gives an electrostatic potential distribution of the three dimensional (3D) mesoporous structures. [3-8] Based on the 3D electrostatic potential distribution, direct information of the detailed structures inside the mesoporous crystals such as diameter, shape and connectivity of the pores can be obtained. Here we show several example of our recent work exploring the use of this method.

Figure 1 shows several 3D structures of mesoporous crystals solved by electron crystallography together with 2D structure (*p6mm* (a)). *Ia*-3*d* (b) and *Pn*-3*m* (c) structures are

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bicontinuous cubic structure composed of an enantiomeric pair of 3D mesoporous networks that are interwoven. Other mesoporous crystals are formed by cage-type pore, which have one or two different sizes of pores packed and connected through the small window, depending on their structures (Figure 1d-g).

References

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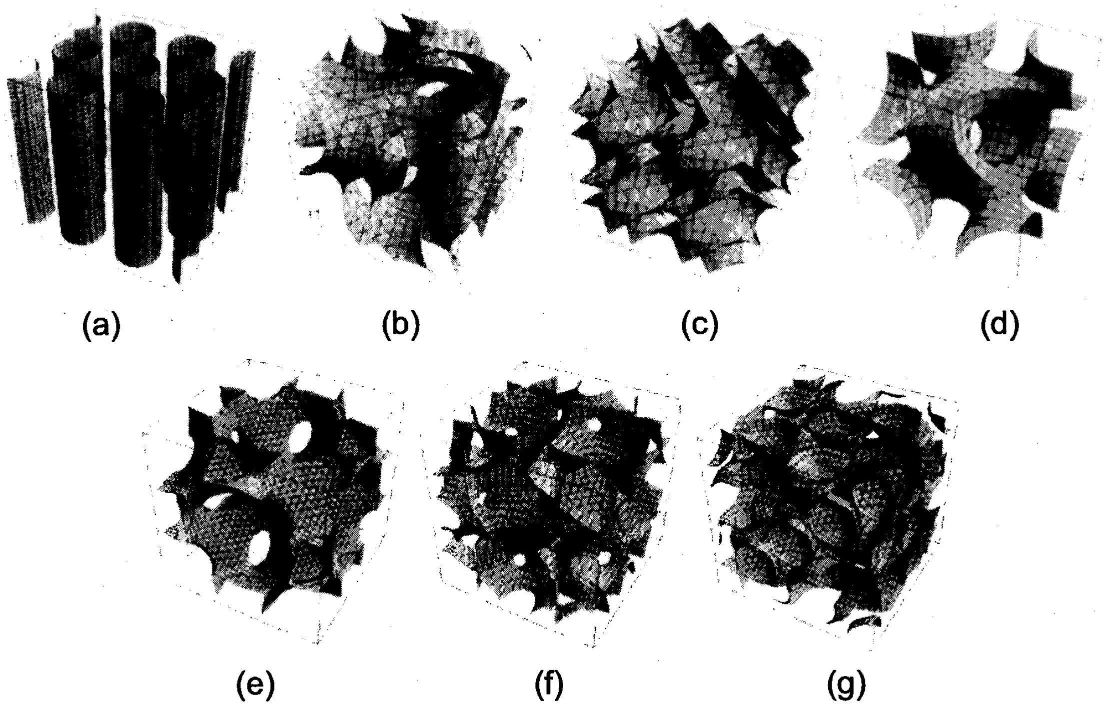

Figure 1. 2D structure (a) and 3D structure of mesoporous crystals, which have *Ia*-3*d* (b), *Pn*-3*m* (c), *Im*-3*m* (d), *Fm*-3*m* (e), *Pm*-3*n* (f), *Fd*-3*m* (g) symmetry.