Ordered mesoporous carbon molecular sieves by templated synthesis: the structural varieties

R. Ryoo[a]*, S. H. Joo[a], S. Jun[a], T. Tsubakiyama[b] and O. Terasaki[b,c]

[a]Department of Chemistry (School of Molecular Science-BK21), Korea Advanced Institute of Science and Technology, Taejon, 305-701, Korea

[b]Department of Physics and CIR, Tohoku University, Sendai 980-8578, Japan

[c]CREST, Japan Science and Technology Corporation, Tohoku University, Sendai 980-8578, Japan

Ordered mesoporous carbons with various structures, designated as CMK-1~5, have been synthesized by carbonization of sucrose, furfuryl alcohol or other suitable carbon sources inside silica or aluminosilicate mesopores that are interconnected into three-dimensional networks such as in MCM-48 (cubic Ia3d), SBA-1 (cubic Pm3n) and SBA-15 (hexagonal p6mm). The mesoporous carbon molecular sieves, obtained after template removal with HF or NaOH solution, show transmission electron micrographs and X-ray diffraction patterns characteristic of the ordered arrangement of uniform mesopores. The structures of these novel carbon materials can be controlled to be negative carbon replicas (CMK-2 obtained from SBA-1, CMK-3 from SBA-15, and CMK-4 from MCM-48) or a network of nano-pipes obtained by uniform deposition of carbon films on the pore walls (CMK-5 from SBA-15), depending on the carbon sources. In a specific case of CMK-1, the synthesis using MCM-48 undergoes the structural transformation to two interpenetrating carbon networks (cubic Ia3d) to an interwoven structure (cubic $I4_132$ or lower). The ordered mesoporous carbons, which are opening up a new area of the nanoporous materials, exhibit BET specific surface areas as high as 2200 $m^2 g^{-1}$, excellent thermal stability in inert atomospheres, strong resistance to attack by acids and bases (standing over a week in boiling 5 M aqueous solution of NaOH, KOH, or H_2SO_4).

1. INTRODUCTION

Many interesting applications for advanced electronic devices, molecular sieving sensors, shape selective catalysts and hydrogen storage systems can be envisioned if carbon nanomaterials are built with three-dimensionally (3-D) ordered pore arrangements, or preferably, with 3-D interconnected pores and atomic orders similar to those in zeolites. Recently, the synthesis of carbon nanomaterials has made very remarkable progresses due to the development of various arc discharge methods and catalytic decomposition of organic compounds on metal particles. However, no such 3-D ordered porous carbon nanomaterials have been obtained yet. Although the fullerenoid-type 3-D porous carbons have not been obtained, some mesoporous carbons exhibiting mesoscopic structural order, that is, materials composed of periodic arrangement of uniform mesopores despite the disordered atomic arrangement, began to appear very recently [1]. These novel mesostructured or nanostructured porous carbons are similar to the well-known MCM-41-type mesoporous silicas, in that uniform mesopores are regularly ordered while the carbon frameworks are constructed with structural disorder in the atomic scale [1-7]. The mesoporous carbons, which are reminiscent of the ordered mesoporous silicas, are indeed obtained by negative replication of the mesoporous silicas with carbon.

As shown by Ryoo et al. using MCM-48 as a template [1], the synthesis of the ordered carbon replicas is accomplished by the carbonization of suitable precursors such as sucrose, furfuryl alcohol and phenol resin inside the 3-D mesoporous network systems. The resultant carbons after the removal of templates with HF or NaOH solution exhibit several X-ray powder diffraction (XRD) lines that are characteristic of the well-ordered pore arrangements. The templated-synthesis technique can now be extended to other 3-D mesoporous silica templates such as SBA-1 (cubic Pm3n, interconnected network of cage-type pores) and SBA-15 (2-D hexagonal p6mm, 1-D channels interconnected randomly by smaller pores). The ordered mesoporous carbons thus obtained correspond to the negative carbon replicas resulting from the pore filling with carbon (CMK-2 obtained from SBA-1, CMK-3 from SBA-15, CMK-4 from MCM-48) [4-6] or a network of nanotubes obtained by uniform deposition of carbon films on the pore walls (CMK-5 from SBA-15) [7], depending on synthesis conditions. In some case of template with bicontinuous structure, such as in the synthesis of CMK-1 with MCM-48, the carbon structure undergoes the transformation from interpenetrating networks of rod-like carbons (cubic Ia3d or lower) to interwoven network (cubic $I4_132$) upon template removal [1-3]. Here we describe the synthesis principle, structures and physical properties of these mesoporous carbons.

2. SYNTHESIS PRINCIPLE

The principle of the templated synthesis is shown in Fig. 1. Various carbon sources such as sucrose solution, furfuryl alcohol, phenol-resin monomers and acetylene gas are polymerized

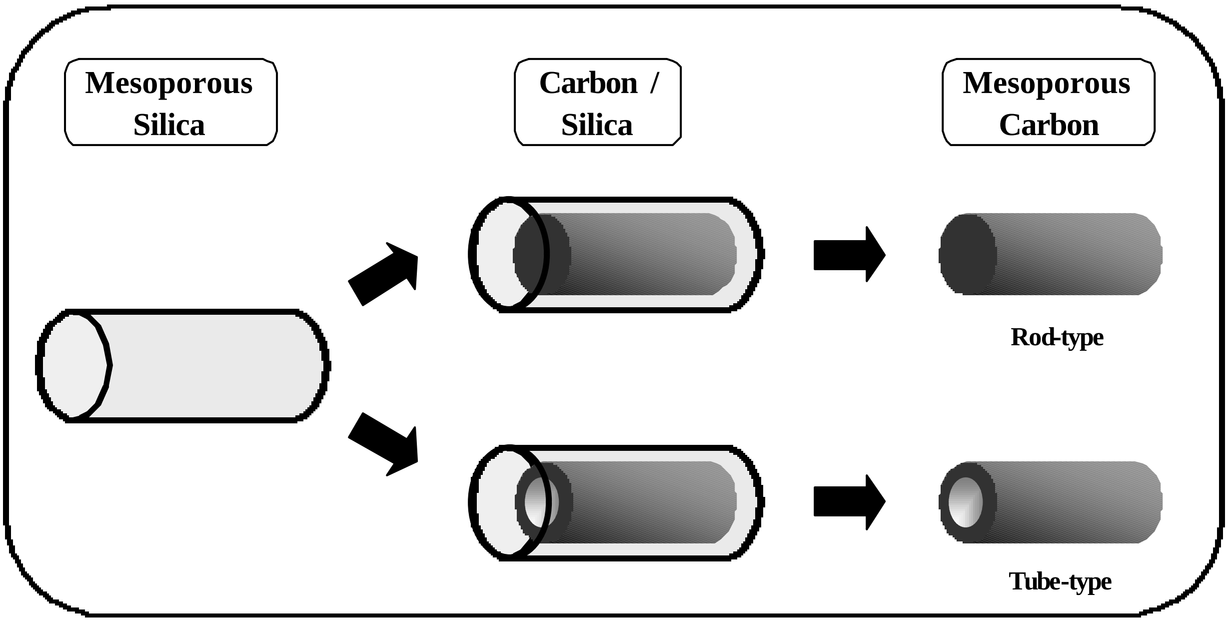

Fig. 1. Schematic representation of the templated synthesis using mesoporous silicas.

with heating inside mesoporous silicas or aluminosilicates. The polymers are then converted to carbon by the pyrolysis, similar to the preparation of ordinary porous carbons materials. However, in the case of the templated synthesis, the pyrolysis should be restricted to inside template pores. An effective method for the restriction of carbonization is to place a suitable catalyst inside pores, such as sulfuric acid for the decomposition of carbohydrates. Alternatively, the silica frameworks can be acidified by the incorporation of alumina. These acid catalysts catalyze the polymerization exclusively inside the region where the catalysts are located, so that subsequent carbonization results in the formation of nanostructured carbons inside the pores. The template can easily be removed at room temperature using a 10 % HF solution in ethanol-water or a hot ethanol-water solution of 1 M NaOH. It is also noteworthy that 3-D pore connectivity is essential for the formation of carbon networks that can retain the structure after the template is removed.

As shown in Fig. 1, either rod- or tube-type carbon materials are obtained depending on synthesis conditions. The rod-type carbons are prepared if carbon precursors such as sucrose and phenol resin are carbonized after template pores are completely filled. On the other hand, the tube-type carbons are obtained if carbon precursors are carbonized as coated on the pore walls. The film coating of carbon precursors is difficult due to capillary condensation or the pore-filling phenomenon. Consequently, the tube type carbons are much more difficult to synthesize than the rod-type. Even if the film is coated, the carbon precursors may undergo the pore filling during subsequent polymerization and carbonization processes, depending on the pore diameters and the nature of the carbon precursors. In fact, all four CMK members except CMK-5 (see Section 3) were thus far obtained as the rod-type.

3. STRUCTURES OF CMK CARBONS

3.1. CMK-1

The CMK-1 carbon can be prepared using sucrose, furfuryl alcohol or phenol resin as a carbon source and high-quality MCM-48 silica as a template [1]. The structure of the MCM-48 silica (cubic Ia3d) consists of an enantiomeric pair of interpenetrating 3-D networks of mesoporous channels, into which the carbon source is filled. The carbonization of the sucrose results in the formation of rod-type carbon inside the silica channels. Because of the

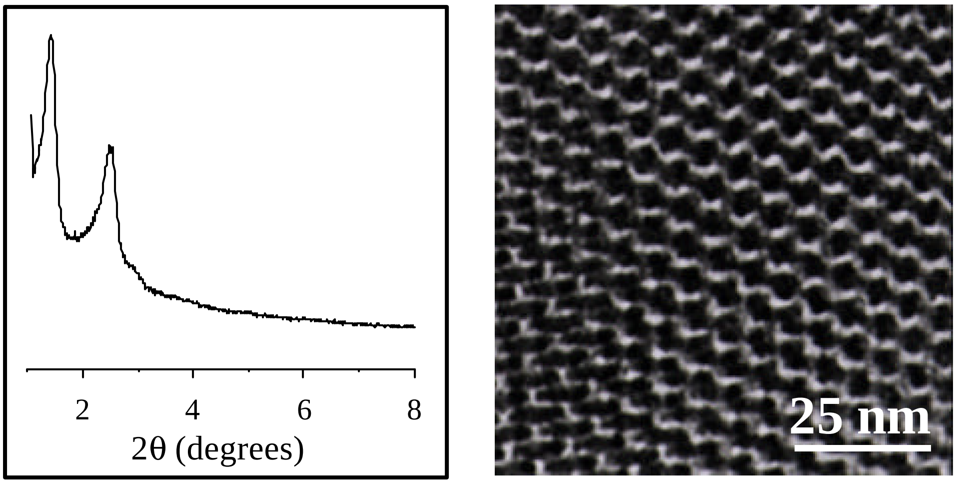

Fig. 2. XRD pattern and TEM image of CMK-1 carbon after the complete removal of template.

bicontinuous nature of the MCM-48 structure [8], the carbon networks formed in the two different kinds of channel systems are not interconnected and the space group, cubic Ia3d, is retained as long as silica frameworks are not removed. However, after the separating silica frameworks are removed, the two carbon networks seem to put together. The joining of the two carbon networks is attributed to the symmetry change from cubic Ia3d to either cubic I4$_1$32 or lower. The new ordered mesoporous structure is indicated by the XRD pattern and transmission electron miscopic (TEM) image shown in Fig. 2. However, it is unclear if the two carbon networks are permanently attached to form a single interwoven network or movable as interpenetrating to each other.

3.2. CMK-2

CMK-2 is an ordered mesoporous carbon obtained using sucrose as a carbon source and the SBA-1 silica as a template [1]. The details of the synthesis conditions and the structure analysis will be reported elsewhere [4]. As shown in Fig. 3, the XRD pattern of the CMK-2 carbon consists of three peaks in the region of 2è = 2 and 5 , similar to that of SBA-1. This silica material gives TEM images that are the reverse contrast to those of SBA-1 silica, as shown in Fig. 3. Recently, the crystal structure of the SBA-1 silica has been solved by electron crystallography [9]. The single crystallographic analysis using electron diffractions shows that the SBA-1 structure is composed of cages (typically 3.3 x 4.1 nm), which are interconnected through two different kinds of uniform pores (mesopores and micropores). Tentatively, the structure of the CMK-2 carbon may be assigned as a negative replica of the SBA-1 silica although rigorous analysis is being performed by the electron diffraction technique.

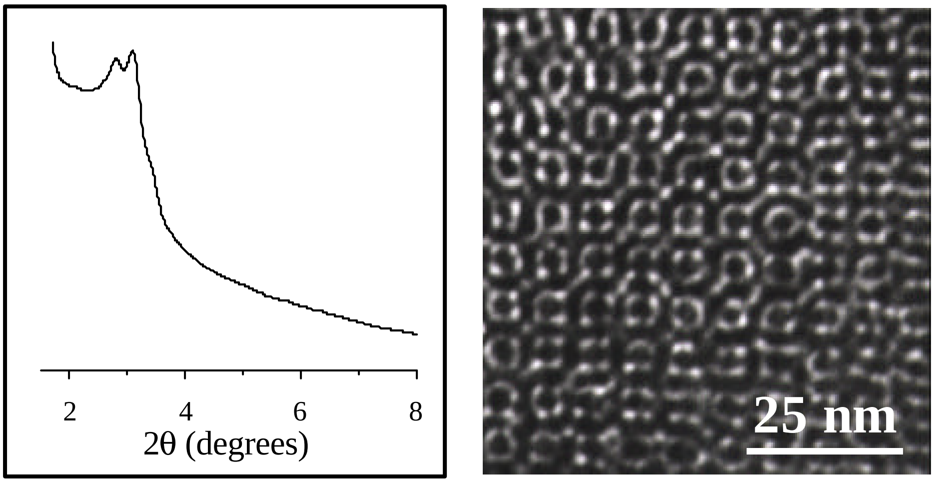

Fig. 3. XRD pattern and TEM image of CMK-2 carbon after the complete removal of template.

3.3. CMK-3

The CMK-3 carbon is a negative replica of the large-pore SBA-15 silica obtained using sucrose as a carbon source [5]. The structure of the carbon is composed of a hexagonal arrangement of 1-D carbon rods as shown by the TEM image and XRD pattern in Fig. 4. Despite the apparently 2-D hexagonal structures, SBA-15 and MCM-41 are distinguished by their markedly different pore connectivity in addition to the difference in the pore diameters. The MCM-41 silica has 1-D channels that are not interconnected. However, the large 1-D mesoporous channels (typically, 9 nm in diameter) of the SBA-15 silica are interconnected through smaller pores, which are various, less than 3.5 nm in diameters, and randomly located perpendicular to the 1-D channels. Because of the 3-D channel structure, the structure of the SBA-15 silica can be converted to the negative carbon replica exhibiting the same kind of structural symmetry. On the other hand, the replication of the MCM-41 silica with carbon results in the formation of carbon fibers that do not retain the 2-D hexagonal arrangement.

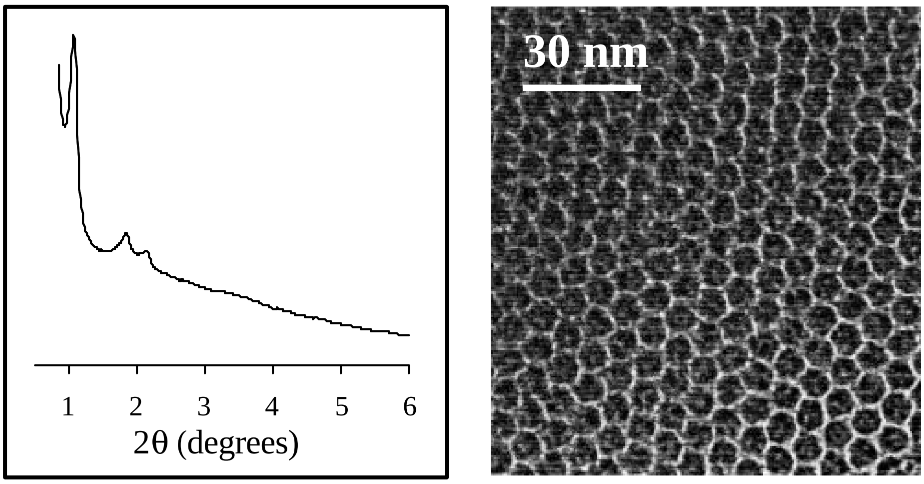

Fig. 4. XRD pattern and TEM image of CMK-3 carbon after the complete removal of template.

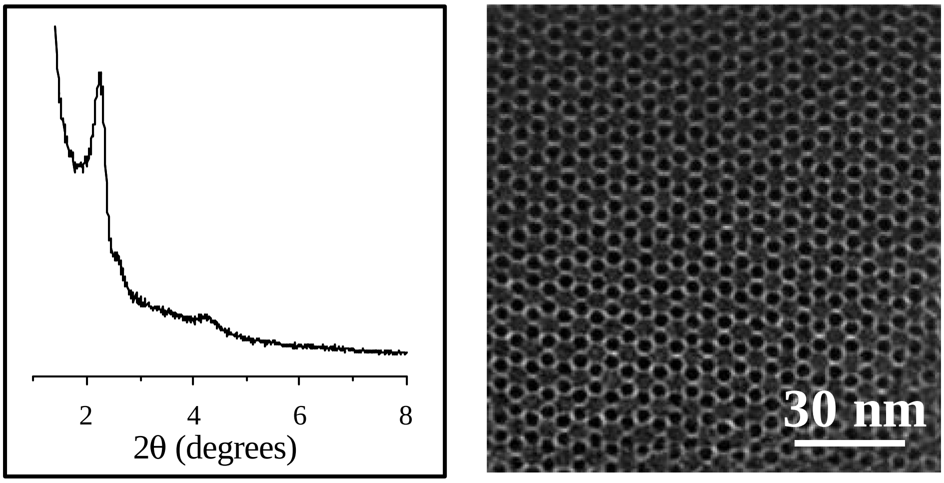

Fig. 5. XRD pattern and TEM image of CMK-4 carbon after the complete removal of template.

3.4. CMK-4

The XRD pattern and TEM image of CMK-4 are shown in Fig. 5. This carbon is prepared with partially disordered MCM-48 silica, which can be obtained by hydrothermal treatments of high-quality MCM-48 [6]. As shown by the XRD pattern and TEM image, the space group does not change even after the complete removal of the silica CMK-4 carbon is a negative replica retaining the cubic Ia3d structure of the MCM-48 template, on the contrary to the case of CMK-1. This fact indicates that the two carbon network systems formed in MCM-48 channels are partly connected by pores that have been generated in the separating silica frameworks.

3.5. CMK-5

This interesting material is constructed with hexagonal arrays of carbon nanotubes or nanopipes as shown by the TEM image in Fig. 6 [7]. The carbon is synthesized with SBA-15 as in the case of CMK-3, but the pore walls of the SBA-15 template are only coated with carbon films instead of the complete filling. The carbon nanopipes retain the hexagonally ordered arrangement permanently, due to interconnection similar to the CMK-3 structure. The wall thickness of the carbon nanopipes can be controlled to a certain degree by the amount of carbon sources. The specific BET surface area of the CMK-5 varies from 1500 to 2200 m^2g^{-1} depending on wall thickness.

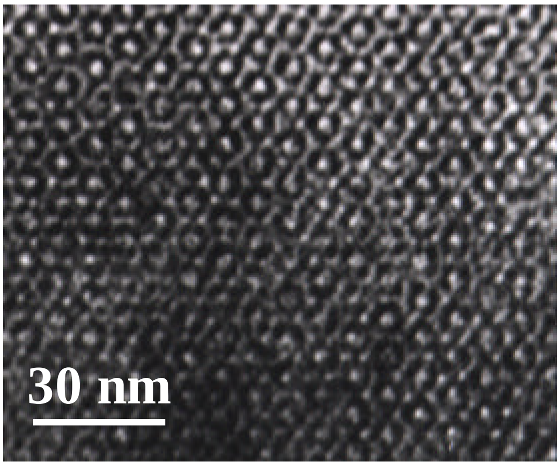

Fig. 6. TEM image of CMK-5 carbon obtained after the complete removal of template.

4. STABILITIES

4.1. Mechanical Stability

The XRD patterns in Fig. 7 show that the frameworks of CMK-1 withstands mechanical pressing for 10 min under pressures as high as 4740 kg cm^{-2}. The mechanical stability of the mesoporous carbon is much higher than that of MCM-48 silicas. The mechanical stability of other CMK materials has not been investigated yet. However, the result for the CMK-1 may be extended to the other carbons.

4.2 Thermal Stability

Recently, the thermal stability of CMK-1 has been investigated by thermogravimetry [2]. The thermal stability in air depends somewhat on the details of synthesis conditions, but in general, the air oxidation of the carbon frameworks begins to cause significant weight losses around 550 °C. The resistance to combustion is somewhat lower than that of the fullerenoid carbon nanotubes. However, the CMK-1 exhibits a very high stability in inert atmospheres. Even after heating in N_2 atmospheres at 1600 °C, the carbon material still gives XRD peaks indicating the structural order although the diffraction intensity is lost as shown in Fig. 8. The material can be heated without losing the structural order in strong acids and bases. The XRD peaks are maintained after the carbon is boiled for a week in 5 M aqueous solution of NaOH, KOH or H_2SO_4 as shown in Fig. 9.

5. CONCLUSIONS

Highly ordered mesoporous carbon materials are now available with rich variety of the structures, by the templated synthesis using mesoporous silica as templates. The templated synthesis of the ordered mesoporous carbons is a remarkable achievement in the field of porous materials. The synthesis is easy, inexpensive and suitable for the large-scale production. The resulting high-surface-area materials with uniform pores promise to be suitable as adsorbents, catalyst supports, and materials for advanced electronics applications.

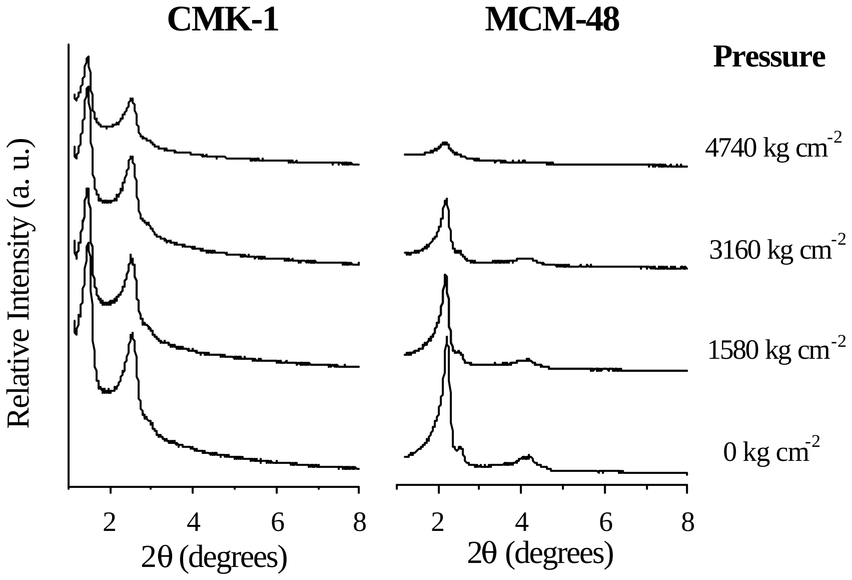

Fig. 7. XRD patterns of CMK-1 and MCM-48 after mechanical pressing for 10 min at given pressures.

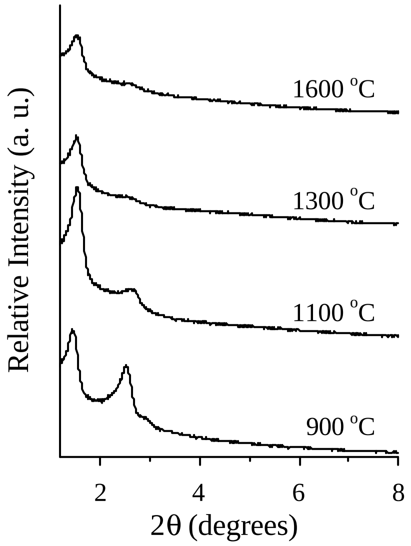

Fig. 8. XRD patterns of CMK-1 after heated in N_2 atmosphere.

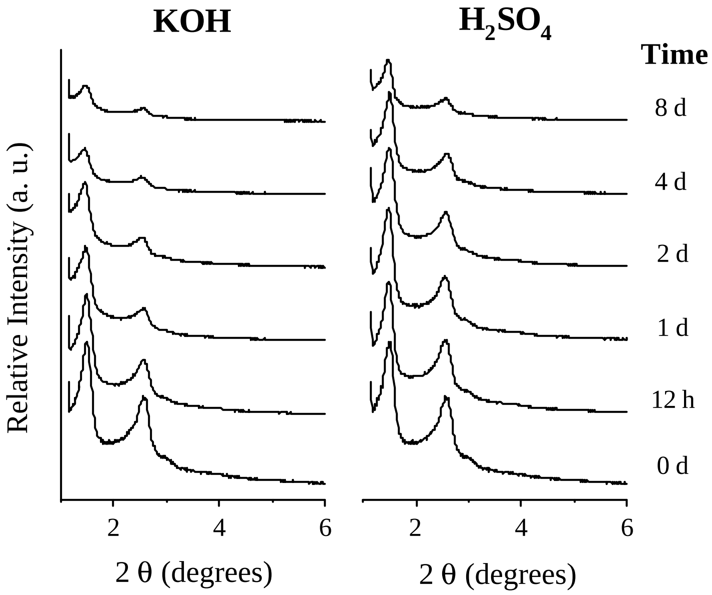

Fig. 9. XRD patterns of CMK-1 after boiled in 5 M aqueous solutions of KOH and sulfuric acid over a week period.

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