Template Synthesis Using Mesoporous Silica

Ryong Ryoo, Shinae Jun, Hongkyu Kang and Jinwoo Cheon
Department of Chemistry, KAIST Taejon, 305-701, Korea
E-mail: rryoo@sorak.kaist.ac.kr

During last decade, there were remarkable progresses on the synthesis of mesoporous silica molecular sieves using surfactants as the structure directing agent.[1-3] The mesoporous materials, composed of silica frameworks, allowed us to control precisely the pore diameters in the range from 2 to 30 nm. These tailorable large pores attracted much attention, providing new possibilities for many applications in adsorption, separation and catalysis. We show in this symposium that the mesoporous silica materials can be used as a template for the synthesis of other new mesoporous materials such as carbons and metals.

The template-synthesis method for carbon uses the carbonization of organic compounds inside the pores of the ordered mesoporous silica. The silica template is subsequently removed with sodium hydroxide solution or hydrofluoric acid. Details of the template synthesis method are described in a recently published paper by Ryoo et al.[4] In this study, sucrose solution was impregnated as a carbon source. The silica template was a cubic mesoporous material referred to as MCM-48. Interestingly, a small amount of sulfuric acid was added to the sucrose solution as the carbonization catalyst. The role of the carbonization catalyst was to convert the sucrose to carbon at possibly low temperatures, without severe volume contraction during the carbonization. Without the sulfuric acid, the resultant carbon material exhibited loss of the structural order. The ordered mesoporous carbon molecular sieve thus obtained was designated as CMK-1 (standing for Carbon Molecular Sieve from KAIST). This carbon material gave three Bragg diffraction lines of x-ray, indicating the highly ordered pore arrangement. The transmission electron microscopy (Figure 1a) and the pore size analysis revealed that the structure of the molecular sieve consisted of a three-dimensional regular array of uniform mesopores about 3 nm in diameter. Although the mesoporous silica MCM-48 was used as the template, the structure of CMK-1 was not simply a negative replica of the silica template. The synthesis mechanism involved an interesting transformation from the cubic Ia3d structure for MCM-48 to a new ordered array of another cubic $I4_132$ structure.

The highly ordered mesoporous texture composed of the carbon framework is not only of scientific interest but also of technological importance for applications as new shape-selective hydrophobic catalyst, catalyst support, adsorbent, sensor, and electrode materials. For example, various noble metals such as Pt, Pd and Ru can be easily supported using the so-call excess-solution wet impregnation technique.[5] According to our very recent studies, the resultant metal dispersion, i.e., the fraction of the metal atoms exposed to the surface of cluster, was surprisingly high. The cluster size was estimated from the chemisorption of H or O, and also using the extended x-ray absorption fine structure at the Pt L_{III} edge. These results showed that the metal clusters consisted of approximately 15 atoms. Such small metal cluster size breaks previous records with carbon support. The size is even smaller than the well-known Pt/Y zeolite system. Our discovery of such small metal clusters is expected to open new possibilities in heterogeneous catalysis. Another example is the surface activation of CMK-1. The surface of the carbon pores can be functionalized in a manner similar to the study of fullerenes.[5] At present, we are investigating the adsorption of hydrogen on this nanostructured carbon material. It is exciting to investigate if the carbon nanopores are suitable for hydrogen storage.

In addition to the CMK-1 synthesis, the template-synthesis strategy can be applied to obtain various types of other ordered mesoporous materials. Using such a simple strategy, we have obtained several types of other ordered mesoporous carbon and platinum (Figure 1b).[5] The structures of the Pt materials are very interesting. The structures consist of face-centered cubic packing of Pt atoms, exhibiting the ordered XRD patterns due to form regular arrays of nanostructured networks. The wire diameter can also be controlled. We expect to discover other nanostructured metal systems such as Pt, Ni and bimetals in due course. Certainly, these new mesoporous materials will extend the scope of mesoporous molecular sieves much further than we have considered hitherto with mainly the silica-based materials such as MCM-41 and MCM-48.

References

1. Beck. J. S. et al., J. Am. Chem. Soc., 114, 10834 (1992).
2. Huo. Q et al., Nature 368, 317 (1994).
3. Zhao, D. et al, Science 279, 548 (1998).
4. Ryoo, R. et al., J. Phys. Chem. B, 103, 7743 (1999).
5. Ryoo, R. et al., manuscripts in preparation.

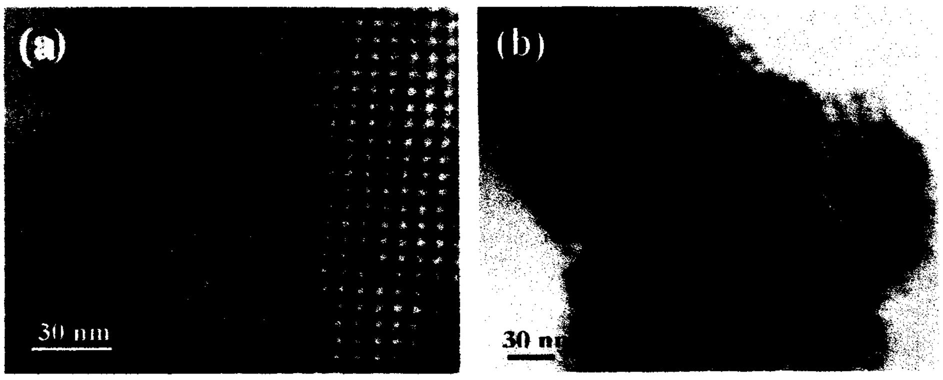
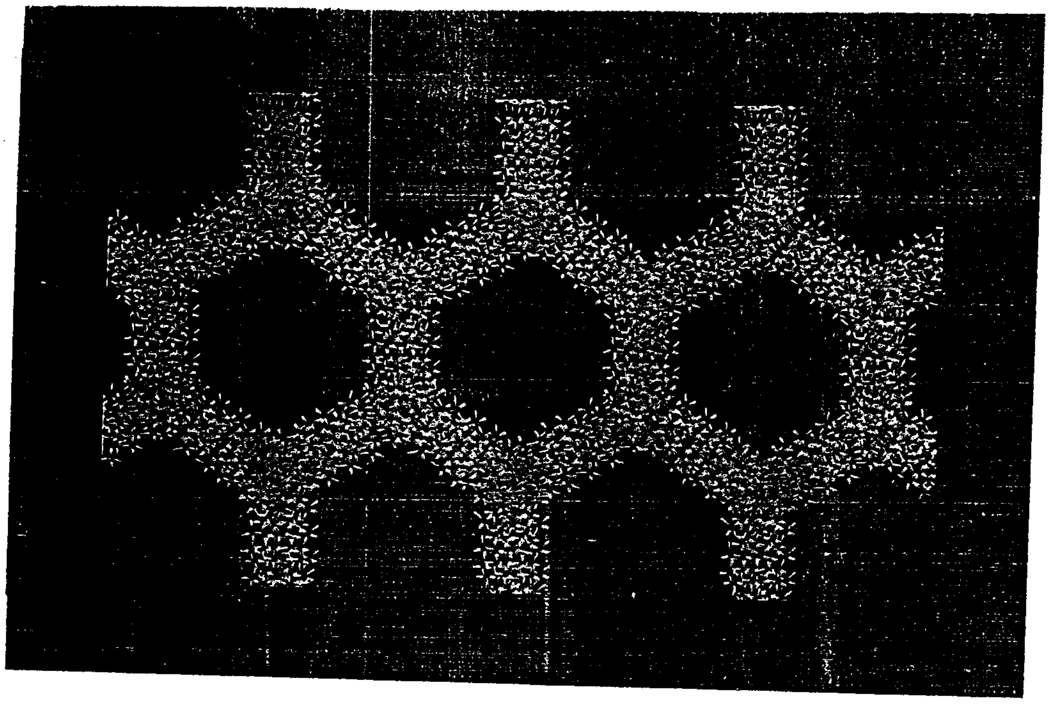
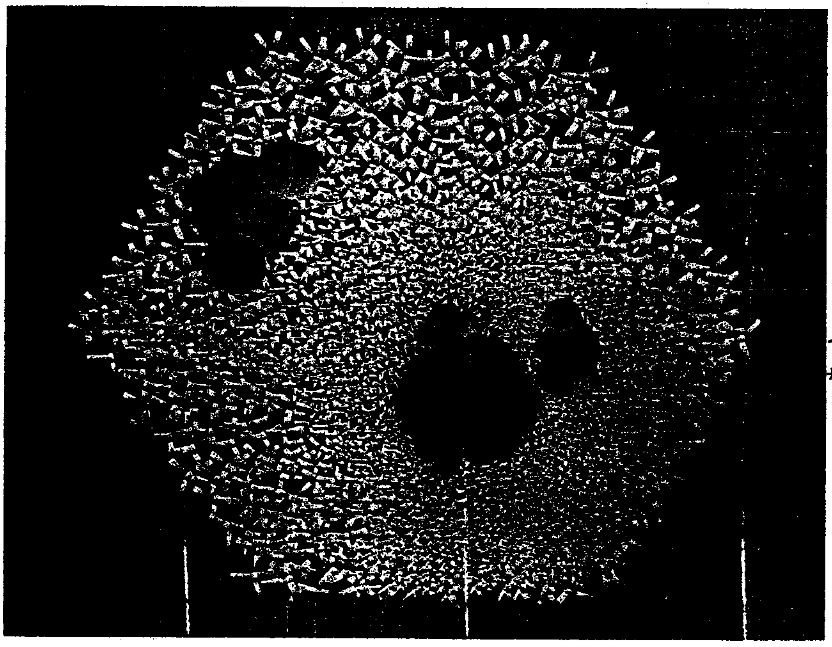
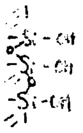


Figure 1. Typical transmission electron micrographs of ordered mesoporous carbon (a) and platinum (b) molecular sieves.







← Al
solid
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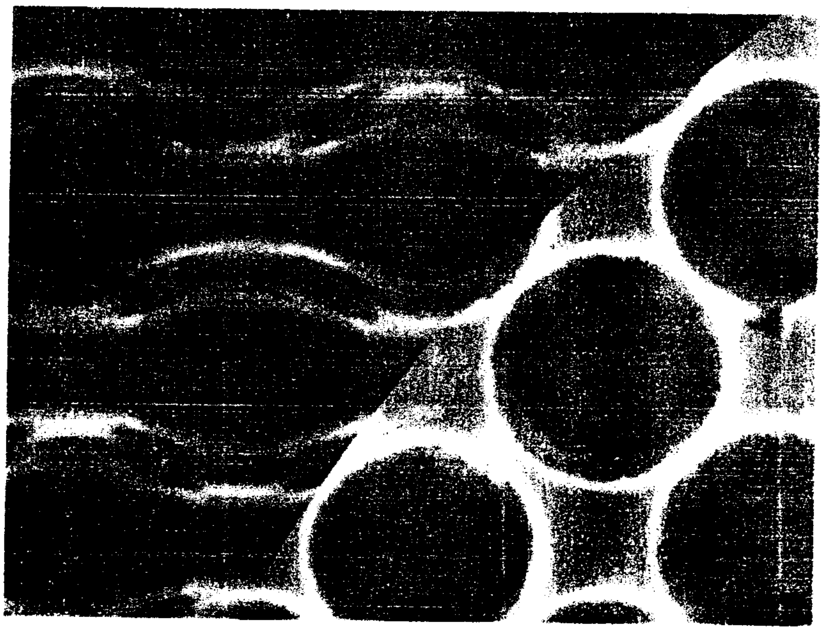
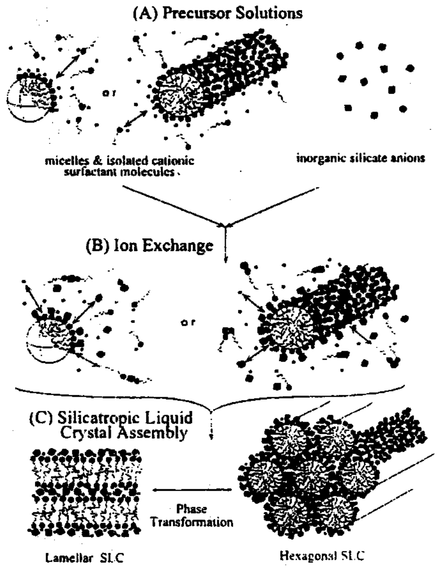


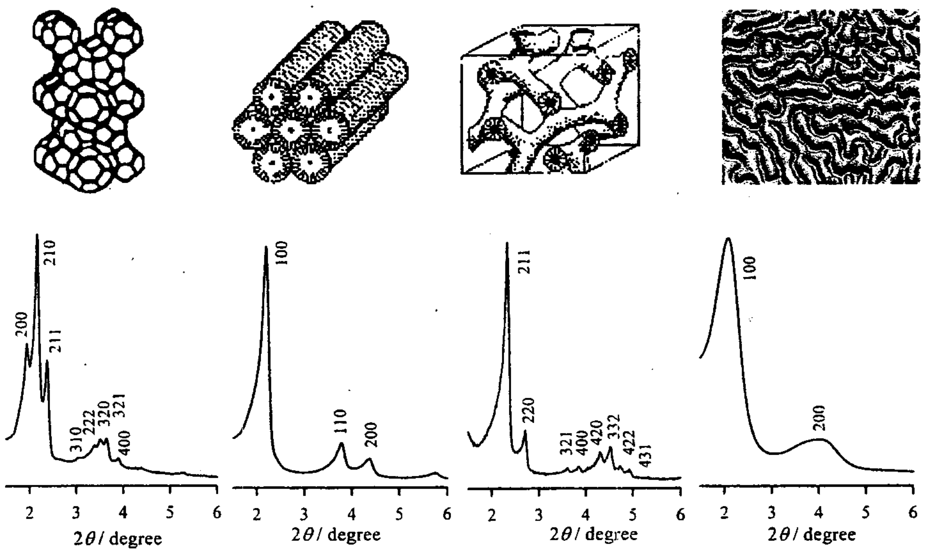
A photonic fcc crystal with calculated electric field amplitudes
Courtesy of Bell Laboratories/Lucent Technologies

Cooperative templating mechanism



(A. Firouzi et al., *Science*, **1995**, *267*, 1138.)

cubic *Pm3n* hexagonal *P6m* cubic *Ia3d* disordered



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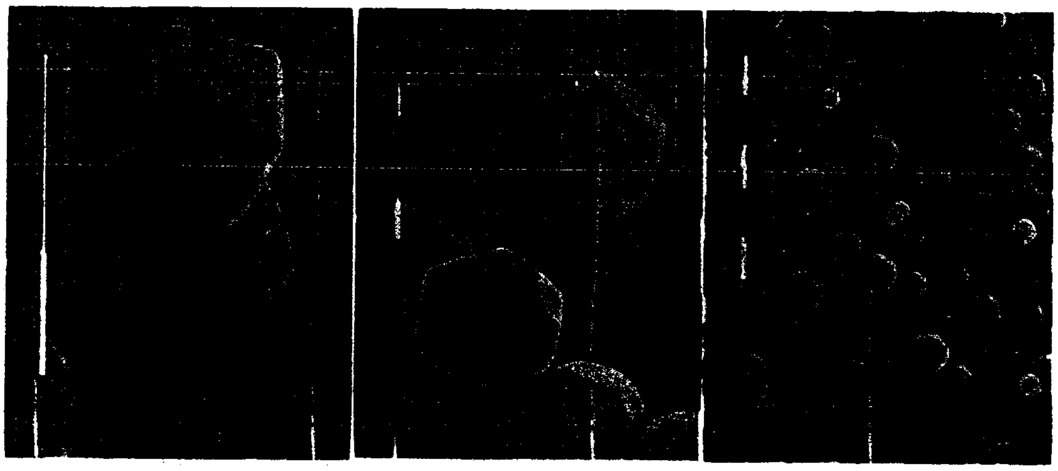

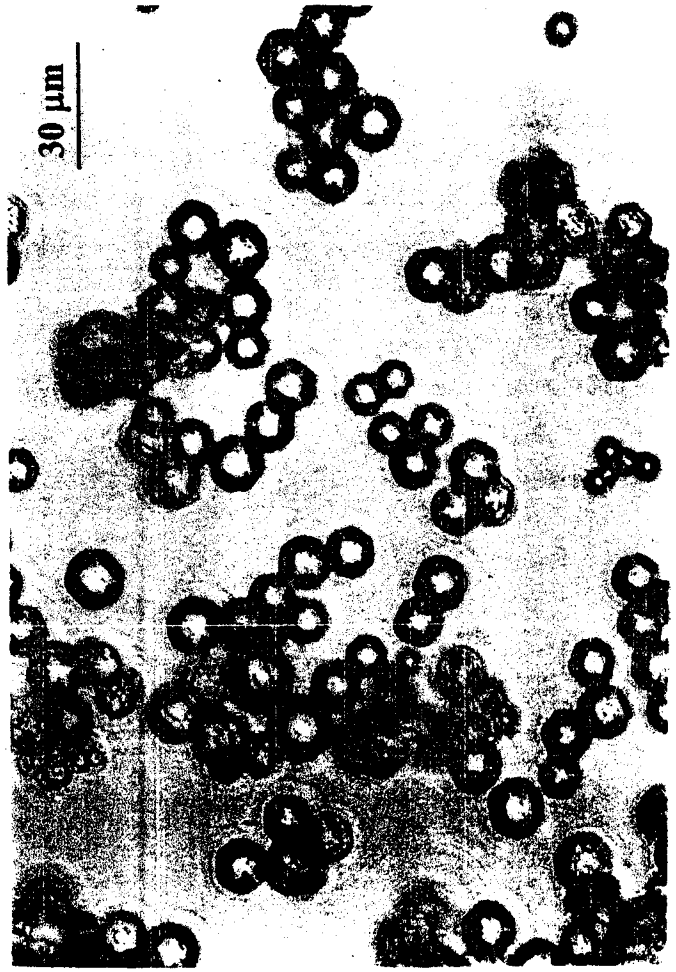

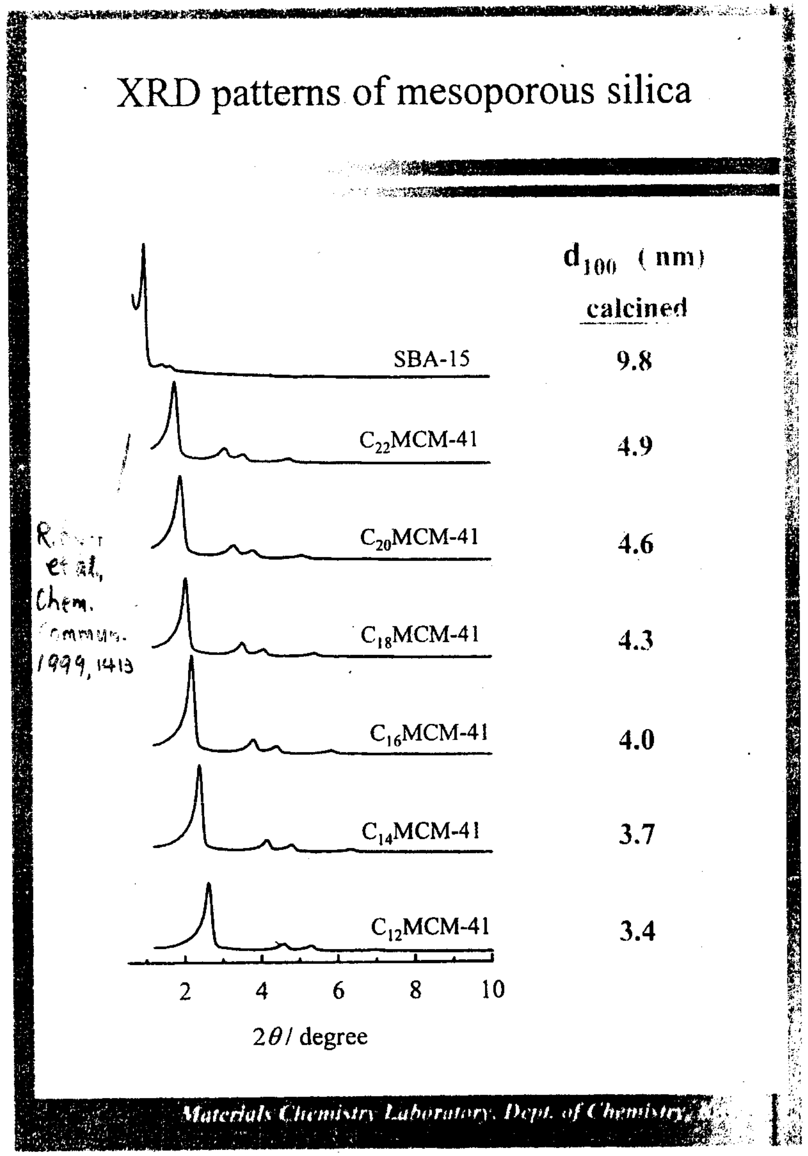

XRD patterns of mesoporous silica

	d_{100} (nm) calcined
SBA-15	9.8
C_{22}MCM-41	4.9
C_{20}MCM-41	4.6
C_{18}MCM-41	4.3
C_{16}MCM-41	4.0
C_{14}MCM-41	3.7
C_{12}MCM-41	3.4

R. [illegible]
et al.,
Chem.
Commun.
1999, 1413

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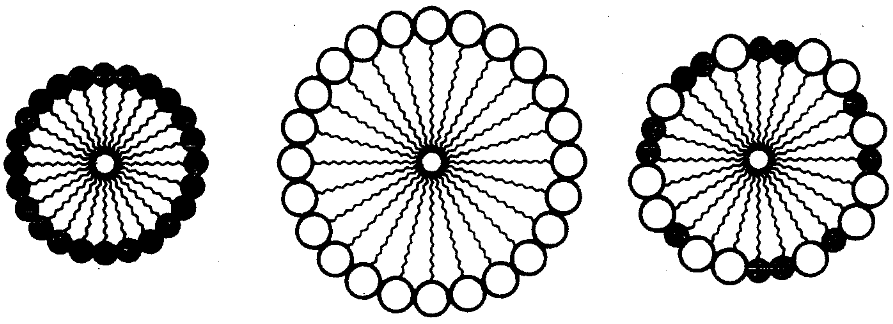
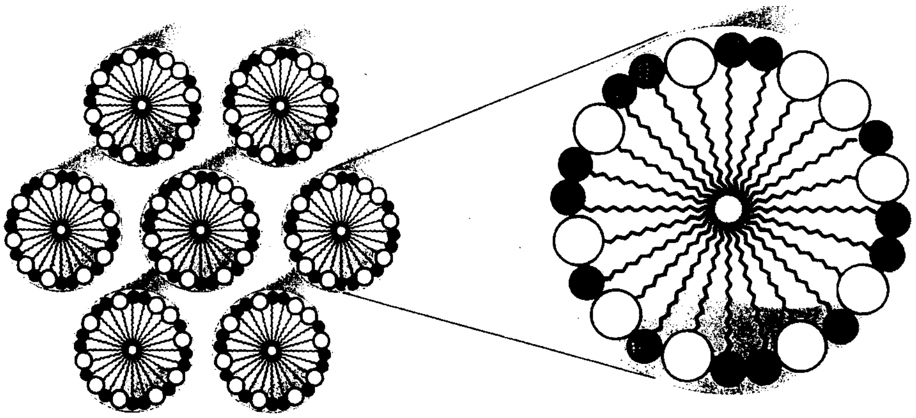
Synthesis of Highly Ordered MCM-41 (R.Ryoo et al. Chem Commun 1999, 1413)

● = $N(CH_3)_3$ ○ = $N(C_2H_5)_3$



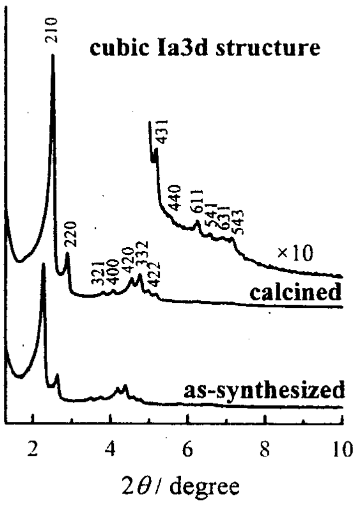
C_{14}MCM-41 C_{22}MCM-41 C_{18}MCM-41



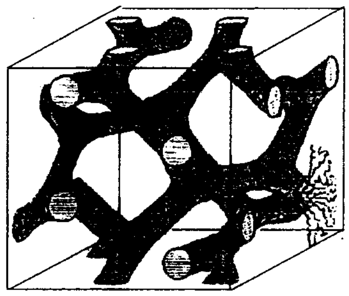
MCM-48 Mesoporous silica with cubic Ia3d structure

C. T. Kresge et al., Nature **359**, 710 (1992)

XRD pattern of MCM-48

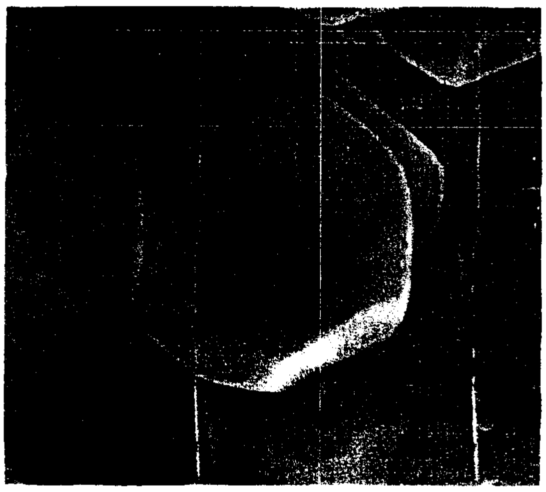


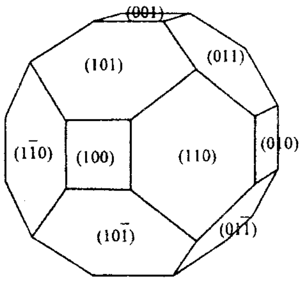
a proposed model for Ia3d mesophase formed by amphiphilic surfactants



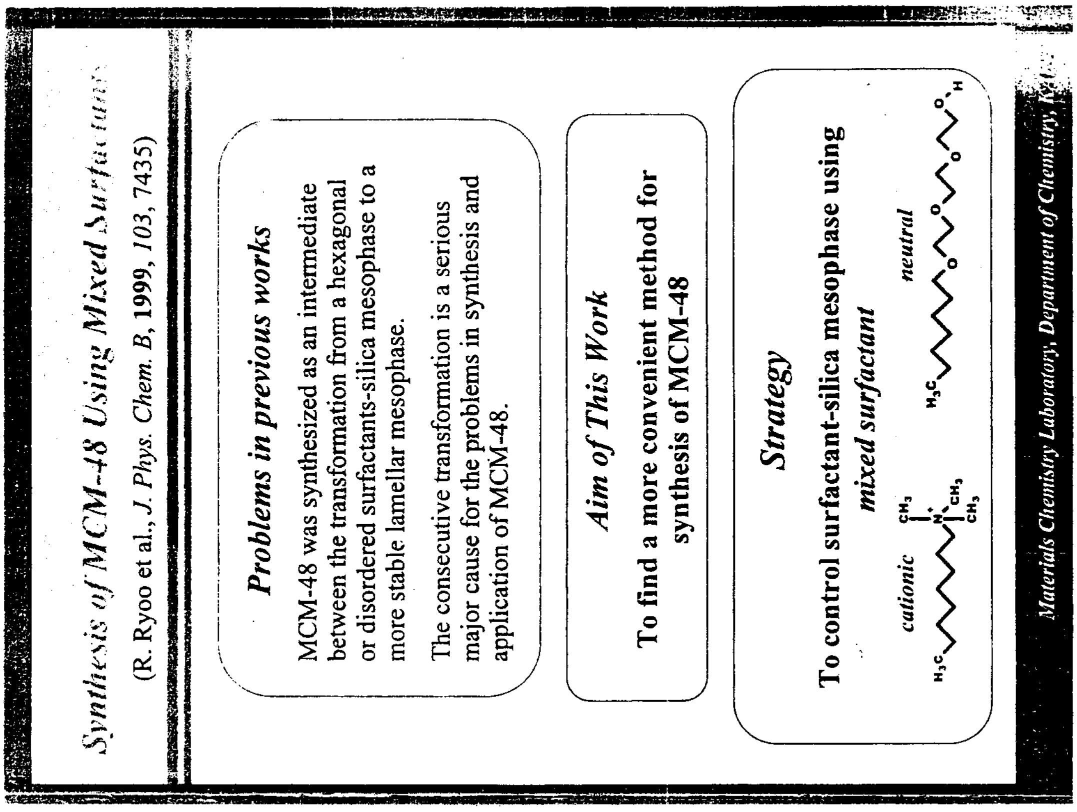
P. Mariani et al., J. Mol. Biol. **204**, 165 (1988)
J. M. Seddon, Biochemistry **29**, 7997 (1990)

1.4 SiO_2 : 1 HTABr : 0.35 Na_2O : 5 EtOH : 140 H_2O
16 h at 413 K





(Kim et al., Chem. Commun. 1998, 259.)



Synthesis of MCM-48 Using Mixed Surfactan

(R. Ryoo et al., *J. Phys. Chem. B*, **1999**, *103*, 7435)

Problems in previous works

MCM-48 was synthesized as an intermediate between the transformation from a hexagonal or disordered surfactants-silica mesophase to a more stable lamellar mesophase.

The consecutive transformation is a serious major cause for the problems in synthesis and application of MCM-48.

Aim of This Work

To find a more convenient method for synthesis of MCM-48

Strategy

To control surfactant-silica mesophase using *mixed surfactant*

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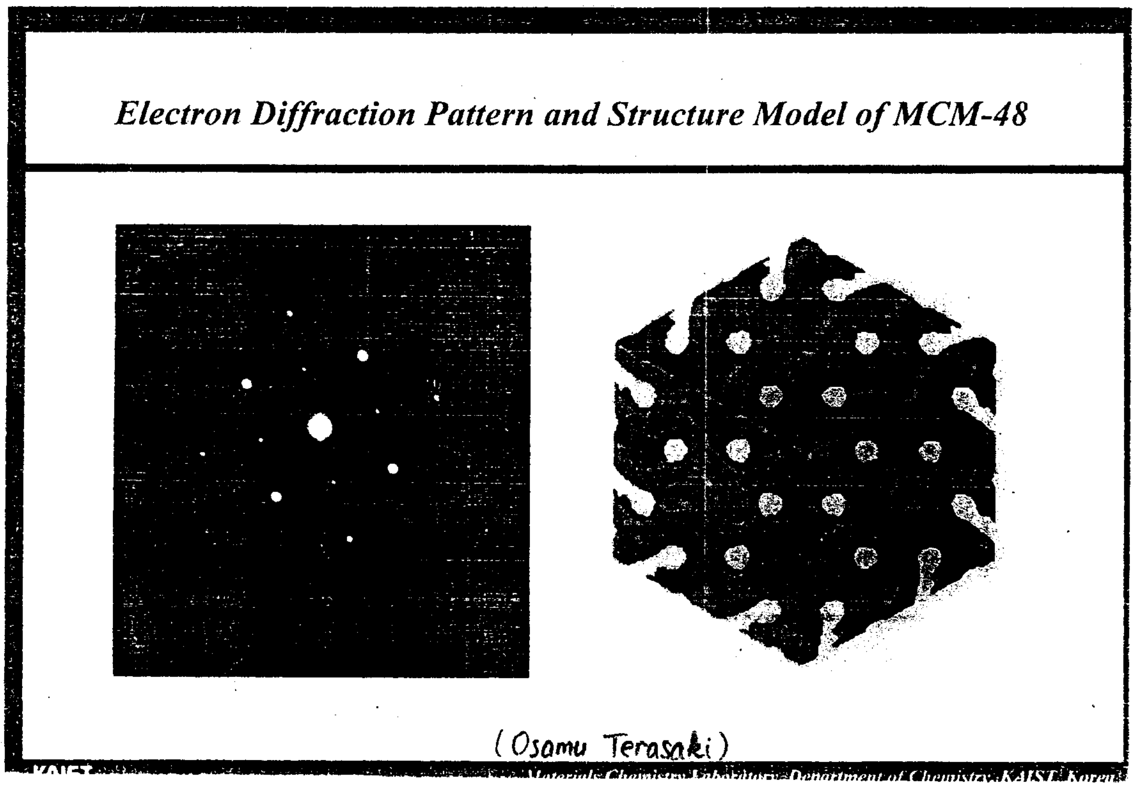

Electron Diffraction Pattern and Structure Model of MCM-48

(Osamu Terasaki)

KAIST

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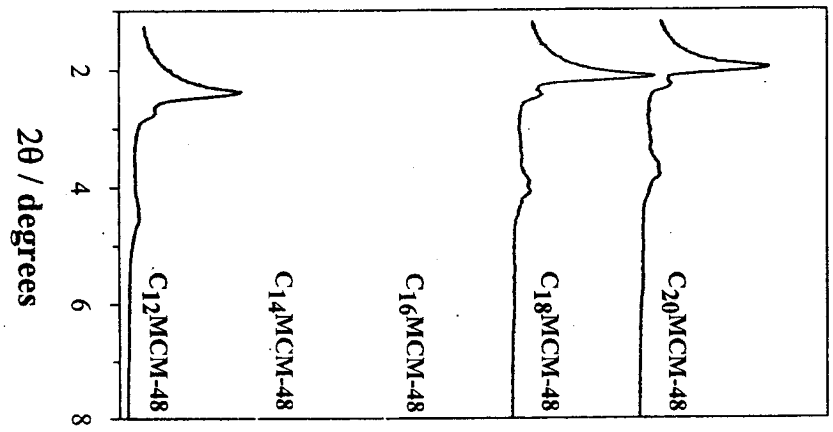
Pore Size Control of MCM-48

(R.Ryoo et al., J. Phys. Chem. B, 1999, 103, 7435)



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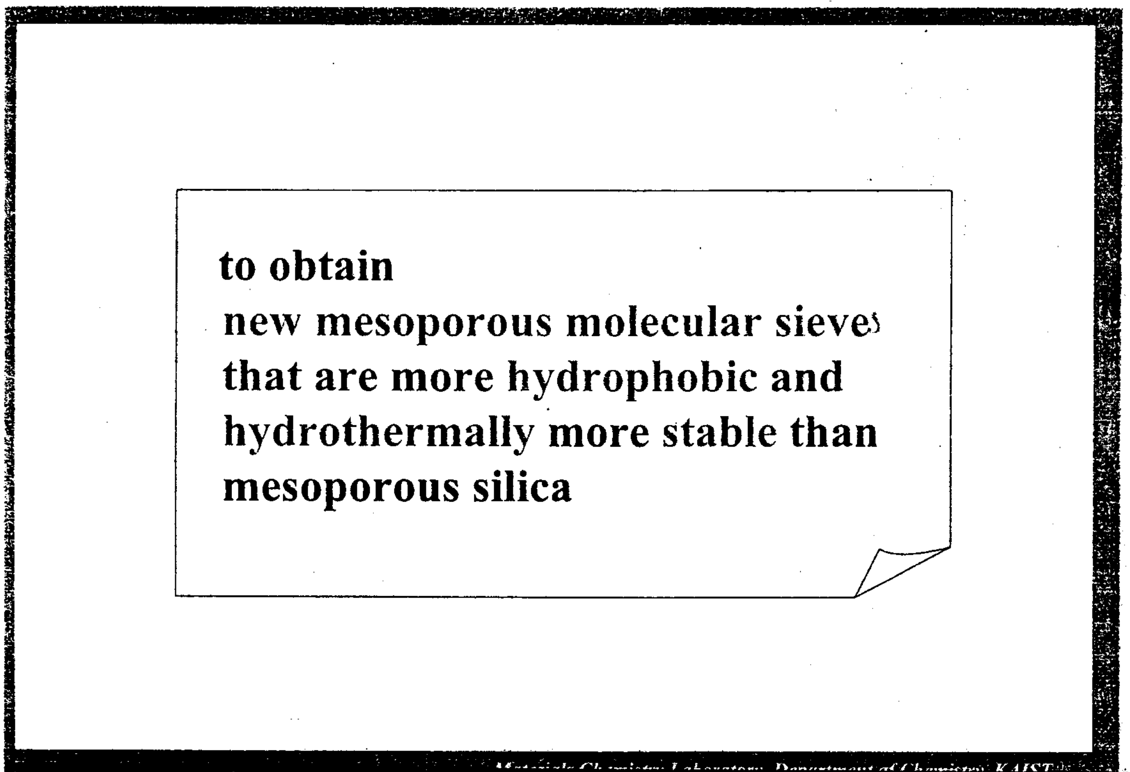
Template Synthesis of Mesoporous Carbon



to obtain
new mesoporous molecular sieves
that are more hydrophobic and
hydrothermally more stable than
mesoporous silica

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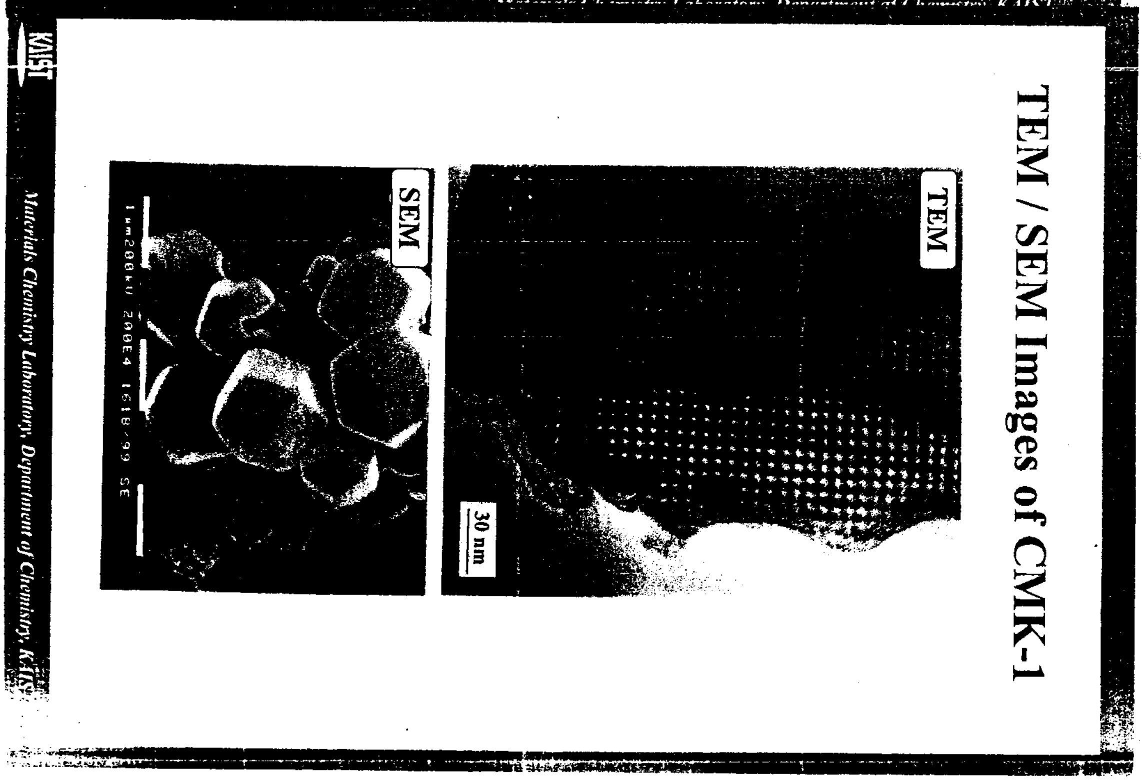

TEM / SEM Images of CMK-1

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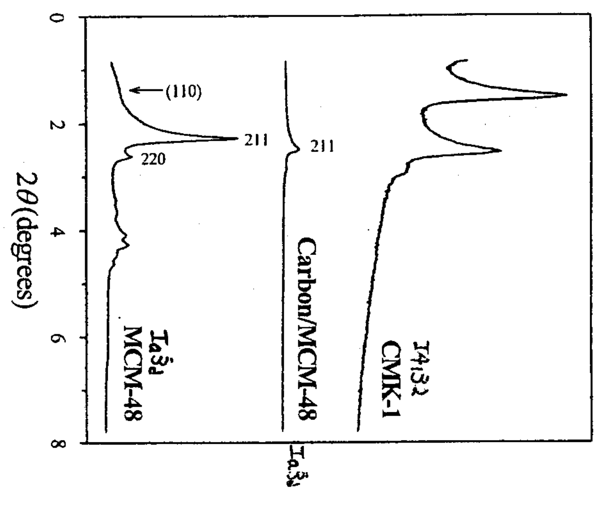
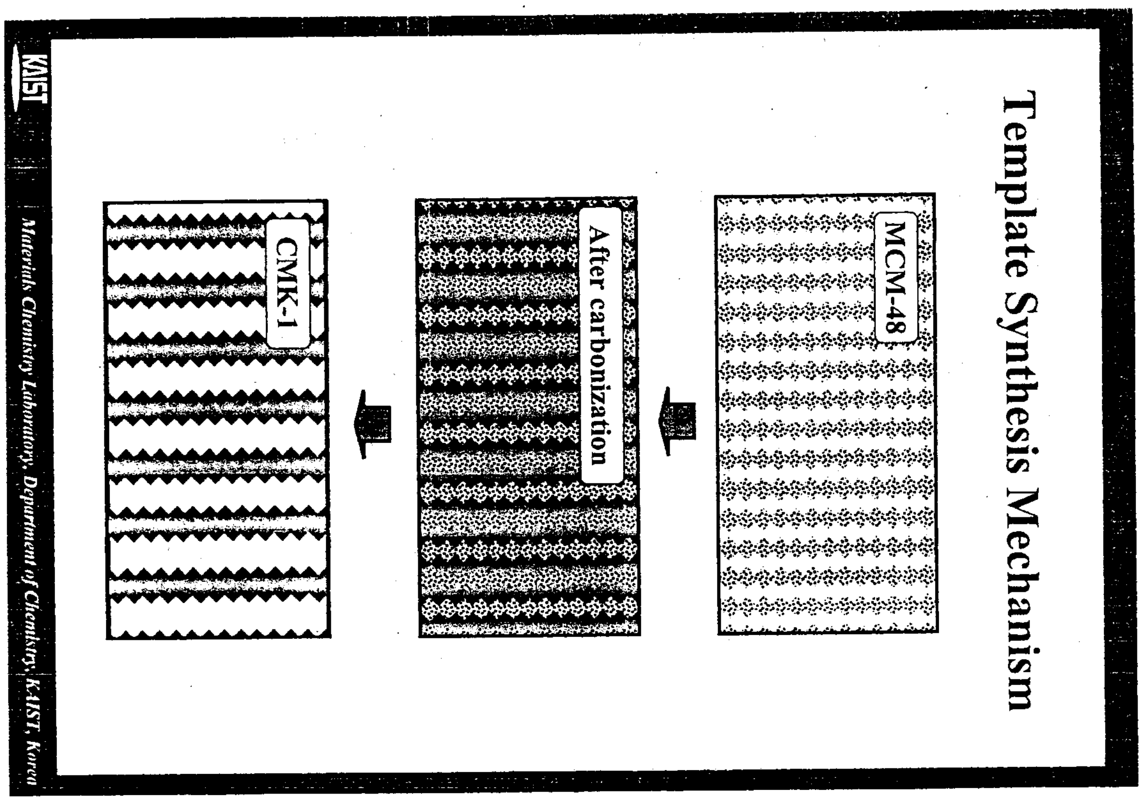


Changes in powder X-ray diffraction patterns during synthesis of the carbon molecular sieve CMK-1 with its silica template MCM-48 : (a) The mesoporous silica molecular sieve MCM-48, (b) MCM-48 after completing carbonization within pores, and (C) CMK-1 obtained by removing silica wall after carbonization.

R. Ryoo et al., *J. Phys. Chem. B*, 103, 7743 (1999).

$$\textbf{Sucrose/MCM-48} \xrightarrow[\textbf{Pyrolysis}]{H_2SO_4} \textbf{Carbon/MCM-48} \xrightarrow[\textbf{Washing with NaOH solution}]{} \textbf{CMK-1}$$

R. Ryoo et al., *J. Phys. Chem. B*, 103, 7743 (1999).



Template Synthesis Mechanism

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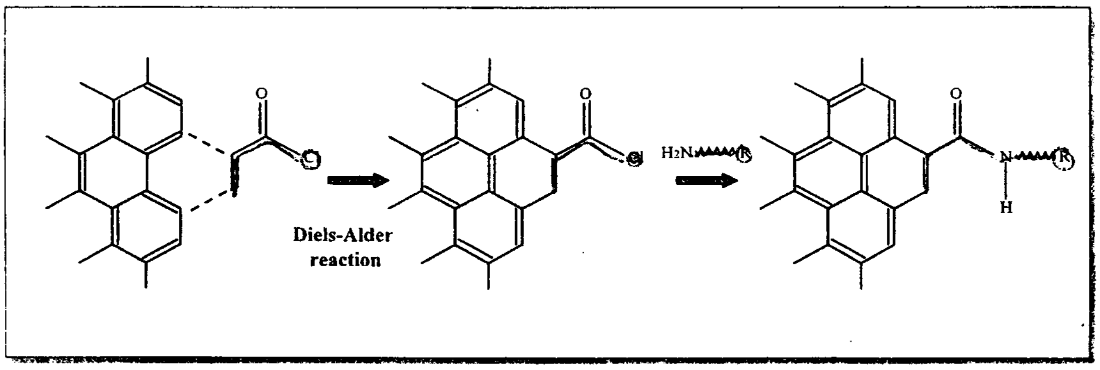
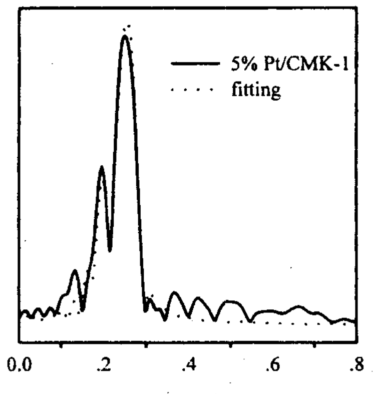
Surface Functionalization of CMK-1



CMK-1 can be functionalized using Diels-Alder reaction with olefinic compounds.

(Manuscript in preparation.)

Pt Cluster on CMK-1



EXAFS Curve Fit

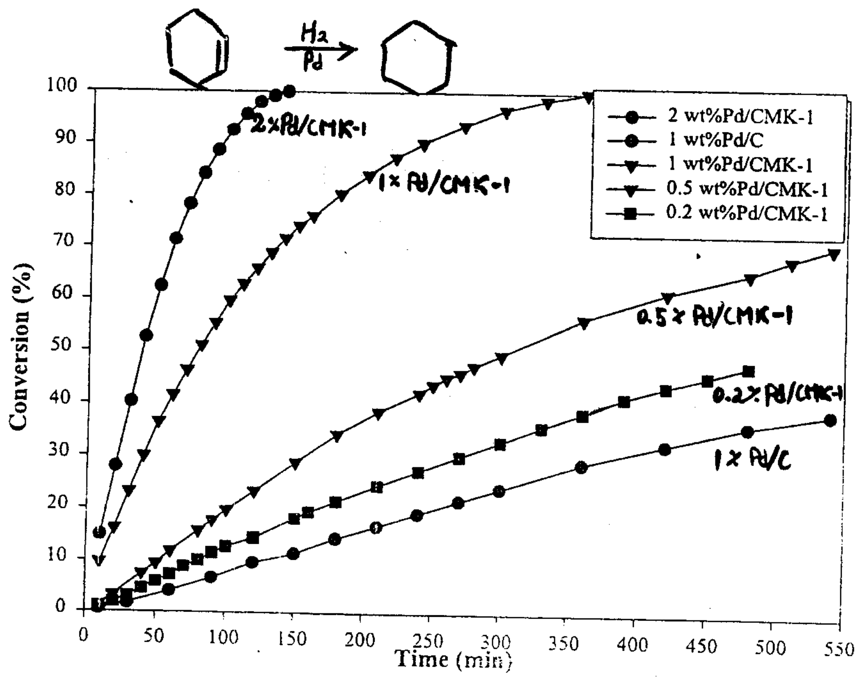
	n	r (nm)
Pt-Pt	5.4	0.27

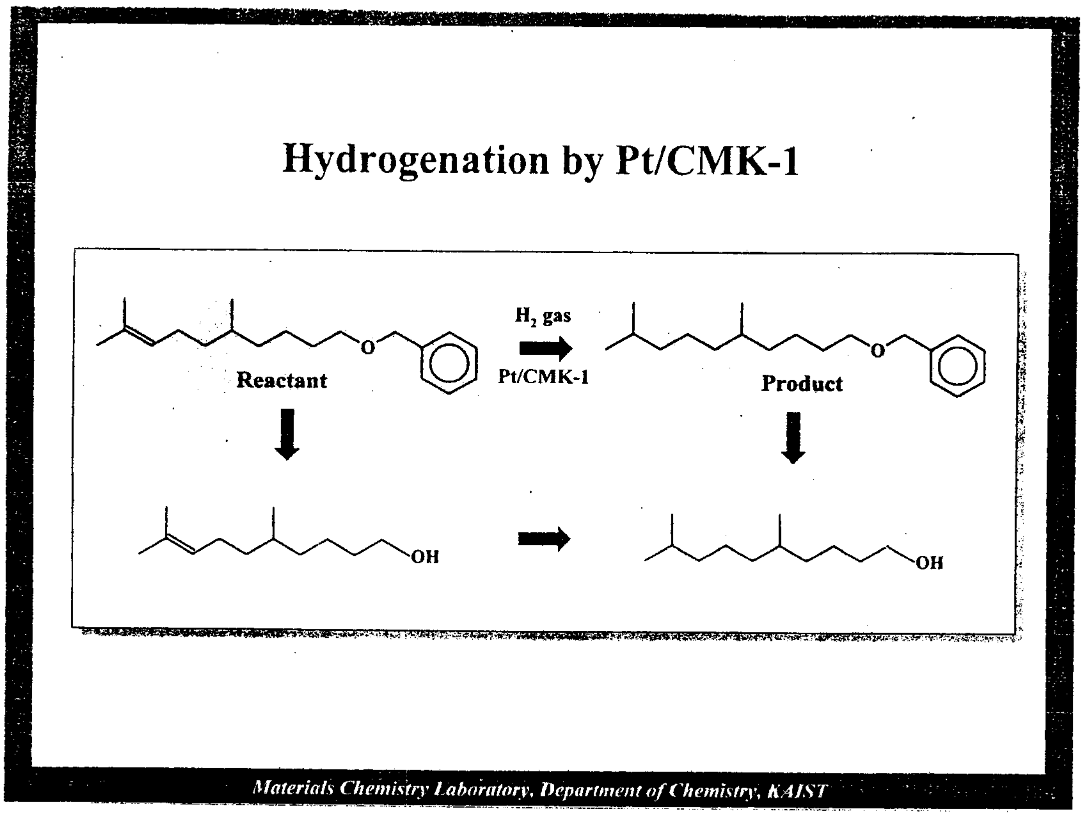
H Chemisorption

Sample	H/Pt
2wt% Pt/CMK-1	1.5
5wt% Pt/CMK-1	1.0

Pt cluster smaller than 1 nm in diameter

Pd, Ru





Hydrogenation by Pt/CMK-1

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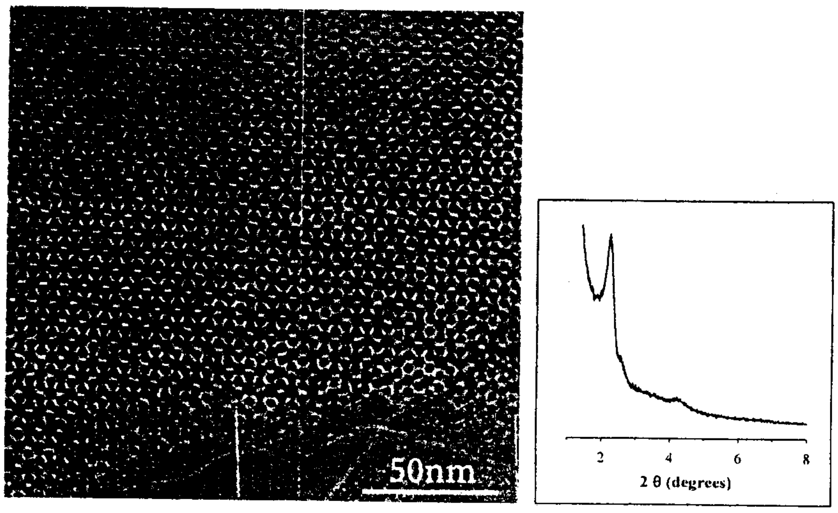
CMK-2 (*Ia3d* structure)



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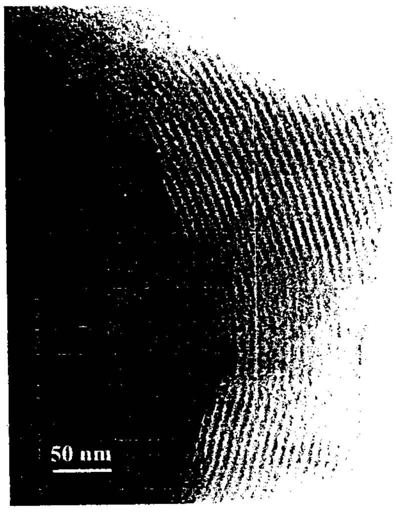
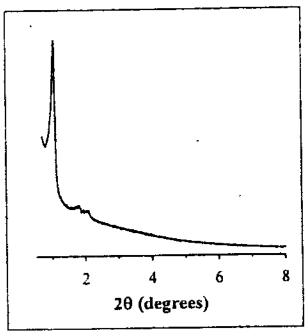
CMK-3 (*hexagonal* structure)





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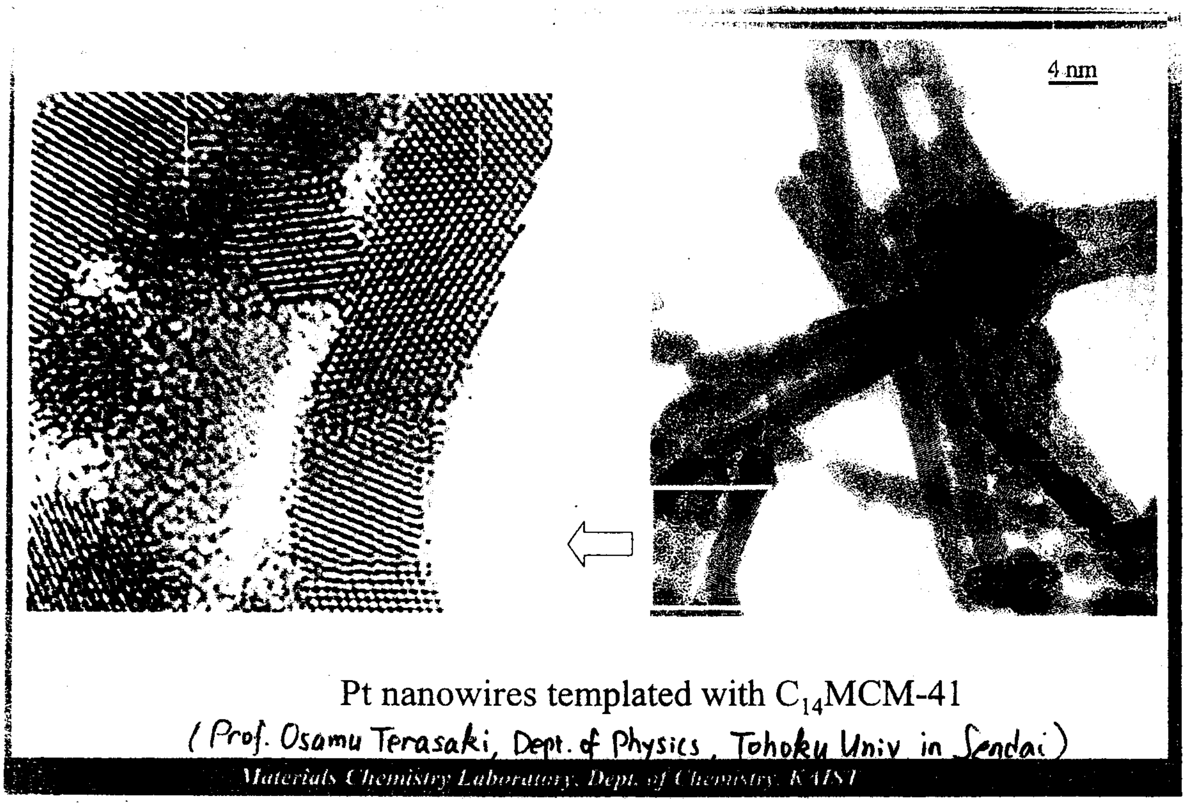
Template Synthesis of Nanostructured Platinum



Pt nanowires templated with C_{14}MCM-41

(Prof. Osamu Terasaki, Dept. of Physics, Tohoku Univ in Sendai)

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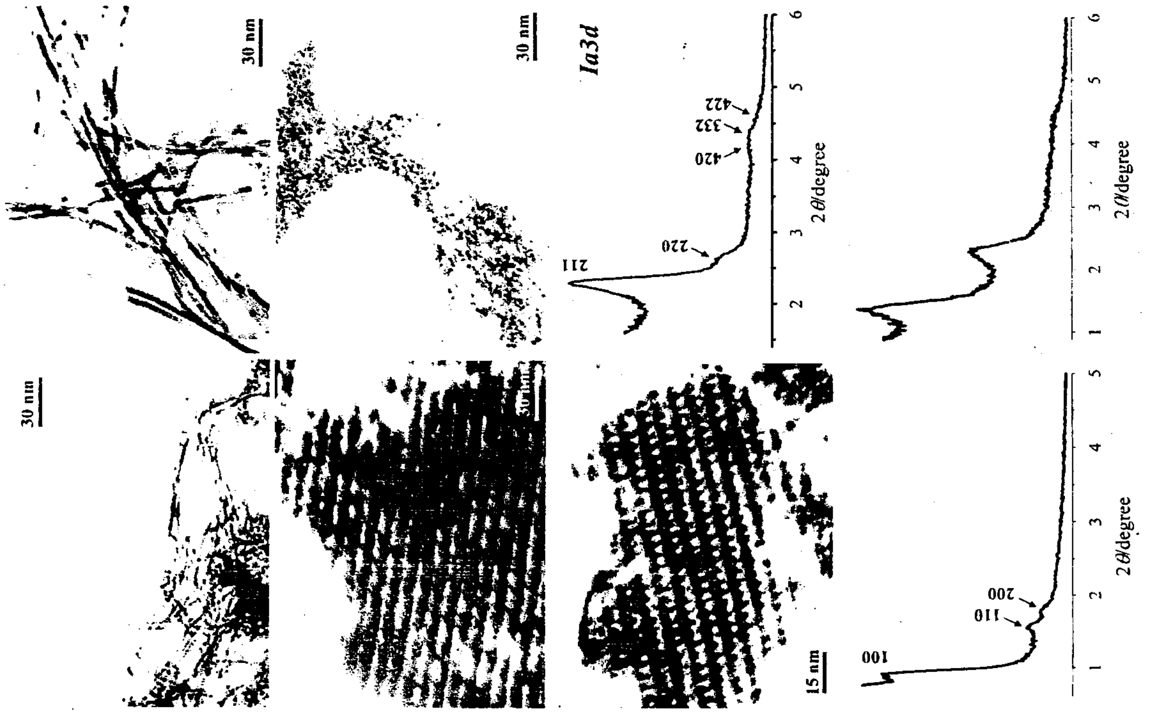
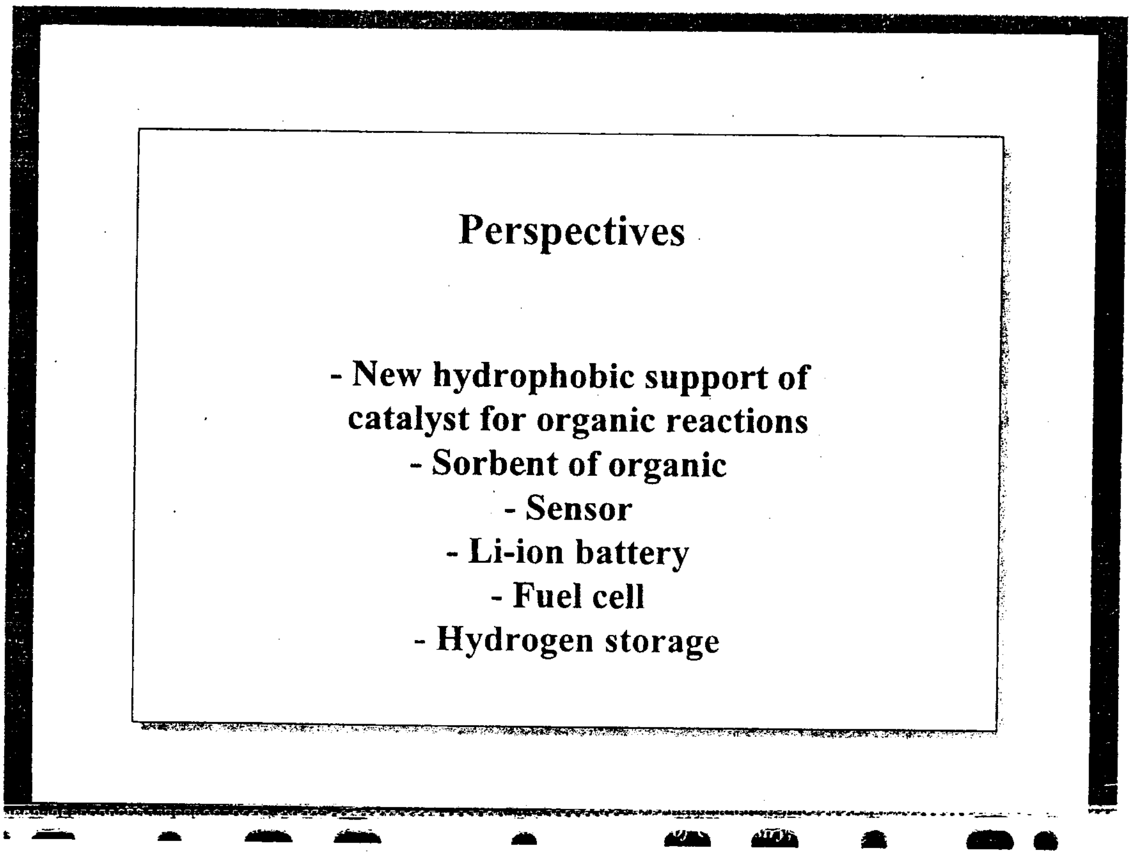
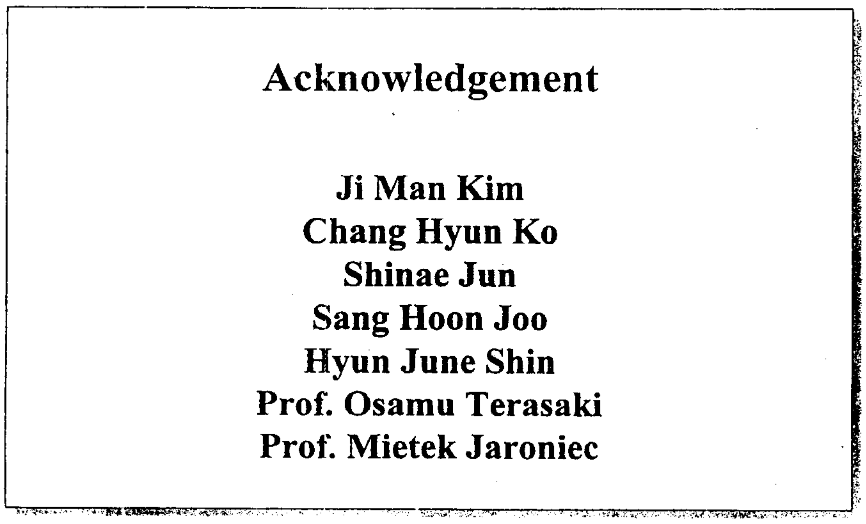




Perspectives

- New hydrophobic support of catalyst for organic reactions
- Sorbent of organic
- Sensor
- Li-ion battery
- Fuel cell
- Hydrogen storage



Acknowledgement

Ji Man Kim
Chang Hyun Ko
Shinae Jun
Sang Hoon Joo
Hyun June Shin
Prof. Osamu Terasaki
Prof. Mietek Jaroniec