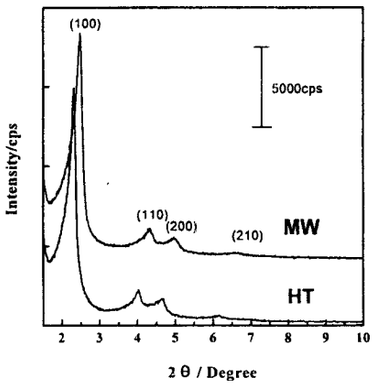
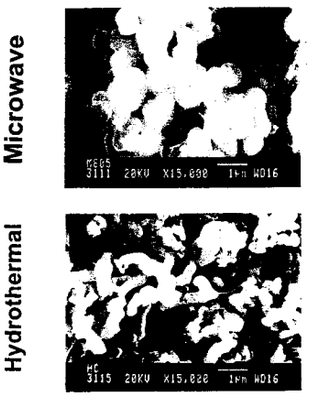
MCM-41 Material Synthesis under Microwave Irradiation

Synthesis Time



MW : 40 min
HT : 2 day

SEM



S.-E. Park et al., *Catal. Today* **44**, 301 (1998)

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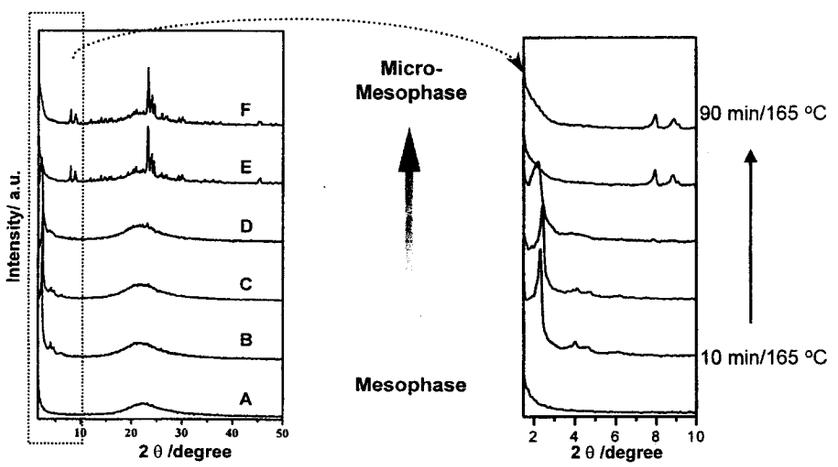
KRI

Micro-Mesoporous Materials by Microwave irradiation



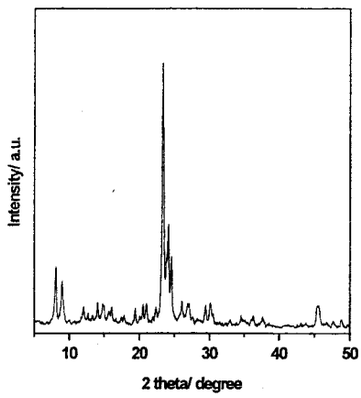
A : Silicalite gel(A) treated by 1 h- MW irradiation(165 °C)
B-F : Mixture for A gel and Micelle according to time of MW irradiation(165 °C)

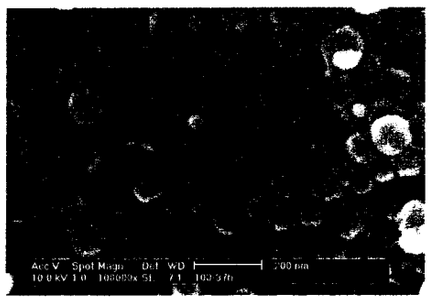
S.-E. Park et al., *Stud. Surf. Sci. Catal* ***in press*** (2000).

Catalysis Center for Molecular Engineering

KRI

Synthesis of Nanosized Si-ZSM-5 by Hydrothermal Heating





- o SEM : about 50-100 nm
- o Dynamic Light Scattering : Av. Size : 83 nm

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SEM Images of Microporous Nickel Phosphates

VSB-1

VSB-5

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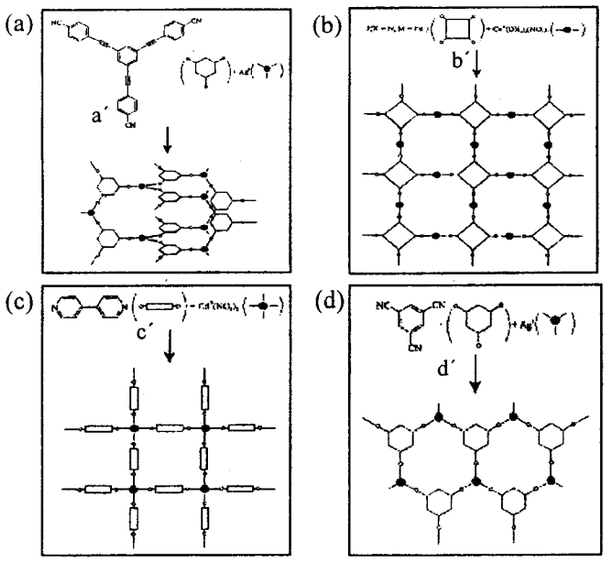
Organic Zeolite Analogues



(a) $ThSi_2$- related structure of a´ • AgOTf (Tf=CF_3SO_2)

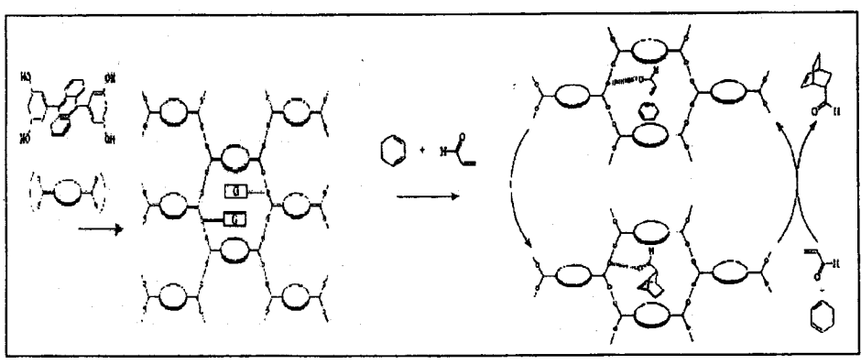
(b) Tetra(4-pyridyl)porphyrin -related structure formed by b´ • $Cd(OH)_2(NO_3)_2$ (X=N and M=Pd^{II})

(c) 4,4-Bipyridine-related structure of c´ • $Cd(NO_3)_2$

(d) Tritopic tricyano derivative -related hexagonal structure of d´ • AgOTf

Application of Organic Zeolitic Catalysis

Suggested mechanism for Diels-Alder reaction catalyzed by microporous zeolite-like acid solid

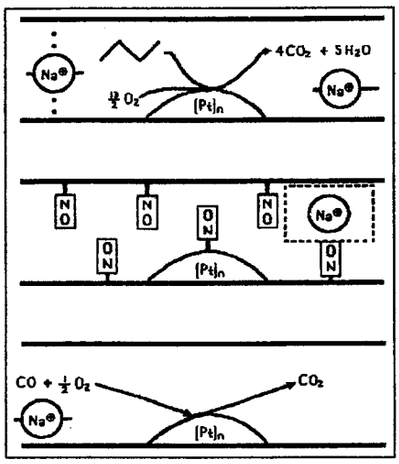


Zeolite-based Gas Sensors

Butane

Nitrogen Oxide

Carbon Oxide



- Decrease of activation energy of Na^+ hopping
- Raise of ionic conductivity
- Raise of polarizability
- Raise of permittivity
- Raise of capacitance

Quasi-irreversible adsorption, blocking of ionic conduction

Fast reaction without great influence on ionic conduction

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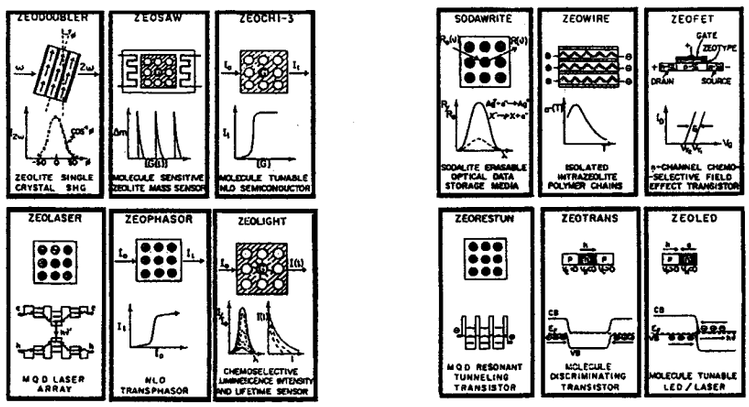
Speculative Nanoscale Device Ideas on Zeolites and Molecular Sieves



G.A.Ozin *Adv. Mater.* 1992, 4(10), 612

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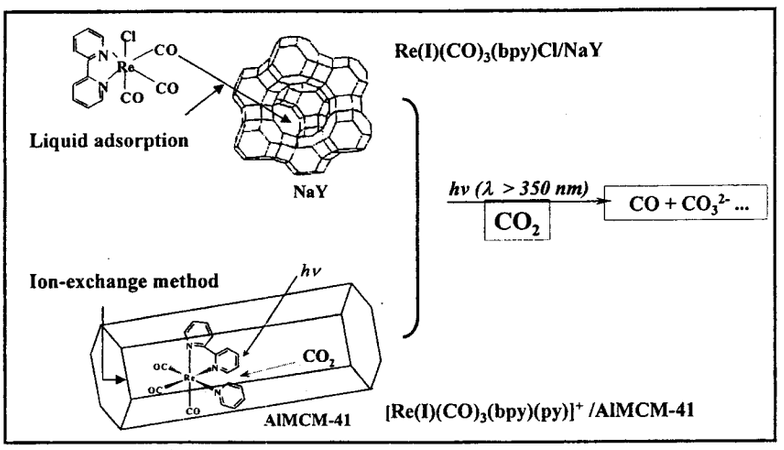
Photochemical Activation & Reduction of CO_2

: over Molecular Sieve-Encapsulated Rhenium Complexes



⇨ *Biomimetic Artificial Photosynthetic System using Supramolecular Assembly of Photosensitizers and Molecular Sieves*

Photoinduced Electron Transfer (PET) of Porphyrins within Mesoporous MCM-41

Long-lived net PET of Porphyrins by Visible Light in Mesoporous MCM-41
⇒ *for photochemical conversion and storage of solar energy*

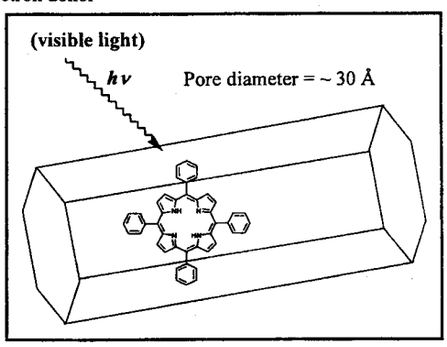
TPP = *meso*-Tetraphenylporphyrin (15 Å) : Electron donor

$$\text{TPP} \xrightarrow{h\nu} \text{TPP}^{+\cdot} + e^-$$
in MCM-41

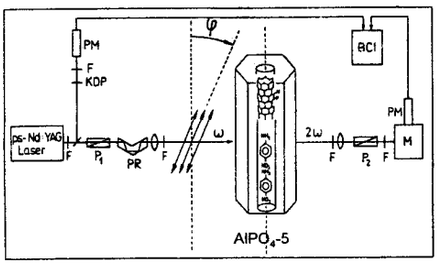
1.$TPP^{+\cdot}$: stable at RT as well as 77 K within MCM-41

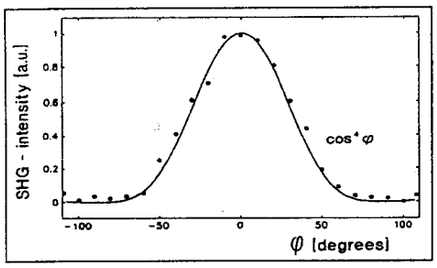
2.MCM-41 framework acts as e^- acceptor

3.$TPP^{+\cdot}$ Photoyield :
TiMCM-41 > MCM-41 > AlMCM-41



Sung-Suh and Kevan, J. Phys. Chem., 102 B, 857 (1998)

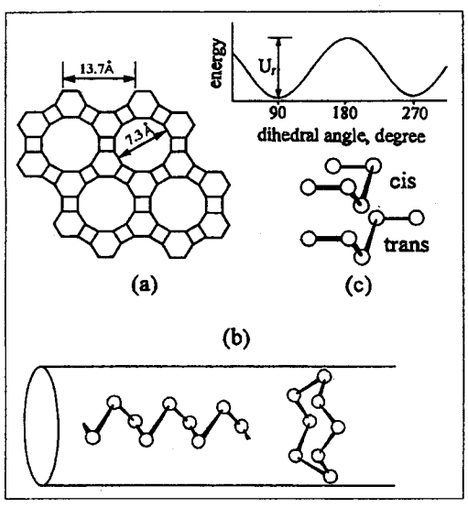




Second Harmonic Generation(SHG) of p-Nitroaniline(PNA) Encapsulated in a Nanochannel of $AlPO_4$-5

(a) PNA molecules have a large anisostropic hyperpolarizability
(b) Since PNA crystallizes centrosymmetrically in a nanochannel of $AlPO_4$-5, the individual molecular dipole moments cancel out
➡ *No SHG signal*
(c) For arrangement of PNA molecules formed in the channels of $AlPO_4$-5, with the strings being longer than the incident wavelength of the laser, the molecular dipole moment are expected to superimpose giving a macroscopic hyperpolarization ➡ SHG effect

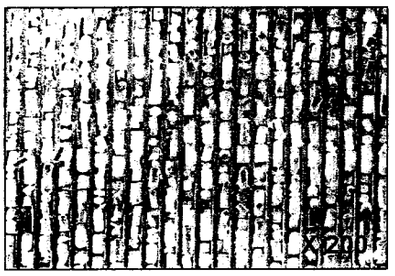
Caro, *et. al. Adv. Mater. Vol. 4,* 273 (1992)

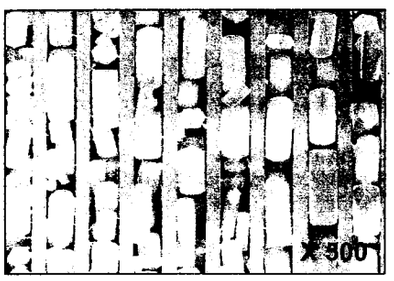


Single Selenium Chains Confined in One-Dimensional Nanochannels of $AlPO_4$-5

(a) $AlPO_4$-5 crystal structure in the plane perpendicular to the c axis
(b) Schematic image of Se chain and Se_8 ring incorporated into $AlPO_4$-5 channel
(c) An approximate dependence of the internal rotational potential of the Se chain vs the dihedral angle
(d) For the temperature dependence of Raman spectrum, the chains are founded to ordered at 77 K, and a phase transition accompanied with a structural relaxation of the chains to the strongly disordered state with unfixed dihedral angles ("torsional melting")

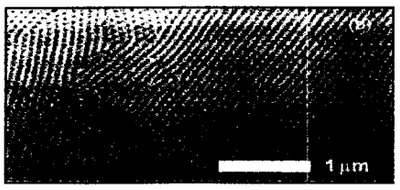
Poborchii, et. al., *Phys. Rev. Lett.*, 82, 1955 (1999)

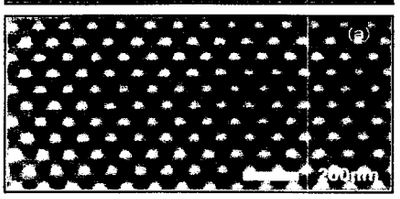


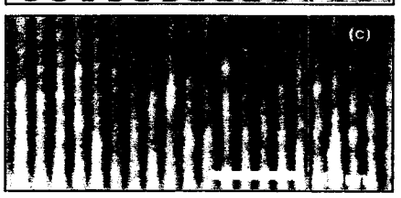


High Ordered $AlPO_4$-5 Single Crystal over Microgrooves of Silicon Wafer

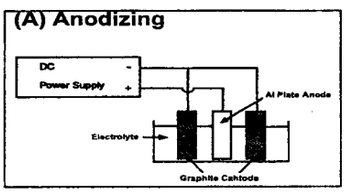
(a) $AlPO_4$-5 dimension: 10 μm x 10 μm x 40 μm
(b) Photolithography of silicon wafer
(c) Vibration alignment using piezoceramic(PZT) actulator at low frequency
(d) UV Raman spectroscopic study of molecules encapsulated in a nanochannel of $AlPO_4$-5

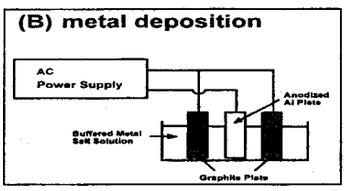


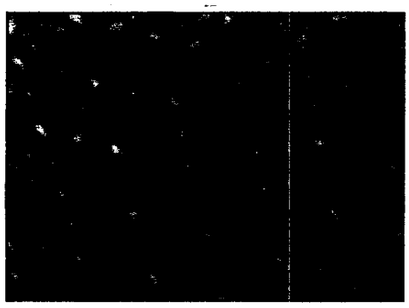




SEM Images of Anodizing Aluminum Oxide (AAO) Nanotemplate as a New Catalyst Support



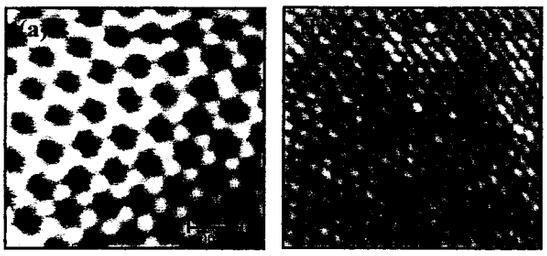


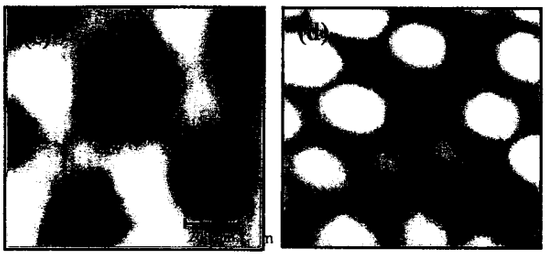


SEM Images of Anodizing Aluminum Oxide (AAO) Nanotemplate depending on Electrolyte

(a) Oxalic Acid
(b) Phosphoric Acid

Electrolyte Concn (temp, °C)	Anodizing ratio ($Å V^{-1}$)	Pore Size ($Å$)
15% Sulfuric Acid (10)	10.0	~ 100
2% Oxalic Acid (24)	11.8	~ 300
4% Phosphoric Acid (24)	11.9	~ 3000



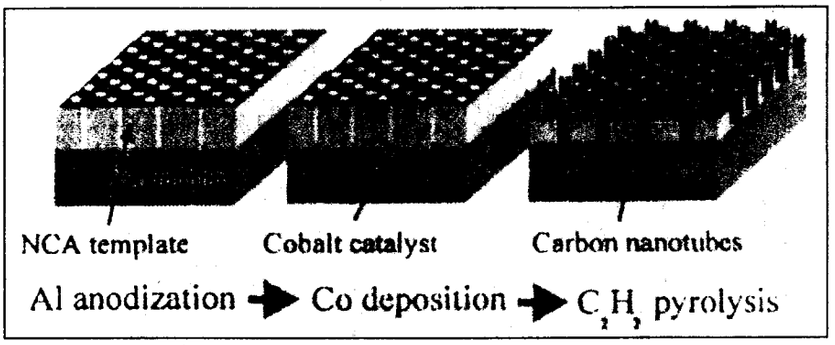


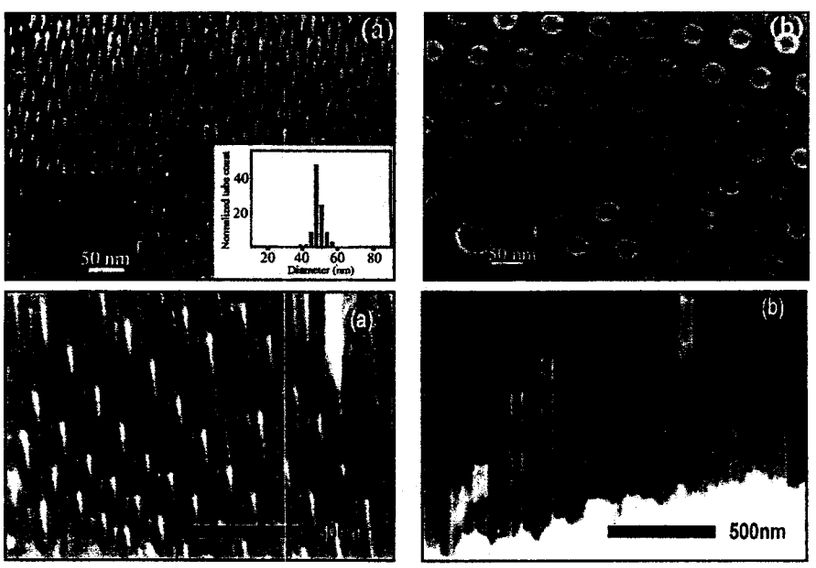
AFM Images of AAO Nanotemplate

In Oxalic Acid
(a) Nanopore (b) Barrier

In Phosphoric Acid
(c) Nanopore (d) barrier

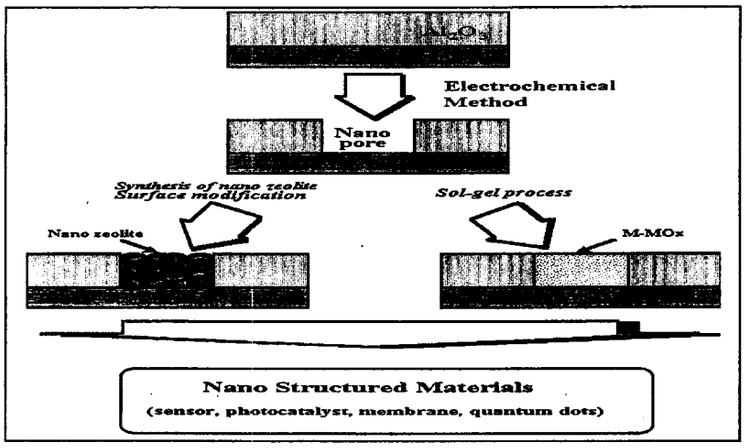
CVD of Carbon Nanotube into AAO Nanotemplate

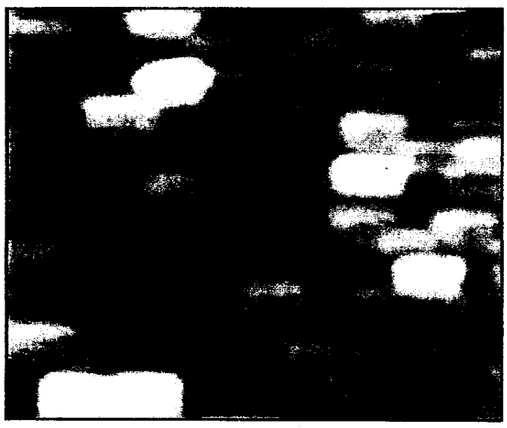




Moskovits, *et. al.*; **Suh**, *et. al. Appl. Phys. Lett.*, **1999**

Fabrication of Zeolite Materials into AAO Nanotemplate



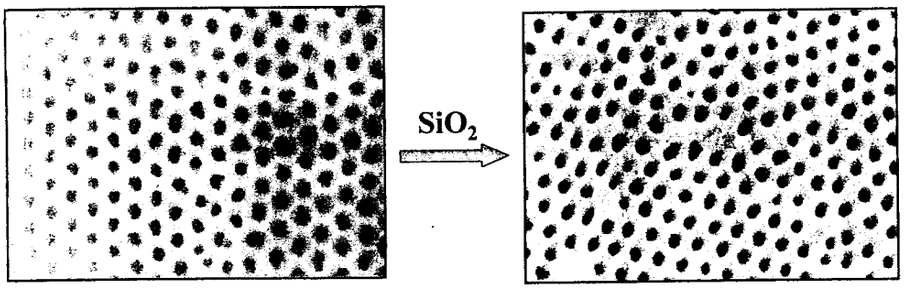


AFM Image of ZSM-5 Thin Film on AAO Nanotemplate

(a) Transparent thin film

(b) Very small size ZSM-5 single crystal : about 20 nm

SEM Images of Mesoporous Silica Thin Film over AAO Nanotemplate



(a) Mesoporous silica thin film in acidic condition
by solvent evaporation method
(b) Mesoporous silica replica of AAO nanotemplate

Conclusion

1. Nano-sized silicalite-1 materials by hydrothermal heating

2. Micro-mesoporous composite materials by microwave Irradiation

•3. Mesoporous MCM-41 by microwave irradiation and
• suggestion of supramolecular templating mechanism

•4. New fabrication of microporous materials and nano reactor for catalyst
•

•5. New anodizing metal Oxide(AAO) nanotemplates for catalysis