D2 Naoya Kumagai

Chance favors only the prepared mind

Recent Advaces in Solid Catalysis

@ Homogeneous

fine chemical synthesis

- metal complexes in solution

⇦

toward general organic reactions

⇩

asymmetric catalysis

TS

model

independent progress
independent profession

⇦⇦⇦
(i)
(ii)

@ Heterogeneous

oil, gas refining

- perovskite
- heteropoly acid
- zeolite ~20Å で 3し

- Mesoporous materials
  20～100 Å の 3し

assessment, design

Enzyme ~20 nm

suface analysis

IR
SEM
STM
XRD
MAS-NMR
EXAFS
DXAFS

近年触媒に関する教科書を調べ直した。期（約3ヶ月の予定で）に、興味ある論文を触媒に関する近年の新展開を紹介する。

□ The Reaction on Solid Surface.

surface · A + S ⟶ $\overset{*}{AS}$ ⟶

enzyme · A + E ⟶ AE ⇄
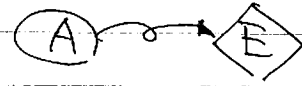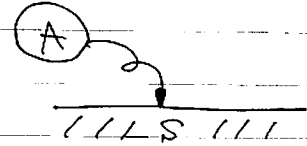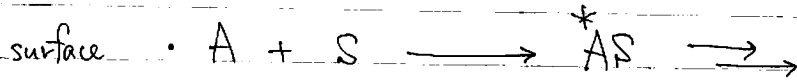
Surface	Solution
· Relatively slow?	· Relatively fast?
	✕ diffusion control ✕
· Adsorption ⟶ Reaction coordination	· Coordination ⟶ Reaction
· Surface design, modification	· Complex design

Haber — Bos. Ammonia Synthesis   1910.

$$3H_2 + N_2 \longrightarrow 2NH_3$$
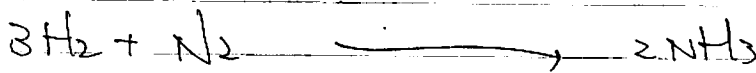
● 3 composite : Fe_3O_4 ⟵ K_2O electrical tuning
⟵ Al_2O_3 : spacer

(c) $�andM⫽ \rightleftharpoons ⫽M^{⊕}⫽ + OH^-$ with $\underset{H}{\overset{O}{|}})\delta-$

(d) $⫽M⫽ \rightleftharpoons ⫽M⫽ + H^+$ with $\underset{H}{\overset{O}{|}})\delta-$ and $O^{⊖}$
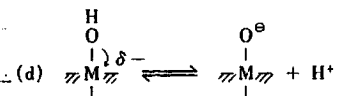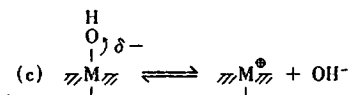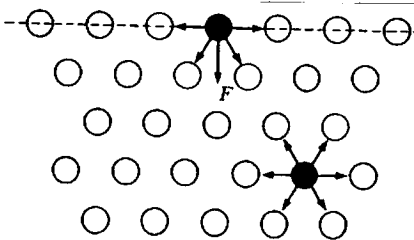
Gas refinement ⟶ Fine chemicals

Heteropoly acid → Perovskite → Zeolites

- Aluminosilicate framework : $[SiO_4]^{4-}$, $[AlO_4]^{5-}$ tetrahedra units
- Highly ordered → 65 defined structure (1996)
- Uniform pore
- 500 – 700 m^2/g surface area
- 2 ~ 10 Å pore size

molecular sieves (分子ふるい)
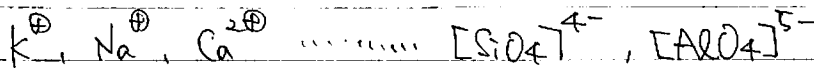
Type 3A Composition 0.6 K_2O: 0.40 Na_2O : 1 Al_2O_3 : 2.0 ± 0.1SiO_2 : x H_2O

Type 4A Composition 1 Na_2O: 1 Al_2O_3: 2.0 ± 0.1 SiO_2 : x H_2O

Type 5A Composition 0.80 CaO : 0.20 Na_2O : 1 Al_2O_3: 2.0 ± 0.1 SiO_2: x H_2O

Type 13X Composition 1 Na_2O: 1 Al_2O_3 : 2.8 ± 0.2 SiO_2 : xH_2O

Type	Pore	adsorbent			
3A	3Å	H_2O NH_3 H_2 He, Ar	CH_4 C_2H_4 C_3H_6 H_2S	C_3H_6 $n-C_{10}H_{22}$ CH_2Cl_2 C_2H_5OH	$iso-C_5H_{12}$ $iso-C_4H_{10}$ $CHCl_3$ $CHBr_3$
4A	4Å		CO_2 CH_3OH O_2, N_2	CH_2Cl_2 CHF_2Cl $(CH_3)_2NH$ CH_3I	$(CH_3)_2CHOH$ $(CH_3)_3N$ CCl_4
5A	5Å				
10X	9Å				
13X	10Å			$(n-C_4H_9N)_2NH$	

$K^{\oplus}$, $Na^{\oplus}$, $Ca^{2\oplus}$ .... $[SiO_4]^{4-}$, $[AlO_4]^{5-}$

↓

cation exchange ability

- high thermal stability
- insoluble version of Bronsted and Lewis acids
- Well defined structure ⟶ shape selectivity.   ~ 1 Å
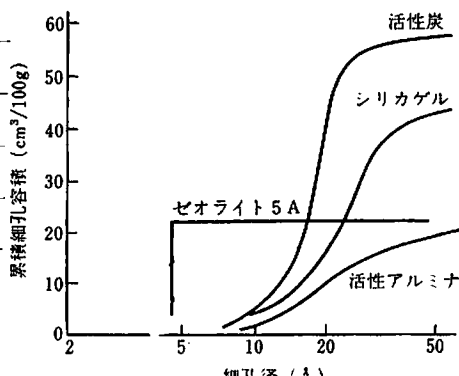
Zeotype : Mn, Co, B, Ga, P ...
⇧
aluminosilicate

Zeolite ——ion exchange→ Na, K, Ca ⇒ Ti, Cu, Mn ...

functions
for organic reactions,
gas refinement
:
ex. NO gas
selective removal

· symmetrical
· small pore 2~10 Å
  o gas refinement
  × fine chemicals

passive support

· Microencapsulated
  Catalyst.
· Review:
  Kobayashi, S.
  chem. Commun.
  2003, 449.

· Metal exchanged.
  (· Hydroxyapatite
    · Montmorillonite (acid)
    · Hydrotalcite (base)

Review:
  Kaneda, K
  有合化 2003, 61.

Homochiral Zeolite
· Unknown
· other approaches
· Inorgano - organo (chiral) material.

examples of homochiral Inorganics.   ⌐JACS 1999, 121, 11235
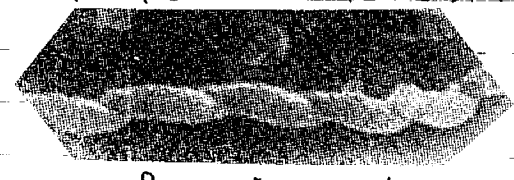 d - or l- Quartz.   Nature 1938, 181, 1193
  · d - or l- NaClO₃   Angew. chem. Int. Ed. 2000, 39, 1540.
  · helical silica.   TL 2003, 44, 721.

Mesoporous Materials

dodec-NH —* : template.   sol-gel method
      HN-dodec   500°C.
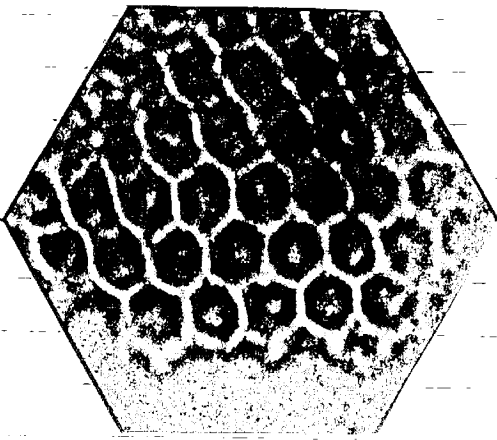
10 ~ 100 nm

· 1st reported in early 1980s.
· mesoporous : 20 - 500 Å   (IUPAC)

⇓ ⌐ Enzyme size
              2 ~ 20 nm

Suitable reaction field
    for organic compounds.

↔ 10 nm

Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$,   Hydrotalcite : $Mg_6Al_2(OH)_{16}CO_3$

Mesoporous Materials

The Preparation of Alkyltrimethylammonium–Kanemite Complexes and Their Conversion to Microporous Materials

Tsuneo YANAGISAWA, Toshio SHIMIZU, Kazuyuki KURODA, and Chuzo KATO*
Department of Applied Chemistry, Waseda University, Ohkubo-3, Shinjuku-ku, Tokyo 169
(Received August 25, 1989)

Preparation of Alkyltrimethylammonium-Kanemite Complexes and the Thermal Treatment. Alkyltrimethylammonium–kanemite complexes were prepared by cation-exchange, as has been described by Beneke and Lagaly.[2] One hundred ml of a 0.1 mol dm^{-3} alkyltrimethylammonium chloride ($C_nH_{2n+1}(CH_3)_3N^+Cl^-$, $n=12, 14, 16,$ or 18) aqueous solution was added to 1 g of kanemite, and then the suspension was stirred for one week at 65 °C. While the suspension was being stirred, this pH was kept between 8 and 9. After the filtration of the product, the same procedure was repeated. Then, the product was washed with an excess of acetone and air-dried.

The complexes were calcined up to 700 °C in air by means of a thermal analyzer, in which the alkyltrimethylammonium ions were pyrolyzed completely.

[handwritten:] NaHSi$_2$O$_5$·3H$_2$O layered polysilicates

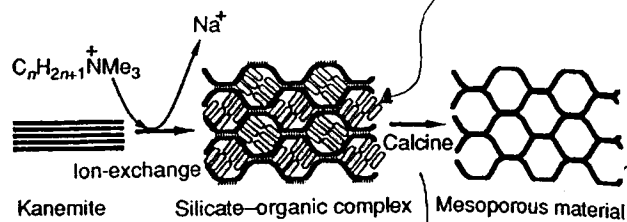*[handwritten:] → template formation*

Fig. 5 Schematic model for the formation of the mesoporous material from kanemite

[handwritten:] J. Chem. Soc. Chem. Commun. 1993. 680. K. Kuroda et al. improved procedure

[handwritten:] • 20 – 40 Å pore size
[handwritten:] • 900 m²/g

[handwritten:] ~N⊕ bigger → larger pore

Pore-size regimes	Definition
macroporous	> 500 Å
mesoporous	20–500 Å
microporous	< 20 Å
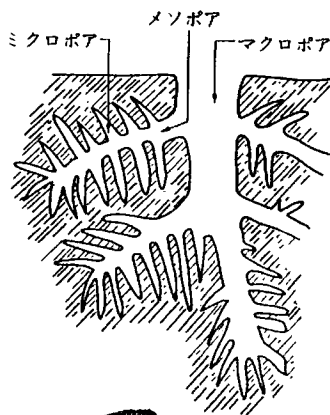
表 5・1 活性炭の各細孔区分の特性値

	細孔半径 (Å)	細孔容積 (ml/g)	比表面積 (m²/g)
ミクロポア	~20	0.25~0.6	700~2000
メソポア	20~1000	0.02~0.2	1~200
マクロポア	1000~	0.2~0.5	0.5~2

図 5・1 活性炭細孔構造のモデル図
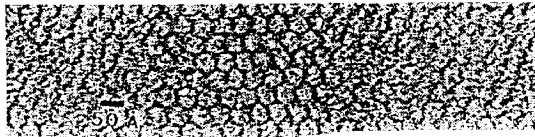
*The second breakthrough.*

Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism

**C. T. Kresge*, M. E. Leonowicz*, W. J. Roth*,
J. C. Vartuli* & J. S. Beck†**

Mobil Research and Development Corporation,
*Paulsboro Research Laboratory, Paulsboro, New Jersey 08066, USA
† Central Research Laboratory, Princeton, New Jersey 08543, USA

Nature 1992, 359, 710.

200 g of a solution containing 26 wt% hexadecyltrimethylammonium ion, as $C_{16}H_{33}(CH_3)_3N^+OH/Cl$ (~30% hydroxide), was combined with 2 g of Catapal alumina, 100 g of tetramethylammonium silicate solution (10% SiO_2, ratio of tetramethylammonium to $SiO_2 = 1$) and 25 g of a precipitated silica (HiSil), with stirring (molar ratio of $C_{16}H_{33}(CH_3)_3N^+$ to Si ≤ 1). This mixture was placed in a static autoclave at 150 °C for 48 hours. After cooling it to room temperature, we recovered the solid product by filtration on a Buchner funnel, washed it with water and dried it in air at ambient temperature. The as-synthesized product was then calcined at 540 °C for one hour in flowing nitrogen, followed by six hours in flowing air. The as-synthesized product contains over 40 wt% of the original surfactant as reflected by its composition (molar): 1 N, 19.6 C, 4.7 Si, 0.27 Al. In general, no special precautions (heating rate, atmosphere) are needed during the temperature ramping (from ambient temperature) and calcination processes.
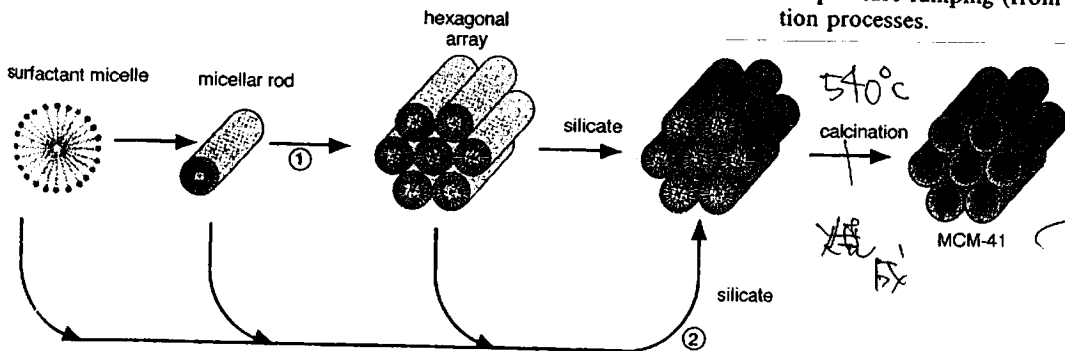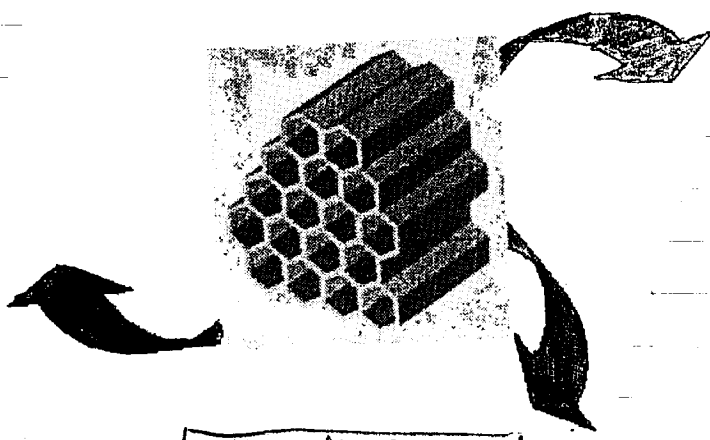

Mobile Catalyst Molecular Sieves

- Pore size 16 Å ~ >100Å
- ≥ 1000 m²/g

⟹ Inspire the widespread research.

all is surface
· High performance
· Supported catalyst

Uniform surface
· Solid catalyst
· Stereoselectivity
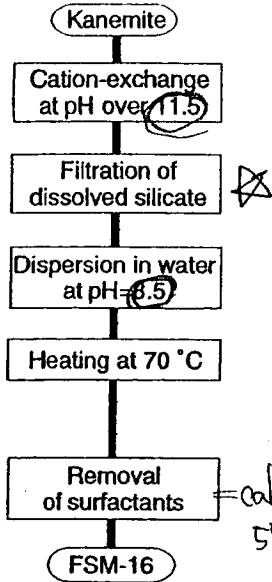· High-level recognition

Ordered Surface
· shape selectivity · Multi-point recognition

Syntheses of Highly Ordered Mesoporous Materials, FSM-16, Derived from Kanemite

[handwritten: Na₂Si₂O₅ layer]

Shinji Inagaki,* Akihiko Koiwai, Noritomo Suzuki, Yoshiaki Fukushima, and Kazuyuki Kuroda†

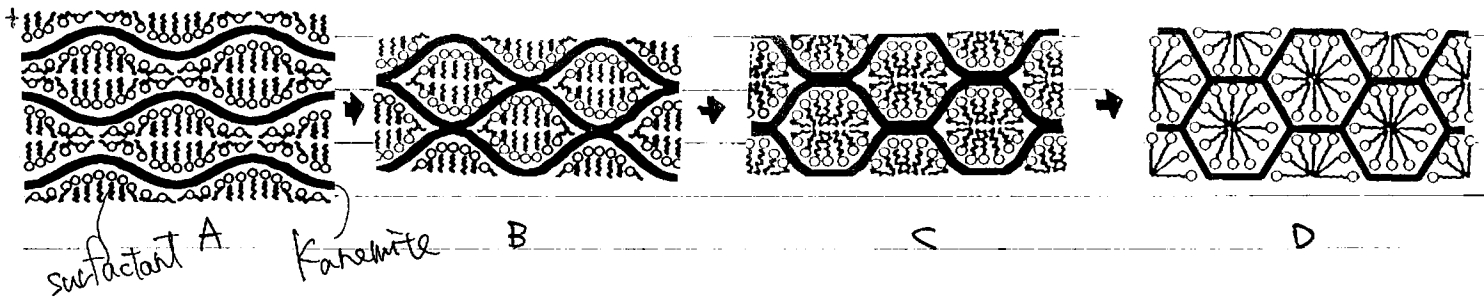Toyota Central R&D Labs., Inc., 41-1, Yokomichi, Nagakute-cho, Aichi 480-11

[handwritten: No. 7]

[handwritten: 5 mm]

Flowchart (Fig. 1):

Kanemite
→ Cation-exchange at pH over *11.5*
→ Filtration of dissolved silicate *[handwritten: ✗]*
→ Dispersion in water at pH=*8.5*
→ Heating at 70 °C
→ Removal of surfactants *[handwritten: = calcination 550 – 900 °C, 6 h]*
→ FSM-16

Fig. 1. Synthetic procedures of FSM-16 and the intermediate silicate/organic complexes.

Table 5. Unit Cell Dimensions, Tentative Pore Diameters, Specific Surface Areas and Pore Volumes of FSM-16 Prepared by Using Various Surfactants with Different Alkyl-Chain Lengths

Surfactant chain length $C_nH_{2n+1}N^+(CH_3)_3$	Unit cell dimensions	Tentative pore diameters	Specific surface areas[a]	Pore volumes
$n=$	nm	Å	$(m^2\,g^{-1})$	$cm^3\,g^{-1}$
8	3.09	<15	680	0.28
10	3.28	16	999	0.47
12	3.68	20	923	0.53
14	3.90	23	1017	0.69
16	4.38	27	1031	0.80
18	4.90	32	929	0.83

a) The specific surface areas were calculated by BET equation using adsorption data at $0.05<P/P_0<0.1$ on $n=8$, $0.05<P/P_0<0.12$ on $n=10$, $0.05<P/P_0<0.15$ on $n=12$, $0.05<P/P_0<0.2$ on $n=14$, $0.05<P/P_0<0.25$ on $n=16$, and $0.05<P/P_0<0.35$ on $n=18$.

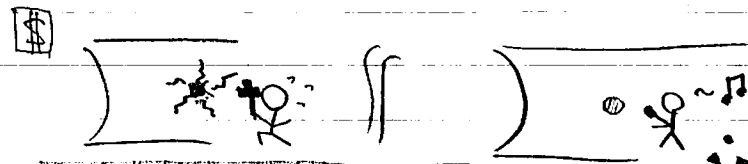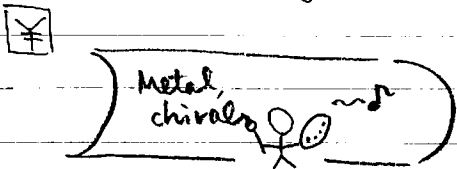*[handwritten annotations below figures:]*

A — Surfactant, Kanemite   B   C   D

• FSM-16 : Folded Sheets Mesoporous Materials.

Now, we got a unit, then ...?   Functionalization

¥   Metal, chiral

• Post-Synthetic modification
• Coating, Grafting

$ Pre-fabricated mesoporous support
• Mesoporous formation with organo-hybridized silica.

Surface properties; Hydrophobicity, philicity, Bind, recognition, activation of guest.

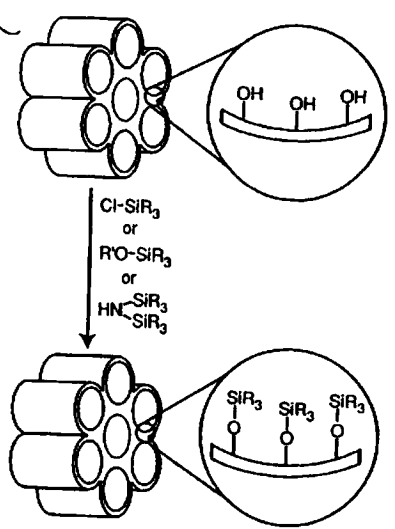(MCM-41, FSM-16 or related...

☒ Post - synthetic modification

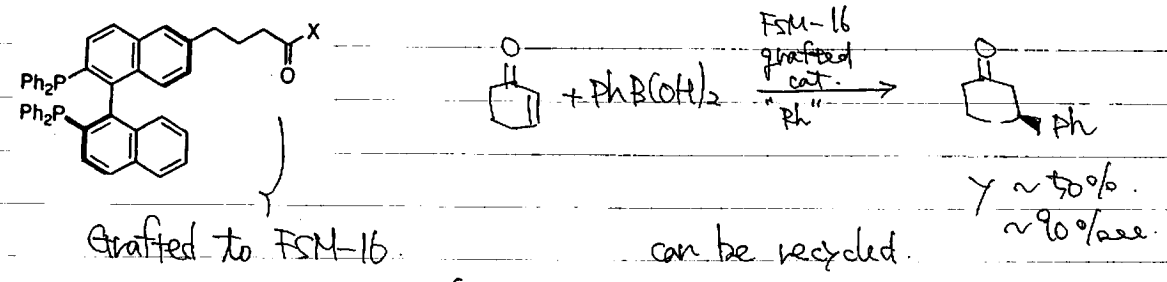Fig. 1. Functionalization of mesoporous silicates by grafting.

CI-SiR₃
or
R'O-SiR₃
or
HN(SiR₃)(SiR₃)

· simple grafting.

· simple coating with Ti, V, Mn, Co, Al
etc.

· simple modification with
$-SO_3H$, $-NR_3^{\oplus}\,^{\ominus}OH$

expected : · Aldol, Michael, Knoevenagel,
oxidation, reduction, ...
· asymmetric epoxidation,
reduction ...
⌐ Hayashi - Miyaura
arylation.

B101

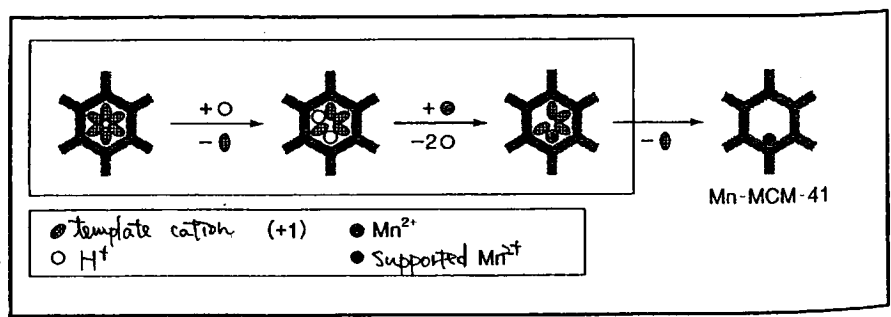## A New Method for Functionalization on Silica Gel with Allylsilanes

Toyoshi Shimada, Kazuko Aoki, Yo Shinoda, Tomoaki Nakamura, Norihito Tokunaga, Shinji Inagaki, and Tamio Hayasi
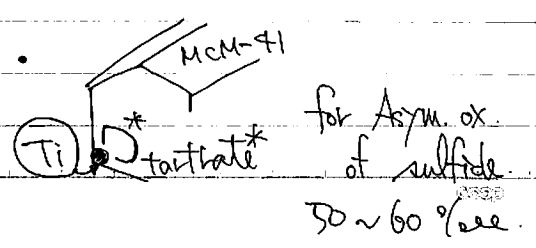Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo, Kyoto 606-8502

Grafted to FSM-16.

$+ PhB(OH)_2 \xrightarrow[\text{"Ph"}]{\substack{\text{FSM-16} \\ \text{grafted} \\ \text{cat.}}}$

can be recycled.

Y ~ 80%.
~ 90% ee.

⌐ Cooperation ⟨ material specialist
asym. cat. specialist

"Idea"
– ▫ Template ion - Exchange method.
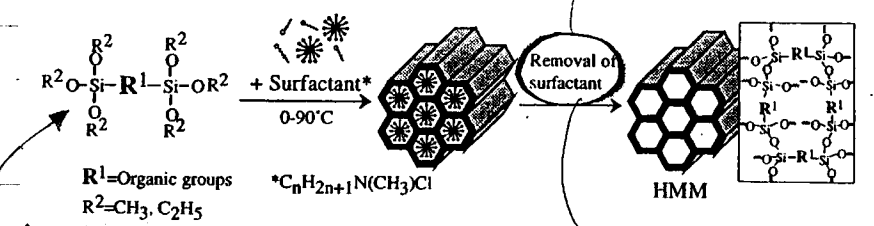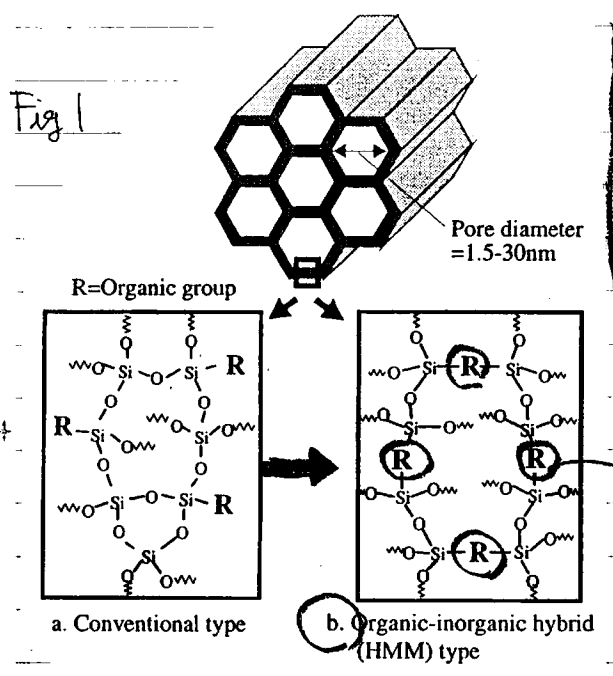
· High - dence incorporation
Si/Mn up to 20

Mn-MCM-41

⊛ template cation (+1)   ● Mn²⁺
○ H⁺   ● Supported Mn²⁺

MCM-41

(Ti)⟨O⟩*tartrate*   for Asym. ox
of sulfide.
50 ~ 60 % ee.

J. Catal. 1998, 178, 207.   Iwamoto et al.

The first HMM (Hybrid Mesoporous Material)

[#] Pre-fabrication method

Novel Mesoporous Materials with a Uniform Distribution of Organic Groups and Inorganic Oxide in Their Frameworks

Shinji Inagaki,*[†] Shiyou Guan,[†] Yoshiaki Fukushima,[†] Tetsu Ohsuna,[§] and Osamu Terasaki[§]

Calcination

Fig 1

Pore diameter = 1.5–30 nm

R = Organic group

a. Conventional type

b. Organic-inorganic hybrid (HMM) type

$R^2O-\overset{\overset{R^2}{|}}{\underset{\underset{R^2}{|}}{\overset{O}{\underset{O}{Si}}}}-R^1-\overset{\overset{R^2}{|}}{\underset{\underset{R^2}{|}}{\overset{O}{\underset{O}{Si}}}}-OR^2$ + Surfactant* → (0-90°C) → Removal of surfactant → HMM

R^1 = Organic groups
R^2 = CH_3, C_2H_5
*$C_nH_{2n+1}N(CH_3)Cl$

Fig 2

$-CH_2-$ $-CH_2CH_2-$ $-CH=CH-$

Synthesis. BTME was added to a mixture of octadecyltrimethylammonium chloride [ODTMA, $C_{18}H_{37}N(CH_3)_3Cl$], sodium hydroxide (NaOH), and water (H_2O) under vigorous stirring at 25 °C. A white precipitate appeared immediately after mixing when the molar ratio of BTME:ODTMA:NaOH:H_2O was 1:0.12:1:231. The suspension was stirred at 25 °C for 24 h. When the molar ratio was 1:0.57:2.36:353, no precipitate appeared during stirring at 25 °C. Heating this clear solution at 95 °C after stirring for 14 h at 25 °C brought precipitation, and the suspension was kept at 95 °C for 21 h. The two kinds of precipitates were filtered and washed with deionized water. The precipitated powders were confirmed to be ordered mesostructures by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM) experiments. The surfactant was removed by stirring 1.0 g of as-synthesized mesoporous materials in 150 mL of ethanol or water with 3.8 g of 36% HCl aqueous solution at 50 °C for 6 h. The filtered sample was washed twice with 150 mL of ethanol or water and dried. Elemental analysis and ¹³C NMR spectra showed that the surfactants were removed completely by repeating this treatment twice. The synthetic yields of mesoporous materials were 43 and 35 mol % for the mixture ratios of 1:0.12:1:231 and 1:0.57:2.36:353, respectively.

- Ordered structure was preserved.
- Incorporated org. group showed outstanding stability.
  ※ -{-CH₂–CH₂-} : stable at < 700°C
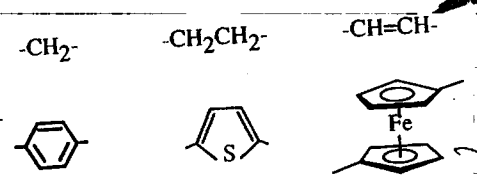
Incorporation of chiral information into mesoporous wall.

+ Various metal exchange method

↓

HMM for Asymmetric catalysis

10.

Inorganics only

☆ Homochiral Zeolite.

Enantiomerically pure Zeolite (Zeotype) have not been synthesized to date.

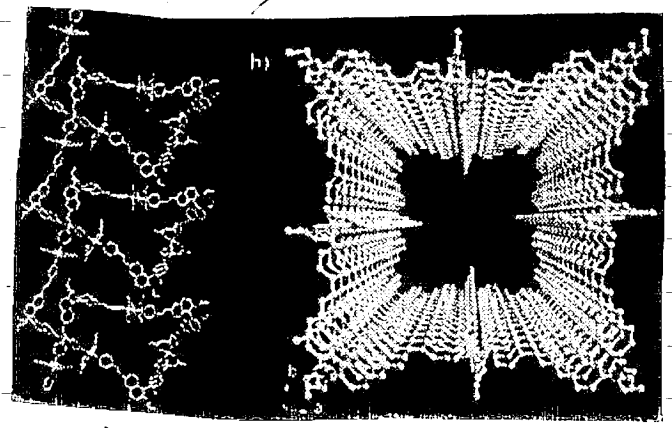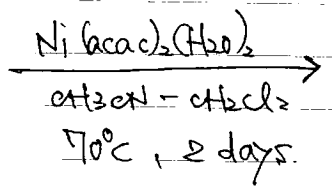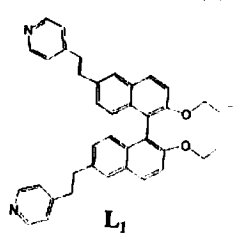② Inorg – Organic chirally ordered porous materials.

Interlocked Chiral Nanotubes Assembled from Quintuple Helices

Yong Cui, Suk Joong Lee, and Wenbin Lin*

Department of Chemistry, CB #3290, University of North Carolina, Chapel Hill, North Carolina 27599
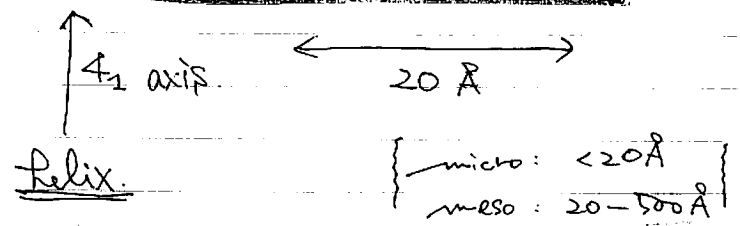
6014 ■ J. AM. CHEM. SOC. 2003, 125, 6014-6015

top view.

$\xrightarrow{\text{Ni (acac)}_2(H_2O)_2 \quad CH_3CN - CH_2Cl_2 \quad 70°C, 2 days}$

L₁

20 Å

Can be used as reaction field?

4₁ axis. 20 Å

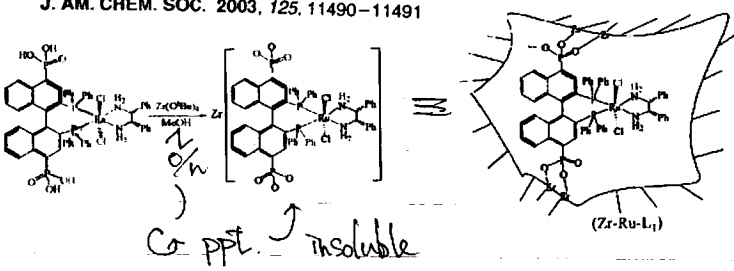Helix.

micro: <20Å
meso: 20 - 500 Å

Chiral Porous Hybrid Solids for Practical Heterogeneous Asymmetric Hydrogenation of Aromatic Ketones

Aiguo Hu, Helen L. Ngo, and Wenbin Lin*

Department of Chemistry, CB#3290, University of North Carolina, Chapel Hill, North Carolina 27599
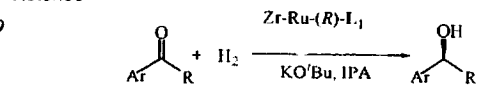
J. AM. CHEM. SOC. 2003, 125, 11490-11491

Co ppt. Insoluble

328 m²/g.

(Zr-Ru-L₁)

Table 1. Heterogeneous Asymmetric Hydrogenation of Aromatic Ketones[a]

$$\underset{Ar}{\overset{O}{\|}}\underset{R}{\quad} + H_2 \xrightarrow[\text{KO'Bu, IPA}]{\text{Zr-Ru-}(R)\text{-I}_1} \underset{Ar}{\overset{OH}{\|}}\underset{R}{\quad}$$

substrate	solid loading (%)	KO'Bu (%)	Zr-Ru-L₁ ee (%)
Ar = Ph, R = Me	0.1	1	96.3 (97.1)[b]
Ar = 2-naphthyl, R = Me	0.1	1	97.1
Ar = 4'-'Bu-Ph, R = Me	0.1	1	99.2
Ar = 4'-MeO-Ph, R = Me	0.1	1	96.0
Ar = 4'-Cl-Ph, R = Me	0.1	1	94.9
Ar = 4'-Me-Ph, R = Me	0.1	1	97.0
Ar = Ph, R = Et	0.1	1	93.1
Ar = Ph, R = cyclo-Pr	0.1	1	90.6
Ar = 1-naphthyl, R = Me	0.1	1	99.2
	0.02	0.4	98.9
	0.005	0.02	98.8 (70)[c]
	0.005	0.02	98.6[d]

Table 2. Recycling and Reuse of Zr-Ru-L₁ Solid Catalyst for Hydrogenation of 1-Acetonaphthone[a]

run	1	2	3	4	5	6	7	8
ee (%)	99.0	99.0	99.1	99.0	99.0	99.2	99.1	99.0
conversion (%)	100	100	100	100	100	100	95	85

[a] The reactions were carried out with 0.1 mol % solid loading and 1% KO'Bu under 700 psi H₂ pressure for 20 h.

0.2% Ru leaching.

[a] All of the reactions were carried out in 20 h, and the ee values were determined by GC on a Supelco β-Dex 120 column. The absolute configurations of the products are identical to those obtained by the Ru-(R)-BINAP-(R,R)-DPEN catalyst. All the conversions were >99% as judged by the integrations of GC peaks. [b] Homogeneous reactions. [c] 70% conversion. [d] 40 h reaction time.

Summary and Perspective ,, Prospective

Highly ordered porous materials
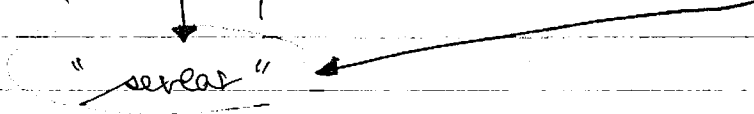
Mesoporous   Inorg — org based assembly.

- Large pore (for organic compounds)
- chiral modification
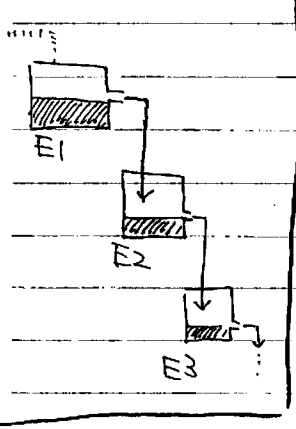- High stability.
- Reaction — Field, multi-point recognition.

• ☒ •

Enzyme : mortality, (← replication) , toward proper equilibria.
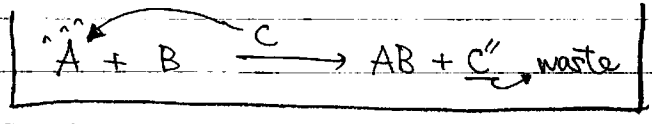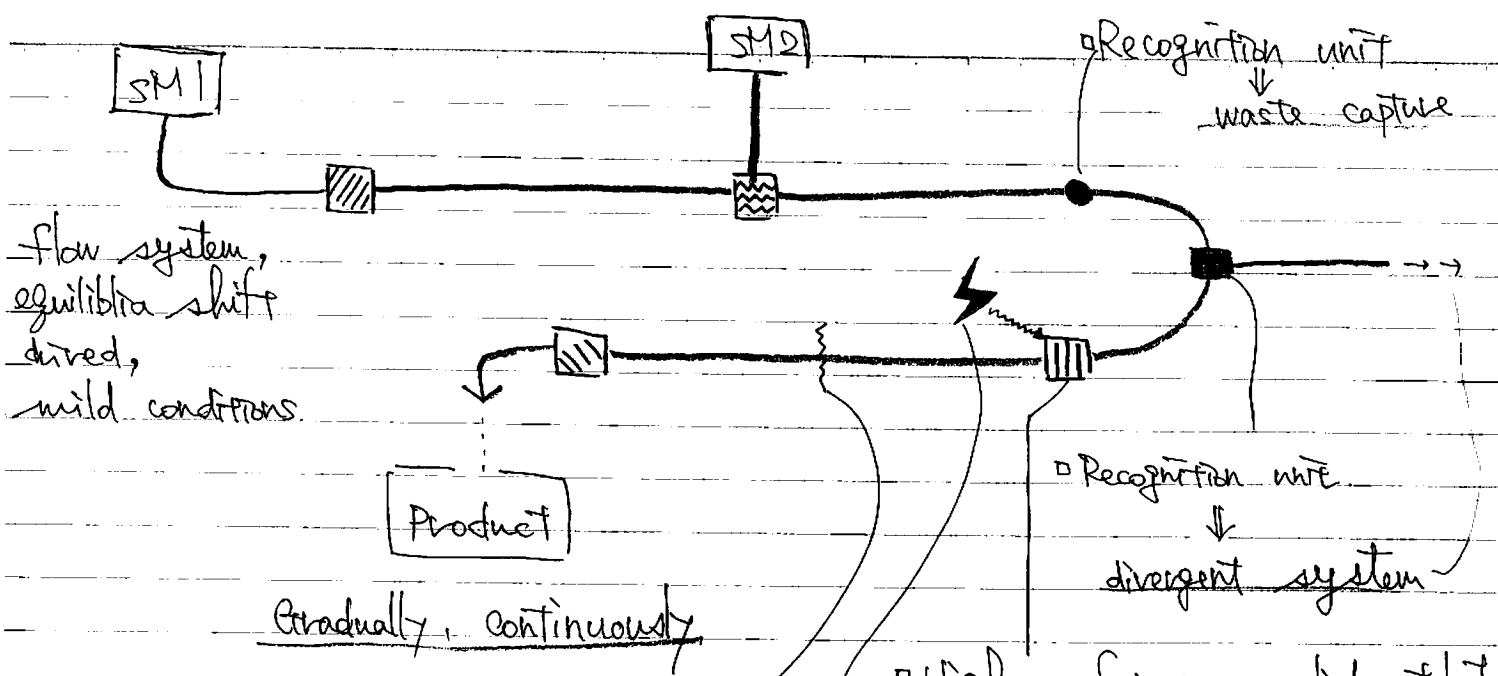Catalyst : immortality, , toward 100 % yield.

"sever"

• our goal ?? ⟶ catalyst with infinity?, 100 % conversion?
or continuous production of target molecules.

• Key of the enzymatic reaction : shift of equilibria, (100% y is not necessary)

• Key of the man-designed reaction : activation by external
reagents.

$$A + B \xrightarrow{\ C\ } AB + C'', \text{waste}$$

E1

E2

E3

SM1

SM2

Recognition unit
⇓
waste capture

flow system,
equilibria shift
drived,
mild conditions.

Product

Gradually, Continuously

▫ Recognition unit
⇓
divergent system

▫ High performance selective
membrane
· equilibrium control
· selective permeability

▫ High performance solid catalyst
· chiral recognition
· No more, fast, 100% reaction
· Selective, mild reaction

▫ MW irradiation unit
· local temp. control.

· oxidation with O_2
· reduction with H_2
· alkylation with R—OH   both $Nu^{\ominus}, E^{\oplus}$

additional ...
▫ [v] chiral switch irradiator : $h\nu^*$ modifies ligands in solid support
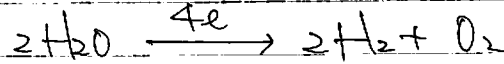enantiomerically.

or,   rac ⟶ $h\nu^*$ ⟶ rac
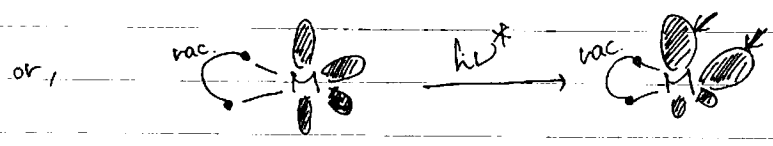
asymmetric MO rearrangement.

enables synthesis of both enantiomers with the same set of units.

Porous material : the best field for metal cluster complex?
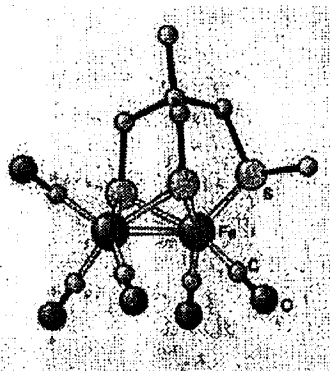
Targets : [Hydrogenase mimic]

⬇

water splitting $2H_2O \xrightarrow{4e} 2H_2 + O_2$

$\underrightarrow{\quad\quad}$ vast energy.
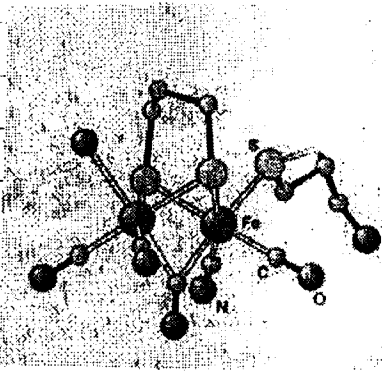
hydrogenase sub-site   **synthetic 2Fe3S assembly**

CHEMICAL
& Engineering News

CONSERVATION OF HELICAL ASYMMETRY

Electronic theory for chiral interactions has powerful consequences for asymmetric catalysis

September 29, 2003.

Wang described the theory earlier this month at the American Chemical Society national meeting in New York City. According to his research adviser, chemistry professor Thomas J. Katz, Wang developed this theory on his own.

optical activity arises when the electrons of a molecule are constrained to a helical path.

For the analyses he has done so far, Wang said all he needed was the reaction mechanism, the relative polarizabilities of relevant groups, pen, paper, and a few minutes. "You can apply the rules even if you don't understand the underlying quantum theory."

"The theory could be very useful to predict the stereochemical outcome of asymmetric reactions," says Cheng Chen, a senior investigator at Merck Research Laboratories,

Applications of the Homohelical Electronic Theory:

David Zhigang Wang *

Scheme 2

Scheme 4

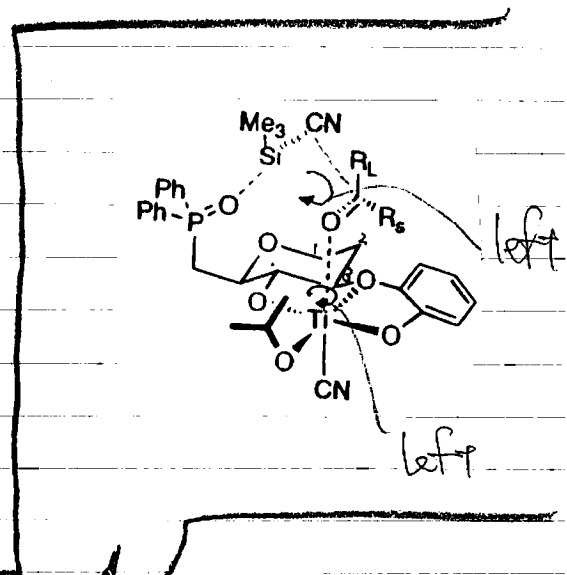Polarizability Matters, Not Sterics !
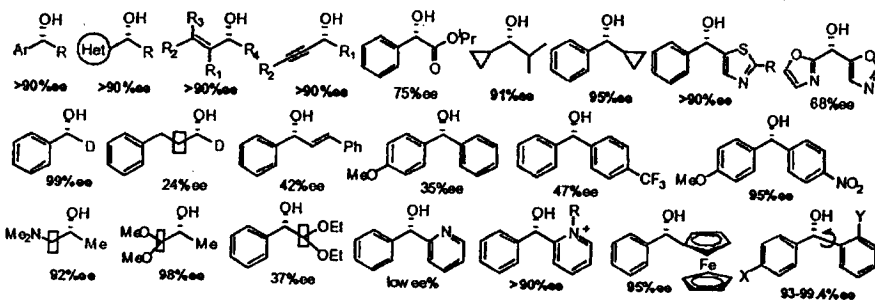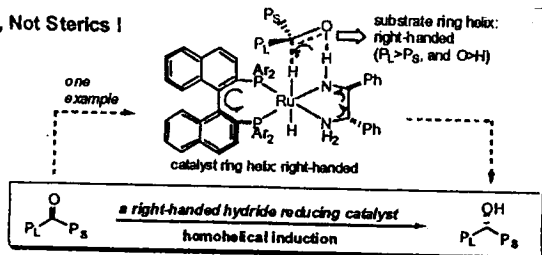
J. Am. Chem. Soc. 2000, *122*, 7412–7413

Catalytic Enantioselective Cyanosilylation of Ketones

Yoshitaka Hamashima, Motomu Kanai, and
Masakatsu Shibasaki*

発見は選択であり、識別である。

Jules Henri Poincaré.