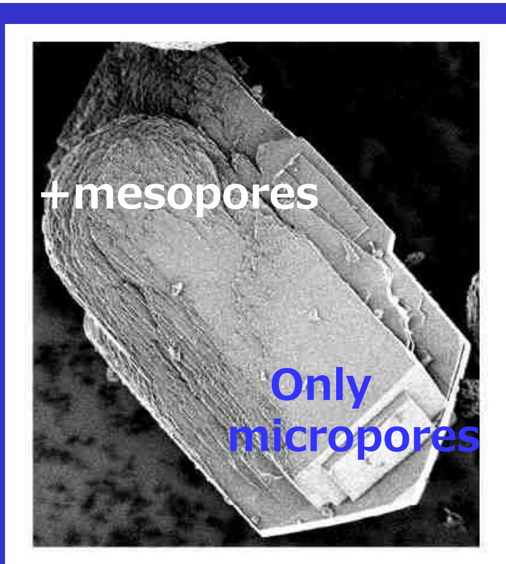
CPM9 9th International Workshop
Characterization of Porous Materials: From Ångströms to Millimeters
May 19 - 22, 2024 | Delray Beach, FL-USA

Adsorption-Biased Characterization of Porous Materials

Katsumi Kaneko

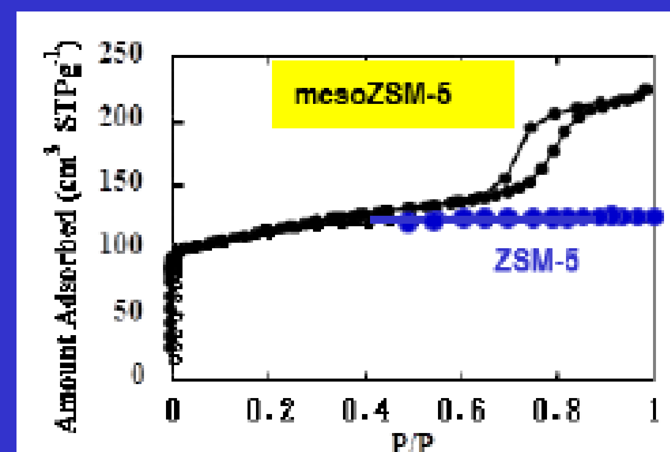
Research Initiative for Supra-Materials, Shinshu University



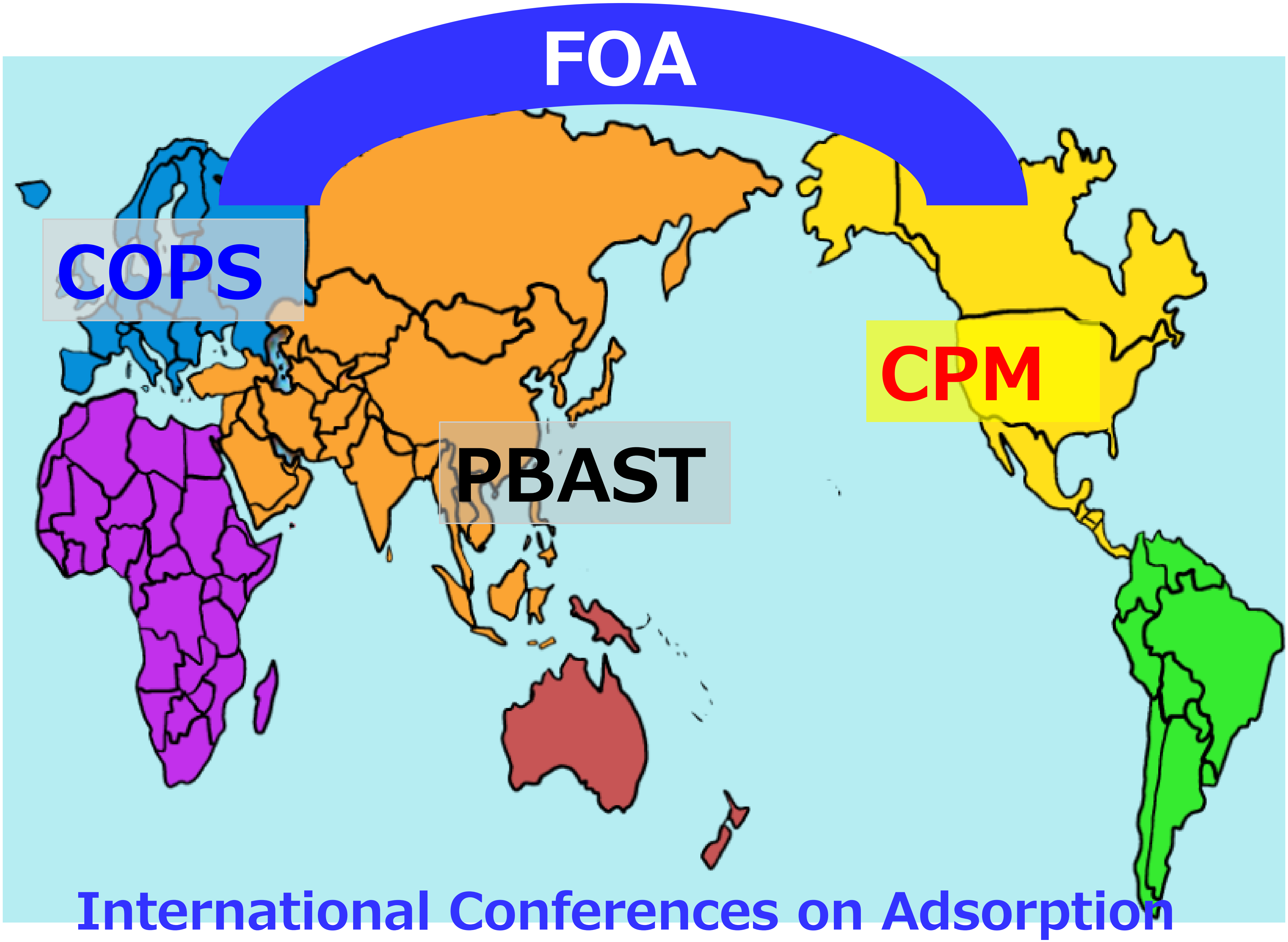
9th CPM

Florida

May 19-23, 2024



Mesoporous ZSM5,
Y. Tao et al, *Chem. Rev.*(2006)


FOA
COPS
CPM
PBAST
International Conferences on Adsorption

International Science Community on Adsorption-Biased Characterization of Porous Solids

COPS: Characterization of Porous Solids Europe

1987(Bad Soden)- Chemistry, Materials science

F. Rodriguez-Reinoso, J Rouquerol, KSW Sing, KK Unger

FOA: Fundamentals of Adsorption World wide

Chemical engineering Materials Science

PBAST: Pacific Basin Adsorption Science and Technology

Asia and Oceania

Chemical engineering Materials Science

Asian countries USA (European countries)

CPM: Characterization of Porous Materials Florida

Materials science, Chemical engineering, Chemistry,--

A.V. Neimark TRI-Princeton(First-5th) 1997—2009

A. V. Neimark, M. Thomas CPM(6th-9th) 2012—2024

COPS: Characterization of Porous Solids

1987(Bad Soden)- Chemistry, Materials science

F. Rodriguez-Reinoso, J Rouquerol, KSW Sing, KK Unger

In front of my poster
with Paco

New Leaders

Tina Düren
(UK)

Maurin Guillaume
(France)

Stefan Kaskel
(Germany)

Joaquin Silvestre
(Spain)

Next COPS
2026, Dresden

Photos from HP

FOA: Fundamentals of Adsorption

FOA 3 1989 Sonthofen, Germany A. B. Mersmann

Chemisorption assisted micropore filling of NO

FOA 4 1992 Kyoto, Japan M. Suzuki

Ultramicroporosimetry of porous solids by He adsorption

FOA 5 1995 California, USA M. D. Le Van

Organize molecular states in micropores

FOA 6 1998 Giens, France F. Meunier

Nanoclathrate-assisted adsorption of supercritical gases in hydrophobic pores

FOA 7 2001 Nagasaki, Japan K. Kaneko

Fundamental problems in high pressure adsorption of supercritical gases

FOA 8 2004 Arizona, USA O. Talu

Plenary: Nanospace molecular science and adsorption

FOA 9 2007 Italy M. Mozzotti

FOA10 2010 Japan M. Miyahara

FOA11 2013 USA P. A. Monson

FOA12 2016 Germany A. Seidel-Morgenstern

FOA 13 2019 Australia P. Webley

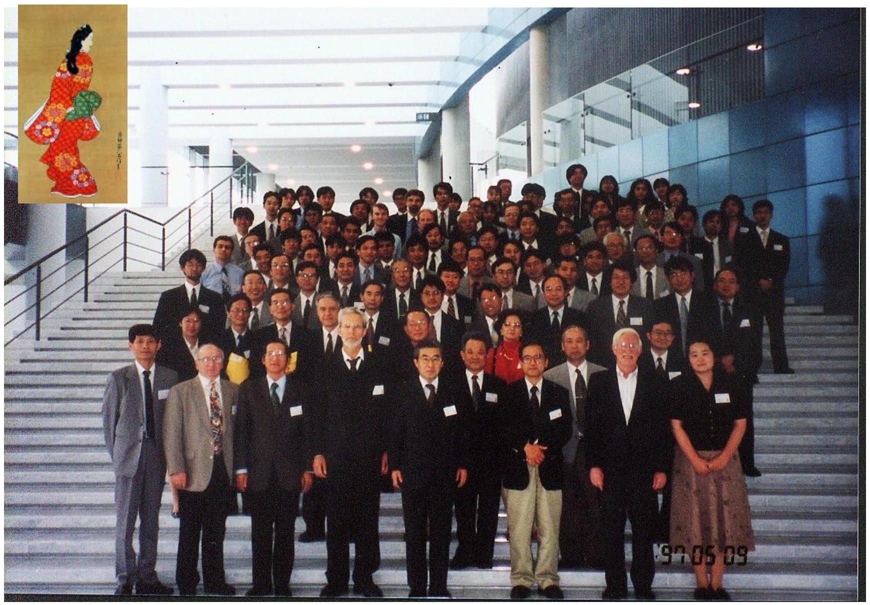
FOA 14 2022 Colorado, USA C. Jones

Plenary: **In-solid Nanostructure-Derived Routes for Future-Responsible Engineering**

FOA 15 2025 Portugal 18 - 23 May 2025 in Porto José Paulo Mota

Pacific Basin Conference on Adsorption Science and Technology

Kisarazu (Chiba) Japan 1997



Prof. D. D. Do (2nd) **Prof. C. –H. Lee (3ird)**

Prof. L. R. Radovic Prof. F. Meunier Prof. Z. Li Prof.T. Bandosz
Prof. M. Jaroniec Prof. M. Suzuki Prof. A. Myers Prof. P. Wu
Prof. W. A. Steele Prof. J.U. Keller Prof. Y. H. Ma Dr. K. S. Knaebel
Prof. S. Sircar Prof. T. Takaishi Prof. K. Ttsutsumi

We have 9th PBAST in Malaysia this fall

Prof Yeoh Fei Yee
University Sains Malaysia

https://pbast2024.eng.usm.my/
email: pbast9.msia@gmail.com

Characterization of Porous Materials: From Ångstromes to Millimeters

Ultrafast graphene wrapped zeolite membrane

R. Kukobat et al. *Sci. Adv*.2022,8. eabl3521

Home Party

at The first Characterization of Porous Materials, Princeton, 1997

Prof. Neimark

Prof. Unger

Prof. Gubbins

Prof. Findenegg

Dear Katsumi,

Time is flying by very fast, and we are pleased to announced that the 6th International Workshop "Characterization of Porous Materials: from Angstroms to Millimeters"(CPM-6) will be held in Palm Beach, Florida, on April 30 - May 2, 2012. The CPM series is organized on a tri-annual basis, alternating with COPS symposiums and FOA conferences. This time, we decided to change the location to make this meeting more attractive for its regular participants, some of whom attended all five previous meetings in New Jersey.

The meeting will take place in a beautiful setting of Delray Beach Marriott located on Florida's Atlantic Ocean Gold Coast,
overlooking sandy beaches in the midway between Ft. Lauderdale and Palm Beach.-------------------------

With warmest wishes,

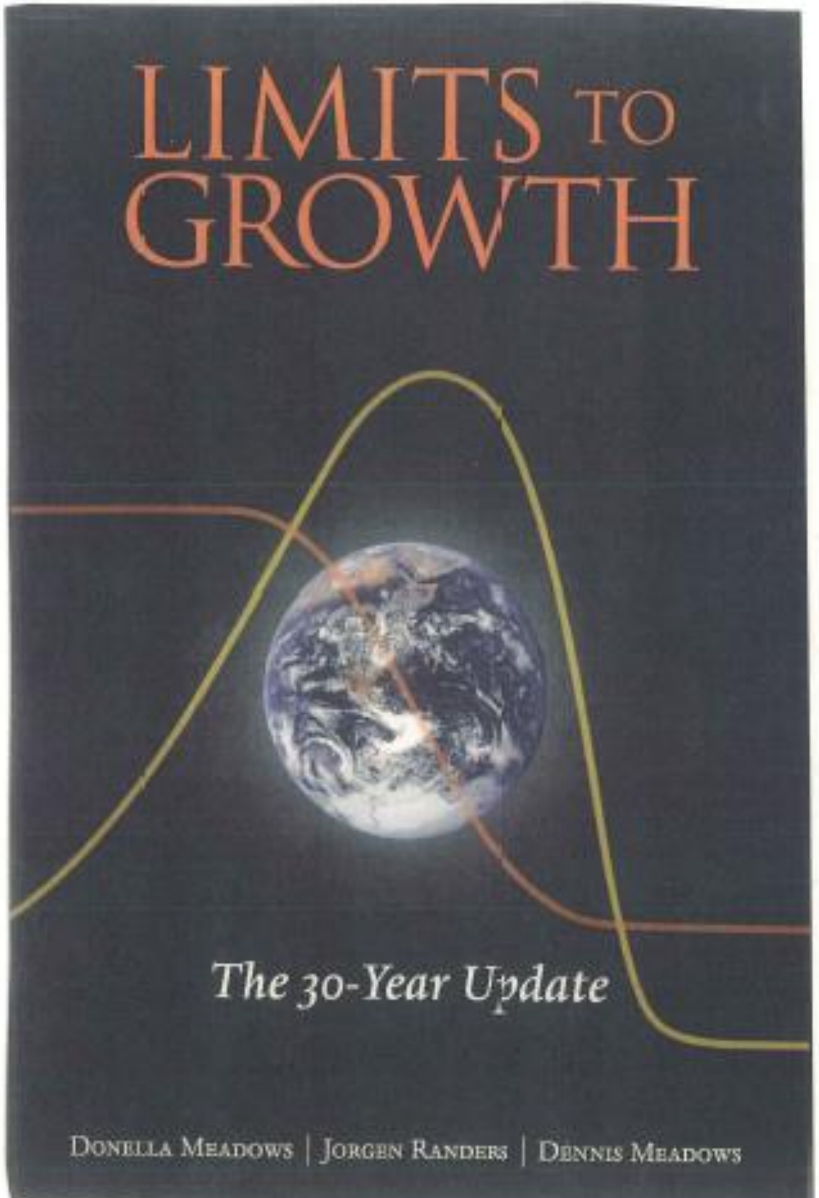
Alex Neimark

Ruthgers The State University of New Jersey

Matthias Thomme

Friedrich-Alexander-University Erlangen-Nürnberg

World wide Issues

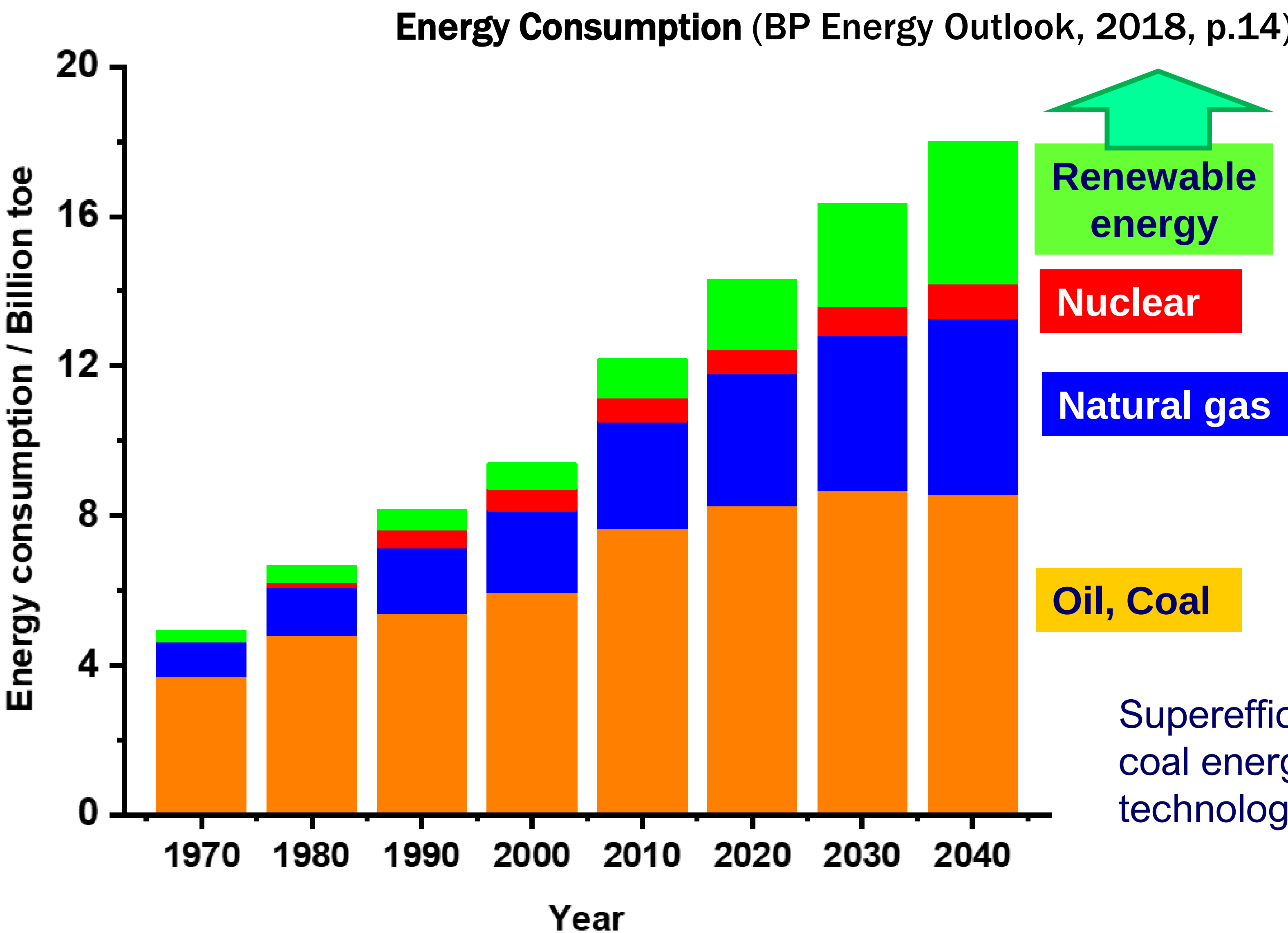


The first text appeared in 1972

The third text

by D. Meadows
J. Raders
D. Meadows
(MIT, USA)
2004
Chelsea Green Pub. Co.

Global Warming
Renewable Energy Technologies



Superefficient coal energy technology

Chemical Industries use Distillation

Distillation

Mixtures

Pure substances

A

Chemical reaction

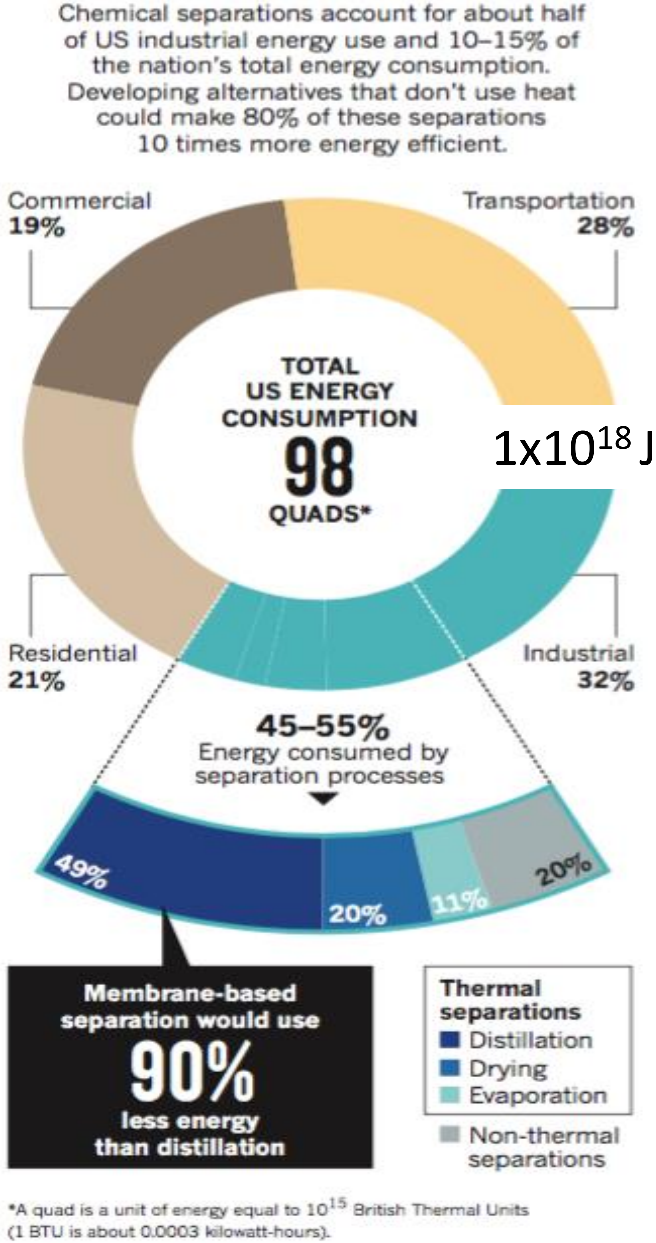
A + B = C

B

Living wares

Separation technologies are *energy-intensive* due to distillation

Energy for Separation of Chemicals is about 50 % of Total Energy Used in Industries



1×10^{18} J

http://enko.co.jp/product/index.html

Energy consumption by

Distillation, Drying,
Evaporation

Energy Saving Separation Technologies

Adsorption separation
Membrane separation

By D. S. Sholl, R.P. Lively, *Nature*, 2016, 532, 435.

Porous Materials

Fundamental of Important Technologies

Adsorption, Storage, Separation

Futuristic Characterization
of Porous Solids

Intensive Demand for Adsorption and Nanoporous Materials

Adsorption

Storage Concentration Separation Removal …..

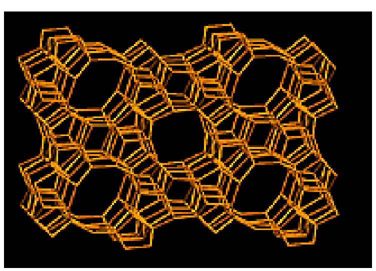
CO_2 Energy (CH_4, H_2, O_2) Water (H_2O, H_2:O_2)

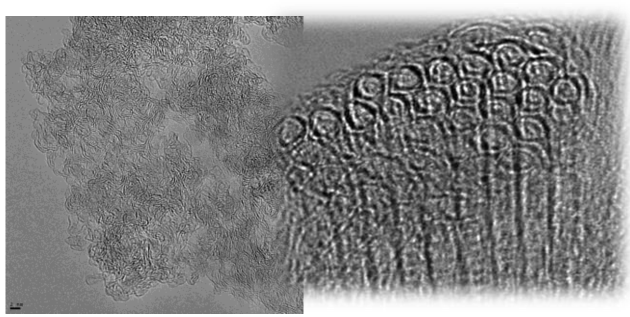
Resources

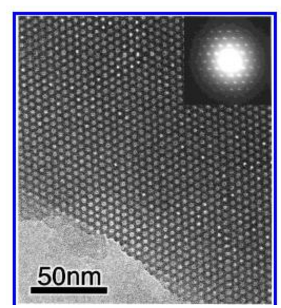
Environmental and Medical Technologies

Nanoporous Materials

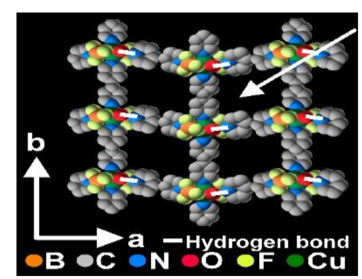
Zeolite Porous carbon m-Silica PCP(MOF)…







S.Inagaki et al, JACS (1999)



Surrounding Situation around 1990

Development of new activated carbons by Industries

Activated carbon fiber (ACF) around 1985

Superhigh surface area carbon 1989

Templating to Template-free synthesis in zeolite

B M Lock et al. Zeolite: Review (1983)

→ H. Awala et al. Nature Mater.(2015)

On stage of well-defined porous solids

Mesoporous Silicas C. Kato:K. Kuroda 1990, K.Kuroda; S. Inagaki 1993

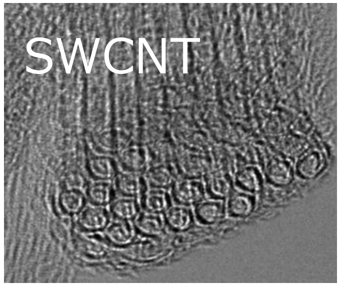
C. T. Kresge et al (Mobil) USA 1992

Carbon nanotube

S. Iijima 1991 : MWCNT, 1993:SWCNT

SWCNT: S Iijima T. Ichihashi, D. S. Bethune et al.

DWCNT (2005) M. Endo et al.



Porous Coordination Polymer (PCP) or Metal organic framework (MOF)

W. Mori (1997) S. Kitagawa O. Yagi G. Férey

(**Gate adsorption** K. Kaneko 2001)

New Attempts in Adsorption Studies around 1990

Theoretical Approaches

Studies with Statistical mechanics on zeolites

R. M. Barrer T. Takaishi D. Ruthven

Molecular simulation and molecular dynamics

W. Steele Adsorption on graphite

D. Nicholson Adsorption in pores

K. E. Gubbins Adsorption in pores

N. Seaton, N. Quirk Pore size distribution of carbons

P. Monson Cavitation, --

A. Neimark Pore size distribution, Cavitation, --

[Now we have powerful and younger leaders]

Fractal analysis D. Avnir P. Pfeifer

No detailed correlation with adsorption mechanism

Experimental Progresses in Adsorption Studies around 1990

Comparison plot analysis K. S. W. Sing

Calorimetric measurement J. Rouquerol

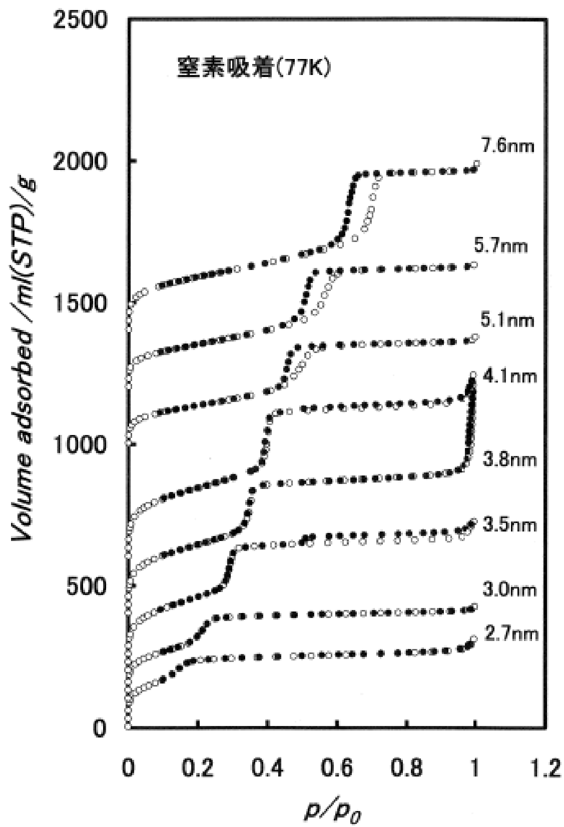
CO_2 adsorption F. Rodriguez-Reinoso

Hot topics around 1990

Adsorption on mesoporous silica (MCM, FSM)

Adsorption hysteresis:

Dependence on temp. and pore width



by Prof. Morishige

K. Kaneko et al: Surface roughness model

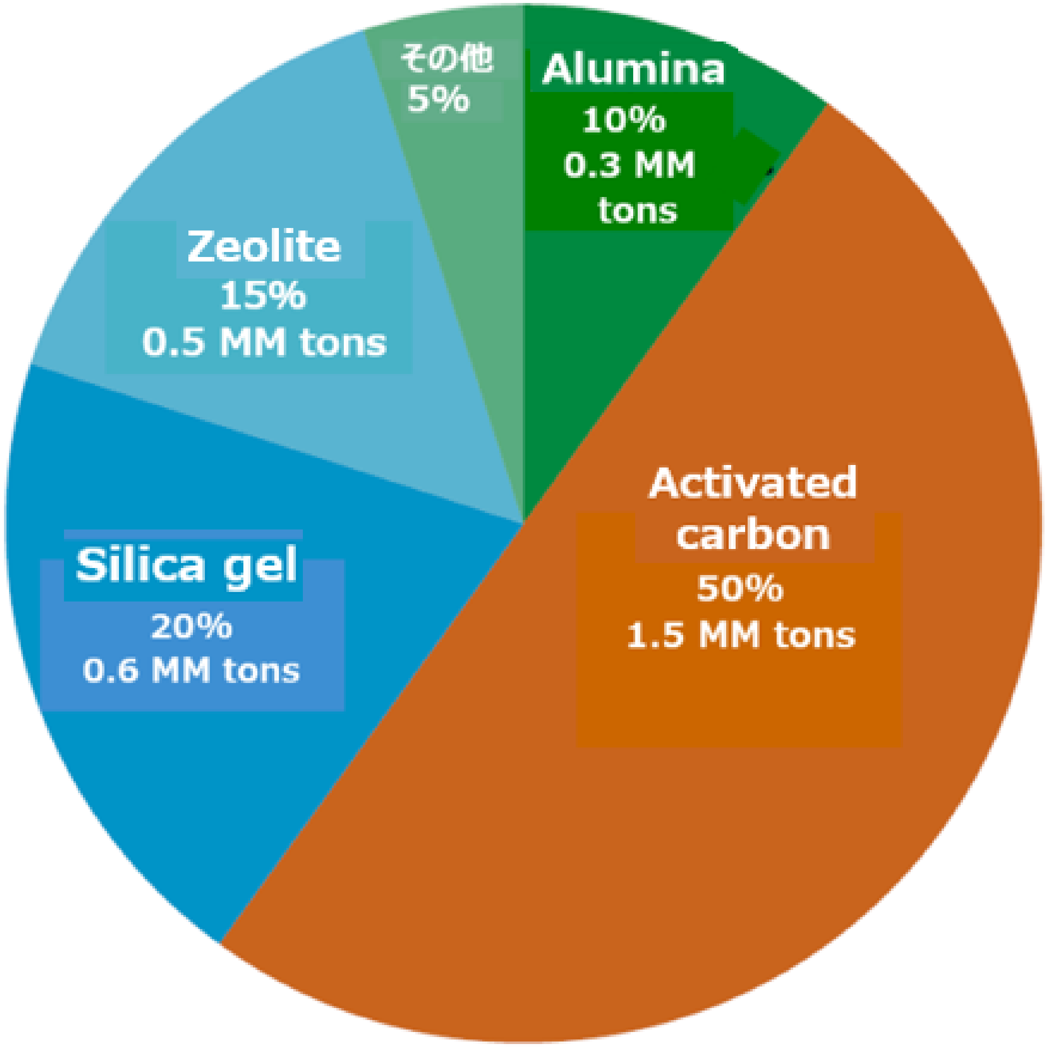
Prediction of Hysteresis Disappearance in the Adsorption Isotherm of N_2 on Regular Mesoporous Silica

Langmuir, **14**, 3079(1998).

Representative Nanoporous Materials

	Zeolite	Carbon	PCP:MOF	Silica
Electrical conductivity	×	◎	△	×
Thermal conductivity	×	◎	△	×
Thermal stability	◎	◎	△	◎
Oxidation resistivity	◎	△	×	◎
Water resistivity	○	◎	△	△
Ion exchangeability	◎	△	△	△
Pore structure	Micro pore	Micro- and mesopore	Micropore	Mesopore
Uniform porosity	◎	×	◎	◎
Tunability of pore size	○	△	◎	◎
high surface area (>1000 m^2 g^{-1})	△	○	◎	○

Industrially Used Porous Adsorbents



Delivered by **Dr. T. Golden** (Air Products and Chemicals, Inc.) in Tutorial lecture at 14th Fundamentals of Adsorption (Colorado, USA, 2022)

Challenges for Better Characterization in Porous Carbons

High resolution N_2 adsorption measurement

Ultramicropore characterization

He adsorption at 4.2 K

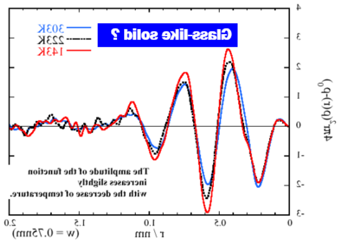
Quantum effect Ne at 23 K H_2 77 K

Superwide P/Po range adsorption from ultrahigh vacuum region

In situ measurement of molecules adsorbed in pores

X-ray diffraction for water inside activated carbon fiber ACF

T.Iiyama et al, J Phys Chem(1995)



Small angle X-ray scattering

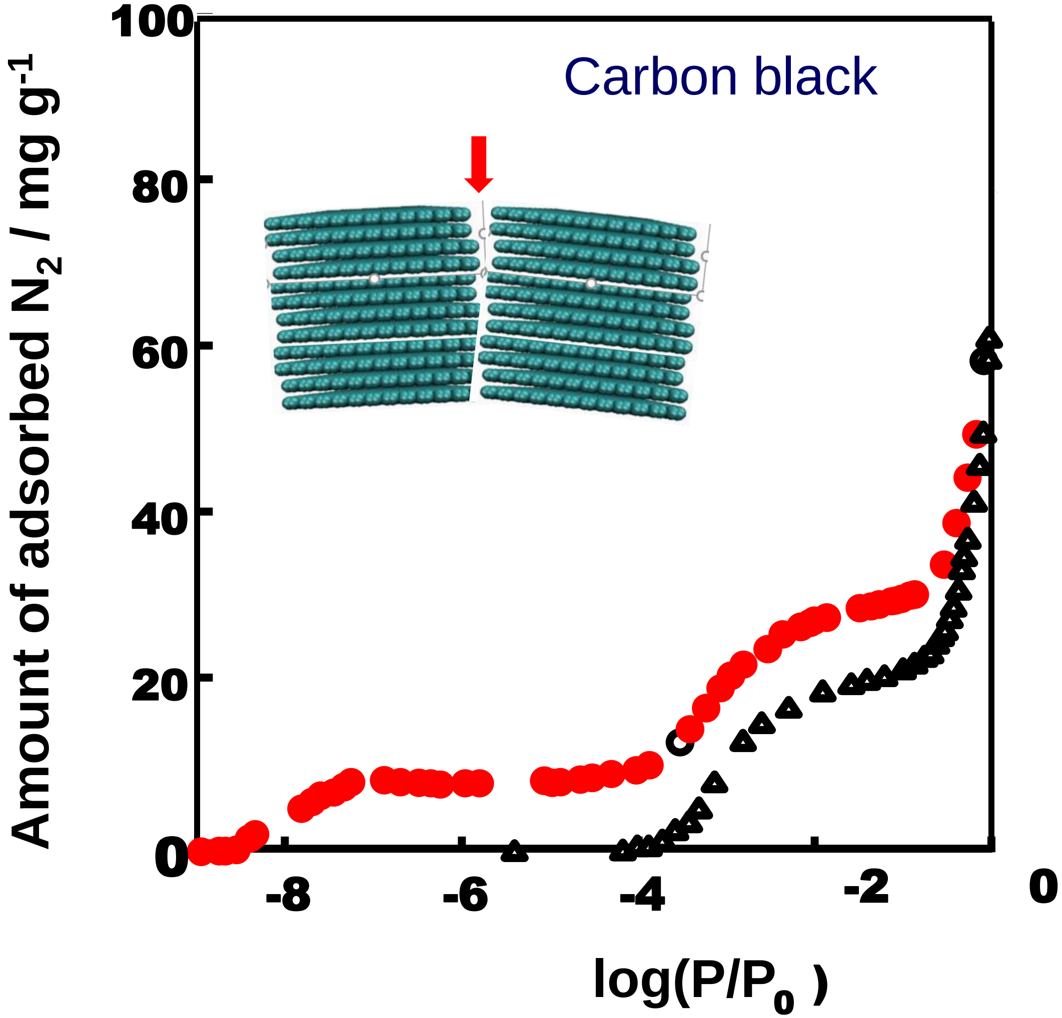
Rotational-vibrational spectral study on CH_4 inside SWCNH

EXAFS

HR-MC simulation aided in situ and/or operand X-ray scattering

Evaluation of Sub-nanometer Pores

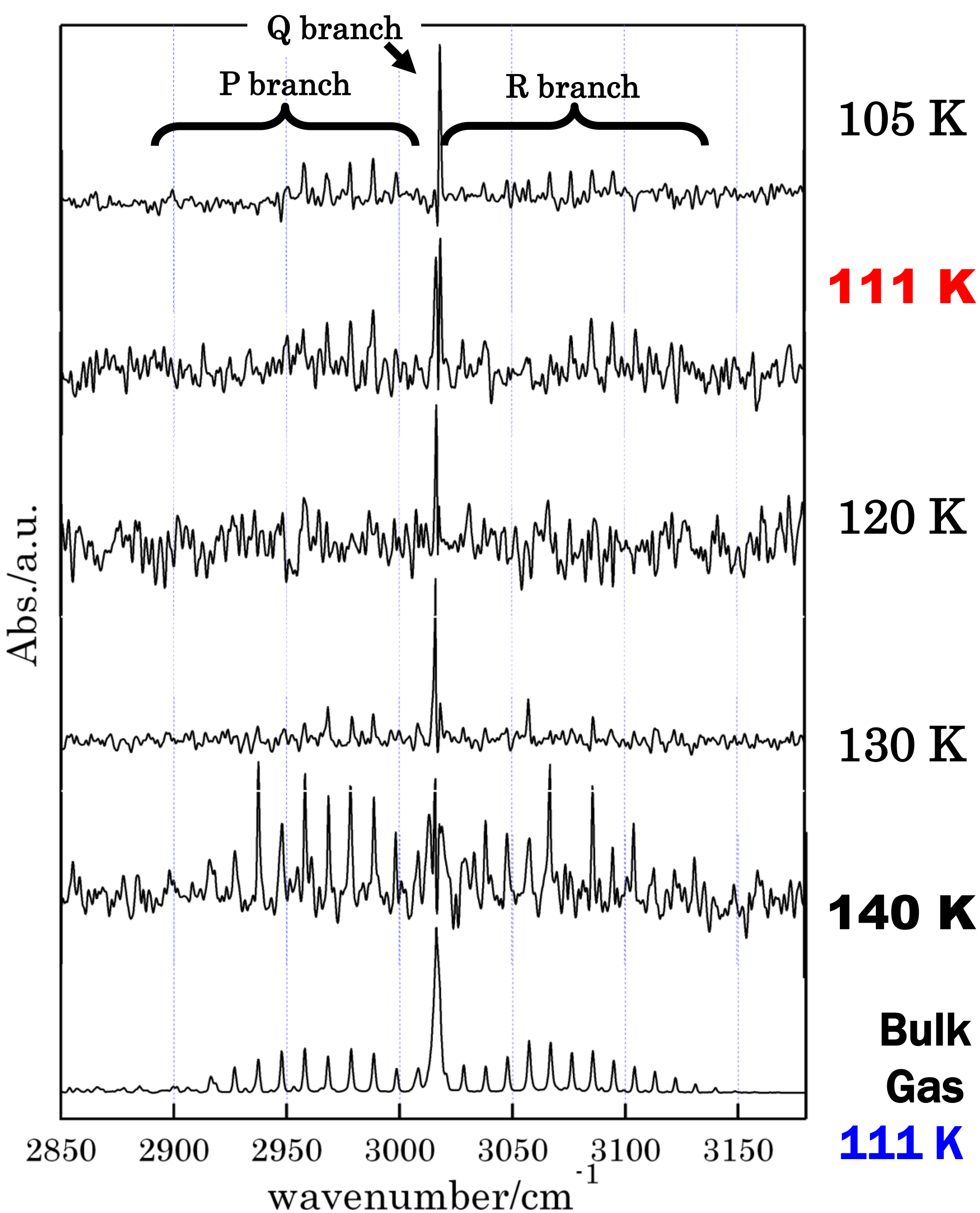
Superwide-pressure range adsorption isotherm $P/P_o = 10^{-9} \sim 1$



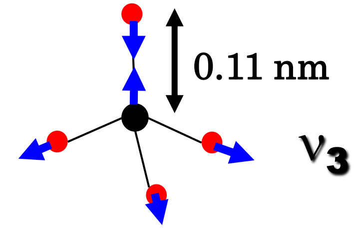
Ultrahigh vacuum system

M. Sunaga,et,
J. Phys. Chem. B, *2004*, ***108, 1065.***

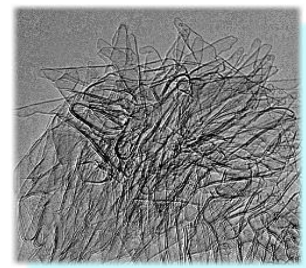
Rotational Vibration Spectra of CH_4 inside SWCNH



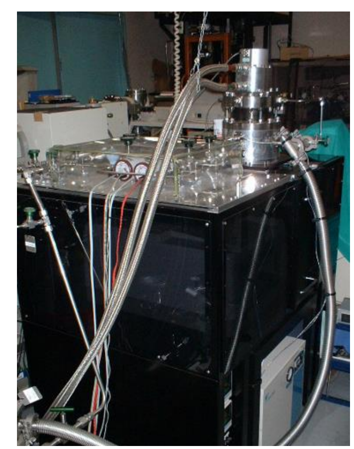
P/Po = 0.05



Asymmetric stretching vibration mode



Single wall carbon nanohorn

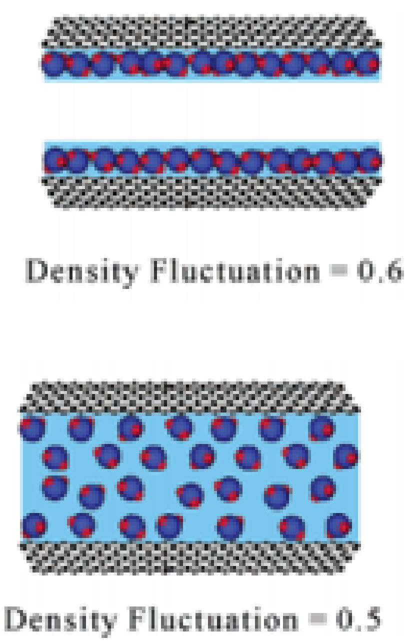


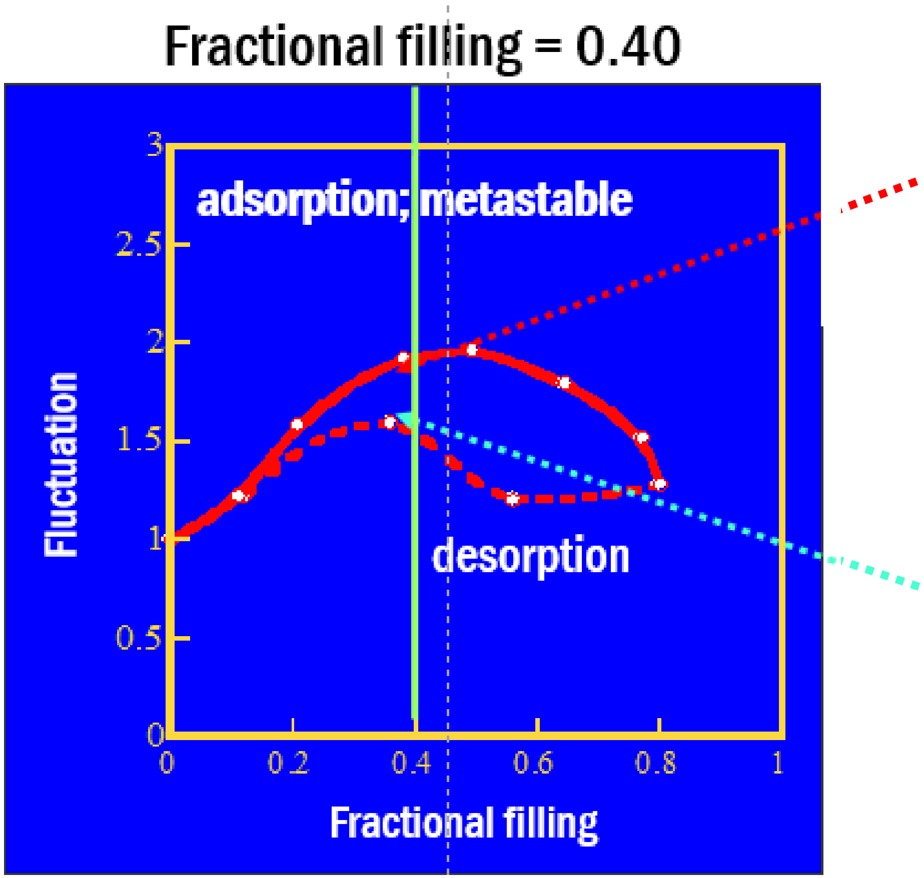
In-situ apparatus

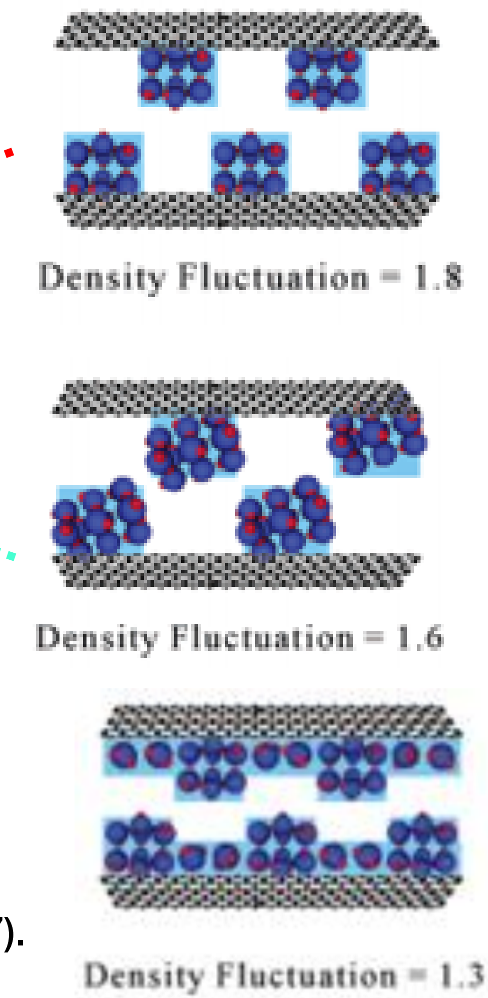
S.Hashimoto et al. *JACS*. 133, 2022 (2011).

Water Adsorbed State from in-situ Small Angle X-ray Scattering

Fluctuation analysis of adsorbed water leads to adsorbed state in carbon micropores



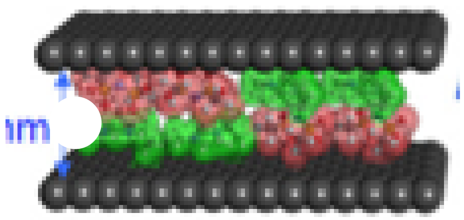




T. Ohba et al. *Nano Lett.* (2004). *Chem. Eur. J.* (2004). *Mol. Phys.* (2007).

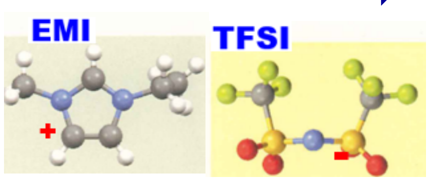
Plausible 3D Structural Information with Hybrid Reverse Monte Carlo (HRMC) Simulation

3D



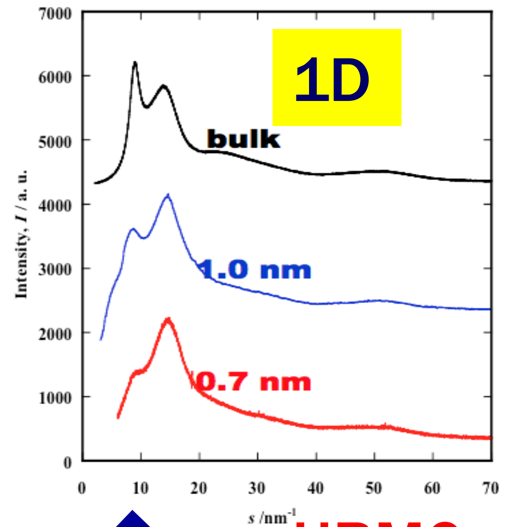
EMI-TFSI in pores
(0.7 nm,1.0 nm)
of nanoporous carbon

Synchrotron
X-ray scattering



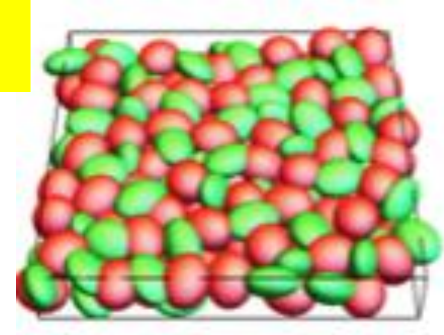
Ionic liquid

1D

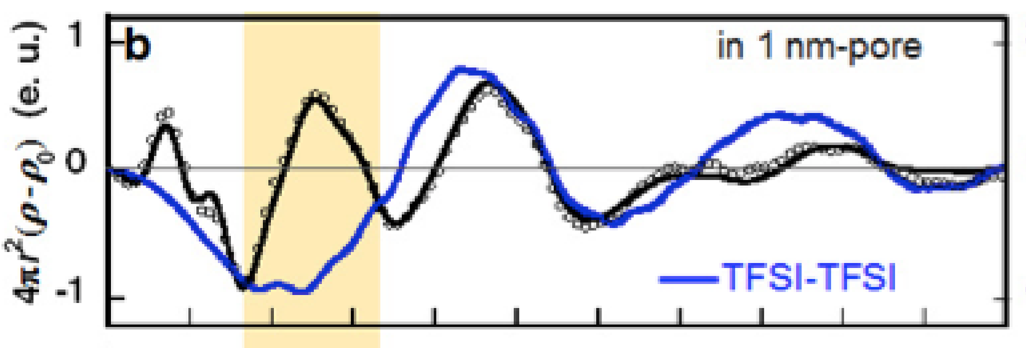


HRMC
LJ, Electrostatic

3D



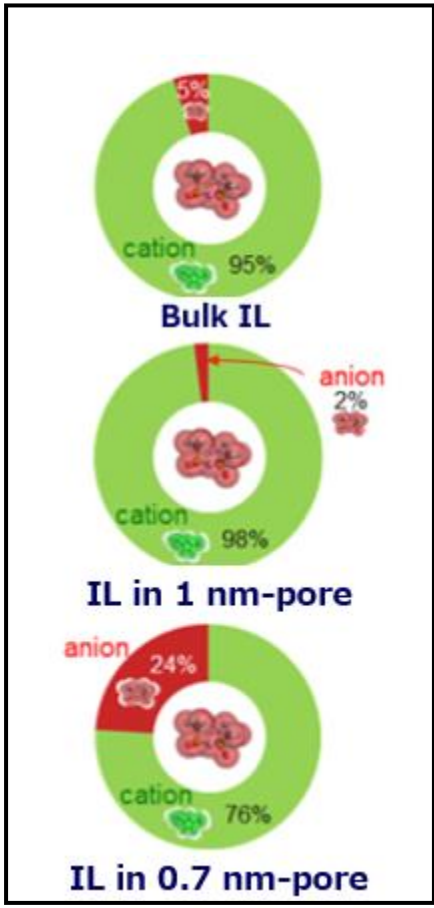
Plausible 3D structure



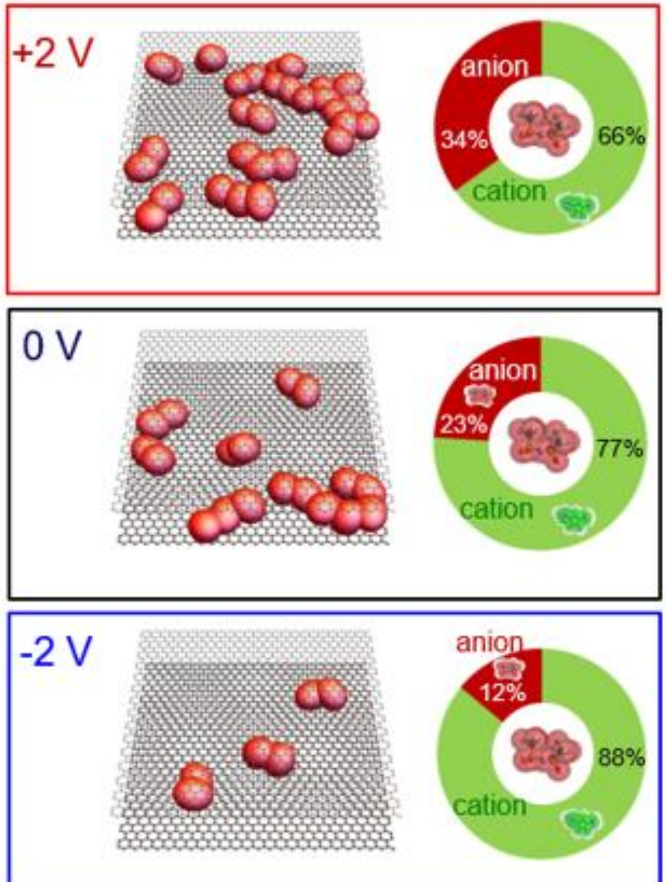
Anion-anion, cation-cation etc structure

Operand-Measurement of Anion Occupancy around an Anion in Narrow Carbon Pores

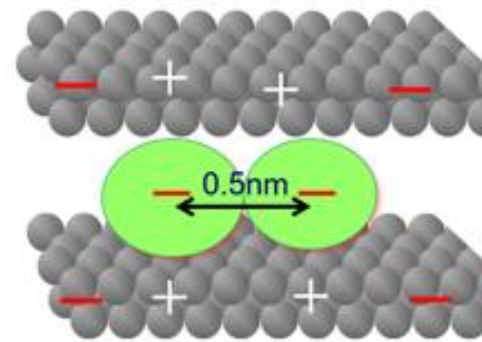
In-situ Synchrotron X-ray scattering



Operando Synchrotron X-ray scattering



Anions (or cations) can gather each other in narrow conductive pores



Apparent breaking of Coulombic law

Understanding high supercapacitance

R. Futamura, et al, *Nature Materials*, **16**, **1225** (**2017**)

Various Properties of Nanoporous Solids

Transient chemical and structural changes in graphene oxide during ripening

GO / Properties	iGO	mGO	tGO	rGO‡	Sigma	NS
π–π^* (nm)	230.5 ± 0.5	< 230.0	> 228.8†	N/A	229.6 ± 0.2	229.6 ± 0.2
Reliability of peak deconvolution	High	Medium	Low	N/A	Medium	High
Oxygen (%)	31 ± 1	< 30		18	27	27
Epoxy (%)	33 ± 4	23 ~ 29	< 23	12	24	29
Hydroxyl (%)	7 ± 4	13 ~ 30	30 ± 2	24	27	6
χ (10^{-8} emu g^{-1})	0.5 ~ 1.8	0 ~ 2.3	0.4 ~ 0.7	0.4	0.83	21.9
Average number of stacking layers	13 ~ 14	8 ~ 13	6 ~ 8	N/A§	12	8
Electrical resistivity (Ω m)	> 0.4	0.1 ~ 0.4	< 0.1	2×10^{-4}	0.31	2.6

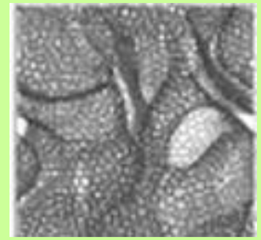
H. Otsuka, et. al. *Nat. Commun.* 15, 1709 (2024).

Adsorption Isotherm leads to Pore Size Distribution and 3D Local Nanostructure

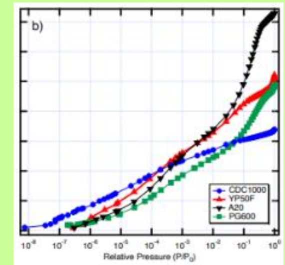
Nanoporous carbons are amorphous

The information on local nanostructures of porous carbon: Useful

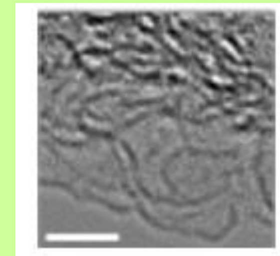
Adsorption isotherms of N_2 at 77 K
with data of model 3D nanostructures and experimental TEM images



Model structure

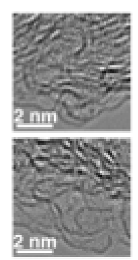


Adsorption isotherms



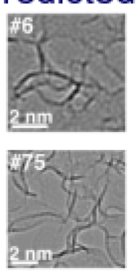
TEM image

experimental



3D nanostructure of carbon samples

Predicted

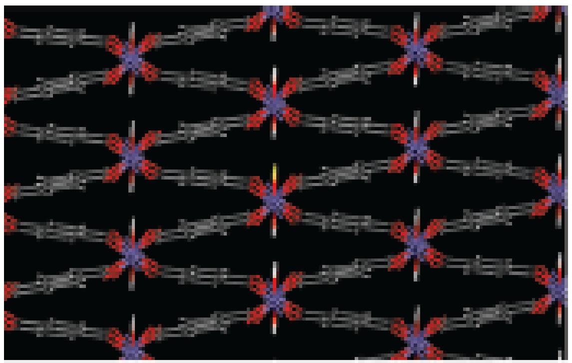


3D Nanostructure Prediction of Porous Carbons via Gas Adsorption

Fernando Vallejos-Burgos et al. *Carbon*, 215, 118431 (1-7) (2023)

Nanoporous Solids are not “solid”

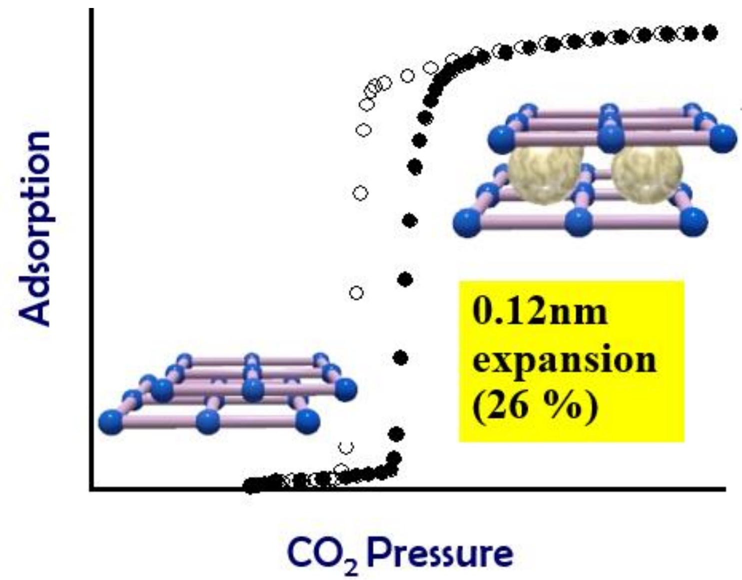
Breathing adsorption on MIL-53



C_2H_6

P.L. Llewellyn et al.
JACS (2009) 131, 13002.

Gate adsorption onMIL-11

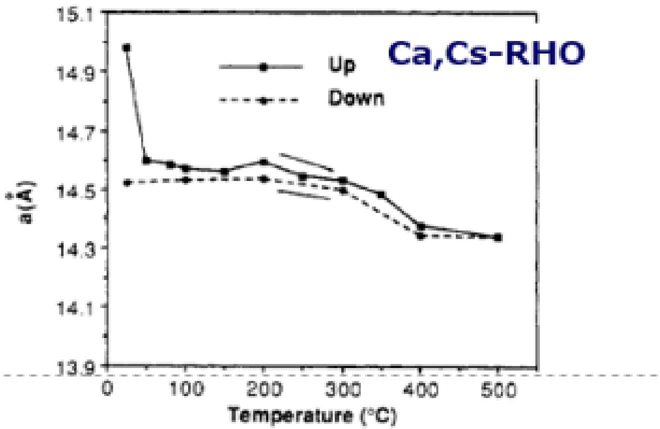


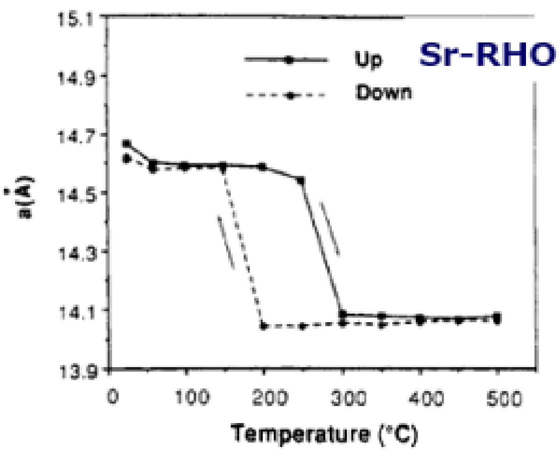
Chem. Phys. Lett. (2001) ,
Nano Lett (2006), JACS, 133 (2011).

Theoretical study by Kyoto Group
S. Hiraide, H. Tanaka et al.
Nature Comm. (2020)

Zeolites are Flexible

Variation of crystal cell dimension with temperature





Flexibility of the Zeolite RHO Framework
D. R. Corbin et al, JACS,112, 4821(1990)

(supported by Dr. L. Abrams)

Visualizing the Flexibility of RHO Nanozeolite: Experiment and Modeling

E. B. Clatworthy,et al. ,
JACS, 145,15313 (2023)

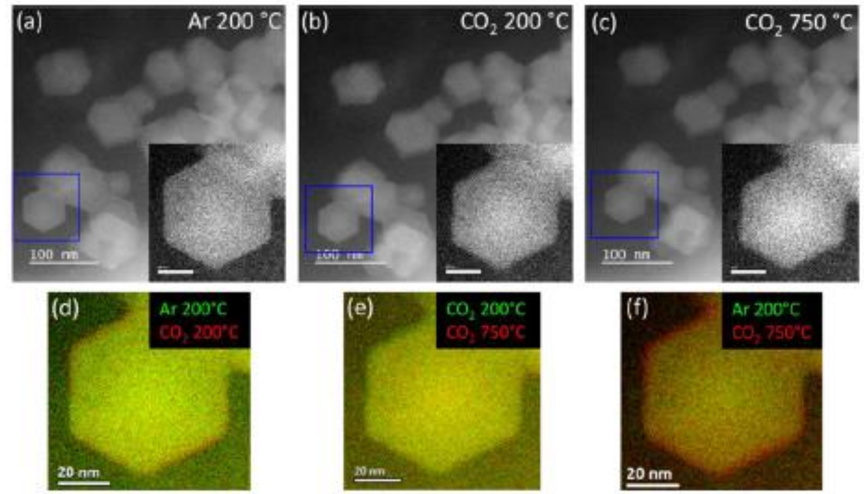


Figure 3. STEM-HAADF micrographs corresponding to the very same region submitted to thermal treatment between 200 and 750 °C under (a) Ar flow at 200 °C, (b) CO_2 flow at 200 °C, and (c) CO_2 flow at 750 °C. (d−f) Superimposed micrographs acquired at different temperatures show the volume expansion of the region displayed in (a−c).

Zeolites are not solid

Adsorption Induced Deformation

G. Reichenauer Experimental studies
A. V. Neimark Theoretical studies

C. Balzer et al. Langmuir, 32, 8265 (2016)
A. V. Neimark, I. Grenev, J.Phys. Chem. C. 124, 749 (2020)

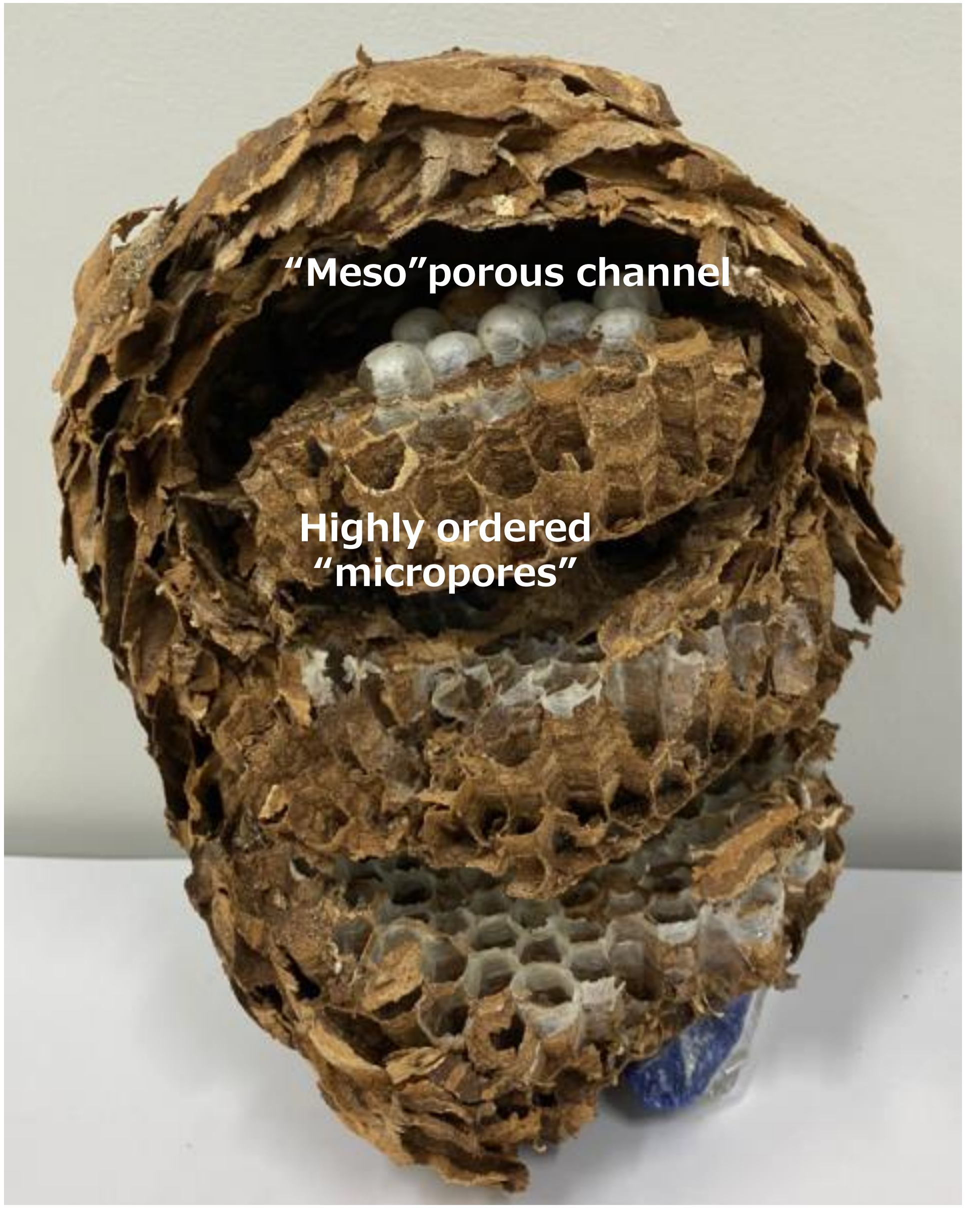
↓

Nanoporous solids of large surface area have superior adaptability to their nanoscale environment

↓

Adsorption-biased characterization with integrated in sit and/or operand approaches

Advanced Porous Materials developed by Hornet Tech.



Layering “Nanostructured” Porous Material

Other merits

Light

Water resistive

Weather resistive

Biomaterials-derived

New challenges for Novel porous materials

Better characterization leads to beyond-porous materials

Scientific Trails are not necessarily easy.

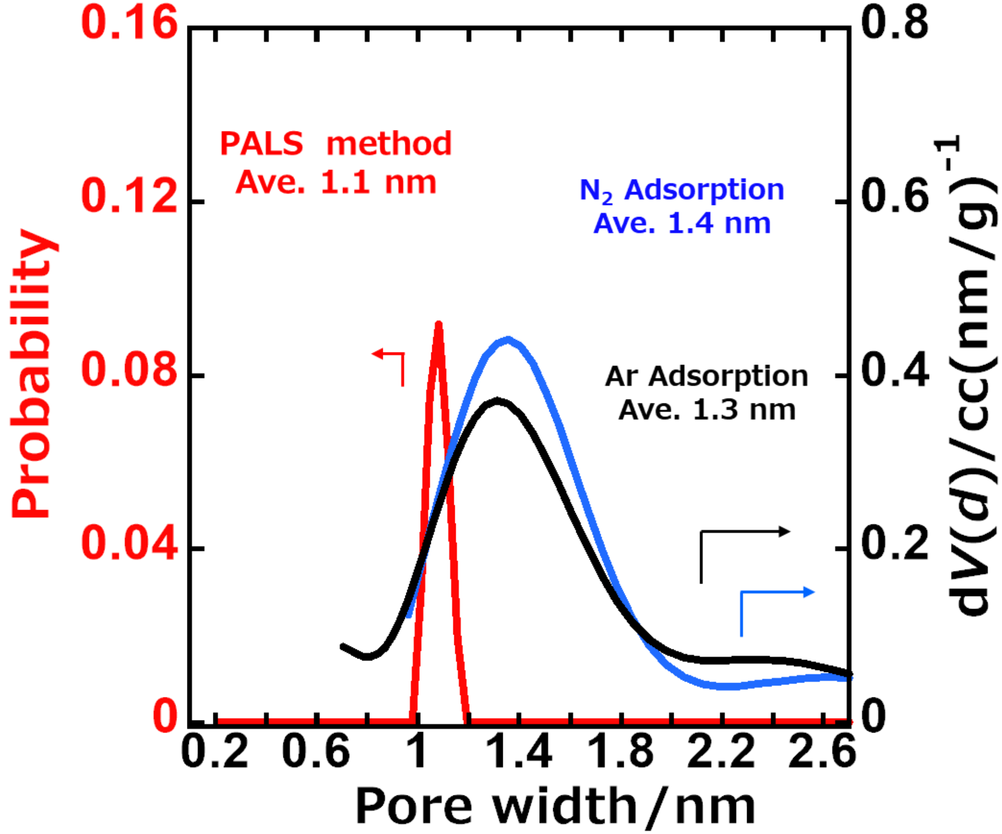
You could get a great pleasure

on finding an excellent route for new science

Looking forward to challenges by young scientists

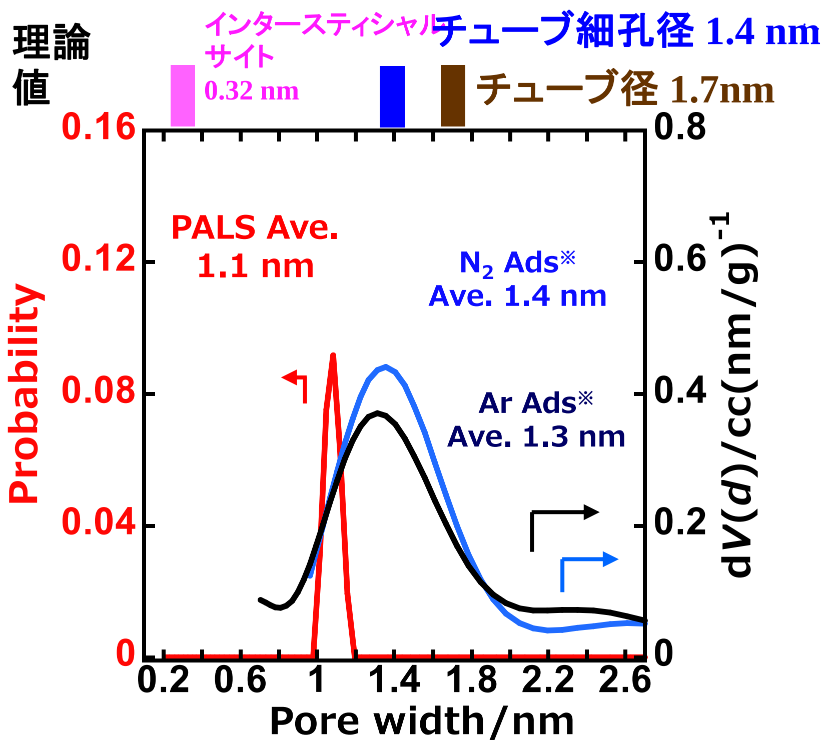
There are so many unsolved issues in this area

SWCNTの細孔構造

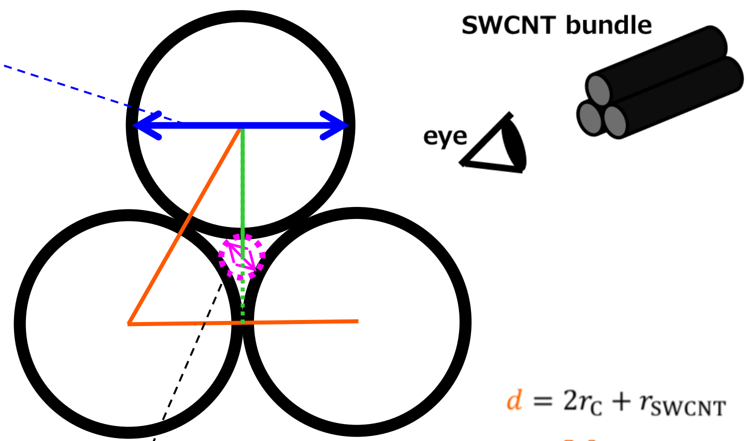


※ N_2 adsorption and Ar adsorption : QSDFT, cylindrical model

SWCNTの細孔構造



※ N2 adsorption and Ar adsorption：QSDFT, cylinderical model



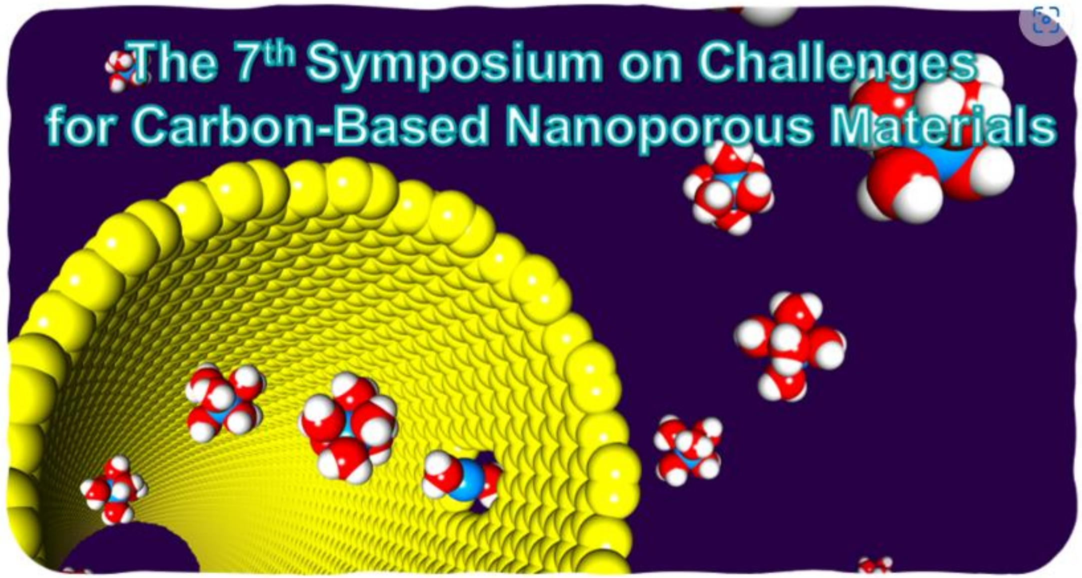
$$d = 2r_C + r_{SWCNT} = 2.0_4\ \mathrm{nm}$$

$$r_{int} = \frac{2\sqrt{3}-3}{3}(2r_C + r_{SWCNT}) = 0.31_6\ \mathrm{nm}$$

$$r_{Ave.} = \frac{n_{SWCNT} r_{SWCNT}^2 \times r_{SWCNT} + n_{int} r_{int}^2 \times r_{int}}{n_{SWCNT} r_{SWCNT}^2 + n_{int} r_{int}^2} = \frac{3 \times 1.36^3 + 6 \times 0.316^3}{3 \times 1.36^2 + 6 \times 0.316^2} = 1.2_5\ \mathrm{nm}$$

≒ 1.1 nm PALS

インタースティシャルサイトを考慮すると、**PALS**は平均細孔径（$r_{Ave.}$）とほぼ一致！



October 18 Wednesday – 21 Saturday, 2023