Carbon Materials for Today and Future Turkish-Japanese Joint Symposium
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Adsorption Properties of Porous Carbons:

Influence of Preadsorbed Water on Gas Adsorption Behavior

Miyawaki, J.; Kanda, T.; Kaneko, K. *Langmuir* **2001**, *17*, 664-669.

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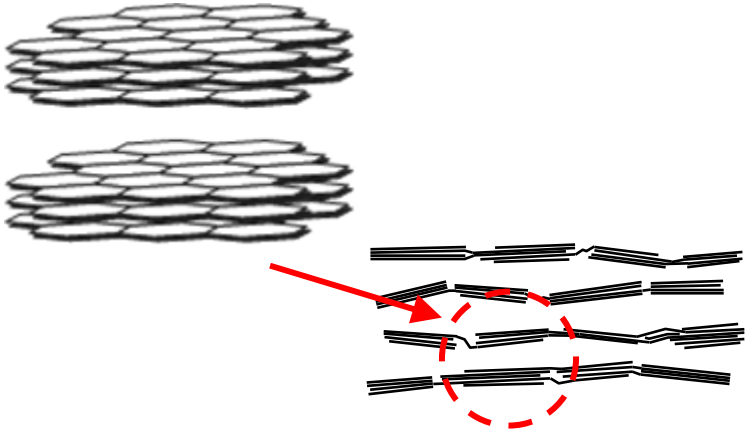
Outline

1. Introduction
   - Characteristics and applications of porous carbons
   - Enhanced interaction potential in micropore
   - Adsorption characteristics of various molecules in micropore
2. Experimental
3. Results
   - Remarkable weight increase for water-preadsorbed ACF
   - Gas composition analyses
4. Hysteresis-assisted pressure-shift-induced water adsorption mechanism
5. Verification of the mechanism
6. Influence of adsorption hysteresis of water or temperature
7. Conclusion

Porous Carbons

Characteristics

- Large surface area
- Confined space
- Surface functionality

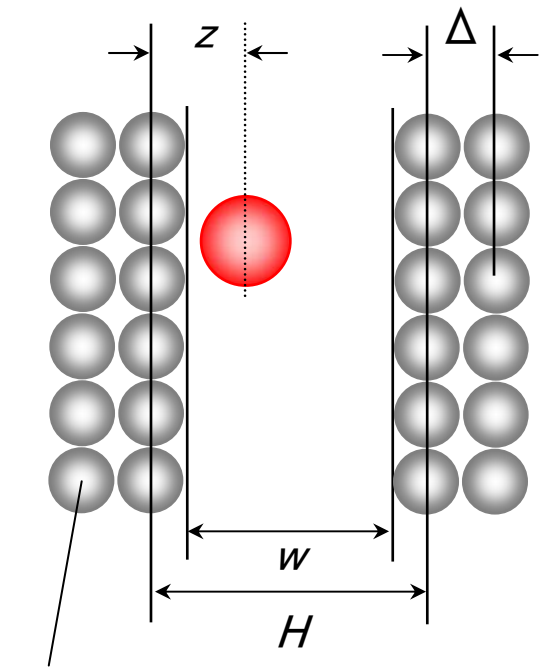


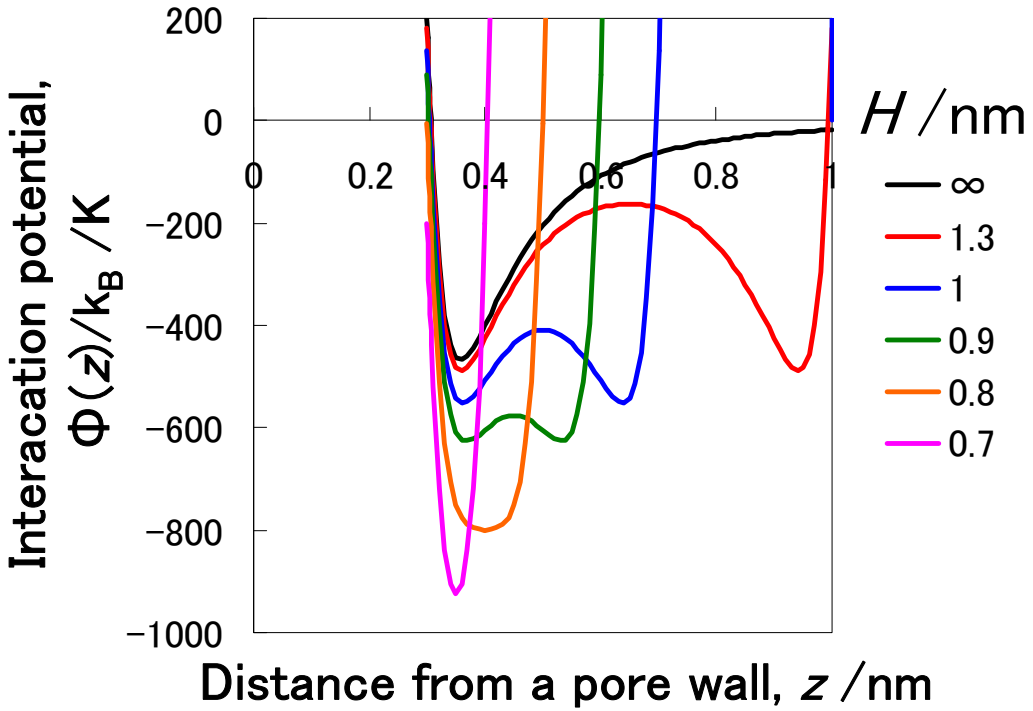
Schematic illustration of slit-shaped graphitic micropore

Applications

- Storage
  - Gas storage
- Separation
  - Decolorization
  - Deodorization
  - Desalination
  - Solvent recovery
  - Desiccation
  - Gas separation
- Catalysis
  - Catalyst
- Support
  - Catalyst support

Micropore –Strong Adsorption Field–





Interaction potentials of a CH_4 molecule in micropores

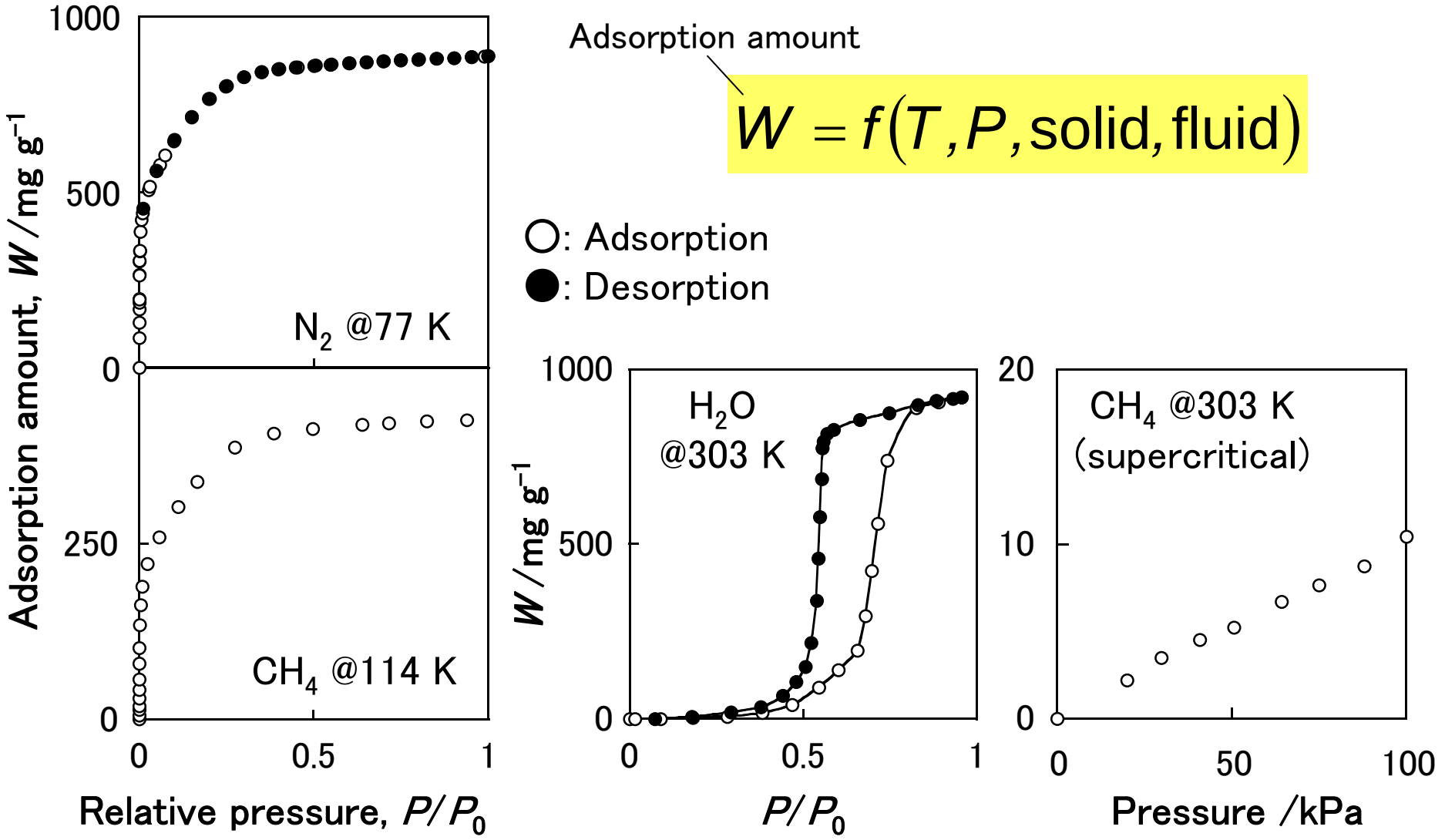
Steele's 10–4–3 potential

$$\Phi(z) = 2\pi\varepsilon_{sf}\rho_s\sigma_{sf}^2\Delta\left\{\left(\frac{2}{5}\right)\left(\frac{\sigma_{sf}}{z}\right)^{10} - \left(\frac{\sigma_{sf}}{z}\right)^4 - \frac{\sigma_{sf}^4}{3\Delta(z+0.61\Delta)^3}\right\}$$

Overlapping of potentials from face-to-face surfaces

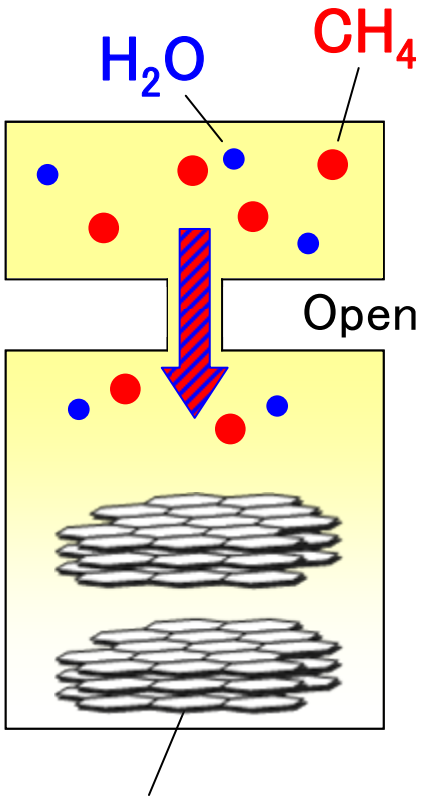
$$\Phi(z)_{pore} = \Phi(z) + \Phi(H-z)$$

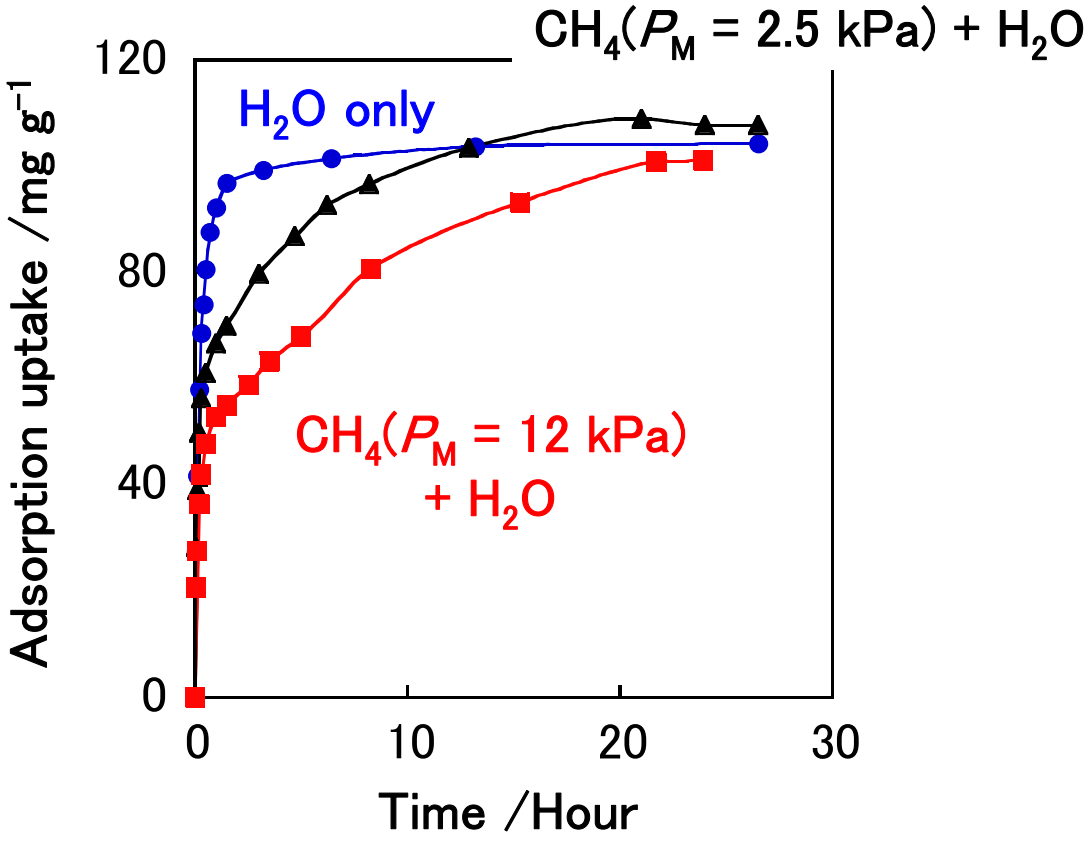
Adsorption Isotherms of Various Gases



Adsorption and desorption isotherms of various gases on ACF P20

Pre-Mixed Gas Adsorption





Time dependence after introduction of pre-mixed gas of CH_4 and H_2O (P_W = 2.5 kPa) to ACF P20 at 303 K
Measured by Mr. T. Kanda

Experimental

- Sample

  Pitch-based Activated Carbon Fiber (ACF): P20

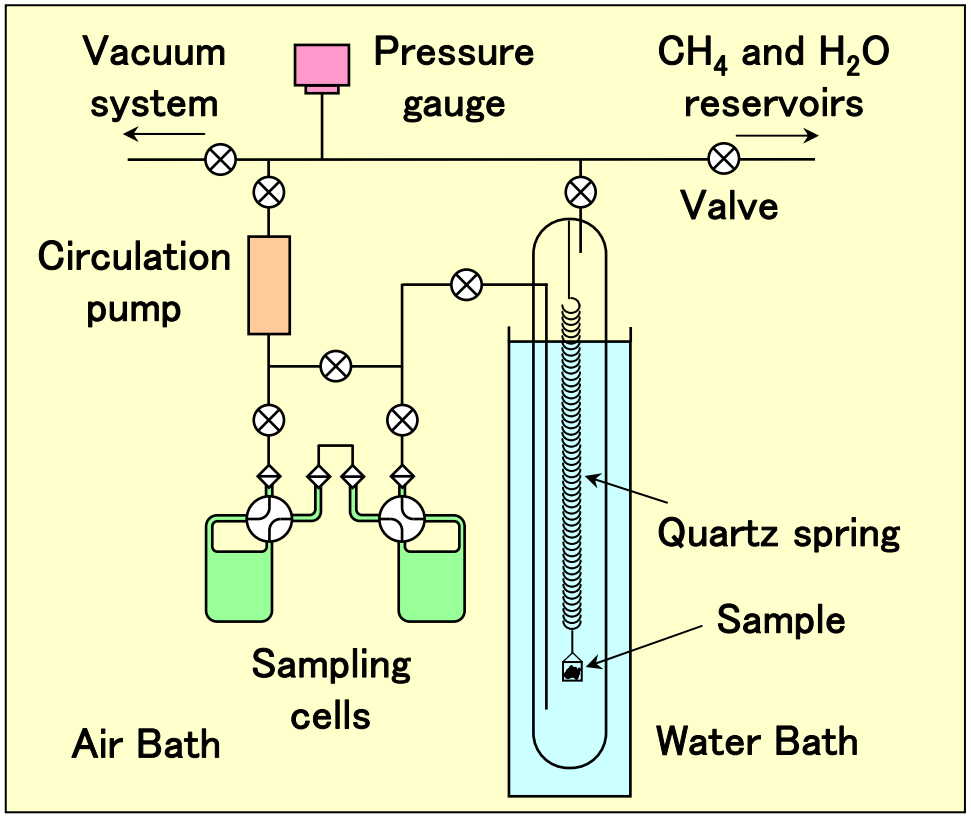
	Specific surface area a_S /m^2 g^{-1}	Micropore volume W_0 /cm^3 g^{-1}	Average pore width w /nm
P20	1800	0.95	1.1

- Pretreatment conditions

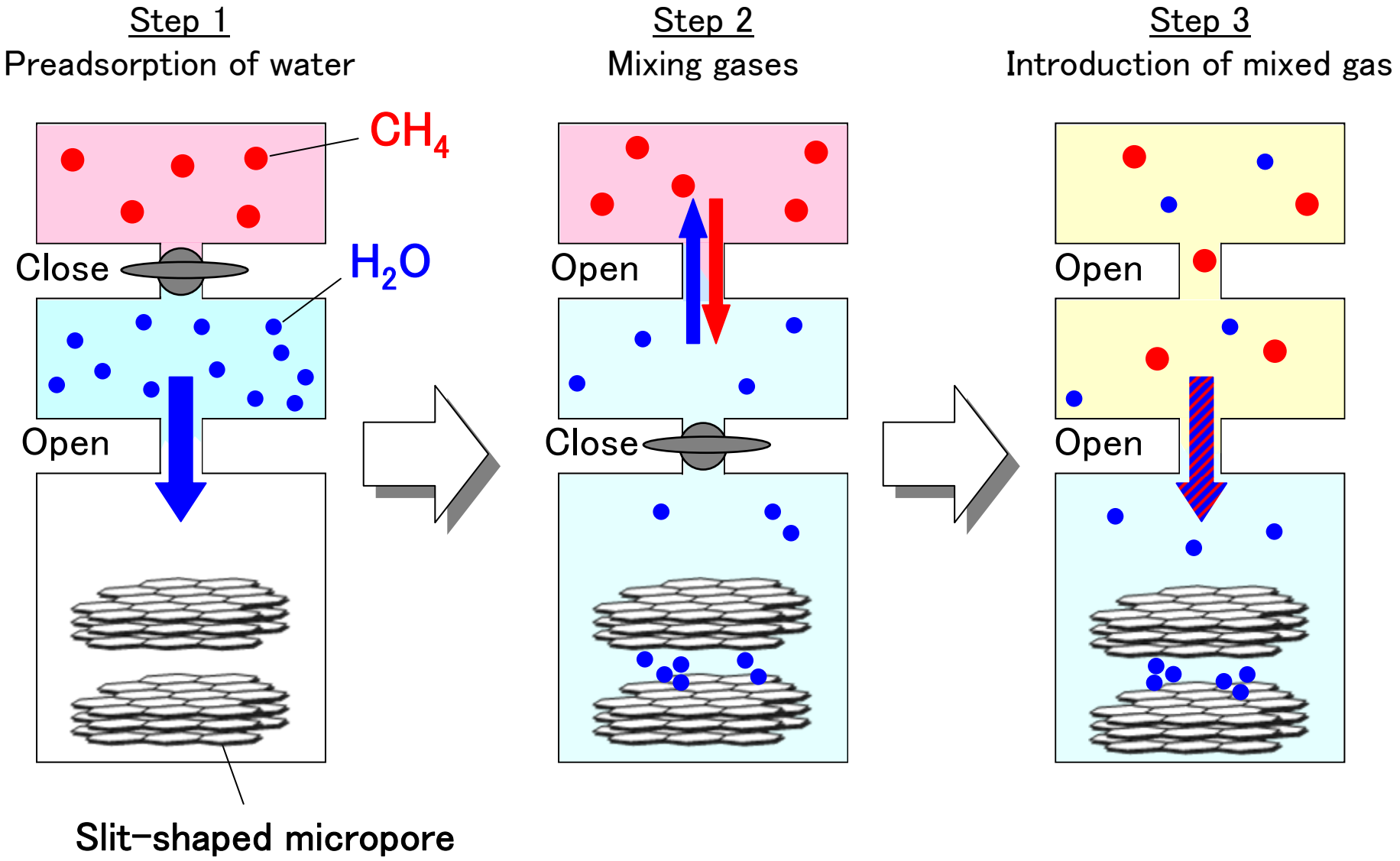
  383 K, ≦ 1 mPa, 2 h

- Apparatuses

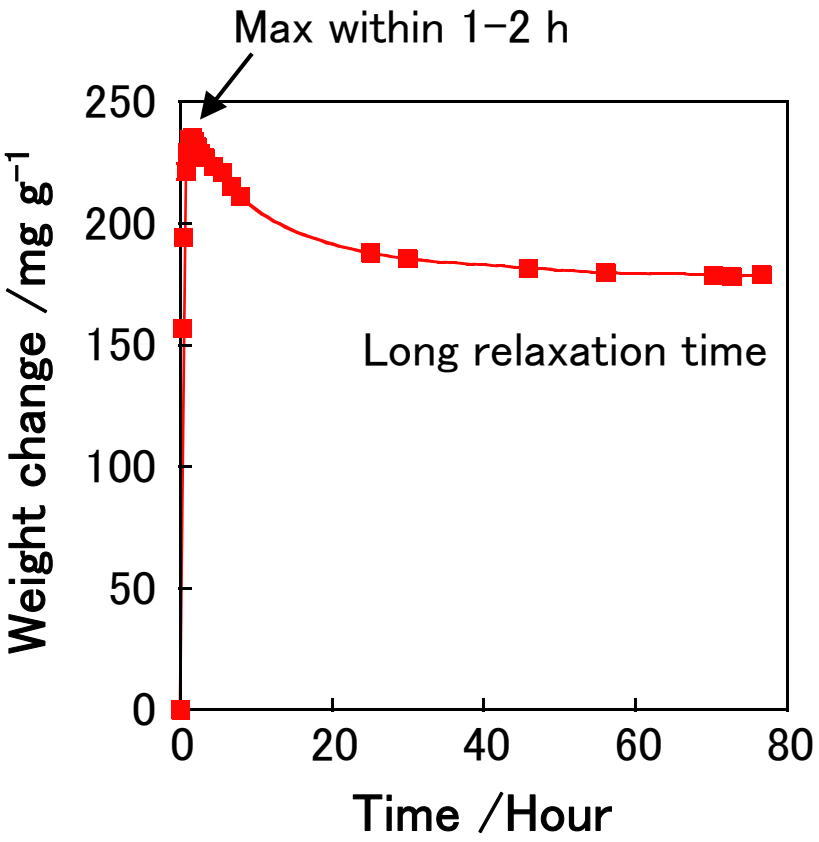
  - Mixed gas adsorption apparatus (gravimetric technique)
  - Gas Chromatography, GC-8AIT (TCD)



Schematic Illustration of Gas Introduction Steps



Effect of Preadsorbed Water



Time dependence of weight change after introduction of mixed gas to H_2O–preadsorbed ACF P20 at 303 K
ϕ_W^{ads} = 0.4, P_M = 4.5 kPa

Possible reason of weight change

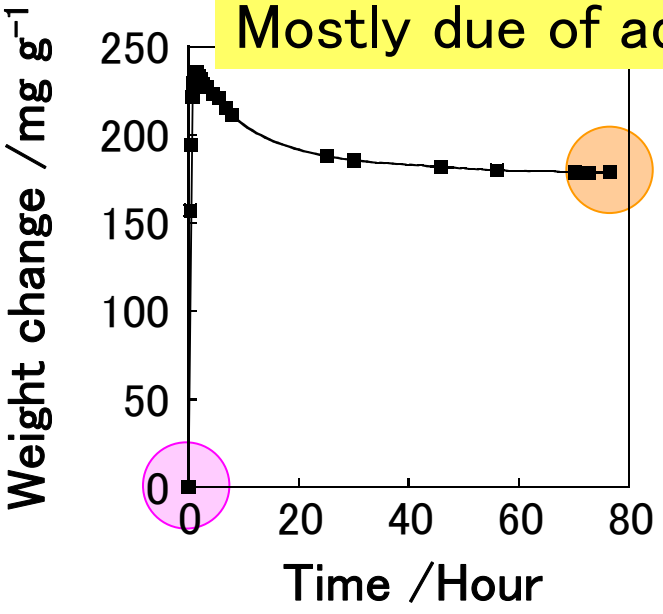
- Enhanced adsorption of CH_4
- Additional adsorption of H_2O

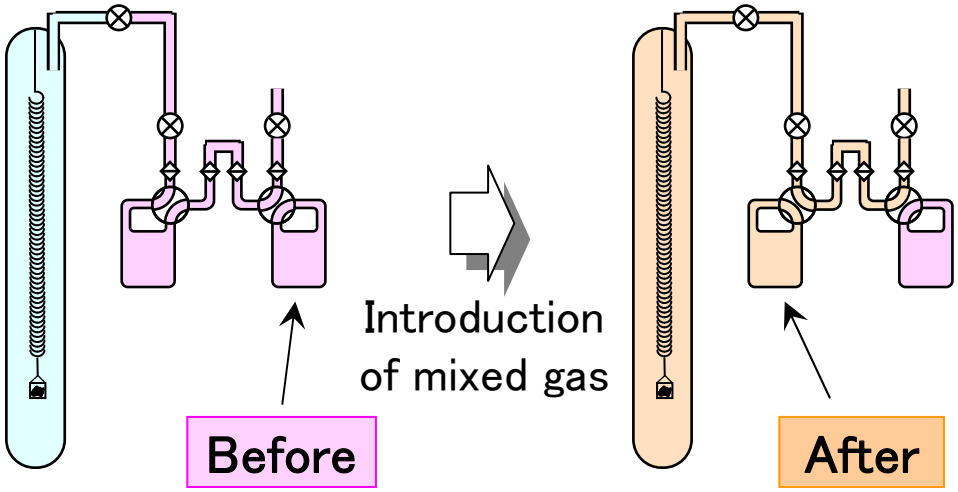
Quantitative analysis of gas composition

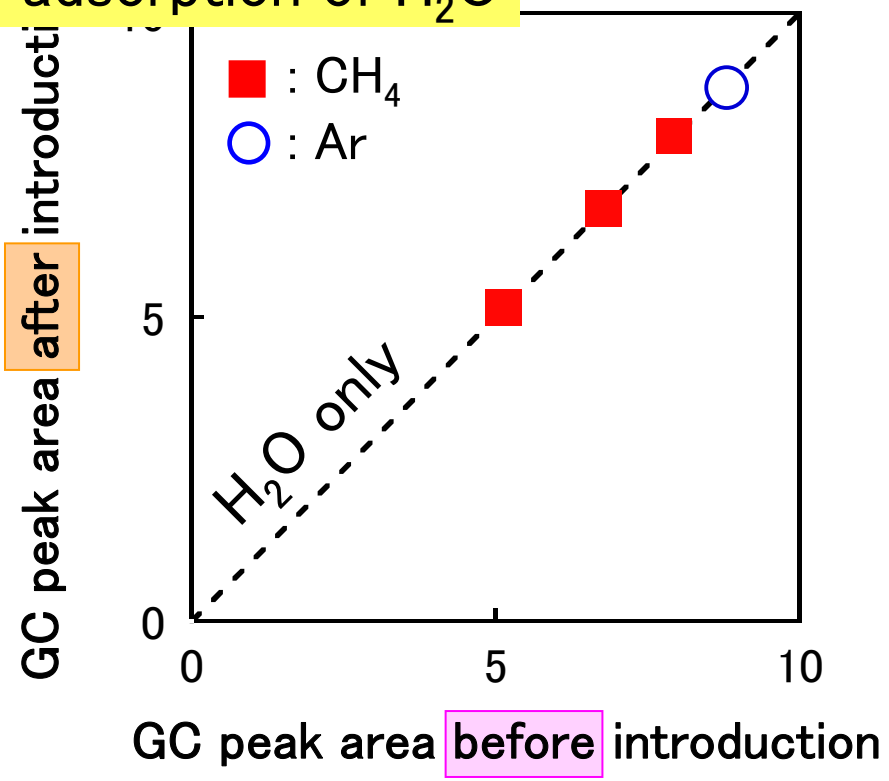
CH_4 ··· Gas Chromatography
H_2O ··· Karl Fischer method

Quantitative Analyses of Gas Composition by GC

Mostly due of additional adsorption of H_2O

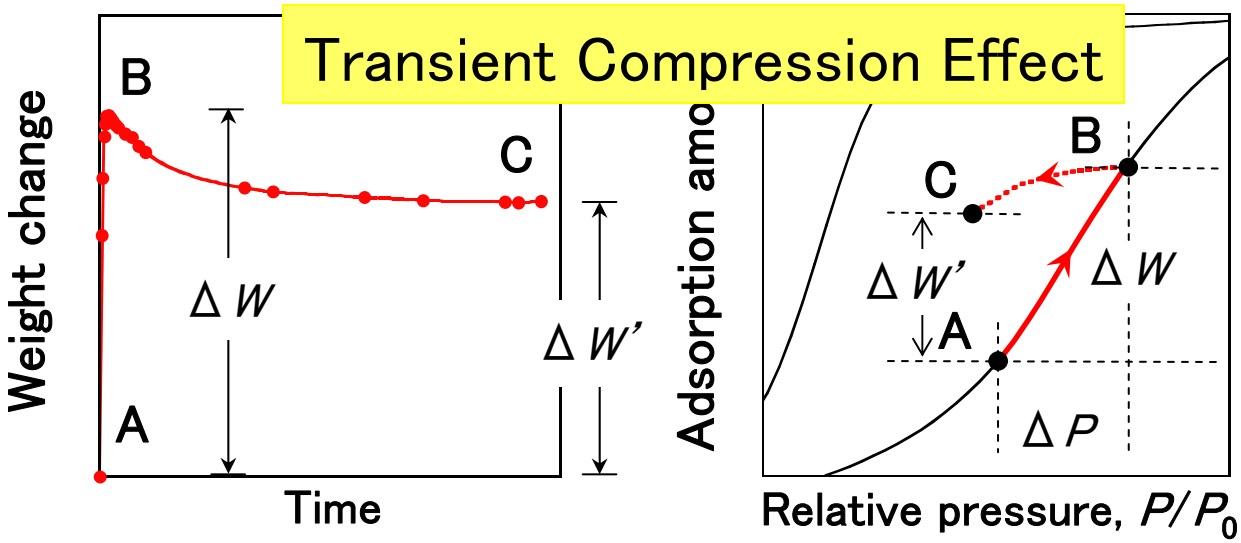






Amounts of Ar or CH_4 in gas phase before and after introduction of mixed gas

Hysteresis-Assisted Pressure-Shift-Induced Water Adsorption Mechanism

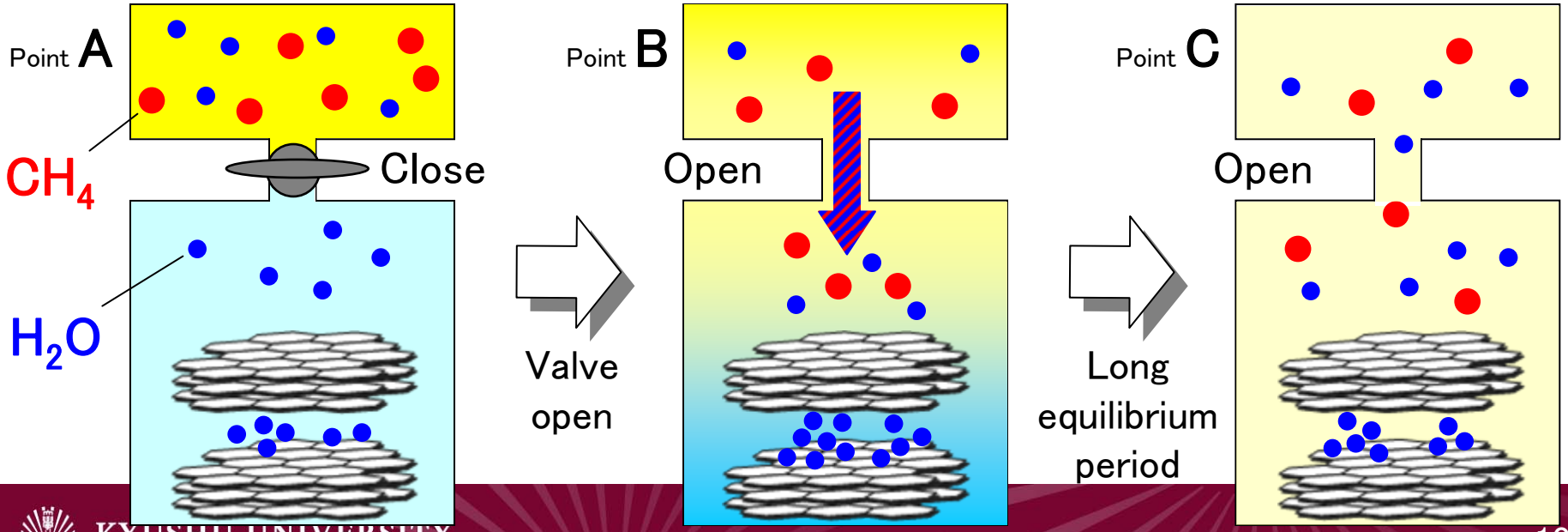


A ⇒ B

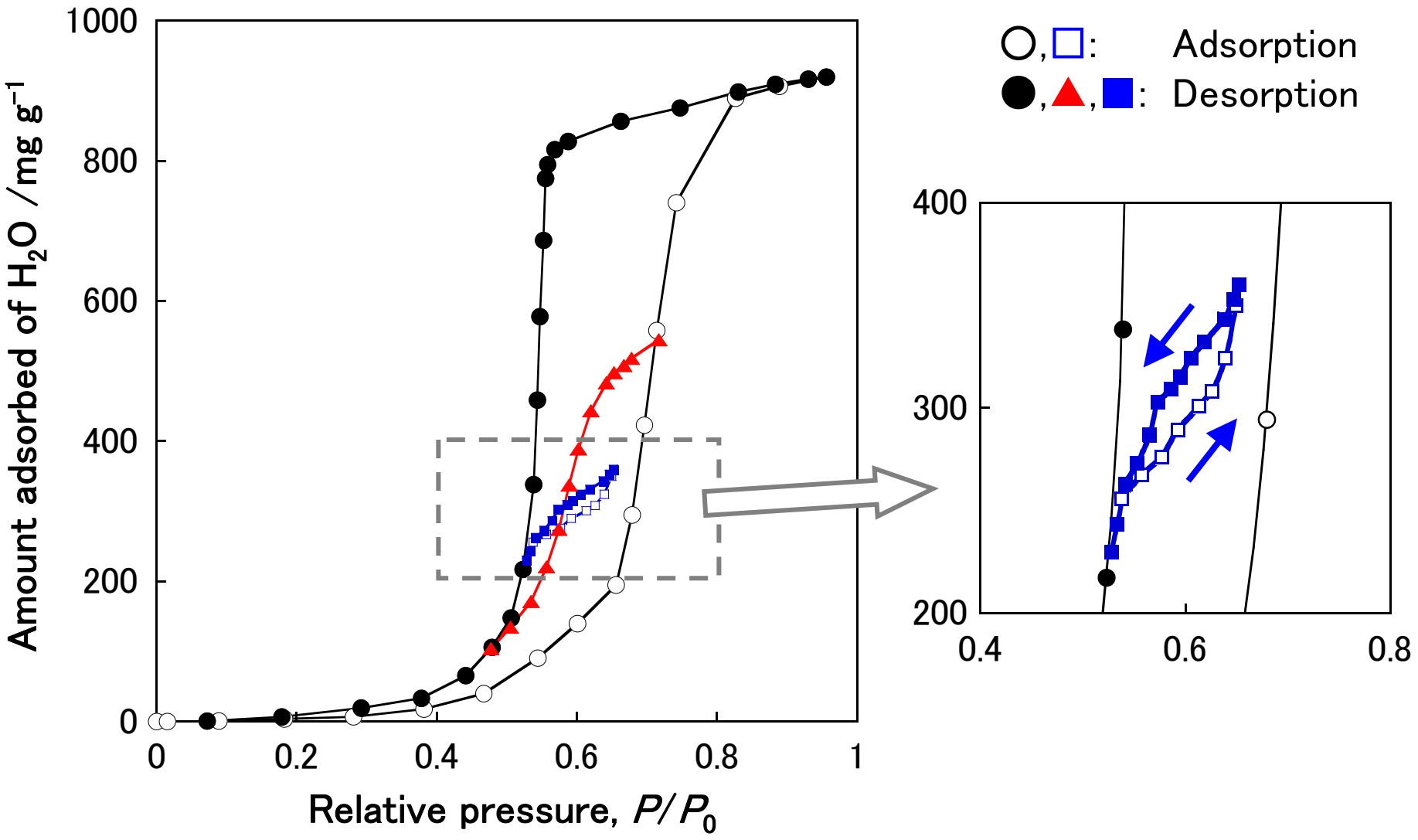
1. Compression of water vapor
2. Increase of effective water pressure around sample (ΔP)
3. Additional adsorption of water (ΔW)

B ⇒ C

4. Relaxation of pressure
5. Partial desorption of water ($\Delta W - \Delta W'$)

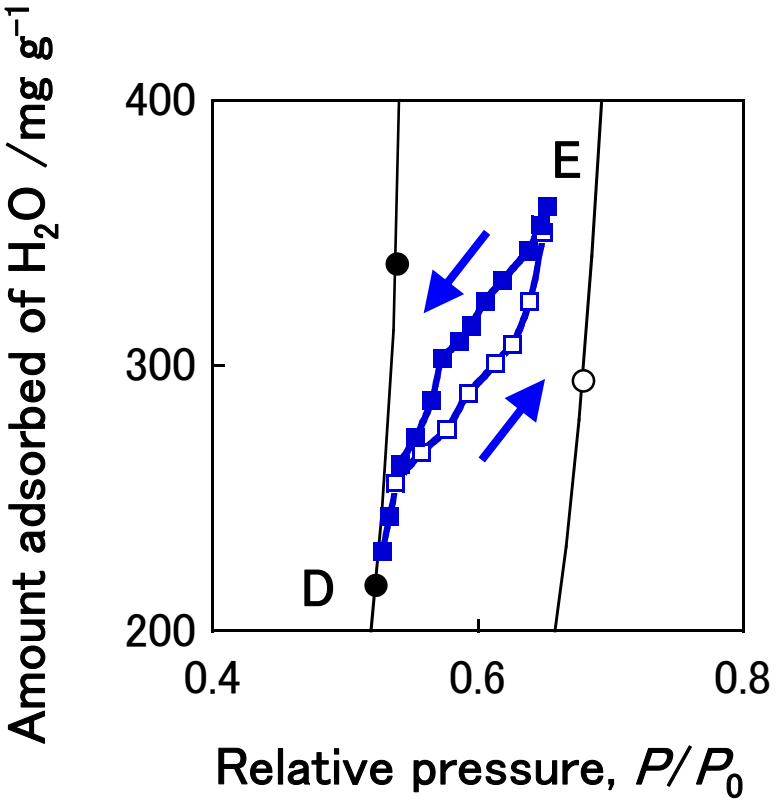


Adsorption and Desorption Scanning Curves of Water



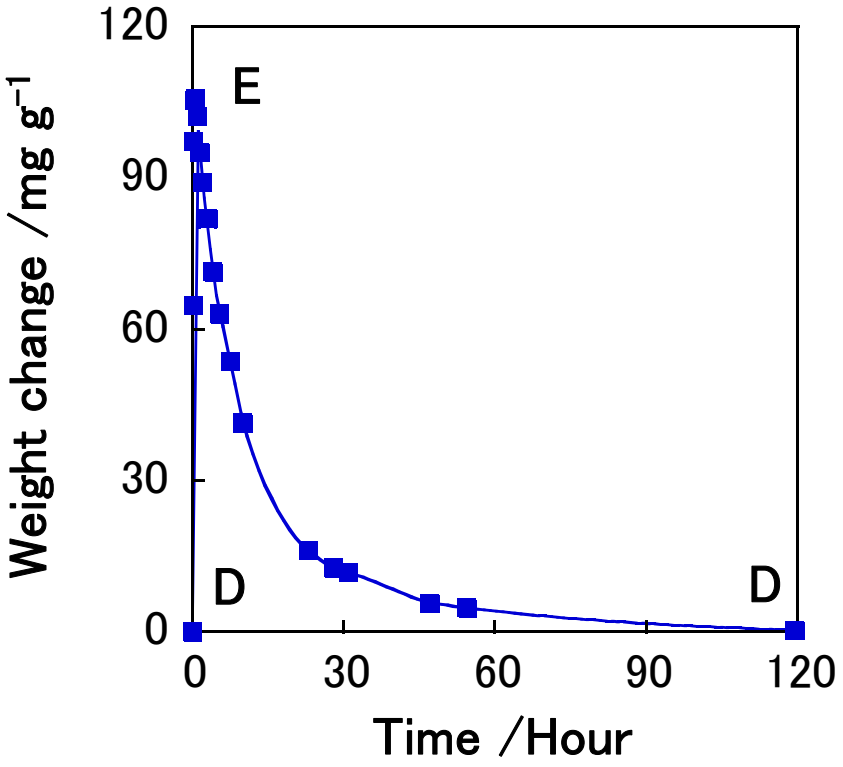
Adsorption and desorption scanning curves of H_2O on ACF P20 at 303 K

Verification of the Mechanism



Adsorption and desorption scanning curves of H_2O on ACF P20 at 303 K

○,□: Adsorption
●,■: Desorption



Time dependence after introduction of mixed gas from H_2O desorption isotherm to H_2O–preadsorbed ACF P20 at 303 K

ϕ_W^{des} = 0.34, P_M = 3.6 kPa

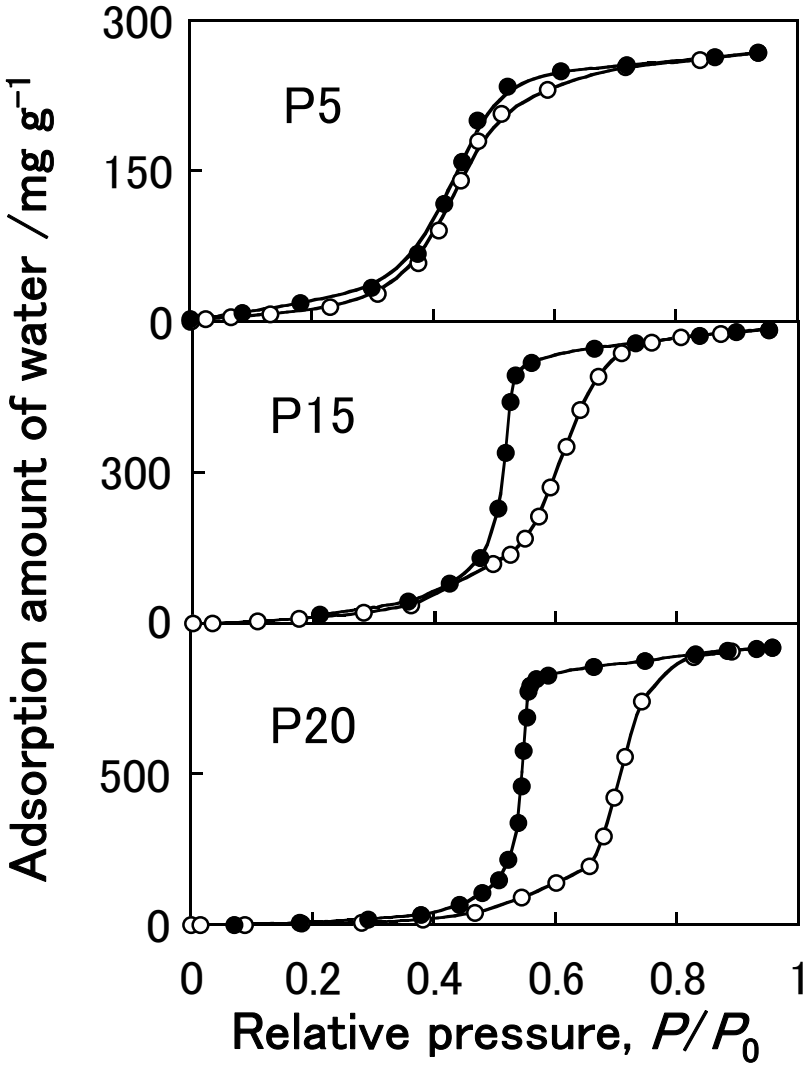
Water Adsorption Isotherms of Microporous Carbons

Pitch-based Activated Carbon Fiber
P5, P10, P15, and P20 (Adol Co.)

KOH-activated Coal-based Activated Carbon
SAC31 (Kansai Coke Co.)

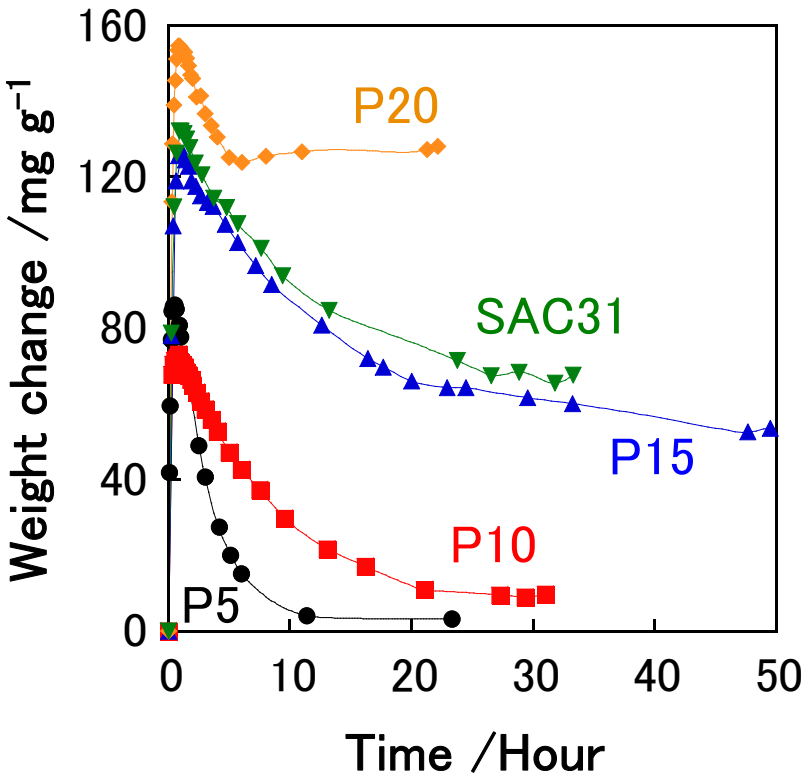
Micropore structural parameters obtained from α_S analysis

	a_S /m^2 g^{-1}	W_0 /cm^3 g^{-1}	w /nm
P5	880	0.29	0.67
P10	960	0.41	0.86
P15	1310	0.60	0.94
P20	1800	0.95	1.1
SAC31	2290	1.33	1.2



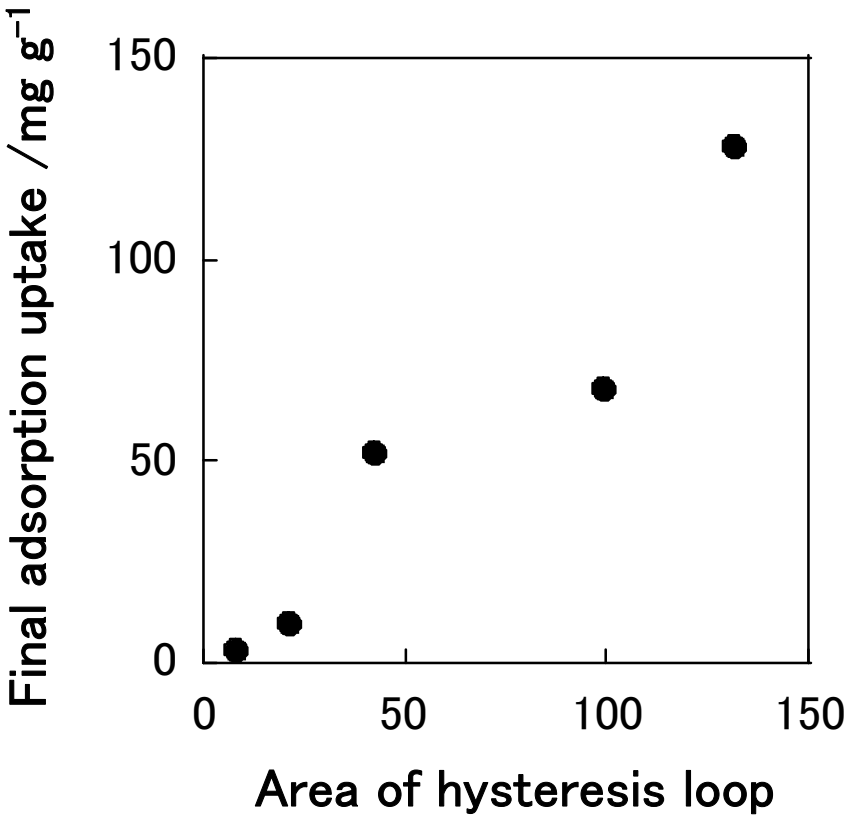
Adsorption and desorption isotherms of H_2O on ACFs at 303 K

Relationship between Adsorption Hysteresis Area and Adsorption Uptake



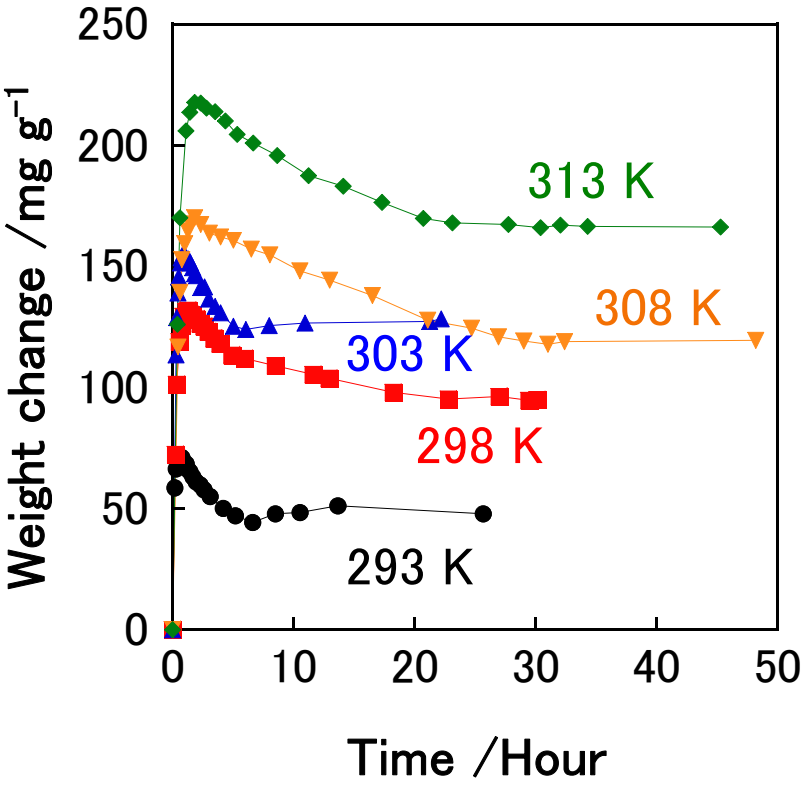
Time dependence after introduction of mixed gas on H_2O–preadsorbed carbons at 303 K

Time dependence for P5 was measured by Mr. T. Kanda.

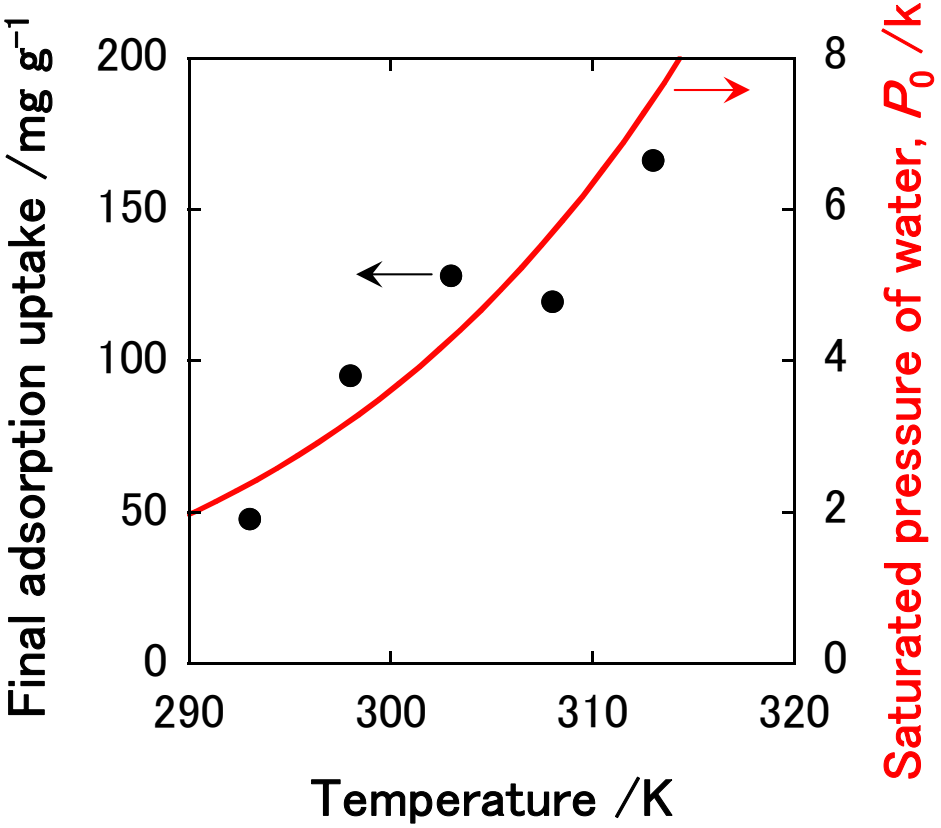


Relationship between area of adsorption hysteresis of H_2O and final adsorption uptake

Temperature Dependence

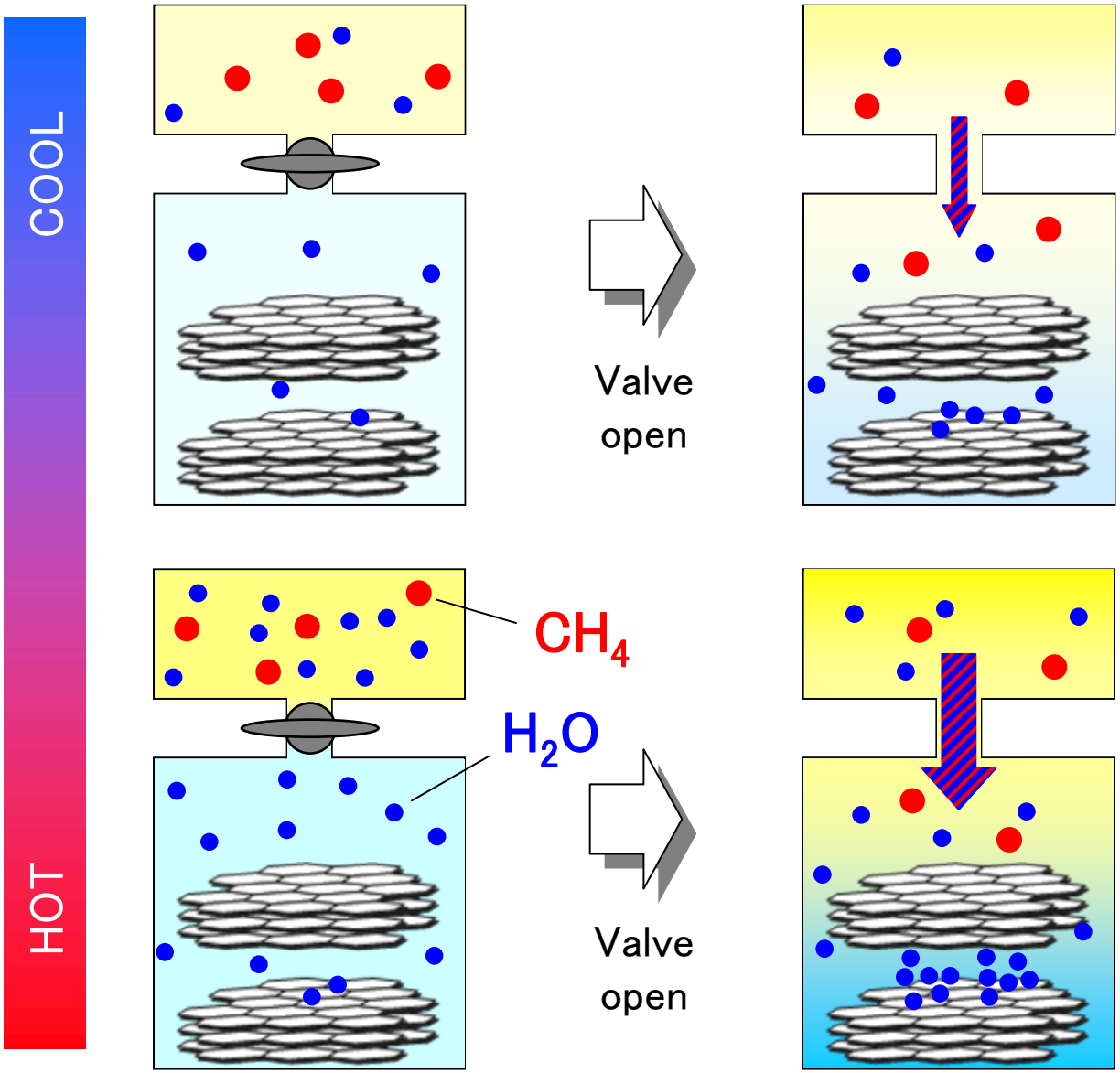


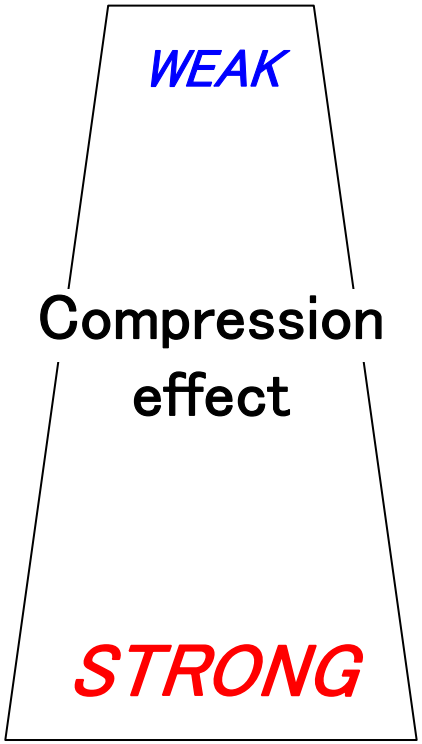
Time dependence after introduction of mixed gas to H_2O–preadsorbed ACF P20 at various temperatures



Relationship between temperature and final adsorption uptake or P_0 of bulk water

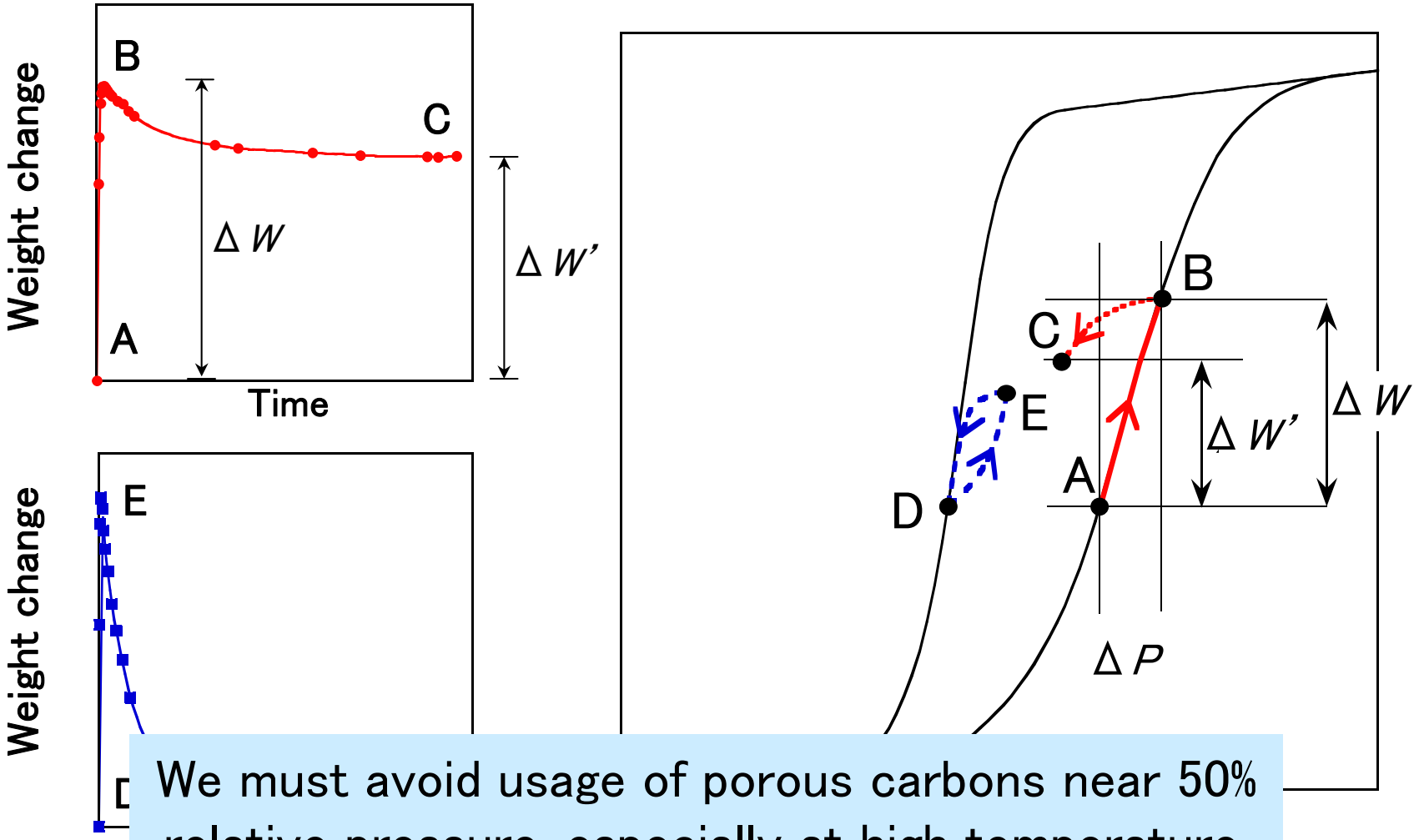
Interpretation of Temperature Dependence





Conclusion

Hysteresis-Assisted Pressure-Shift-Induced Water Adsorption Mechanism



We must avoid usage of porous carbons near 50% relative pressure, especially at high temperature.

Thank you for your attention.

İlginiz için teşekkür ederiz.

ご静聴ありがとうございました。