Adsorption and Desorption Isotherms

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- Basic concepts

- Classification of gas adsorption isotherms

- Classification of adsorption-desorption hysteresis loops

- Physical phenomena behind the isotherms

- Gas adsorption for COFs/MOFs

Adsorbate + Adsorbent $\underset{\text{Desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}}$ Adsorption

$A + B \rightleftharpoons AB$
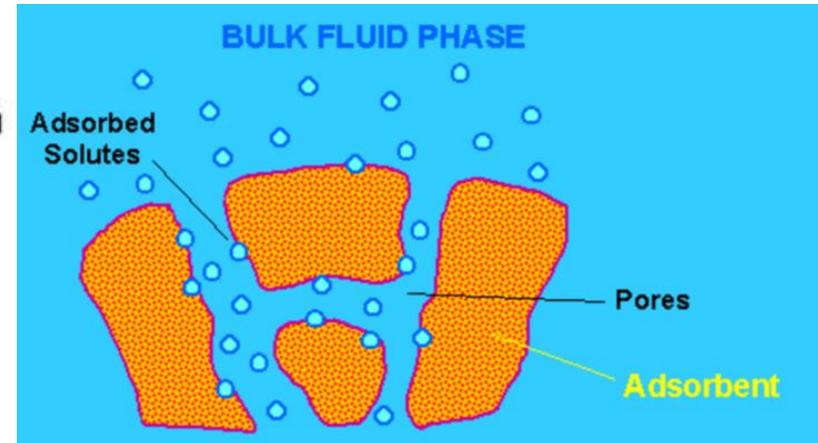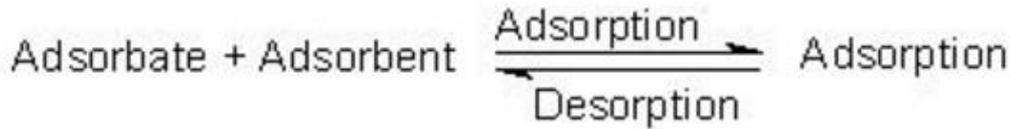
Adsorbent: The substance on whose surface the adsorption occurs is known as adsorbent. Examples: activated charcoal, mesoporous Silica

Adsorbate: The substance whose molecules get adsorbed on the surface of the adsorbent (i.e. solid or liquid) is known as adsorbate.

Adsorption ≠ absorption: In absorption, the molecules of a substance are uniformly distributed in the bulk of the other, whereas in adsorption molecules of one substance are present in higher concentration on the surface of the other substance.
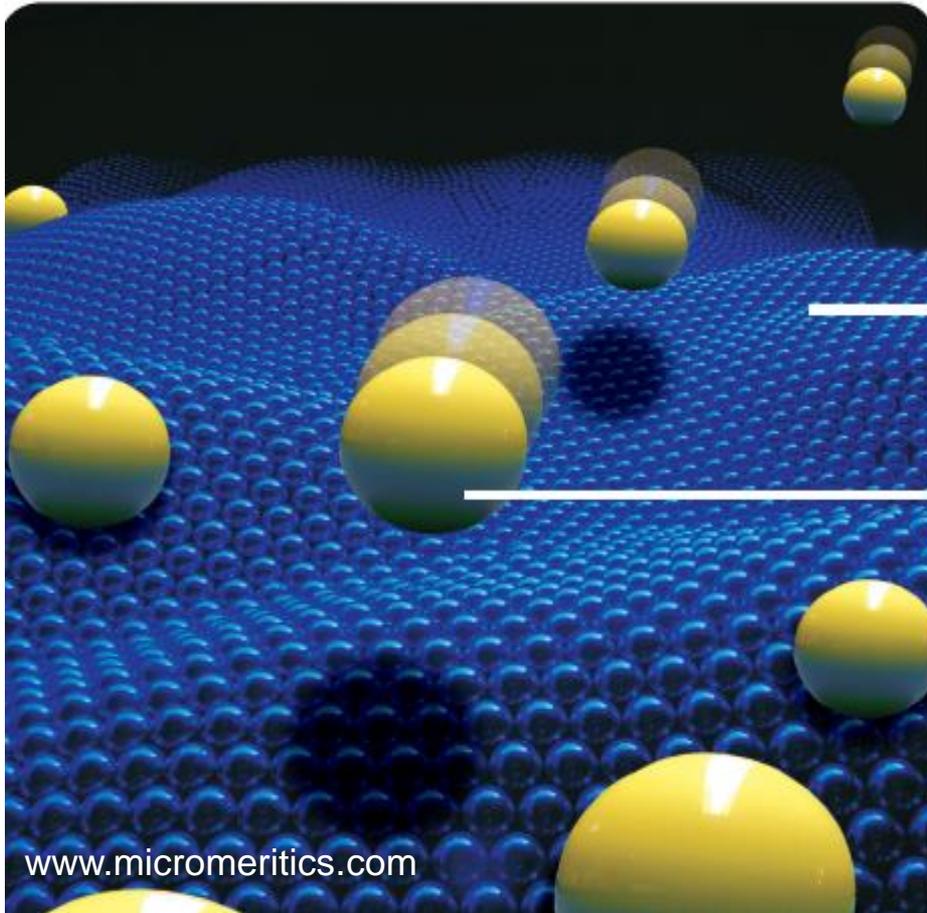
Why Adsorption happens?

These surface molecules (in blue) are experiencing a bond deficiency, thus it is energetically favorable for them to adsorb molecules. (in yellow)

Adhesion of atoms, ions, bimolecules or molecules of gas, liquid or dissolved solids to a surface is called adsorption. This process creates a film of the adsorbate –the molecules or atoms being accumulated, on the surface of the adsorbent.

www.micromeritics.com

General factors affecting adsorption: Nature of adsorbate and adsorbent. The surface area of adsorbent. Activation of adsorbent. Experimental conditions. E.g., temperature, pressure, etc.

Physisorption: physical adsorption	Chemisorption: chemical adsorption
1.Low heat of adsorption usually in the range of 20-40 kJ mol^{-1}	High heat of adsorption in the range of 40-400 kJ mol^{-1}
2.Force of attraction are Van der Waal's forces	Forces of attraction are chemical bond forces
3.It usually takes place at low temperature and decreases with increasing temperature	It takes place at high temperature
4.It is reversible	It is irreversible
5.It is related to the ease of liquefaction of the gas	The extent of adsorption is generally not related to liquefaction of the gas
6.It is not very specific	It is highly specific
7.It forms multi-molecular layers	It forms monomolecular layers
8.It does not require any activation energy	It requires activation energy

Adsorption stages

Stage 1
Isolated sites on the sample surface begin to adsorb gas molecules at low pressure.

Stage 2
As gas pressure increases, coverage of adsorbed molecules increases to form a monolayer.

Stage 3
Further increasing gas pressure will cause the beginning of multi-layer coverage. Smaller pores in the sample will fill fist.

Stage 4
A further increase in the gas pressure will cause complete coverage of the sample and fil all the pores

Stage 1

Stage 2

Stage 3

Stage 4

Increasing gas pressure

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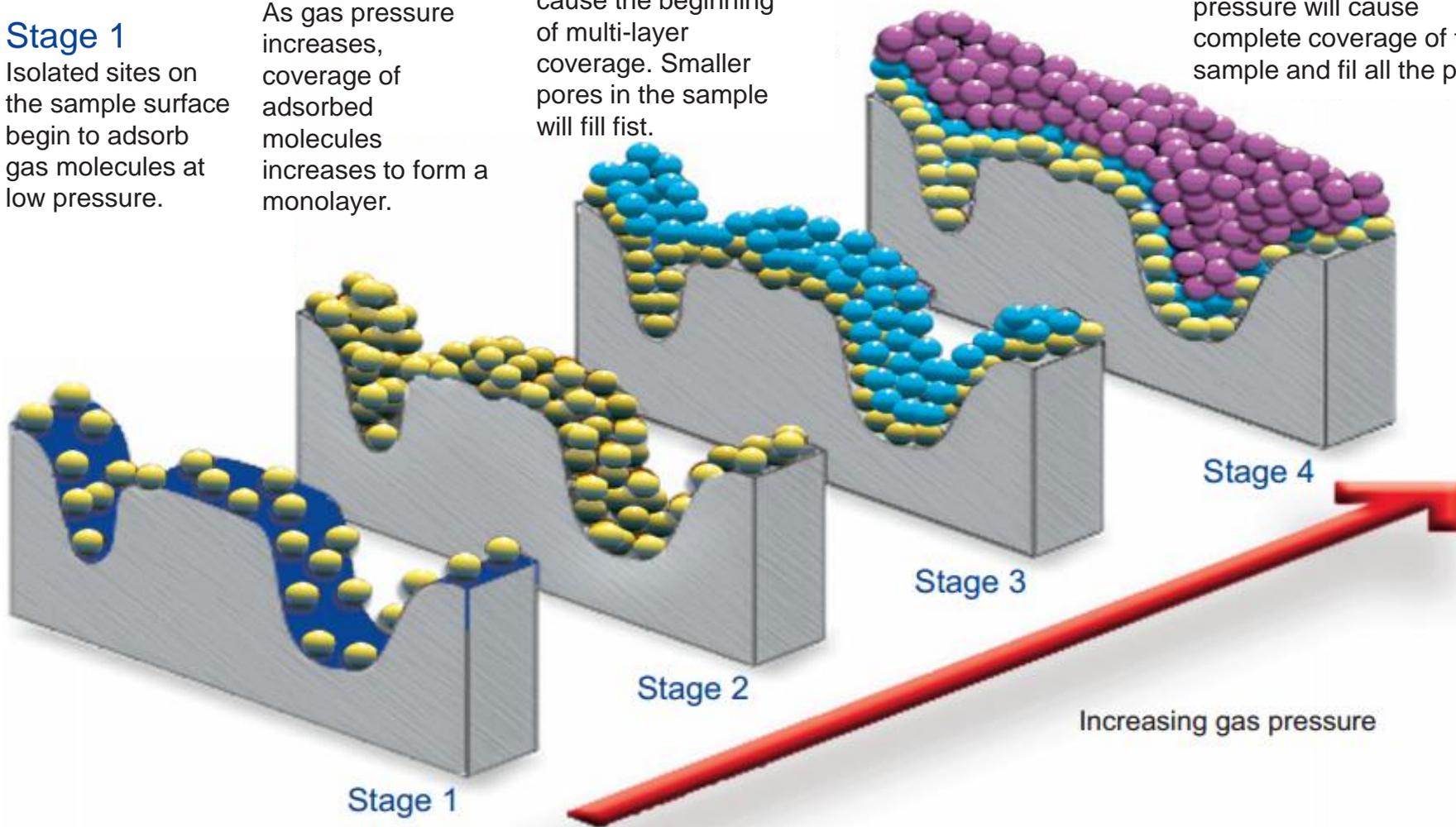
Henry's (Linear) adsorption isotherm, early 19th century

$$X = K_H P$$

Freundlich adsorption isotherm, 1909, purely empirical

$$\frac{x}{m} = K p^{1/n}$$

Langmuir adsorption model, 1918, semi-empirical
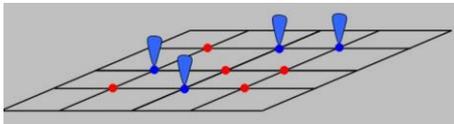
The adsorption sites (heavy dots) are equivalent and can have unit occupancy. Also, the adsorbates are immobile on the surface.

$$\theta_A = \frac{V}{V_m} = \frac{K_{eq}^A \, p_A}{1 + K_{eq}^A \, p_A}$$

Brunauer–Emmett–Teller (BET) theory, 1938, JACS
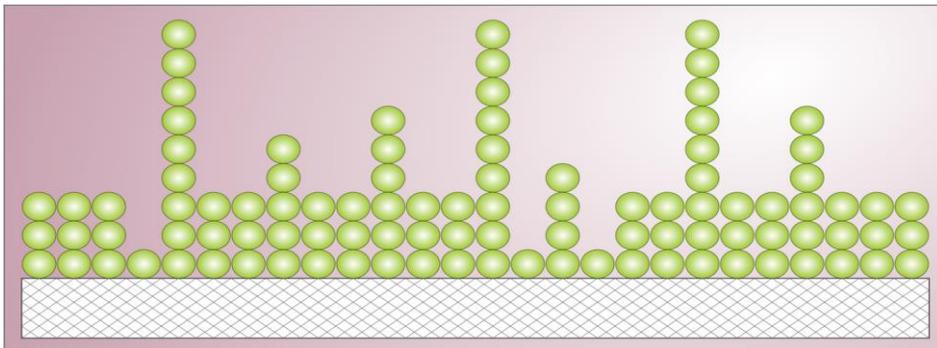
1. gas molecules physically adsorb on a solid in layers infinitely;
2. there is no interaction between each adsorption layer; and
3. the Langmuir theory can be applied to each layer.

$$\frac{1}{v\left[(p_0/p) - 1\right]} = \frac{c-1}{v_m c}\left(\frac{p}{p_0}\right) + \frac{1}{v_m c}$$

https://en.wikipedia.org/wiki/Langmuir_adsorption_model   https://en.wikipedia.org/wiki/BET_theory

Classification of pore sizes:
micropores (< 2 nm)
mesopores (2~50 nm)
macropores (> 50 nm)
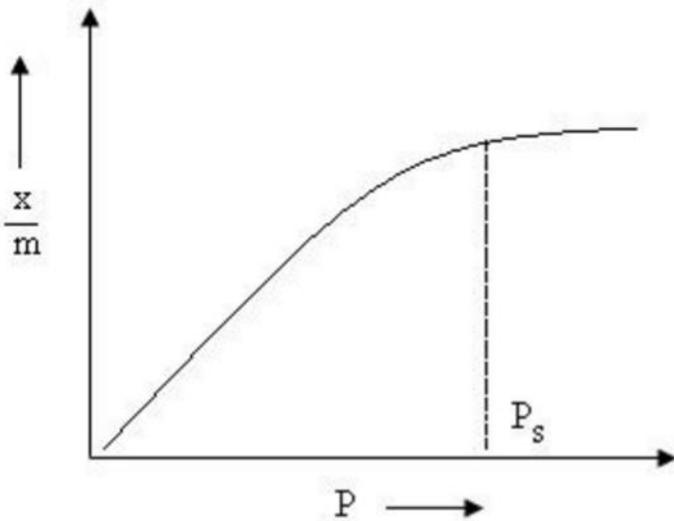
The reversible Type I isotherm is concave to the relative pressure, $p/p_\circ$ axis and a approaches a limiting value as $p/p_\circ \sim 1$.

Type I isotherms are given by microporous solids having relatively small external surfaces (e.g.activated carbons, molecular sieve zeolites, COFs/MOFs and certain porous oxides), the limiting uptake being governed by the accessible micropore volume rather than by the internal surface area.

The above graph depicts Monolayer adsorption.
This graph can be easily explained using Langmuir Adsorption Isotherm.
If BET equation, when $P/P_0 \ll 1$ and $c \gg 1$, then it leads to monolayer formation and Type I Adsorption Isotherm is obtained.

II

$\frac{x}{m}$

P_s

P

III

$\frac{x}{m}$

P_s

P
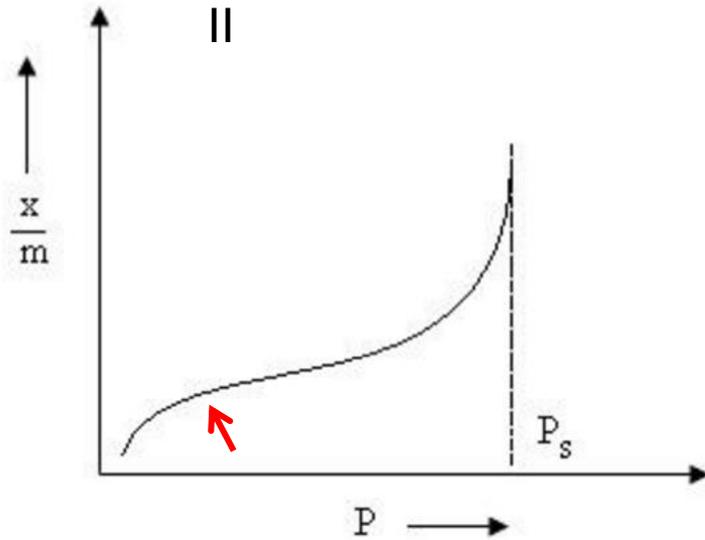
The reversible Type II isotherm is the normal form of isotherm obtained with a non-porous or macroporous adsorbent.

The Type II isotherm represents unrestricted monolayer-multilayer adsorption.

The arrow point, the beginning of the almost linear middle section of the isotherm, is often taken to indicate the stage at which monolayer coverage is complete and multilayer adsorption about to begin.
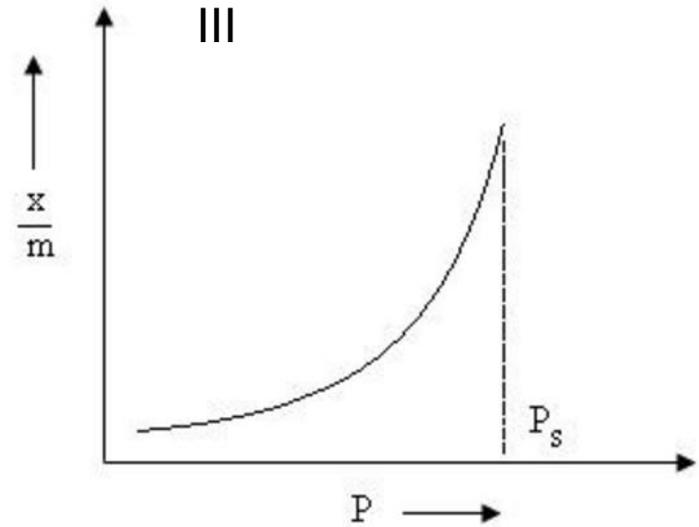
The reversible Type III isotherm is convex to the x axis over its entire range.

It also indicates unrestricted multilayer formation process.

It forms because lateral interactions between adsorbed molecules are strong in comparison to interactions between the adsorbent surface and adsorbate.
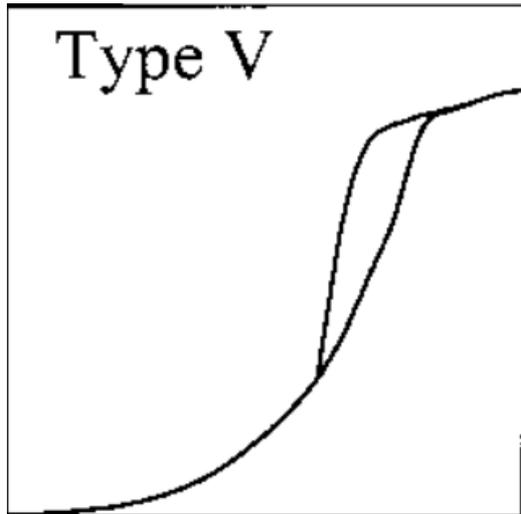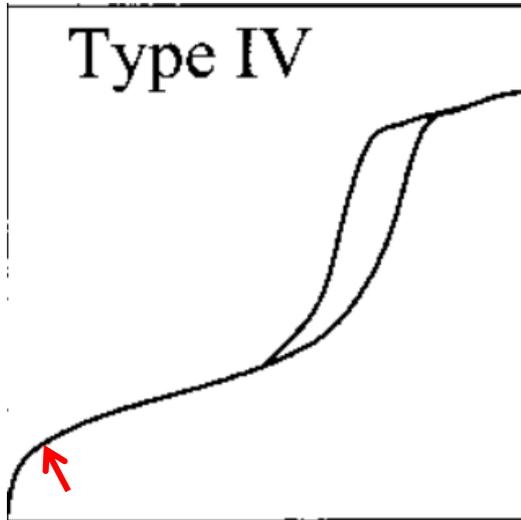
Adsorption on mesoporous solids proceeds via multilayer adsorption followed by capillary condensation, resulting in Type IV and V isotherms.

Characteristic features of the Type IV isotherm are its hysteresis loop, which is associated with capillary condensation taking place in mesopores, and the limiting uptake over a range of high P/P_0.

The initial part of the Type IV isotherm is attributed to monolayer-multilayer adsorption since it follows the same path as the corresponding part of a Type II isotherm obtained with the given adsorptive on the same surface area of the adsorbent in a non-porous form.

The distinction between Types IV and V is analogous to that between Types II and III.

Kruk et.al., *Chem. Mater.* **2001**, 13, 3169-3183
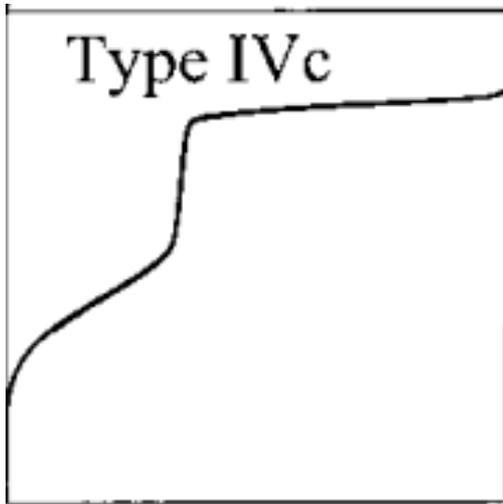
The capillary condensation-evaporation in mesopores may also be reversible, resulting in Type IVc isotherms.
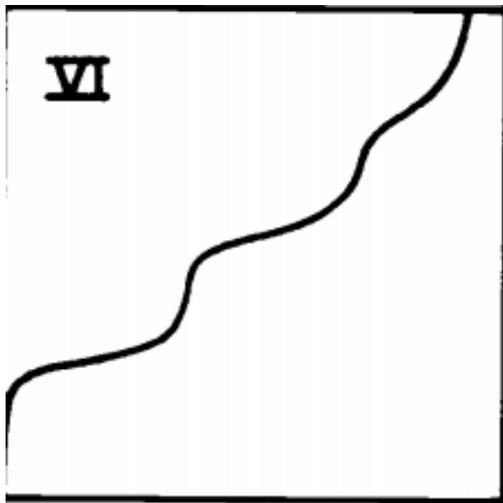

The Type VI isotherm, in which the sharpness of the steps depends on the system and the temperature, represents stepwise multilayer adsorption on a uniform non-porous surface.

The step-height now represents the monolayer capacity for each adsorbed layer and, in the simplest case, remains nearly constant for two or three adsorbed layers.
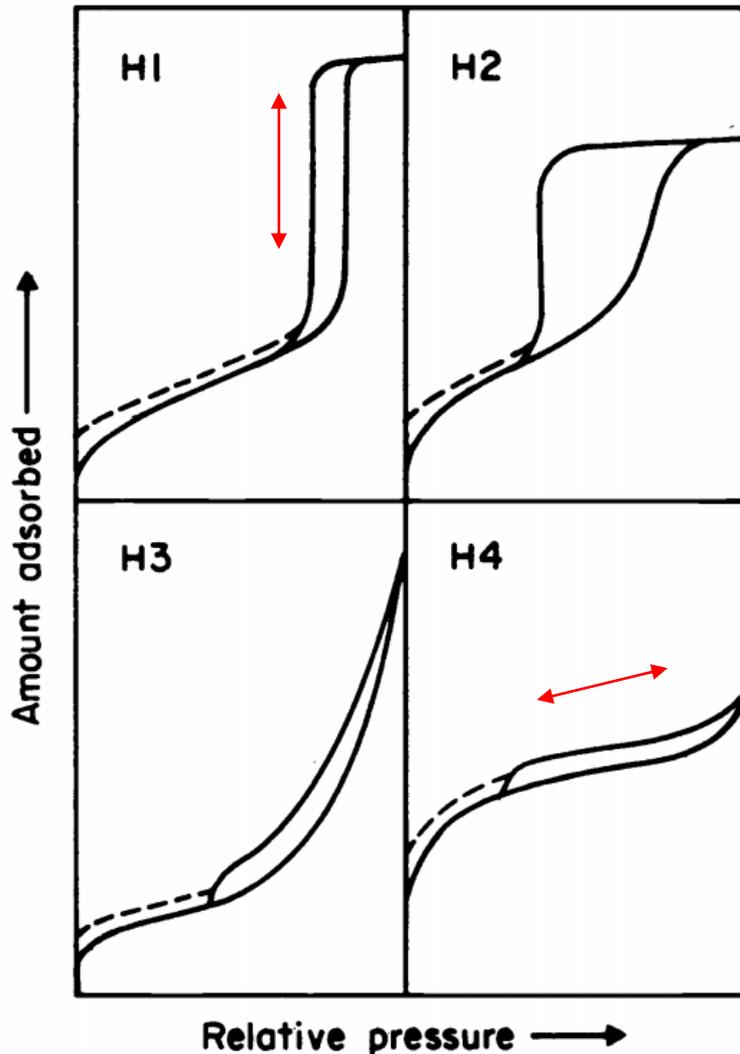
Steepness of the isotherms decreases from H1 to H4.

The hysteresis is usually attributed to the thermodynamic or network effects or the combination of these two effects.

H1: agglomerates or spherical particles arranged in a fairly uniform way, cylindrical pore geometry, indicating relatively high pore size uniformity and facile pore connectivity

H2: pores with narrow mouths (ink-bottle pores), relatively uniform channel-like pores, pore network (connectivity) effects

H3: aggregates (loose assemblages) of platelike particles forming slit-like pores

H4: narrow slit-like pores, particles with internal voids of irregular shape and broad size distribution, hollow spheres with walls composed of ordered mesoporous silica

Sing et.al, *Pure & Appl. Chem.*, **1985**, 57, 603-619

Once condensation has occurred, a meniscus immediately forms at the liquid-vapor interface which allows for equilibrium below the saturation vapor pressure.
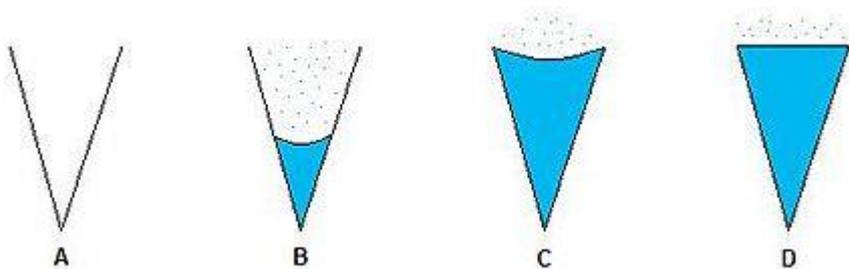

Relation of equilibrium vapor pressure to the saturation vapor pressure can be thought of as a relative humidity measurement for the atmosphere.

Microporous silica plugs

Microporous pore wall

6-8 nm

3-4 nm

Open mesopore Blocked mesopore
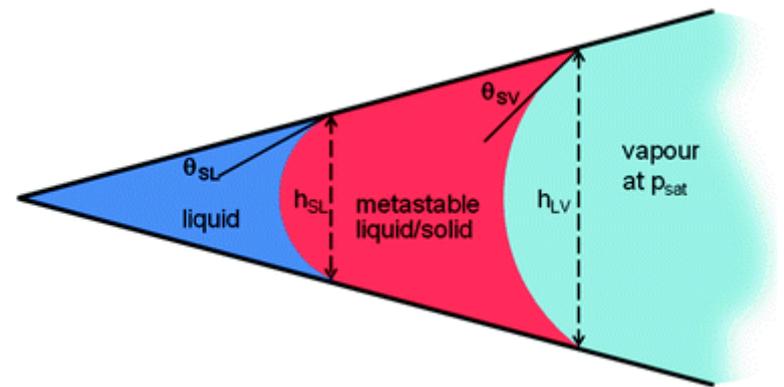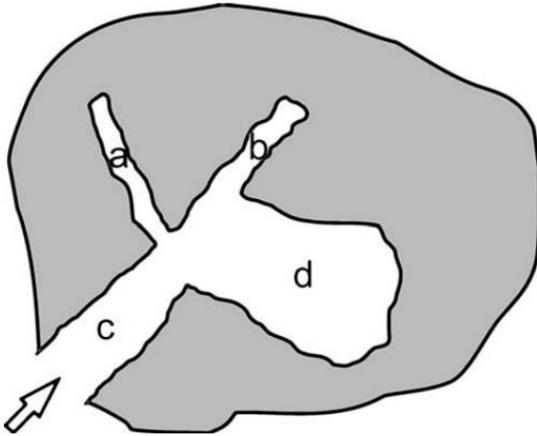
During desorption, the smaller pores a and b will empty at their corresponding pressure, being lower than that needed for emptying of pore c. How ever, pore d can only empty via pore c and accordingly will empty at lower pressure.


vol. gas adsorbed (cm³ STP/g)

N_{open}

$N_{blocked}$

N_{micro}

encapsulated mesopores empty at lower pressure than the open pores of similar size.

p/p_0

J.C. Groen et al., *Microporous and Mesoporous Mater.,* **2003**, 60, 1–17
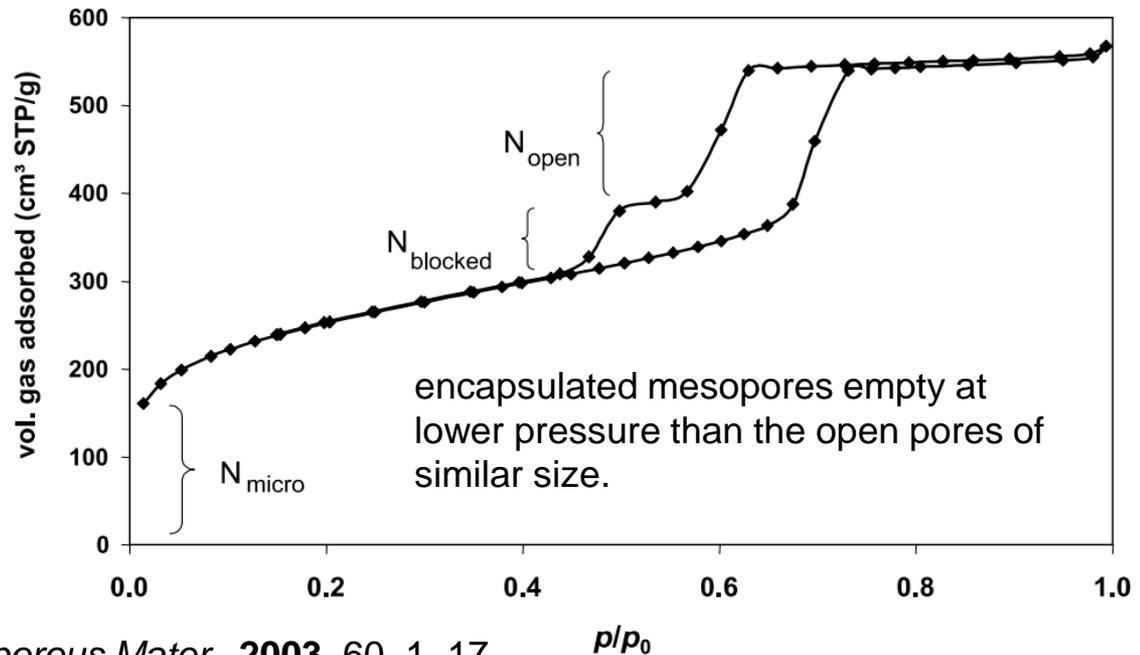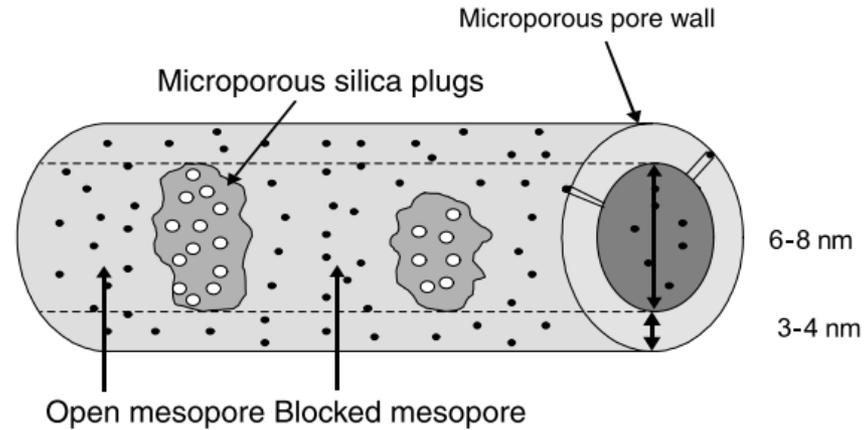
Pore sizes and adsorption

N₂ adsorption

MCM 41 (2nm)

MCM 41 (3nm)

H1 loop

SBA 15 (8nm)

MCM 41

SBA 15 (8nm)

J.C. Groen et al., *Microporous and Mesoporous Mater.,* **2003**, 60, 1–17
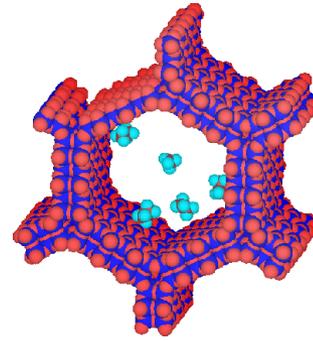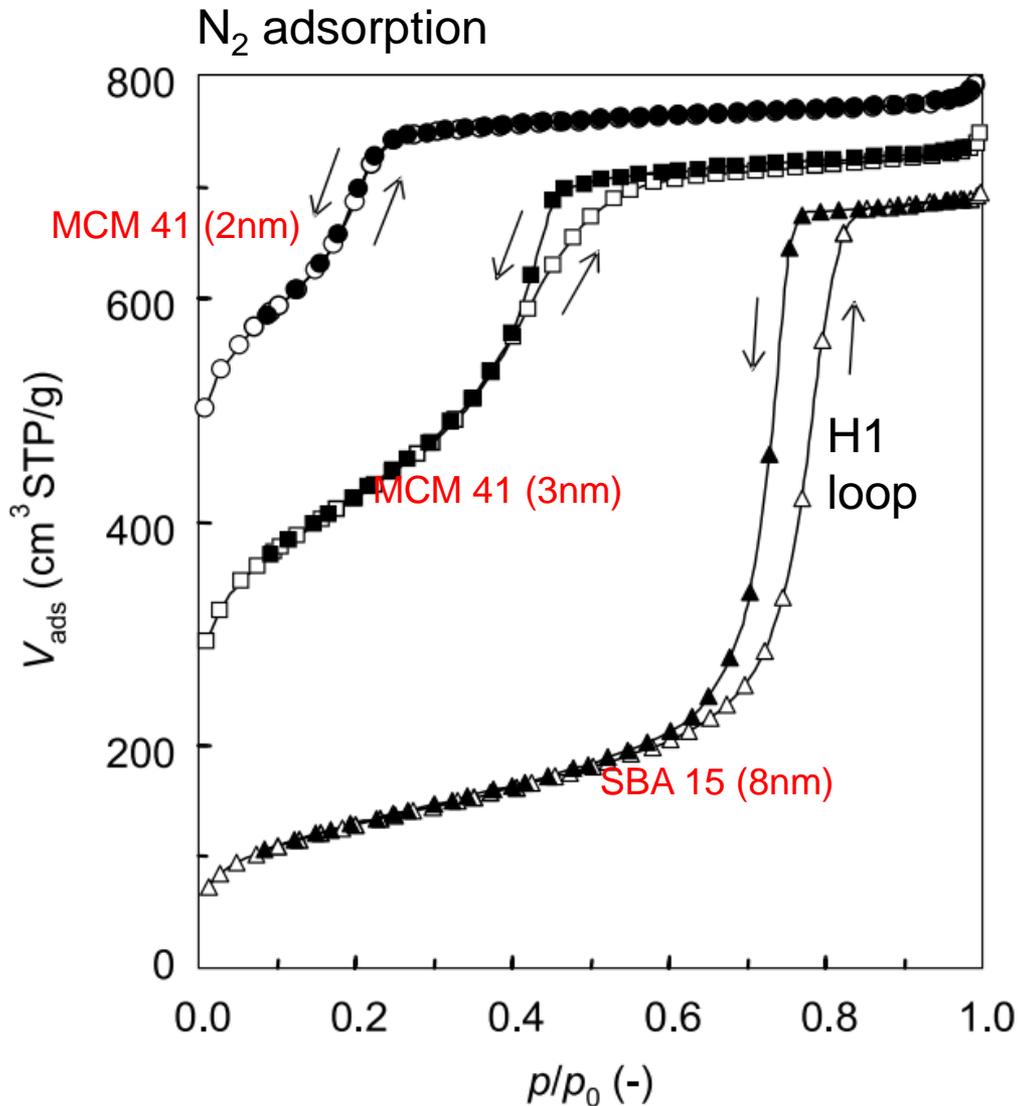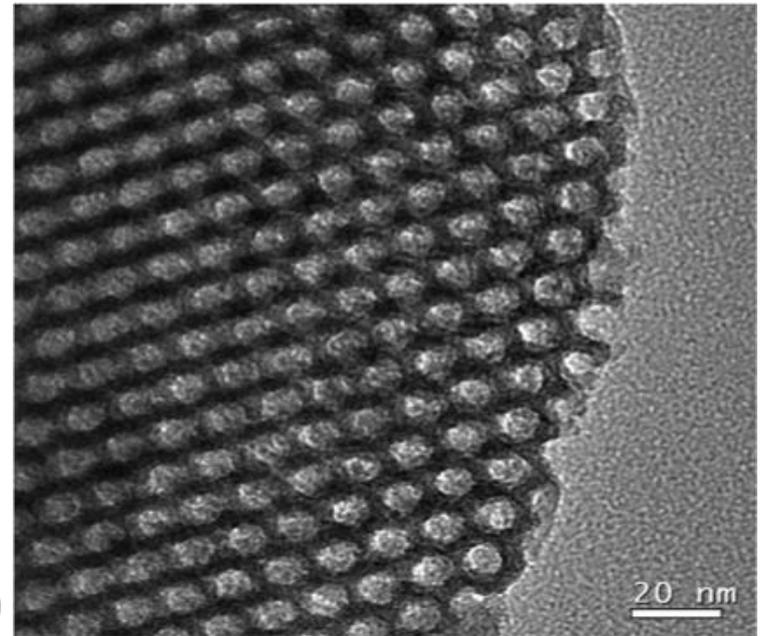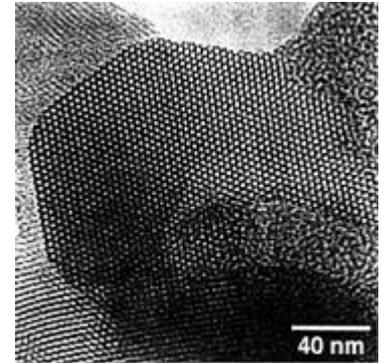
High-resolution N_2 and Ar adsorption isotherms of silicalite-1
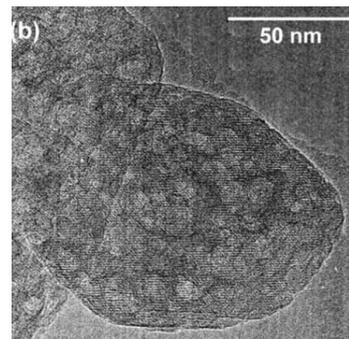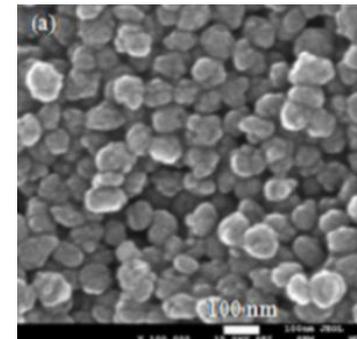
Adsorption (open symbols) and desorption (solid symbols) isotherms at 77 K of alkaline-treated ZSM-5

J.C. Groen et al., *Microporous and Mesoporous Mater.,* **2003**, 60, 1–17

ZSM-5

silicalite-1
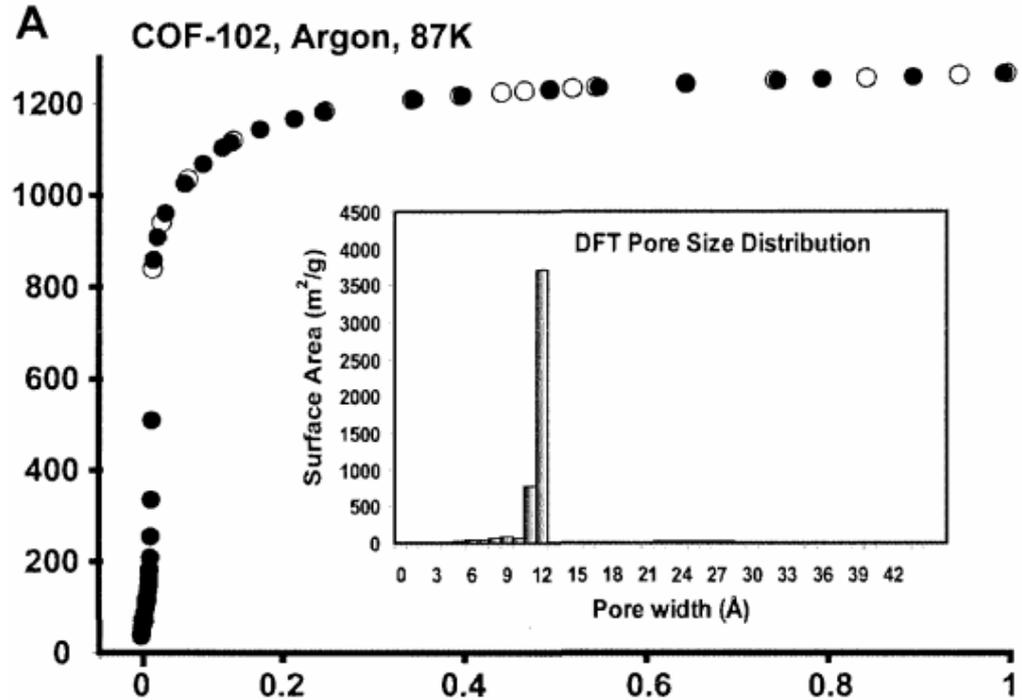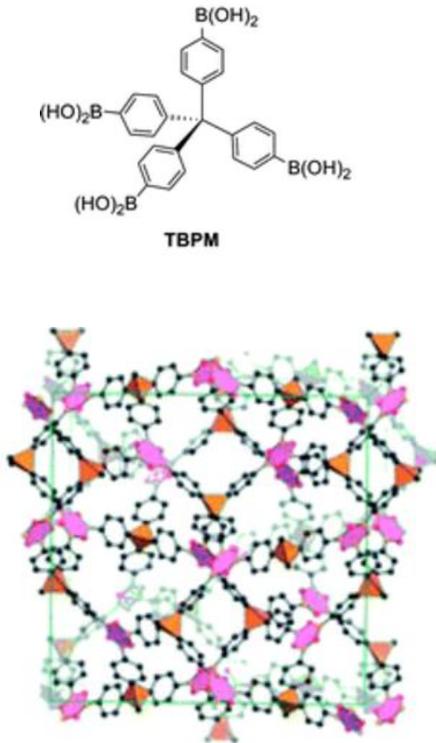
Usually Type I, with very large surface areas

Joseph Ray Hunt, *UCLA PhD thesis*, **2009**
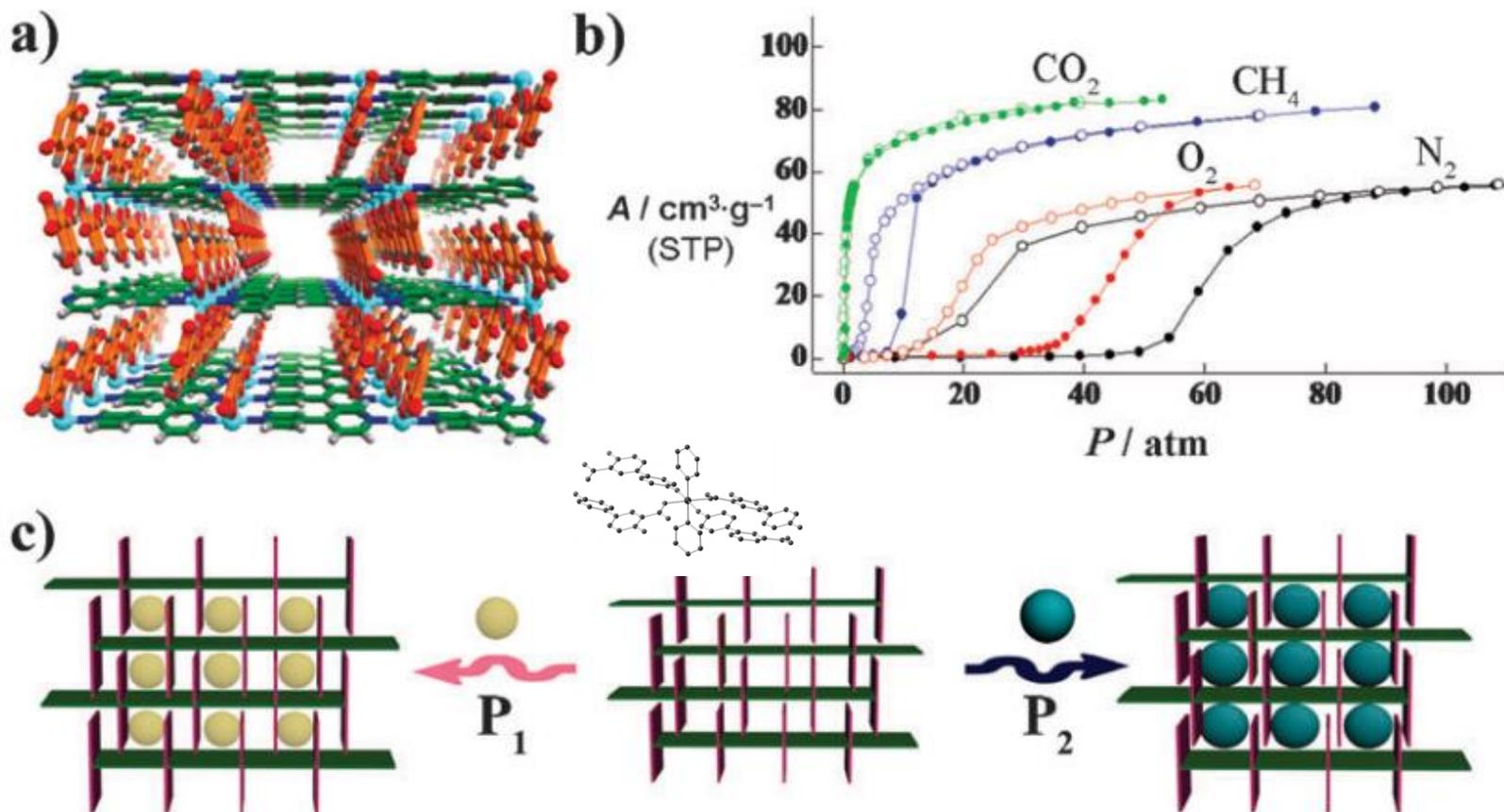
3D π-stacked pillared layer structure of Cu(dhbc)₂(4,4'-bpy). (b) Gas adsorption (filled circles) and desorption (open circles) isotherms at 298 K. (c) Schematic representation of the gas selective adsorptions in the dynamic framework Cu(dhbc)₂(4,4'-bpy) whose gap open size depends on the guest molecules at special pressure.

Kitaura et.al, *Angew. Chem., Int. Ed.,* **2003**, 42, 428–431

- Understanding different types of adsorption isotherms

- Classification of adsorption-desorption hysteresis loops

- Estimating the porous structures based on the shapes of isotherms and hysteresis loops

- Systematical references for future BET measurements

- Q: Why Langmuir surface area > BET surface area for mesoporous Silica while with similar value for COFs?