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A4.4

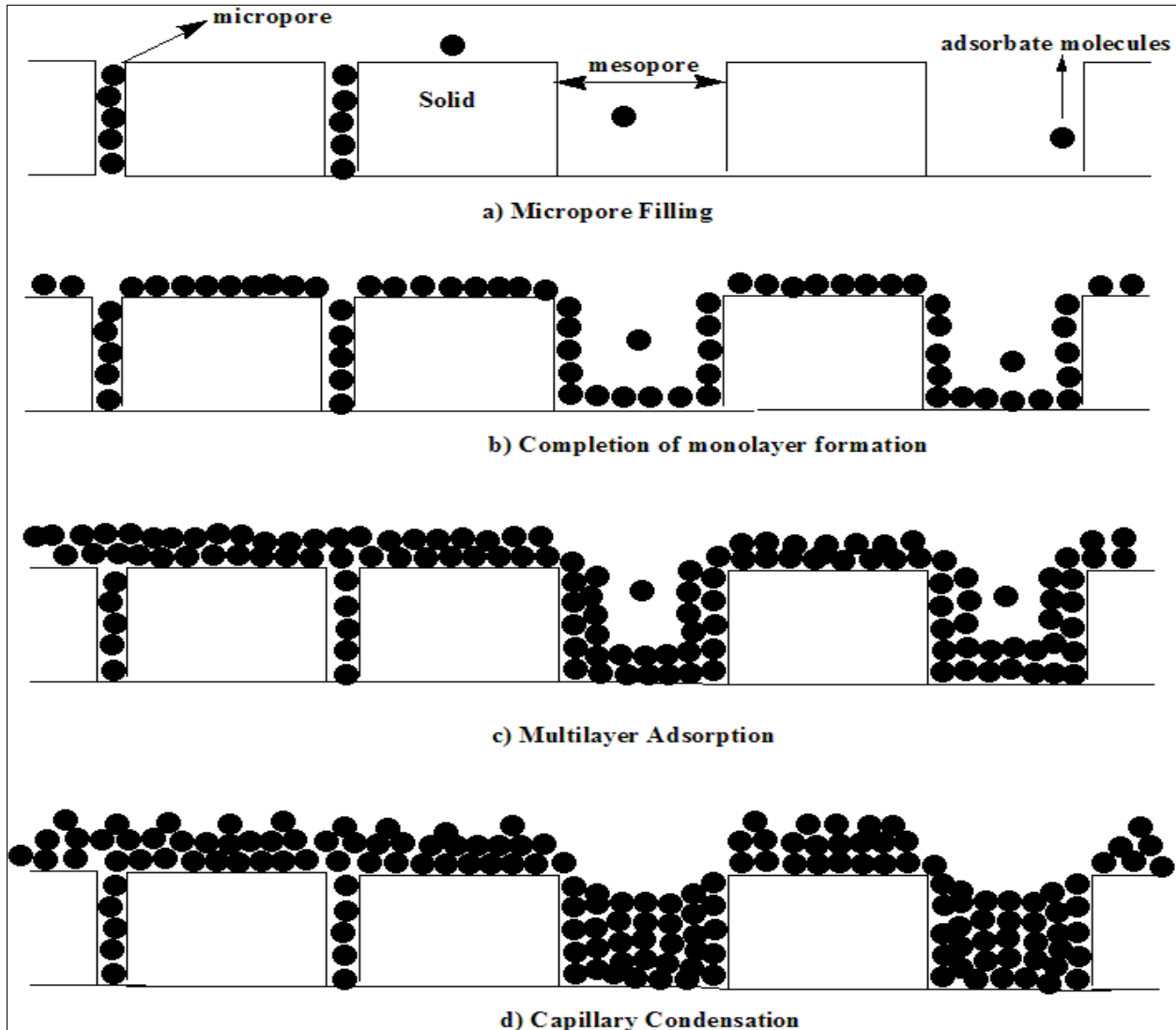


Fig.1: molecules being adsorbed on a porous solid

With increase in pressure, adsorption proceeds as:

- 1) Micropore Filling
- 2) Monolayer Formation
- 3) Multilayer Adsorption
- 4) Capillary condensation taking place in mesopores

Physisorption: is a process in which the electronic structure of the atom or molecule is barely perturbed upon adsorption. When a molecule approaches a surface, the electrons in the particle—due to quantum fluctuations—set up a dipole, which induces an image dipole in the polarizable solid. Since this image dipole has the opposite sign and is correlated with fluctuations in the particle, the resulting force is attractive. This weak bonding (also known as van der Waals force) is the cause for physisorption. In **Fig. 1(a), right hand side**, when a molecule approaches the surface, at a certain distance from surface van der Waals forces are strongest. This helps the molecule to stay near the surface or in other words, get adsorbed.

Chemisorption: is an adsorption process in which an adsorbate is held on the surface of an adsorbent by chemical bond. These bonds are either ionic or covalent, depending on the reactive chemical species involved. Since this type of adsorption involves bond formation, it is characterized by monolayer formation. If only chemisorption would have been taking place, the process in figure 1 would have stopped after **1(b)** i.e monolayer formation.

a) Yes, molecules undergo chemisorptions only until a monolayer is formed because it involves formation of chemical bonds between the adsorbate and adsorbent.

b) It is not possible to predict number of layers adsorbed directly. It depends on factors like temperature, pressure, nature of adsorbent and adsorbate.

For type II adsorption isotherms Kuratov et al proposed a way to determine number of layers using t_δ -method.

For that we need to obtain the adsorption value (a) in the multi-layer filling experimentally. This multi-layer filling area lies in a certain range of relative pressure (x)

And that range is given by $0.5 < x < 0.8$.

$$n = \frac{\ln\left(1 - \frac{a_m t_\delta}{a}\right)}{\ln x}$$

Where n = no. of layers

a = adsorption value

x = relative pressure

a_m = monolayer capacity

$$t_\delta = \frac{35x}{(1-x)(1-x+35x)}$$

= for multilayer adsorption in range $0 < x < 0.8$

References:

- 1) Oura, K.; V.G. Lifshits; A.A. Saranin; A.V. Zotov; M. Katayama (2003). *Surface Science, An Introduction*. Berlin: Springer

- 2) V.V.Kutarov, E.Robens and B.M.Kats; *Journal of Thermal Analysis and Calorimetry*, Vol.86(2006)1, 35–38
 - 3) Pickett, G. , *J. Amer. Chem. Soc.*, 67, 1958
 - 4) I. Chorkendorff, J.W. Niemantsverdriet (2003). *Concepts of Modern Catalysis and Kinetics*. Weinheim: WILEY VCH
 - 5) Rolando M.A. Roque-Malherbe (2007). *Adsorption and Diffusion in Nanoporous Materials* .Boca Raton: CRC Press
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A.4.6 One gram of Alumex has

$$\text{Surface Area} = 500 \text{ m}^2 = 5 \times 10^{20} \text{ nm}^2; \quad \text{Volume} = 0.4 \text{ mL}$$

a) Calculating Weight of Ni(NO₃)₂ required:

$$\text{Loading} = 2 \text{ Ni atoms/ nm}^2$$

For 1 gm of Alumex

$$\begin{aligned} \text{Total Ni atoms required} &= \text{Loading} \times \text{Surface Area} \\ &= 10^{21} \end{aligned}$$

$$\begin{aligned} \text{Moles of Ni required} &= \text{Total atoms/ Avogadro's number} \\ &= 10^{21}/6.022 \times 10^{23} = 1.66 \times 10^{-3} \end{aligned}$$

$$\text{Moles of Ni(NO}_3)_2 = 1.66 \times 10^{-3}$$

$$\begin{aligned} \text{Weight of Ni(NO}_3)_2 \text{ required} &= \text{Mol. Wt} \times \text{moles} \\ &= 182.7 \times 1.66 \times 10^{-3} = 0.303 \text{ gm} \end{aligned}$$

Since, 1 gm of Alumex requires 0.303 gm of Ni(NO₃)₂

Total weight of catalyst formed = 1.303

For 5 gm of catalyst

$$\begin{aligned} \text{Alumex required} &= (1/1.303) \times 5 \\ &= 3.83 \text{ gm} \end{aligned}$$

$$\begin{aligned} \text{Ni(NO}_3)_2 \text{ required} &= (0.303/ 1.303) \times 5 \\ &= 1.16 \text{ gm} \end{aligned}$$

Calculating No. of impregnation cycles:

0.3 gm of Ni(NO₃)₂ dissolves in 1 gm of water

$$\begin{aligned} \text{Water required for 1.16 gm} &= (1/0.3) \times 1.16 \\ &= 3.86 \text{ gm} \end{aligned}$$

$$\text{Density of water} = 1 \text{ gm/mL}$$

$$\text{Volume of water required} = 3.86 \text{ mL}$$

$$\begin{aligned} \text{Pore volume of Alumex} &= 0.4 \times 3.83 \\ &= 1.53 \text{ mL} \end{aligned}$$

$$\begin{aligned} \text{Volume available for impregnation} &= 0.9 \times 1.53 \\ &= 1.377 \text{ mL} \end{aligned}$$

$$\begin{aligned} \text{No. of impregnation cycles} &= \text{Total volume/ Volume available per impregnation} \\ &= 3.86/ 1.377 = 2.803 \end{aligned}$$

Approx no. of impregnation cycles required = 3

b) Calculating Weight of Copper phthalocyanine :

Loading = 2 Cu atoms/ nm²
For 1 gm of Alumex
Total Cu atoms required = 10²¹
Moles of Cu required = Total atoms/ Avogadro's number
= 10²¹/6.022 x 10²³ = 1.66 x 10⁻³
Moles of copper phthalocyanine = 1.66 x 10⁻³
Weight of copper phthalocyanine required = Mol. Wt x moles
= 576.08 x 1.66 x 10⁻³ = 0.956 gm
Since, 1 gm of Alumex requires 0.956 gm of copper phthalocyanine
Total weight of catalyst formed = 1.956
For 5 gm of catalyst
Alumex required = (1/1.956) x 5 = 2.55 gm
Copper phthalocyanine required = (0.956/ 1.956) x 5
= 2.45 gm

Calculating No. of impregnation cycles:

0.002 gm of copper phthalocyanine dissolves in 1 gm of water

Water required for 2.45 gm = (1/0.002) x 2.45
= 1225 gm

Volume of water required = 1225 mL

Pore volume of 2.55 gm Alumex = 0.4 x 2.55
= 1.02 mL

Volume available for impregnation = 0.9 x 1.02 = 0.918

No. of impregnation cycles = Total volume/ Volume available per impregnation
= 1225 / 0.918 = 1334.4

Approx no. of impregnation cycles required = 1335

NOTE : Pore Diameter = 6.0 A and typical C-C bond length = 1.54 A

Copper phthalocyanine side length = 12 A [1]

It would be impossible for copper phthalocyanine molecule to enter pore and get adsorbed. **The dimensions of adsorbate must be small compared to the pore diameter. Thus copper phthalocyanine is not a suitable precursor for making Cu/ Alumex catalyst.** Also, the number of impregnation cycles required in case of copper phthalocyanine is large as compared to case to Ni(NO₃)₂.

Reference:

1) M.Moors, A.Krupski, S.Degen, M.Kralj, C.Becker, K.Wandelt; Applied Surface Science 254(2008) 4251–4257