Lecture 7

Pore analysis

In general, catalyst consists of pore in the range of, micropore, mesopore or macropore depending on the preparation conditions and compositions. To determine the pore size distribution within the catalyst, pore analysis is essential. Knowing the pore size distribution gives an idea about accessibility of the reactants to the active sites. The pore analysis consist of determining the average pore size, average pore volume and pore size or pore volume distribution.

Total pore volume and average pore size

Total pore volume is defined as the liquid nitrogen volume at a certain p/p_o (=0.95).Total gas adsorbed at certain p/p_o (=0.95) is converted to liquid volume assuming pores are filled with liquid adsorbate

$$V_p = V_{liq} = \frac{V_{gas}(STP)}{22.4 \times 10^3} \times 34.6 = V_{gas} \times 1.54 \times 10^{-3} \text{ cm}^3$$

where, **34.6** $cm^3/mol =$ **molar volume of liquid nitrogen**

Average pore size can be estimated from the pore volume. Assuming cylindrical pore geometry average pore radius (**r**) can be expressed as: $r = \frac{2V_p}{S}$

Pore size

(a) By gas adsorption

Pore size and pore size distribution can be determined using Kelvin equation. Kelvin equation relates equilibrium vapor pressure (**p**) of a liquid contained in a capillary to equilibrium pressure of the same liquid over a free surface (**p_o**) :

$$\ln \frac{p}{p_o} = \frac{-2\gamma V_{liq} \cos \theta}{rRT} \text{ -------------------- (1)}$$

$\gamma =$ surface tension of liquid nitrogen
$\theta =$ contact angle (usually zero for liquid N_2)
$V_{liq} =$ the molar volume of liquid nitrogen
r = radius of pore
R = gas constant

At any equilibrium pressure, **p**, the pore of radius less than '**r'** will be filled with the condensed vapor. Application of Kelvin equation to all points of an isotherm at relative pressure greater than that corresponding to monolayer volume where capillary condensation begins to occur, will yield information concerning the volume of gas adsorbed in pores of different radii. For nitrogen as adsorbate and substituting values of various constants, the Kelvin equation can be written as

$$\ln \frac{P}{P_o} = \frac{-2\gamma V_{liq} \cos\theta}{rRT}$$

Or $r_k\,(nm) = 0.41\ \log \dfrac{p}{p_0}$ (2)

$\gamma = 8.72$ mN/m

$\theta = 0$

$V_{liq} = 34.68 \times 10^{-6}$ m^3 / mol

$T = 77\ K$

R=8.314 $J / K\ mol$

The '**r$_k$**' is the radius into which condensation occurs at the required relative pressure. This radius is called Kelvin radius. However, Kelvin radius is not the actual pore radius since some adsorption has already occurred on the pore wall prior to condensation leaving a central core of radius **r$_k$** . Conversely, an adsorbed film remains on the wall when evaporation of the centre core takes place.
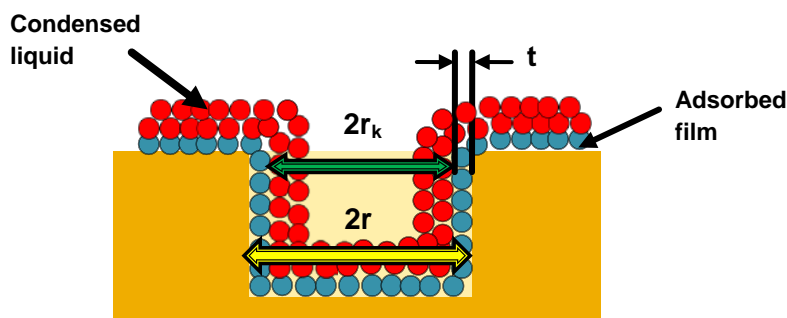

Fig. 3. Schematic showing Kelvin radius and actual pore radius during pore condensation

Then if '**r**' is the actual pore radius and the thickness of the adsorbed film is t (Fig. 3) then

$$r\ (nm) = r_k + t = \frac{2\gamma V_{liq}}{RT \ln \frac{p}{p_o}} + t = 0.41\ \log \frac{p}{p_0} + t \tag{3}$$

Pore size distribution can be obtained by the analysis of either adsorption or desorption isotherm branches. Kelvin equation as described is applied to the desorption branch of hysteresis loop as it is more appropriate to assign wetting angle to a pore filled with liquid that possess a well defined meniscus. If '**h**' is the effective height of a monolayer, then the thickness of adsorbed layer '**t**' is given as $t = \left(\frac{V}{V_m}\right)h$. Here 'V' is the volume of gas adsorbed and 'V_m' is the volume of adsorbed monolayer. When the packing of adsorbate is hexagonal, then for nitrogen h = 3.6 A^0 and for cubic packing h= 4.3 A^0 = 0.43 nm. The '**t**' at a given relative pressure can also be calculated using Halsey equation

$$t = 3.54 \times \left[\frac{5}{2.303 \times \log \frac{p_0}{p}}\right]^{\frac{1}{3}} (\overset{o}{A}) = 0.354 \times \left[\frac{5}{2.303 \times \log \frac{p_0}{p}}\right]^{\frac{1}{3}} nm \tag{4}$$

Pore size distribution

Most common method for determination of pore size distribution is BJH (Barrett-Joyner-Halenda) method. Assumptions are:

(i) Condensation occurs in pores when a critical relative pressure is reached corresponding to the Kelvin radius 'r_k'

(ii) When evaporation or condensation occurs, a multilayer of adsorbed film exist on the pore wall and this film has same depth/thickness as the adsorbed film on a non porous surface

(iii) Actual pore volume evaporation is composed of the volume evaporated out of the central core plus the volume desorbed from the film left on the pore walls

Steps for determination of pore size distribution are as follows:

1. p/p_0 and V_{gas} (STP, cm^3/g) data obtained directly from isotherm.
2. Then Kelvin radius 'r_k' is calculated from Kelvin equation using zero wetting angle for N_2 from equation(2).
3. Then, the film thickness t calculated from Halsey equation (4) at each p/p_0.
4. Then the pore radius r calculated from equation (3).
5. Mean values of r_k and r in each decrement are calculated from successive entries.
6. Change in film thickness Δt is calculated from difference of successive values of t .
7. Then ΔV_{gas} , that is the change in adsorbed volume between successive p/p_o values, is determined by subtracting successive values .
8. Thereafter, ΔV_{liq} that is the volume of liquid corresponding to ΔV_{gas} is calculated as follows

$$\Delta V_{liq} = \frac{\Delta V_{gas}}{22.4 \times 10^3} \times 34.6 = \Delta V_{gas} \times 1.54 \times 10^{-3} \ \text{cm}^3 / g$$

9. Then $\Delta t \Sigma S$ is determined. This represents the volume change of the adsorbed film remaining on the walls of the pores from which the central core has previously evaporated . This volume is the product of the film area $\sum S$ and the decrease in film depth Δt

10. Actual pore volume evaporated, V_p. is then determined. Actual pore volume evaporated is composed of the volume evaporated out of the centre core plus the volume desorbed from the film left on the pore walls, For a pore of length L,
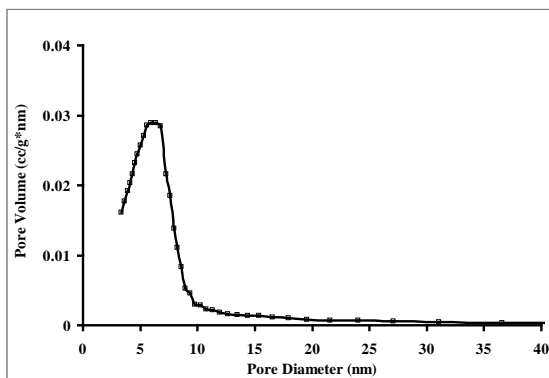
$$\Delta V_{liq} = \pi r_k^2 L + \Delta t \Sigma S$$

Now , $V_p = \pi r^2 L$. By combining $V_p = \left[\dfrac{\bar{r}}{\bar{r_k}} \right]^2 \left[\Delta V_{liq} - \left(\Delta t \Sigma S \times 10^{-4} \right) \right] \ \text{cm}^3 / g$

11. The surface area of the pores walls can be calculated from pore volume by :

$$S = \frac{2V_p}{\bar{r}} \times 10^4 \quad m^2, \; V_p \text{ in cm}^3/\text{g and } r \text{ in A}^0$$

An elaborate example of pore size distribution work table can be seen in Lowell et al. for more understanding.
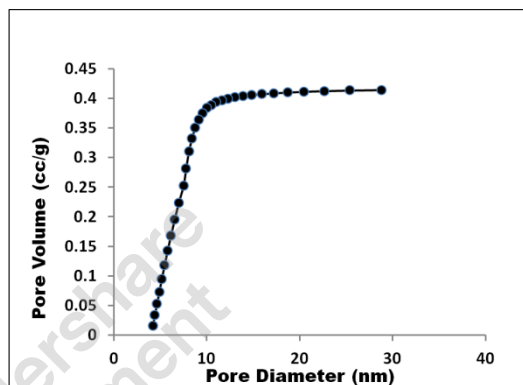
(a)   **(b)**

Fig. 4. Pore volume distribution of titania samples calcined at 400 ^{0}C

(a) differential (b) cumulative

Pore size distribution can be represented both in differential and cumulative ways. The Fig. 4(a) shows the differential BJH pore distribution of titania sample calcined at 400 ^{0}C. The figure shows that for the given sample pores were in the range of 2-10 nm. The corresponding cumulative pore distribution is shown in Fig. 4(b).
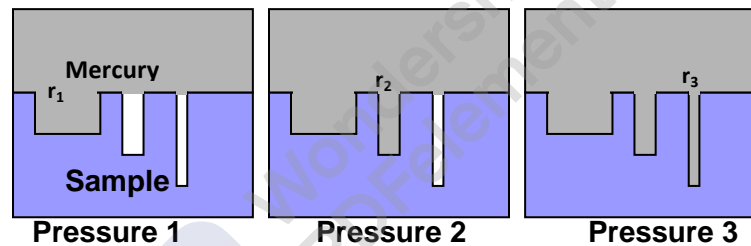
(b) By mercury intrusion

For macropores materials with pore diameter greater than 50 nm, the mercury intrusion method is preferred. Due to non-wetting nature of mercury on oxide supports, intrusion is met with resistance and mercury is forced to enter the pores of material under pressure. The pore radius 'r' is related to the applied pressure P as

$$P = \frac{(-2\gamma \cos \theta)}{r} \text{----------------(5)}$$

The wetting or contact θ angle between mercury and solid is on average lies in the range 130-140^0 and surface tension of mercury is 0.48 N/m^2. **p** is in atm and **r** in nanometers.

As can be observed from equation (5) smaller the pore radius higher is the pressure needed for mercury to intrude in the pore. At low pressure of 0-2 atm, mercury penetrates voids between particles. At moderate pressure range of 3-500 atm large macro pores are filled. At further higher pressure range of 500-2000 atm, smaller macro pores and large mesopores are progressively filled. This technique is satisfactory for pores down to 3-5 nm dia . Maximum diameter that can be measured is usually 10^5 nm. Mercury intrusion method is carried out in the instrument known as mercury porosimeter. In a typical mercury porosimeter data, volume of mercury penetrating into pores is plotted as a function of applied pressures.

Pressure 1< Pressure 2 < Pressure 3 as **r$_1$ > r$_2$ > r$_3$**

Fig. 5. Intrusion of mercury into pores of various sizes. Here 'r' represents the radius of pores.

The pressure required for filling up the pores as a function of pore size is schematically shown in Fig.5. As pore radius decreases in the order r$_1$ > r$_2$ > r$_3$, requried pressure for filling the pores increases in order of Pressure 1< Pressure 2 < Pressure 3.The available instruments can measure pore size up to 2 nm using a maximum operating pressure of about 400 MPa.

Table 1. Typical pore volume values of different support and catalyst.

Support/catalyst	Pore volume cm^3/g	Application
Activated carbon	0.6-0.8	Used as support for various process
Zeolites	0.5-0.8	Used as catalyst and support
Al_2O_3-SiO_2-Zeolites	0.1-0.9	Fluid catalytic cracking catalysts