

SOLID CATALYSTS AND ITS CHARACTERISATIONS

Catalysts

- ❖ Speed up the reaction
- ❖ Lower activation energy
- ❖ Cost saving for industrial processes

Fundamental Properties required to a catalyst

- Activity
- Selectivity
- Stability
- Morphology
- Mechanical Strength
- Thermal Properties
- Regenerability
- Originality
- Cost

Activity

High activity of a catalyst defines as:

High productivity

✓ from a smaller reactor

or

✓ at milder reaction condition

Selectivity

High selectivity

- ✓ High yield of desired product
- ✓ Suppression of undesired reactions
- ✓ Reduction of internal diffusion to mass transfer

Stability

Good stability of a catalyst:

- ✓ Stability should change very slowly with the course of reaction and regeneration

Causes to change activity, selectivity and stability of a catalyst

- Coke forms on catalysts in different reactions such as cracking, hydrogenolysis, polymerization, cyclisation etc.
- Reactants, products or poisons may attack active agents or the support.
- The crystals of a deposited metal may become enlarged or regrouped.
- A change in the crystalline structure of the support can cause a loss of mechanical strength.
- Progressive adsorption of trace poisons in the feed or products may reduce activity.

Morphology

External morphological characteristics of a catalyst must be suited to the process

- Moving bed: Spherical form
- Fluidised bed: Spherical powder
- Fixed bed: Beads, rings, pellets, extrudates, flakes etc. depending on the pressure drop allowed

Shapes of the catalyst and pressure drop in reactor

Ascending order of relative pressure drop in reactor
for different catalyst forms

Rings< Beads< Pelletes< Extrudates< Crushed

Mechanical Strength

Mechanical strength of a catalyst is defined by the resistance to :

- Crushing (to sustain from compressive strength)
- Attrition (wearing out of the particle from solid surface by touching of another solid)
- Abrasion (wearing out by rubbing or friction)
- Erosion (wearing by contact with fluids)

Thermal Characteristics

High Thermal conductivity & Specific heat of catalyst cause:

- Reduced temperature gradient within grains as well as catalyst bed
- Improvement in heat transfer for exothermic or endothermic reactions

Regenarability

- All the catalysts age during the process
- Regeneration is done when the properties of the catalyst is insufficient for the process
- Suitable treatment to gain the part or all of the catalytic properties (activity, selectivity etc.)
- Must preserve the mechanical strength also during regeneration

Originality

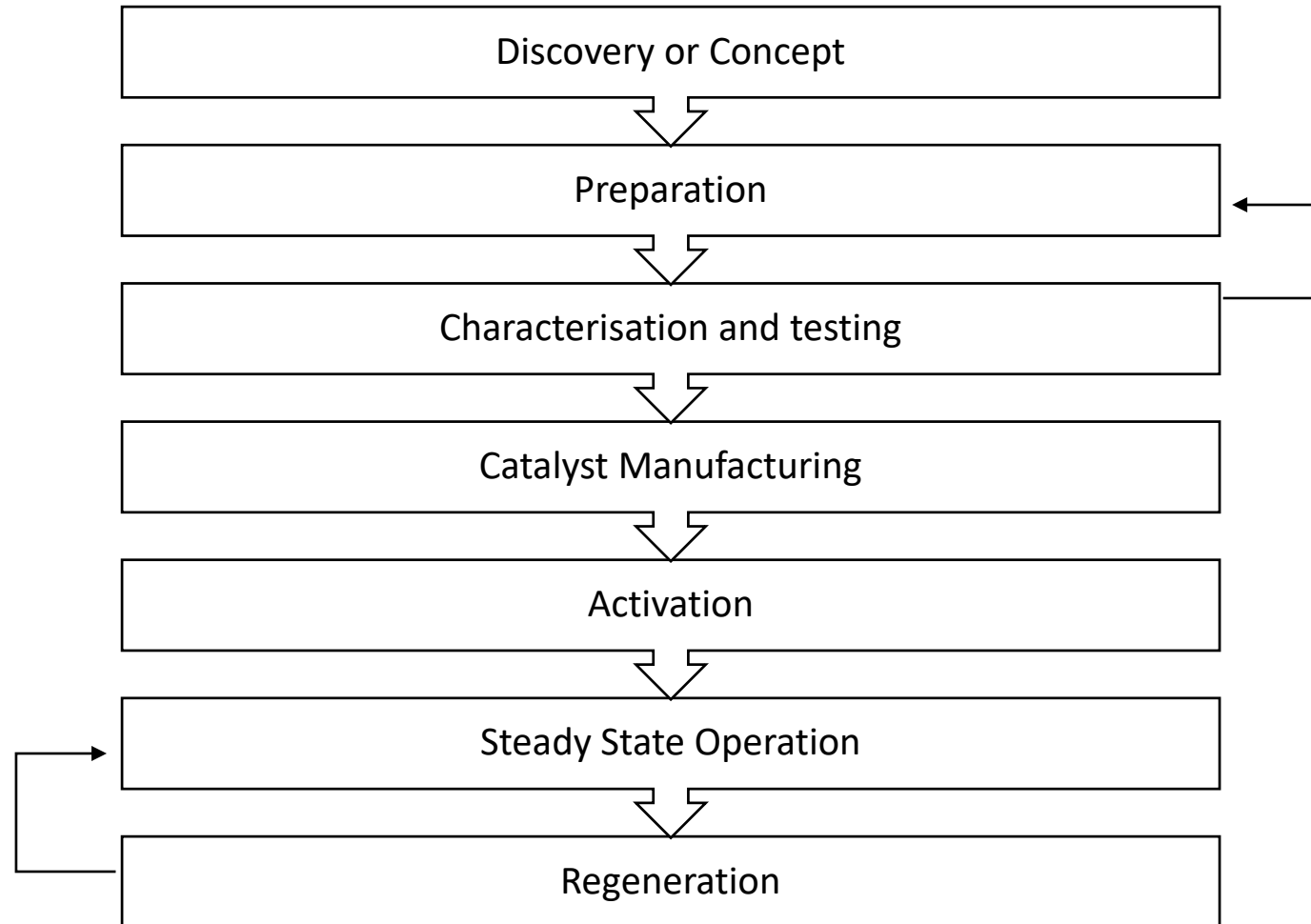
Catalysts and process should be licensed

- Either catalyst is original
- Or, if obtained from public domain, should be used legally

Cost

- Catalysts must be cheap compared to the competitive catalysts
- Should not pose heavy burden on the process economics

Catalyst Development Steps



Beginning of developmental process

- Discovery of a new material with attractive catalytic properties
- Adaptation of an existing catalyst to a new reaction

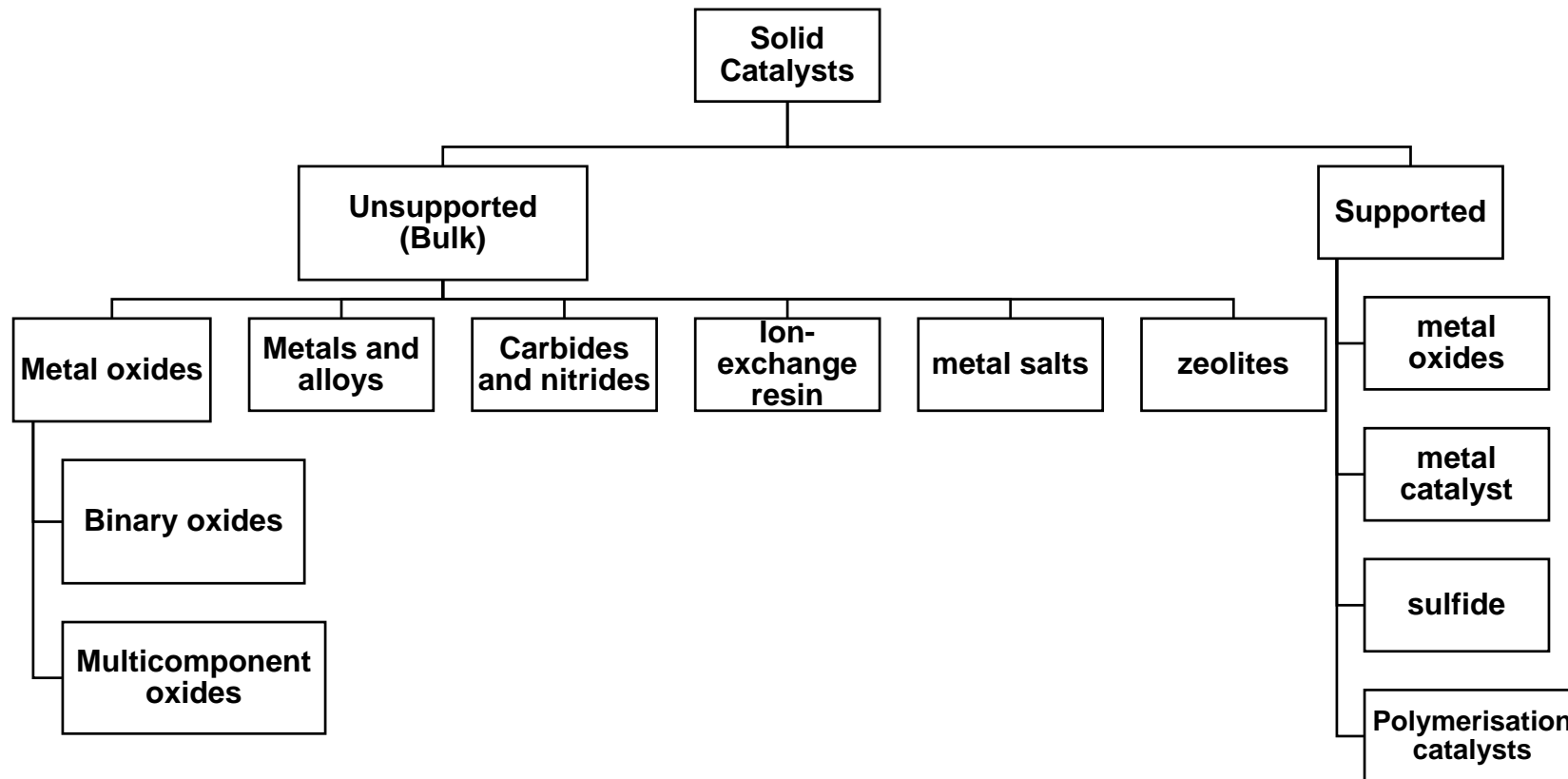
Features of Catalyst Manufacture

Catalyst is a chemical product characterised by its composition and method of preparation

Operations used in manufacturing:

Precipitation, Impregnation, Ripening, Filtration,
Washing, Drying, Calcination, Activation

Types of Heterogeneous Catalysts



Synthesis of Catalysts

Sl. No.	Goal	Possible approach	Example
1	High activity per unit weight of active component	Disperse active component on a high surface area support	V_2O_5/TiO_2 for oxidation
2	Increased particle Strength	Add stable inorganic matrix	FCC Catalysts
3	Increased pellet porosity	Add burnouts	--
4	Decreased reactor pressure drop	Use monolithic supports	Catalytic converters
5	Increased thermostability of supported Catalysts	Enhance chemical bonding between support and active phase	Add K^+ to reforming Catalyst
6	Modified reactant binding to catalyst surface	Add promoters specific for the target molecule	Ni/Co to Mo/Al_2O_3 for hydrodesulfurization of fuel
7	Increased activity or selectivity	Many approaches, depending on reaction and catalyst	Shape selective molecular sieves

Bulk Catalysts

Comprise of active substances (may or may not need any inert binder)

✓ Bulk catalysts without binder:

High temperature fusion (iron catalyst for ammonia synthesis)

✓ Bulk catalysts with binder:

Depends on the strength required under reaction condition and reactor type (pelletizing)

Supported Catalysts

Reasons for preparation:

- For obtaining bifunctional catalyst
- High dispersion of active phase
- Better diffusion of gases through the bed
- Better mechanical resistance to attrition
- Better thermal conductivity
- Improved catalytic properties by active phase-support interaction

Catalyst Supports, Promoters and Inhibitors

➤ Carrier/Support

Early notion about support

- ✓ The supports were assumed to be inert
- ✓ Only a means of spreading of an expensive active material
- ✓ To give mechanical strength to the catalyst
- ✓ No attention was paid to the influence of support on catalyst behaviour.

Contd...

Newer aspects of catalyst support

- ✓ Average pore size and pore size distribution should be such that physical limitations are not placed on the conversion
- ✓ Supports may have low/high surface area
- ✓ Low surface area supports are used where high activity per unit mass is less important
- ✓ Low surface area supports are considered when cost is one of the major factors.

Contd...

➤ Promoters

Imparts improved characteristics to the catalyst (better activity, selectivity or stability)

Action of promoters

- The promoters may change the electronic structure of the solid in such a way that the activity per unit area is increased.
- The promoter may catalyze an intermediate step in the reaction.
- The promoter may slow down or otherwise influence crystal formation and growth or produce lattice defects. These effects may lead either to a higher activity per unit area or to a higher specific surface area.

Contd...

➤ Inhibitors

- ✓ Inhibitors are a type of promoters who may influence the selectivity by poisoning undesired reactions.
- ✓ Example is: Addition of halogen compounds to the catalyst used for oxidation of ethylene to ethylene oxide ($\text{Ag/ Al}_2\text{O}_3$). Halogens prevent complete oxidation of ethylene to CO_2 and H_2O , thus permitting the use of the catalyst for industrial purpose.

Contd...

➤ Stabilizers

- ✓ Inhibits the loss of active surface area during operation
- ✓ Inhibits the sintering of active sites
- ✓ Inhibits the growth of microcrystalline regions
- ✓ These actions as a whole enhance the catalyst stability

Catalyst Characterisation

- Surface area
- Void Volume
- Solid Density
- Pore size
- Pore Volume Distribution

Surface Characterisation

- It is difficult to obtain surface area more than $1 \text{ m}^2/\text{g}$ of a non porous material
- To be effective, the catalyst should have surface area in the range of $5\text{-}1000 \text{ m}^2/\text{g}$
- For highly porous catalysts the global rate of reaction is dependent on the geometrical properties of catalyst pores
- Surface area has pronounced effect on the amount of gas adsorbed on the catalyst

Contd..

- Rate of adsorption of gas is dependent on the internal pore surface
- More the rate of adsorption, more will be the rate of chemical reaction
- Heat and mass transfer effects on the reaction rate is dependent on the internal pore geometry (distribution of void spaces within the catalyst)

Determination of Surface Area

- Standard method for measuring surface area is based on the physical adsorption of a gas
- Usually amount of N_2 adsorbed on solid surface is measured at its normal b.p ($-195.8^{\circ}C$) over a range of pressures below 1 atm
- In order to determine surface area of solid, monolayer adsorption should be identified

BET Surface Area

- Brunauer-Emmett and Teller (BET) method is the pioneer
- The method is standard and reproducible
- Nitrogen is physically adsorbed on the solid surface
- It is difficult to find out actual catalytic area by BET method

Classical BET Method

- ✓ Measuring the volume of gas adsorbed on a sample of solid
- ✓ Operating temperature is normal b.p of N_2 ($-195.8^{\circ}C$)
- ✓ Operating pressure may vary from 0-1 atm
- ✓ The data obtained are a series of gas volumes at different pressures and at a particular temperature

Contd...

- ✓ The volumes obtained are corrected to cm^3 at 0°C and 1 atm (STP)
- ✓ Plot is made by the volumes against pressure to vapour pressure

BET-Flow Method

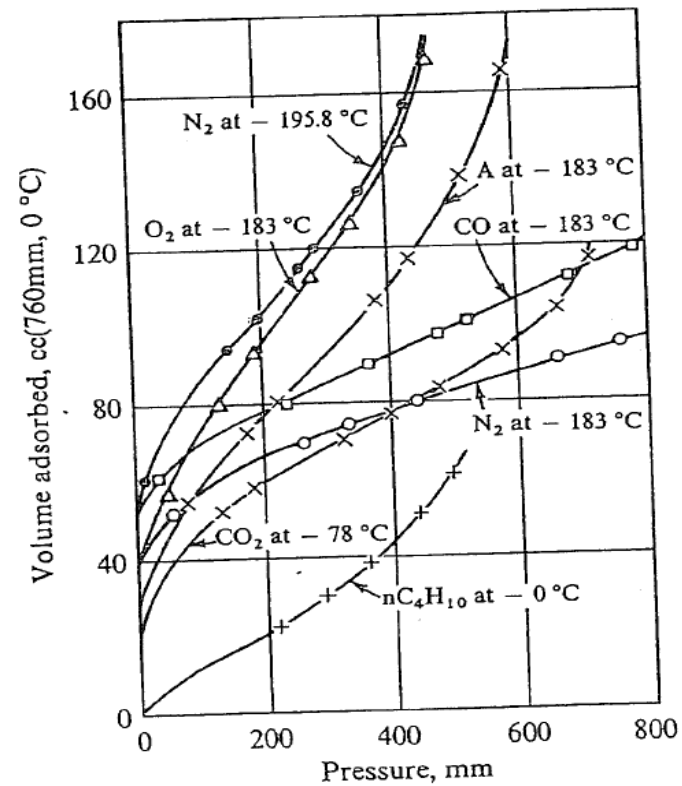
❑ Simplification of classical BET method

- Mixture of non-adsorbable gas (He) and adsorbable gas (N_2) is passed over the solid
- The partial pressure of the adsorbable gas is varied keeping total pressure constant
- The adsorption is done until equilibrium is reached at a particular partial pressure.
- The adsorbed gas is desorbed by heating the sample
- The desorbed volume is collected by passing He on it

Contd....

- The volume desorbed is measured by a thermal conductivity cell or other detector
- This volume gives a single point on the isotherm
- This process can be repeated at successive partial pressures (different compositions of gases)
- Volumes at different pressures construct the isotherm

Langmuir Isotherm



Langmuir Plot for Different gases

Langmuir Isotherm

- Isotherm equation (for monolayer adsorption)

$$\frac{kp}{1 + kp} = \frac{v}{v_m}$$

$$\frac{p}{v} = \frac{1}{kv_m} + \frac{p}{v_m}$$

Where,

$K = \frac{k}{k'}$ = adsorption equilibrium constant,
 v = volume of gas adsorbed at any time,
 v_m = monomolecular layer volume,
 p = pressure of the gas (or concentration)

BET Equation

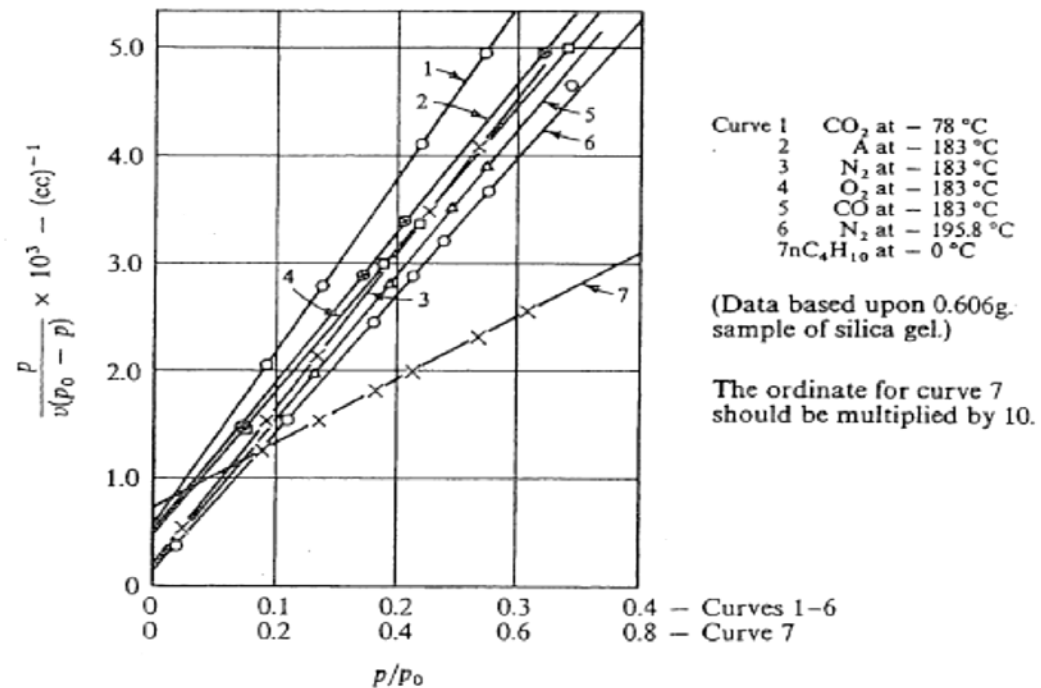
- BET Equation (For multilayer adsorption)

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m C} + \frac{(C - 1)p}{C v_m p_0}$$

Where p_0 is the saturation or vapor pressure and C is a constant for the particular temperature and gas-solid system

BET Plot

A plot of $\frac{p}{v(p_0 - p)}$ vs $\frac{p}{p_0}$ should give a straight line



Contd...

Intercept $I = \frac{1}{v_m c}$ at $\frac{p}{p_0} = 0$

and

Slope $S = \frac{c-1}{v_m c}$

Hence, the monolayer volume is,

$$v_m = \frac{1}{I + S}$$

Contd...

Monomolecular layer volume can be converted to the number of molecules adsorbed

$$S_g = \left[\frac{v_m N_0}{V} \right] \alpha$$

Where N_0 = Avogadro's number, 6.023×10^{23} molecules/mol, V = volume per mole of gas at conditions of v_m and α = the area covered by one adsorbed molecule

Contd...

Considering two dimensional packing of molecules on the surface and α as the projected area of a molecule,

$$\alpha = 1.09 \left[\frac{M}{N_0 \rho} \right]^{2/3}$$

Where M is the molecular weight and ρ is the density of the adsorbed molecules.

- The term in bracket represents the volume of one adsorbed molecule.
- The density is normally taken as that of the pure liquid at the temperature of the adsorption experiment.

Void Volume and Solid Density

Helium-Mercury Method of determination of void volume or pore volume:

- ✓ The volume of helium displaced by a sample of catalyst is measured
- ✓ Then the helium is removed and the volume of mercury that is displaced is measured
- ✓ The volume of helium displaced is a measure of the volume occupied by the solid material
- ✓ From this and the weight of the sample, the density of the solid phase ρ_s , can be obtained

EXPLANATION

The diagram illustrates the measurement of catalyst pellet volume using two different liquids: Helium (He) and Mercury (Hg).

Left side (Helium displacement):

- A catalyst pellet (porous) is shown at the top.
- An arrow points down to a container filled with He.
- The pellet is submerged in the He, and the displaced volume is indicated by a dashed line and labeled "He displacement volume".
- Below this, text states: "He enters into the pores leaving the solid part of the pellet. Hence, He displaced is solid volume".

Right side (Mercury displacement):

- An arrow points from the left side to a container filled with Hg.
- The pellet is submerged in the Hg, and the displaced volume is indicated by a dashed line and labeled "Hg displacement volume".
- Below this, text states: "Hg, as a heavy liquid can not enter into the pores of the pellet at atmospheric pressure. Hence, Hg displacement volume is the total volume of the pellet i.e., Pore volume + Solid volume".

Porosity

Void fraction or porosity of the particle ϵ_p

$$\epsilon_p = \frac{\text{void (pore) volume of particle}}{\text{total volume of particle}}$$

$$= \frac{m_p V_g}{m_p V_g + m_p (1/\rho_s)}$$

$$\epsilon_p = \frac{V_g \rho_s}{V_g \rho_s + 1}$$

Where m_p = mass of the particle

V_g = void volume per gram of particles

Contd...

Sample mass divided by the mercury volume gives the density ρ_p of the porous particles.

$$\text{Then, } \varepsilon_p = \frac{\text{Void volume}}{\text{total volume}} = \frac{V_g}{1/\rho_p} = \rho_p V_g$$

Pore System

- Monodisperse pore system

Catalyst particle containing single type of void region (micropore)

- Bidisperse pore system

Catalyst pellet containing two void regions (micro and macropore)

- ✓ Micropore is void space within the particle

- ✓ Macropore is void space between the particles

(Macropore and macroporosity depends on pelleting pressure)

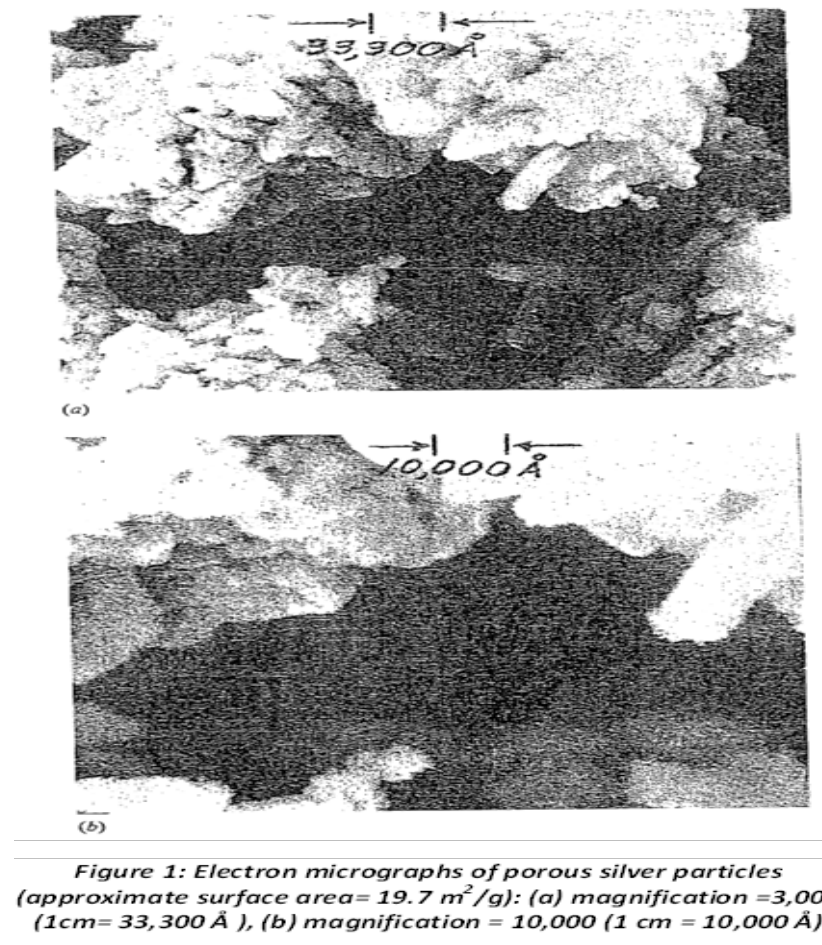
Pore volume distribution

- Distribution of pore volume according to pore size is important parameter
- Pores are non-uniform in size, shape, length and are interconnected to each other
- These characteristics change from catalyst to catalyst
- Hence, it is not possible to find out quantitative description of the void structure

Contd...

- Hence, a simplified pore model is assumed, so that the diffusion rates of reactants through the void space can be evaluated
- Here, the pores are simulated as cylindrical pores with radius 'a'
- Pore radius is variable
- The distribution of void volume is defined in terms of this pore radius

The actual void spaces are far from this assumption



SEM images of porous silver particles at different magnifications

Surface area, pore volume, and mean pore radii for typical solid catalysts

Table

Catalyst	Surface Area, m ² /g	Pore volume, cm ³ /g	Mean pore radius, Å
Activated carbons	500-1,500	0.6-0.8	10-20
Silica gels	200-600	0.4	15-100
SiO-Al ₂ O ₃ cracking catalysts	200-500	0.2-0.7	33-150
Activated clays	150-225	0.4-0.52	100
Activated alumina	175	0.39	45
Celite (Kieselguhr)	4.2	1.1	11,000
Synthesis ammonia Catalysts, Fe	...	0.12	200-1,000
Pumice	0.38
Fused copper	0.23

Determination of Pore Volume

- Mercury penetration method
- Nitrogen adsorption-desorption method
 - Pore sizes in a catalyst may range from 10-10000 Å or more.
 - Hg has a significant surface tension which prevents it to go into most of the pores.

Hence, N₂ is needed at that condition

Contd...

- ✓ The pore volume from the largest pore size down to about 200-100Å can be done with a simple Hg-porosimeter.
- ✓ But high pressure apparatus is needed to find out pore volume of the pore size below 200Å by Hg
- ✓ At this pore size range N₂ adsorption is used to determine pore volume

N₂ adsorption method

- This method is similar to surface area determination
- N₂ adsorption is continued until N₂ pressure approaches the saturation pressure (P_0 , 1 atm at normal b.p)
- At $P/P_0 \rightarrow 1.0$, all the pores are filled up with adsorbed and condensed N₂
- At this condition, a desorption isotherm is established

Contd...

- Desorbed N_2 at each increment is measured
- Vapour pressure of a liquid evaporating from a capillary (cylindrical pore) is proportional to the radius of capillary
- Hence, the volume desorbed can be plotted against pore radius
- This way the pore volume according to the pore radius is measured

Contd...

A combination of N_2 adsorption-desorption and Hg penetration method cover the whole range of pore volume

- ✓ This combination process is necessary for determination of pore volume of a bidisperse catalyst (alumina pellet)
- ✓ For monodisperse catalyst, only N_2 adsorption-desorption process is sufficient (silica gel)

Principle of Hg Penetration Process

It is to equate force due to surface tension of Hg with the applied force

$$\pi a^2 p = -2\pi a \sigma \cos\theta$$
$$a = \frac{-2\sigma \cos\theta}{p}$$

Where, a = pore radius in Å, σ = surface tension of mercury, p = applied pressure, psi, and θ = contact angle between mercury and pore wall.

Taking the value of θ as 140° as a good average,

$$a (\text{Å}) = \frac{8.75 \times 10^5}{p (\text{psi})}$$

Application Example

Example:

The mercury penetration data given in the following table were obtained on a 0.624 g sample of uranium dioxide pellet formed by sintering particles at 1000°C for 2hr. Since the particles were nonporous, the void space was entirely between the particles (that is, in macropores). At the beginning of the experiment (when the pressure was $1.77 \text{ lb/in}^2 \text{ abs}$) the amount of mercury displaced by the sample was found to be 0.190 cm^3 . Calculate the porosity and pore volume distribution of the pellet.

Hg porosimeter data for UO_2 sample

Pressure lb/in ²	Mercury concentration cm ³	Penetration cm ³ /g	ΔV	a (Å)
116	0.002	0.003	0.196	7543
310	0.006	0.010	0.189	2822
344	0.010	0.016	0.183	2543
364	0.014	0.022	0.177	2403
-	-	-	-	-
-	-	-	-	-
-	-	-	-	-
1540	0.118	0.189	0.010	568
1900	0.122	0.196	0.003	460
2320	0.124	0.198	0.001	377
3500	0.125	0.199	0	250

Contd...

- At $p = 1.77$ psi, only pores larger than 500000 \AA will be filled with Hg,

$$a(\text{\AA}) = \frac{8.75 \times 10^5}{1.77} \approx 500000$$

At largest pressure, 3500 psi, the pores just smaller than 250 \AA will remain unfilled

Distribution and Penetration Curves

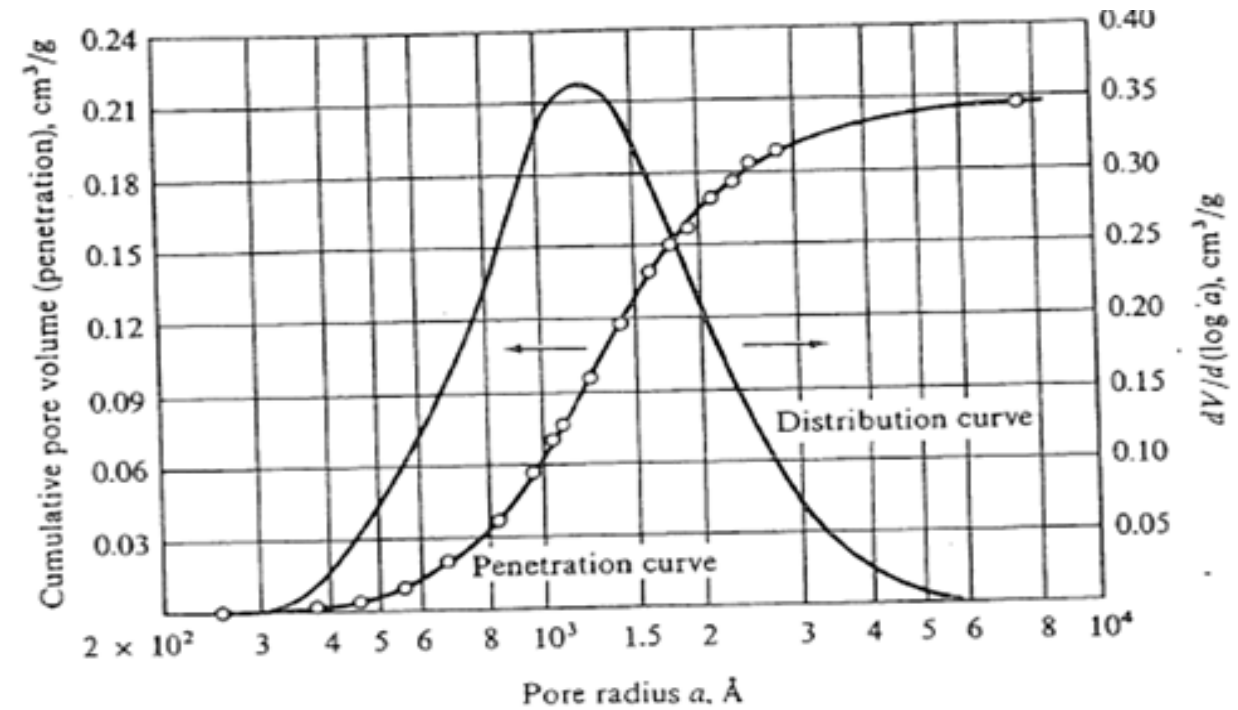


Figure 1: pore-volume Distribution in UO_2 pellet

Contd...

- Plot of Cumulative Pore Volume against Pore Radius is Penetration Curve
- The penetration volume at any pore radius 'a' is the volume of pore just larger than 'a'.
- The derivative of this curve, i.e, $\Delta V / \Delta a$ is the volume of pores between a and (a + Δa) divided by Δa
- This is the derivation function of the pore volume according to pore radius

Contd....

- Plot of pore radius on logarithmic scale and the derivative of distribution function, $dV/d(\log a)$, gives the distribution curve
- This curve shows the rate of change of pore volume with change in pore radius

Parallel pore Model

- Average pore radius \bar{a} is assumed, rather than the distribution of pores
- All pores are considered to be straight, cylindrical, not interconnected
- They have same pore radius \bar{a} and pore length \bar{L}
- To get average pore radius, determination of only surface area and pore volume are necessary

Contd...

This model is called Wheeler Parallel Pore Model

This is a hypothetical model

Equations,

$$m_p s_g = (2\pi \bar{a} \bar{L})n$$

And

$$m_p V_g = (\pi \bar{a}^2 \bar{L})n$$

Where m_p and n are the mass and number of pores per particle respectively

The average pore radius,

$$\bar{a} = \frac{2V_g}{s_g}$$

This model agrees well with monodisperse catalyst

Tutorials

1. Calculate the external surface area of nonporous spherical particles of 2 microns dia. What size particles would be necessary if the external surface is to be 100 m²/g. The density of the particles is 2.0 g/c.c.

Solution:

External surface area per unit volume of a spherical particle of dia d is

$$\frac{6\pi d^2}{\pi d^3} = \frac{6}{d}$$

Contd...

If the particle density is ρ_p , then surface area per g of particle is

$$S_g = \frac{6}{d\rho_p}$$

$d = 2$ microns (2×10^{-4} cm) and $\rho_p = 2$ g/cc

$$\text{Hence, } S_g = \frac{6}{2(2 \times 10^{-4})} = 1.5 \times 10^4 \text{ cm}^2$$

If surface area of $100 \text{ m}^2/\text{g}$ is required, the spherical particles would have a diameter of

$$d = \frac{6}{\rho_p \cdot S_g} = \frac{6}{2(100 \times 10^4)} = 0.03 \times 10^{-4} \text{ cm} = 0.03 \text{ micron}$$

2. In an experiment to determine the pore volume and catalyst particle porosity the following data were obtained on a sample of activated silica:

Mass of catalyst sample = 101.5 g,

Volume of helium displaced by the sample = 45.1 cm³,

Volume of mercury displaced by sample = 82.7 cm³

Calculate the required properties.

Solution: The volume of mercury displaced minus the helium displacement volume is the pore volume.

$$V_g = \frac{82.7 - 45.1}{101.5} = 0.371 \text{ cm}^3/\text{g}$$

The helium volume is also a measure of the density of the solid material in the catalyst, that is,

$$\rho_s = \frac{101.5}{45.1} = 2.25 \text{ g/cm}^3$$

The porosity is calculated as,

$$\varepsilon_p = \frac{V_g \rho_s}{V_g \rho_s + 1} = \frac{0.371 \times 2.25}{0.371 \times 2.25 + 1} = 0.455$$

3. An 8.01 g sample of catalyst is studied with N_2 adsorption at -195.8°C . the following data are obtained:

Pressure, mm Hg	6	25	140	230	285	320
Volume adsorbed, cm^3 (at 0°C and 1 atm)	61	127	170	197	215	230

The vapor pressure of N_2 at -195.8°C is 1 atm and density is 0.808 g/cm^3 . Estimate the surface area (m^2/g) of the sample.

Solution:

For monomolecular adsorption, we consider,

$$\frac{p}{v} = \frac{1}{kv_m} + \frac{p}{v_m} ,$$

Where, v_m = volume of gas adsorbed at complete monomolecular layer adsorption.

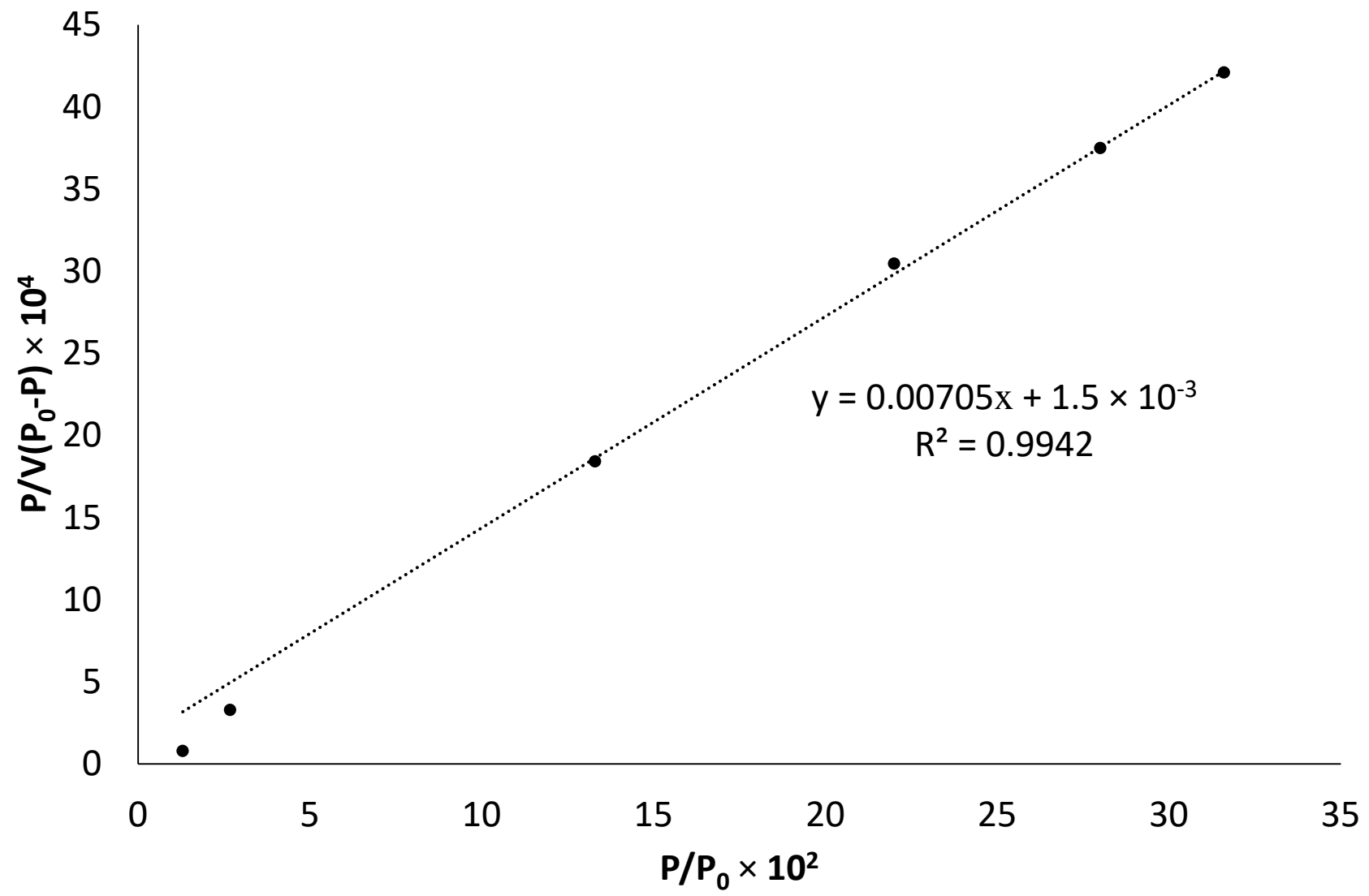
But in reality, multilayer adsorption occurs and the adsorption isotherm equation is,

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{(C - 1)p}{(cv_m)p_0}$$

C is constant.

From the plot between $\frac{p}{v(p_0 - p)}$ vs $\frac{p}{p_0}$, we get a straight line

$\frac{p}{v(p_0 - p)}$	0.00013	0.00026	0.00133	0.0022	0.0028	0.00316
$\frac{p}{p_0}$	0.00789	0.03289	0.1842	0.3026	0.375	0.4210



Intercept (I) = $\frac{1}{v_m c} = 0.15 \times 10^{-3}$ at $\frac{p}{p_0} = 0$ for
8.01g sample.

Slope (S) = $\frac{c-1}{v_m c} = 7.2727 \times 10^{-3}$ for 8.01 g sample.

$$\begin{aligned}\therefore v_m &= \frac{1}{I + S} = \frac{10^3}{(0.15 + 7.27)} \times \frac{1}{8.01} \frac{\text{cm}^3}{\text{g}} \text{ of catalyst} \\ &= 16.819 \frac{\text{cm}^3}{\text{g}} \text{ of catalyst}\end{aligned}$$

Hence, surface area $S_g = v_m \left(\frac{N_0 \alpha}{v} \right)$

and $\alpha = 1.09 \left(\frac{M}{N_0 \rho} \right)^{2/3}$

α = projected area of N_2 molecule on the surface,

N_0 = Avogadro's number,

V = volume per mole of gas at the condition of v_m ,

Since, v_m is recorded at the standard condition,

$$\therefore v = 22400 \text{ cm}^3 / \text{gmol}$$

M = molecular weight of N₂,

ρ = density of N₂ at (-195.8°C)

$$\therefore \alpha = 1.09 \left[\frac{28}{2.303 \times 10^{23} \times 0.808} \right]^{\frac{2}{3}}$$

$$= 16.2 \times 10^{-16} \text{ cm}^2/\text{molecule}$$

$$\therefore S_g = 16.819 \left[\frac{2.303 \times 10^{23} \times 16.2 \times 10^{-16}}{22400} \right] \text{ cm}^2/\text{g}$$

$$= 73.16 \text{ m}^2/\text{g cat}$$

Hence, the surface area of the catalyst is 73.16 m²/g.

4. The true density of the solid material in an activated alumina particle is 3.675 g/cm^3 . The density of the particle determined by mercury displacement is 1.547 . The surface area by adsorption measurement is $175 \text{ m}^2/\text{g}$. From this information compute the pore volume per gram, the porosity of the particles and the mean pore radius. The bulk density of a bed of the alumina particles in a 250 cm^3 graduate is 0.81 g/cm^3 . What fraction of the total volume of the bed is void space between the particles and what fraction is void space within the particles?

Solution:

True density of solid material of the alumina particle

$$\rho_s = 3.675 \text{ g/cm}^3 \text{ (obtained from He displaced volume)}$$

$$\rho_p = 1.547 \text{ g/cm}^3, S_g = 175 \text{ m}^2/\text{g}.$$

Basis: 1g sample

$$\text{Solid volume} = \frac{1}{3.675} \text{ cm}^3 = 0.272 \text{ cm}^3$$

Particle volume(solid phase + pore)

$$= \frac{1}{1.547} \text{ cm}^3 = 0.6464 \text{ cm}^3$$

$$\begin{aligned} \therefore \text{pore volume} &= \frac{1}{1.547} - \frac{1}{3.675} \\ &= 0.3743 \text{ cm}^3/\text{g} \end{aligned}$$

$$\text{Porosity } \varepsilon_p = \frac{\text{pore volume}}{\text{total volume}} = \frac{0.3743}{0.6464} = 0.579$$

Bulk density of alumina bed = 0.81 g/cm³

Volume of alumina bed = 250 cm³

Mass of the alumina = 0.81 × 250 = 202.5 g

Fraction of void space within the particle

Porosity of the particle = 0.579

Fraction of void space between the particles

$$= \frac{202.5}{0.81} - \frac{202.5}{1.547} = 0.4764$$

5. Two samples of silica-alumina cracking catalysts have particle densities of 1.126 and 0.962 g/cm³ respectively, as determined by mercury displacement. The true density of the solid material in each case is 2.37 g/cm³. The surface area of the first sample is 467 m²/g and that of the second is 372 m²/g. Which sample has the larger mean pore radius?

Solution

$$\text{Sample 1: } \rho_{p_1} = 1.126 \frac{\text{g}}{\text{cm}^3}, \quad S_{g_1} = 467 \frac{\text{m}^2}{\text{g}}$$

Sample 2: $\rho_{p_2} = 0.962 \frac{\text{g}}{\text{cm}^3}$

$$S_{g_2} = 372 \frac{\text{m}^2}{\text{g}}$$

According to Wheeler's parallel pore model, average

pore radius $\bar{a} = \frac{2V_g}{S_g}$,

V_g = pore volume, S_g = surface area.

Pore volume = particle volume – solid volume

Basis: 1 g of sample each

$$\text{particle volume} = \frac{1}{\text{particle density}}$$

$$V_1 = \frac{1}{1.126} = 0.888 \text{ cm}^3$$

$$V_2 = \frac{1}{0.962} = 1.0395 \text{ cm}^3$$

$$\text{Solid volume } (V_s) = \frac{1}{\text{solid density}} = \frac{1}{2.37} = 0.4219 \text{ cm}^3$$

Pore volume of samples,

$$V_{g_1} = V_1 - V_s = 0.888 - 0.4219 = 0.4661 \text{ cm}^3$$

$$V_{g_2} = V_2 - V_s = 1.0395 - 0.4219 = 0.6176 \text{ cm}^3$$

∴ Pore radius of sample,

$$\begin{aligned}\overline{a_1} &= \frac{2V_{g_1}}{S_{g_1}} = \frac{2 \times 0.4661}{467 \times 10^4} = 0.00199 \text{ cm} \\ &\approx 2 \times 10^{-3} \text{ cm}\end{aligned}$$

$$\begin{aligned}\overline{a_2} &= \frac{2V_{g_2}}{S_{g_2}} = \frac{2 \times 0.6176}{372 \times 10^4} = 0.0033 \text{ cm} \\ &\approx 3.3 \times 10^{-3} \text{ cm}\end{aligned}$$

Therefore, the second sample has larger mean pore radius.