

Solid catalysts

3) Texture of the catalyst (surface area, pore size, pore volume, metal dispersion)

Surface area determination

- Surface area has a pronounced effect on the activity of a catalyst
- It is one of the first properties that need to be determined
- Estimated surface area includes both internal and external area. External surface area is so small compared to internal area that it can be ignored
- Standard method of measuring surface area is based on the physical adsorption of a gas on the solid surface
 - The amount of nitrogen (N₂) adsorbed at equilibrium at the normal boiling point (-195.8°C) is measured over a range of N₂ pressures below 1 atm
 - Under these conditions, several layers of molecules may be adsorbed on top of each other on the surface
 - As a result of multilayer adsorption, the BET equation is used for surface area determination

$$\frac{p_A}{v(p_o - p_A)} = \frac{1}{v_m c} + \left(\frac{c-1}{v_m c}\right) \frac{p_A}{p_o}$$

where p_o = saturation vapour pressure,
 v_m = volume of gas adsorbed at monolayer

- Most systems follow the equation in the $\frac{p_A}{p_o}$ range of 0.05 to ~ 0.35
- The experimental data gives us the values of volume (v) of gas adsorbed at a particular pressure p_A
- The value of $\frac{p_A}{v(p_o - p_A)}$ can be plotted versus $\frac{p_A}{p_o}$ to yield a straight line with $\left(\frac{c-1}{v_m c}\right)$ as the slope $\frac{1}{v_m c}$ as the intercept

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$$\text{Intercept } (I) = \frac{1}{v_m c}$$

$$\text{Slope } (S) = \left(\frac{c-1}{v_m c}\right)$$

$$\therefore v_m = \left(\frac{1}{I+S}\right) \quad (\text{based on 1 gm catalyst})$$

- Number of molecules of gas adsorbed to form a monolayer $= \frac{v_m}{V} \times N_o$ where $N_o = \text{Avogadro number} = 6.023 \times 10^{23}$ molecules/mol
 $V = \text{volume per mol of gas at conditions of } v_m$
- Surface area per gram of catalyst, S_g**

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

where $\alpha = \text{surface area covered by one molecule}$

- Projected cross-sectional area, α is given as

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

where $M = \text{molecular weight}$
 $\rho = \text{density of adsorbed molecule}$

$$\text{For } N_2 \text{ at } -195.8^\circ\text{C (77 K), } \rho = 0.808 \text{ g/cm}^3, \quad \alpha = 16.2 \text{ \AA}^2$$

$$\therefore S_g = 4.35 \times 10^4 v_m \quad (\text{cm}^2/\text{g})$$

If the gas is changed, the surface area is found to be different

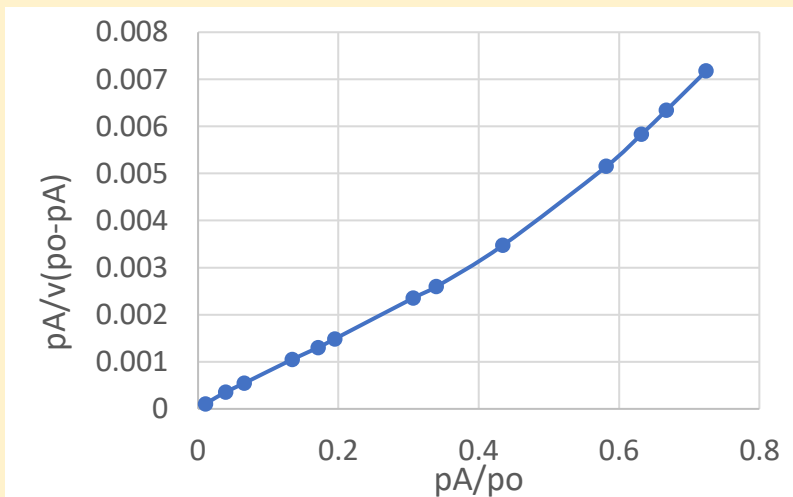
Example

Low temperature (-195.8°C) nitrogen adsorption data were obtained for an Fe-Al₂O₃ ammonia catalyst. The adsorption data for 50.4 g catalyst sample were

Pressure, mm Hg	8	30	50	102	130	148	233	258	330	442	480	507	550
Volume adsorbed, cm³ (at 0°C, 1 atm)	103	116	130	148	159	163	188	198	221	270	294	316	365

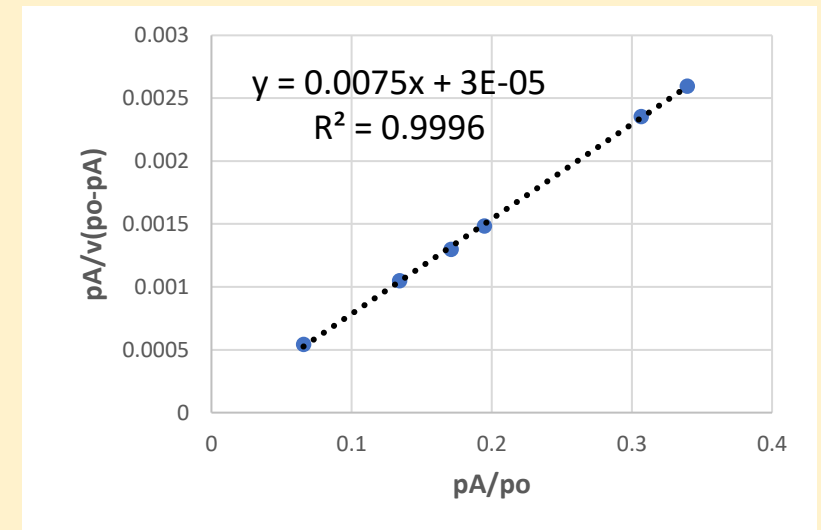
Estimate the surface area for this catalyst.

The vapour pressure of N₂ at -195.8°C (p_o) is 1 atm (760 mm Hg)



The plot shows a curvature when the entire range of $\frac{p_A}{p_o}$ is considered

The plot shows a straight line in the $\frac{p_A}{p_o}$ range of 0.05 to 0.35



$$\text{Slope } (S) = 0.0075$$

$$\text{Intercept } (I) = 0.00003$$

$$v_m = \left(\frac{1}{0.00003 + 0.0075} \right) \times \frac{1}{50.4} = 2.6203 \text{ cm}^3/\text{g}$$

$$\text{Surface area, } S_g = \left[\frac{v_m N_o}{V} \right] \alpha$$

$$\text{For N}_2, \alpha = 16.2 \text{ \AA}^2$$

$$S_g = 4.35 \times 10^4 \times v_m \text{ (cm}^2/\text{g)}$$

$$= 4.354.35 \times 10^4 \times 2.6203 = 11.40 \times 10^4 \text{ (cm}^2/\text{g)}$$

$$= 11.40 \text{ (m}^2/\text{g)}$$

Pore (Void) volume and solid density

- The void volume of a porous solid is measured by the **helium-mercury method**
- The volume of helium displaced by the catalyst is measured
- Then the helium is removed and the volume of the mercury that is displaced is measured. Since mercury does not fill the pores at atmospheric pressure, the difference in volume gives the pore volume of the catalyst sample
- The volume of helium displaced is a measure of the volume occupied by the solid material
- Knowing the mass of the catalyst sample (m_p) and this volume (helium displaced), it is possible to calculate the **density of the solid material (ρ_s)**
- The mass of catalyst (m_p) and the volume of mercury displaced gives the **density of the porous particles (ρ_p)**
- The **void fraction or porosity of the solid catalyst (ϵ_p)** can be calculated as

$$\epsilon_p = \frac{\text{void volume of particle}}{\text{total volume of particle}} = \frac{m_p v_g}{m_p v_g + m_p \left(\frac{1}{\rho_s}\right)}$$

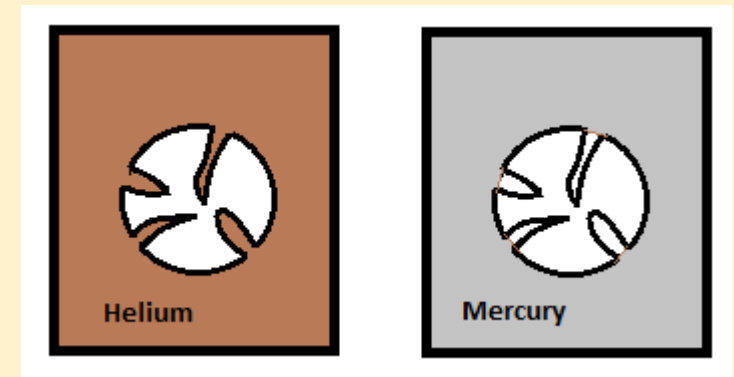
$$\text{or, } \boxed{\epsilon_p = \frac{v_g \rho_s}{v_g \rho_s + 1}}$$

- Also, $\epsilon_p = \frac{\text{void volume of particle}}{\text{total volume of particle}} = \frac{m_p v_g}{\frac{m_p}{\rho_p}} = \rho_p v_g$

$$\text{or, } \boxed{\epsilon_p = \rho_p v_g}$$

- The average pore radius, r (considering the pore to be cylindrical) can be estimated as,

$$\boxed{r = \frac{2v_g}{S_g}}$$



Example

In an experiment to determine the pore volume and 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 sample = 45.1 cm³

Volume of mercury displaced by sample = 82.7 cm³

Calculate the required properties.

$$\text{Pore volume per gram catalyst } (v_g) = \frac{82.7 - 45.1}{101.5} = \mathbf{0.371} \frac{\text{cm}^3}{\text{g}}$$

$$\text{Density of the solid material } (\rho_s) = \frac{101.5}{45.1} = 2.25 \frac{\text{g}}{\text{cm}^3}$$

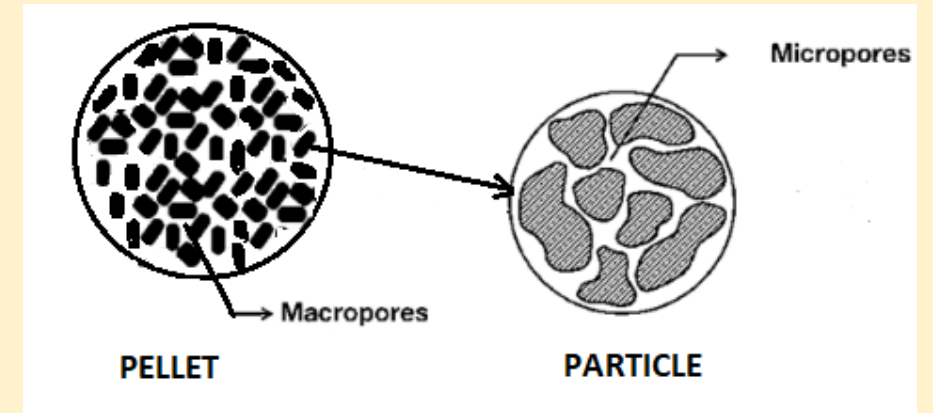
$$\text{Particle porosity = Void fraction } (\epsilon_p) = \frac{v_g \rho_s}{v_g \rho_s + 1} = \frac{0.371 \times 2.25}{0.371 \times 2.25 + 1} = \mathbf{0.455}$$

$$\text{Density of porous material } (\rho_p) = \frac{101.5}{82.7} = 1.227 \frac{\text{g}}{\text{cm}^3}$$

$$\text{Again, } \epsilon_p = \rho_p v_g = 0.371 \times 1.227 = \mathbf{0.455}$$

Micropore and macropores

- Agglomeration of porous particles to form pellets leads to formation of two types of void regions –
 - Small void spaces within the individual particles called **micropores**
 - Void region between particles in the pellet called **macropores**
- The macro-porosity and macropore diameter depends on the pelleting pressure
- Increasing the pressure decreases the macropore volume with the micropore volume remaining almost unchanged
- Macro and micropore volumes and porosities for bi-disperse catalyst pellets are calculated by the same methods as used for monodisperse pore systems



Example

A hydrogenation catalyst is prepared by soaking alumina particles (100-150 mesh size) in aqueous NiNO_3 solution. After drying and calcining, the particles contain 7 wt% NiO. The catalyst is then made into pellets. The measurements for one pellet are:

Mass = 3.15 g Thickness = $\frac{1}{4}$ " Diameter = 1" Volume = 3.22 cm^3

The Al_2O_3 particles have micropores and pelleting introduces macropores. From experimental methods, the macropore volume of the pellet is found to be 0.645 cm^3 and the micropore volume is $0.40 \text{ cm}^3/\text{g}$ of particles. Based on this data calculate the following:

Data: Mass of pellet = 3.15 g Thickness = ¼" Diameter = 1" Volume = 3.22 cm³
 Macropore volume of the pellet is found to be 0.645 cm³ Micropore volume is 0.40 cm³/g of particles

- (a) **Density of the pellet, $\rho_p = \frac{3.15}{3.22} = 0.978 \text{ g/cm}^3$**
- (b) **Macropore volume per gm catalyst $(v_g)_M = \frac{0.645}{3.15} = 0.205 \text{ cm}^3/\text{g}$**
- (c) **Macropore void volume in the pellet, $\varepsilon_M = \frac{\text{macropore volume}}{\text{total volume}} = \frac{(v_g)_M}{1/\rho_p} = \frac{0.205}{1/0.978} = 0.2$**
- (d) **Micropore void fraction in the pellet, $\varepsilon_\mu = \frac{\text{micropore volume}}{\text{total volume}} = \frac{(v_g)_\mu}{1/\rho_p} = \frac{0.4}{1/0.978} = 0.391$**
- (e) **Solid fraction, $\varepsilon_S = 1 - \varepsilon_M - \varepsilon_\mu = 1 - 0.2 - 0.391 = 0.409$**
- (f) **Density of the particles, $\rho_{pr} = \frac{3.15}{3.22 - 0.645} = 1.22 \text{ g/cm}^3$**
- (g) **Density of the solid phase, $\rho_S = \frac{\text{mass of pellet}}{\text{volume of pellet} \times \varepsilon_S} = \frac{3.15}{3.22 \times 0.409} = 2.39 \text{ g/cm}^3$**
- (h) **Void fraction of the particles, $\varepsilon_p = \frac{(v_g)_\mu}{1/\rho_{pr}} = \frac{0.4}{1/1.22} = 0.49$**