

## Lecture 6

### Catalyst characterization

Characterization of heterogeneous catalyst refers to the determination of its physical and chemical characteristics, which are responsible for its performance in a reaction.

Characteristics of catalysts include:

- Chemical composition of the bulk and surface of the solids
- Surface area and porosity ( micro, meso and macro)
- Bulk solid structure, phase composition, crystallite size
- Surface morphology
- Surface chemical properties such as:
  - location and oxidation state of active metals
  - acid-base property
  - reducible – oxidizable property
- Aggregate properties such as aggregate or particle size, density, mechanical strength and attrition resistance
- Catalytic properties : activity , selectivity, stability

#### Objectives of characterization

The primary objective of catalyst characterization is to understand the relationship among physical, chemical and catalytic properties. For this purpose, the physical and chemical properties are determined by various characterization techniques and related to its activity and selectivity. This is essential for design and process optimization. The characterization is also done to monitor the changes in physical and chemical properties of the catalyst during preparation, activation and reaction stages for better understanding and quality control. Determination of the extent of deactivation of catalysts during the reaction process is also important. Characterization of used catalysts can help to determine the causes of deactivation and minimize it. It also helps to design procedures for catalysts regeneration.

## Characterization Techniques

In this section some of the characterization techniques that are most commonly used will be discussed. These techniques are summarized below.

### 1. Structural analysis

#### (a) Surface area

- widely accepted BET ( Brunauer, Emmet and Teller) method used for analyzing multilayer physisorption isotherms of inert gases to determine the surface area

#### (b) pore analysis by

- BJH method
- mercury intrusion method

#### (c) X-Ray Diffraction (XRD) :

- can detect crystalline materials having crystal domains greater than 3-5 nm.
- characterization of bulk crystal structure and chemical phase composition.

### 2. Chemisorption technique

- determines dispersion of metal in catalysts
- determination of surface metal area

### 3. Thermal analysis

#### (a) temperature programmed reduction (TPR) :

- measures the rate of reduction of active metals as function of temperature.
- can be correlated with activity of catalysts

#### (b) temperature programmed desorption (TPD) :

- measurement of rate of desorption of adsorbed molecules as function of temperature
- mainly used to study acid –base property of catalysts

#### (c) Thermo Gravimetric Analysis (TGA) :

- measurement of weight loss (or gain) as a function of temperature in a controlled gaseous atmosphere;

- process associated with mass change can be detected and analyzed
- (d) Differential Thermal Analysis (DTA)
- monitoring the temperature difference between sample and reference
  - process associated with latent heat of transition can be detected and analyzed

#### **4. Spectroscopic techniques**

(a) Infra red spectroscopy

- identify compounds and investigate sample composition
- Study of structure and bonds

(b) Raman spectroscopy :

- study of oxidation state and interaction of metal oxides

#### **5. Microscopic technique**

(a) Scanning electron microscopy (SEM):

- image the topography of solid surface
- resolution better than 5 nm.

(b) transmission electron microscopy (TEM) :

- determines the micro –texture and micro structure
- resolution better than 0.2 nm

## Surface area, pore size, pore volume determination

Determination of surface area and pore distribution of catalysts is important to understand the extent of dispersion possible for the active metals. Higher surface area of support results in higher dispersion of the active metals. Hence supports of higher surface area are desirable.

Pores are usually formed during drying or calcination of hydroxides precipitates or gel. The size and number of pores determines the internal surface area. Pore size also determines the accessibility of reactants to the active sites and the ability of diffusion of products back to the bulk fluid. Hence pore structure and surface area must be optimized to provide maximum utilization of active sites for a given feed stock.

## Working principle and instrumentation

The basic components of volumetric physical adsorption analyzer as shown in Fig. 1 are:

- 1) Analysis manifold of accurately known volume and temperature
- 2) Vacuum system with valve to manifold
- 3) Source of adsorptive gas (typically, N<sub>2</sub>) with valve to manifold
- 4) Pressure transducer and temperature sensor
- 5) Sample tube connected to analysis manifold
- 6) Liquid nitrogen bath

Determination of internal surface area is based on adsorption and condensation of N<sub>2</sub> at liquid N<sub>2</sub> temperature, 77K. Initially, the sample is evacuated at 293-523 K (120-250 °C) followed by cooling to 77 K by liquid N<sub>2</sub>. Then gradually the partial pressure of nitrogen above the sample is increased. Some quantity of gas will be adsorbed by the sample and removed from the gas phase. After stabilization the equilibrated pressure is recorded and amount of nitrogen adsorbed at each equilibrated pressure is noted. The isotherm, volume adsorbed as function of relative pressure  $p/p_0$ , is plotted from the data. The pressure over the sample is gradually increased until pressure reaches near saturation pressure, by when

the complete adsorption isotherm is developed. The desorption isotherm is measured by a step-wise reduction in pressure until a low pressure over the sample is achieved. Although the volumes are adsorbed at different conditions, the values are reported at STP conditions. Fig. 2 shows a typical  $N_2$  adsorption and desorption isotherm at 77 K for alumina.

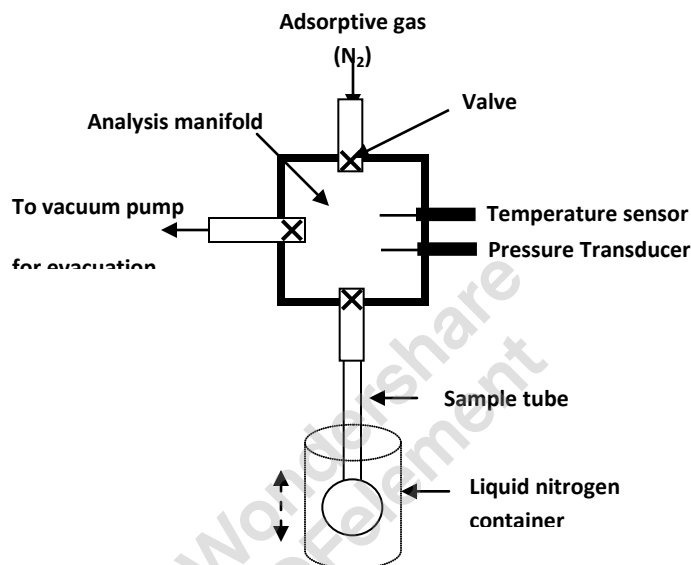


Fig. 1. Basic components of volumetric physical adsorption analyzer

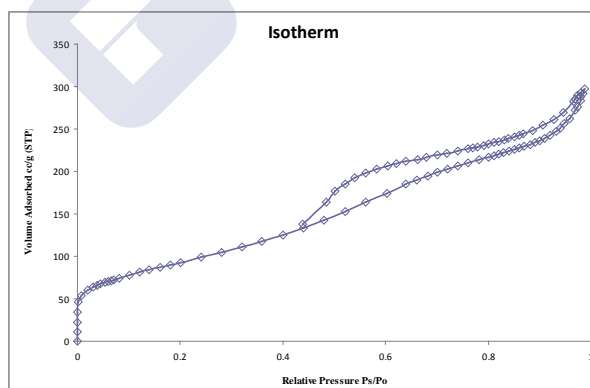


Fig. 2. A typical  $N_2$  adsorption and desorption isotherm at 77 K for alumina

### Adsorption using Argon and Krypton

Krypton is used as adsorbate at 77 K for low surface area analysis while, Argon adsorption at 77 K and liquid argon temperature (87K) is often used for micro and mesopores analysis.

To measure very low surface area the number of molecules trapped in the void volume of sample cell needs to be reduced. The number of molecules left in void volume can be reduced by using adsorbate such as Krypton with low vapor pressure at liquid nitrogen temperature. The saturation pressure of Krypton at liquid nitrogen temperature is 0.35 kPa which is much lower compared to that of N<sub>2</sub> (101.3 kPa). Consequently the number of Krypton molecules in free space of sample cell, at any given relative pressure, is significantly reduced compared to that of nitrogen at liquid nitrogen temperature, though amount of adsorption will be only slightly less. Hence, Krypton adsorption at 77 K is much more sensitive and can be applied to measure surface areas down to 0.05 m<sup>2</sup>. The cross sectional area used for Krypton is 0.202 nm<sup>2</sup>.

For analysis of ultramicropores less 0.7 nm, the nitrogen adsorption at 77 K is not satisfactory. The pore width of 0.7 nm corresponds to bilayer thickness of nitrogen molecule. For ultramicropores, pore filling occurs at relative pressure of 10<sup>-7</sup> to 10<sup>-5</sup>, where the rate of diffusion and attainment of adsorption equilibration is very slow. Consequently measurement becomes time consuming and may also cause non-equilibrated adsorption isotherms with erroneous results. On the other hand argon fills the micropores of dimension 0.4-0.8 nm in most cases at much higher relative pressure as compared to nitrogen. This leads to accelerated diffusion and equilibration process and result in reduction of analysis time as well as increase in accuracy. Argon adsorption is advantageous for pore size analysis of zeolites and other microporous materials.

The typical surface area values of different supports and catalysts are summarized in Table 1.

Table 1. Typical surface area values of different support and catalyst.

Support/catalyst	BET surface area $\text{m}^2/\text{g}$	Application
Activated carbon	500-2000	Used as support for various process
Zeolites	500-1200	Used as catalyst and support
$\text{Al}_2\text{O}_3\text{-SiO}_2\text{-Zeolites}$	100-600	Fluid catalytic cracking catalysts
$\text{Ni}/\text{Al}_2\text{O}_3$	100-150	Methanation catalyst
$\text{Cu}/\text{Zn}/\text{Al}_2\text{O}_3$		Methanol synthesis catalyst
$\text{MnO}_x/\text{Al}_2\text{O}_3$	140-180	Catalyst for total oxidation of volatile organic carbon
$\text{Fe}/\text{K}/\text{Al}_2\text{O}_3$	20	Ammonia synthesis catalyst

### Determination of surface area using BET Equation

As discussed earlier (lecture 4), the BET equation describes the relationship between volume adsorbed at a given partial pressure and the volume adsorbed at monolayer coverage. BET equation can be written in the form :

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

$p$  = partial pressure ;  $p_0$  = saturation pressure at the experimental temperature ;

$v$  = volume adsorbed at  $p$ ;  $v_m$  = volume adsorbed at monolayer coverage ;  $c$  = constant

Monolayer coverage is determined using BET equation. The  $\frac{p}{v(p_0 - p)}$  is plotted as a function of  $\frac{p}{p_0}$ . The plot is linear in the range of relative pressures  $\frac{p}{p_0} = 0.05 - 0.3$ . At higher relative pressure  $p/p_0$ , the BET plot deviates from linearity as non-ideality or pore condensation was not accounted for the derivation of BET equation.

Slope and intercept of this linear plot is used for determination of monolayer capacity  $v_m$ .

The intercept and slope from the plot is given as

$$\text{Intercept} = \frac{1}{cv_m} \quad \text{Slope} = \frac{(c-1)}{cv_m}$$

Then the monolayer volume  $v_m$  is given as,  $v_m = \frac{1}{\text{slope} + \text{intercept}} (STP)$

The total number of  $N_2$  molecules adsorbed corresponding to monolayer volume  $v_m$  can be calculated as

$$\text{No. of } N_2 \text{ molecules} = \frac{v_m (m^3) \times 6.02 \times 10^{23} (\text{molecules} / \text{mol})}{0.0224 (m^3 / \text{mol})}$$

Now, each adsorbed  $N_2$  molecule occupies an area of surface comparable to its cross section area of  $0.162 \text{ nm}^2$ .

$$SA(m^2) = \left[ \frac{v_m (m^3) \times 6.02 \times 10^{23} (\text{molecules} / \text{mol})}{(0.0224 m^3 / \text{mol})} \right] \times 16.2 \times 10^{-20} (m^2 / N_2 \text{ molecule})$$

$$\text{Or } SA(m^2) = v_m (m^3) \times 4.36 \times 10^6 (m^{-1}) = 4.36 \times 10^6 v_m$$



**Solved problem :**

1. Nitrogen was employed to determine the surface area of 1.0 g sample of silica gel and results obtained shown in table below. The sample of silica gel was maintained at the normal boiling point of liquid nitrogen (77K). One molecule of nitrogen occupies  $16.2 \times 10^{-20} \text{ m}^2$  area of plane surface. Calculate the specific surface area of silica gel by the BET method. The saturated vapor pressure  $p_0$  of nitrogen at 77K is 101.3 kPa.

Equilibrium Pressure, $p$ [kPa]	5.0	6.3	7.5	9.0	11.2
Volume adsorbed, (STP), $V \times 10^6$ [m <sup>3</sup> ]	6.7	7.0	7.2	7.4	7.7

**Solution :**

The BET equation in following form is used. 
$$\frac{p}{V(p_0 - p)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \frac{p}{p_0}$$

The  $\frac{p}{V(p_0 - p)}$  is plotted as function of  $\frac{p}{p_0}$ . The plot is shown in Fig. 3.

Table 1. Calculation for plot of BET equation

$v$ $m^3$	$p$ $kPa$	$p_0$ $kPa$	$p/p_0$	$p/[v(p_0-p)]$ $m^{-3}$
6.7E-06	5	101.3	0.049	7.75E+03
7.0E-06	6.3	101.3	0.062	9.47E+03
7.2E-06	7.5	101.3	0.074	1.11E+04
7.4E-06	9	101.3	0.089	1.32E+04
7.7E-06	11.2	101.3	0.111	1.61E+04

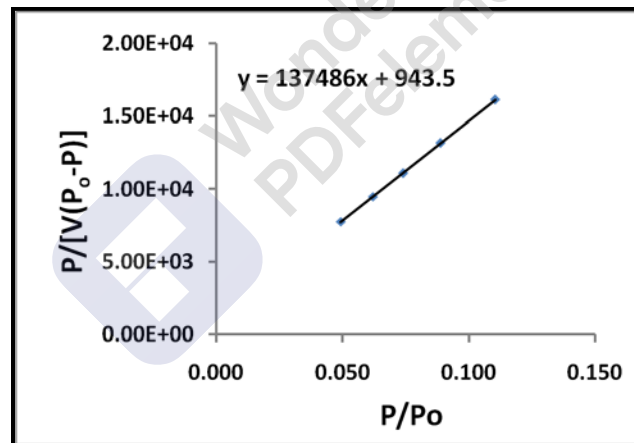


Fig. 3. Linear plot of BET equation

Intercept =  $943.5 \text{ m}^{-3}$  ; Slope =  $137486 \text{ m}^{-3}$

$$\text{Monolayer volume } V_m = \frac{1}{\text{slope} + \text{intercept}} = \frac{1}{137486 + 943.5} = 7.22 \times 10^{-6} \text{ m}^3 \text{ (STP)}$$

Then surface area for 1 gm sample can be determined as :

$$SA = \left[ \frac{7.22 \times 10^{-6} \text{ m}^3 \times 6.02 \times 10^{23} \text{ molecules / mol}}{22400 \times 10^{-6} \text{ m}^3 / \text{mol}} \right] \times 16.2 \times 10^{-20} \text{ m}^2 / N_2 \text{ molecule}$$

**= 31.4 m<sup>2</sup>**

As initially 1 gm sample was used, specific surface area of sample = 31.4 m<sup>2</sup>/g

