




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, N₂) 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 N₂ at liquid N₂ temperature, 77K. Initially, the sample is evacuated at 293-523 K (120-250 °C) followed by cooling to 77 K by liquid N₂. 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 N₂ adsorption and desorption isotherm at 77 K for alumina.

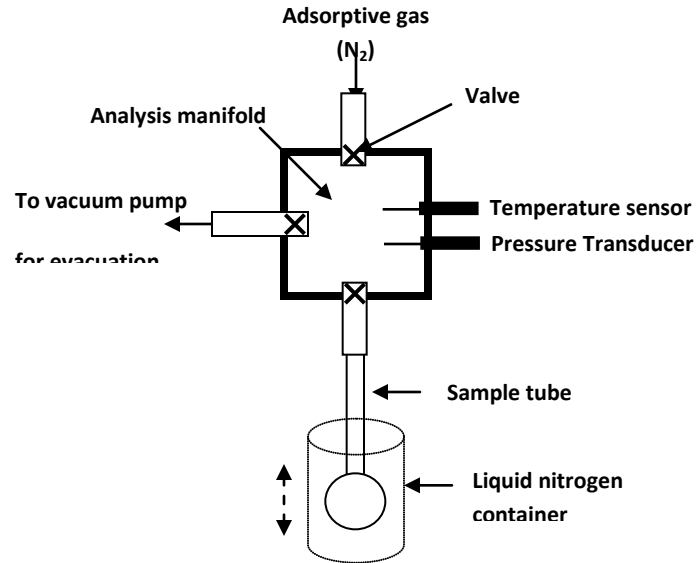


Fig. 1. Basic components of volumetric physical adsorption analyzer

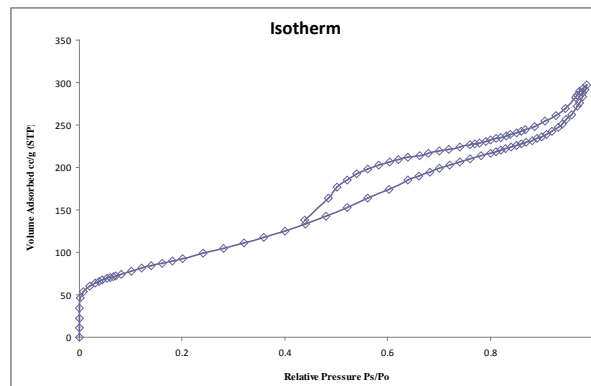


Fig. 2. A typical N₂ adsorption and desorption isotherm at 77 K for alumina