CATALYSTS

Ph.D course/ Physical Chemistry
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- **There are four basic ways of fixing transition metal complexes on a matrix:**

- 1) Chemical bonding on inorganic or organic supports.

- 2) Production of highly dispersed supported metal catalysts.

- 3) Physisorption on the surface of oxidize supports (supported solid phase catalysts, SSPC).

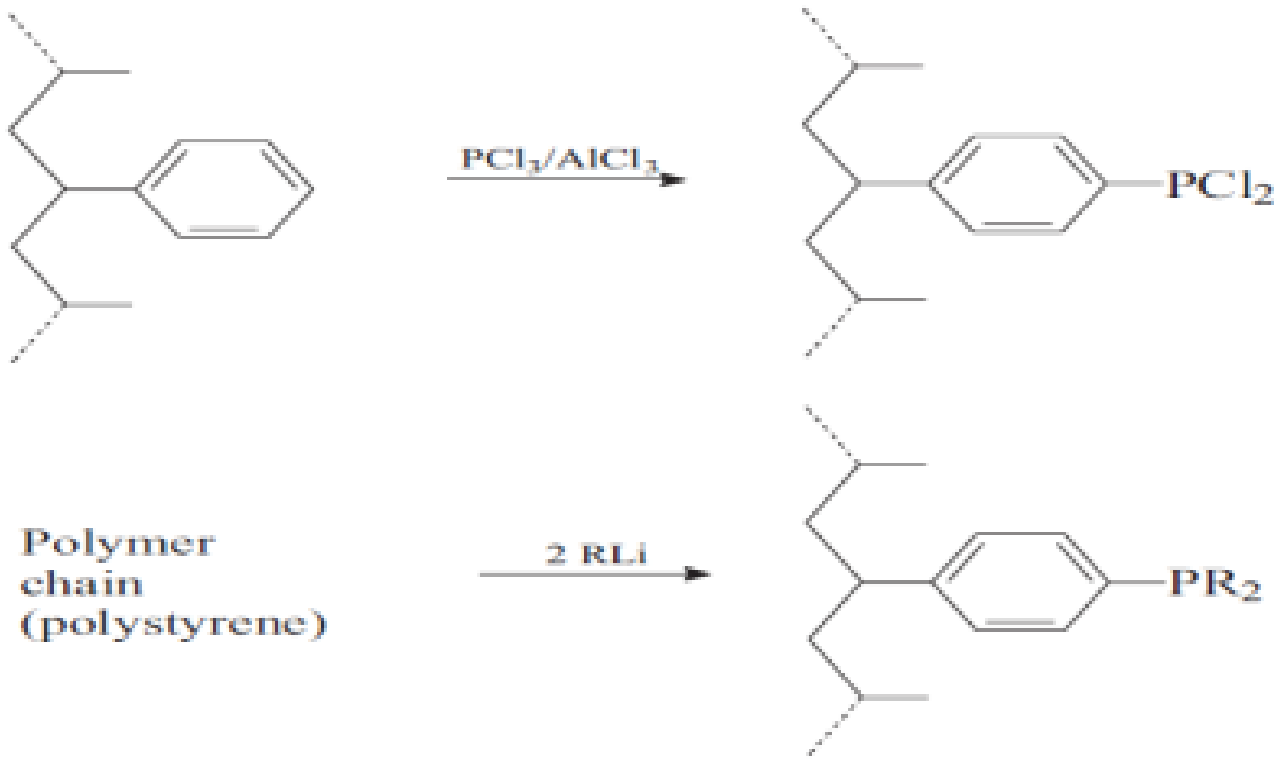
- 4) Dissolution in a high-boiling liquid that is adsorbed on a porous support (supported liquid phase catalysts, SLPC)

1- Chemical bonding:

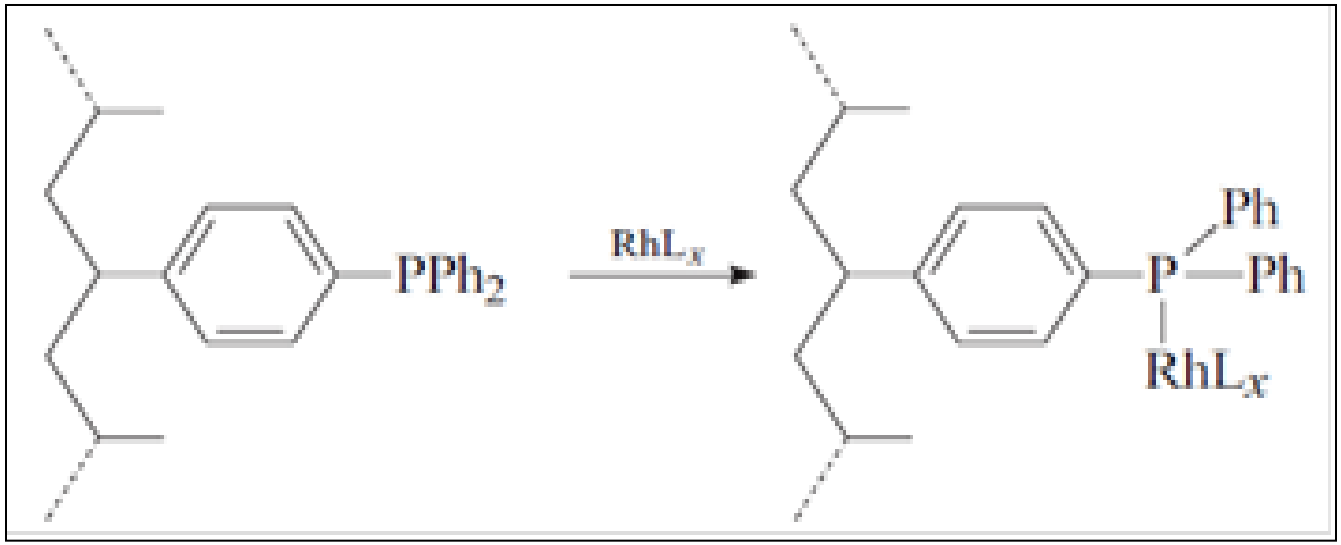
The immobilization of organometallic complexes on inorganic or organic supports is the most widely used method. Basically the supports act as high molecular mass ligands and are obtained by controlled synthesis. The bonding can be ionic or coordinative.

- The main aim of the process is to bind the complexes on the solid surface in such a manner that its chemical structure is retained as far as possible.
- A common method is the replacement of a ligand by a bond to the surface of the solid matrix. This means that a reactive group must be incorporated in the surface during production of the support.

Numerous polymer synthesis and orgamometallic synthesis are available for the construction of functionalized supports; the equation below gives just one example;



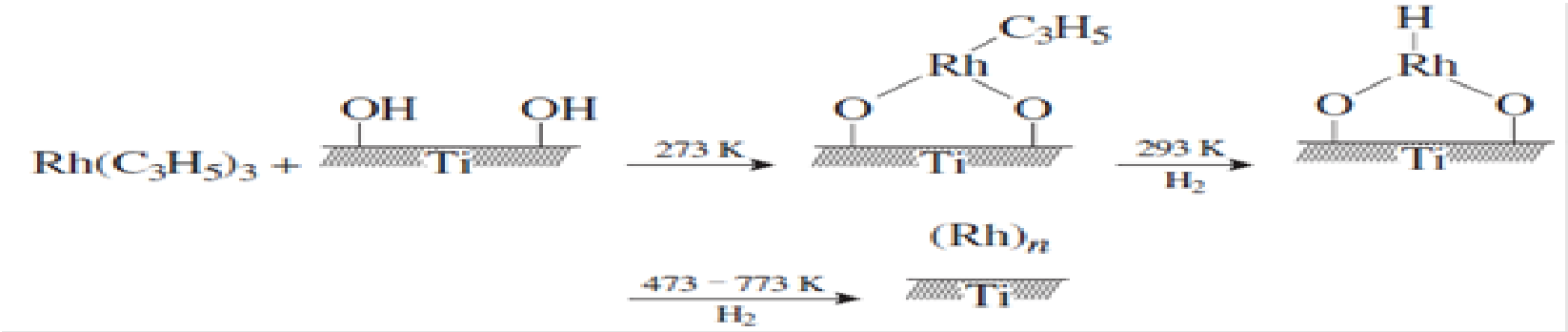
- Here triphenylphosphine, the most important ligand in organometallic catalysis, is coupled to the benzene rings of cross-linked polystyrene.



Hard copolymers of this type take up metal complexes only on the surface. The physical properties of the support can be varied by means of the polymerization method; the metal loading can also be controlled well.

2- Highly Dispersed Supported Metal Catalysts

This method is used to obtain a very fine distribution of metal on a support by decomposition of organometallic compounds (so-called grafted catalysts). For example, by treating TiO_2 with η^3-allyl complexes of rhodium followed by decomposition, highly active hydrogenation and hydrogenolysis catalysts are obtained. Similar catalysts based on polysiloxanes are produced by Degussa; Pd, Rh, and Pt systems are available.



(Rh)*n* = small aggregates of 25 or more Rh atoms with particle diameters of ca. 1.4 nm.

3- SSP Catalysts

- In this group of catalysts, organometallic complexes are anchored on the inner surface of porous supports, mainly by physisorption. These catalysts can be used as catalyst beds through which the reaction medium flows.
- For example, the complex $[Rh(\eta^3\text{-}C_3H_5)(CO)(PPh_3)_2]$ is adsorbed on $\gamma\text{-}Al_2O_3$ and used as a hydrogenation catalyst. The fixed complexes often exhibit considerably lower activity and selectivity than in the homogeneous phase, and this limits their range of applications. The SLP catalysts are a better alternative.

- 4- ***SLP Catalysts***
- **In this process a solution of the complex in a high-boiling solvent spreads out on the inner surface of a porous support, which generally consists of an inorganic material such as silica gel. The reaction takes place in the liquid film, which the starting materials reach by diffusion. The products are also transported away by diffusion out of the film, which is retained on the support.**

- **- The use of SLP catalysts is generally restricted to the synthesis of low-boiling compounds. Oxo synthesis with SLP catalysts has been the subject of much interest. An example is the hydroformylation of propene with $[RhH(CO)(PPh_3)_3]$ in liquid triphenylphosphine on γ-Al_2O_3. Further examples are the oxidation of ethylene to acetaldehyde with aqueous solutions of $PdCl_2$ and $CuCl_2$ on kieselguhr, and the oxychlorination of alkenes with a $CuCl_2$/CuCl/KCl/rare earth halide melt on silica gel.**

Loading of the Support

- Loading of the active component on the support can also be carried out in a variety of ways. These can be classified as:
- 1- Traditional chemical methods such as grafting, precipitation and impregnation that have been discussed earlier.
- 2- Modern methods (based on the methods employed in electronics industry) like physical and chemical vapour deposition and atomic layer deposition.
- Anchoring and grafting are the methods based on stable covalent bond formation between homogenous transition metal complex .

3- Micro emulsion method

- Water, oil and amphiphile, (Surfactant) constitute a micro-emulsion system. Such system are optically isotropic and thermodynamically stable. At macroscopic level, micro-emulsion looks like a homogenous solution , but at moleculare state, it is heterogenous. The internal structure of the micro-emulsion at any temperature is dependent on the ratio of the constituents. The structure can be either nano-spherical nano-sized droplets or a bi- continuous phase . At high concentration of water, the internal structure of micro-emulsion consists of small oil droplets in a continuous water phase. At increased oil concentration a bi- continuous phase without any clear defined shape is formed . At high oil concentration the system transforms to small water droplets(reverse micelles).

- The size of droplets varies from 10 to 100 nm depending on the type of surfactant employed. In the hydrophilic interior of these droplets a certain amount of water soluble material like transition metal salts is dissolved. Two preparation methods possible. These are:

1- Mixing two micro-emulsions, one containing the precursor and the other containing the precipitating agent.

2- Adding the precipitating agent directly to the micro- emulsion containing the metal precursor

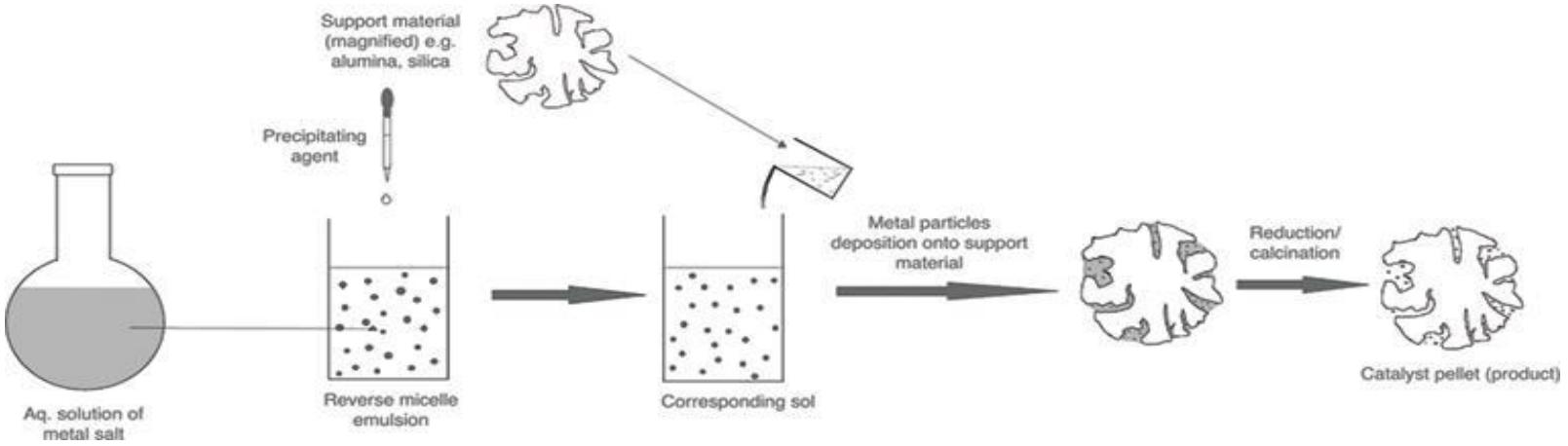


Fig ( ): mechanism where a reverse micro emulsion can be used for the preparation of solid catalyst .

- **There are some advantages and disadvantages of the micro emulsion technique. They are:**

1- The metal particles are reduced directly in the micro-emulsion and can be used as a catalyst in suspension without further thermal treatment.

2- A narrow particle size distribution can be obtained.

3- The particle size can be controlled to a great extent Bimetallic particles can be obtained at room temperature.

4- No effect of the support is found on the formation of the particles.

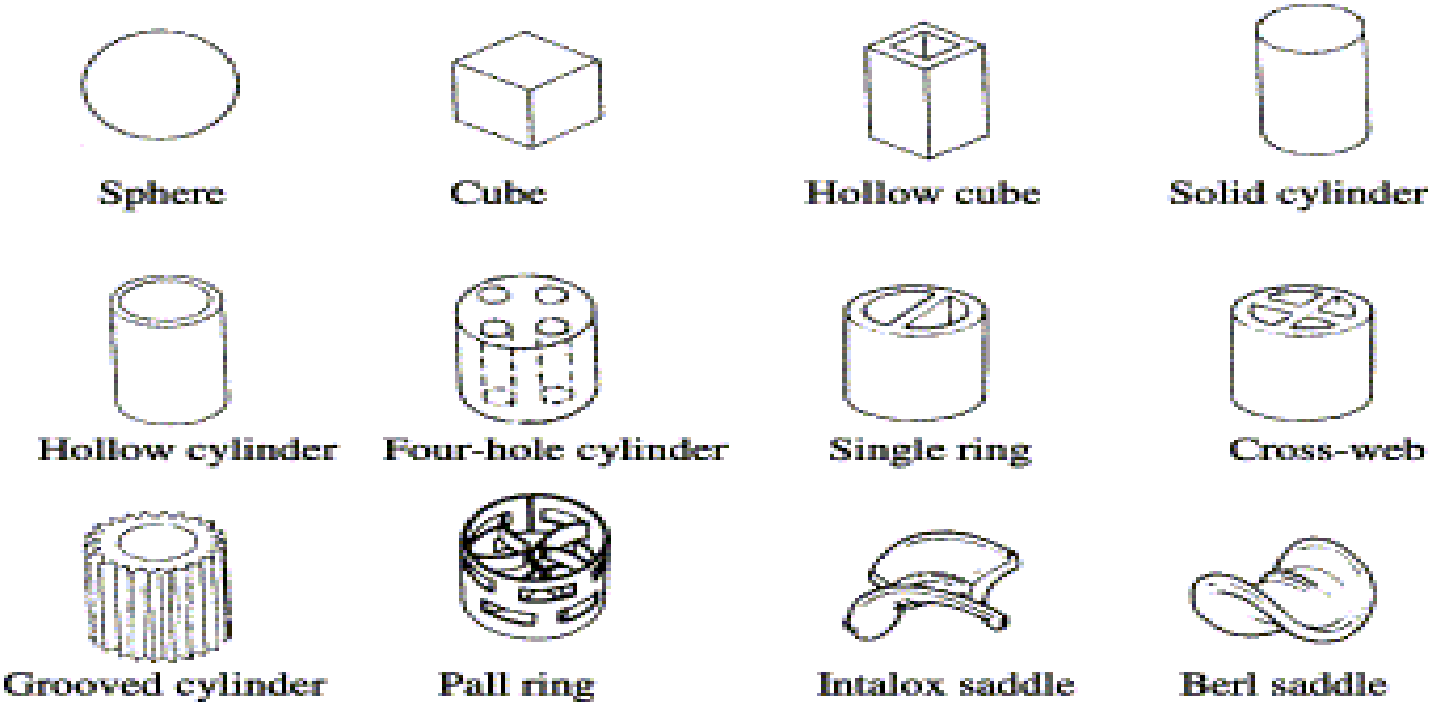
- **Limitations of this method are:**

1- The amount of the catalyst prepared from a single micro-emulsion may be limited.

2- Recovery and recycling of the liquid phase may be difficult.

Catalyst Shapes

Industrial catalysts are generally shaped bodies of various forms, e. g., rings, spheres, tablets, pellets, Honeycomb (Fig. 6-1).



Characterization of Heterogeneous Catalysts

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

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

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.

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.

Physical Characterization

- In any heterogeneous catalytic system, the reactant must first be adsorbed on the catalyst surface. This is why surface characterization is so important.
- The main terms for describing physical catalyst properties are as follows:
- – Morphology: steric conditions and topology of the surface
- – Texture Properties: generally refers to catalyst surface area, the pore structure of the particles (pore size, pore size distribution, pore shape). Share of the hollow space (pore volume) of a catalyst pellet.

Determining the Surface Area:

- The total surface area of a solid is related to the volume (the amount) of gas that is adsorbed on this surface at a given temperature and pressure. An adsorption isotherm is a graph which shows how the amount adsorbed depends on the equilibrium pressure of the gas, at constant temperature.
- **The determination of physisorption isotherms**
- The quantity of gas adsorbed is measured in any convenient units, but for the presentation of the data, it is recommended that the amount adsorbed should be expressed in moles per gram of outgassed adsorbent. If possible, the composition of the adsorbent should be specified and its surface characterized.

- To facilitate the comparison of adsorption data, it is recommended that adsorption isotherms are displayed in graphical form with the amount adsorbed (preferably in mol g^{-1}) plotted against the equilibrium relative pressure (p/p^0), where p^0 is the saturation pressure of the pure adsorptive at the operational temperature, or against p, when the temperature is above the critical temperature of the adsorptive.
- If the adsorption measurements are made under conditions where the gas phase deviates appreciably from ideality (e.g., at high pressure), it is desirable that the isotherms should be presented in terms of gas fugacity rather than pressure.

Classification of physisorption isotherms

- An adsorption isotherm is a graph which shows how the amount adsorbed depends on the equilibrium pressure of the gas, at constant temperature.
- In the 1985 IUPAC recommendations physisorption isotherms were grouped into six types. However, over the past years various new characteristic types of isotherms have been identified and shown to be closely related to particular pore structures.
- Therefore, in 2015 IUPAC refine its original classifications of physisorption isotherms and associated hysteresis loops. The proposed updated classification of physisorption isotherms is shown in Fig below:

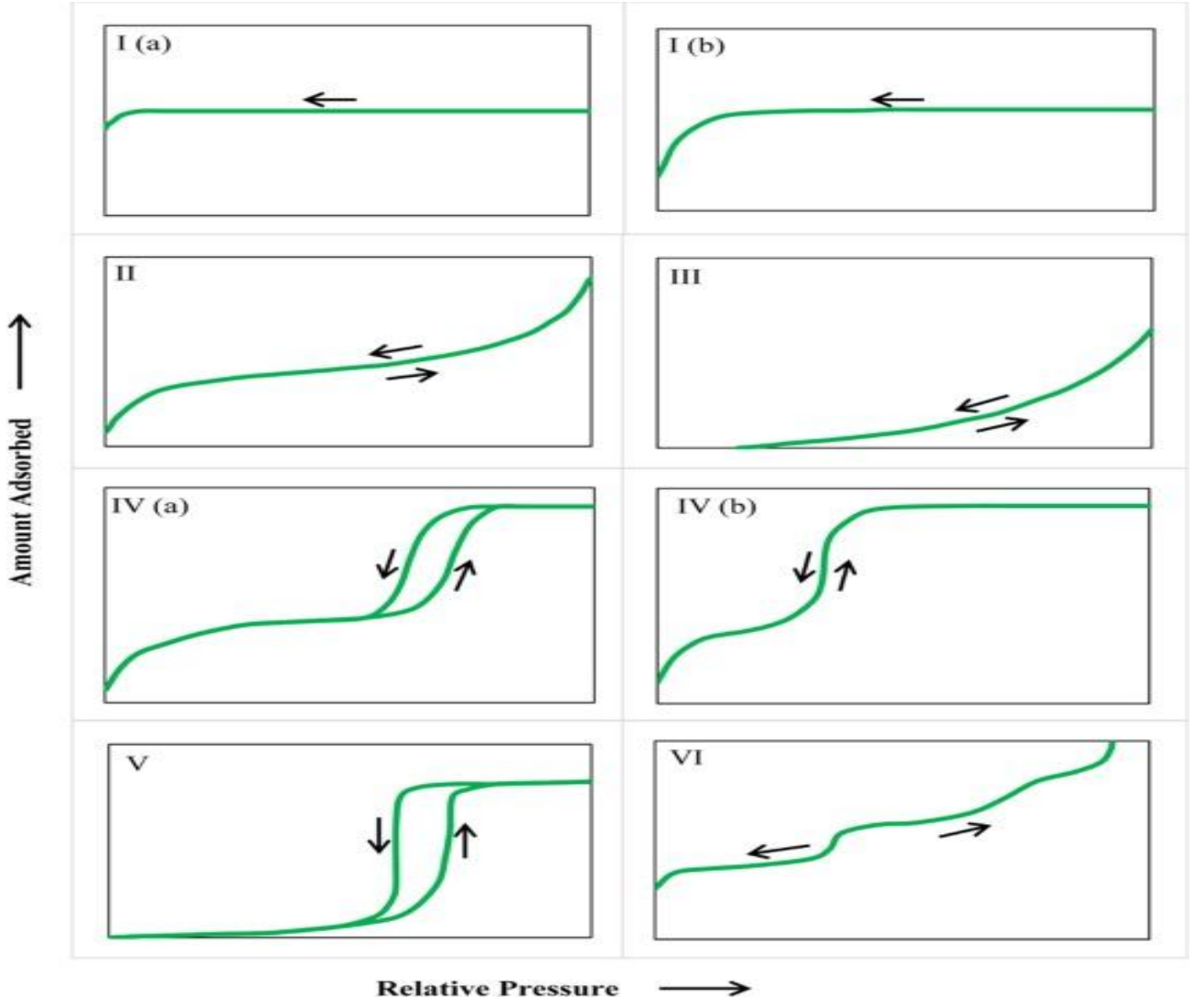


Fig. Classification of physisorption isotherms.

- Reversible Type I isotherms are given by microporous solids having relatively small external surfaces (e.g., some activated carbons, molecular sieve zeolites and certain porous oxides).
- - A Type I isotherm is concave to the p/p^0 axis and the amount adsorbed approaches a limiting value. This limiting uptake is governed by the accessible micropore volume rather than by the internal surface area.
- - A steep uptake at very low p/p^0 is due to enhanced adsorbent-adsorptive interactions in narrow micropores (micropores of molecular dimensions), resulting in micropore filling at very low p/p^0.

- - For nitrogen and argon adsorption at 77 K and 87 K, Type I (a) isotherms are given by microporous materials having mainly narrow micropores (of width < ~ 1 nm).
- -Type I (b) isotherms are found with materials having pore size distributions over a broader range including wider micropores and possibly narrow mesopores (< ~ 2.5 nm).

- - Reversible Type II isotherms are given by the physisorption of most gases on nonporous or macroporous adsorbents.
- - The shape is the result of unrestricted monolayer-multilayer adsorption up to high p/p^0. If the knee is sharp, Point B – the beginning of the middle almost linear section – usually corresponds to the completion of monolayer coverage.

- A more gradual curvature (i.e., a less distinctive Point B) is an indication of a significant amount of overlap of monolayer coverage and the onset of multilayer adsorption. The thickness of the adsorbed multilayer generally appears to increase without limit when $p/p^0 = 1$.

- - In the case of a Type III isotherm, there is no Point B and therefore no identifiable monolayer formation; the adsorbent-adsorbate interactions are now relatively weak and the adsorbed molecules are clustered around the most favorable sites on the surface of a nonporous or macroporous solid.
- - In contrast to a Type II isotherm, the amount adsorbed remains finite at the saturation pressure (i.e., at $p/p^0 = 1$).

- Type IV isotherms are given by mesoporous adsorbents (e.g., many oxide gels, industrial adsorbents and mesoporous molecular sieves).
- - The adsorption behavior in mesopores is determined by the adsorbent adsorptive interactions and also by the interactions between the molecules in the condensed state. In this case, the initial monolayer-multilayer adsorption on the mesopore walls, which takes the same path as the corresponding part of a Type II isotherm, is followed by pore condensation. (pore condensation is the phenomenon whereby a gas condenses to a liquid-like phase in a pore at a pressure p less than the saturation pressure p^0 of the bulk liquid).

- - A typical feature of Type IV isotherms is a final saturation plateau, of variable length (sometimes reduced to a mere inflexion point).
- - In the case of a Type IVa isotherm, capillary condensation is accompanied by hysteresis. This occurs when the pore width exceeds a certain critical width, which is dependent on the adsorption system and temperature (e.g., for nitrogen and argon adsorption in cylindrical pores at 77 K and 87 K, respectively, hysteresis starts to occur for pores wider than ~ 4 nm).

- With adsorbents having mesopores of smaller width, completely reversible Type IVb isotherms are observed. In principle, Type IVb isotherms are also given by conical and cylindrical mesopores that are closed at the tapered end.
- In the low $p/p0$ range, the Type V isotherm shape is very similar to that of Type III and this can be attributed to relatively weak adsorbent–adsorbate interactions. At higher $p/p0$, molecular clustering is followed by pore filling. For instance, Type V isotherms are observed for water adsorption on hydrophobic microporous and mesoporous adsorbents.

- The reversible stepwise Type VI isotherm is representative of layer-by-layer adsorption on a highly uniform nonporous surface.
- - The step-height now represents the capacity for each adsorbed layer, while the sharpness of the step is dependent on the system and the temperature.
- - Amongst the best examples of Type VI isotherms are those obtained with argon or krypton at low temperature on graphitised carbon blacks.