

# Chemisorption

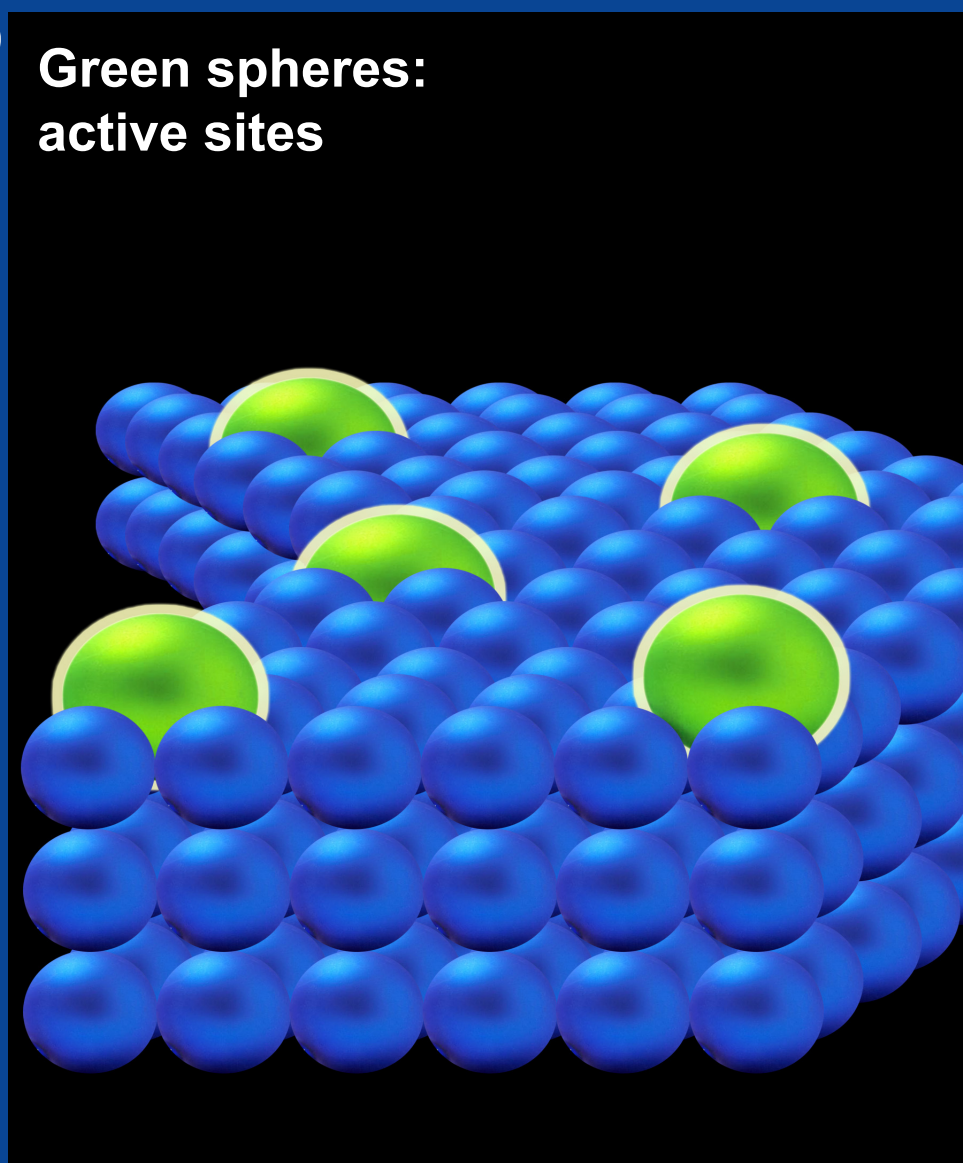
Presented by Micromeritics Instrument Corporation

**Chemisorption:** Chemical adsorption is an interaction much stronger than physical adsorption. In fact, the interaction is an actual chemical bond where electrons are shared between the gas and the solid surface. While physical adsorption takes place on all surfaces if temperature and pressure conditions are favorable, chemisorption only occurs on certain surfaces and only if these surfaces are clean. Chemisorption, unlike physisorption, ceases when the adsorbate can no longer make direct contact with the surface; it is therefore a single layer process.

Blue spheres: surface molecules

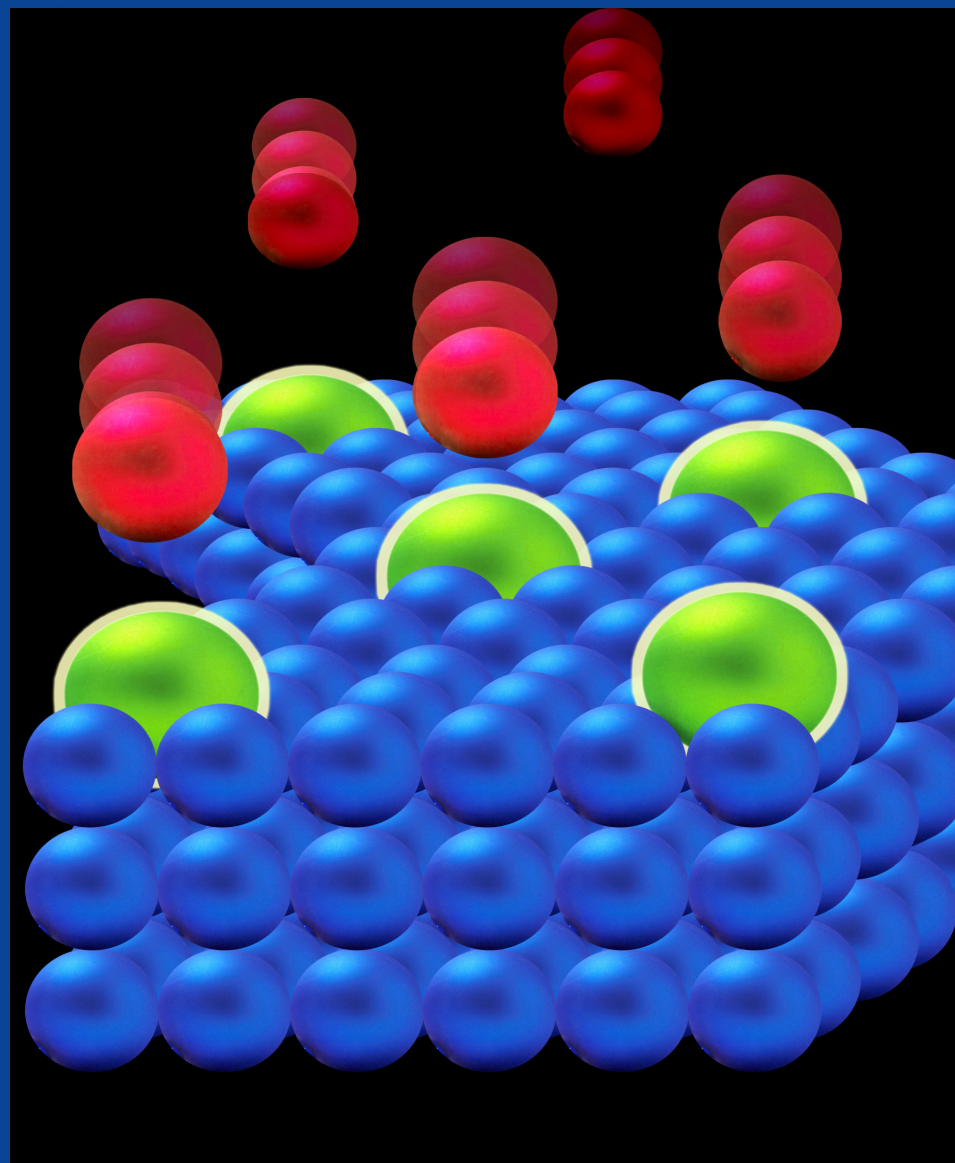
1.)

Green spheres: active sites



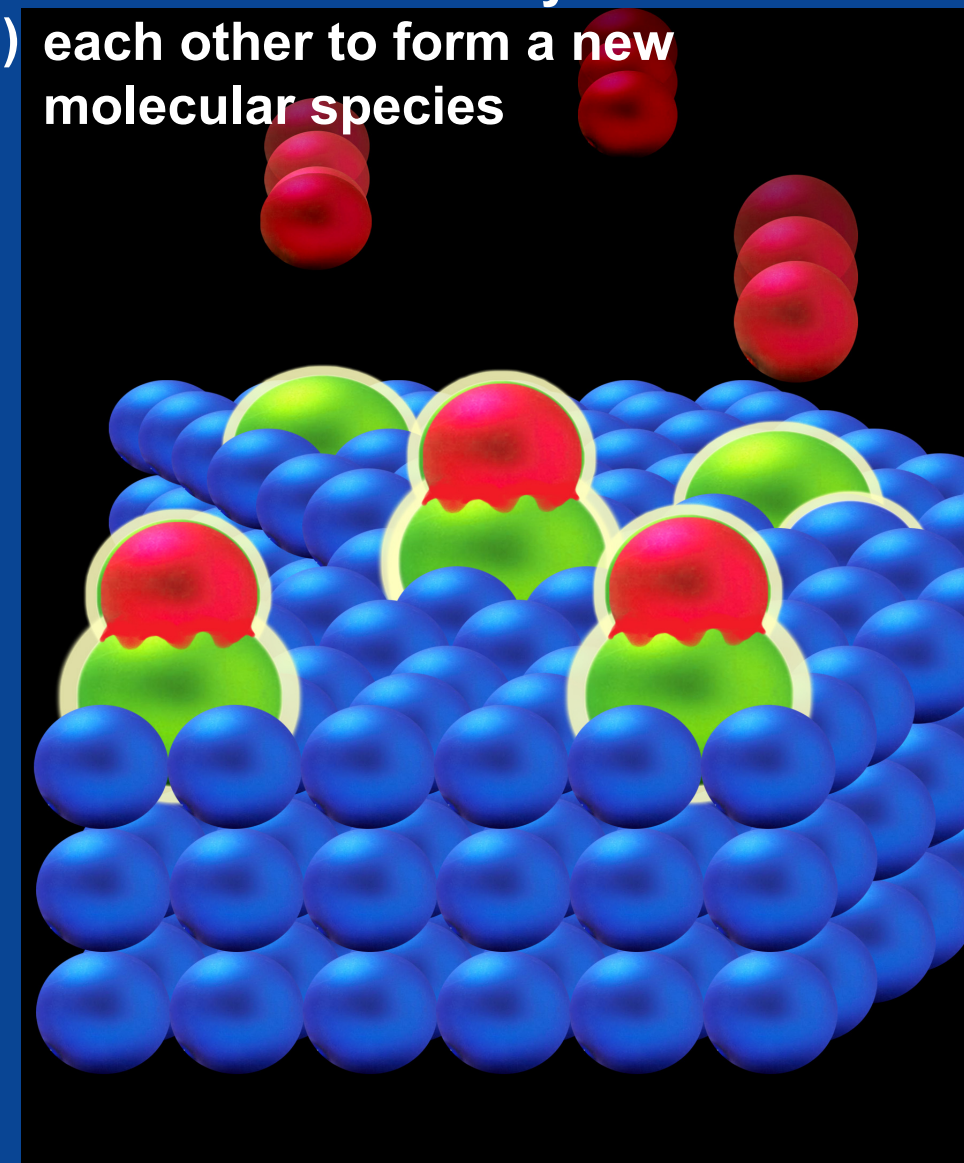
Red spheres: gas molecules

2.)



Red and Green: molecules react only with each other to form a new molecular species

3.)



Most medicinal, chemical, and petroleum-derived items in common usage are dependent at some stage in their manufacture on a heterogeneous catalytic process. High octane gasoline, plastics, fertilizers, and herbicides would either be prohibitively expensive or unobtainable without them. Likewise, pollution control would be almost nonexistent were it not for catalysts.

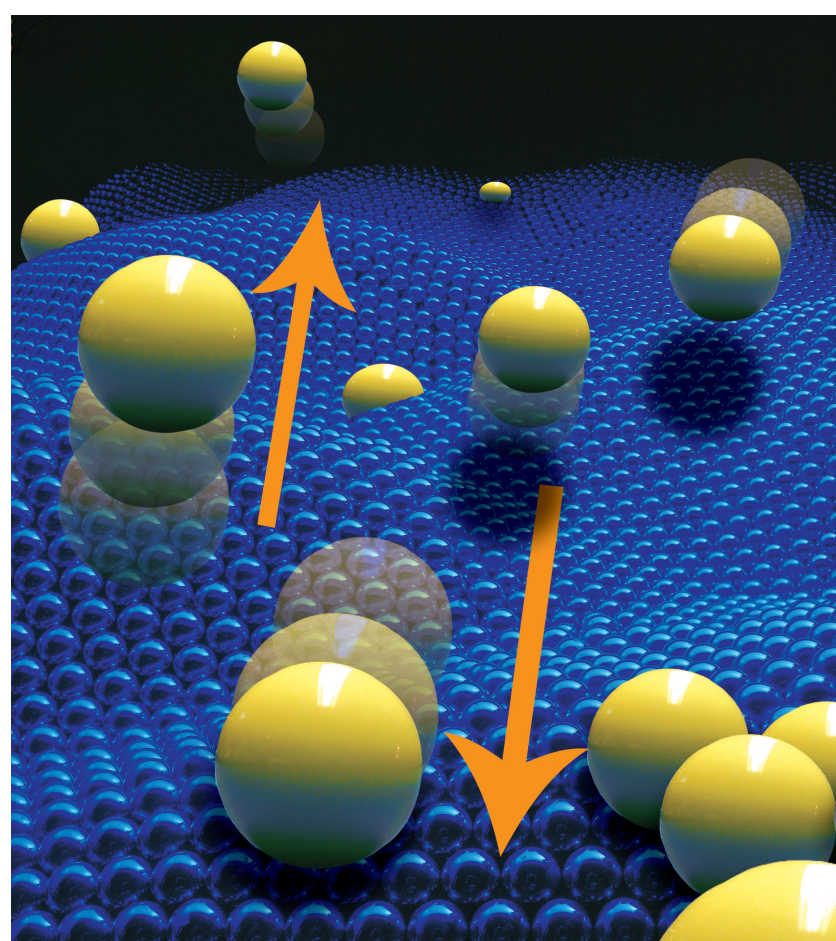
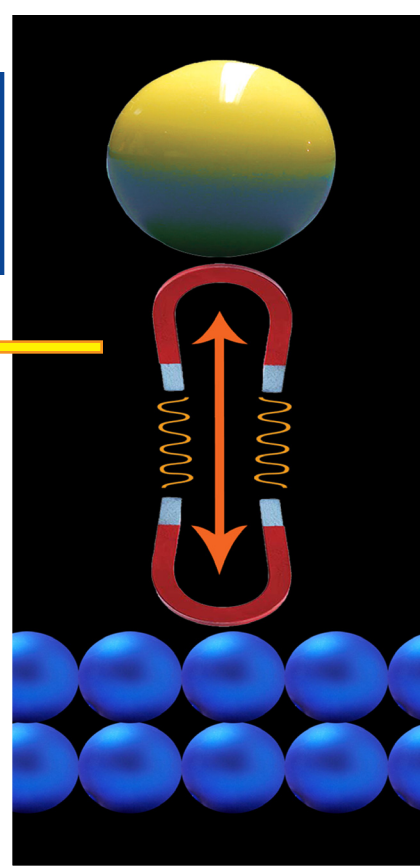
## Physical and Chemical adsorption differentiated

### Physisorption

(by van der Waals and electrostatic forces) This is the most common form of adsorption. The molecules are attracted by van der Waals forces, and attach themselves to the surface of the solid. The molecules remain intact, and can be freed easily (the forces are small, and short-range).

Physical adsorption is the result of a relatively weak interaction between the solid surface and the gas - a physical attraction. Physically attractive forces involve relatively weak van der Waals forces and low heats of adsorption usually not exceeding 80 kJ/mole. Physical adsorption does not affect the structure or texture of the adsorbent, and desorption takes place as conditions are reversed.

**Chemical adsorption** is a much stronger interaction than physical adsorption with heats of adsorption up to 800 kJ/mole. But heat of adsorption values less than 80 kJ/mole do not necessarily rule out chemisorption. During the chemisorption process the adsorbing gas or vapor molecule splits into atoms, radicals, or ions that form a chemical bond with the adsorption site. This interaction involves the sharing of electrons between the gas and the solid surface and may be regarded as the formation of a surface compound.



	Chemisorption	Physisorption
Temperature Range:	<b>Unlimited</b>	Near or above dew point of gas
Enthalpy of Adsorption:	<b>Typically (80 - 800 kJ/mol)</b>	Typically (5 - 80 kJ/mol)
Nature of the adsorption:	<b>Irreversible</b>	Reversible
Saturation:	<b>Limited to one layer</b>	Multilayer formation
Adsorption kinetics:	<b>Variable Activated process</b>	Fast Non - Activated process

Unlike physical adsorption, chemisorption is difficult to reverse. In fact, when sufficient energy is applied to remove the adsorbed molecules, atoms of the surface material may be carried away with them. For example, when oxygen is chemisorbed on charcoal, the application of heat and vacuum results in desorption of carbon monoxide.

Physical adsorption takes place on all surfaces provided temperature and pressure conditions are favorable. Chemisorption, on the other hand, is localized and occurs only on certain surfaces or surface sites. Meaningful examination of the energies and sites involved can be achieved only if these sites are cleansed of previously adsorbed molecules. Thus, before a chemisorption analysis can proceed, removal from the active sites of any existing atmospheric contamination must be achieved.

Under proper conditions physical adsorption results in adsorbed molecules forming multiple layers. Chemical adsorption occurs only if the adsorbate makes direct contact with the active surface; therefore it is a single-layer process. But physical and chemical adsorption processes are not exclusive. A layer of molecules may be adsorbed physically on top of an underlying chemisorbed layer, or physical adsorption may occur on non-active sites of a substrate while chemisorption is occurring on the active sites.

Physical adsorption diminishes rapidly with temperature elevation; chemisorption, on the other hand, is enhanced by high temperature. Furthermore, the same surface can display physical adsorption at one temperature and chemisorption at a higher temperature. For example, at liquid nitrogen temperature (77 K) nitrogen gas is adsorbed physically on iron but at 800 K, an energy level too high for physical adsorption bonds, nitrogen is adsorbed chemically to form iron nitride.

Many molecules must be activated before they will react according to present theories. Activation energy is a measure of the energy which must be supplied to them to bring about reaction. In some cases the activation energy requirement is such that reaction will proceed only at a measurable rate above a certain temperature. In others, reaction proceeds rapidly at low temperature, hydrogen on platinum being an example of a chemisorption reaction where the activation energy approaches zero.

### Summary:

#### • Chemisorption:

- is a strong (chemical) interaction between the adsorbed molecule and the surface molecule of the active site.
- is selective and occurs only on certain clean surfaces.
- is a single layer process.
- often requires an activation energy.
- can take place at elevated temperatures.
- is always localized.
- sites may be homogeneous or heterogeneous according to the energy characteristics of the adsorption site.
- can be used to measure the area of active metal of a catalyst.
- can be used to determine relative activity among several catalysts.
- can be used to study degradation of catalytic activity due to time of use and poisoning.
- A catalyst accelerates a chemical reaction without being consumed in the process.
- A homogeneous catalyst is one which is of the same phase as the reactant; for example, a liquid-liquid solution.
- A heterogeneous catalyst is one which is of different phase as the reactant; for example, a solid-gas interaction.
- A catalyst employs a chemisorption process.
- The strength and velocity of the chemisorption determines catalytic activity.
- The total surface of a catalysts may be metallic or metallic clusters may be distributed on the surface of a supporting material.
- Catalysts of practical interest are characterized by high specific surface area.
- TPD and TPR employ chemisorption and investigate desorption and reduction as a function of temperature.
- TPD provides information about the number, strength and heterogeneity of chemisorption sites.
- TPR is used to gain information on the reducibility of oxidic species and provides such information as the number of reducible species, the activation energy of the site, and the quantity of hydrogen consumed by the site.

## Applications

### Catalysts

The active surface area and porous structure of catalysts have a great influence on production rates. Limiting the pore size allows only molecules of desired sizes to enter and leave; creating a selective catalyst that will produce primarily the desired product. Chemisorption experiments are valuable for the selection of catalysts for a particular purpose, qualification of catalyst vendors, and the testing of catalyst performance over time to establish when the catalyst should be reactivated or replaced.

### Fischer-Tropsch Synthesis

Cobalt, iron, etc. based catalysts are used to convert syngas (carbon monoxide and hydrogen) to hydrocarbons larger than methane. These hydrocarbons are rich in hydrogen and do not contain sulfur or nitrogen. The characterization of these materials includes:

- Temperature-programmed desorption
- Pulse chemisorption

### Isomerization

Catalysts such as small-pore zeolites (mordenite and ZSM-5) containing noble metals (typically platinum) are used to convert linear paraffins to branched paraffins. This increases the octane number and value for blending gasoline and improves the low temperature flow properties of oil. The characterization of these materials includes:

- Temperature-programmed reduction
- Pulse chemisorption

### Fuel Cells

Platinum-based catalysts including Pt/C, PtRu/C, and PtRuIr/C are often characterized by temperature-programmed reduction to determine the number of oxide phases and pulse chemisorption to calculate:

- Metal surface area
- Metal dispersion
- Average crystallite size

### Partial Oxidation

Manganese, cobalt, bismuth, iron, copper, and silver catalysts used for the gas-phase oxidation of ammonia, methane, ethylene, and propylene are characterized using:

- Temperature-programmed oxidation
- Temperature-programmed desorption
- Heat of desorption of oxygen
- Heat of dissociation of oxygen

### Catalytic Reforming

Catalysts containing platinum, rhenium, tin, etc. on silica, alumina, or silica-alumina are used for the production of hydrogen, aromatics, and olefins. These catalysts are commonly characterized to determine:

- Metal surface area
- Metal dispersion
- Average crystallite size

### Catalytic Cracking

Acid catalysts such as zeolites are used to convert large hydrocarbons to gasoline and diesel fuel. The characterization of these materials includes:

- Ammonia chemisorption
- Temperature-programmed desorption of ammonia
- Temperature-programmed decomposition of alkylamines
- Temperature-programmed desorption of aromatic amines

### Hydrocracking, Hydrodesulfurization, and Hydrodenitrogenation

Hydrocracking catalysts typically composed of metal sulfides (nickel, tungsten, cobalt, and molybdenum) are used for processing feeds containing polycyclic aromatics that are not suitable for typical catalytic cracking processes. Hydrodesulfurization and hydrodenitrogenation are used for removing sulfur and nitrogen respectively from petroleum feeds. The characterization of these materials includes:

- Temperature-programmed reduction
- Oxygen pulse chemisorption

