10. Surface Chemistry and Catalysis

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Abstract:

Heterogeneous catalysis is a major factor these days. Most industrial chemical processes share a common catalytic genesis. These processes include the production of clean fuels, medicines, commodity chemicals, and pollution abatement technology. Gaining insight into the basic principles of local surface chemistry is crucial since catalysis occurs at the surface, as it determines the catalytic performance. A thorough understanding of a catalyst surface at the atomic level may open the door to the creation of innovative catalytic systems with practical energy and environmental applications. We will talk about in this essay. Surface Catalysis and Chemistry.

Keywords:

Surface Chemistry, Catalysis, Heterogeneous, Chemical Processes, Colloid Formation, Electrode Reactions, Chromatography, Enzymatic, Absorption, Physisorption, Pressure, Gas, Adsorbent, Solid, Isotherm.

10.1 Introduction:

10.1.1 Surface Chemistry:

The study of chemical interactions at interfaces can be a rough definition of surface chemistry. Surface engineering, which seeks to alter the chemical composition of the surface by incorporating certain elements or functional groups that have a variety of desirable effects or enhance surface or interface qualities, is closely associated with surface chemistry. Surface chemistry and electrochemistry are related. The field of heterogeneous catalysts places significant emphasis on surface chemistry. Adsorption is the process of bringing molecules of a gas or liquid to the surface; this can happen via chemisorption or physio absorption. Surface chemistry includes these two. [1]

Surface science is the study of chemical processes that take place at the interface between two phases (liquid-gas, solid-liquid, solid-vacuum, and solid-solid). Although we understand far more about reactions that take place in homogenous phases, chemistry at interfaces is widespread in nature. It's not that I'm not interested in or trying hard enough; the issue is that studying interfaces is harder than studying bulk samples. A few decades ago, a new paradigm was ushered in with the invention of innovative spectroscopies that are specifically tailored to discriminate and isolate information from surfaces.

However, the majority of those spectroscopies are vacuum-dependent, meaning they cannot be used in conditions that are pertinent to many of the systems of interest. Though the quest for a molecular-level explanation of the processes and energetics of interfacial reactions rages on, more recent developments have opened up new possibilities for the characterization of gas–solid and, more specifically, liquid–solid interfaces. We present three perspectives on surface phenomena related to heterogeneous catalysis in this issue of The Journal of Physical Chemistry Letters, which highlight the current state of the field as well as future directions of research and development. [2]

10.1.2 Applications of Surface Chemistry:

In a broader sense, surface chemistry is the study of how the surfaces of different systems interact with one another. Certain phenomena operate according to this theory, like:

- Catalysis
- Colloid Formation
- Electrode Reactions
- Chromatography

Chemical processes that include surface chemistry include the following:

- Enzymatic processes occurring at the biological interfaces present in the membranes and walls of cells.
- They are utilized in the surface and interface of computer microchips in the electronics sector.
- The heterogeneous catalysts in the catalytic converter remove pollutants from vehicle exhaust. [3]

10.2 Types of Absorption:

10.2.1 Physical Adsorption or Physisorption:

"Physisorption" is the word for the process when gas, solid, or liquid are kept to a solid surface by weak vander wall forces. H2 on charcoal, for instance.

A. Characteristics:

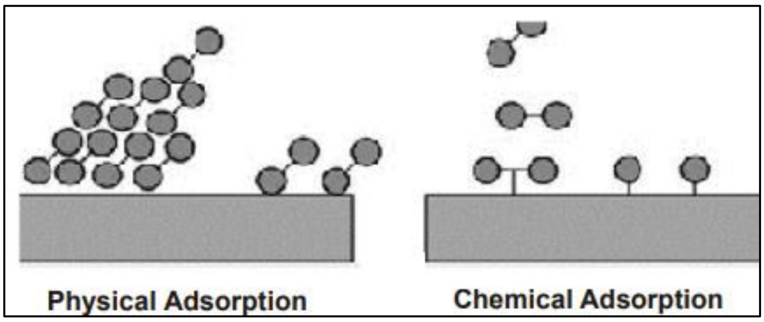
- Nature of forces: Weak van der Waals forces
- Specificity: It is not specific in nature
- Reversibility: The process is reversible
- Layer: It is a multi-layered process
- Enthalpy of adsorption: Low enthalpy of adsorption [20 – 40 KJ/mole]
- The energy of activation: Very low
- Desorption: Very easy
- Factors affecting: Surface area of adsorbent nature of adsorbate, pressure, temperature. [4]

10.2.2 Chemical Adsorption or Chemisorption:

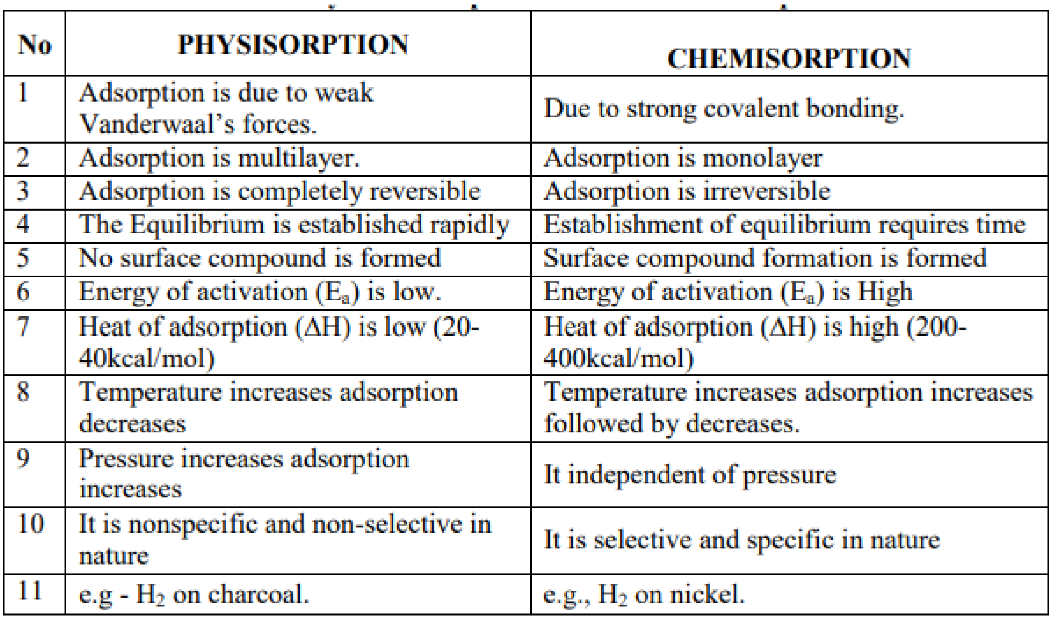
Chemisorption is the process by which gas, solid, or liquid are retained on a solid surface by strong chemical covalent bonds. H2 on nickel, for instance.

A. Characteristics:

- Nature of forces: Strong chemical forces
- Specificity: Highly specific nature
- Reversibility: It is irreversible
- Layer: It is a single-layered process
- Enthalpy of adsorption: High enthalpy of adsorption [40 – 400 KJ/mole]
- The energy of activation: Very high
- Desorption: Very difficult
- Factors affecting: Surface area of adsorbent, nature of adsorbate temperature. [5]



The distinction between chemical and physical adsorption [6]



No	PHYSISORPTION	CHEMISORPTION
1	Adsorption is due to weak Vanderwaal's forces.	Due to strong covalent bonding.
2	Adsorption is multilayer.	Adsorption is monolayer
3	Adsorption is completely reversible	Adsorption is irreversible
4	The Equilibrium is established rapidly	Establishment of equilibrium requires time
5	No surface compound is formed	Surface compound formation is formed
6	Energy of activation (E_a) is low.	Energy of activation (E_a) is High
7	Heat of adsorption (ΔH) is low (20-40kcal/mol)	Heat of adsorption (ΔH) is high (200-400kcal/mol)
8	Temperature increases adsorption decreases	Temperature increases adsorption increases followed by decreases.
9	Pressure increases adsorption increases	It independent of pressure
10	It is nonspecific and non-selective in nature	It is selective and specific in nature
11	e.g - H_2 on charcoal.	e.g., H_2 on nickel.

10.3 Factors Affecting Adsorption:

10.3.1 Effect of Temperature:

$$adsorption \propto \frac{1}{Temperature}$$

10.3.2 Effect of Pressure:

At constant temperature: Adsorption $\propto$ Pressure

A. Nature of Gas or Adsorbent [7]

Adsorption $\propto$ Critical temperature of the gas α

Liquation of the Gas

For example, [NH_3, Cl_2, HCl] > [N_2, O_2, H_2]

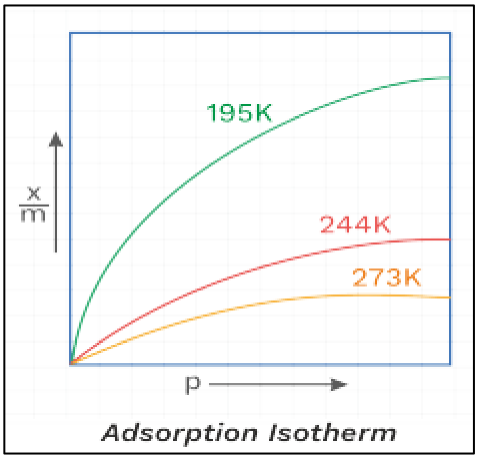
B. Surface area of Adsorbent: Greater surface area of the adsorbent will result in a higher number of active centers and a faster rate of adsorption.

C. Activation of Solid Adsorbent: The adsorbent becomes activated and the rate of adsorption rises when it is divided or when gases that have previously been adsorbed are removed.

D. Adsorption Isotherm [8]: At constant temperature, the plot illustrates the extent of adsorption (x/m) against pressure.

Here, x = Mass of gas adsorbed

m = Mass of adsorbent



E. Freundlich Adsorption isotherm [9]

At low pressure, graph is almost straight

$$\frac{x}{m} \propto P$$

$$\frac{x}{m} \propto KP$$

Here, K = Constant.

At high pressure $\frac{x}{m}$ becomes almost constant and does not change with pressure

$$\frac{x}{m} \propto \ P^o \ \frac{x}{m} \propto \ KP^o$$

At intermediate value of pressure

$$\frac{x}{m} \propto \ P^{\frac{1}{n}}$$

$$\frac{x}{m} = \ KP^{\frac{1}{n}}$$

(n>1)

n is constant and solely dependent on the adsorbent and adsorbate's properties.

The values of K and n are calculated as follows:

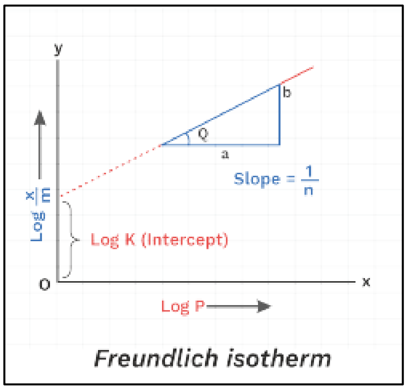
When we take equation (1)'s logarithm, we get

$$\log_e \frac{x}{m} = log_e\ K + \frac{1}{n} log_e\ P$$

As a result, a straight line appears when a graph between loge x/m and loge P is created.

Here, slope

$$= \frac{1}{n}\ \left(\frac{1}{n} = 0\ to\ 1\right); Intercept = \log_e K$$



If pressure is substituted with concentration

$$\frac{x}{m} = KC^{\frac{1}{n}}$$

Langmuir adsorption isotherm

$$\frac{x}{m} = \frac{a\,P}{1 + b\,P}$$

$$\frac{x}{m}/P = \frac{a\,P}{1 + b\,P}$$

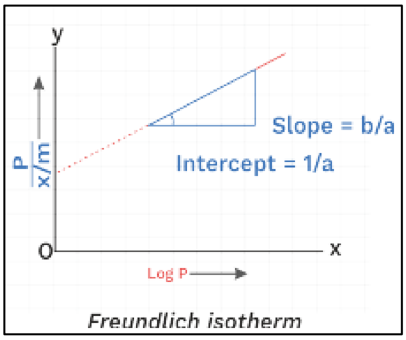
When we reverse the equation, we obtain,

$$\frac{P}{x/\,m} = \frac{1 + b\,P}{a} = \frac{1}{a} + \frac{b}{a}P$$

Here, the constants a and b are shown on a graph between

$$\frac{P}{x\,/\,m}\,and\ P$$

The slope of the straight line is equal to b/a, and the intercept is equal to 1/a.



Adsorption isobars are the charts that show the relationship between temperature and x/m at constant pressure.

10.4 Catalysis:

A catalyst is a material that speeds up reactions and, most of the time, can be retrieved in its pure form at the conclusion of the reaction. It might, nevertheless, participate in a reaction that is used up in one phase and then renewed in a subsequent one. We call this process "catalysis."

If a substance quickens the rate of a chemical reaction, it is referred to as a positive catalyst, or just a catalyst. However, if the extra material slows down the rate of a chemical reaction, it is referred to as a negative catalyst. [10]

Example of Negative Catalysts:

1. Acetanilide or H_3PO_4 in the breakdown of H_2O_2.
2. Alcohol in the process of oxidizing chloroform, which produces phosgene.
3. In internal combustion engines, tertraethyl lead or nickel carbonyl serve as antiknock materials.
4. Antifreezes, such as glycerol, which stop the machines from rusting.

Catalytic Promoters:

Some compounds can increase a catalyst's activity even when they are applied in very small amounts. It's possible that this material isn't a catalyst. These compounds are known as catalytic promoters because they enhance a catalyst's activity. For instance, in Haber's procedure, molybdenum is used as a promoter for the Fe catalyst.

Catalytic Inhibitors or Poisons:

The presence of modest amounts of other compounds known as inhibitors significantly lowers the rates of several processes. Poisoning is the term for substances whose presence reduces or eliminates a catalyst's action. In the Haber process, CO or H_2S in hydrogen gas poisons the Fe catalyst.

10.4.1 Types of Catalysis:

There are basically two categories of catalysis:

(A) Homogeneous Catalysis:

A catalyst is referred to as homogeneous if it is present in the same phase as the reactants; this kind of catalysis is known as homogeneous catalysis.

Ex:

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{H_2SO_4} \underset{\text{Glucose}}{C_6H_{12}O_6(aq)} + \underset{\text{Fructose}}{C_6H_{12}O_6(aq)}$$

$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$

$$CH_3COOCH_3(\ell) + H_2O(\ell) \xrightarrow{HCl(\ell)} CH_3COOH(aq) + CH_3OH(aq)$$

(B) Heterogeneous Catalysis:

The catalyst and reactants are present in different phases during this form of catalysis. In heterogeneous catalysis, the reactants are often gasses, though occasionally liquid reactants are also employed. The catalyst is typically a solid. Another name for it is surface catalysis.

Ex:

i) Methyl alcohol (CH_3OH) synthesis from CO and H_2 with a catalyst mixture of copper, Z_nO and Cr_2O_3.

$$CO(g) + 2H_2(g) \xrightarrow{Cu,ZnO-Cr_2O_3} \text{CH3OH}(l)$$

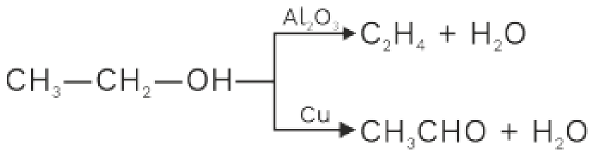
ii) Haber's technique, which uses iron as a catalyst to produce ammonia from N_2 and H_2.

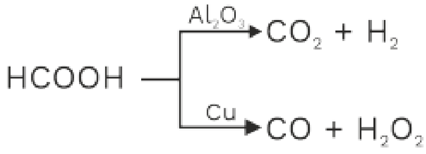
$$N_2(g) + 3H_2(g) \overset{Fe}{\leftrightarrow} 2NH_3(g)$$

10.4.2 Properties of a Catalyst:

- At the conclusion of a reaction, the mass or chemical composition Report Phrase of a catalyst remains unchanged.
- The degree of chemical adsorption determines a catalyst's activity; hence, adsorption should always be somewhat strong but not very strong.
- Since it is very specialized, a catalyst may be useful for one reaction but ineffective for another. We refer to this as catalyst specificity.

For instance, the enzyme invertase is capable of catalyzing the hydrolysis of sucrose but not maltose.





Due to its increased surface area and thus higher number of active centers, catalyst works best in solid powder form.

- A temperature is known as the optimal temperature at which a catalyst functions best.
- By altering the activation energy, the catalyst's inclusion causes the reaction to follow an alternative course.

10.4.3 Enzyme Catalysis:

For a variety of processes, many enzymes also serve as catalysts. Since many processes that occur in plants, animals, and our bodies are catalyzed by enzymes. Thus, the phenomena are referred to as biochemical catalysis, and they are known as biochemical catalysts.

A. Characteristics of Enzyme Catalysis:

- High effectiveness One million molecules of reactant can be changed by one enzyme molecule every minute.
- Highly specific nature No enzyme catalyst has the ability to catalyze more than one reaction at once.
- Optimum temperature At the ideal temperature of 298–310 K, an enzyme catalyst yields a greater product. The temperature of the human body, or 310 K, is ideal for processes catalyzed by enzymes.
- Ideal pH An enzyme-catalyzed reaction reaches its maximal pace in an optimum pH range of 5 to 7.
- Activators Ions like Na+, Ca2+, and Mn2+ are activators that aid in the activation of enzymes that are unable of acting on their own.
- Co-enzyme The presence of co-enzymes, which are substances with an enzyme-like nature, boosts the activity of the enzyme. Vitamins mostly function as co-enzymes.
- Inhibitors' Effect The rate of an enzyme reaction is slowed down by inhibitors. Many medications' mechanism of action is based on the inhibition of specific enzymes in the body.

B. Enzyme Catalysis and Its Mechanism:

Enzymes are essential biological catalysts for all biological activities. They expedite metabolic reactions inside living things and are incredibly specialized. By forming complexes between the enzyme and the substrate, enzyme catalysis lowers the activation energy needed for the process. Enzymes help cells react, which makes sure metabolic pathways run smoothly. [11]

10.5 Conclusion:

Surface chemistry is the study of chemical and physical events that take place at the interface between two phases, such as liquid-gas and solid-liquid and solid-vacuum and solid-liquid interfaces. Surface Physics and Surface Chemistry are fields that fall under the umbrella of Surface Chemistry.

The 2D coverings have been shown to dramatically influence surface chemistry and catalysis, leading to improved surface reactions and weakened molecule adsorption.

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