HETEROGENEOUS CATALYSIS
Contents

Chapter 1. General Revision.

Chapter 2. Active sites of Heterogeneous Catalysis.

Chapter 3. Multiplet Theory.
  3.1 Geometric Factor  3.2 Energy Factor

Chapter 4. Electronic Theory.

Chapter 5. Active Ensemble Theory.
General Revision
1.1 Characteristics of Catalysts
1.2 Mechanism of Chemical Reactions on Solid Catalysts
1.3 Physical & Chemical Adsorption
1.4 Chemical Adsorption
1.5 Langmuir Adsorption Isotherm
1.6 Types of Chemical Reactors
1. A catalyst is a substance that changes the rate of a chemical reaction to reach equilibrium. It participates in reaction, effecting intermediate chemical interaction with the reagents. It is both a reactant and a product. The catalyst undergoes no net change.

N.B
It is worthy to note that the word ‘catalysis’ is used to describe the action of the catalyst. Catalysis is said to be positive if the reaction rate increases. Negative catalysis implies a decrease in the chemical reaction rate due to catalyst action.
2. A catalyst accelerates reaction by providing alternative path to products, the activation energy of each catalytic step being less than that for the homogeneous (non-catalytic) reaction.

Example:

\[ A + B \xrightarrow{k_1} C \xleftarrow{k_2} \]

\[ A : C_2H_4, \quad B : H_2, \quad C : C_2H_6 \]

For non-catalytic reaction (thermal)

\[ A + B \xleftrightarrow{k_1} C \xleftrightarrow{k_2} \]

Where \( \Delta E \) is the activation energy and \( AB^* \) is an activated complex.
If present CuO-MgO as catalyst and its active center (site) as X, then the reaction path is changed.

The closed sequence will be

**Adsorption of A**

\[ A + X \xrightarrow{\Delta E_1} AX^* + AX \]

**Surface reaction**

\[ B + AX \xrightarrow{\Delta E_2} ABX^* + CX \]

**Desorption of C**

\[ CX \xrightarrow{\Delta E_3} CX^* \xrightarrow{} C + X \]

**Net**

\[ A + B + X \xrightarrow{\Delta E_1 + \Delta E_2 + \Delta E_3} C + X \]

and

\[ \Delta E_1 + \Delta E_2 + \Delta E_3 = \Delta E \]
Remark:
In general, in order to effect reactions with a sufficient rate under normal production conditions, the activation energy has to be less than 40Kcal/mole.
3. A catalyst can increase the rate of only those processes that are thermodynamically favorable; it cannot initiate reactions that are not thermodynamically feasible. Thus equilibrium conversion is not altered by catalysis. A catalyst accelerates the forward reaction in an equilibrium system is a catalyst for reverse reaction.

\[
K = \frac{k_1}{k_2} = \frac{k_1'}{k_2'} = \frac{[B]}{[A]} = \frac{[B][X]}{[A][X]}
\]

where \(K\) is thermodynamic equilibrium constant.
4. For a given reactant or group of reactants there may be several reaction paths, and by appropriate choice of catalyst any one of these paths may be “selected”.

**Example 1:**

**Without catalyst**

\[ \text{C}_2\text{H}_5\text{OH} \xrightarrow{450^\circ\text{C}} \text{H}_2, \text{CH}_4, \text{C}_2\text{H}_4, \text{CO}, \text{CO}_2, \text{H}_2\text{O}, \text{CH}_3\text{CHO}, \ldots \]

**With proper catalysts**

\[ \text{C}_2\text{H}_5\text{OH} \xrightarrow{350^\circ\text{C}} \frac{\text{Al}_2\text{O}_3}{\text{C}_2\text{H}_4 + \text{H}_2} \]

\[ \text{C}_2\text{H}_5\text{OH} \xrightarrow{350^\circ\text{C}} \frac{\text{Cu}}{\text{CH}_3\text{CHO} + \text{H}_2\text{O}} \]
Example 2:

Feed: 100% $n-C_5H_{10}$, at 400°C, 1 atm, the product distribution are

Without catalyst (thermal reaction)

- $n-C_5$: 9.2%
- $i-C_5$: 70.8%
- neo-$C_5$: 20.0%

At refinery, by using a proper catalyst

- $n-C_5$: 11.5%
- $i-C_5$: 88.5%
- neo-$C_5$: 0.0%
1.2 Mechanism of Chemical Reactions on Solid Catalysts

Steps in a heterogeneous catalytic reaction.
Step 1: Transport of reactants from the bulk fluid to the fluid-solid interface

Step 2: Intraparticle transport of reactants into the catalyst particle (If it is porous)

Step 3: Adsorption of reactants at interior of the catalyst particle

Step 4: Chemical reaction of adsorbed reactants to adsorbed products (surface reaction)

Step 5: Desorption of adsorbed products

Step 6: Transport of products from the interior sites to the outer surface of the catalyst particle

Step 7: Transport of products from the fluid-solid interface into the bulk fluid stream
## 1.3 Physical & Chemical Adsorption

<table>
<thead>
<tr>
<th></th>
<th>Physical Adsorption</th>
<th>Chemical Adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Adsorbent</td>
<td>All solid</td>
<td>Active centers</td>
</tr>
<tr>
<td>2. Adsorbate</td>
<td>All gases</td>
<td>Reactive gases</td>
</tr>
<tr>
<td>3. Temperature</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>4. ΔH</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>5. Rate</td>
<td>Very rapid</td>
<td>Slow</td>
</tr>
<tr>
<td>6. E</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>7. Coverage</td>
<td>Multi-layer</td>
<td>Mono-layer</td>
</tr>
<tr>
<td>8. Reversibility</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>9. Importance</td>
<td>Surface area</td>
<td>Active-center area</td>
</tr>
<tr>
<td></td>
<td>Pore size</td>
<td>Information for kinetics</td>
</tr>
</tbody>
</table>
1.4 Chemical Adsorption

1.4.1 General Phenomena

Equilibrium curve of physical adsorption

Equilibrium curve of chemical adsorption

Laboratory experiment data (in a finite time)
1.4.2 Heat of adsorption

1. The heat of chemisorption is a measure of the strength of the bonds formed between adsorbent and adsorbate. The variation of heat of adsorption with surface coverage is a measure of surface heterogeneity.

*Example: Hydrogen on the metal film*
2. The maximum reaction rate is obtained when the bonds between the adsorbed complex and the catalyst are neither too strong nor too weak.

Example: Activity of various metals for the decomposition of formic acid as a function of the heat of formation of their formates.
If $(-\Delta H)_{\text{ads}}$ is very large for a given situation, it is clear that catalysis will be hindered precisely because that species is too tenaciously held at the surface. If, on the other hand, $(-\Delta H)_{\text{ads}}$ is very low, the species in question may not be desorbed on the catalyst surface for a time long enough to facilitate reaction.
11.5 Langmuir Adsorption Isotherms

A. The Langmuir treatment of adsorption

1. Sweeping assumptions
   a. The entire active center is energetically uniform.
   b. There is no interaction between adsorbed molecules.
   c. All the adsorption occurs by the same mechanism.
   d. Coverage is less than one complete mono-layer.

2. Langmuir isotherm

\[ A + X \rightleftharpoons_{k}^{k'} A - X \]
where $\theta_A$ : the fraction covered by adsorbed molecules

adsorption rate : $r_a = k P_A (1-\theta_A)$

desorption rate : $r_d = k' \theta_A$
At steady-state (at equilibrium)

\[ r_a = r_d \]

\[ \dot{\theta}_A = \frac{kP_A}{k' + kP_A} = \frac{K P_A}{1 + K P_A} = \frac{V}{V_m} \]

where \( K = \frac{k}{k'} = \) equilibrium constant
\( V = \) volume of gas adsorbed
\( V_m = \) maximum volume (complete mono-layer) can be adsorbed

or in the concentration form

\[ \theta_A = \frac{K C_A}{1 + K C_A} \]

Remark:
By thermodynamics \( K = A \exp(-\Delta H_{ads} / RT) \)

For Langmuir isotherm, we assume \( \Delta H_{ads} \neq f(\theta) \)
i.e. for a given temperature, \( K = \) const.
\[ \frac{V}{V_m} \rightarrow 1.0 \quad \text{at} \quad P \rightarrow \text{large} \]
\[ \frac{V}{V_m} = KP \quad \text{at} \quad P \rightarrow 0 \]

slope = K
Asymptotic solution

For $\phi_1 \rightarrow \text{large } (> 5)$

$$\tanh \phi_1 = 1 - e^{-2\phi_1} + e^{4\phi_1} - \ldots \approx 1$$

$$\therefore \eta = \frac{1}{\phi_1} \quad (\text{for } \phi_1 > 5)$$
1.6 Types of Catalytic Chemical Reactors

- Inverted cup screwed on to bottom plate
- Composition is uniform at $X_{A\text{out}}$, $C_{A\text{out}}$
- Four rapidly spinning wire baskets containing catalyst pellets, $W$

Fluid in, $F_{A0}$, $X_{A\text{in}}$, $C_{A\text{in}}$

Spinning shaft

Fluid out, $X_{A\text{out}}$, $C_{A\text{out}}$

Product

Spinning paddle

Catalyst, $W$

Recycle pump

Fluid in, $X_{A\text{in}} = 0$
Chapter Two

Active Sites of Heterogeneous Catalysis
Active sites of Heterogeneous Catalysis

1. Taylor’s Theory of active Sites
2. Adsorption Heterogeneity of Surface
3. Poisoning of Catalysts Surfaces
4. Relation between Parameters of the Arrhenius Equation
5. Theory of Super saturation "Sintering"
1. Taylor’s Theory of active Sites

According to his theory (the 1920's), the surface atoms of a crystal may be higher than the mean level of the surface act as the active sites of a catalyst. Such crystal "peaks" have free valences and are capable of forming reactive intermediates.

This idea has been confirmed by a number of qualitative experiments. For example, W. Palmer and F. Constable, investigating the dehydration of alcohols on metallic copper, i.e.

\[
R \text{— CH}_2 \text{— OH} \rightarrow R \text{— CH = O + H}_2
\]

It was found that methods leading to the formation of a sufficiently "smooth" surface; electrolytic deposition, reduction of a solution of \([\text{Cu(NH}_3\text{)}_4]^{2+}\) with hydrazine hydrate, etc. give inactive specimens.
Any changes take place in the lattice dimensions can lead to lattice imperfections.
Taylor’s Theory of

If the preparation is carried out by:

(i) passing of ammonia over a copper screen at 820 °C,
(ii) rapid reduction of copper salts and CuO with carbon monoxide, or
(iii) thermal decomposition of the copper salts of monobasic fatty acids

Imperfections in the crystal lattice, may be improved and a catalytically active surface is obtained.

Taylor was the first to put forward the idea of the existence of an active centre and to characterize its structure.
2-Adsorption Heterogeneity of Surface.

(a) Adsorption Isotherm.
(b) Heat of Adsorption.
(c) Differential –isotope Method.
2(a) Adsorption Isotherm

In the Langmuir adsorption theory a surface is assumed to be homogeneous, i.e. all its parts are considered to have identical adsorption potentials.

The equation of the Langmuir adsorption isotherm, having the form

\[ \theta = \frac{Kp}{1 + Kp} = \frac{V}{V_m} \]

can be written in the form

\[ \frac{P}{V} = \frac{P}{V_m} + \frac{1}{KV_m} \]

Where \( V \) = volume of adsorbate at pressure \( p \)

\( V_m \) = the same in case of saturation.
It can be seen that there is no linear relation between $p/V$ and $p$, within small pressure intervals linear sections of the isotherms can conditionally be separated.

Fig. 1. Isotherms of adsorption of chlorine on silica gel
1- at 88.5 °C; 2-at 66.5 °G; 3- at 51 °C; 4- at 35.9 °C
By extrapolation of each of these sections toward the axis of ordinates, we can see that the smaller the pressure, the smaller is the value of $1/Vm$ for the given section of the isotherm and, therefore, the greater is the value of the adsorption coefficient, $K$.

For this reason the non-linear isotherms shown in Fig. 1 can be explained if it is considered that different sections of a surface have different adsorption potentials.
Figure 2 shows data of H. S. Taylor on the heats of adsorption of ammonia on an iron catalyst obtained as follows. The ammonia was adsorbed on the catalyst in consecutive portions of two cubic centimeters, and each time the heat of adsorption was determined.

It can be seen that as the surface is covered, the heat of adsorption regularly decreases, i.e. less and less active sections of the surface are covered by the adsorbate (Fig.2).
It can be seen that as the surface is covered, heat of adsorption regularly decreases, i.e. less and less active sections of the surface are covered by the adsorbate.
**Adsorption** first proceeds on sites of most strong adsorption potential. **Desorption**, on the contrary, first starts from the most weak active sites. Experiments, thus, show that the real surface of an adsorbent is heterogeneous i.e. different parts of the surface give different **heats of adsorption**.
This method of detecting the heterogeneity of a surface is developed by S. Roginsky and N. Keyer. A definite portion of a gas of a certain isotope composition is first adsorbed on the surface, and then a portion having another isotope composition. Separate portions of the gas are desorbed and their isotope compositions are analyzed.
The surface is homogeneous, the composition of the desorbed gas should be the average one of all the portions adsorbed at different times. Desorption proceeds uniformly from all the occupied sites of the surface.

The surface is heterogeneous, the sequence of desorption should be the reverse to that of adsorption.

Experiments show that the real surface of an adsorbent is heterogeneous and different parts of it have different adsorption potentials.
3. Poisoning of Catalysts

The action of poisons on the catalytic activity of different parts of the surface is heterogeneous.

Fig. 3. Dependence of activity of platinum Catalyst on poison content.
The poisoning action of carbon monoxide on copper catalyzing the hydration of ethylene. The adsorption of 10 cm³ of carbon monoxide corresponds to the adsorption saturation of the surface of 100g of copper (i.e. $V_m = 10$ cm³)

The adsorption of 0.05 cm³ of CO already suppresses the initial catalytic activity of the copper by 90%. Consequently, 10 cm³ of CO corresponds to the total number of adsorption sites while 0.05 %, to the 90 % of the active sites.
Amount of CO that adsorbed on catalytically active sites = 
\[
\frac{100 \times 0.05}{90} = 0.055 \text{ cm}^3
\]

Amount of active sites participates = 
\[
\frac{100 \times 0.05}{10} = 0.55\%
\]
ONLY those adsorption sites are catalytically active on which the adsorbate molecules are capable of forming an active intermediate for the desired catalytic reaction.
4. Relation between Parameters of the Arrhenius Equation

When the same process is conducted on different catalysts (of a different chemical nature or prepared in different ways), there is a relation between the parameters $C$ and $E$ in the Arrhenius equation $k = C e^{-E/RT}$ that is described by the equation $C = a e^{E/h}$ or in the logarithmic form $\ln C = \ln a + E/h$

The quantity $E$ is connected with the energy nature of an active centre, while $C$, is the number of active sites per unit of catalyst surface.

The greater the value of $E$ for a given catalyst from among a series of catalysts with a different activity of their sites, the higher is the value of $C$ that can be expected.
5. Theory of Super saturation "Sintering".

According to this theory, all catalytically active systems have an increased Helmholtz energy $A_{\text{sup}}$ in comparison with the minimum Helmholtz energy $A_0$ of the thermodynamically equilibrium state, i.e. are supersaturated.

A measure of super saturation and, therefore, of the activity of a specimen is the excess of Helmholtz energy

$$\Delta A = A_{\text{sup}} - A_0$$

Super saturation may occur in the process of preparation of a catalyst. Its cause may be the presence of metastable phases, lattice imperfections, impurities, an increased dispersity and the like, etc.
Fig. 4. Kinetics of sintering of platinum black:
Fig. 4 shows that at 200 °C assumed that here there are indeed no equilibrium relations between the crystalline phase of the catalyst and the active sites on its surface, and that the system consecutively passes through metastable states. Out at higher temperatures a certain stationary state of the lattice is maintained with a definite number of active sites on its surface.
The specific activity, depending on the temperature of preliminary calcination of the catalyst, frequently has a maximum. Figure 5 shows an example of such a relation for silver catalysts of the decomposition of formic acid. As the temperature increases the number of active sites per unit of surface area first grows and then, beginning from a definite temperature, decreases. This phenomenon was considered from the standpoint of thermodynamics by O. Poltorak, who adopted the following model. The active sites are an "atomic phase" that is adsorbed on the surface of a crystal. It was found that for finely dispersed crystals the amount of "atomic phase" per unit of surface area decreases with a growth of the crystals competing.
Fig. 5. Dependence of specific activity and specific surface area of silver catalyst on temperature of preliminary calcinations.

Temperature of preliminary calcinations, °C
Thanks

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HETEROGENEOUS CATALYSIS

Multiplet Theory
Geometric Factor

Prof. Shawky M. Hassan
Professor of Physical Chemistry
1- Multiplet Theory

1.1-Geometric Factor
Principal of geometrical similarity (conformity).

1.2-Energy Factor
Principal of energy similarity.

This theory was been advanced by A. Balandin in 1927 and developed by his students and co-workers.
1.1-Geometric Factor

The term geometric factor has become synonymous with lattice spacing of atoms at a catalyst surface.

1.1.1- Experimental Evidence

The accumulated experimental data made it possible to define more specifically the concept of active site from the geometric point of view. For example:
a- Only hydrocarbons of six-membered ring are capable of dehydrogenation and of producing aromatic ring.

i-

\[ \text{Cyclohexane} \xrightarrow{\text{Ni}} \text{Benzene} + 3\text{H}_2 \]

\[ \text{Chemical Reaction:} \quad \text{C}_6\text{H}_{12} + 3\text{H}_2 \rightarrow \text{C}_6\text{H}_6 + 3\text{H}_2 \]

\[ 250 \degree \text{C} \]

ii-

\[ \text{1.2- dimethylcyclohexane} \xrightarrow{\text{Ni}} \text{O-Xylene} + 3\text{H}_2 \]

\[ \text{Chemical Reaction:} \quad \text{C}_10\text{H}_{14} + 3\text{H}_2 \rightarrow \text{C}_8\text{H}_{12} + 3\text{H}_2 \]
b- Heterocyclic compounds of six or four carbon atoms may be dehydrogenated.
1.1.2- Theoretical Basis

Adsorption of Hydrogen gases

Activation energy of adsorption = 14 k cal mol$^{-1}$
Separation distance = 3.6 Å
Activation energy depends on the spacing of Ni atoms in the lattice.
1.1.2- Theoretical Basis

Adsorption of Hydrogen gases

i-

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{C} & \quad \text{C} \\
\end{align*}
\]

\[
\begin{align*}
\text{C} & \quad \text{C} \\
\end{align*}
\]

Activation energy of adsorption = 14 k cal mol$^{-1}$
Separation distance = 3.6 Å

ii-

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{Ni} & \quad \text{Ni} \\
\end{align*}
\]

\[
\begin{align*}
\text{Ni} & \quad \text{Ni} \\
\end{align*}
\]

Activation energy depends on the spacing of Ni atoms in the lattice.
iii- Dehydrogenation of cyclohexane on metal catalysts.

\[ C_6H_{12} = C_6H_6 + 3H_2 \]

\[ \text{C-----C} \quad 1.53 \times 10^{-8} \]

<table>
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<tr>
<th>Catalyst</th>
<th>Pt</th>
<th>Pd</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r \times 10^{-8}, \text{cm} )</td>
<td>2.77</td>
<td>2.74</td>
<td>2.48</td>
</tr>
<tr>
<td>( E_{\text{act}}, \text{kJ/mol} )</td>
<td>75.3</td>
<td>64.0</td>
<td>40.6</td>
</tr>
</tbody>
</table>
Balandin Mechanism

- Carbon atom
- Hydrogen atom
- Platinum atom
1.1.3- The main Hypotheses of the Theory

The concepts of an adsorption and of catalytic active centers are not equivalent.

Molecules are adsorbed on several adsorption centers by several sections, as a result of which weakening of the bonds occur and in the limiting case their redistribution.

A complex of a definite number of adsorption centers arranged in geometrical conformity with the arrangement of the atoms in a molecule being catalyzed is a catalytically active centers are called duplets, quadruplets, sextets, etc and in general multiplet.
1.14- Examples

Example i:

\[ i: \text{H} - \text{H} - \text{C} - \text{C} - \text{O} \quad \xrightarrow{\text{Cu}} \quad \text{H} - \text{C} - \text{C} = \text{O} \]

Example ii:

\[ ii: \text{H} - \text{H} - \text{C} - \text{C} - \text{H} \quad \xrightarrow{\text{Al}_2\text{O}_3} \quad \text{H} - \text{C} = \text{C} - \text{H} - \text{H} - \text{O} - \text{H} \]
iv-
THANKS

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HETEROGENEOUS CATALYSIS

Multiplet Theory

Energy Factor
1.2- **Energy Factor**

A second tenet of the multiple theory is the principle of energy similarity (1935). It depends on activation energy.

Activation energy of a heterogeneous reaction is a complex quantity consisting in the first approximation of two addends, one of which depends only on the energy of the bond between the composite parts of the reacting molecules, and the other on the energy of interaction between a catalyst and the composite parts of a multiplet complex.
According to this principle, a heterogeneous catalytic reaction can be represented by the following scheme:

Reactants + Catalyst

First stage

Multiplet complex

Second stage

Catalyst + Products
Polanyi proposed a scheme of a heterogeneous catalytic reaction of the type:

$$AB + CD \rightarrow AD + BC$$

He postulated that the process requires the existence on the surface of the catalyst of groups of four catalyst atoms, each of the latter having one free valence:
First stage
Second stage

A

Cat

Cat

Cat

Cat

B

C

D

E_2

A

B

C

D
1- $E_1 = $ Energy of formation of multiplet adsorption complex.

$E_1 = (Q_{A\text{cat}} + Q_{B\text{cat}} + Q_{C\text{cat}} + Q_{D\text{cat}}) - Q_{AB} - Q_{CD}$

or

$E_1 = -Q_{AB} - Q_{CD} + q \quad (1)$

2- $E_2 = $ Energy of dissociation

$E_2 = Q_{AB} + Q_{CD} + (Q_{A\text{cat}} + Q_{B\text{cat}} + Q_{C\text{cat}} + Q_{D\text{cat}})$

or

$E_2 = +Q_{AB} + Q_{CD} - q \quad (2)$
\[ E_2 = \text{Total energy of reaction} \]

\[ E = E_1 + E_2 = -Q_{AB} - Q_{CD} + Q_{AD} + Q_{BC} \quad \text{-------(3)} \]

If \( Q_{AB} + Q_{CD} > Q_{AD} + Q_{BC} \) \( \text{endothermic} \)

and

If \( Q_{AB} + Q_{CD} < Q_{AD} + Q_{BC} \) \( \text{exothermic} \)

When \( E_1 = E_2 \)

\[ q = \frac{1}{2} (Q_{AB} + Q_{CD} + Q_{AD} + Q_{BC}) \]

or

\[ q = \frac{1}{2} E \quad \text{-----------------------------------------(4)} \]

Where, \( q = \text{adsorption potential of the catalyst} \)
\[ q = \frac{1}{2} (Q_{AB} + Q_{CD} + Q_{AD} + Q_{BC}) \]

\[ q = Q_{Acat} + Q_{Bcat} + Q_{Ccat} + Q_{Dcat} \]
The principal of energetic correspondence:

For the selection of an active catalyst for an endothermic reaction. It is necessary for the adsorption potential of the catalyst $q$ to approach as closely as possible one-half of the energy of the reacting bonds ($1/2 S$).
Thanks

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HETEROGENEOUS CATALYSIS

THE ELECTRONIC THEORY CATALYSIS

Prof. Shawky M. Hassan
Professor of Physical Chemistry
3.1. Relation Between Catalytic and Physical Properties of Transition Elements
   - 3.1.1 Structure of Electron Shells.
   - 3.1.2 Magnetic Properties.
   - 3.1.3 Work Function.
   - 3.1.4 Adsorption Intermediates.

3.2. Mechanism of Chemisorption on Semiconductors (assumptions of the theory)

3.3. Mechanism of Catalytic Reactions on Semiconductors.

- The transition elements (especially triad ones') have the most characteristic catalytic properties among the metals.

- A feature of the transition elements is the incompleteness of their d-electron shells, which determines their chemical properties.

- Table 1 gives the distribution of electrons in the atoms of elements catalytically active in the metal state, and also some of their properties connected with the electron structure.
• The easiness of formation of unoccupied d-shells, and also transitions of electrons from s-shells to d-shells lead to the formation of unpaired electrons on the outer s- and d-shells. As a result, the atoms of the transition elements are free to form covalent bonds at the expense of these unpaired electrons.

• Increase of the weight of the d-states (defined as the degree, in per cent, of participation of the d-shell electrons in the formation of the valence bonds) leads to greater catalytic activity (Fig. 1).
Fig. 1 Relation between catalytic activity and 'weight' of d-state in dehydrogenation
3.1.2. Magnetic and Catalytic Properties of the Transition Metals

when unpaired electrons are present in the outer shell and paramagnetic properties are displayed in an external magnetic field.

The formation of an intermediate should be facilitated when there are free valences on the surface of a catalyst, an increase in the number of unpaired electrons in the general case should result in an increase in the catalytic activity.

Therefore, parallelism of the catalytic and paramagnetic properties of substances should be expected. Such correlation was actually observed in a number of cases.

e.g. for Pd $4p^6\ 4d^{10} \rightarrow 4p^64d^94s^1$
3.1.3. Work Function of Electron and Catalytic Properties of Transition Metals and Semiconductors.

- The work function of an electron in a metal is the smallest energy which must be imparted to a conduction electron of the metal for it to be able to emit from the metal into a vacuum. Thus transition of an electron from the metal to a molecule being catalyzed is possible in certain processes at definite conditions.

- It is assumed that the decomposition of hydrogen peroxide on metals with a comparatively low work function of an electron includes the following initial stage:

\[
\text{H}_2\text{O}_2 + \text{e}^- \rightarrow \text{OH} + \text{OH}^- \quad \text{Cu (4.1 eV) < Ni (4.9 eV)}
\]

Catalytic activity of copper and nickel alloys considerably drops with increasing nickel concentration.
The catalytic deuterium exchange between deuterium molecules and ammonia includes the following initial step:

\[
\frac{1}{2} D_2 + NH_3 \rightarrow NH_3D^+
\]

Figure 2 shows how the activation energy of deuterium exchange on various metals depends on the work function of an electron.
Fig. 2. Dependence of activation energy of deuterium exchange in ammonia on work function of an electron
3.1.4. Formation of Adsorption Type Intermediates On the Surface of a Transition Metal.

Two different mechanisms of the chemisorption process are possible from the viewpoint of electron notions.

- The surface of the metal has a lower affinity to an electron than the atom being adsorbed. A typical example of is the chemisorption of oxygen on a metal surface.
- The surface of the metal has a greater affinity to an electron than the atom being adsorbed, for example, the adsorption of hydrogen on a metal surface.
Examples

• 1- Figure 3a shows the increase in the resistance of a transparent nickel film on which oxygen was adsorbed. The increase in the resistance is irreversible.

The oxygen atoms pull out electrons from the surface of the metal, and a stable surface oxide film is formed.
Fig. 3 Change in resistance of thin nickel films upon adsorption 
(A = inlet of gas, B = suction away of gas): 
\(a\)–adsorption of oxygen at 90.5 K; \(b\)–adsorption of hydrogen at 294.3 K
Figure 3b shows similar experimental results for the adsorption of hydrogen. The theoretically expected diminishing of the resistance is quite clearly seen. Attention is drawn to a certain incomplete.

Nitrous oxide carbon monoxide, similar to oxygen, increase the resistance. (Fig. 4a)
Fig. 4 Change in resistance of thin nickel films in adsorption and a catalytic process
(A = inlet of gas; B = suction away of gas):
a—adsorption of butadiene at 200 °C; b—hydrogenation of butadiene at 200 °C
**Figure 24.** Activation energy for the catalytic oxidation of carbon monoxide and electrical conductivity for zinc oxide doped with oxides of gallium and lithium [97].
1. 4-The hydrogenation of butadiene (fig.4b)

\[ \text{C}_4\text{H}_6 + 2\text{H}_2 \rightarrow \text{C}_4\text{H}_{10} \]

The reaction of catalytic hydrogenation proceeds between the adsorbed hydrogen atoms and the molecules of butadiene approaching them from the gaseous phase.


There are several conceptions describing the adsorption and catalytic
Wolkenstein formulated an elegant theory to account for observed adsorption and catalytic phenomena on semiconductors. He assumed that adsorbed species may be chemisorbed to the surface of a semiconductor in essentially three ways to form different types of bonds.
1. Weak chemisorption in which a weak homopolar bond is formed when a valence electron of an adsorbed atom is drawn into the conduction band of the semiconductor. The adsorbed atom remains electrically neutral, and the free electrons or holes of the lattice do not involve in the chemisorptions.
2. Strong chemisorption in which the adsorbed species captures a free electron of the lattice which participates in the chemisorption bond.

3. Strong chemisorption in which the adsorbed species captures a free hole of the lattice which participates in the chemisorption bond.

4. All the three types of bonds can transform into one another.
Fig. 101. Diagram showing transition of a “weak” homopolar bond into a “strong” one as a result of the transition of an electron from a conduction band (1) or from a valence band (2).
fig. 26. Three ways in which, according to Wolkenstein [113], a sodium atom may be adsorbed by a semiconductor.
5. The Fermi level determines the magnitude and sign of the surface charge for a given coverage of chemisorbed species, the total number of chemisorbed particles and the reactivity of these particles. Thus, Fermi level acts as a regulator of the chemisorptive and catalytic properties of the surface.
3.3 Mechanism of Catalytic Reactions of Semiconductors:

The assumption of the electronic theory of WolRenstein may be used to account for the radical mechanism of some heterogeneous catalytic reactions.
Fig. 13.16. Diagram of heterogeneous catalytic reaction of exchange on a semiconductor:
$AB + CD \rightleftharpoons AC + BD$

Fig. 104. Two kinds of surface reactions:

(a) complete formation of products on the surface; (b) partial formation of the products on the surface and partial formation of them when molecules in the gaseous phase react with the adsorbed radicals
Fig. 103. Scheme showing electron mechanism of reaction of a molecule with a free valence of a surface:

\(a\)—molecule with a single bond; \(b\)—molecule with a double bond
FIG. 27. Wolkenstein’s radical mechanism [113] for the catalysed reaction: $\text{C}_2\text{H}_6 + \text{Cl}_2 \rightleftharpoons \text{C}_2\text{H}_5\text{Cl} + \text{HCl}$. 
HETEROGENEOUS CATALYSIS

Theory of Active Ensemble

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This theory is concerned with the metal-supported catalysts, those which are contain metal(s) loaded on a support.
Contents

1) Physical fundamentals of the theory.
   a) Catalyst on support.
   b) Poisson’s distribution law.

2) Fundamental equation of the theory.

3) Active centers of catalytic processes.
Physical fundamentals of the theory.
a) Catalysts on supports

i. These are catalysts in which the metal is loaded on the surface of a solid called support or carrier.

- Support is catalytically **inactive** and has high surface area.
  - **ex.** Silica, Alumina, Active Carbon, …… etc

- Metal is the **active** substance
  - **ex.** Nickel, Nickel oxide, platinum, …… etc

\[
\begin{align*}
\text{Ni(OH)}_2 & \xrightarrow{\Delta} \text{Ni(OH)}_2 \\
\text{Ni(NO)}_3 & \xrightarrow{\Delta} \text{NiO} \\
\text{Ni(CO)}_3 & \xrightarrow{H_2, \Delta} \text{Ni}
\end{align*}
\]
Activity of the catalyst depends on the amount of metal content.
iii. The support does not capable only of changing catalytic activity within small limits but it has a rule or sometimes promotes the selectivity of the catalyst.

iv. Thermal stability of a supported catalyst, as a rule, sharply increases in comparison with that of the solid (support) and the metal (catalyst), by preventing sintering and increasing the temperature range which can be applied to the reaction.

v. N. Kobzhev proposed the so-called “block structure” for the support surface to explain its behavior in the catalytic reactions.
Surface defects limit the surface mobility of the applied atoms (metallic atoms), which are localized in the surface blocks-regions of free migrations.

Thus increase of temperature leads to the formation on the support surface of geometrical and energy barriers.

These prevent thermal motion along the surface and do not allow the metal atoms to “sinter” into an inactive or only slightly active complex of atoms (clusters), as would occur on an ideal crystal surface.
b) Poisson’s distribution law.

The distribution of metal atoms on the surface of a support was studied on the basis of the block structure by finding the probability of the formation of an n-atomic ensemble in a migration region.

If we have

\[ N = \text{no. of metal atoms on the surface} \]
\[ A_s = \text{total surface area of the support} \]
\[ \Delta = \text{average area of migration region} \]
\[ \nu = \text{average no. of metal atoms in one region} \]
\[ Z_o = \text{no. of migration regions on the surface of one gram of the support.} \]

\[ Z_o = \frac{A_s}{\Delta} \]

\[ \nu = \frac{N}{Z_o} = \frac{\Delta}{A_s} N \]
The probability of an \( n \)-atomic ensemble being formed in a region having area \( \Delta \) is:

\[
P = \left( \frac{\Delta}{A_s} \right)^n \left( \frac{A_s - \Delta}{A_s} \right)^{N-n}
\]

where

\( n \) = no. of atoms in the region having area \( \Delta \)

\( N \) = average no. of metal atoms in a migration region
\[ P = \frac{N_l}{n_l \cdot (N - n)} \cdot \left( \frac{\Delta}{A_s} \right)^n \left( \frac{A_s - \Delta}{A_s} \right)^{N-n} \]

and,

\[ \frac{\nu}{N} = \frac{\Delta}{A_s} \]

\[ P = \frac{\nu^n}{n_l} \cdot \frac{N_l}{N^n (N - n)} \cdot \left( 1 - \frac{\nu}{N} \right)^{N-n} \]
Finally we get:

\[ P_n = \frac{\nu^n}{n!} e^{-\nu} \]

Poisson's law
The probability of the formation of an ensemble consisting of a no. of atoms from (1) to (6) depending on the concentration "..." of the applied metal.
Relation between Total catalytic activity \((A)\) or Specific activity \((a)\) and the fractional coverage of surface \((\theta)\).

\[
\theta = \frac{N A_{\text{cat}}}{A_s}
\]

and

\[
a = \frac{A}{\theta}
\]
That means

\[ a = f(\theta) \quad A = f(\theta) \]

"The catalytic activity of certain catalyst depends on the fractional coverage of surface with the metal atoms (catalyst)."

So, we have two cases
On the basis of the Poisson's distribution law

If

\[ N = \text{atoms of catalyst on surface of 1g support.} \]
\[ Z_o = \text{no. of migration region.} \]
\[ Z_n = \text{no. n-atomic ensemble.} \]

\[ Z_n = Z_o P_n = Z_o \left( \frac{N}{Z_o} \right)^n e^{-N/Z_o} \]
Denoting

\[ r_n = \text{activity of one } n\text{-atomic ensemble} \]

\[ \therefore A_n = r_n Z_n = r_n Z_o \frac{1}{n^l} \left( \frac{N}{Z_o} \right)^n e^{-N/Z_o} \]

and

\[ a_n = \frac{A_n}{N} = r_n \frac{1}{n^l} \left( \frac{N}{Z_o} \right)^{n-1} e^{-N/Z_o} \]
Then

\[
\frac{dA_n}{dN} = r_n \left( \frac{N}{Z_o} \right)^{n-1} \frac{1}{n!} e^{-N/Z_o} \left( n - \frac{N}{Z_o} \right)
\]

\[
\frac{dA_n}{dN} = zero
\]

when

\[
n = \frac{N_A^{max}}{Z_o}
\]

\[\text{(1)}\]
Similarly

\[
\frac{d a_n}{dN} = r_n \left( \frac{N}{Z_o} \right)^{n-2} \frac{1}{n!} e^{-N/Z_o} \left( n - 1 - \frac{N}{Z_o} \right)
\]

when

\[
n - 1 = \frac{N_{\text{max}}^a}{Z_o} \]

\[(2)\]
By solving (1) & (2), We get:

\[ n = \frac{N^A_{\text{max}}}{N^A_{\text{max}} - N^a_{\text{max}}} \]

and

\[ Z_0 = N^A_{\text{max}} - N^a_{\text{max}} \]

also,

\[ \frac{N}{Z_0} = \frac{\Delta}{A_{\text{cat}}} \quad \theta_c = S \theta_c \]

where

\[ S = \frac{\theta}{A_{\text{cat}}} \]
Finally

\[ \theta = \frac{\theta_A^{\max}}{\theta_A^{\max} - \theta_a^{\max}} \]

and

\[ S = \frac{1}{\theta_A^{\max} - \theta_a^{\max}} \]
example

\[ 3H_2 + N_2 \xrightarrow{\text{Fe/Al}_2\text{O}_3} 2\text{NH}_3 \]

From experimental data,

\[ N_{\text{max}}^A = 8.8 \times 10^{18} \]

\[ N_{\text{max}}^a = 6.1 \times 10^{18} \]

\[ \therefore n = \frac{8.8}{8.8 - 6.1} = 3.25 \approx 3 \]

Means, the synthesis of ammonia proceeds on triatomic ensembles of iron \([\text{Fe}]_3\).
b- The number of migration region

\[ Z_o = (8.8 - 6.1) \times 10^{18} = 2.7 \times 10^{18} \]

c- The absolute activity, \( r_n \), of one n-atomic center is determined from:

\[
\log \left( \frac{A_n}{N^n} \right) = \log \left( r_n Z_o^{1-n} \right) - \frac{N}{2.3Z_o}
\]

\( Z_o = 3.1 \times 10^{18} \) from slope

\( r_n = 0.49 \) from intercept (molecule/ensemble/s)
Active centers of catalytic processes
It was found that, the composition of an active ensemble (center) is mainly determined not by the geometry of the molecules being catalyzed, but the number and kind of the bonds broken in the initial act of activation.

A monoatomic ensemble is a typical active center for all oxidation process, where Bakh consider the first act of an oxidation process to be the activation of the oxygen by formation of an intermediate peroxide compound.
Example

Oxidation process of SO$_2$ on Pt or Pd can be explained as follows:

1-Activation of oxygen

\[ \text{Pt} + \text{O}_2 \rightarrow \text{PtO} \]

2-Transfer of active oxygen to a molecule of SO$_2$

\[ \text{PtO} + \text{SO}_2 \rightarrow \text{PtO} + \text{SO}_3 \]
PtO + SO$_2$ $\rightarrow$ Pt + SO$_3$

Since O$_2$ molecule react with _one_ atom of metal then the active center has the simplest monoatomic structure.
Exam 2000

• State the assumptions of the theory of active ensembles and derive the fundamental equation. Give examples.

• Discuss the mechanism of catalysis on semiconductors.

• Explain the role of point defects of crystal lattices in catalysis.
Exam 2001

• Discuss why the transition elements have the most characteristic catalytic properties among the metals.

• Explain briefly the Multiplet theory of catalysis.

• Using Poison's distribution law derive a mathematical equation for the determination of the number of metal atoms in the active ensemble.

• Explain what do you understand by the term lattice dislocations in catalysis.
Exam 2002

• Discuss the various experimental data which explain that only a small part of the catalyst surface participates in the process of catalysis.

• Explain the principles of the multiple theory of catalysis.

• Write on the different types of point defects in crystal lattices giving different examples. Discuss their role in heterogeneous catalysis.
• From the catalytic data of the Fe/Al$_2$O$_3$ catalyst in ammonia synthesis $N^A_{\text{max}}$ and $N^a_{\text{max}}$ were found to be $8.8 \times 10^{18}$ and $6.1 \times 10^{18}$ respectively. Determine both the types and activity if the n-atomic ensemble.

Exam 2003

• Explain why the elements of group VIII of the periodic system have the most characteristic catalytic properties among the metals
Discuss the experimental data that made it possible to assume each of the following.

• The principle of geometrical similarity.
• The theory of active ensembles.

State the assumption mode in each case.

• Explain what do you understand by the term "poisoning of catalysts".
• Derive the Fundamental equations of the theory of active ensembles and discuss their applications.
Exam 2004

State the assumptions of the theory of active ensembles and derive equations for the total and specific activities of n-atomic ensemble. Discuss how the mechanism of reaction can depend on the type of ensemble.

Explain briefly the principle of energy similarity in heterogeneous catalysis.

Discuss the different phenomena that explain the heterogeneity of catalytic surfaces of solids.
HETEROGENEOUS CATALYSIS

Thanks

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