§ 8.4 adsorption at gas / solid interface

Levine:

pp. 397–402 section 13.5 adsorption of gases on solids
§ 8.4 adsorption at gas / solid interface

Powder explosion in Baxian, Xinbei, Taiwan

http://www.iqiyi.com/w_19rt68ph15.html
8.4.1 Solid surface and specific surface area

(1) Surface of solid: unbalanced force and suspending bond

Matter that is at or near an interface is not in the same state as those in the interior of a phase. Owing to the suspending bond, solid surface is apt to react with other substances.

How do we stabilize the solid surface?
§ 8.4 adsorption at gas / solid interface

8.4.1 Solid surface and specific surface area

(2) Degree of subdivision

<table>
<thead>
<tr>
<th>arris</th>
<th>Surface area</th>
<th>Surface atom %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 cm</td>
<td>6 cm²</td>
<td>3 × 10⁻⁸</td>
</tr>
<tr>
<td>1 μm</td>
<td>6 × 10⁴ cm²</td>
<td>30%</td>
</tr>
<tr>
<td>1 nm</td>
<td>6 × 10⁷ cm²</td>
<td>~ 100%</td>
</tr>
</tbody>
</table>

(3) Specific area:

\[ S_v = \frac{S}{V} \quad S_w = \frac{S}{W} \]

The surface-to-volume / mass ratio

Micropowder explosion: micropowder is thermodynamically unstable.
§ 8.4 adsorption at gas / solid interface

8.4.1 Solid surface and specific surface area

Solid can not lower surface energy by shrinking its surface. How can solid lower its surface energy?

Adsorption of gas molecules
### 8.4.1 Solid surface and specific surface area

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific surface area (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbons from Iris tectorum doped with ferric nitrate</td>
<td>1371</td>
</tr>
<tr>
<td>Activated carbon prepared from lignin</td>
<td>931.53</td>
</tr>
<tr>
<td>Activated Carbon Fiber</td>
<td>1153.25</td>
</tr>
<tr>
<td>Activated Carbons from Agricultural Residues</td>
<td>821</td>
</tr>
<tr>
<td>MnFe₂O₄/activated carbon magnetic composites</td>
<td>553</td>
</tr>
<tr>
<td>Powdered activated carbon</td>
<td>1100---1230</td>
</tr>
<tr>
<td>Commercial activated carbon</td>
<td>1200</td>
</tr>
<tr>
<td>NaOH-activated carbon produced from macadamia nut shells</td>
<td>1524</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>sample</th>
<th>$S_{BET}^a$ (m²/g)</th>
<th>$d_p^b$ (nm)</th>
<th>$V_r^c$ (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-BN</td>
<td>627</td>
<td>2.7</td>
<td>0.42</td>
</tr>
<tr>
<td>c-BN</td>
<td>25</td>
<td>10.6</td>
<td>0.07</td>
</tr>
<tr>
<td>AC$^f$</td>
<td>106</td>
<td>5.1</td>
<td>0.14</td>
</tr>
<tr>
<td>MS$^g$</td>
<td>389</td>
<td>2.5</td>
<td>0.25</td>
</tr>
<tr>
<td>SiO₂</td>
<td>229</td>
<td>7.7</td>
<td>0.44</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>124</td>
<td>6.9</td>
<td>0.21</td>
</tr>
<tr>
<td>α-Fe₂O₃</td>
<td>109</td>
<td>14.6</td>
<td>0.40</td>
</tr>
<tr>
<td>Co₂O₃</td>
<td>61</td>
<td>9.9</td>
<td>0.15</td>
</tr>
<tr>
<td>TiO₂ (P25)</td>
<td>47</td>
<td>9.2</td>
<td>0.11</td>
</tr>
<tr>
<td>CeO₂</td>
<td>14</td>
<td>11.0</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Metal catalyst: Pt, Pd, Ni, Fe Oxide: Al₂O₃, SiO₂ Activated carbon: charcoal Catalysts or catalyst support

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§ 8.4 adsorption at gas / solid interface
§ 8.4 adsorption at gas / solid interface

8.4.2 Kind of adsorption

Sorption: movement of a material from one phase to another. Adsorption vs. absorption

Adsorbate: the material being adsorbed. Adsorbent: the material doing the adsorbing.

chemical adsorption, physical adsorption, chemisorption, physisorption
Chemisorption involves the formation of chemical bonds between adsorbed molecule and solid surface, and often involving the breaking of preexisting bonds in the adsorbed molecule. In some cases the chemisorption step requires an activation energy.

Physi-sorption involves forces similar to the intermolecular forces / weak interaction that lead to condensation of vapors to liquid.
### § 8.4 adsorption at gas / solid interface

8.4.2 Kind of adsorption

**Comparison between chemical and physical adsorption**

<table>
<thead>
<tr>
<th>sorption</th>
<th>physisorption</th>
<th>chemisorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>interaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal effect</td>
<td></td>
<td></td>
</tr>
<tr>
<td>temperature</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorbed layer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>reversibility</td>
<td></td>
<td></td>
</tr>
<tr>
<td>selectivity</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
8.4.2 Kind of adsorption

Transition from physisorption to chemisorption

By following the transition from physical absorption to chemical adsorption, catalysts can activate reactant molecules at relatively mild conditions. This is the basic principal for heterogeneous catalysis.
§ 8.4 adsorption at gas / solid interface

### 8.4.3 Thermodynamic aspects of adsorption

\[ \Delta G = \Delta H - T\Delta S \]

- Adsorption is spontaneous, \( \Delta G < 0 \)
- Entropy decreases during adsorption, \( \Delta S < 0 \)
- Therefore: \( \Delta H < 0 \)

adsorption is a exothermic process

#### Conditions for chemisorption

\[ 2W + N_2 = 2 \, W - N_{ad} \]

\[ \Delta_{ads}H_m = D(N_2) - 2X (W-N) < 0 \]

\[ X_{W-N} > \frac{D_{N_2}}{2} \]
§ 8.4 adsorption at gas / solid interface

8.4.4 Description of adsorption

The amount of adsorption \( a \) of a certain kind of solid for certain gases is a function of \( T \) and \( p \).

\[ a = a(T, p) \]

For constant pressure: **isobar** \( a \sim T \)

For constant adsorption: **isochore** \( T \sim p \)

Clausius-Clappeyron equation:

\[
\left( \frac{\partial \ln p}{\partial T} \right)_a = -\frac{\Delta_{ads} H_m}{RT^2}
\]
Adsorption increases with increase of pressure under low pressure. While at high pressure, adsorption attains maximum value.

8.4.4 Description of adsorption

Adsorption isotherm:
8.4.4 Description of adsorption

Types of adsorption isotherm:

Brunauer: five types of isotherms

- Type I: 78 K N₂/silica gel or iron catalyst
- Type II: 78 K N₂/active carbon
- Type III: 323 K benzene/Fe₂O₃
- Type IV: 352 K Br₂/silica gel
- Type V: 373 K water/active carbon
§ 8.4 adsorption at gas / solid interface

8.4.5 adsorption isotherm—Langmuir

(1) Degree of coverage

\[ \theta = \frac{S_1}{S} \]

$S$: the total adsorption sites

$S_1$: sites occupied by adsorbed molecules

(2) The basic assumptions

(1) The solid surface is uniform

(2) monolayer adsorption

(3) no intermolecular interaction

The uniform surface contains a fixed number of adsorption sites. Each site holds only one adsorbed molecule. The heat of adsorption is the same for all sites and does not depend on the fraction coverage $\theta$.
§ 8.4 adsorption at gas / solid interface

8.4.5 adsorption isotherm—Langmuir

(3) Adsorption and desorption rate and equilibrium

\[ r_{ads} = k_1 (1 - \theta) p \]

\[ r_{des} = k_2 \theta \]

\[ r_{ads} = r_{des} \]

Langmuir isotherm

\[ \theta = \frac{k_1 p}{k_2 + k_1 p} = \frac{bp}{1 + bp} \]

\[ b = \frac{k_1}{k_2} \]

\( b \) (adsorption coefficient):

the kinetic equilibrium constant of the adsorption and desorption
§ 8.4 adsorption at gas / solid interface

8.4.5 adsorption isotherm—Langmuir

\[ \theta = \frac{bp}{1 + bp} \quad a = k\theta = \frac{kbp}{1 + bp} \]

at low pressure, \( bp \ll 1 \),

\[ a = kbp \]

at high pressure, \( bp \gg 1 \),

\[ a_m = k \]

\[ \theta = \frac{V}{V_m} \]
§ 8.4 adsorption at gas / solid interface

8.4.5 adsorption isotherm—Langmuir

For monolayer adsorption, the specific area can be thus estimated according to

\[ S_W = \frac{V_m}{22400} \frac{L\sigma_0}{W} \]

\[ \frac{V}{V_m} = \frac{bp}{1+bp} \]

\[ \frac{p}{V} = \frac{1}{bV_m} + \frac{p}{V_m} \]

For Langmuir adsorption, when plotting \( p/V \) against \( p \), straight line can be obtained.
Adsorption heat depends on the coverage, which suggests that the surface of adsorbent is not uniform. Some sites are more active than the other.
8.4.5 adsorption isotherm—BET

(1) BET isotherm: Brunauer-Emmett-Teller (1938)

1) Basic assumptions

(1) uniform surface;
(2) multilayer adsorption;
(3) the heat of the layer other than the first layer is the condensation heat;
(4) desorption only occur at the layer exposed to the gas

Multilayer adsorption = condensation?

8.4.5 adsorption isotherm—BET

\[
\frac{V}{V_m} = \frac{Cp}{(p_0 - p) \left[ 1 + (C - 1) \frac{p}{p_0} \right]}
\]

\[
\frac{(p_0 - p)V}{p} = \frac{CV_m}{1 + (C - 1) \frac{p}{p_0}}
\]

\[
\frac{p}{(p_0 - p)V} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \frac{p}{p_0}
\]

\[S_g = \sigma_a L \frac{V_m}{22400}\]

BET absorption isotherm is valid for type I through type III.
8.4.5 Adsorption Isotherm—BET

Measurement of specific area of solid with BET

Fig. 1. Isotherms for hydrogen and deuterium adsorption and desorption on activated carbon at 77 K [4].
8.4.5 adsorption isotherm—BET

Fig. 1. Nitrogen-adsorption isotherms at -195°C

Fig. 2. Linear B.E.T. plots of the isotherms from figure 1:
8.4.5 adsorption isotherm—BET

\[ \frac{V}{V_m} = \frac{C}{1 - \frac{p}{p_0}} \]

<table>
<thead>
<tr>
<th>RH/%</th>
<th>$\frac{V}{V_m}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.997</td>
</tr>
<tr>
<td>40</td>
<td>1.30</td>
</tr>
<tr>
<td>50</td>
<td>1.68</td>
</tr>
<tr>
<td>60</td>
<td>2.22</td>
</tr>
<tr>
<td>70</td>
<td>3.08</td>
</tr>
<tr>
<td>80</td>
<td>4.76</td>
</tr>
<tr>
<td>90</td>
<td>9.75</td>
</tr>
</tbody>
</table>

图3 不同C值时界面覆盖度（$\frac{V}{V_m}$）与相对湿度（$\frac{p}{p_0}$）的关系
Both Langmuir and BET isotherms are based on the assumption that the surface of the solid is uniform and the adsorption heat is independent of coverage.

\[ \Delta_{\text{ads}} H_m = \Delta_{\text{ads}} H_0^0 - \beta \ln \theta \]

\[ a = kp^n \]

\[ \ln a = \ln k + \frac{1}{n} \ln p \]

\[ \ln a = \ln k + \frac{1}{n} \ln c \]

Valid for adsorption in solution

Fig. 8. Comparison between experimental and computed equilibrium data derived from the modified Freundlich model in the case of adsorption of mixtures
8.4.5 adsorption isotherm—Temkin

(3) Temkin adsorption isotherm

Temkin adsorption isotherm can be derived on the assumption that:

$$\Delta_{ads} H_m = \Delta_{ads} H_m^0 (1 - \beta \theta)$$

$$a = k \ln(bp)$$

Brunauer–Emmet–Teller Adsorption Isotherm Model
Freundlich Adsorption Isotherm Model
Frenkel–Halsey–Hill Adsorption Isotherm Model
Hygroscopic Growth Theory
§ 8.4 adsorption at gas / solid interface

8.4.6 Some phenomena for heterogeneous catalysis

(1) basic principal of heterogeneous catalysis

The potential curve of adsorption

Interaction between molecule and catalyst on catalytic activity
Mechanism of heterogeneous catalysis

A *surface reaction* can usually be divided into five elementary steps:

1) **diffusion** of reactants to surface;
2) **adsorption** of reactants at surface;
3) **reaction** on the surface;
4) **desorption** of product from surface;
5) **diffusion** of product from surface.

Which is r.d.s.?
Many surface reactions can be treated successfully on the basis of the following assumptions:

1) the r.d.s. is a reaction of adsorbed molecules;
2) the reaction rate per unit surface area is proportional to $\theta$.

For unimolecular reaction over catalyst

Catalyzed isomerization or decomposition
8.4.6 Some phenomena for heterogeneous catalysis

(2) Mechanism of heterogeneous catalysis

For bimolecular reaction over catalyst

**Langmuir-Hinshelwood mechanism (L-H mechanism)**

\[
A (g) + B (g) \rightarrow A \cdots B \rightarrow A-B
\]

**Langmuir-Rideal mechanism (L-R mechanism)**

\[
A (g) + \rightarrow A \rightarrow A + B (g) \rightarrow A-B + \]

§ 8.4 adsorption at gas / solid interface
§ 8.4 adsorption at gas / solid interface

8.4.6 Some phenomena for heterogeneous catalysis

Langmuir-Hinshelwood mechanism (L-H mechanism)

Synthesis of ammonia

Langmuir-Rideal mechanism (L-R mechanism)

Hydrogenation of ethylene
In middle 1970s, Ertl began to studied the mechanism of Haber-Bosch process. Ertl used LEED, AES, UPS, TDS to study this process and measured the work function of N adsorption on Fe(111), Fe(100) and Fe(110). He found the dissociation of N\textsubscript{2} on Fe surface, and the Haber-Bosch process obeyed L-H mechanism.

He won 2017 Noble Prize.
8.4.6 Some phenomena for heterogeneous catalysis

(3) kinetics for heterogeneous catalysis

For unimolecular reaction

\[ r \propto \theta_A \quad r = k\theta_A \]

According to Langmuir isotherm

\[ \theta = \frac{bp}{1 + bp} \quad r = \frac{kb_A p_A}{1 + b_A p_A} \]

Under low pressure, when \( b_A p_A << 1 \)

At high pressure, when \( b_A p_A >> 1 \)
8.4.6 Some phenomena for heterogeneous catalysis

When competing adsorption exists:

\[ \theta_A = \frac{b_A p_A}{1 + b_A p_A + b_B p_B} \]

\[ r = \frac{kb_A p_A}{1 + b_A p_A + b_B p_B} \]

When \( b_A p_A << 1 + b_B p_B \)

\[ r = \frac{kb_A p_A}{1 + b_B p_B} \]

The adsorption of competing species inhibits the reaction.

For example:

Decomposition of \( \text{N}_2\text{O} \) over Ag, CuO or CdO.

\[ r = \frac{k[\text{N}_2\text{O}]}{1 + b[\text{O}_2]} \]

When \( b_B p_B >> 1 \)

\[ r = \frac{kb_A p_A}{1 + b_B p_B} \]

\[ r = \frac{k' p_A}{p_B} \]

For example

Decomposition of ammonia over Pt

\[ r = k \frac{[\text{NH}_3]}{[\text{H}_2]} \]
§ 8.4 adsorption at gas / solid interface

8.4.6 Some phenomena for heterogeneous catalysis

The situation of the L-R mechanism is the same as that of unimolecular reaction over catalyst.

For **L-H mechanism**, small modification should be made.

\[
 r = k \theta_A \theta_B \\
 r = \frac{kb_A p_A b_B p_B}{(1 + b_A p_A + b_B p_B)^2}
\]

Rate~ partial pressure relation of **L-H mechanism**
§ 8.4 adsorption at gas / solid interface

8.4.6 Some phenomena for heterogeneous catalysis

(4) Active sites

Ununiformity of solid surface and catalysis

10^{-9} \text{PH}_3, which is insufficient for formation of monolayer, can destroy completely the activity of Pt catalyst toward oxidation of ammonia.

In 1926, Taylor proposed the active site model

1) Only the molecules adsorbed on the active sites can lead to reaction.

2) The fraction of active sites on the catalyst surface is very low.
§ 8.4 adsorption at gas / solid interface

8.4.6 Some phenomena for heterogeneous catalysis

The active site is in fact an atom cluster comprising of several metal atoms.

Increase of the degree of subdivision will increase the ununiformity of catalyst surface and increase the number of active sites.
§ 8.4 adsorption at gas / solid interface

8.4.6 Some phenomena for heterogeneous catalysis

检索结果: 139
(来自所有数据库)
您的检索: 标题
: (catalyst) AND 标题
: (single atom) ...

Fig. 8 Charge differences (isosurface value 0.0015 e Å⁻³) for (a) O₂@V/g-C₃N₄, (b) O₂@Cu/g-C₃N₄, (c) CO@V/g-C₃N₄, and (d) O@V/g-C₃N₄. The red and green colors represent charge accumulation and depletion, respectively.
If $b_B$ is very large, even at low $p_B$, $\theta_A$ will be very small. The reaction of A will be greatly retarded. The impurities with high $b$ is catalyst poison.

$$r = \frac{kb_A p_A}{1 + b_A p_A + b_B p_B}$$
Homework

Deduce the following relations.

**When dissociation occur during adsorption:**

\[ \theta = \frac{b_A^{1/2} p_A^{1/2}}{1 + b_A^{1/2} p_A^{1/2}} \]

Dissociative adsorption

**Adsorption of mixed gases**

For gas A and B: \( \theta_A, \theta_B, p_A, p_B \)

\[ \theta_A = \frac{b_A p_A}{1 + b_A p_A + b_B p_B} \]

\[ \theta_B = \frac{b_B p_B}{1 + b_A p_A + b_B p_B} \]

**Competing adsorption**

\[ \theta_A = \frac{b_A p_A}{1 + \sum_{i=1}^{n} b_i p_i} \]