The Concepts of Heterogeneous Catalysis

What is catalysis?

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What is catalysis

• The potential energy picture
• The kinetic picture
• The chemical bonding picture
What is catalysis

• The potential energy picture
• The kinetic picture
• The chemical bonding picture
Langmuir - Hinshelwood Kinetics

1915 Langmuir: Adsorption Isotherm
1927 Hinshelwood: Kinetics of Catalytic Reactions

• Consistent with Sabatier’s Principle
• Coverage dependence: Volcano plot
• Temperature dependence: Volcano plot
Reaction Mechanism:

\[ A + * \rightleftharpoons A_{ads} \quad \text{equilibrium; } K_A \]

\[ B + * \rightleftharpoons B_{ads} \quad \text{equilibrium; } K_B \]

\[ A_{ads} + B_{ads} \rightarrow AB_{ads} + * \quad \text{r.d.s; } k \]

\[ AB_{ads} \rightarrow AB + * \quad \text{fast} \]

Coverages:

\[ \theta_A = K_A p_A \theta_* \quad \theta_B = K_B p_B \theta_* \quad \theta_* = \frac{1}{1 + K_A p_A + K_B p_B} \]

Reaction rate:

\[ r = \frac{N_* k K_A K_B p_A p_B}{(1 + K_A p_A + K_B p_B)^2} \]
Irving Langmuir
(1881 - 1957)

- worked at General Electrics
- oxygen adsorption on tungsten filaments of light bulbs
- 1932: Nobel Prize in Chemistry
- Langmuir Adsorption Isotherm:

\[ \theta_A = \frac{K_A [A]}{1 + K_A [A]} \]
Rate of reaction, Activation energy, Order of reaction:

\[ r = \frac{N_* k K_A K_B p_A p_B}{(1 + K_A p_A + K_B p_B)^2} \]

\[ E_a^{app} = -R \frac{\partial \ln r}{\partial (1/T)} = RT^2 \frac{\partial \ln r}{\partial T} \]

\[ = E_a^{rds} + (1 - 2\theta_A) \Delta H_A + (1 - 2\theta_B) \Delta H_B \]

\[ n_A = \frac{\partial \ln r}{\partial \ln p_A} = p_A \frac{\partial \ln r}{\partial p_A} = 1 - 2\theta_A \]
Rate of a Catalytic Reaction: Pressure Dependence

\[ E_{\text{ads}}(A) = E_{\text{ads}}(B) = 125 \text{ kJ/mol} \]
\[ s(B) = s(A) ; \quad E_{\text{act}} = 50 \text{ kJ/mol} \]
\[ T = 600 \text{ K}; \quad p_B \text{ is fixed} \]
Rate of a Catalytic Reaction: Temperature Dependence

\[ E_{ads} (A) = 135 \text{ kJ/mol} \]
\[ E_{ads} (B) = 125 \text{ kJ/mol} \]
\[ s(B) p_B = 10 s(A) p_A \]
\[ E_{act} = 50 \text{ kJ/mol} \]

**reaction order**
- negative in \( p_A \)
- positive in \( p_B \)

**reaction order**
- positive in \( p_A \) and \( p_B \)
The Sabatier Effect

optimum interaction
catalyst - adsorbate:
• *not too strong*
• *not too weak*

![Catalytic activity vs. metal-adsorbate bond strength](image)

- **catalytic activity**
- **metal - adsorbate bond strength**
Catalysis by Metals: Trends in Reactivity

strong, dissociative adsorption
stable oxides, carbides, nitrides

Cr, Mn, Fe, Co, Ni, Cu, Mo, Tc, Ru, Rh, Pd, Ag, W, Re, Os, Ir, Pt, Au

Weak, molecular adsorption
stable against oxide, carbide, nitride formation
What is catalysis

• The potential energy picture
• The kinetic picture
• The chemical bonding picture
Example: CO Oxidation

What is the most essential thing that the catalyst does?
a catalyst breaks bonds........

......and lets other bonds form
The minimum you need to know about . . . . . .

Molecular Orbitals

Overlap:

- Much overlap
- Little overlap

Filling:

- Strong bond
- Weak bond
- No bond

Atom    molecule    atom

Atomic orbital    molecular orbitals    atomic orbital

anti bonding

bonding
and about . . . .

Bonding in Metals

4p

4s

3d

atom

metal

sp - band

d-band

density of states
Work Function: Ionization Potential of a Metal

\[ \varphi : \text{energy barrier for electrons leaving the surface} \]
Strength of metals:
Filling of bands
Atomic Adsorption in the ‘Resonant Level Model’

(the simplest description)

**Diagram:**
- **$E_{Vac}$:** Vacuum level
- **$E_F$:** Fermi level
- **$sp$-band:**
- **Core level 1**
- **Core level 2**
- **Work function**
- **Ionization energy**
- **$e_a$:** Ionization energy

**Annotations:**
- Jellium has no $d$-band (e.g. Al)
Atom on free-electron metals (no d-band):
Molecules on free-electron metals (no d-band):

a) Molecules on free-electron metals (no d-band):

b) Molecules on free-electron metals (no d-band):
Atom on d-metal:

a) 
- $E_{\text{vac}}$
- $E_F$
- d-band
- s-band
- antibonding
- bonding

b) 
- $E_{\text{vac}}$
- $E_F$
- antibonding
- bonding

<table>
<thead>
<tr>
<th>d-metal</th>
<th>adsorbed atom</th>
<th>free atom</th>
<th>d-metal</th>
<th>adsorbed atom</th>
<th>free atom</th>
</tr>
</thead>
<tbody>
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</table>
Molecular Adsorption on a d-metal

\[ \sigma \text{-orbitals} \quad \sigma^* \text{-orbitals} \]

\[ E_{\text{vac}} \]

\[ E_F \]

d-metal

adsorbed molecule

free molecule

antibonding

bonding

1s

1s

\( \sigma \)

\( \sigma^* \)
CO adsorption on a d-metal

$d-5\sigma$  
$d-2\pi^*$  

$E_{\text{vac}}$  
$E_F$

d-metal  
adSORBED molecule  
free molecule

"relieved repulsion" favors on-top adsorption, often called "donation"  
"back donation" binds molecule to surface, weakens internal CO bond, favors multiple coordination

This picture is the key to understanding catalysis in terms of orbital theory.
a catalyst breaks bonds........

How?
Atoms prefer high coordination sites

Carbon on Rh(111)

<table>
<thead>
<tr>
<th>Coordination</th>
<th>Energy (eV)</th>
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<tbody>
<tr>
<td>hcp</td>
<td>0.00</td>
</tr>
<tr>
<td>fcc</td>
<td>0.24</td>
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<tr>
<td>top</td>
<td>1.99</td>
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<tr>
<td>bridge</td>
<td>0.67</td>
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</table>

Nitrogen on Rh(111)

<table>
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<th>Coordination</th>
<th>Energy (eV)</th>
</tr>
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<tbody>
<tr>
<td>hcp</td>
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<tr>
<td>fcc</td>
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<tr>
<td>top</td>
<td>2.13</td>
</tr>
<tr>
<td>bridge</td>
<td>0.72</td>
</tr>
</tbody>
</table>

Paco Ample, Dani Curulla, Josep Ricart, Hans Niemantsverdriet, 2002
The CO molecule dissociates in the transition state: optimal overlap between d- and $2\pi^*$-orbitals
Energetics of Dissociation
on a transition metal such as Fe, Ru

$\Delta H_{\text{ads}}(AB)$
-150 kJ/mol

$E_{\text{act}}$
75 kJ/mol

Driving Force

$\Delta H_{\text{ads}}(A+B)$
-600 kJ/mol
Trends in chemisorption

Strong atomic adsorption

Cr Mn Fe Co Ni Cu
Mo Tc Ru Rh Pd Ag
W Re Os Ir Pt Au

N/Metal, kJ/mo

Weaker adsorption

585 564
543
531 531

d-band < half filled
strong bond

d-band > half filled
weaker bond

d-metal adsorbed atom free atom
Evac EF
antibonding bonding

Evac EF
antibonding bonding
Dissociation on Different Metals

\[ \Delta H_{ads} (AB) \]

\[ \delta E_{act} \]

\[ \delta \Delta H_{ads} (A+B) \]

Bronstedt-Polanyi Relation

\[ \delta E_{act} \approx \frac{1}{2} \delta \Delta H_{ads} (A+B) \]
<table>
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<tr>
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<td>Ru</td>
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<td>Pd</td>
<td>Ag</td>
</tr>
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<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
<td>Au</td>
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</table>

**easy dissociation**

**no dissociation**

### Dissociation on Different Metals

E.g. Rh and Fe

\[
\Delta H_{\text{ads}} (AB) \quad \delta \Delta H_{\text{ads}} (A+B) \quad \delta E_{\text{act}} \quad \frac{1}{2} \delta \Delta H_{\text{ads}} (A+B)
\]

**Bronstedt-Polanyi Relation**
Coordinative unsaturation: higher reactivity

- **fcc (111)**
  - 9 neighbours per atom

- Less dense surface or defects
  - <9 neighbours per atom

- **Fermi level**
  - **sp-band**
  - **d-band**

- **Energy** vs. **Density of states**
Coordinative unsaturation: higher reactivity

fcc (111) 9 neighbours per atom

less dense surface or defects <9 neighbours per atom

E_{vac}  
E_F

bonding  antibonding

stronger bond!
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If you can explain catalysis along these three lines you have a pretty good understanding of what catalysis on metals means.