Catalysis for gas-solid interactions

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Catalysis for gas-solid interactions

1/ General concepts:
   Adsorption
   Mechanisms

2/ Main families of catalysts

3/ Catalysts properties
   Structure/texture
   Acido-basicity (Lewis, Bronsted)

4/ Kinetic measurements

5/ Characterizations
1/ General concepts
CATALYSIS: A catalyst is a substance which accelerates the thermodynamic equilibrium approach. It only acts on reaction kinetic.

A catalyst decreases the activation energy

**Catalyst**: solid, liquid or gas

A catalyst is not consumed by the reaction

A **catalyst can orientate a chemical reaction**

**Activity & Selectivity**
Example: \[ \text{NO} + \frac{1}{2} \text{O}_2 \rightarrow \text{NO}_2 \]

Catalyst: Pt / oxide supports

![Graph showing NO conversion vs. temperature for different oxide supports.](image)

- **NO conversion / %**
- **Temperature / °C**

Materials:
- SiO$_2$
- Al$_2$O$_3$
- CeO$_2$
- ZrO$_2$
- YSZ
- Al$_2$O$_3$-SiO$_2$

Thermodynamic equilibrium line.
The catalyst changes the reaction route
The catalyst orientates the reaction

2 thermodynamically possible reactions

```latex
\begin{align*}
A & \xrightarrow{r_1} B \\
& \xrightarrow{r_2} C
\end{align*}
```

The catalysts changes the $r_2/r_1$ ratio

Modification of the selectivity

Selectivity = kinetic

Example:
Isopropanol decomposition

Deshydratation

Deshydrogenation
Homogeneous reactions: all species are in a single physical state

Heterogeneous reactions: 2 phases (gas / solid)

Homogeneous Catalysis: the catalyst is dissolved in a media where takes place the reaction

Heterogeneous Catalysis: the catalyst is separated from the reactive mixture.
Adsorption process

Atoms on the surface of a solid are less stable (less neighbored atoms) vs bulk atoms.
In contact with a fluid, the surface atoms try to catch molecules of the fluid to more stable.

Physical adsorption: Van der Waals type strengths (no alteration of the molecule) = PHYSISORPTION
Chemical adsorption: chemical bond (modification of the molecule) = CHEMISORPTION
Physisorption can take place before chemisorption
### Adsorption enthalpy

<table>
<thead>
<tr>
<th>Adsorbant</th>
<th>Molécule sorbée</th>
<th>Physisorption (kJ·mol⁻¹)</th>
<th>Chimisorption (kJ·mol⁻¹)</th>
<th>T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fer</td>
<td>oxygène</td>
<td>17</td>
<td>500</td>
<td>−183</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>30</td>
<td>130</td>
<td>−78</td>
</tr>
<tr>
<td>ZnO</td>
<td>hydrogène</td>
<td>5</td>
<td>-</td>
<td>−191</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>85</td>
<td>−200</td>
</tr>
<tr>
<td>Cuivre</td>
<td>hydrogène</td>
<td>4</td>
<td>-</td>
<td>78</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>-</td>
<td>−50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>160-300</td>
</tr>
</tbody>
</table>

**Physisorption vs Chemisorption**

Physisorption: enthalpy < 30 kJ/mol
Adsorption process

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

Molecule adsorption = immobilization = Entropy drop: \( \Delta S < 0 \)
\( \Delta G < 0 \), Free energy drop
then \( \Delta H < 0 \) (Adsorption heat)

Adsorption: equilibrium process
\[ \Delta H = \Delta H_d - \Delta H_a \]

**Physisorption:**
- low adsorption heats (5 - 30 kJ/mole)
- process closed to liquefaction but takes place before reaching the saturating vapor pressure.
- Physisorbed gas properties closed to those of free molecules.
- REVERSIBLE process.

**Chimisorption:**
- High adsorption heat (> 80 kJ/mole): HIGH ENOUGH TO IMPROVE REACTION RATE
- Intermediate step of heterogeneous catalysis: often rate-determining step
- deep modification of electronic properties of the adsorbed molecule
- Often needs an activation energy
Adsorption process

**Physisorption isotherm**

**Chemisorption isotherm**

- **Condensation**
- **T = constante**
- **Pression**
- **liquefaction**
- **Saturation**
- **Monolayer**
Two kinds of chemisorption

Saturated molecules are dissociatively adsorbed (alkane): fragments of the dissociative molecules create new chemical bonds on the surface.

Unsaturated molecules (free orbitals, alkene) can be adsorbed associatively.
Adsorption process

Catalytic rate = kinetic

Linked with the reactant adsorption
**Langmuir Model**

**Langmuir assumptions (1915):**

The solid surface is uniform

The adsorption heat depends on the surface coverage

The adsorption leads to the formation of a monolayer

There is an equilibrium between adsorbed and gas phase molecules

\[
G + S \leftrightarrow GS
\]
Langmuir Model

S / solid surface

θ: fraction of the surface covered: coverage

The adsorption rate is proportional to the free surface and to the gas partial pressure

The desorption rate is proportional to the covered surface

Equilibrium: adsorption rate = desorption rate

\[ K_{\text{ads}}P(1-\theta)S = K_{\text{des}}\theta S \]

\[ \theta = \frac{K_{\text{ads}}P}{(K_{\text{des}} + K_{\text{ads}}P)} = \frac{\lambda P}{1+\lambda P} \]

\[ \theta/(1-\theta) = \lambda P \]

with \( \lambda = \frac{K_{\text{ads}}}{K_{\text{des}}} \)
Langmuir model

Dissociative adsorption (H$_2$ on Pt)

$\theta = (\lambda P)^{1/2} / [1+(\lambda P)^{1/2}]$

Two gas adsorbed on same sites with two different adsorption constants $K_1$ and $K_2$

$\theta_1 = \frac{K_1 P_1}{1 + K_1 P_1 + K_2 P_2}$ et $\theta_2 = \frac{K_2 P_2}{1 + K_1 P_1 + K_2 P_2}$
Mechanism of a catalytic reaction

Reaction takes place on the surface (gas/solid interface)

1: transfer of gaseous reactants onto the catalytic surface
2: adsorption of reactants
3: interaction between chemisorbed reactants: surface reaction
4: desorption of products
5: transfer of products our of the reactor

Steps 2,3 et 4: chemistry (the catalyst plays a role)
Step 1 and 5: physic (transport of matter: diffusion control)

The kinetic law (reaction rate) depends on the rate-determining step
Mechanism of a catalytic reaction

\[ [A]+[S] \xrightarrow{A^*} \text{A}_{\text{ads}} \]

E = Ed – Ea : Adsorption heat
Mechanism of a catalytic reaction

**Langmuir-Hinshelwood**: \( A^* + B^* \rightarrow \text{Products} \)

1 adsorption site = competitive adsorption of the two reactants onto the catalyst surface

Surface reaction onto the catalyst surface

\[ \theta_A : \text{Coverage of reactant } A \]

\[ V = k \theta_A \cdot \theta_B \]

\[ \theta_A = \frac{K_A P_A}{1 + K_A P_A + K_B P_B} \text{ et } \theta_B = \frac{K_B P_B}{1 + K_A P_A + K_B P_B} \]

If one reactant is weakly adsorbed, the coverage is near zero and the catalytic rate is negligible

**Eley-Rideal**: Reaction between an adsorbed reactant and another one in the gas phase

\[ A^* + B \rightarrow P \text{ with } v = k \theta_A \cdot P_B \]
Mars et Van Krevelen Mecanism : Redox mecanism

The catalyst presents two adsorption sites: an oxidized site Cat-O and a reduced one : Cat

Transition metal oxide based catalysts: oxidation degree change

\[
HC + \text{Cat-O} \rightarrow HCO + \text{Cat} \\
\text{Cat} + \frac{1}{2} \text{O}_2 \rightarrow \text{Cat-O}
\]

Example : \( \text{V}_2\text{O}_5 \), \( 4 \text{V}^{5+} + 2 \text{O}^{2-} \rightarrow 4 \text{V}^{4+} + \text{O}_2 \) (g)
Partial oxidation of butene \( \text{C}_4\text{H}_8 \) in maleic anhydride \( \text{C}_4\text{H}_2\text{O}_3 \)

Charge transfer
2/ Main families of catalysts
CATALYST = SOLID

Advantages:  - easy separation,  
  - mechanical resistance,  
  - chemically stable (P, T)  
  - good interactions with gases or liquids

Drawbacks:  - preparation repetability (oxides)  
  - homogeneity (particles size)  
  - Aging, sintering.

Needs to maintain a high surface of contact between the catalyst and the reactant

Utilisation of support to disperse the active phase
Nature of the catalysts

**METALS**
- Mainly at the zero oxidation degree,
- Mainly used in reducing conditions

<table>
<thead>
<tr>
<th>VIIA</th>
<th>VIII</th>
<th>IB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe $^{3d^64s^2}$</td>
<td>Co $^{3d^74s^2}$</td>
</tr>
<tr>
<td></td>
<td>Ru $^{4d^75s^1}$</td>
<td>Rh $^{4d^85s^1}$</td>
</tr>
<tr>
<td>Re $^{4f^{14}5d^56s^2}$</td>
<td>Os $^{4f^{14}5d^66s^2}$</td>
<td>Ir $^{4f^{14}5d^76s^2}$</td>
</tr>
<tr>
<td></td>
<td>Cu $^{3d^{10}4s^1}$</td>
<td>Ag $^{4d^{10}5s^1}$</td>
</tr>
</tbody>
</table>

Main reactions: dehydrogenation, combustion, reforming, Automotive post-treatment…

Activity linked with the exposed metallic fraction or dispersion
SUPPORTS

**ALUMINA**

Intensive used support

Many kinds, various physichemical properties (porous or not)

γ-Al$_2$O$_3$ : surface specific area : 100 - 200 m$^2$/g

**SILICA**

SiO$_2$

Amorphous, 150 - 300 m$^2$/g

Inert support

**ZEOLITHE**

Cristallised Silicoaluminates, microporous

Na$_x$(AlO$_2$)$_x$(SiO$_2$)$_x$, z H$_2$O

Tridimensional netwoks of tetraede AlO$_4$ et SiO$_4$

Exchange Na$^+$ ↔ Mn$^+$ Catalytic propery

Surface specific area: 800 – 1000 m$^2$/g

Carbon, ceria, zirconia....
OXIDES

Used as un-supported catalyst

Oxides of Sc, Ti, V, Cr : partial oxidation

Oxides of Co, Ni, Cu, Pd : Combustion

Examples :
(VO)$_2$P$_2$O$_7$ : partial oxidation of butane in maleic anhydride.
Perovskites LaMnO$_3$, LaCoO$_3$ : combustion of hydrocarbons

Activity linked to surface specific area
# Main families of catalysts

## Catalyst families

<table>
<thead>
<tr>
<th></th>
<th>Métaux</th>
<th>Sulfures</th>
<th>Oxydes</th>
<th>Ions supportés</th>
<th>Acides</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Principales phases actives</strong></td>
<td>Ni, Co, Fe, Pd, Rh, Ru, Pt, Ir, Cu, Ag</td>
<td>Ni$_3$S$_2$, Co$_3$S$_8$ MoS$_2$ WS$_2$</td>
<td>ZnO CuO, Cr$_3$O$_3$ Fe$_2$O$_3$ V$_2$O$_5$, MoO$_3$</td>
<td>Ni$^{2+}$ Mo$^{6+}$ Cr$^{3+}$ Ti$^{3+}$ Zr$^{4+}$ Re$^{7+}$</td>
<td>Alumine modifiée (Cl, F) Silice-alumine Silice-magnésie Acide phosphorique supporté Zéolithes Réines sulfoniques</td>
</tr>
<tr>
<td><strong>Réactions</strong></td>
<td>Hydrogénations Déshydrogénations Hydrogénolyses Oxydations Cyclisations</td>
<td>Hydrogénations Déshydrogénations Hydrogénolyses</td>
<td>Oxydations Hydrogénations Déshydrogénations Cyclisations</td>
<td>Oligomérisations Métathèses Polymérisations Oxychlorations</td>
<td>Hydratations Déshydratations Étherifications Isomérisations Oligomérisations Alkylations Craquage Estérisations</td>
</tr>
<tr>
<td><strong>Principales applications industrielles</strong></td>
<td>Synthèse de l’ammoniac Raffinage pétrolier Hydrogénations en chimie fine Postcombustions (1) Oxydations menagées Production du gaz de synthèse</td>
<td>Hydrotraitements en raffinage (2) Hydrocraquage</td>
<td>Oxydations Synthèse du méthanol Destruction de SO$_2$/NO$_x$ Production d’oléfines</td>
<td>Dimérisation des oléfines Métathèses Polymérisation de l’éthylène Polymérisation du propylène Polymérisation du chlorure de vinyle</td>
<td>Production d’éthers composites de l’essence Craquage catalytique Alkylation de l’isobutane par les oléfines Alkylation des aromatiques Isomérisation de paraffines et d’alkylaromatiques</td>
</tr>
</tbody>
</table>

(1) Pots catalytiques en automobile.
(2) En particulier : hydrodésulfuration (HDS) hydrodésazotation (HDN) et hydrodémétallation (HDMe).
Zeolithes

Microstructured network of Al and Si
Channel diameter < 1 nm (Microporosity)

- Faujasite Y: $\text{Na}_{56}\text{Al}_{56}\text{Si}_{136}\text{O}_{384}$, $\approx 240$ H$_2$O
- Mordenite: $\text{Na}_8\text{Al}_8\text{Si}_{40}\text{O}_{96}$, $\approx 24$ H$_2$O
- ZSM-5 (MFI): $\text{Na}_x\text{Al}_x\text{Si}_{96-x}\text{O}_{192}$, $\approx 16$ H$_2$O ($x < 27$)

Na can be exchanged with metallic cations ($\text{Co}^{2+}$, $\text{Cu}^{2+}$, …)
3/ Catalysts properties
Metal supported catalysts

Heterogeneous catalysis = surface process
Catalysts properties = textural and structural

**Structural** = nature and arrangement of atoms not only in the solid but also on the surface: adsorption sites

**Texture** = Agglomerates and grains morphology as well as pores (inter or intra-grains)
Catalyst structure

Adsorption site = 1 single atom or clusters of atoms

The adsorption stops when all sites are filled (monolayer)

Simple relationship between the saturated number of adsorbed molecule and the number of surface atoms.

For pure metals:
   Number of sites = number of surface atoms

For oxides:
   Adsorption site concentration 100 to 1000 as for metals: defects (oxygen vacancies, ...), cations, anions, ...
Catalyst structure

Adsorption of H$_2$ on cuivre (110)
HP-STM

# Catalyst structure

<table>
<thead>
<tr>
<th>Element</th>
<th>Metallic atomic radius (Å)</th>
<th>Ionic radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>1.44</td>
<td>+1: 1.26</td>
</tr>
<tr>
<td>Al</td>
<td>1.43</td>
<td>+3: 0.51</td>
</tr>
<tr>
<td>Au</td>
<td>1.45</td>
<td>+: 1.37; +3: 0.85</td>
</tr>
<tr>
<td>Ba</td>
<td>2.23</td>
<td>+2: 1.34</td>
</tr>
<tr>
<td>Co</td>
<td>1.25</td>
<td>+2: 0.75; +3: 0.63</td>
</tr>
<tr>
<td>Cr</td>
<td>1.30</td>
<td>+2: 0.84; +3: 0.66; +4: 0.56; +6: 0.49</td>
</tr>
<tr>
<td>Cu</td>
<td>1.28</td>
<td>+1: 0.96; +2: 0.70</td>
</tr>
<tr>
<td>Fe</td>
<td>1.26</td>
<td>+2: 0.75; +3: 0.64</td>
</tr>
<tr>
<td>Mn</td>
<td>1.36</td>
<td>+2: 0.80; +3: 0.66; +4: 0.57; +7: 0.40</td>
</tr>
<tr>
<td>Pt</td>
<td>1.39</td>
<td>+2: 0.80; +4: 0.65</td>
</tr>
<tr>
<td>Sr</td>
<td>2.15</td>
<td>+2: 1.12</td>
</tr>
<tr>
<td>Ti</td>
<td>1.70</td>
<td>+2: 0.90; +3: 0.76; +4: 0.64</td>
</tr>
</tbody>
</table>
Catalyst structure

Pt atoms, surface density depends on the exposed plan

Paramètre de maille: \( a_0 = 3.923 \, \text{Å} \)

\[
\begin{align*}
\langle 100 \rangle & : \\ & 2r.2r=4r^2=S \\
& S=2\pi r^2=12.08 \, \text{Å}^2 \\
& A<100>=a_0^2=15.39 \, \text{Å}^2 \\
& \text{N at Pt} / \text{m}^2=0.65.10^{19} \\
\langle 110 \rangle & : \\ & 2r.a_0=S \\
& A<110>=10.88 \, \text{Å}^2 \\
& \text{N at Pt} / \text{m}^2=0.92.10^{19} \\
\langle 111 \rangle & : \\ & 2r.2r.rac(3)=4r^2.rac(3)=2S \\
& A<111>=6.64 \, \text{Å}^2 \\
& \text{N at Pt} / \text{face}=1.50.10^{19} \\
\end{align*}
\]

Equi-distribution des faces: \( \text{N at Pt} / \text{m}^2=1.024.10^{19} \)
Surface structure: well defined crystallographic plans
Many metals crystallise in CFC systems (Ni, Pt, Cu, Ag, Pd…)

Each face has a different structure
Heterogeneous surface: needs to know the contribution of each face in the overall surface

Active sites:
Atoms at the corner and in the edges
Steps between plans
Catalyst structure

TOF of cyclohexene (CHE) and cyclohexane (CHA) formation during benzene hydrogenation

Catalyst texture

Agglomerates, grains, pores:
- Granulometry
- Size and shape of agglomerates
- Overall area
- Volume and shape of pores

Main parameters:
- Specific surface area = surface / mass in m²/g
- Porous volume = pore volume / mass in cm³/g
Dispersion = accessible metallic fraction
For metal supported catalysts

Depend on:
  • Nature of the metal
  • Size of metallic particles

Varies with the temperature (sintering process)

Measured from Chemisorption techniques: adsorption of probe molecules (H₂, CO, O₂,...)
Acido-basicity

Two definitions:
Bronsted acid / base: donor / acceptor of protons
Lewis acid / base: acceptor / donor of electrons

Surface of solid catalysts can present acidic and basic sites:
- acidic sites: positives charges
- basic sites: negatives charges
- Example: OH groups on silica
  (Bronsted acidic sites, positive charge on Si)
Surface catalyst properties: acido-basicity

Hammet classification
Surface catalyst properties: acido-basicity

- γ- Al₂O₃ : a common support in catalysis

- At atmospheric pressure and room temperature: the surface is covered with H₂O
- From 100°C, H₂O desorbs but hydroxide groups remain on the surface (Lewis)

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

\[
\begin{align*}
\text{O} & \quad \text{OH} \\
\text{Al} & \quad \text{Al} & \quad \text{Al} \\
\end{align*}
\]

- When the temperature increases: two neighbored OH groups react to form H₂O : formation of Al³⁺ cations (Lewis acid) and O²⁻ (Lewis base)

These sites are very reactive
4/ Kinetic measurements
Kinetic measurements

Measurements of the reaction rates as a function of the temperature and on reactant concentrations

\[ A + B \leftrightarrow C + D \]

Reaction rate:

\[ r = k [A]^{nA}[B]^{nB} \text{ (POWER LAW)} = k' \exp(-E_a/R.T) \]

Temperature / °C

\[ \begin{array}{cccc}
0 & 10 & 20 & 30 \\
60 & 70 & 80 & 90 \\
100 & 250 & 300 & 350 & 400 & 450 & 500
\end{array} \]

\[ \text{C}_3\text{H}_6 \text{ conversion / %} \]

Ir / ZSY

Ir-20-LP

Ir-40-HP

Ir-90-LP

Ir-150-HP

Conversion: fraction of a reactant consumed

\[ \text{Conversion} = \frac{100 \times (\text{P}_{\text{C}_3\text{H}_6})_i - (\text{P}_{\text{C}_3\text{H}_6})_f}{(\text{P}_{\text{C}_3\text{H}_6})_i} \]

Yield: conversion into a specific product

\[ \text{C}_3\text{H}_6 + 4.5 \text{ O}_2 \rightarrow 3 \text{ CO}_2 + 3 \text{ H}_2\text{O} \]

\[ \%\text{TTG} = 100 \times \frac{\text{P}_{\text{CO}_2}}{\text{P}_{\text{CO}_2} + 3 \times \text{P}_{\text{C}_3\text{H}_6}} \]
Yield and selectivity

Example: Nitric oxide abatement (car exhaust treatment)

Selective catalytic reduction of NO by propene under lean-burn conditions

18 NO + 2 C₃H₆ → 9 N₂ + 6 CO₂ + 6 H₂O
14 NO + C₃H₆ → 7 N₂O + 3 CO₂ + 3 H₂O

NO + ½ O₂ → NO₂

Yieldₙ₂ = 2×Pₙ₂/(PₙO)  N₂ yield

N₂ Selectivity: fraction of consummed NO converted into N₂

SN₂ = 100×Pₙ₂/(Pₙ₂+Pₙ₂O+PₙO₂)

Selectivities can only be compared at similar conversions
T50 : Temperature at 50% of conversion : light-off temperature

Pt/Al₂O₃ + Na

T50 : Temperature at 50% of conversion : light-off temperature

C₃H₆ conversion / %

Temperature / °C

sans Na
0.12% Na
1% Na
5% Na

TOF : Turn over frequency : number of molecules of products/ time/ active site

Space velocity: gas flow/ volume of catalyst
Activity ≠ conversion

Specific activity = catalytic reaction rare per unit of mass (mol/s/g)

Intrinsic activity = Number of reactant moles converted per unit of time and area (mol/s/m²)

\[
\text{Intrinsic activity} = \frac{\text{specific activity}}{\text{surface specific area}}
\]

TOF = specific activity / dispersion
Materials for catalytic air depollution

- Noble metals / support
  - **Platinum**
    - Most oxidation reactions
  - **Palladium**
    - Oxidations \((\text{CH}_4)\)
  - **Rhodium**
    - DeNOx
  - **Ruthenium**
    - DeNOx. Oxidation.

Spivey, 1987, 2005

**Shape:** powder beads, extrudates, pellets wash-coated on monoliths
General considerations:

- strongly exothermic reactions
  (Ex: $\Delta H = -282 \text{ kJ mol}^{-1}$ for CO oxidation
   $-802 \text{ kJ mol}^{-1}$ for CH$_4$ oxidation)
- no thermodynamic limitations
- often sensitive to particle sizes

\[
\text{Rate} = k \ P_{O_2}^m \ P_{HC}^n
\]
CO oxidation over Metal/Al₂O₃

Mécanisme de Langmuir-Hinshelwood

<table>
<thead>
<tr>
<th>Metal</th>
<th>Pd</th>
<th>Pt</th>
<th>Rh</th>
</tr>
</thead>
<tbody>
<tr>
<td>m (O₂)</td>
<td>+ 0.9</td>
<td>+1.0</td>
<td>+1.0</td>
</tr>
<tr>
<td>n (CO)</td>
<td>− 0.9</td>
<td>− 0.9</td>
<td>− 0.8</td>
</tr>
<tr>
<td>E (kJ mol⁻¹)</td>
<td>108-133</td>
<td>104-125</td>
<td>92-117</td>
</tr>
</tbody>
</table>

\[
r_{CO} = k \frac{K_{CO} P_{CO} \sqrt{K_O P_O}}{(1 + K_{CO} P_{CO} + K_O P_O^{1/2})^2}
\]

If \( K_{CO} P_{CO} \gg 1 + K_O P_O^{1/2} \)

\[
r_{CO} = k \frac{K_O P_O^{1/2}}{K_{CO} P_{CO}}
\]

Barbier Jr and Duprez

Europacat 2009
Catalytic oxidation of Hydrocarbons and Alcohols

Light-off temperatures (50% conversion)
Catalyst: commercial Pt-Rh/CeO$_2$-Al$_2$O$_3$

From Bart et al., in *Catalytic Control of Air Pollution, ACS Symp.Series 495*

<table>
<thead>
<tr>
<th>n-alkanes</th>
<th>T50</th>
<th>Alkenes alkynes</th>
<th>T50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>515°C</td>
<td>Ethylene</td>
<td>205°C</td>
</tr>
<tr>
<td>Ethane</td>
<td>435°C</td>
<td>Propene</td>
<td>185°C</td>
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<tr>
<td>Propane</td>
<td>290°C</td>
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<td>285°C</td>
</tr>
<tr>
<td>Hexane</td>
<td>195°C</td>
<td></td>
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</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aromatics</th>
<th>T50</th>
<th>Alcohols</th>
<th>T50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>205°C</td>
<td>Methanol</td>
<td>195°C</td>
</tr>
<tr>
<td>Toluene</td>
<td>220°C</td>
<td>Ethanol</td>
<td>200°C</td>
</tr>
<tr>
<td>O-Xylene</td>
<td>225°C</td>
<td>Propanol</td>
<td>205°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Butanol</td>
<td>210°C</td>
</tr>
</tbody>
</table>
CH₄ and C₃H₈ oxidation over Metal/Al₂O₃

TOF (s⁻¹) @ 400°C

TOF (s⁻¹) @ 250°C

Yao and Yu Yao
Barbier et al
Hicks et al
C₃H₈ oxidation: kinetics and mechanism

No well-established mechanism.
Most probable: "oxygenolysis" mechanism analogous to that of hydrogenolysis

<table>
<thead>
<tr>
<th>Metal</th>
<th>Pd</th>
<th>Pt</th>
<th>Rh</th>
</tr>
</thead>
<tbody>
<tr>
<td>m (O₂)</td>
<td>+ 0.1</td>
<td>-1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>n (C₃H₈)</td>
<td>+ 0.6</td>
<td>+2.0</td>
<td>+0.5</td>
</tr>
<tr>
<td>E (kJ mol⁻¹)</td>
<td>66-96</td>
<td>84-105</td>
<td>95-105</td>
</tr>
</tbody>
</table>

Pt: strong O₂ adsorption
(with respect to C₃H₈)
Pd and Rh: O₂ adsorption moderately higher.

Steps 1
1a: dehydrogenative HC adsorption
\[ C_3H_8 + \ast \rightarrow C_3H_{8-x} -\ast + \frac{x}{2}H_2 \]

1b: O₂ adsorption
\[ \frac{1}{2}O_2 + \ast \rightarrow O -\ast \]

Step 2
C-C bond cleavage by O₂
\[ C_3H_{8-x} -\ast + O_2 \rightarrow C_2H_y -\ast + (CO, CO₂, H₂O) \]

Step 3
Oxidation of adsorbed C₂ fragments (fast)

\[ \text{Rate} \approx A \frac{P_C}{P_{O_2}^{1/2}} \]
C₃H₆ oxidation over Metal/Al₂O₃ catalysts

<table>
<thead>
<tr>
<th>Metal</th>
<th>Pd</th>
<th>Pt</th>
<th>Rh</th>
</tr>
</thead>
<tbody>
<tr>
<td>m (O₂)</td>
<td>+1.5</td>
<td>+2.0</td>
<td>−0.8</td>
</tr>
<tr>
<td>n (C₃H₆)</td>
<td>−0.5</td>
<td>−2.0</td>
<td>+0.9</td>
</tr>
<tr>
<td>E (kJ mol⁻¹)</td>
<td>67-117</td>
<td>67-125</td>
<td>67-92</td>
</tr>
</tbody>
</table>

Pd and Pt:
- strong adsorption of the olefin
- very weak particle size effect

Exactly the reverse for Rh
Relative adsorption constants

On Pd and Pt

On Rh
Kinetic study: an example

\[ \text{C}_3\text{H}_6 + 4.5 \ \text{O}_2 \rightarrow 3 \ \text{CO}_2 + 3 \ \text{H}_2\text{O} \]

Catalyst: Pt / \( \gamma \)-Al\(_2\)O\(_3\)

![Graph showing the variation of propene conversion versus temperature for three Pt/Al\(_2\)O\(_3\) catalysts, with different Pt loadings.](image)

Variation of the C\(_3\)H\(_6\) conversion versus temperature for three Pt/Al\(_2\)O\(_3\) catalysts, with different Pt loadings (■ P8 – 0.5 wt. %, ▲P5 – 1 wt. %, ♦P1 –1.5 wt. %). Reactive mixture:

\[ \text{C}_3\text{H}_6/\text{O}_2 : 1000 \text{ ppm}/9 \% \text{. Total gas flow rate: } 120 \text{ mL.min}^{-1}. \]
Kinetic study: an example

Variation of the intrinsic catalytic activity versus temperature for three Pt/Al₂O₃ catalysts, with different Pt loadings (■ P8 – 0.5 wt. %, ▲ P5 – 1 wt. %, ◆ P1 –1.5 wt. %). Reactive mixture: C₃H₆/O₂: 1000 ppm/9 %. Total flow rate: 120 mL.min⁻¹.
Determination of partial order in O\textsubscript{2} for the catalyst P5 diluted. (♦ 150°C, ■ 155°C, ▲ 160°C, × 165°C, ● 168°C). Reactive mixture: 1000 ppm C\textsubscript{3}H\textsubscript{6} and O\textsubscript{2} concentration varies between 0.5 and 6 %.
Kinetic study: an example

Kinetic study: an example

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>n (O₂)</th>
<th>p (C₃H₆)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>1.02</td>
<td>-0.45</td>
</tr>
<tr>
<td>155</td>
<td>1.12</td>
<td>-0.45</td>
</tr>
<tr>
<td>160</td>
<td>0.92</td>
<td>-0.42</td>
</tr>
<tr>
<td>165</td>
<td>1.09</td>
<td>-0.39</td>
</tr>
<tr>
<td>168</td>
<td>0.84</td>
<td>-0.44</td>
</tr>
</tbody>
</table>

\[ v = k' C_n^{O_2} C_p^{C_3H_6} \]

Assumptions: Langmuir-Hinshelwood

LH1: Non dissociative adsorption of propene and O₂
LH2: Dissociative adsorption dissociative of propene and O₂
LH3: Non dissociative adsorption of propene and dissociative of O₂
LH4: Dissociative adsorption of propene and non dissociative of O₂

n = 1, p = -0.4
Mathematic modelling can determine the mechanism

Adjustment of experimental data with calculated ones for the L-H mechanism with dissociative $\text{C}_3\text{H}_6$ and non-dissociative $\text{O}_2$, for propene oxidation after simplification

(+ experimental rates, — calculated rates)
5/ Characterizations
Dispersion measurements: probe molecule adsorption

Example: Pt / alumina (2 wt%)

Dispersion = Pt$_s$ / total Pt avec Pt$_s$ : surface Pt

Procedure: reduction of the catalyst and desorption under vacuum

- Adsorption of H$_2$ at room temperature (HC): Pt$_s$ + $\frac{1}{2}$ H$_2$ → Pt$_s$-H
- Titration with oxygen at room temperature: Pt$_s$-H + $\frac{3}{4}$ O$_2$ → Pt$_s$-O + $\frac{1}{2}$ H$_2$O
- Titration with H$_2$ at room temperature (HT): Pt$_s$-O + $\frac{3}{2}$ H$_2$ → Pt$_s$-H + H$_2$O

M$_W$ Pt = 195.09 g/mol, total Pt = 102.52 µmol / g of catalyst
HC = 20.6 µmol H$_2$ / g of catalyst
OT = 30.8 µmol O$_2$ / g of catalyst
HT = 62.1 µmol H$_2$ / g of catalyst then dispersion = 40 %

Problems: ratio O or H / Pt not equal to 1 and spillover of H$_2$ on the support (overestimation of the H$_2$ quantity)

Other techniques: CO adsorption, Transmission Electronic Microscopy
Dispersion measurements: Temperature-programmed methods

Adsorption of probe molecules (O₂, H₂, acido-basic molecules…).
Heating of the catalyst in inert conditions (He) or under vacumm induces the desorption
Detection with a mass-spectrometer
→ quantity of molecule adsorbed
→ desorption temperature = strength of the chemical bond
Adsorption of O₂ and TPD of O₂: metal/support interactions

Two kinds of oxygen species

Pt / YSZ [(ZrO₂)₀.₉₂(Y₂O₃)₀.₀₈] An O²⁻ conductor

Pt / Al₂O₃

O₂ / 10⁻¹¹ mol/s

Temperature / °C

O(g)
B.E.T. (Brunauer, Emmet et Teller) Model

Measurement of the surface specific area

Generalization of the Langmuir model to multilayers adsorption

\[ \frac{\theta}{1-\theta} = \lambda P \]

- \( n_0 \): number of free sites
- \( n_1 \): number of molecules on the solid
- \( n_2 \): number of molecules in contact with the first layer
- \( n_3 \): ...

Langmuir Equilibrium for each layer
First layer: \( \lambda_1 \) (adsorption heat of the 1st layer) \( \lambda_1 = K_{ads,1}/K_{des,1} \)

For the followings: \( \lambda_2 = \lambda_3 = \ldots = \lambda \) (liquefaction heat) \( E_1 \geq E = E_L \)
\( \lambda_1 \geq \lambda \), if \( \lambda_1 = c \times \lambda \) with \( c \geq 1 \)
B.E.T. (Brunauer, Emmet et Teller) Model

1st layer $n_1 - n_2 / n_0 = \lambda_1 \cdot P = c \cdot \lambda \cdot P$

$n_1 - n_2 (\theta)$: coverage ($n_1$ can desorb if $n_2$ is removed), $n_0 (1-\theta)$: free sites

2nd layer $(n_2 - n_3) / (n_1 - n_2) = \lambda \cdot P$

3rd layer $(n_3 - n_4) / (n_2 - n_3) = \lambda \cdot P$

ird layer $(n_i - n_{i+1}) / (n_{i-1} - n_i) = \lambda \cdot P$

$N = n_0 + n_1$: Overall number of sites

- $n_1 - n_2 = c \cdot \lambda \cdot P \cdot n_0$
- $+ (n_2 - n_3) = \lambda \cdot P \cdot (n_1 - n_2) = c \cdot (\lambda \cdot P)^2 \cdot n_0$
- $+ (n_i - n_{i+1}) = c \cdot (\lambda \cdot P)^i \cdot n_0$

Geometrical suite

$\lambda P < 1$

$(\lambda P + (\lambda P)^2 + \ldots + (\lambda P)^{i-1}) = \lambda P / (1 - \lambda P)$

When $i$ tends to $\infty$, $n_i$ tends to 0

$n_1 = c \lambda P n_0 / (1 - \lambda P)$
B.E.T. (Brunauer, Emmet et Teller) Model

\[ n_1 = \frac{c \lambda P n_0}{(1-\lambda P)} \]

\[ n_2 = \frac{c(\lambda P)^2 n_0}{(1-\lambda P)} \]

\[ n_i = \frac{c(\lambda P)^i n_0}{(1-\lambda P)} \]

Quantity of adsorbed gas

\[ n = n_1 + n_2 + \ldots + n_i = \frac{c n_0}{(1-\lambda P)} \sum_{i=1}^{\infty} (\lambda P)^i = \frac{c \lambda P n_0}{(1-\lambda P)^2} \]

\[ \frac{n}{N} = \frac{[c \lambda P/(1-\lambda P)^2][1/(1+c \lambda P/(1-\lambda P))]} \]

\[ \frac{n}{N} = \frac{c \lambda P}{[(1-\lambda P)(1+(c-1)\lambda P)]} \]
When \( P = P_o \) (saturated vapour pressure at \( T \)), liquid condensates on the solid. All surface atoms are adsorption sites.

\[
1 = \lambda P_0, \quad \lambda = 1/P_0
\]

\( (\lambda P = P/P_0 < 1 \text{ as assumed!}) \)

\[
V/V_M : \text{monolayer capacity}
\]

\[
V: \text{quantity of adsorbed gas at } P
\]

\[
V_M: \text{quantity of gas required for a monolayer}
\]

\[
n/N = V/V_M = cP/P_o / [(1-P/P_o)(1+(c-1)P/P_o)]
\]

B.E.T. method
\[ \lambda_1 = c \lambda \]
\[ C = \exp \left( \frac{E_1 - E_L}{RT} \right) \]

\( E_L \): heat of gas liquefaction

If the first layer is much more strongly adsorbed than the others:
\( E_1 >> E_L \) donc \( c >> 1 \)

If similar adsorption strengths, \( c=1 \)

\[ V/V_m \]
\[ P/P_0 \]

\( C = 1000 \), type II
We form a monolayer

\( C = 1 \), type III
We start with a multilayer
B.E.T. (Brunauer, Emmet et Teller) Model

\[
\frac{V}{V_M} = \frac{cP}{P_0} / \left[ (1-P/P_0)(1+(c-1)P/P_0) \right]
\]

\[
P/[V(P_0-P)] = \frac{1}{cV_M} + \frac{c-1}{(cV_M)} \frac{P}{P_0}
\]

\[
\beta = \frac{1}{cV_M}
\]

\[
\beta = \frac{1}{cV_M}
\]

\[
V_M = \frac{1}{(\alpha + \beta)}
\]

if \( c \gg 1 \)

\[
P/[V(P_0-P)] = \epsilon + \left( \frac{1}{V_M} \right) \frac{P}{P_0}
\]

Only 1 point of the isotherm is sufficient to find \( V_M \)
B.E.T. (Brunauer, Emmet et Teller) Model

\[ S (m^2) = V_M (cm^3, CNTP) \times Na \times \sigma / \text{molar volume (22400 cm}^3) \]

- \( Na \): Avogadro number
- \( \sigma \): area filled with a physisorbed molecule

\[ \sigma = 13.8 \text{ Å}^2 \text{ at 77K for Ar} \]
\[ \sigma = 20.2 \text{ Å}^2 \text{ at 77K for Kr} \]
\[ \sigma = 16.2 \text{ Å}^2 \text{ at 77K for N}_2 \]

For nitrogen at 77K, \( S(m^2) = 4.35 \times V_M (cm^3 \text{ CNTP}) \text{ (BET AREA)} \)

**Validity**: \( 0.05 < P/P_0 < 0.3 \) (\( P > 0.3 \) risq to condensate into the mesopores, \( P < 0.05 \) less than one monolayer adsorbed (not enough sites))

This method is not valid for micropores (\( c=1 \))
Electronic microscopy

SEM (Scanning electronic microscopy): texture

TEM: Transmission electronic microscopy: active site
Environmental Transmission Electronic Microscopy: in-situ observations of the reaction