DICP Course - Dalian, 2012
Preparation of solid catalysts
Part 6

Supported by the Chinese Academy of Sciences

Charles Kappenstein, Professor Emeritus, University of Poitiers, France

DALIAN INSTITUTE OF CHEMICAL PHYSICS,
CHINESE ACADEMY OF SCIENCES

1431
Université
de Poitiers

中國科学院
CHINESE ACADEMY OF SCIENCES

cnrs
dépasser les frontières

Faculté des Sciences
Fondamentales
et Appliquées
UFR SFA
Université
de Poitiers

Institut de Chimie
des Milieux et Matériaux de Poitiers
IC2MP

Outline

Introduction and general aspects

Interfacial chemistry – Electrostatic adsorption

Impregnation, drying, calcination and/or reduction

Sol-gel chemistry processing

Deposition – Precipitation and Coprecipitation

➡ Preparation of bimetallic catalysts

Outline

Zeolite-based catalysts

Characterization – High throughput experimentation

Case studies:

- **Noble metal catalysts**
- **Methanol catalysts**
- **Hydrotreating catalysts**
- **……**

Outline

Preparation of bimetallic catalysts

➡ 1) Introduction

2) Redox preparation

3) Surface organometallic chemistry (SOMC)

Introduction

Bimetallic catalytic systems are proposed to improve
Catalysts activity,
Selectivity,
Stability.

Selectivity depends on specific sites

- **low coordination sites: edges, corners, adatomes**
- **high coordination sites: faces, terraces**

Stability depends on catalyst resistance

- **to poisoning**
- **to sintering**
- **to structural or composition modification**

➔ How to prepare bimetallic catalysts to achieve these aims?

Introduction

Classical Methods:

- **Co-impregnation**
- **Co-precipitation**
- **Successive impregnations**

But

➔ Heterogeneous particles
➔ Random location of the second metal

Optimization of the preparation procedure: Controlled Surface Reactions

Two main ways:

1- Redox preparation

2- Surface organometallic chemistry

Outline

Preparation of bimetallic catalysts

1) Introduction

2) Redox preparation
    direct redox reaction
    refilling
    metal support redox reaction

3) surface organometallic chemistry (SOMC)

Redox preparation: direct redox reaction

- Prepare metal M_1 on the support

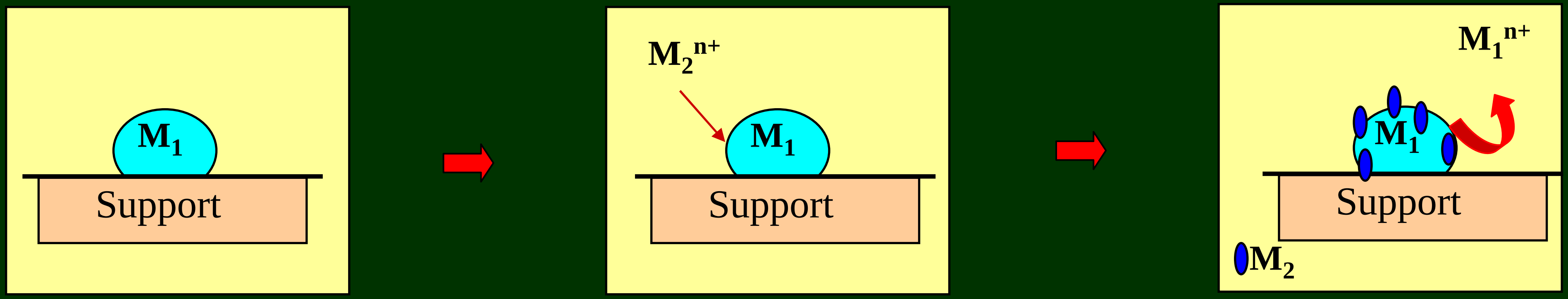
- Add the precursor of metal M_2

The redox reaction happens on the surface of metal M_1

$$(M_1)\text{-}M_1(s) + M_2^{n+}(aq) \rightarrow M_1^{n+}(aq) + (M_1)\text{-}M_2(s)$$

Thermodynamic condition?

$$E°(M_2^{n+}/M_2) > E°(M_1^{n+}/M_1)$$



Redox preparation: direct redox reaction

Ex.: Pt-Pd/Al_2O_3

1) Prepare a 1 wt.-% Pd/Al_2O_3

2) Introduction of the solvent and N_2 (1 h)

3) Introduction of the solution of H_2PtCl_6 (contact time 20 min)

$$2\,Pd(s) + [PtCl_6]^{2-}(aq) + 2\,Cl^-(aq) \rightarrow 2\,[PdCl_4]^{2-}(aq) + Pt(s)$$

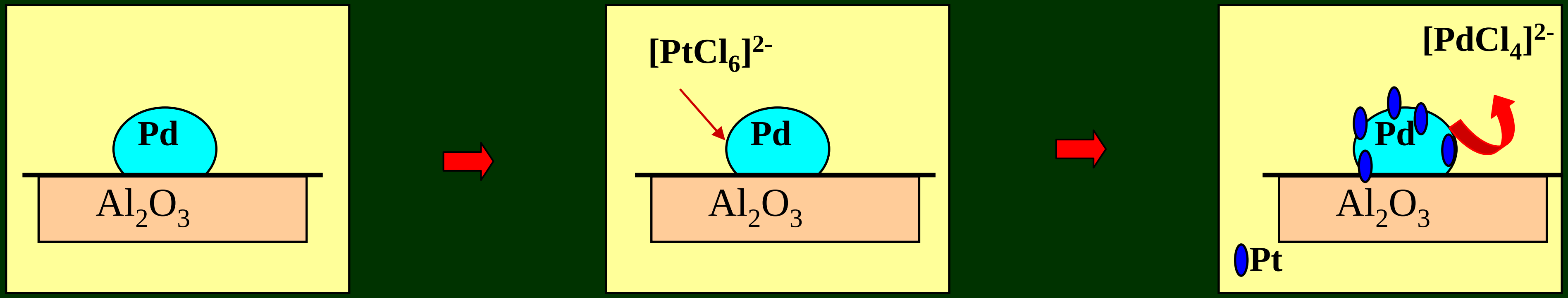
Is the thermodynamic condition on redox potential in agreement

$$E°([PtCl_6]^{2-}/Pt) = 0.74\ V > E°([PdCl_4]^{2-}/Pd) = 0.62\ V$$

4) Washing

5) Drying at 120 °C

6) Reduction at 400 °C → 0.2%Pt-0.8%Pd/Al_2O_3



Redox preparation: refilling

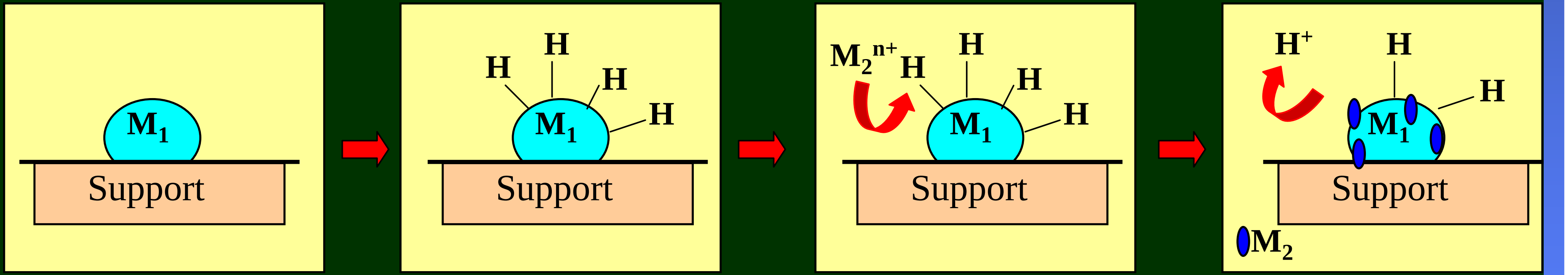
- Prepare metal M_1 on the support
- Chemisorption of H_2 on metal M_1
- Add the precursor of metal M_2

The redox reaction happens on the surface of metal M_1

$$(M_1)\text{-}(H)_n(s) + M_2^{n+}(aq) \rightarrow (M_1)\text{-}M_2(s) + n\,H^+(aq)$$

Thermodynamic condition?

$$E°(M_2^{n+}/M_2) > E°(H^+/H_2) = 0.00\ V$$



Redox preparation: refilling

Ex.: Pt-Pd/Al_2O_3

1) Prepare a 1 wt.-% Pd/Al_2O_3

2) Introduction of the solvent and N_2 (1 h)

3) Introduction of H_2 (1 h)

4) Evacuation of H_2 by N_2 flow

5) Introduction of the solution of H_2PtCl_6 (contact time 20 min)

$$\text{Pd-(H)}_4\text{(s)} + [\text{PtCl}_6]^{2-}\text{(aq)} \rightarrow \text{Pd-Pt} + 6\ \text{Cl}^-\text{(aq)} + 4\ \text{H}^+\text{(aq)}$$

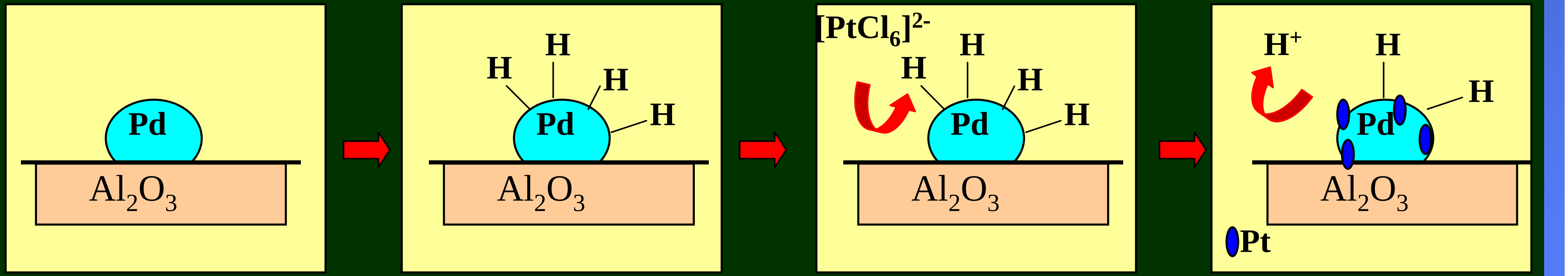
Is the thermodynamic condition on redox potential in agreement

$$E°([\text{PtCl}_6]^{2-}/\text{Pt}) = 0.74\ \text{V} > E°(\text{H}^+/\text{H}_2) = 0.00\ \text{V}$$

4) Washing

5) Drying at 120 °C

6) Reduction at 400 °C → 0.2%Pt-1%Pd/Al_2O_3



Redox preparation: Comparison direct redox reaction and refilling

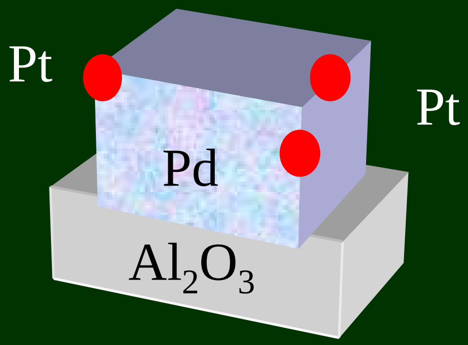
Ex.: Pt-Pd/Al_2O_3

Application: Hydrogenation of aromatics to decrease their content in diesel fuel

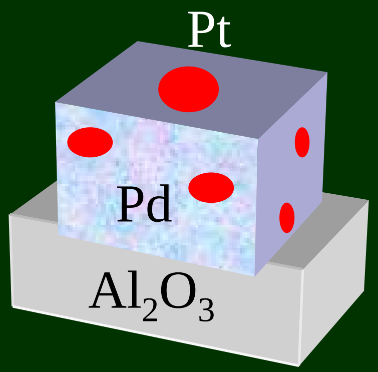
➔ Refilling ⇨ Pt deposited on low Pd coordination sites (edges and corners)

➔ Direct redox reaction ⇨ Pt on high coordination sites (111 faces)

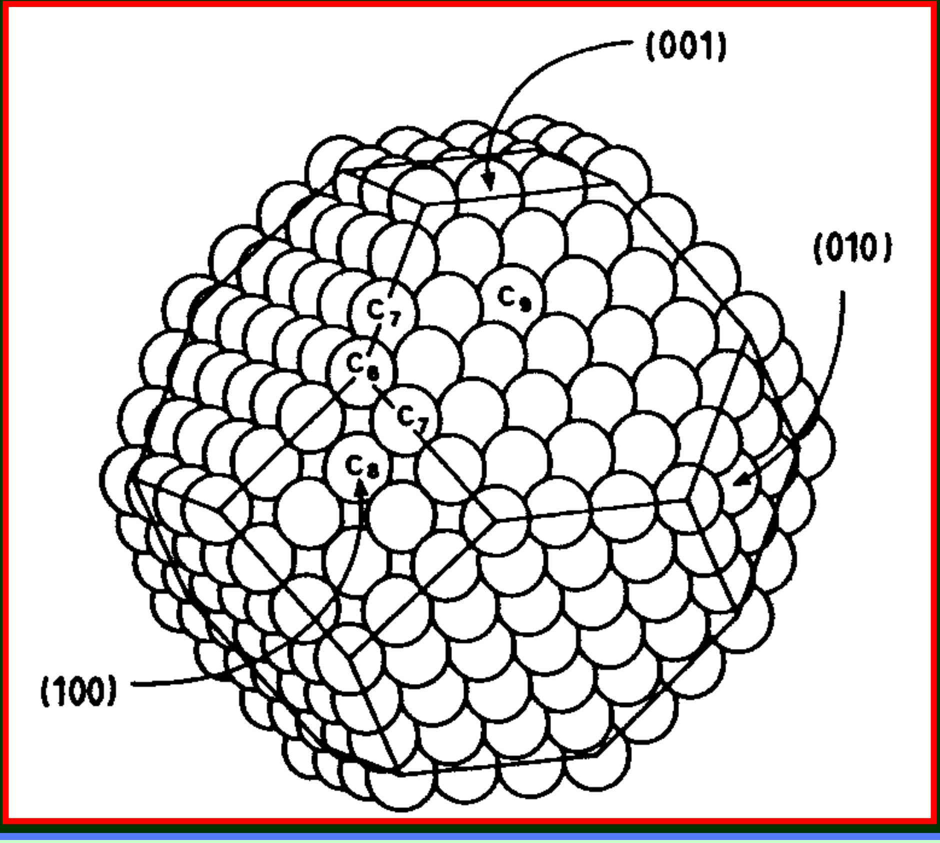
Models



Refilling



Direct redox reaction



Redox preparation: Metal-support redox reaction (MSR)

The support or a part of the support is reducible

- Prepare metal M_1 on the support

- Reduce a part of the support with H_2

support + $H_2(g)$ ➔ reduced support + $H_2O(l)$

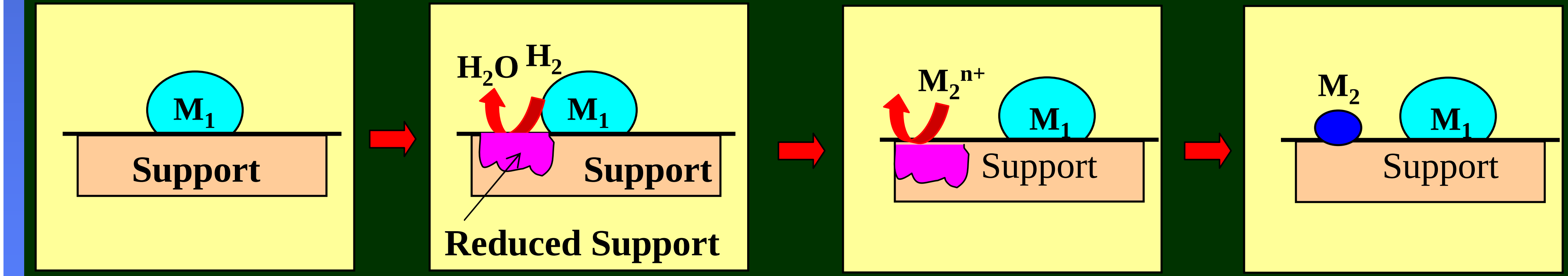
- Add the precursor of metal M_2

reduced support + $M_2^{n+}(aq)$ ➔ support + $M_2(s)$

Thermodynamic condition?

$$E°(M_2^{n+}/M_2) > E°(\text{support/reduced support})$$

➔ M_1 and M_2 are separated



Redox preparation: Metal-support redox reaction (MSR)

Ex.: Rh-Pt/Al_2O_3-12%CeO_2

1) Prepare a 1 wt.-% Pt/Al_2O_3-12%CeO_2

- Impregnation of H_2PtCl_6,
- Calcination and reduction, at 500 °C

$$CeO_2(s) + x\ H_2(g) \rightarrow CeO_{2-x}(s) + x\ H_2O(g) \quad \text{(x close to 0.2)}$$

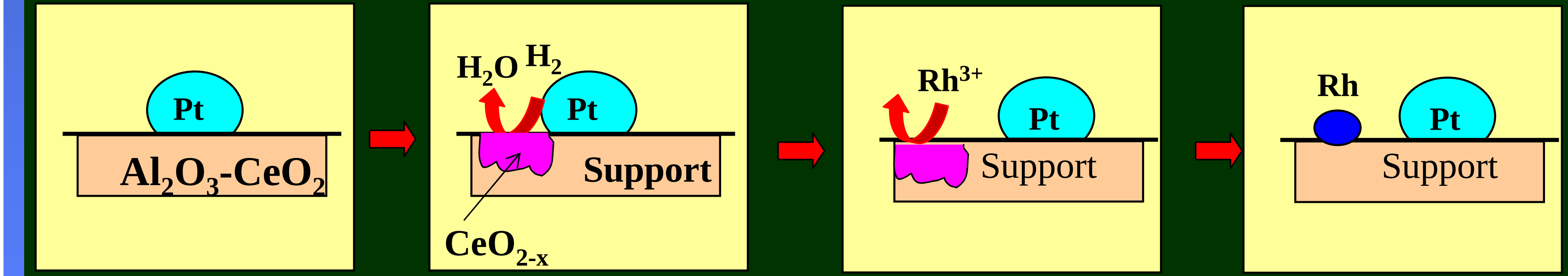
2) Impregnation of $RhCl_3$

$$3\ CeO_{2-x}(s) + 2x\ Rh^{3+}(aq) + 3x\ H_2O(l) \rightarrow 3\ CeO_2(s) + 2x\ Rh(s) + 6x\ H^+(aq)$$

Is the thermodynamic condition on redox potential in agreement

$$E°(Rh^{3+}/Rh) = 0.76\ V > E°(CeO_2/CeO_{2-x}) = -0.07\ V$$

3) Final reduction at 500 °C → 0.2%Rh-1%Pt/Al_2O_3-CeO_2



Redox preparation: Metal-support redox reaction (MSR)

Ex.: Rh-Pt/Al_2O_3-12%CeO_2

Compare with coimpregnated catalyst:

- Co-impregnation of H_2PtCl_6 and $RhCl_3$
- Calcination and reduction at 500 °C

➔ Rh-Pt alloy formation

For metal-support redox reaction

➔ Pt and Rh particles are separated

Interest:

Three-way catalyst (TWC)

- Pt for hydrocarbon and CO oxidation
- Rh for NO_x reduction
- Al_2O_3 as support promoted by CeO_2

Objectives :

- Resistance to Pt-Rh alloy formation (no activity)
- Resistance to sulfur poisoning

Outline

Preparation of bimetallic catalysts

1) Introduction

2) Redox preparation

3) Surface organometallic chemistry (SOMC)
  - **Pt catalysts modified by Ge**
  - **Rh catalysts modified by Ge**

Surface organometallic chemistry (SOMC)

Two types of surface controlled reactions

- Redox reaction

⇒ Limitation linked by the redox potential value

- Surface Organometallic Chemistry (SOMC)

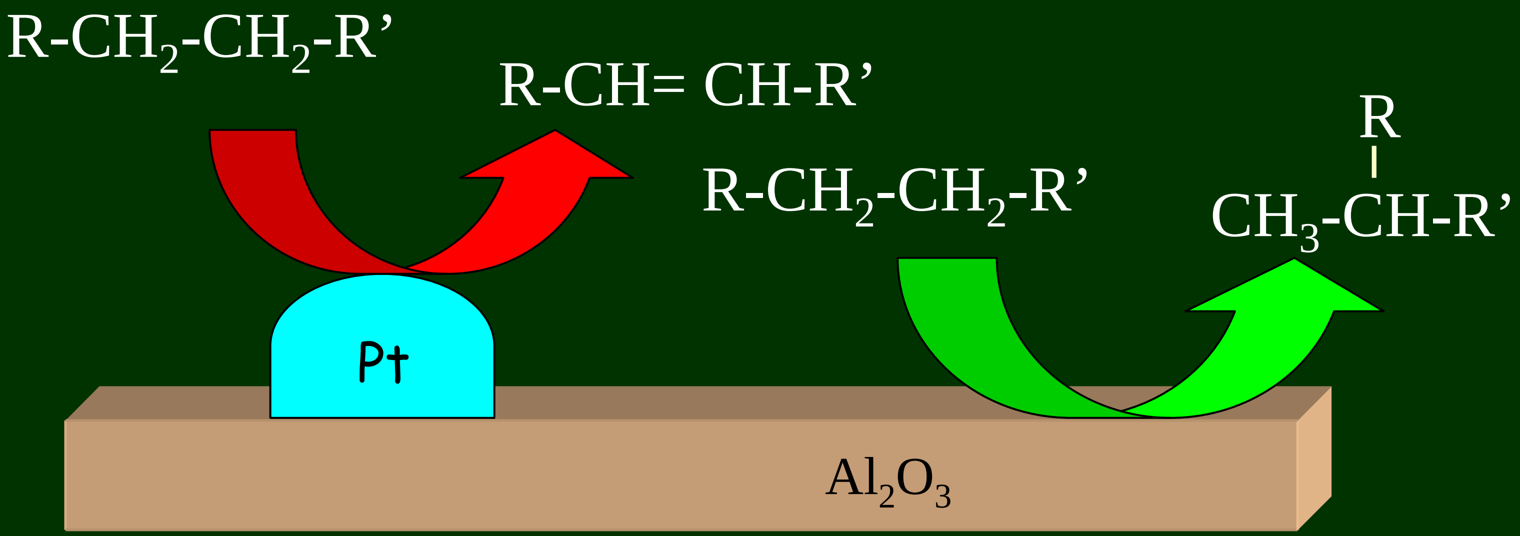
⇒ Use of organometallic precursors

Surface organometallic chemistry: Pt catalysts modified by Ge

Application: Reforming of gazoline

Objectives:

- ➔ **To enhance deshydrogenation reactions (metal)**
- ➔ **To favor isomerisation reaction (acidic support)**



$R\text{-}CH_2\text{-}CH_2\text{-}R'$ ➔ $R\text{-}CH{=}\,CH\text{-}R'$

$R\text{-}CH_2\text{-}CH_2\text{-}R'$ ➔ $CH_3\text{-}\overset{\overset{R}{|}}{C}H\text{-}R'$

How to increase the catalyst performances?

➔ add a second component to Pt

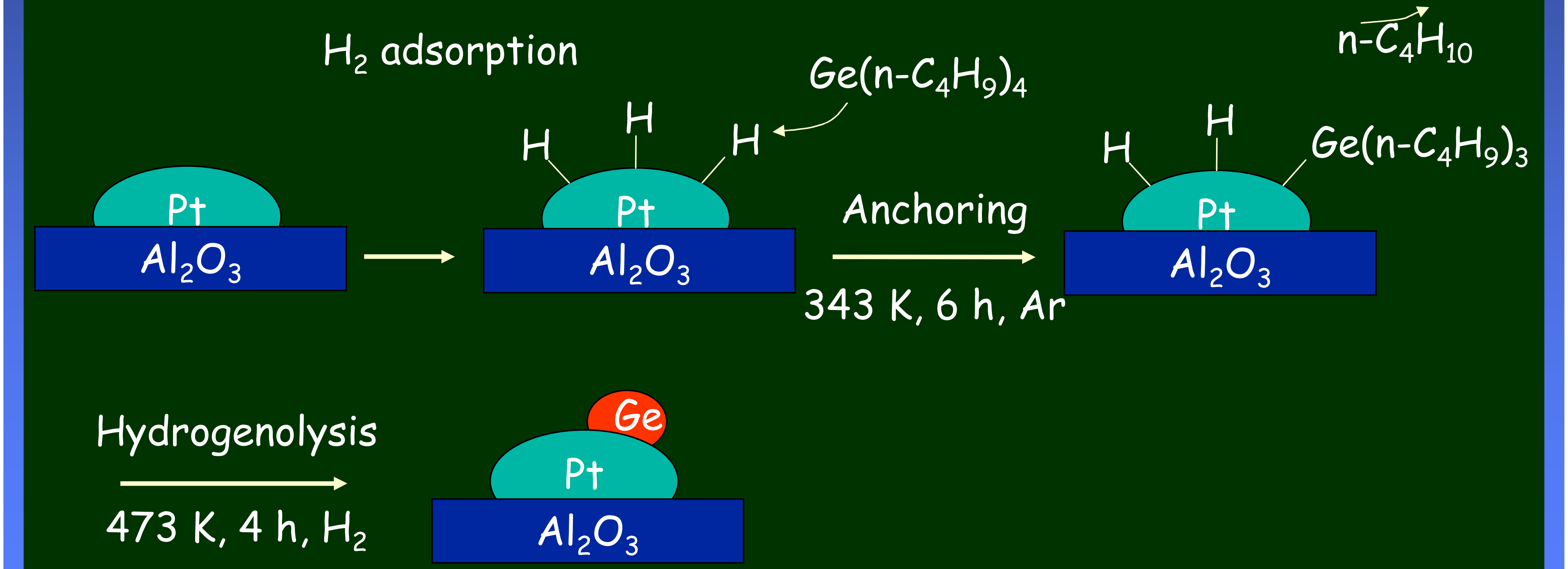
Promoting effect ➔ ↗ Activity ↗ Selectivity

Stabilisation effect ➔ ↘ Coking deactivation ↗ Regeneration ability

Surface organometallic chemistry: Pt catalysts modified by Ge

1) prepare a Pt/Al_2O_3 catalyst
2) adsorb hydrogen
3) react wih Ge-(n-C_4H_9)$_4$
4) finish with hydrogenolysis ➔ formation of Ge-Pt/Al_2O_3 catalyst

Perform all the steps in an unique reactor ➔ *in-situ* preparation in a dynamic reactor



Surface organometallic chemistry: Rh catalysts modified by Ge

Catalyst preparation steps for in situ preparation

1) prepare a 1 % Rh/Al_2O_3 catalyst (reduction at 400 °C)
2) Add the solvent heptane (C_7H_{16}) under Argon
3) Introduce H_2 (1 h) at 25 °C
4) Evacuate H_2 by an argon flow
5) Introduce the solution of tetrabutylgermanium (6 h, 70 °C)
6) Wash with heptane
7) Dry at 120 °C
8) Reduce at 200 °C under H_2

➔ 1 % Rh - x % Ge/Al_2O3 x = 0.02 % (i.e. 200 ppm) to 0.15 %

Catalytic performances in 2,2,3-trimethylbutane hydrogenolysis

Particles < 1.5 nm ➔ CH_4 + C6

Particles > 2.5 nm ➔ i-C4 + C3

End of part 6