

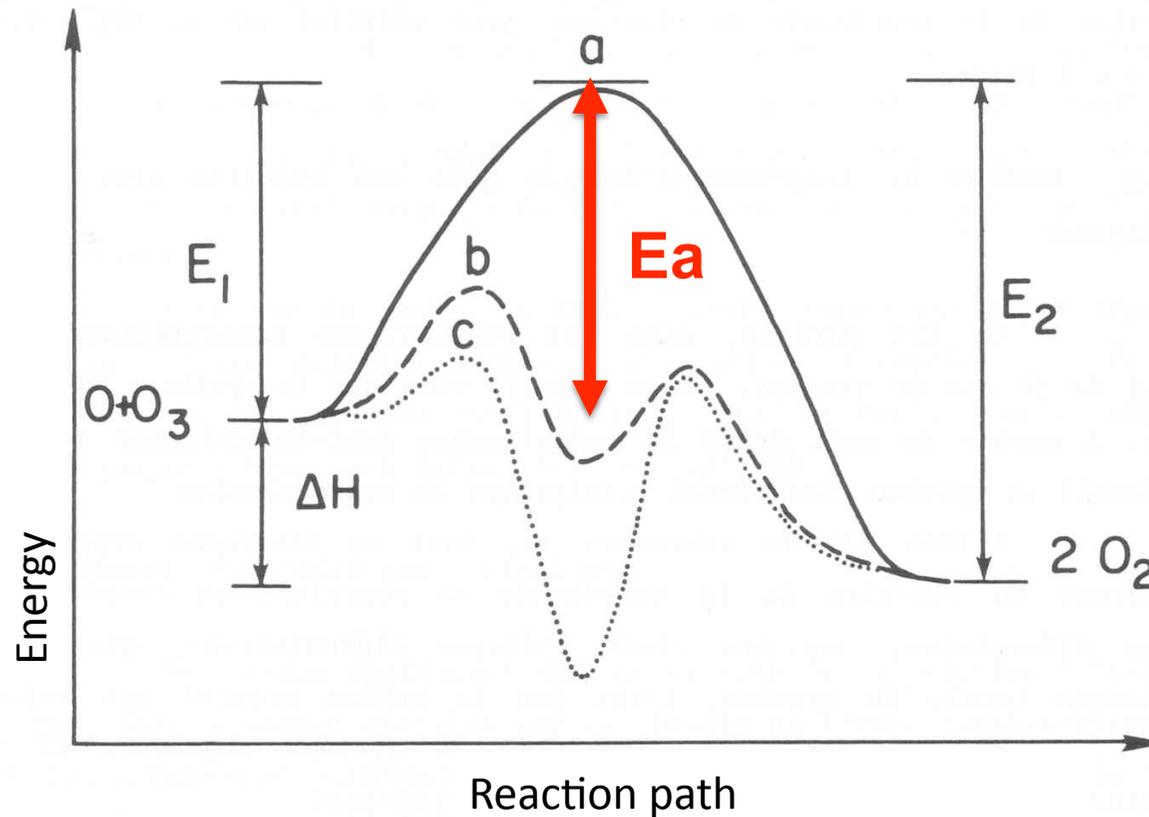
# Catalyse hétérogène: une affaire de surface(s)

Journées de Chimie ENS-X-ESPCI  
Paristech

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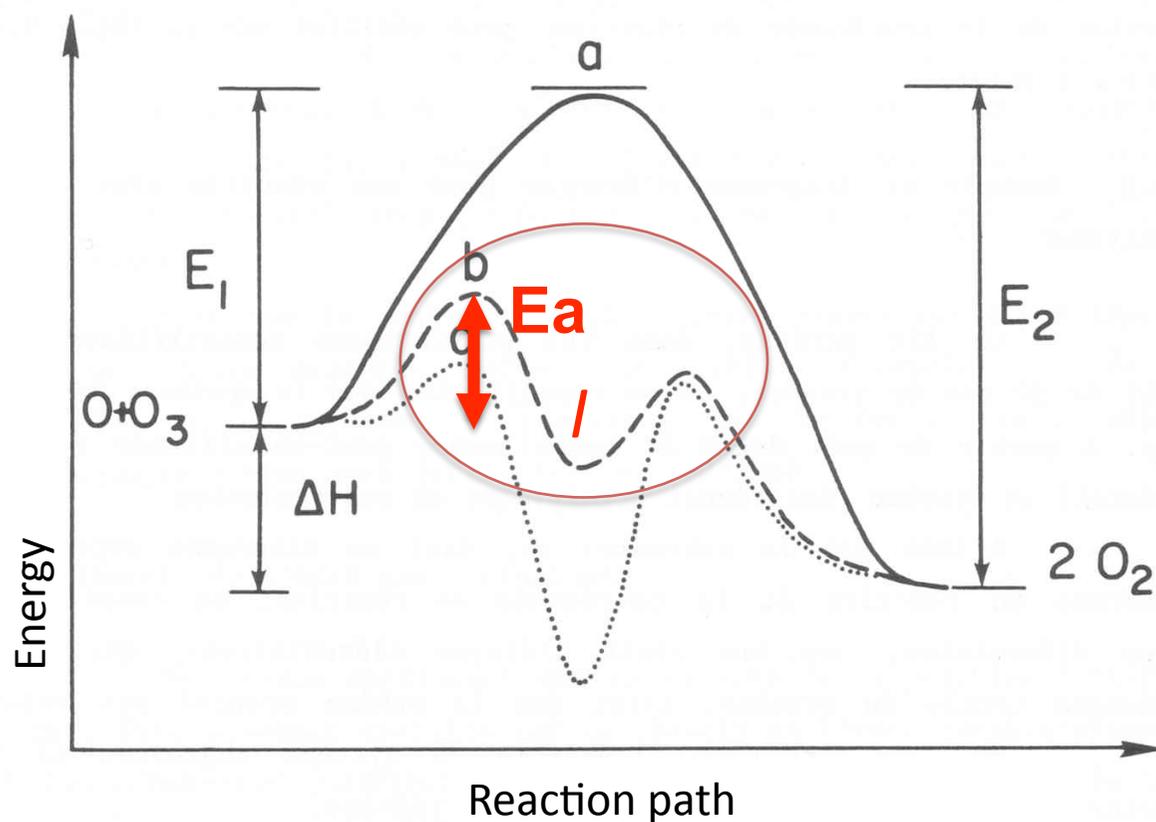
# Qu'est-ce qu'un catalyseur?



chemin réactionnel « normal »:  $k = A \exp(-E_a/RT)$  (équation d'Arrhenius)

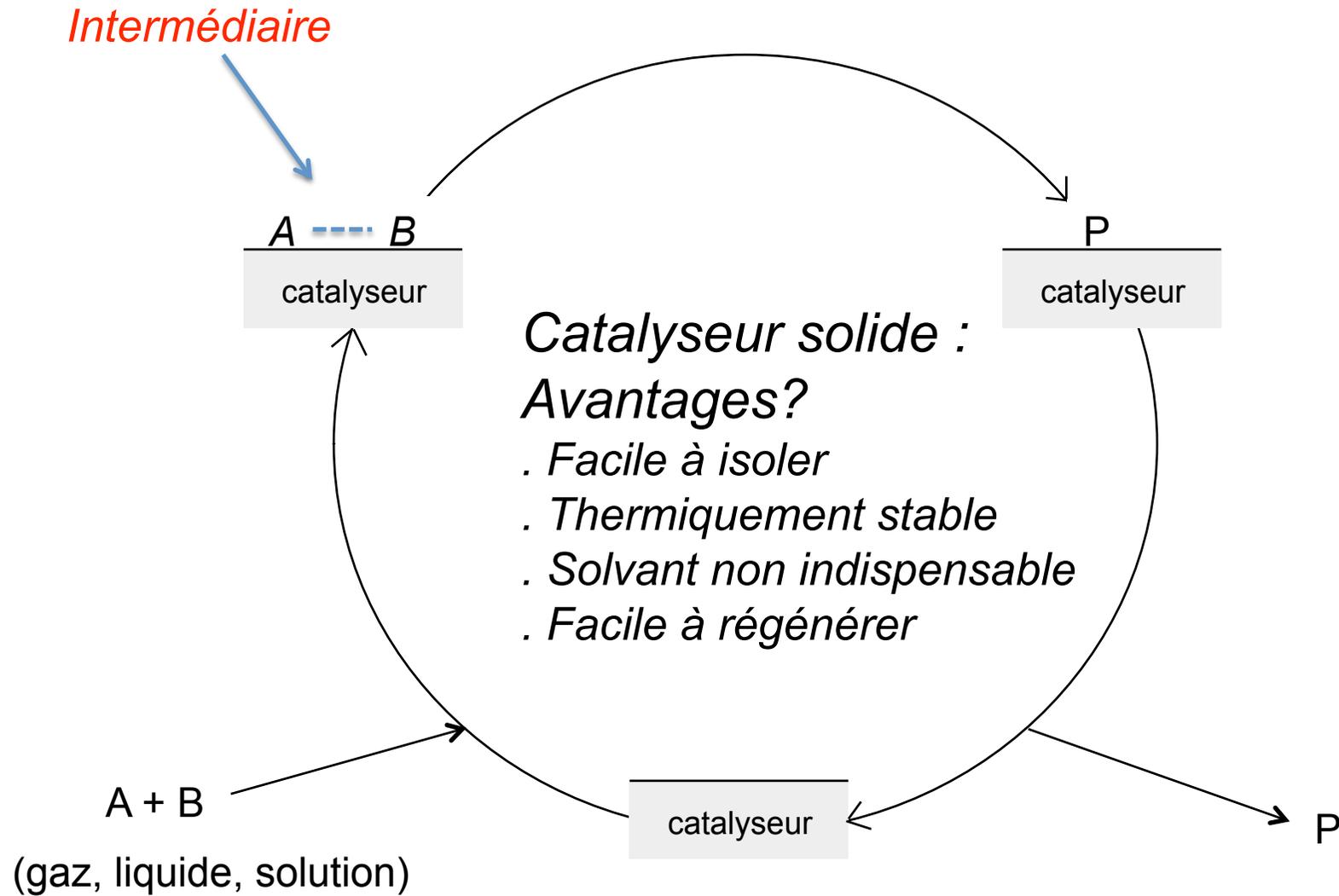
quand  $E_a$  est élevée,  $k$  est faible, la réaction est lente

## Qu'est-ce qu'un catalyseur?

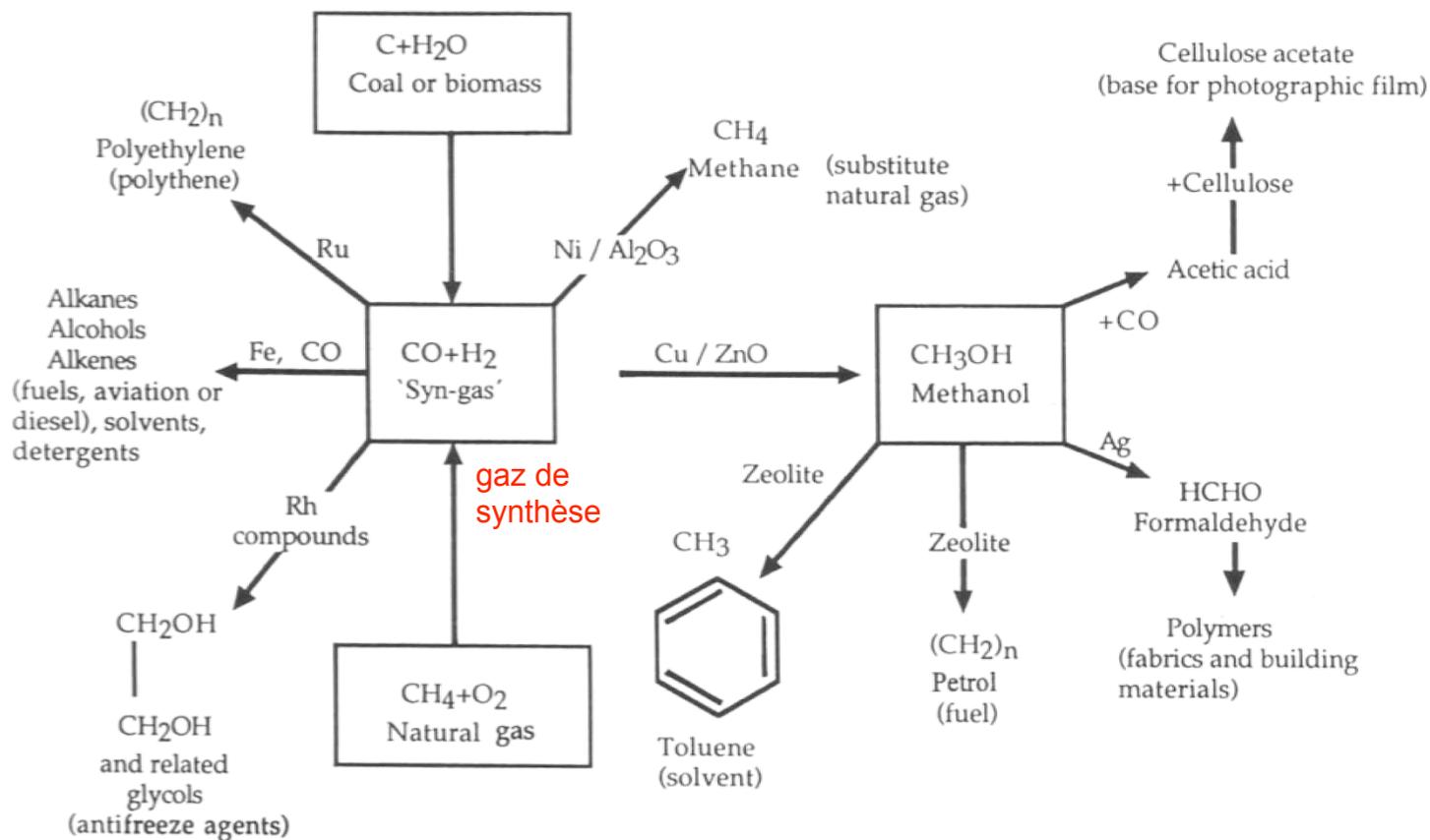


La même réaction avec un catalyseur: sur le nouveau chemin de réaction,  
Ea est maintenant faible, la réaction est rapide  
Le catalyseur forme un intermédiaire I avec les réactifs

# Cycle catalytique et catalyse hétérogène



# Sélectivité d'un catalyseur



**Scheme 1.4** Synthesis gas (abbreviated 'syn-gas') is a mixture of carbon monoxide and hydrogen and may be produced either by oxidising coal with steam, or by burning methane. A wide diversity of products can be generated from 'syn-gas', using the appropriate catalyst, as shown here.

## Le premier procédé commercial en catalyse hétérogène: le briquet Döbereiner (1823)



An incidental result of Döbereiner's discoveries was his invention of the first lighter. This employed hydrogen, generated from zinc and sulphuric acid, passing over finely divided platinum which then glowed sufficiently to ignite the gas. A number of different types produced in Germany and in England became very popular and many thousands of them were in use over a long period of time. Döbereiner refused to file a patent for his lighter with the comment "I love science more than money". These are but three of the many designs that were produced

# Importance actuelle de la catalyse hétérogène

1 exajoule (EJ) =  $10^{18}$  Joule  
consommation annuelle d'énergie aux USA: 94 EJ

synthèse de  $\text{NH}_3$

+ obtention de  $\text{C}_2\text{H}_4$  et  $\text{CH}_3\text{-CH=CH}_2$

+ synthèse de  $\text{CH}_3\text{OH}$

actuellement

5,9 EJ/an

soit

. **62%** de la consommation d'énergie

700 millions t  $\text{CO}_2$ /an

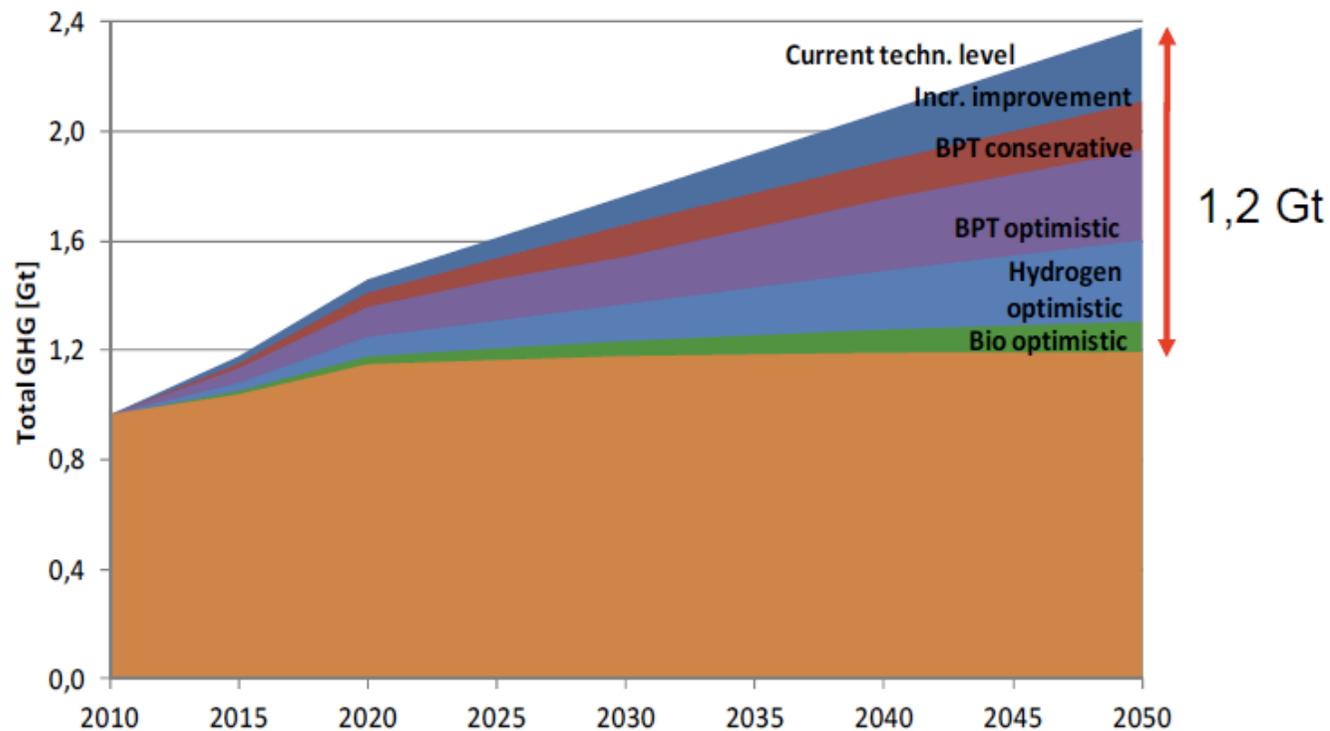
soit

. **73%** de la production de gaz à effet de serre

**de l'industrie chimique**

# Importance environnementale de la catalyse hétérogène

catalyse appliquée à la valorisation des ressources renouvelables  
= stabilisation des émissions de gaz à effet de serre  
(séquestration de CO<sub>2</sub> par la biomasse)



(... mais stabilisation de la quantité d'énergie dépensée pas garantie, si la demande continue d'augmenter)

# Zoom sur un catalyseur automobile « 3 voies »

agit sur les gaz d'échappement

- . réduction de  $\text{NO}_x$  en  $\text{N}_2$  sur **Rh**
- . oxydation de  $\text{CO}$  en  $\text{CO}_2$  sur **Pt**
- . oxydation des hydrocarbures imbrûlés sur **Pt**

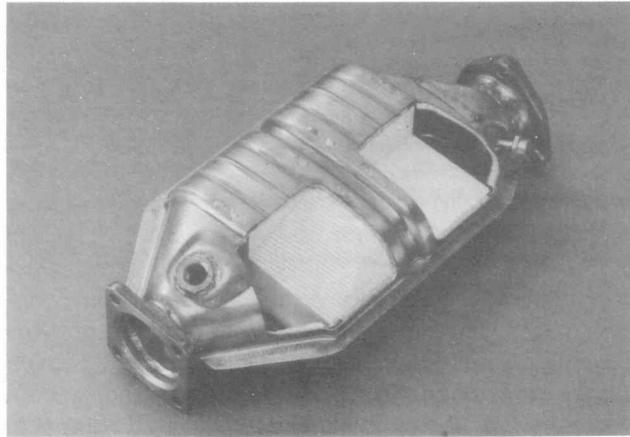


Figure 27. Cutaway view of ceramic monolith based converters for the catalytic aftertreatment of exhaust gases.

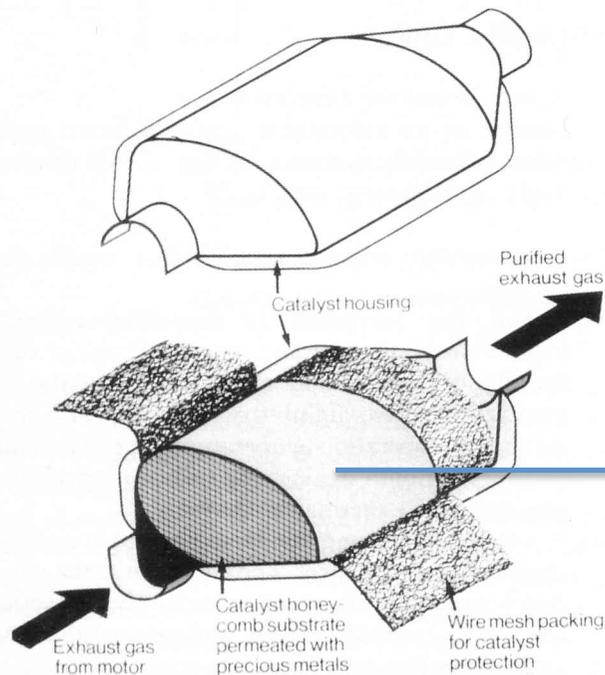


Figure 28. Design principle of a ceramic monolith based converter for the catalytic aftertreatment of exhaust gases.

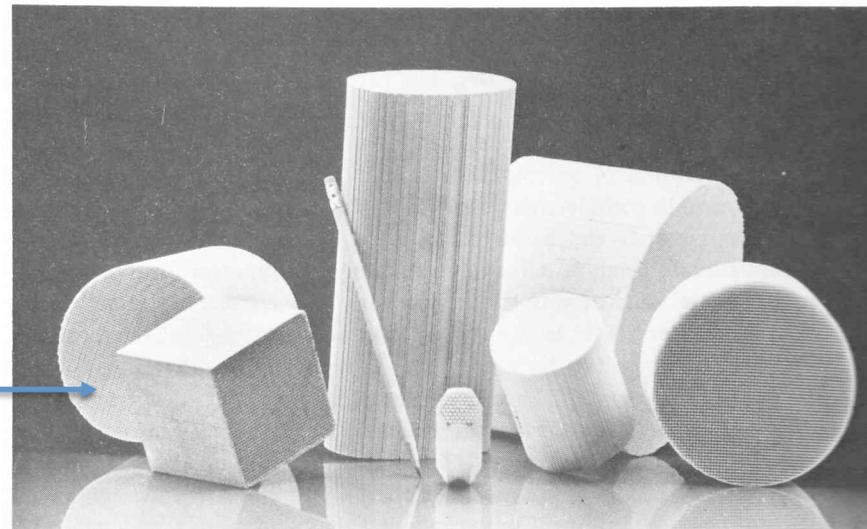


Figure 4.13 Representative monolith shapes. (Courtesy of Corning Glass Works.)

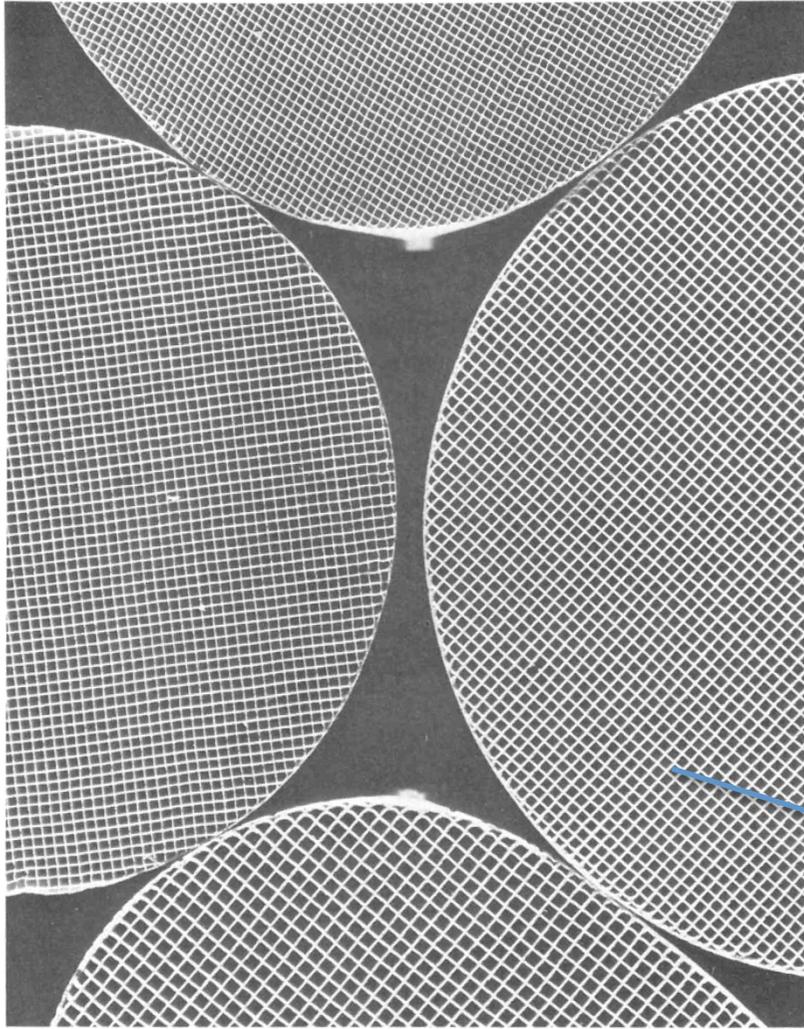


Figure 4.14 Monolith cross sections of different cell sizes. (Courtesy of Corning Glass Works.)

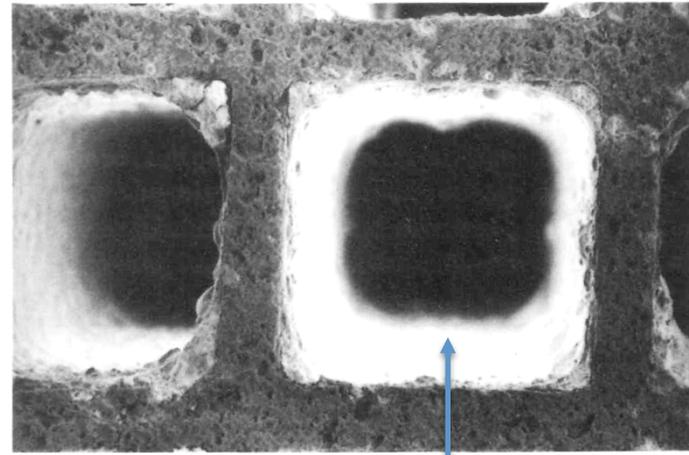
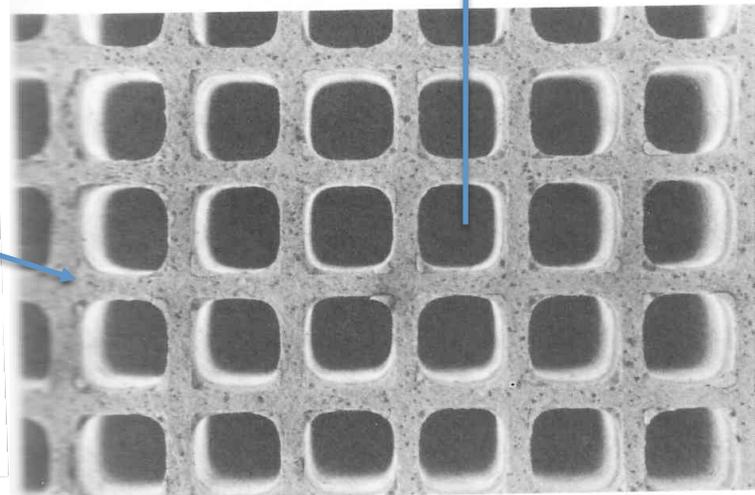


Figure 36. Close-up view of a channel of a washcoated ceramic monolith.



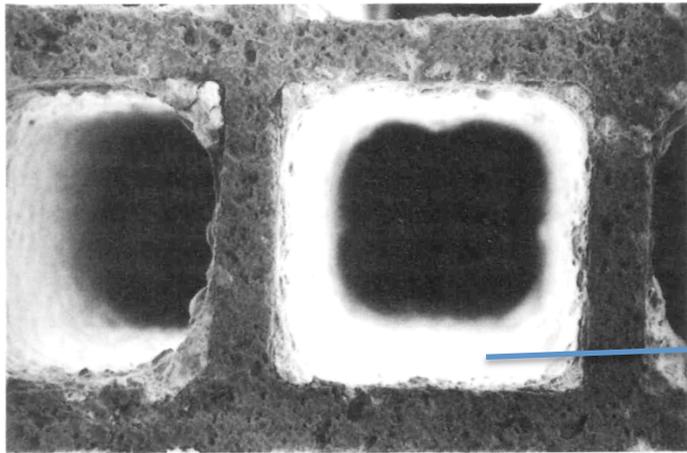


Figure 36. Close-up view of a channel of a washcoated ceramic monolith.

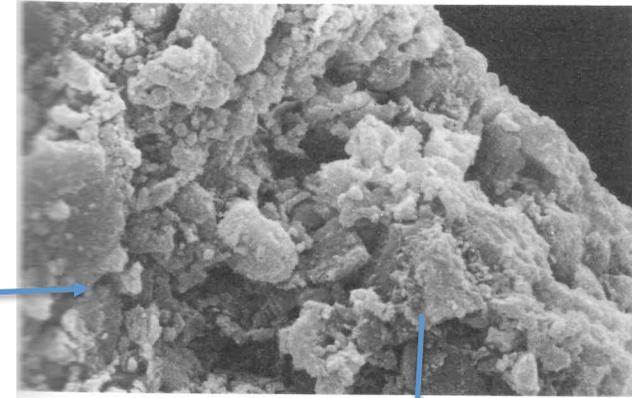


Figure 38. Scanning electron microscope view of a washcoat layer.

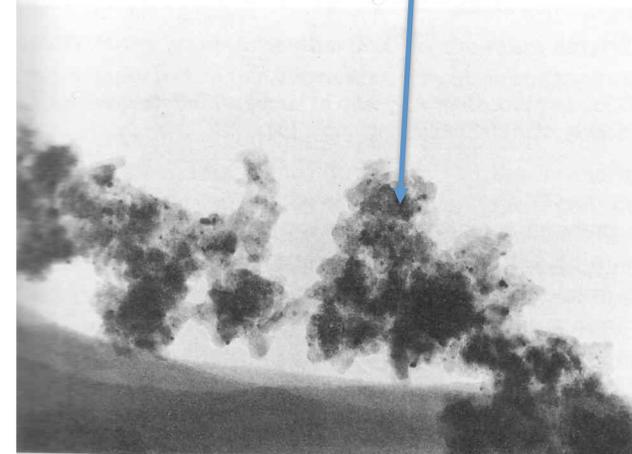


Figure 39. Transition electron microscope picture of precious metals on a washcoat particle.

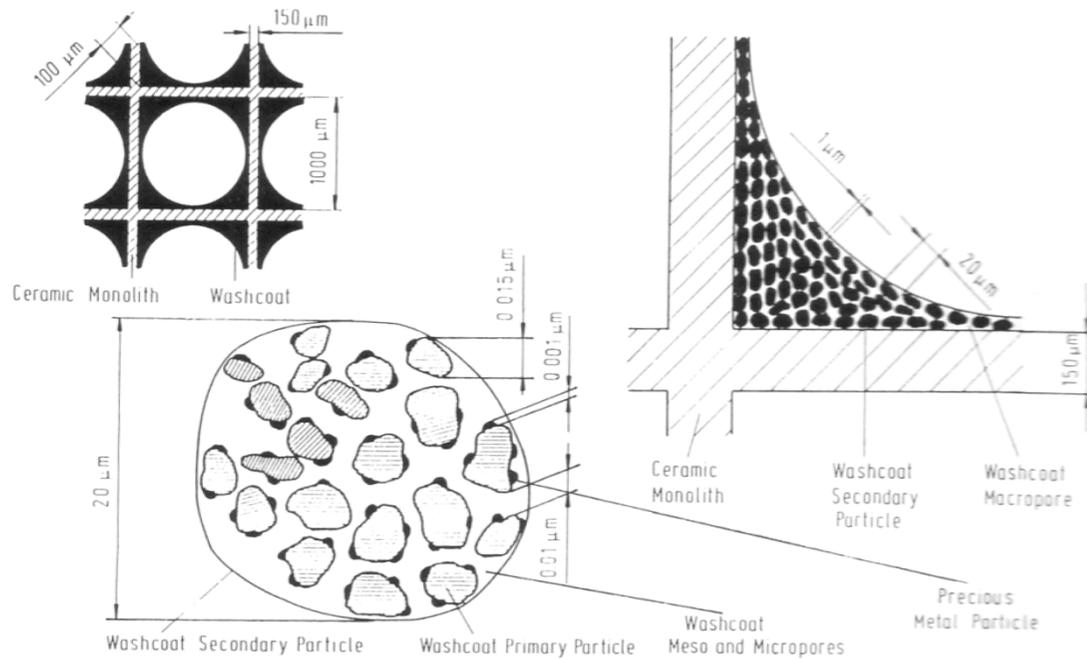
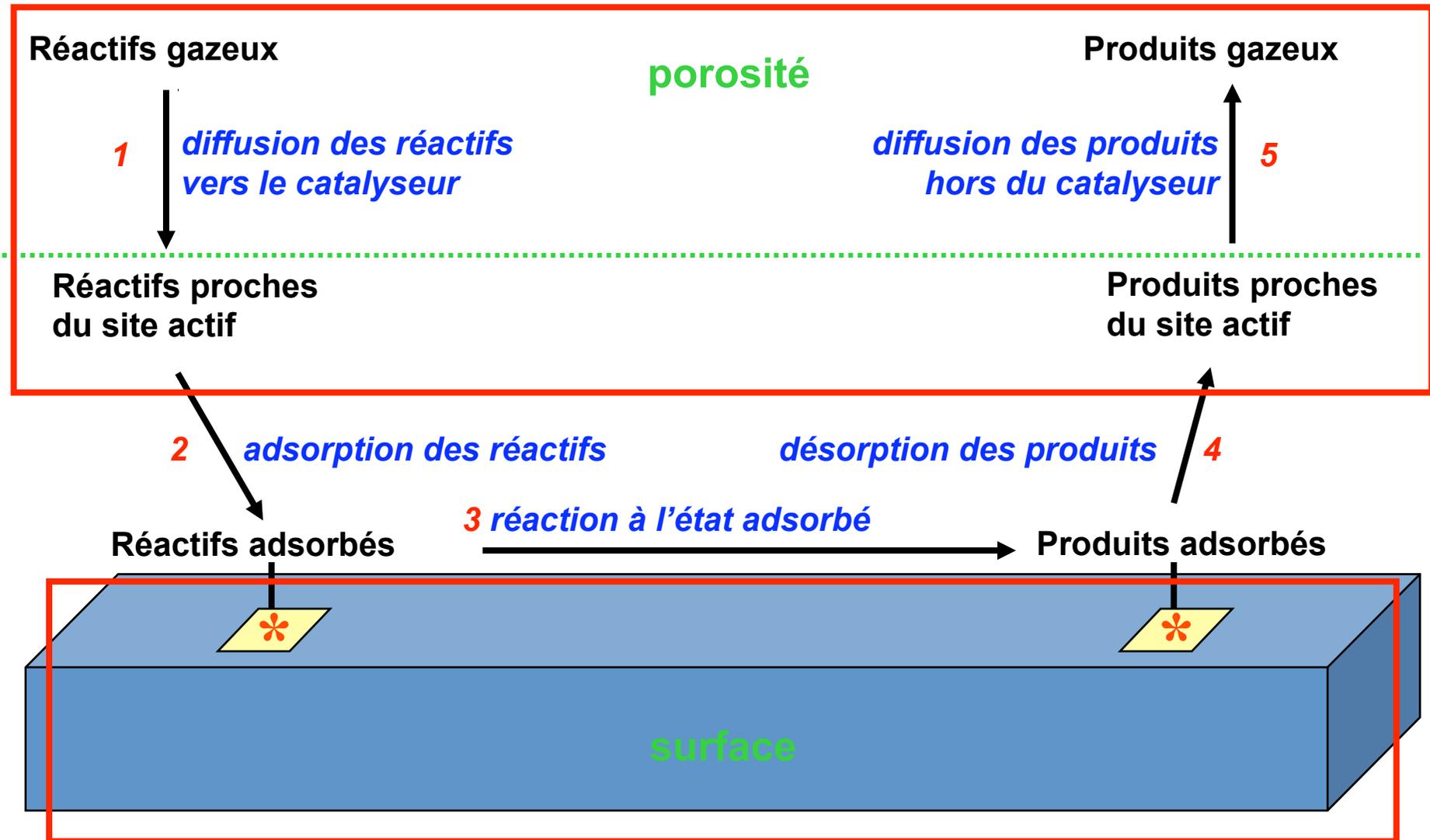


Figure 37. Dimensional relationships of a washcoat on a ceramic monolith.

# Les 5 étapes d'une réaction catalytique



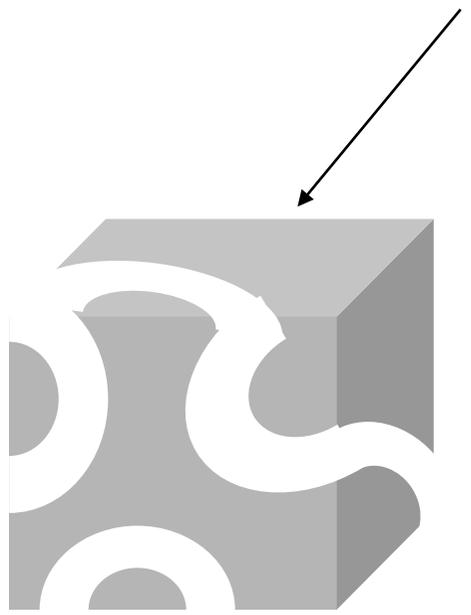
## Dispersion d'une phase catalytique

$$\text{Dispersion} = \frac{\text{Nombre d'atomes de surface accessibles}}{\text{Nombre total d'atomes}}$$

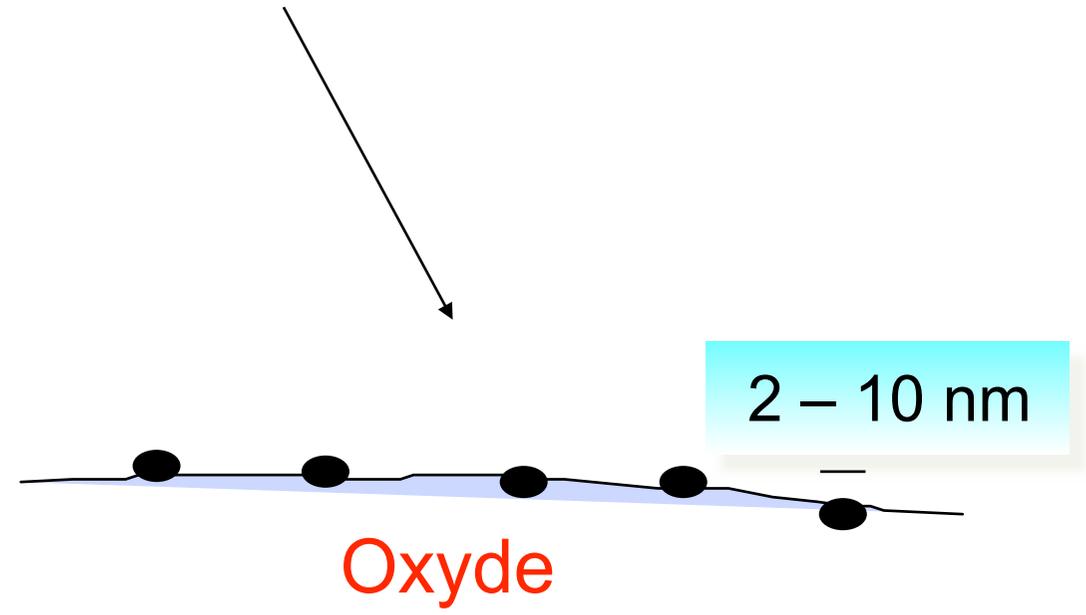
- . Sites ★ complètement isolés : dispersion maximale
- . Quand la taille d'une particule de phase active **diminue**, la dispersion **augmente**

# Comment augmenter le nombre de sites actifs accessibles?

Catalyseurs massiques



Catalyseurs **supportés**



# Catalyseurs pour l'oxydation de $\text{NH}_3$ (synthèse de $\text{HNO}_3$ )



**toile de Pt – Rh**

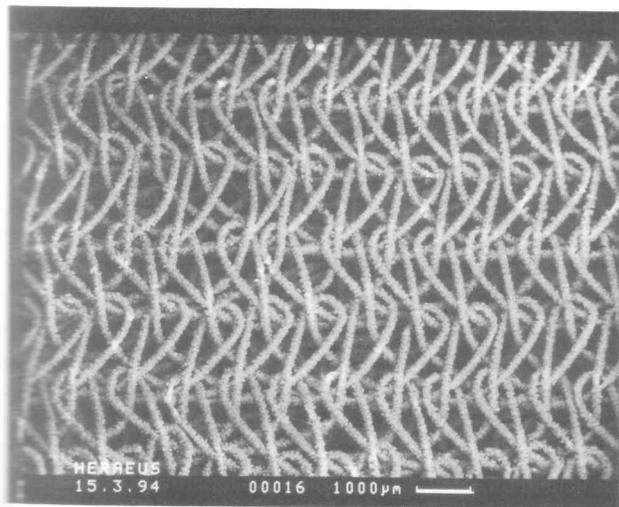
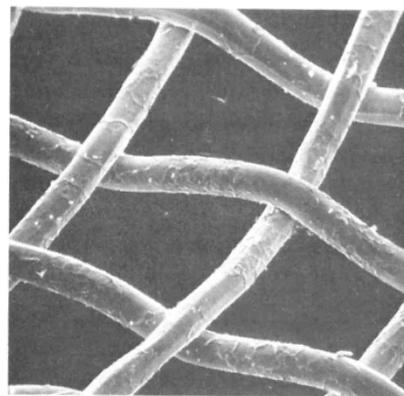
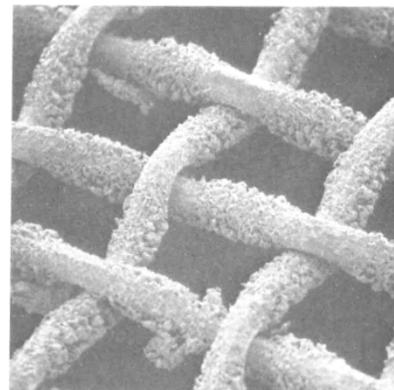


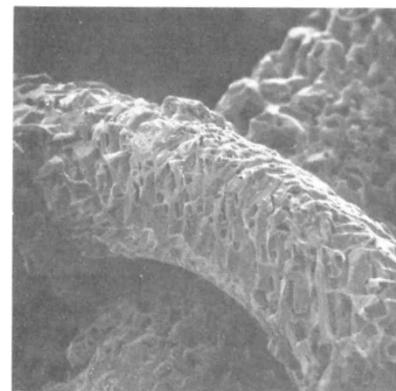
Figure 6. Warp-knitted platinum–rhodium catalyst gauze (courtesy of Heraeus, Hanau, Germany).



(a)



(b)



(c)

Figure 8.11 Scanning electron micrographs of 10% Rh–90% Pt gauze wire 0.075 mm (0.003 in) in diameter. (a) Original gauze, as drawn, showing uniform grain structure and absence of nodules on the wires. (b) The gauze of Fig. 8.11a after one-half the normal gauze life installed in a nitric acid plant, showing the nodular pattern typical of an active gauze. (c) An enlarged view of the crossover point of two gauze wires in Fig. 8.11b showing the characteristic octagonal crystal structure and the nodules, which are concentrated on the wire surfaces between crossover points. [Courtesy of *Platinum Metals Review*, 15(2), 52 (1971).]

# Catalyseurs pour l'oxydation de $\text{NH}_3$ (synthèse de $\text{HNO}_3$ )



dispersion du métal: 10 ppm!

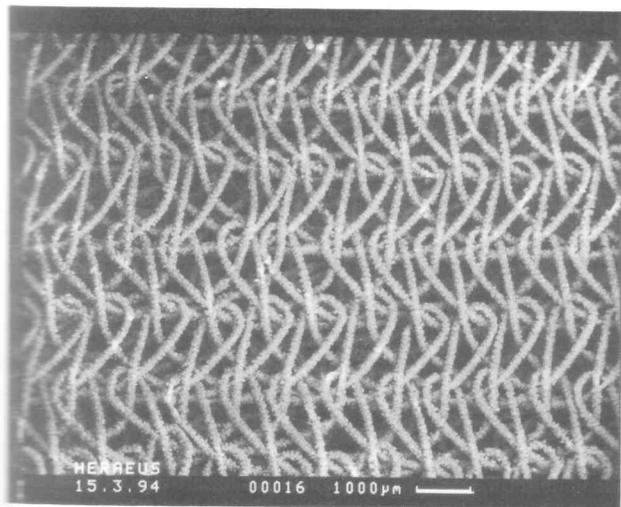
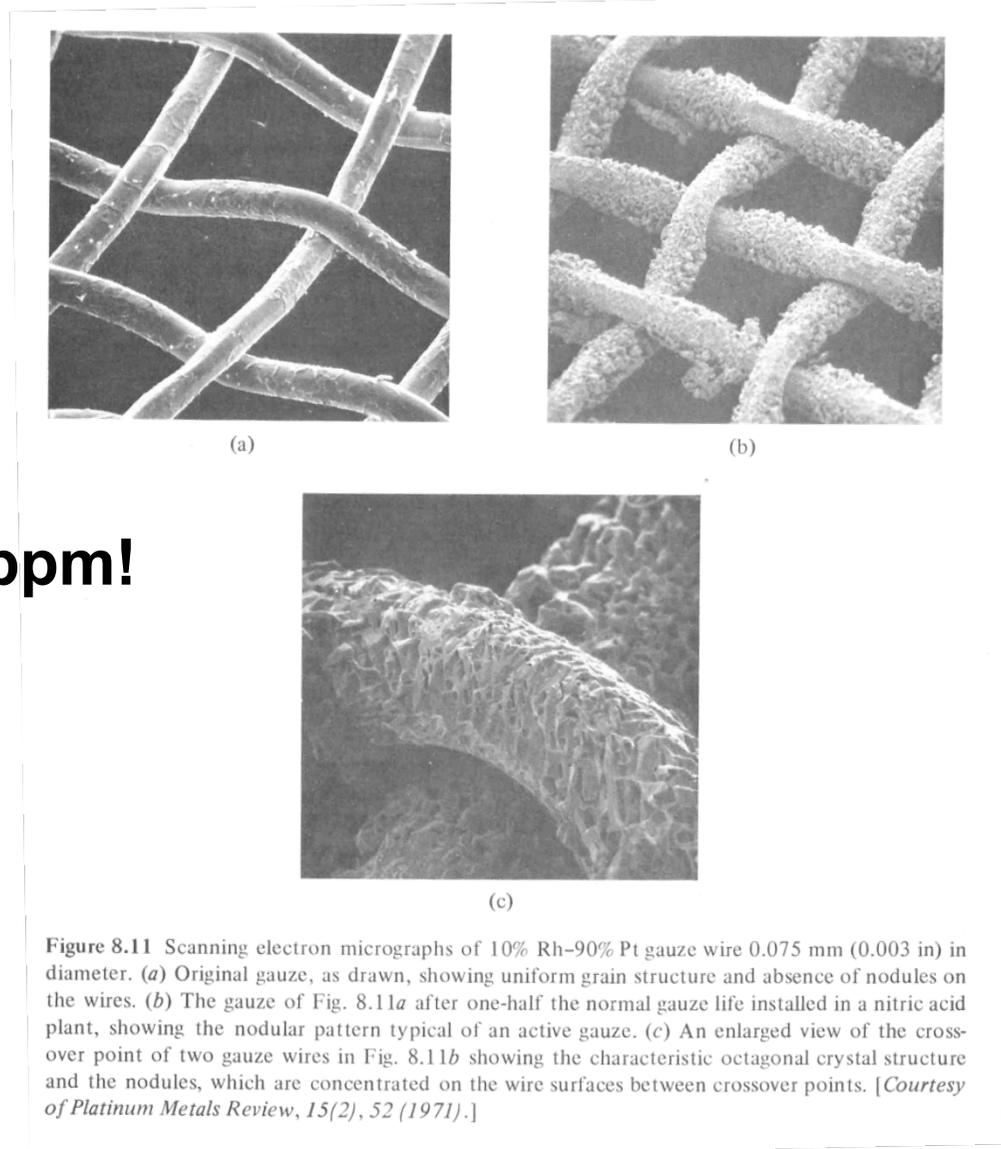


Figure 6. Warp-knitted platinum-rhodium catalyst gauze (courtesy of Heraeus, Hanau, Germany).



## Catalyseurs pour le procédé Haber-Bosch (synthèse de $\text{NH}_3$ )

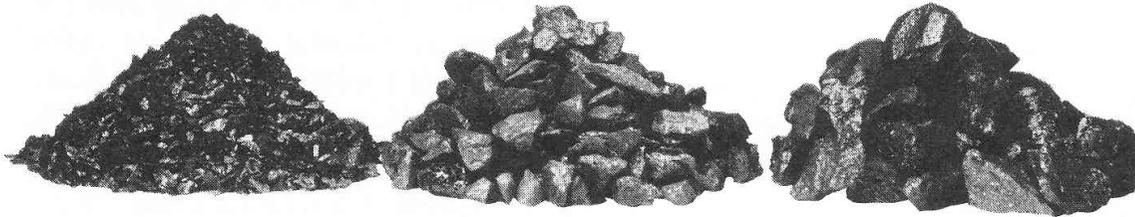


Figure 4.10 Topsøe ammonia synthesis catalyst KMI. The three sizes are about 1.5 to 3 mm, 6 to 10 mm, and 12 to 21 mm. (Courtesy of Haldor Topsøe A/S.)

Oxydes de fer +  $\epsilon$  oxydes

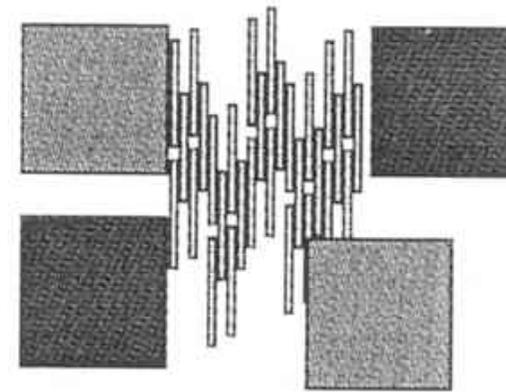
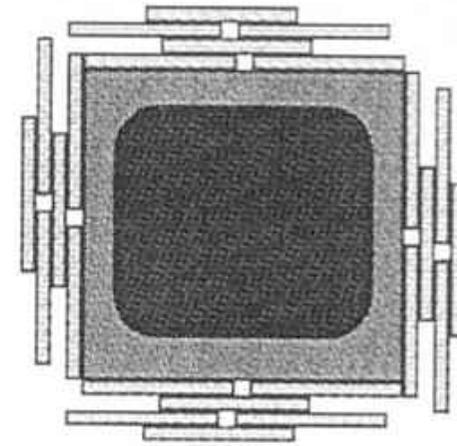
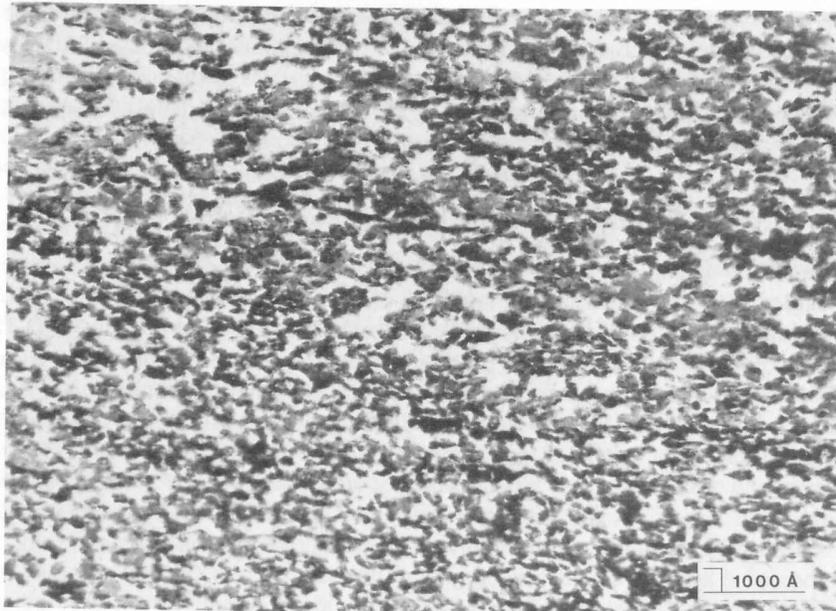
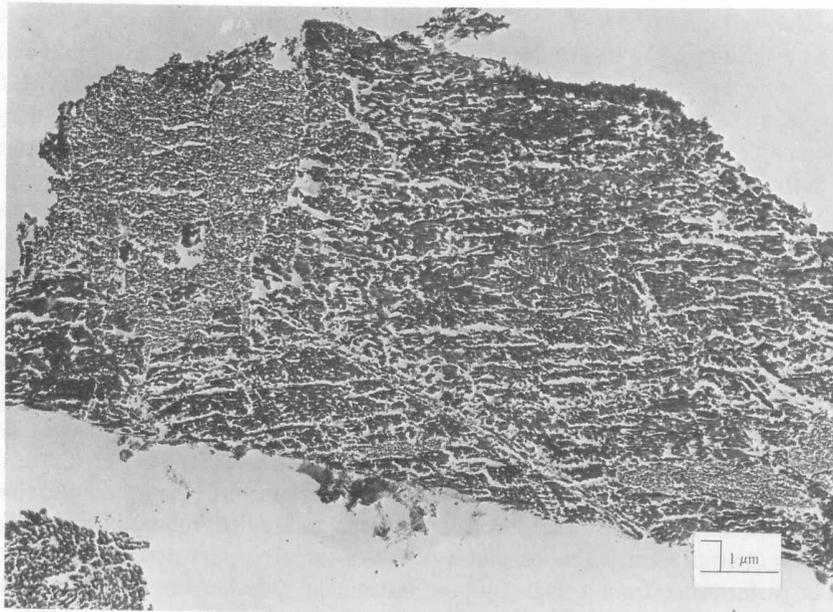
fusion, broyage

$\text{Fe}_3\text{O}_4$  + promoteurs

réduction par  $\text{H}_2$

$\text{Fe}^\circ$  +  $\epsilon$   $\text{Al}_2\text{O}_3$

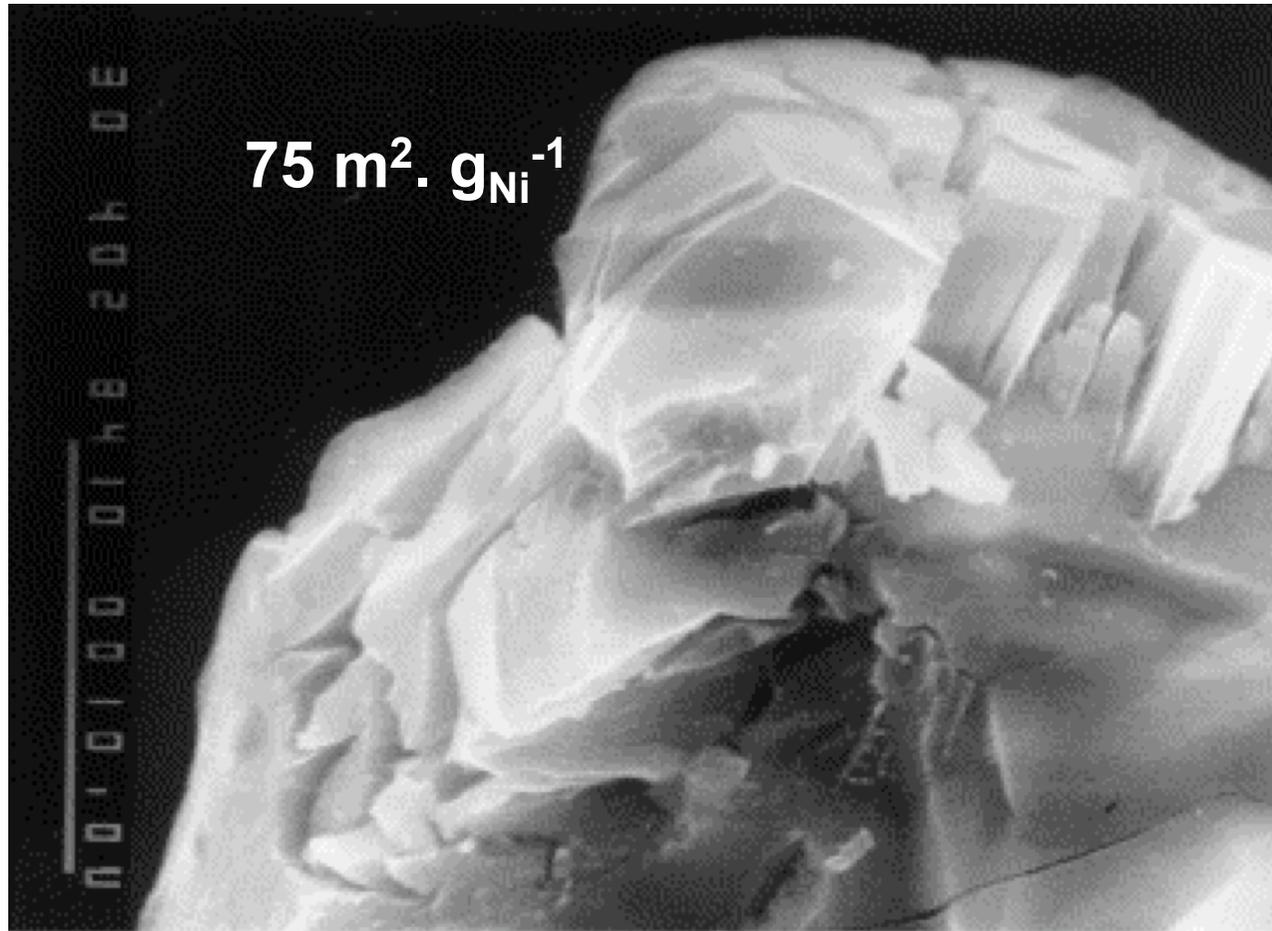
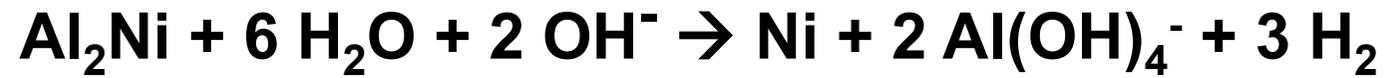
+  $\epsilon\epsilon$   $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{MgO}$



$20 \text{ m}^2 \cdot \text{g}_{\text{Fe}}^{-1}$

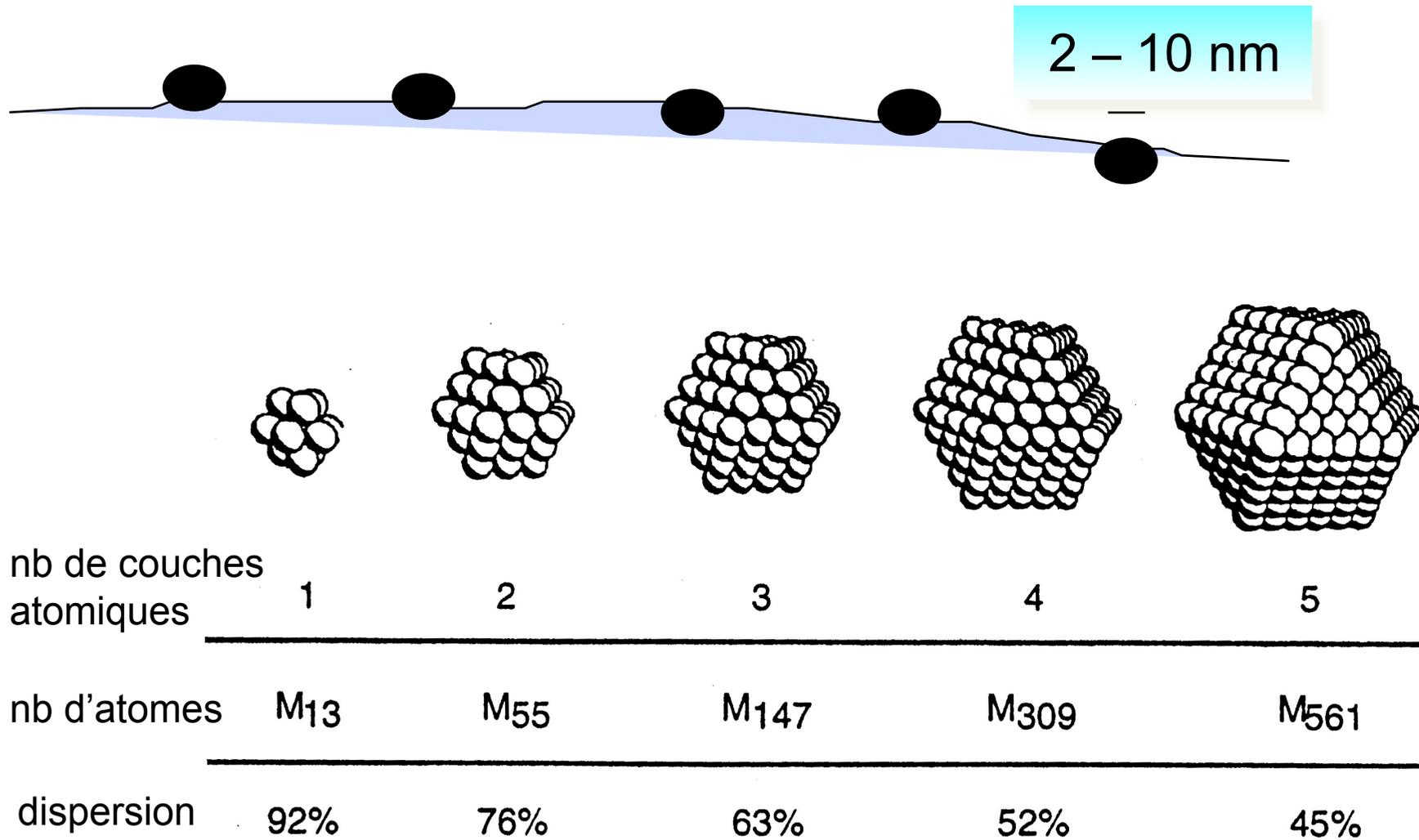
Figure 5.9 Electron micrograph of thin section of Topsøe ammonia-synthesis catalyst KMIR. (Nielsen, 1968.)

## Un catalyseur d'hydrogénation : le nickel de Raney

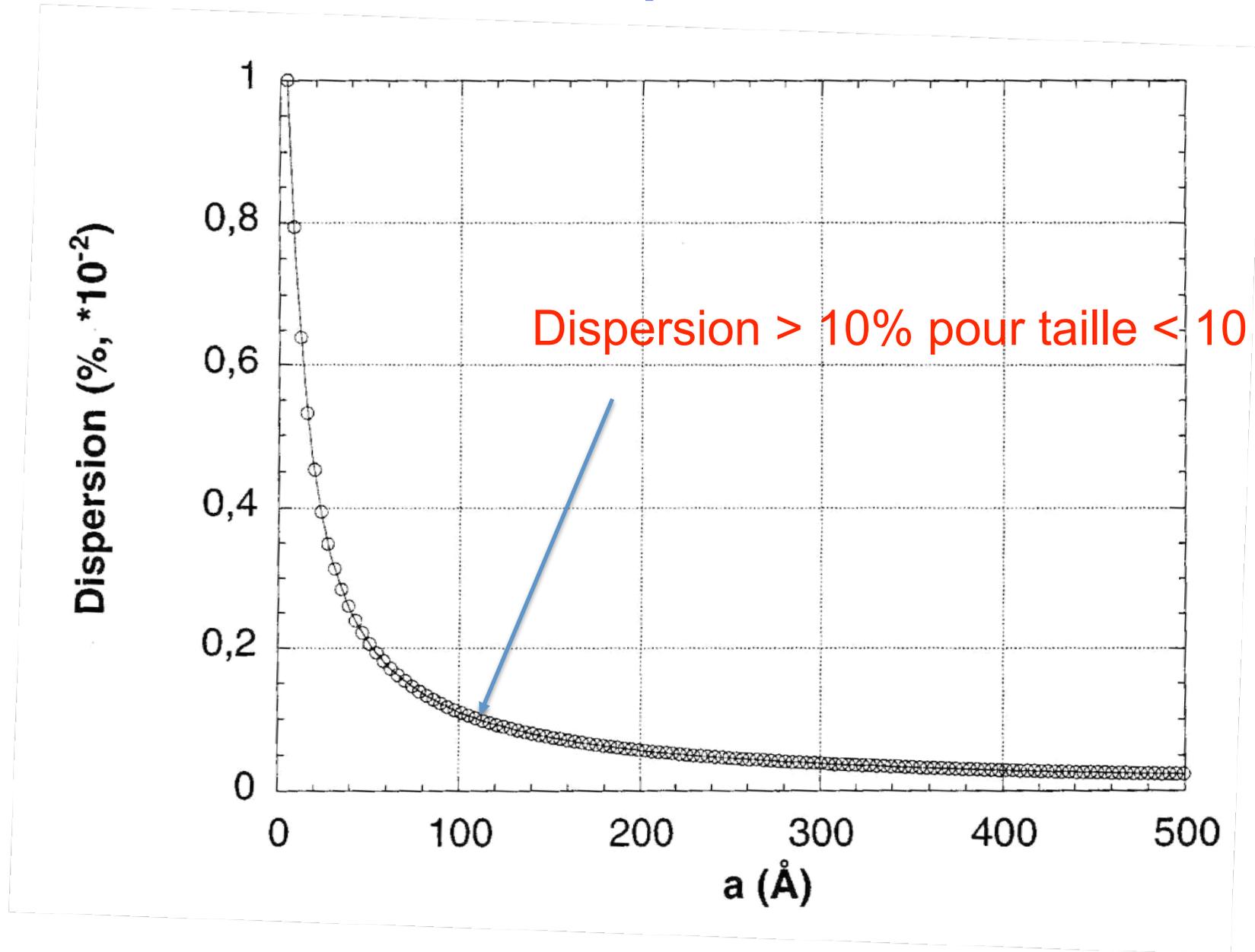


**Dispersion:**  
**8-10%**

# Les nanoparticules



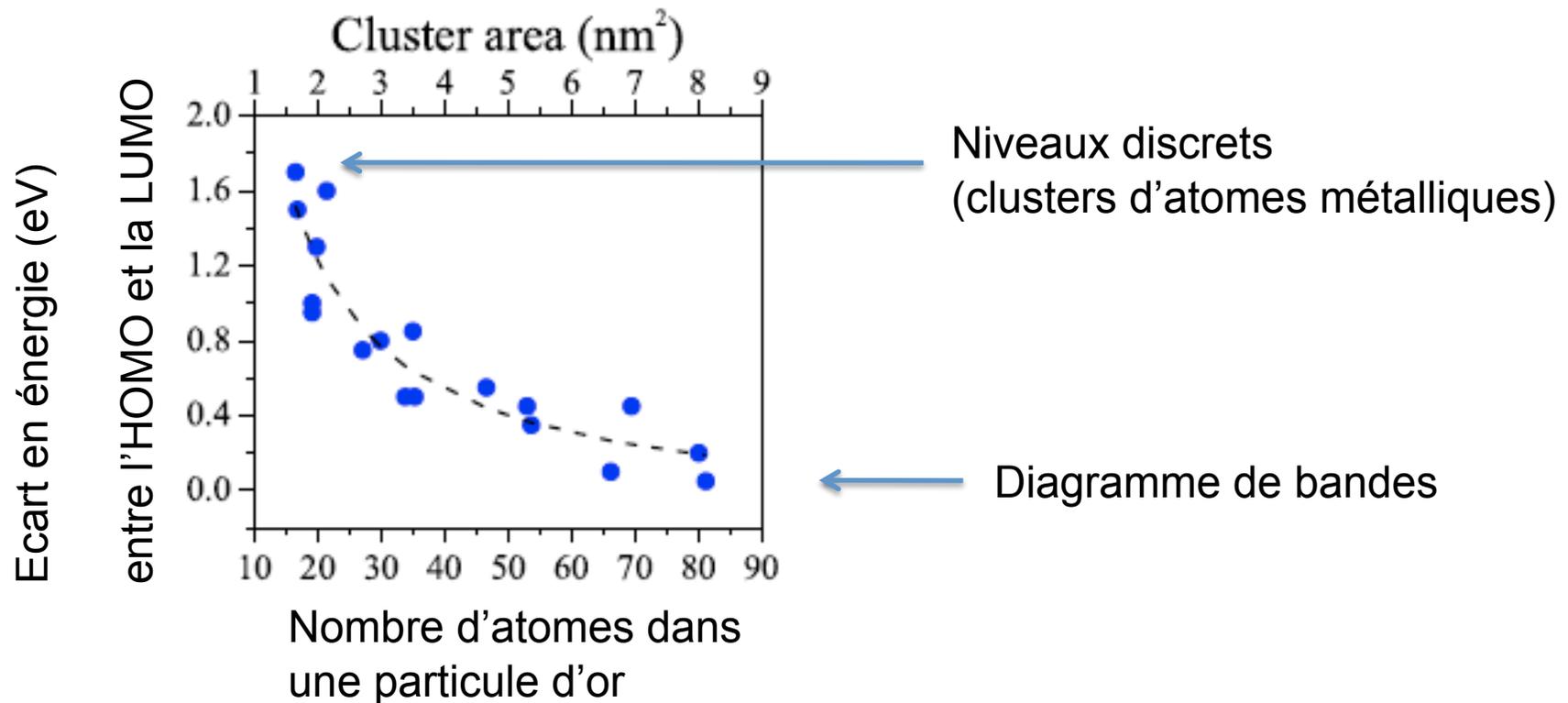
# Les nanoparticules



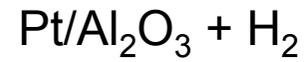
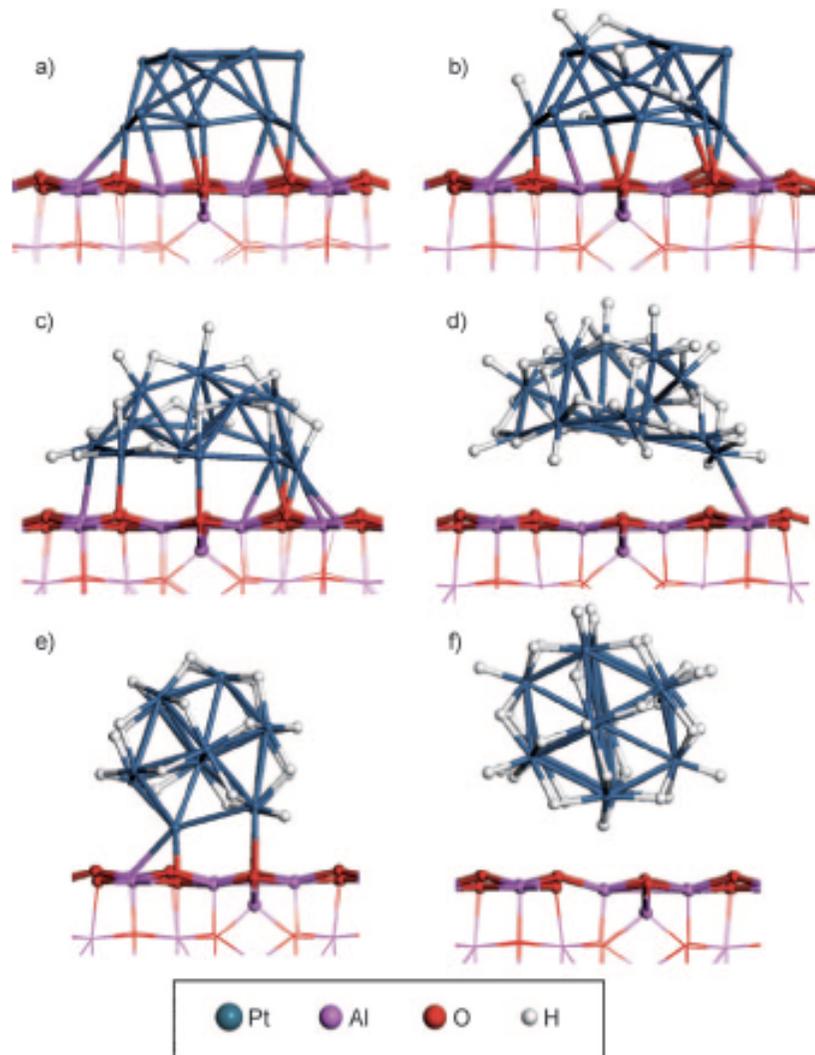
# N atomes de surface

= N sites catalytiques également actifs?  
pas si simple...

1. Les propriétés électroniques des particules changent avec leur taille



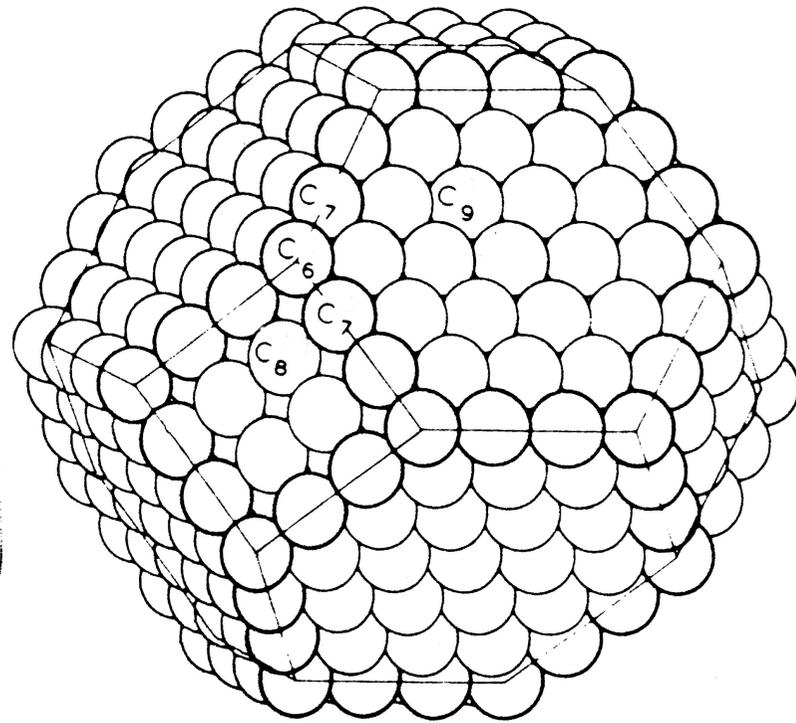
## 2. Une petite particule métallique peut changer de forme pendant la réaction



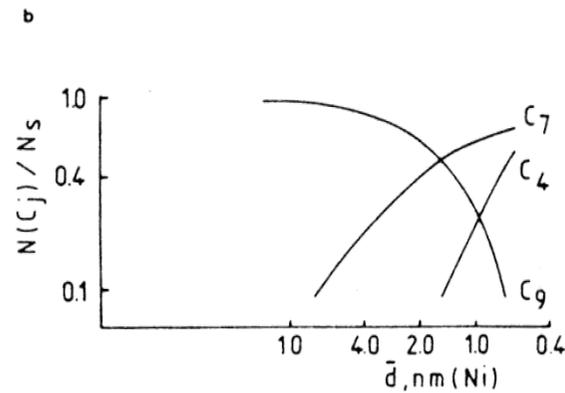
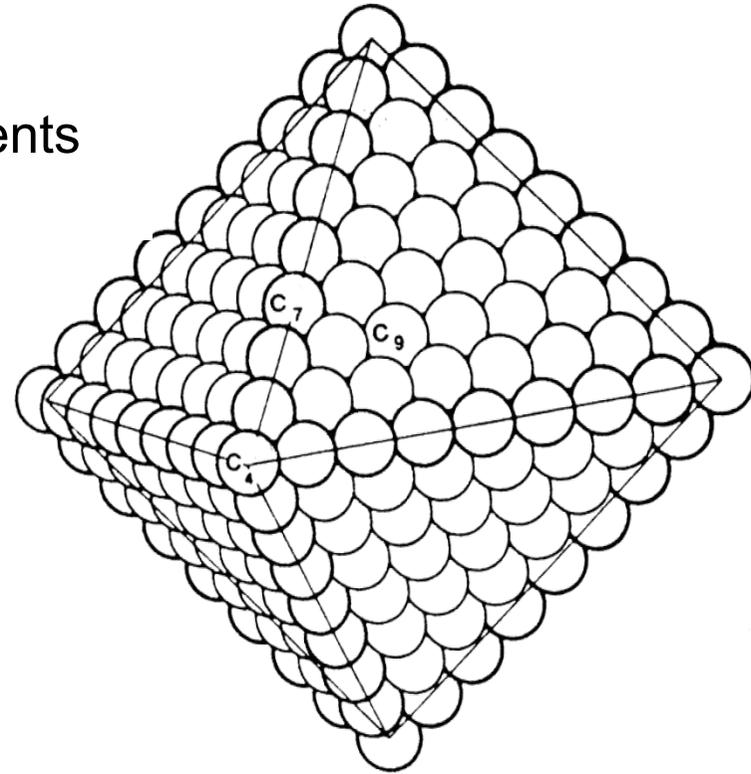
**Figure 1.** Calculated structures for hydrogen-covered  $\text{Pt}_3\text{H}_n$  clusters ( $n$  is the number of hydrogen atoms) supported on  $\gamma\text{-Al}_2\text{O}_3$  (100) surface, with  $n=0$  (a),  $n=6$  (b),  $n=18$  (c),  $n=38$  (*meta-stable*) (d),  $n=20$  (e),  $n=34$  (f).

C. Mager-Maury et al., ChemCatChem 3, 200 (2011)

3. Une particule de grande taille n'est pas « sphérique » ; tous les atomes ne sont pas équivalents en termes de coordinence

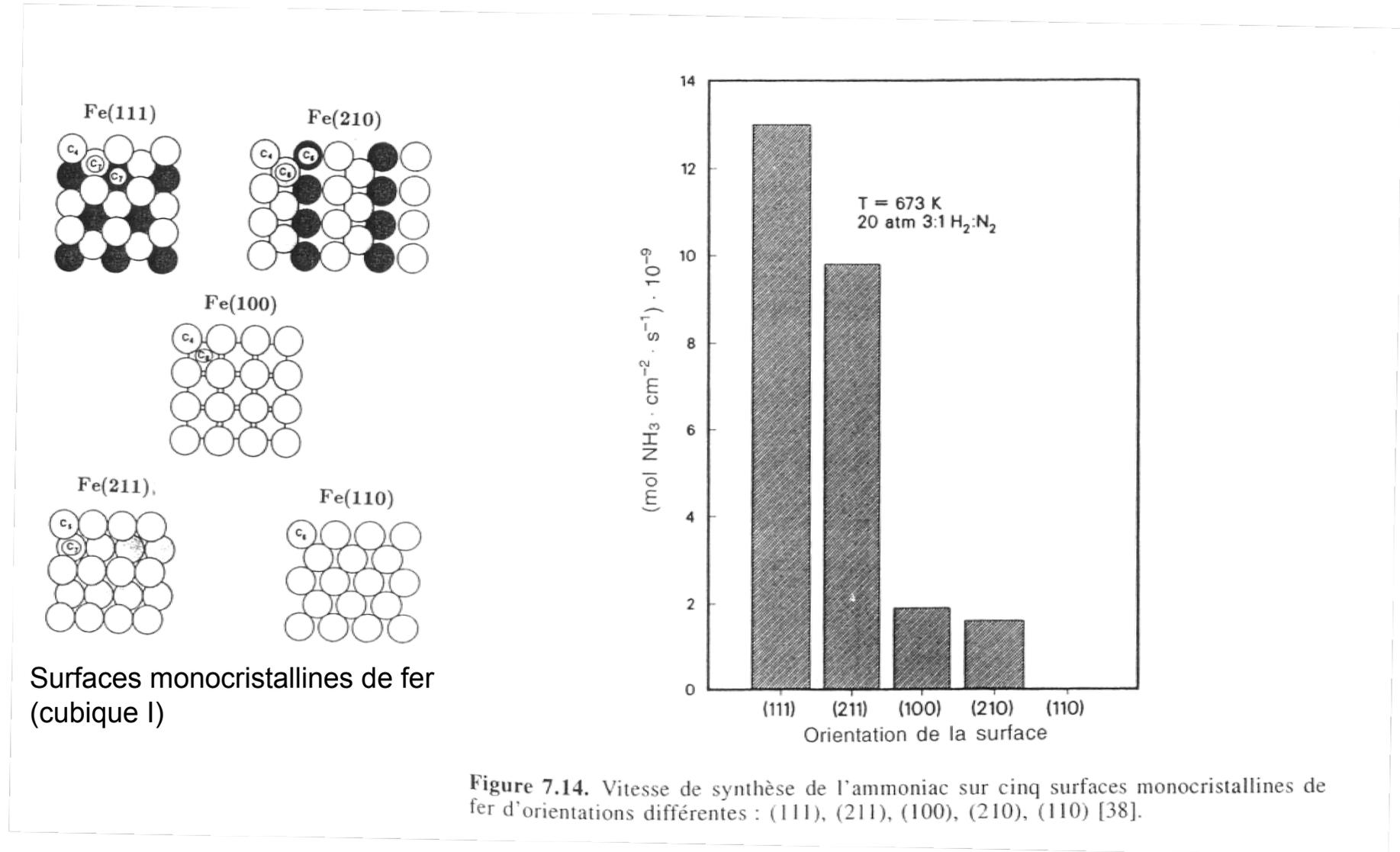


Face-centered cubic (fcc) cubooctahedron



(a) Face-centered cubic (fcc) octahedron.  $m = 9$  ( $m$  is the number of atoms along  $\bar{d}$ ). From Ref. 20. (b) Coordination of surface atoms versus the mean particle size  $\bar{d}$

#### 4. Conséquences: réactions « sensibles à la structure »



# Les supports

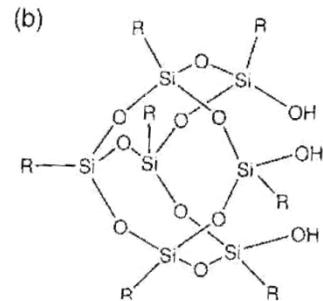
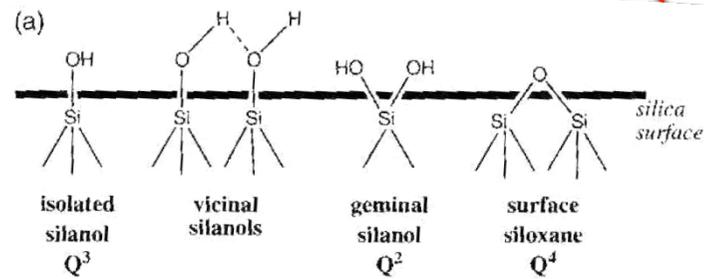
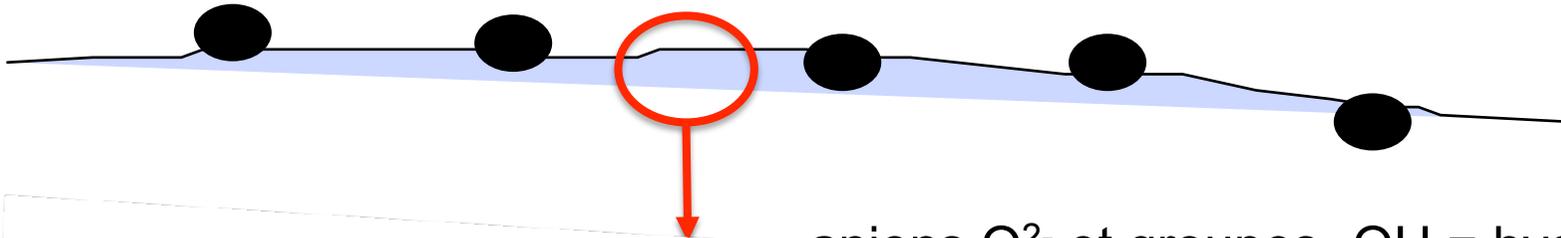


Figure 8.2 (a) Type of groups at the silica surface (the  $Q^n$  terminology stems from NMR, and is used to describe the number of O-bridges around the central Si atom) and (b) the trisilanol silsesquioxane  $(R_7Si_7O_9)(OH)_3$  as a model for silica surfaces.

silice  $SiO_2$

anions  $O^{2-}$  et groupes  $-OH =$  hydroxyles

peuvent avoir des propriétés acidobasiques

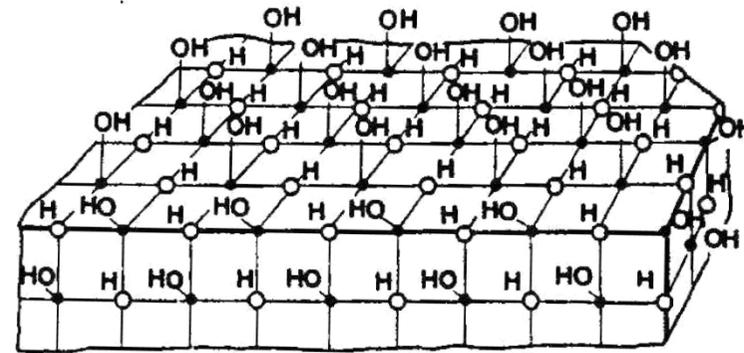
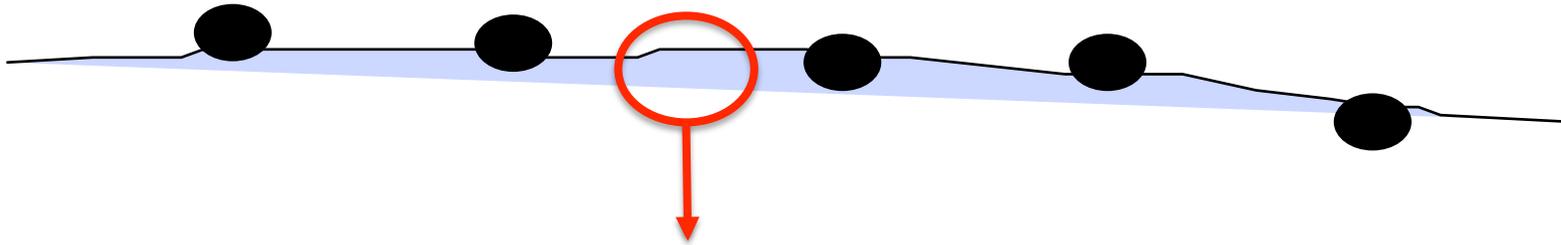


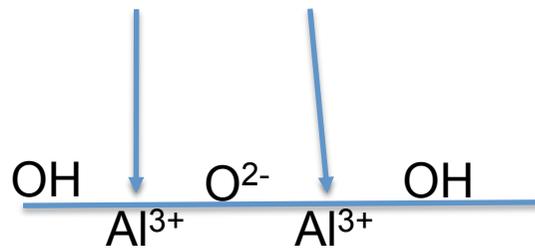
Fig. 4. Model of part of an ideal microcrystal with fully hydroxylated cube faces showing hydroxyls on extended  $\{100\}$  faces and on edges and corners.

MgO

## Les supports



après déshydratation,  
cations accessibles

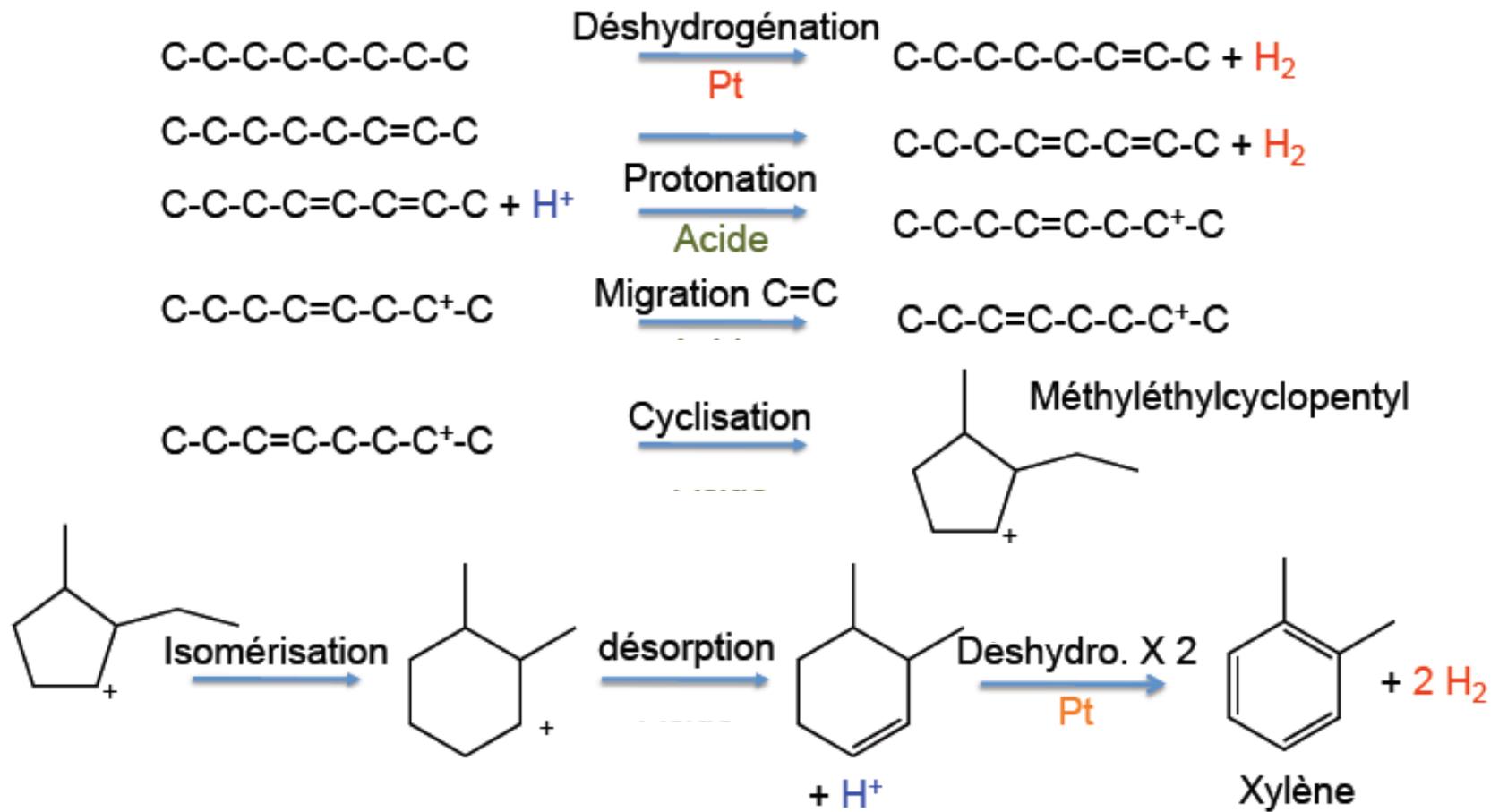


peuvent présenter une acidité  
de Lewis  
(adsorber des molécules  
via une paire électronique)

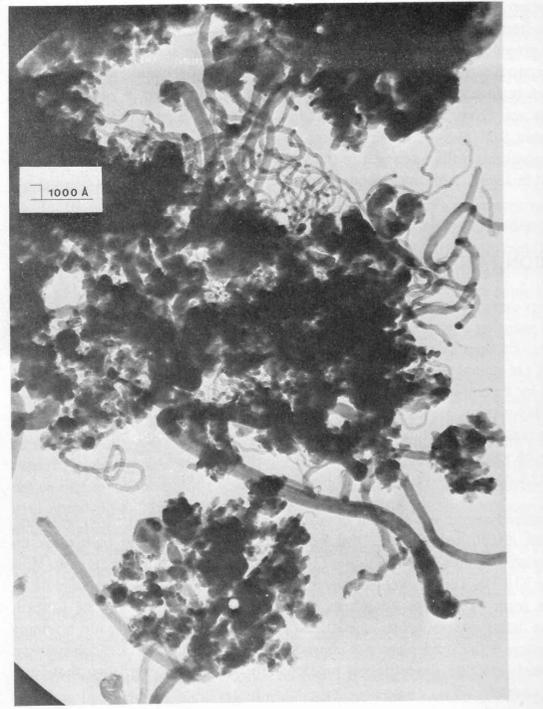
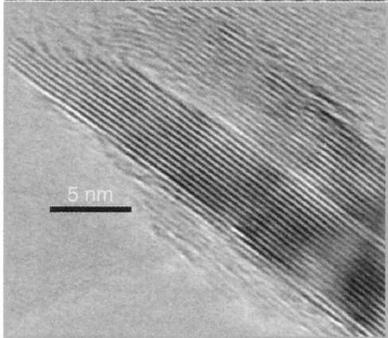
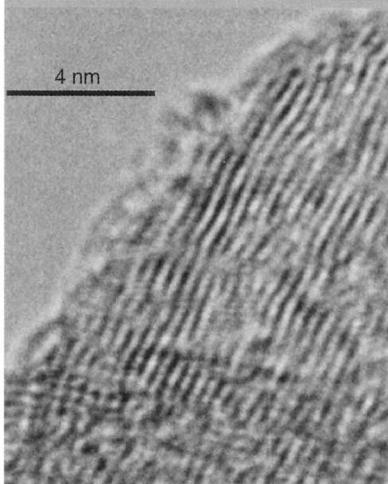
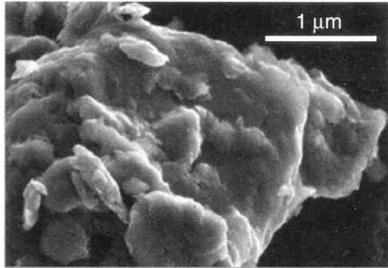
→ catalyse bifonctionnelle

# Exemple de mécanisme bifonctionnel

reformage de l'essence : alcane linéaire → aromatique



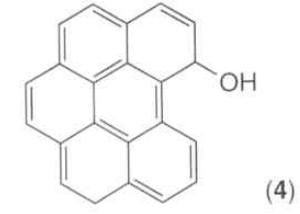
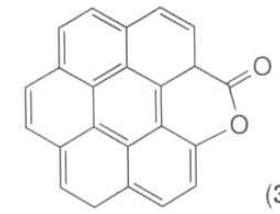
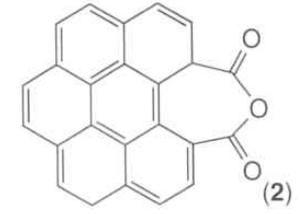
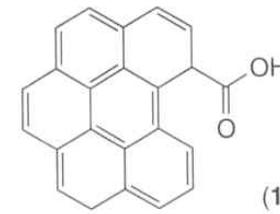
## Supports : surtout des oxydes, mais aussi du carbone



nanofibres, synthétisées  
par décomposition  
catalytique du méthane ou de l'éthane

carbones  
graphitiques

### Fonctions de surface



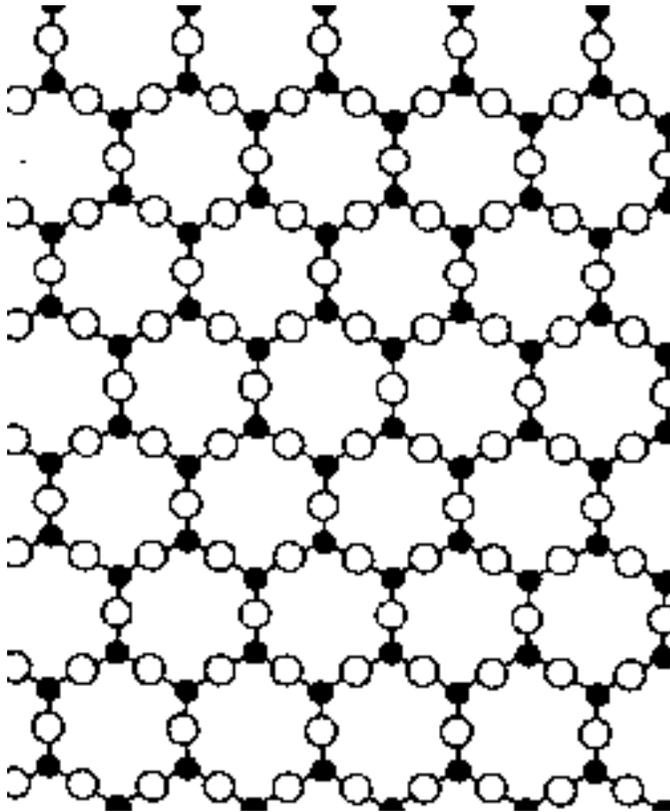
## Exemples de supports oxyde: silice, silicoaluminates

catalyse hétérogène = phénomène de surface

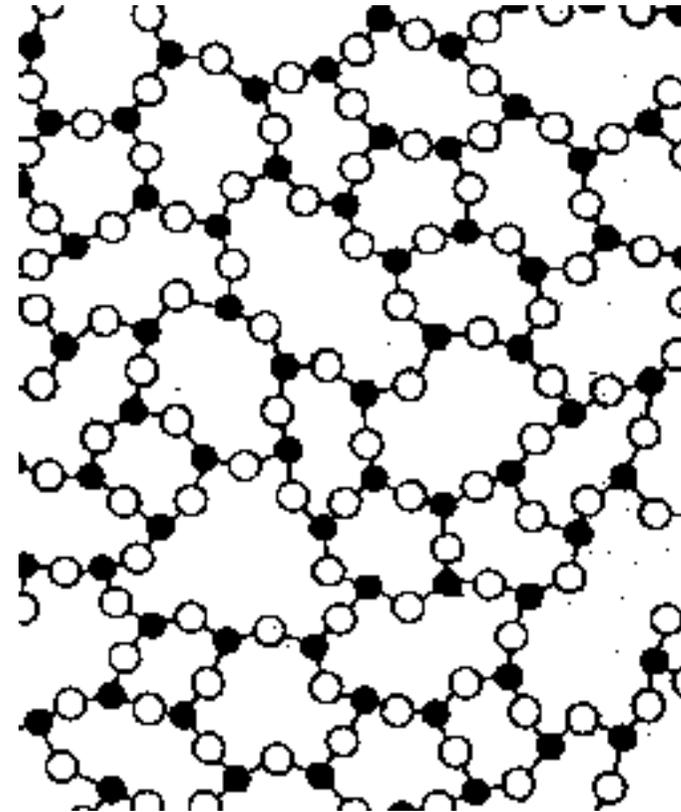
Le matériau doit présenter une surface spécifique élevée, qu'il soit :

- lui-même le catalyseur
- un support pour une phase active dispersée

## Supports amorphes ou peu cristallisés

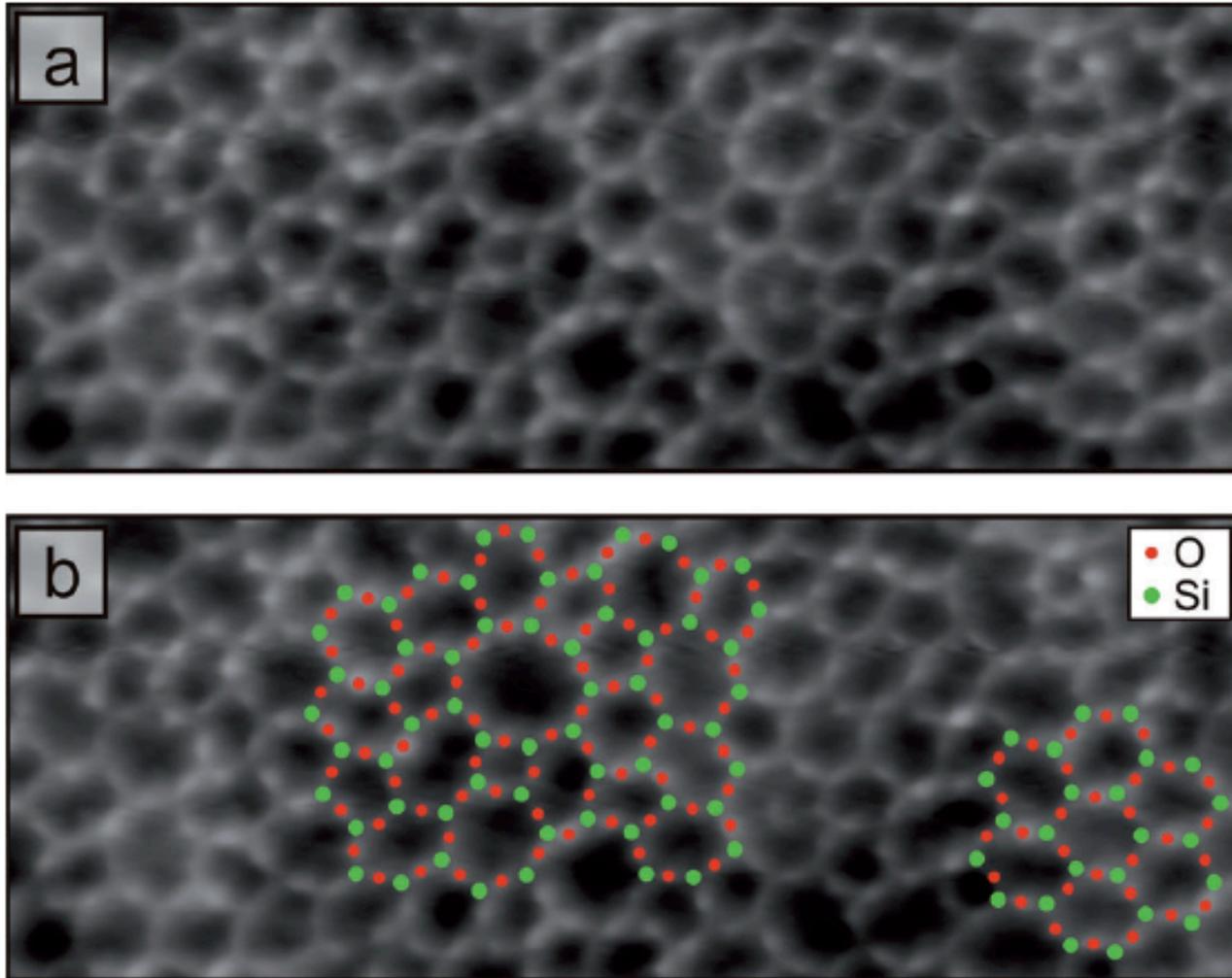


SiO<sub>2</sub> cristallisée (schématique)



SiO<sub>2</sub> amorphe (schématique)

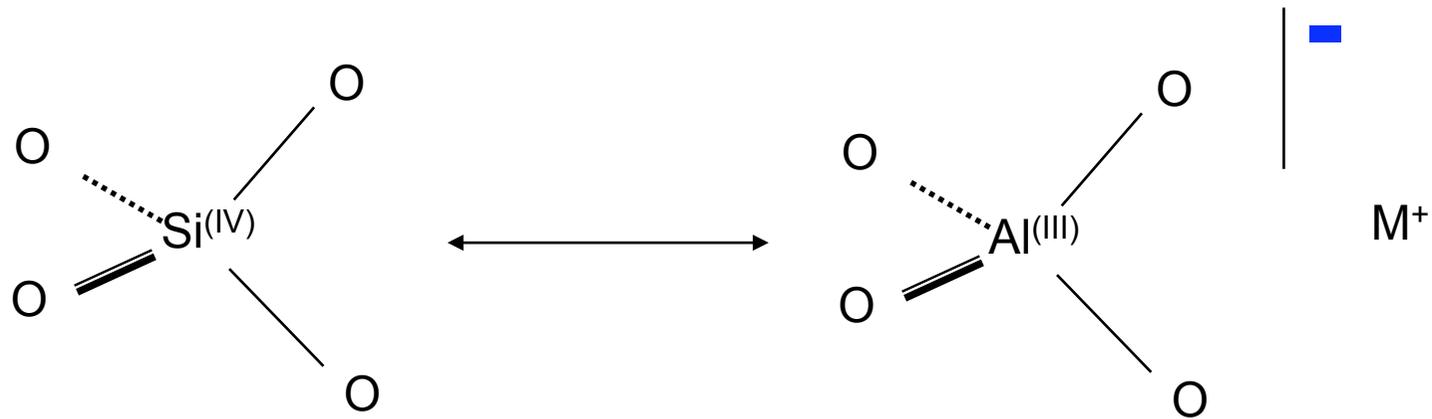
## Une silice amorphe... en photo



**film de silice sur Ru(0001) (microscopie à effet tunnel)**

## Supports microporeux ( $\emptyset \leq 2$ nm): les zéolithes

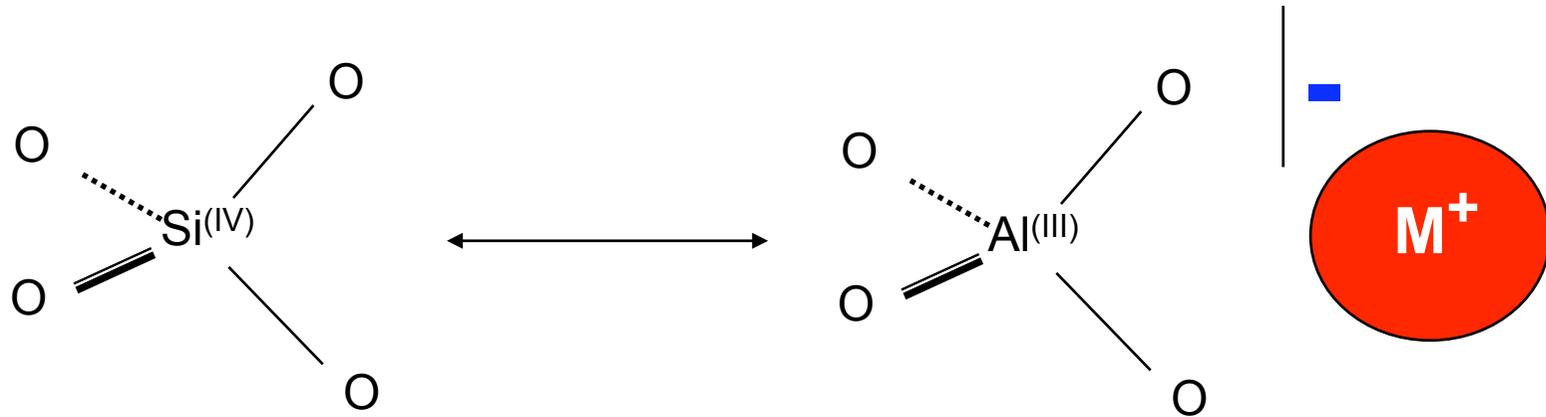
aluminosilicates: substitution Si(IV) – Al(III) dans la structure



A chaque Al correspond une charge négative qui doit être compensée par un cation

# Supports microporeux organisés: les zéolites

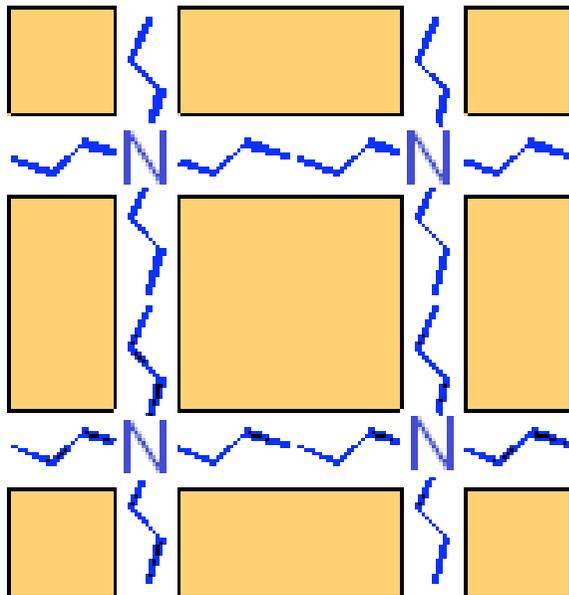
Dans une zéolithe, le cation ( $\text{Na}^+$ ,  $\text{K}^+$ ...) peut être...



- échangé par un autre cation actif en catalyse  
ex. cation de métal de transition pour **catalyse rédox** ( $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ...)
- échangé par  $\text{NH}_4^+$ , puis calciné  
 $\text{NH}_3$  part, il reste  $\text{Si}(\text{O}^-\text{H}^+)-\text{Al}$  = **catalyse acide**

# Supports microporeux organisés: les zéolithes

structuration appropriée par choix d'un template = **cation, ou molécule organique**



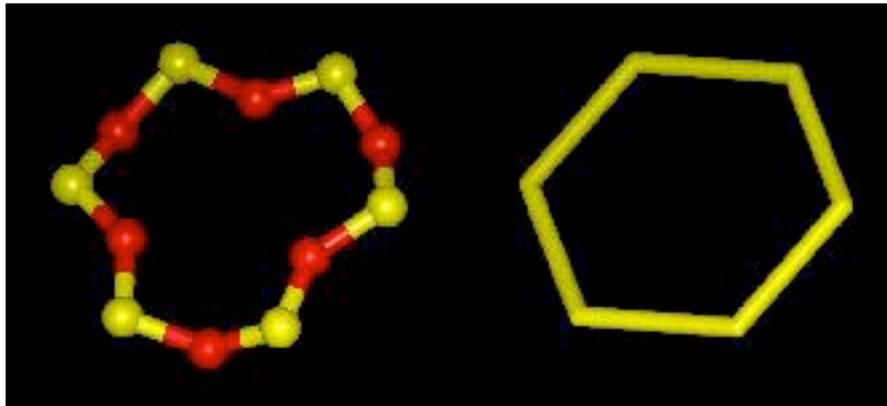
Ex : ion  $\text{NPr}_4^+$

destruction ultérieure du template  
par calcination dans l'air

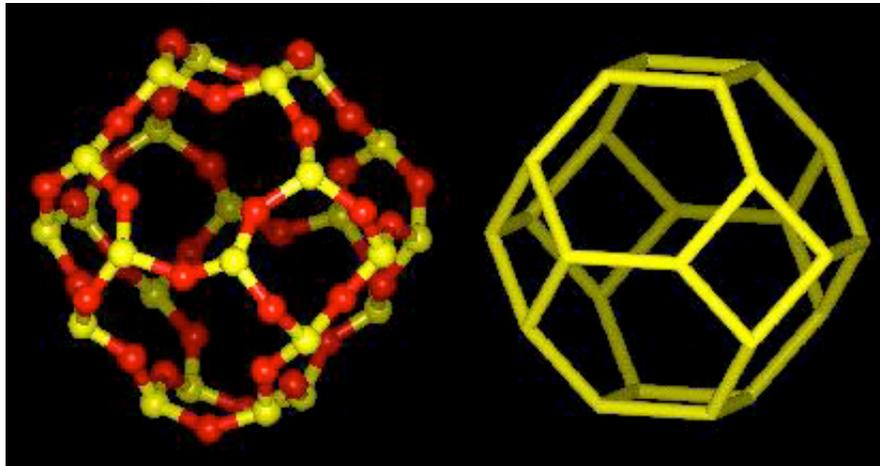
1<sup>re</sup> zéolithe purement artificielle :  
 $\text{H}^+$ -ZSM-5

(utilisée dans sa forme acide  
pour le craquage pétrolier)

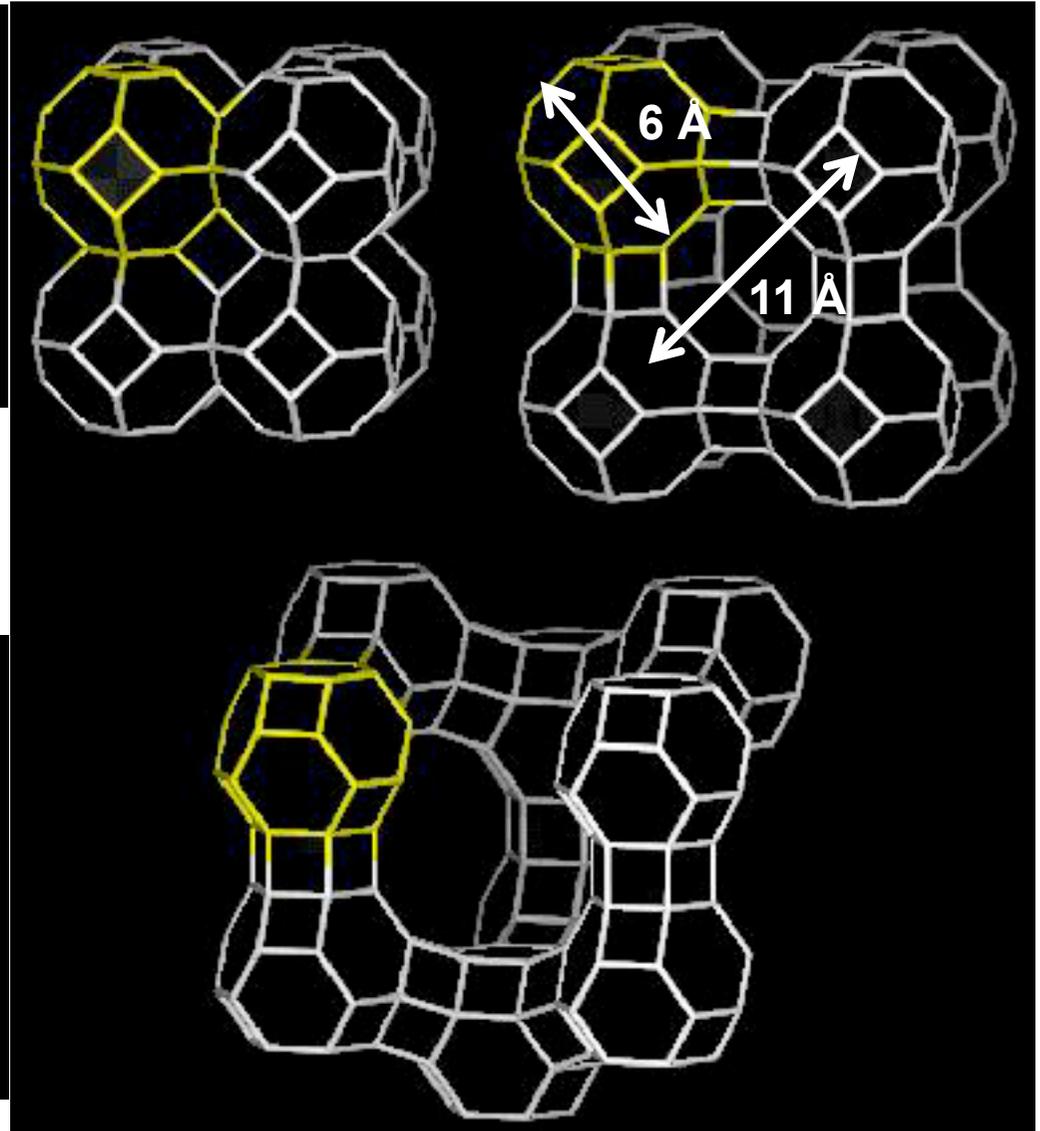
## Réseaux microporeux 3D



Cycle ( $\text{Si}_6\text{O}_6$ )



Cage sodalite



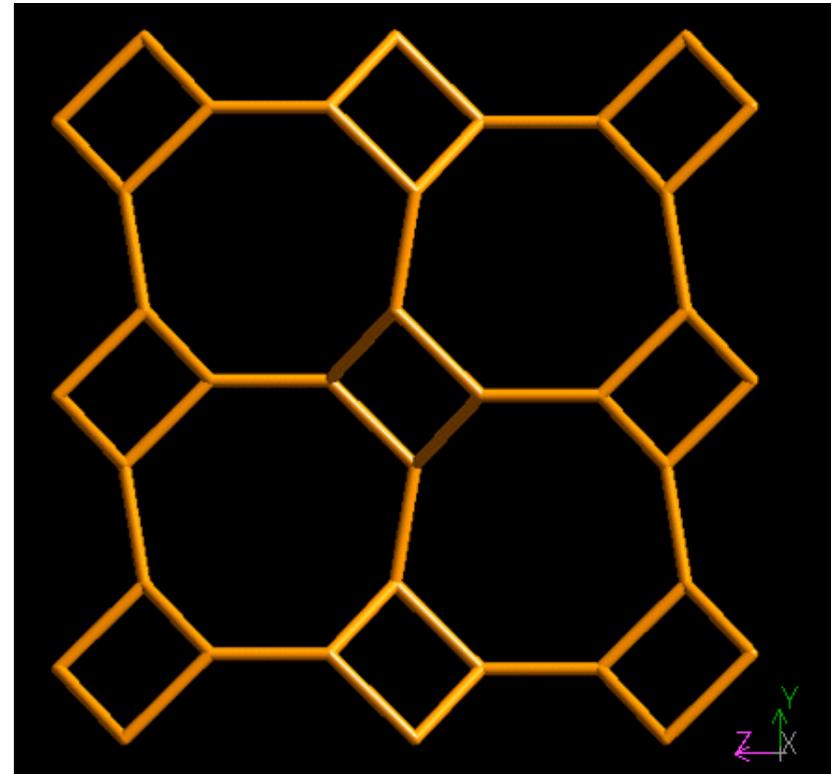
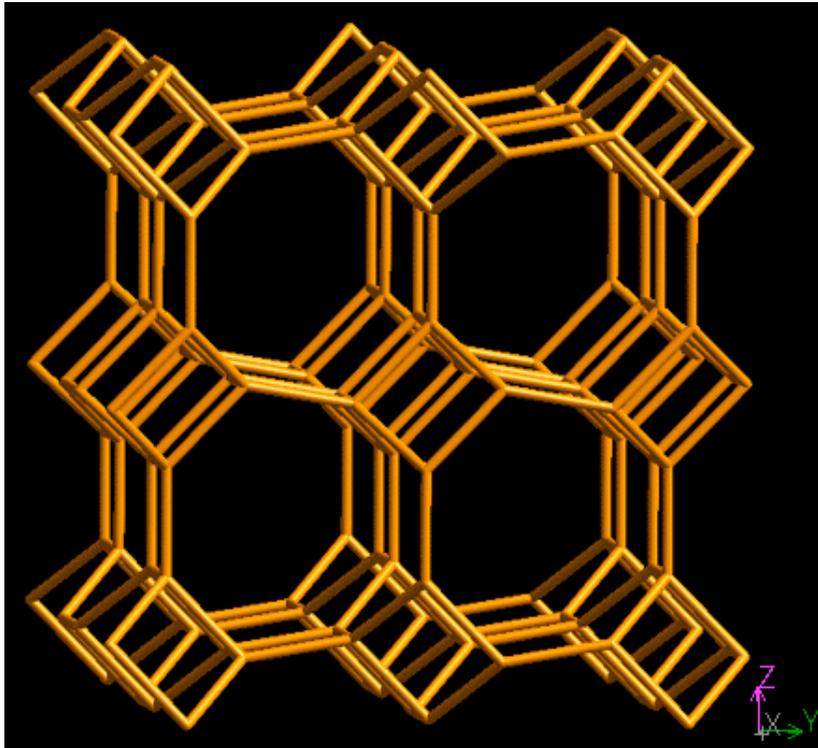
nombreuses combinaisons



Zéolithes naturelles :  
chabazite

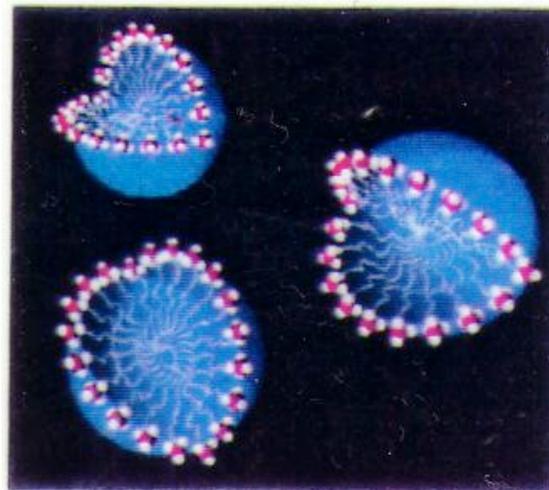
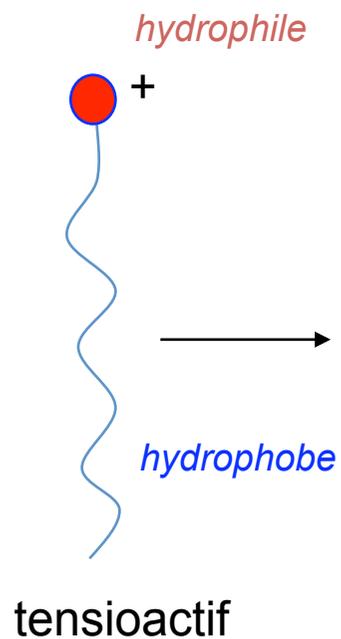


phillipsite

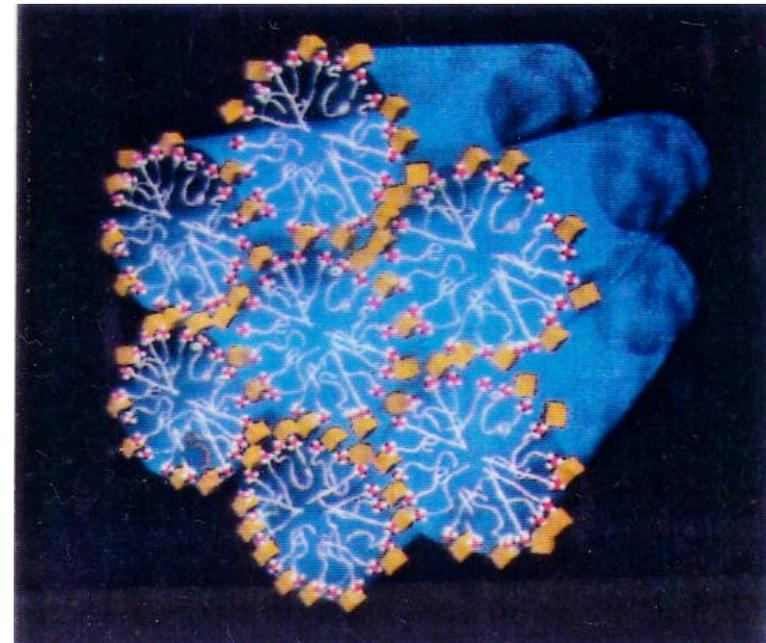


# Les matériaux mésoporeux ( $2 \leq \emptyset \leq 50 \text{ nm}$ )

mésopores > micropores, d'où templates plus gros, MAIS toujours hydrosolubles

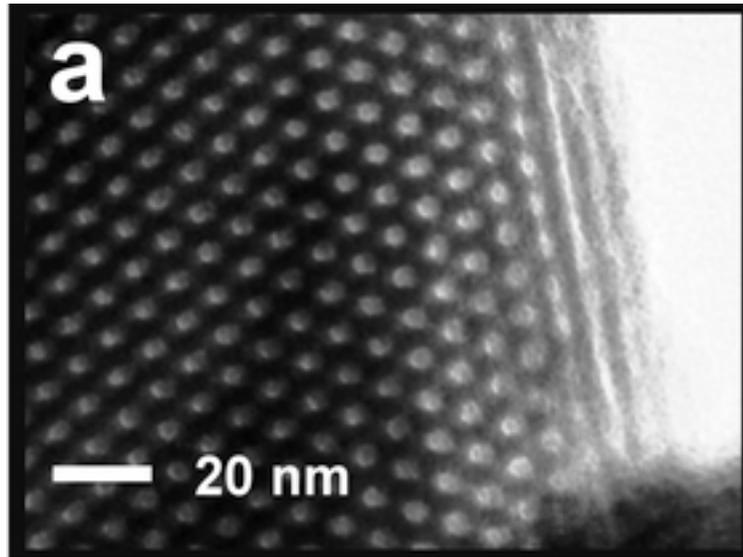


micelle

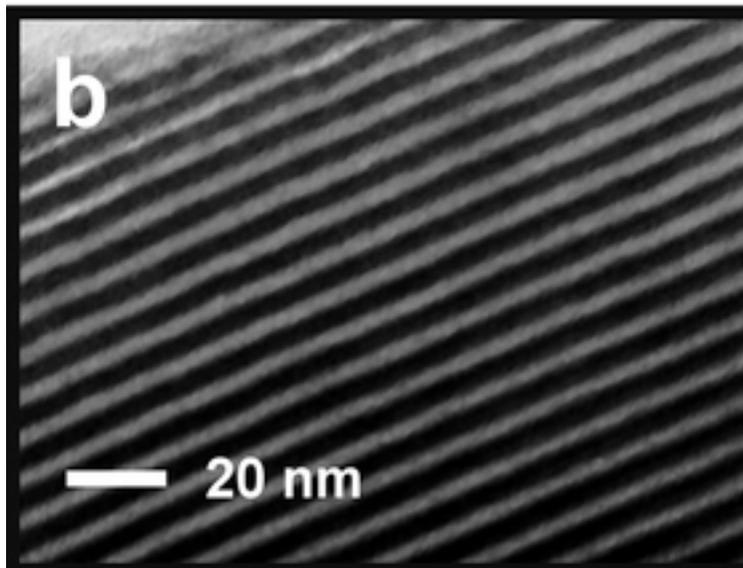


au-dessus d'une certaine concentration, formation de micelles cylindriques autour desquelles **les ions silicate** s'organisent

# Silice mésoporeuse SBA-15



$\emptyset$  pore = 6 nm

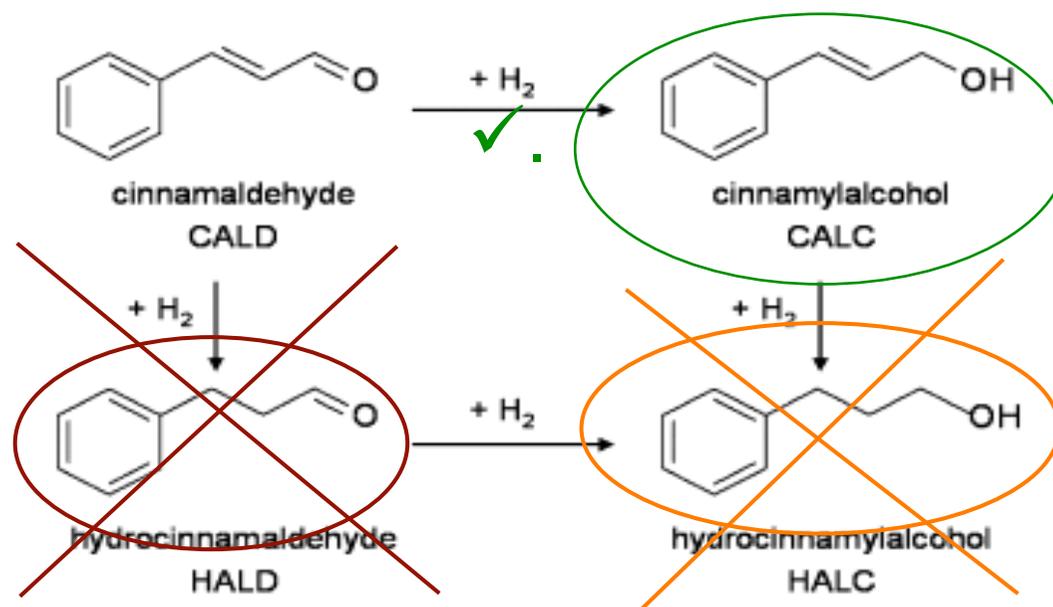


template : copolymère tribloc  
(polyoxyde d'éthylène)- *hydrophile*  
(polyoxyde de propylène)- *hydrophobe*  
(polyoxyde d'éthylène) *hydrophile*

Juan A. Melero, Galen D. Stucky, Rafael van Grieken  
et Gabriel Morales  
J. Mater. Chem., 2002, 12, 1664 - 1670

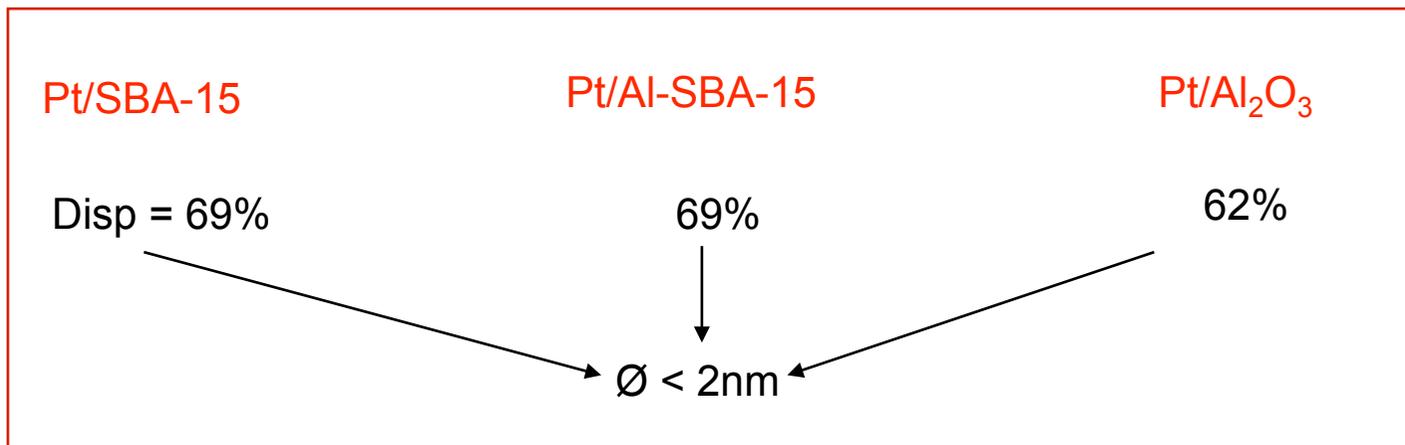
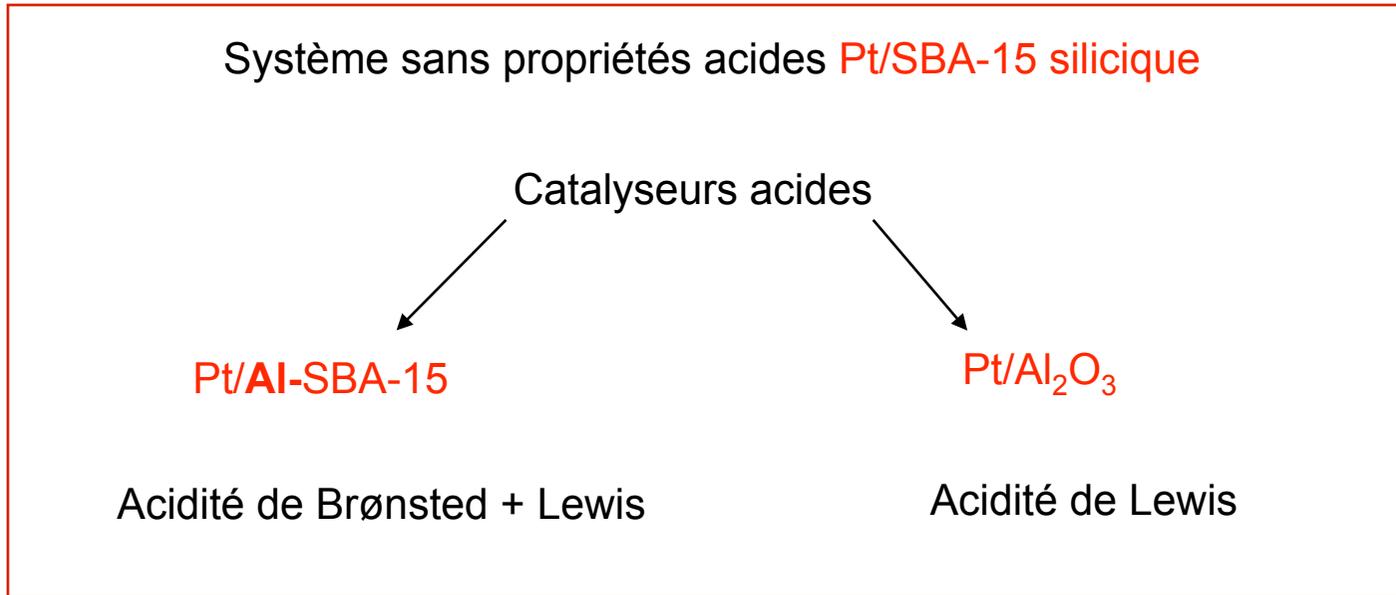
# Catalyse hétérogène: une affaire de surface(s) (coll. Åbo Akademi, Finlande)

Hydrogénation du cinnamaldéhyde sur catalyseurs au Pt

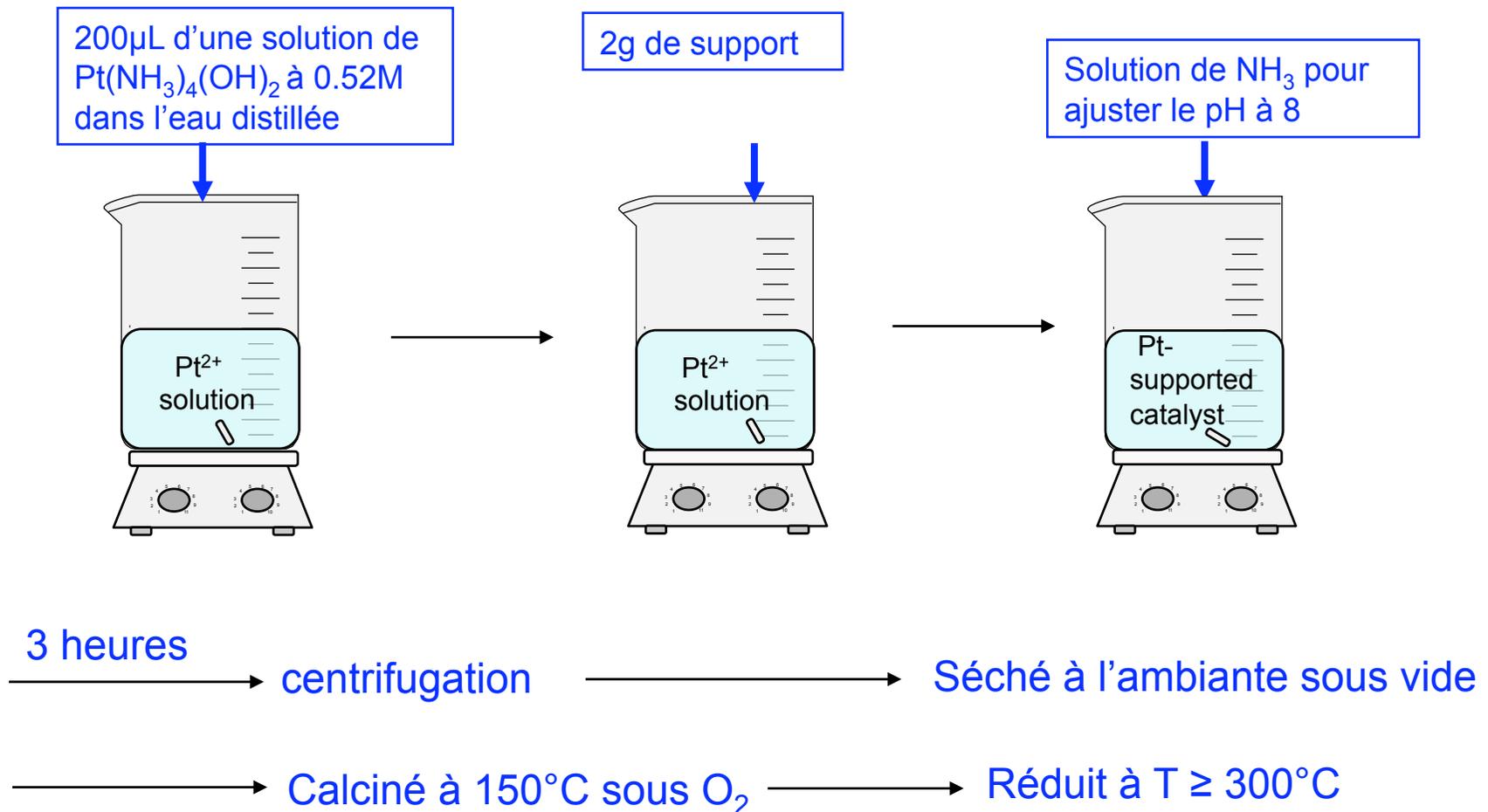
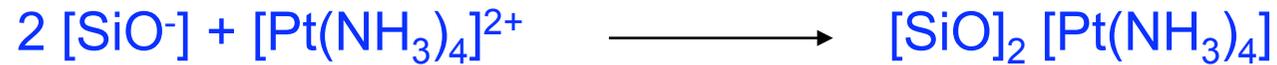


T réaction = 100 °C, P(H<sub>2</sub>) = 30 bar, solvant = 2-pentanol

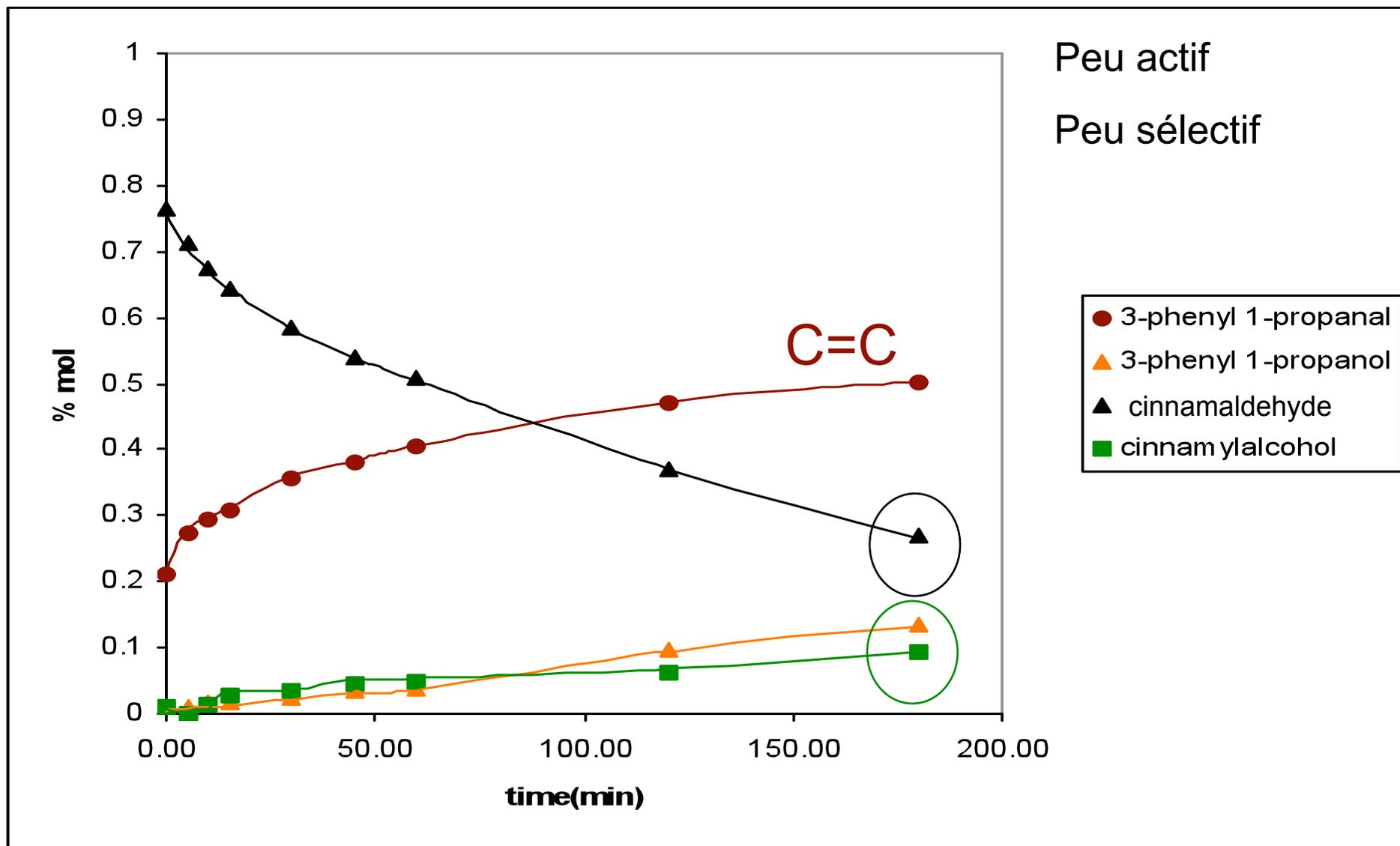
### 3 catalyseurs supportés au Pt



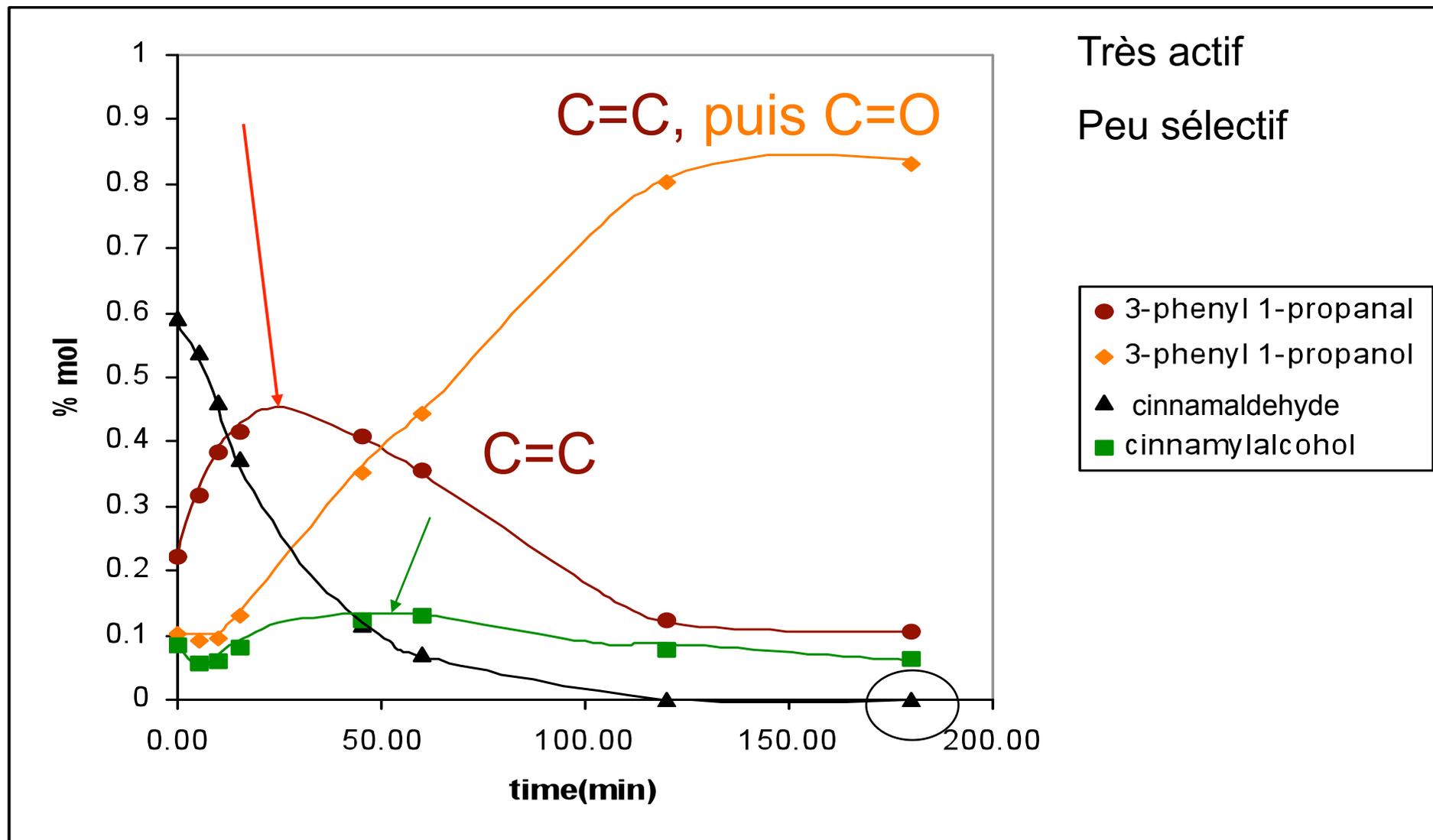
# Introduction du platine sur les supports SBA-15



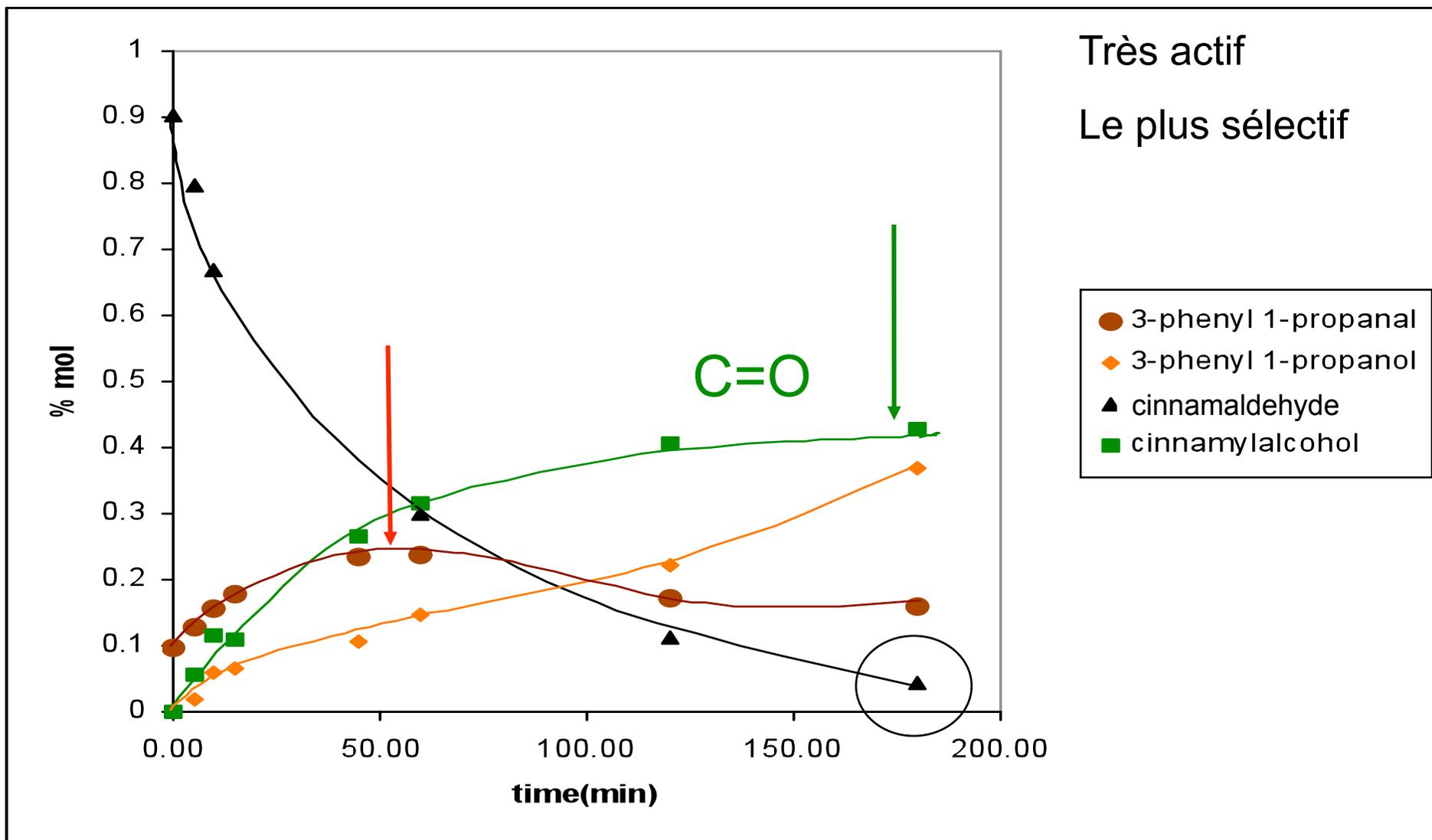
# Pt/SBA-15



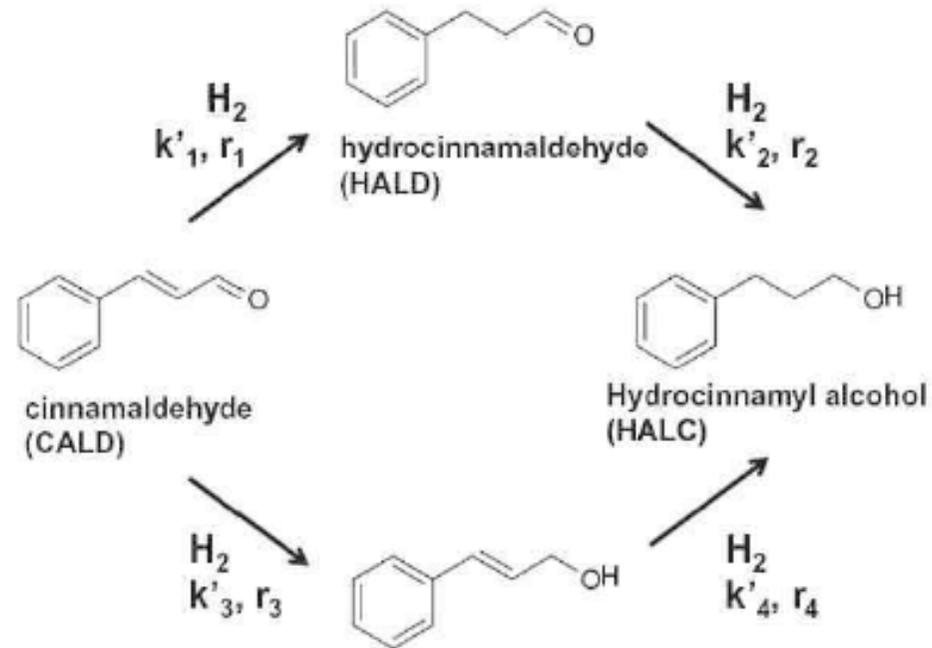
# Pt/Al-SBA-15



# Pt/Al<sub>2</sub>O<sub>3</sub>



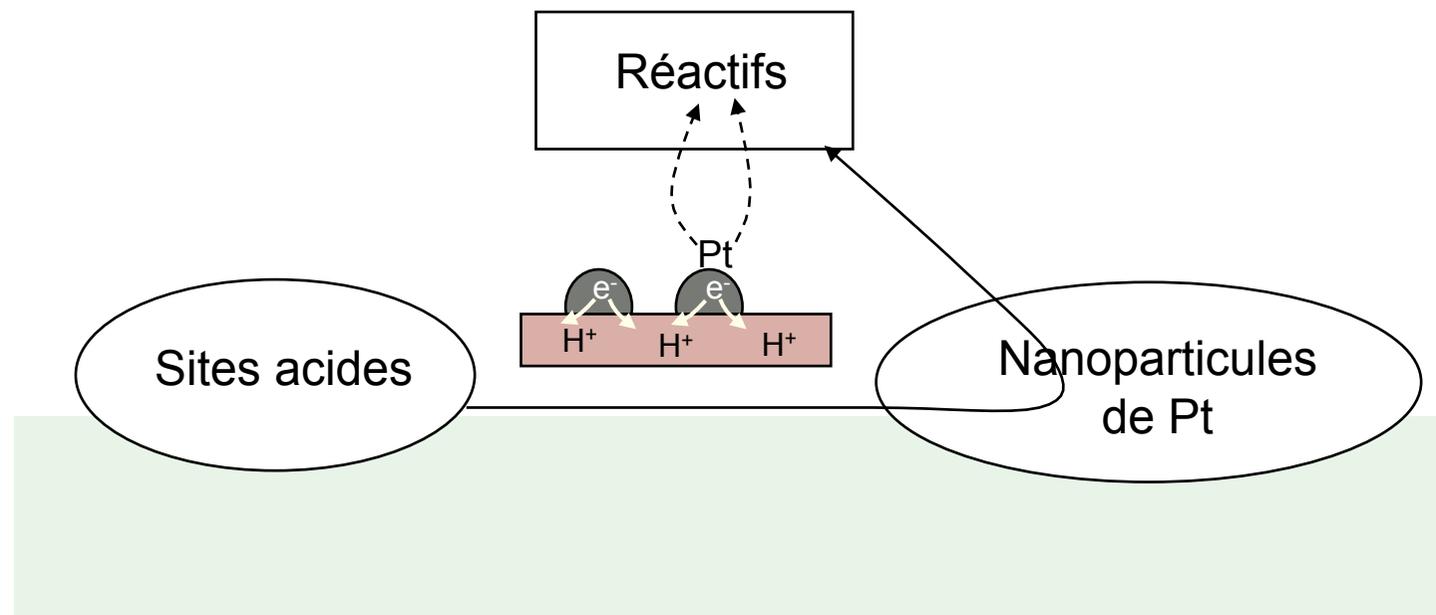
## Constantes apparentes de vitesse



|                                   | $k'_1$                  | $k'_2$                  | $k'_3$                  | $k'_4$                  | ( $\text{min}^{-1}$ ) |
|-----------------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-----------------------|
|                                   | CALD $\rightarrow$ HALD | HALD $\rightarrow$ HALC | CALD $\rightarrow$ CALC | CALC $\rightarrow$ HALC |                       |
|                                   | (C=C)                   | (C=O)                   | (C=O)                   | (C=C)                   |                       |
| Pt/SBA-15                         | 12                      | 1                       | 3                       | 0                       |                       |
| Pt/Al-SBA-15                      | <b>34</b>               | 1                       | <b>16</b>               | 2                       |                       |
| Pt/Al <sub>2</sub> O <sub>3</sub> | 8                       | <b>10</b>               | <b>9</b>                | 1                       |                       |

# Augmentation de la vitesse d'hydrogénation:

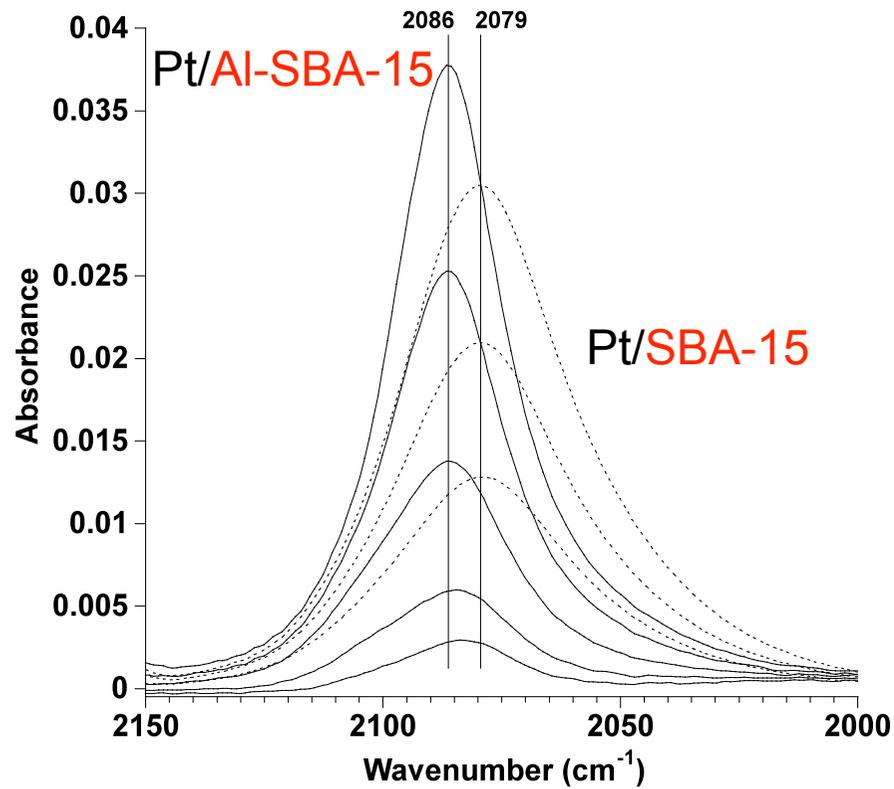
Pt/**Al-SBA-15** vs. Pt/**SBA-15**



Polarisation des nanoparticules métalliques par le support acide



Rétrodonation plus faible



adsorption de CO,  
spectroscopie IR

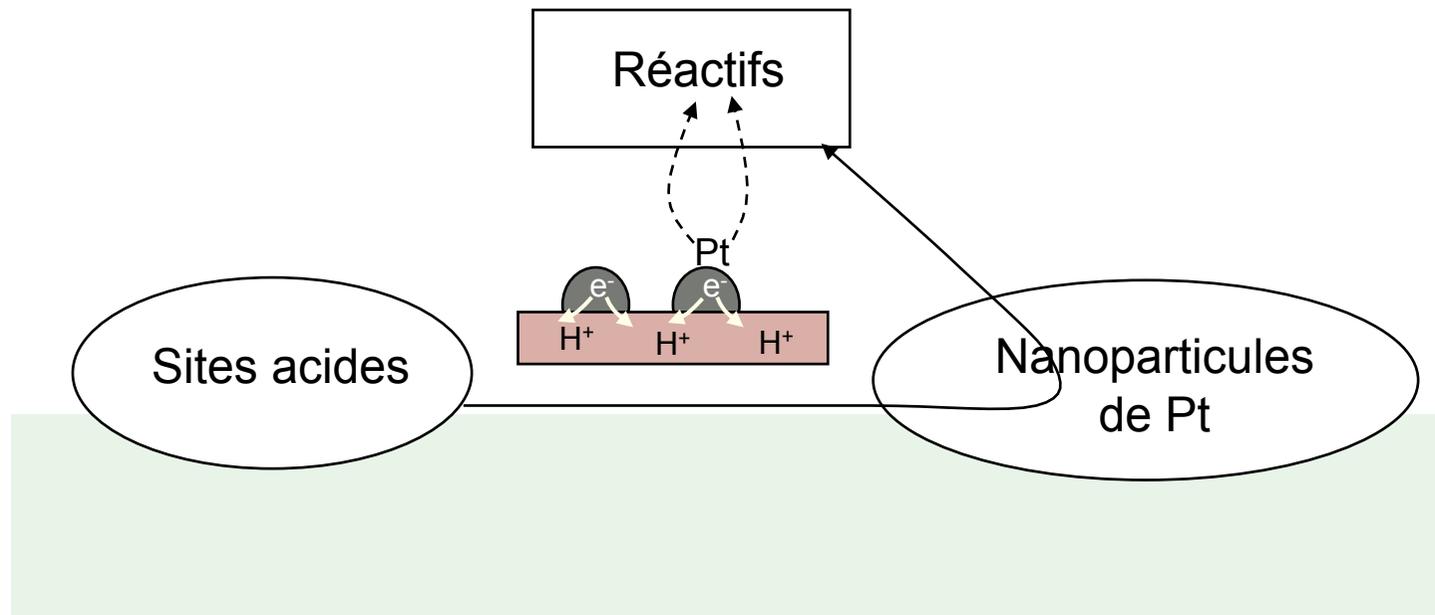
Polarisation des  
nanoparticules  
métalliques par le  
support acide



Rétrodonation  
plus faible

# Augmentation de la vitesse d'hydrogénation:

Pt/**Al-SBA-15** vs. Pt/**SBA-15**



Polarisation des nanoparticules métalliques par le support acide

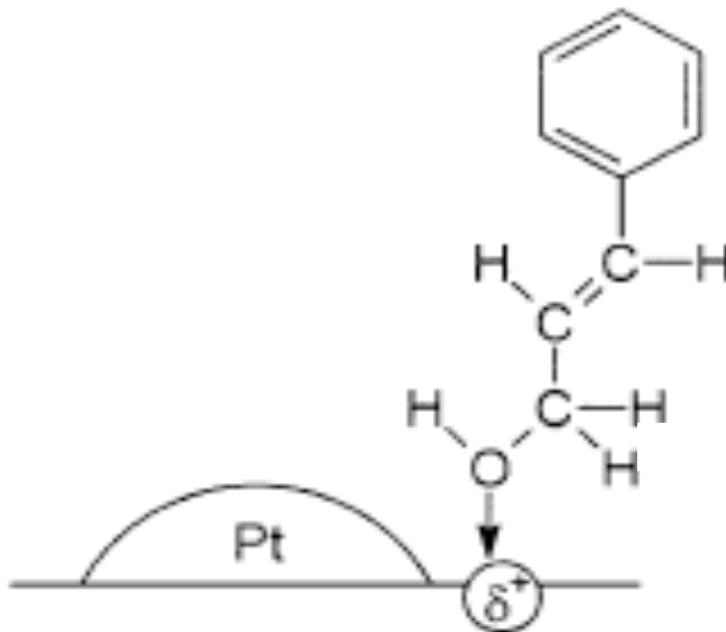


Rétrodonation plus faible  
Désorption facilitée



Augmentation de la vitesse de réaction

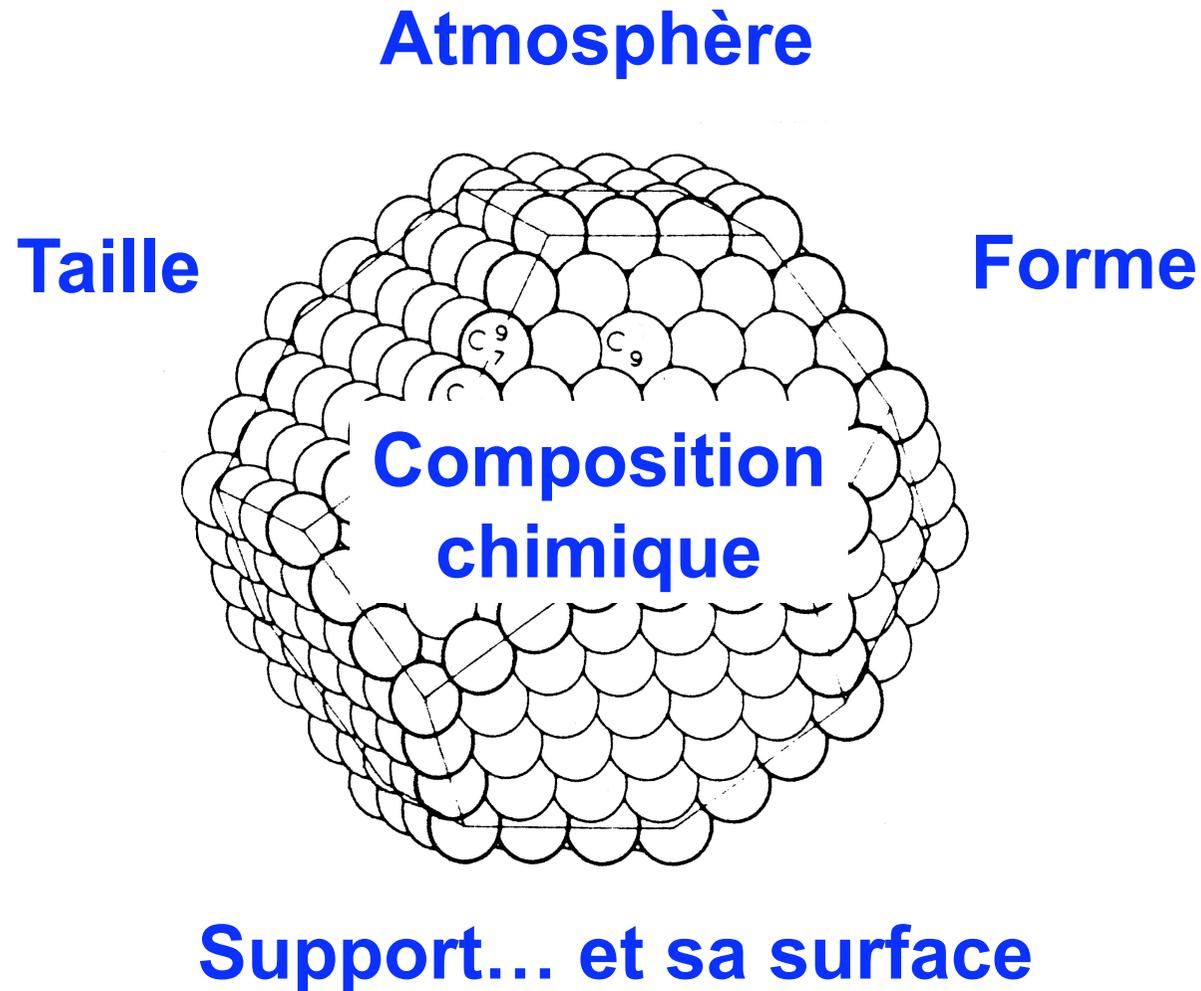
## Augmentation de la sélectivité sur Pt/ $\text{Al}_2\text{O}_3$ vs. Pt/SBA-15



Szollosi. et al. ,*J. Catal.*, 179, 1998, 619-623

Nombreux sites acides de Lewis près des nanoparticules de Pt :  
favorise l'adsorption du cinnamaldéhyde **par la liaison C=O**

# Conclusions: Qu'est-ce qui gouverne une phase catalytique?



***Merci pour votre attention!***