DICP Course - Dalian, 2012
Preparation of solid catalysts
Part 1

Supported by the Chinese Academy of Sciences

Charles Kappenstein, Professor Emeritus, University of Poitiers, France

Outline

Introduction and general aspects

Interfacial chemistry – Electrostatic adsorption

Impregnation and drying

Sol-gel chemistry processing

Deposition – Precipitation – Coprecipitation

Shaping of solid catalysts – Monolith-based catalysts

Outline

Zeolite-based catalysts

Characterization – High throughput experimentation

Case studies:

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

Outline

Introduction and general aspects

1) Importance and development of solid catalysts

2) What is catalysis ?

A short introduction

Surface reactions, physisorption, chemisorption

Kinetics and catalysis

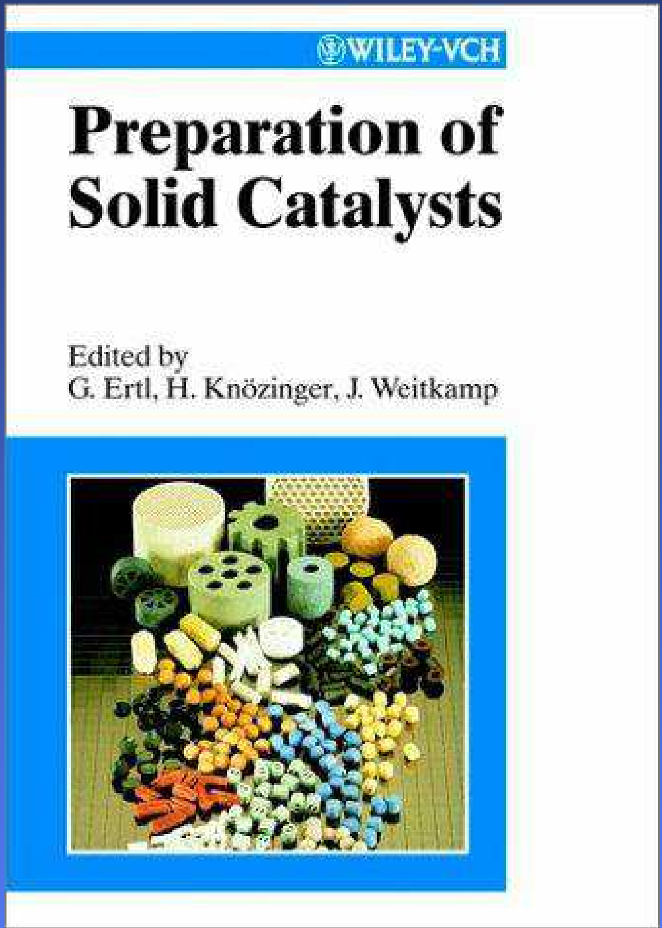
3) What is a solid catalyst ?

Preparation : carrier, precursor, active phase

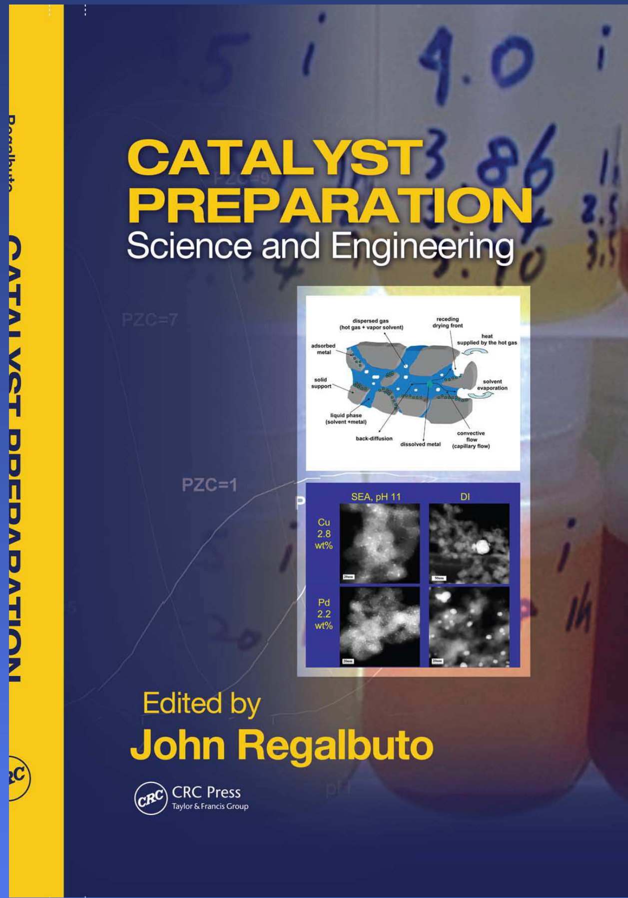
Characterization : surface area, metallic area, size, porosity

Active centers : stability, activity, selectivity

Importance and development of solid catalysts: some books

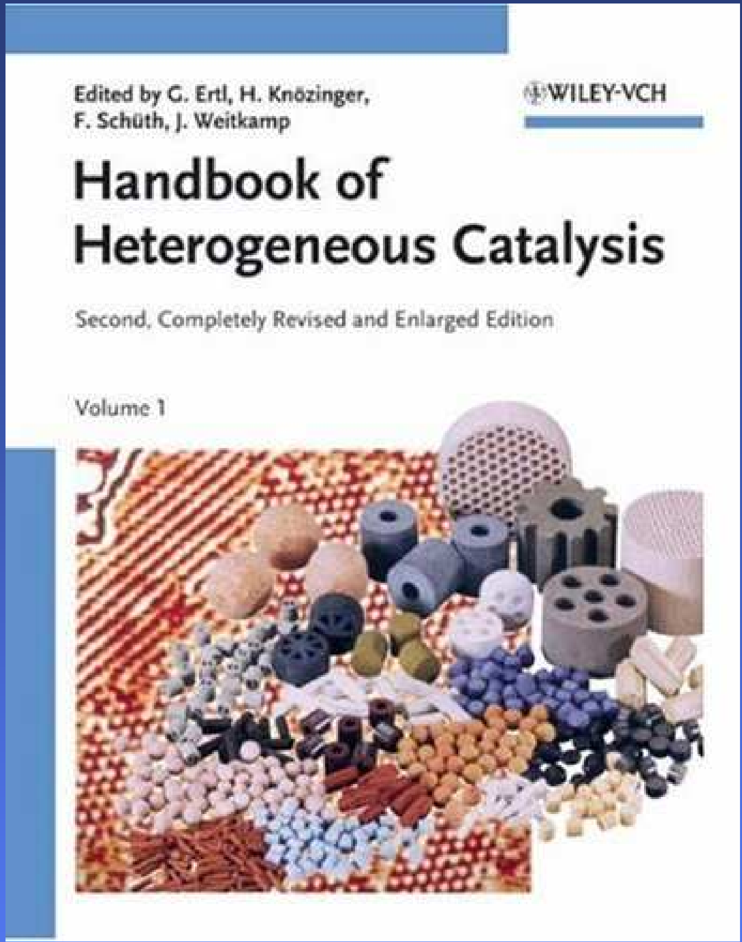


1999

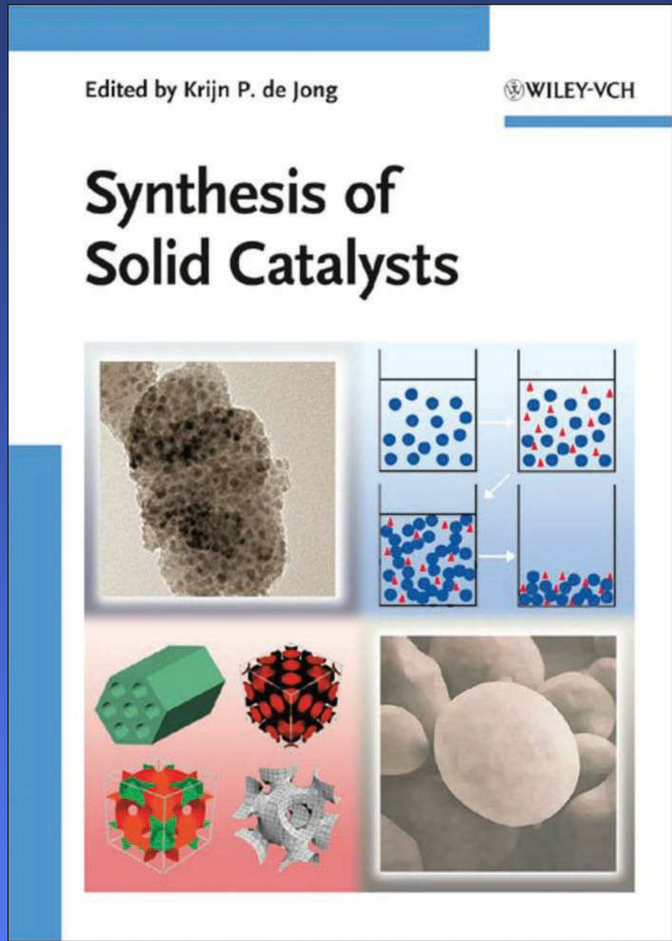


2007

Importance and development of solid catalysts: some books



2008



2009

Importance and development of solid catalysts

•About 85 % of all chemical processes make use of catalysts

•All molecules of modern fuels have been confronted at least with one catalyst

World catalyst demand and forecast (billion US $/year) by application [de Jong, 2009]

	2007	2010	2013	
Refining	4.35	4.98	5.85	
Petrochemicals	3.03	3.64	4.34	
Polymers	3.24	3.75	4.30	
Fine chemicals/other	1.47	1.59	1.70	
Environmental	5.51	6.28	6.93	
Total	17.6	20.2	23.1	

Importance and development of solid catalysts

Chemical	Application reaction	Catalyst
C_2H_4, C_3H_6	hydrocarbon cracking	$Pt/SiO_2\text{-}Al_2O_3$
H_2SO_4	$SO_2 + 0.5\ O_2 \rightarrow SO_3 \rightarrow H_2SO_4$	V_2O_5
Ammonia	$N_2 + H_2 \rightarrow NH_3$	$K_2O/Fe/Al_2O_3$
Nitric acid	$NH_3 + O_2 \rightarrow NO_2 \rightarrow HNO_3$	Pt-Rh
Saturated chemicals	hydrogenation	Ni/SiO_2
Polymers	polymerization	CrO_x/SiO_2
Epoxide	$C_2H_4 + O_2 \rightarrow C_2H_4O$	$Ag/\alpha\text{-}Al_2O_3$
Methanol	$CO + 2\ H_2 \rightarrow CH_3OH$	$Cu/ZnO/Al_2O_3$
Fuel, gazoline	hydrotreating	$CoMoS_2/\gamma\text{-}Al_2O_3$
Gazoline	Fischer-Tropsch synthesis	Co/SiO_2
Gazoline	hydroisomerization	Pt/mordenite
Gazoline	catalytic cracking	Zeolite Y based
Clean air	NO_x abatement	V_2O_5/TiO_2

The Past

- Use of catalytic reactions since ancient time but not recognized due to the lack of scientific knowledge. Ex.: fermentation to produce ethanol.
  - $C_6H_{12}O_6(aq) \rightarrow 2\ C_2H_5OH(l) + 2\ CO_2(g)$
- Use of sulfuric acid to catalyze the synthesis of diethylether (16th century).
  - $2\ C_2H_5OH(l) \rightarrow C_2H_5\text{-}O\text{-}C_2H_5(l) + H_2O(l)$
- Production of sulfuric acid using nitrogen oxides (18th century).

19th century. Discoveries in chemical reaction rates
(Humphry Davy, Michael Faraday)

The Davy lamp: can burn methane without flame

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$$

use of platinum gauze to control this reaction
without flame propagation

➔ First use for human safety: the presence of methane pockets in mines could be detected before the explosion happens.

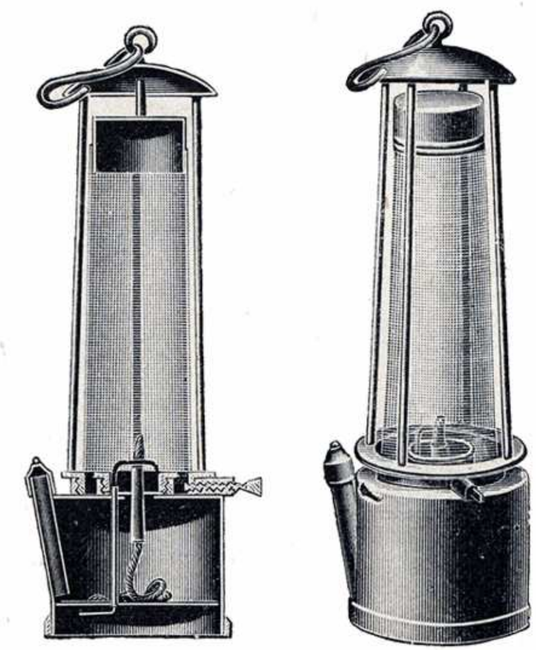


Fig. 192. Davyſche Sicherheitslampe

The definition of catalysis

J. Berzelius introduce the word "catalysis" in 1836.

Catalysis derived from Greek roots: ***cata*** = down, ***lysein*** = split or break

Example: decomposition of H_2O_2:

$$H_2O_2(l) \rightarrow H_2O(l) + 1/2\ O_2(g)$$

"Catalytic power actually means that substances are able to awaken affinities which are asleep at this temperature by their mere presence and not by their own affinity."

Usually accepted definition :

A **catalyst** is a substance that increases the **rate** at which a chemical system approaches **equilibrium**, without being consumed in the process.

Catalysis is the phenomenon of a catalyst in action.

The definition of catalysis

The original text (translated in English)

"This is a new power to produce chemical activity belonging to both inorganic and organic nature, which is surely more widespread than we have hitherto believed and the nature of which is still concealed from us. When I call it a new power, I do not mean to imply that it is a capacity independent of the electrochemical properties of the substance. On the contrary, I am unable to suppose that this is anything other than a kind of special manifestation of these, but as long as we are unable to discover their mutual relationship, it will simplify our researches to regard it as a separate power for the time being. It will also make it easier for us to refer to it if it possesses a name of its own.

I shall therefore using a derivation well-known in chemistry, call it the catalytic power of the substances, and the decomposition by means of this power catalysis, just as we use the word analysis to denote the separation of the component parts of bodies by means of ordinary chemical forces. *Catalytic power actually means that substances are able to awaken affinities which are asleep at this temperature by their mere presence and not by their own affinity.*

Classification of catalytic systems

Heterogeneous catalysis (80 wt.-%)

The reactants and the catalyst are present in different phases:

➔ reactants: gas or liquid phase

➔ catalyst: solid phase

The catalytic reactions happen at the surface of the solid.

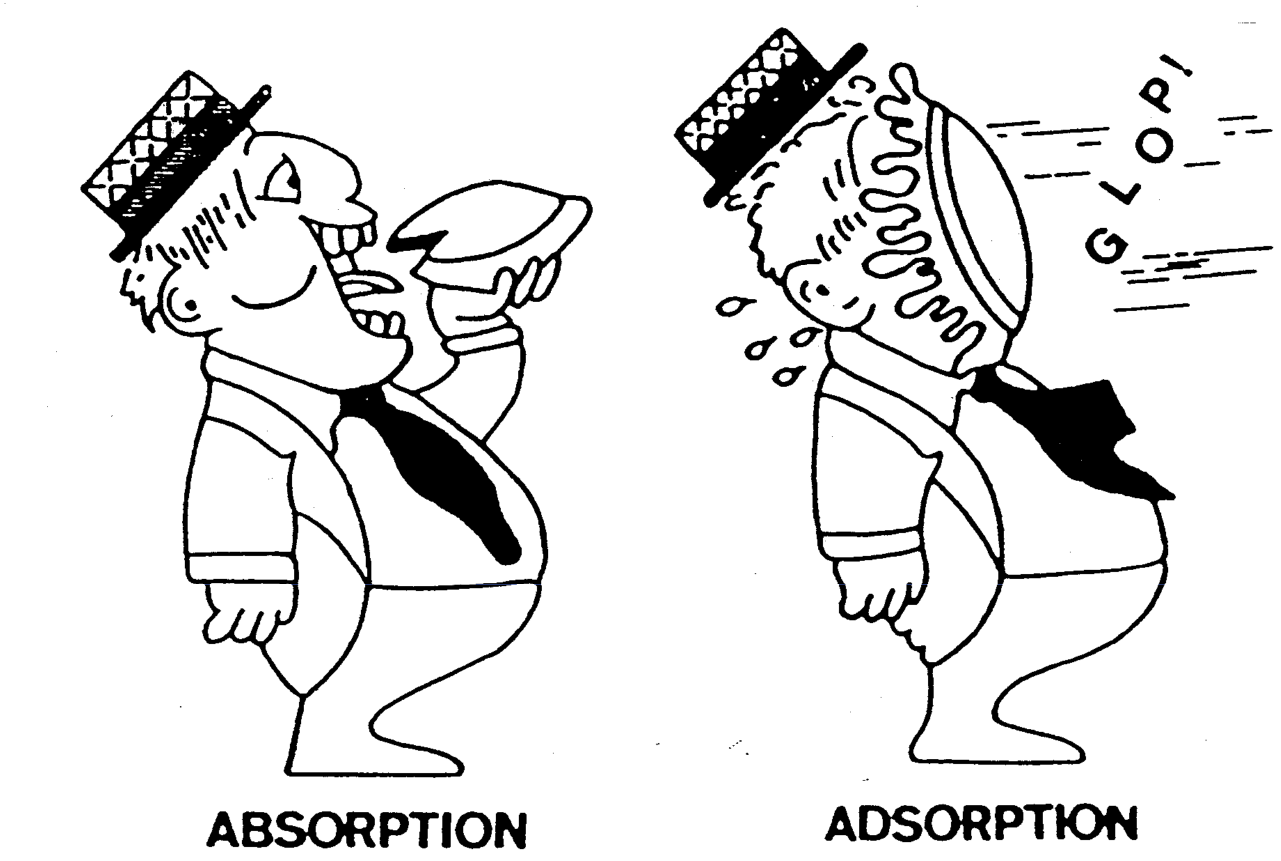
Homogeneous catalysis (17 %) and biocatalysis (3 %)

The reactants and the catalyst are present in the same phase : liquid phase.

The catalyst is a solute of the system.

Surface reactions

Difference between absorption and adsorption

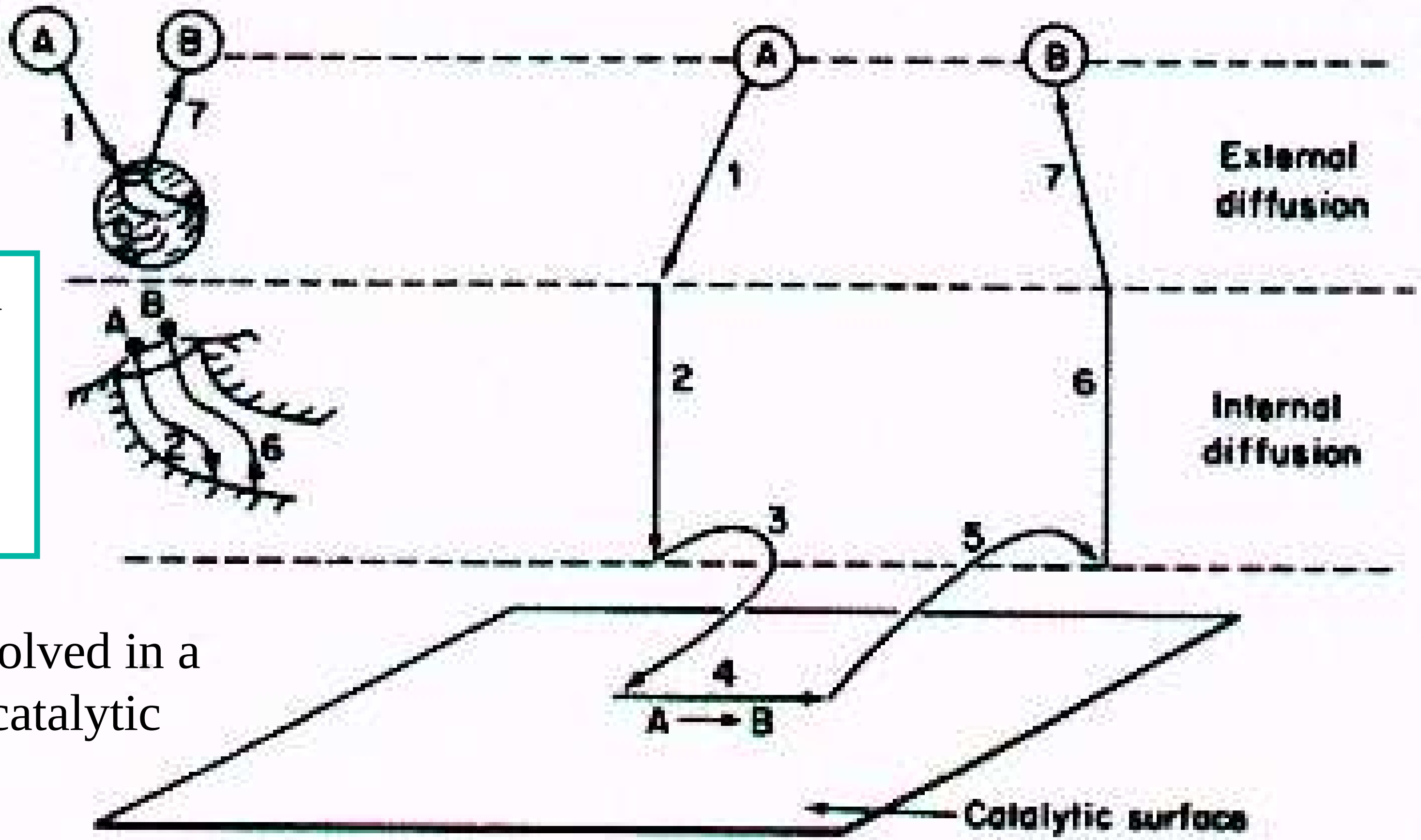


➔ An adsorption is a surface reaction

The solid is the adsorbent | **The molecule is the adsorbate**

Mechanism of catalytic reactions

The essence of catalysis is a cycle of reactions that consumes the reactants, forms the products and regenerates the catalytic species for a new cycle [Bond, 1987].



A reaction takes place on The surface, but the species involved in the reaction must get ***to*** and ***from*** the surface

Seven steps involved in a heterogeneous catalytic reaction

Limiting steps:

Chemical reaction at surface	➔ rate limitation through chemistry	4
Transport of molecules to and from surface	➔ rate limitation through diffusion	1, 2, 6, 7

Volcano plot

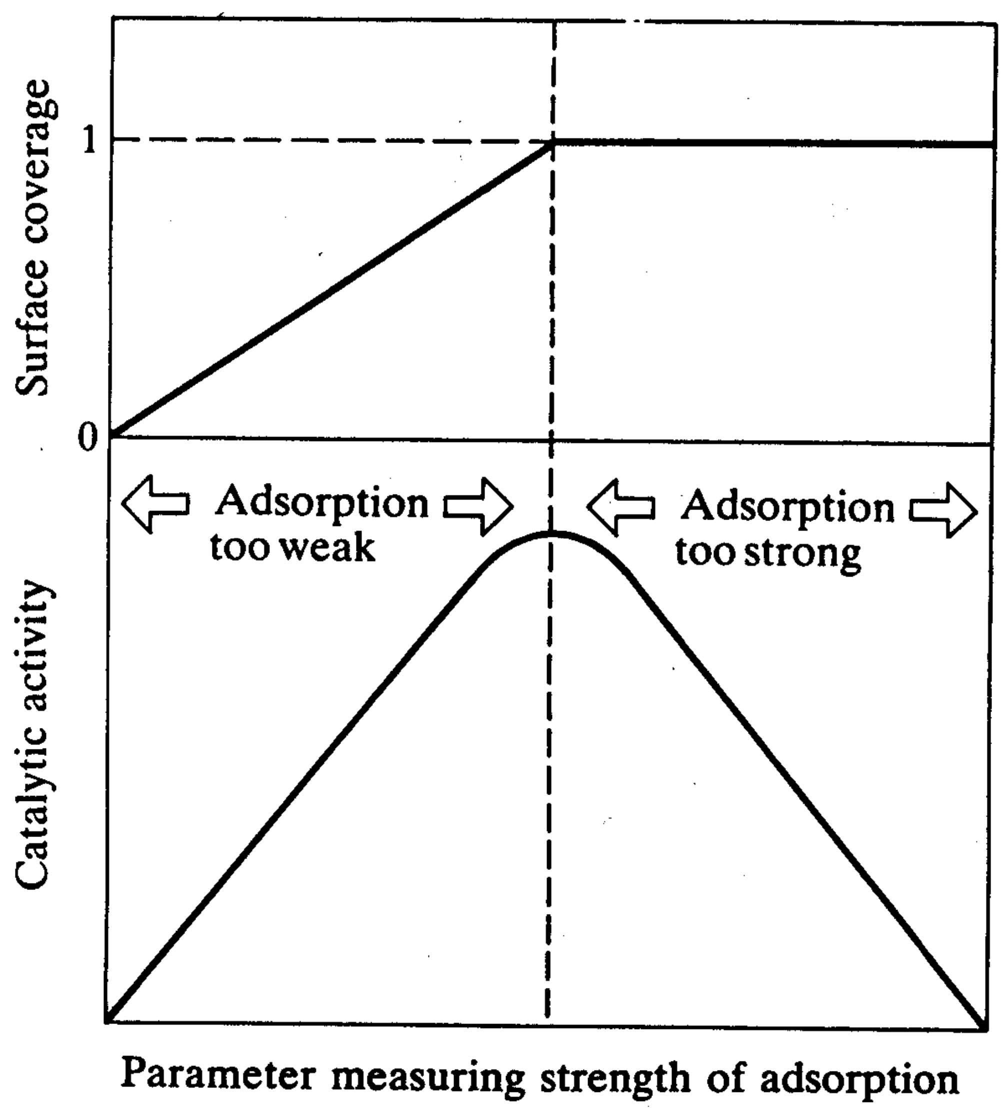
Which metal is the best catalyst for a given reaction ?

The catalytic activity is inversely related to the strength of chemisorption of the reactants providing that adsorption is sufficiently strong for the adsorbate to achieve high surface coverage.

(Balandine, 1925)

The volcano curve:

dependence of catalytic activity upon strength of reactant adsorption (lower part) and the corresponding variation in surface coverage (upper part).



What is catalysis?

An example of volcano plot

Catalytic decomposition of formic acid in gas phase

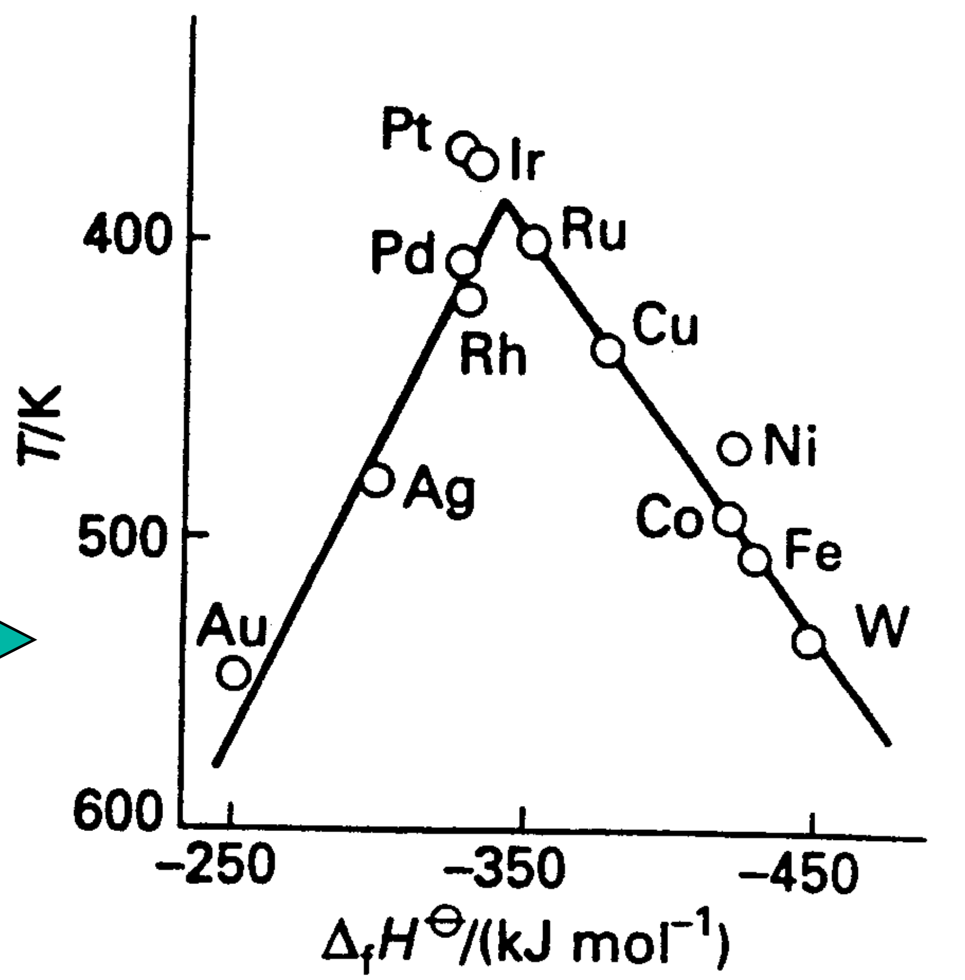
HCOOH(g) ➔ H_2O(g) + CO(g)

A volcano diagram.

The reaction temperature for a set rate of formic acid decomposition is plotted against the stability of the corresponding metal formate, as judged by enthalpy of formation.

[Bond 1987]

Temperature for 50 % decomposition



Outline

Session I – Catalysis and Catalysts

1) What is catalysis ?

A short introduction

Surface reactions, physisorption, chemisorption

Kinetics and catalysis

2) What is a solid catalyst ?

Preparation : carrier, precursor, active phase

Characterization : surface area, metallic area, size, porosity

Active centers : stability, activity, selectivity

Characteristics

- High surface area
- Low pressure drop
- High number of active sites

Classification of heterogeneous catalysts

Class	Functions	Examples
Metals, alloys conductors	hydrogenation dehydrogenation hydrogenolysis	Fe, Ni, Pd, Pt, Ag
Oxides and sulphides block d Semiconductors	oxidation dehydrogenation desulphurization	NiO, ZnO, MnO2 Cr_2O_3, Bi_2O_3-MoO_3 WS_2
Insulator oxides blocks s and p	dehydration	Al_2O_3, SiO_2, MgO
Acids, zeolites	polymerization isomerization cracking, alkylation	H_3PO_4, H_2SO_4 SiO_2-Al_2O_3

The periodic table

																	18
1	2							H				13	14	15	16	17	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Lr															
s block		d block										p block					

lanthanides	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
actinides	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No
	f block													

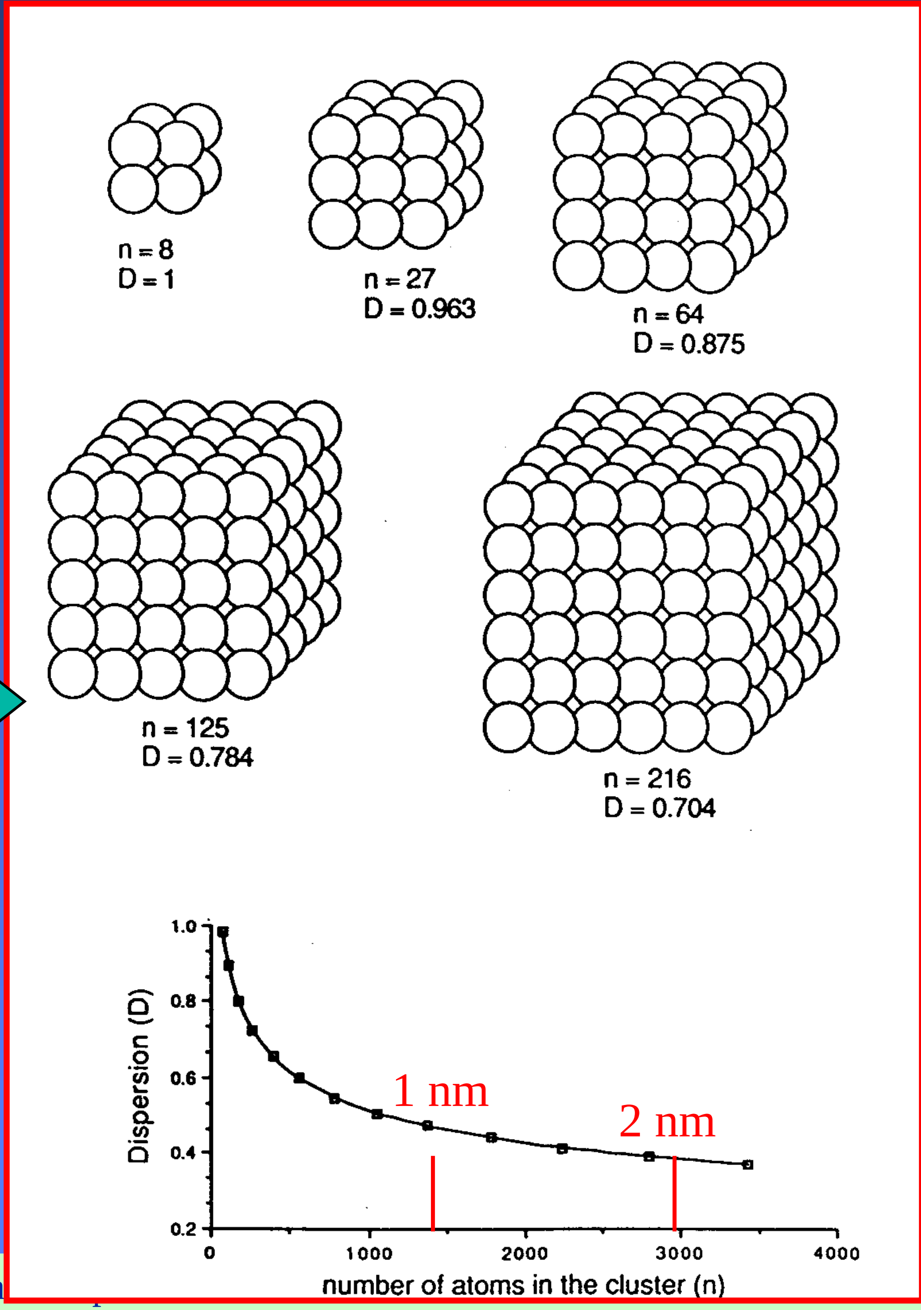
What is a solid catalyst ?

Metal dispersion

For metal catalysts:

$$\text{Dispersion} = \frac{\text{number of surface atoms}}{\text{total number of metal atoms}}$$

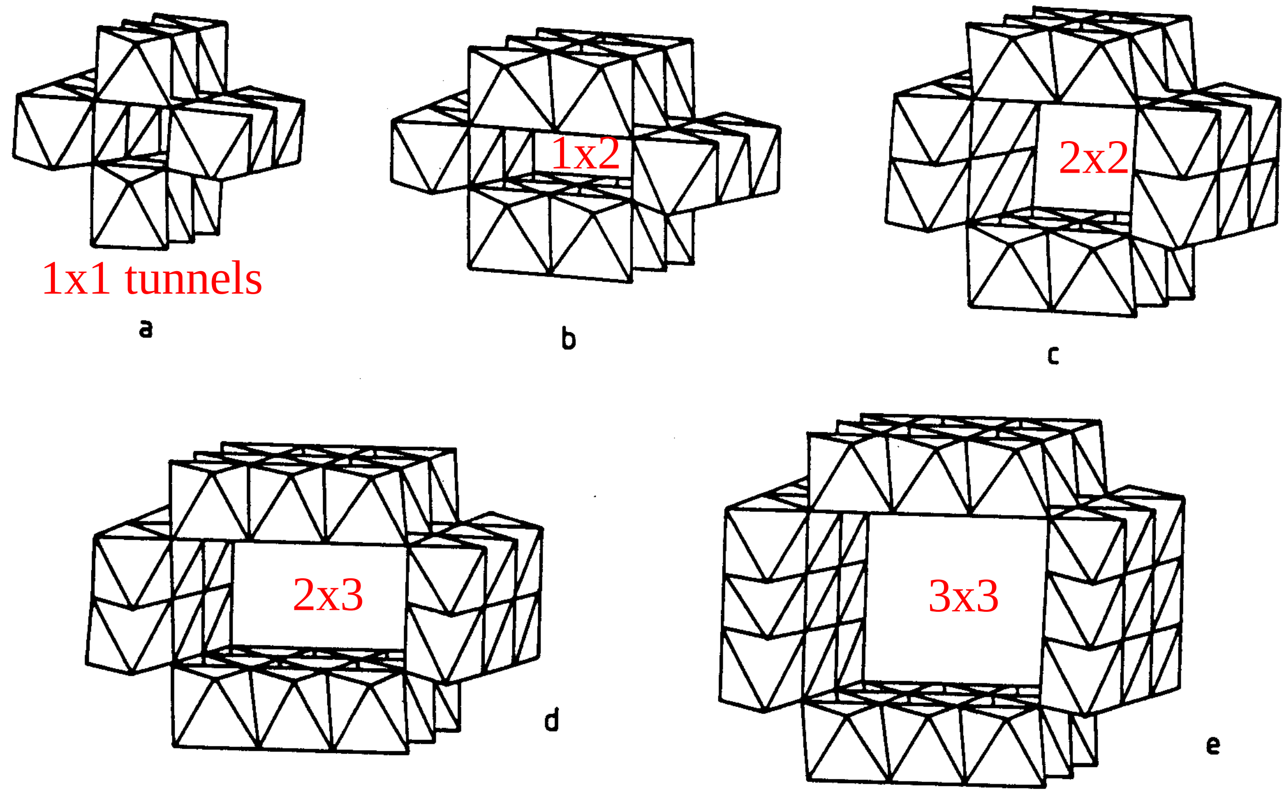
Clusters of atoms with single cubic packing having 8, 27, 64, 125 and 216 atoms.
In an 8-atom cluster, all the atoms are on the surface. However, the dispersion declines rapidly with increasing cluster size [Somorjai, 1994].



Semiconducting oxides

Example: manganese oxides (decomposition of H_2O_2)

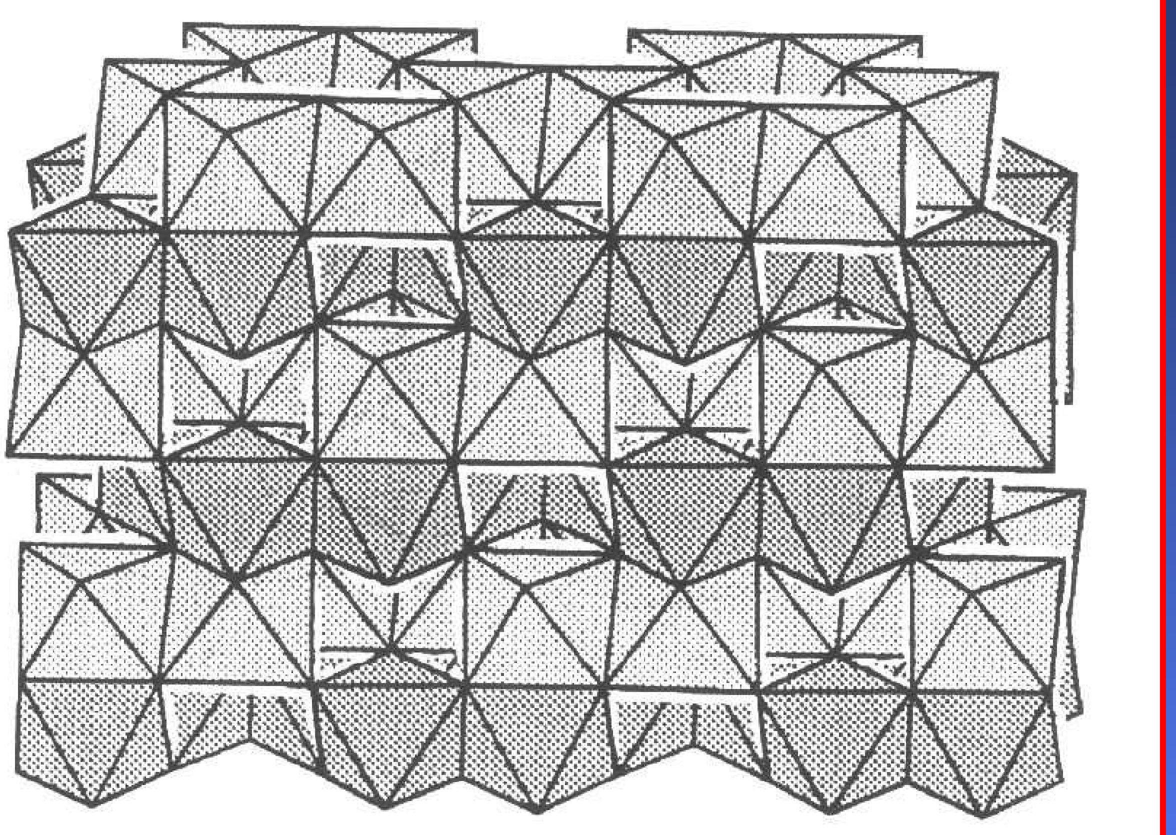
Polymorphs of MnO_2 [Thomas & Thomas, 1997]



(a) Pyrolusite β-MnO_2 has the rutile structure;
(b) ramsdellite γ-MnO_2 has the structure of the mineral diaspore;
(c) hollandite α-MnO_2 has tunnels circumscribed by a 2 x 2 arrangement of edge-sharing octahedra;
(d) romanechite displays 2 x 3 tunnels;
(e) todorkite displays 3 x 3 tunnels.

➔ **What is the best structure for the decomposition of hydrogen peroxide?**

Insulator oxides



Alumina

Linked octahedra in **corundum α-Al_2O_3**. The Al atoms are at the centers and the O atoms at the corners of the octahedra. (U. Müller, Inorganic structural chemistry, Wiley, 1992, p. 171).

➔ **Low specific surface area**

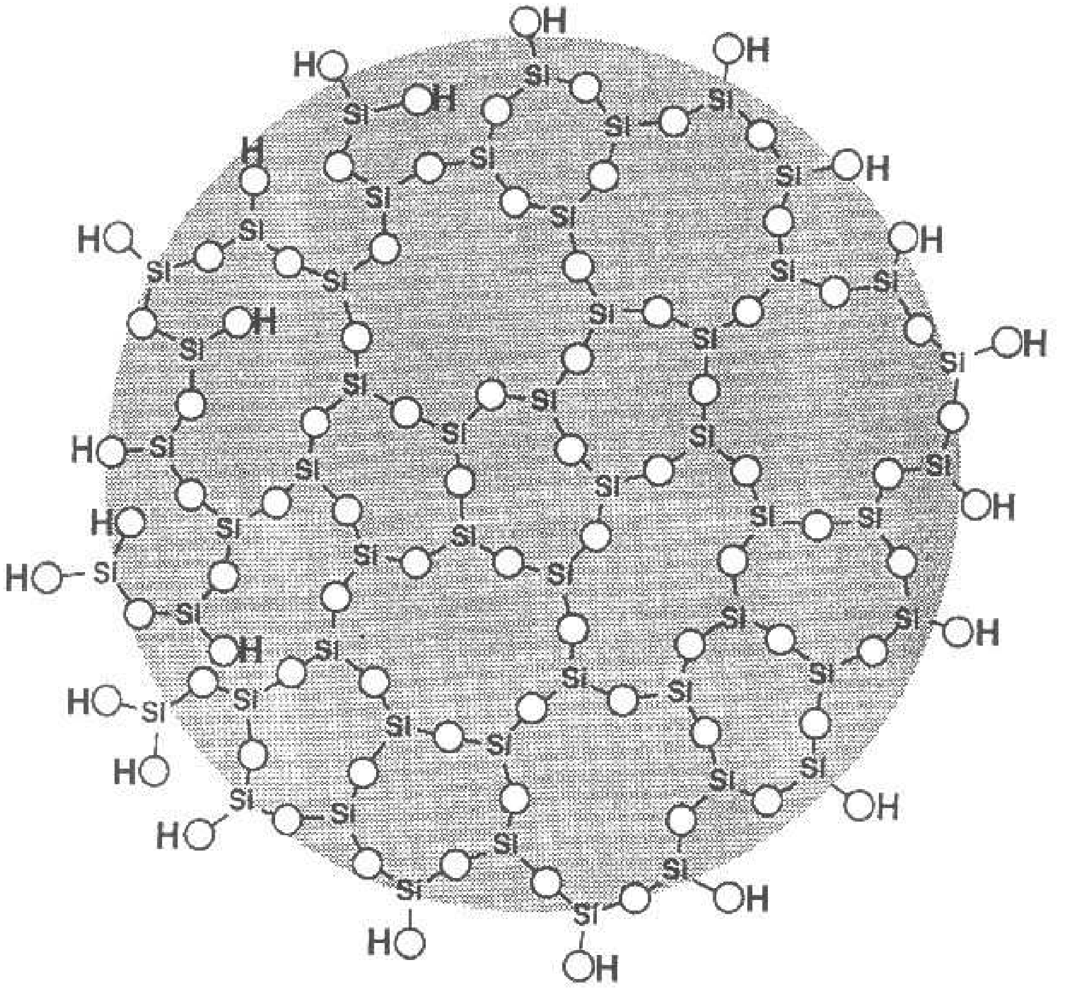
➔ **High thermal stability**

Insulator oxides

Silica

Schematic representation of a dehydrated but fully hydroxylated **colloidal silica particle**. The 4th oxygen coordinated with Si is above or below the plane. The Si-O-Si bond angle may vary, but the Si-O distances are constant.
(H. Bergna, The Colloid Chemistry of Silica, ACS, 1994, p. 9.)

- ➔ **Low thermal stability**
- ➔ **Large specific surface area**

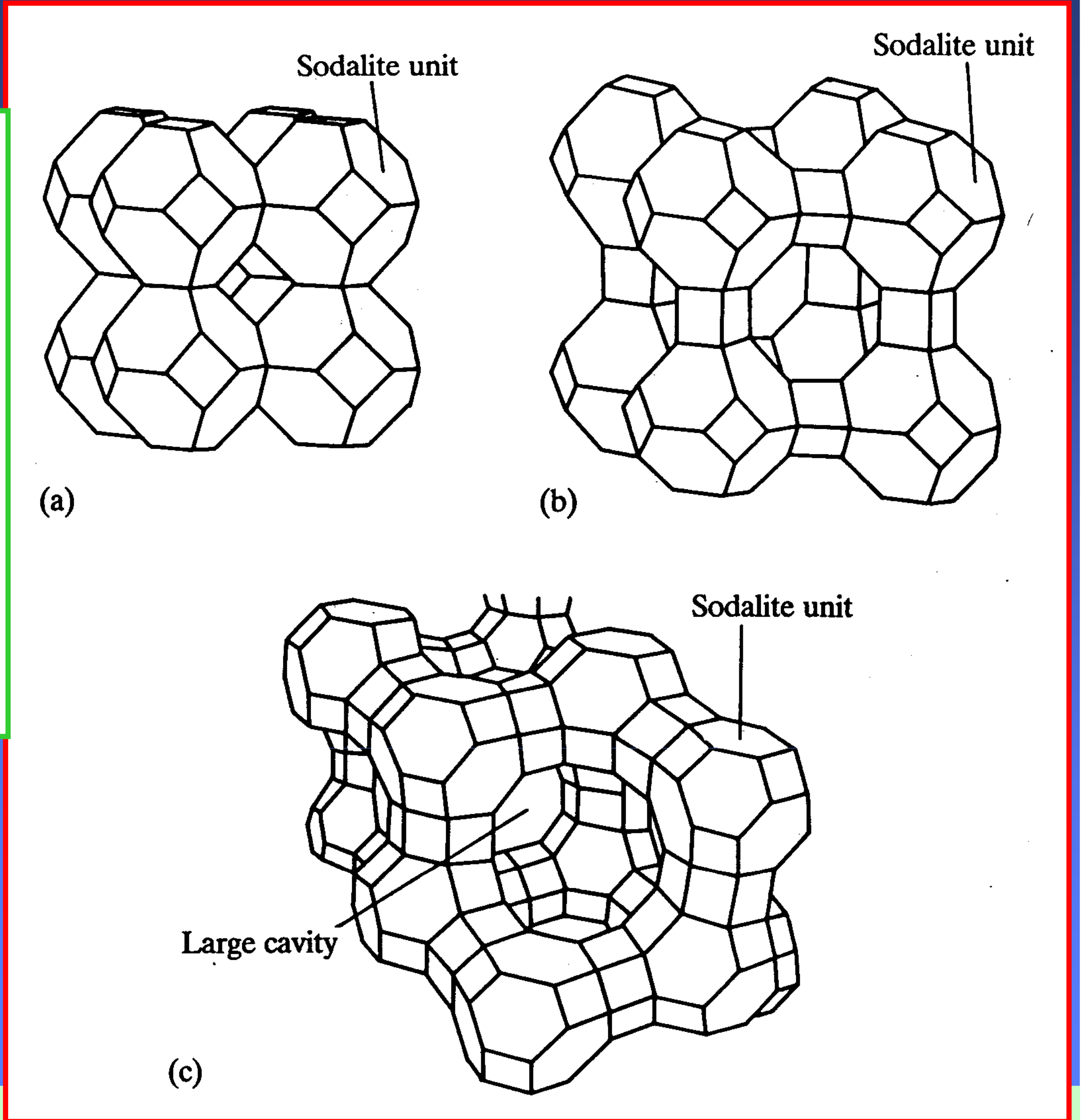


Zeolites

Aluminosilicates

Zeolite frameworks buit up from sodalite units:
(a) sodalite,
(b) A-zeolite,
(c) faujasite (X- and Y-zeolite).
(L. Smart, E. Moore, 'Solid State Chemistry', Chapman et Hall, 1992)

➔ **Low thermal stability**
➔ **Very large surface area**



Preparation of metal supported catalysts

➔ **Impregnation of the support with the precursor of the active phase.**

Support: high surface area oxide (100 - 400 $m^2.g^{-1}$), high internal porosity (1 $mL.g^{-1}$).

Precursor: soluble in the solvent and firmly bonded on the surface after the impregnation.

Active phase: obtained after transformation of the precursor (activation of the catalyst).

Ex.: **Shell 405 catalyst for N_2H_4 decomposition**:

Support: gamma alumina, specific surface area: 100-200 $m^2.g^{-1}$.

Precursor: hexachloroiridic acid H_2IrCl_6 in aqueous solution.

Impregnation procedure: wetness impregnation procedure. The volume of the impregnating solution corresponds to the volume of the porosity.

Drying: fixation of the precursor on the hydroxyl groups present at the alumina surface.

Activation, reduction in H_2, formation of iridium crystallites onto the surface of alumina.

The procedure is repeated in order to obtain the expected load on the alumina surface.

Preparation of metal supported catalysts

Two procedures for the impregnation:
- Impregnation with a solution excess;

➔ Dilute solution.
- Wetness impregnation;

➔ Concentrated solution

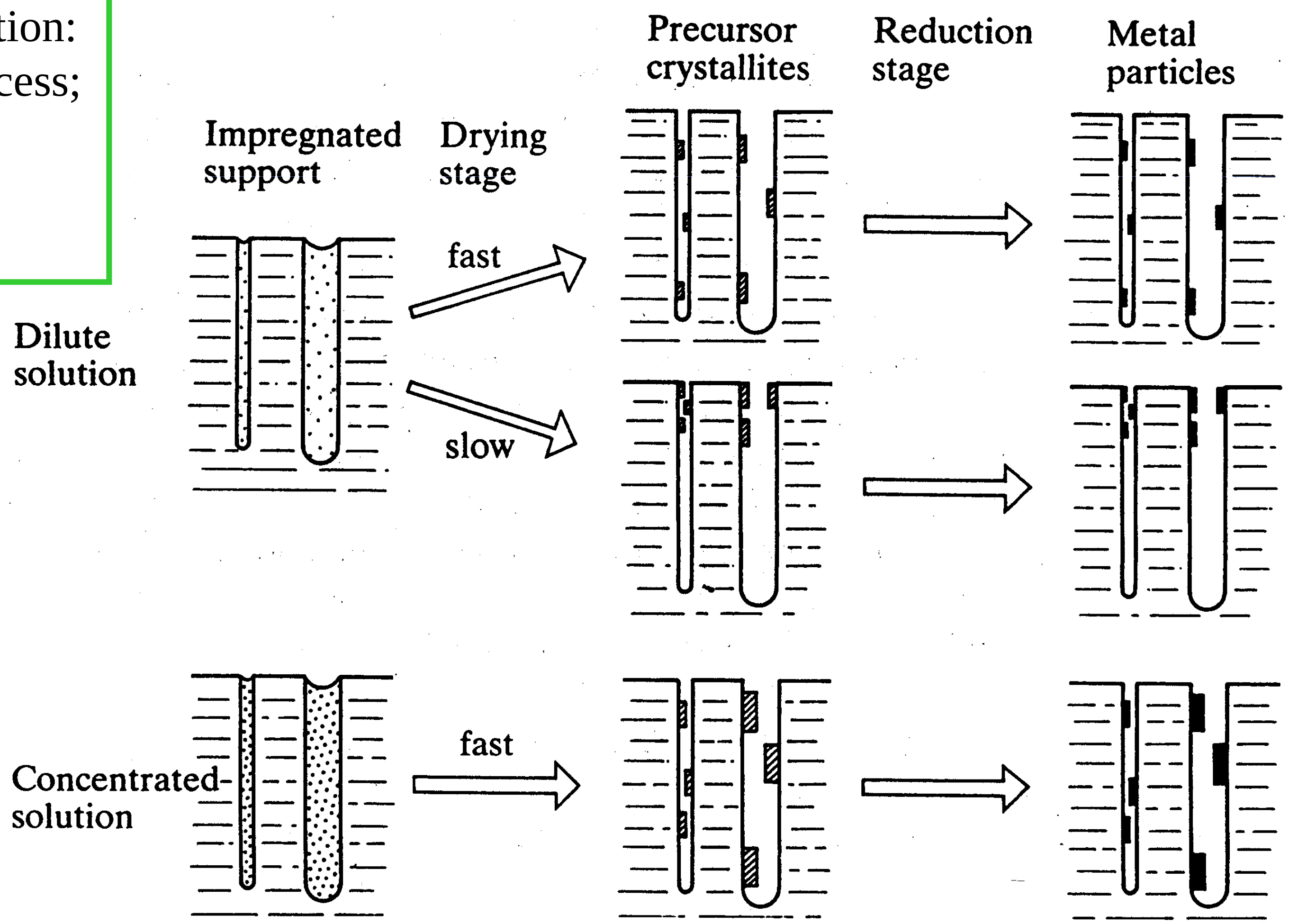
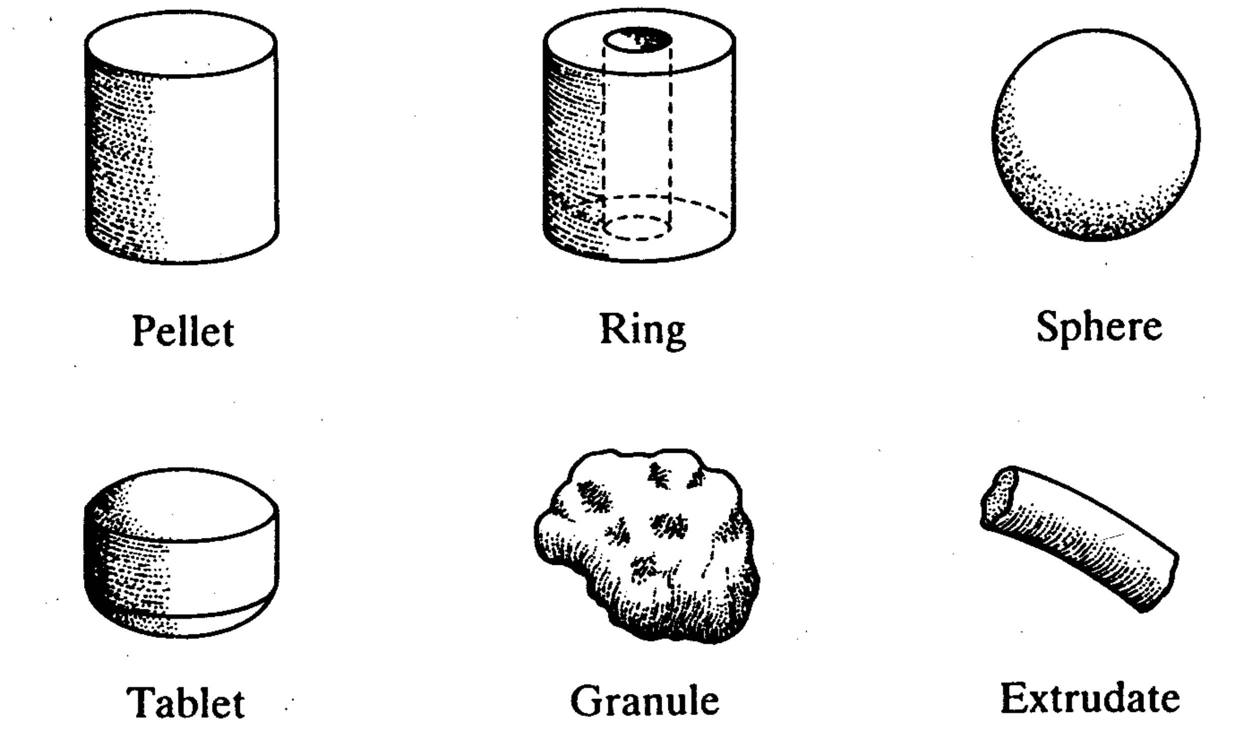
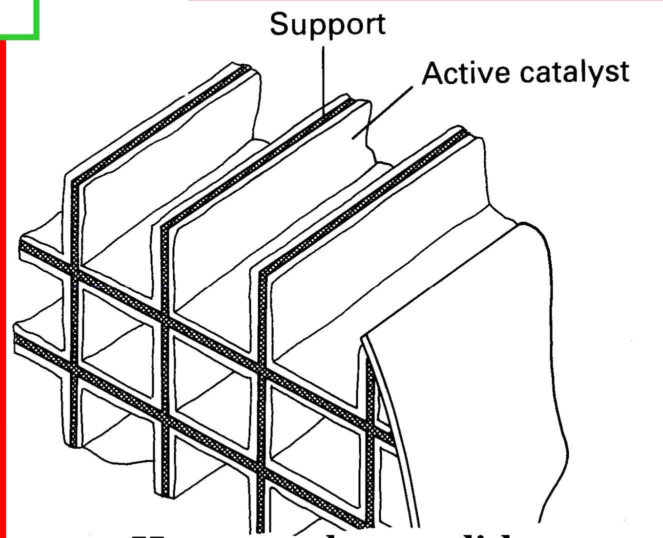


Illustration of the stages in the preparation of supported metal catalysts: the pores of the support are initially impregnated with either a dilute or a concentrated solution of the metal precursor [88-B].

Forms and shapes of catalysts

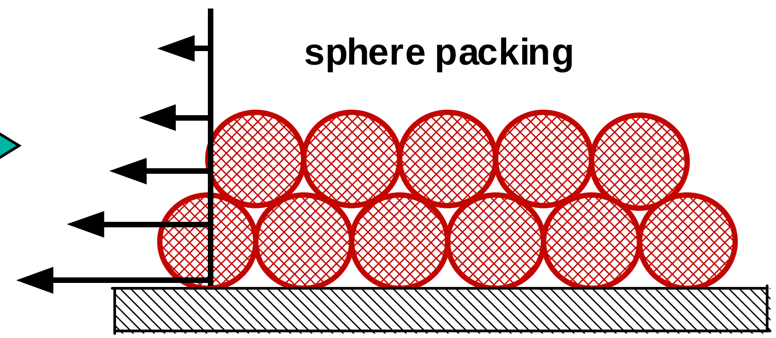
Various forms of coarse catalyst particles [Bond, 1987]



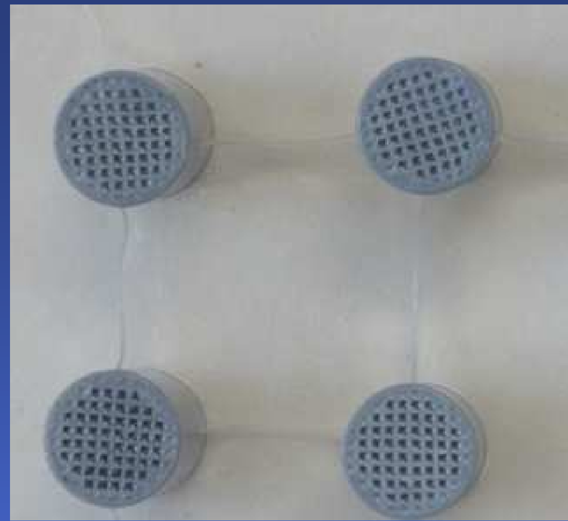


Honeycomb monolith

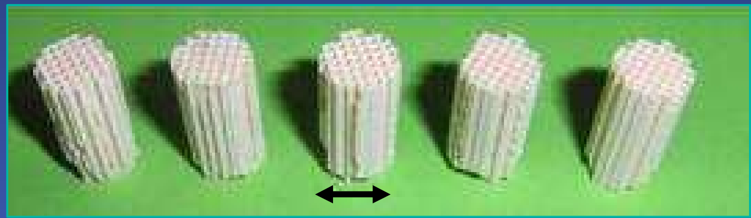
Influence of the shape on
- Pressure drop
- Diffusion effect
- Boundary effect (particles size = 1/10 diameter)



Cellular ceramics



1) Small honeycomb monoliths: square channels



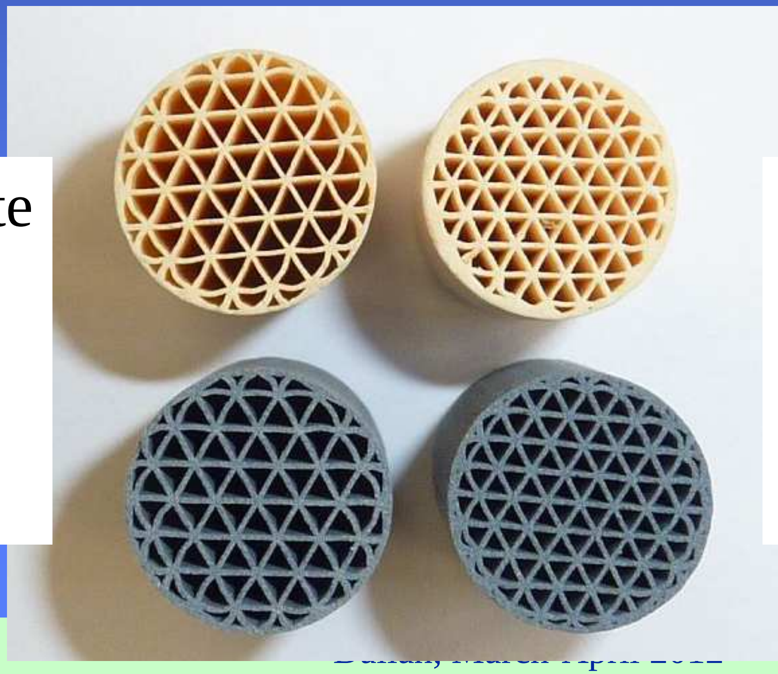
10 mm

2) Small honeycomb monoliths: triangular channels

Cordierite

400 cpsi

SiC



Cordierite

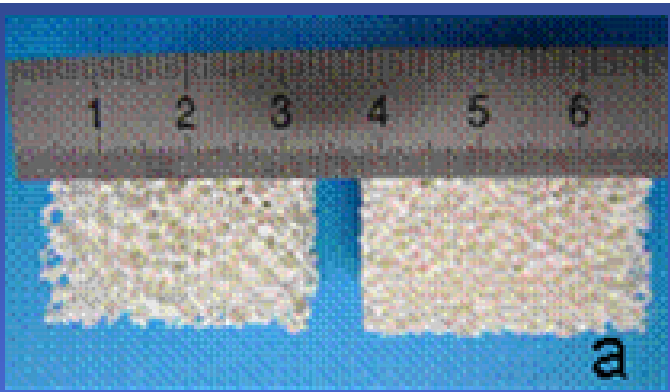
600 cpsi

SiC

Cellular ceramics

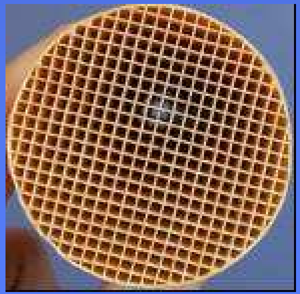
3) Foams: interconnected pores

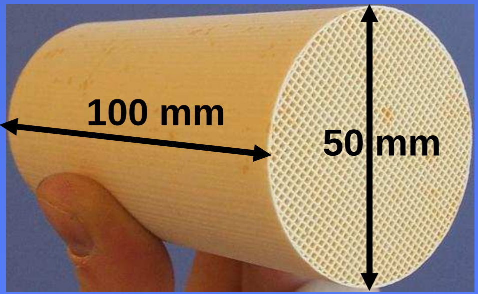
block of foam (alumina) cylindrical-shaped foam (mullite).



4) Large honeycomb monoliths

Monolith before preparation
100 or 400 cpsi
Cordierite or mullite



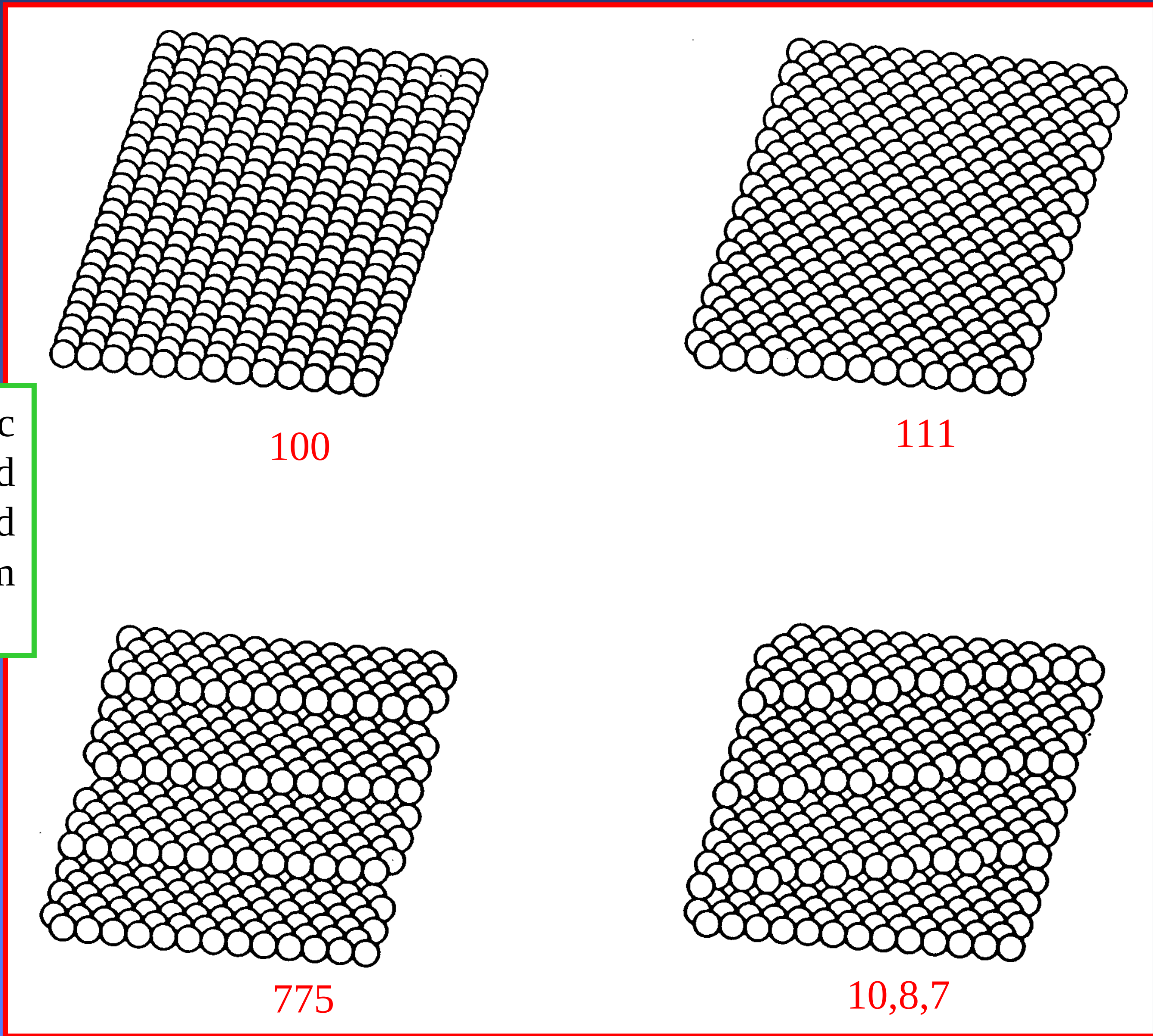


Characterization

Different tools are necessary to characterize the catalysts and their surfaces

Technique	Property probed
	Bulk information:
Elemental analysis	chemical composition:
Powder X-ray diffraction	phase composition, average crystallite size
Electron microscopy	texture, porosity, crystallite size distribution
EXAFS	environment of the target atoms
Infrared and Raman spectroscopy	structure
	Surface information
Physisorption	total surface area, pore volume, pore size distribution
Chemisorption	active surface area, dispersion
Work function	direction of flow of electrons to or from the surface
XPS	surface composition, oxidation states
Probe molecules (NH_3, CO,…)	acidity, basicity, metal surfaces

Ideal surfaces



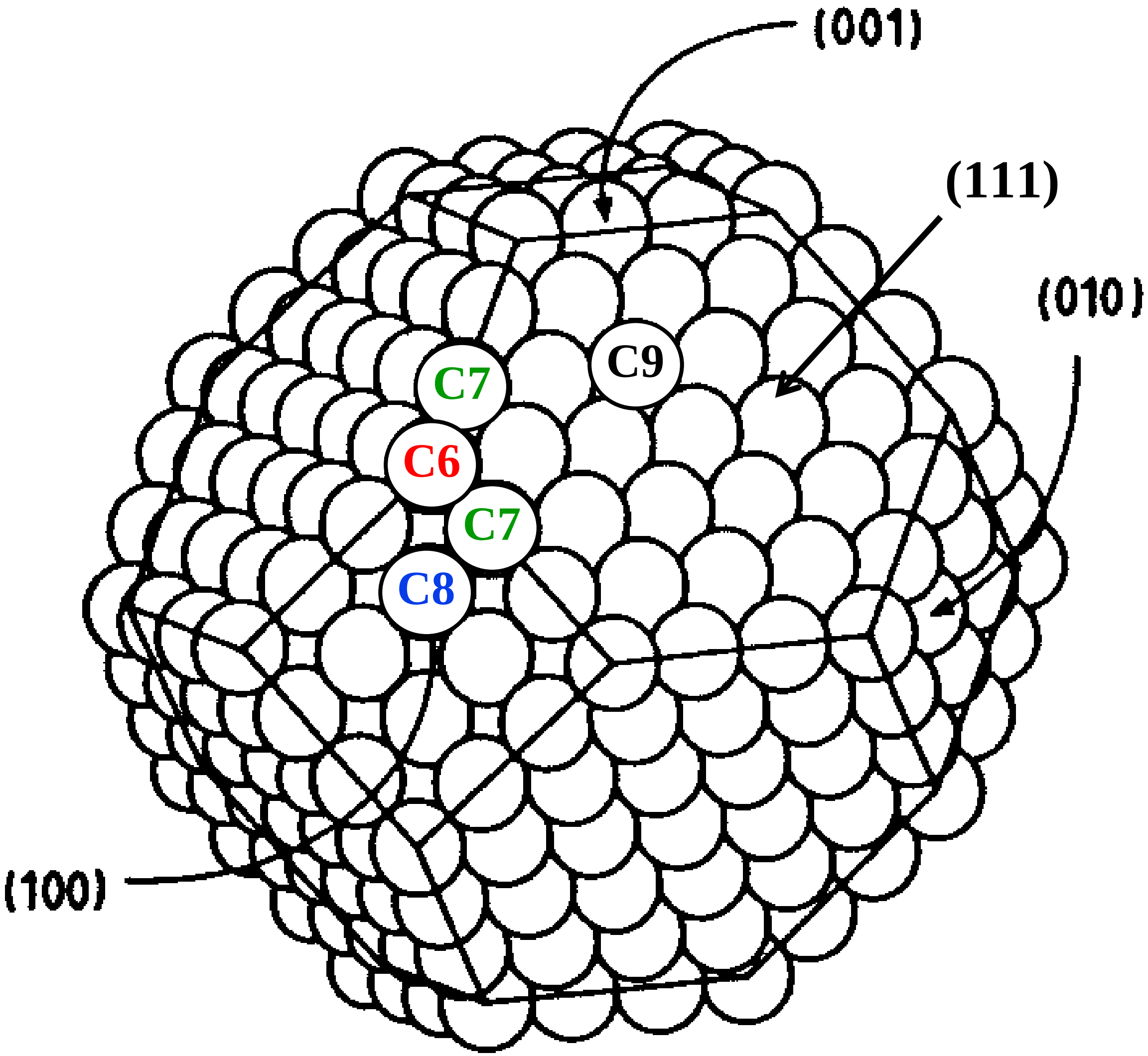
Ball model of idealized atomic structures of the **platinum** (111) and (100) crystal faces, the stepped platinum (775) and kinked platinum (10,8,7) surfaces [Campbell, 1988]

Ideal three-dimensional model

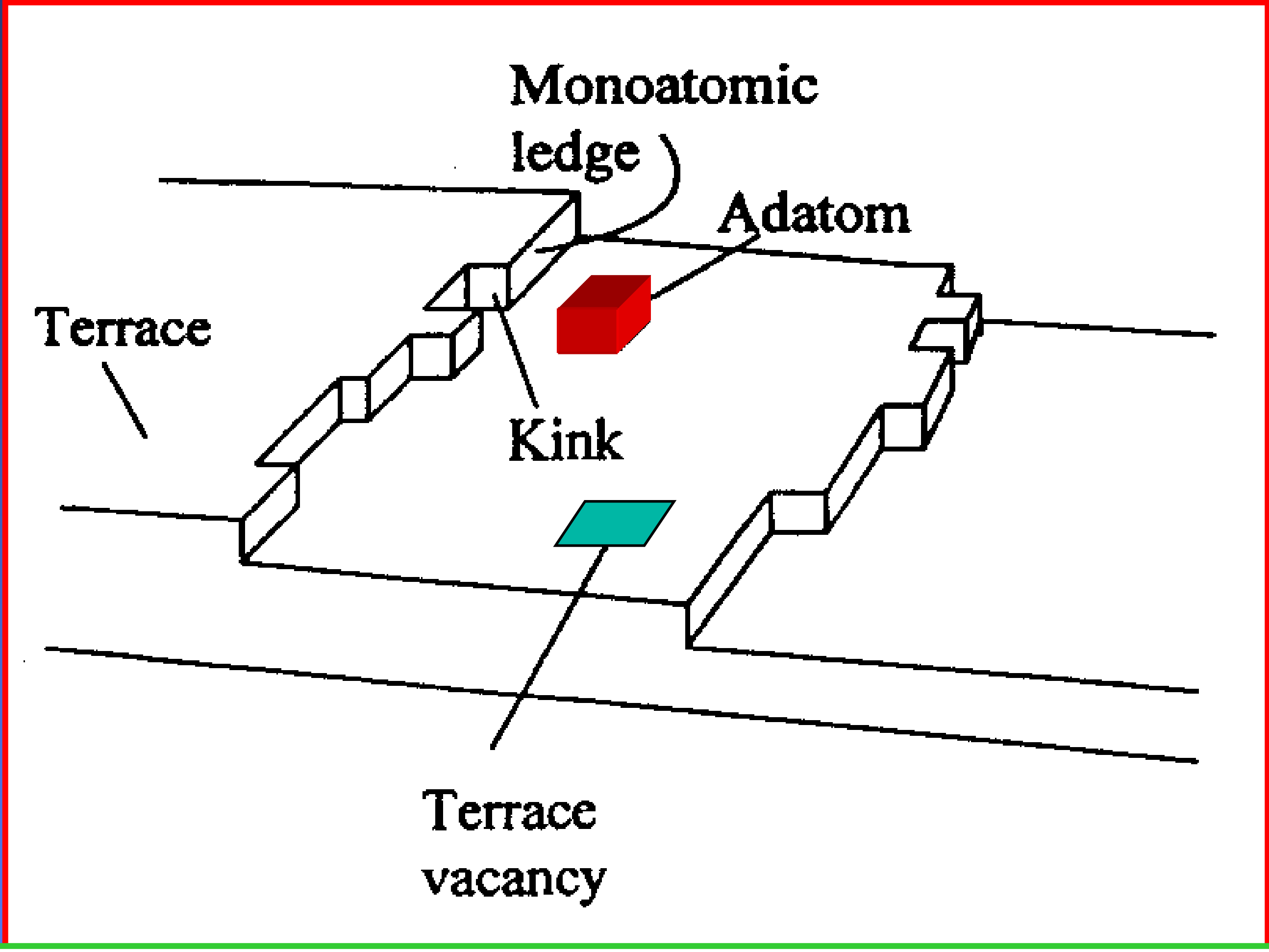
Close packed cubic arrangement. Truncated octahedron with faces (100) and (111)
[Thomas & Thomas, 1997]

Neighbour number

C6 (corner)	6
C7 (edge)	7
C8 (square surface)	8
C9 (hexagonal surface)	9
Bulk	12



Real surfaces

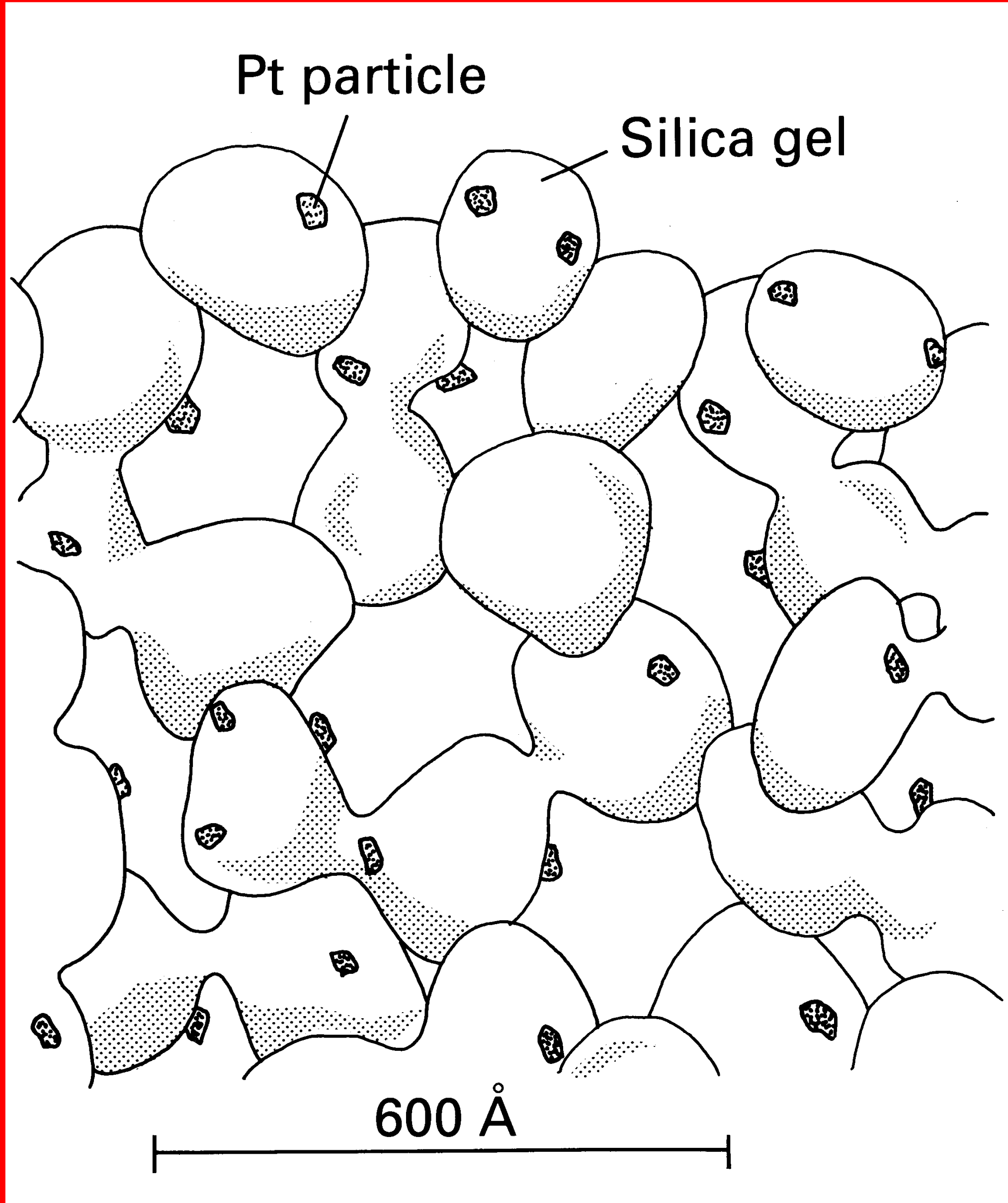


(111)

Model of a heterogeneous solid surface depicting different surface sites.
These sites (step, kink, terrace, adatom and vacancy) are distinguishable by their number of nearest neighbors [Attard & Barnes, 1998].

What is a solid catalyst ?

Model of supported catalysts



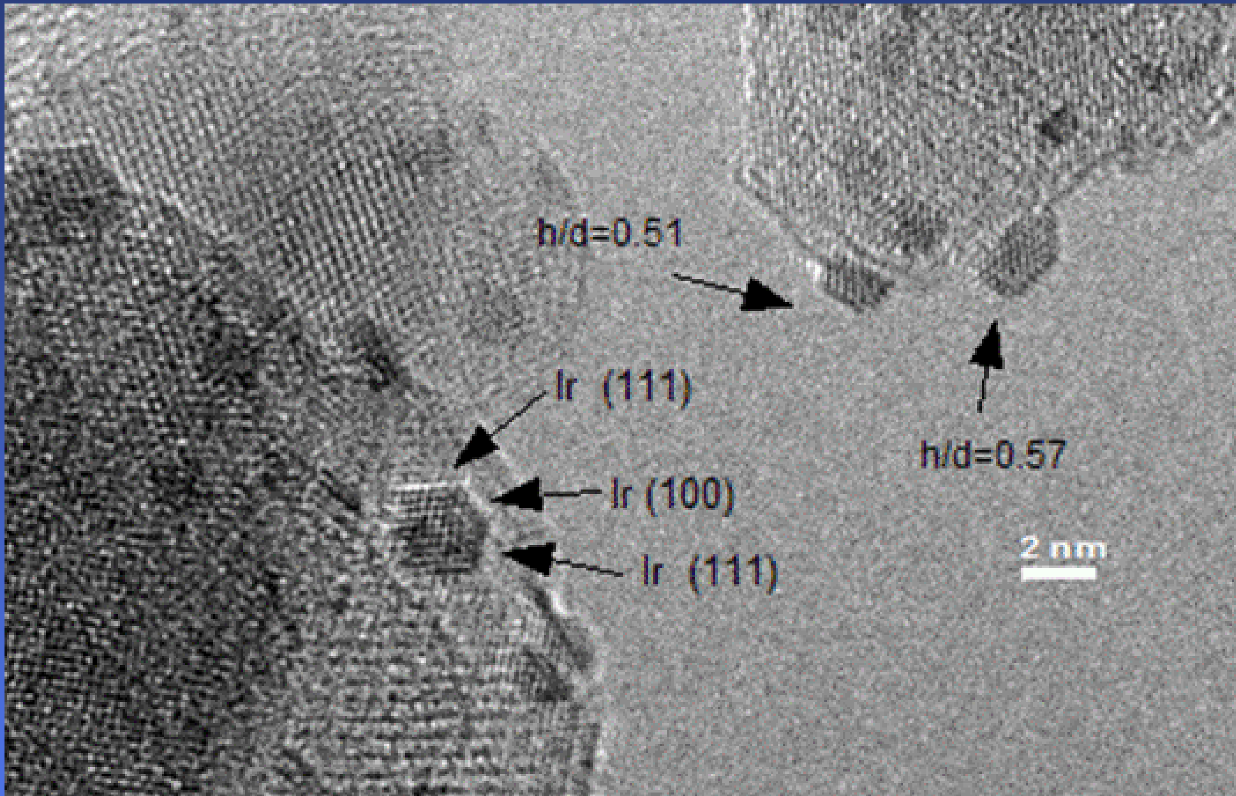
Schematic diagram of **platinum particle** supported on silica gel Pt/SiO_2

We have the same model for Ir/Al_2O_3.

Real surfaces probed by electron microscopy

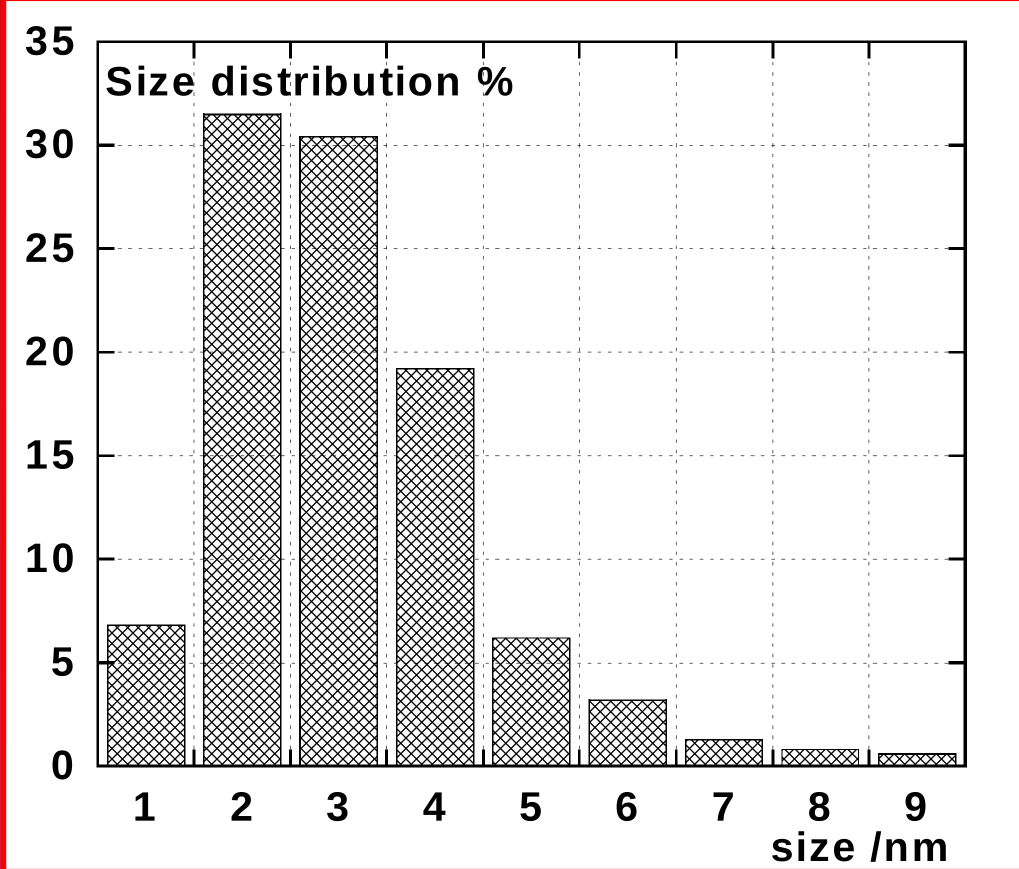
Transmission electron micrograph of an **Ir/Al_2O_3** catalyst.
the bar indicates the scale 100 nm.

Real surfaces probed by electron microscopy



TEM picture of Ir/Al2O3 sample showing the hemi-cuboctahedral shape of iridium crystallites.

Particle size distribution



Particle size distribution of a **Ir/Al_2O_3 catalyst**. The data are from the previous micrograph (manual counting).

Different mean sizes (values in nm):	**calculated**	**experimental**
Number $\Sigma x_i d_i$ (x_i = number fraction)	3.1	
Surface $\Sigma x_i d_i^3 / \Sigma x_i d_i^2$	4.7	4.7 (dispersion)
Volume $\Sigma x_i d_i^4 / \Sigma x_i d_i^3$	5.6	5.5 (XRD)

The active centers

Activity:

specific activity (per g of catalyst)
intrinsic activity (per active center)
transformation rate:
$\%\text{-}R_A$ = 100 x number of A-mol converted/ total number of A-mol

Selectivity:

choice between several paths
A ➔ B or A ➔ C
selectivity factor $S_B = x_B/(x_B + x_C)$ x_B = mol-fraction of B
depends on the activation energies
selective poisoning

Stability:

thermal stability: sintering effect
mechanical stability: attrition
chemical stability: modification of the active sites
poisons (sulfur, ammonia, carbon monoxide, …)

➔ Influence of dispersion or crystallite size on activity?

Example: decomposition of hydrazine

Two successive reactions:

$$3\ N_2H_4 \rightarrow 4\ NH_3 + N_2 \qquad (1)$$

$$4\ NH_3 \rightarrow 2\ N_2 + 6\ H_2 \qquad (2)$$

Study of step 1: decomposition of hydrazine into ammonia

Catalysts: 1 %-Ir/Al_2O_3 diluted in alumina (1 to 20)

catalyst	**dispersion** in %	**activity** mol/g.h	**intrinsic activity** (mol-N_2H_4)/(mol-Ir).h
A	48	2.2	88400
B	10	0.50	96000
C	3	0.13	95000
D	40	1.9	95000

➔ Different specific activities

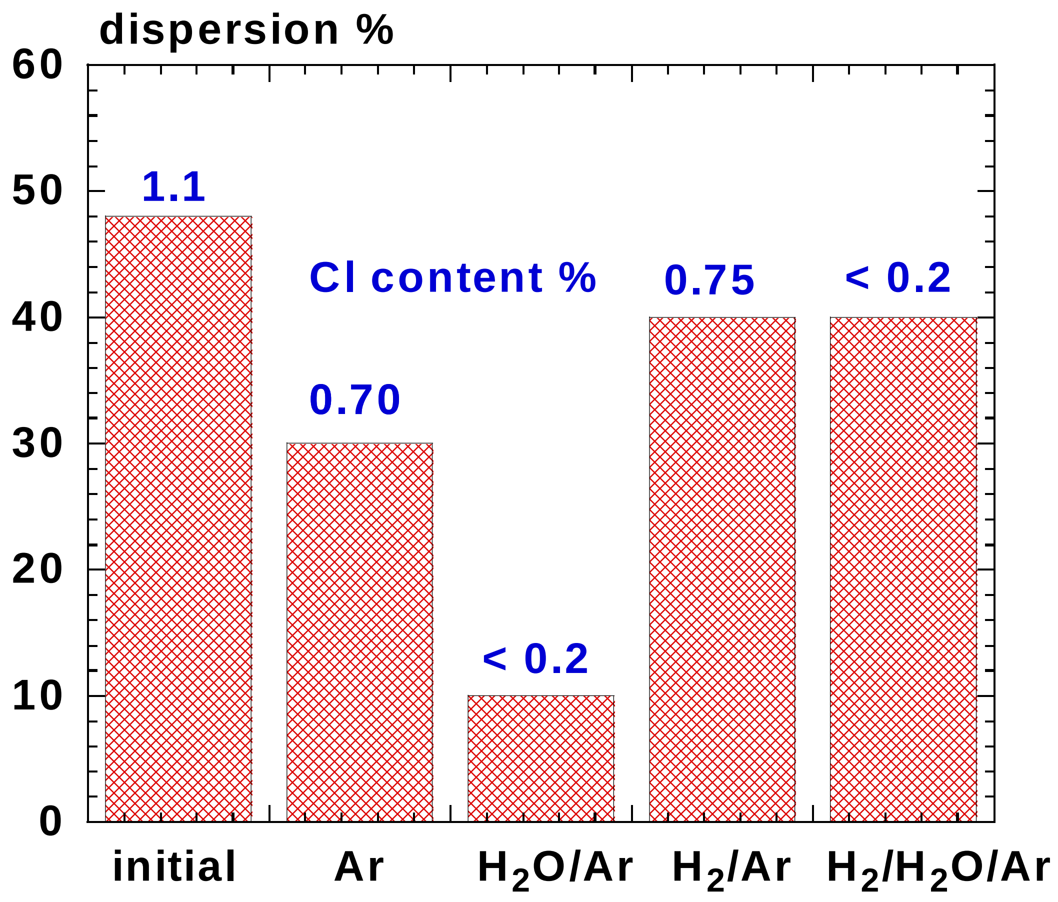
➔ Same intrinsic activity

➔ No influence of crystallite size

Catalyst stability

•Influence of thermal treatment on dispersion.
•Influence of the nature of the gas.

Conditions: 1 % Ir/Al_2O_3; 20 h; 500 °C

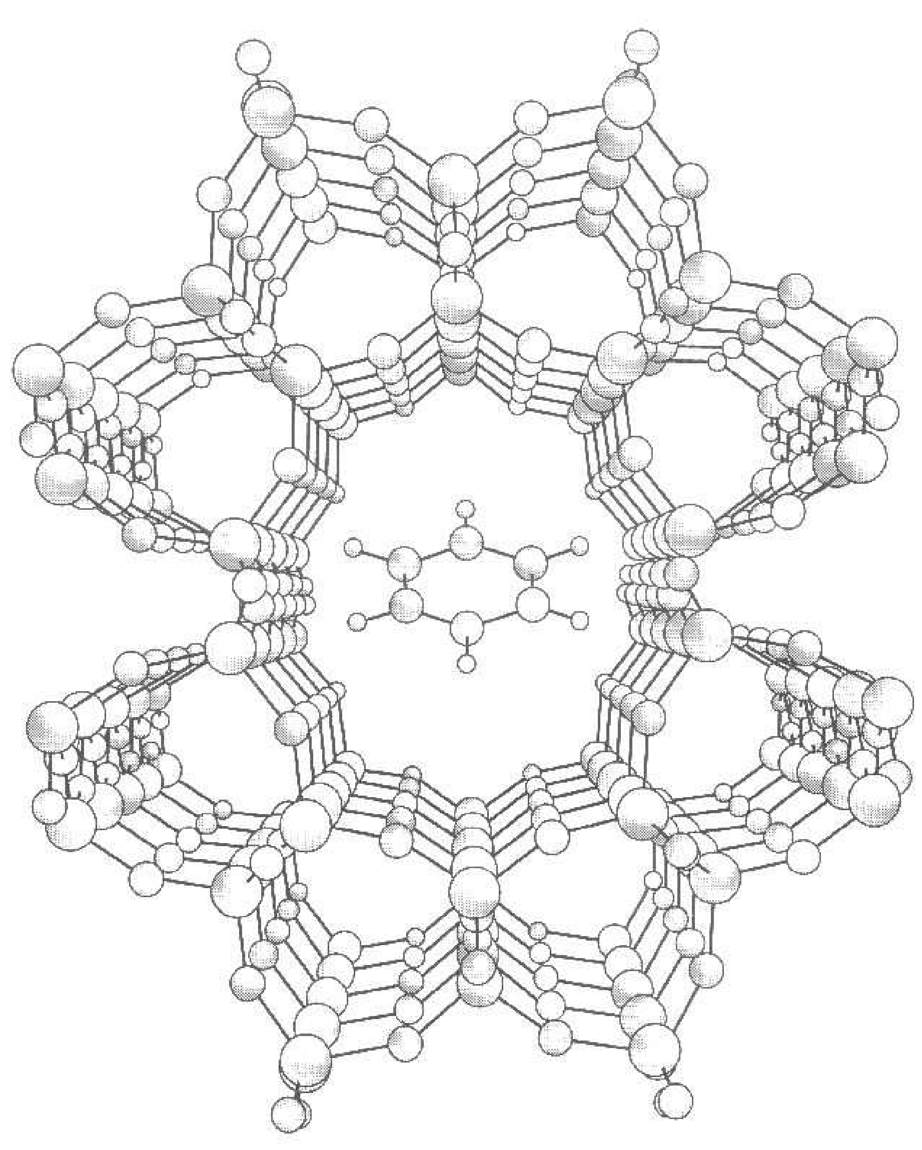


- ➢ Role of H_2O in sintering
- ➢ Role of surface OH group in pure Ar
- ➢ Protection against sintering in H_2
- ➢ Decrease of Cl content

Catalyst selectivity

Shape selectivity in zeolites

A view through the channels of theta-1 zeolite with an adsorbed benzene molecule in one of the channels
[Shriver, Atkins, 1994]
Opening of the channels typically 3 to 10 Å for different zeolites.
➔ **Microporous materials**



- ➔ Absorption of molecules small enough to enter the channels.
- ➔ Exclusion of larger molecules.
- ➔ Control over catalytic reactions unattainable with silica or alumina.

Other examples of selectivity

$$C_2H_5OH(g) \xrightarrow{Cu} CH_3CHO(g) + H_2(g)$$

$$\xrightarrow{Al_2O_3} C_2H_4(g) + H_2O(g)$$

$$\xrightarrow{MgO\text{-}SiO_2} CH_2{=}CH\text{-}CH{=}CH_2 + H_2O$$

$$\xrightarrow{\text{Zeolite ZSM-5}} \text{synthetic gasoline} + H_2O$$

$$N_2H_4 \rightarrow NH_3 + N_2$$

$$\rightarrow H_2 + N_2$$

$NH_3OH^+NO_3^-$ (HAN)

$$\rightarrow N_2 + 2\,H_2O + O_2$$

$$\rightarrow 2\,NO + 2\,H_2O$$

$$\rightarrow NO_2 + 0.5\,N_2 + 2\,H_2O$$

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End of Lecture 1