

# Heterogeneous catalysis (I)

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## Contents

1. Introduction: the importance of catalysis and some historical data.
2. Concepts:
  - Catalyst
  - Activation energy
  - The catalytic cycle
3. The catalyst selection
4. Heterogeneous catalysis and surface science
  - Structural consideration
  - Surface and adsorption

## **Contents**

5. About the “active sites” of surfaces
  - Relationships of crystal defects and catalytic activity
  - The nature of the crystallographic layer
  - The geometric factor
  - Bi - functional catalysts
  - Acid sites in zeolites
  - Electronic properties
6. Catalysts preparation:
  - Bulk catalysts
  - Supported catalyst
7. The catalysts deactivation / regeneration

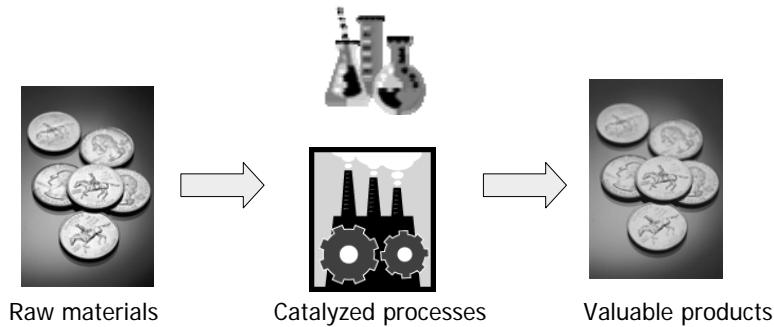
3

## **■Introduction**

4



## The importance of catalysis

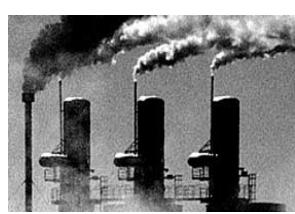
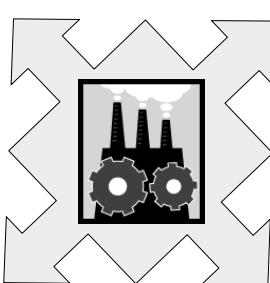


- More than 90% of the industrial processes are catalyzed (chemical, pharmaceuticals, materials, polymers, energy, etc)

5



## The importance of catalysis



Environmental  
Catalysis

## What to know ?



There is no a single theory of heterogeneous catalysis, but only a series of principles to interpret and predict the processes that occur, mainly in the gas – solid interface.

### Catalysis is an inter-disciplinary science!!!

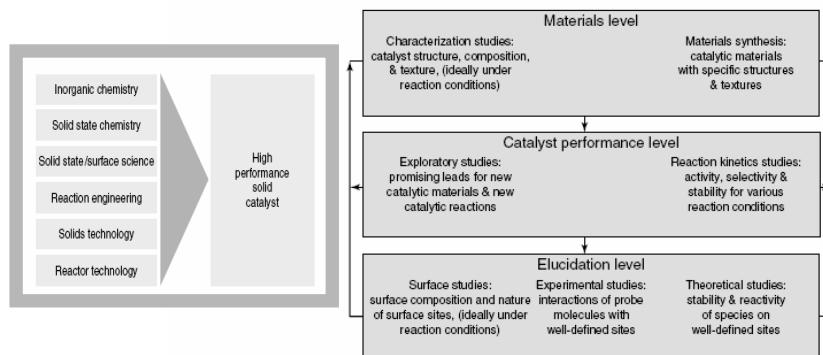


Fig. 6 Levels of study in heterogeneous catalysis research.

## Some historical data



Historical summary of the development of industrial biocatalytic processes

Year	Process	Micro-organism/Enzyme
-6000	Beer brewing by malting procedure	Malt enzymes
-3000	Wine making by fermentative conversion of grape juice sugars	Yeast a.o.
-2000	Alcohol(ic drinks) by fermentation various carbohydrate sources Bread and other leavened bakery products by carbon dioxide and alcohol	Yeast a.o. Baker's yeast
-800	Vinegar (acetic acid) by aerobic fermentation of ethanol Cheese making (coagulation) by casein hydrolysis with calf stomach extract	Acetobacter Calf rennet (chymosin)

Fermentation is the oldest type of catalytic processes. Several thousand years BC beer, bread and winemaking were typical fermentation processes. Today, thousands of different catalysts (enzymes) are available to perform these transformations, which has been classified by six major groups of reactions:

Oxidation and reduction	Oxidoreductases
Transfer of functional groups	Transferases
Hydrolysis	Hydrolases
Addition and elimination	Lyases
Isomerisation	Isomeraseas
Carbon bond formation	Ligases



## Industrial catalyzed processes

Historical summary of the development of industrial processes

Year	Process	Catalyst
1750	H <sub>2</sub> SO <sub>4</sub> lead chamber process*	NO/NO <sub>2</sub>
1870	SO <sub>2</sub> oxidation	Pt
1880	Deacon process (Cl <sub>2</sub> from HCl)	ZnCl <sub>2</sub> /CuCl <sub>2</sub>
1885	Claus process (H <sub>2</sub> S and SO <sub>2</sub> to S)	Bauxite
1900	Fat hydrogenation	Ni
1910	Methane from syngas	Ni
	Coal liquefaction	Fe
	Upgrading coal liquids	WS <sub>2</sub>
	Ammonia synthesis (Haber-Bosch)	Fe/K
	NH <sub>3</sub> oxidation to nitric acid	Pt
1920	Methanol synthesis (high pressure process)	Zn, Cr oxide
	Fischer-Tropsch synthesis	Promoted Fe,Co
	SO <sub>2</sub> oxidation	V <sub>2</sub> O <sub>5</sub>
	Acetaldehyde from acetylene*	Hg <sup>2+</sup> /H <sub>2</sub> SO <sub>4</sub>
1930	Catalytic cracking (fixed bed, Houdry)	Clays
	Ethene epoxidation	Ag
	Polyvinyl chloride*	Peroxide
	Polyethylene (low density, ICI)*	Peroxide
	Oxidation of benzene to maleic anhydride	V
	Alkylation*	HF/H <sub>2</sub> SO <sub>4</sub>
1940	Hydroformylation, alkene to aldehyde*	Co
	Catalytic reforming (gasoline)	Pt

Among the first industrial catalytic processes are a few inorganic oxidation processes, as the Deacon process (HCl into Cl<sub>2</sub>) and the production of sulfuric acid. The production of sulfuric acid was commercialized in the mid-18th century. In the so-called lead chamber process the oxidation of SO<sub>2</sub> into SO<sub>3</sub> was catalyzed by NO.



Many reasons underlie the development of the science and technology of catalysis.

One of the main driving forces is the availability of the raw materials.  
As an example, in the energy field:

Biomass was originally predominant.  
Later coal became the most important industrial feedstock.  
Coke oven gas components played the role of base chemicals.  
Subsequently, oil took over the place of coal and the technological scene changed profoundly (petrochemical industry)  
More recently, natural gas resources appear to have become much more important and a lot of research in catalysis is aimed at processes based on natural gas.

It is also clear that biomass is experiencing a revival as an environmental care alternative to oil (biodiesel, syngas and Fischer – Tropsch synthesis, etc.

In recent years environmental considerations have been also the major driving force for novel catalytic processes.

## ■ Concepts

11

### What is a catalyst?



The name 'catalysis' was coined by Berzelius in 1836. He concluded that besides 'affinity' a new force is operative, the 'Catalytic Force'. With this, try to focus the behavior of some substances that permit initiate reaction of decomposition or synthesis. At that time no understanding existed, on a molecular level, of reaction rates.

### Definition of catalyst

According to the IUPAC (1976) a catalyst is a substance that, being present in small proportions, increases the rate of attainment of chemical equilibrium, without itself undergoing chemical change.

### Comments

- This means that catalyst is not a reactant (is not consumed by the reaction)
- In fact, catalyst undergoes transitory changes to catalyze the reaction, and permanent changes which typically leads to the catalyst deactivation

12

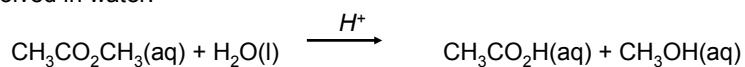


## Types of catalysts:

Catalytic processes can be divided in three main types: heterogeneous homogeneous and enzymatic processes.

→ In a **heterogeneous reaction**, the catalyst is in a different phase from the reactants. Normally, the catalyst is a solid and reactants are fluids (liquids or gases). It is characterized by the presence of "active sites" on the catalyst surface.

→ In a **homogeneous reaction**, the catalyst is in the same phase as the reactants (as the hydrolysis of esters by acid catalysts, all reactants and catalyst are dissolved in water):



→ The **enzymatic catalysis (biocatalysis)** have an intermediate character between homogeneous and heterogeneous processes, because although the enzymes and reactants are in the same phase (solution), they have "active sites" in their structures.

13



## Kinetic Vs. Thermodynamic: the necessity of catalysts

A reaction may have negative  $\Delta G$ , but the reaction rate may be so slow that there is no evidence of it is occurring.

Conversion of diamond to graphite is a thermodynamic favor process ( $\Delta G < 0$ ).

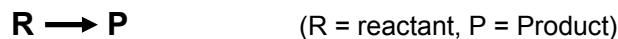


**Kinetics makes this reaction nearly impossible**  
*(Fortunately, one diamond is forever)*

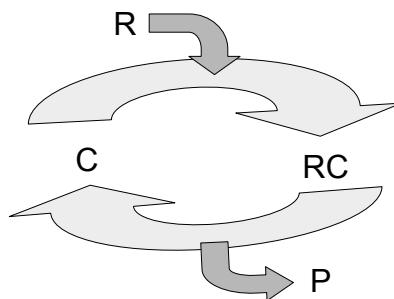
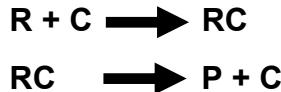
14



Thus, for a given reaction:



where the reaction rate is null or negligible, the use of a catalyst (C) provides a new reaction pathway through the formation of an intermediate species on the catalyst surface



A catalyzed reaction is therefore a sequence of elemental steps, continuously repeated, where the catalyst is regenerated after each reaction cycle.

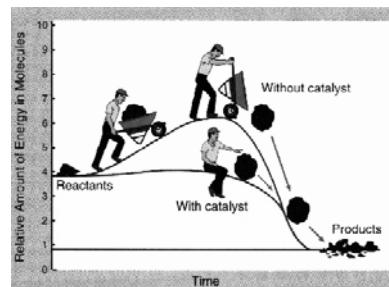
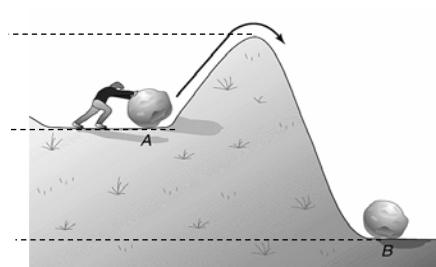
15

## Activation Energy



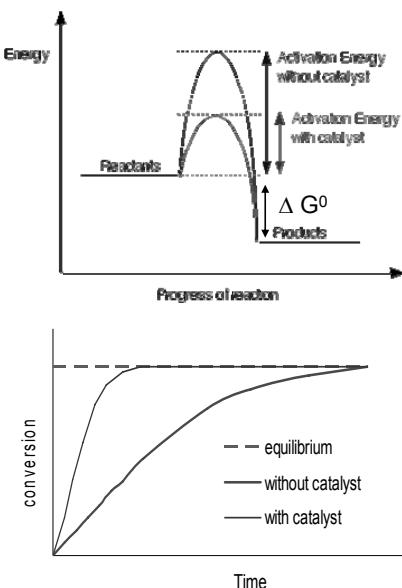
**Activation Energy** : The energy required to overcome the reaction barrier. Usually given a symbol  $E_a$  or  $\Delta G^\ddagger$

The Activation Energy ( $E_a$ ) determines how fast a reaction occurs.  
**The lower the Activation barrier, the faster the reaction**



16

## Activation Energy



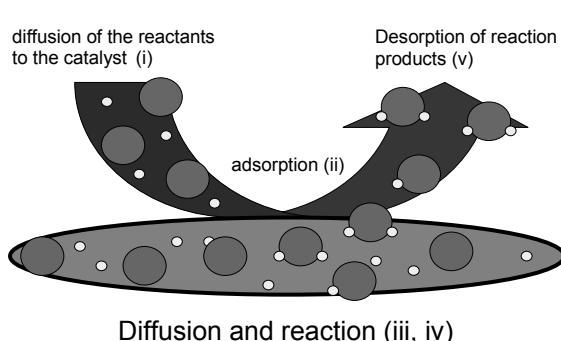
Nevertheless, taking into account that the initial and final states are the same by both un-catalyzed and catalyzed process, the overall free Gibbs energy,  $\Delta G^0$  is therefore identical.

This means that all the thermodynamic parameters, including the equilibrium constant

$$K = \exp(-\Delta G^0/RT)$$

were not affected and catalysts only permit to attain the equilibrium more quickly.

17



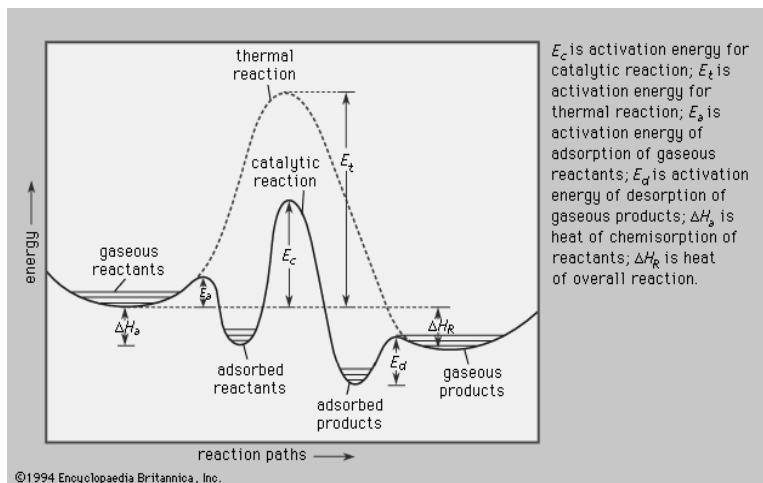
The progress of a heterogeneous catalytic reactions can be resolved into at least five distinct steps:

- (i) Diffusion of the reactants to the catalyst
- (ii) Adsorption of reactants (reactant-surface)
- (iii) The chemical changes on the surface, formation of the adsorbed complex
- (iv) Decomposition of the adsorbed complex (product-surface)
- (v) Desorption and diffusion of the reaction products from the catalyst

18



Each step of the heterogeneous catalytic cycle involves a characteristic energy.



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19

### Steps of reaction

(i, ii) diffusion and adsorption

If no diffusion restriction occurs, one or more of the reactants are **adsorbed** on to the surface of the catalyst

**Be careful!**

Adsorption is where something sticks to a surface. It isn't the same as Absorption where one substance is taken up within the structure of another.

Differences between physisorption and chemisorption will be analyzed before.

**Heterogeneous Catalysis Must Always  
be Preceded by Adsorption!!!**

20

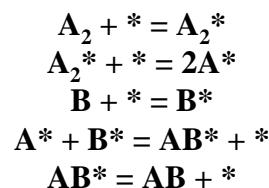


How adsorption is produced on the catalyst surface  
determine the reaction mechanism:

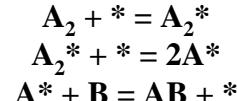
Example: The Reaction



**Langmuir-Hinshelwood mechanisms**



**Eley-Rideal mechanism:**



21

## Eley-Rideal or Langmuir-Hinshelwood?



**For the Eley-Rideal mechanism:**

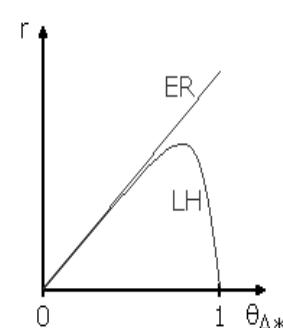
the rate will increase with increasing coverage until the surface is completely covered by  $A^*$ .

**For the Langmuir-Hinshelwood mechanism:**

the rate will go through a maximum and end up at zero, when the surface is completely covered by  $A^*$ .

This happens because the step  $B + * = B^*$

cannot proceed when  $A^*$  blocks all sites.



The trick is that the step  $B + * = B^*$

requires a free site.

22



(iii, iv) The adsorbed species can move, interacting between them and with the catalyst surface and **reaction happens** through the formation and decomposition of an intermediate adsorbed specie.

At this stage, both of the reactant molecules might be attached to the surface, or one might be attached and hit by the other one moving freely in the gas or liquid.

The mobility of chemical species on the catalyst surface is also noticeable, phenomena such the spillover of hydrogen atoms play an important role in hydrogenation reactions.

The apparition of bonds or interactions with the catalyst surface debilitates or destroys the intra-molecular bonds, inducing the reactions.

(v) The product from the decomposition of the intermediate specie should be **desorbed and diffuse in the flow**.

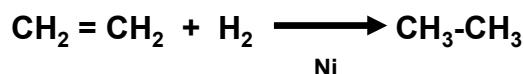
Desorption simply means that the product molecules break away. This leaves the active site available for a new set of molecules to attach to and react.

23



### Example:

#### *The hydrogenation of a carbon-carbon double bond*



The simplest example of this is the reaction between ethene and hydrogen in the presence of a nickel catalyst.

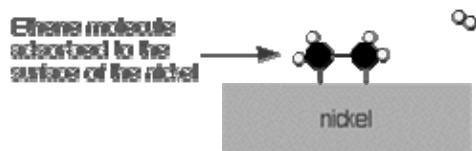
In practice, this is a pointless reaction, because you are converting the extremely useful ethene into the relatively useless ethane.

Ethene hydrogenation is widely used as reaction test of new hydrogenation catalysts

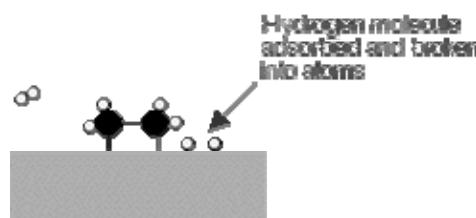
24



Ethene molecules are adsorbed on the surface of the nickel. The double bond between the carbon atoms breaks and the electrons are used to bond it to the nickel surface

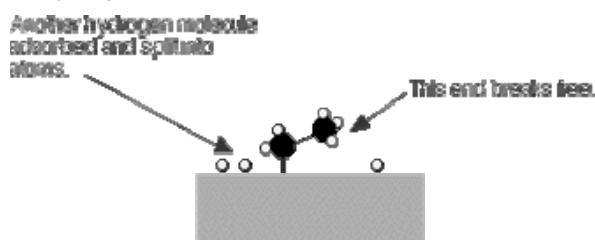


Hydrogen molecules are also adsorbed on to the surface of the nickel. When this happens, the hydrogen molecules are broken into atoms. These can move around on the surface of the nickel.

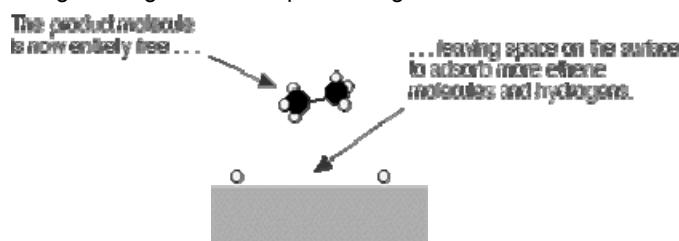


25

If a hydrogen atom diffuses close to one of the bonded carbons, the bond between the carbon and the nickel is replaced by one between the carbon and hydrogen



As before, one of the hydrogen atoms forms a bond with the carbon, and that end also breaks free. There is now space on the surface of the nickel for new reactant molecules to go through the whole process again.



26

## ■ The catalyst selection

27

### Criteria for a good catalyst

Chemical related aspect

Activity

Selectivity

Stability (thermal properties)

Non-chemical

Morphology

Mechanical strength

Cost

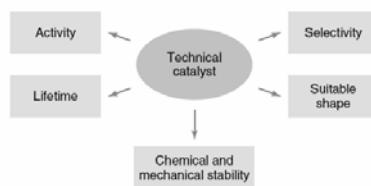
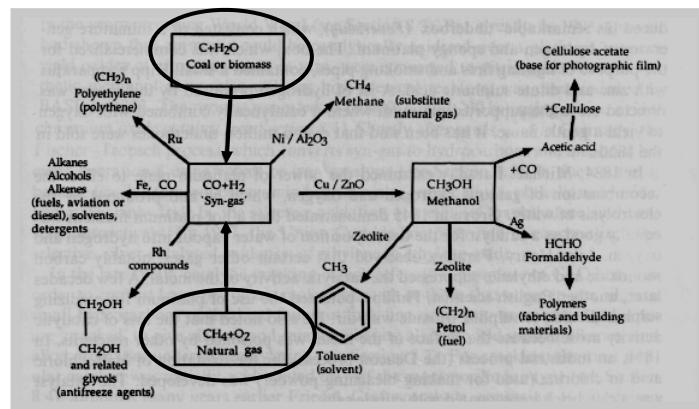


Fig. 5 Catalyst properties.

28



## About the catalyst selection

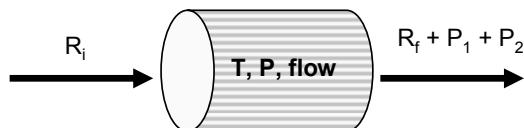


Example: Transformations of "syngas" obtained by gasification on steam of coal or biomass, or by partial oxidation of natural gas. Depending on the catalyst used, a wide diversity of products can be generated.

29



## Definitions of conversion and selectivity



Conversion is defined as the fraction of reactant transformed:

$$\text{Conversion (\%)} = X_T = [R_i] - [R_f] / [R_i] * 100$$

While selectivity is defined for each product on the basis of its formation:

$$\text{Selectivity (\% } P_x) = [P_x] / \sum [P] = [P_1] / [R_i] - [R_f] * 100$$

The reaction yield (or partial conversion) for a given product is therefore:

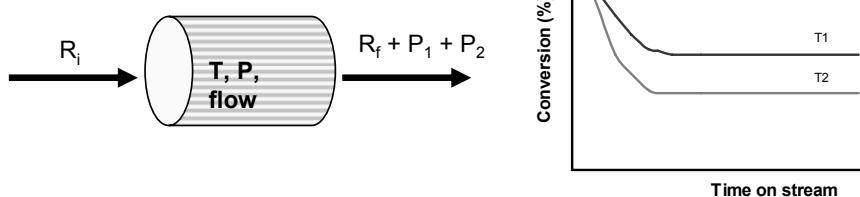
$$Y (\% i) = X_T S_i = [P_1] / [R_i]$$

30



### Be careful with the meaning of the curves X vs time!!

Continuous flow reactors



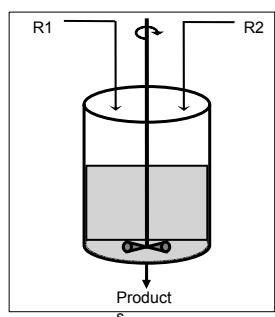
Curves of conversion vs reaction times are often used to determine the catalyst stability. In continuous flow reactors conversion tends to decrease until reaching the stationary state at each experimental conditions. The longer time at constant conversion values, the more stable catalysts.

31



### Be careful with the meaning of the curves X vs time!!

Semicontinuous reactors



In semicontinuous reactors where reactants are loaded initially, conversion vs time curves indicates the conversion of this charge until the equilibrium is reached, then, the reactor is discharged.

Obviously, catalysts are not activated during reaction.

32



## The catalytic activity

In general, the rate of any gas-solid or liquid-solid-catalyzed reaction can be expressed as the product of the apparent rate coefficient  $K$  and a pressure- (or concentration-) dependent term:

$$r = K P_i \quad \begin{matrix} K, \text{ apparent rate coefficient} \\ P_i, \text{ Partial pressure of reactant } i \end{matrix}$$

this rate coefficient ( $K$ ) will change as the prevailing conditions of the reaction vary, and it is convenient to use the Arrhenius equation:

$$k = A' \exp(-E'/RT)$$

where  $A'$  is a temperature-independent **pre-exponential factor** and  $E'$  is the **apparent** activation energy of the catalytic reaction.  $E'$  cannot be expected to be the true activation energy because the concentration of reactant at the catalyst surface will be temperature-dependent.

Thus, the catalytic activity can not be defined  
in terms of apparent activation energy.

33



## Turnover frequency

Far more convenient is the use of the concept of turnover frequency or turnover number. The turnover frequency (often designated TOF) is simply the number of times  $n$  that the overall catalytic reaction in question takes place per catalytic site per unit time for a fixed set of reaction conditions (temperature, pressure or concentration, reactant ratio, extent of reaction).

$$\text{TOF} = \frac{\text{number of molecules of a given product}}{(\text{number of active sites}) \times (\text{time})}$$

It is sometimes difficult to determine the number of active sites. For such situations,  $S$  is often replaced by the total, readily measurable, area  $A$  of the exposed catalyst.

or

$$\text{TOF} = \frac{1}{S} \frac{dn}{dt}$$

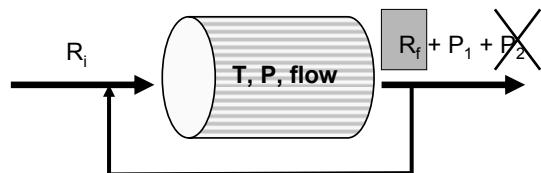
where  $S$  is the number of active sites.

Note that TOF is a rate, not a rate coefficient, so that it is necessary to specify all the prevailing conditions of the catalytic reaction.

34



## About the catalyst selection



A good catalyst must possess both high activity and long-term stability. But its single more important attribute is selectivity.

Selectivity is more important than activity:

- The unconverted reactant can be re-circulated.
- It is not interesting the transformations of reactants in valueless products.
- The selective transformation of reactants facilitate the final separation process.

35

■ Heterogeneous catalysis  
and Surface Science

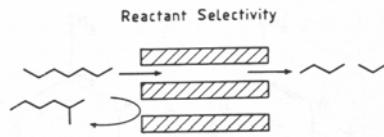
36



## Heterogeneous Catalysts is a Surface Science!!!

The catalytic processes develops ONLY on the catalyst surface.

Therefore, the catalyst surface should be as large as possible, but moreover, surface must be accessible to the reactants.



**Figure 1.1** A shape-selective catalyst, such as a synthetic zeolite with cylindrical pores of *ca* 5.5 Å diameter, permits ready ingress of straight-chain reactant alkanes (e.g. *n*-heptane) but not of branched isomers (e.g. 2-methylhexane). The acid centres lining the pores can therefore catalyse the cracking of the *n*-heptane but not of the branched hexane.

37

## Surface heterogeneity

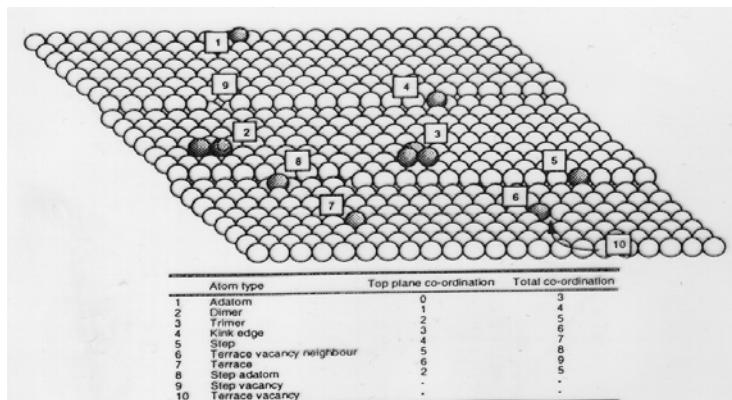


Fig. 2.2 Crystal surface structure, based on the fcc (111) plane with (100) steps, showing different types of atomic environment.

Reactants will be chemisorbed preferentially in the more energetic sites

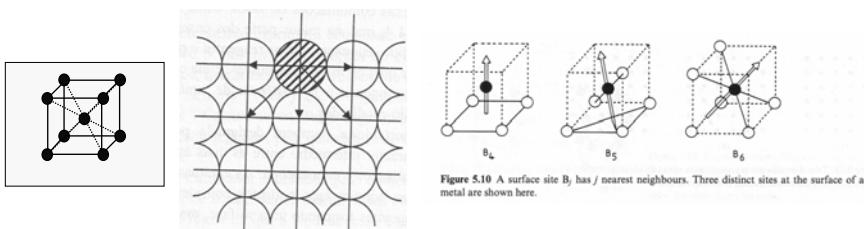
38



## Surface energy of solids

The coordination number is 12 for fcc and hcp and 8 for bcc, but, it is clear the smaller coordination of surface atoms (in the plane 4 for bcc and 6 for fcc and hcp).

The resulting force unbalance at the surface is responsible of the interactions of the solid with the environment (adsorption).



Schematic representation of the surface energy of solids.

Figure 5.10 A surface site  $B_j$  has  $j$  nearest neighbours. Three distinct sites at the surface of a bcc metal are shown here.

A surface site  $B_j$  has  $j$  nearest neighbors.  
Three distinct sites at the surface of a bcc metals are showed here.

39



## The adsorption process

Table 1.1. Definitions: adsorption

Term	Definition
Adsorption	Enrichment of one or more components in an interfacial layer
Adsorbate	Substance in the adsorbed state
Adsorptive <sup>a</sup>	Adsorbable substance in the fluid phase
Adsorbent	Solid material on which adsorption occurs
Chemisorption	Adsorption involving chemical bonding
Physisorption	Adsorption without chemical bonding
Monolayer capacity	either Chemisorbed amount required to occupy all surface sites or Physisorbed amount required to cover surface
Surface coverage	Ratio of amount of adsorbed substance to monolayer capacity

<sup>a</sup> Translated into French as 'adsorbable'.

Adsorption is brought about by the interactions between the solid and the molecules in the fluid phase. Two kinds of forces are involved, which give rise to either physisorption or chemisorption.

Physisorption forces are mainly dispersion and van der Waals attractive forces, which do not depend on the polar nature of the adsorbent or adsorptive and are therefore regarded as *non-specific*, whereas chemisorption interactions are essentially responsible for the formation of chemical compounds.

40

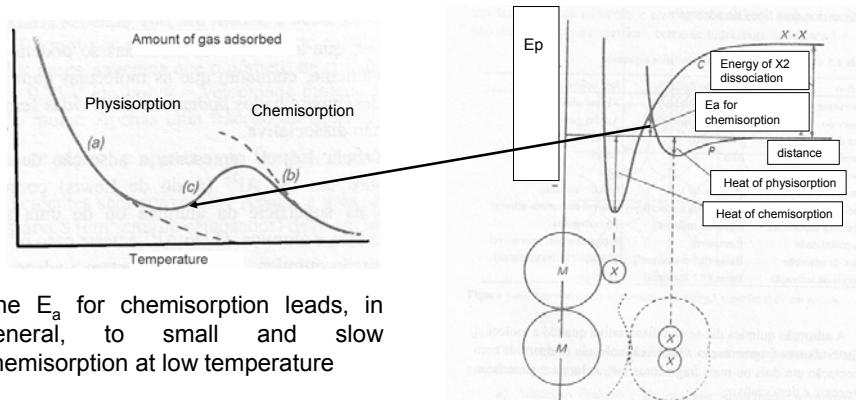


## The adsorption process

Adsorption is an spontaneous process,  $\Delta G < 0$

$$\Delta G = \Delta H - T \Delta S$$

Because  $\Delta S$  decrease with adsorption (the adsorbed molecules moves on the catalysts surface, but not freely as in gas phase)  $\Delta S < 0$  and consequently  $\Delta H < 0$ , adsorption is an exothermic process, and the adsorption capacity therefore decrease when the temperature increase (Le Chatelier-van't Hoff Principle)



The  $E_a$  for chemisorption leads, in general, to small and slow chemisorption at low temperature



## Comparison between physical and chemical adsorption

Parameter	Physisorption	Chemisorption
Adsorbent	All solids	Some solids
Adsorbate	All vapors	Some gases
Temperature	Low	High
Amount adsorbed	High	Low
Amount (%) adsorbed at low pressure	Low	High
Influence of P o the amount adsorbed (high P)	High	Low
Specificity	None (all the surface)	High (only on some specific sites)
Reversibility	Reversible	irreversible
Heat of adsorption	Low (0.5-5 Kcal/mol)	High (5 – 100 Kcal/mol)
Surface coverage	multilayer	monolayer

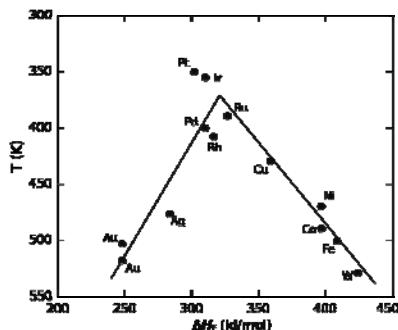
Nevertheless, the strongest adsorption sites are not necessarily the best catalytic sites. A good catalyst needs to adsorb the reactant molecules strongly enough for them to react, but not so strongly that the product molecules stick more or less permanently to the surface.

Gold, isn't a good catalyst because it doesn't form strong enough attachments with reactant molecules.

Tungsten, isn't a good catalyst because it adsorbs too strongly.

Metals like platinum or iridium make good catalysts because they adsorb strongly enough to hold and activate the reactants, but not so strongly that the products can't break away.

### The Sabatier principle



Volcano plot for the decomposition of formic acid on transition metals.

T corresponds to the T needed to obtain a  $\lg r = -0.8$ , and  $\Delta H_f$  is the heat of formation of the metal formate salt (intermediate Metal-acid formic), that is to say, the strength of the M-reactant interaction.

43

### The catalytic surface: Structural considerations

On the basis of their chemical nature, heterogeneous catalyst can be classified as:

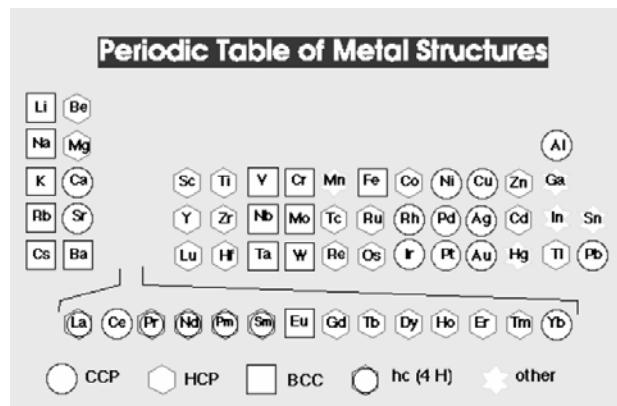
Catalyst type	Reactions	Catalytic phases
Metals	Hydrogenation /dehydrogenation, oxidations, hydrogenolysis	Fe, Ni, Pd, Pt, Ag, Au, Cu
Non - stoichiometric oxides and sulphurs	Oxidations, desulfurizations	NiO, ZnO, MnO <sub>2</sub> , WS <sub>2</sub> , MoS <sub>2</sub>
Stoichiometric oxides	Polymerization, Isomerization, cracking, alkylation	SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , zeolites

The crystalline structure of the catalyst will define the catalytic active surface

44



## Structure of metals



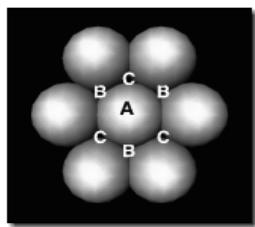
Metal present only three main structures. Most of them (71%) adopt a packing arrangement which maximizes the occupation of space: ccp or hcp. Alternatively, alkali metals and some transitions metals present bcc structure.

45

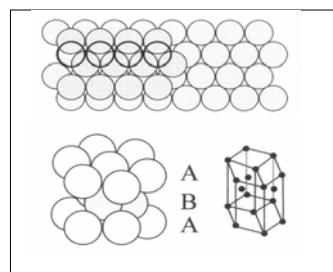


## Structure of metals

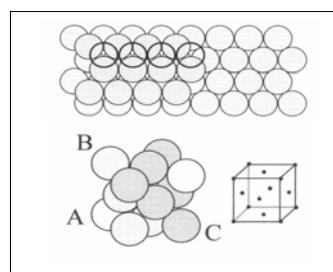
The compact layers are packed with a sequence ABAB leading to the hexagonal (hcp) structure, or ABCABC, leading to the cubic (ccp or fcc) structure.



hcp



ccp



The coordination number is in both cases 12 and the fraction of occupied volume of 74%

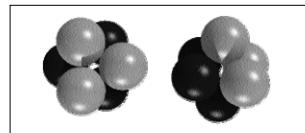
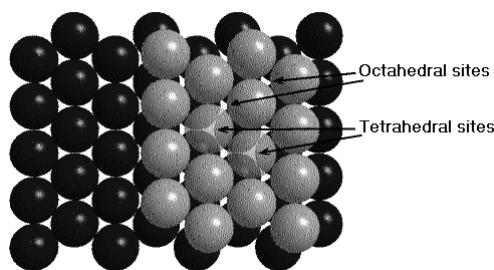
46



## Hole distributions in close packed structures

Two distinct types of interstices appears: tetrahedral and octahedral.

$$N \text{ atoms} = N \text{ oct holes} = 2N \text{ td holes}$$



$$D = 0.414r$$

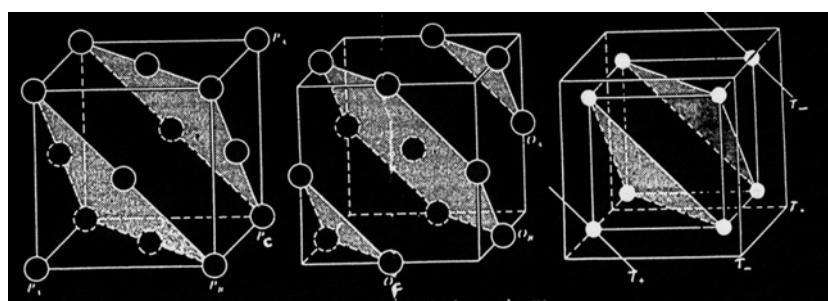
$$D = 0.225r$$

47



## Hole distribution

The interstices also form layers between the atom layers, located at  $\frac{1}{4}d$  Td+  $\frac{1}{2}d$  Oct and  $\frac{3}{4}d$  Td-. The occupation of these holes will determine the structure of metal compounds.



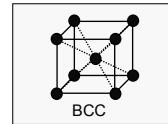
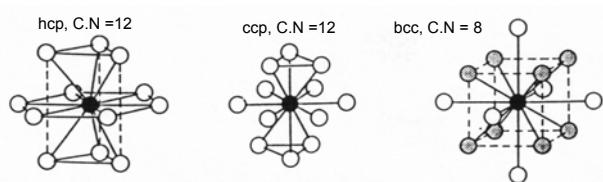
Analysis of the FCC structure: a) primitive sites b) octahedral holes c) tetrahedral T+ and T- holes

48



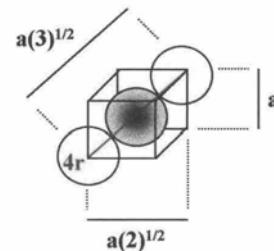
## Structure of metals

### BCC structure



The BCC structure is not a close packing structure, the coordination number decrease from 12 to 8 and the fraction of the occupied volume from 74 to 68%.

Metal atoms are in contact only along the diagonals of the cube.



49

## Some oxides of interest in heterogeneous catalysis

Many oxides are of interest in catalysis, they are widely used in oxidations or hydrogenation / dehydrogenation processes.

In contrast to the simplicity of the structural characteristics of metals, metal oxides and sulfurs present a wide variety of structures, and most of them present polymorphism.

Table I Crystal structures and ion coordinations in simple solid oxides of interest in heterogeneous catalysis<sup>a</sup>

Cation valence	Structure name	SG	z	Coordination		Cation radius/ $\text{\AA}$	Ion packing	Examples
				Cation	Oxide			
1	Cuprite <i>Pm3</i>	2	2 (linear)	4	0.5	M = csp	Cu <sub>2</sub> O, Ag <sub>2</sub> O	
	Rock salt <i>Fm3m</i>	4	6 (oct.)	6 (oct.)	0.65	O = csp	MgO, CaO, SrO, BaO, MnO, FeO, CuO, NiO, CdO	
	Zinc blende <i>F43m</i>	4	4 (tet.)	4 (tet.)	~0.3	O = csp	BeO (II)	
	Wurtzite <i>P6<sub>3</sub>mc</i>	2	4 (tet.)	4 (tet.)	0.68	O = hep	BeO (I), ZnO	
	Tenovite <i>C2/c</i>	4	4 (sq. pl.)	4	0.62	(O = dist. csp)	CuO	
3	Corundum <i>R-3c</i>	3	3 (trig.)	1.2	0.02	M = hcp	$\text{Al}_2\text{O}_3$ , $\text{Cr}_2\text{O}_3$ , $\gamma\text{-Fe}_2\text{O}_3$ , $\alpha\text{-Ga}_2\text{O}_3$	
	Dolomite spinel-type	6	6 (oct.)	4	0.5 - 0.65	O = csp	$\gamma\text{-Al}_2\text{O}_3$ , $\delta\text{-Al}_2\text{O}_3$ , $\beta\text{-Al}_2\text{O}_3$ , $\eta\text{-Al}_2\text{O}_3$ , $\theta\text{-Al}_2\text{O}_3$ , $\gamma\text{-Fe}_2\text{O}_3$ , $\text{MgAl}_2\text{O}_4$	
	"A" <sup>b</sup>	1	7	6.4	0.99 - 1.2	M = hcp		
	"B"	3	6	7.6	6.5-7.4	M = hcp		
	"C" - bustbyte	6	6 (oct.)	4	0.6 - 0.72	O = def. cub.		
2,3	Spiral <i>Fd3m</i>	8	6 (oct.)	4	0.6 - 0.65	O = csp		
	o-Quartz <i>P3<sub>1</sub>21</i>	3	4 (tet.)	2 (hex.)	0.3 - 0.4	O = csp		
	Rutile <i>P4<sub>3</sub>mm</i>	2	6 (oct.)	3	0.5 - 0.85	O = hep	$\text{TiO}_2$ , $\text{GeO}_2$ , $\text{SnO}_2$ , $\text{B-PbO}_2$	
	Anatase <i>I41/amnd</i>	4	6 (oct.)	3	0.65	O = hep	$\text{TiO}_2$	
	Fluorite <i>Fm3m</i>	4	8 (oct.)	4	0.8 - 1.0	O = prim. cub.	$\text{TiO}_2$ , $\text{CaO}$ , $\text{HfO}_2$ , $\text{ZrO}_2$ , (H)	
	Baddleyite <i>R3c</i>	4	7	3.4	0.8	M = csp	$\text{ZrO}_2$ (I)	
5	$\text{P}_2\text{O}_{10}$ <i>P2<sub>1</sub>2<sub>1</sub>2</i>	2	4 (tet.)	1.2	0.17	Molecular		
	V <sub>2</sub> O <sub>5</sub> <i>Pmm</i>	2	4 (tet.)	1.2	0.33			
	H-Ni <sub>2</sub> O <sub>3</sub> <i>P2</i>	14	6.8	3.2	0.6 - 0.7	Layered	$\text{V}_2\text{O}_5$ , $\text{R-Nb}_2\text{O}_5$	
	B-Ni <sub>2</sub> O <sub>3</sub> <i>B2</i>	4	6	3.2	0.6 - 0.7		$\text{H-Nb}_2\text{O}_5$	
	MoO <sub>3</sub> -type <i>Pmm</i>	4	5 (8)	2	0.6 - 0.7	O = dist. hep	$\text{B-Nb}_2\text{O}_5$ , $\text{Sb}_2\text{O}_3$	
	MoO <sub>3</sub> <i>C2m</i>	4	4 (tet.)	1.2	0.6	O = def. dist. csp	$\text{ReO}_3$ , $\text{WO}_3$	
				1.2	0.7	Layered	$\text{MoO}_3$	
						Chains	$\text{CrO}_3$	

<sup>a</sup> SG = space group; L = low temperature form; H = high temperature form; P = high pressure form; oct. = octahedral; tetr. = tetrahedral; sq. pl. = square planar; trig. = trigonal; cub. = cubic; dist. = distorted; " = metastable phase; prim. = primitive; def. = deformed.

50



## Structural consideration of metal oxides

By "simple" we mean oxides formed from a single metallic element and where the degree of departure from exact stoichiometry ( $MO$ ,  $MO_2\dots$ ) may be quite small.

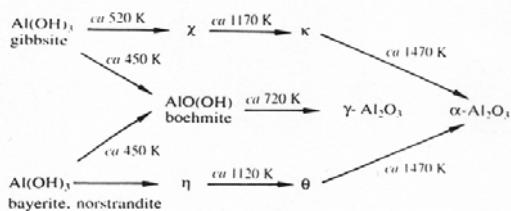
Table 1.5 Structures related to close-packed arrangements of anions					
Formula	Cation/anion coordination	Type and number of holes occupied	Examples	Cubic close packing	Hexagonal close packing
$MX$	6:6	All octahedral	Sodium chloride	Nickel arsenide; $Na_2AlO_4$ , $FeS$ , $NiS$	
	4:4	Half octahedral; every alternate site occupied	$ZnS$ , $CuCl_2$ , $Y_2O_3$	Zinc blende; $ZnS$ , $\beta-Al_2O_3$	
$MX_2$	8:4	All tetrahedral	Fergusonite: $CaAl_2O_4$ , $ThO_2$ , $ZrO_2$ , $CeO_2$		Wurtzite: $ZnS$
	6:3	Half octahedral; alternate layers have fully occupied sites	Cadmium iodide: $CdCl_2$		
$MX_3$	6:2	One-third octahedral; adjacent pairs of layers have two-thirds of the octahedral sites occupied		Bismuth iodide: $BiI_3$ , $FeCl_3$ , $TiCl_3$	Cordmann iodide; $CdI_2$ , $TlI_2$
		Two-thirds octahedral			
$M_2X_3$	6:4	Two-thirds octahedral			Corundum: $Al_2O_3$ , $Fe_2O_3$ , $Cr_2O_3$
$ABO_3$		Two-thirds octahedral			Ilmenite: $FeTiO_3$
$\Delta B_2O_4$		One-third octahedral and one-half octahedral	Silicon: $MgAl_2O_4$ , Inverse spinel: $Mg_2SiO_4$		Olivine: $Mg_2SiO_4$

51



## Structural consideration of metal oxides

Alumina ( $Al_2O_3$ ) have considerable prominence in heterogeneous catalysis.



Thermal dehydration process in air of  $Al(OH)_3$

All the crystallographic forms are based on close packed  $O^{2-}$  ions with  $Al^{+3}$  in O and T sites, the differences arise when  $O^{2-}$  layers are superposed in different sequences:  $\alpha$  -  $Al_2O_3$  (corindon) ABAB,  $\beta$ -series ( $\chi$ - $\eta$  phases) ABACABAC,  $\gamma$  -  $Al_2O_3$  ABCABC.

52

## Structural consideration of metal oxides

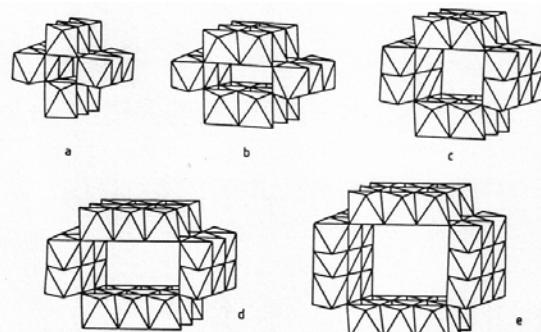


Figure 5.16 Mineral structures composed essentially of the oxides of manganese exhibit an interesting trend. Pyrolusite ( $\beta\text{-MnO}_2$ ) has the rutile structure (a); ramsdellite ( $\gamma\text{-MnO}_2$ ) has the structure of the mineral diaspore shown in (b); hollardite ( $\alpha\text{-MnO}_2$ ) has rectangular tunnels circumscribed by a  $2 \times 2$  arrangement of edge-sharing octahedra (c). In romanechite (d) and todorkite (e), the tunnels are  $2 \times 3$  and  $3 \times 3$  octahedra respectively.

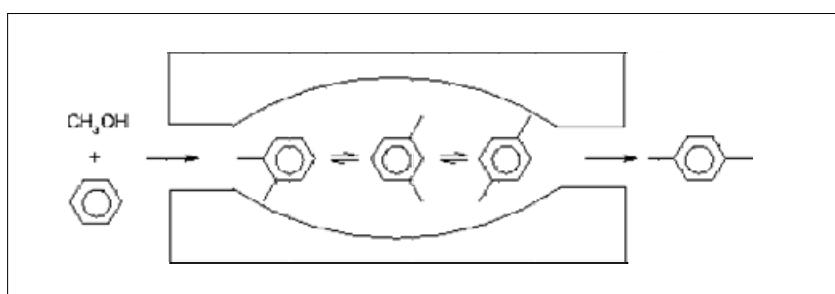
It is noteworthy that “designed” catalysts, possessing desired diameters of tunnels and requisite composition of their inner walls can be obtained. The catalyst characteristic can be tailored knowing the structure transformations.

53

## Structural effects



Schematic diagram of product **shape selectivity**: Para-xylene diffuses preferentially out of the zeolite channels

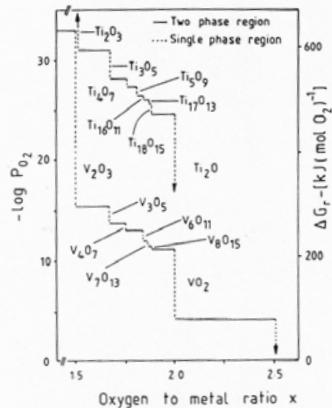


54



## Structural consideration of metal oxides

In some oxide, the degree of non-stoichiometry may be gross. For example, ferrous oxide retains the rock salt structure over the composition range  $\text{Fe}_{0.82}\text{O}$  to  $\text{Fe}_{0.96}\text{O}$



Careful thermodynamic measurements leave no doubt about the existence of numerous non-stoichiometric materials of general formula  $\text{Ti}_n\text{O}_{2n-1}$  and  $\text{V}_n\text{O}_{2n-1}$

**Figure 5.15** Equilibrium oxygen pressures in the Ti-O and V-O systems at 1000 K as a function of the metal/oxygen ratio.

55



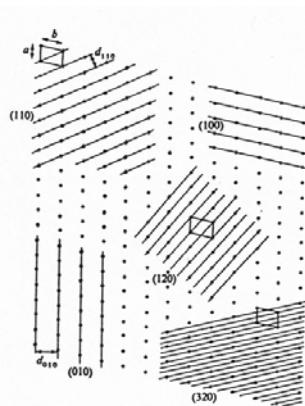
## Miller indices

Planes in a crystallographic structure are labeled using Miller indices

Calculations:

- Measure the interception of the plane with the axis  $(abc, xyz)$
- Take reciprocal of the indices
- Rationalize the dividends
- Place the rationalized dividend in parenthesis

Example: for a plane with intercepts  $(3a, 2b, \infty c)$ , the reciprocal are  $(1/3, 1/2, 1/\infty)$  and clearing the fractions yield  $(2, 3, 0)$

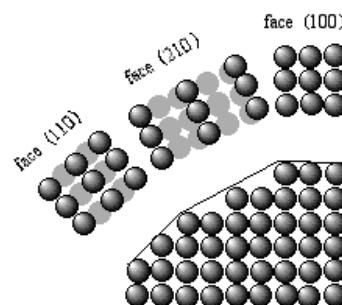
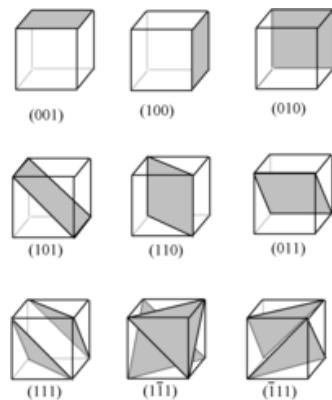


The higher the value of  $(hkl)$  indices, the smaller the inter-planar distance between the planes in that direction.

56



Planes with different Miller indices in cubic crystals



Dense crystallographic planes

57



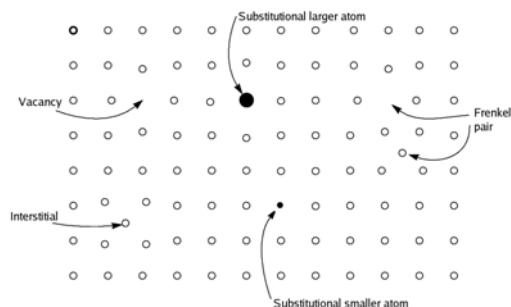
## Classification of crystal imperfections

1. **point defects**, which are places where an atom is missing or irregularly placed in the lattice structure. Point defects include lattice vacancies, self-interstitial atoms, substitution impurity atoms, and interstitial impurity atoms
2. **linear defects**, which are groups of atoms in irregular positions. Linear defects are commonly called dislocations.
3. **planar defects**, which are interfaces between homogeneous regions of the material. Planar defects include grain boundaries, stacking faults and **external surfaces**.

58



## Point defect: Frenkel and Schottky defects



$$n_v = n \exp\left(\frac{-Q}{RT}\right)$$

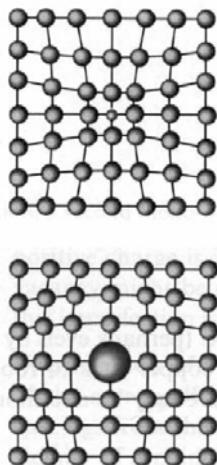
The number of vacancies present in a material increases exponentially as the temperature increases

A Schottky defect is simply an unoccupied lattice site. In ionic solids defects in the cation lattice balances out the number in the anion lattice. The Frenkel defect also implies the combination of a vacancy with interstitial defects. Point defects may combine or associate, forming clusters.

59



## Substitutional defects



Substitutional defects are produced when one atom is replaced by a different type of atom.

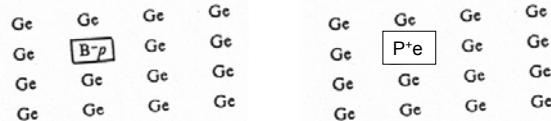
- If the substitutional atom is smaller than the original atom then the lattice is in tension.
- If the substitutional atom is larger than the original atom then the lattice is in compression.

60



## Substitutional defects

But substitutional defect also produce strong changes in the conductivity of the solids:



When Ge structure is doped with P or As, which have five valence electrons, four of them are shared with germanium atoms forming covalent bonds, while the fifth becomes quasi-free. This type of impurities is known as a "donor impurity" and it confers n-type semiconductivity.

On the contrary, when Ge is doped with B, Ga or In, each trivalent impurity atom accommodated, there would be one positive hole formed into the valence band. This type of impurity is known as an "acceptor impurity" and it confers p-type semiconductivity.

61

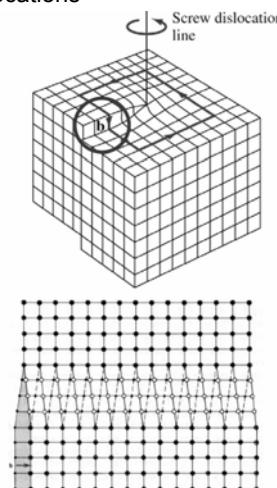
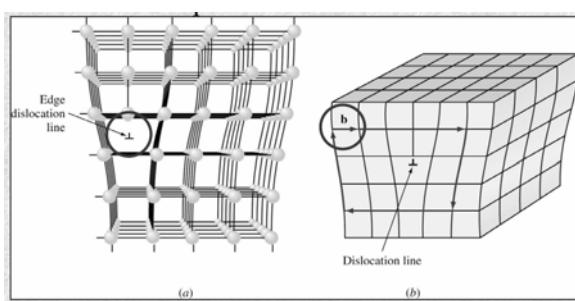
## linear defects



### Screw dislocations

#### Edge dislocations

Edge dislocations are caused by the termination of a plane of atoms in the middle of a crystal



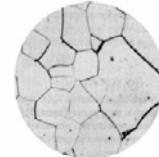
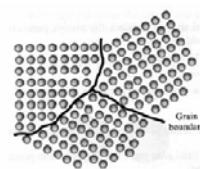
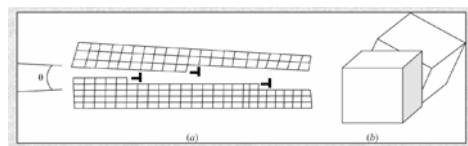
The screw dislocation is more difficult to visualize, but basically comprises a structure in which a helical path is traced around the linear defect (dislocation line) by the atomic planes of atoms in the crystal lattice

62



## Polycrystalline catalysts: Grain Boundaries

- The crystalline structure of each grain is identical but their orientations are not
- The grain boundary is a narrow zone where the atoms are not properly spaced
- The misorientation angle  $\theta$  is generally  $< 10^\circ$ .



Boundaries are regions of high energy, and consequently, with strong interactions with the environment.

63

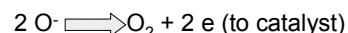


## Relationship of crystal defects and catalytic activity

The overall decomposition of nitrous oxide is:

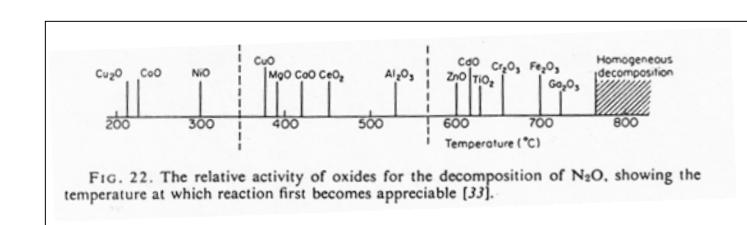


Followed by



Or by

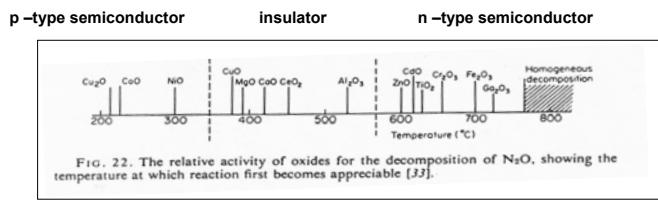
And the reaction mechanism may be written:



64

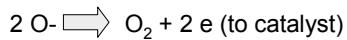


## Relationship of crystal defects and catalytic activity

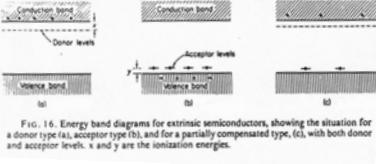


The activity of different metal oxide in this reaction can be divided into three group: p-type semiconductor, insulator, n-type semiconductor. The most active catalyst are p-type semiconductor.

It is assumed that the slow step is:



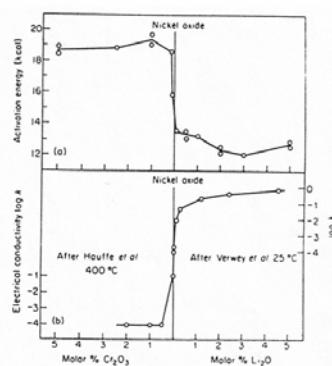
If this transfer of electrons is the slow step, the higher activity of p-semiconductors is related with their lower lying energy levels.



65

## Relationship of crystal defects and catalytic activity

Oxidation of CO on NiO: the doping of NiO catalyst with  $\text{Li}^+$  results in an increase of positive holes enhancing the electrical conductivity, this favour the catalytic activity because the  $E_a$  for the CO oxidation simultaneously decreases . The contrary effect is obtained by doping with  $\text{Cr}^{+3}$ .



66

Now a break before....

## ■ Looking for the active site nature

67

### The active sites and chemisorption



The catalyst surface is heterogeneous. Not all the surface will participate on the reactions, but reactions will be developed on the “active sites” or “active centers”

These terms are widely used, but with wider meanings related to the activation / deactivation of the catalysts.

The crystal defects are the genesis of the active sites concept, associated to chemisorption sites, but remember that strong chemisorption avoid the reactions and deactivates the catalysts by blocking the active sites.

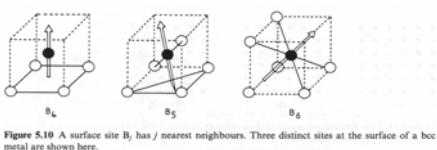
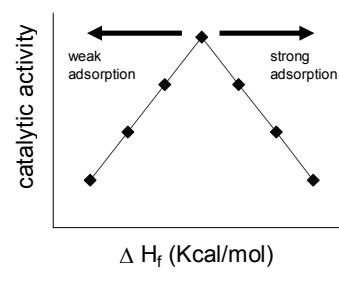


Figure 5.10 A surface site  $B_j$  has  $j$  nearest neighbours. Three distinct sites at the surface of a bcc metal are shown here.



Volcano plots

68



## The active sites: unsaturation

Taylor attributed special activity to those atoms which, because of the uneven geometry of the surface (Fig. 9), have low coordination to other catalyst atoms (unsaturation), and these are the atoms that were attributed to provide the seat of most catalytic conversions.

This view focused attention on the heterogeneity of the surface of almost all catalysts, and the fact that the total surface would not be equally active in effecting chemical reactions.

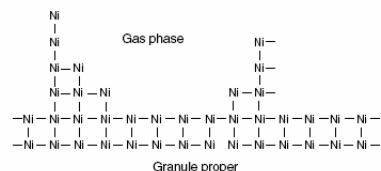


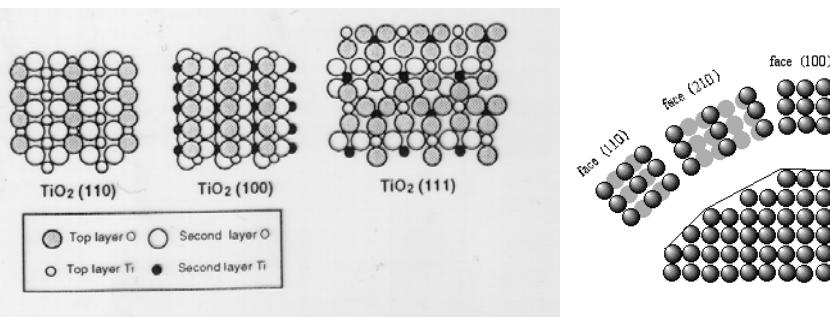
Fig. 9 Taylor's representation of heterogeneity and the presence of various types of active site on a nickel catalyst. (Reproduced from Ref. [62].)

69



## The active sites: crystallographic layer

The nature and characteristics of the catalyst surface, and consequently the nature and strength of the interactions with the environment, strongly depends on the crystallographic plane where reactions will occur



Boudart divides the catalytic reaction in two classes: Structure sensitive and structure insensitive, if reaction rate changes markedly or not as the particle size of the catalyst is changed, or as the crystallographic face of the catalyst surface is altered.

70

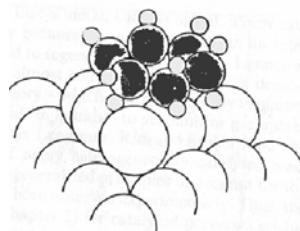


## The active sites: Geometric factor

The catalytic activity depends on the presence on surface of correctly spaced groups of atoms to accommodate the reactant molecules.

Balandin in the mid-1940's predict that metals with interatomic distances ranging from 2.48-2.77 Å should exhibit catalytic activity for the hydrogenation of benzene an the dehydrogenation of cyclohexane, since, for these reactions, the metal spacing match the interatomic distances in the cyclic molecules.

Schematic illustration of the Balandin concept of multiplets involved in the molecular bonding. "Sextet complex"



71



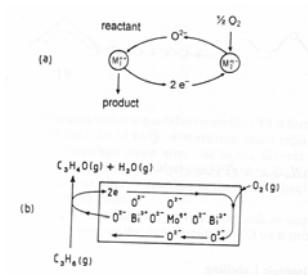
## The active sites: the oxide surface

Numerous surface entities may be present on reacting catalysts but this entities mustn't to be always the active sites for different reactions.

Certain oxidations catalyzed by oxides occurs in two steps, according to the so-called Mars-van Krevelen mechanism: first, a reaction between the oxide catalysts and the hydrocarbon, in which the later is oxidized and the former reduced, followed by the reaction of the reduced oxide with  $O_2$  to restore the initial state.

Mars-van Krevelen mechanism:

Conversion of propylene to acroleine by bismuth molybdate catalyst



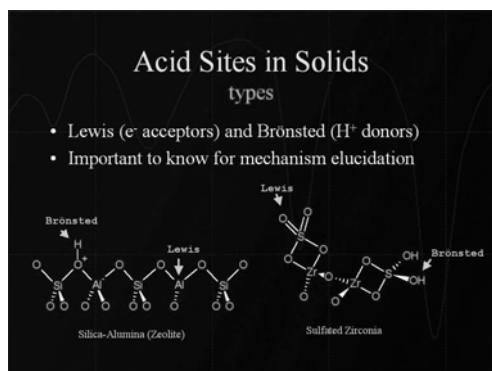
The redox cycle undergoes by the catalyst surface determine the activity and selectivity of the reaction. Easily reducible oxides are quite active, but poorly selective, if reduction is not facile enough, catalyst is poorly active, if reduction is too easy, the activity increase but probably with formation of undesired compounds, and if re-oxidation is not appropriate, catalyst is quickly deactivated. The catalytic behavior depends on the mobility of ions and electrons.

72



## The active sites: acidity in zeolites

The acid-base character of the catalyst surface must be also take into account. The catalytic behavior of many solids is associated to this character.



There is one acid hydrogen for every tetrahedrally bonded aluminium. These active sites are distributed uniformly throughout the bulk and are bridging hydroxyl groups. These are the classic Bronsted acid sites, the intrinsic strength of which is a function both of the particular local environment and also the Si/Al ratio.

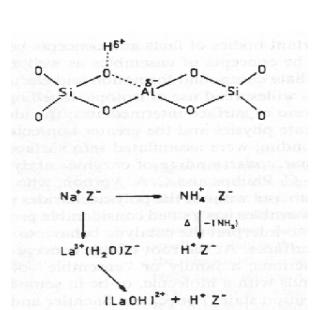
73

## The active sites: acidity in zeolites

### Some acid catalyzed reactions

Table 8.4. Acid-catalysed reactions giving hydrocarbon products.

Reaction	Zeolite catalyst	Temperature [°C]
1 Ethylbenzene from benzene and ethylene	ZSM-5	400
2 Xylenes production, isomerization (including ethylbenzene) and disproportionation	Various modified ZSM-5	300–600
3 p-Ethyltoluene from toluene plus ethylene	ZSM-5	400
4 New routes to aromatics paraffins, olefins, alcohols, etc.	ZSM-5	400–600



Acidity can be introduced in four ways:

- Ion exchange with  $NH_4^+$  followed by thermal decomposition.
- Hydrolysis of ion-exchanged polivalent cations followed by partial dehydration
- Direct proton exchange
- Reduction of exchanged metal ions to a lower valence state:





## The active sites: conductivity

The idea that catalytic activity could be related to the bulk electronic properties of the catalyst (electronic band structure) leads to divide the catalyst into metals, semiconductors and insulators (Dowden, 1950's)

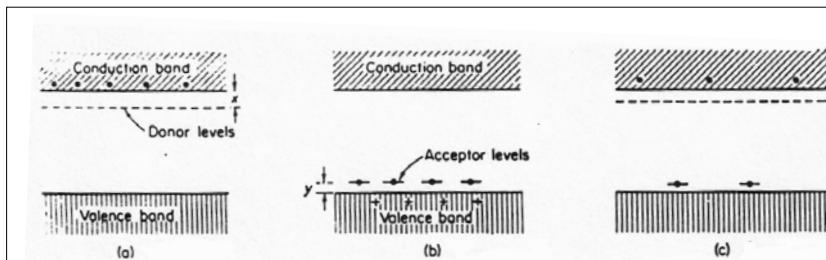


FIG. 16. Energy band diagrams for extrinsic semiconductors, showing the situation for a donor type (a), acceptor type (b), and for a partially compensated type, (c), with both donor and acceptor levels. x and y are the ionization energies.

Donor (n-semiconductors) or acceptor levels (p-semiconductors) can be generated by doping catalysts, as previously showed. This means that the electronic properties of the catalyst can be also tailored.

75



## The active sites: electronic properties

When chemisorption occurs on a semiconductor surface, the resulting change in electrical conductance of the solid yields unambiguous information concerning the type of electronic rearrangement, or the direction of the charge transfer at the surface.

A fall in the conductivity of n-type semiconductor as a result of chemisorption, signifies an electron transfer from the conduction band of the catalyst to the adsorbed species (the concentration of electrons from the donor levels decreases and anionic species are formed on surface).

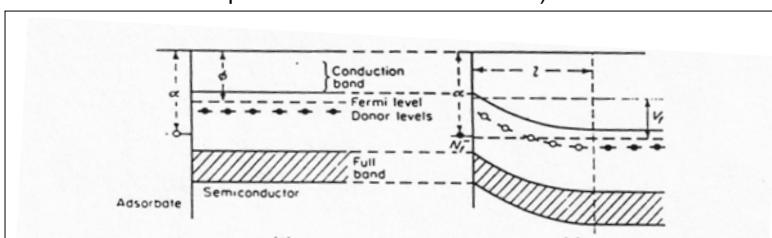


FIG. 17. Diagrammatic representation of anionic chemisorption on an n-type semiconductor; (a) before chemisorption, and (b) after chemisorption [33].

76



## The active sites: electronic properties

A fall in conductivity of a p-type semiconductor signifies an electron transfer from the chemisorbed gas to the solid leading to a fall in the surface concentration of positive holes in the full band due to the entry of electrons from the adsorbate.

In both cases, chemisorption leads to a depletion of carriers in semiconductors, and both are examples of depletive chemisorption. The reverse process, namely cumulative adsorption, distinguished by a rise in conductivity because the surface concentration of carriers has increased.

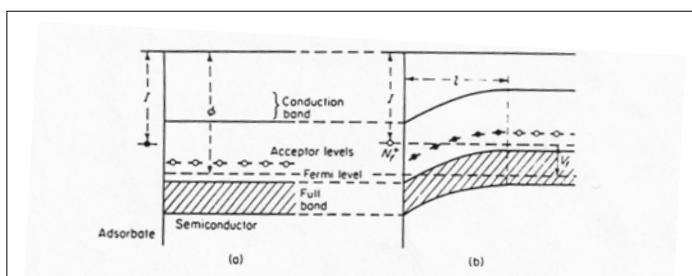
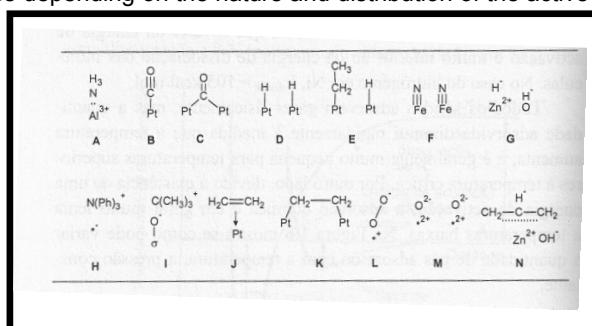


FIG. 18. Diagrammatic representation of cationic chemisorption on a p-type semiconductor; (a) before chemisorption, and (b) after chemisorption [33].

77

## The active sites

The concept of “active site” is therefore very wide. Some examples of adsorbed surface complex are showed, you can observe how reactants interact with the catalysts surface depending on the nature and distribution of the active sites.



- A.**  $\text{NH}_3$  (Lewis base) coordinately linked to  $\text{Al}^{3+}$  ions (Lewis acid) on  $\text{Al}_2\text{O}_3$  surface. **B and C.** Linear and bridge adsorption of CO on Pt. **D and E.** Dissociative adsorption on Pt of  $\text{H}_2$  or alkanes. **F.** Dissociative adsorption of  $\text{N}_2$  on Fe. **G.** Heterolytic dissociative adsorption of  $\text{H}_2$  on the  $\text{ZnO}$  surface. **H.** Adsorbed complex with charge transference. **I.** Adsorption of isobutene on silica alumina where the acid surface proton ( $\sigma\text{-OH}$ ) was transferred to the isobutene. **J and K.** Possibilities of ethylene adsorption on Pt. **L.** Adsorption of  $\text{O}_2$  on metal oxides with charge transference. **M.** Dissociative adsorption of  $\text{O}_2$ . **N.** Heterolytic dissociative adsorption of propylene on  $\text{ZnO}$ .



## The active sites: bifunctional catalysts

Another question is the notion of bifunctional or multifunctional catalysts, namely in the case of supported catalyst.

Example: the  $\text{Al}_2\text{O}_3/\text{Pt}$  catalysts used in the hydroprocessing of petrochemicals, the metal serves to dissociate  $\text{H}_2$ , while the acid support serves to catalyse the build-up of vital carbonium ion intermediates.

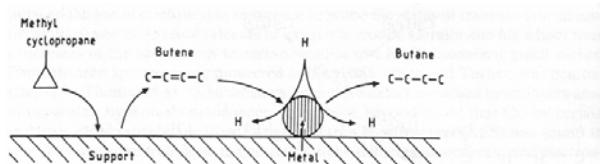


Figure 1.17 A bifunctional catalyst such as platinum on  $\text{Al}_2\text{O}_3$  facilitates the isomerization of methylcyclopropane to 2-butene as well as the hydrogenation of 2-butene to butane (after Boudart).

In this case catalyst, electron transfers between both phases can also modify the overall reaction.

79

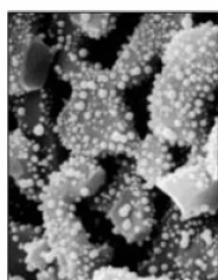


## Preparation of catalysts

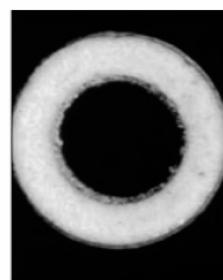
### Types of solid catalysts



Carrier-free catalyst



Supported catalyst



Coated catalyst

80



## Preparation of solids catalysts

The development of a solid catalyst requires knowledge of the parameters which have the greatest influence on catalyst performance.

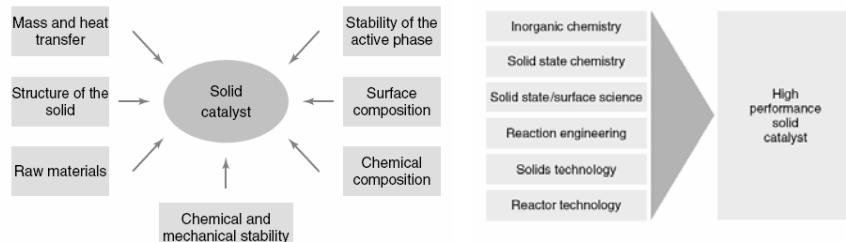


Fig. 16 The development of a solid catalyst.

Fig. 6 The properties that control a catalyst's performance.

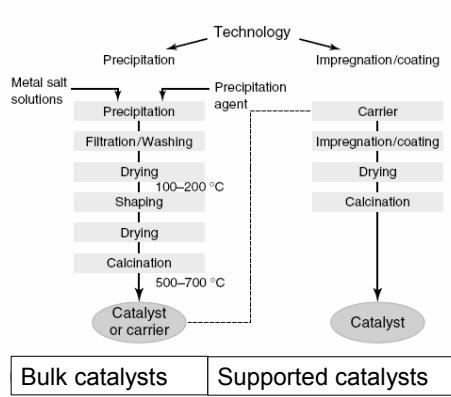
The main objective of catalyst development is optimization of the various different catalyst properties, an essential precondition for achieving such an objective is a close cooperation between experts working in very different fields of scientific research.

81



## Preparation of solids catalysts

Currently, two principal routes exist for the production of technical catalysts:



The first route, yielding bulk catalysts, starts with the precipitation of a catalyst precursor, which is filtered, dried, and shaped. Calcination steps may be included after drying or after shaping.

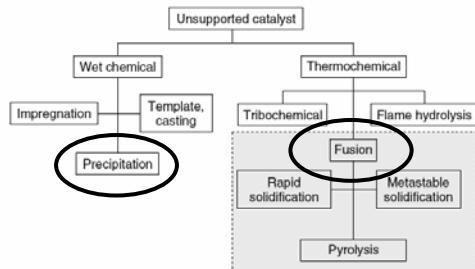
The second route starts with a carrier material, which can be impregnated with salt solutions or coated with powders. Drying and calcination give the final supported catalyst.

82



## Preparation of solids catalysts

### Preparation of bulk catalysts



Bulk catalysts can be prepared from two routes, precipitation is the most common but a small number of heterogeneous catalysts is prepared by the fusion of mixtures of oxidic or metallic precursors.

83



## Bulk Catalysts and Supports

### Fused Catalysts

Among the thermochemical methods, the fusion processes are rarely applied as they require extensive special equipment which is generally unavailable to research groups, and difficult to use in industry.

### Metallic Glasses

Amorphous metals can be prepared in a wide variety of stable and metastable compositions, with all catalytically relevant elements.

The function of the fused amorphous alloys is to serve as a precursor material for the formation of a metastable active phase characterized by an intimate mixture of phases with different functions (synergism).

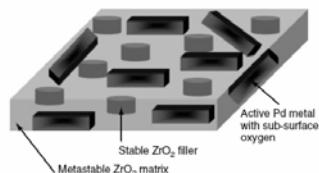


Fig. 6 Schematic arrangement of the surface of a partly crystallized E-L TM amorphous alloy such as Pd-Zr. A matrix of zirconia

84



## Precipitation and Co-precipitation

Precipitation is the process in which a phase-separated solid is formed from homogeneous solution, after super-saturation.

The main advantage of precipitation is the possibility of creating very pure materials.

Tab. 1 Some industrially relevant catalysts and supports obtained by precipitation and coprecipitation techniques

Material	Use	Important examples
$\text{Al}_2\text{O}_3$ , mostly $\gamma$ , in special cases $\alpha$ or $\eta$	Support, catalyst	Claus process, dehydration of alcohols to alkenes and ethers, support of hydrotreating catalysts, support for three-way catalyst
$\text{SiO}_2$	Support	Noble metal/ $\text{SiO}_2$ for hydrogenation reactions, $\text{Ni}/\text{SiO}_2$ for hydrogenation reactions, $\text{V}_2\text{O}_5/\text{SiO}_2$ for sulfuric acid production, support for Ziegler catalysts
$\text{Al}_2\text{O}_3/\text{SiO}_2$	Catalyst	Acid-catalyzed reactions, such as isomerization, component of FCC catalysts
$\text{Fe}_2\text{O}_3$	Catalyst, catalyst component	Fischer–Tropsch reactions, major component of catalyst for ethylbenzene dehydrogenation to styrene
$\text{TiO}_2$	Support, catalyst, catalyst component	Major component of $\text{DeNO}_x$ catalyst, photocatalyst
$\text{ZrO}_2$	Catalyst, support	Acid catalyst after sulfate modification, component of three-way catalyst support
$\text{Cu/ZnO}$	Catalyst	Methanol synthesis, methanol steam reforming
$(\text{VO})_2\text{P}_2\text{O}_7$	Catalyst	Selective oxidation (e.g., butane to maleic anhydride)
$\text{Cu-Cr}$ -oxides	Catalyst	Combustion reactions, hydrogencations
$\text{AlPO}_4$	Support, catalyst	Polymerization, acid-catalyzed reactions
$\text{Sn-Sb}$ -oxides	Catalyst	Selective oxidation (e.g., isobutene to methacrolein)
Bi-molybdates	Catalyst	Selective oxidation (e.g., propene to acrolein), mostly supported in thin-layer on non-porous carriers

FCC = fluid catalytic cracking.

63

## Precipitation and Co-precipitation

Precipitation is – and probably will remain – one of the most important methods for the synthesis of solid catalysts.

For the industrial preparation of catalysts by precipitation, the ease and cost of the operation must always be balanced against the catalyst performance.

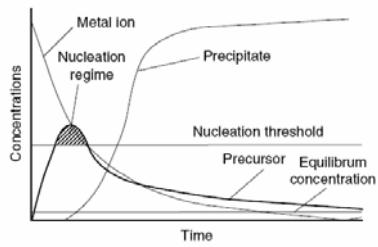
Advanced precipitation methods, such as microemulsion synthesis, in most cases do not yield catalysts of sufficiently superior quality to compensate for the higher efforts required in the synthesis. Moreover, the more complex a synthetic process is, the less robust it is usually, and this represents a major obstacle for industrial implementation.

Hence, conventional precipitation and coprecipitation from aqueous solution will most likely continue to be the “workhorse” of catalyst synthesis for many years.

86



## Precipitation and Co-precipitation



Simplified scheme for the formation of a solid product from solution.

The final particle size is determined by the interplay between nucleation and growth. The more particles nucleate, the smaller the resulting particles will be.

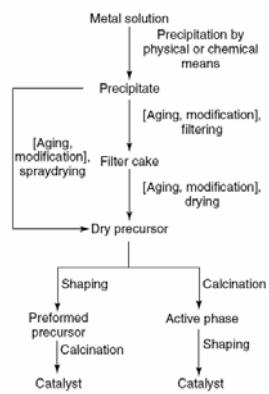


Fig. 1 Preparation scheme for precipitated catalysts. Optional steps are indicated by square brackets.

87

## Precipitation and Co-precipitation

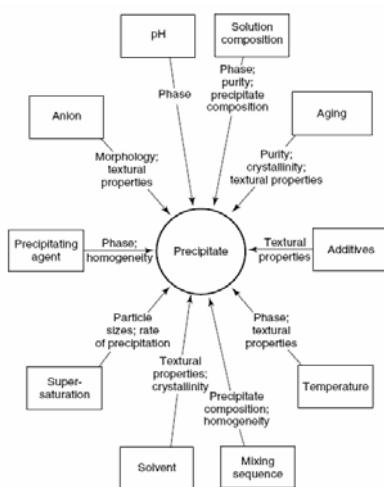


Fig. 4 Parameters affecting the properties of the precipitate, and the main properties influenced.

Usually, precipitates with specific properties are desired.

These properties include chemical composition, purity, morphology, homogeneity, particle size, pore sizes and pore volume, crystallinity, surface area, separability from the mother liquor,

To obtain these properties, many parameters such as solvent, saturation, precipitating agent, mixing sequence, pH, aging, calcination temperature, etc, must be optimized.

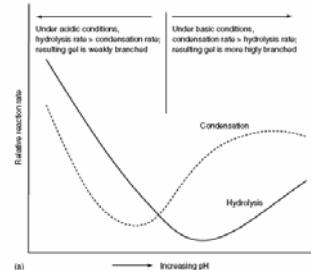
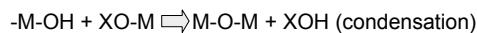
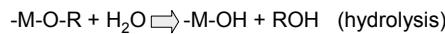
88



## Sol gel Process

Sol-gel processing is one of the routes for the preparation of porous materials by solidification (without precipitation) from a solution phase.

The reaction proceed in two steps:



Ex. Synthesis de Silica gel

Precursor: tetraethylortosilicate ( $\text{Si}(\text{OC}_2\text{H}_5)_4$ ) (TEOS)



**The characteristics of the gel depend on the balance between both hydrolysis and condensation rates**

89

## Sol gel Process

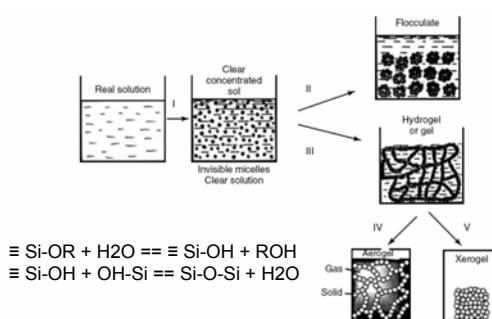


Fig. 1 General scheme of sol-gel processing in the preparation of solid materials. I, colloidization; II, flocculation; III gelation; IV, supercritical fluid processing; V, drying by evaporation.

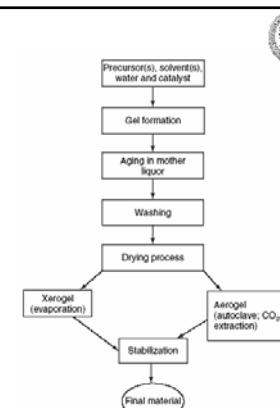


Fig. 2 The sequence of steps involved in sol-gel processing for the synthesis of porous solid catalytic phases. (Adapted from Ref. [6].)

First appear a clear colloidal solution due to primary condensation of dissolved molecular precursors. These colloidal particles, during gelation, forms polymeric chains by chemical bonding between local reactive groups at their surface. This prevents flocculation, that is a result of isotropic micelle aggregation.

The porous solids (xero- or aerogels) are produced in the next step – desolvation – depending on the drying mode.

90



## Sol gel Process

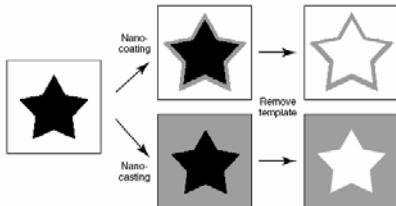
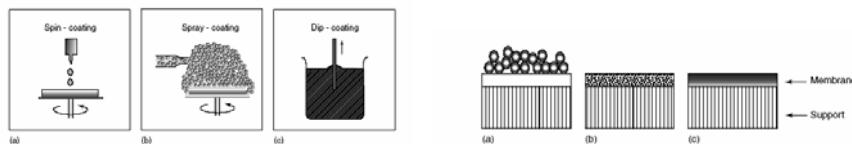


Fig. 16 Templating steps involved in nano-coating and nano-casting strategies for the preparation of sol-gel-derived porous solids.  
(Reproduced from Ref. [25].)

One of the advantages of the sol-gel process is the flexibility of the process, that permits to obtain catalysts in different configurations by templating or coating methods.

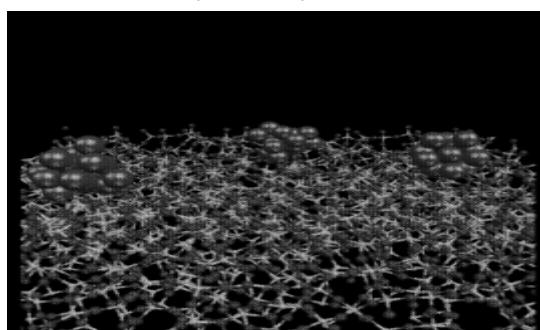


91

## Supported Catalysts

Many industrial catalysts consist of metals or metal compounds finely dispersed on an appropriate supports.

The role of the support is not merely that of a carrier; it may actually contribute catalytic activity. Further, the interaction between the active phase and the support phase can affect the catalytic activity.



The advantage of spreading the active phase on a support is to disperse it throughout the pore system, to obtain a large active surface per unit weight used.<sub>92</sub>



The selection of the support is based on a series of desirable characteristics:

- ➡ stability under reaction and regeneration conditions
- ➡ appropriate physical form for the given reactor
- ➡ adequate mechanical properties
- ➡ high surface area and porosity
- ➡ inertness
- ➡ chemical nature

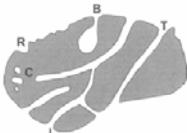
93



Porous solids are used as bulk catalysts or as catalyst supports.

94

## The surface area of the solids is located inside the pores



## Concepts

Figure I.1. Cross-section of a hypothetical porous grain showing various types of pores: closed (C), blind (B), through (T), interconnected (I), together with some roughness (R) (Rosquerol, 1990).

Table I.3. Definitions: porous solids

Term	Definition
Porous solid	Solid with cavities or channels which are deeper than they are wide
Open pore	Cavity or channel with access to the surface
Interconnected pore	Pore which communicates with other pores
Blind pore <sup>*</sup> (Dead-end pore)	Pore with a single connection to the surface
Closed pore	Cavity not connected to the surface
Void	Space between particles
Micropore	Pore of internal width less than 2 nm
Mesopore	Pore of internal width between 2 and 50 nm
Macropore	Pore of internal width greater than 50 nm
Pore size	Pore width (diameter of cylindrical pore or distance between opposite walls of slit)
Pore volume	Volume of pores determined by stated method
Porosity	Ratio of total pore volume to apparent volume of particle or powder
Total porosity	Ratio of volume of voids and pores (open and closed) to volume occupied by solid
Open porosity	Ratio of volume of voids and open pores to volume occupied by solid
Surface area	Extent of total surface area as determined by given method under stated conditions
External surface area	Area of surface outside pores
Internal surface area	Area of pore walls
True density	Density of solid, excluding pores and voids
Apparent density	Density of material including closed and inaccessible pores, as determined by stated method

\* In the sense of the French word 'borene'.

95

## Some typical porous solids



### Zeolites

Zeolites are microporous crystalline solids with well-defined structures. Generally they contain silicon, aluminum and oxygen in their framework and cations, water and/or other molecules within their pores

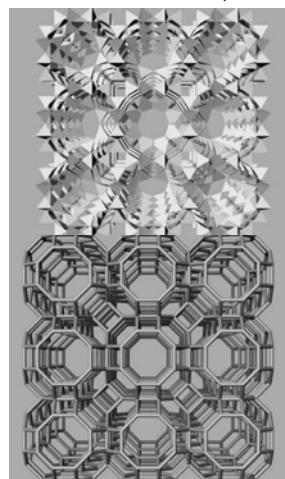
#### Framework Structure

A defining feature of zeolites is that their frameworks are made up of 4-connected networks of atoms.

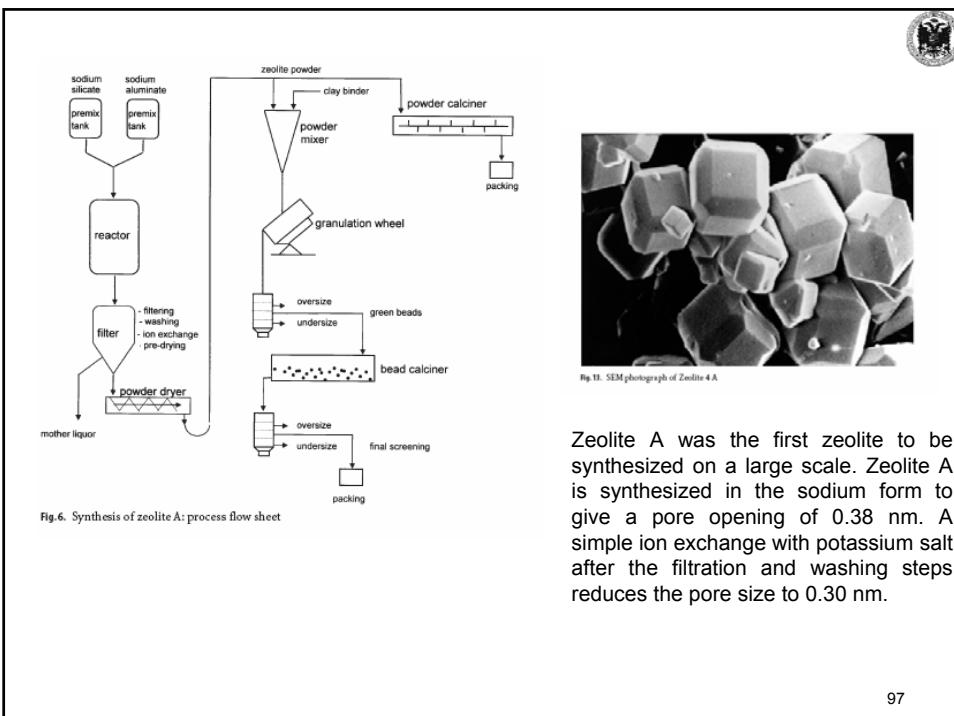
One way of thinking about this is in terms of tetrahedra, with a silicon atom in the middle and oxygen atoms at the corners. These tetrahedra can then link together by their corners to form a rich variety of beautiful structures.

The framework structure may contain linked cages, cavities or channels, which are of the right size to allow small molecules to enter

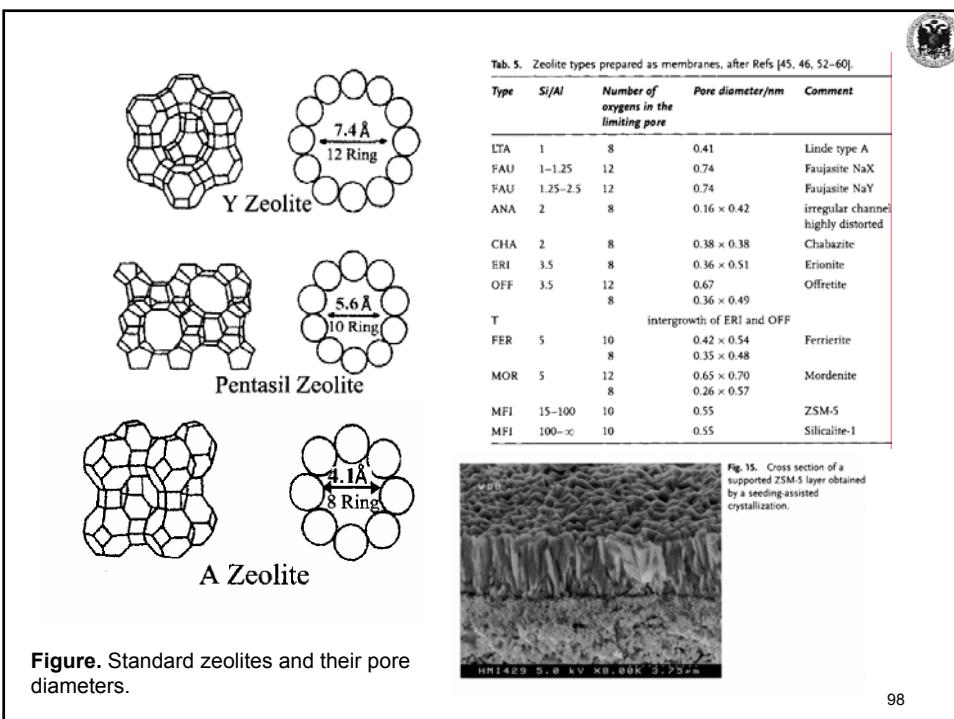
In all, over 130 different framework structures are now known.



LTA: Structure and Framework Figures <sup>96</sup>



97



98



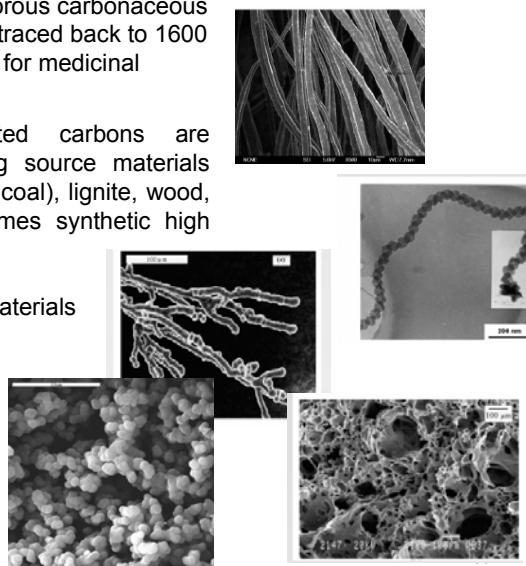
## Some typical porous solids

### Carbon materials

Activated carbons are the microporous carbonaceous adsorbents whose history can be traced back to 1600 B.C. when wood chars were used for medicinal purposes in Egypt.

Commercially available activated carbons are prepared from carbon containing source materials such as coal (anthracite or brown coal), lignite, wood, nut shell, petroleum and sometimes synthetic high polymers.

There are many types of carbon materials with different origins, thermal resistance, morphology, porosity, etc and in different configuration such as nanonubes, nanoparticles, foams, powders, pellets, etc



## Some typical porous solids

### Carbon materials

Tab. 4 Types of carbon support and their geometric surface areas

Carbon	Surface area/m <sup>2</sup> g <sup>-1</sup>
Natural graphite	0.1–20
Synthetic graphite	0.3–300
Graphitized carbon blacks	20–150
Carbon blacks	40–250
Activated carbon from wood	300–1000
Activated carbon from peat	400–1200
Activated carbon from coal (coke)	200–1000
Activated carbon from coconut shells	700–1500

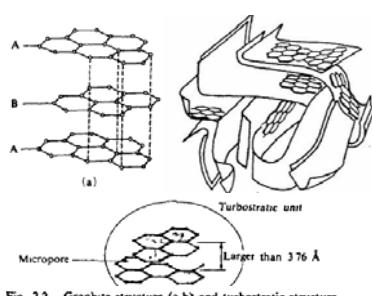


Fig. 2.2. Graphite structure (a,b) and turbostratic structure

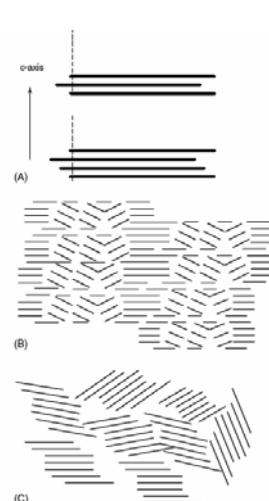


Fig. 9. Stacking variants of graphite carbon. (A) ideal stacking of large graphene units in hexagonal (AB) or rhombohedral (ABC) sequence. (B) Partly graphitized hard carbon with stacks of small graphite units. (C) Pre-graphitic stage with irregular stacks of basic units; hexagonal defects and few  $sp^3$  bridging functions keep the metastable nanostructure in place.

100



## Characterization of porous texture

There are different techniques to evaluate the type and pore volume:

### ADSORPTION ISOTHERMS

Adsorption isotherms describe the relation between the amount of molecules adsorbed on a unit mass of the solid and the adsorbate equilibrium pressure (or relative pressure) at a given temperature ( $V_{\text{STP}}$  vs  $P/P_0$ ).

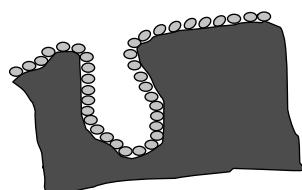
Intuitively, it is straightforward to see that the amount of adsorbed molecules forming a dense monolayer on the surface of a solid can be used to calculate its specific surface area, A. The monolayer capacity it is related to the specific surface area A (m<sup>2</sup>/g) by the simple equation:

$$A = n_m a_m L$$

Where  $n_m$ , the monolayer capacity (mol<sub>sorbate</sub> / g<sub>solid</sub>),  $a_m$  is the average area occupied by a molecule of adsorbate in the completed monolayer and L is the Avogadro constant

101

## Types of adsorption isotherms



Monolayer adsorbed molecules

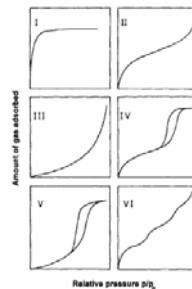


Fig. 13.3. The six types of adsorption isotherms following the Brunauer, Deming, Deming, Teller notation.

*Isotherm I* is typical of adsorption in micropores

*Isotherm II* represents multilayer physisorption on a flat surface (valid for many nonporous substances).

*Isotherms III and V* are characteristics of weak gas-solid interactions

*Isotherm IV* is frequently observed in the study of practical heterogeneous catalysts. It is characteristic of multilayer adsorption accompanied by capillary condensation in mesopores.

*Isotherm VI* is obtained when the surface of a nonporous adsorbent is energetically uniform, the isotherm may have a step-like shape associated to multilayer formation.

102



## MERCURY POROSIMETRY

Mercury porosimetry is used for the determination of the pore volume and the size distribution of meso- and macropores.

The technique uses progressive increase of the external pressure to force mercury into the pores of the sample studied. An inverse relationship exists between the pressure applied  $P$  and the pore radius  $r_p$ . For cylindrical pores this is the Washburn equation:

$$r_p = (2\gamma/P) \cos\theta$$

where  $\gamma$  is the surface tension and  $\theta$  the contact angle

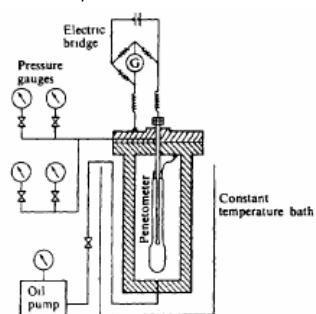


Fig. 211 Mercury penetration apparatus.

## Why supported Catalysts?

The activity of solid catalysts is usually proportional to the active surface area per unit volume of catalyst, provided that transport limitations are not present.

Remember the idea that one isolated atom can be an active site.

A high activity per unit volume calls for small particles.

As most active species sinter rapidly at the temperatures at which the thermal pretreatment and the catalytic reaction proceed, small particles of the active species alone generally do not provide thermostable, highly active catalysts.

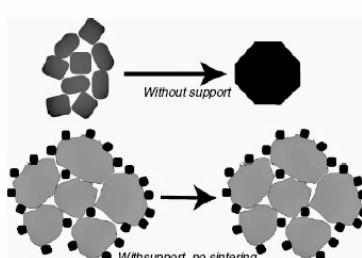


Fig. 1 Top: Rapid sintering of unsupported active particles.  
Bottom: Supported thermostable active material.



## Supported Catalysts

### The concept of dispersion

The degree of dispersion, defined by the ratio of the number of surface atoms to the total number of atoms in the polyhedron under consideration,  $N_s/N_t$ .

Dispersion needs to be as close as possible to unity so as to maximize the utilization of a catalyst.

For very small clusters it is not crystallographically sensible to talk of planes with Miller indices. Small particles may not be favorable when the reaction is structure-sensitive, and larger particles may exhibit a higher activity and/or selectivity per unit surface area.

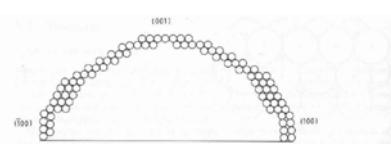
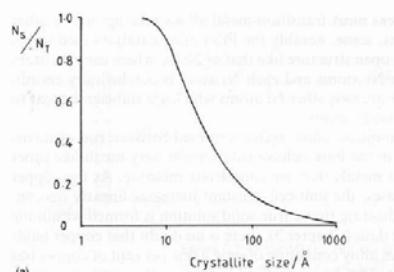


Figure 5.3 Hard-sphere model of a tungsten tip, showing cross-section of distinct crystallographic faces (see text).



For a crystallite of cubic shape  $N_s/N_t$  reaches unity when the size approaches 10 Å (assuming a unit cell spacing of 2.5 Å).

105



## Supported Catalysts

The procedures used to prepare supported catalysts can be divided into two main groups:

- (i) the selective removal of one or more component of usually non-porous bodies of a compound containing precursors of the support and the active component(s);
- (ii) the application of a precursor of the active component(s) onto a separately produced support

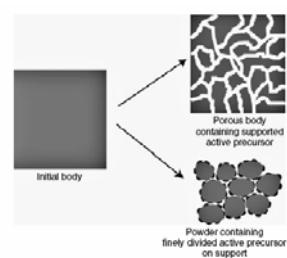
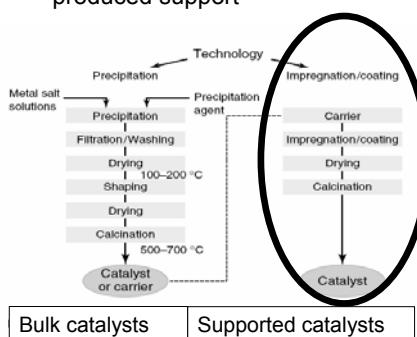


Fig. 4 Production of supported catalysts by selective removal of components from non-porous precursor leading to either porous bodies (top) or powder (bottom) of a supported active component.

106



## Supported Catalysts

The procedures used to load separately produced supports are:

- Contacting with a solution of an active precursor and drying
- Precipitation of an active precursor in the presence of a support suspended in the solution
- Decomposition of a gaseous active precursor on the support surface

There are also different techniques and the results depend also of many factors such as porosity, interactions between both phases, nature of precursors, thermal treatments, etc

**Chemical Vapor Deposition**

**Solid-State Ion Exchange in Zeolites**

**Incipient Impregnation**

**Precipitation onto a Suspended Support**

**Grafting and Anchoring of Transition Metal Complexes to Inorganic Oxides**

**Deposition–Precipitation within Pre-Shaped Support Bodies**

107

## Grafting and Anchoring of Transition Metal Complexes to Inorganic Oxides

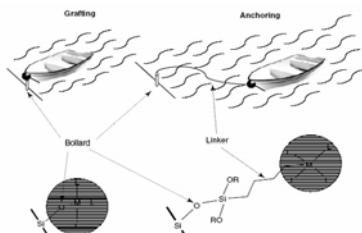


Fig. 1 Representation of "grafting" and "anchoring" of bollards and complexes to a pier and an oxide support, respectively.

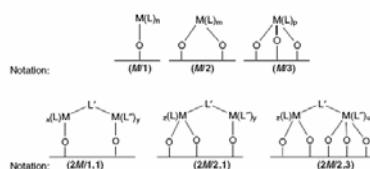


Fig. 2 Examples of mono- and polymolecular species grafted to an oxide support and proposed nomenclature.

108



## Supported Catalysts from Chemical Vapor Deposition and Related Techniques

According to IUPAC, deposition which occurs by adsorption or reaction from the gas phase is referred to as chemical vapor deposition (CVD).

In CVD, the correct choice of reactants (the precursors) is very important. These precursors fall into several general major groups, which include the halides, carbonyls, alkoxides, acetates, and organic complexes.

The choice of a precursor is governed by certain general characteristics, including:

- stability at room temperature;
- Sufficient volatility at low temperature so that it can be easily transported to the reactor;
- a capability of being produced at very high degrees of purity;
- an ability to react cleanly on or with the support
- an ability to react without producing side reactions or parasitic reactions

Tab. 1 CVD precursors

Al	AlCl <sub>3</sub> , AlEt <sub>2</sub>
B	BCl <sub>3</sub> , B(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> , BEt <sub>2</sub>
Bi	BiPh <sub>3</sub>
Ca	Ca(DPM) <sub>2</sub>
Co	Co(acac) <sub>3</sub> , Co(CO) <sub>4</sub> , Co(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> , Co(acac) <sub>2</sub> , Co <sub>2</sub> (acac) <sub>3</sub> , Co <sub>2</sub> (acac) <sub>2</sub> (CO)
Cr	Cr(CO) <sub>6</sub> , CrCl <sub>3</sub> O <sub>2</sub> , Cr(acac) <sub>3</sub>
Cu	Cu(acac) <sub>2</sub> , Cu(AcO) <sub>2</sub> , Cu(DPM) <sub>2</sub> , CuCl, Cu <sub>2</sub> (CH <sub>3</sub> CH <sub>2</sub> NMe <sub>2</sub> ) <sub>2</sub>
Fe	Fe(CO) <sub>5</sub> , Fe <sub>3</sub> (CO) <sub>12</sub> , Fe(acac) <sub>3</sub> , FeCp <sub>2</sub> , FeCl <sub>3</sub>
Ge	Ge(acac) <sub>3</sub> , GeMe <sub>3</sub>
Ir	Ir(acac) <sub>3</sub> , IrCl(CO) <sub>2</sub> , Ir(acac) <sub>2</sub> (CO) <sub>2</sub> , Ir(allyl) <sub>3</sub> , Ir(Cp) <sub>2</sub> ( <i>t</i> - <i>s</i> -COD), IrCp <sup>*</sup> ( <i>t</i> , <i>s</i> -COD), Ir( <i>p</i> -SCMe <sub>2</sub> ) <sub>2</sub> (CO) <sub>2</sub>
Mn	Mn <sub>2</sub> (CO) <sub>10</sub>
Mo	Mo(C <sub>2</sub> H <sub>5</sub> ) <sub>6</sub> , MoCl <sub>5</sub> , Mo <sub>2</sub> (AcO) <sub>8</sub> , MoO <sub>3</sub> (nhd) <sub>2</sub> , MoO <sub>5</sub>
Nb	NbCl <sub>5</sub> , Nb(OEt) <sub>5</sub>
Ni	Ni(CO) <sub>4</sub> , Ni(acac) <sub>3</sub> , Ni(allyl) <sub>2</sub> , NiCP <sub>2</sub>
Os	Os(CO) <sub>4</sub> , Os(acac) <sub>3</sub> , Os(CO) <sub>2</sub> (acac) <sub>2</sub>
Pd	Pd(acac) <sub>2</sub> , Pd(AcO) <sub>2</sub> , Pd(hfac) <sub>2</sub> , Pd(allyl) <sub>2</sub> , Pd(Cp) <sub>2</sub> , Pd(allyl) <sub>2</sub> , Pd(allyl) <sub>2</sub> Cp, Pd(allyl) <sub>2</sub>
Pt	Pt(CO) <sub>4</sub> , PtCl <sub>2</sub> (CO) <sub>2</sub> , Pt(acac) <sub>2</sub> , Pt(hfac) <sub>2</sub> , Pt(Cp) <sub>2</sub> , Pt(nhd) <sub>2</sub> , PtBu <sub>2</sub> , PtCp <sup>*</sup> Me <sub>2</sub> , PtMe <sub>2</sub> ( <i>t</i> - <i>s</i> -COD)
Rh	Rh <sub>2</sub> (CO) <sub>10</sub> , RhReO <sub>3</sub> , Re <sub>2</sub> O <sub>7</sub>
Ru	Ru(CO) <sub>4</sub> , Ru(acac) <sub>3</sub> , Ru(CO) <sub>2</sub> (acac) <sub>2</sub> (CO) <sub>2</sub> , Ru(allyl) <sub>3</sub> , Ru(CO) <sub>2</sub> Cl, Ru(CO) <sub>2</sub> (acac) <sub>2</sub> , Ru(allyl) <sub>2</sub> , Ru(Cp) <sub>2</sub>
Ru	Ru(CO) <sub>5</sub> , Ru <sub>2</sub> (CO) <sub>10</sub> , Ru( <i>t</i> , <i>s</i> -COD), Ru( <i>t</i> , <i>s</i> -COD)(acac) <sub>2</sub> , Ru(Cp) <sub>2</sub>
Sb	Sb(OEt) <sub>3</sub> , Sb(O <sub>2</sub> CMe <sub>2</sub> ) <sub>3</sub> , SbEt <sub>3</sub> , Si(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> , Si(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> O, Si(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Pr <sub>2</sub>
Sm	Sm(acac) <sub>3</sub>
Sn	Sn(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> , SnMe <sub>4</sub> , Sn-Et <sub>2</sub>
Ti	TiCl <sub>4</sub> , Ti(OEt) <sub>4</sub> , Ti(OPr) <sub>4</sub>
V	V(CO) <sub>5</sub> , VC <sub>4</sub> , VOCl <sub>3</sub> , VO(Pr') <sub>3</sub>
W	W(CO) <sub>6</sub> , WC <sub>6</sub>
Zr	Zr(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> , Zr(O <sub>2</sub> SMe <sub>2</sub> ) <sub>2</sub> , ZrCl <sub>4</sub> (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> , Zr(OEt) <sub>4</sub> , Zr(OBu') <sub>4</sub> , Zr(Cp <sub>2</sub> Cl) <sub>2</sub> , Zr(Cp <sub>2</sub> Me) <sub>2</sub>

Acac, acetylacetone; hfac, hexafluoroacetylacetone; tmdm, 2,2,6,6-tetramethyl-3,3-dione; DPM, dipropylamine; Me, methyl; Et, ethyl; Pr, propyl; P*r*, isopropyl; Bu, butyl; Bu', ter-butyl; Cp, cyclopentadienyl; Cp', pentamethylcyclopentadienyl.



## From the Precursor to the Final Catalyst

In general, the impregnated support are not yet actives. The catalyst precursor deposited on the support must be transformed to a suitable compound (metal oxides, sulfurs) in order to acquire the desired activity.

These last stages, calcination, reduction and sulfidation, are usually called Activation, and their effect strongly depends of experimental conditions and interactions active phase and supports. (ex. Sintering is favored with long calcinations and treatment temperature, stabilization of crystallographic phases, different degrees of reduction / non stoichiometry, or the formation of solid solutions by diffusion of the active phase on the supports can occurs )

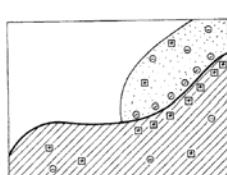


Figure 4. Supported phase-support interaction: electronic interaction.

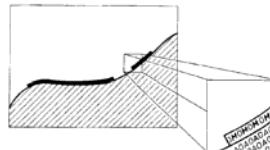
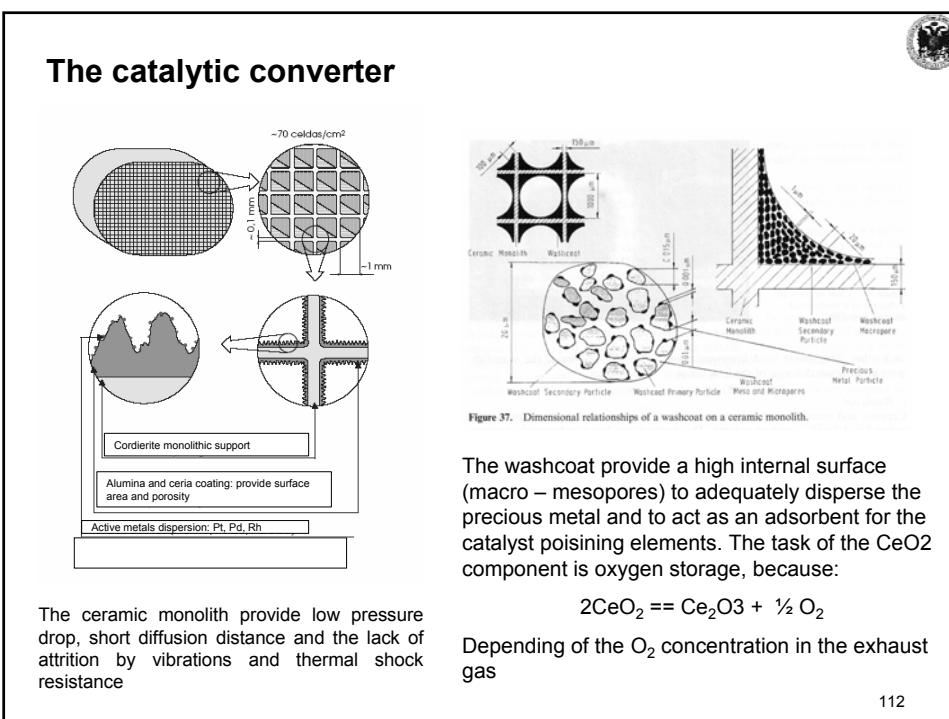
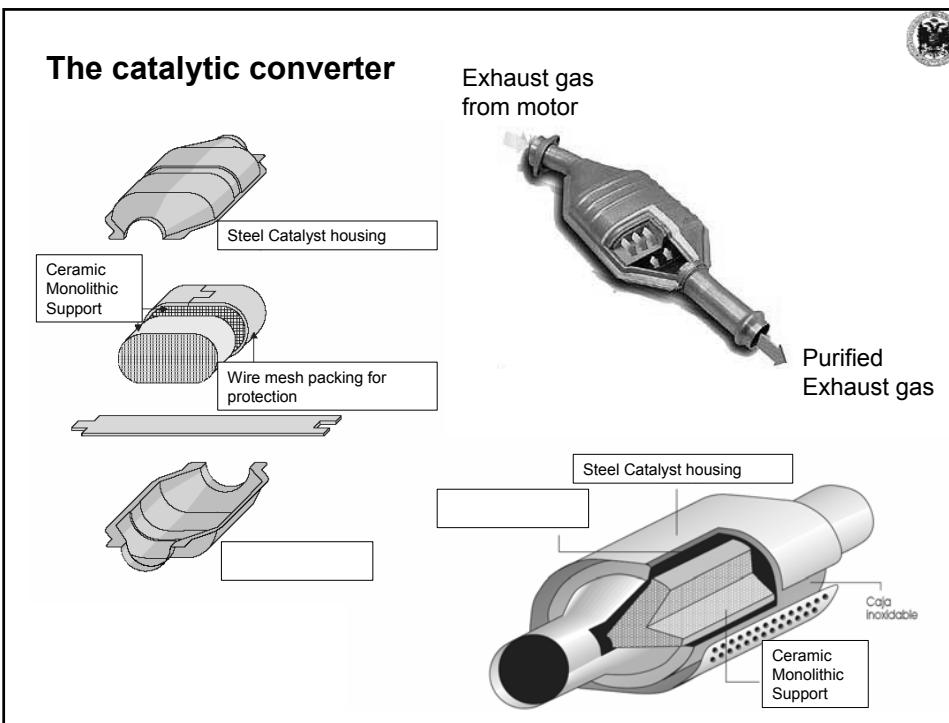


Figure 6. Supported phase-support interaction: patches of monolayer (rafts) or complete monolayer.



Figure 8. Supported phase-support interaction: partial formation of solid solutions.





## The catalytic converter

Three-way catalysts contain Pt : Rh : Pd in proportions that varies with the properties of fuels, the catalysts operating conditions or the emissions targets to be reached.

Both Pt and Pd are common elements in oxidations catalysts, with an increasing proportion of Pd vs Pt because this metal is cheaper. The Rh enhance the selective reduction of NO to N<sub>2</sub>.

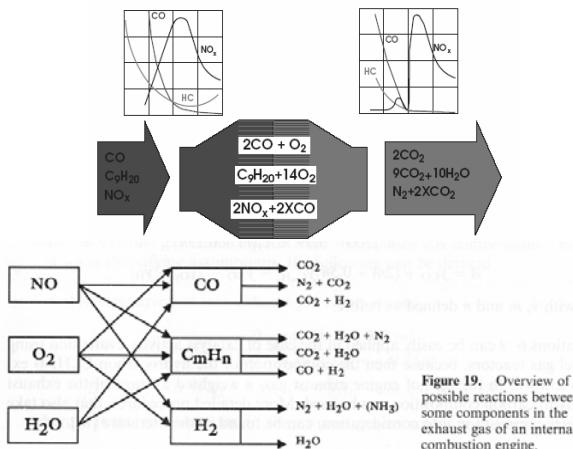


Figure 19. Overview of the possible reactions between some components in the exhaust gas of an internal combustion engine.

Three-way catalysts: NO reduction and CO and hydrocarbons (VOC's) oxidations

113



## Catalyst deactivation

The activity and selectivity of heterogeneous catalysts may change during the course of reaction. Usually activity decreases due to either chemical or physical reasons, or a combination both factors.

However, sometimes the selectivity increases, and therefore, is not to be viewed as an entirely negative effect.

Example: In zeolitic and other acid catalysts such as Al<sub>2</sub>O<sub>3</sub>, there is a loss in their activity for the cracking of hydrocarbons, but an improvement in their isomerisation facility, upon exposure to nitrogenous bases such as pyridine or quinoline.

114

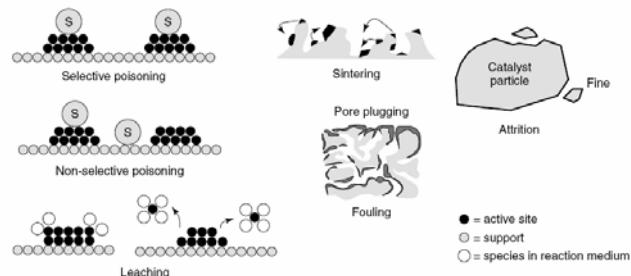


## Catalyst deactivation

Catalyst deactivation can be caused by:

- (i) a decrease in the number of active sites
- (ii) A decrease in the quality of the active sites
- (iii) degradation of accessibility of the pore space

The main causes of deactivation can be classified as:



115



## Catalyst deactivation

**Poisoning:** The active sites of a catalyst may become inactive by the adsorption of impurities in the feed stream

Tab. 2 Examples of catalyst poisons

Type of poison	Examples	Reaction
Strong chemisorbers	H <sub>2</sub> S in Pt catalysts H <sub>2</sub> S in Ni catalysts NH <sub>3</sub> in acid catalysts CO in Fe catalysts	Hydrogenation, catalytic reforming Hydrogenation, steam reforming Hydrocracking Ammonia synthesis
Metals	V, Ni in Co and Mo sulfides Pb in noble metal catalysts	Hydrotreating Oxidation of CO, hydrocarbons
High molecular weight product	Coke from dienes, acetylenes Coke in acid catalysis	Pyrolysis gas selective hydrogenation FCC

It is useful to distinguish between temporary and permanent poisoning.

In the case of temporary poisoning, adsorption of the poison is relatively weak and reversible and removal of the poison from the fluid phase results in restoration of the original catalytic activity.

If adsorption of the poison is strong and not readily reversed, the poisoning is called permanent.

116



## Catalyst deactivation

### Formation of Deposits

The formation of deposits can be of a physical or a chemical nature.

So-called catalyst fouling is a physical process, which covers all phenomena in which material is deposited on the surface of the catalyst to block active sites and/or pores.

In most cases, the catalyst causes the formation of undesired by-products that lead to deposits. The most commonly encountered is so-called coke, which is formed by chemical reactions of hydrocarbons at relatively high temperature.

When large amounts of coke are deposited, the diffusion characteristics change as a result of narrowing or even complete blocking of the catalyst pores.



117

## Catalyst deactivation



### Thermal Degradation

Thermal degradation is a physical process leading to catalyst deactivation because of high-temperature-induced sintering, chemical transformations, evaporation, etc.



Sintering is the loss of catalyst active surface due to crystallite growth of either the support material or the active phase.

Initially, the metal is supposed to be present as small clusters of atoms (or small metal particles), termed monomer dispersion. Surface diffusion of the atoms will lead to two-dimensional clusters and, upon further diffusion, three-dimensional particles will be formed

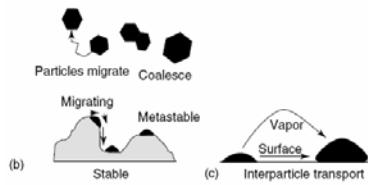
118



## Catalyst deactivation

### Thermal Degradation

Sintering resembles crystallization: larger particles grow at the expense of smaller ones. Particles might move and coalesce or atoms move from one particle to another, either by volatilization or by surface migration.



The position of the particle contributes to the ease of sintering. A "valley" position is stable, whereas an "on-top" position is highly unstable.

Sintering is a function of time, temperature, atmosphere, interaction metal – support, porosity and morphology of the support, etc

119



## Catalyst deactivation

### Thermal Degradation

**Chemical transformations**, reactions in which the support is directly involved can also take place. An example is alumina-supported cobalt oxide. At high temperatures ( $>800$  K), solid-state diffusion becomes noticeable and Co ions diffuse into the support, generating a spinel. It is not surprising that in this process catalytic activity is lost

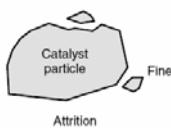
**Evaporation**, leads to a progressive loss of the active phase and of course, is most important in high temperature processes, the major examples being steam reforming and catalytic combustion. By a high-temperature treatment (up to 920 K) in an oxygen-containing gas, platinum is slightly vaporized because of the formation of Pt oxides.

120



## Catalyst deactivation

### Mechanical Deactivation



Mechanical strength is important in giving the catalyst resistance against *crushing*. In a fluidized-bed reactor, *attrition* will always occur and the fines formed will be carried away with the product flow.

The shape and porosity of the catalyst particles influence mechanical strength: a spherical shape is most favorable, while the higher the porosity, the lower is the mechanical strength. In particular, macropores will lead to reduced strength.

In washcoat monoliths, the adherence of the coating to the monolith is very important. The washcoat may be fractured and/or separated from the monolith because of thermal stresses.

This is particularly relevant in automotive applications, in which the catalyst is subject to a wide range of temperatures that change very often and very rapidly (engine on – off).

121



## Catalyst deactivation

### Corrosion / Leaching

Particularly in liquid-phase catalysis, leaching of the active metal by dissolution into the surrounding liquid reaction mixture is often a concern.

In most cases, leaching is the result of solvolysis of metal–oxygen bonds through which the catalyst is attached to the support. This not only causes loss of catalyst activity, but also results in contamination of the product.

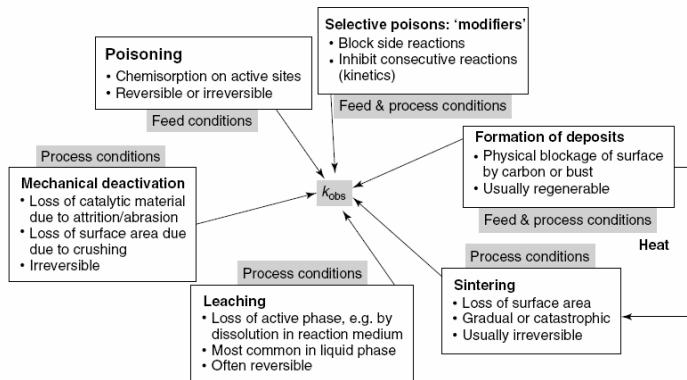
The support material itself may be also subjected to leaching. The reaction medium can be corrosive. Consider alumina at high or low pH. Above pH 12 it will dissolve.

122



## Catalyst deactivation

### Summary



Deactivation phenomena, their causes and effects

123



**What can be done to eliminate or in any case reduce the catalyst deactivation?**

If the cause of deactivation is understood, logical measures can be contrived:

- At the catalyst level
- In the reactor selection and process design
- In the optimization of the operating conditions.

124



## What To Do?

When poisoning is the problem, a more robust active phase or support might be selected. Example: Alumina forms a surface sulfate with sulfur oxides, whereas titania is inert.

When fouling is the problem, the option is to optimize the catalyst texture (wide / narrow pores). The coke deposition can be prevented by tuning the reaction conditions or by alloying the metal particles.

Sintering is more easily prevented than cured, as it is often irreversible. Sintering can be reduced by structural promoters or stabilizers. Example, the addition of Re to the Pt/alumina catalyst leads to strongly improved stability.

The crushing strengths and attrition resistances of catalysts can be significantly improved, for example by using different preparation or shaping methods

125



## What To Do?

It will be clear that the time-scale of deactivation influences the choice of reactor type, the mode of operation and regeneration.

Tab. 6 Relationship between time-scale of deactivation and reactor type (solid catalysts)

Time-scale of deactivation	Typical reactor type
Years	Fixed-bed reactor, no regeneration
Months	Fixed-bed reactor, regeneration while reactor is off-line
Weeks	Fixed-bed reactors in swing mode, moving-bed reactor
Minutes–days	Fluidized-bed reactor, slurry reactor; continuous regeneration
Seconds	Entrained-flow reactor (riser) with continuous regeneration

Tab. 7 Operating conditions in catalytic reforming

	Semi	Fully	Continuous
Feed H <sub>2</sub> :HC/mol:mol	10	4–8	4–8
Pressure/MPa	1.5–3.5	0.7–1.5	0.3–0.4
Temperature/K	740–780	740–780	770–800
Catalyst life	0.5–1.5 years	Days–weeks	Days–weeks

With increasing the deactivation rate, the choice of the reactor type changes from fixed bed to the riser with continuous regeneration.

The correct choice of the operating conditions strongly influences the catalyst life, which vary from years to days.

126

## PGM = Platinum group metals (noble metals)



Tab. 1 Important application segments for PGM process-catalysts [6]

Application	Catalyst type support	Precious metals (PM)	PM loading/%	Catalyst life/years
<b>Oil refining</b>				
• Reforming	Al <sub>2</sub> O <sub>3</sub>	Pt; Pt/Rh; Pt/Ir	0.02–1	1–12
• Isomerization	Al <sub>2</sub> O <sub>3</sub> ; zeolites	Pt; Pt/Pd		
• Hydrocracking	SiO <sub>2</sub> ; zeolites	Pd; Pt		
• Gas to liquid (GTL)	Al <sub>2</sub> O <sub>3</sub> ; (SiO <sub>2</sub> , TiO <sub>2</sub> )	Co + (Pt or Pd or Ru or Re)		
<b>Bulk and specialities</b>				
• Nitric acid	Gauzes	Pt/Rh; Pd	100	0.5
• H <sub>2</sub> O <sub>2</sub>	Powder (black)	Pd	100	1
• HCN	Al <sub>2</sub> O <sub>3</sub> or gauzes	Pt; Pt/Rh	0.1; 100	0.2–1
• PTA	Carbon granules	Pd	0.5	0.5–1
• VAM	Al <sub>2</sub> O <sub>3</sub> ; SiO <sub>2</sub>	Pd/Au	1–2	4
• Ethylene oxide	Al <sub>2</sub> O <sub>3</sub>	Ag	10–15	
• KAAP	Activated carbon	Ru		
<b>Homogeneous</b>				
• Oxo alcohols	Homogeneous	Rh	100–2000 ppm (in process solution)	1–5
• Acetic acid	Homogeneous	Rh; Ir/Ru		
<b>Fine chemicals</b>				
• Hydrogenation	Activated carbon (powder)	Pd; Pt; Pd/Pt; Ru; Rh; Ir	0.5–10	0.1–0.5
• Oxidation				
• Debenzylation etc.				
<b>Automotive</b>				
• Catalysts	Cordierite monolith ceramic pellets	Pt/Rh	0.1–0.5	>10
• Diesel particulate filter	Metallic monolith SiC or cordierite monolith	Pt/Pd/Rh Pt Pt/Pd		

127

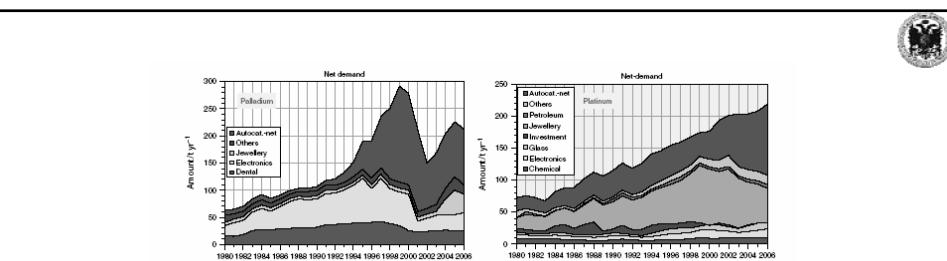


Fig. 2 Development of net demand for Pt and Pd by application (data based on Ref. [1]).

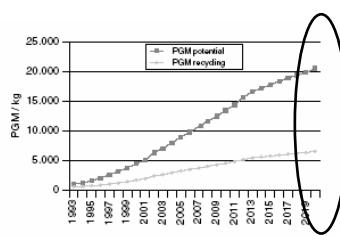
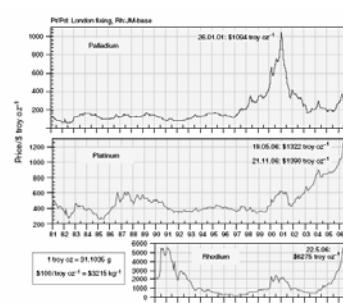


Fig. 13 Theoretical recycling potential for PGM from autocatalysts and forecast of real recycling volumes (at current lifecycle efficiencies) for Germany [9].



In spite of the increasing price and demand of noble metals (platinum group, PGM) the real recycling degree only reach about 30% of the potential

128

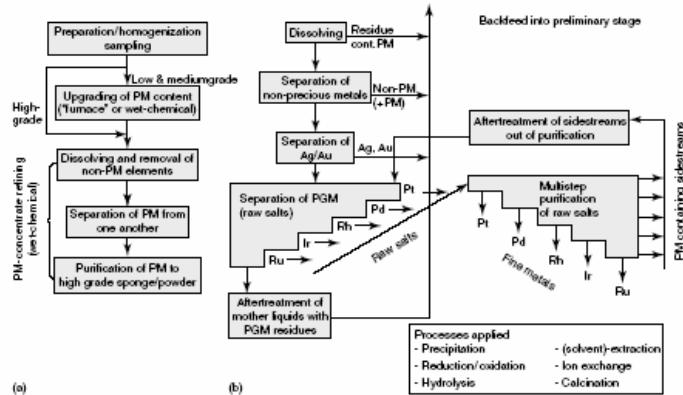


Fig. 4 (a) Main steps in PM refining and (b) sequence of PM concentrate processing [5].

129



Tab. 2 Overview of treatment and refining methods for precious metals catalysts

Substrate/catalyst type	Main sampling method	Preconcentration	PGM separation and purification out of	PGM yield/% (after sampling step)
Activated carbon	Out of ash after incineration or from suspension of original catalyst	Incineration or, "smelting"	PGM concentrate or collector metal with PGM	96–99
Al <sub>2</sub> O <sub>3</sub> ( $\gamma$ -type)	Screening or blending	Dissolution of substrate by NaOH or H <sub>2</sub> SO <sub>4</sub>	PGM concentrate	98–99
Zeolite, SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> (all types), ZrO <sub>2</sub> , BaSO <sub>4</sub> , CaCO <sub>3</sub>	Screening, blending (milling)	Pyrometallurgy (smelting)	Collector metal with PGM	94–98.5
Gauzes	Dissolution or melting	–	PGM solution or PGM alloy	98–99
Homogeneous	Out of mixed pulp or after incineration	Chemical collection or incineration or "smelting"	PGM concentrate or collector metal with PGM	85–98

130



### Some final remarks:

- Catalysis is essential to maintain our quality of life.
- The catalyst only increases the reaction rate
- Selectivity is most important than activity
- Catalysis is a surface phenomenon. The catalyst surface is heterogeneous and active sites of variable strength are related to geometric, electronic, acid-basic aspects, etc
- Different kinds of catalysts: bulk and supported, can be prepared
- The catalytic behavior can be tailored by fitting the catalyst characteristics (porosity, electronic parameters, etc)
- The catalyst is finally deactivated and the recycling the spent catalyst is necessary from an economic and environmental point of view.

131

Thanks for your attention!!!



132