روش های سنتز و شناسایی کاتالیزورهای هتروژن

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سنتز کاتالیزورهای هتروژن

INTRODUCTION

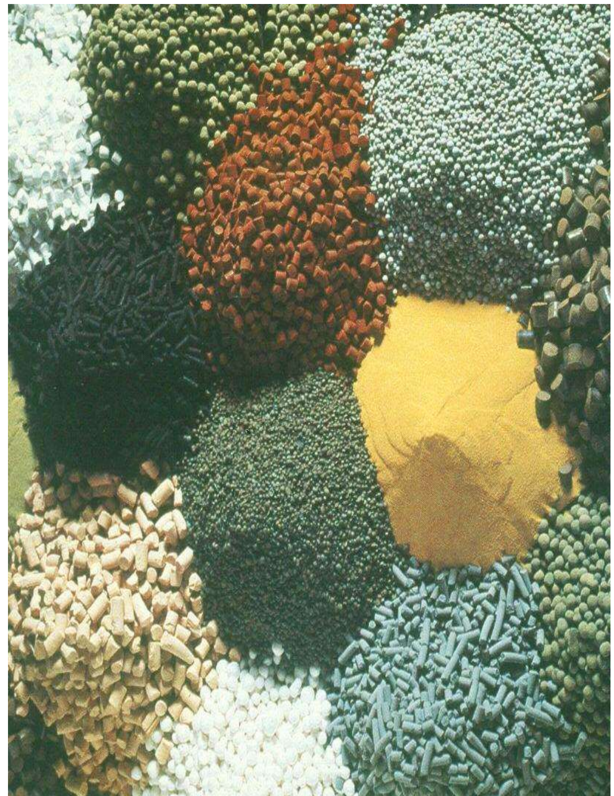
- Industrial catalysts are generally shaped bodies of various forms,

e. g., rings, spheres, tablets, pellets.

- The production of heterogeneous catalysts consists of numerous physical and chemical steps.

- The conditions in each step have a decisive influence on the catalyst properties.

- the main physical properties of a catalyst that are influenced by the production Conditions are: Active surface area; pore structure; mechanical strength.



TYPES OF CATALYSTS

(1) Unsupported Catalyst

Usually very active catalyst that do not require high surface area

e.g., Iron catalyst for ammonia production (Haber process)

(2) Supported Catalyst

requires a high surface area support to disperse the primary catalyst

the support may also act as a co-catalyst (bi-functional)

or secondary catalyst for the reaction (promoter)

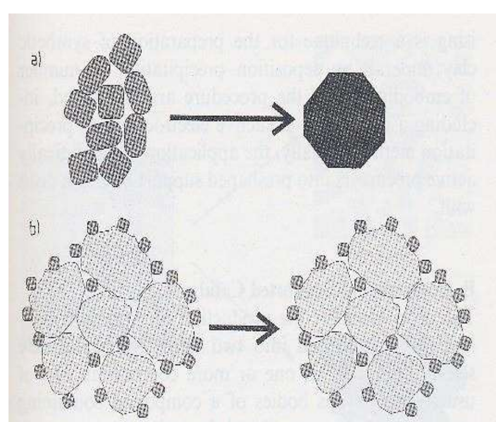


Figure 1. (a) Rapid sintering of unsupported active particles. (b) Supported thermostable active material.

TYPES OF CATALYSTS

Bulk Catalysts

Metal oxides

Metals (skeletal catalysts)

Noble metal gauze

Supported Catalysts

Often noble metals

Systems which cannot be dispersed by other methods

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

Rule of thumb for specific surface area with respect to particle size:

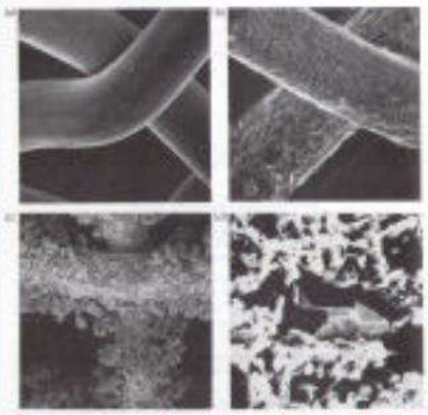
- 1 µm ˜ 1 m²/g $A = 6/(\rho \cdot d)$
- one magnitude higher/lower particle size corresponds to one magnitude lower/higher specific surface area

TARGETS FOR CATALYST PREPARATION

- Activity
- Selectivity
- Stability
  - coking
  - poisoning by reactands
  - sintering
  - poisoning by impurities
- Morphology
- Mechanical strength/resistance
- Thermal properties
- Regeneration
- Reproducibility
- No patent / patentable
- Costs

BULK CATALYSTS: FUSED CATALYSTS

- Important for preparation of metal alloys for gauzes
- High dispersion of elements (in melt)
- Ostwald process (Pt/Rh)
- Andrussov process (Pt or Pt/Rh)
- Sulfuric acid catalyst ($V_2O_5/M_2S_2O_7$)
- Typically high costs of energy, process control difficult



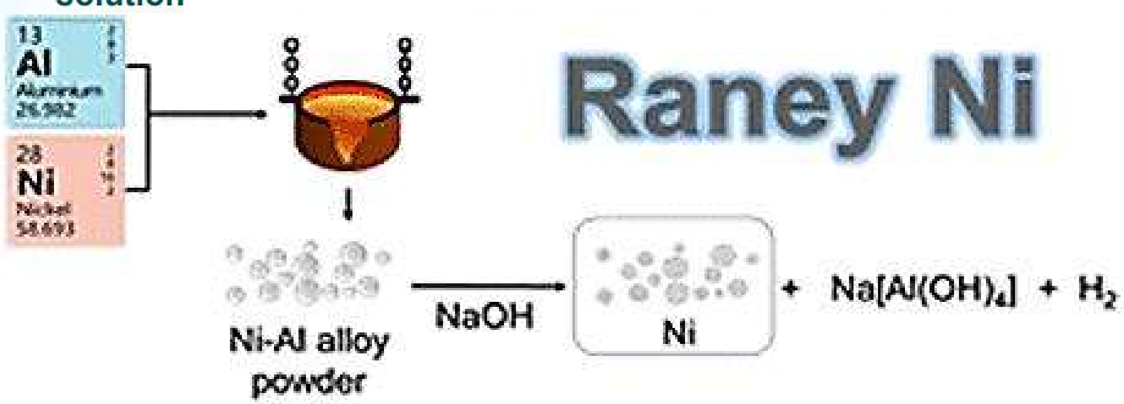
Pt/Rh gauze unactived , partially activated, well-activated, and with Rh_2O_3 crystals on surface

Installation gauze pad

from Catalyst Handbook, 2nd Ed., M.V. Twygg (ed), Wolfe Publishing Ltd., 1989

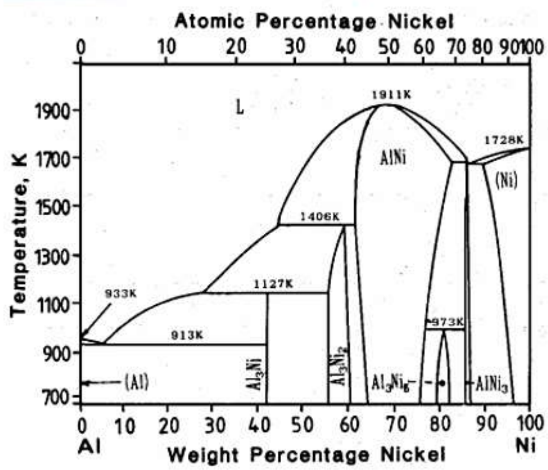
BULK CATALYSTS: RANEY CATALYSTS

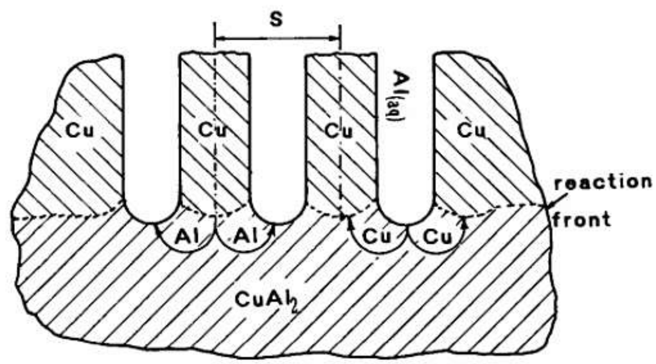
- Principle: Formation of alloy in a melt, then extraction of one component
- usually: Ni/Al alloy, extraction of Al with alkali hydroxide solution



BULK CATALYSTS: RANEY CATALYSTS

- Principle: Formation of alloy in a melt, then extraction of one component
- usually: Ni/Al alloy, extraction of Al with alkali hydroxide solution
- Other systems known, technically Raney-Cu is used for the reduction of organic nitro compounds and nitriles

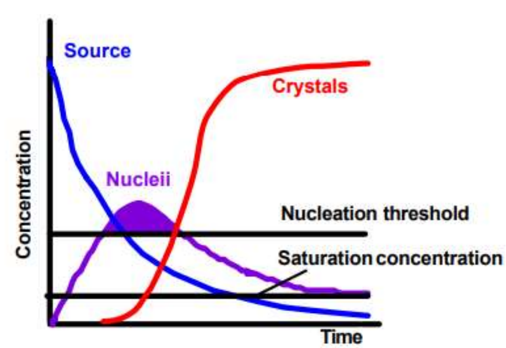




BULK CATALYSTS: PRECIPITATED CATALYSTS

- Precipitated Catalysts

  Nucleation is decisive



(simplified!)

- Problems:
  - Quality varies because of changing concentrations

    ➡ continuous precipitation
  - Inclusion of ions

    ➡ decomposable couter ions, NO_3^-, NH_4^+, oxalate, citrate...
  - Local supersaturation

    ➡ homogeneous precipitation, e.g. with urea
  - component with low K_{sp} precipitates first in co-precipitation

    ➡ Precipitation at high supersaturation or continiuously

BULK CATALYSTS: PRECIPITATED CATALYSTS

» Nowadays increasing use of organic solvents, e.g. in production of VPO($(VO)_2P_2O_7$) catalysts or Ziegler (zirconocene/MAO/SiO_2 - catalyst) catalysts

» Precipitation of defined precursor compounds followed by thermal decomposition or transformation into final catalyst

Examples:

Ni/Al_2O_3

Hydrotalcites, such as $Ni_6Al_2(OH)_{16}CO_3 \cdot 4\ H_2O$, have different calcination and reduction behavior than mixtures of components due to dispersion of elements on atomic level

Methanol catalyst (Cu/ZnO)

Depending on precipitation conditions many different phases with strongly varying catalytic properties can be obtained in dependence of conditions during transformation into catalyst

BULK CATALYSTS: SOL-GEL MATERIALS

- Sol-Gel process produces typically highly porous materials with high specific surface areas
- Precursors mostly metal alkoxides, but could as well be simply salts

Hydrolysis: $M\text{-}OR + H_2O \longrightarrow MOH + ROH$

Condensation: $MOH + XO\text{-}M \longrightarrow M\text{-}O\text{-}M + XOH$ X=H,R

- Both steps proceed simultaneously, relative reaction rate important for product properties

if hydrolysis faster than condensation ➡ less branched material

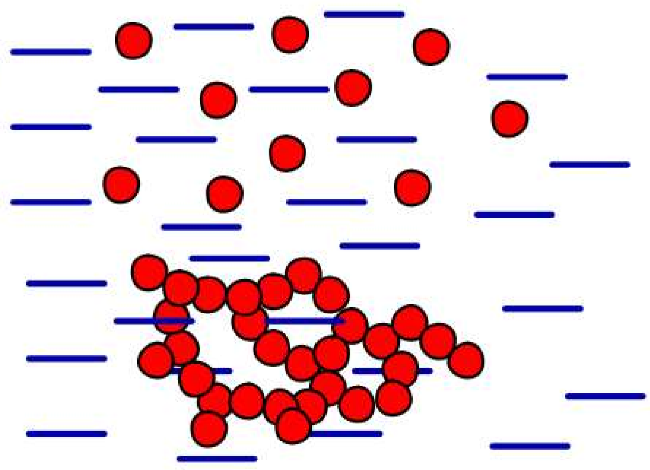
if hydrolysis slower than condensation ➡ highly branched material

J. Brinker, W. Scherer, Sol-Gel-Science, Academic Press 1990;
J. Livage, M. Henry, C. Sanchez, Progr. Solid St. Chem. 18, 259 (1988)

SOL-GEL FORMATION

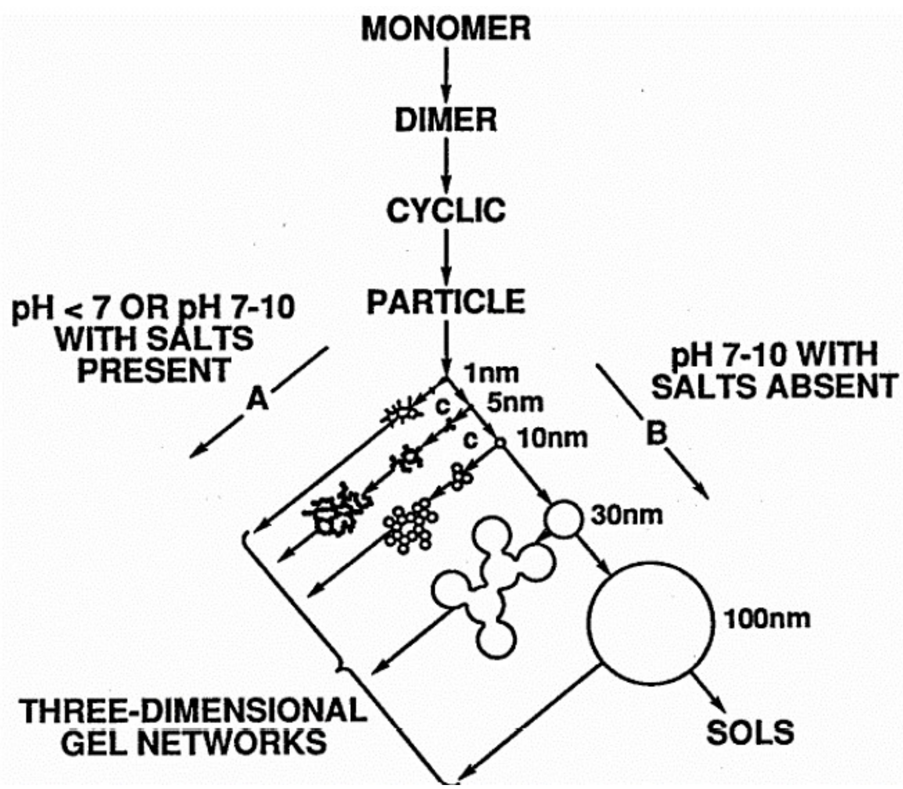
1. Sol Formation

2. Gelation

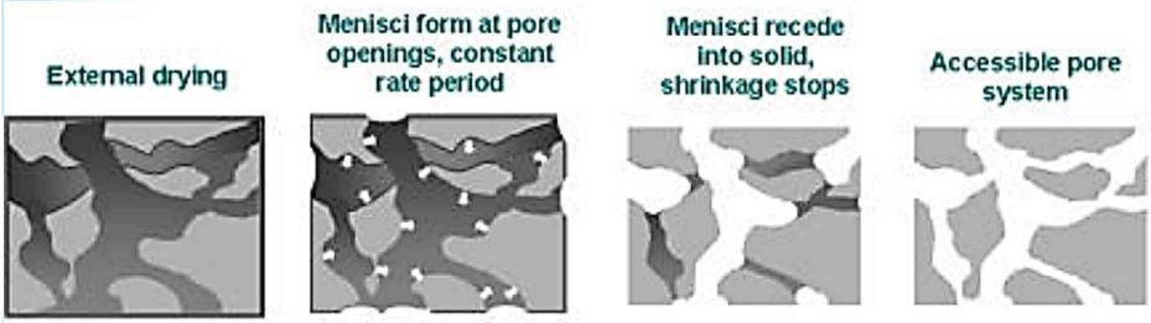


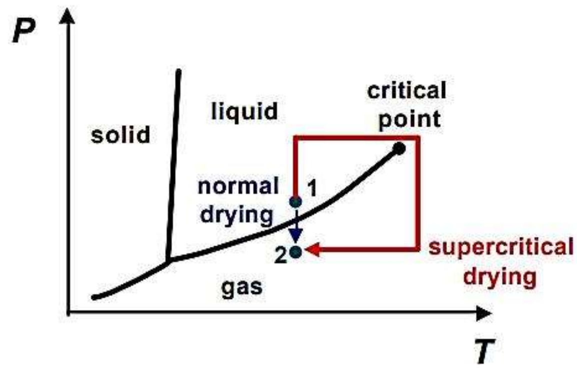
Advantage: High degree of control over product properties easy preparation of mixed oxides with atomic dispersion of elements

GELATION OF SILICA



GEL DRYING / AEROGELS





BULK CATALYSTS: HYDROTHERMAL SYNTHESIS

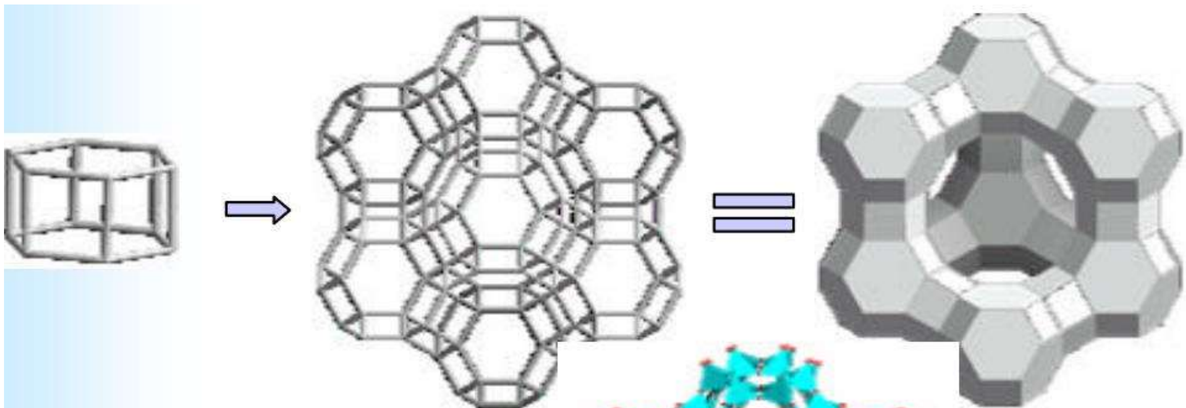
- Discrimination against precipitation sometimes difficult; typically higher temperature, often pressure, longer reaction time than for precipitation
- Crucial for zeolite synthesis (crystalline, microporous aluminosilicates)

Lab autoclaves
50 - 250 ml

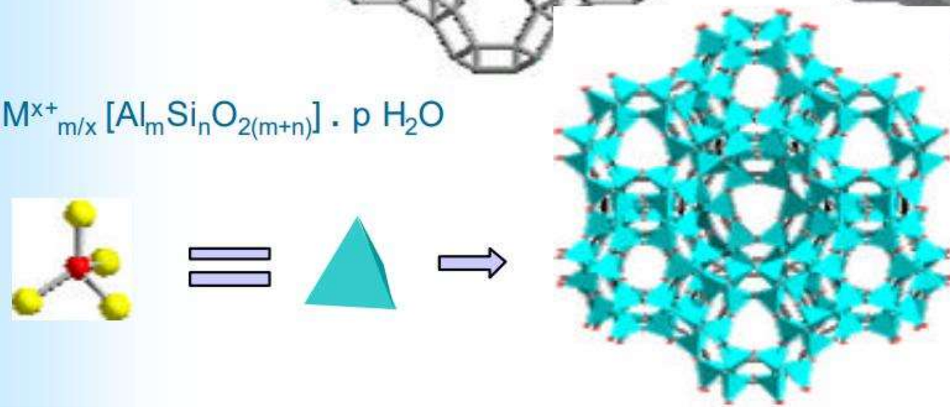
Stirred autoclave
1.5 - 2.5 l

Industrial stirred reactors
50 - 5000 l

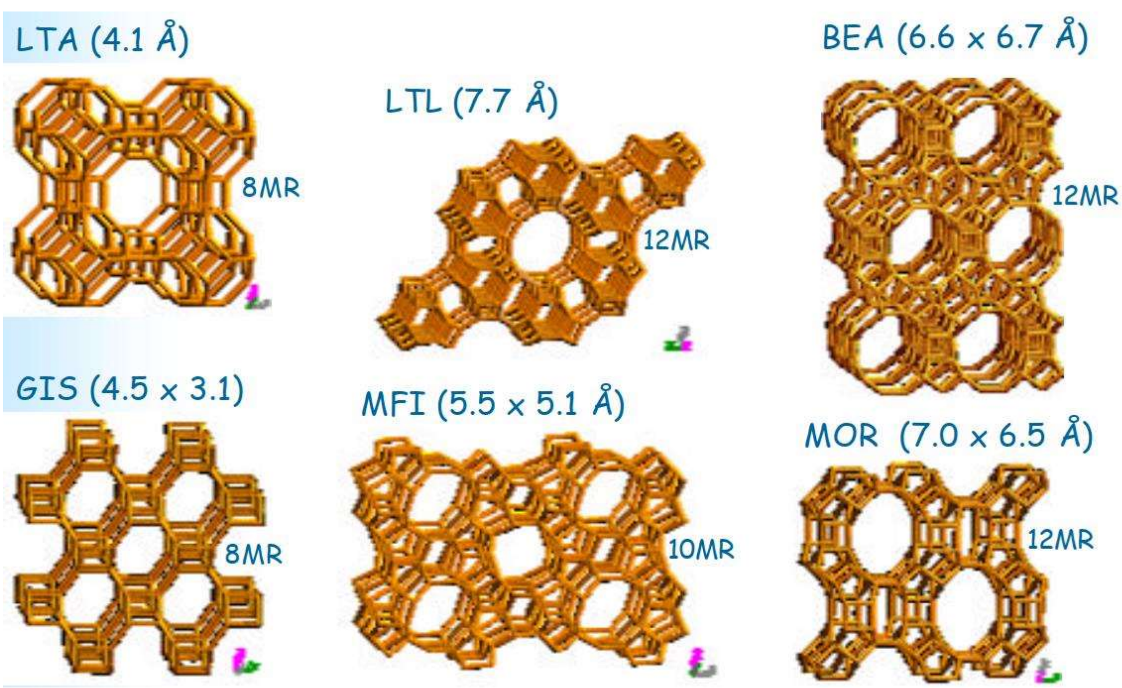
ZEOLITES



$M^{x+}_{m/x}\,[Al_mSi_nO_{2(m+n)}]\,.\,p\,H_2O$

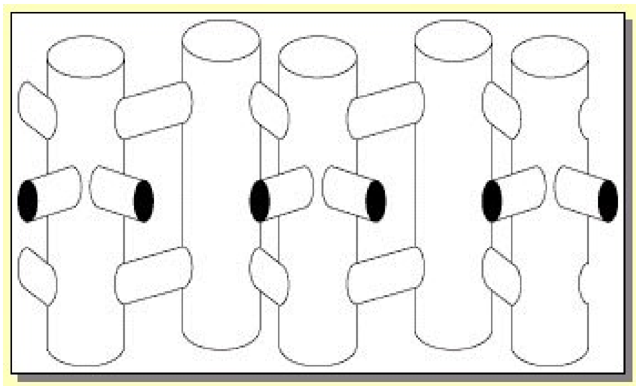


ZEOLITES



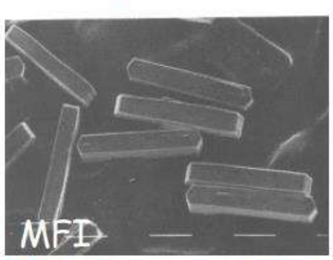
WHAT IS ZSM-5 CATALYST ?

- It is an abbreviation for (Zeolite Scony Mobile Number 5)
- First synthesized by Mobil Company in 1972
- It replaces many Homogeneous Catalysts were used in many petrochemical processes
- ZSM-5 has two diameters for its pores : d_1= 5.6 Å , d_2= 5.4 Å
- Where as, Zeolite Y has a diameter = 7.4 Å

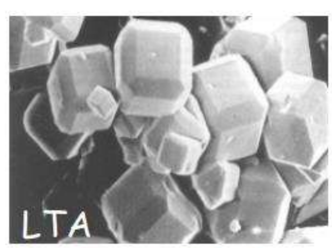


BULK CATALYSTS: HYDROTHERMAL SYNTHESIS

- Discrimination against precipitation sometimes difficult; typically higher temperature, often pressure, longer reaction time than for precipitation
- Crucial for zeolite synthesis (crystalline, microporous aluminosilicates)
- Cristallization from silicion and aluminum containing solutions, mainly under alkaline conditions
- minimum Si/Al ratio is 1
- Often "template" required (organic additive, e.g. tetraalkylammonium ions), mainly for high silica zeolites
- Many parameters affect zeolite synthesis
  - reagents
  - pH
  - mixing sequence
  - temperature
  - heating rate
  - concentrations
  - template
  - ...



ZSM-5, Silicalite-1 (150μm)



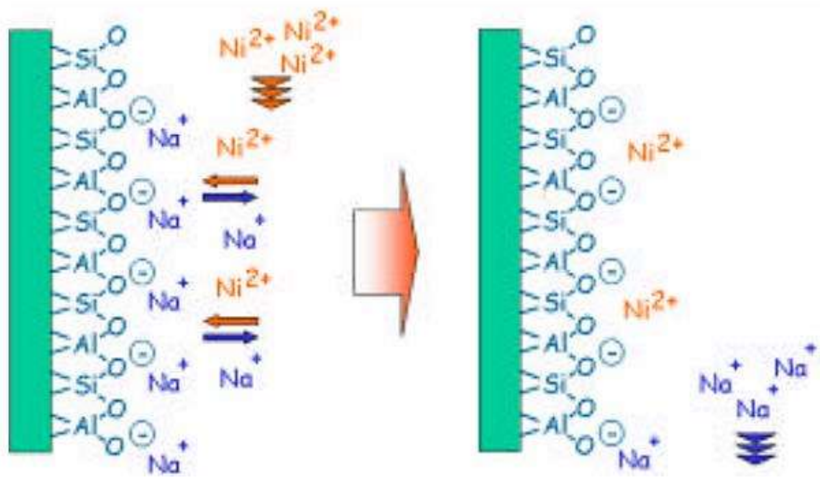
Linde Type A (0.2 - 2 μm)

BULK CATALYSTS: SOLID STATE REACTIONS

- Transformation of definied Precursors s.o.
- also reaction of mixtures of oxides obtained by milling

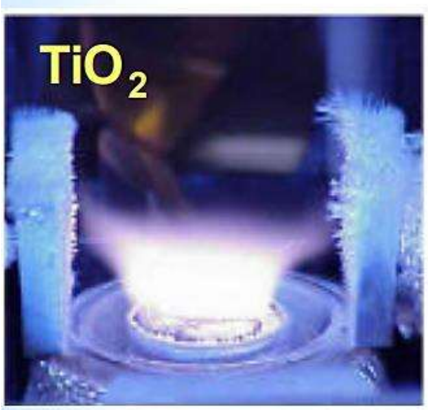
  example: Styrene catalyst
  milling of KOH + FeO_x + CrO_x, then calcination at 900 - 1300 K
- Solid state ion exchange

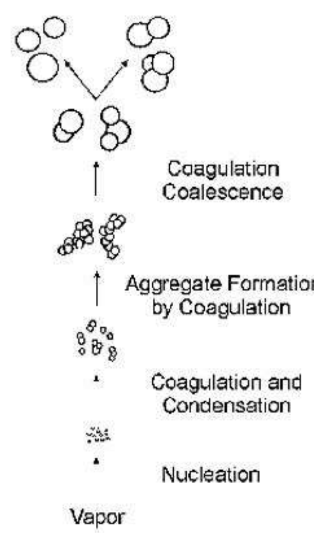
  example: zeolites, 600-700 K)



BULK CATALYSTS: OTHER METHODS

- Flame hydrolysis (Aerosil...)
- Sputter processes
- Spezial processes for Carbides, Nitrides
- ...





http://www.engin.umich.edu/~cre/web_mod/aerosol/frame08_pics/pict.htm

SUPPORTED CATALYSTS: SUPPORTS

- γ-,η- or α -Al_2O_3, SiO_2, TiO_2, ZrO_2, MgO, C
- Surface functionality typically -OH for Oxides, oxo-functionality for Carbons
- Oxidic surfaces in electrolytes generally charged

$$M\text{-}OH \longrightarrow M\text{-}O^- + H^+$$
$$M\text{-}OH + H^+ \longrightarrow MOH_2^+$$

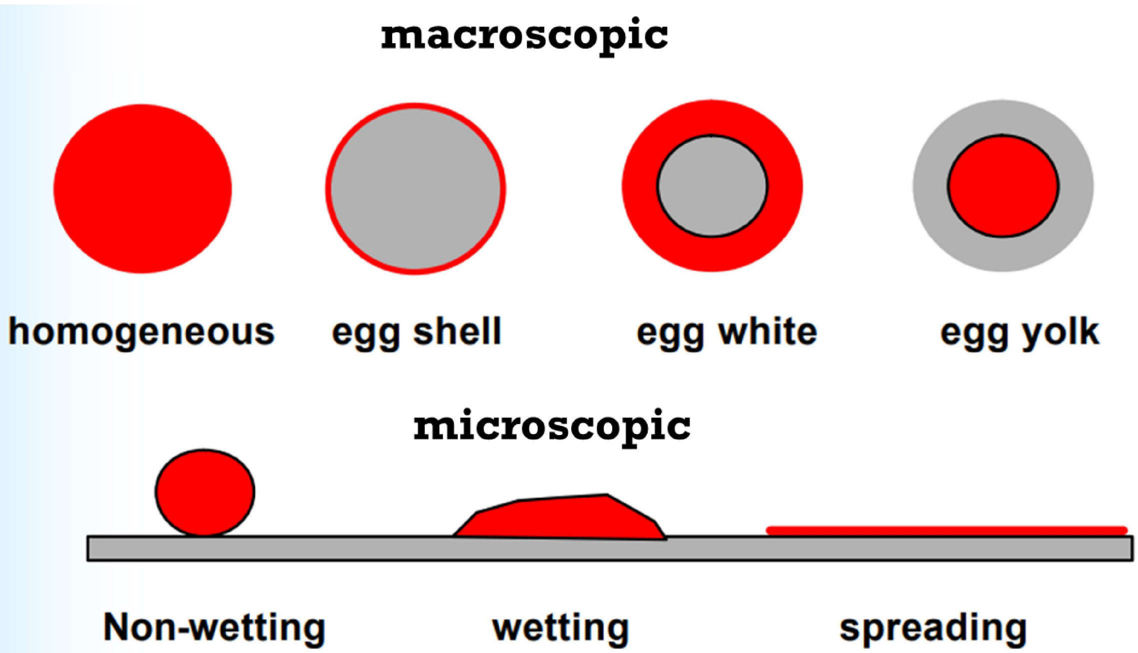
=> decisive for loading, since no adsorption if wrongly charged!

PZC (Point of zero charge) = particle is not charged at this pH
G.A. Parks, Chem. Rev. 65, 177 (1965)

Rule of thumb:

M_2O			PZC > pH 11.5
MO	8.5	<	PZC < 12.5
M_2O_3	6.5	<	PZC < 10.4
MO_2	0	<	PZC < 7.5
M_2O_5			PZC < 0.5

DISTRIBUTION OF ACTIVE COMPONENT ON SUPPORT



Examples for spreading: V_2O_5 on TiO_2, MoO_3 on Al_2O_3 or on TiO_2, not on SiO_2

SUPPORTED CATALYSTS: PREPARATION

- **Wet Impregnation, Ion Exchange, Equilibrium Adsorption**
  - Often discriminated but in principle all very similar
  - Principles:

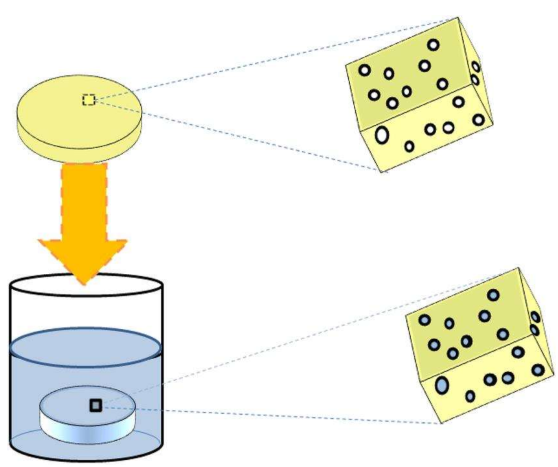
    Wet Impregnation (incipient wetness/dry impregnation)
    - Support with as much solution to just imbue support; porous material with as much solution that pores are just filled, then drying
    - Drying rate can strongly affect metal distribution

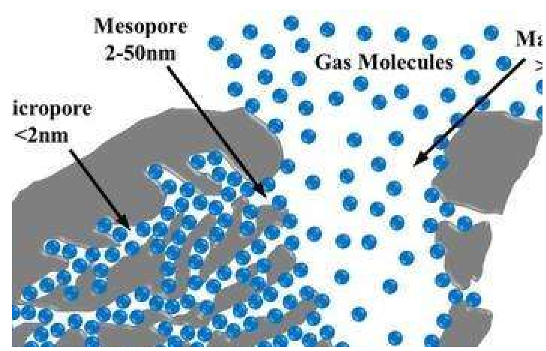
    Ion Exchange and Equibibrium Adsorption
    - Basically the same: Ion exchange if structural charges present (zeolites)
    - Support with excess solution, wait until equilibrium reached, filtration, drying

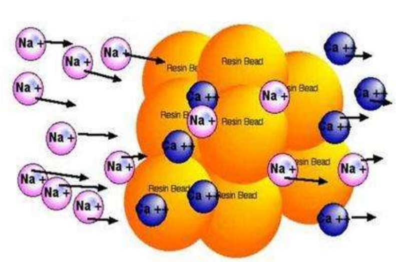
  - But: During Wet Impregnation also always Adsorption
    During drying after Ion Exchange/Adsorption also always Wet impregnation

SUPPORTED CATALYSTS: PREPARATION

Wet Impregnation, Ion Exchange, Equilibrium Adsorption







SUPPORTED CATALYSTS: PROBLEMS

Ion Exchange

» Achievable loading is limited by ion exchange capacity or saturation concentration of solution

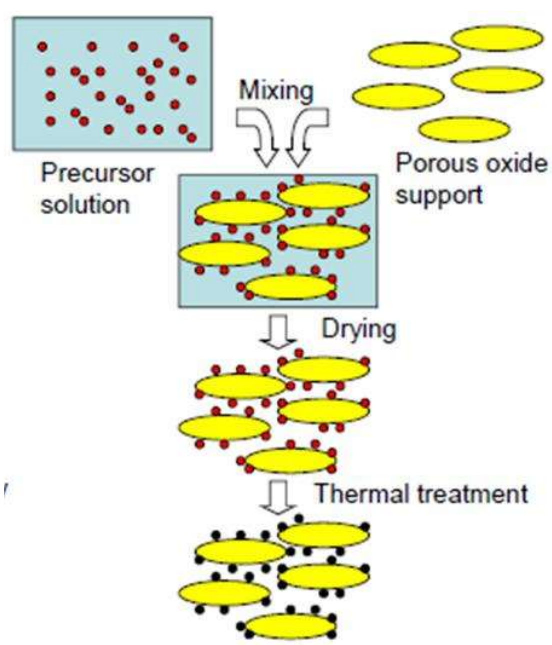
→ **Multiple exchange / loading**

» Ion exchange strongly binds ions which can result in irreversible occupation of first exchange sites; might result in inhomogeneous loading

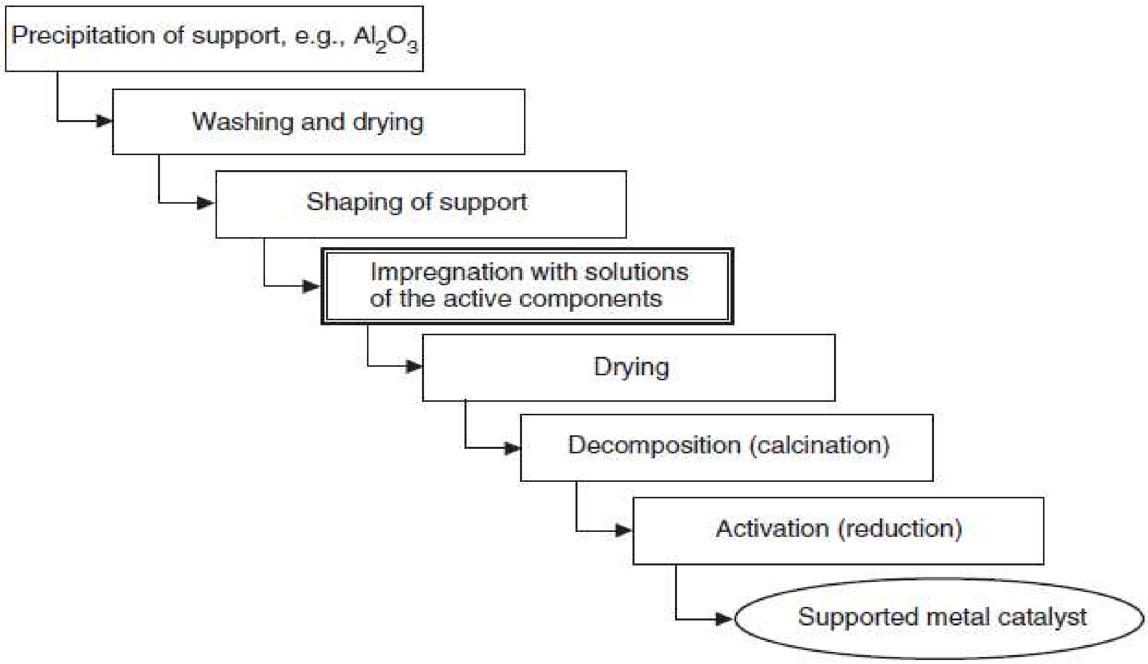
→ **Taking advantage of competetive ions, such as NH_4^+ at Ion Exchange of $[Pt(NH_3)_4]^{2+}$ in zeolites**

IMPREGNATION

- The support is immersed in a solution of the active component under precisely defined conditions (concentration, mixing, temperature, time). Depending on the production conditions, selective adsorption of the active component occurs on the surface or in the interior of the support. The result is non uniform distribution.



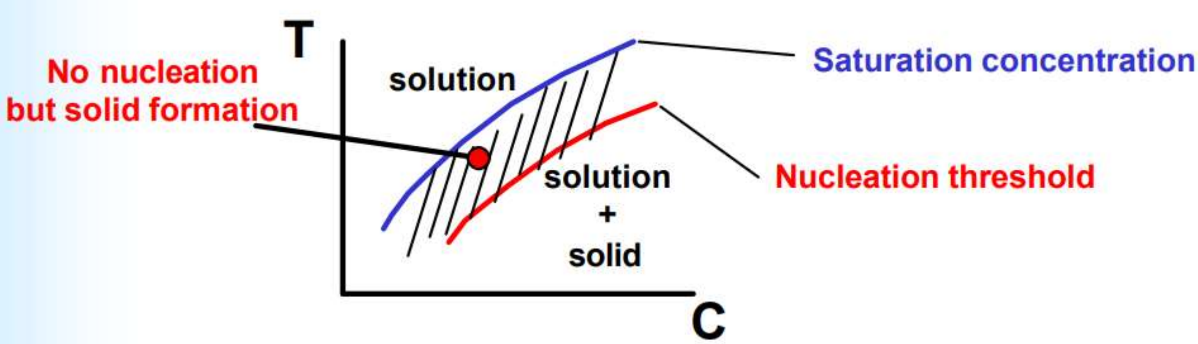
SUPPORTED METAL CATALYST



Scheme 6-2 Production of supported metal catalysts by impregnation

SUPPORTED CATALYSTS: PRECIPITATION-DEPOSITION

- Support is dispersed in solution, then precipitation is started by addition of precipitation agent
- Problem can be:
  - Precipitation off support
  - Precipitation only on external surface of porous supports



Precipitation-Deposition ideally in concentration range between saturation concentration and nucleation threshold; if interaction between support and species in solution good, then only precipitation on support.

SUPPORTED CATALYSTS: PRECIPITATION-DEPOSITION

Ideal precipitation if precipitation is initiated at the same time in whole solution (homogeneous precipitation)

pH:

Urea $CO(NH_2)_2 \rightleftarrows NH_4^+ + CNO^-$

$CNO^- + 3\ H_2O \rightleftarrows NH_4^+ + 2\ OH^- + CO_2$

$NaNO_2^-$ $3\ NO_2^- + H_2O \rightleftarrows 2\ NO + NO_3^- + 2\ OH^-$ (no air!)

Oxidation state:

Fe^{2+} more soluble than Fe^{3+}, Mn^{2+} more than Mn^{3+}/Mn(IV), M^{n+} may get oxidized in solution (e.g. O_2 from air)

Removal of complexation agents:

desorption of NH_3 from ammine complexes,
oxidation of inorganic complexing agents with H_2O_2

SUPPORTED CATALYSTS: GRAFTING

- Grafting (or Anchoring): Deposition involving the formation of a strong ("covalent") bond between support and active element (J. Haber, Pure&Appl.Chem). Results in definied, good isolated species on surface
  - Typically reaction of OH-group with active species. If Silanol reacts, water usually does as well
    => exclusion of water
  - mostly metal organic reactions

    $S\text{-}OH + MX_n \longrightarrow S\text{-}O\text{-}M\text{-}X_{n-y} + y\ HX$

    $S\text{-}OH + M(CO)_n \longrightarrow S\text{-}O\text{-}MHCO_{n-2} + 2\ CO$
  - further modication by elmination or decomposition of of remaining ligands
  - Typical reactions
    - Chlorides and oxychlorides of transition metals
    - Metal alkoxides from gas phase
    - Metal allyles (Mo, Cr) or carbonyles mostly from pentane etc.

ACTIVATION / CALCINATION

- Irrespective of the preparation method of solid, additional steps, such as thermal treatment, are necessary after combination of components
- Easiest Case: Activation under reaction conditions. Relatively rare, in most cases customer wants equilibrated catalyst
- Calcination
  - » Can be decisive for properties of catalyst
  - » Many possible prozesses (decomposition of precursor, spreading, sintering, formation of new phases from active material and support, destruction)
  - » Specific for each system
  - » depends on gas phase; often air, but also inert gas or controlled water vapor atmosphere

REDUCTION

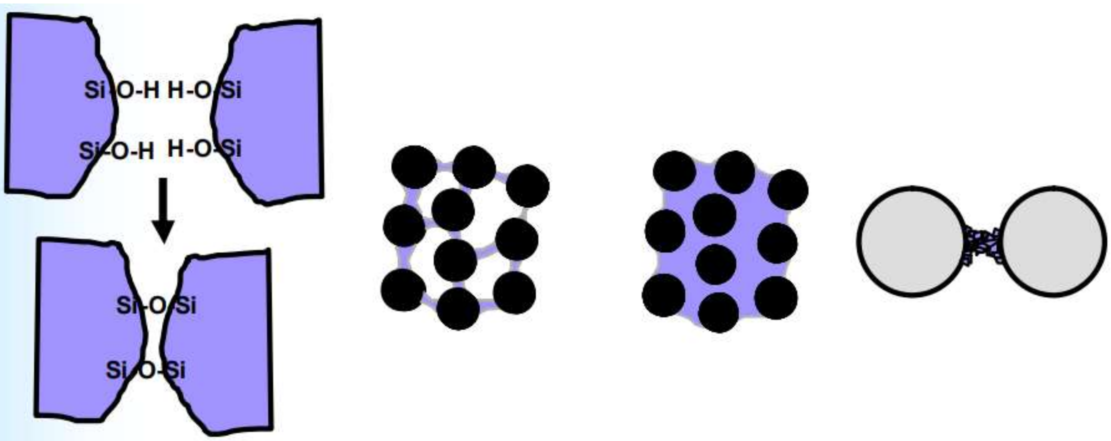
- One of the most important steps in preparation of metal catalysts
- Starts typically from oxide (after calcination), for noble metals from chloro compounds or oxychloride
- Reduction mostly with H_2
  - » often: Dispersion higher with higher reduction rate
  - » However, can be inverted if nucleation is limiting factor
  - » Reducibility might be different to bulk material
- SMSI (strong metal support interaction) might occur
  - » Mainly for TiO_2, ZrO_2
  - » H_2 sorption suppressed
  - » Explanation: electronic effect, alloy, decoration of noble metal with sub-oxides (Ti_4O_7)

SHAPING OF CATALYSTS

- Very important, but basically empirical knowledge
- Often additives, such as oil, graphite, steatite, talc, wasser glass, starch for activated carbon (binder). (additive best protected know-how of producers)
- Shape defines pressure drop in reactor

monoliths < rings < spheres < pellets < extrudates < broken material

FORCES BETWEEN PARTICLES



Chemical Bonds Solvent Bridges Capillarity Solids bridges

Principles of Agglomeration: S.M. Iveson et al., Powder Technology 117, 3 (2001)

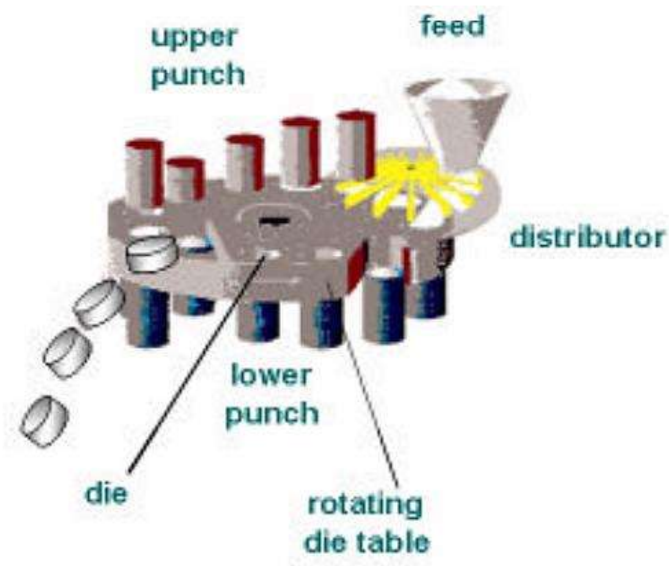
FORCES BETWEEN PARTICLES

Mechanism	Strength	Comment
Van der Waals forces	medium at short distances, rapid decay with distance	Magnitude depends on the interaction potentials
Electrostatic forces	Weak, but dominant for distances approaching µm	Can be repulsive, if charging of particles with same sign occurs; different for conductors and insulators
Liquid bridges	Strong	
Capillary forces	Very strong	Full saturation of granule with liquid
Solid bridges	Variable	Depends very much on conditions of solvent evaporation and crystallizing solid in bridge
Covalent bonds	Very strong	

METHODS OF SHAPING

- Breaking / Milling
- Spray Drying results in small particles (7 - 700 µm)
- Tabletting: Pressing in moulds
- Extrusion: Principle of "Spätzlemaschine"
  - » press for highly viscous media
  - » screw for less viscous / thixotropic media
- Oil drop coagulation
- Pelletier pan: Snow ball principle

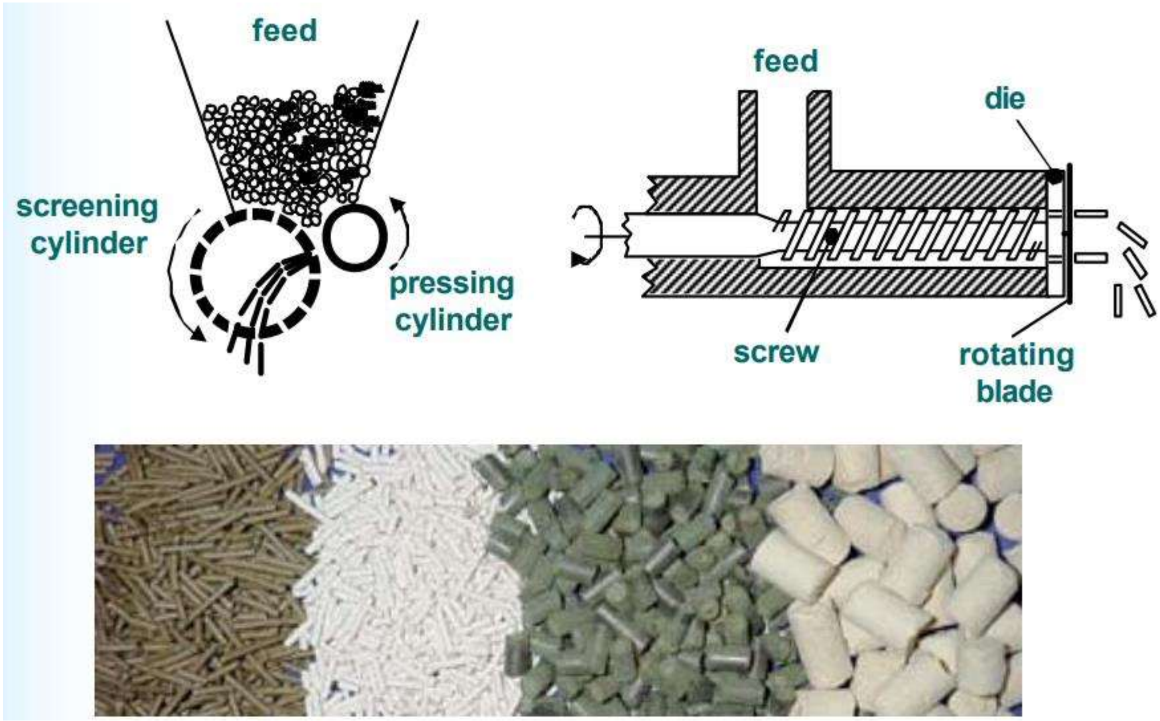
ROTARY TABLET PRESS



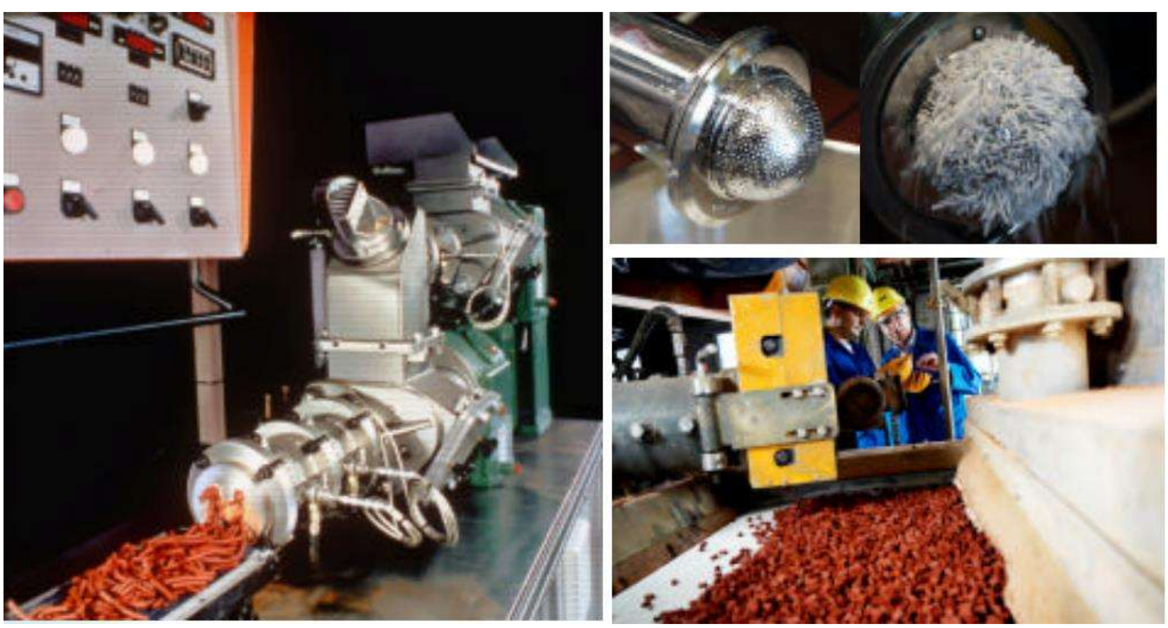
Good Review: S. Jain, Pharm. Sci. Technol. Today 2, 20 (1999)

INDUSTRIAL TABLETING MACHINE

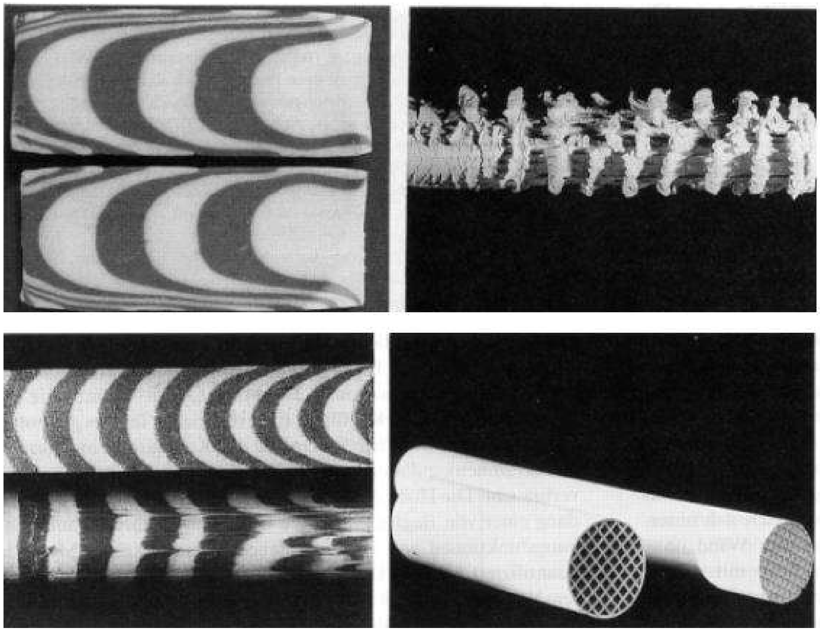
EXTRUSION



EXTRUDERS



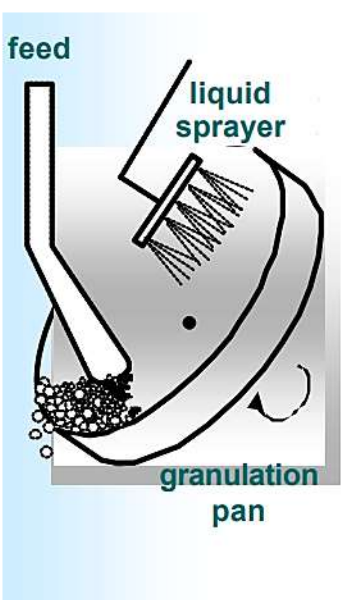
EXTRUDATES / MONOLITHS



Bad extrusion characteristics

Good extrusion characteristics

GRANULATION / PELLETIZING



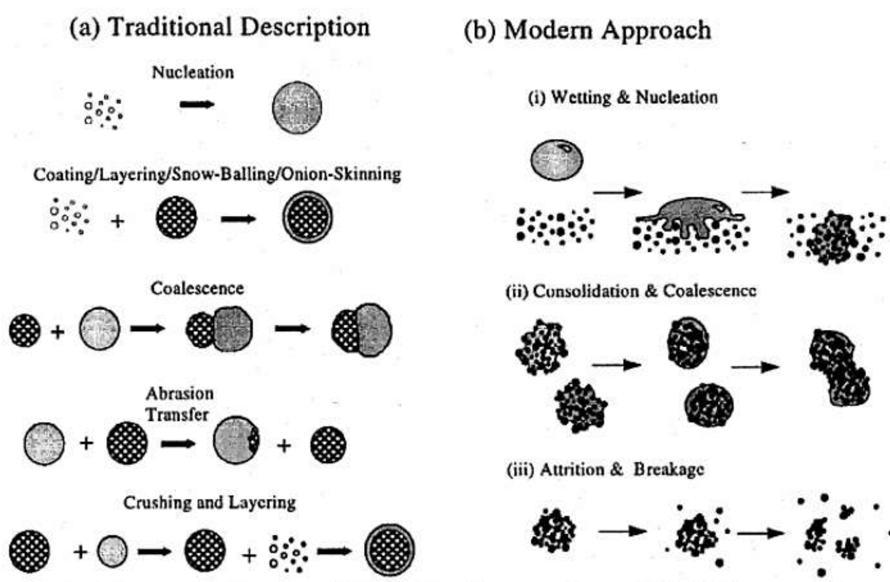
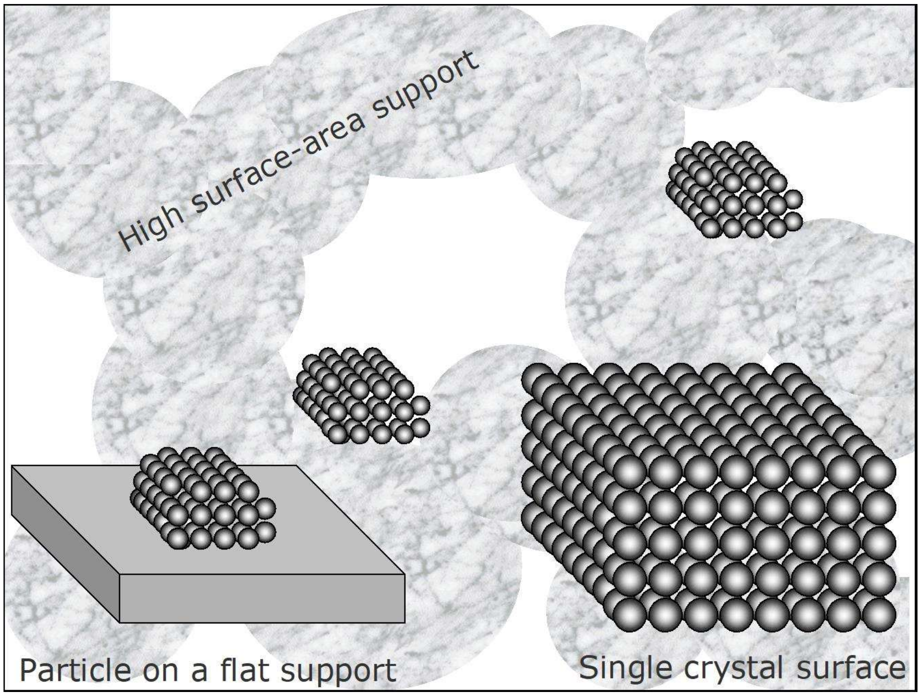


Fig. 1. Schematic of granulation processes (a) Traditional view (after Sastry and Fuerstenau [26]); (b) Modern approach [1].

INDUSTRIAL SPHERONIZER

شناسایی کاتالیزورهای هتروژن

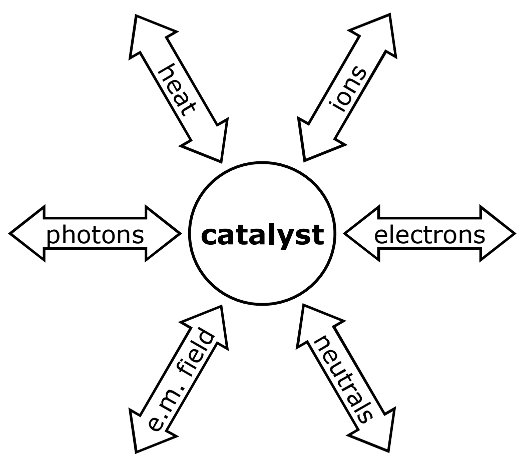
CATALYSTS ARE COMPLEX NANO-MATERIALS



CHARACTERIZATION OF HETEROGENEOUS CATALYSTS

Investigate:

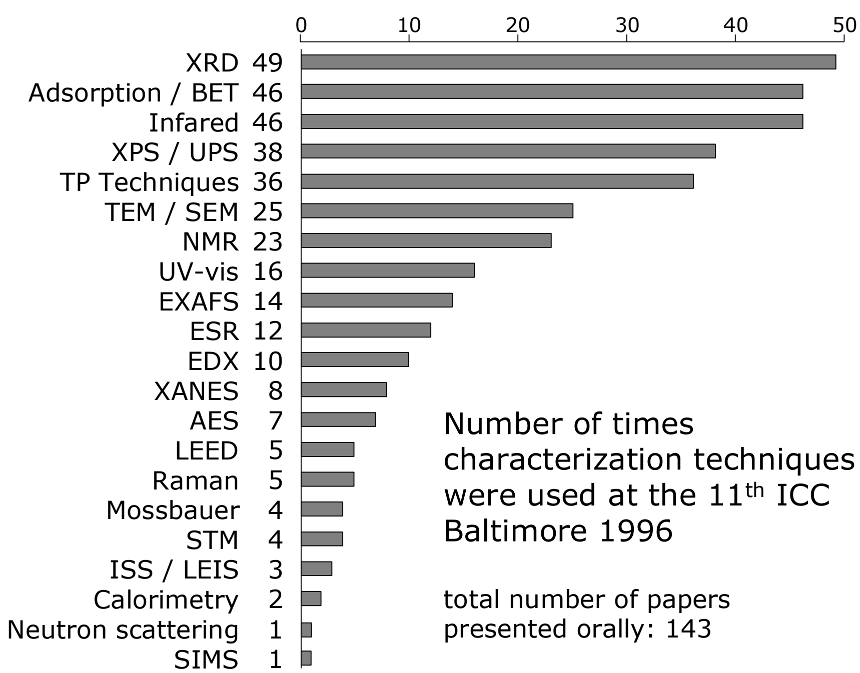
- Structure/morphology
- Surface area
- Number of active sites
- Pore distributions
- Nature of active site
- Overall reactivity
- Turn over frequency (TOF)
- Selectivity
- Stability
- Heat and mass transport
- ?
- ?



CHARACTERIZATION OF HETEROGENEOUS CATALYSTS

- Physical properties: pore size, surface area, and morphology of the carrier; and the geometry and strength of the support
- Chemical properties: composition, structure, and nature of the carrier and the active catalytic components
- Changes during the catalysis process: deactivation

MOST OFTEN USED METHODS



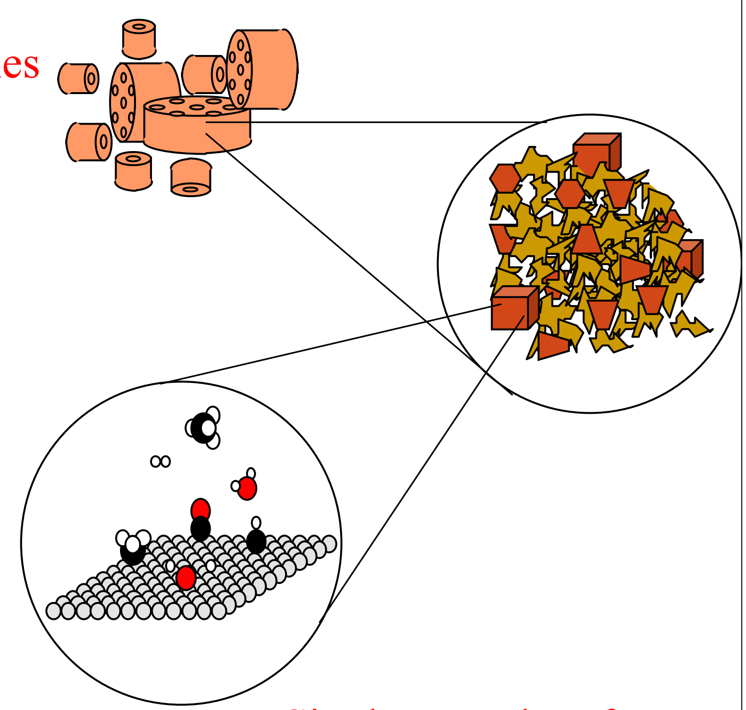
PHYSICAL PROPERTIES OF CATALYSTS

Surface Area and Pore Size of the Carrier

- Surface area
- Pore size: (Pore size distribution ,Pore structure, Pore volume)
- It is usually advantageous to have high surface area (large number of small pores) to maximize the dispersion of catalytic components.
- If the pore size is too small, diffusion resistance will becomes a problem.

THE SURFACE SCIENCE APPROACH

- Simpler system - Detailed studies
  - Fundamental insight
  - Input to catalyst design

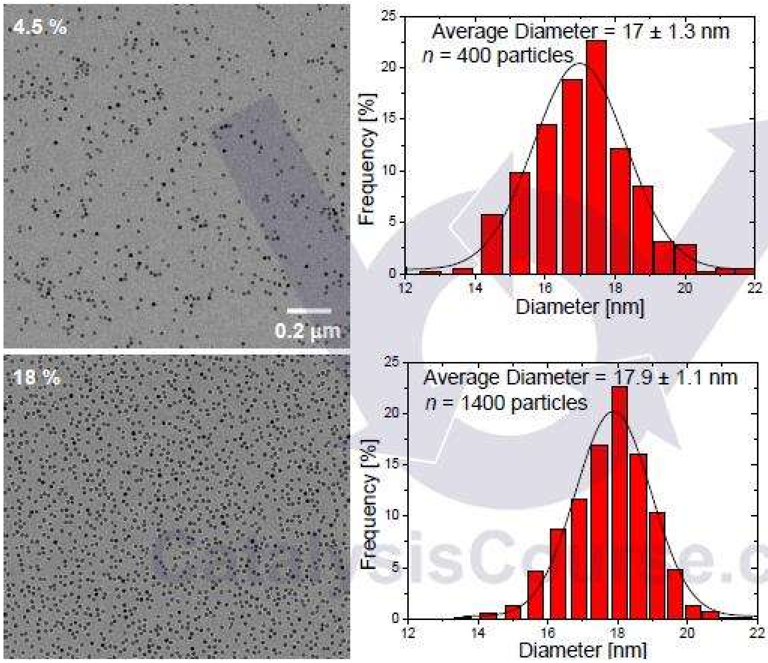


- The structure gap
- The pressure gap
- The materials gap

Single crystal surfaces as model catalysts.

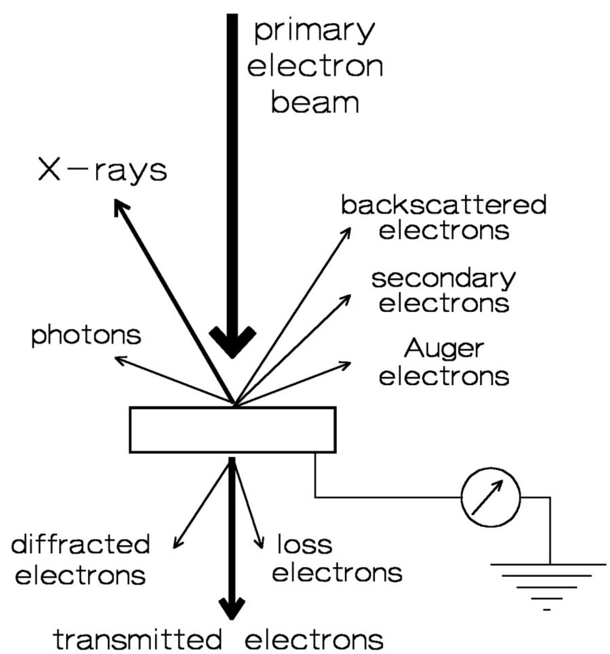
Particle Size Distributions

TEM of iron oxide nano particles



ELECTRON MICROSCOPY

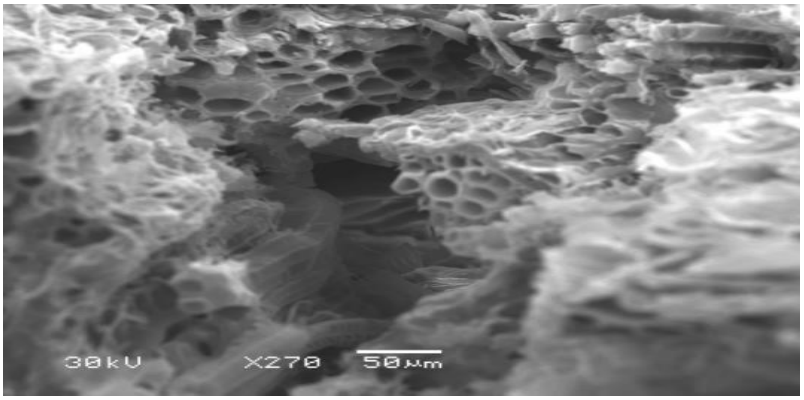
Does not work *in situ*



Gives information on particles size, shape, composition.

SCANNING ELECTRON MICROSCOPE (SEM)

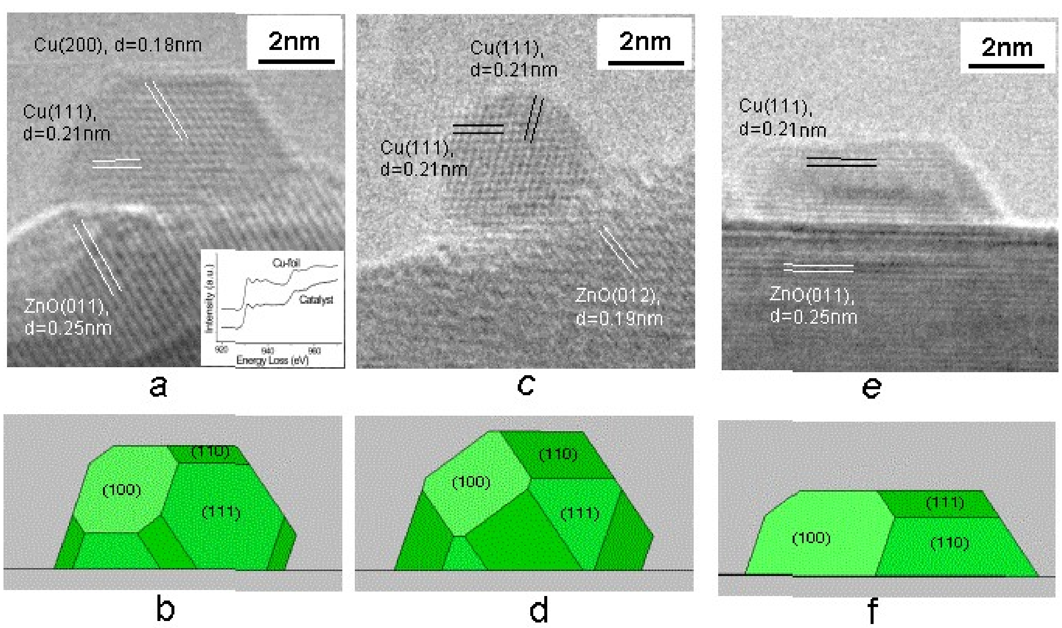
- Scanning electron microscope (SEM) is equipped with an energy dispersive analyzer or wavelength dispersive analyzer.
  The bombardment of a sample with electrons generates X rays characteristic of the elements present.



peanut shells

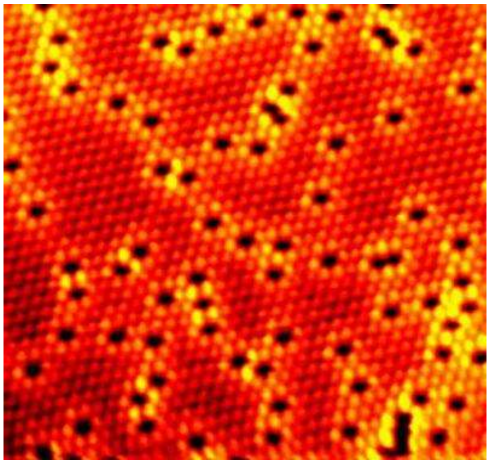
TRANSMISSION ELECTRON MICROSCOPE (TEM)

TEM images of Cu on ZnO (a model methanol catalyst).

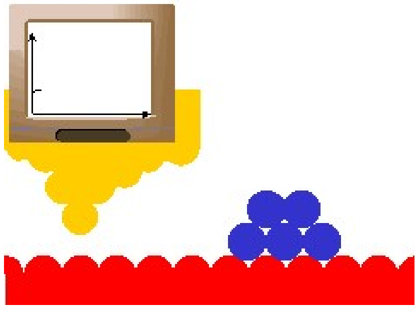


SCANNING TUNNELING MICROSCOPY (STM)

Length scales
”Seeing” atoms
Electron tunneling
Hardware realisation
Applications
Basic research

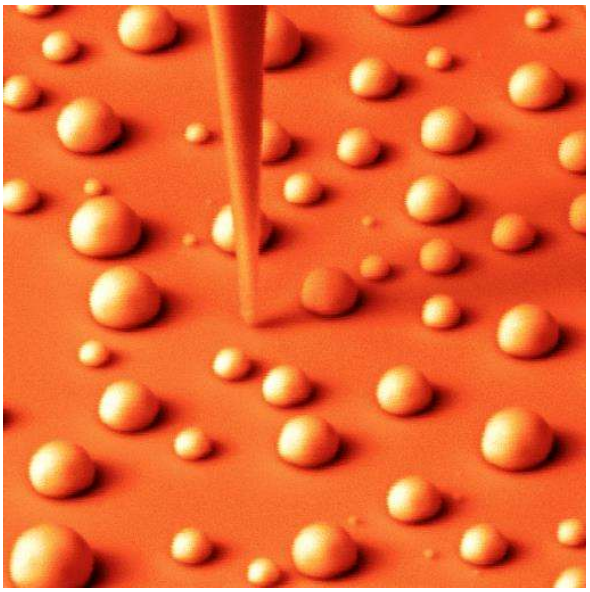


L. P. Nielsen University of Århus (80Åx80Å)



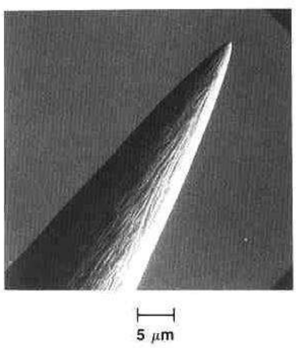
CRYSTALLITES AND STM-TIP

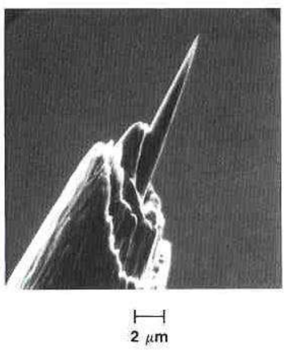
STM image



35 micrometer
A. Emundts und H.P. Bonzel

A sharp tip

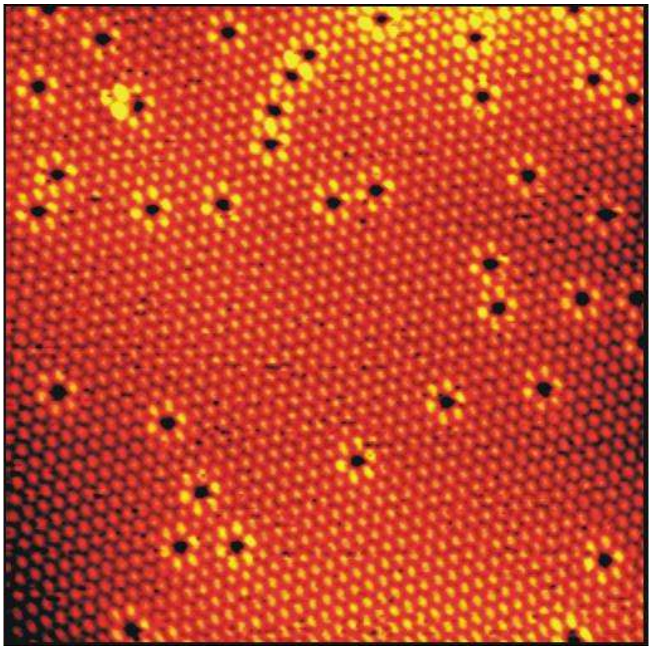




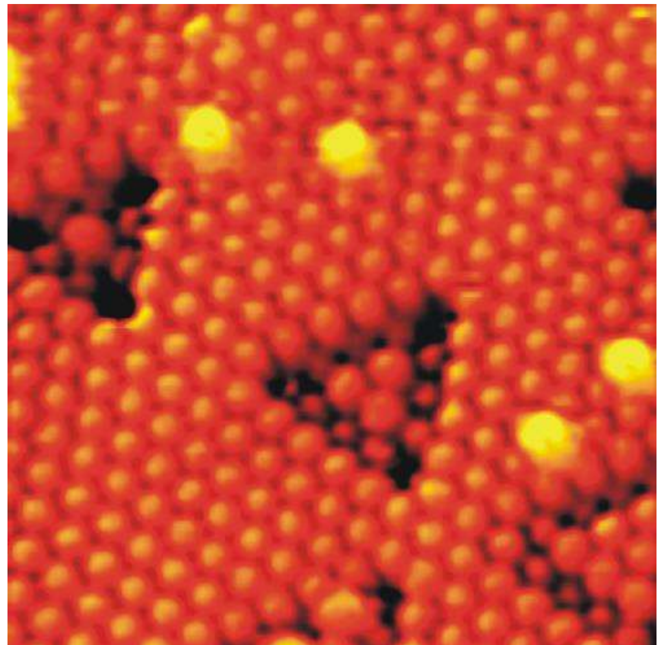
STM AU/NI(111)

Let you sometime, but not always, see the atoms

0.02ML Au



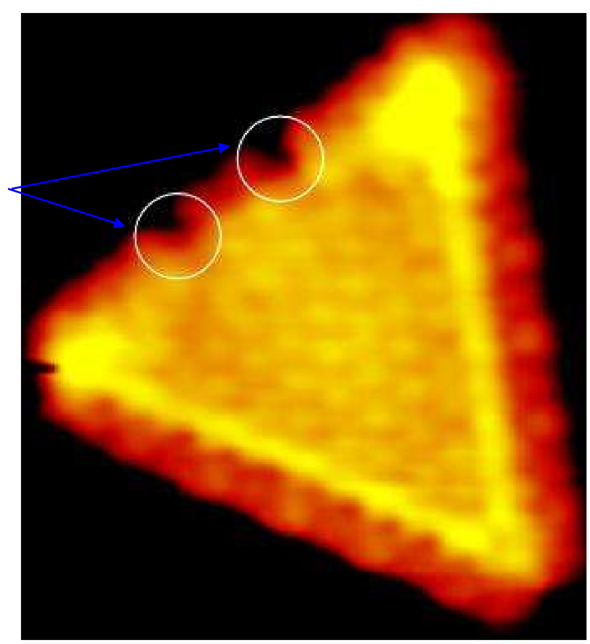
0.8 ML Au

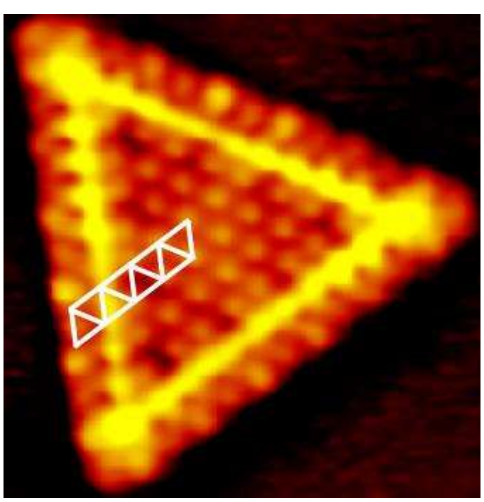


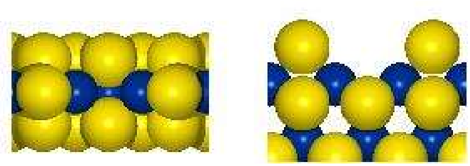
STM MODEL CATALYST

MoS_2 on Au(111)

Sulfur removed by atomic hydrogen





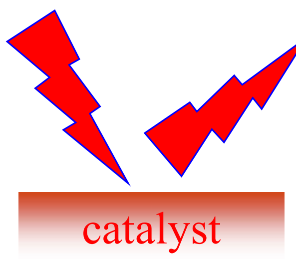


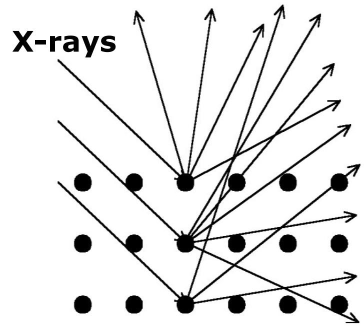
X-RAY DIFFRACTION (XRD)

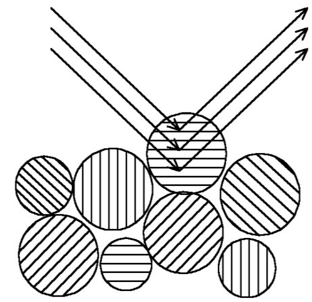
Bragg´s Law

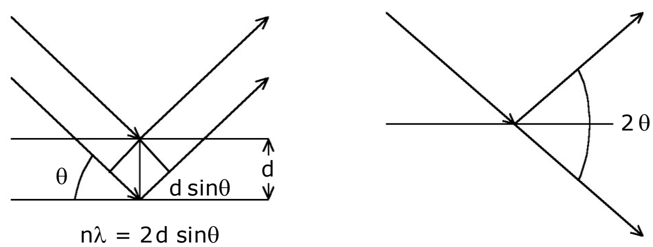
$$n\,\lambda = 2d\,\sin\theta\,; \quad n = 1, 2, \ldots$$

X-rays in X-rays out









Can be used *in situ*

Gives information on phases and sizes of particles if big enough.

X-RAY DIFFRACTION (XRD)

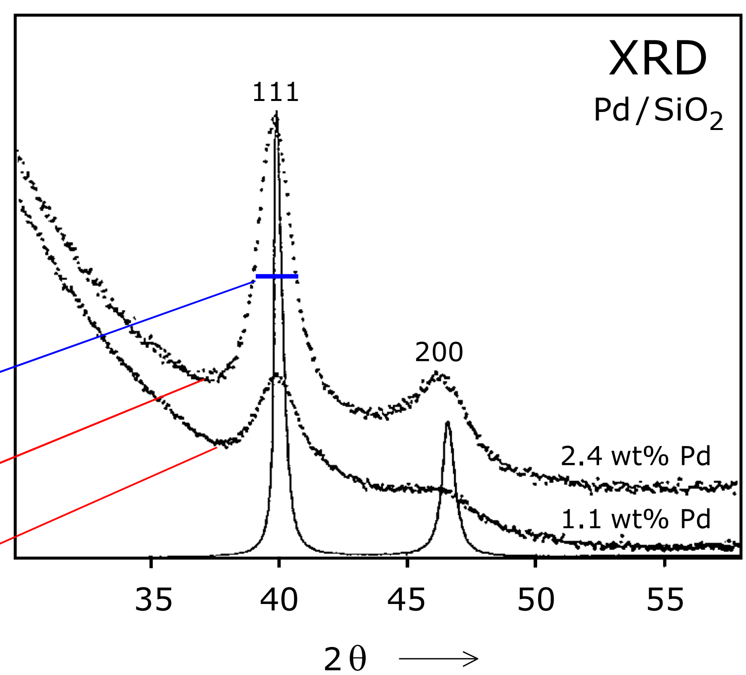
Peaks position reveals crystalline structure

Width of peaks reveals particle size

$$\langle L \rangle = \frac{K\,\lambda}{\beta\cos\theta}$$

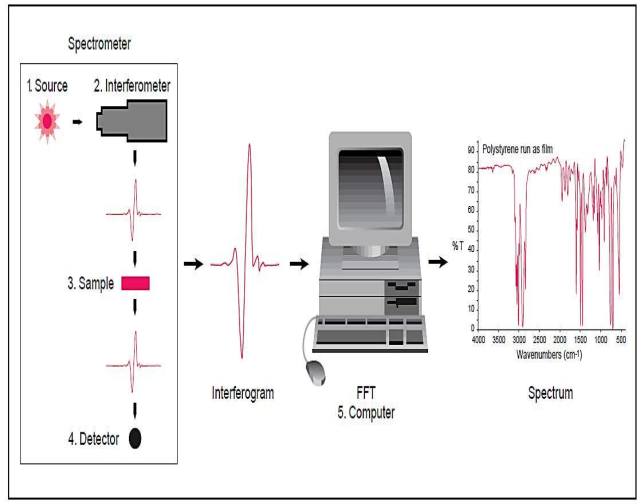
4.5 Å

2.5 Å

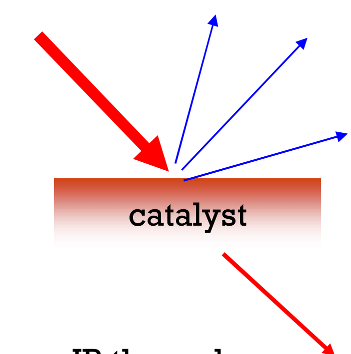


FTIR (FOURIER TRANSFORM INFRA RED)

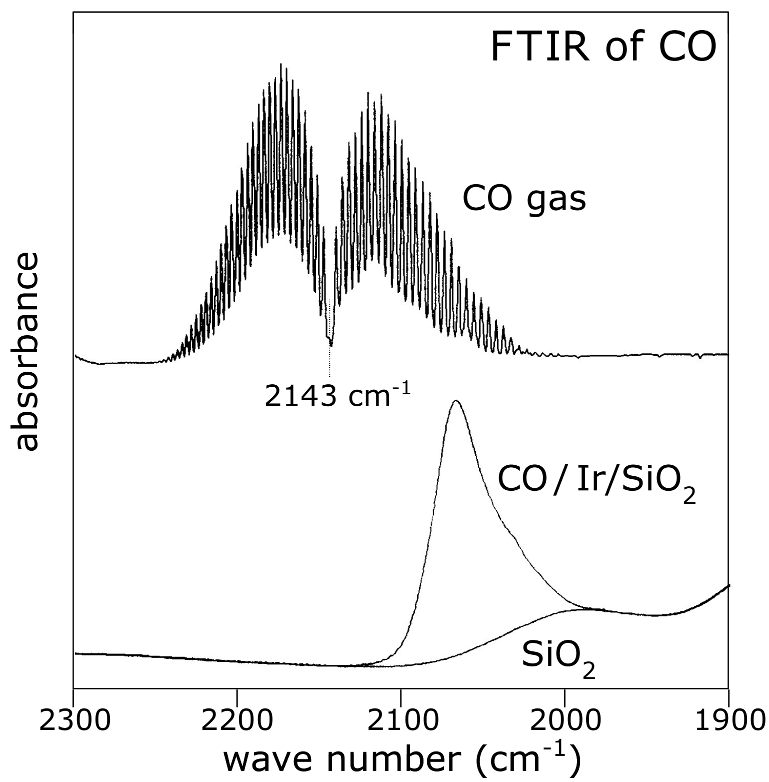
- FT-IR stands for Fourier Transform Infra Red, the preferred method of infrared Spectroscopy.
- *So, what information can FT-IR provide?*
  - It can identify unknown materials
  - It can determine the quality or consistency of a sample
  - It can determine the amount of components in a mixture



INFRARED SPECTROSCOPY



An *in situ* method



Any Question?