Metal Surface area

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Types of Catalysts

Type	Examples	Applications
Supported metal catalysts	Pt/Al_2O_3, Pd/Al_2O_3 Ni/Al_2O_3 Fe/Co	Dehydrogenation Hydrogenation Oxidation, FTS
Metal oxide /sulfide/ chloride catalysts	V_2O_5, Ag/Al_2O_3 Bi-Mo Oxide Co-Mo/Al_2O_3 $CuCl_2$-KCl/Al_2O_3	Oxidation, Epoxidation Ammoxidation HDS, HDN,HDC Oxychlorination
Zeolite catalysts	Zeolite Y, REY, USY, ZSM-5 Mordenite	FCC, MTG, MTO, Alkylation, Aromatization Isomerization

Wide Spectrum of Applications

Catalysts- Characteristics

- **Chemical composition**
- **Phase composition, Crystalline/Amorphous**
- **Structural features, Phase transformations**
- **Surface composition, Co-ordination, Structure**
- **Dispersion& distribution of active phases**
- **Electronic properties**
- **Textural properties-Surface area, Pore-size**
- **Physical properties-Size, Shape, Strength**
- **Chemical properties- Surface reactivity/Acidity**

Enabling Structure-Activity correlations

Catalysis & Analytical Chemistry

Preparation	Characterization	Evaluation	Ageing	Spent
Concn. of active elements	Phase composition	In-situ Spectroscopy	Solid state transformations	Inactive phases
Species in Solution phase	Electronic state	Transient surface species	Structural transformations	Poisons
Solid state transformations	Structural features	Reactants & Products	Surface composition	Analysis of coke
Preparation techniques	Dispersion & Distribution	Kinetics & mechanism		
	Surface composition			
Evolve active phase	*Ensure desired characteristics*	*Surface reactions*	*Catalyst life*	*Deactivation*

Application of Analytical Techniques- From Cradle to Coffin

Supported metal catalysts

Characteristics

- Metal dispersion/Crystallite size (XRD, XPS)
- Metals distribution / Profile (EDXA)
- Metal support interactions (XPS)
- Metal-Promoter interactions (XPS)
- Nature of coke deposits (HPLC, TGA, NMR)

Metal surface area

- What do we mean by metal surface area ?
- How it is related to catalytic activity?
- How do we measure metal surface area?

Metal surface area

Supported metal catalysts

- Active metals- Pt, Pd, Ni, Co, Cu, Ag, Au, Rh, Ru
- Supports- Alumina, Silica, Activated carbon, Titania, Zeolites
- Impregnation/loading of active metals on support

  < 1 wt % for Pt, Pd ; 1-20 wt% for base metals, Ni, Co,Cu

- Metal salt/Support- Impregn.- drying- calcination- reduction- Metal/Support
- Dispersion of active metals on the support - Preparation conditions
- Dispersion- Distribution/spreading of metal particles as fine /small

  crystallites over the surface of support

  crystallite size- 1 – 100 nm in size, varying shape

- Support- Total surface area- BET method
- Metal surface area- Contribution due to metals alone- Crystallite size
- Metals - Crystallites- Active sites- Activity
- Total activity = Activity per site X Number of active sites

  (TON)   ????

  Turn Over Number- No.of molecules converted per sec. per site

Adsorption Mechanism

Step 1: Diffusion to Adsorbent Surface

Step 2: Migration into Pores of Adsorbent

Step 3: Monolayer Buildup of Adsorbate

Contaminant Molecules
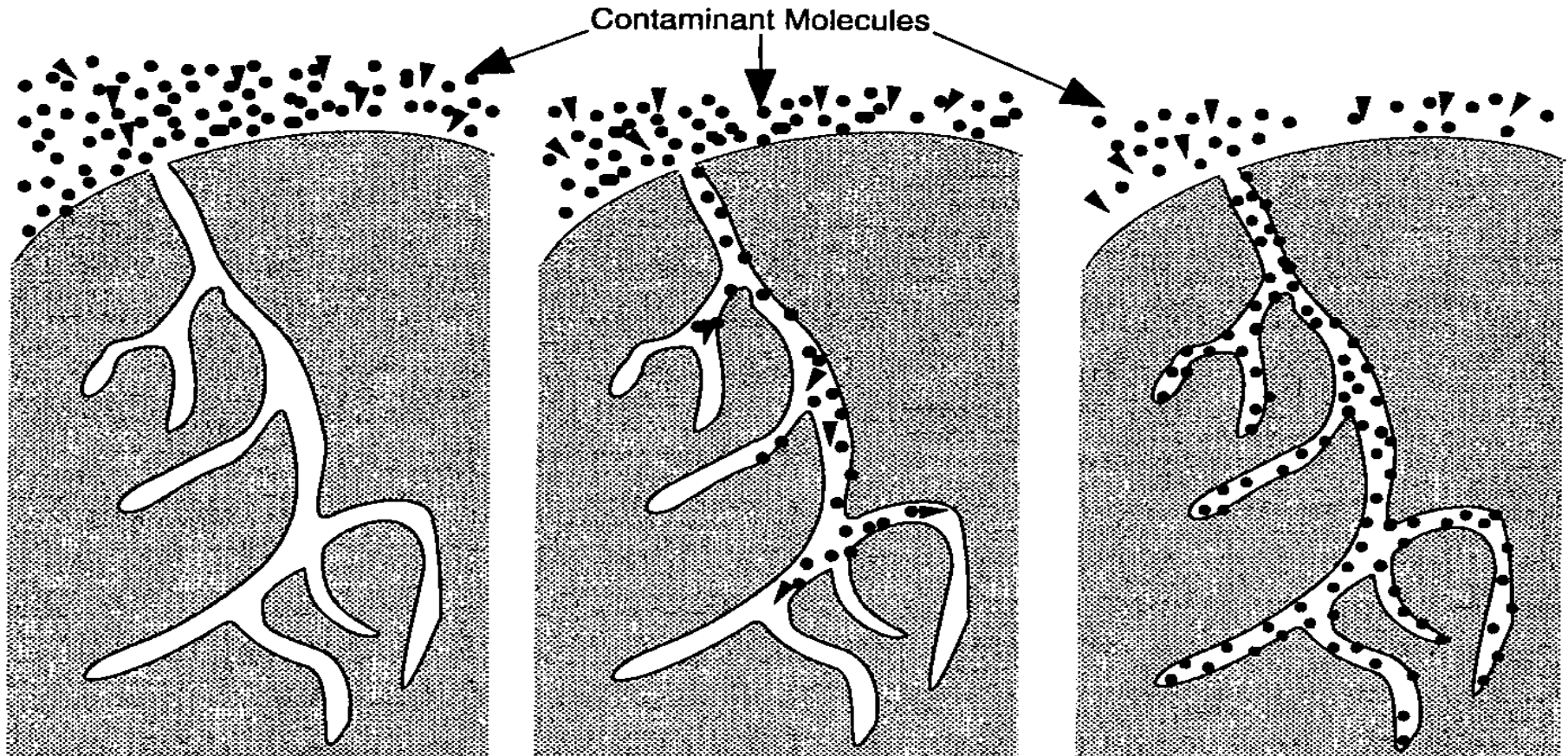
The above adsorption process represents the diffusion of metal salt/impregnation solution into the pores of the support

8

Supports

❖ High surface area oxidic compounds: zeolites, SiO_2, Al_2O_3, TiO_2, ZrO_2, CeO_2, ZnO

❖ Carbon materials
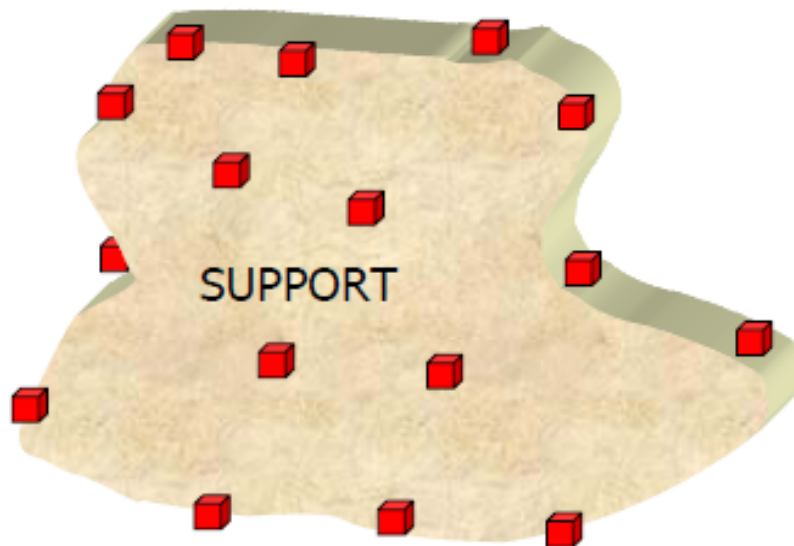
SUPPORT

Dispersed phase

❖ Increased surface area

❖ Stabilized

❖ Goal: disperse an *active phase* on an inexpensive and inert (?) *support*

Area occupied by metal crystallites is responsible for activity

Metal Crystallites - Features

- **Crystal-** Specific arrangement of atoms/ions as per stoichiometry
  Long range order-fcc,bcc,hexagonal-Specific geometry, morphology, shape
- **Particles** – Primary/Secondary- Particle size- Measurement methods- Support particle size- Std. Test Sieves- Instrumental methods-Sedimentation
- **Crystallite**- Cluster of metal atoms- No stoichiometry-Specific shape – related to bulk metal structure, short range order, varying size & co-ordination No.- higher degree of co-ordinative unsaturation- active sites
- **Crystallite size control**
  - Preparation methods
  - Nature of support
  - Metal loading
  - Metal precursor
- **Parameters**
  - Crystallite size- d- nm
  - Metal area S-m^2/g
  - Dispersion % D
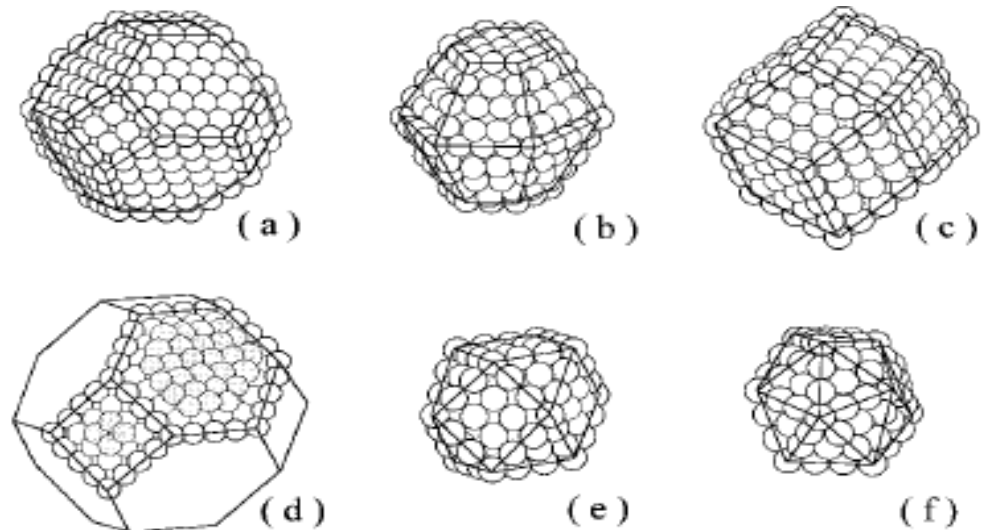
Figure 2. Types of crystallites considered in Figure 1: (a) VH cubooctahedron; (b) VH hcp truncated bipyramid; (c) VH bcc rhombic dodecahedron; (d) VH cubooctahedron max-B5; (e) MM cubooctahedron; and (f) MM icosahedron.

Active sites on the surface

Supported metal catalysts-guiding principles

Pt metal-Bulk Crystal-Crystal planes- Surface structure--active sites
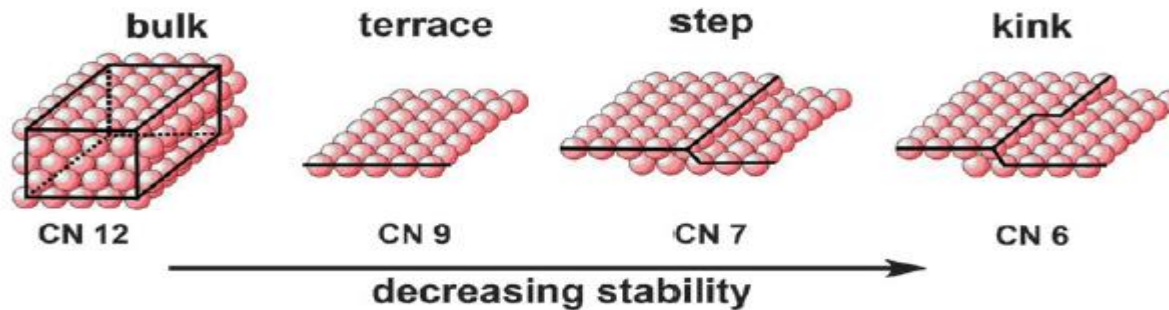
- Bonding/Reactivity of reactants on terrace/step/kink sites is determined by the co-ordination numbers/co-ordinative unsaturation

- For cyclic hydrocarbon reactant
- C-H bond activation – step sites- Dehydrogenated product
- C-C- bond activation - kink sites- Ring opening
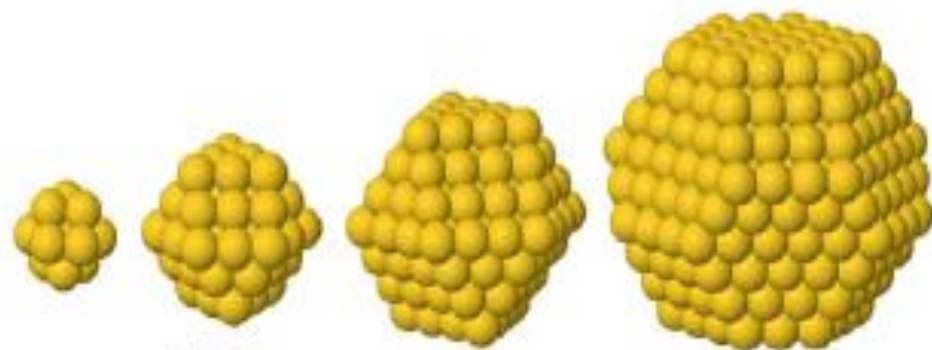
Active phase composition-Structure-Size-Shape
Surface structure-Selectivity
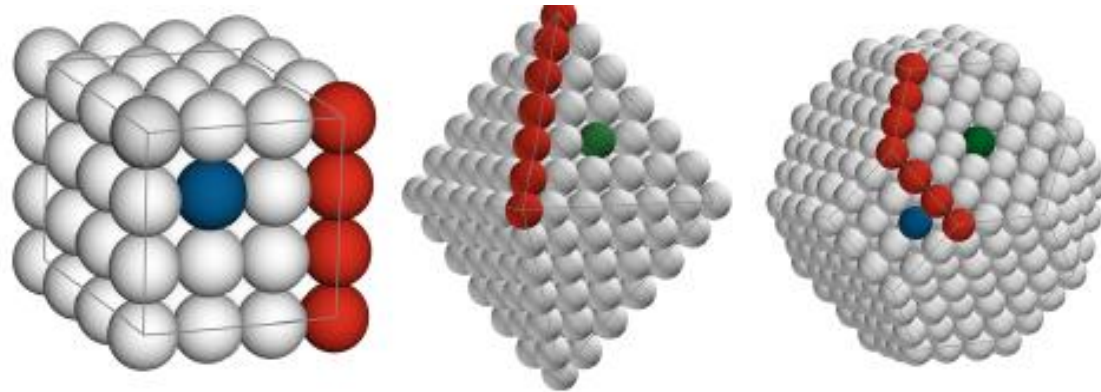
Figure 2.1: Schematic representation of the surface atoms found on three common *fcc* crystallites. ● low coordination number atoms, such as corner and edge atoms, ● (111) plane atoms and ● (100) plane atoms.

$N_S=12$
$N_T=13$
$d=0.86$ nm

$N_S=42$
$N_T=55$
$d=1.44$ nm

$N_S=92$
$N_T=147$
$d=2.02$ nm

$N_S=146$
$N_T=405$
$d=2.67$ nm
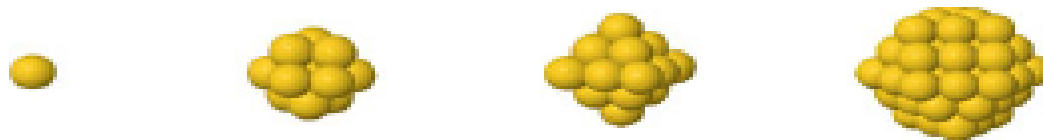
1 atom
$d=0.288$ nm

13 atoms
$d=0.86$ nm

19 atoms
$d=1.10$ nm

55 atoms
$d=1.44$ nm

		Fractions of Surface Atoms (N_S) that have low Coordination numbers (CN) situated at:					
		Corners			Edges	Terraces	
N_T	N_S	CN=4	CN=5	CN=6	CN=7	CN=8	CN=9
13	12	-	1.00	-	-	-	-
19	18	0.33	-	0.67	-	-	-
55	42	-	0.29	-	0.57	0.14	-
79	60	-	-	0.40	0.20	-	0.40

Topics in Catalysis,53,848,2010
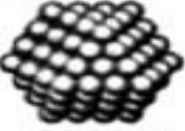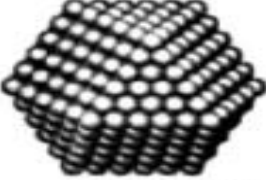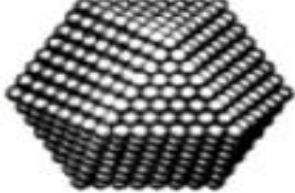
CORNER CATALYSIS

Gold atoms sitting at the corners of catalyst particles are most able to participate in a chemical reaction. So using smaller clusters of gold atoms can maximize the number of these active atoms.

Nature, 495, S 10 (2013)
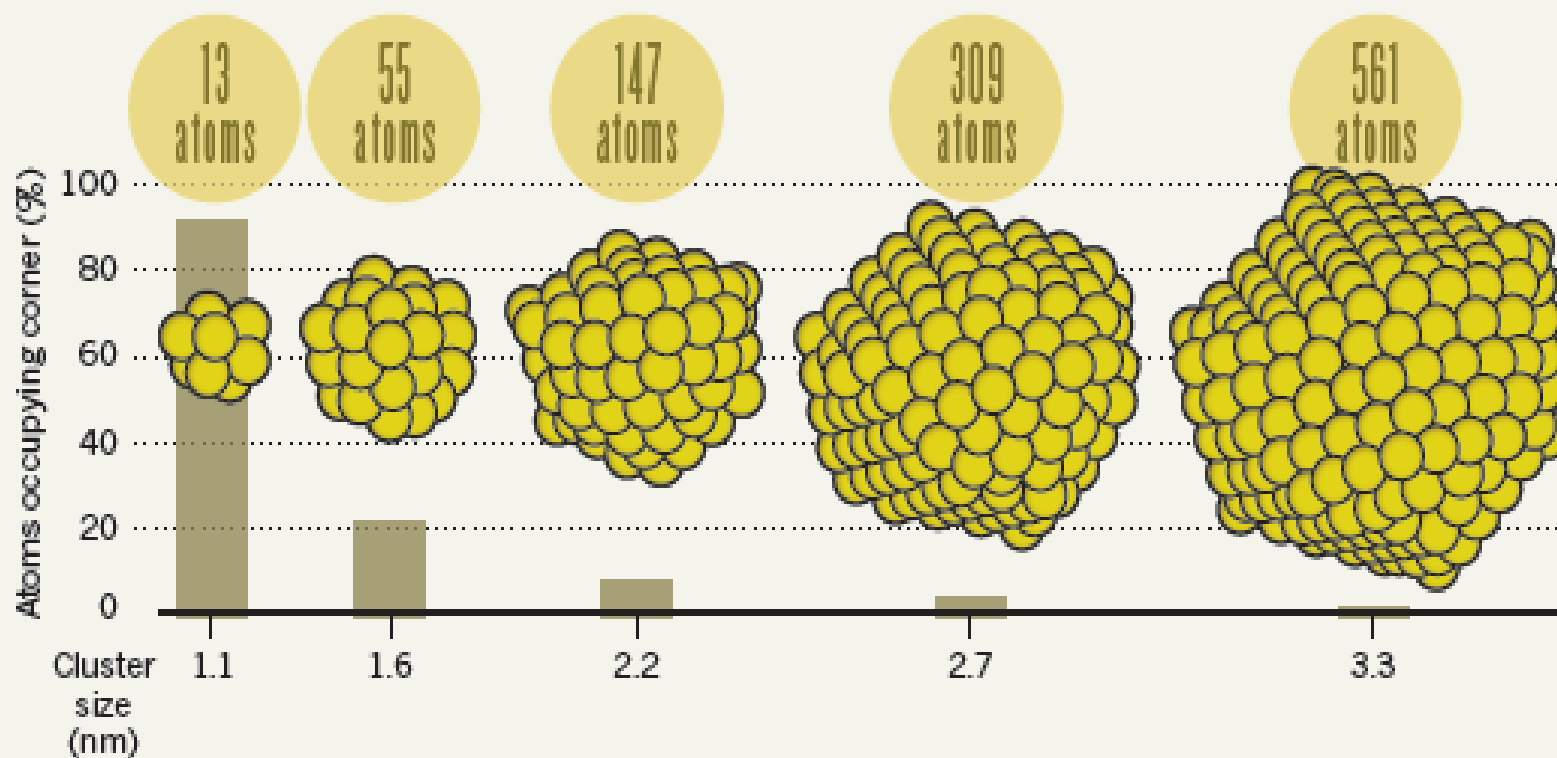
Total Vs Exposed metal atoms

The relation between the total number of atoms in full shell clusters and the percentage of surface atoms (reprinted from [5] with permission from John Wiley & Sons)

Full shell clusters	Total number of atoms	Surface atoms (%)
One shell	13	92
Two shells	55	76
Three shells	147	63
Four shells	309	52
Five shells	561	45
Seven shells	1415	35

Aiken, J. D., III; Finke, R. G. *Journal of Molecular Catalysis A: Chemical* **1999, 145, 1-44.**

Dispersion decreases as crystallite size increases

Crystallite geometry, dispersion & co-ordination number


Truncated Octahedron
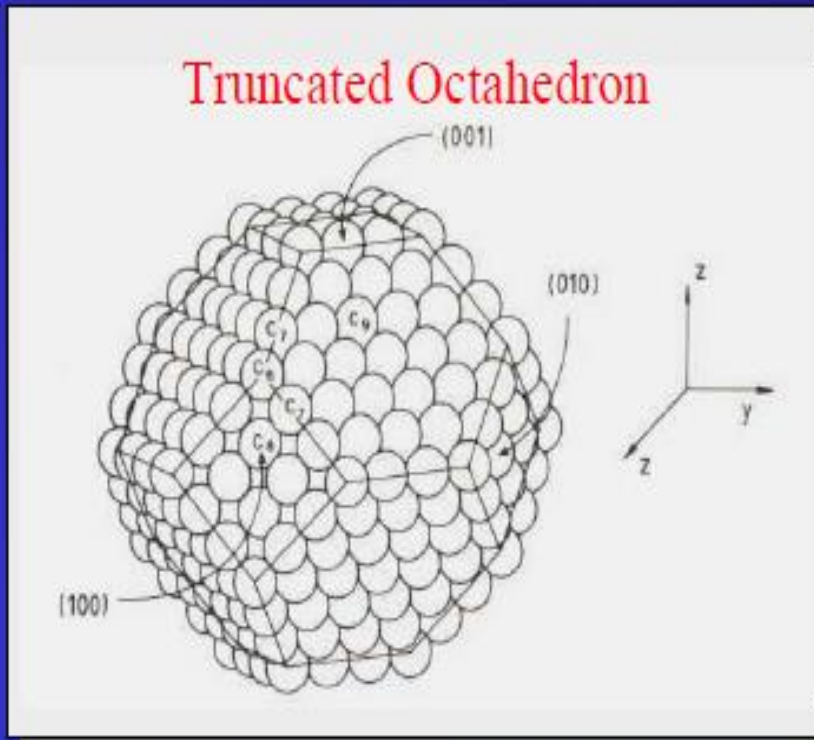
Crystal size ↓ then N_S/N_T ↑
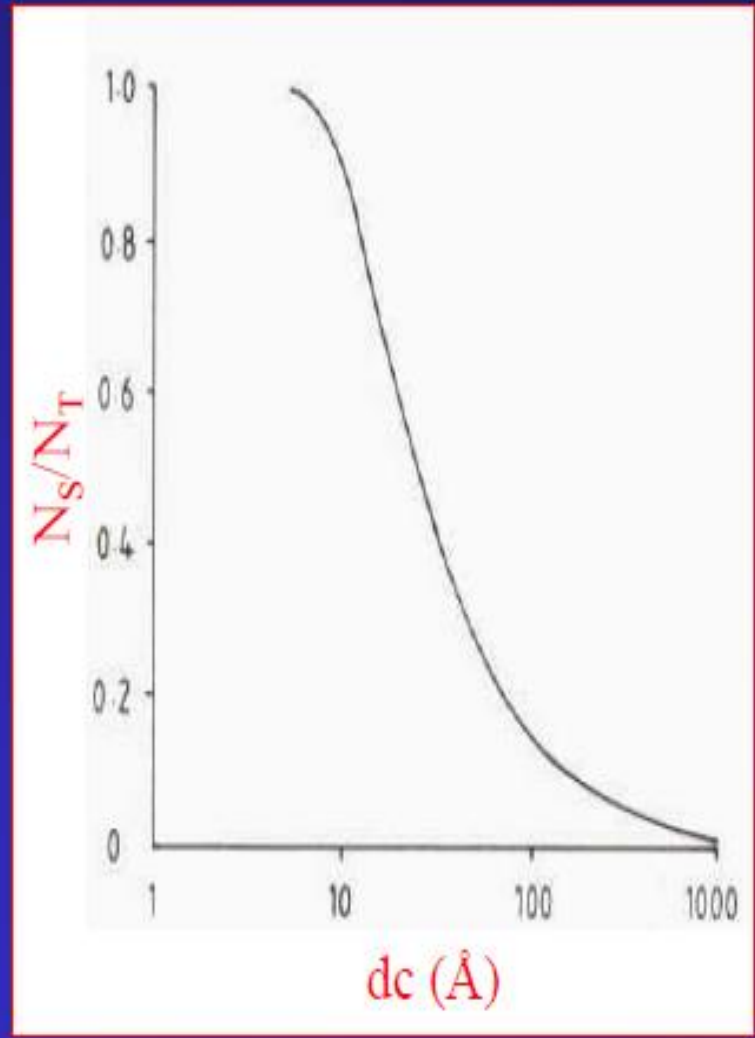
Lower co-ordination number- higher unsaturation -Higher activity
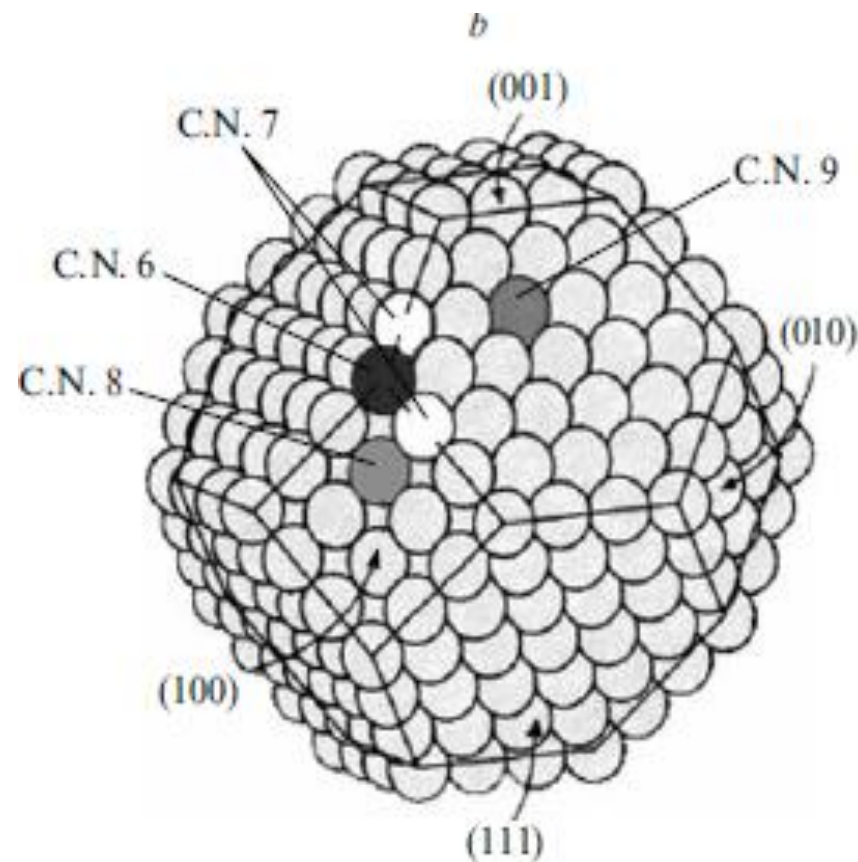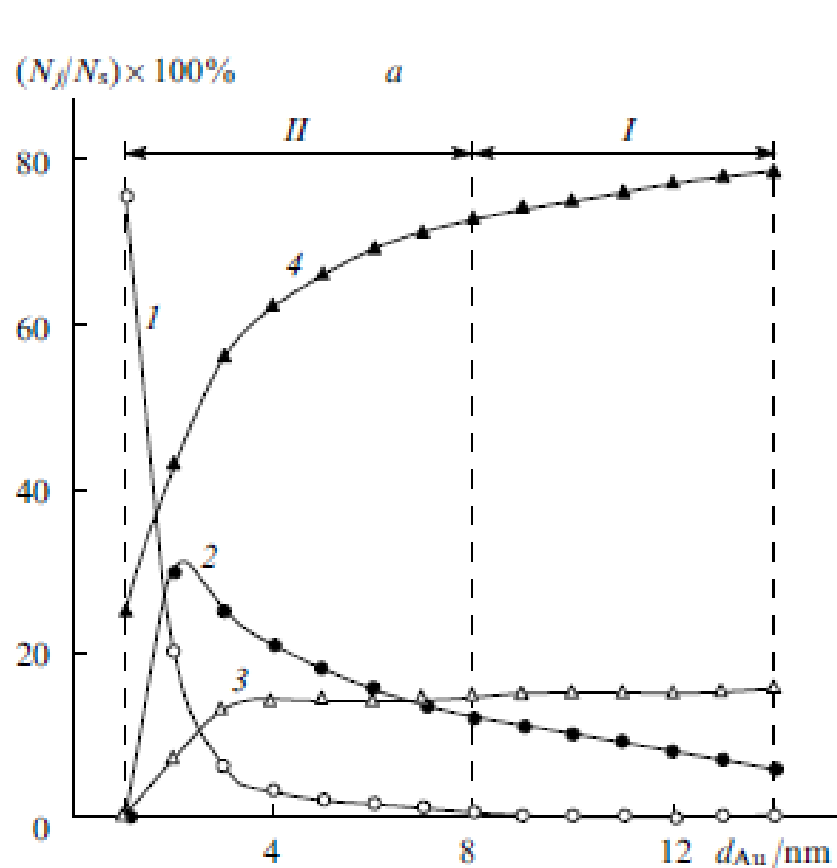
Figure 7. Relative concentrations of gold surface atoms N_j/N_s with coordination numbers of 6 (curve *1*), 7 (curve *2*), 8 (curve *3*) and 9 (curve *4*) *vs.* the diameter of gold nanoparticles d(Au) [(*a*) data of C Mohr, P Claus. *Sci. Progr.* **84** 311 (2001)]; the equilibrium cubocta-hedral shape for Au particles was used in calculations (*b*) from Ref. 124).

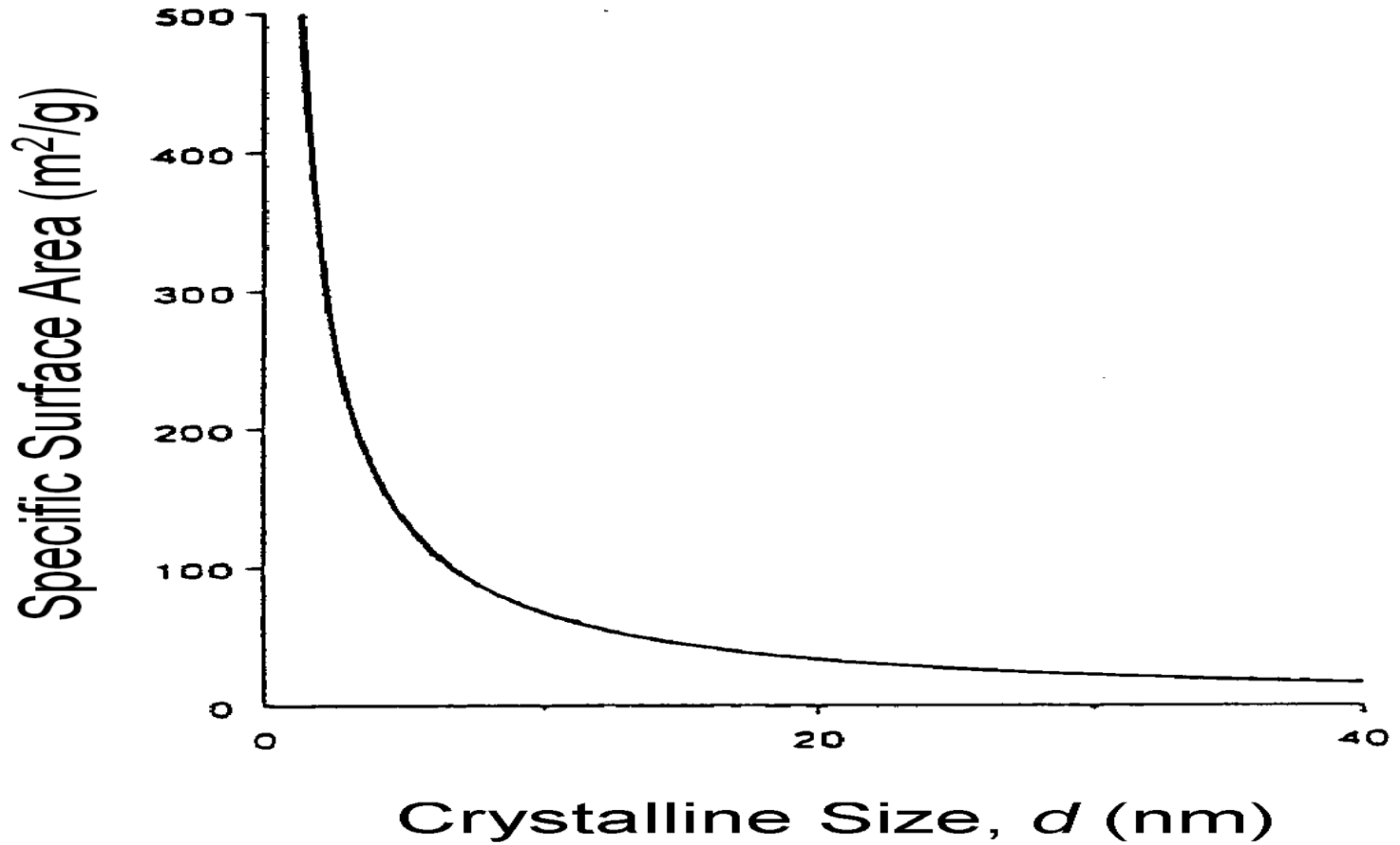N_j is the number of atoms with C.N. of j, N_s is the number of surface atoms.

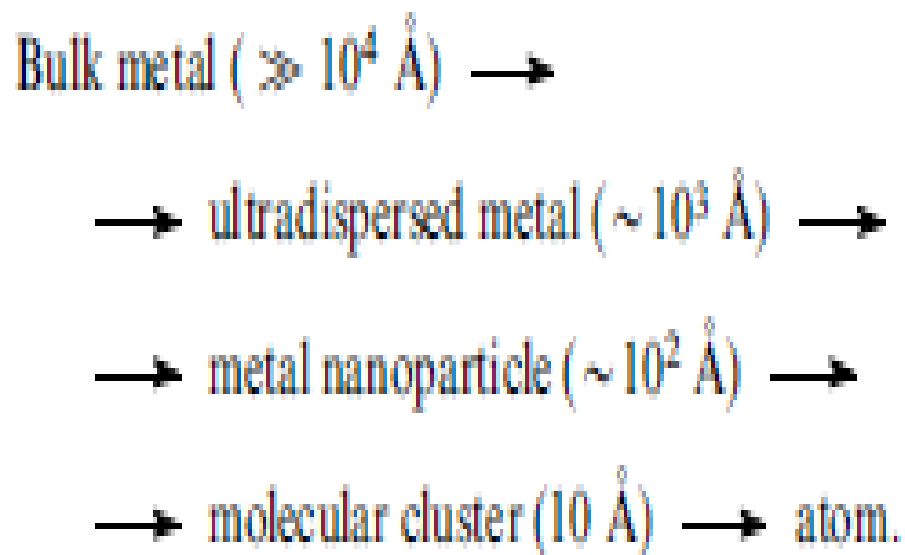# Crystallite size data for Au/TiO$_2$ - Illustration
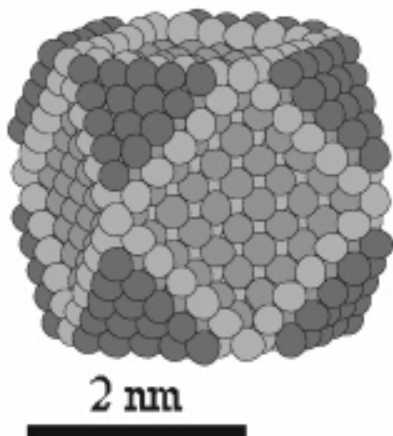
Crystallite size   3.41 nm
Total no of Au atoms 893
No of atoms on surface 468 –(Exposed atoms)
Co ordination number- 5.7,11
% Dispersion- 468/893 - 52
No.of exposed atoms = No.of active sites

2 nm

Crys.size nm	Surf.area m^2/g	CO Oxidn %
3.41	108.2	99
4.09	87.7	93
3.79	84.8	63
5.21	56.1	14
5.63	53.5	1

X. Bokhimi et.al, J.Phys.Chem.
C111,15210,2007

Crystallite size Vs.Activity- Supported Ni catalyst

Concept of size in metals

Bulk metal ($\gg 10^4$ Å) $\longrightarrow$

$\longrightarrow$ ultradispersed metal ($\sim 10^3$ Å) $\longrightarrow$

$\longrightarrow$ metal nanoparticle ($\sim 10^2$ Å) $\longrightarrow$

$\longrightarrow$ molecular cluster (10 Å) $\longrightarrow$ atom.

S A Nikolaev, L N Zanaveskin, V V Smirnov, V A Averyanov, K L Zanaveskin
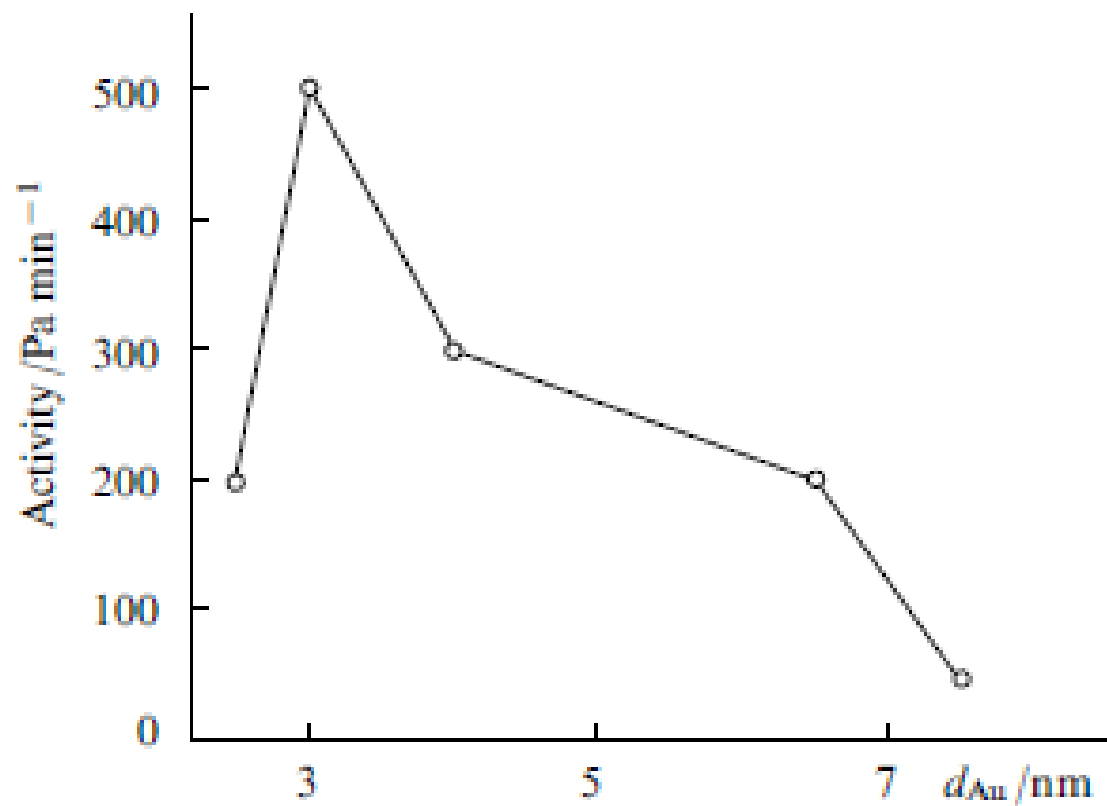
Figure 8. Activity of gold nanoparticles in acetylene hydrogenation at 523 K *vs.* size of Au particles immobilized on alumina.[152]

Support Surface Area Vs Dispersion
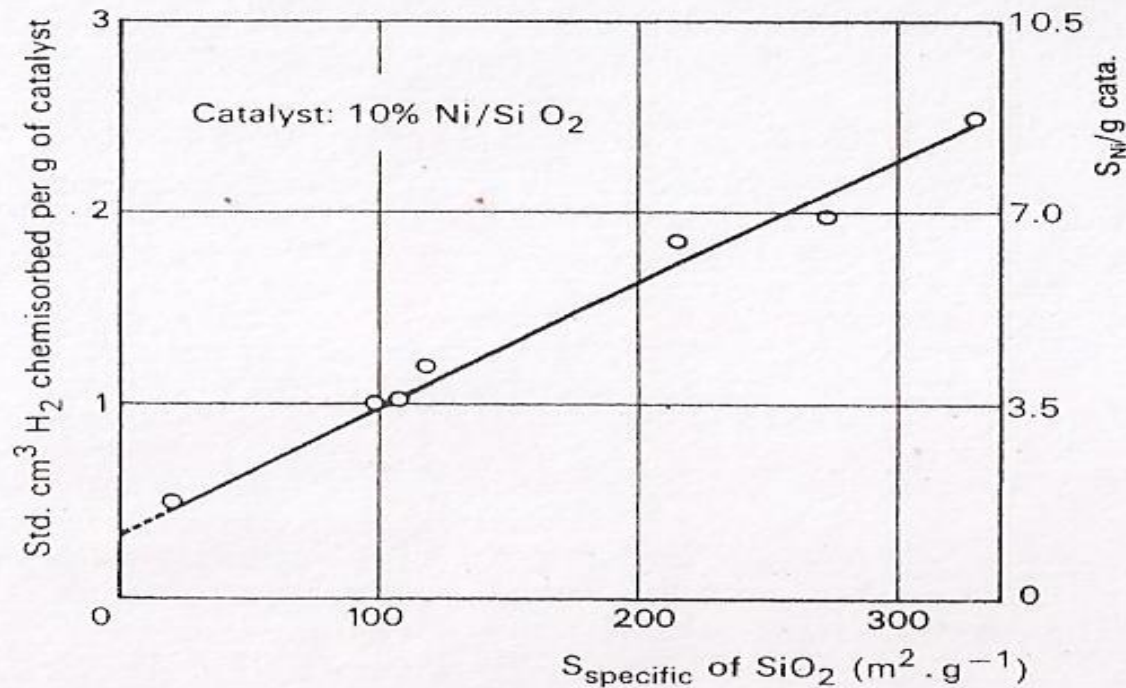
FIG. 7.11   Influence of the support surface on the dispersion of the active agent (10% nickel on a silica support).

The supports are impregnated by a nickel nitrate solution with no excess. The impregnated catalysts are dried at 80° C. calcined at 500° C, and reduced. Tests plotted above show that the volume of hydrogen chemisorbed per gram of catalyst, i.e., the nickel surface accessible to the hydrogen, increases with the specific surface of the support. The plot suggests that the catalytic surface at zero support surface corresponds to the surface offered by solid nickel obtained from nitrate after the same treatments.

Rao, S., Cosyns, J., IFP unpublished results.
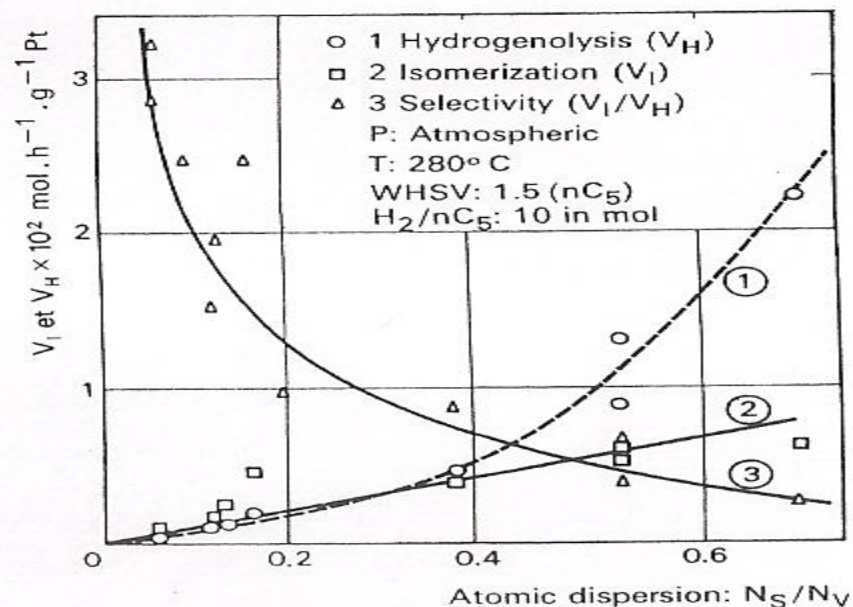
FIG. 7.12 Effects of atomic dispersion on activity and selectivity of platinum for the hydrogenolysis of *n*-pentane.

Normal pentane is treated with hydrogen in a differential fixed-bed reactor at low conversion rates, at the operating conditions shown in the figure, and the production of light products and isopentane is measured as indications of hydrogenolysis and isomerization respectively.

The rate of isomerization increases linearily with the dispersion of the metal, and the rate of hydrogenolysis increases much more rapidly. This can be interpreted by assuming the hydrogenolysis operates preferentially on atoms at the corners or edges of the crystallites, while the isomerization uses any of the surface atoms without discrimination:

$$V_I \quad = \text{rate of isomerization, mol} \cdot h^{-1} \cdot g^{-1} \, Pt$$
$$V_H \quad = \text{rate of hydrogenolysis, mol} \cdot h^{-1} \cdot g^{-1} \, Pt$$
$$V_I/V_H \; = \text{selectivity}$$
$$N_S/N_V = \text{accessibility} = \text{atoms of surface/total atoms}$$

N_S is obtained from CO chemisorption by assuming an average stoichiometric ratio of (Pt atoms/molecule of CO) = 1.15 as valid for the range of aggregates studied in this example.

Brunelle, P., Sugier, A., Montarnal, R., *J. Catal.* Vol. 43 p. 273, 1976.
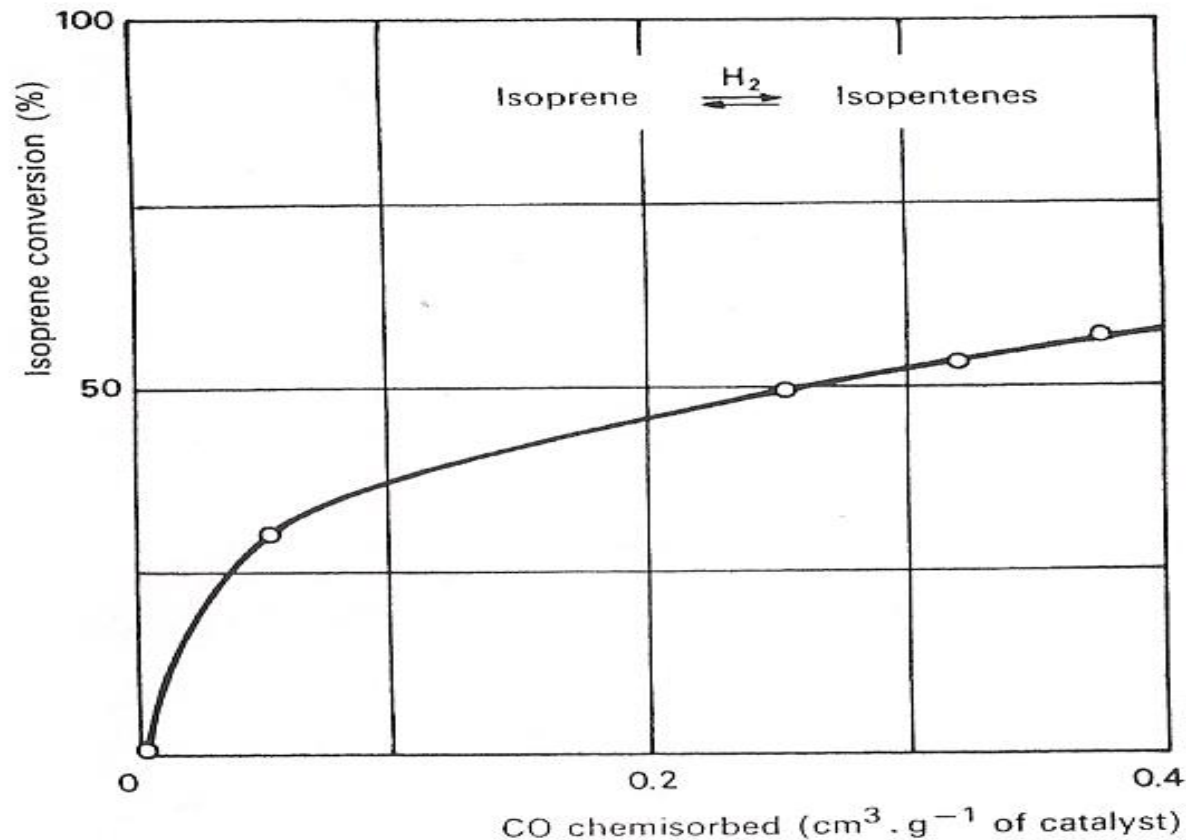
FIG. 7.13 Effects of Pd dispersion on the selective hydrogenation of isoprene.

Operating conditions: $P = 20$ bar; $T = 60°$ C; LHSV $= 10$/h; H_2/HC in moles $= 3$; feed $= 10$ vol.% isoprene in 90% benzene; additive: 5,000 ppm thiophene added to feed by wt.

Each of the four data points represents a catalyst corresponding to a particular method of impregnation. The conversion increases with the amount of CO chemisorbed, but very moderately, because of the intervention of diffusional phenomena on the overall rate of hydrogenation.

Derrien, M., Cosyns, J., IFP results.
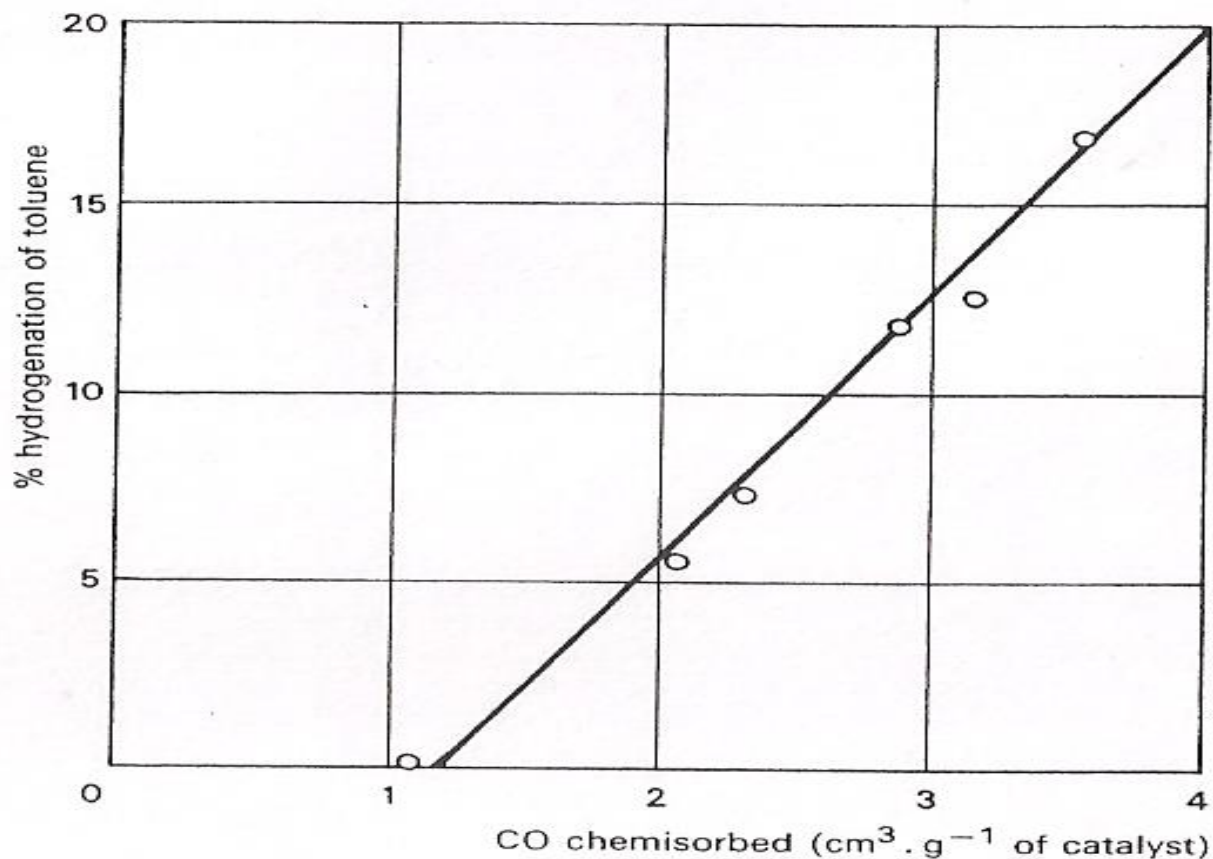
FIG. 7.14   CO chemisorption as a measure of hydrogenating activity.

Toluene was hydrogenated over sulfided Co-Mo supported on alumina, under the following conditions: feed = 79.5% cyclohexane, 20% toluene, and 0.5% thiophene, all by wt; total pressure = 60 bar; $T = 350°$ C; $H_2/HC = 450$ by vol; LHSV = constant.

The CO chemisorbed was measured by a volumetric method at ambient temperature. The data obtained for the different catalysts show that the hydrogenating activity varies linearly with the CO chemisorbed at ambient temperature, when allowance is made for the chemisorption of the support.

Miquel, J., Franck, J. P., IFP results.
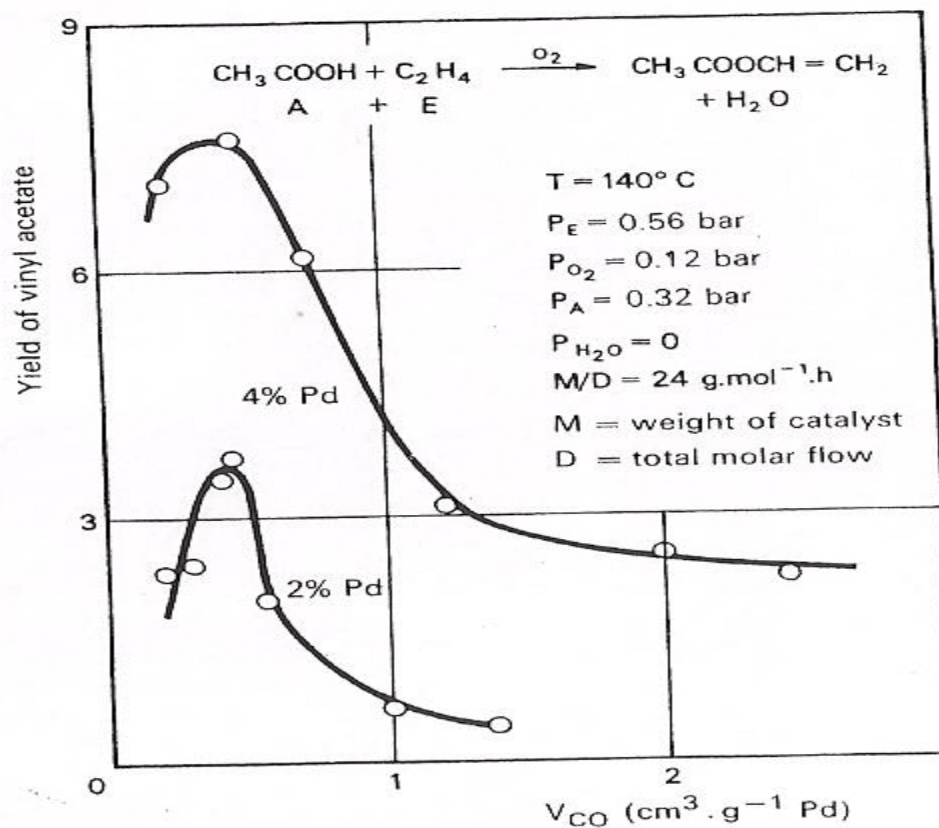
FIG. 7.18 Effect of crystallite dimensions on the synthesis of vinyl acetate by gas-phase acetoxidation of ethylene.

The catalysts were made by successive deposits on a 220 m^2 . g^{-1} silica, as follows: (a) deposit of palladium by cationic exchange followed by calcination at various temperatures, then reduction at 150° C; (b) deposit of 15% by weight of CH_3COONa by impregnating without excess solution, followed by drying. The sodium acetate plays the role of activator in this reaction.

The curves connecting the data points show that the yield of vinyl acetate passes through a maximum for an optimum crystallite dimension expressed in terms of CO chemisorption.

Samanos, B., Thesis, Paris, 1971.
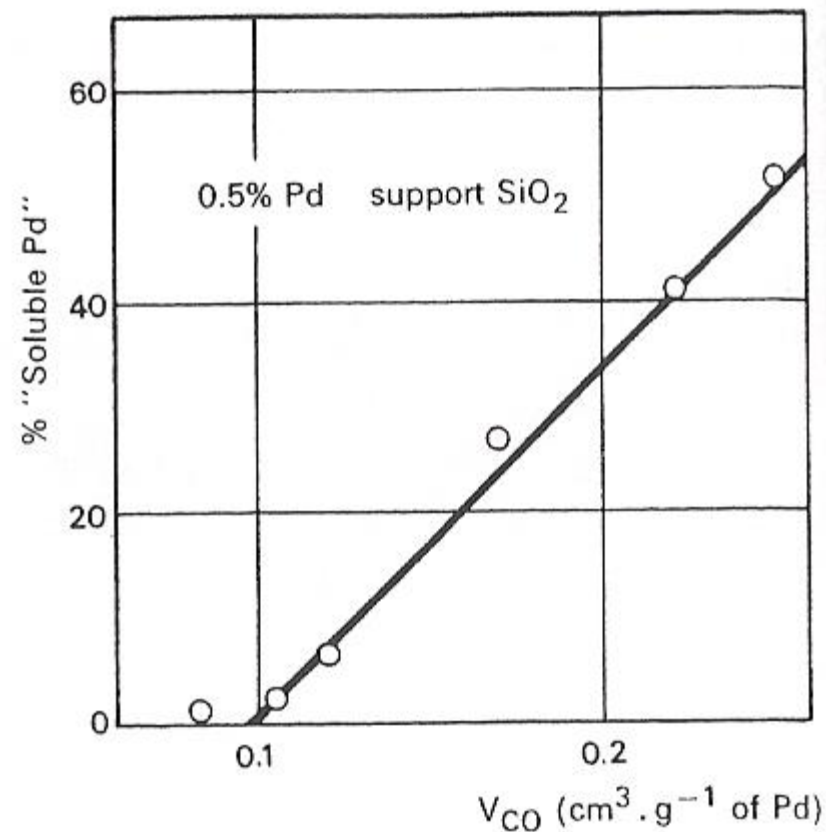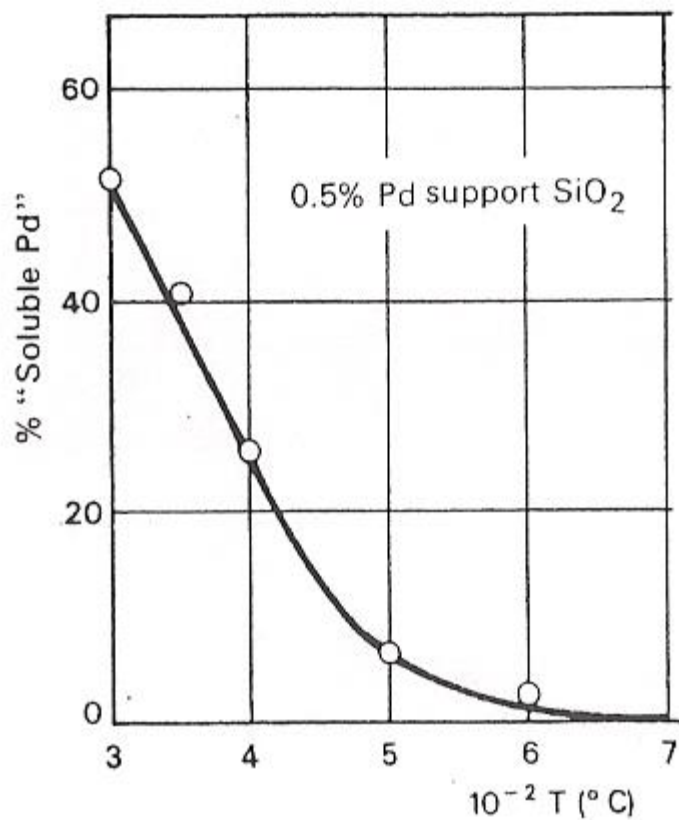
FIGS 7.20 and 7.21   Correlation between the chemical solubility of deposited palladium and its dispersion.

Figure 7.20 shows that the solubility of palladium in a solution of 5% $SnCl_2$ decreases as the calcination temperature increases. The linear relation between the percentage of soluble Pd and the quantity of CO chemisorbed in Fig. 7.21 shows that solubility reflects the dimensions of the crystallites.

Samanos, B., Thesis, Paris, 1971.

Crystallite size measurements
- Experimental techniques

- X-ray line broadening Analysis –XLBA

- Transmission electron microscopy- TEM

- Chemisorption methods

- X-ray photo electron spectroscopy

Crystallite size measurement- Methods

X-ray line broadening analysis-XLBA

Crystallite/Particle size is inverse proportional to line width- FWHM

Debye- Sherrer formula- Size (d) = $k\lambda /\beta Cos\theta$

- k- constant-0.94or to 1; β- angular width at half-height, λ- X-ray   wave length , $\beta = (B^2-b^2)$; B- FWHM for sample & b-FWHM for standard
- Applicable range- 3-100 nm
- Not applicable for catalysts with low metal loading
- Only average value is obtained
- d- gives length; Shape/Geometry factor to be included
- d_m = d x g
- Particle size/crystallite size could

   be measured
- Average value from different

   d-lines
- High temperature/in-situ studies

Crystal geometry	Factor **g**	Definition
Sphere	4/3	Diameter
Hemisphere	4	Diameter
Cube 100	1	Cube edge
110	1.061	Cube edge
111	1.155	Cube edge

- Small angle X-ray diffraction
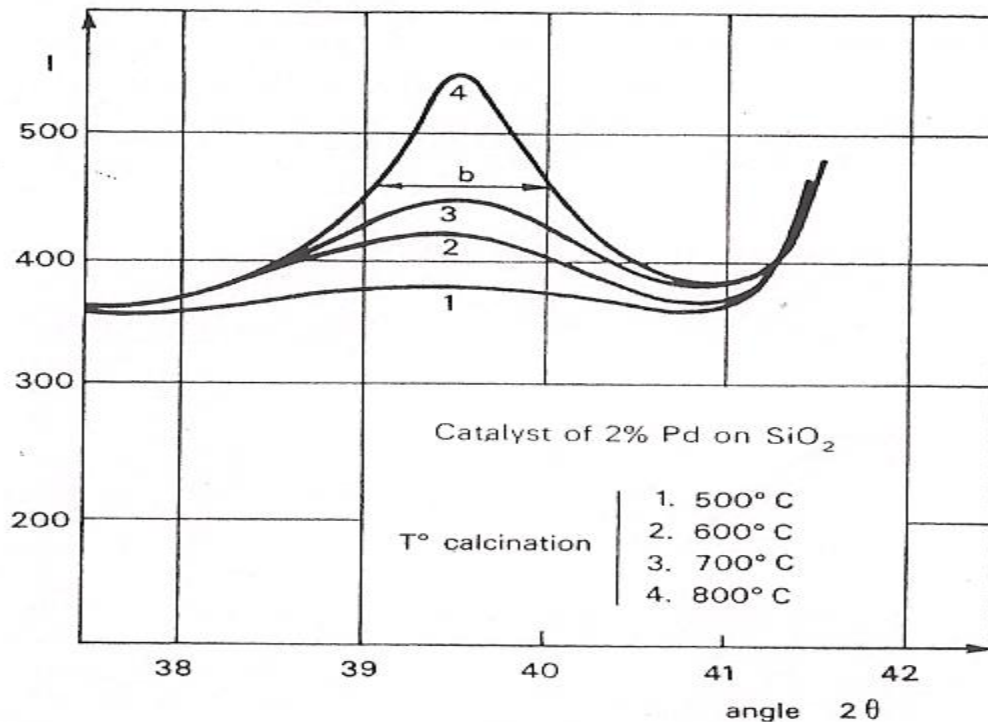
FIG. 7.15   Determining the average size of palladium crystallites from the mid-height width (b) of X-ray diffraction lines.

An estimate of the dimension of the crystallites, d, is first approximated by the Scherrer formula.

$$d = \frac{k_\lambda}{b \cos \theta}$$

where b represents the angular width of the X-ray line at mid-height, θ, the corresponding Bragg angle, and k is a constant close to one. This method applies particularly well for crystallite dimensions between 5 nm and 50 nm. The average dimensions of the crystallites of four catalysts of this figure appear in Table 7.6, which shows the importance of the calcining temperature on the enlargement of the palladium crystallites and hence on the surface that they offer for the access of the reactants.

Samanos, B., Thesis, Paris, 1971.
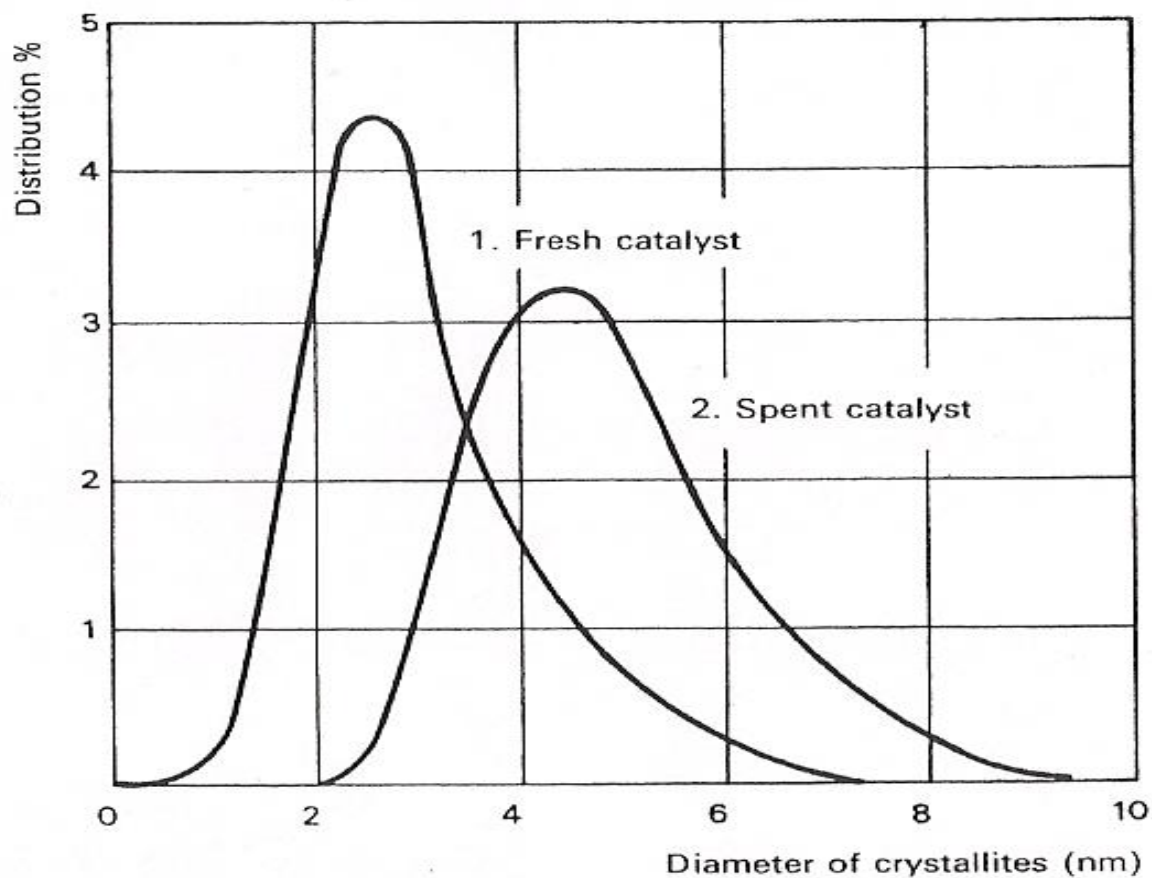
FIG. 7.19 Dispersion of platinum on a reforming catalyst by the Small Angle X-ray Scattering (SAXS) method.

The figure shows the crystallite distribution according to dimension for both a fresh catalyst and a spent catalyst that has undergone six regenerations. The support is η alumina; and unwanted diffusion of the alumina pores is suppressed by previous adsorption of C_4H_9I, whose electronic density is close to that of alumina.

White, T. E., Kirklin, P. W., Gould, R. W., Heinemann, H., *J. Catalysis*, 25, 407, 1972.

Transmission Electron Microscopy

Direct observation of crystallite size & shape; Sampling technique is critical
Size range upto 1 nm & below
Small sample- May not be representative; in-situ studies possible

FIG. 7.17   Electron microscope photograph of platinum deposits on zeolite
(1 mm = 3.3 nm).
Gallezot, P., Dalmai-Imelik, G., Imelik, B., *Institut de recherche sur la catalyse*, Lyon,
Unpublished results.

Transmission Electron Microscopy
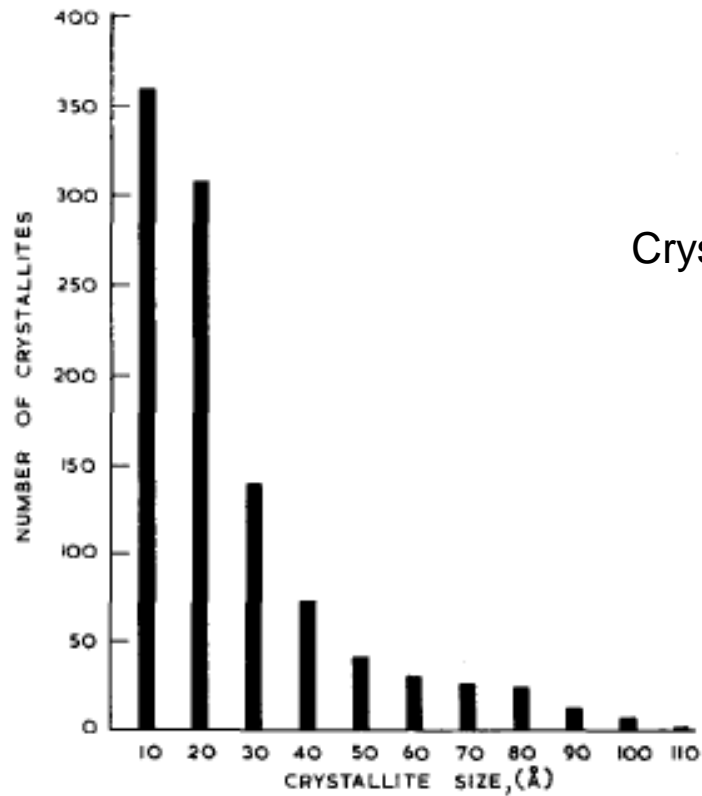
Crystallite size distribution-Histogram

FIG. 2. Size distribution of platinum crystallites in 3% Pt/silica catalyst derived from Fig. 1.

J.Catal.7,378,1967

Crystallite size analysis by TEM
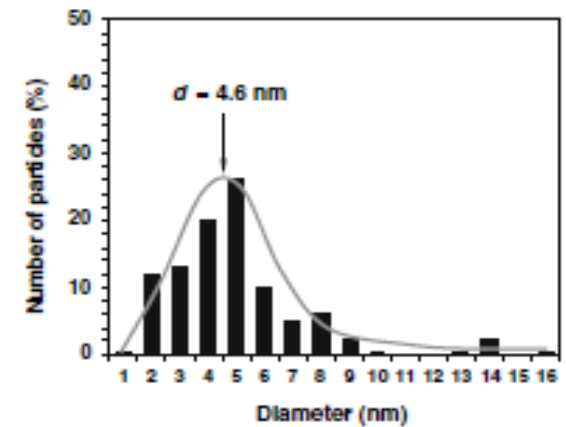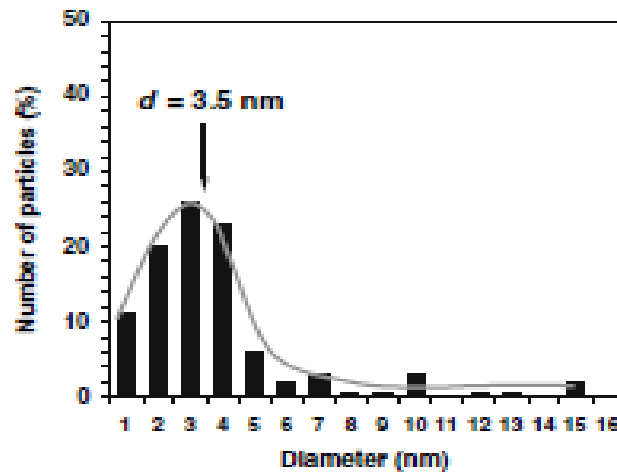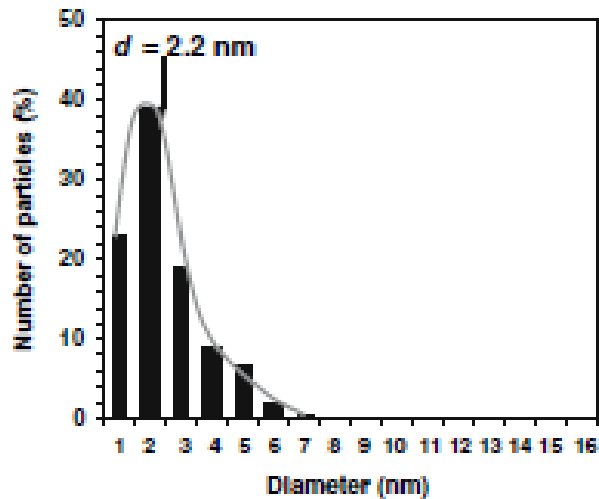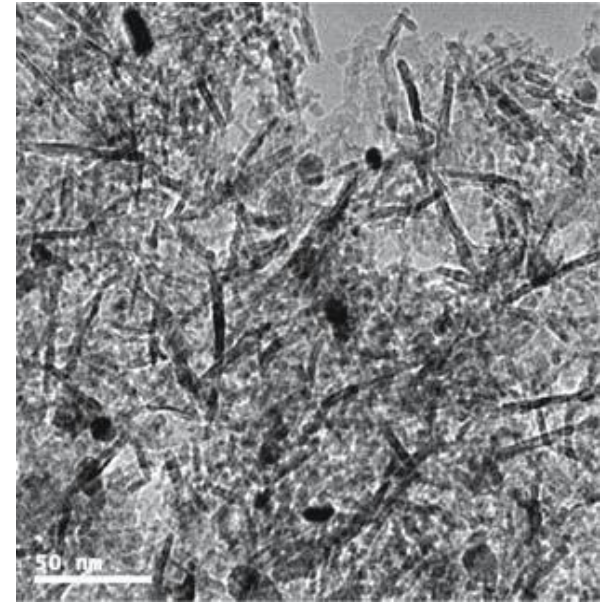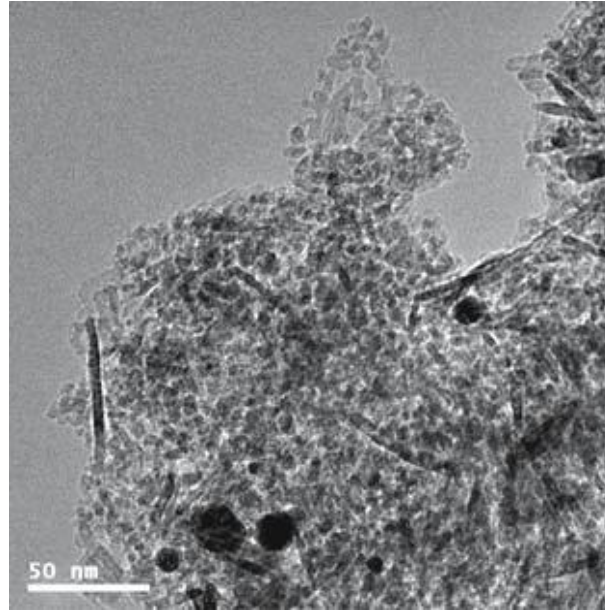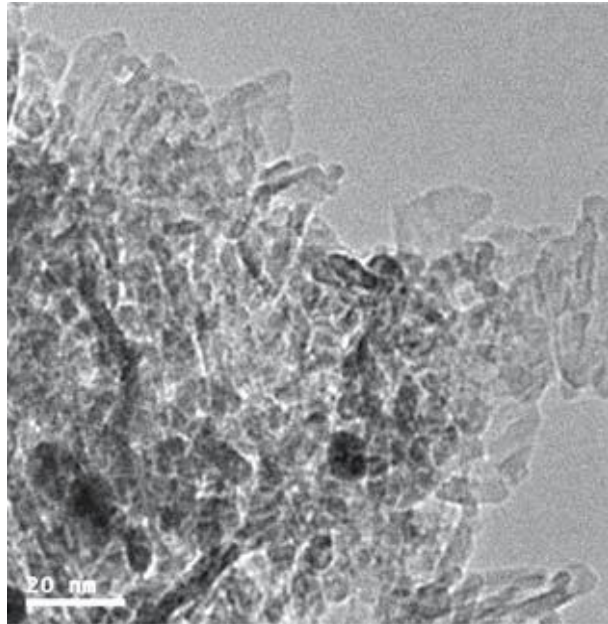
Fig. 2 Selected TEM images and particle size distributions of the reduced samples. (a) 1.9 wt.% Ru (2.2 nm); (b) 4.7 wt.% Ru (3.5 nm); (c) 7.0 wt.% Ru (4.6 nm)
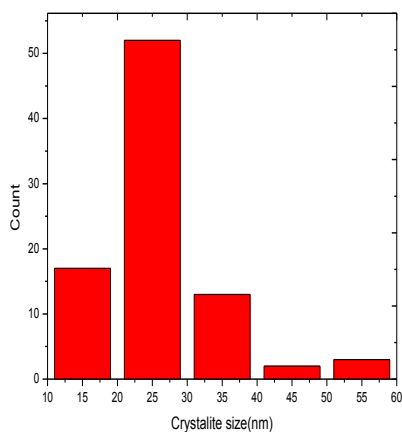
W.Zhang et.al,
Catal.Lett., 119,311,2007
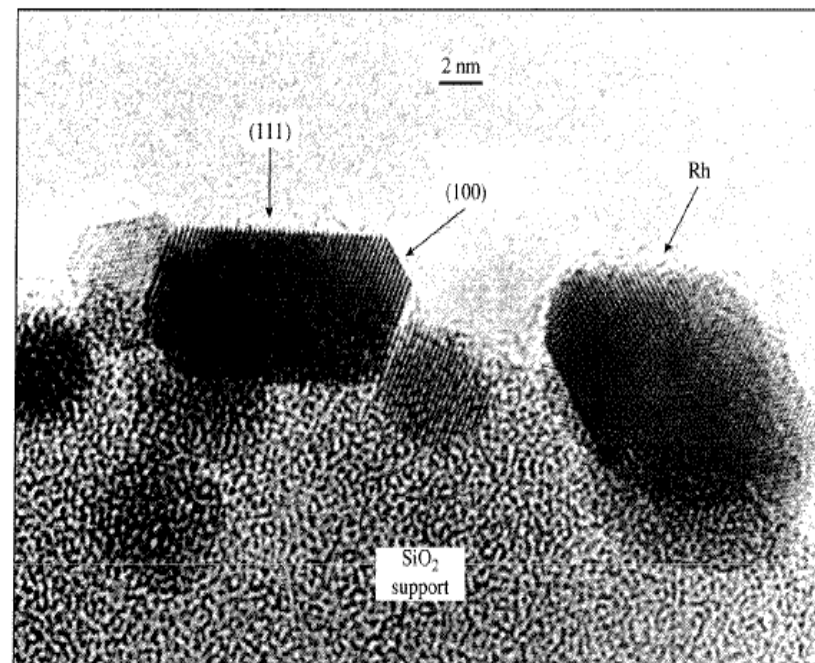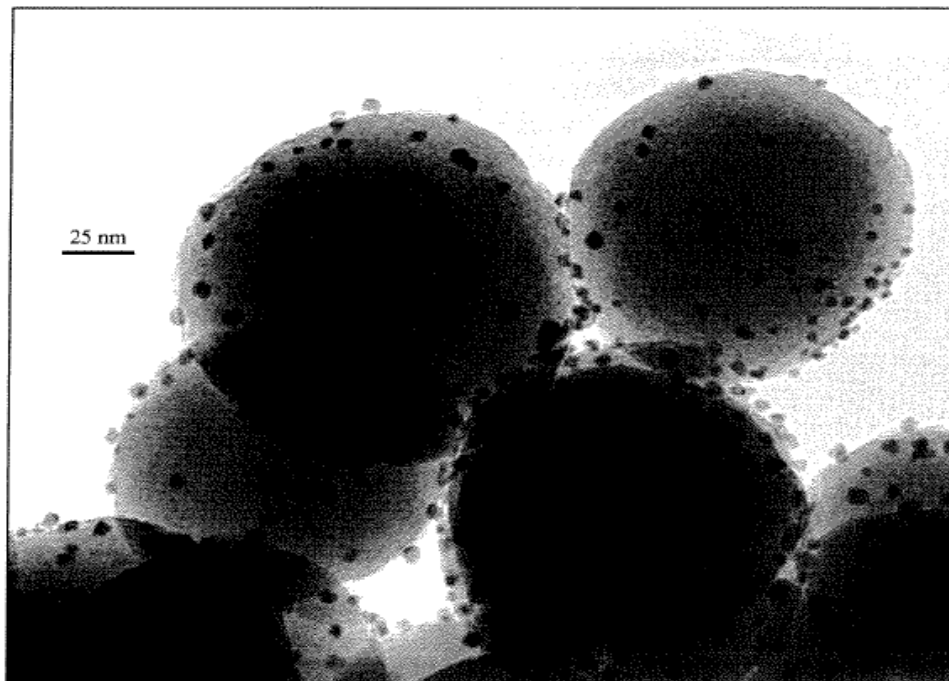
(a) Rhodium metal particles supported on silica carrier. **(b)** High-resolution electron micrograph shows how small supported Rh crystallites expose low-index faces. (Top photo courtesy of A. K. Datye. Bottom photo from "Modeling of heterogeneous catalysts using simple geometry supports" by A. K. Datye in *Topics in Catalysis*, vol. 13:131, copyright © 2000 by Kluwer Academic, reproduced by permission of the publisher and the author.)
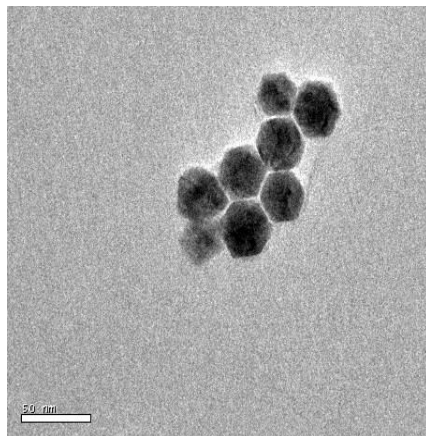
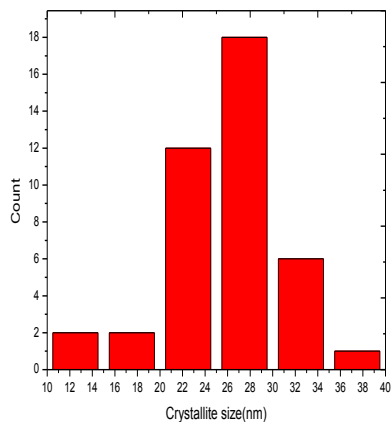# Shape controlled Pd nano particles on Hydrotalcite & Titania
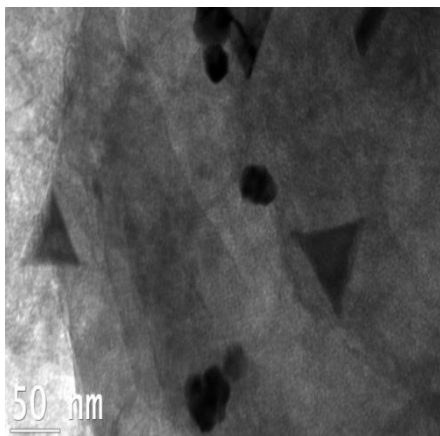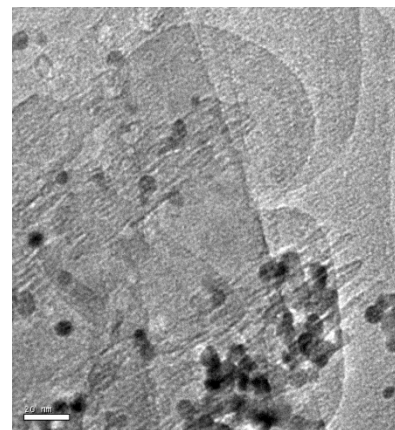

Tetrahedral
Mean- 27.2 nm
± 11.04 nm

Octahedral
Mean- 25.73 nm
± 5.06 nm

Spherical
Mean- 6.4 nm
± 2.24 nm
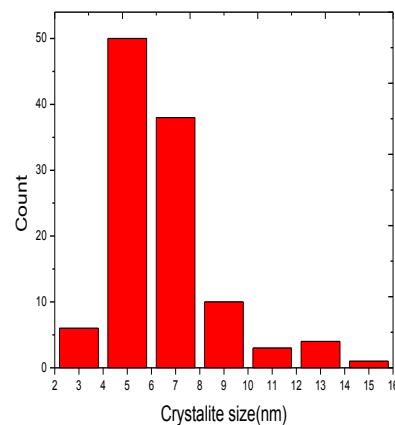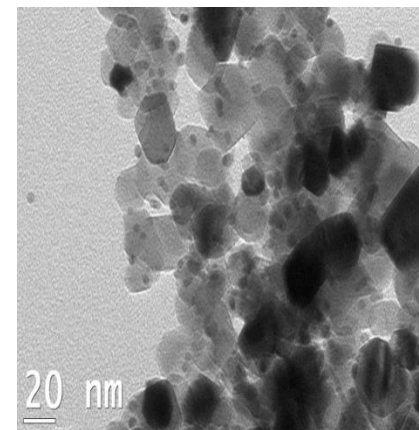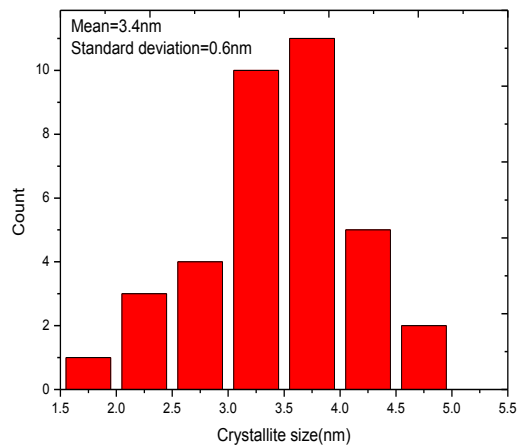
Spherical-P-25
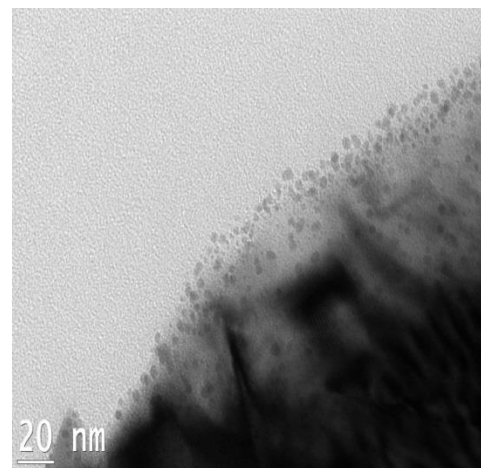**Mean- 3.43 nm**
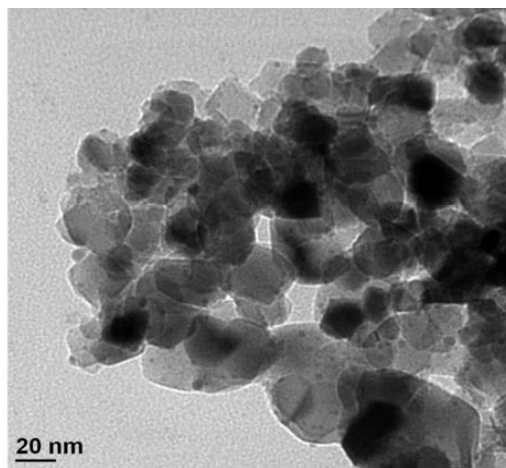**±1.43 nm**

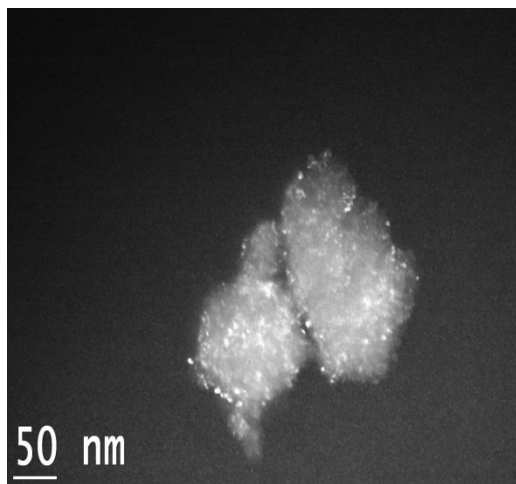(25-45 nm) *

(30-50 nm)*

(8-40 nm)*
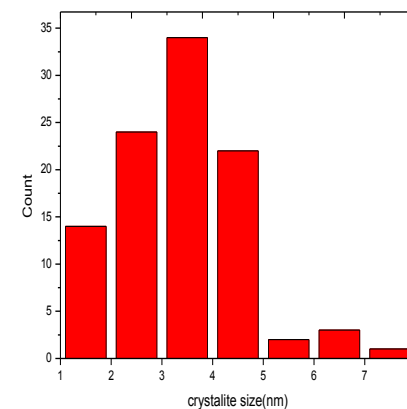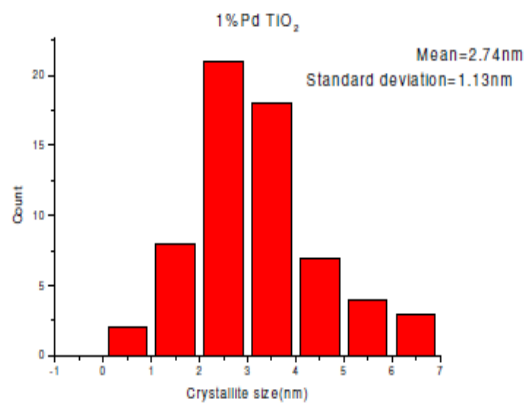
Pd loading
HTC-3.6 %; P-25-1.5%

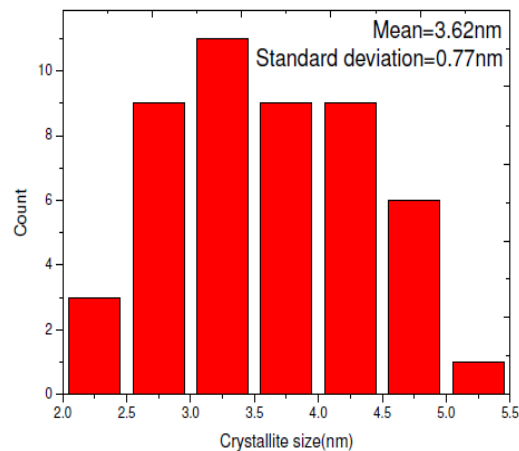* - Size values reported in Appl. Catal. A 413-414, 10,2012

TEM data for 1%Pd on polymorphs of TiO$_2$ as supports

Anatase
3.4± 0.6 nm

P-25
2.74±1.13 nm

Rutile
3.62±0.6 nm

TEM data for 1%Pd on polymorphs of TiO$_2$ as supports
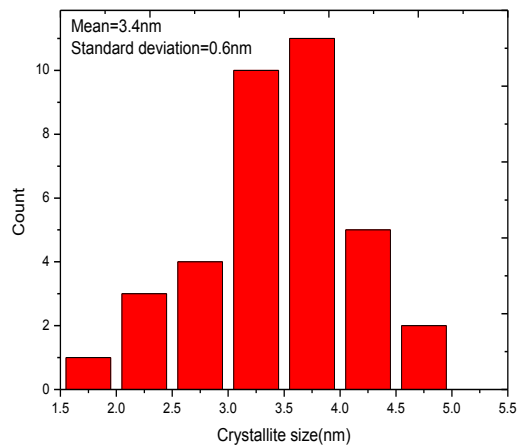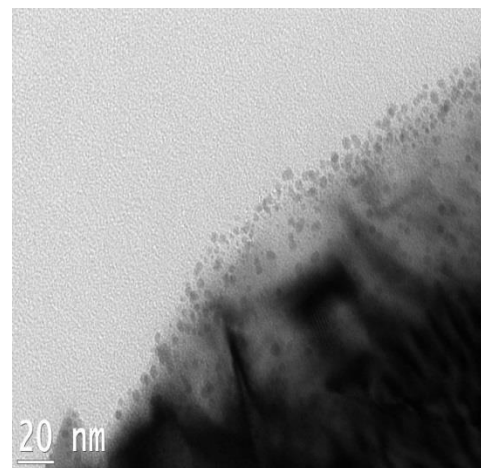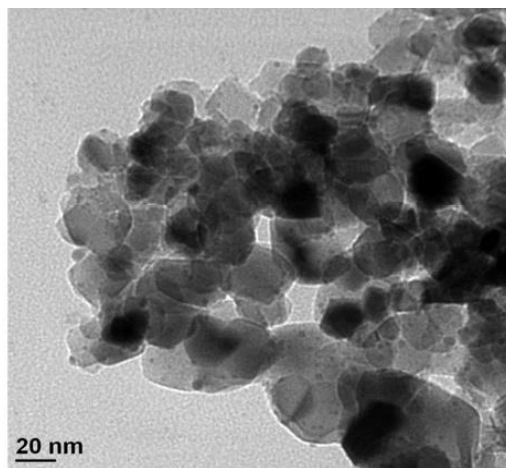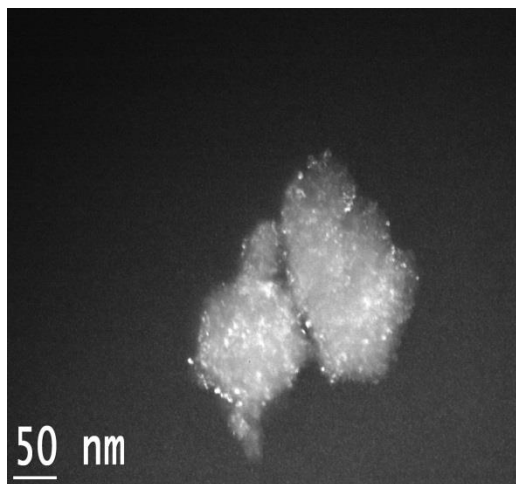
Anatase
3.4± 0.6 nm
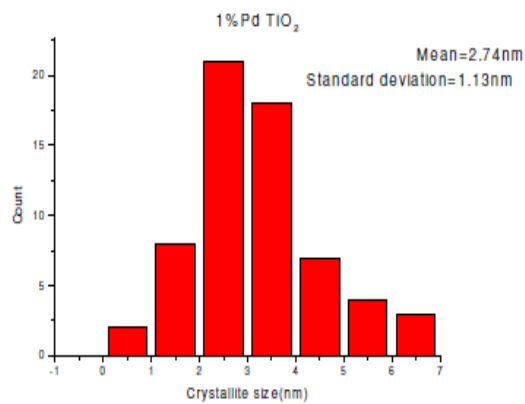
P-25
2.74±1.13 nm
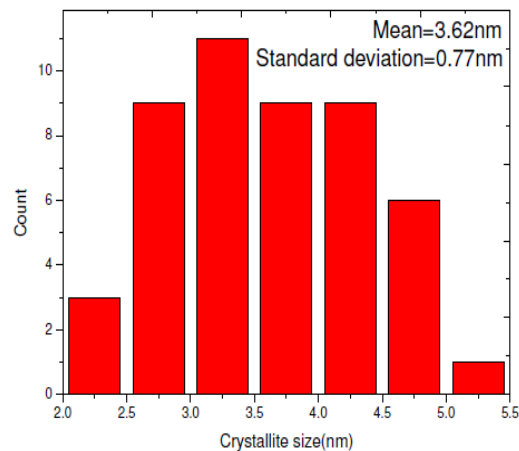
Rutile
3.62±0.6 nm

n-Hexadecane –Conversion & Selectivity on ZSM-12-Role of SDAs
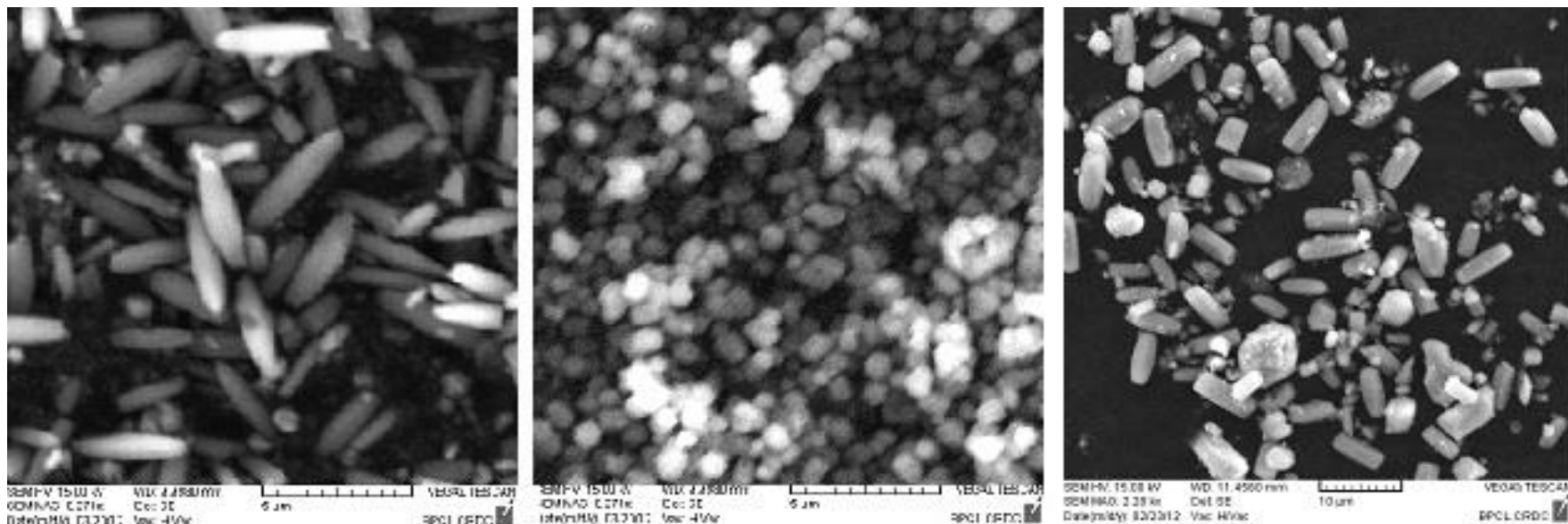
Crystal morphologies of ZSM-12 (L to R)- BTMACl-ZSM-12: Rice shaped , TEABr-ZSM-12: Cuboidal shaped &MTEABr-ZSM-12: Elongated cuboidal shaped crystallites

Catalyst	Template	Crystallite Size (µm)	Zeolite Acidity (µmol/g)	External SA (m²/g)	BET Total SA (m²/g)
CAT-1	BTMACl	3 – 4	107	40	260
CAT-2	TEABr	1 – 2	80	69	220
CAT-3	MTEABr	6 – 7	115	38	260
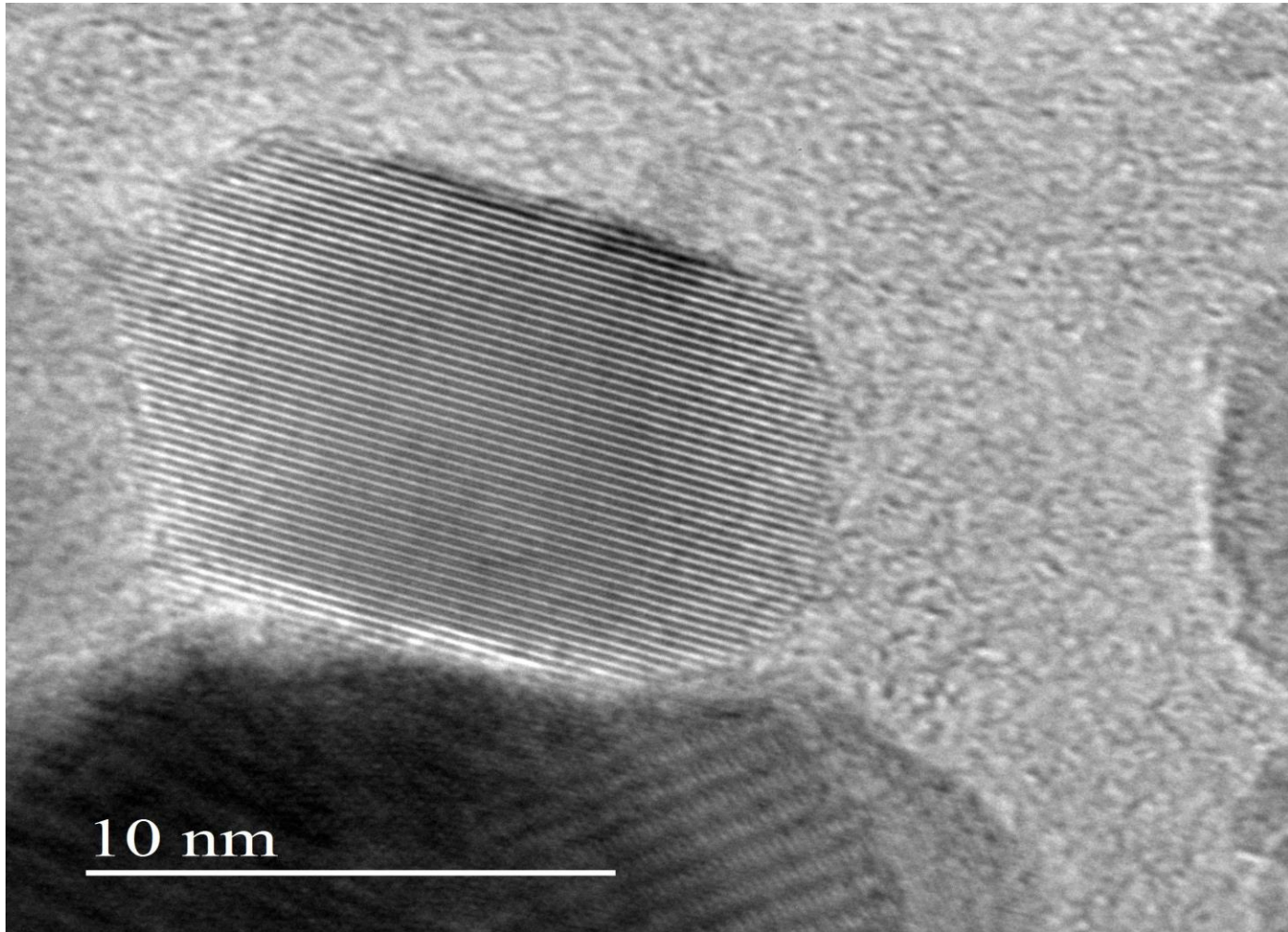
Nano size cobalt oxide prepared in the laboratory

Morphology of $Na_{(1-x)}La_xTaO_{(3+x)}$ (a) SEM image, b) TEM image, (c) SAED (d) HRTEM
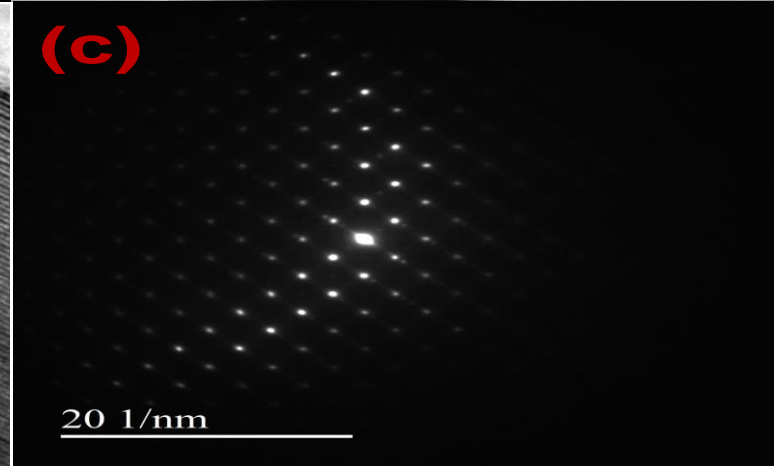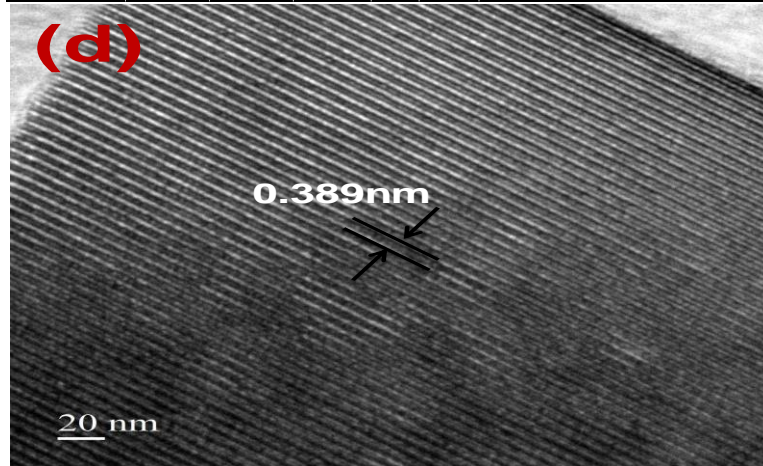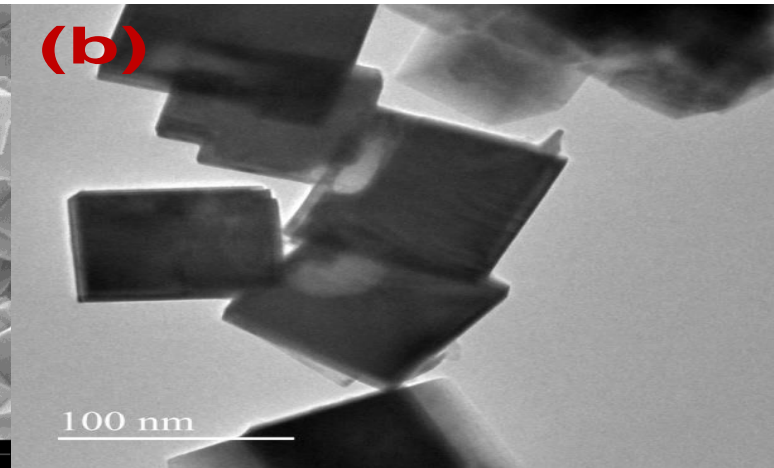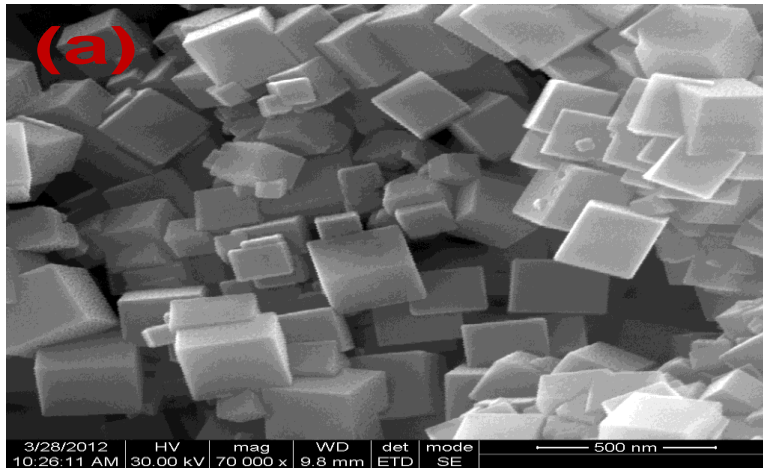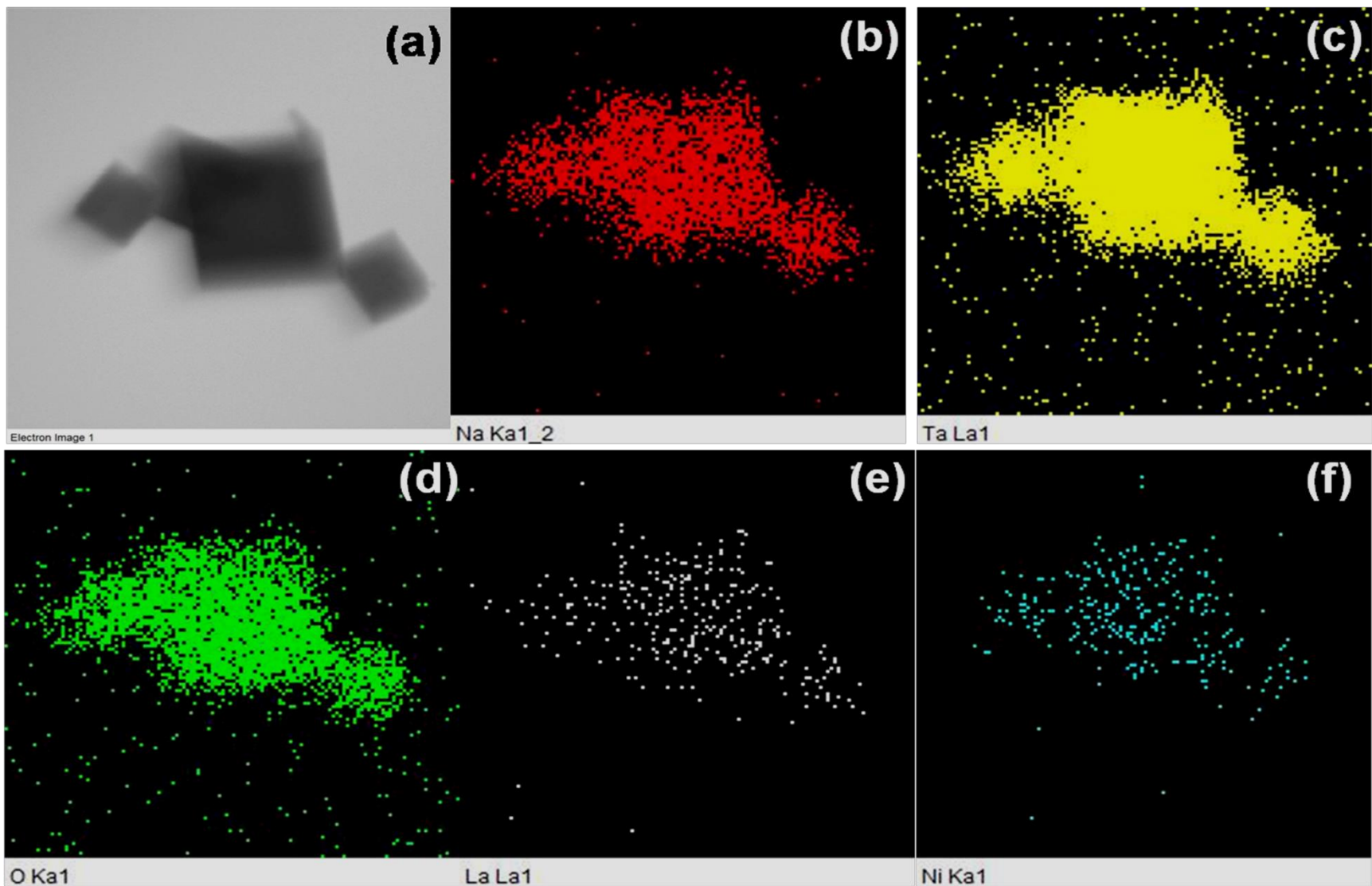
STEM (a) and Elemental mapping (b) Na-Kα (c) Ta-Lα (d) O-Kα (e) La-Lα (f) Ni-Kα for 0.2Wt% NiO/Na$_{(1-x)}$La$_x$TaO$_{(3+x)}$.

20 nm
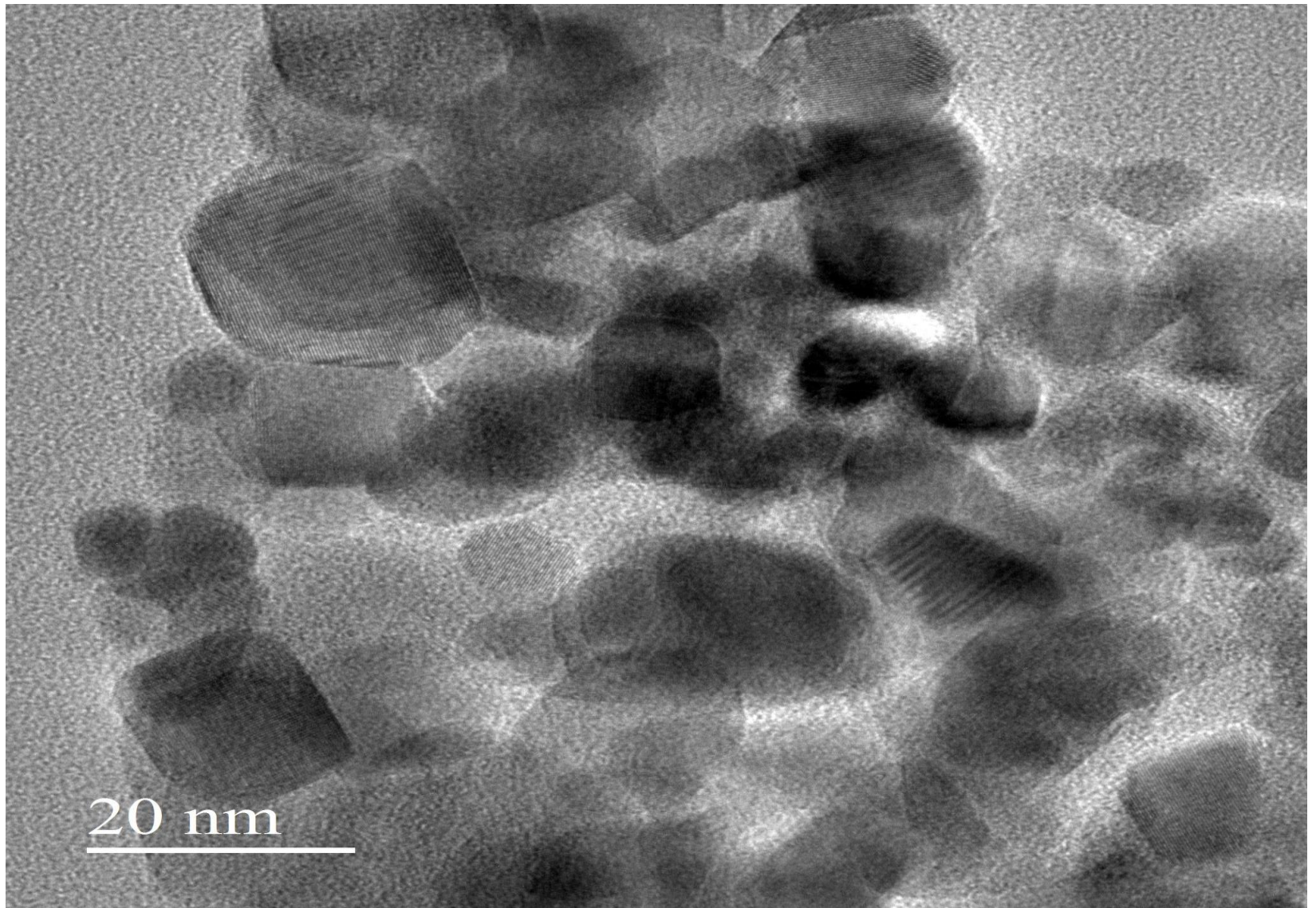
Nano size cobalt oxide prepared in the laboratory

Metal surface area by Chemisoprtion

□ CO molecules

Metal particles

Support (e.g. oxide) surface
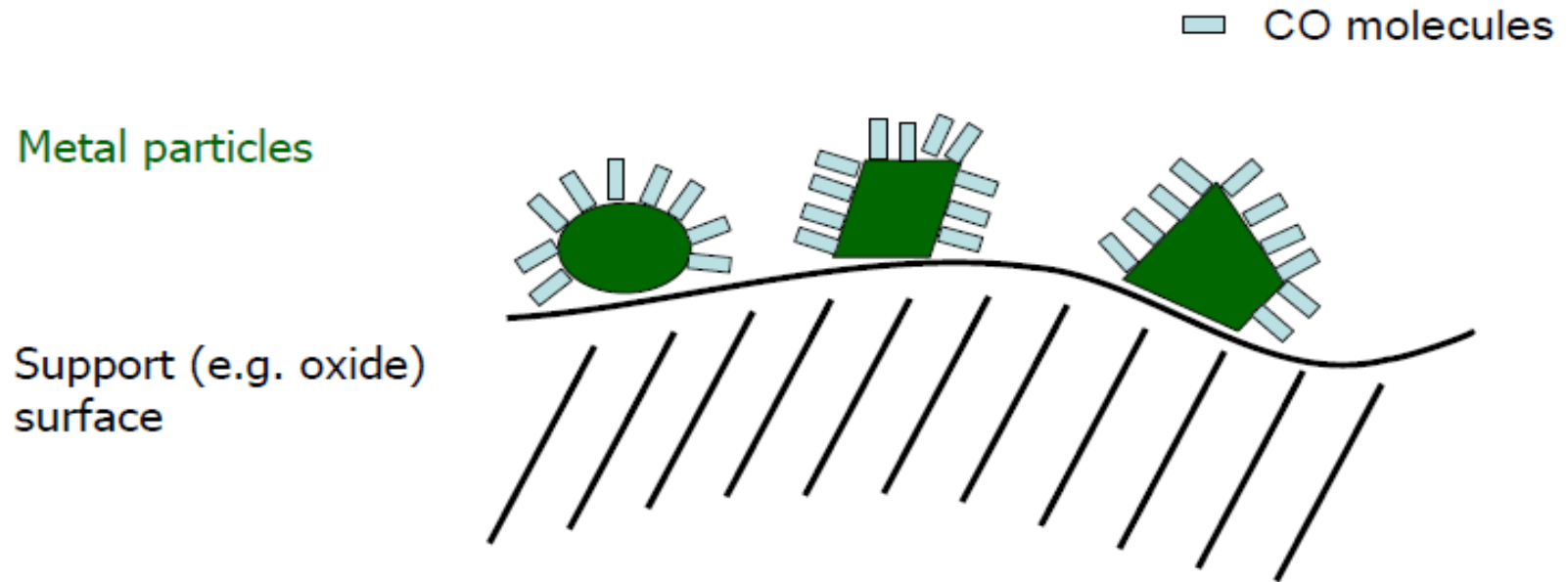
❖ specific adsorption of probe on only one type of site (e.g. on metal and not on support): depends on strength of interaction of probe with metal/support sites, conditions (T, p) can be optimized

Physical adsorption - Non specific/selective
Chemisorption- Selective / specific w.r.t adsorbate/adsorbent

Crystallite size by Chemisorption

- Volumetric (static) / Flow (dynamic) method/ Volume desorbed (TPD)
- Measurement of monolayer volume
- Adsorption specific to metal sites only
- Static method- Irreversibly adsorbed Hydrogen is measured by ASTM-D32 /ASTM D-3980-82,1998 method for H_2 adsn on supported Pt- Euro-Pt standard
- Adsorption isotherm- Total and after evacuation of physisorbed part
- Dynamic method- Pulse technique- Saturation of surface with adsorbate with repeated pulses
- Data for calculation-
  - Vol.of adsorbate consumed at specific pressure & temperature
  - Metal: Adsorbate- Stoichiometry at mono layer coverage-
  - No of metal atoms involved in adsorption for one molecule of adsorbate
  - n_s- No.of metal atoms per unit area of surface
    - ❖ if adsorption is specific, number of sites can be derived from isotherm (no site heterogeneity, no spill-over)

Adsorption isotherm- Static method
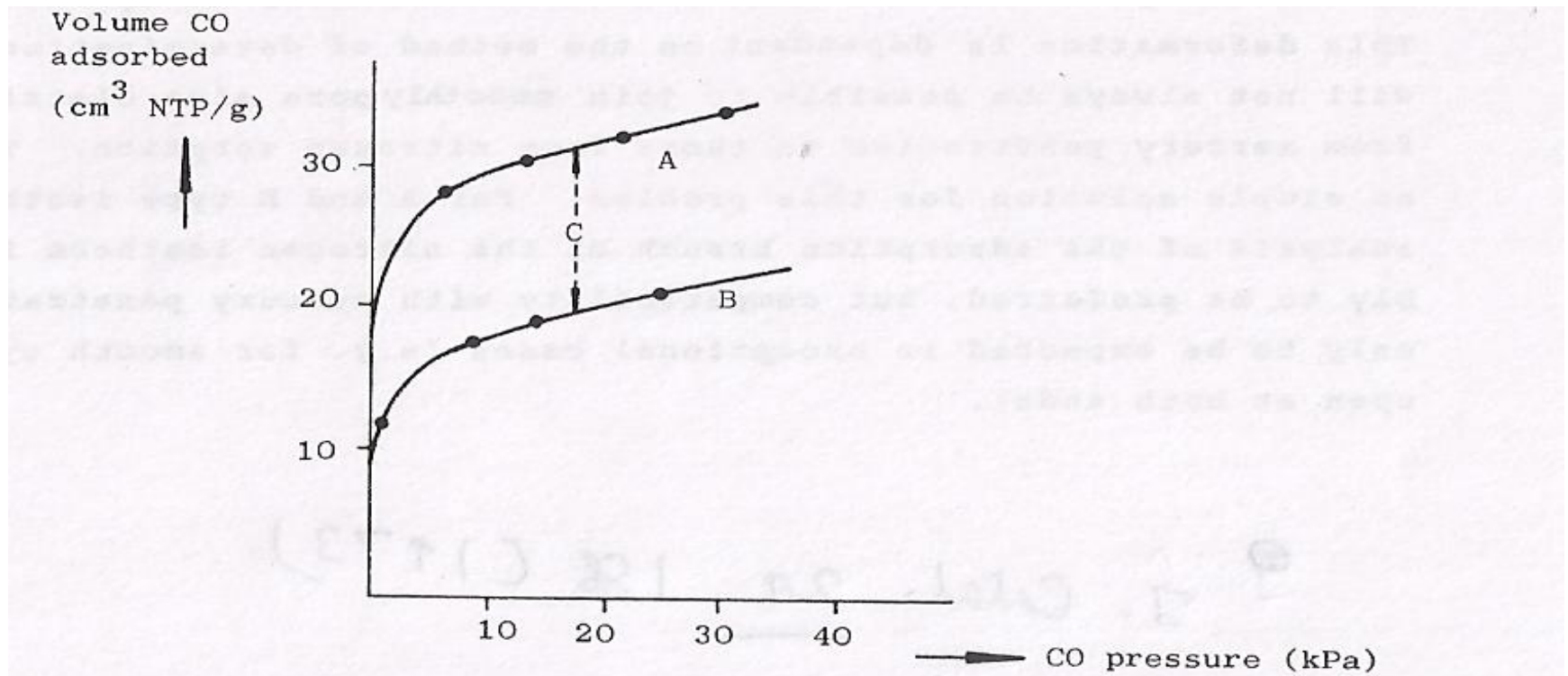
Fig. 1. Adsorption of carbon monoxide on a singly promoted ammonia synthesis catalyst. From lit. 3.
A. Total adsorption at 90 K.   C. Volume CO chemisorbed.
B. Physical adsorption, after evacuation at 195 K.

Adsorption isotherm- Static method
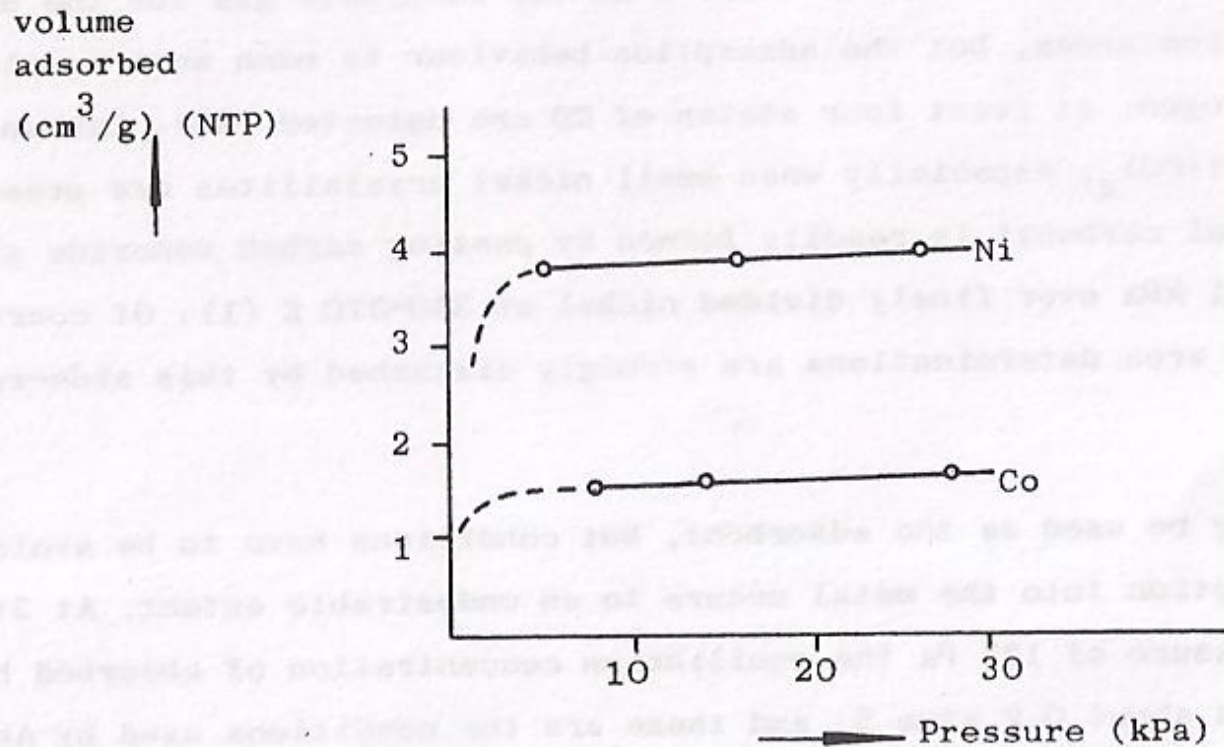
Fig. 6. Adsorption isotherms for hydrogen on silica-supported nickel and cobalt at 291 K. The samples are prereduced in flowing hydrogen, to 643 K. Evacuation at the same temperature (lit. 20).

Measurement of chemisorption
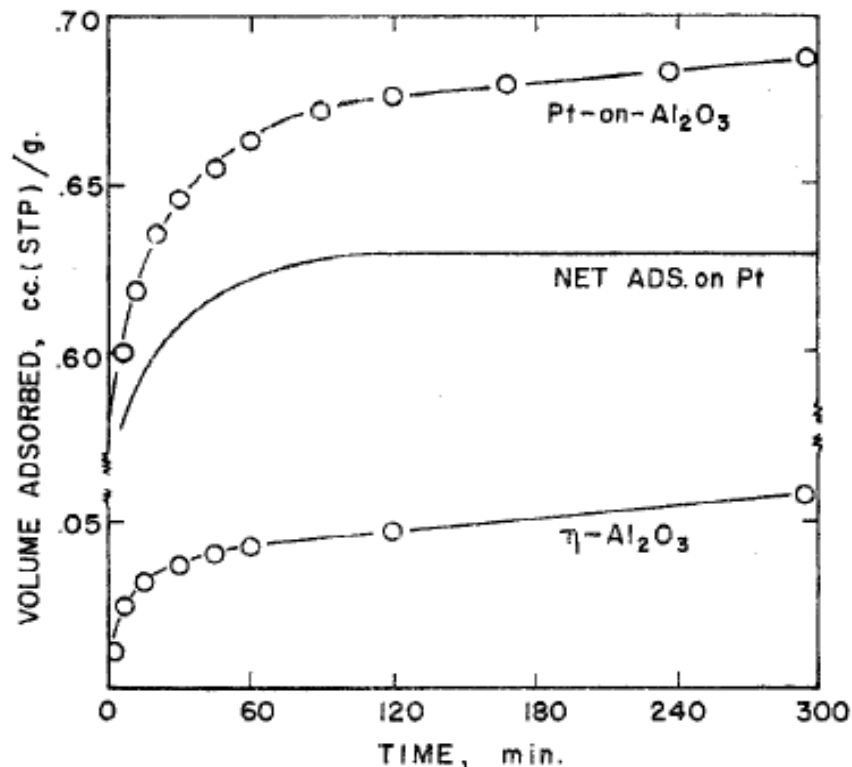
Fig. 3.—H_2 adsorption, 250°, 200 mm.

Pt-on-Al_2O_3

NET ADS. on Pt

η-Al_2O_3

(●) THIS WORK, 1.10% Pt, 250°
(○) SPENDEL[10], 0.60% Pt, 250°
(△) ADLER[11], 0.58% Pt, 200°
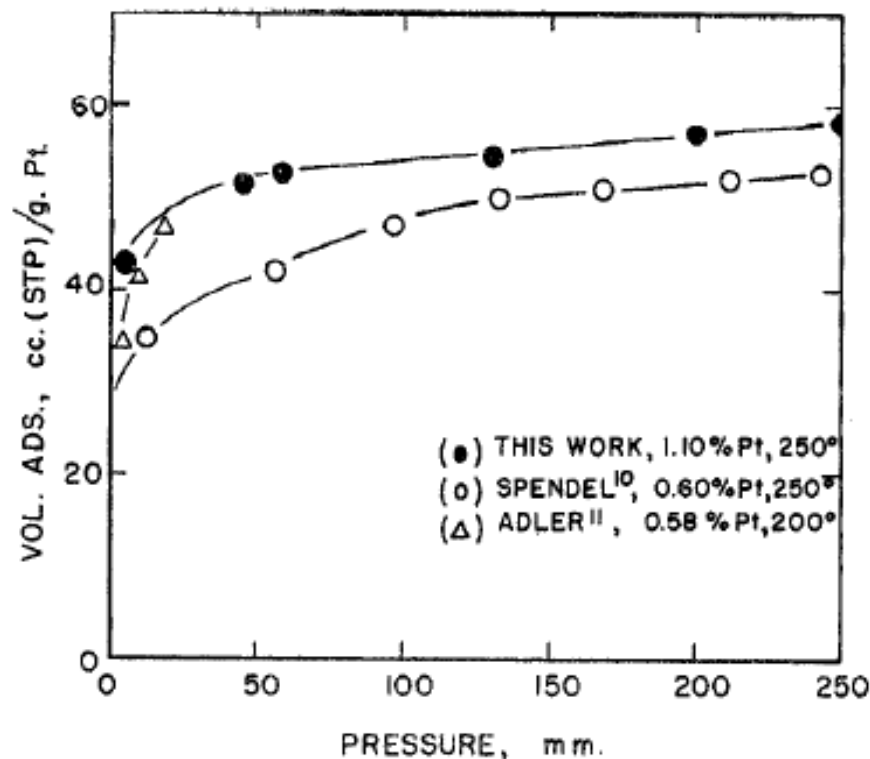
Fig. 2.—H_2 adsorption isotherms on platinum-on-alumina.

Extrapolation of linear region of isotherm to $P_{eq}=0$ gives V_m

HL.Gruber, J.Phys.Chemistry, 66,48,1962

Stoichiometry for chemisorption

Metal	Gas	Operating conditions		Stoichiometry n
		T°C	Press torr	
Cu	CO	20	10	1-2
Ag	O_2	200	10	2
Co	H_2	20	10	2
Ni	H_2	20	10	2
Ni	C_2H_4	0	100	2
Rh	CO	20	10	2
Pd	CO	20	10	1-2
Pt	H_2	20	10	>2
Pt	H_2	250	100	2
Pt	O_2	25	100	2
Cu	N_2O	Pulse mode		2

n- No of surface metal atoms per molecule of adsorbate

No.of surface metal atoms

No. of surface metal atoms per unit area of Polycrystalline metals (n_s) X 10^{15}

Metal	Equal proportions of (100),(110 & 111)	25%(100),5% (110) 70% (111)*
Co	1.51	-
Ni	1.54	1.75
Pt	1.25	1.42
Pd	1.27	1.45
Ru	1.63	-
Ir	1.30	1.48
Rh	1.33	1.55
Cu	1.47	1.67
Os	1.59	-

* Based on morphology of metal crystallites by TEM

Cross sectional area = $1/n_s$

For Pt - $1/(1.25 \times 10^{15})$ = 8 $\AA^2$

For Ni - $1/(1.54 \times 10^{15})$ = 6.5 $\AA^2$

Chemisorption method-Assumptions

- Surface metal atoms are free from any other adsorbates /poisons- Evacuation-Purging
- Suitable activation/pre-treatment/pre-reduction procedures to be adopted
- All metal atoms are in zero oxidn state/completely reduced- Check by TPR

    Noble metals Vs Base metals – Pt-Ni –Presence of Ni ions in supported Ni-
- Adsorption stoichiometry for specific adsorbate-metal system is known and is independent of crystallite size- CO chemisorption- stoichiometry dependence on size
- In the case of measurements on used/spent catalysts, proper pre-treatment procedure is to be evolved so that the dispersion is not affected
- Adsorption due to support, hydrogen spill over effects and metal support interactions are to be factored in
- Euro Pt standards could be used for calibrations.

Pulse chemisorption set up
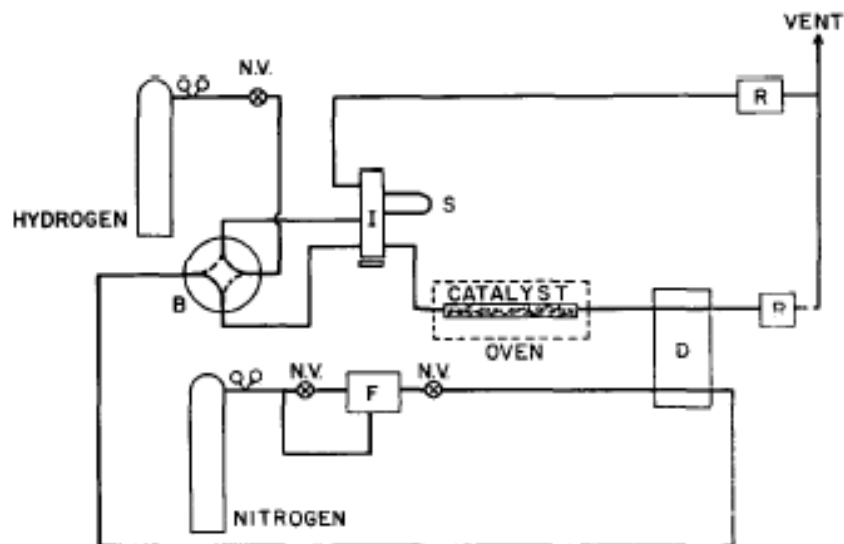
FIG. 1. Schematic of the flow system. F = "Moore" flow controller, N.V. = needle valve, D = thermal conductivity detector, B = glc backflush valve, I = 6-port "Varian" sample-injector, S = sample loop, R = rotameter. The setup for hydrogen adsorption is shown. Prereduction was carried out with the valve B in its alternate position. Oxygen chemisorption was studied by replacing the hydrogen source with oxygen.
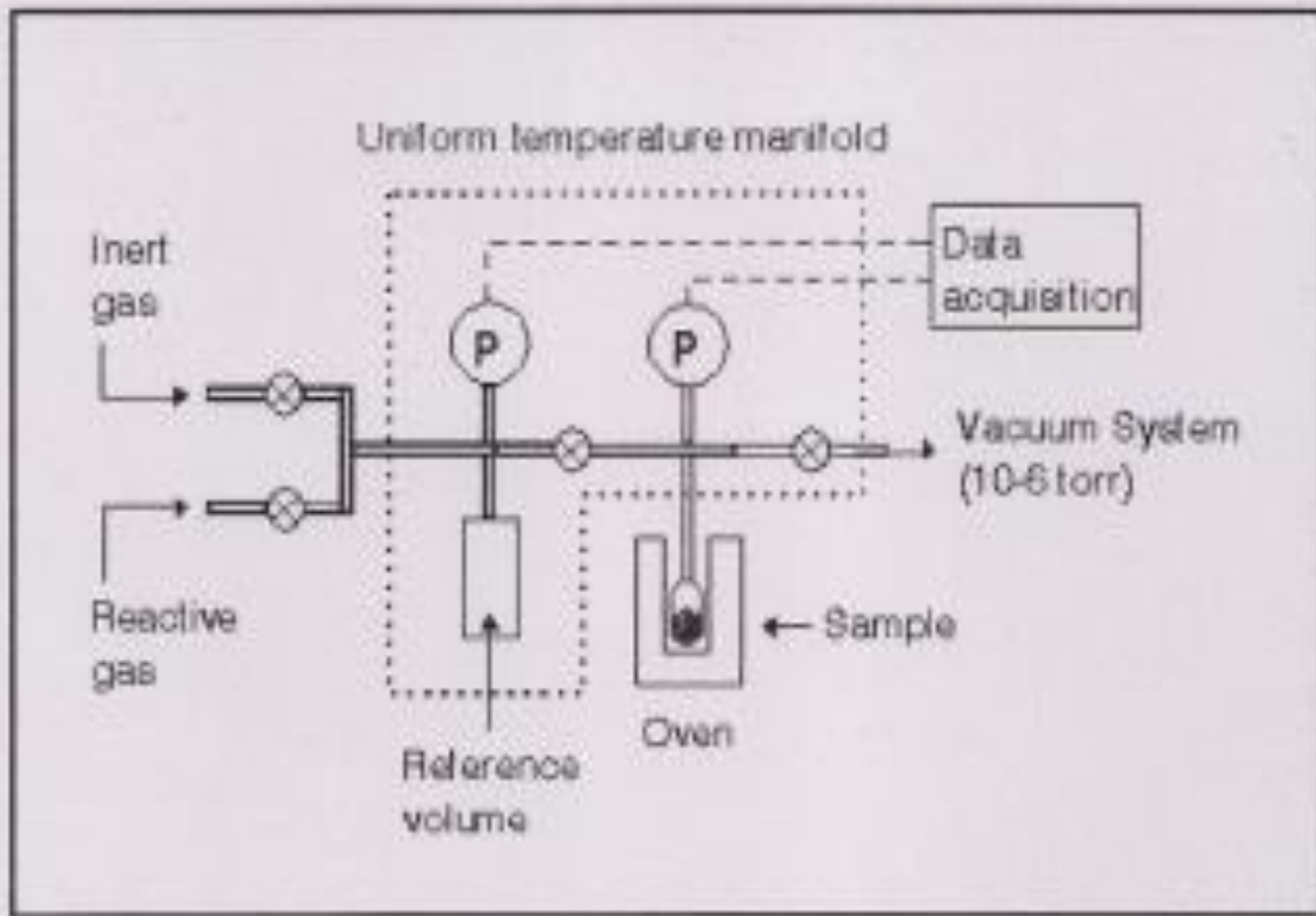
Static chemisorption unit
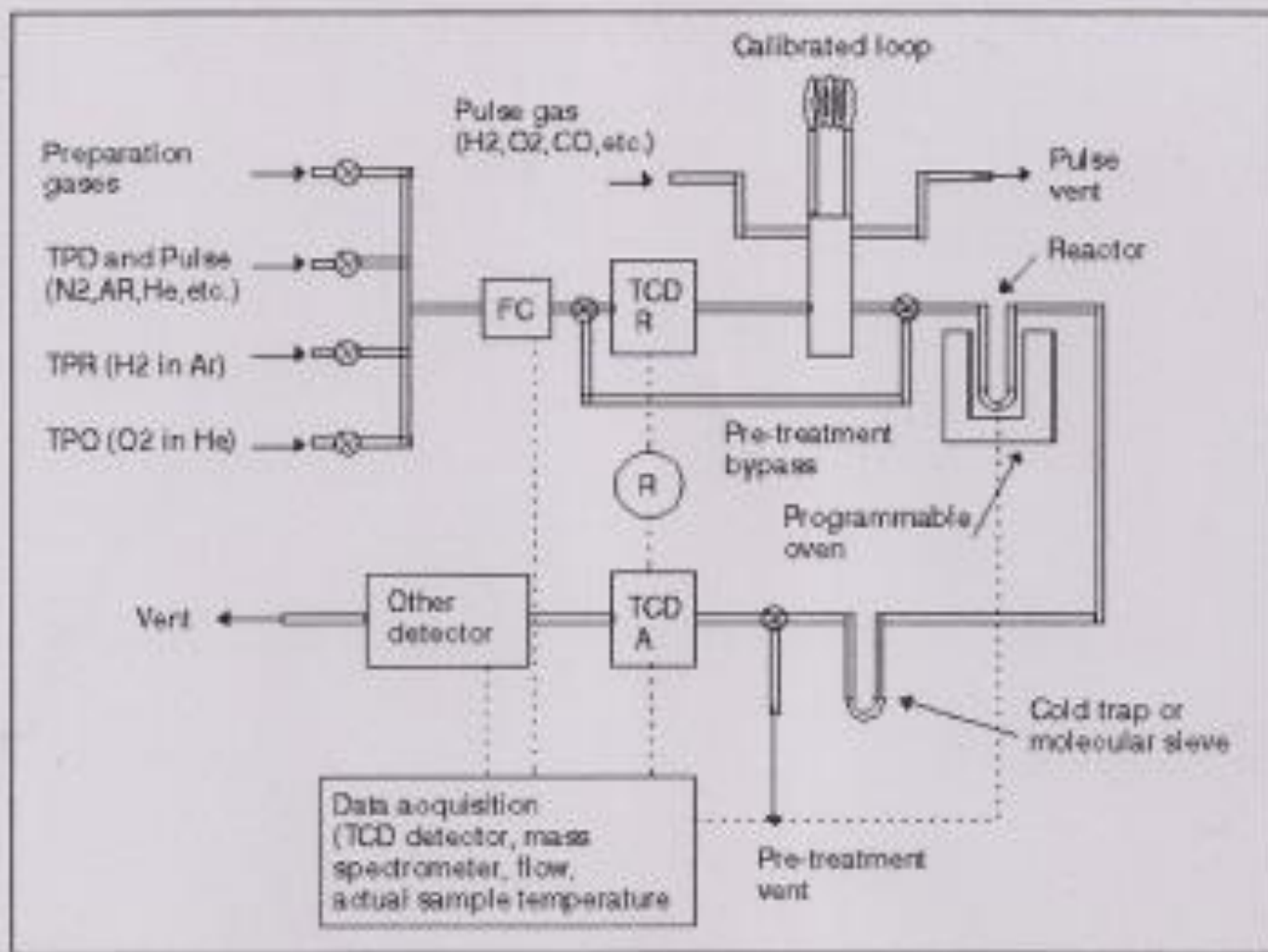
Figure 6. Diagram of a multipurpose apparatus for pulse chemisorption, TPD, TPR and TPO.

Chemisorptive titration

- Pt adsorbs H_2 & O_2 reversibly at RT
- Titration cycles are possible

$$Pt + H \longrightarrow Pt....H$$

$$Pt....H + O_2 \longrightarrow Pt...O + H$$

$$Pt...O + 3H \longrightarrow Pt....H + H_2O$$
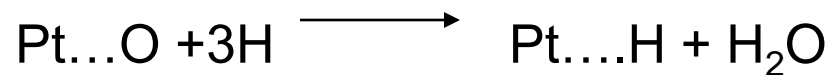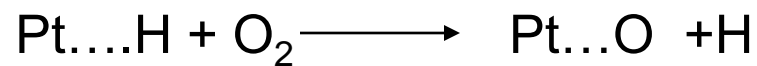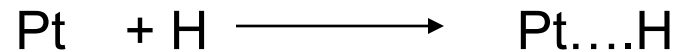
O_2 & H_2 cycles to be repeated up to saturation

H_2 consumed in titration is 3 times higher than that in chemisorption
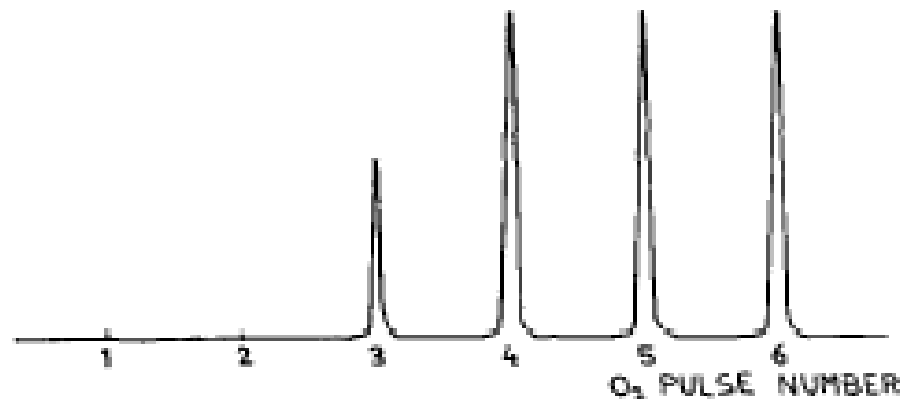
FIG. 2. Typical chromatogram for O_2-titration of a Pt- - -H surface.
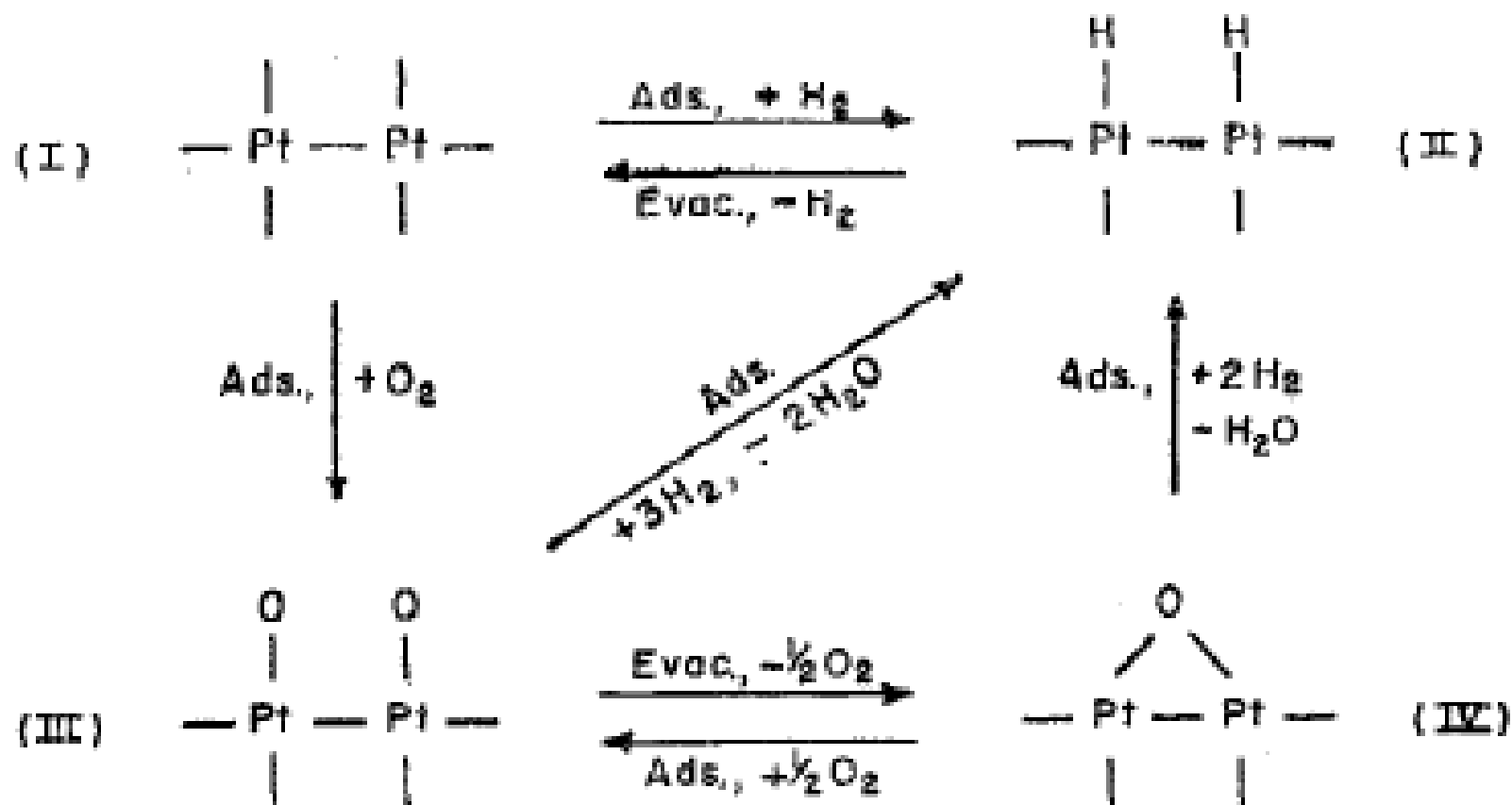
Fig. 4.—Reaction scheme for oxidation-reduction cycle.

HL.Gruber, J.Phys. Chem., 66,48,1962

Mono metallic Pt- Dispersion

TABLE 1

COMPARISON OF Pt DISPERSION VALUES FROM DIFFERENT METHODS[a]

Method	Measured by	Gas adsorbed, ml STP/g cat.	Dispersion, %
A	Goldstein	0.282	82
B	Boudart *et al.*		73
C	This work	0.278	81
D	This work	0.271	79

[a] Methods: A, volumetric chemisorption; B, H_2-titration of Pt- - -O surface volumetrically; C, H_2-titration of Pt- - -O surface gas chromatographically; D, O_2-titration of Pt- - -H surface gas chromatographically. Note that the pretreatments of the catalyst in A and B were extensive and more severe than those in C and D. Catalyst: Cyanamid-Ketjen reforming catalyst CK-306

Well established- Static & Dynamic methods

TABLE 7.5

A COMPARISON OF CRYSTALLITE DIAMETERS BY DIFFERENT METHODS OF MEASUREMENT

(Pt dispersed on an SiO_2 support by cationic exchange, calcined at the indicated temperatures, and reduced at 400 °C for 6 h).

Pt (%)	Calcination (3 h) (T, °C)	Diameter of crystallites (Φ, nm)			
		1	2	3	4
1.26	350	2.0	2.4	—	2.5
1.53	450	5.5	5.5	6	6.5
1.26	520	6.9	6.8	10	8.2
1.26	600	9.2	9.0	11	11.2
1.26	700	14.8	14.6	18	18.5

1. Φ is calculated from the volume of adsorbed CO, assuming cubic crystallites with one face resting on the support.
2. Φ is calculated by the formula:

$$\Phi = 6\ V/S = \frac{6 \cdot (\%\ Pt)}{10^2 \cdot S \cdot d}$$

where Φ is in nm, S in $m^2 \cdot g^{-1}$, and $d = 21.45$ (the density of Pt).
3. The diameter is determined by X-ray diffraction.
4. Φ is calculated from the volume of adsorbed CO, assuming an octahedral shape more probable than a cubic one.

Brunelle, P., Sugier, A., Montarnal, R., Unpublished results.

TABLE 7.6

COMPARING DIFFERENT METHODS OF CRYSTAL MEASUREMENT

(A catalyst of 2% Pd impregnated on SiO_2 by cation exchange is calcined at seven different temperatures; and the diameters of the crystallites are estimated by CO chemisorption, electron microscope (EM), and X-ray diffraction (XR). All catalysts were reduced at 150° C for 1.5 h).

T (°C)	CO chemisorbed $(cm^3 . g^{-1})$	Φ by chemisorption [1] (nm)	Φ by EM (nm)	Φ by XR [2] (nm)
300	1.3	2.7	2	—
350	1.15	3.1	2.5	—
400	1	3.7	3	—
500	0.55	7.2	5	5.5
600	0.42	9.7	6	7
700	0.31	12.5	7	7.5
800	0.25	15.8	14	14

[1] Φ is calculated by assuming that the crystallite is cubic with one face resting on the support.
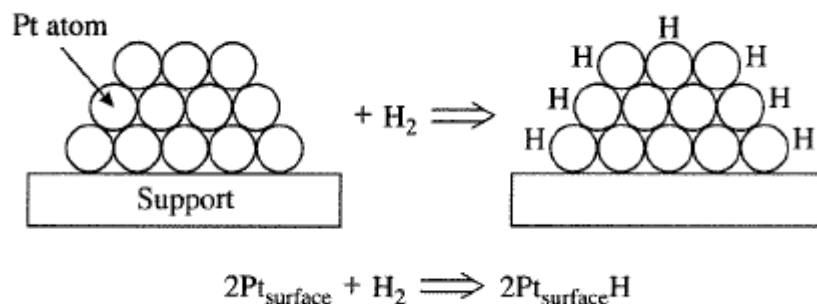[2] Φ is calculated with the Scherrer formula:

$$\Phi \text{ (nm)} = \frac{k\lambda}{b \cos \theta}$$

where b is the width of the line at mid-height, λ is the wave length (0.154 nm) of the K_α line of copper, and θ the corresponding Bragg angle.

Samanos, B., *L'acétoxydation de l'éthylène en phase gazeuse*. PhD. thesis, Paris, 1971, and Montarnal, R.

$$2Pt_{surface} + H_2 \implies 2Pt_{surface}H$$

$$\text{Fraction exposed} = \text{Dispersion} = \frac{2 \times (H_2 \text{ molecules chemisorbed})}{\text{Total number of Pt atoms}}$$

Table 5.1.1 | Determination of metal particle size on Pt/Al$_2$O$_3$ catalysts by chemisorption of H$_2$ and CO, X-ray diffraction, and transmission electron microscopy.
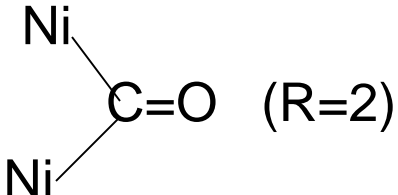
	Diameter of Pt particles (nm)			
% Pt	H$_2$	CO	X-ray diffraction	Electron microscopy
0.6[a]	1.2	1.3	1.3	1.6
2.0[a]	1.6	1.8	2.2	1.8
3.7[a]	2.7	2.9	2.7	2.4
3.7[b]	3.9	—	4.6	5.3

[a]Pretreatment temperature of 500°C.
[b]Pretreatment temperature of 800°C.
Source: Renouprez et al., *J. Catal.*, **34** (1974) 411.

Chemisorption- Limitations

- Metal- adsorbate stoichiometry

- Types of adsorbed species- CO, linear & bridged form & dependence on experimental conditions-Pressure &Temp.

- Ni=C=O (R=1) Ni

$$\underset{Ni}{\overset{Ni}{>}} C=O \quad (R=2)$$

- $N_2O + 2Cu \longrightarrow (Cu)_2O + N_2$ (R=2)

- Weakly adsorbed Vs strongly adsorbed

- Hydrogen spill-over to the support

- SMSI effects- Lower adsn- size- Direct observation by TEM

- To be supported by TEM data

- Bi-metallic clusters/alloys- Specific methods to be developed

Chemisorption stoichiometry – Variations- Experimental conditions need to be defined
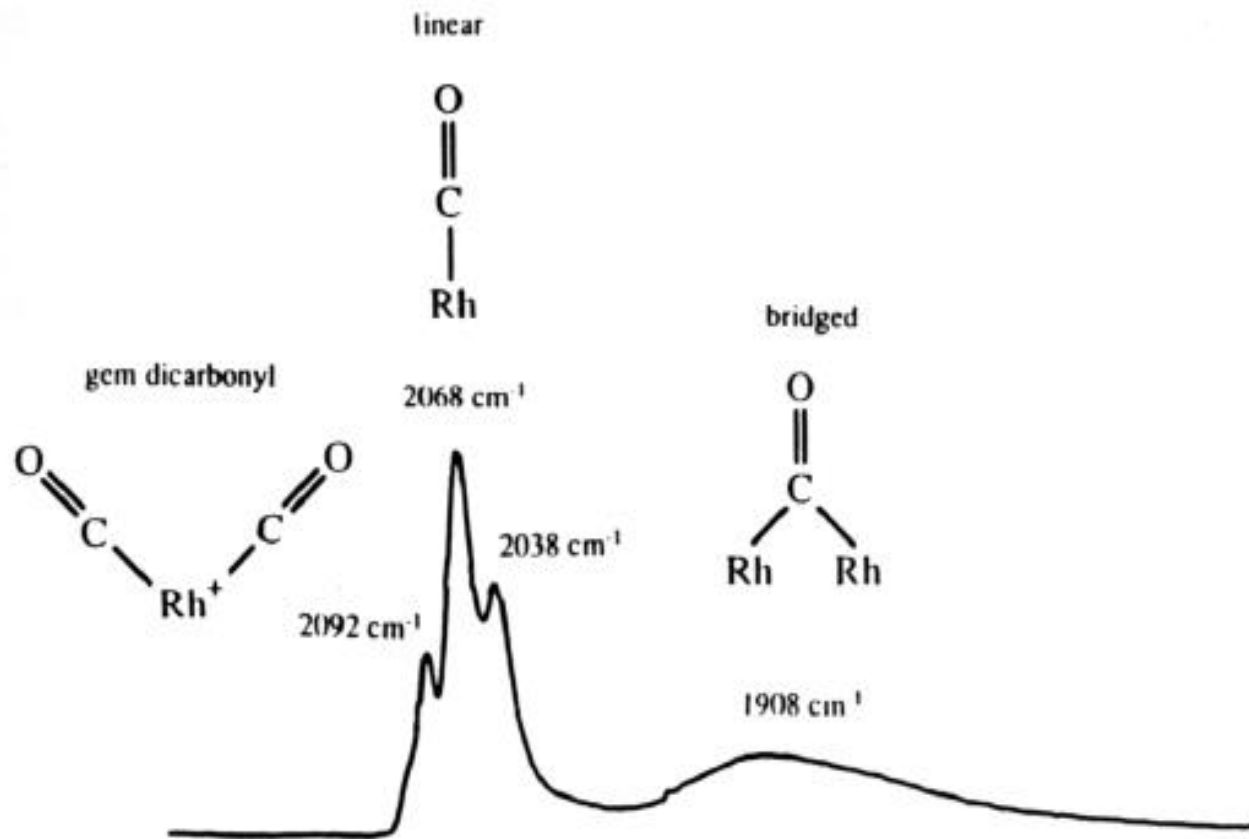
Fig.8. Transmission-absorption infrared spectrum of carbonyl species a Rh/SiO₂ catalyst.

Calculations

Metal surface area, $S = (N_A \sigma /M) \times R$

  N_A Avogadro Number, σ −cross sectional area per metal atom in Å^2

  M- Mol. Weight of metal & R- ratio of adsorbate atoms adsorbed per metal atom

Crystallite size $d = 5V/S = 5/(S \times \rho)$ where ρ −density of the metal & S metal area per gram

  It is assumed that metal particle is a cube with 6 sides and one side/face rests on support and the remaining 5 faces exposed

  Dispersion/Fraction of metal exposed = N_S /NT

  N_s- No.of metal atoms exposed as per the stoichiometry

  N_T- No.of total metal atoms, as per loading

Effect of promoter metals on Pt

Pt catalysts promoted by Re, Sn etc highly active and stable for catalytic reforming. Possible reasons are: (Pt-Sn, Pt-Re, Pt-Sn-Re)

- Increase the dispersion/activity of Pt- Geometric effect
- Form alloys and retard sintering of Pt
- Decrease the deep dehydrogenation capacity of Pt and thus decrease the formation of unsaturated coke precursors.
- They decrease the hydrogenolysis capacity and therefore also decrease the formation of light gases.
- They modify the concentration of surface hydrogen which has an effect on the relative production of different reaction intermediates and therefore on the final reaction selectivity.
- A portion of the additives remains oxidized on the surface and modifies the amount and strength of the acid sites of the support.

How do we measure the dispersion of bi- & trimetallic catalysts?
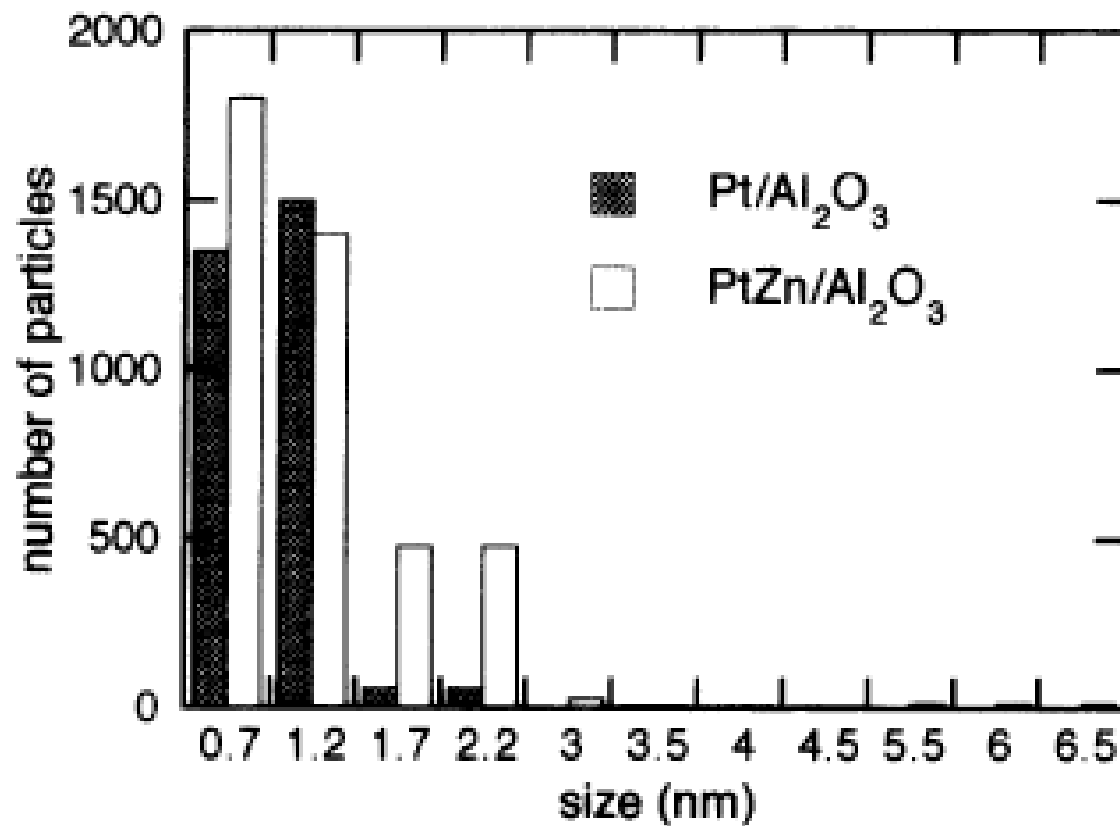
Distribution of particle sizes for a parent platinum catalyst and the same modified by addition of zinc.
B. Coq, F. Figueras / Coordination Chemistry Reviews 178–180 (1998) 1753–1783

Pt-Re- Metal dispersion

- Pt adsorbs H_2 & O_2 reversibly
- Re does not adsorb H_2 ; but adsorbs O_2 irreversibly
- Saturate the surface with H_2 pulses
- Titrate with O_2
- Go through next H_2 cycle- for Pt only
- 2 nd O_2 cycle- due to Pt only
- Difference in O_2 uptake is due to Re.
- Calcualte dispersion of Pt & Re separately
- Total Oxygen uptake could be used
  for dispersion calculation

JOURNAL OF CATALYSIS 29, 188-1~ (1973)

TABLE 2
OXYGEN TITRATION OF Pt AND Re IN Pt–Re–Al₂O₃ CATALYSTS AT 25°C[a]

	Re 0.0	0.1	0.3	0.6	1.0
Pt					
0.0			(0.06)	(0.24)	
0.1	0.06	0.03			
		(0.07)			
0.3	0.19	0.18	0.18	0.18	0.23
		(0.12)	(0.20)	(0.39)	(0.39)
0.6	0.39			0.30	
				(0.47)	

[a] Catalysts prepared by impregnation on γ-Al₂O₃. Metal contents in wt%. Titer values in ml STP/g catalyst Titer values for Re are shown in brackets.

Dispersion- bi metallics- Simple systems

TABLE 1
SUMMARY OF BIMETALLIC CATALYSTS INVESTIGATED

Catalyst system[a]	Metal content wt%	Atomic ratio of metals	
		Cu/Ru	Cu/Os
Ru–Cu	1 Ru, 0 Cu	0	
	1 Ru, 0.126 Cu	0.20	
	1 Ru, 0.315 Cu	0.50	
	1 Ru, 0.63 Cu	1.00	
Os–Cu	1 Os, 0 Cu		0
	1 Os, 0.082 Cu		0.25
	1 Os, 0.166 Cu		0.50
	1 Os, 0.33 Cu		1.00

[a] All catalysts supported on silica.
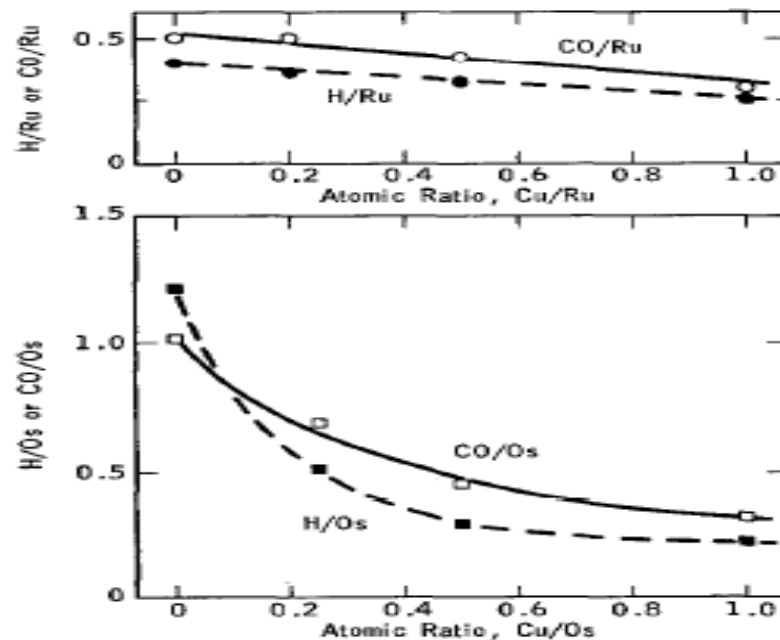
Dispersion- bi metallics- Simple systems

FIG. 2. The chemisorption of hydrogen and carbon monoxide at room temperature on silica-supported ruthenium–copper and osmium–copper catalysts. The catalysts all contain 1 wt% ruthenium or osmium, with varying amounts of copper. The adsorption data are expressed by the quantities H/Ru, CO/Ru, H/Os, and CO/Os, which refer respectively to the number of hydrogen atoms or carbon monoxide molecules chemisorbed per atom of ruthenium or osmium in the catalyst.

Expts on Cu/silica show that Cu does not adsorb H_2 or CO

Bimetallics- Chemisorption Vs Dispersion

Table 1

Fraction of Pt exposed to hydrogen (H/Pt) and mean metal particle size by TEM of some catalysts

Catalyst	H/Pt	Mean particle size (nm)
Pt	0.42	1.8
Pt–Re	0.19	1.5
Pt–Sn	0.00	1.8
Sn–Pt–Re	0.26	2.0
Re–Pt–Sn	0.08	1.9
Pt–Sn–Re	0.10	1.9
Pt–Re–Sn	0.21	2.0

Bi & Tri metallic catalysts

Dispersion measurements by hydrogen chemisorption

- Exhibit lower hydrogen uptakes, though , Pt crystallite sizes are smaller than Pt alone

Possible reasons

- Alloy formation- electronic effect affecting the adsorption of H2

- Geometric effect- increasing dispersion- decreases no.of adjacent Pt atoms- essential for dissociative adsorption

  - Pt-Sn- H2 uptake half of ethylene uptake

- Changes in electronic state of Pt^0 - $Pt^{\delta+}$ or $Pt^{\delta-}$ Both 2nd metal or support can change the electronic state of Pt

- Adsorption behavior of Re & Sn- Active for O_2 chemisorption, but not active for H_2

- Do not get reduced completely

- Chemisorption data may not represent actual dispersion

Metal dispersion- Bi & Tri metallics

Table 1

Chemisorption of CO and H_2 by a Pt/Al$_2$O$_3$ catalyst subjected to different thermal treatments

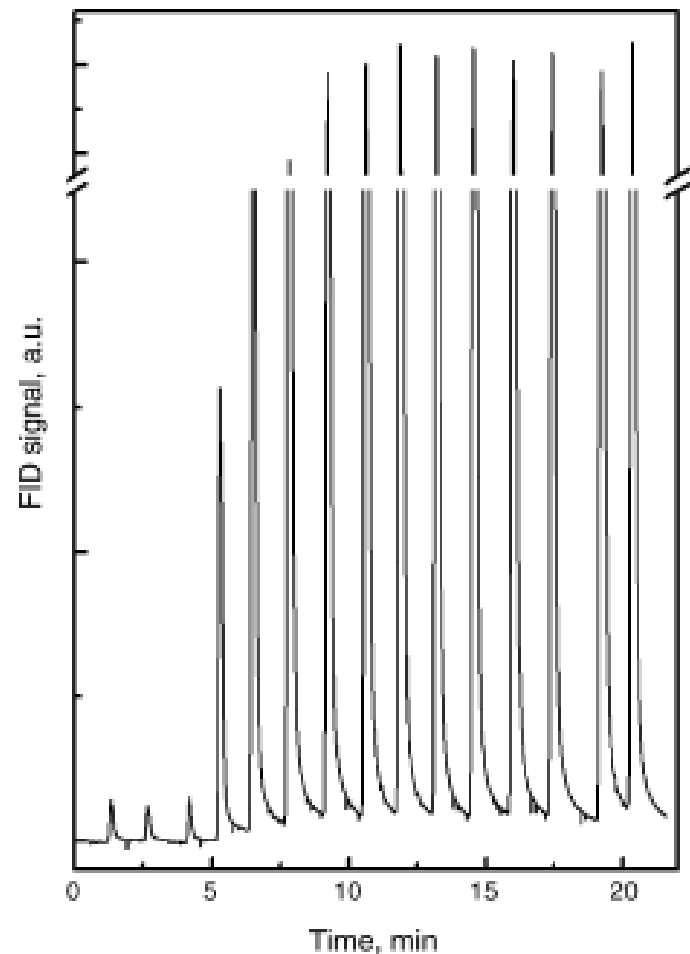| Treatment	CO/Pt (dynamic method)	H/Pt (static method)
None	54	52
600 °C, 2 h, air	40	44
600 °C, 6 h, air	10	11

Fig. 2. CO chemisorption in the pulse chemisorption apparatus. FID signal evolution as a function of time (pulse number).

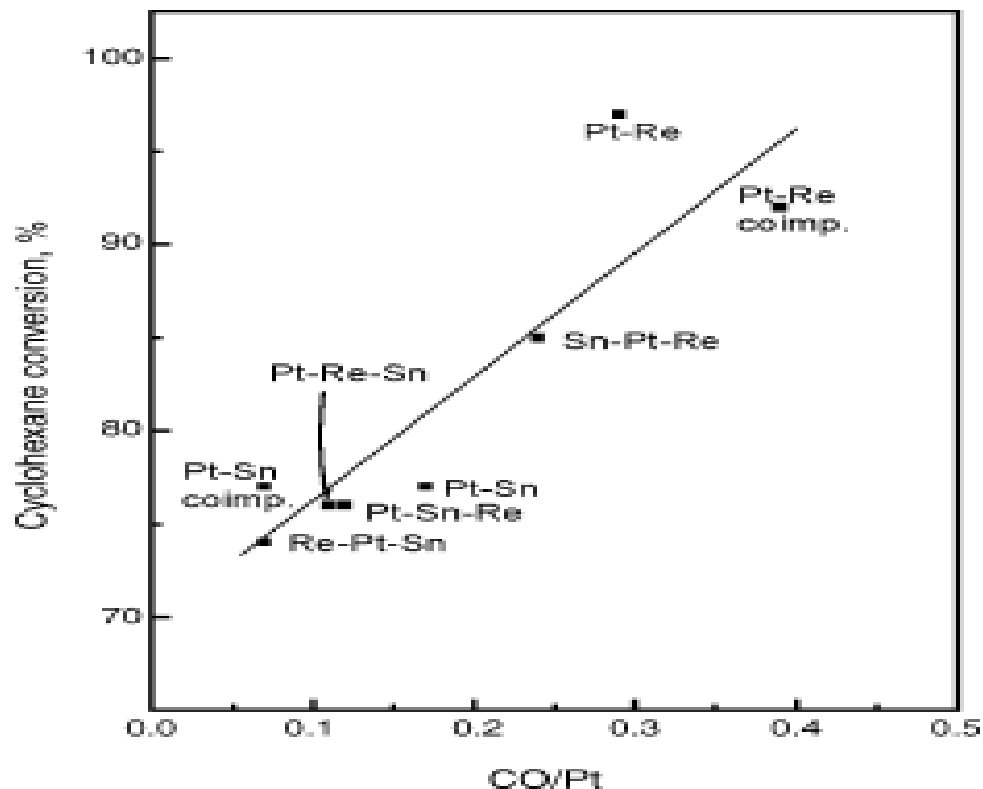# Metal dispersion- Bi & Tri metallics

Fig. 3. Activity during dehydrogenation of cyclohexane as a function of the CO/Pt ratio. Stable conversion value all throughout the time span of the reaction. Regression coefficient, $R^2 = 0.934$. Coimp., catalysts prepared by coimpregnation of metal precursors; Suc., catalysts prepared by successive impregnations of metal precursors in the order indicated. Temperature = 400 °C, pressure = 0.1 Mpa, H_2/CH molar ratio = 30.

Energy Dispersive X-ray Analysis-EDXA

- Identification of elements based on their characteristic X-ray emission lines

- After due calibration concentration of elements can be measured

- EDXA is attached to SEM or TEM

- Qualitative as well as quantitative analysis can be done in a selected volume of 1 μm^3 of the sample

- Applications spread over several fields like metallurgy, materials and catalysis

- Applications in catalysis

  - Identification of impurities

  - Concentration profile of elements- preparation & manufacture

  - Characterization- fresh & spent catalysts – deactivation phenomenon
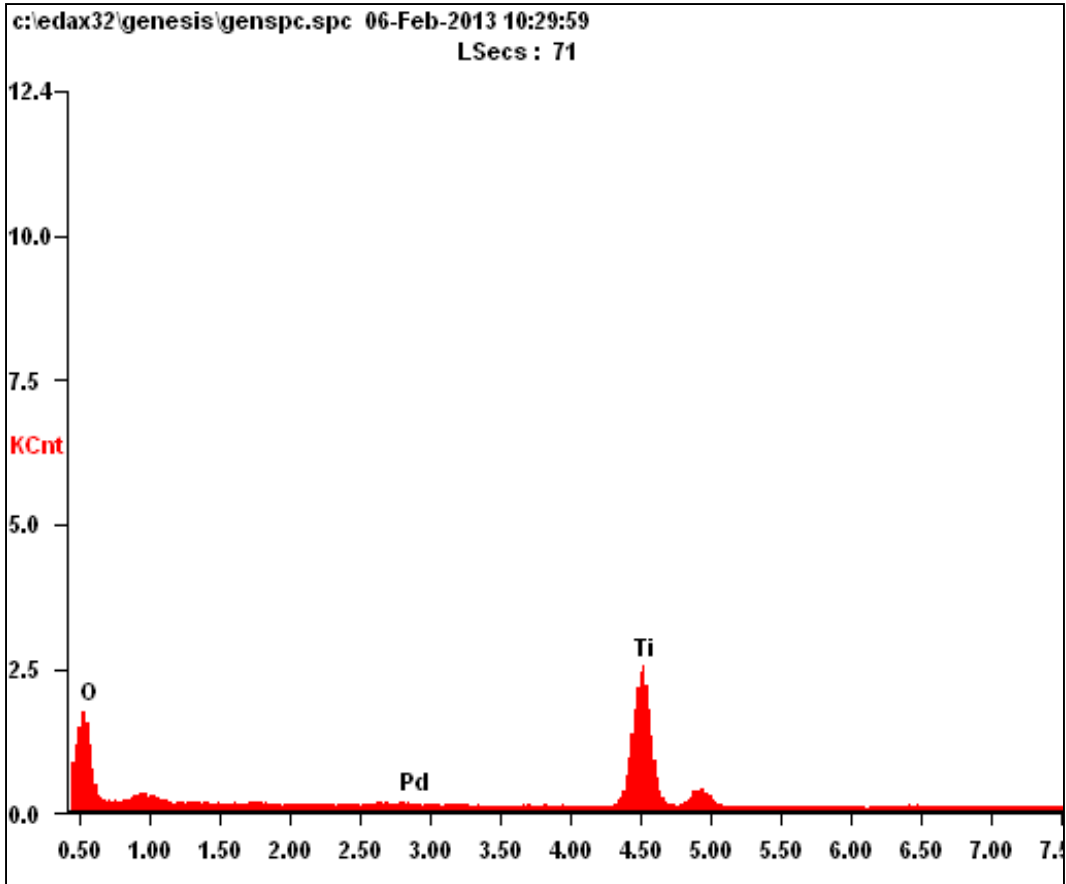
Characteristic X-Rays
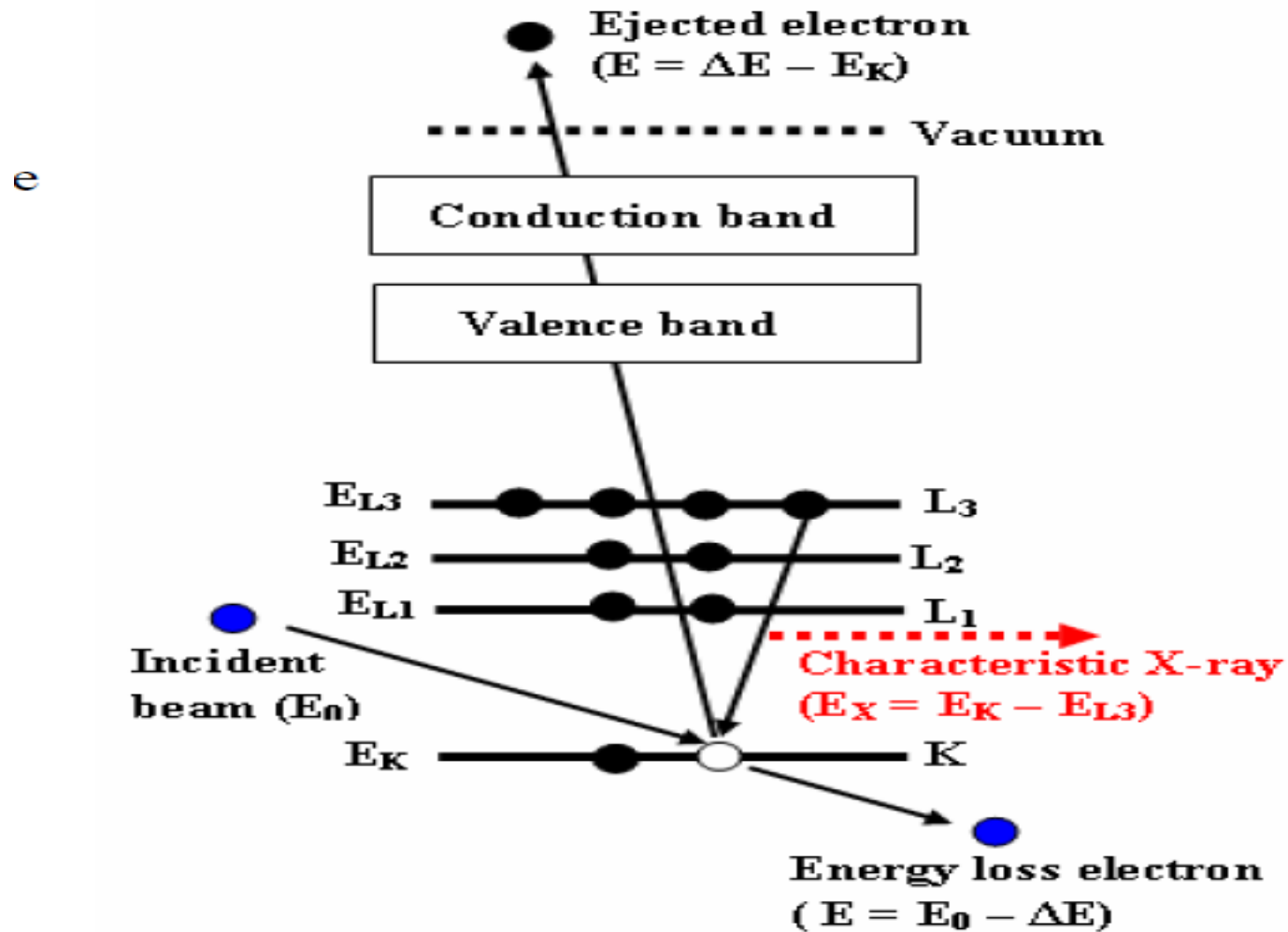
Characteristic X-Ray lines
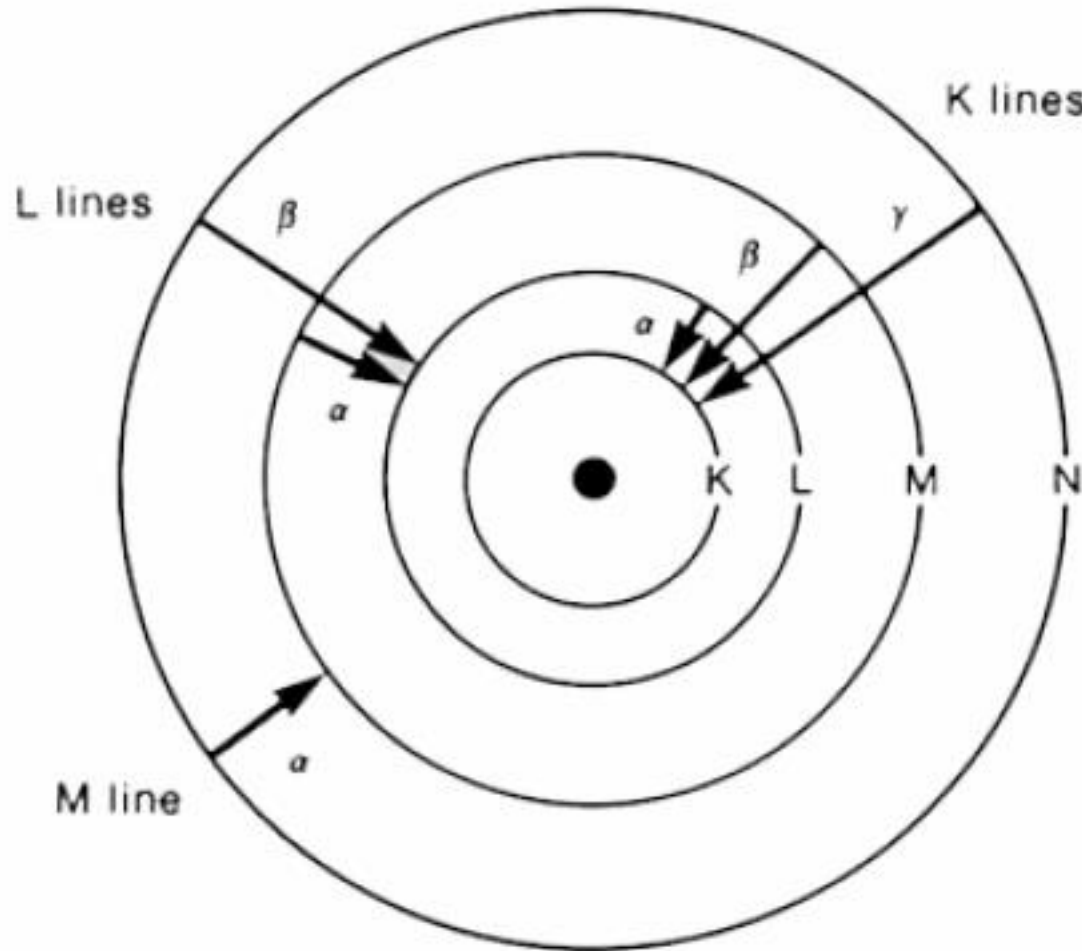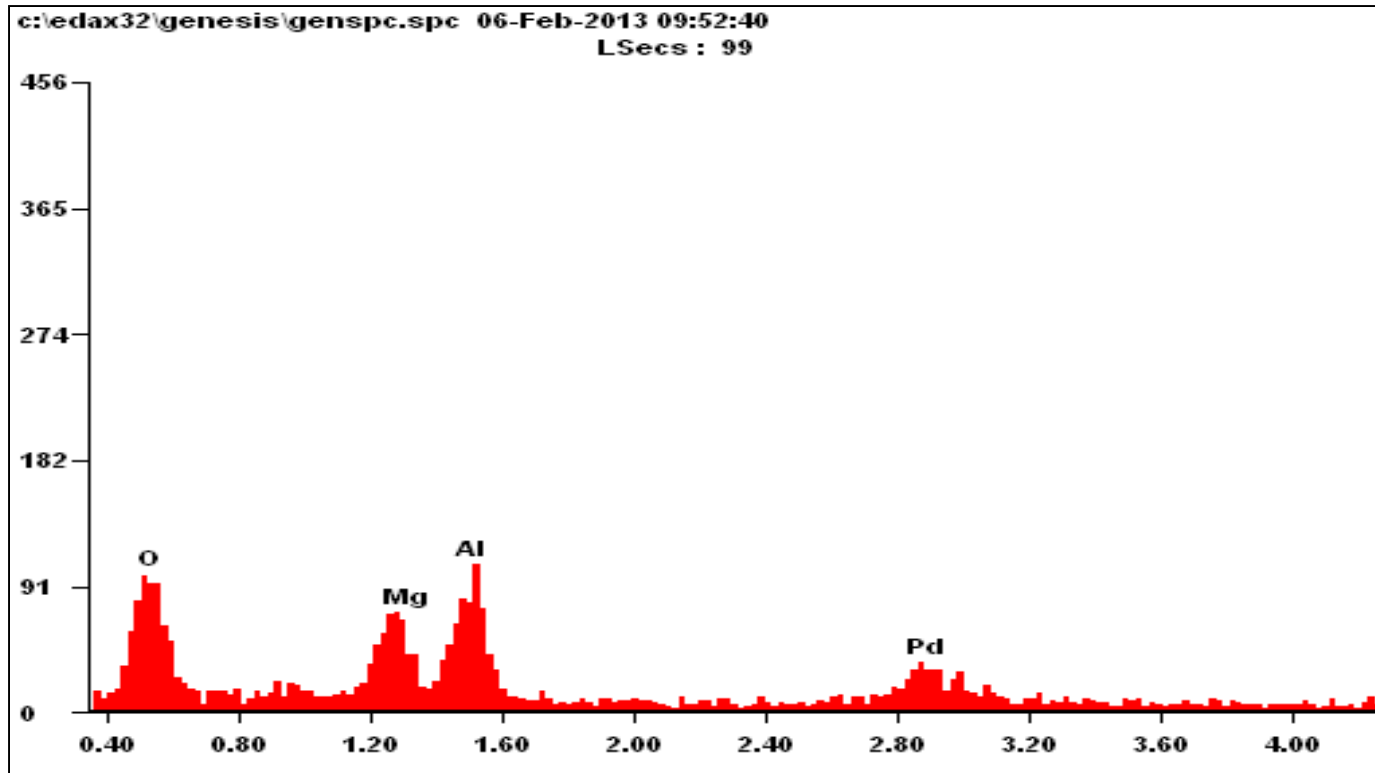
EDXA pattern for Pd-Mg-Al-O

Elem	Weight %	Atomic %
O K	20.90	36.80
MgK	26.50	30.80
AlK	23.80	24.80
PdL	28.90	07.70

EDAX pattern for Pd-TiO$_2$

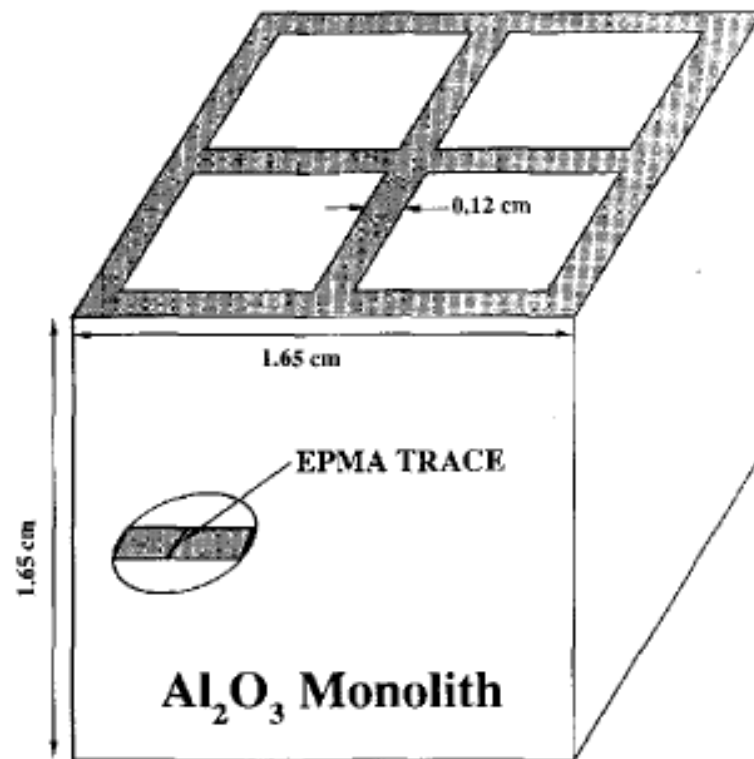| Elem	Weight %	Atomic %
O K	31.90	59.20
PdL	04.20	01.20
TiK	63.90	39.60

Metal Impregnation- Concentration profile

Factors affecting the metal distribution

(i) the method of impregnation- wet or dry,

(ii) the duration of the impregnation,

(iii) the nature of the precursor and support, , pH of impregn soln.

   precursor species in solution, $PtCl_6^-$ or $Pt(NH_3)_4^+$ - Alumina/Silica

(iv) Added salts/acids as competing anions

(v) the subsequent drying, calcination, and activation steps.

Performance of the catalyst depends on the optimum distribution of active metal within the geometry of the support pellet

Concentration of impregnating solutions

Solution	Precursor conc. (mol/cm³)	HF conc. (mol/cm³)
1	$3.8 \cdot 10^{-5}$	0
2	$3.8 \cdot 10^{-5}$	$3.32 \cdot 10^{-3}$
3	$3.8 \cdot 10^{-5}$	$6.64 \cdot 10^{-3}$
4	$3.8 \cdot 10^{-5}$	$9.96 \cdot 10^{-3}$

0.12 cm

1.65 cm

1.65 cm

EPMA TRACE

Al_2O_3 Monolith

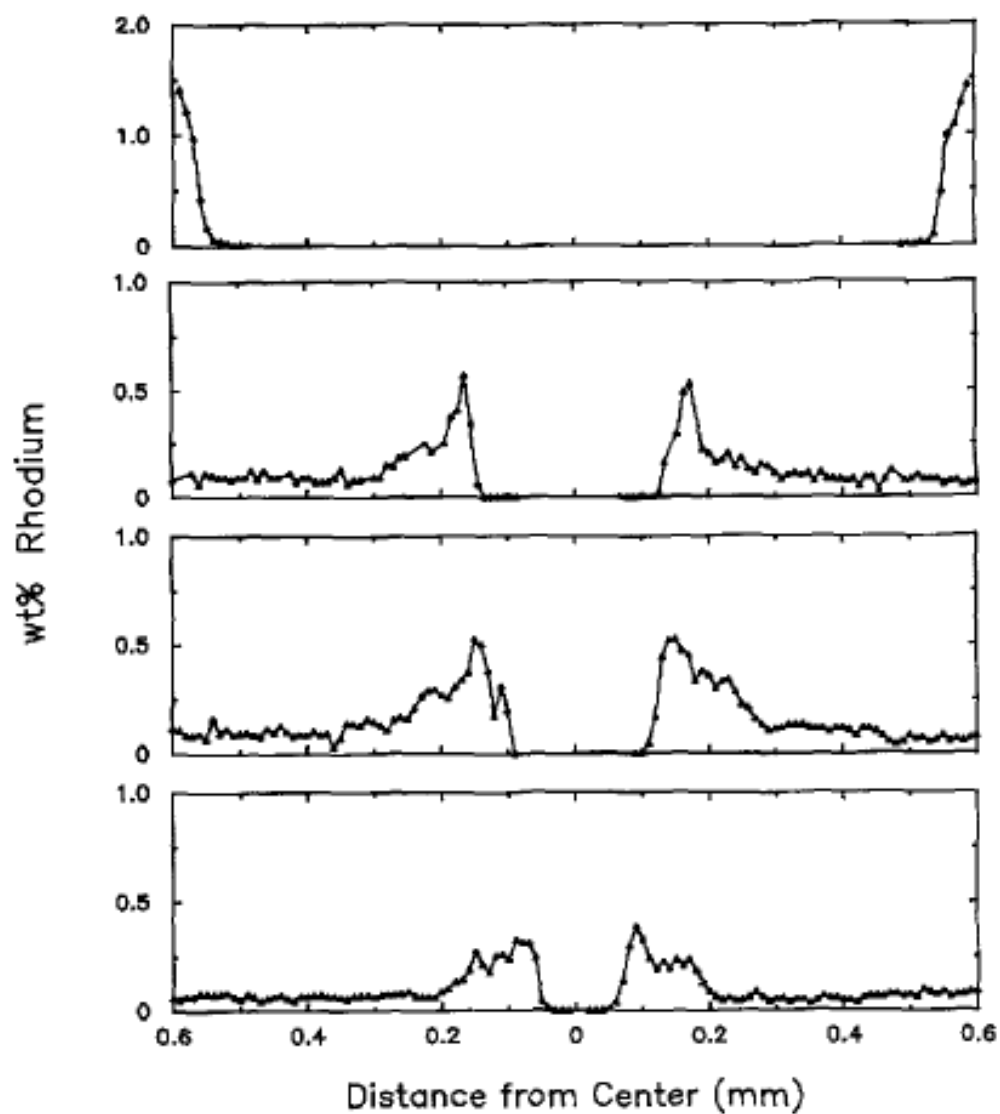JS Hepburn, Appl.Catal.55,271,1989; 71,205,1991

Fig. 4. Rhodium distributions. Top graph: solution 1, second graph: solution 2, third graph: solution 3, bottom graph: solution 4.
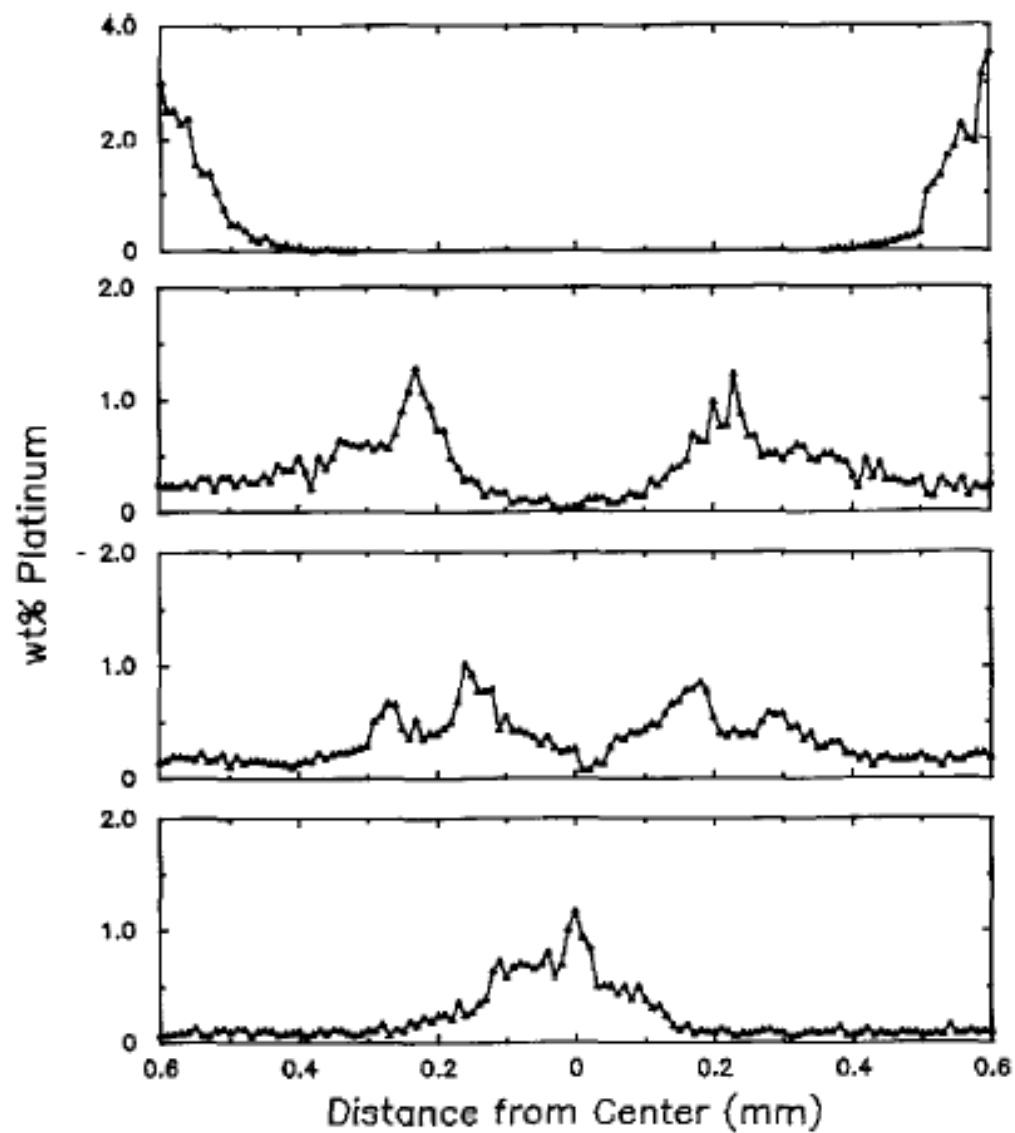
Fig. 5. Platinum distributions: Top graph: solution 1, second graph: solution 2, third graph: solution 3, bottom graph: solution 4.
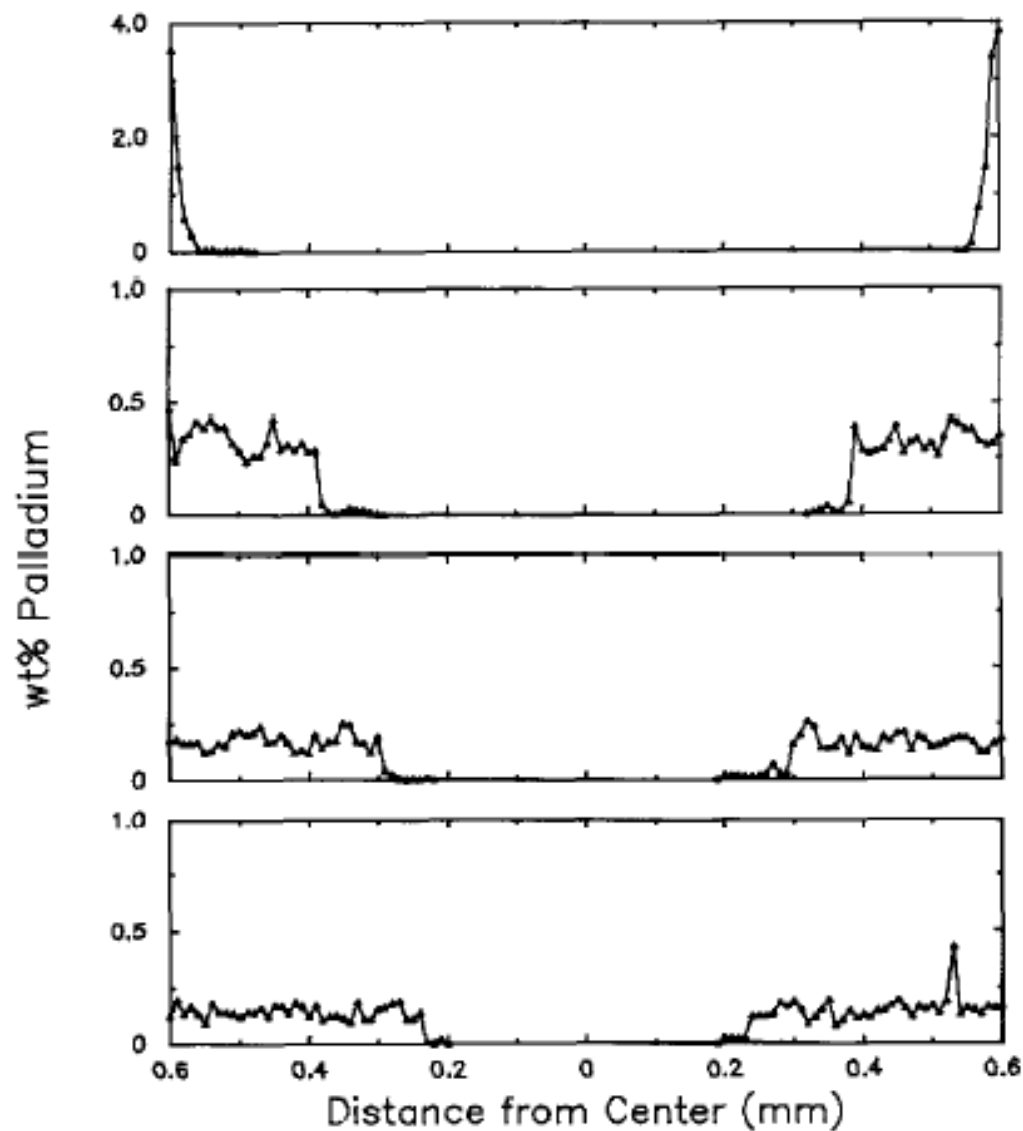
Fig. 6. Palladium distributions: Top graph: solution 1, second graph: solution 2, third graph: solution 3, bottom graph: solution 4.
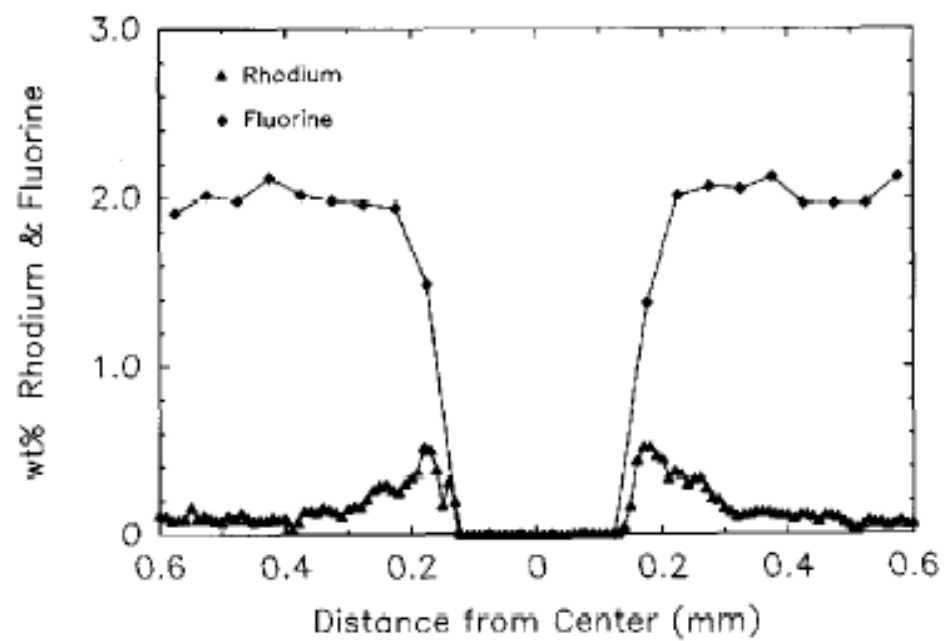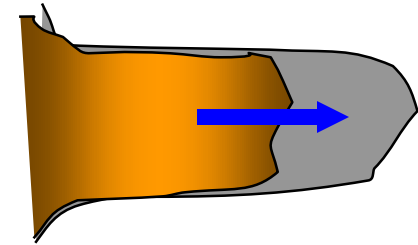
Fig. 7. Fluorine and rhodium distributions for solution 3.
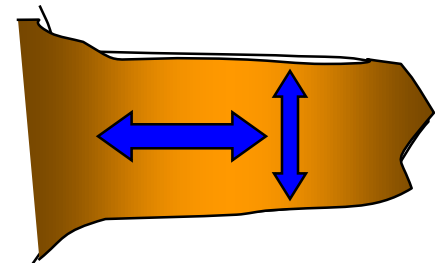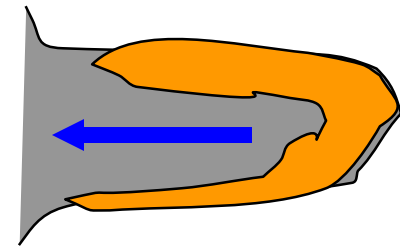
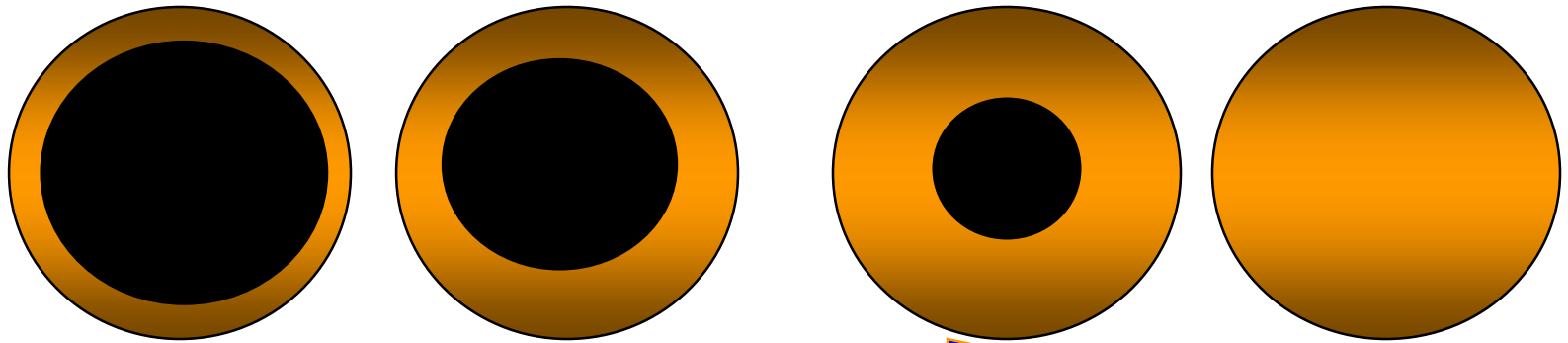# Impregnation process

Solution flows
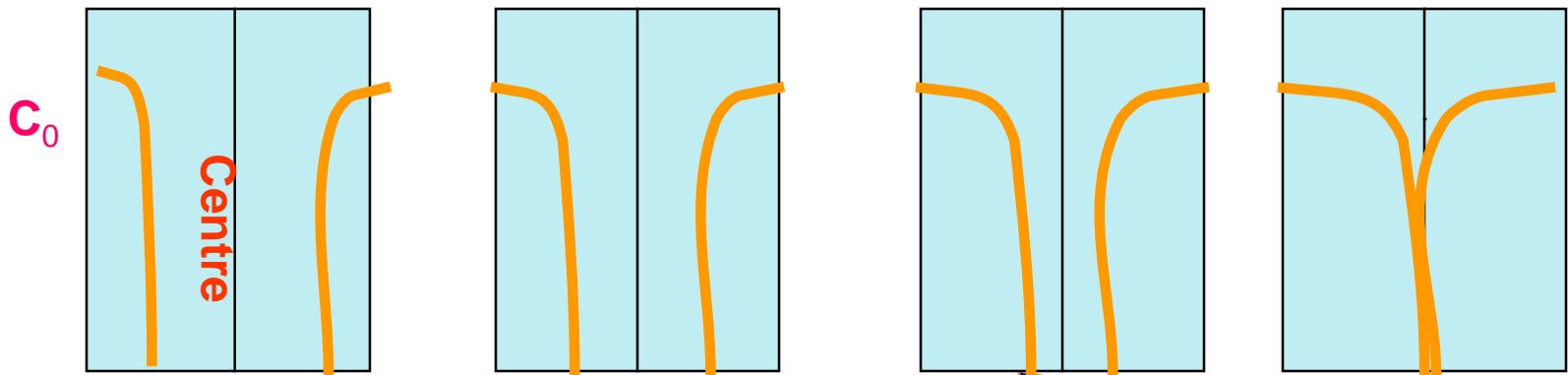Into the pores

Adsorption
Desorption
Diffusion

Evaporation
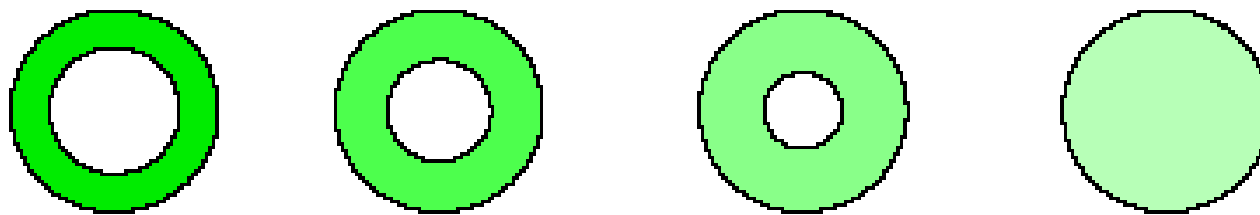
Effect of Drying

Drying time after impregnation

C_0

Centre

Concentration profile after Drying

Active Phase Profiles

- Start from egg-shell catalyst Pt/Al_2O_3 (from H_2PtCl_6)

Increasing impregnation time →
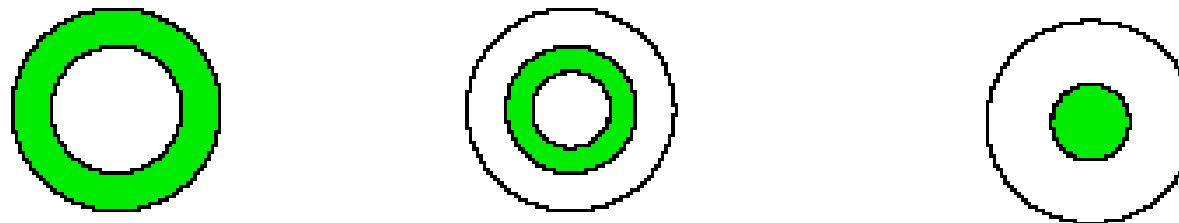
Increasing citric acid concentration →

Concentration profiles by EDXA

FIG. 4. Types of Pt profiles obtained in coimpregnation experiments.
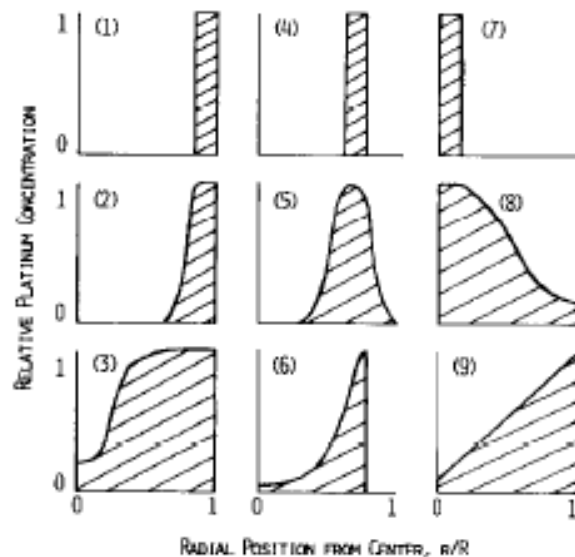
Type 1—Outer shell, sharply defined
Type 2—Outer shell, diffuse
Type 3—Outer shell, diffuse to center
Type 4—Inner shell, sharply defined
Type 5—Inner shell, diffuse
Type 6—Inner shell, diffuse to center
Type 7—Core, sharply defined
Type 8—Core, diffuse
Type 9—Linearly increasing from center

Concentration profiles by EDXA

TABLE 1

Properties of Coimpregnated Catalysts

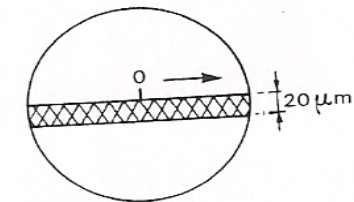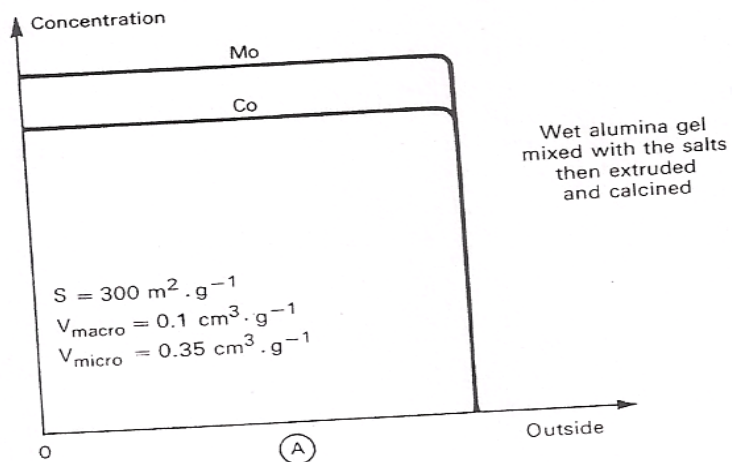| Acid or salt	Impregnation time, 1 hr					Impregnation time, 22 hr		
	Conc (M)	Pt (wt%)	Pt band, r/R			Conc (M)	Pt (wt%)	Pt band
			Begins at	Ends at	Type			Type
None	—	0.51	1	0.77	1	—	0.51	2
AlCl$_3$	0.01	0.50	1	0.56	1	0.01	0.51	2
HCl	0.01	0.51	1	0.67	1	0.01	0.50	2
NaCl	0.01	0.49	1	0.81	1	0.01	0.51	2
HF	0.01	0.50	—	—	5	0.01	0.50	5
NaF	0.01	0.51	1	0.83	1	0.01	0.51	2
NaBr	0.01	0.50	1	0.77	1	0.01	0.50	9
HNO$_3$	0.01	0.50	1	0.50	1	0.01	0.51	3
NaNO$_3$	0.008	0.49	1	0.79	1	0.008	0.51	2
Na$_3$PO$_4$[a]	0.01	0.31	0.83	0	7	0.01	0.10	8
Na benzoate	0.01	0.48	1	0.78	1	0.01	0.50	2
Acetic acid	0.01	0.51	—	—	3	0.01	0.50	uniform
Citric acid	0.01	0.49	0.84	0.44	4	0.01	0.48	6
Na citrate[a]	0.02	0.19	0.33	0	7	0.01	0.14	8
Tartaric acid	0.01	0.49	—	—	6	0.01	0.51	7

[a] The 22-hr sample was prepared using a fresh solution of Na$_3$PO$_4$ (or Na citrate) and H$_2$PtCl$_6$ while the 1-hr sample was prepared using a portion of that same solution after it had been stored for 2 or 3 days.

YS Shyr & WR Erst, J.Catal.63,425,1980

Concentration

Mo

Co

Wet alumina gel
mixed with the salts
then extruded
and calcined

$S = 300\ m^2 \cdot g^{-1}$
$V_{macro} = 0.1\ cm^3 \cdot g^{-1}$
$V_{micro} = 0.35\ cm^3 \cdot g^{-1}$

Outside

O

(A)

$O \longrightarrow$
$20\ \mu m$

Catalyst cross-section
illustrating the path
of the electron microprobe

Concentration

Mo

Co

Alumina supports
impregnated in
two stages:

1. Solution of ammonium molybdate
2. Calcination
3. Solution of cobalt nitrate

$S = 230\ m^2 \cdot g^{-1}$
$V_{macro} = 0.15\ cm^3 \cdot g^{-1}$
$V_{micro} = 0.40\ cm^3 \cdot g^{-1}$

Outside

O

(B)

Concentration

Co   Mo

$S = 300\ m^2 \cdot g^{-1}$
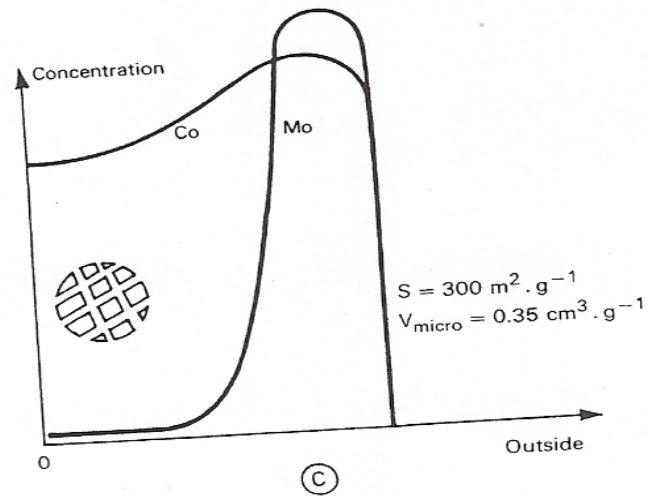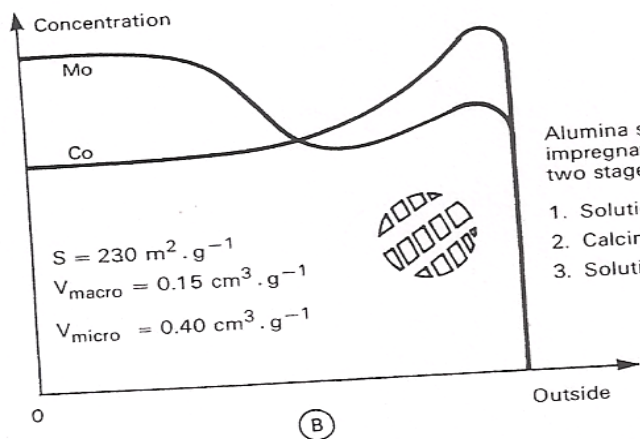$V_{micro} = 0.35\ cm^3 \cdot g^{-1}$

Outside

O

(C)

FIG. 7.23 Analysis of metal distribution from center to periphery in cobalt-molybdenum-alumina type catalysts.

(A) Homogeneous distribution such as is obtained by mixing salts with the wet gel before forming. (B) The distribution obtained by impregnating a catalyst with two pore systems, $\varnothing < 15$ nm and $\varnothing > 100$ nm. A fairly homogeneous distribution is obtained. (C) The distribution obtained by impregnating a microporous support (average $\varnothing = 4.6$ nm).
The small diameter of the micropores and the absence of macropores block diffusion of the large highly adsorbed molybdate ion, and molybdenum is deposited in a layer at the exterior of the grain. (The curves for Mo and Co are drawn with different scales).
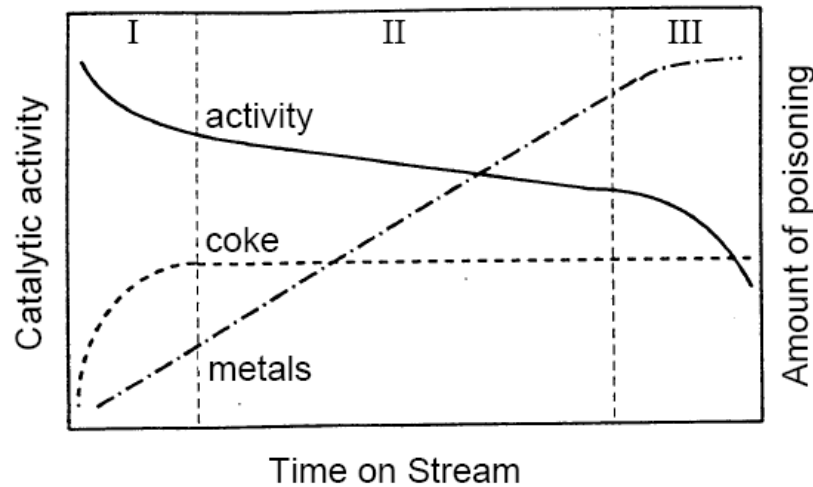
Jacquin, Y., Chenebaux, M. T., IFP unpublished results.

Influence of Pore Size on Vanadium Deposition Hydrotreating of Heavy Feedstock
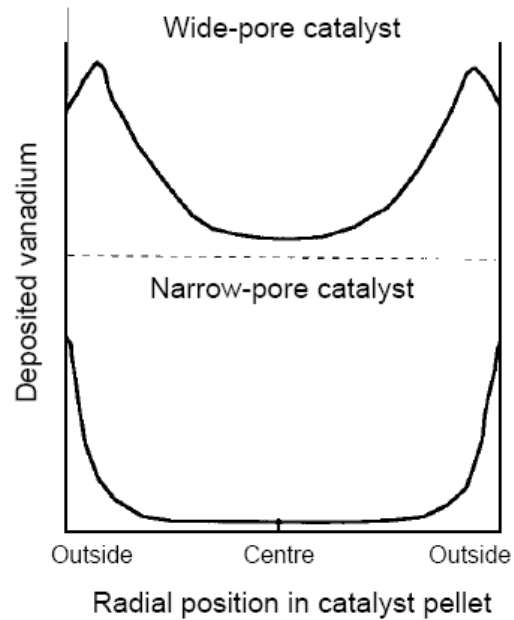
Typical Stability Profiles in Hydrotreating

Initially high rate of deactivation

• mainly due to coke deposition

Subsequently coke in equilibrium

• metal deposition continues