Catalysis and Nanoscience

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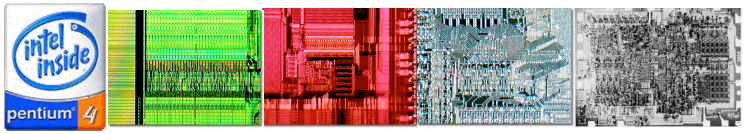
Lawrence Berkeley National Laboratory

Technically and Biologically Important Length Scales

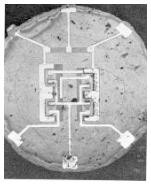
Intel Processors

P 4 **P 3** **486DX** **8088** **4004**



2003 **1999** **1989** **1981** **1969**

First Fairchild IC

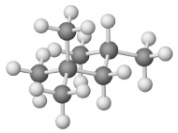


1961

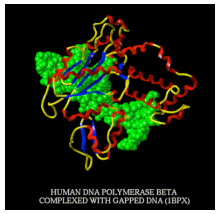
Nanotechnology

1 Å | 1 nm | 10 nm | 100 nm | 1 μm | 10 μm | 100 μm | 1 mm | 1 cm

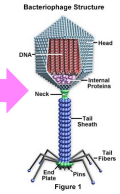
isooctane



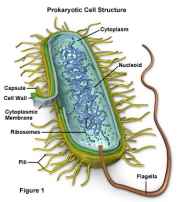
Hydrocarbon Fuel of today



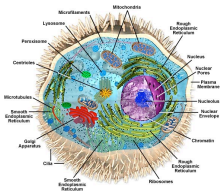
Enzyme



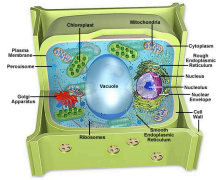
Virus



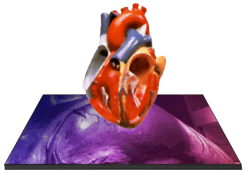
Bacterium



Animal Cell

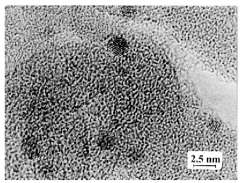


Plant Cell



Tissue & Organ

H_2 - Fuel of tomorrow



Pt/SiO_2 catalyst

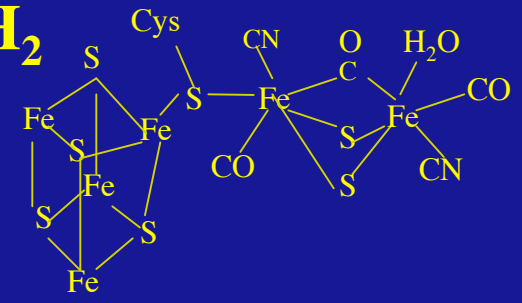
Catalysis

Catalysis is an integral part of nanotechnology. Biological catalysts – enzymes – are the foundation of biological systems, while synthetic heterogeneous catalysts –metal or metal oxide nanoparticles supported on oxides – are the foundation of the chemical industry.

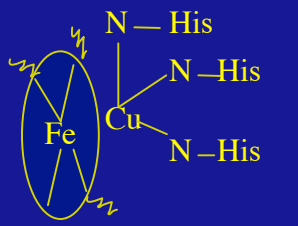
Active sites of various enzymes

hydrogenase

H_2

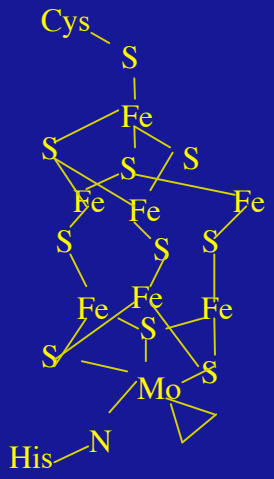


O_2



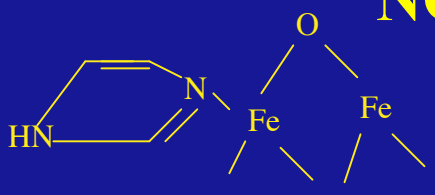
cytochrome C oxidase

N_2



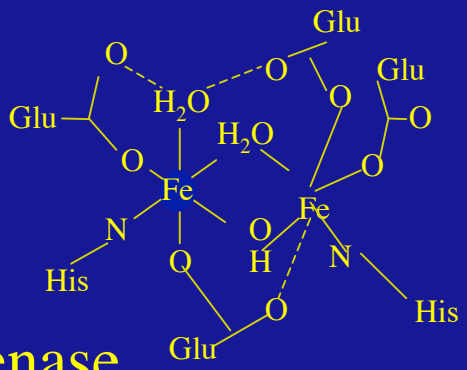
cofactor of nitrogenase

NO



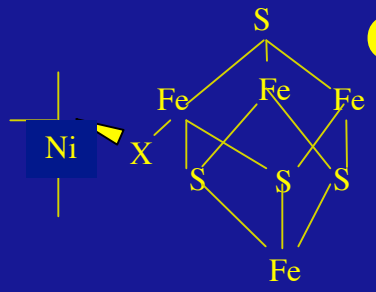
nitric oxide reductase

CH_4



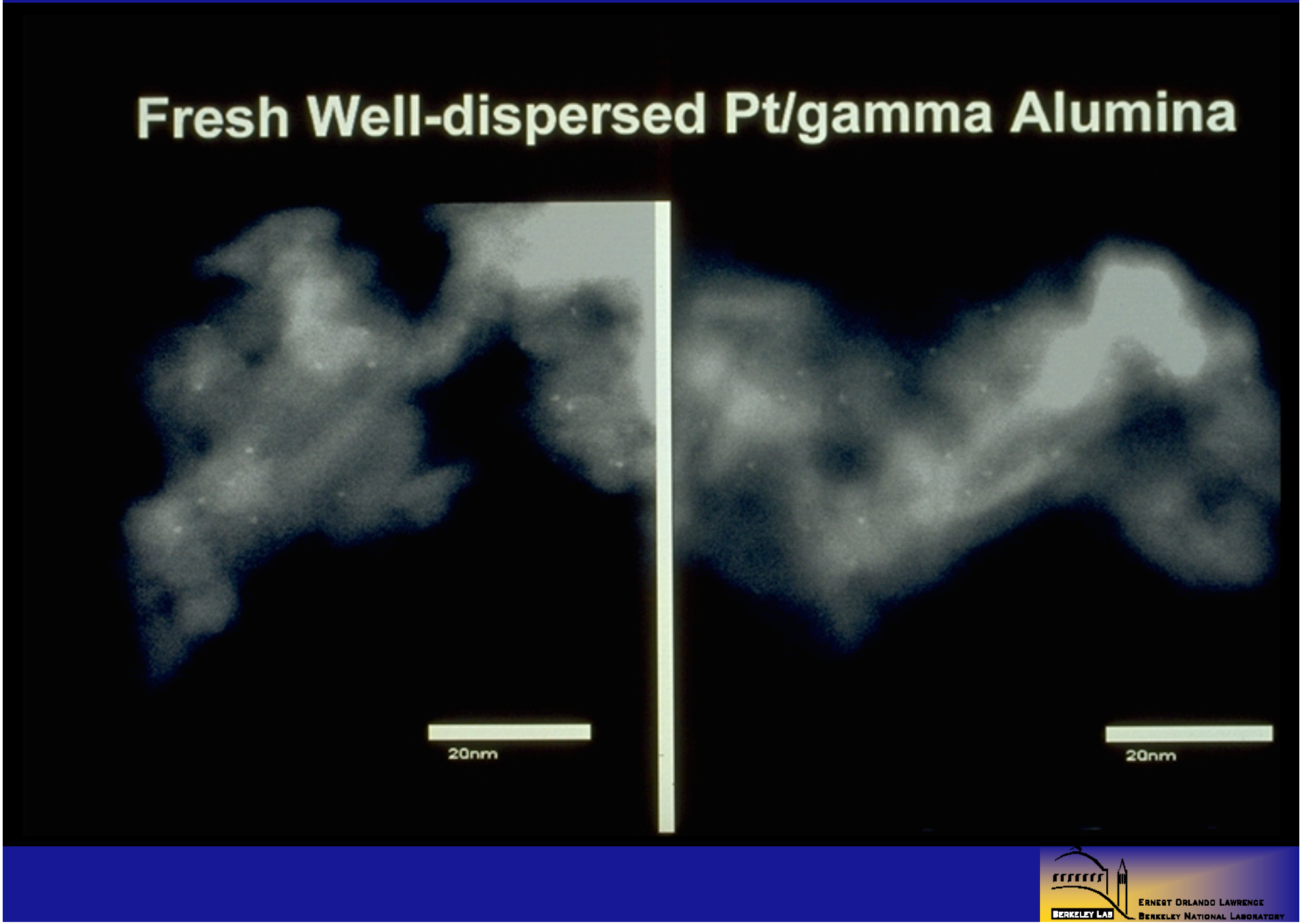
methane monooxygenase

CO

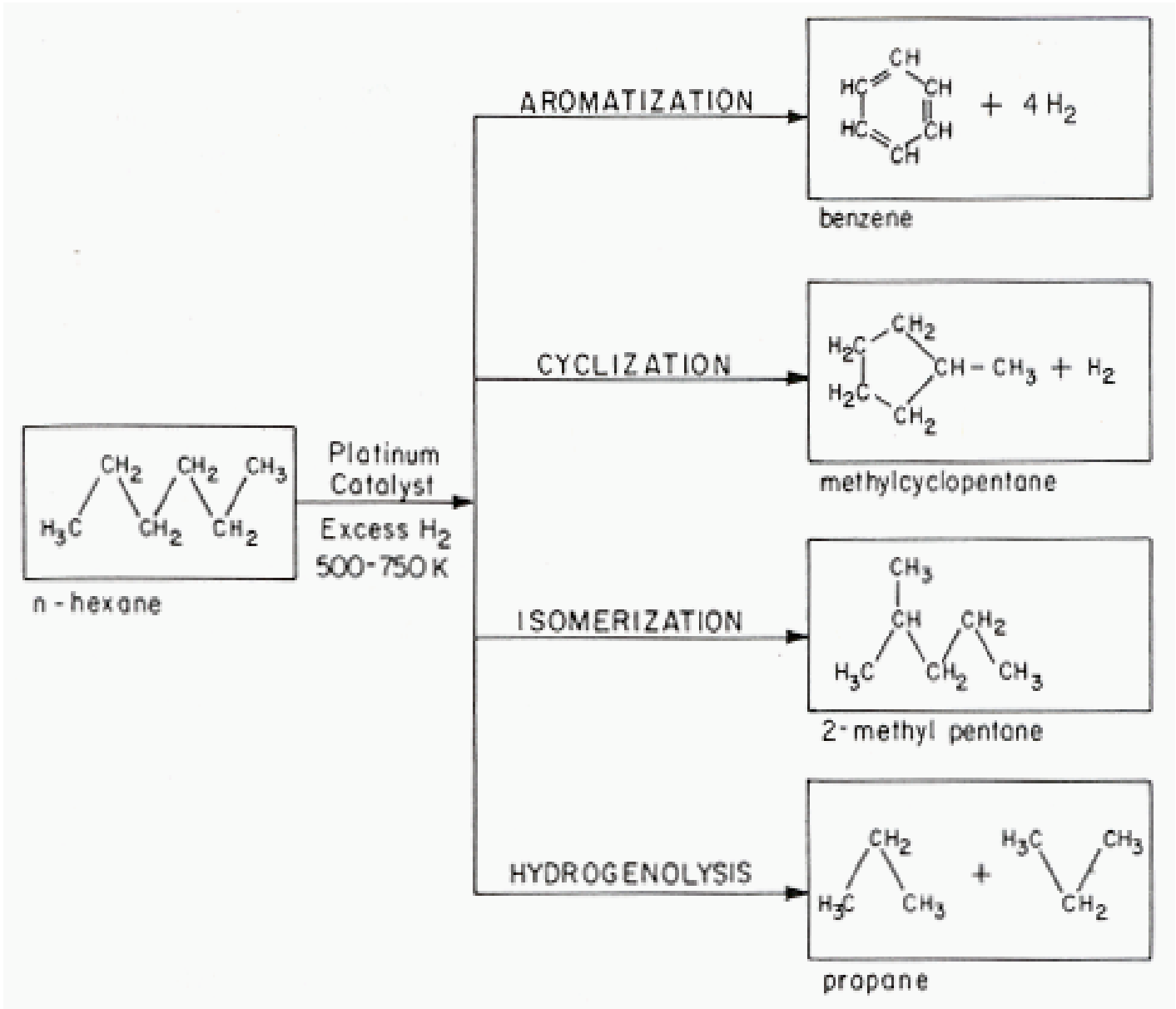


carbon monoxide dehydrogenase

Fresh Well-dispersed Pt/gamma Alumina



Reforming with Pt Catalyst



Octane Rating

110

93

78

N/A

Catalysis in the 21st Century

100% Selectivity for
All Catalyst-Based Processes

Clean Manufacturing

No Byproducts

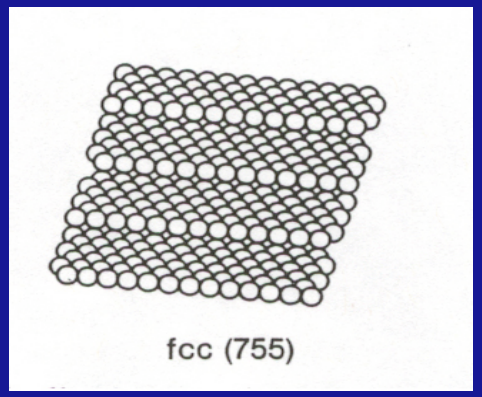
Molecular Ingredients of Catalytic Activity and Selectivity

- Metal Surface Structure
- Bonding Modifiers
- Mobility
- Selective Site Blocking
- Bifunctional Catalysis
- Oxide-Metal Interface Sites

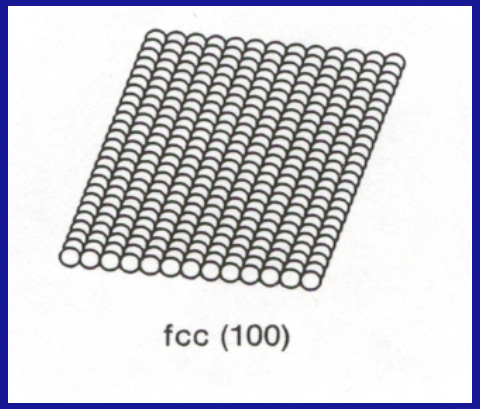
Structure Sensitivity of H_2/D_2 Exchange

Reaction Probability

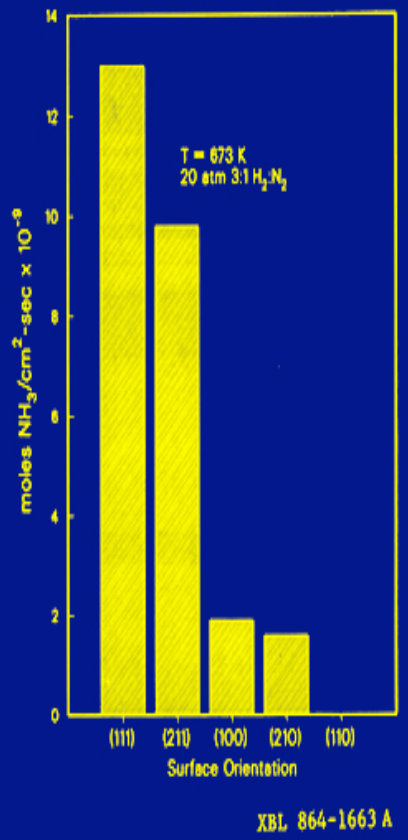
0.9

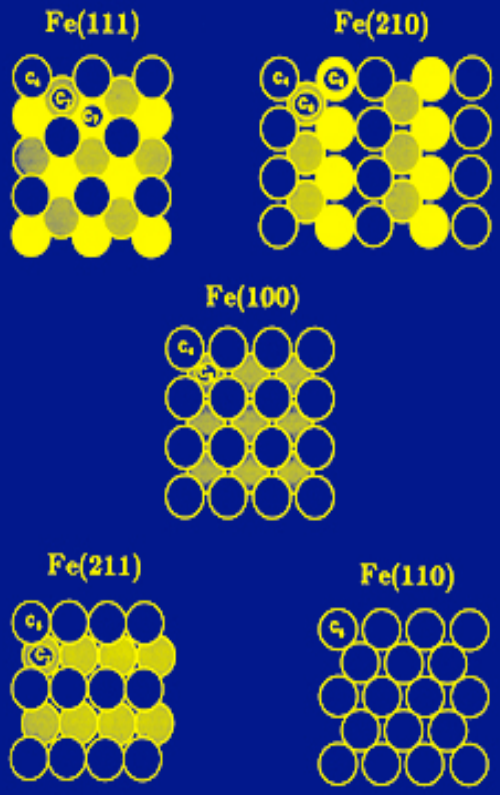


$\leq 10^{-3}$



Structure Sensitivity of Ammonia Synthesis

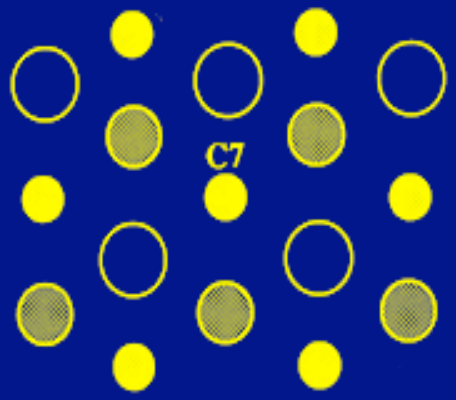




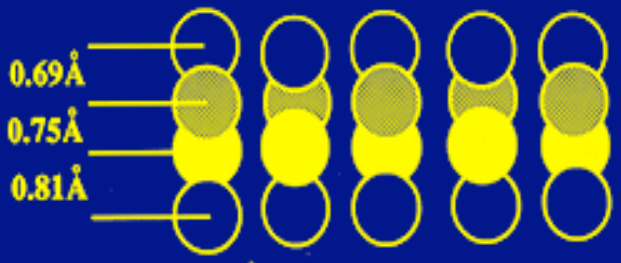
Surface Structure of Clean Iron Surfaces

Fe(111)

Top View



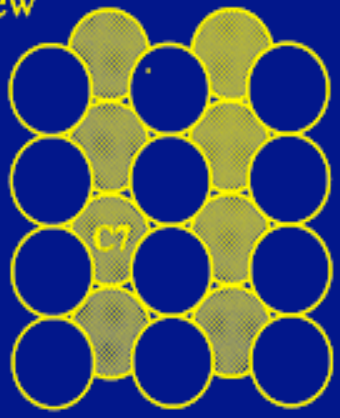
Side View



Bulk Value 0.827Å

Fe(211)

Top View



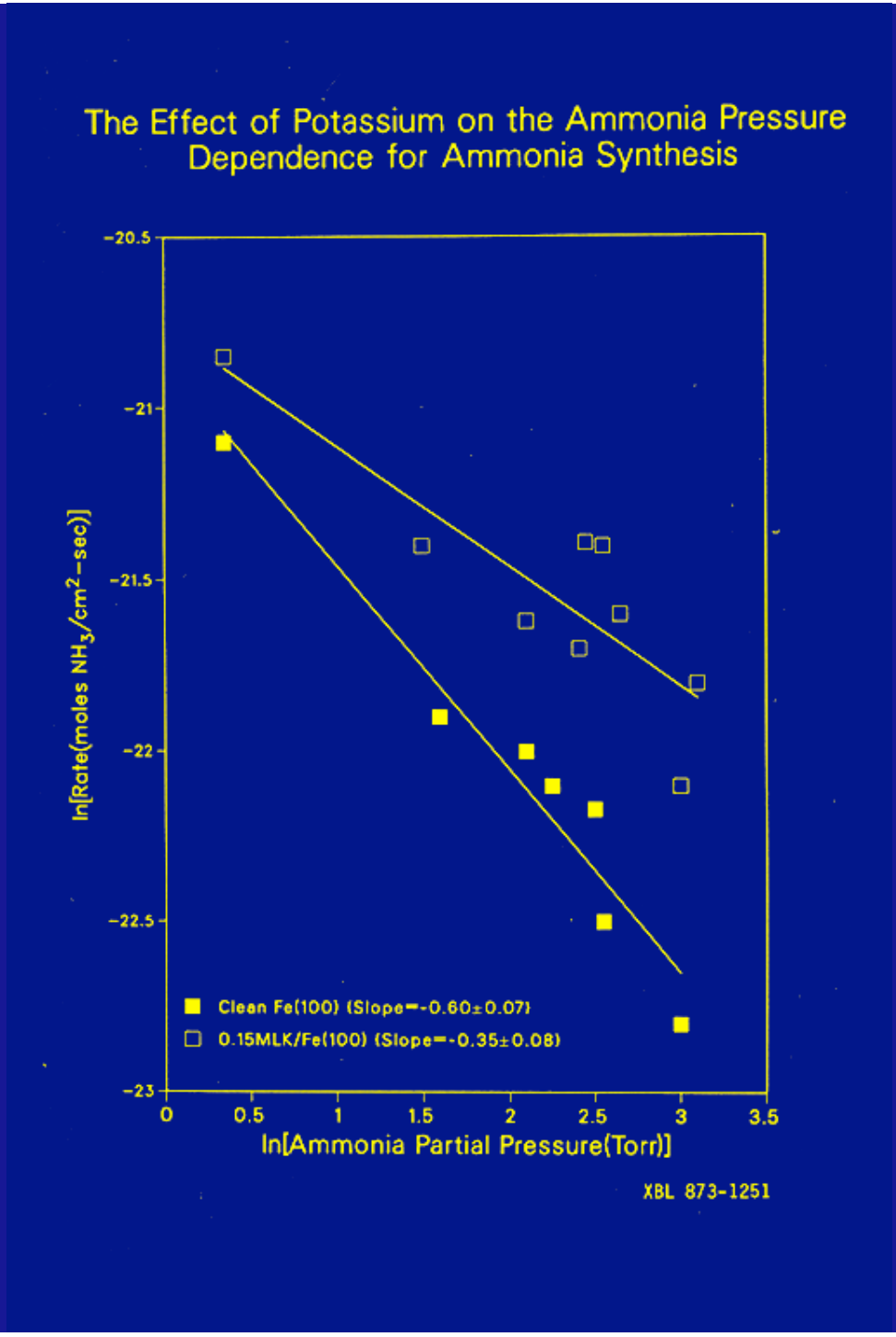
Side View

Bulk Value 1.17Å

J. Sokolov, F. Jona and P.M. Marcus *Phys. Rev. B* Vol 23, No 2 1986

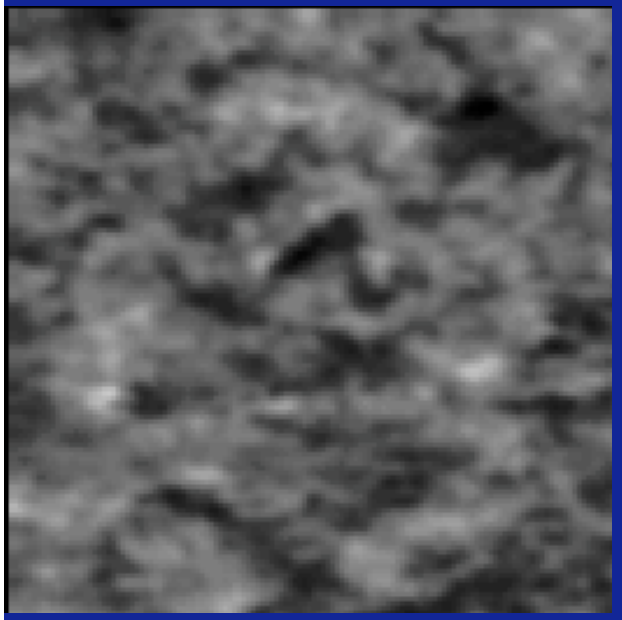
J. Sokolov, H.D. Shih, U. Bardi, F. Jona and P.M. Marcus *J. Phys C : Solid State Phys.*, 17 (1984) 371-383

XBL 938-1286

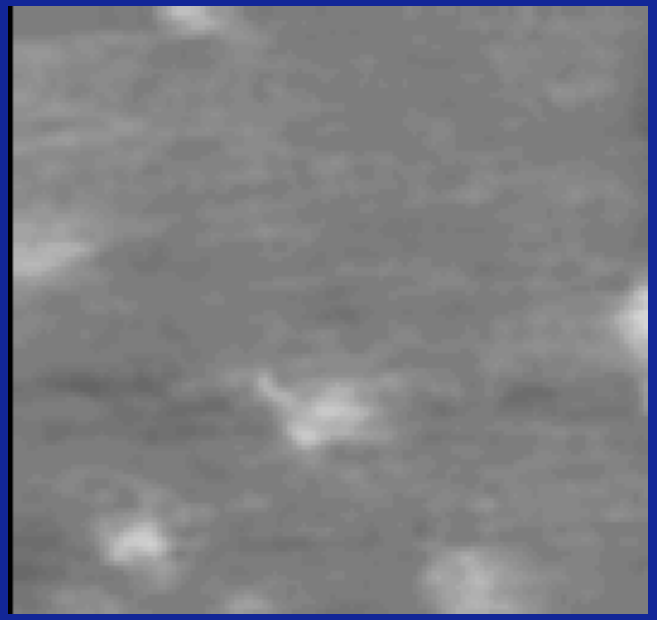


Potassium is Bonding Modifier of Adsorbed Ammonia

CO Poisons Ethylene Hydrogenation and Induces Surface Order on Rh(111)

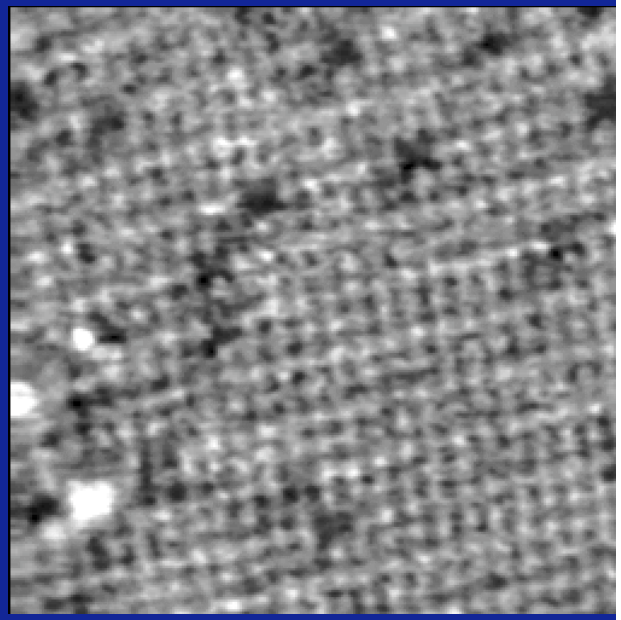


20 mTorr H_2



20 mTorr H_2
+
20 mTorr C_2H_4

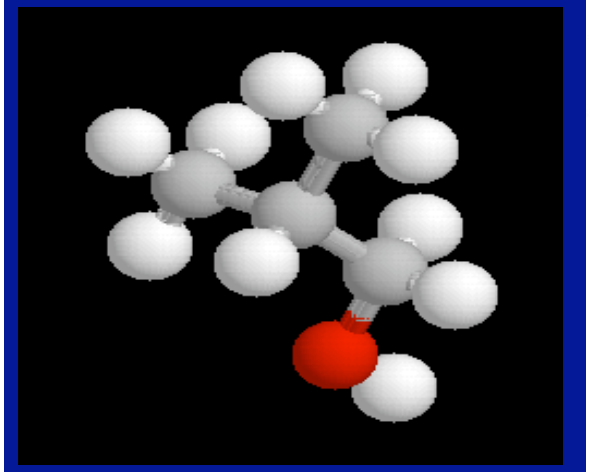
(100 Å)^2 images



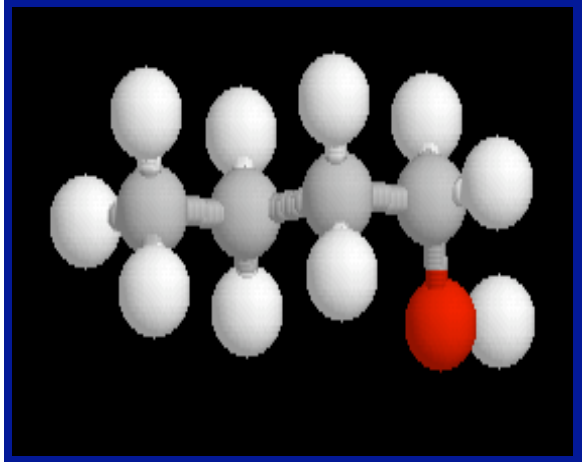
20 mTorr H_2
+
20 mTorr C_2H_4
+
5.6 mTorr CO

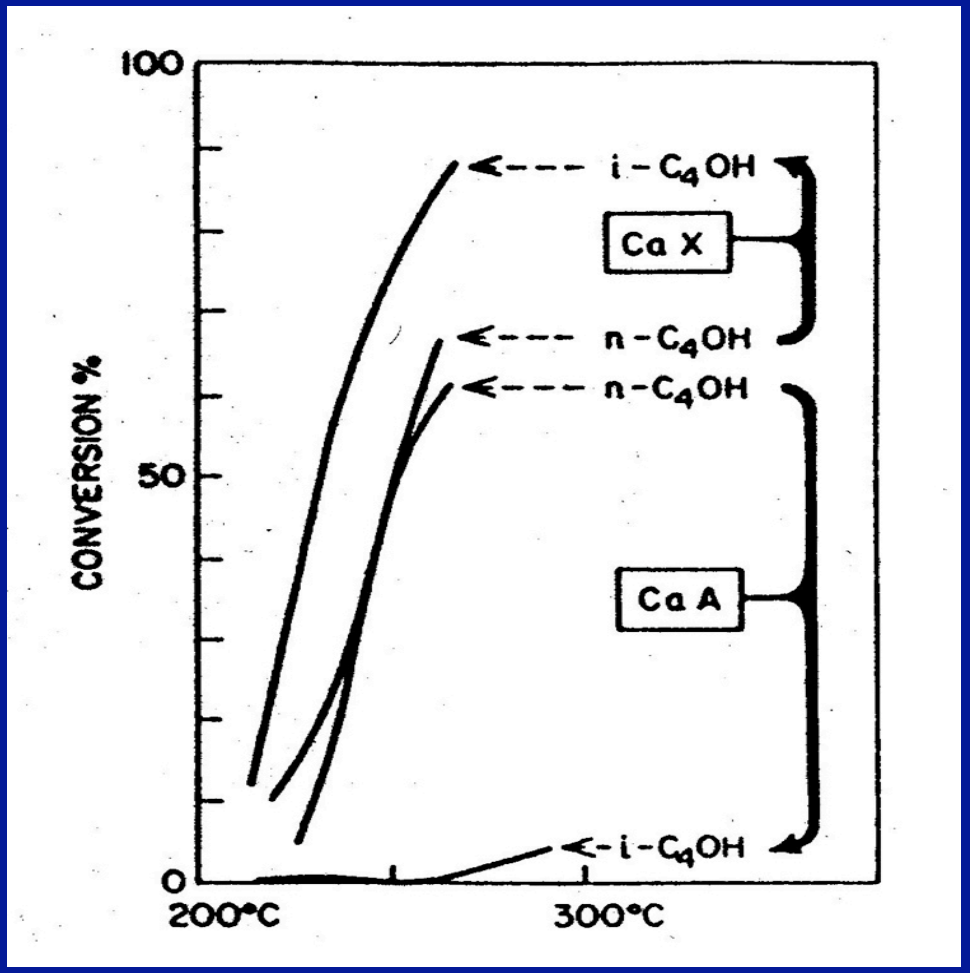
Dehydration of *n*-butanol without reaction of *i*-butanol on Linde 5A zeolite

i-butanol



n-butanol

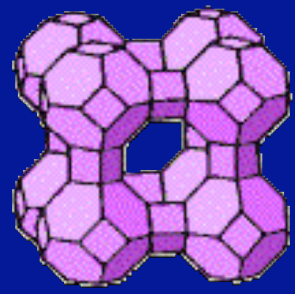




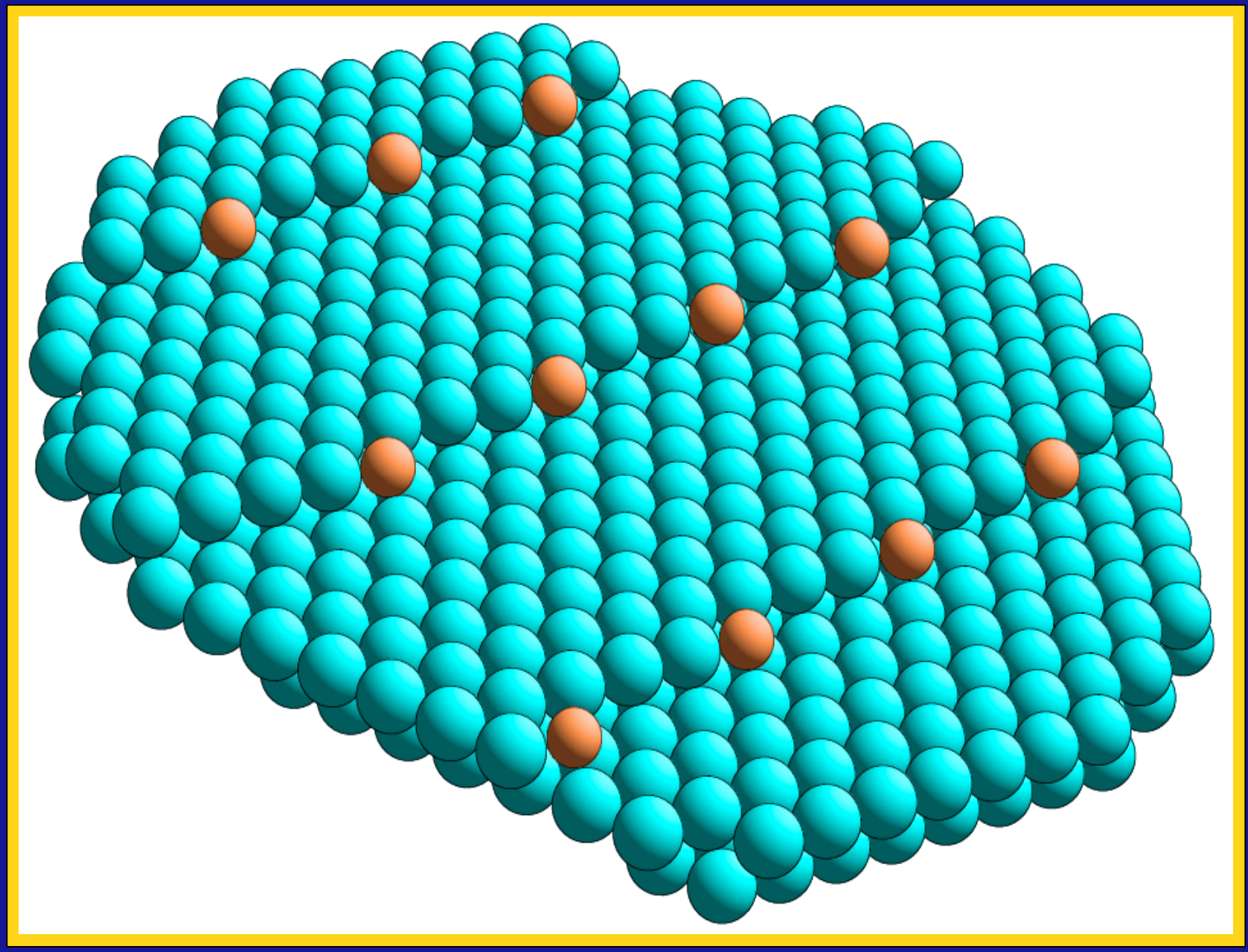
Ca^{2+} radius: 1.05 Å

CaX:
8-12 Å
pore size

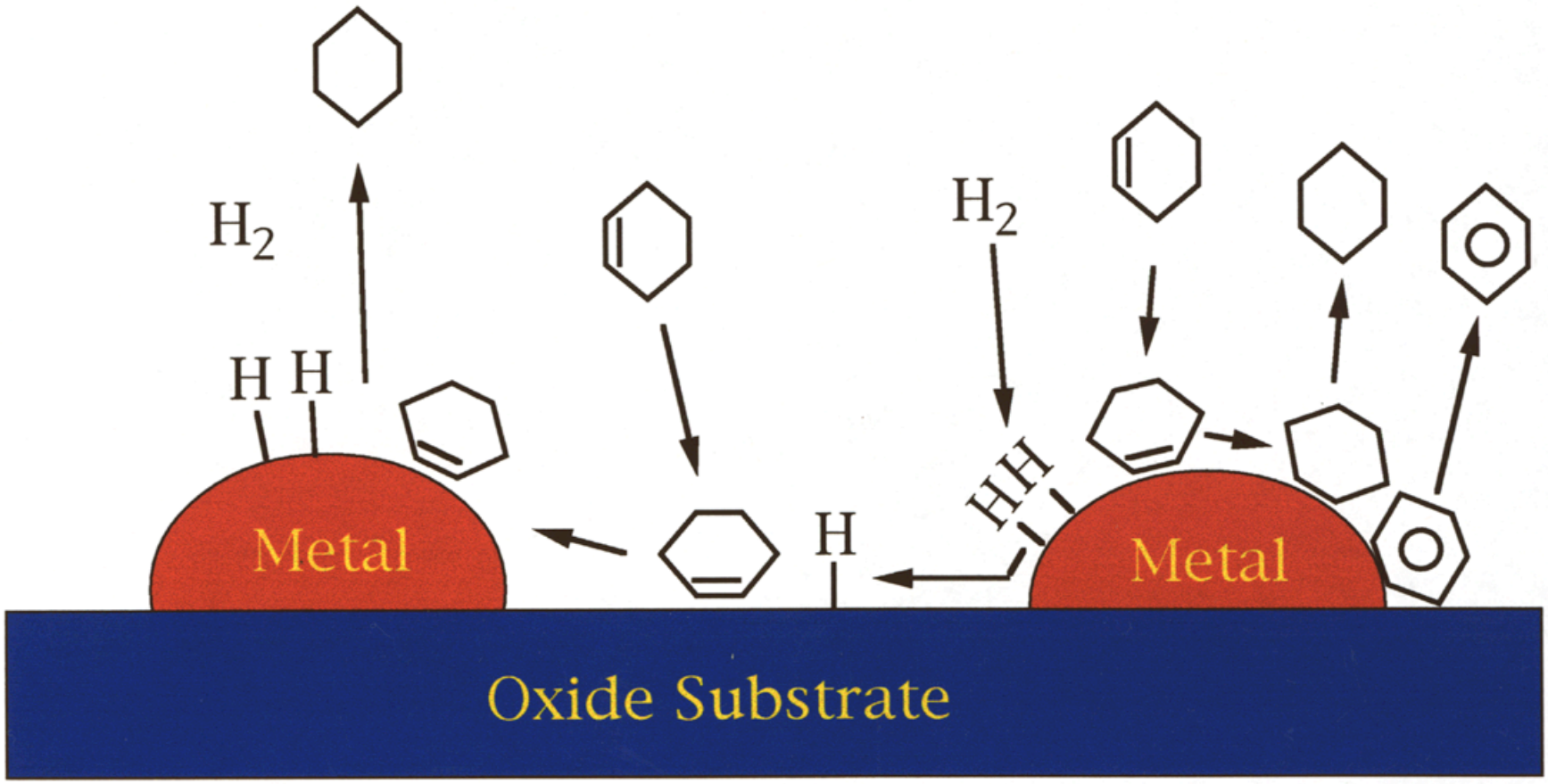
CaA:
5 Å
pore size



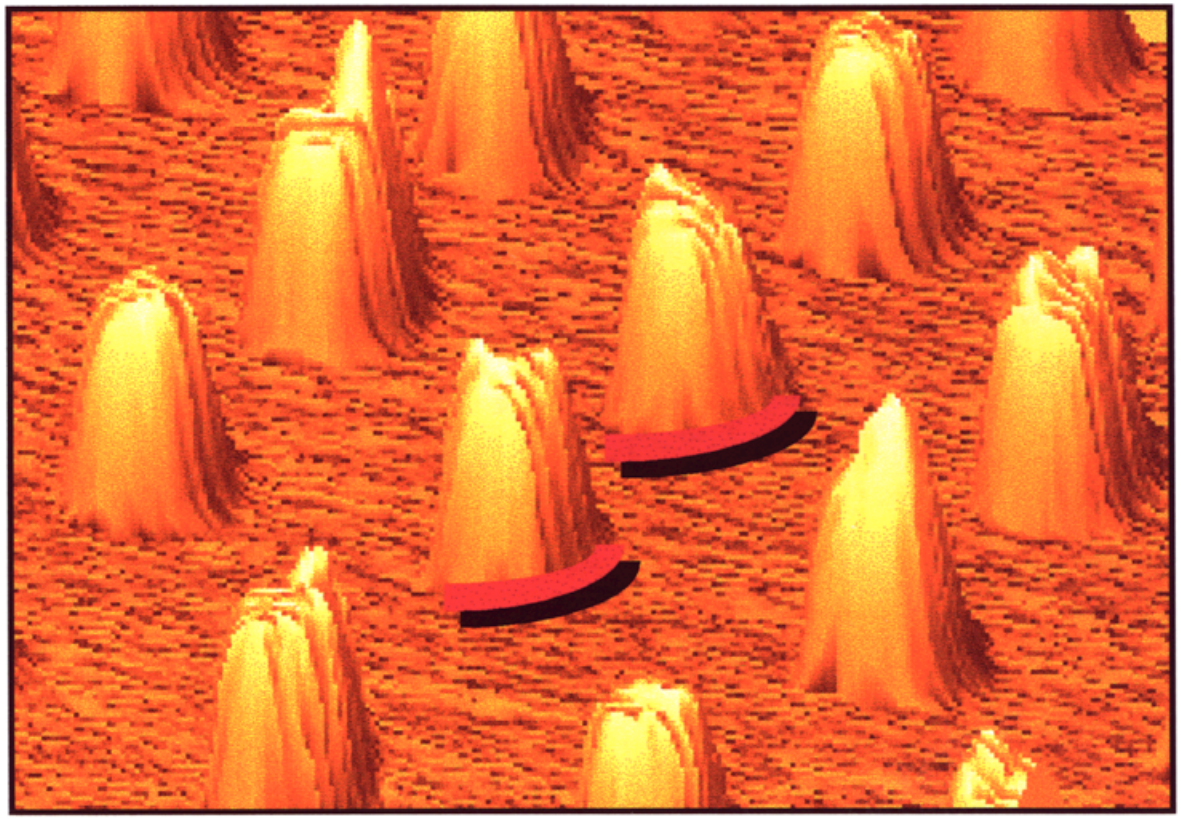
V. J. Frilette, P. B. Weisz, R. L. Golden, *J. Catal.* **1**, (1962) 301



Bifunctional Catalysis

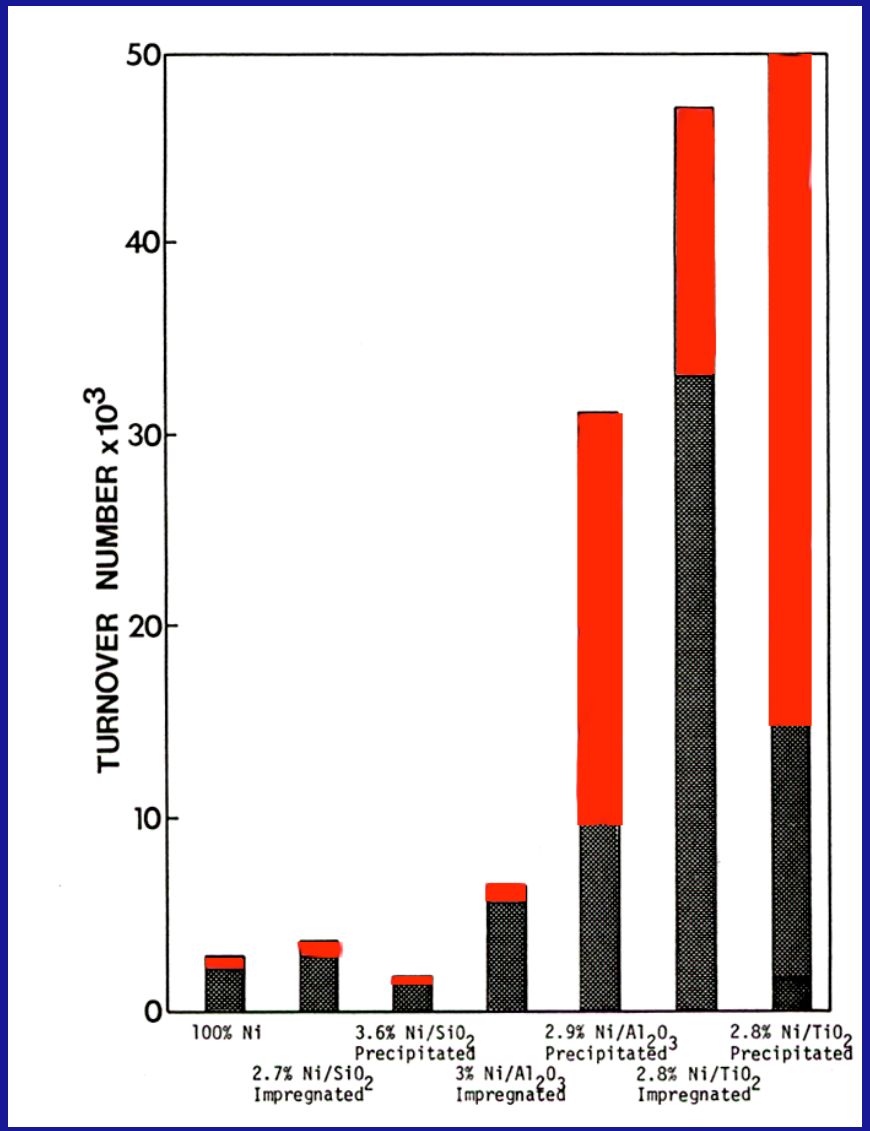


Active Sites at the Metal-Oxide Interface



100 nm

Effect of support on CO Hydrogenation over Ni Catalysts at 525K: Note Changes of Activity and Selectivity



C_{2+} hydrocarbon turnover no.

CH_4 turnover no.

Bartholomew, C.H., Pannell, R.B., and Butler, J.L., *J. Catal.*, **65**, 335 (1980)

Fabrication of High Technology Catalysts

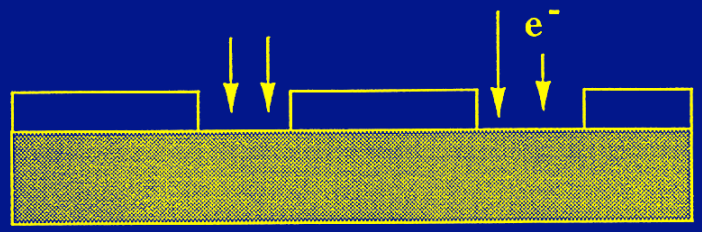
Molecular Control

- Size
- Location
- Structure
- Promoters

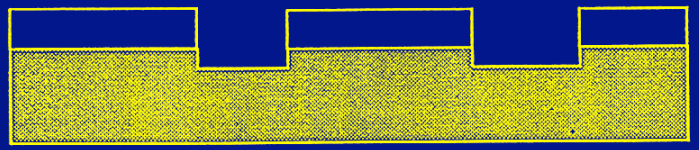
Fabrication of 2-Dimensional and 3-Dimensional Catalysts Toward 100% Selectivity

Electron beam lithography:

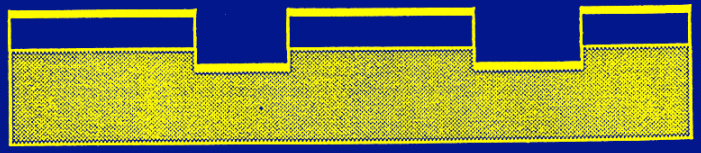
Coat substrate with resist



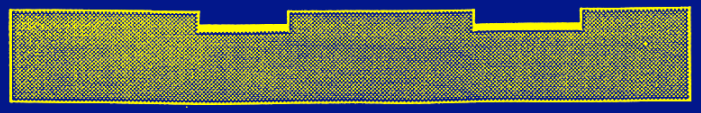
Expose and develop resist



Etch substrate (optional)



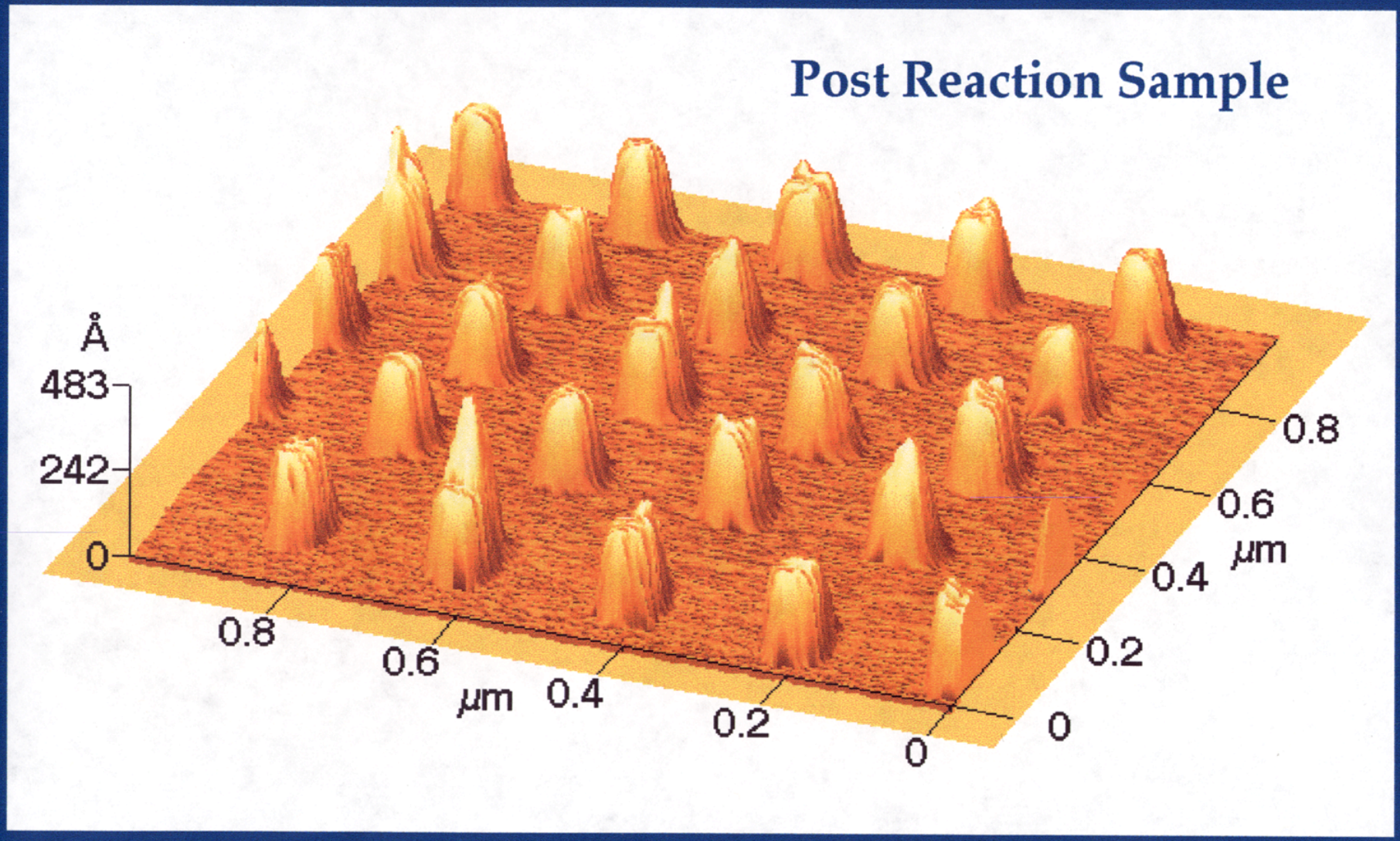
Evaporate metal film



Lift off remaining resist

XBD 9611-05348.TIF

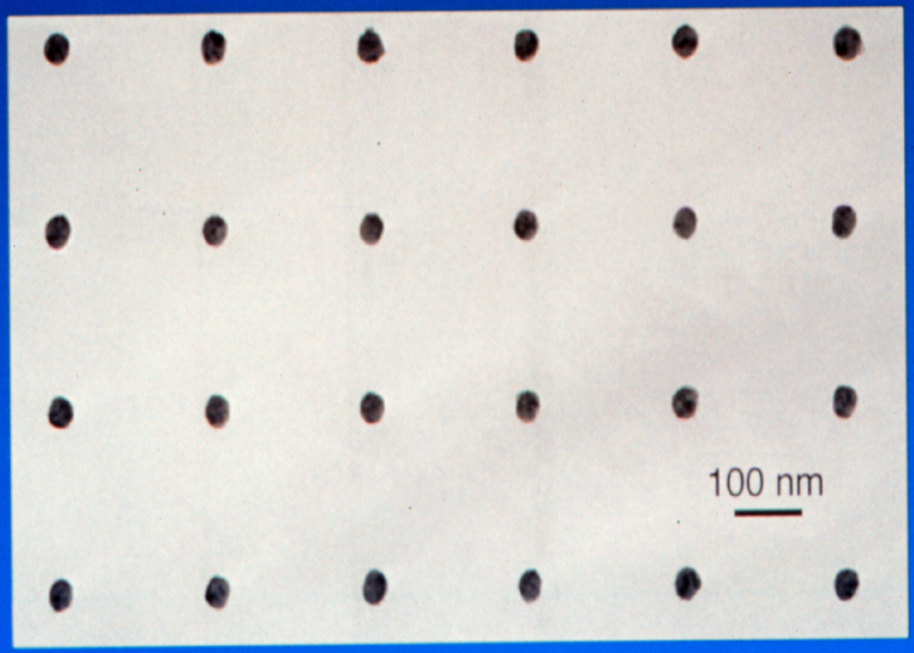
AFM Image of Pt Nanoparticles/SiO_2 Fabricated using Electron Beam Lithography



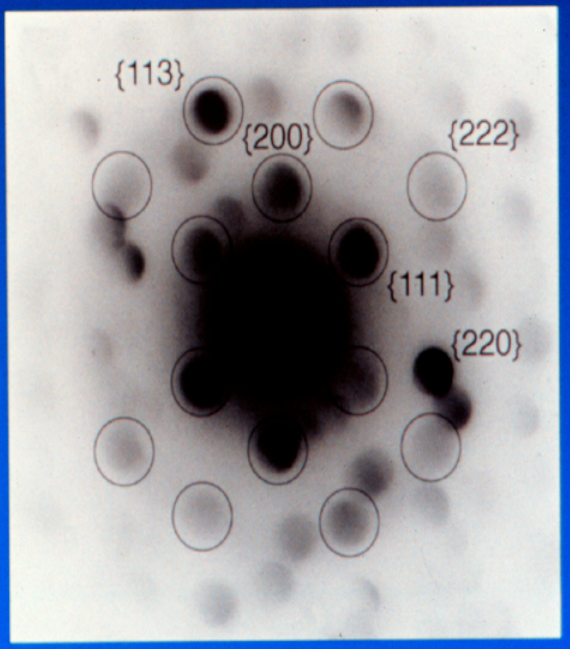
50 nm particles; 200 nm interparticle distance

BERKELEY LAB

Model catalysts fabricated by electron beam lithography: Pt nanocluster arrays on Si(100)



transmission electron micrograph



microdiffraction pattern

(particle size 40 nm, particle distance 230 nm, sample size 1 cm^2)

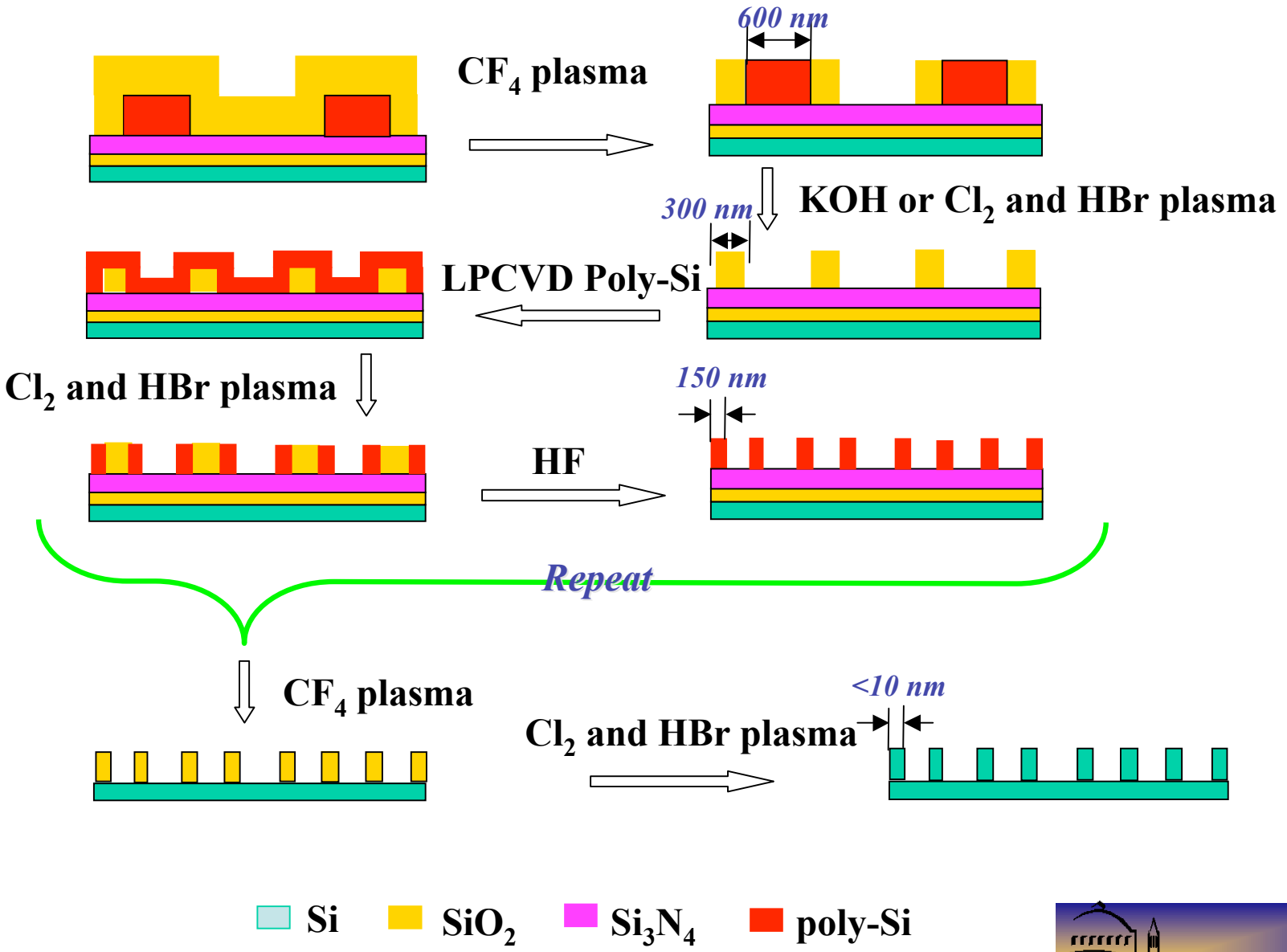
G. Rupprechter, A. Eppler & G. A. Somorjai
Materials Sciences Division, Lawrence Berkeley National Laboratory, USA

10^9 nanoparticles ~ 1 mm^2 surface area
produced by e^--beam lithography in one day

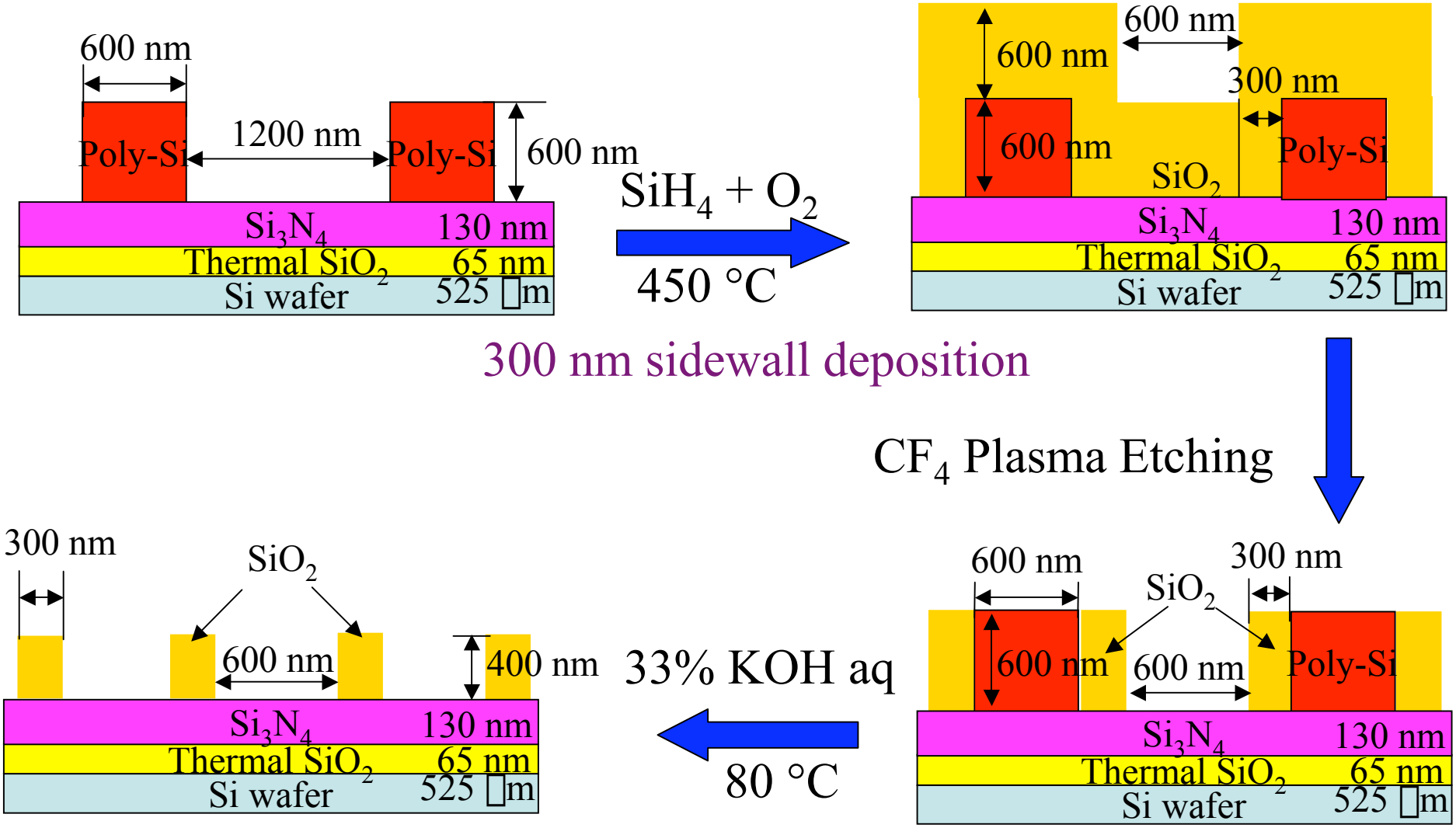
10^{11} nanoparticles ~ 1 cm^2 surface area
suitable for model catalytic studies

10^{15} nanoparticles ~ 1 m^2 surface area
technologically significant catalyst system

Scheme of Multiple Size Reduction Lithography

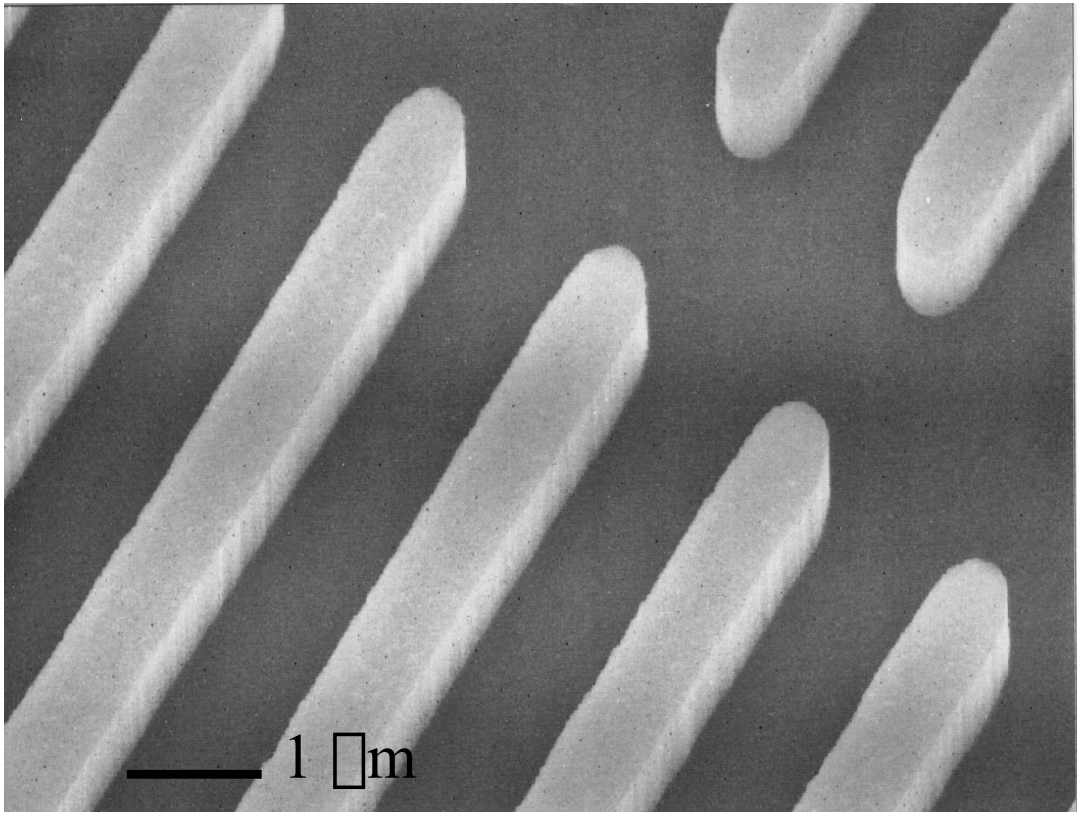


Size Reduction Lithography II

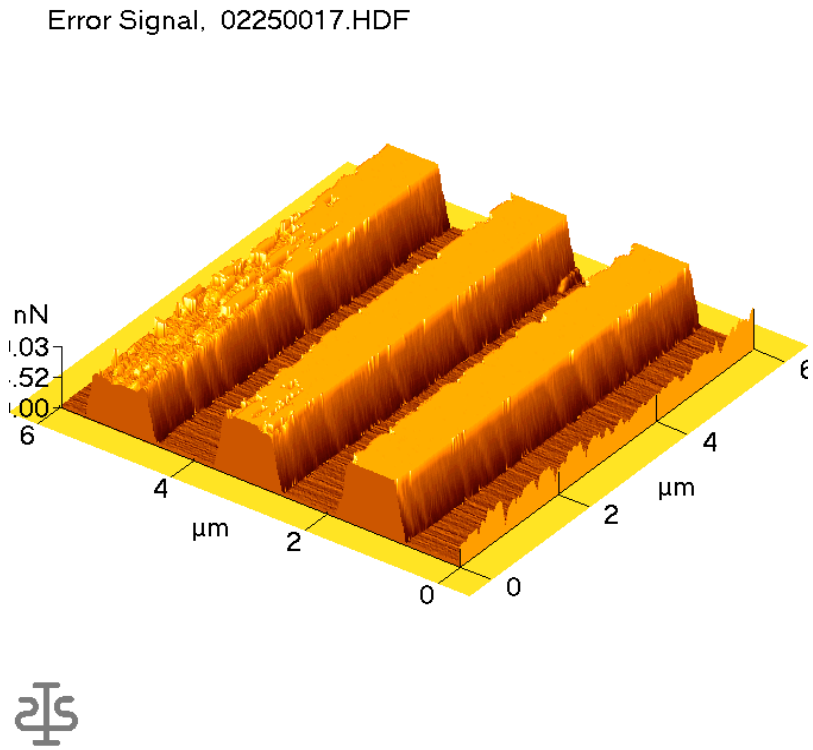


Optical Lithography Defined Poly-Si Pattern

SEM picture

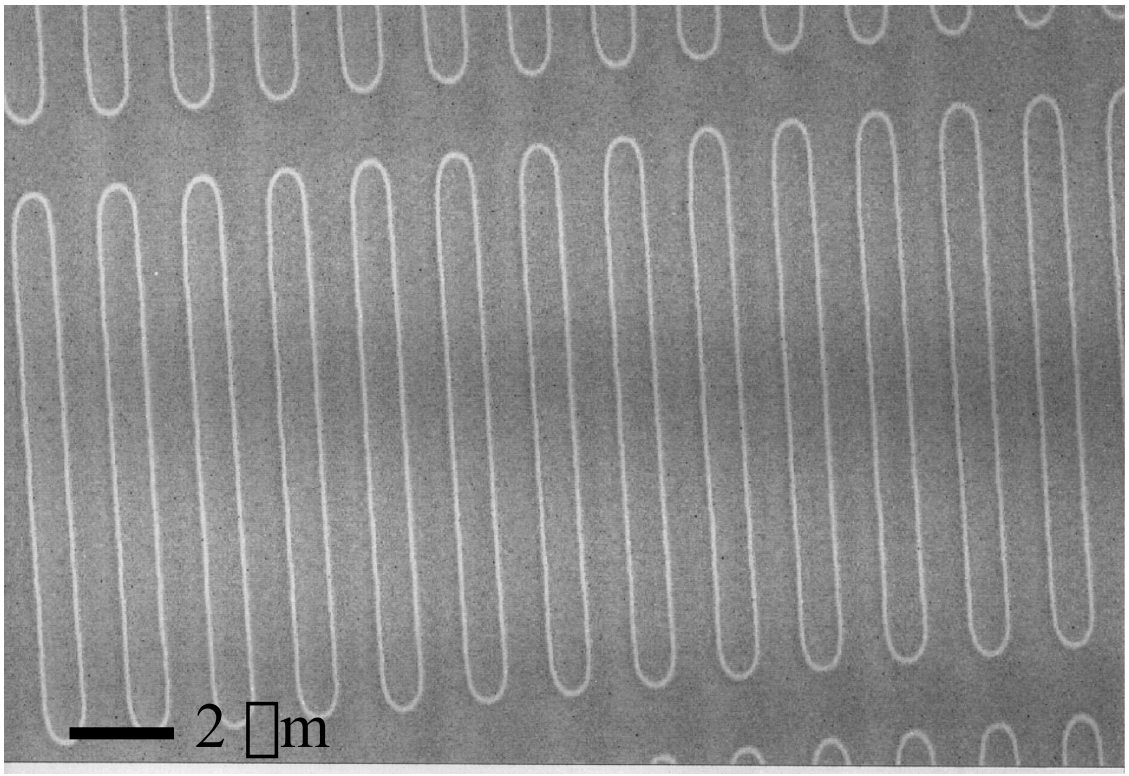


AFM picture

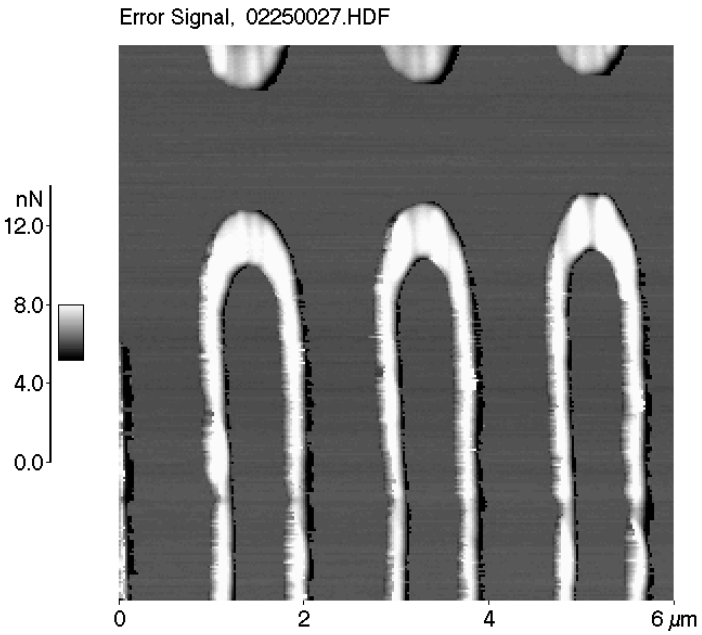


SiO_2 Nanowire Pattern After 1st Size Reduction Lithography Process

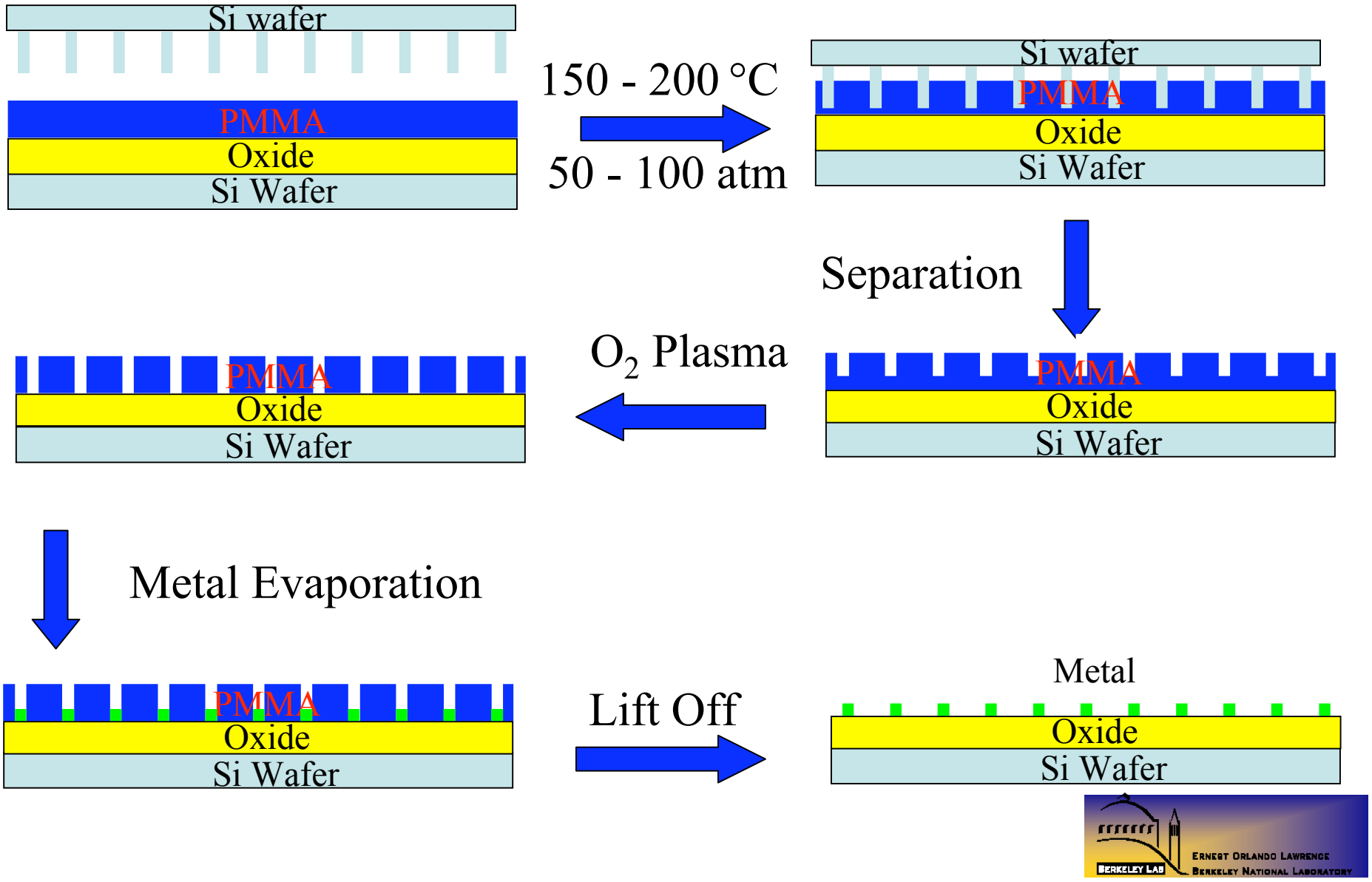
SEM picture



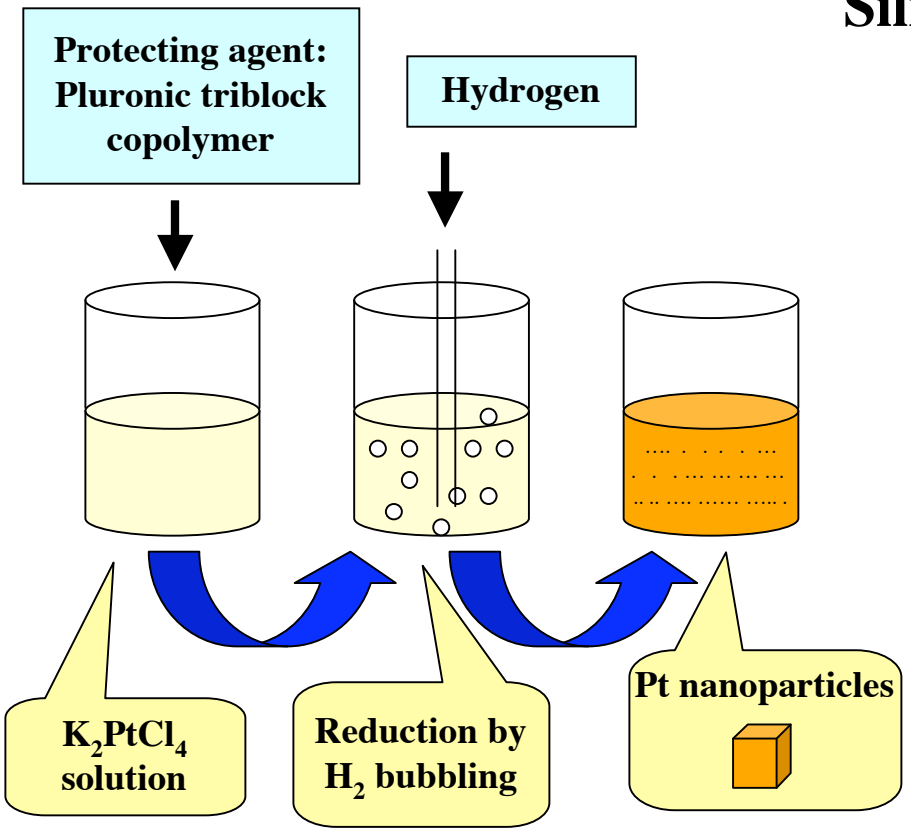
AFM picture

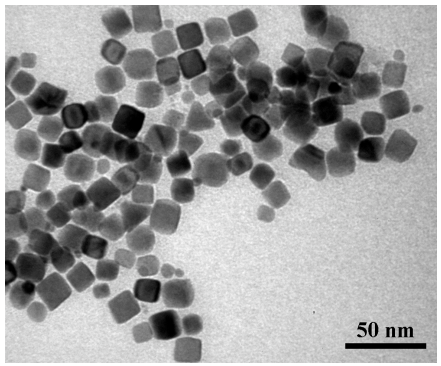


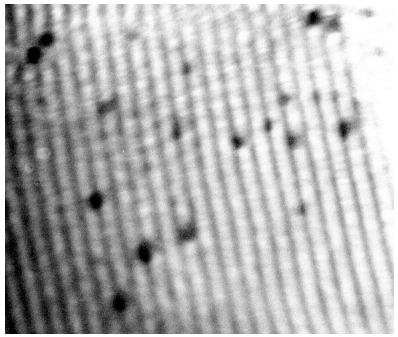
Pattern Transfer with Nanoimprint Lithography

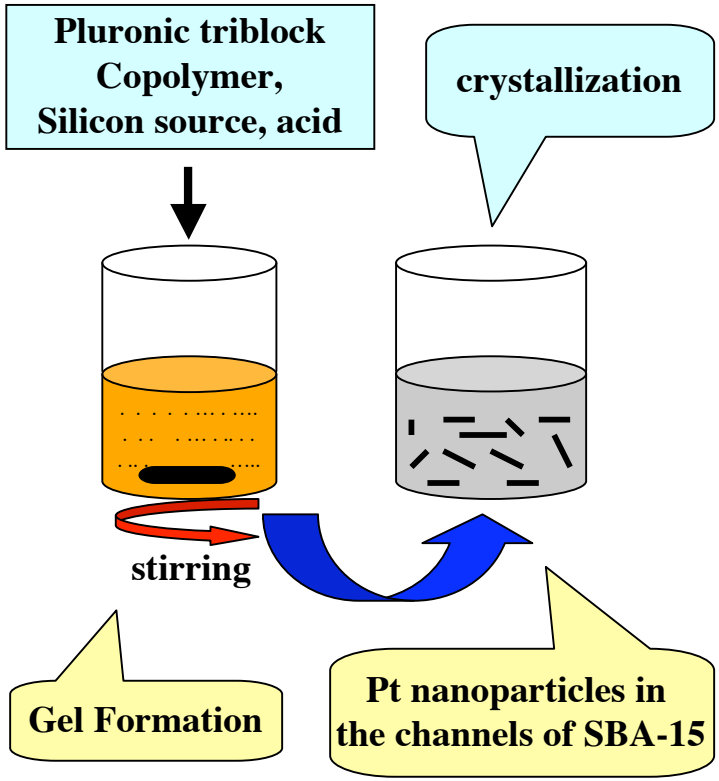


Synthesis of Pt Nanoparticles and their Encapsulation in Mesoporous Silicate









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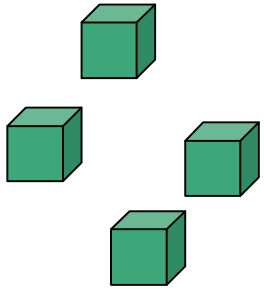
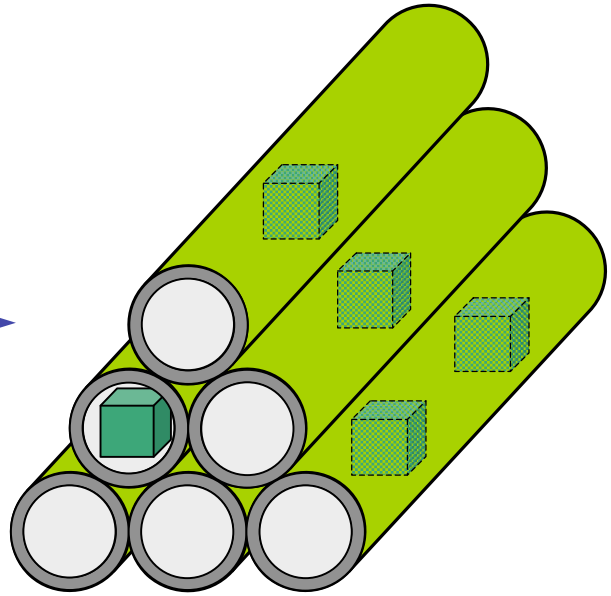
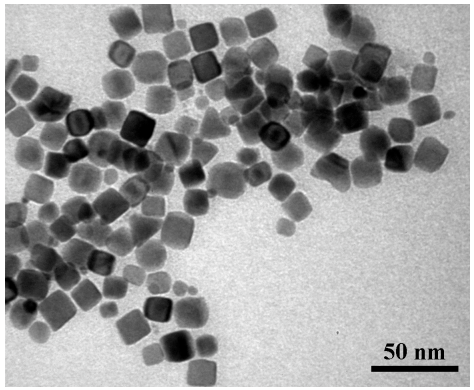
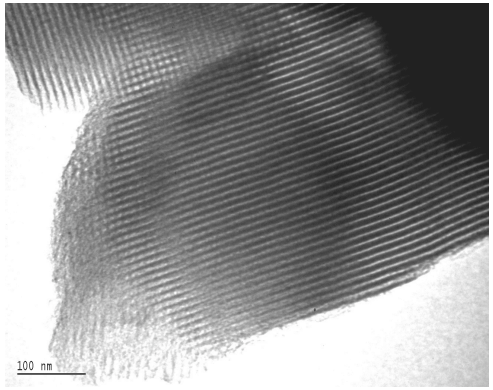


SiO_2 precursor

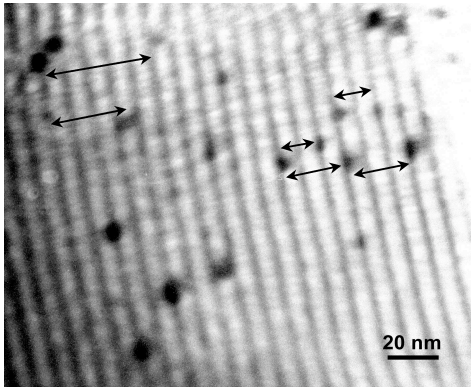




Pt Nanoparticles



Mesoporous Silicate
SBA-15 channels



Mesoporous Silicate
Encapsulated
Pt Nanoparticles

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