「表面の科学とエコテクノロジーに対する分子的理解」

米国カリフォルニア大学バークレー校化学科教授

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Molecular Understanding of the Science and Ecotechnologies of Surfaces

Commemorative lecture at the 32nd Honda Prize
Award Ceremony on the 17th November 2011

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Curriculum Vitae for Dr. Gabor A. Somorjai

■生まれ

1935年5月4日　　（76歳）ハンガリー・ブダペスト（米国市民）

■学　歴

1956年　　　　　ハンガリー・ブダペスト工科大学化学工学科卒業

1960年　　　　　米国カリフォルニア大学バークレー校化学科博士課程修了

■職　歴

1960年〜64年　　IBM 研究員（ニューヨーク州ヨークタウンハイツ）

1964年〜現在　　カリフォルニア大学バークレー校化学科教授

1964年〜現在　　ローレンスバークレー国立研究所上級科学者兼ディレクター

■経　歴

　1956年、ブダペスト工科大学化学工学科4年在学時にハンガリー革命が勃発し米国へ移住。1960年にカリフォルニア大学バークレー校で博士号を取得。

　卒業後はニューヨーク州ヨークタウンハイツにある IBM 研究所で研究員として勤務。1962年、米国市民権を取得。1964年、カリフォルニア大学バークレー校化学科助教授に就任（1967年同科准教授、1972年同科教授）。同時にローレンスバークレー国立研究所先端材料センター材料科学部門の上席科学者兼表面科学・触媒化学プログラム・ディレクターを兼務。

　表面科学、不均一系触媒、固体化学の分野で1,000以上の科学論文を発表し、「表面科学の父（もしくは開拓者）」とも呼ばれる。ソモルジャイ博士の下で140名が博士号を取得し、250名以上の博士研究員（ポスドク）が学んだ。その内、現在約100名が大学で教鞭をとる他、産業界でも多くの卒業生が活躍中。

　世界中の研究者が読む博士が著した教科書には、「表面化学の原則」Prentice Hall 社(1972年)、「モノグラフ・固体表面の吸着単分子膜」Springer-Verlag 社(1979年)、「二次元の化学〜表面」Cornell 大学出版(1981年)、「表面化学と触媒入門」Wiley-Interscience 社(1994年)、「表面化学と触媒入門・第2版」Wiley 社(2010年)等がある。

■BORN

4th May, 1935, Budapest, Hungary (U.S. citizen)

■DEGREES

1960　　Ph.D., Chemistry, University of California, Berkeley (UC Berkeley), CA

1956　　B.S., Chemical Engineering, Technical University, Budapest, Hungary

■APPOINTMENTS

1964 – Present　　Professor, Department of Chemistry, UC Berkeley

1964 – Present　　Faculty Senior Scientist, Lawrence Berkeley National Laboratory

1960 –1964　　Research Staff, IBM, Yorktown Heights, New York

■SELECTED HONORS

Somorjai was born in Budapest, Hungary, on May 4, 1935. He was a fourth year student of Chemical Engineering at the Technical University in Budapest in 1956 at the outbreak of the Hungarian Revolution. He left Hungary and emigrated to the United States, where he received his Ph.D. degree in Chemistry from the University of California, Berkeley in 1960. He became a U.S. citizen in 1962.

After graduation, he joined the IBM research staff in Yorktown Heights, NY, where he remained until 1964. At that time, he was appointed Assistant Professor of Chemistry at the UC Berkeley. In 1967, he was named Associate Professor, and in 1972 promoted to Professor. Concurrent with his faculty appointment, he is also a Faculty Senior Scientist in the Materials Sciences Division, and Director of the Surface Science and Catalysis Program at the Center for Advanced Materials, at the Lawrence Berkeley National Laboratory. He was appointed University Professor by the UC Board of Regents in March of 2002.

Somorjai has educated 140 Ph.D. students and more than 250 postdoctoral fellows, about 100 of which hold faculty positions and many more are leaders in industry. He is the author of more than 1000 scientific papers in the fields of surface chemistry, heterogeneous catalysis, and solid state chemistry. He has written three textbooks, *Principles of Surface Chemistry*, Prentice Hall, 1972; *Chemistry in Two Dimensions: Surfaces,* Cornell University Press, 1981 *Introduction to Surface Chemistry and Catalysis*, Wiley-Interscience, 1994 and *Introduction to Surface Chemistry and Catalysis*, Second Edition, Wiley 2010; and a monograph, *Adsorbed Monolayers on Solid Surfaces*, Springer-Verlag, 1979

■受賞歴 **Awards and Honors**

2011　　ENI New Frontiers of Hydrocarbons Prize
　　　　BBVA Foundation Frontiers of Knowledge Award in Basic Sciences
2009　　Senior Miller Fellow, Miller Institute, UC, Berkeley
　　　　Japanese Society for the Promotion of Science Award
　　　　Excellence in Surface Science Award from the Surfaces in Biointerfaces Foundation
　　　　Fellow of the American Chemical Society
　　　　Honorary Membership, Chemical Society of Japan
2008　　Priestley Medal from the American Chemical Society
2007　　Langmuir Prize from the American Physical Society
2006　　Remsen Award from the Maryland Section of the ACS
　　　　Honorary Fellow, Cardiff University
2003　　Cotton Medal, Texas A&M University
2002　　National Medal of Science
2000　　American Chemical Society Award for Creative Research in Homogeneous or Heterogeneous Catalysis
　　　　Linus Pauling Medal for Outstanding Accomplishment in Chemistry, American Chemical Society,
　　　　Puget Sound, Portland and Oregon Section
1998　　Wolf Prize in Chemistry
1997　　Von Hippel Award, Materials Research Society
1995　　Chemical Pioneer, American Institute of Chemists
1994　　Adamson Award in Surface Chemistry, American Chemical Society
1990　　Honorary Membership in Hungarian Academy of Sciences
1989　　Peter Debye Award in Physical Chemistry, American Chemical Society
　　　　Senior Distinguished Scientist Award, Alexander von Humboldt Foundation
　　　　E.W. Mueller Award, University of Wisconsin
1986　　Henry Albert Palladium Medal
1983　　Member, American Academy of Arts and Sciences
1982　　Fellow, American Association for the Advancement of Science
　　　　Distinguished Scholar for Exchange with China
1981　　Colloid and Surface Chemistry Award, American Chemical Society
1979　　Member National Academy of Sciences
1978　　Miller Professorship, UC Berkeley
1977　　Emmett Award, American Catalysis Society
1976　　Kokes Award, Johns Hopkins University, Baltimore, Maryland
　　　　Elected Fellow, American Physical Society
1972　　Unilever Visiting Professor, University of Bristol, United Kingdom
1969　　Guggenheim Fellowship
　　　　Visiting Fellow, Emmanuel College, Cambridge, United Kingdom
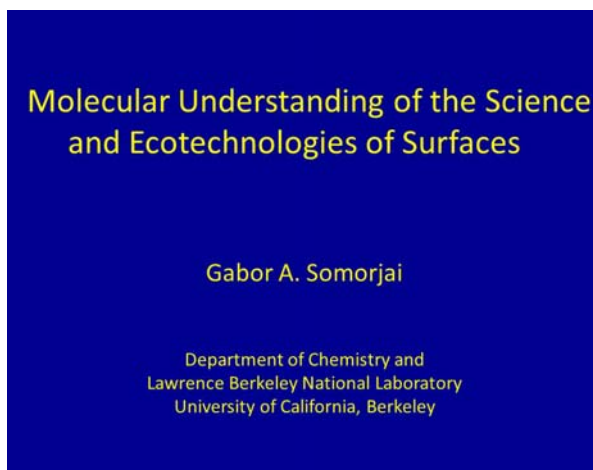
■会員 **Memberships**

　　　　National Academy of Science
　　　　American Academy of Arts and Sciences
　　　　American Chemical Society
　　　　American Physical Society (Fellow)
　　　　American Association for the Advancement of Science (Fellow)
　　　　Cosmos Club, Washington DC

Molecular Understanding of the Science and Ecotechnologies of Surfaces

Gabor A. Somorjai

I am deeply honored and grateful to receive the Honda Prize for my research in surface science and catalysis, which has led to a molecular understanding of these important fields of science and ecotechnologies. The ecotechnology concept of the Honda Foundation that leads to the implementation of technologies for sustainable development is very important in the 21st Century. In this lecture, I would like to suggest that the success rate of eco-engineering is greatly increased by connecting it to science pursued on the atomic and molecular level. In turn, pursuit of ecotechnological goals has led to some of the most innovative science. (Fig 1)
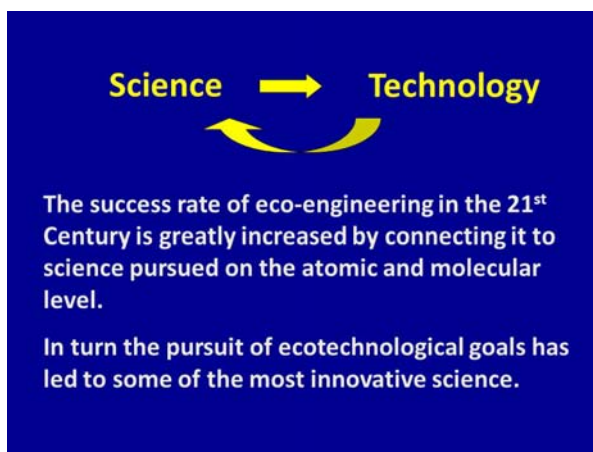
Fig 1
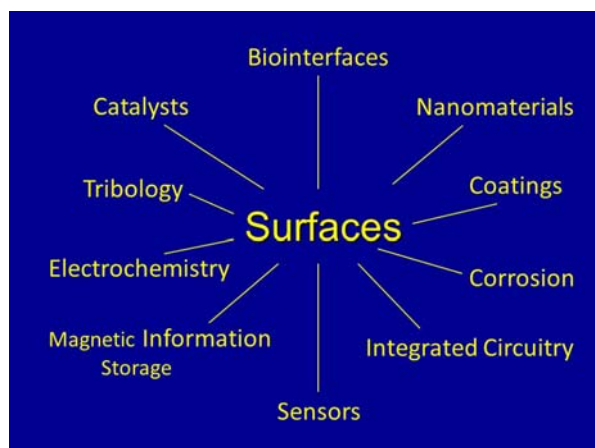
Fig 2 Major Applications of Surfaces

Surfaces have many applications that impact our daily lives (Fig 2). Of these many applications I chose catalysis and biointerfaces as the focus of my investigations over the decades. This lecture deals with catalysis and, by necessity, nanomaterials because most catalysts are nanoparticles. I shall attempt to explain what catalysis is and why it is playing such an important role in human life, including the ecotechnologies developed by Honda Motor Co., Ltd. I will also explain how a combination of developments of experimental studies and instrumentation led to an understanding of this phenomenon at the molecular level, which in turn propelled catalysis to the frontier of science and technologies in broad fields of human enterprise.

Evolution and achievements of Surface Science

What are surfaces? Figs 3a, 3b, and 3c show three types of surfaces. Fig 3a shows external surfaces ranging from single crystals (flat, stepped and kinked platinum surfaces) to the green leaf.
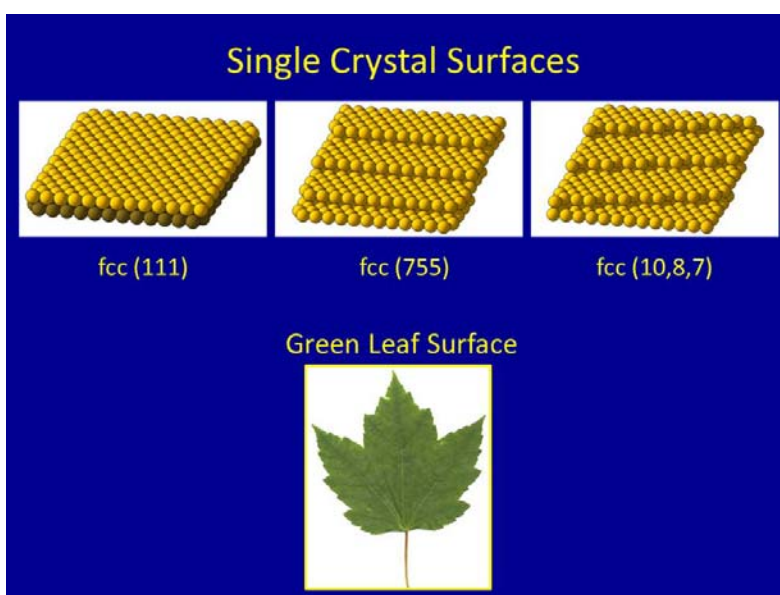
Fig 3a External Surfaces
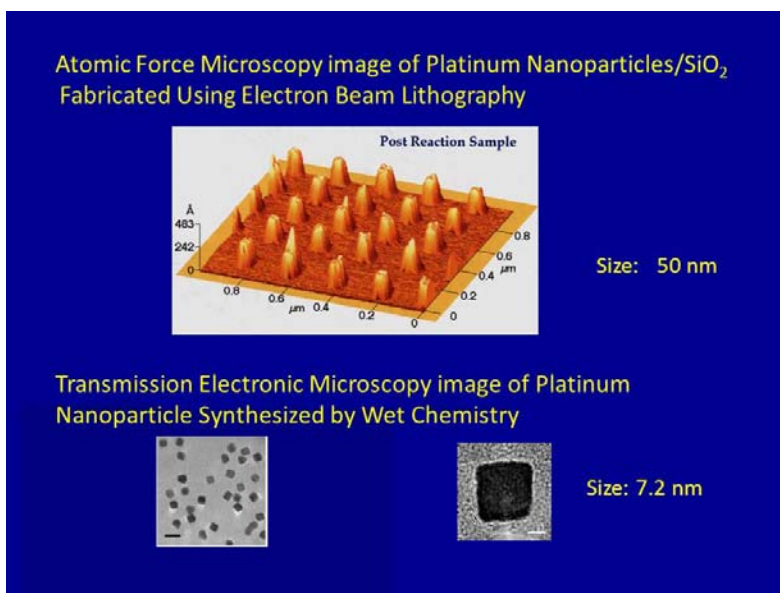
Fig 3b Nanoparticle Surfaces
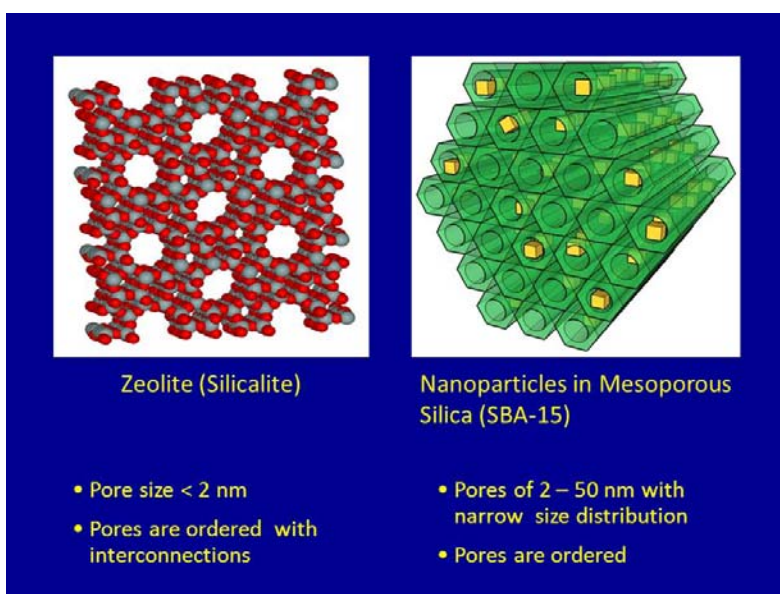
Fig 3c Internal Surfaces

Fig 3b shows nanoparticle surfaces that can be catalysts and also provide the ordered transistor components in the integrated circuit elements of a computer. Fig 3c shows internal surfaces of solids full of micropores or mezopores, such as the structures of the human bone or devices that adsorb large amounts of gases or fluids. The study of modern surface science began with the discovery of the transistor, an amplifier device to be substituted for the radio tube, and through the practice of space sciences. As transistors were made smaller and smaller, they became faster and faster as the transmission of electrons became more rapid. This gave rise to the technology quest of ever larger surface to volume ratios. Using the

ultrahigh vacuum technology developed by space sciences, device surfaces could be studied free of impurities to determine and control their properties on the atomic scale.

Nanosciences
Monodispersed nanoparticles 2D and 3D

Applications in <u>Catalysis</u>, <u>Tribology</u>, <u>Polymers</u>, <u>Biointerfaces</u>, <u>Microelectronics</u>, <u>Energy Conversions</u>, <u>Environmental Chemistry</u>

<u>Surface Instruments at High Pressures</u>, <u>Liquid Interfaces</u> (STM, SFG, AFM, QCM, RAIRS)

<u>Surface Dynamics</u>
Rapid energy transfer between incident and product molecules
Mobility of the adsorbed molecules along surfaces during catalytic turnover

<u>Surface Thermodynamics</u>
Adsorbate coverage dependent heats of adsorption
Coadsorption induced ordering
Surface segregation

<u>Surface Structure and Bonding</u>
Clean surface reconstruction
Adsorbate induced restructuring
Surface defects (steps, kinks) are chemically active

<u>Model Surfaces - Single crystals</u>, (Metals, Semiconductors)

<u>Surface Instruments in Vacuum</u> (XPS, AES, LEED, SIMS)

Fig 4 Evolution of Surface Science

Fig 4 shows the surface science evolution in the 1965-1985 periods. The techniques to study surfaces were electron, ion and molecule scattering, from clean surfaces of metals and semiconductors. These studies uncovered the structure and bonding of surface atoms and molecules, and the thermodynamics and dynamics of their adsorption, energy transfer and mobility that leads to surface chemical reactions.

However, the most important surface phenomena that are part of our everyday lives occur at high pressures and liquid interfaces, and not in vacuum, which was the focus of the early surface science studies. In order to understand the molecular surface properties that play key roles in corrosion, energy conversion, biointerfaces, environmental chemistry, friction and lubrication I spent the next 25 years developing techniques that could be utilized *to study the molecular properties of surfaces at the buried solid-gas and solid-liquid interfaces (Fig 4).* Since I wanted to understand catalytic reactions on surfaces I had to extend my studies to nanomaterials in the 1990s, since most catalysts are nanoparticles.
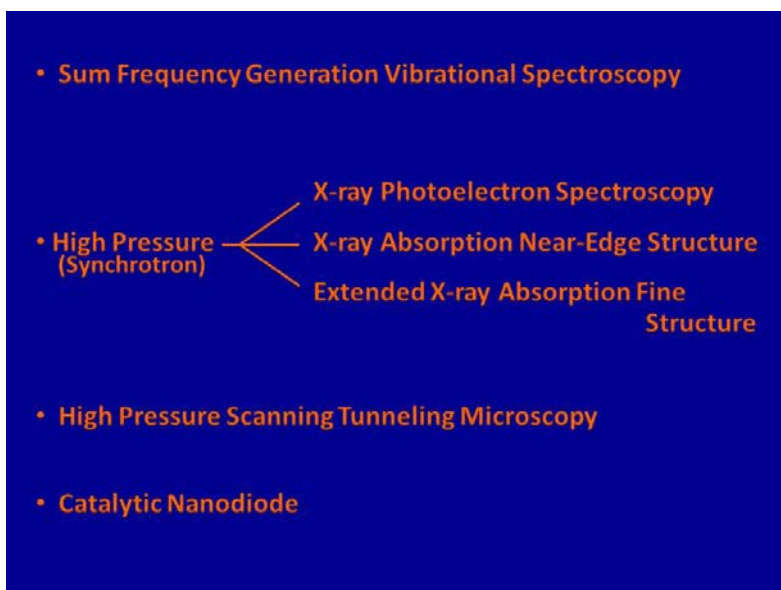
Fig 5 In-situ techniques for molecular studies of high-pressure gas and liquid interfaces

The techniques I utilized in Berkeley, some of which were developed there, are shown in Fig 5, and I shall show their applications in molecular studies later.

I would like to introduce briefly some of the ecotechnologies that use surfaces almost exclusively. These include the catalytic converter on automobiles (Fig 6a) that is responsible for removal of pollutants in urban areas like the Los Angeles basin (Fig 6b).
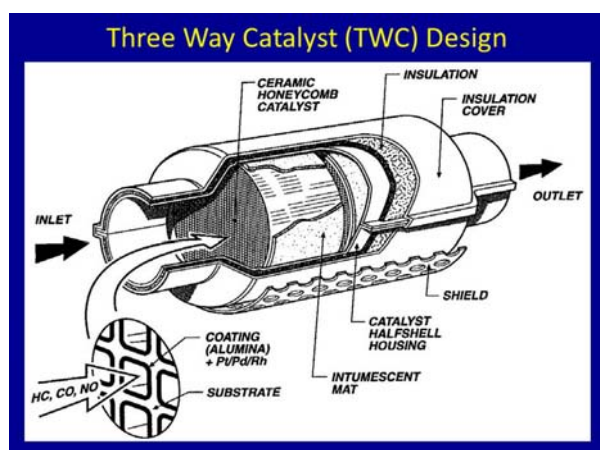
Fig 6a Three-way Catalyst (TWC) Design
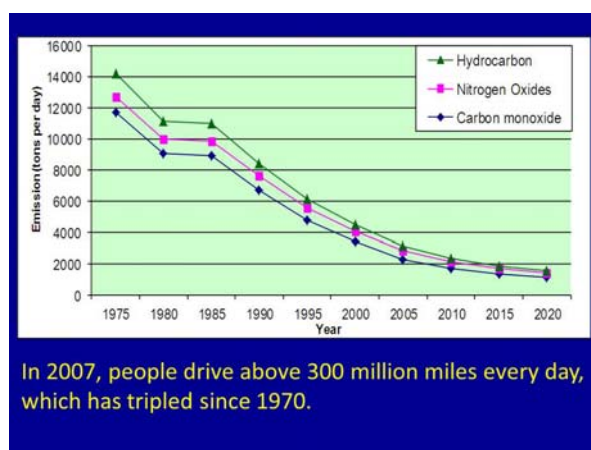
Fig 6b Emission from Automobiles in Los Angeles

Energy efficiency through reaction selectivity, commonly called "clean manufacturing" or "green chemistry," means chemistry that yields only the desired molecule without any waste by-products.

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Examples include the production of high-octane gasoline (Fig 7a), isotactic polymerization (Fig 7b), and synthetic fuel production from synthetic gas, CO and H_2 (Fig 7c). Biointerfaces produced via implant technologies (Fig 7d) is a rapidly growing area of biotechnology that is responsible for the steadily growing life expectancy of humans.
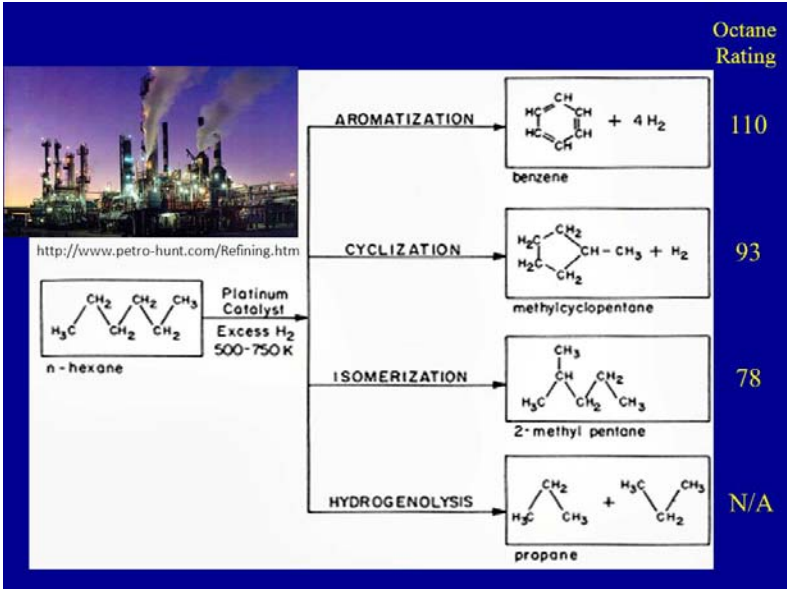
Fig 7a Reforming with Pt. catalysts
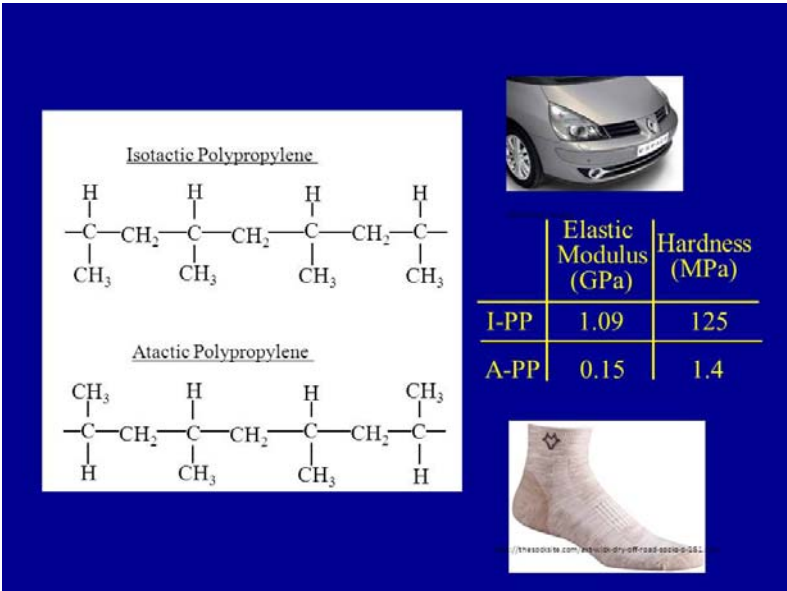
Fig 7b Tacticity of Polypropylene
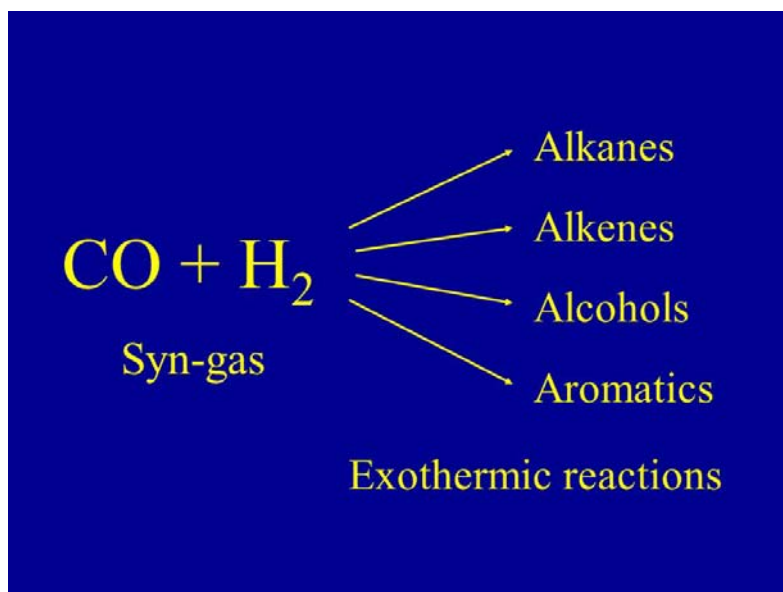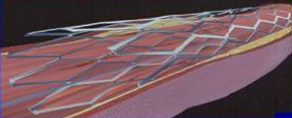
Fig 7c Fuels and Chemicals
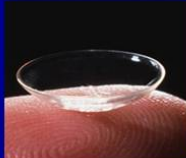
Fig 7d Biointerfaces and Medical Devices

Approaches to nanoparticle catalyst

Let me turn to catalysis, which has been the focus of most of my studies past and present. Catalysts are nanoparticles usually categorized into three distinct classifications: enzyme, homogeneous and heterogeneous. Examples in Fig 8 show that sizewise, these nanoparticles are in the 1-8 nanometer range.
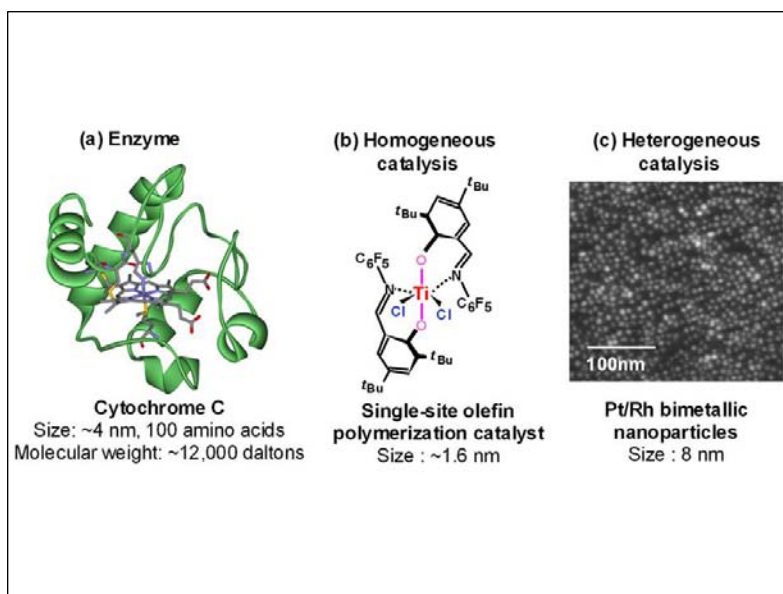
Fig 8 Catalysts are Nanoparticles

In attempting to move from single crystals surfaces to nanoparticles (NPs) for utilization as heterogeneous catalysts (Fig 9a), our early efforts to synthesize them following the nanolithography technology practiced in the microelectronic industry did not succeed. The smallest nanofeatures (dots, rods) we could produce were 25 nm, much larger than the particle sizes of catalysts which are in the 1-10 nm range (Fig 9b).
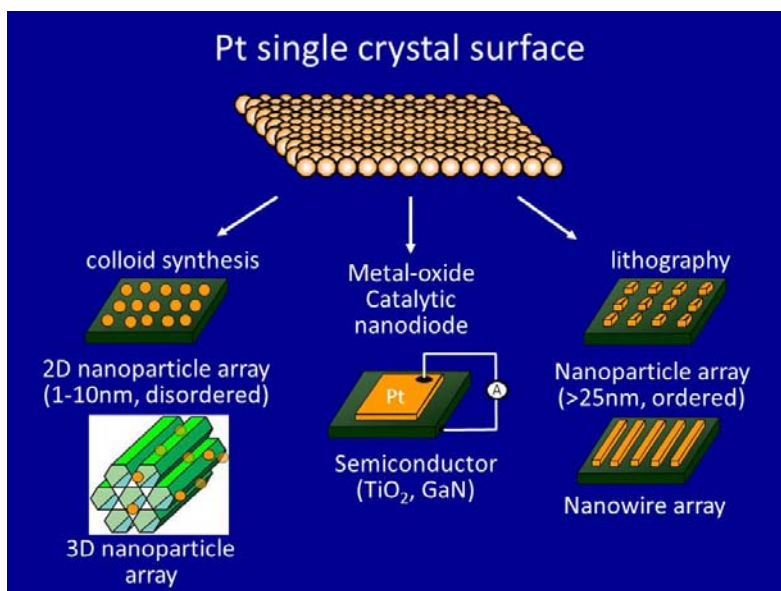
Fig 9a Evolution of the Model Catalyst System
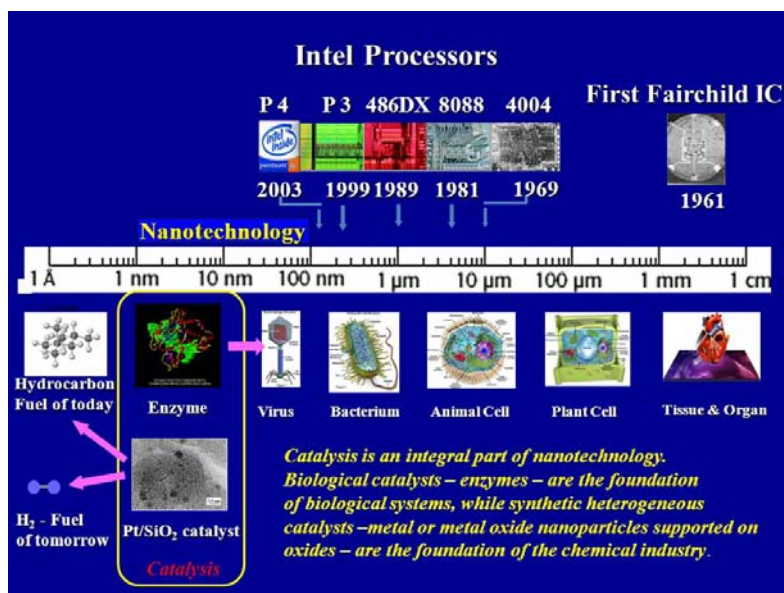
Fig 9b Technically and Biologically Important Length Scales

We then turned to colloid science technologies, which are shown in Figs 10a, 10b, 10c, 10d, and 10e. This proved very successful. The metal nanoparticles are capped by an organic surfactant or polymer that prevents their aggregation and permits their storage. The porous nature of these caps allows molecular penetration and reactions on the metal surface. A cap can also be removed to obtain clean NPs.
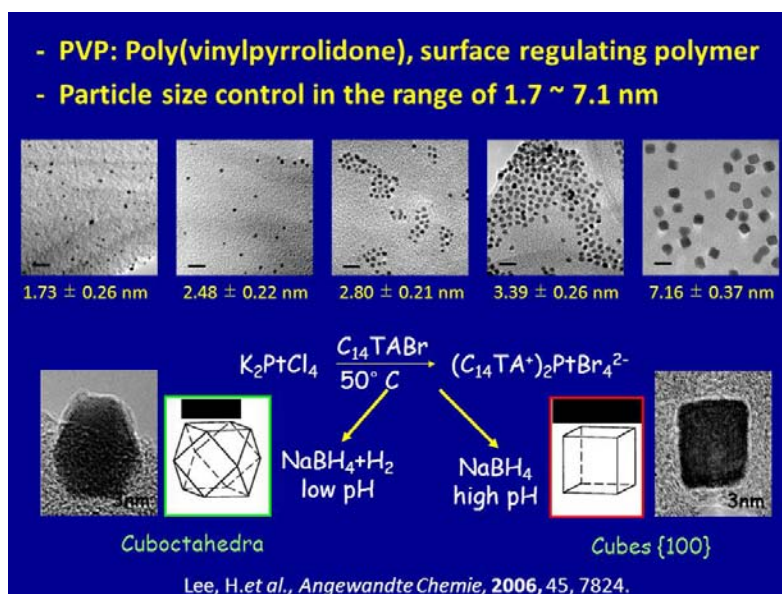
Fig 10a Control of Size and Shape of Pt Nanoparticles
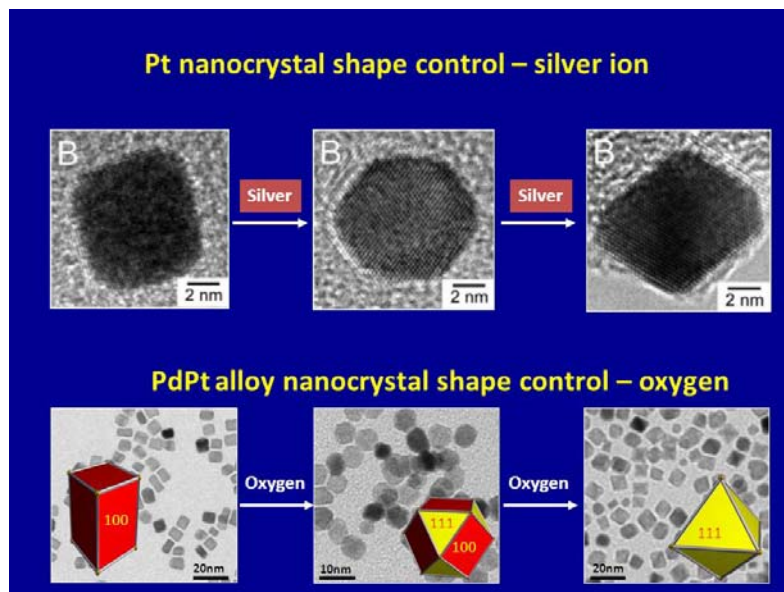
Fig 10b Pt and PdPt Alloy Nanocrystal Shape Control
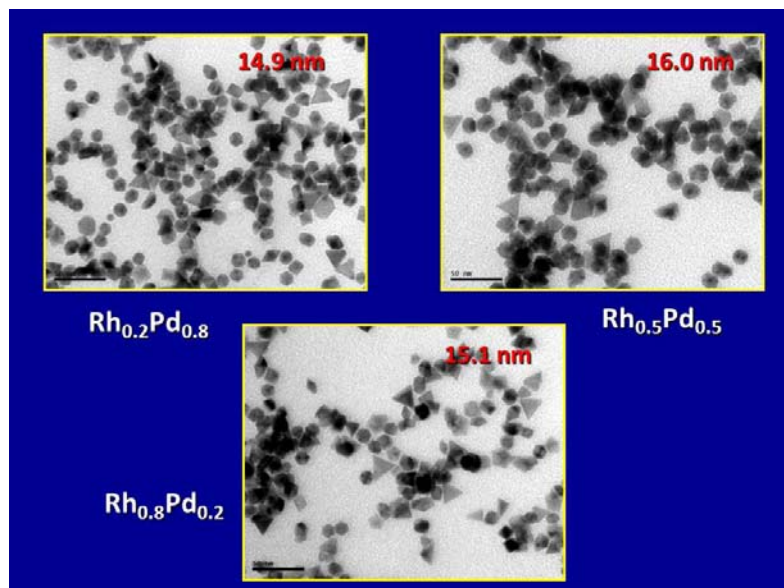
Fig 10c TEM Images of Rh_xPd_{1-x} Nanocrystals

Using inorganic oxide caps, which are also porous, the thermal stability of the metal NPs can be greatly improved (Fig 10d) to overcome the low melting points associated with the small size NPs (Fig 10e).
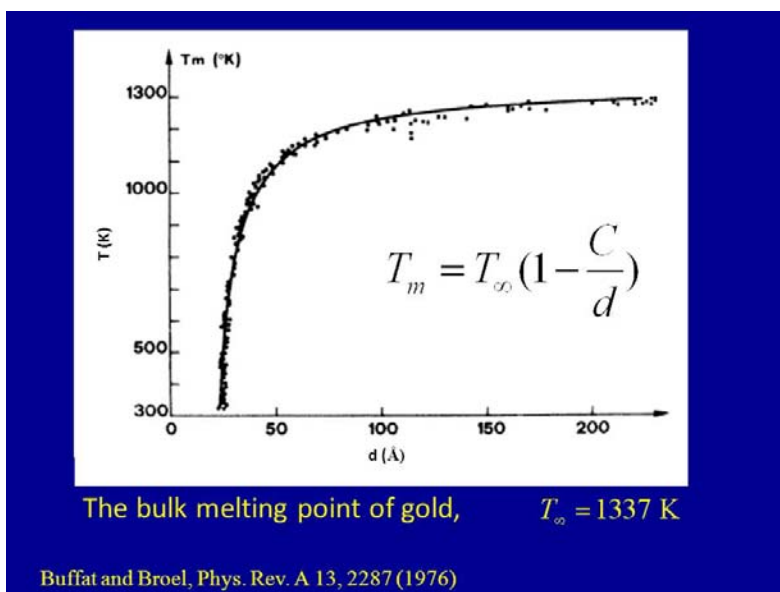
Fig 10d The Size Effect on the Melting Point of gold
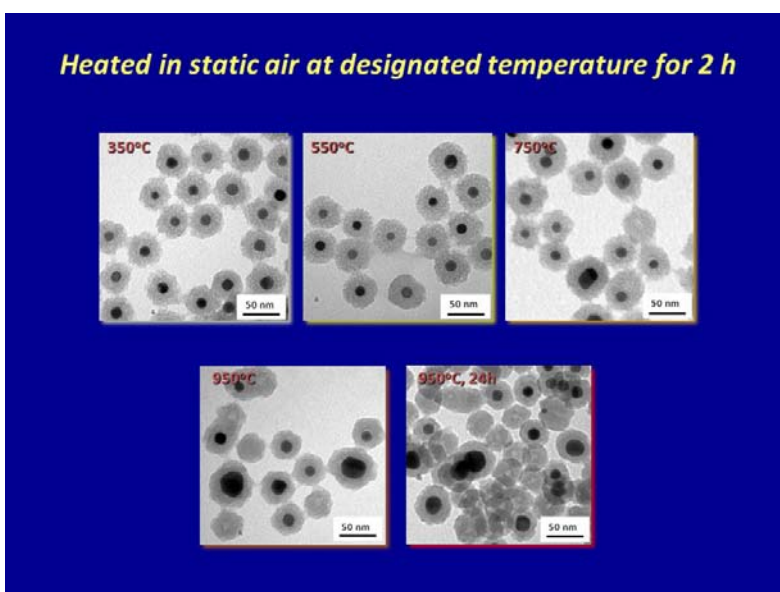
Fig 10e Pt@SiO$_2$ core shell structures of NPs with increased thermal stability

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Catalytic selectivity of metal nanoparticles

In the 20th Century much of catalysis science focused on understanding reactions that formed one product; ammonia synthesis, ethylene hydrogenation, carbon monoxide oxidation. In the 21st Century the focus is on catalytic selectivity; how to make only one molecule out of several possible product molecules. (Fig 11).
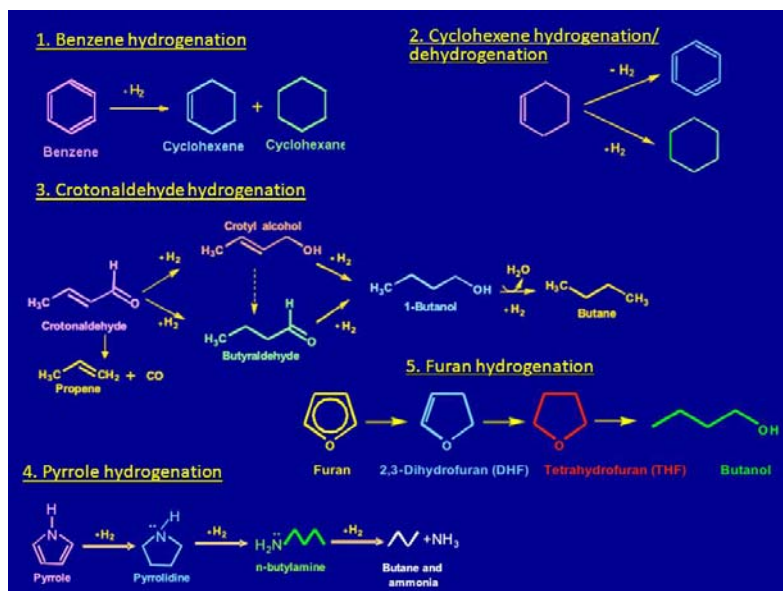
Fig 11 Reaction product selectivity in Multipath catalytic reactions

We studied many multipath reactions and the conclusion of the studies is that *size and shape of metal nanoparticles control both catalytic reaction rates and selectivities.*

We show a few examples of this finding (Figs 12a, 12b, 12c, 12d, and 12e). Clearly, the size and shape of the nanoparticles control the product distribution.
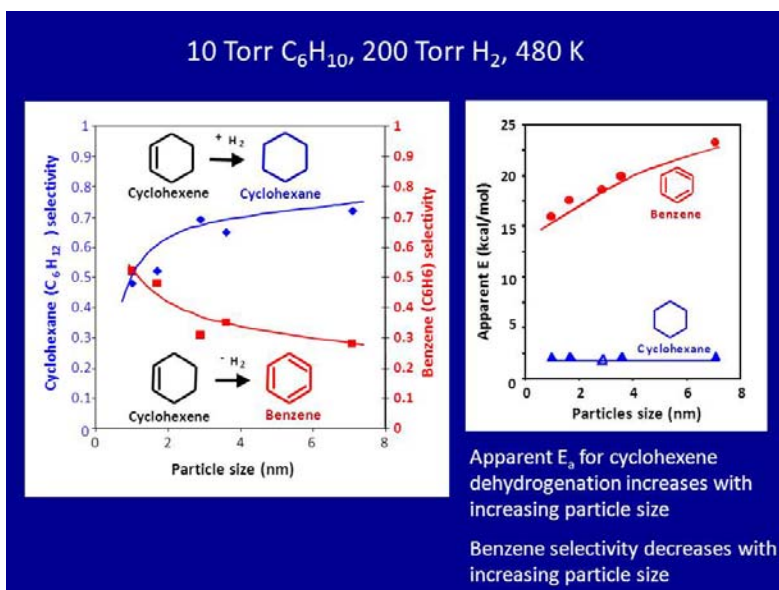
Fig 12a Effect of Pt Particle Size on Selectivity in Hydrocarbon Conversion Reactions: Cyclohexene Hydrogenation/Dehydrogenation
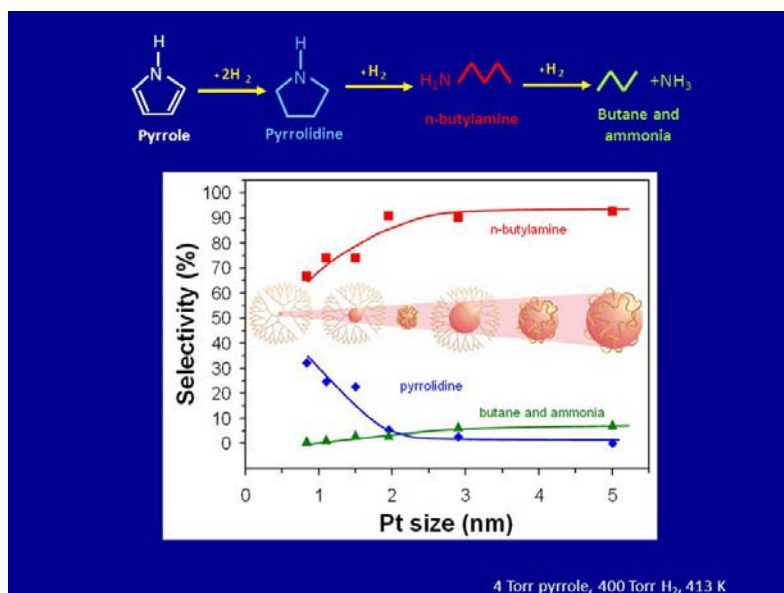
Fig 12b Pyrrole Hydrogenation over Pt NPs: Effect of Particle Size
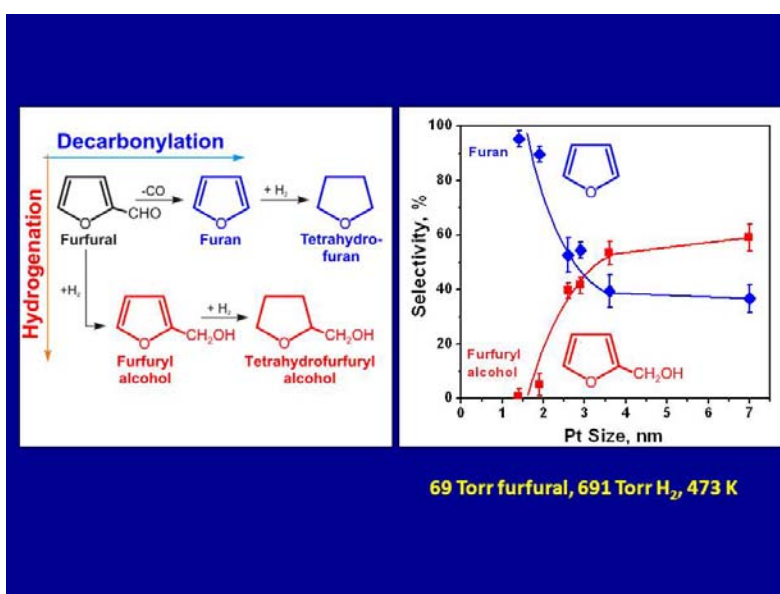
Fig 12c Catalytic Furfural Chemistry over Pt NPs. Effects of Particle Size
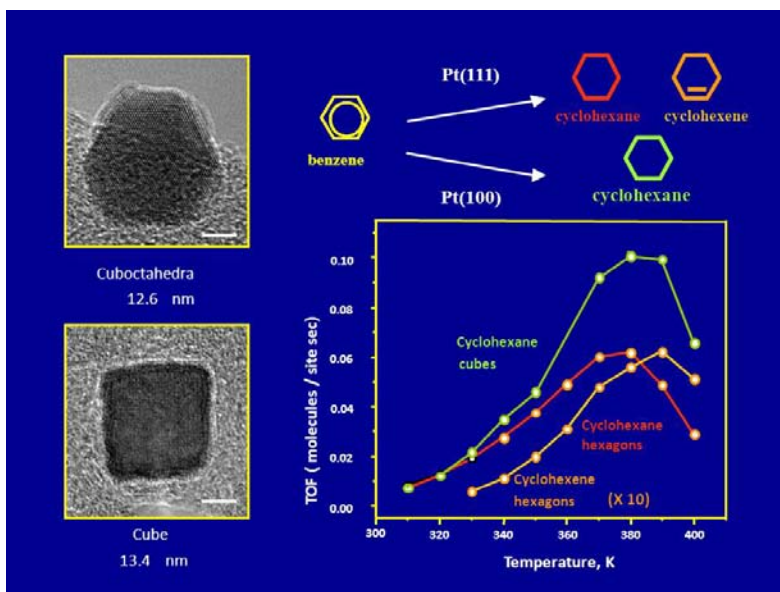
Fig 12d Benzene Hydrogenation over Platinum Single Crystals and Different Shapes of NPs
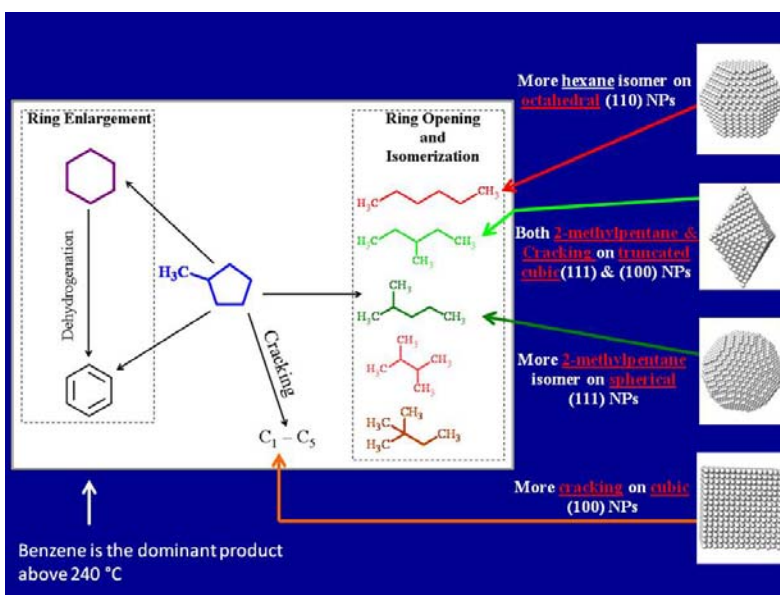
Fig 12e Selective rearrangements of Methylcyclopentane in the presence of hydrogen
on platinum nanoparticles of 6 nm Size and different shapes

The process of this control of product distribution by using selected NP sizes and shapes, we call nanocatalysis (Fig 13)
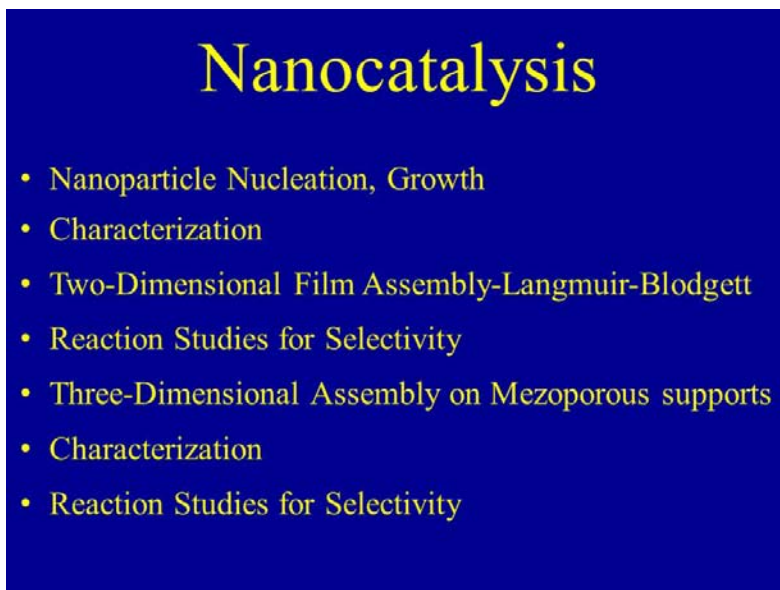
Fig 13

The question is why this is happening and why it was not utilized for the selective production of molecules earlier. This brings to focus the flaw of catalytic studies in the past. Catalysts were usually studied before-use and after-reaction. The lack of instruments and experimental techniques to study the working catalyst while the catalytic reaction is in progress was the reason for focusing on prenatal and postmortem studies.

The many techniques that are presently available to elucidate the structural and chemical dynamics of the catalytic process. Below we show how the new techniques identify the molecular factors that control catalytic selectivity.

Sum Frequency Generation (SFG) Vibrational Spectroscopy

The unique surface sensitivity of SFG permits detection of reaction intermediates in catalytic surface reactions (Figs 14a, 14b, 14c, 14d, 14e and 14f).
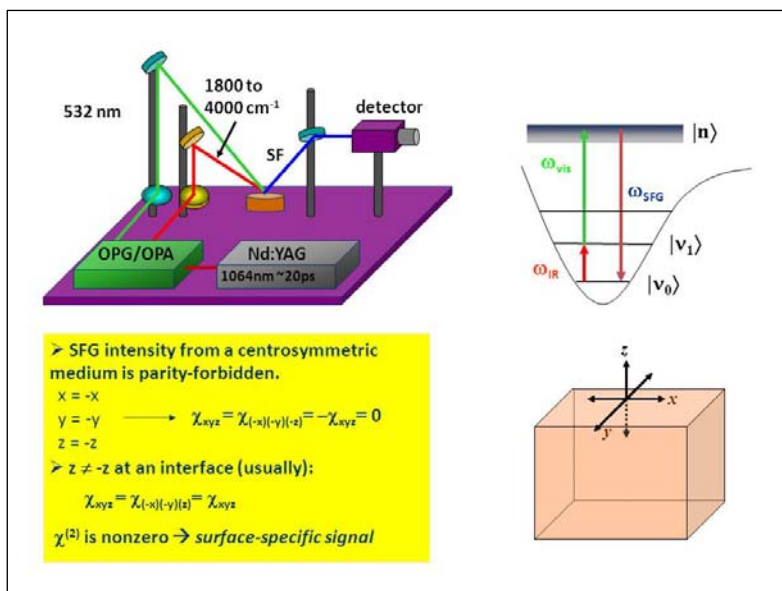
Fig 14a Sum Frequency Generation *in situ* Surface-Specific Vibrational Spectroscopy
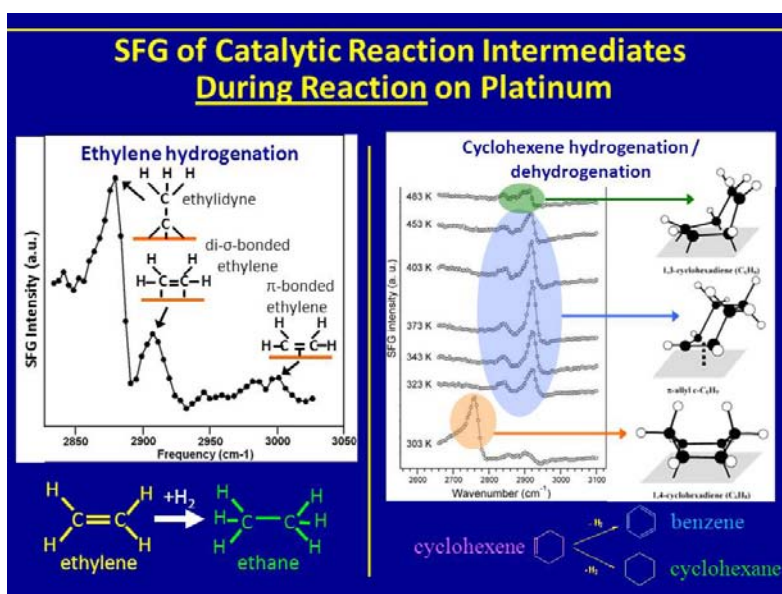
Fig 14b and 14c   Reaction intermediates during ethylene hydrogenation
and cyclohexene hydrogenation and dehydrogenation
on platinum surfaces
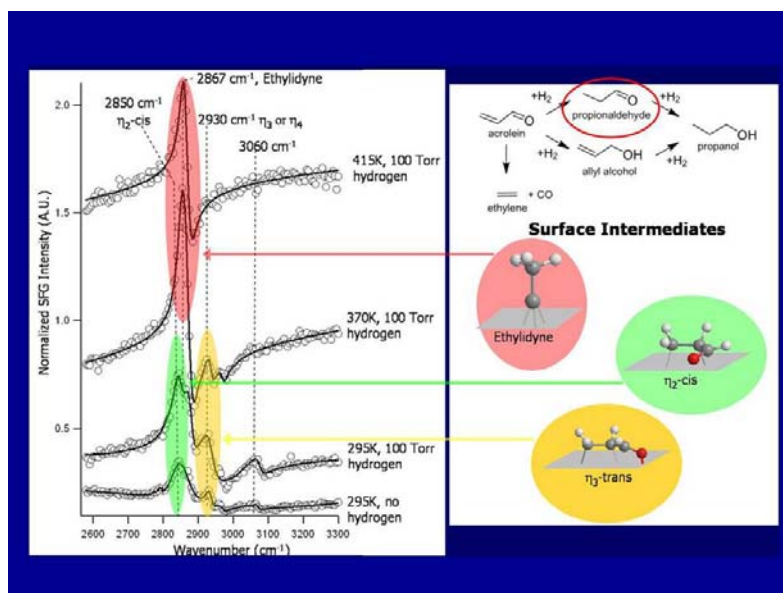
Fig 14d   Reaction intermediates during acrolein hydrogenation over Pt.
temperature dependence.
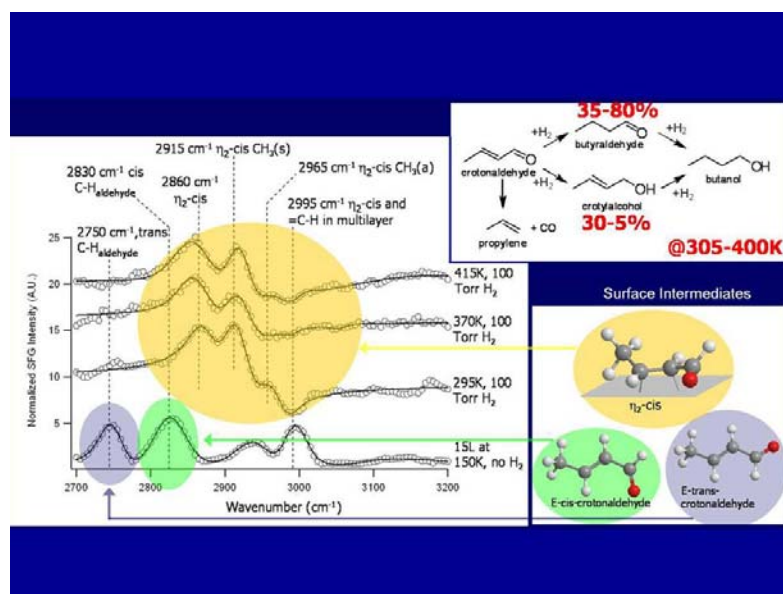
Fig 14e Reaction intermediates during crotonaldehyde Hydrogenation on Pt.
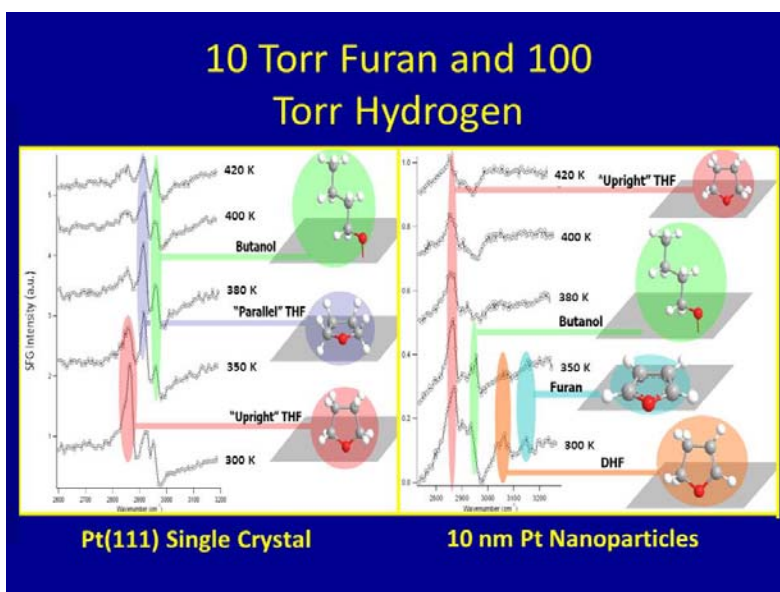
Fig 14f   Reaction Intermediates during furan hydrogenation over Pt (111)
single crystal and 10 nm size Pt nanoparticle

Surface composition detected under reaction conditions by ambient pressure X-ray photoelectron spectroscopy
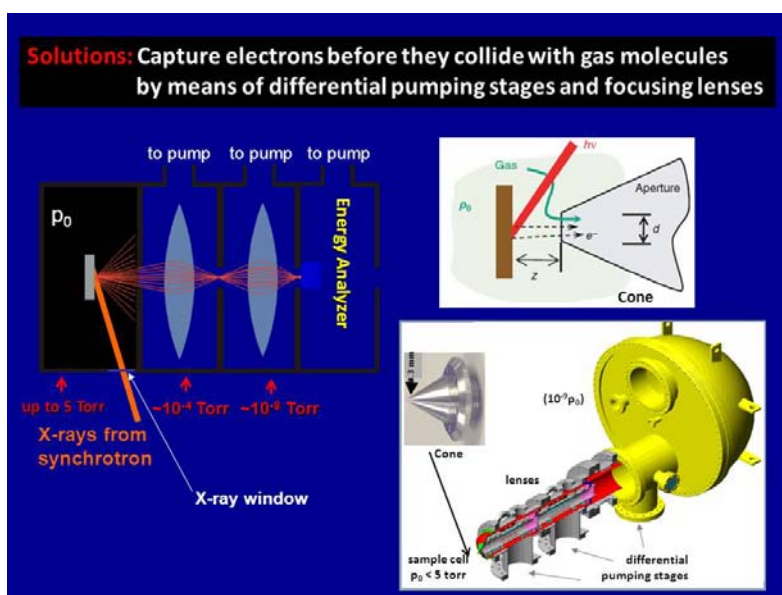
Fig 15a Ambient-pressure X-ray photo- Electron spectroscopy techniques (XPS)

Bimetallic nanoparticles undergo surface composition change driven by changing chemical (oxidizing and reducing environment) (Figs 15a, 15b and 15c)
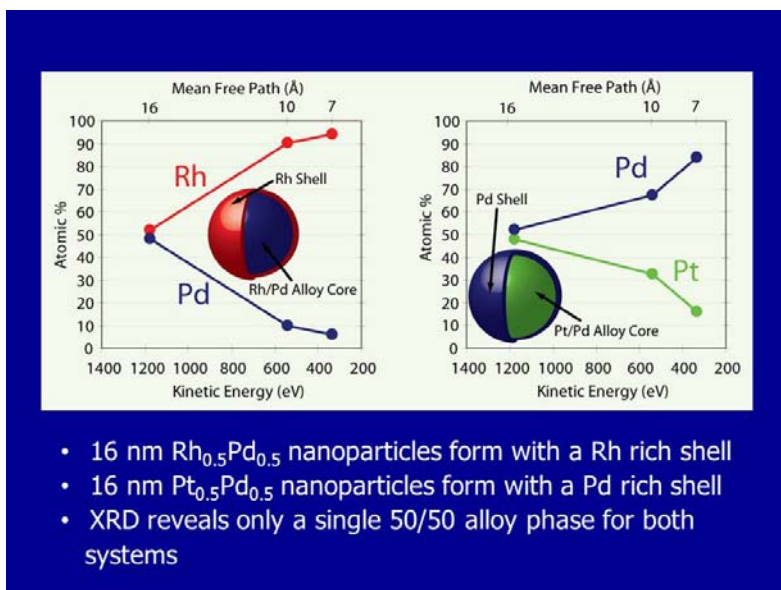
Fig 15b Core-Shell Structure Probed by Synchrotron XPS.
Surface segregation of Rhodium in $Rh_{0.5}Pd_{0.5}$ and palladium in $Pd_{0.5}Pt_{0.5}$ in vacuum.
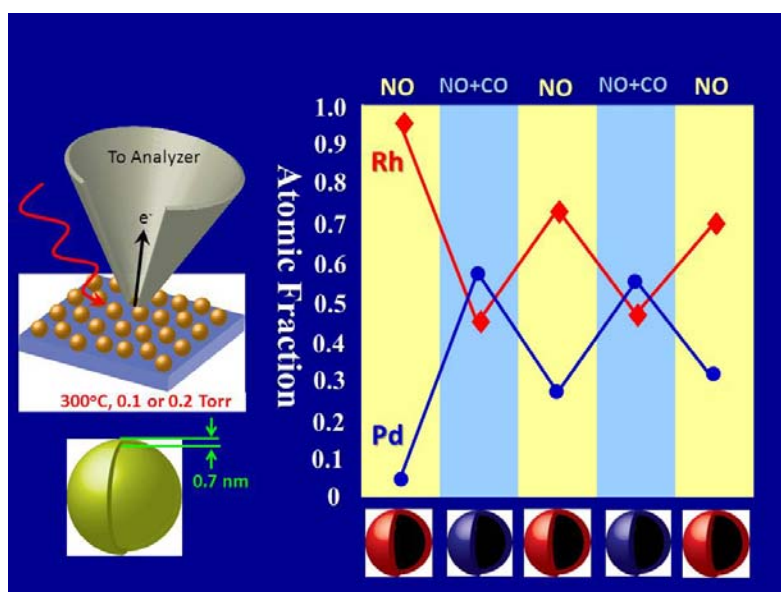
Fig 15c Restructuring of $Rh_{0.5}Pd_{0.5}$ nanoparticles during reactions with oxidizing NO and reducing CO

High Pressure Scanning Tunneling Microscopy Detects Adsorbate Mobility and Adsorbate-Induced Restructuring of Metal Surfaces
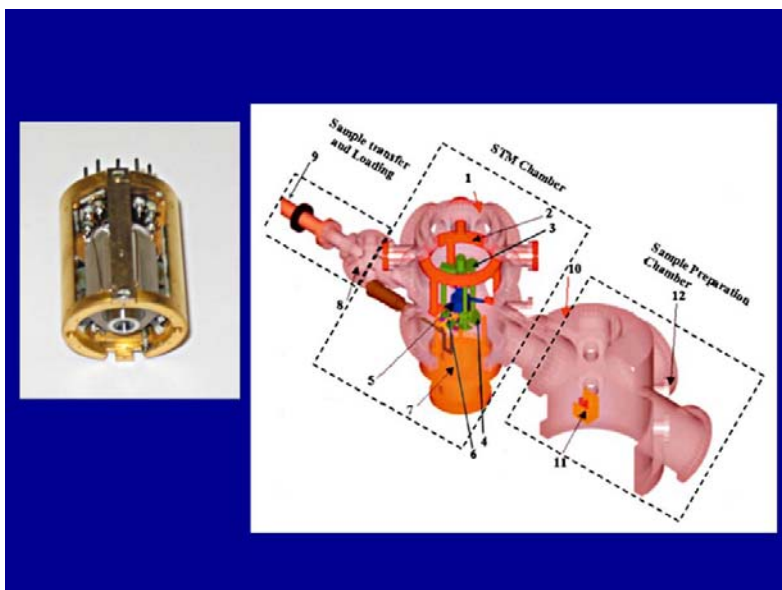
Fig 16a Scanning tunneling microscopy working under high-pressure conditions
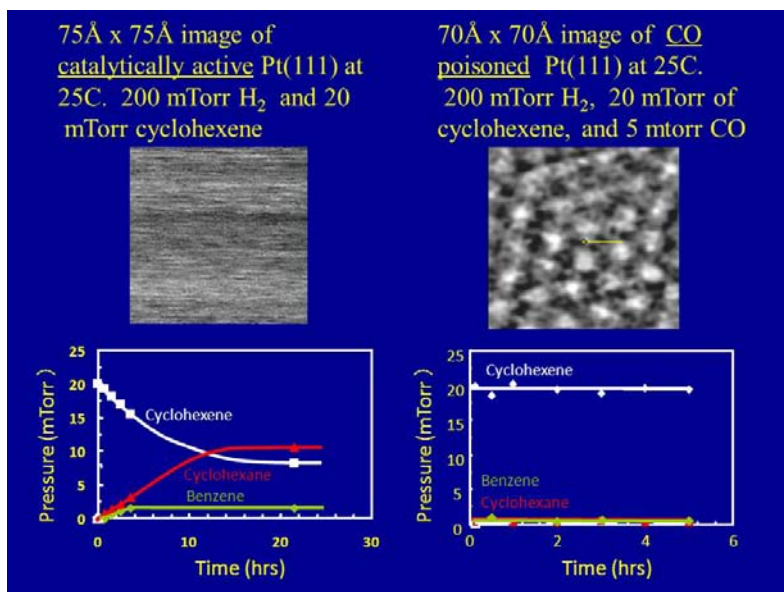
Fig 16b High-pressure STM reaction studies:
The role of surface mobility under reaction conditions.
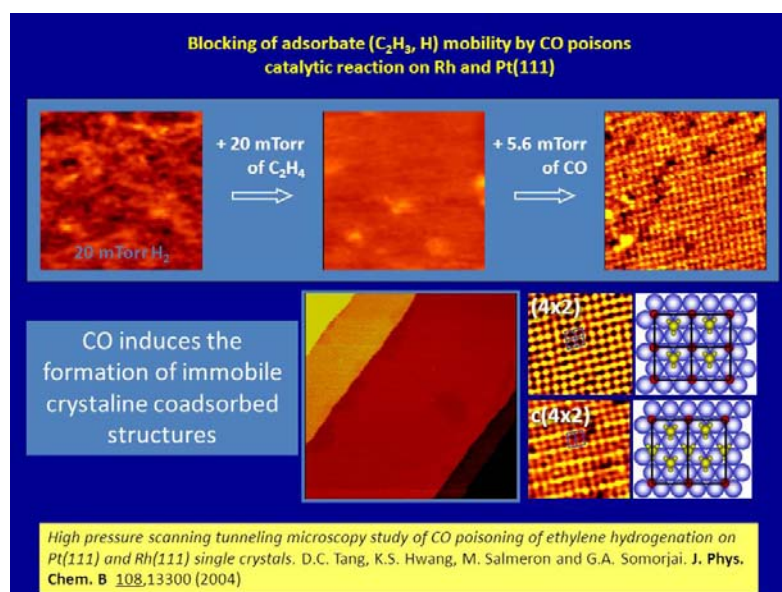
Fig 16c   Blocking of adsorbate (C2H3 H) Mobility by CO poisons catalytic
reaction of Rh and Pt
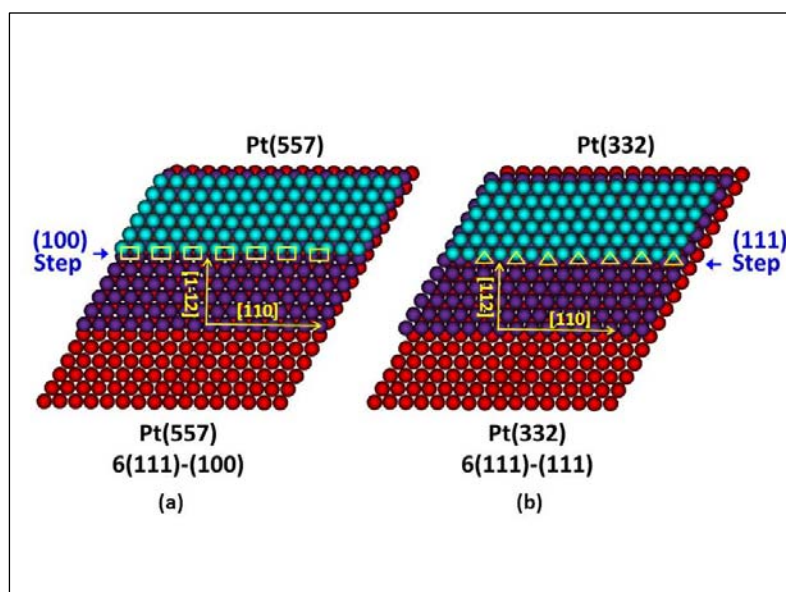
Fig 16d Surface structure of Pt (557) and Pt (332) stepped crystal surfaces.
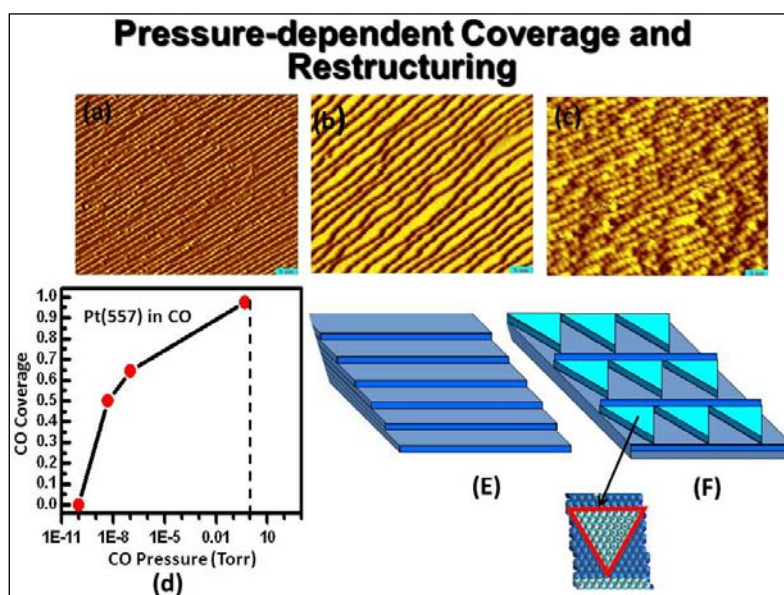
Fig 16e Pressure-dependent CO coverage and clustering of platinum atoms
at high coverage of CO
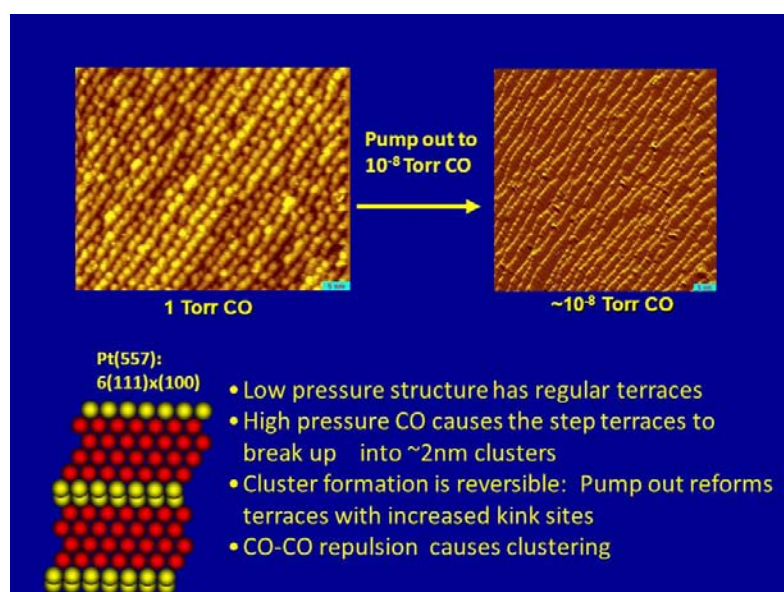
Fig 16f Reversible CO-induced Restructuring of stepped platinum surface

There are several molecular factors that control catalytic selectivity, which could be detected by techniques that monitor the catalyst surfaces under reaction conditions (Fig 17). In addition, there are two more important molecular factors that could be identified in catalytic reactions.
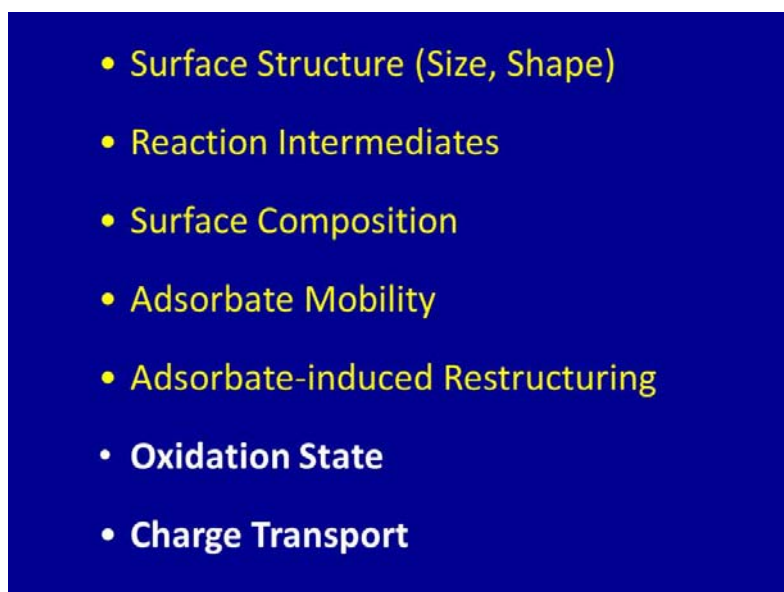
Fig 17 Molecular factors that control catalytic selectivity at surfaces

Change of Metal Oxidation State with Decreasing Size of Metal Nanoparticles which also Permits Heterogenizing Homogeneous Catalysts.

High oxidation state of small size nanoparticles permits their ability to carry out homogeneous catalytic reactions using small (0.8 nm to 1.5 nm) size heterogeneous NP metal catalysts (Figs 18a, 18b and 18c).
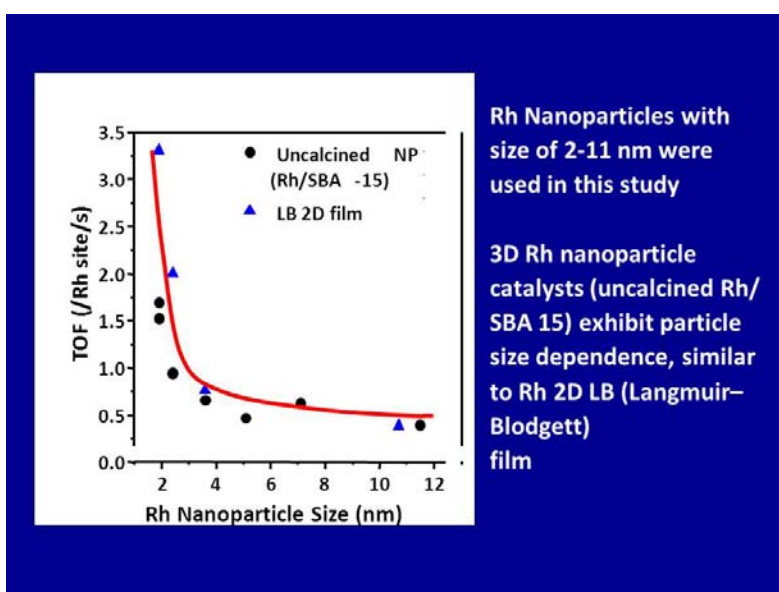
Fig 18a Size dependence of CO oxidation state activity
(100 Torr of O_2, 40 Torr of CO, and 443K) on rhodium nanoparticles.
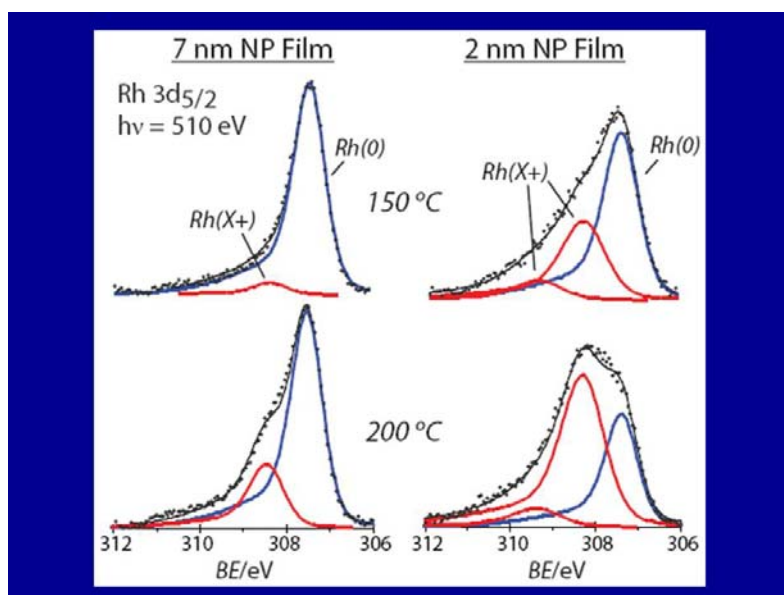
Fig 18b Change of rhodium nanoparticle state oxidation state with NP size
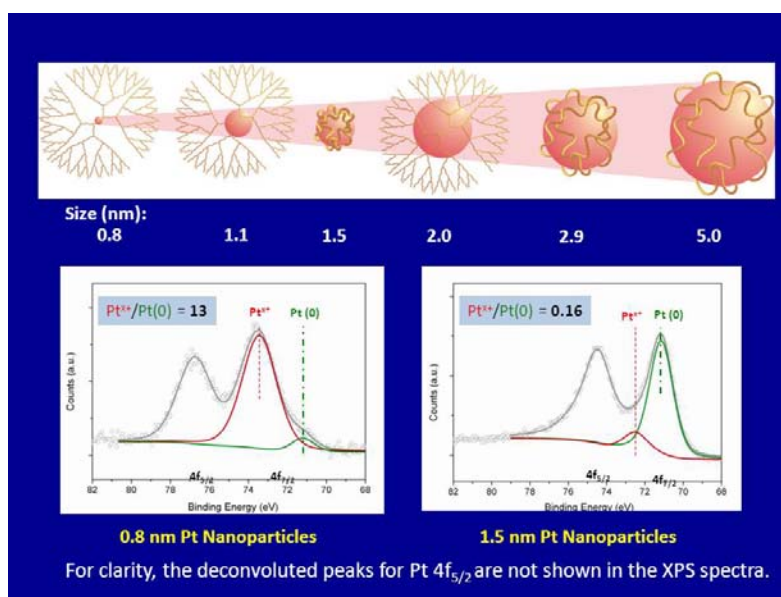
Fig 18c Oxidation state changes with the size of Pt nanoparticles

Conversion of Homogeneous to Heterogeneous Catalysis using Dendrimers
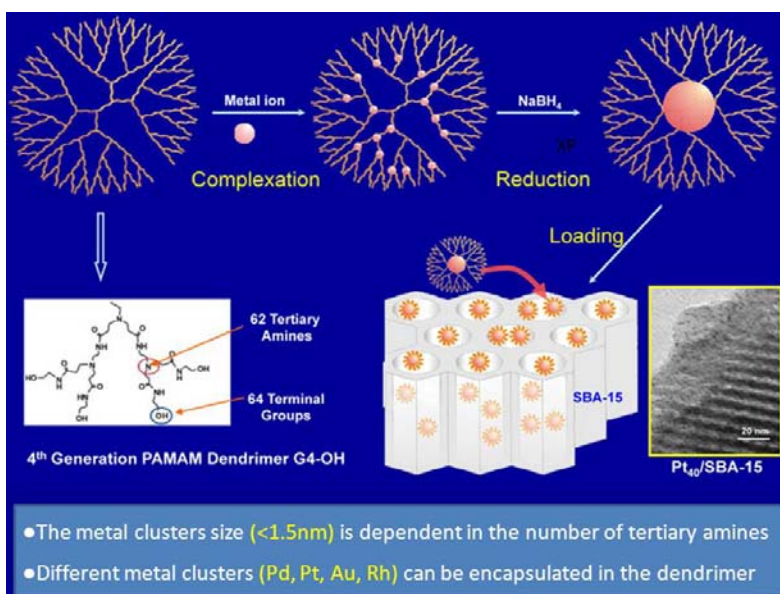
Fig 19a Catalyst Preparation and Characterization
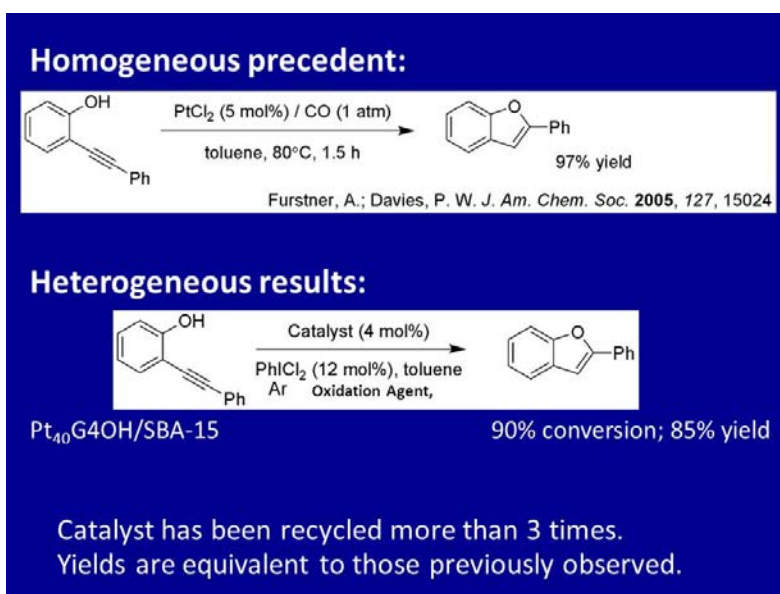
Fig 19b Solution-phase heterogeneous catalysis of homogeneous reaction with dendrimer encapsulated ~ 1 nm Pt_{40} nanoparticles supported on SBA-15
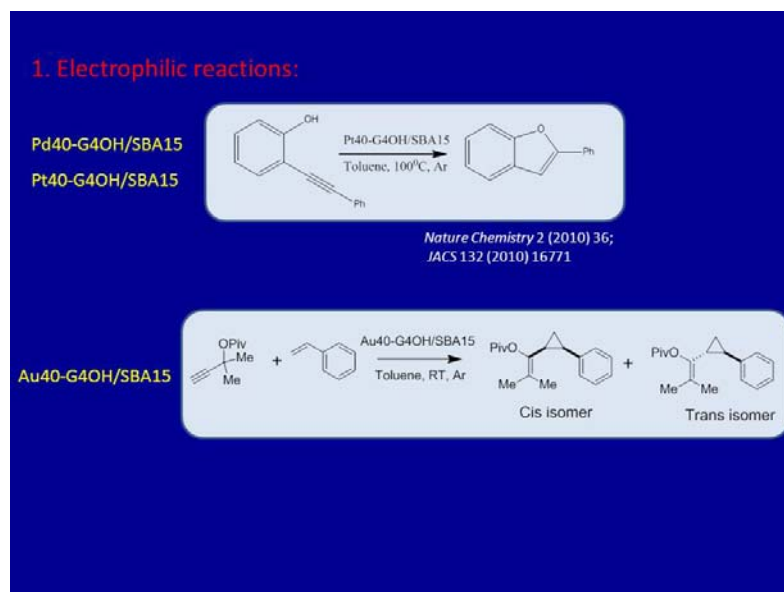
Fig 19c Heterogenization of homogeneous reactions (Electrophilic reactions)
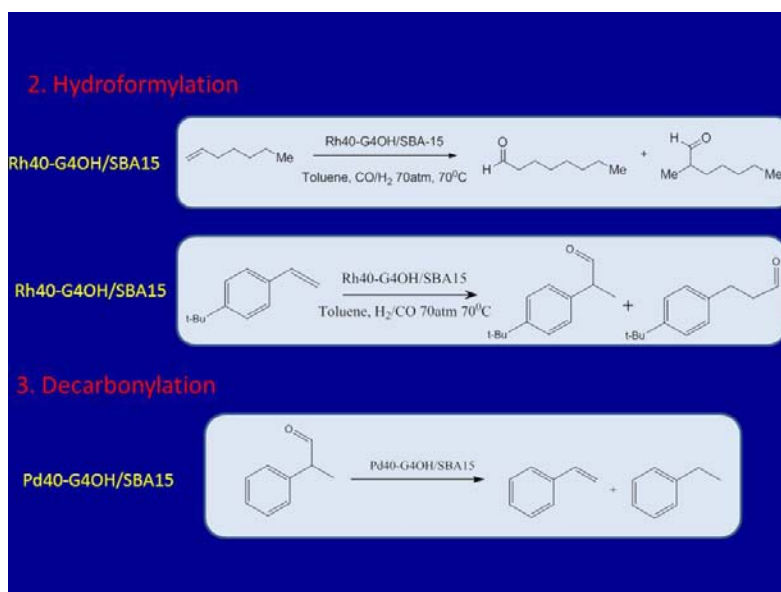
Fig 19d Heterogenization of homogeneous reactions (Hydroformylation and Decarbonylation)
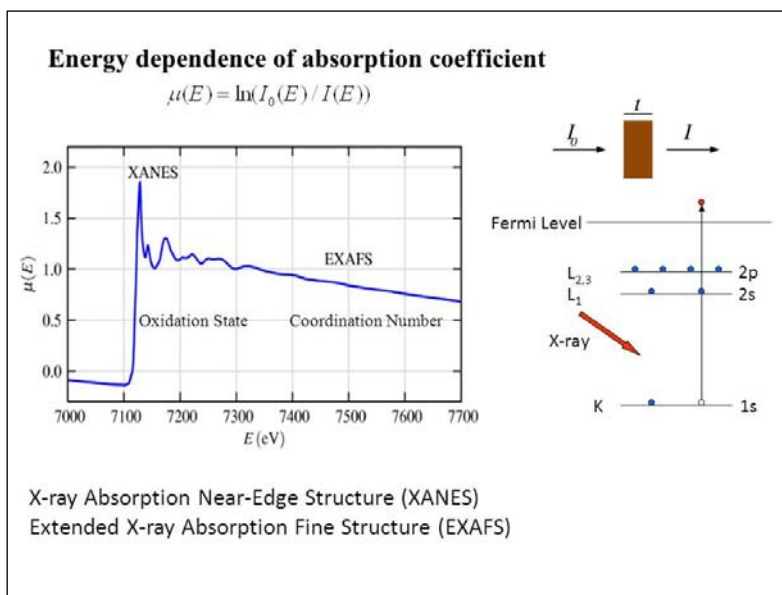
Fig 19e X-Ray Absorption Spectroscopy (XAS): What we measure?
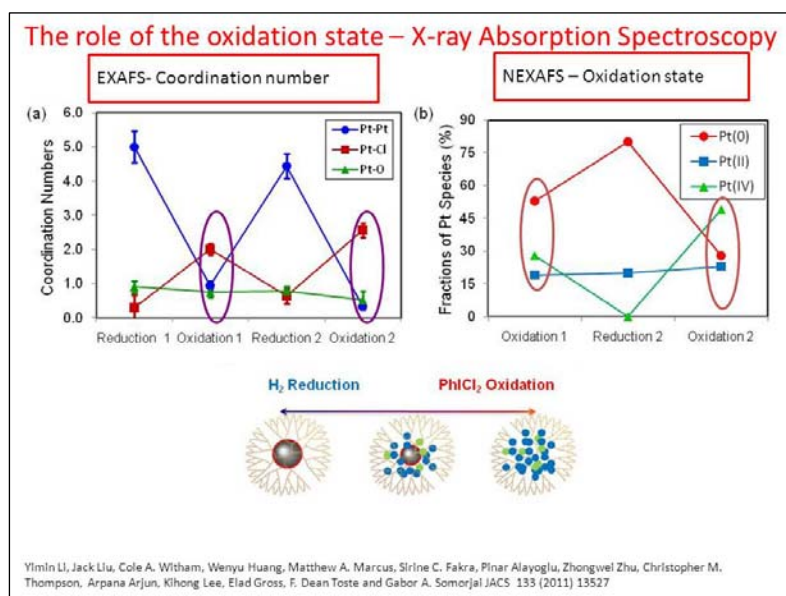
Fig 19f The role of the coordination number and oxidation state during heterogenizing homogeneous reactions using metal cluster on dendrimer supports.

Charge transport and catalysis at oxide-metal interfaces
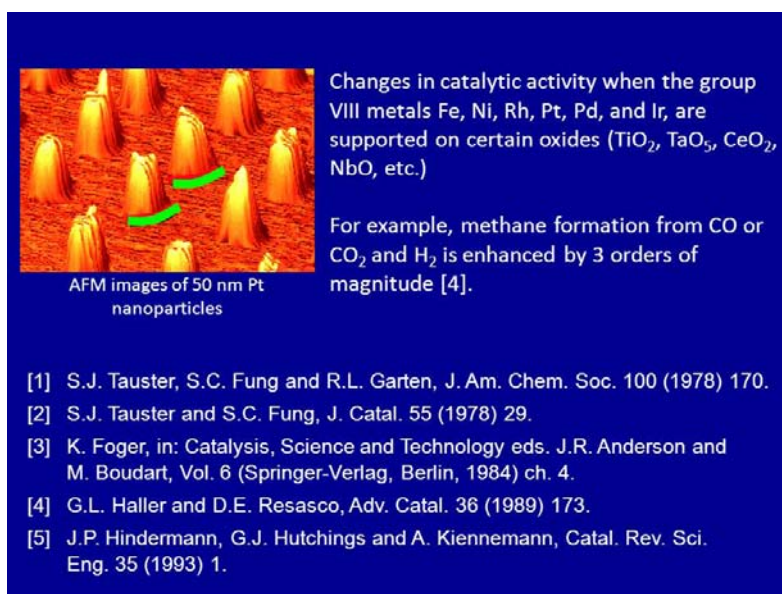
Fig 20a Strong Metal-Support Interaction (SMSI) Effect

Hydrogen and carbon monoxide catalytic oxidation generates a steady electron flow across platinum (or other metals)/titanium oxide (or other oxides) Schottky diode. The thin metal film (~ 4nm) provides the hot electrons (> 1 eV) that render the oxide-metal interfaces active reaction sites (Figs. 20a, 20b, 20c, 20d and 20e).
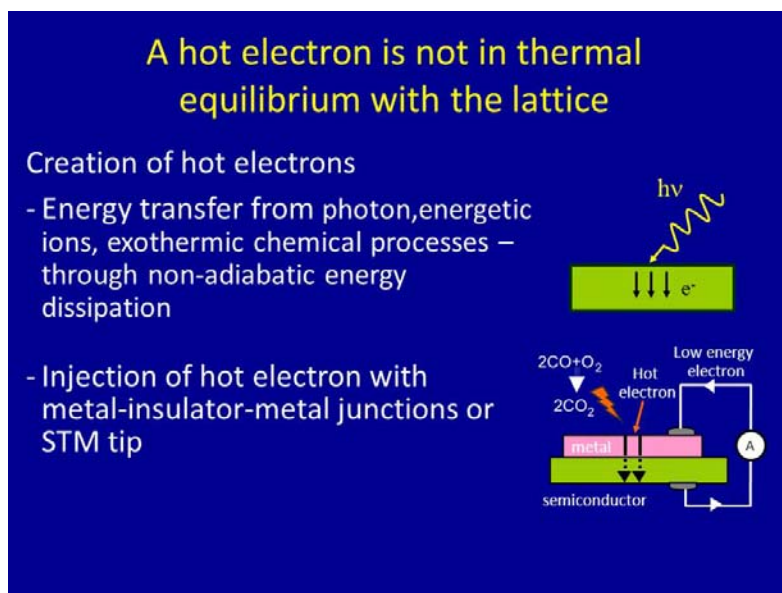
Fig 20b Hot electron generation in metals
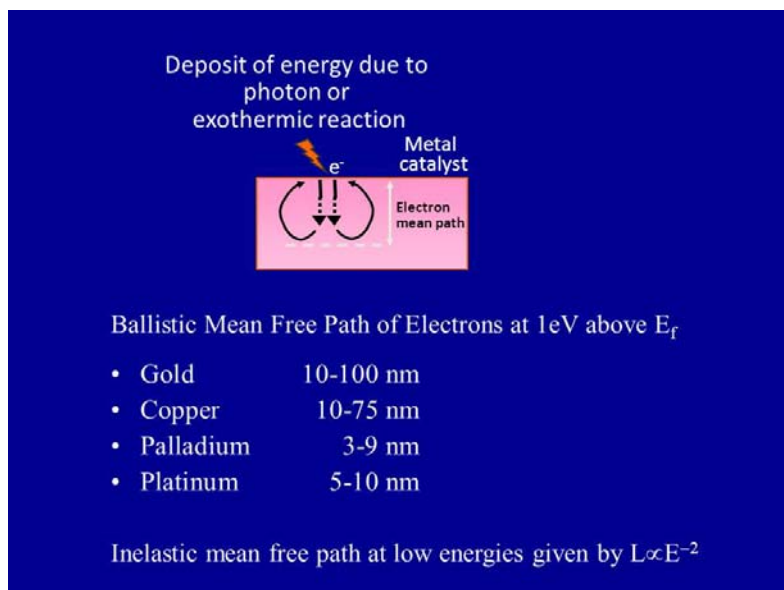
Fig 20c Mean free path of hot electrons in metal surfaces
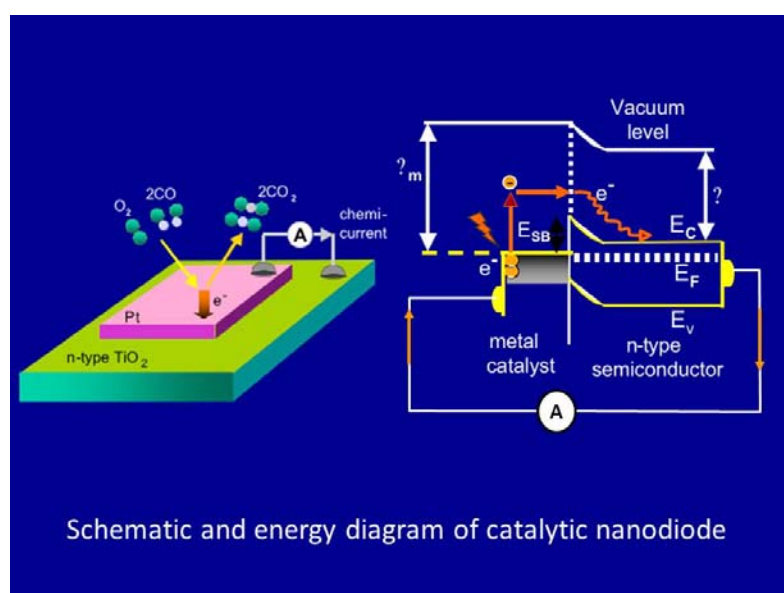
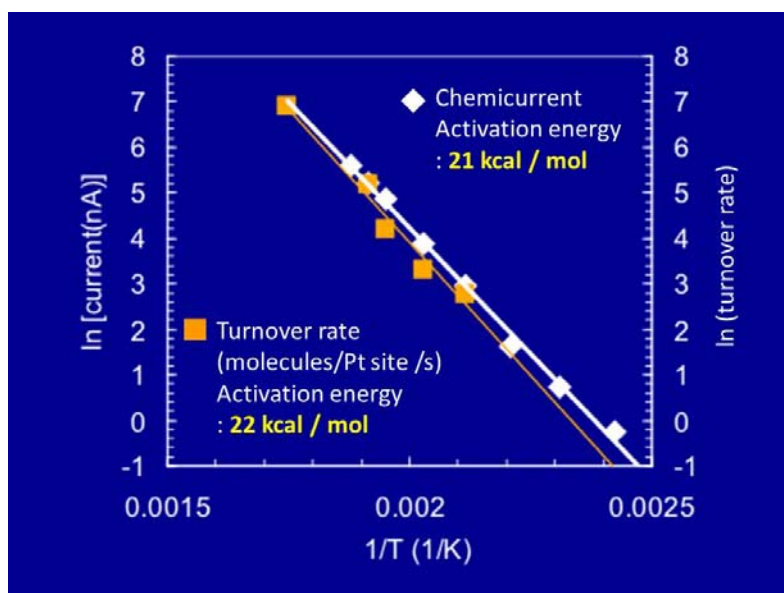Fig 20d Hot electron generation by exothermic catalytic reactions

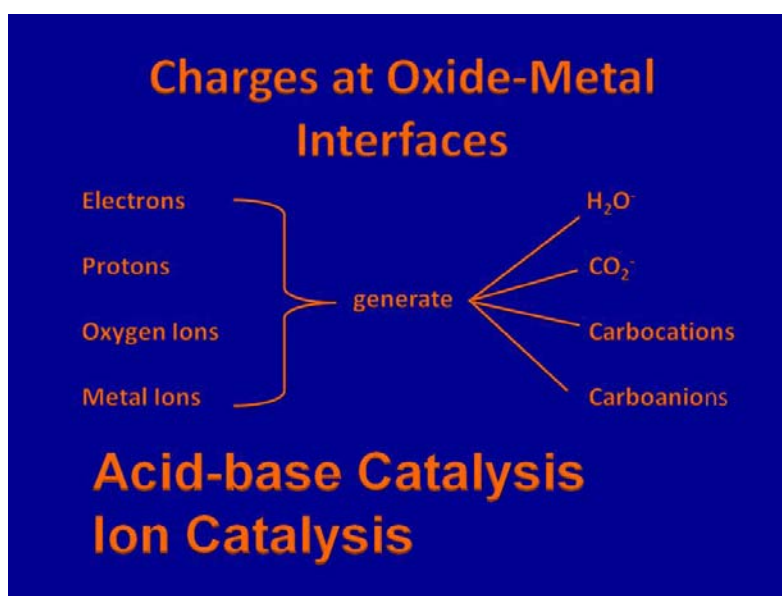Fig 20e Chemicurrent and turnover rate measure during carbon monoxide oxidation

Fig 21

Charge transport at oxide-metal interfaces lead to the formation of charged molecules and to acid-base catalysis (Fig 21).

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