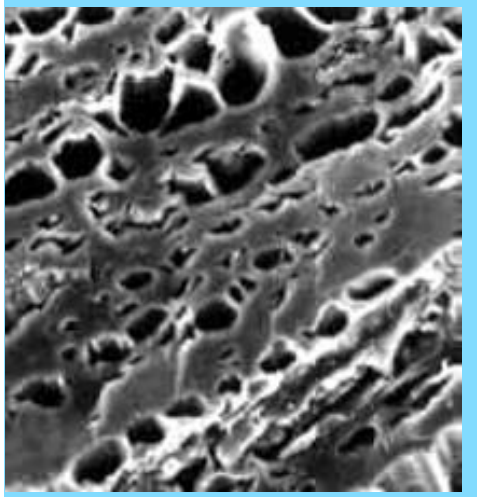
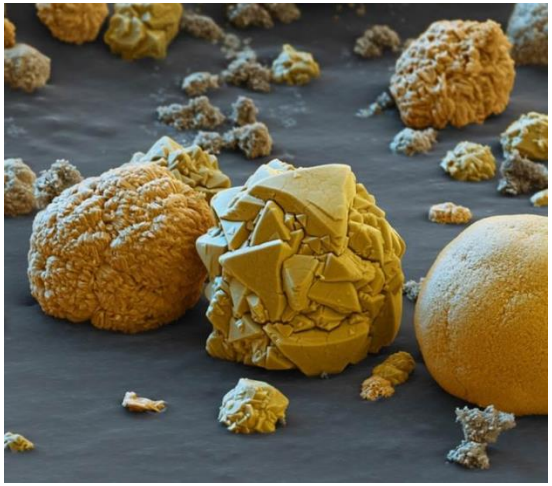


Production process for precious metal catalysts

Dr. Giovanni Iacono

Rome 23/03/2017



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List of subjects

- Precious metals catalitic activity
- Activated carbon structure
- Activated carbon surface chemistry
- Isoeletric point and point of zero charge
- Industrial production methods for catalyst
- Bimetallic Pd-Au catalyst
- Vinyl Acetate Monomer (VAM)

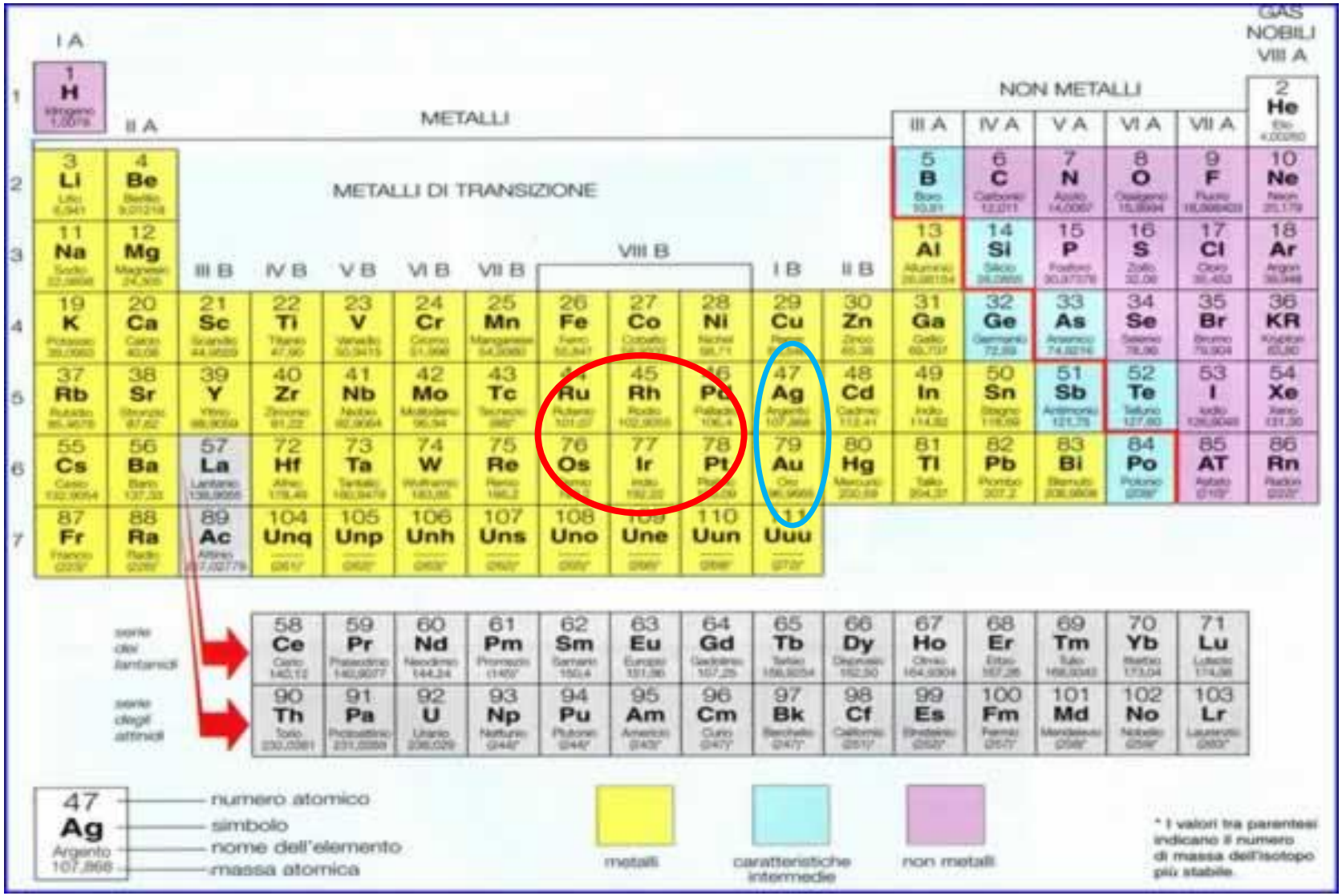
The first precious metal used in the history: gold !

- Shiny, malleable, and resistant to corrosion, gold has been the most desired precious metal since the time of the Pharaohs.
- For example, gold alloy nanoparticles (defined as particles from 1 – 100nm in size) in the glass of the famous Lycurgus cup (c.a. 4th century AD) cause the color to change from green for reflected light to red for transmitted light.
- C. Freyschlag, Materials Today, April 2011, col.14, 4, pp. 134-142.

Industrial application of precious metals

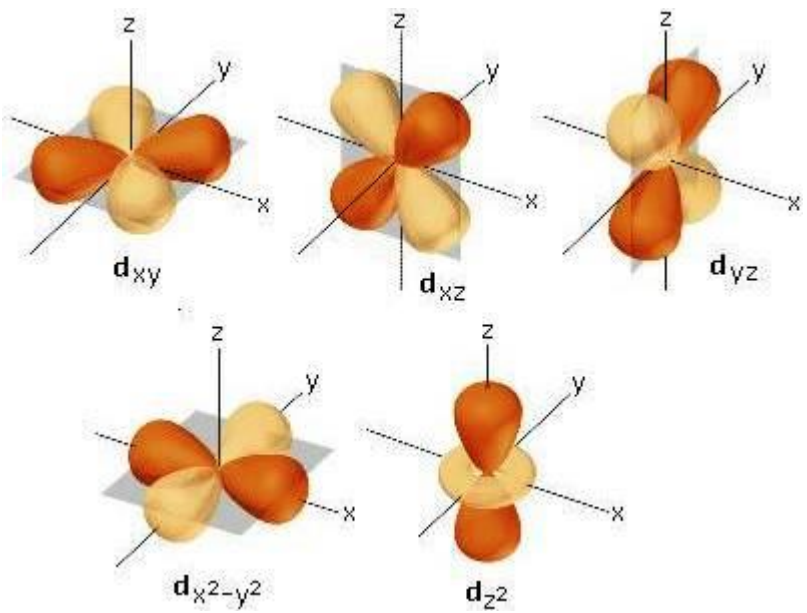
- Platinum was one of the first to be used for catalysis.
- In 1831, Peregrin Phillips patented the use of Platinum as a catalyst for production of sulfuric acid via the oxidation of SO_2 in the contact process.
- The recent interest in Gold as a catalyst was ignited by the discovery that gold nanoparticles on reducible oxides were effective catalysts for CO oxidation at low temperatures.

The periodic table of the elements



Chemical properties and electronic structure of PGM

- **In the group VIIIB there are the 6 noble metals PGM: Ru, Rh, Pd, Os, Ir, Pt**.
- Ruthenium [Kr] $4d^7\ 5s^1$
- Rhodium [Kr] $4d^8\ 5s^1$
- Palladium [Kr] $4d^{10}\ 5s^0$
- Osmium [Xe] $4f^{14}\ 5d^6\ 6s^2$
- Iridium [Xe] $4f^{14}\ 5d^7\ 6s^2$
- Platinum [Xe] $4f^{14}\ 5d^9\ 6s^1$
- **Gold and Silver are in the Group IB:**
- Silver [Kr] $4d^{10}\ 5s^1$
- Gold [Xe] $4f^{14}\ 5d^{10}\ 6s^1$



Precious metals as catalyst

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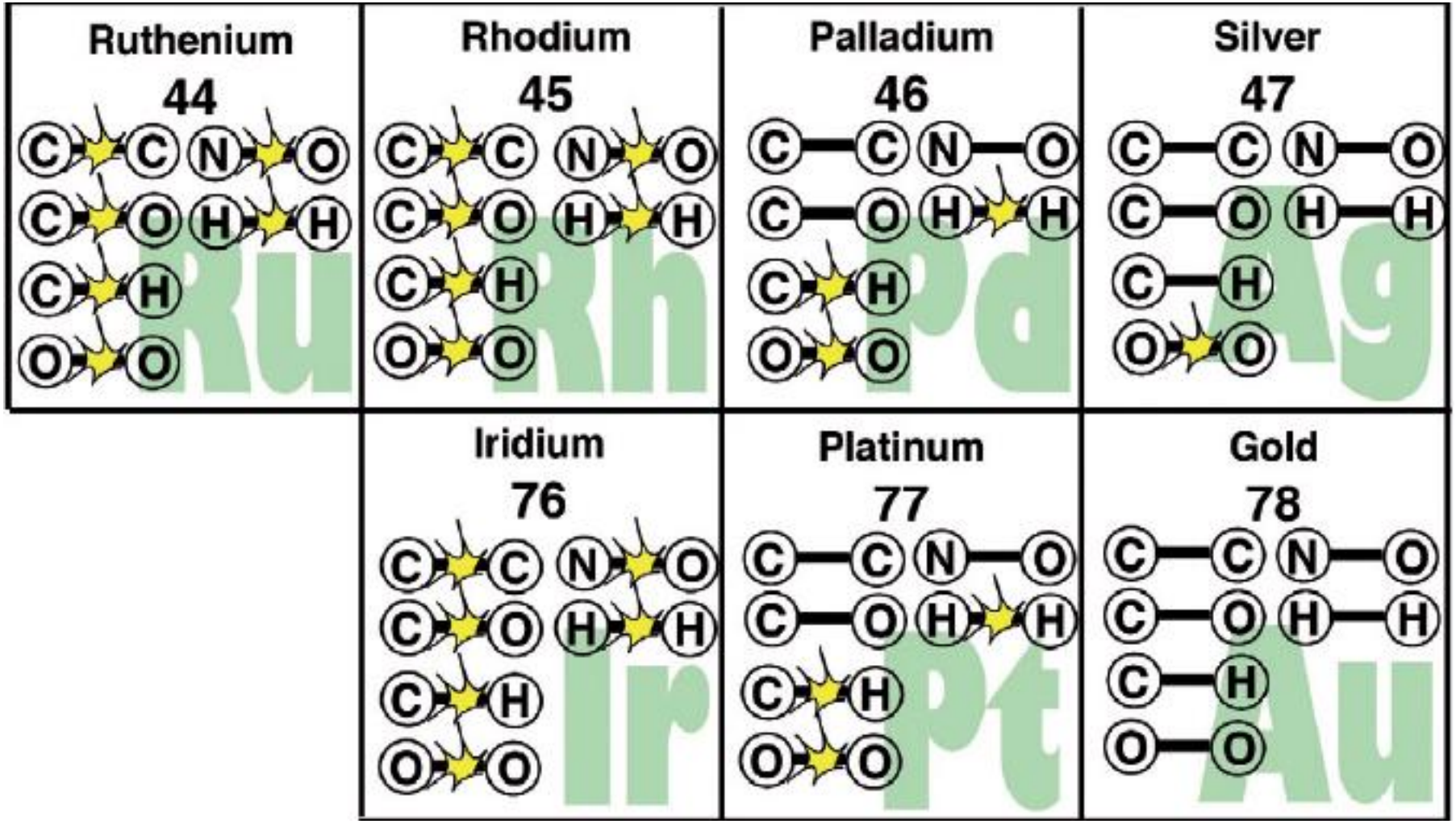
- The catalytic behavior is revealed to be somewhat different for each precious metal.
- PGMs exhibit distinct patterns that can be used to design new catalytic systems.
- This process requires varying levels of selectivity and specificity of the catalyst to cleave bonds of one type and reform others.
- One useful way to think about the differences between noble metals is to classify them in terms of bond-breaking capability.

Bond-breaking capability of precious metals



Bond-breaking capability of precious metals

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- The precious metals used in catalysis can be "ranked" by their bond-breaking abilities. The capacity of each metal to break specific chemical bonds is indicated clearly.
- Note the increasing "inertness" in progressing from left to right in this series.
- Most of them are able to dissociate O_2.
- Some of them are able to dissociate H_2, expecially the Palladium.

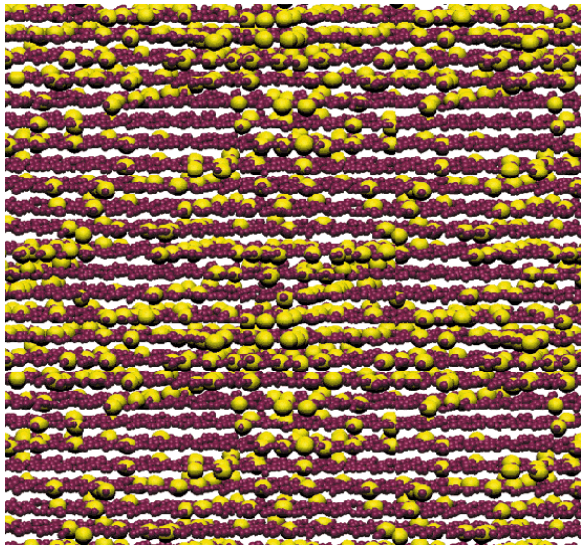
Palladium as sponge

- Palladium soaks up hydrogen like a **sponge**.
- At room temperature and atmospheric pressure, palladium can absorb up to 900 times its own volume of hydrogen.
- When palladium is saturated with hydrogen, it becomes a polymorphic material and hydride transformations may be induced in it by processes of heating/cooling and/or saturation/desaturation.
- There are differences between the specific volumes of the α-hydrogen solid solution and β-hydride phases in the palladium.

- V. A. Goltsov, Platinum Metals Rev., 1999, 43, (3), 116-8.

β-hydride formation

- Onset of the beta phase in palladium hydride at 300 degrees Kelvin.
- This phase change occurs as the concentration of hydrogen atoms (yellow) in the palladium (purple) increases.
- At early stages (the α phase), hydrogen atoms randomly populate small interstices in the lattice structure.
- At a critical point, the lattice expands, allowing hydrogen to cluster at higher density (the β phase).



Hydrogen storage on activated carbon

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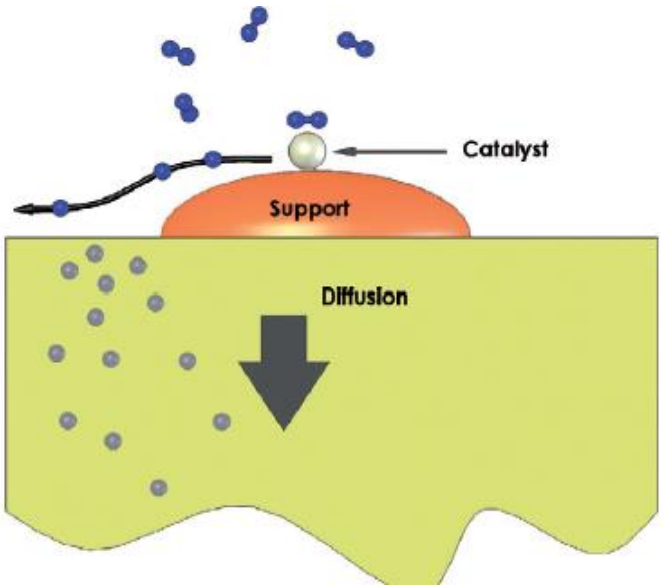
- Carbon offers the advantages of being lightweight and inexpensive, while exhibiting reversibility and rapid sorption kinetics.
- The phenomenon of physical adsorption is essentially the accumulation of undissociated hydrogen molecules upon a surface of microporous carbon.
- Hydrogen uptake in carbon is proportional to its surface area and pore volume.

Hydrogen spillover

- The metallic doping of carbon materials results in the following phenomena, which are collectively termed as the hydrogen spillover mechanism:
- (i) H_2 molecules dissociate on the metal catalyst particles;
- (ii) H atoms migrate from the metal catalyst particles to the carbon substrate material;
- (iii) H atoms diffuse on the substrate.



Advantages of Pd on carbon

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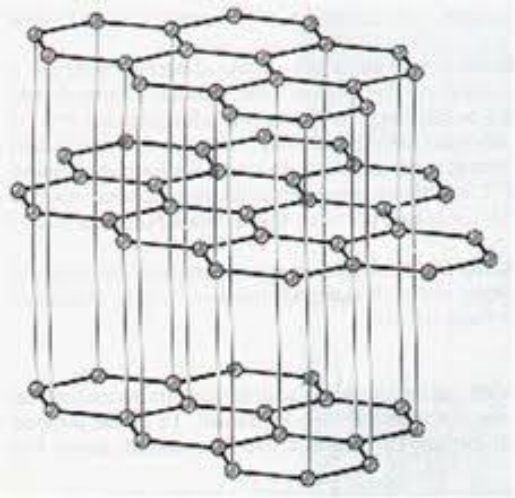
- The hydrogen capacity of the combined system (carbon + metal) will typically exceed that of the individual components.
- An advantage is provided by the use of Pd as the catalyst is that a portion of the hydrogen is stored within the catalyst itself (as PdHx).
- Hence, the capacity of the overall material is likely to be higher than that of a nonabsorbing metal.

Honors to Paul N. Rylander

- Dr. Paul N. Rylander was one of the best researcher In Engelhard Industries, New Jersey, where he also headed the organic reactions section from 1956 to 1972.
- He received his B.Ch.E. from Johns Hopkins and Ph.D. from Indiana, and was a post-doctoral fellow at Rochester and Harvard.
- Dr. Rylander was the author of numerous papers and patents and of books about catalytic hydrogenation with noble metals catalysts.

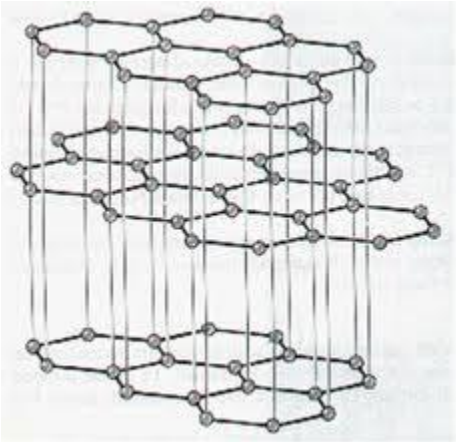
Insight into carbon structure : the graphite structure

- The structure of activated carbon is based on a defective graphite lattice.
- In graphite the individual carbon atoms link up to form sheets of carbon atoms. Each sheet of carbon atoms is translated (offset) by one-half of a unit such that alternate sheets are in the same position.
- Within each sheet every carbon atom is bonded to three adjacent carbon atoms that lie at the apices of equilateral triangles. This produces hexagonal rings of carbon atoms with aromatic electronic structure.



Graphite structure

- The spacing between the sheets of carbon atoms is greater than the diameter of the individual atoms.
- Weak bonding forces (van der Waals forces) hold the sheets together.
- Because these forces are weak, the sheets can easily slide past each other.
- The sliding of these sheets gives graphite its softness for writing and its lubricating properties.



Porous structure of activated carbon

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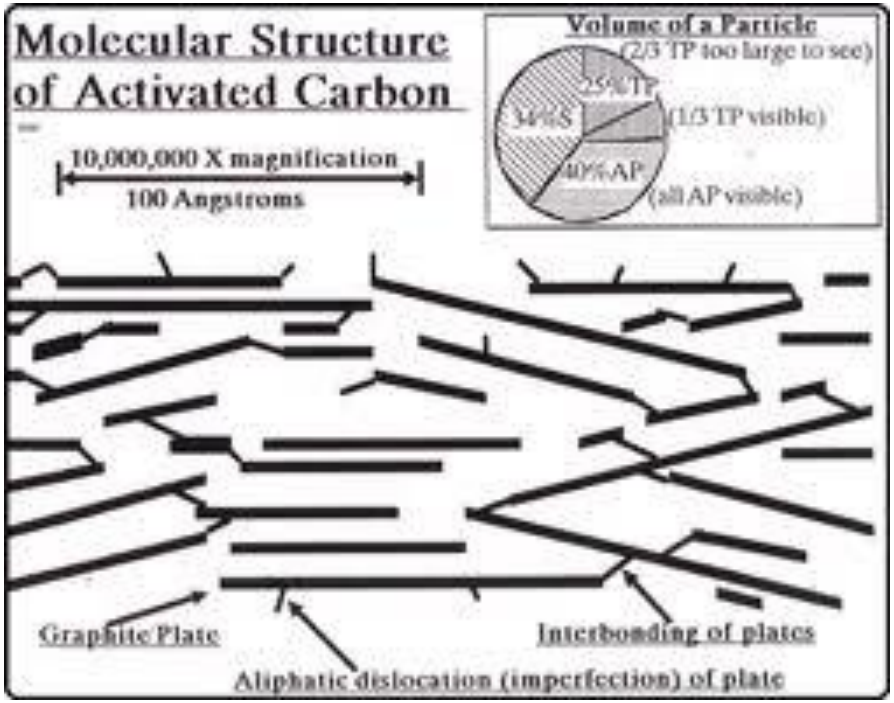
- The structure of activated carbon is based on a defective graphite lattice.
- During heat treatment the macromolecular structure remains and some cross-linking is developed. Residual elementary carbon atoms are grouped into stacks of aromatic sheets cross-linked randomly.
- Because of irregular arrangement, there are free interstices between stacks that can be filled by with tars and decomposition products, which become disorganized carbon.
- The disorganized carbon in the char is the first to react with gases during the activation process, clearing the porosity of the final activated carbon.

- F. Rodriguez-Reinoso, *Activated Carbon and Adsorption*, in Encyclopedia of Materials: Science and Technology (second edition), 2001, pp. 22-34.

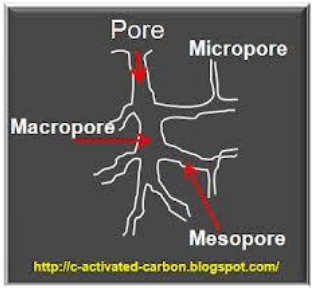
Pores dimensions (IUPAC)

- Micropores : ϕ < 2,0 nm
- Mesopores : 2,0 < ϕ < 50,0 nm
- Macropores : ϕ > 50,0 nm



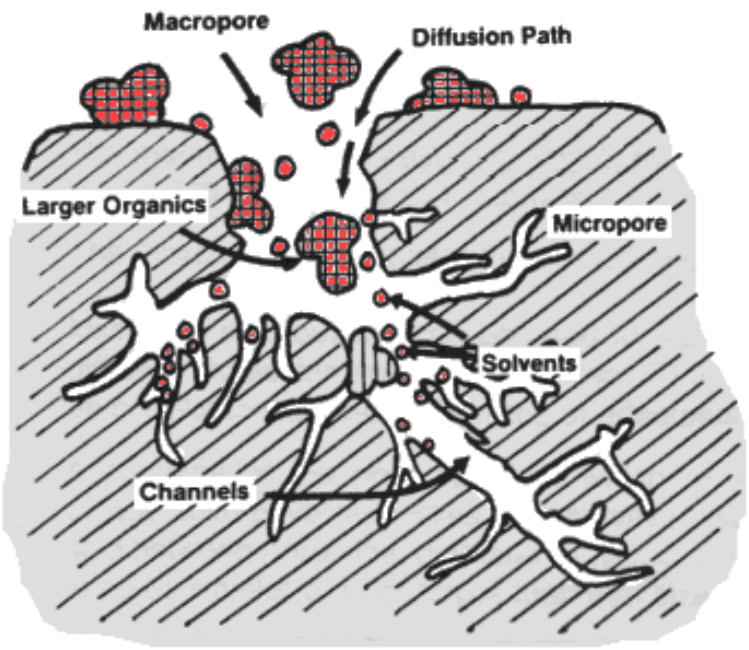
Industrial process for activated carbon production

- Raw materials of different origin (vegetal or mineral or synthethic).
- **Steam activation** :1) Low temperature treatment for charcoal production , 2) Physical activation with steam at HT
- **Chemical activation** (H_3PO_4, $ZnCl_2$):
- No charcoal production for chemical activation, but direct contact between raw material and chemicals.

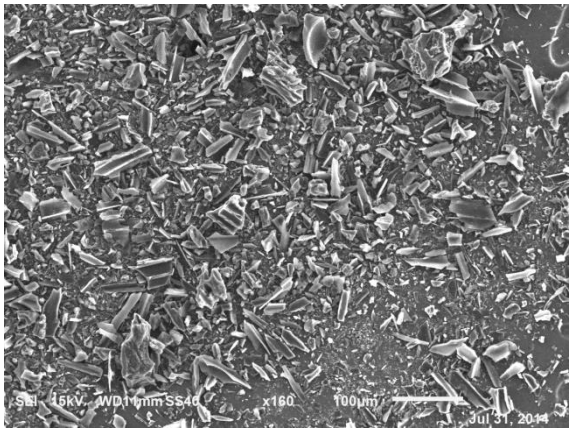


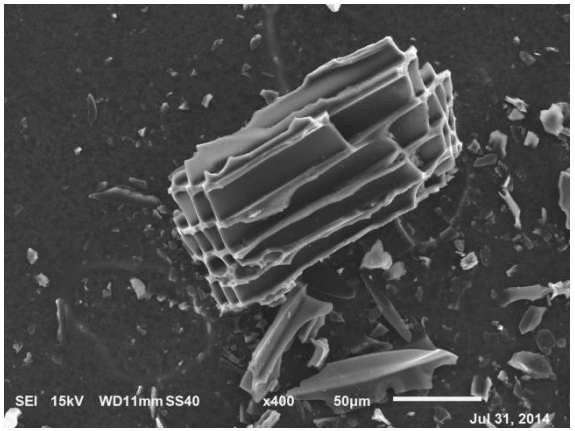
Source of raw material for activated carbon production

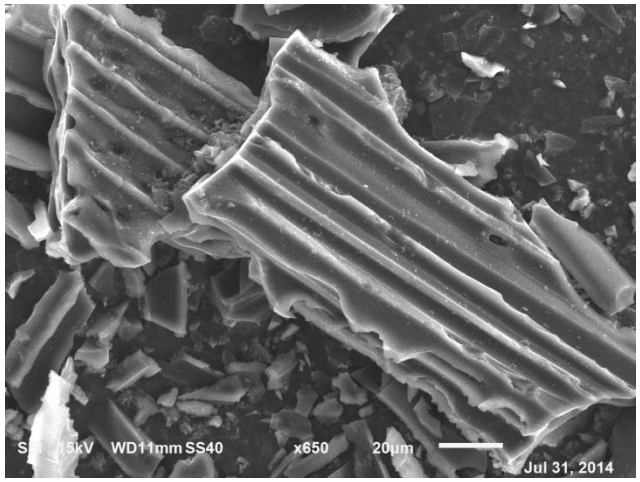
- Usually from wood and vegetal source (coconut shell).
- Only one supplier in the world using material from mining : peat.
- Pet-coke : residual material into the bottom of column for fractional distillation of petrol.
- Products of pyrolysis of organic materials (e.g. acetylene, macroreticular polymers)



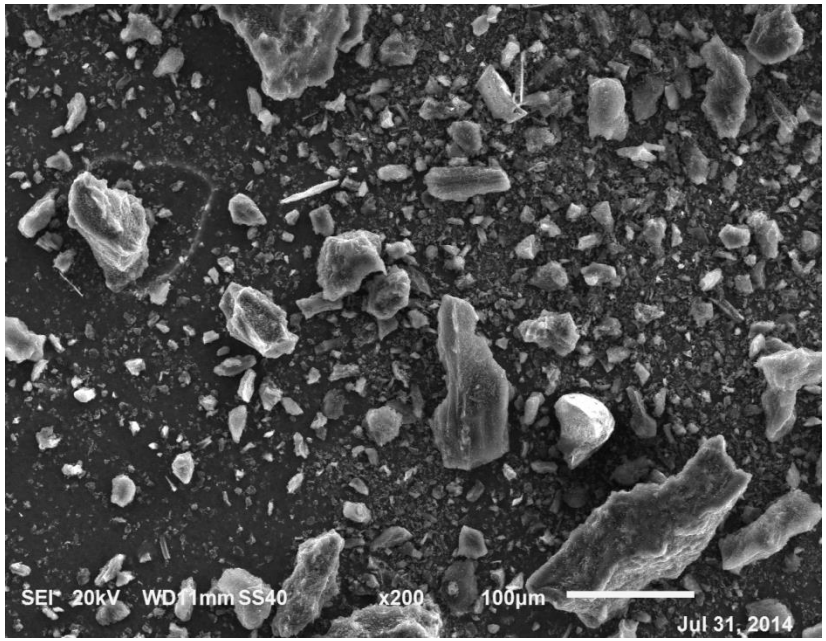
SEM pictures of steam activated carbon (wood)

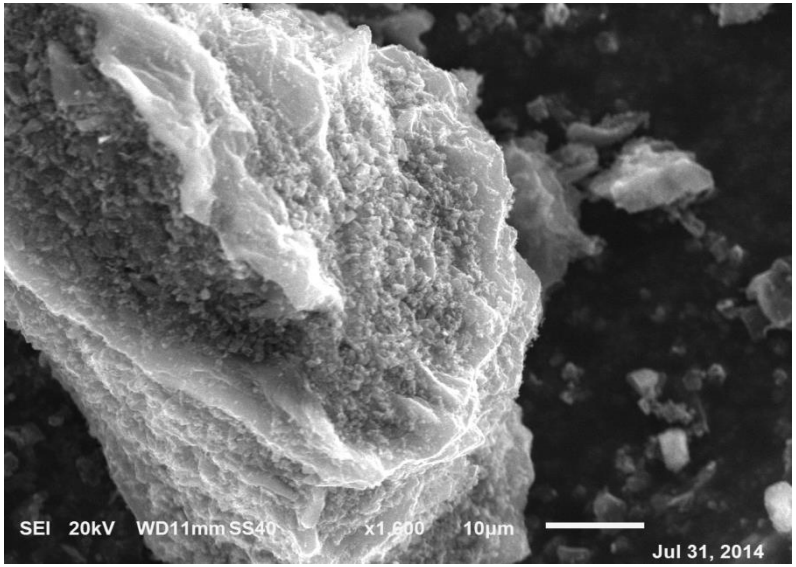




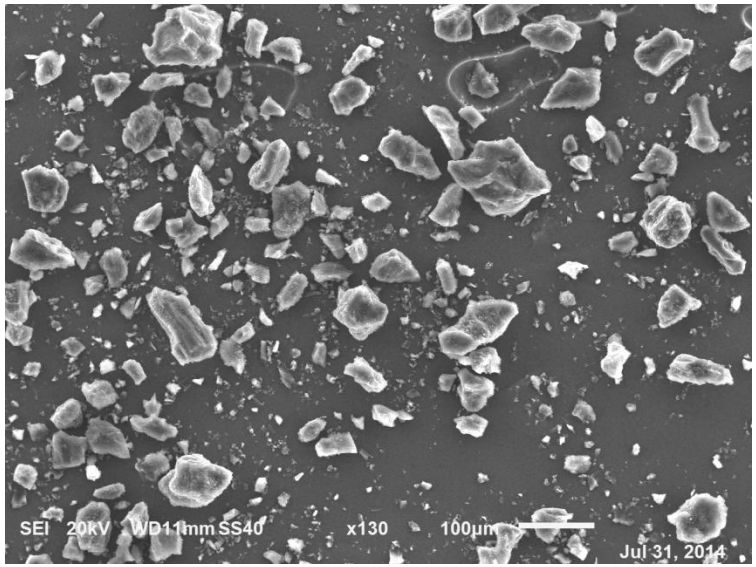


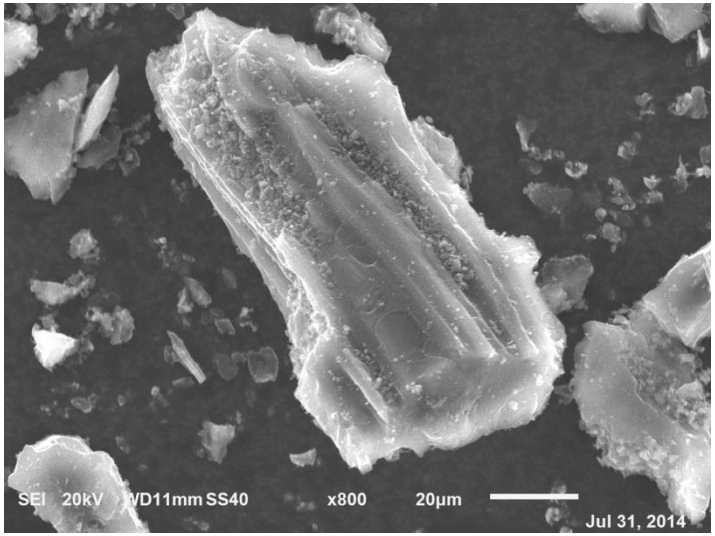
SEM pictures of steam activated carbon (peat)





SEM pictures of acid activated carbon (AAC)





Comparison of main physical and chemical characteristics of steam activated carbons

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Carbon origin	Ash content (%)	Iron content max (ppm)	T.S.A. (m2/g)	Pore volume (cc/g)	Diameter < 50% (μ)
Vegetal	2	300	900	0,6	28
Mineral	6	500	900	0,6	22

- As far as activation grade of carbons is concerned, all the products show the same values.
- The main difference is about the ash content because of different origin. Difference in PSD.
- Full characterization about chemical and physical properties.

Surface chemistry and adsorptive properties

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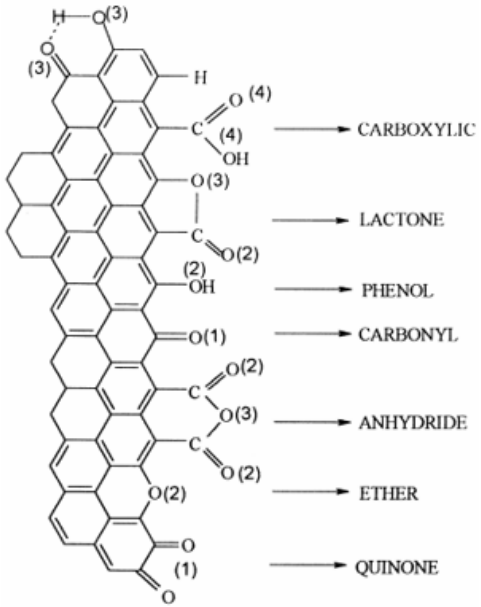
- The normal carbon surface is hydrophobic, i.e. repels water.
- If the carbon is extensively covered with oxigen assumes a hydrophilic behaviour, i.e. can be easily dispersed in water.
- A sample of carbon black Spheron 6 has been treated to cover its surface with appreciable quantity of oxigen.
- 2 samples of untreated and oxigenated Spheron were tested for adsorption of methanol and benzene.
- The oxygen containing sample showed a preferential adsorption of methanol.
- The untreated sample showed a preferential adsorption of benzene.

- Th. Van Der Plas, «The texture and the surface chemistry of carbons» in Physical and Chemical Aspects od Adsorbents and Catalyst, edited by B.G. Linsen, chapter 9, p. 456, AP (1970).

Oxygenated functional groups

- The oxygenated functional groups on the activated carbon surface chemistry can be the following:
- Carboxylic acid
- Lactone
- Phenol
- ketone
- anhydride
- ether
- quinone



- U. Zielke, K. J. Huttinger And W. P. Hoffman, *Surface-Oxidized Carbon Fibers: I. Surface Structure and Chemistry*, Carbon Vol. 34, No. 8, 983-998, 1996 .

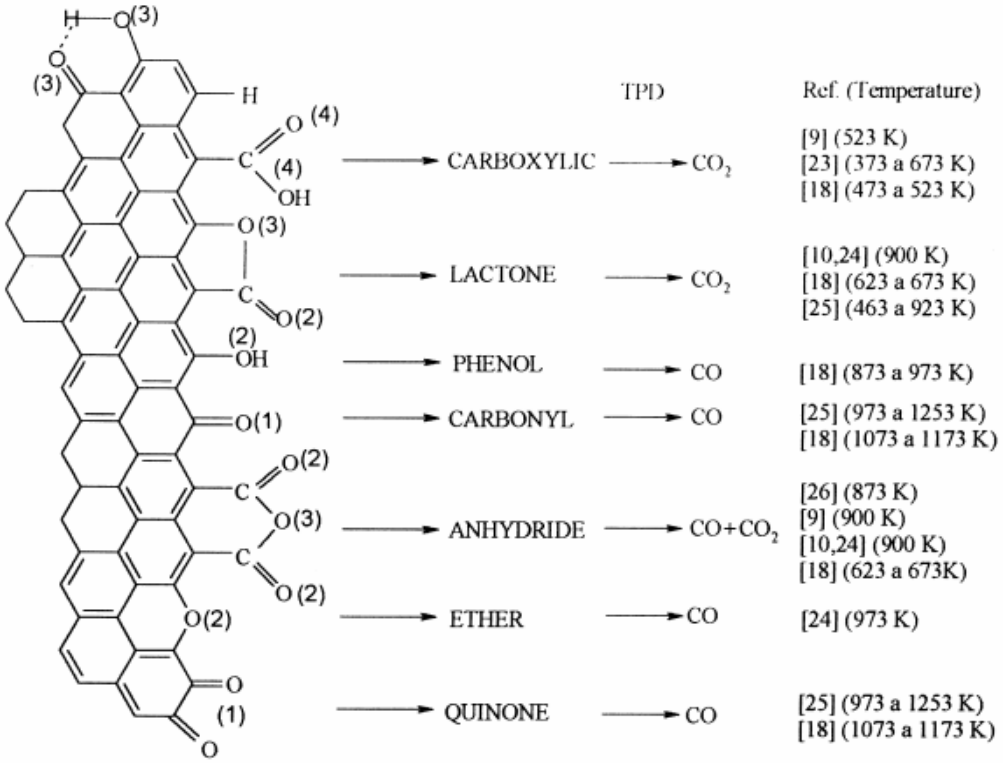
Thermal Programmed Desorption

- The TPD (Thermal Programmed Desorption) is an useful method for characterization of active carbons.
- Surface oxygen groups on carbon materials decompose upon heating by releasing CO and CO_2 at different temperatures.
- Each functional group can evolve, if the sample is heated at the right temperature , CO or CO_2 or H_2O.

Surface groups in activated carbon

- Different functional groups can evolve on heating the same gas , but at a different temperature, that accounts for the different bond energy.

- J.L. Figueiredo , M.F.R. Pereira, M.M.A. Freitas, J.J.M. Orfao, *Modification of the surface chemistry of activated carbons*, Carbon 37 (1999) 1379–1389.



Modification of surface chemistry for activated carbons

- The modification of surface chemistry of activated carbons can be made in 2 different ways:
  - Oxidation in gas phase
  - Oxidation in liquid phase
- As far as oxidation in gas phase is concerned, the carbon is flowed with an oxidant reactant, air or O_2 diluted in N_2 ; during the oxidation the burn off is controlled (main parameter).
- As far as oxidation in liquid phase is concerned, several oxidant in solution are used, for instance HNO_3, H_2O_2, $Ca(ClO)_2$ and peroxides.

Comparison between air and liquid phase oxidation

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- Gas phase oxidation of activated carbons increases mainly the concentration of hydroxyl and carbonyl surface groups[1];
- Oxidation in the liquid phase increases especially the concentration of carboxylic acids.
- HNO_3 hot treatment is able to introduce a large quantity of carbonyl and carboxylic groups.
- H_2O_2 treatment of carbon at room temperature can introduce a lower quantity of carbonyl and carboxylic groups than HNO_3.

- [1] J.L. Figueiredo , M.F.R. Pereira, M.M.A. Freitas, J.J.M. Orfao, *Modification of the surface chemistry of activated carbons*, Carbon 37 (1999) 1379–1389.

Various carbon based materials

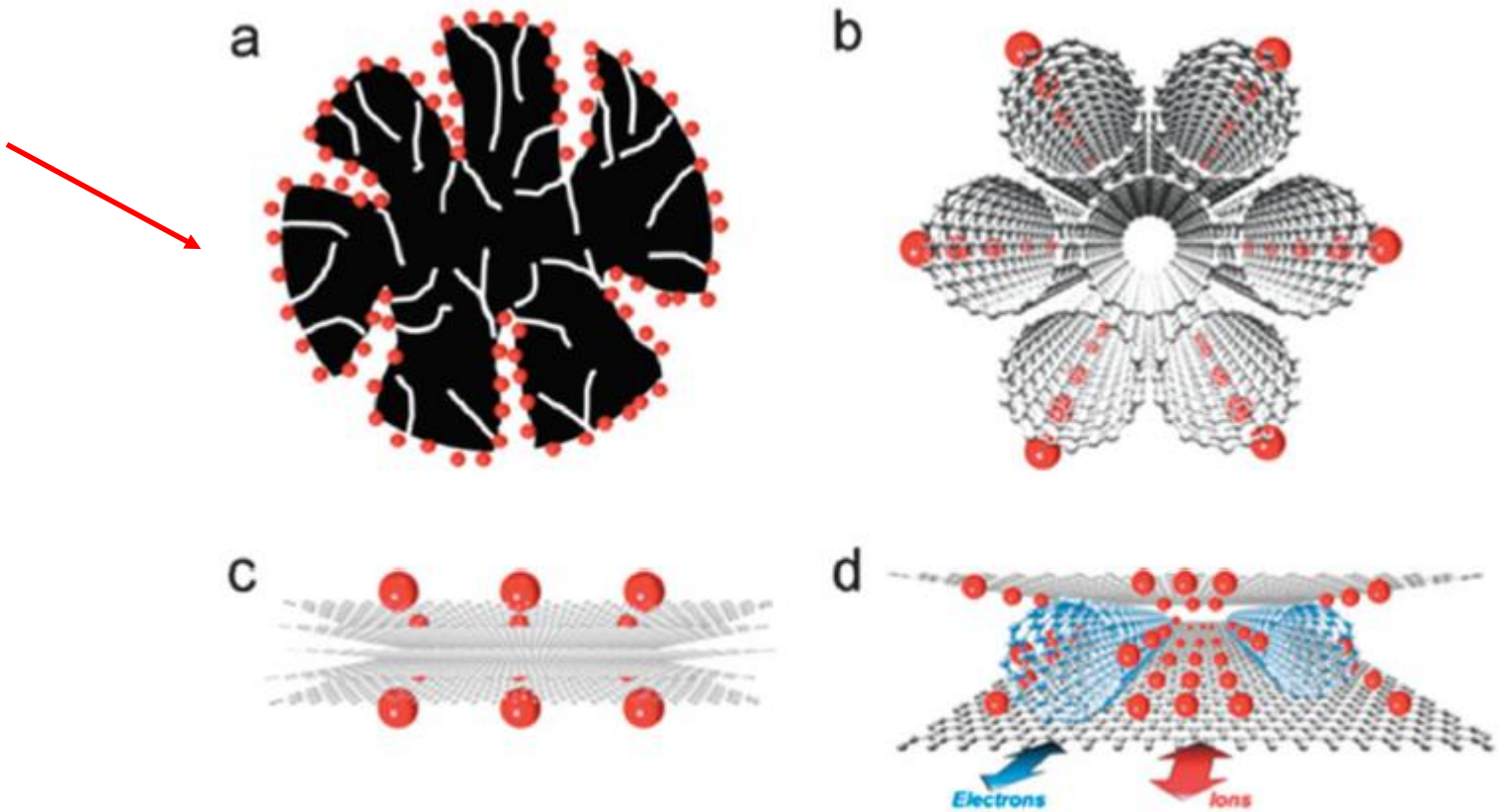
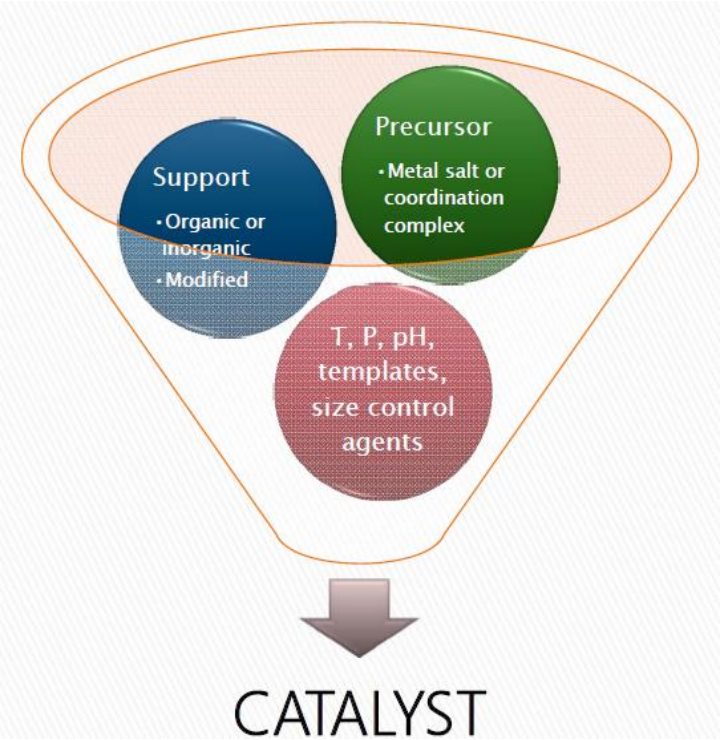


Fig. 24 Structural representation of various carbon-based nanomaterials, including (a) activated carbon, (b) single walled carbon nanotubes, (c) pristine graphene and (d) graphene/nanotube composites. Reproduced

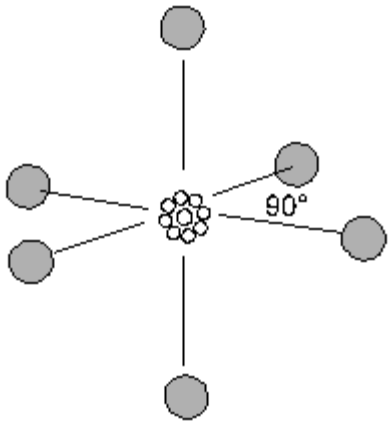
Main parameters for catalyst preparation

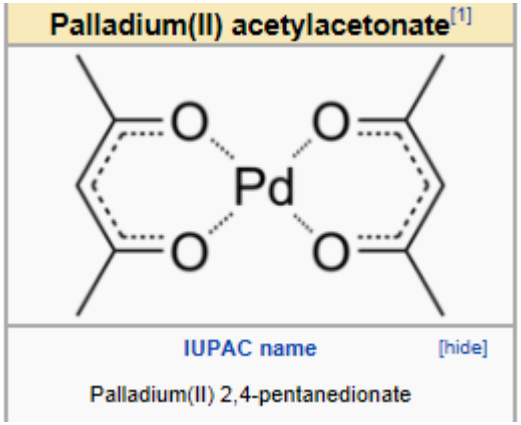
- Major parameters for catalyst preparation are:
  - A) Carrier
  - B) PGM salt
  - C) method



Palladium precursors

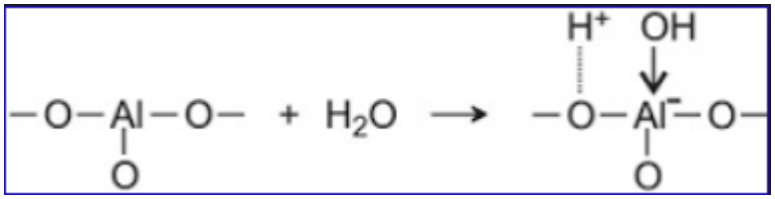
- $Pd(NH_3)_4^{2+}$: charge positive; stable in neutral and moderately basic enviroment.
- $PdCl_4^{2-}$: palladium complex negatively charged; stable in acidic and neutral solution, if Cl^-/Pd^{2+} ratio is high enough to avoid hydrolysis.
- $Pd(acac)_2$: neutral Palladium complex.





Iso Electric Point (IEP) and Point of Zero Charge (PZC): oxide carriers

- The surface of most oxides is hydroxylated or becomes hydroxylated upon contact with water.
- These hydroxyl groups can be classified as acid, neutral and basic (Bronsted sites).
- Moreover coordinately unsaturated metal sites can be present, which may act as Lewis-acidic centers.
- When dispersed in aqueous solutions the surface of particles of mineral amphoteric oxides such as silica and alumina becomes generally charged.



$$M{-}OH + H^+ \rightleftarrows M{-}OH_2^+$$

$$M{-}OH \rightleftarrows M{-}O^- + H^+$$

Iso Electric Point (IEP) and Point of Zero Charge (PZC)

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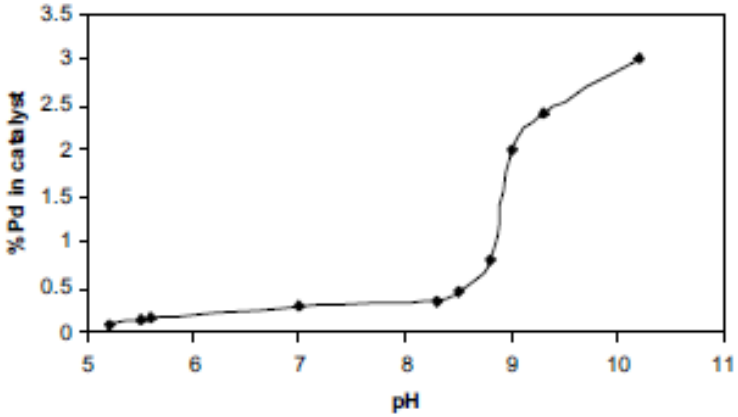
- The charged surface in combination with the charged layer around the particle is called the electrical double layer.
- The pH value at which the net surface charge is zero, is referred to as the point of zero charge (PZC) or often loosely the iso-electric point (IEP).
- At pH values below its IEP an oxidic particle acquires a net positively charge and tend to adsorb compensating anions, like $PdCl_4^{2-}$.
- At pH values above its IEP, the surface acquires a net negatively charge and cations like $Pd(NH_3)_4^{2+}$ can be adsorbed.

IEP of various oxides as catalyst carriers

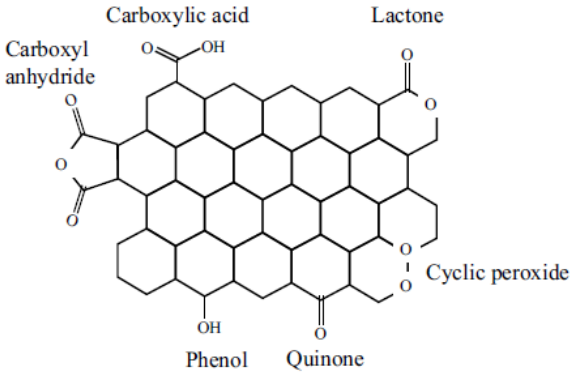
Type	Oxide	IEP	Adsorption
Acidic	Sb_2O_3	<0.4	Cations
	WO_3	<0.5	
	SiO_2	1.0-2.0	
Amphoteric	MnO_2	3.9-4.5	Cations or Anions
	SnO_2	~5.5	
	TiO_2	~6	
	γ-Fe_2O_3	6.5-6.9	
	ZrO_2	~6.7	
	CeO_2	~6.75	
	α,γ-Al_2O_3	7.0-9.0	
Basic	Y_2O_3	~8.9	Anions
	α-Fe_2O_3	8.4-9.0	
	ZnO	8.7-9.7	
	La_2O_3	~10.4	
	MgO	12.1-12.7	

Effect of impregnation pH on extent of $Pd(NH_3)_4^{2+}$ adsorption on γ-alumina : direct relationship between pH and Pd assay !



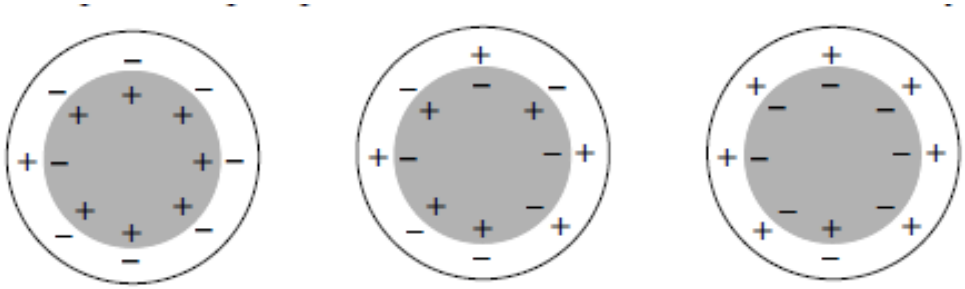
What happens for activated carbon ?

- Structure of activated carbon, consisting of aromatic sheets and strips, containing various slit-shaped voids, i.e. the micropores.
- Oxygen-containing surface groups are by far the most important groups influencing the surface characteristics and adsorption behavior of activated carbon.



IEP for activated carbons

- The oxygen-containing surface groups can be divided in acid, neutral and basic ones.
- This implies that the carbon surface may have different amounts and types of oxygen surface groups and, consequently, both negatively and positively charged surface sites can exist in aqueous solution, depending on the pH.
- At pH>pHIEP the carbon surface, covered by deprotonated acidic groups, will attract cations from solution; at pH<pHIEP it will attract anions.



Acidic medium ($pH < pH_{IEP}$) | $pH = pH_{IEP}$ | Basic medium ($pH > pH_{IEP}$)

Carbon surface groups and metal dispersion

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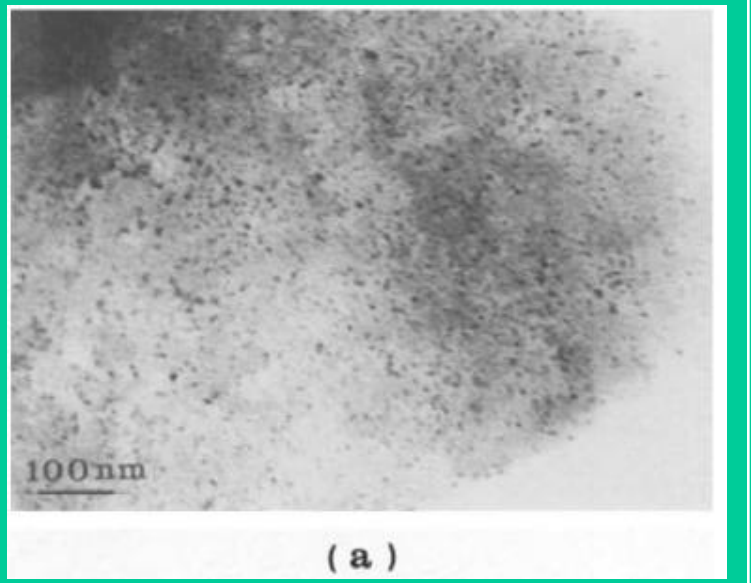
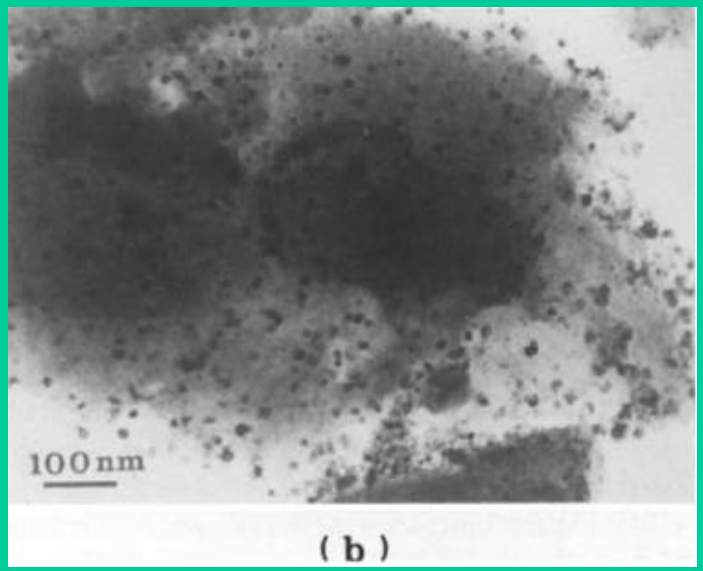
- Carboxylic, quinone and lactone groups are acidic. Because of their negative charge they enhance the interaction between the carbon surface and positively charged metal precursors.
- Furthermore, they decrease the hydrophobicity of the carbon material, thus making the surface more accessible for aqueous metal precursor solutions
- It has been proven for Pd on activated carbon that the metal dispersion increases with increasing amounts of surface oxygen groups.

Suh (Carbon1993): Electron micrographs of the Pd particles on activated carbon support





on nitric acid-treated support	On original untreated support

IEP values for various activated carbons

3.6 Carbon-rich materials						
3.6.4.1	ACF-10 activated carbon from American Kynol[be]			pH*		8.3
3.6.4.1.2	OLC activated carbon from Calgon			pH*		8.9
3.6.4.2.1	Activated carbon[bf]	None		pH*		11.9
	Activated carbon[bg]			pH(?)*		2.7–7.9
3.6.4.2.1.2	Activated carbon[bh]			pH*		5.6–9
	Activated carbon[bi]			cip (?)*		5.3
3.6.4.2	Activated carbon[bj]	None		pH*	1 day equilibration	8.9
						9
						8
						7
						6.8
3.6.4.2.2	Spherical activated carbon[bk]		pH*			7.6
						8.9
						10.2
3.6.4.2.2	activated carbon[bl]	0.1 M NaCl	25	pH		8
3.6.4.2.2	Carbon xerogels[bm]			pH		9.4

Kosmulski, J. Coll. And Int. Sci., 337 (2009) 439-448

Interactions between Pt salt and carbon surface

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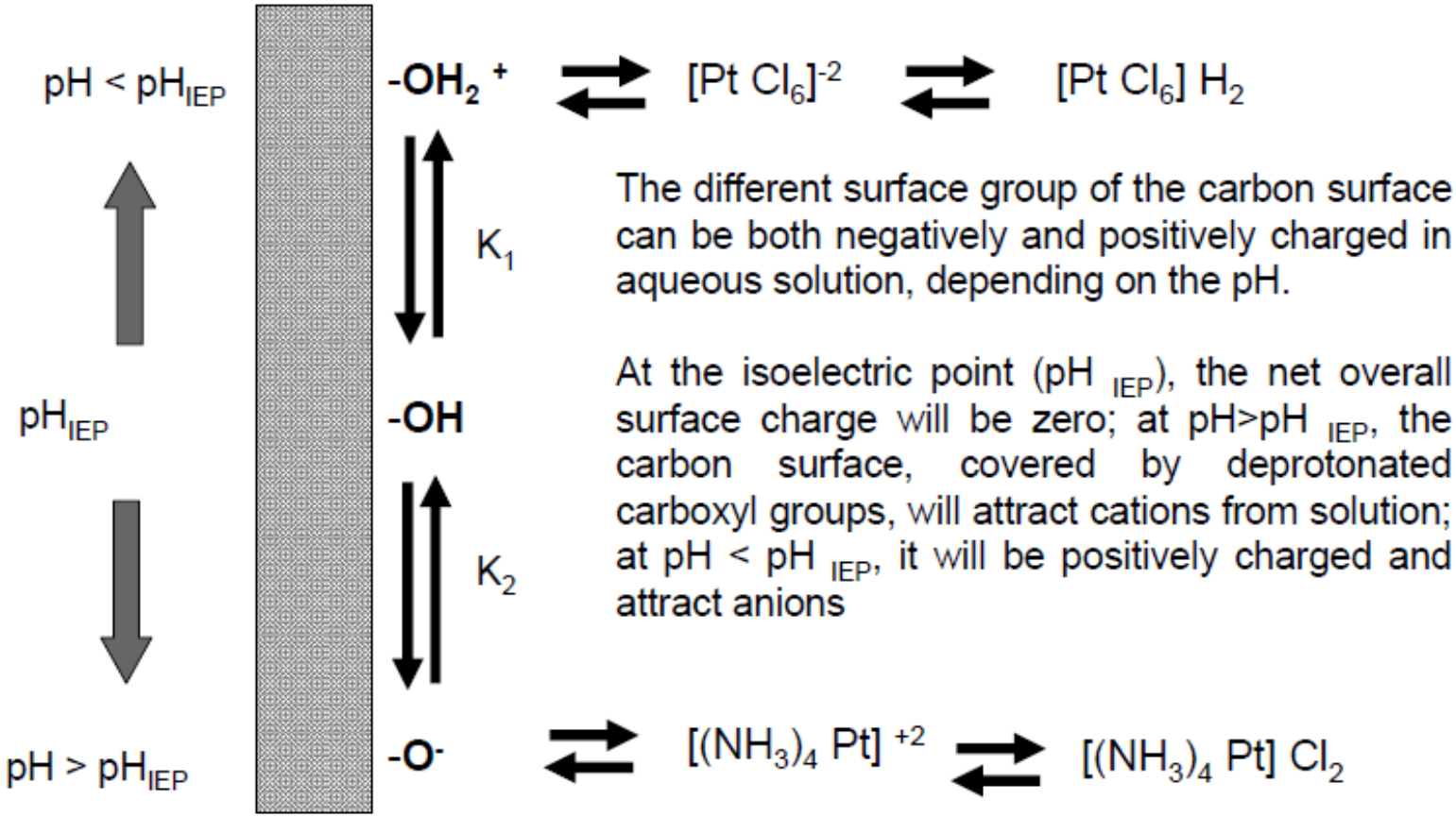
Effect of carbon surface chemistry



The different surface group of the carbon surface can be both negatively and positively charged in aqueous solution, depending on the pH.

At the isoelectric point (pH_{IEP}), the net overall surface charge will be zero; at $pH > pH_{IEP}$, the carbon surface, covered by deprotonated carboxyl groups, will attract cations from solution; at $pH < pH_{IEP}$, it will be positively charged and attract anions

Other surface groups (not oxygenated)

- Other surface groups are the basic groups, due to the graphitic carbon.
- Basic surface groups are localized at the same edges as acidic groups, although their quantity is lower.
- The basicity of graphitic carbon is explained in terms of the π sites of the graphite basal plane interacting with water.
- Increasing of the amount of basic sites on the basal plane surface will both enhance the electrostatic attraction with metal anion complexes (e.g. CπH3O^{+} - $PdCl_4^{2-}$) and diminish repulsive interactions (e.g. COO^{-} - $PdCl_4^{2-}$), thus increasing the dispersion.

$$C_\pi + 2\,H_2O \longrightarrow C_\pi H_3O^+ + OH^-$$

Basic sites = reducing sites (graphitic carbon)

- Chemical processes occur when H_2PdCl_4 from aqueous solution is adsorbed on the surface of graphite-like carbon materials.
- They found that adsorption proceeds via two competitive pathways:
- Reduction to form metallic Pd particles (process 1) or formation of π-complexes of $PdCl_2$ with C=C fragments of the carbon matrix (process 2).
- The first process takes place near the exterior surface of the carbon particles. Reduction of palladium occurs as a result of the high reducing power and the conductivity of graphitic carbon → Pd mirror.
- The spontaneous reduction of H_2PdCl_4 results in Pd^0 particles with a broad size range of 6-100 nm.

$$PdCl_2/C + 2HCl \underset{(2)}{\rightleftharpoons} H_2PdCl_4 + C \underset{(1)}{\rightleftharpoons} Pd^0/C + 2Cl^-/2C^{\oplus} + 2HCl$$

Summary of interactions

Maximum catalyst dispersion and resistance to sintering can be obtained by either:

(1) oxidation of the carbon typically renders the carbon surface more acidic. This in turn results in electrostatic repulsion of the $PtCl_6^{-2}$ anions and will favor electrostatic attraction of the $[Pt(NH_3)_4]^{2+}$ cations, maximizing catalyst dispersion.

(2) increasing the basic C, sites on the basal plane surface of oxygen-free carbon will maximize the electrostatic attraction with the metal anion (C_{Π} - H_3O^+ - $PtCl_6^{-2}$)

(3) C=O groups acting as anchoring centers hinder agglomeration and surface diffusion of catalyst particles across the graphene layers.

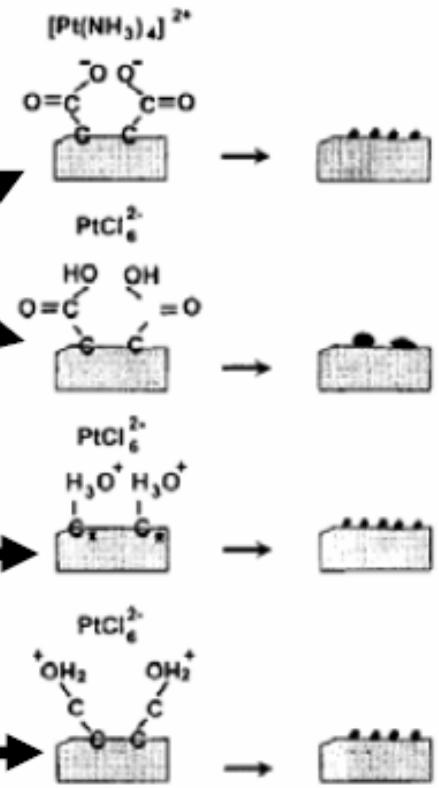


Fig. 12. Schematic representations of the more common interactions between the active sites of a carbon surface and metal ions.

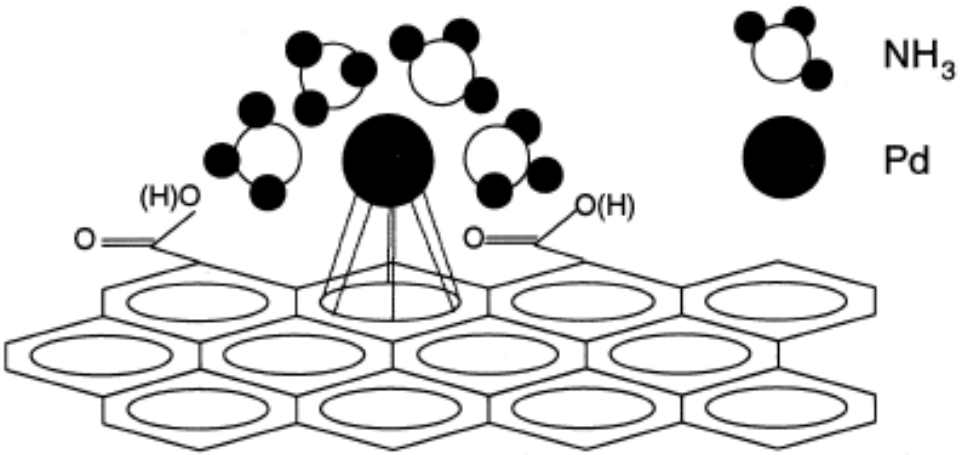
Different methods for catalyst preparation

- 1) Adsorption / ion exchange
- 2) Deposition /precipitation
- 3) Deposition/reduction
- 4) Colloid deposition
- 5) Incipient wetness impregnation

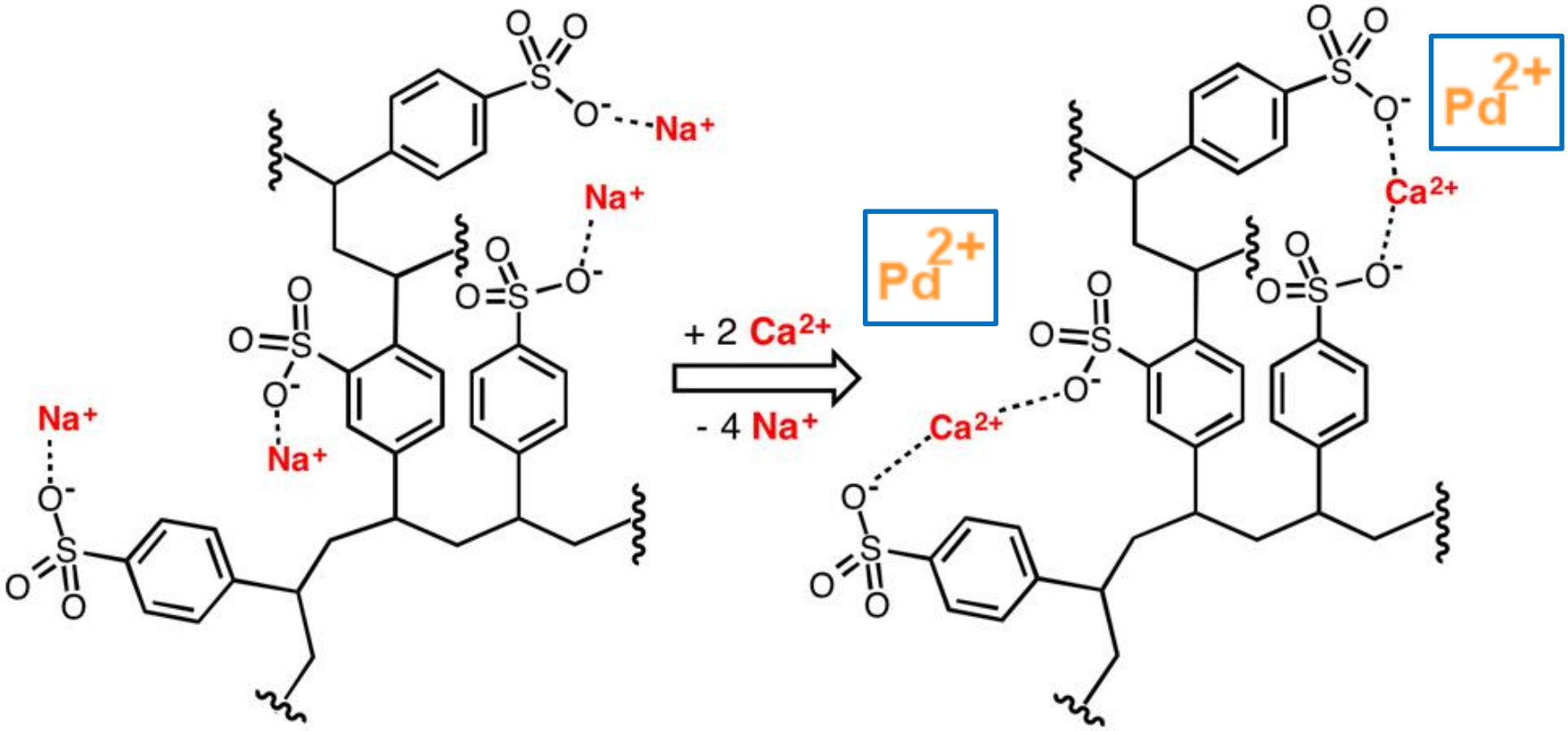
- M. L. Toebes at all, Synthesis of supported palladium catalysts, J. Mol. Cat. A: Chemical 173 (2001) 75-98.

Ionic adsorption

- Adsorption of ionic species such as $[Pt(NH_3)_4]^{2+}$, $[PtCl6]^{2-}$, $[Pd(OH)4]^{2-}$ onto the carbon support occurs via the functional groups on the surface.
- By this mechanism, uniformly impregnated catalysts are available because of an equilibrium between adsorbed and free ions exists; diffusion into the core of each individual support particle can occur.



Active carbons as cation exchanger resin



The deposition of ultrafine platinum particles on carbon black by surface ion exchange—increase in loading amount

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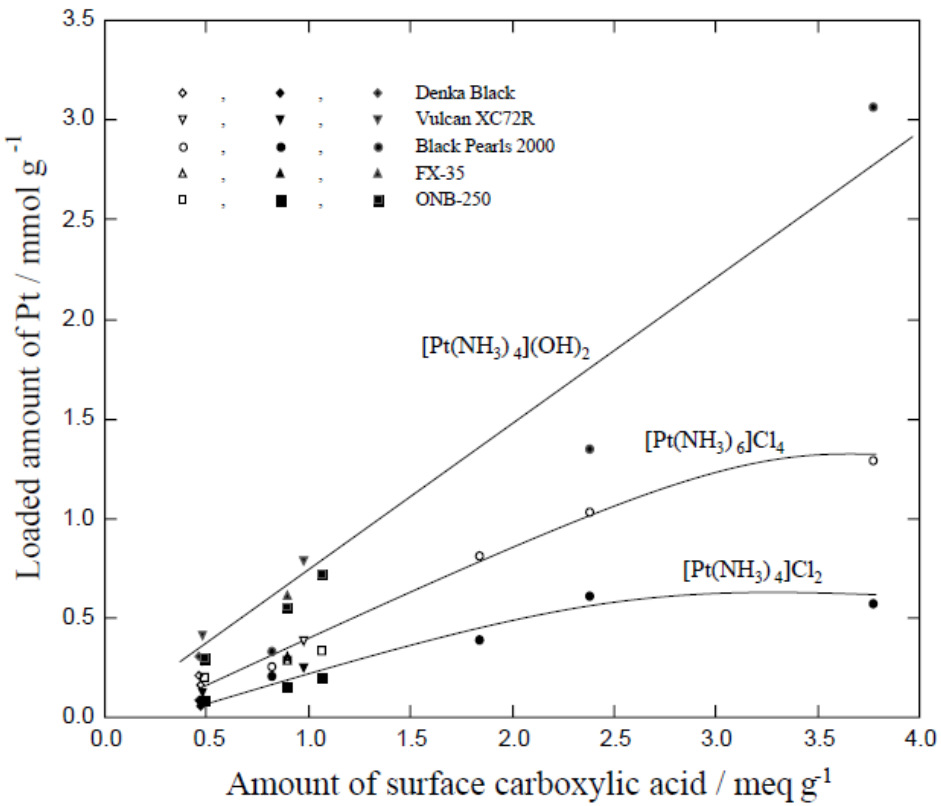
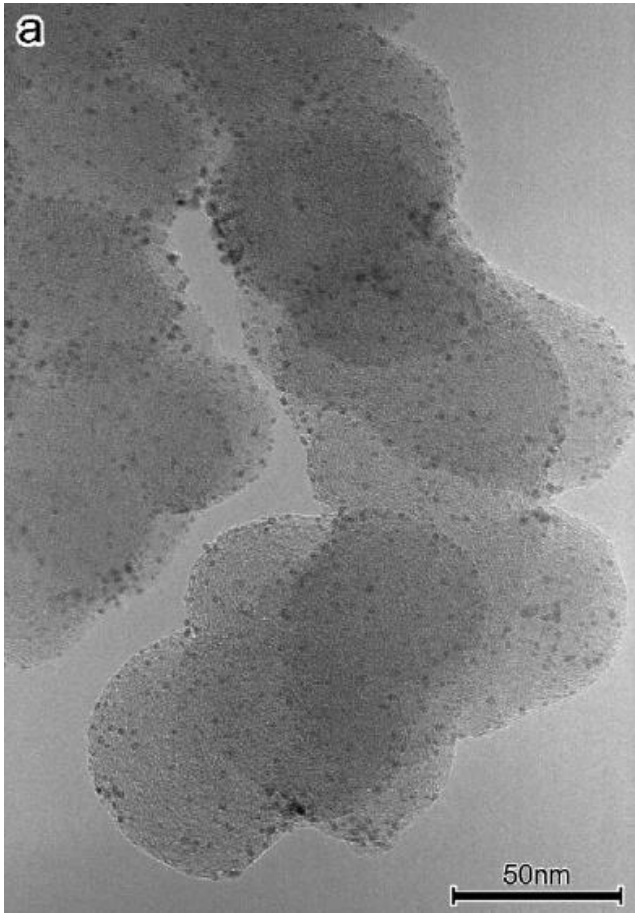
- Carbon black-supported platinum electrocatalysts were prepared by an ion-exchange technique.
- The platinum loading amount was up to 37.4 wt.% using this technique.
- Carbon blacks were first oxidized by the liquid phase method before the ion exchange;
- The oxidized carbon blacks were immersed in a solution of the platinum cation-complex salt; dried in the oven at 110 ◦C.
- Reduction of the adsorbed platinum complex precursor to its metallic form was carried out by the treatment with hydrogen gas at elevated temperature.

- Kazuaki Yasuda∗, Yasuo Nishimura, Materials Chemistry and Physics 82 (2003) 921–928.

K. Yasuda, Y. Nishimura / Materials Chemistry and Physics 82 (2003) 921–928





Deposition / precipitation

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- Palladium on carbon using deposition/precipitation.
- Activated carbon pre-treated with HNO_3.
- The palladium precursor, K_2PdCl_4, was added to an aqueous suspension of the support
- The pH of the solution was adjusted to 10–11 by addition of a KOH-solution.
- Precipitated $Pd(OH)_2$ into porous texture was reduced by HCOONa or H_2 gas.

Reduction step

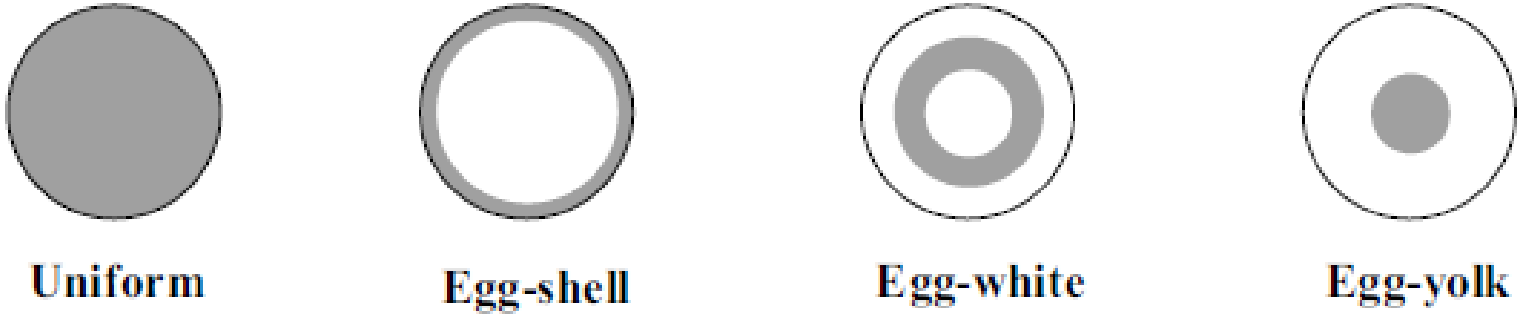
- From the table it can be concluded that reduction by hydrogen results in a much higher dispersion than reduction by HCOONa.
- G. Farkas, L. Hegedus, A. Tungler, T. Mathe, J.L. Figueiredo, M. Freitas, J. Mol. Catal A: Chem. 153 (2000) 215.

Effect of support activation and reduction procedure on Pd dispersion[a]

Support	S_{BET} ($m^2\ g^{-1}$)[b]	Dispersion Pd (%, H_2 chemisorption)	
		Reduction H_2	Reduction HCOONa
Activated carbon HCl	1000	48	10
Activated carbon O_2/N_2	1130	41	20
Activated carbon HNO_3	910	50	20
Graphite	8.4	48	20
Carbon black	36	43	10

Different distribution of PGM crystallites on activated carbon

- When using **impregnation** for catalyst preparation, it is important the distribution of the precursor over the macroscopic support bodies.
- Four types of distribution are available:
  - Uniform
  - Egg-shell
  - Egg-white
  - Egg-yolk



The best PGM distribution onto the carrier

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- For large catalyst bodies, a homogeneous distribution of the active phase is only preferential for relatively slow catalytic reactions, providing reactants time to diffuse to the active sites.
- If the reaction is fast or if secondary reactions are problematic, a different macroscopic distribution of the active phase might be preferred, such as an eggshell distribution or an egg-white distribution, if the catalyst is prone to attrition.
- If the reactants contain poisons, an egg-yolk distribution may be favorable so that the poison can be captured at the edge of the catalyst body, where few active sites are present .

- Peter Munnik, Petra E. de Jongh, and Krijn P. de Jong, Recent Developments in the Synthesis of Supported Catalysts ,Chem. Rev. 2015, 115, 6687−6718

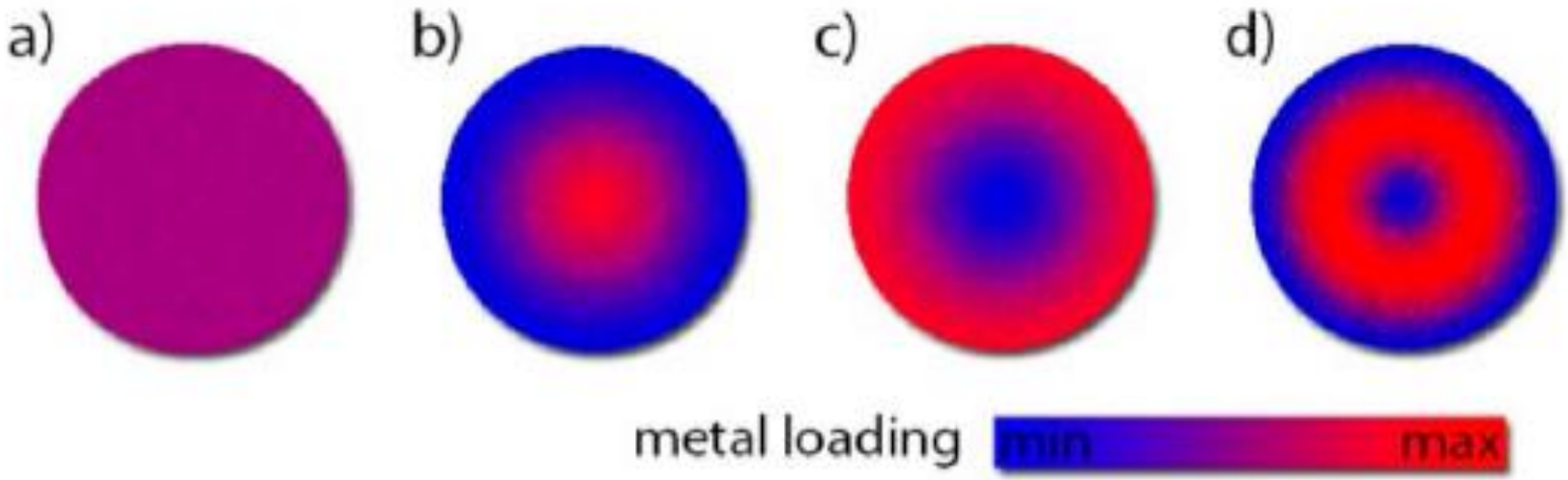

Figure 1. Different types of macroscopic metal distributions across a support body: (a) homogeneous distribution, (b) egg-yolk distribution, (c) eggshell distribution, (d) egg-white distribution (red, high concentration of metal; blue, low concentration of metal).

Preparation method: Deposition/reduction

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- Preparation of 5% Palladium on activated carbon catalysts.
- In a suspension of activated carbon an aqueous solution of Na_2PdCl_4 was dropped and stirred.
- Then reducing agent (sodium hypophosphite or formaldehyde) was added rapidly.
- The precipitation step is missing !
- G.R. Heal, L.L. Mkayula, Carbon 26 (1988) 815.

Preparation method: Deposition/reduction

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- It may already occur when the first metal ions reach a virgin support surface and come into contact with redox active sites (formation of π-complexes of $PdCl_2$ with C=C fragments).
- In this way, nucleation centers are generated.
- Further deposition of metal atoms on these metal clusters or crystallites by a redox mechanism can be achieved by adding a reducing agent to the reaction mixture.
- This method is also very effective for the site selective deposition of a second metal on preformed metal crystallites.

Preparation method: Colloid deposition

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- Deposition of a preformed or in situ generated precious metal colloid.
- These colloid particles readily adsorb on the external surface of the support particles and in their porous structure.
- The size of the colloid particles controls their penetration into the pore system.
- If the size of the colloid particles is large, the accessibility of the inner pore system is only very limited, which leads to egg-shell distribution of the metal.

BASF patent

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(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
6 August 2009 (06.08.2009)

PCT

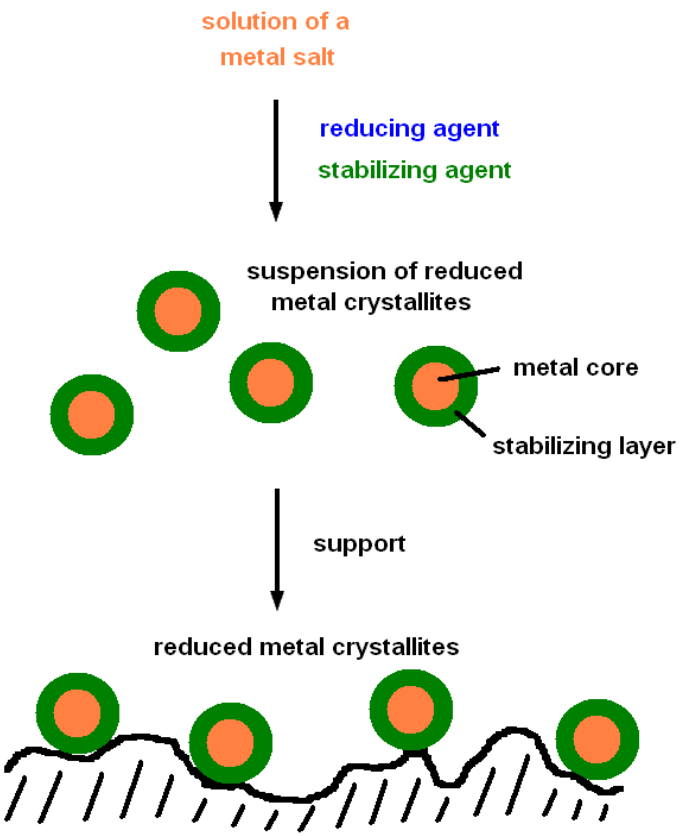
(10) International Publication Number
WO 2009/096783 A1

(54) Title: PROCESS FOR THE PREPARATION OF AN AQUEOUS COLLOIDAL PRECIOUS METAL SUSPENSION

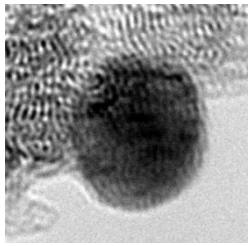
(57) Abstract: The invention is directed to a process for the preparation of an aqueous colloidal precious metal suspension, which process comprises reducing a precious metal salt in aqueous solution using a functionalised, water soluble quaternary ammonium salt in the absence of organic solvents, to form elementary nanoparticles.

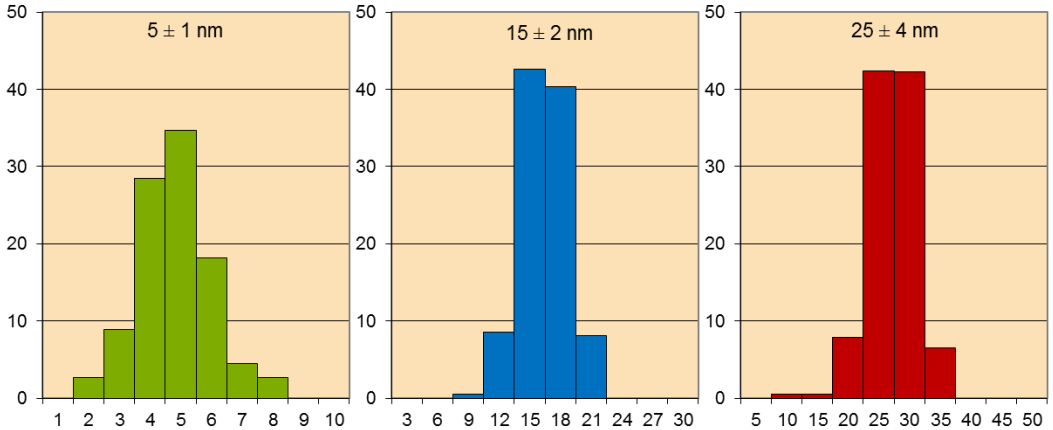
"Colloidal" preparation

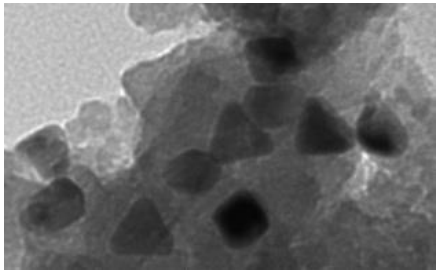
- Step 1: reduce metal in solution
- Step 2: deposit metal on support



NanoSelect Pd catalysts
Tuning of metal crystallite size I





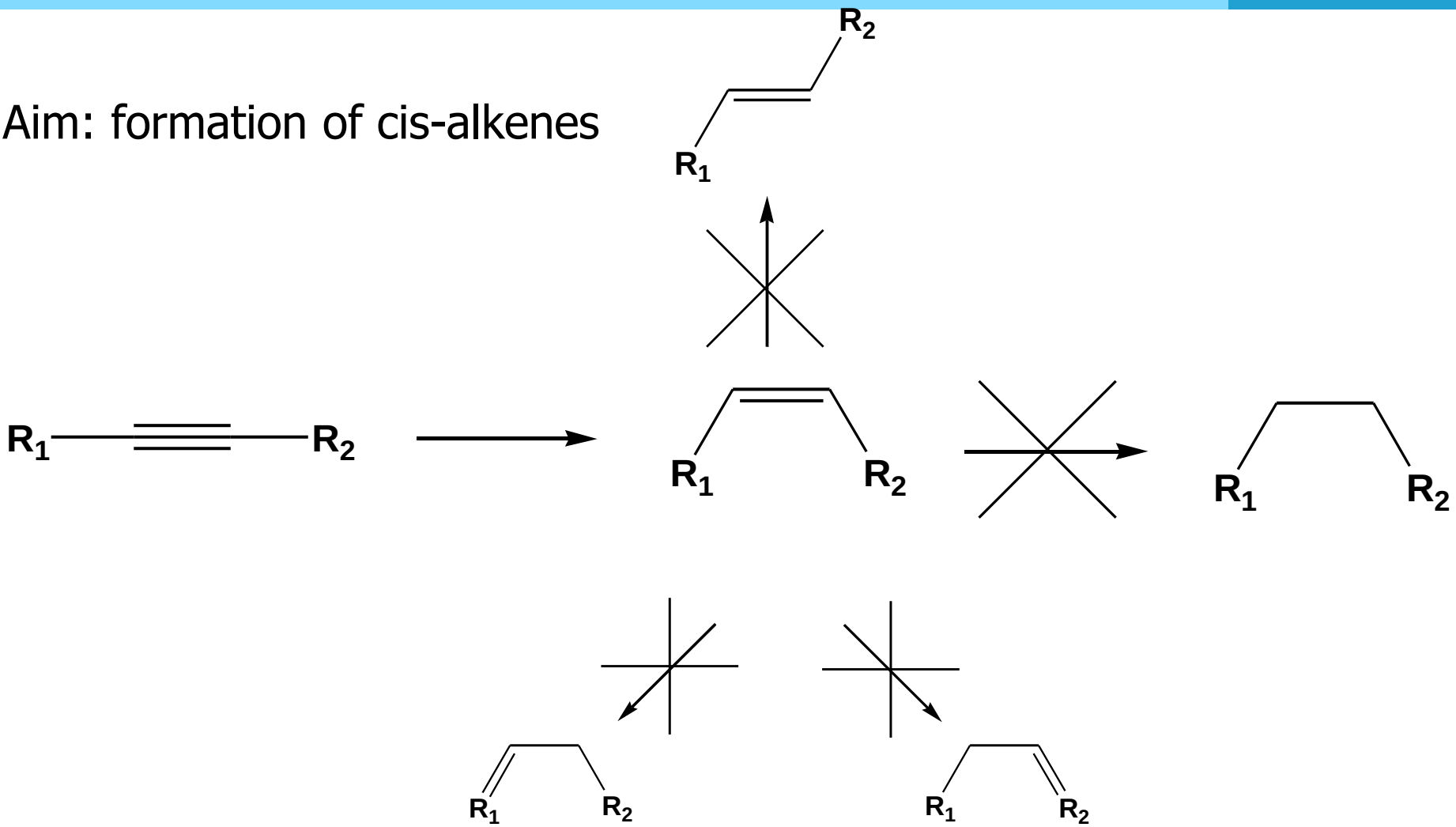


- A narrow distribution of Pd cristallites is obtained.
- The size of Pd cristallites can be tuned from 5 to 25 nm.
- Selective catalyst.

Semi-hydrogenation of alkynes

Reaction scheme

Aim: formation of cis-alkenes



Incipient wetness impregnation

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- IWI, also called capillary impregnation or dry impregnation.
- The carriers are usually spheres or other geometrical shapes.
- The adsorption power of carrier is measured; i.e. the volume of solution that can be adsorbed by carrier, remaining dry.
- Typically, the active metal precursor is dissolved in an aqueous or organic solution.
- The metal-containing solution is added to a catalyst support. Capillary action draws the solution into the pores.
- The catalyst can then be dried and calcined to drive off the volatile components within the solution, depositing the metal on the catalyst surface.

Bimetallic catalyst : Gold and Palladium

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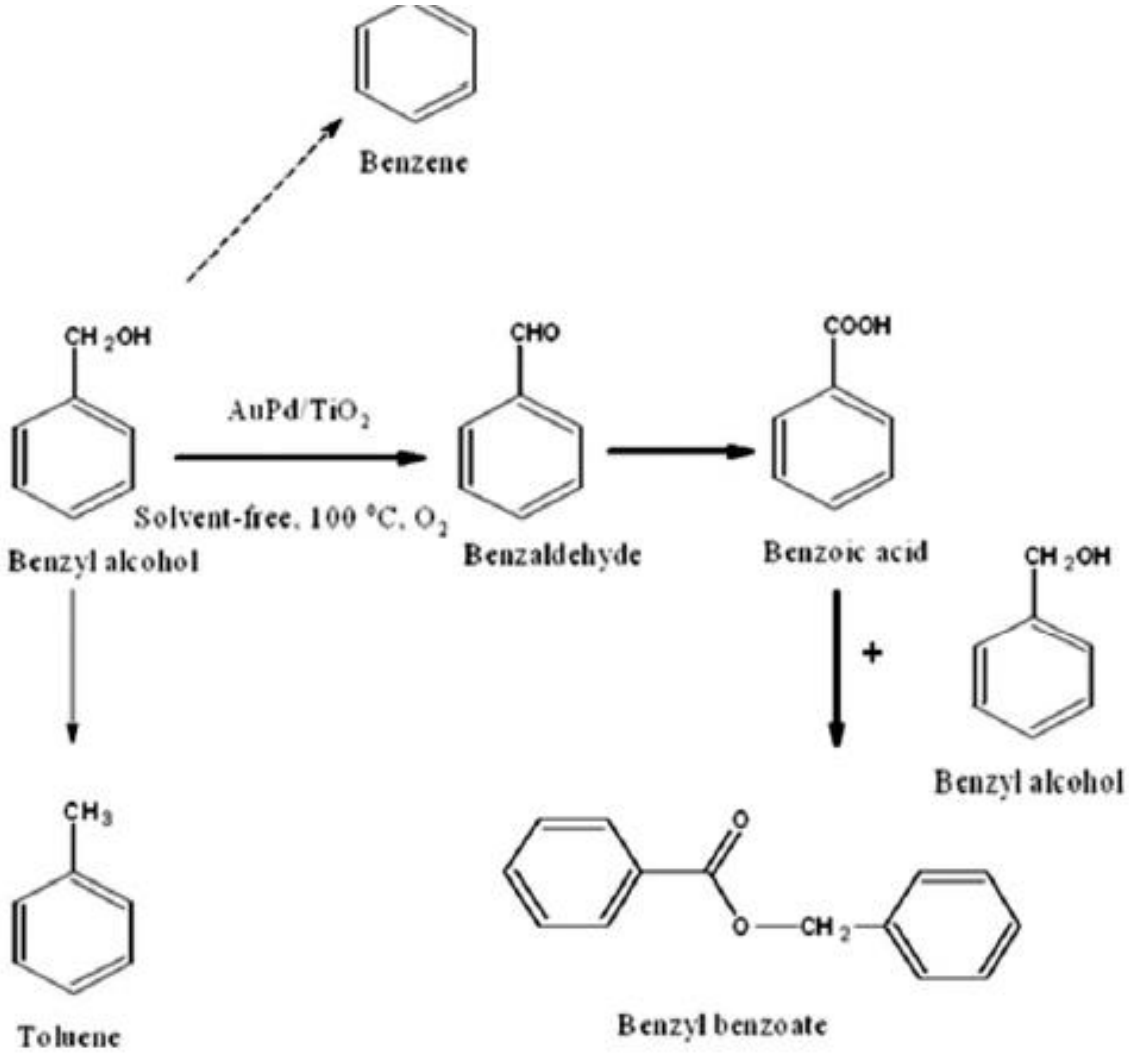
- Increasing interest in the synthesis of supported bimetallic Au–Pd catalyst.
- (i) Au and Pd can form solid solutions in the whole range of Au/Pd atomic ratio;
- (ii) the addition of second metal can alter the electronic and geometrical properties of the synthesized nanoparticle with the formation of alloy and core–shell structures.
- The main application is the selective oxidation of alcohols.
- Selectivity and catalyst stability are affected depending on the final morphology of the nanoparticles.

- Federica Menegazzo,∗, Maela Manzolib, Michela Signoretto,Francesco Pinna, Giorgio Strukul, H2O2DIRECT SYNTHESIS UNDER MILD CONDITIONS ON PD–AU SAMPLES: EFFECTOF THE MORPHOLOGY AND OF THE COMPOSITION OF THE METALLIC PHASE; Catalysis Today 248 (2015) 18–27

Oxidation of benzyl alcohol to benzaldehyde

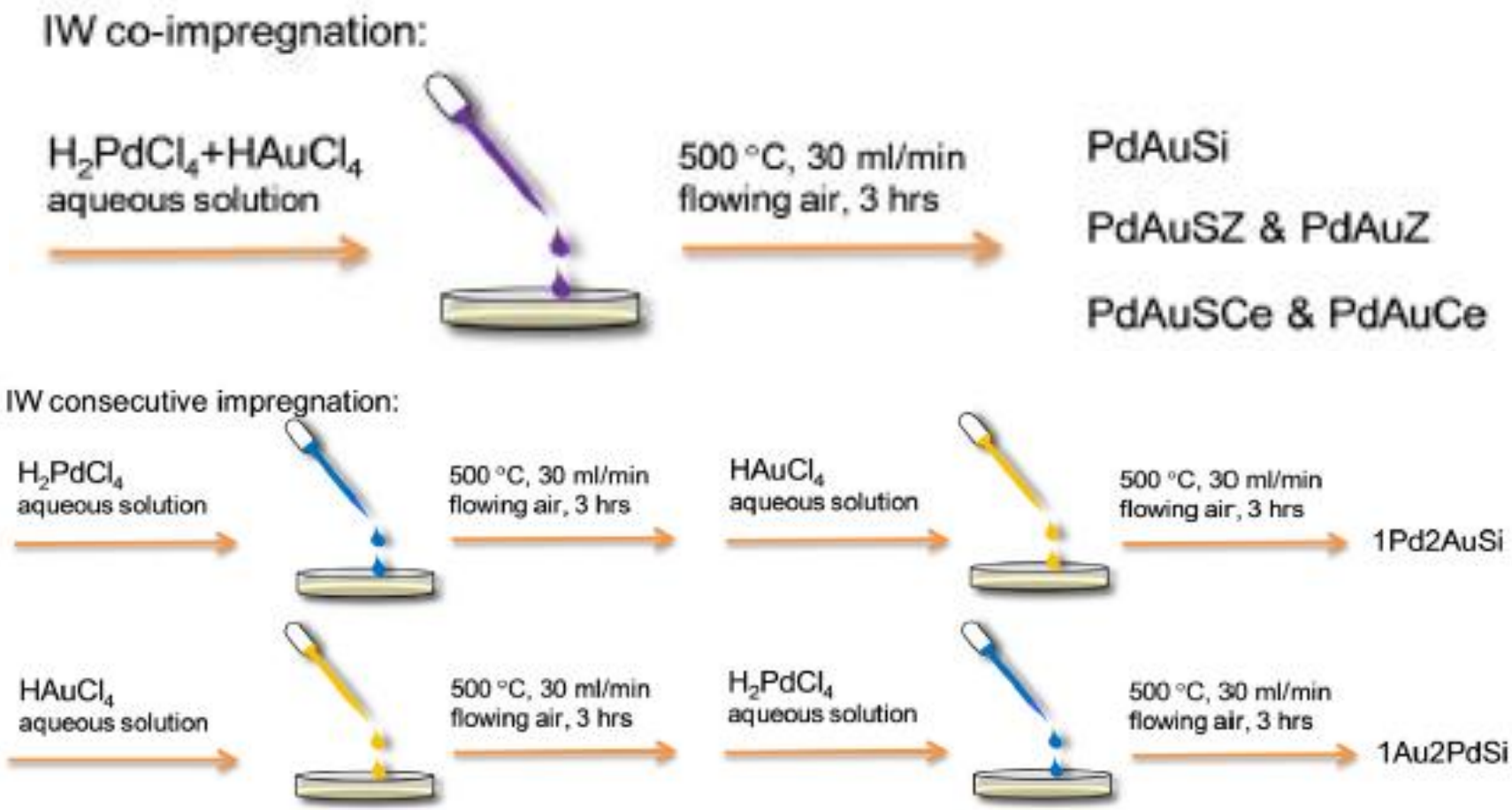


Oxidation test results

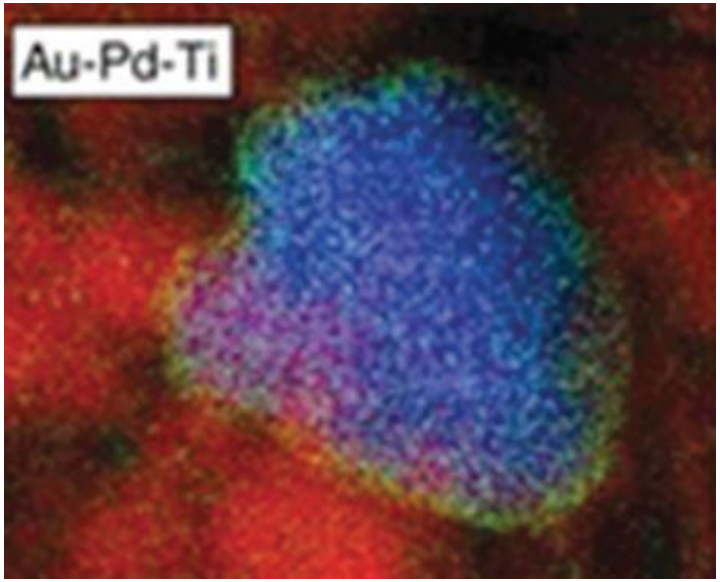
- The higher activity of the supported Au–Pd catalysts synthesized by the colloidal method instead of the impregnation method was attributed primarily to the significant smaller particle size, narrow particle size distribution and metallic oxidation state of the two metals.

Catalyst	T (°C)	Solvent	Conv. (%)	Sel% aldehyde
Au–Pd/TiO_2	100	Solvent free	90	95
Au–Pd/C	120	Solvent free	80	65
Au–Pd/C	60	H_2O/NaOH	95	94
Au_{80}–Pd_{20}/C	60	$C_6H_5CH_3$	90	99
Au–Pd/PI	100	H_2O/Na_2CO_3	99	98
Au–Pd/SBA-15	80	Solvent-free	40	99
Au–Pd/Fe_3O_4	100	Solvent-free	65	94
Au–Pd/TiO_2	90	H_2O	75	96
Au–Pd/MgO	90	H_2O/K_2CO_3	75	95
Au@Pd@Ph-PMO	80	Solvent-free	100	93
Au@8Pd/SiO_2	90	Solvent-free	91	87
Au–Pd–GO/TiO_2	120	H_2O/NaOH	89	71

Au-Pd catalyst prepared by IWI



SEM pictures



Ti in red, Au in blu, Pd in green

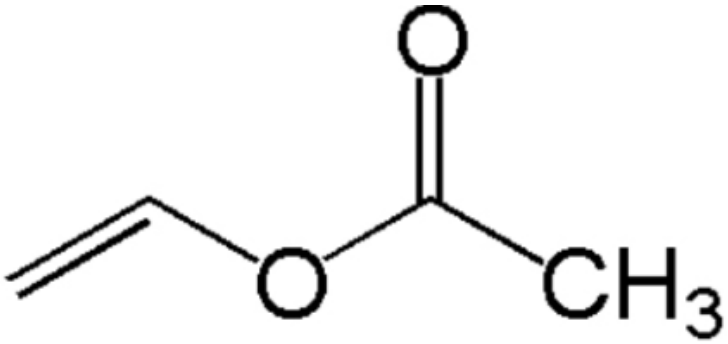
Vinyl Acetate Monomer (VAM)

- The vinyl acetate monomer (VAM) is large - scale commodity chemical mostly used in manufacturing polyvinyl acetate, the basic ingredient in water - soluble acrylic paints.
- Other applications are coatings for textile and paper industries, laminated safety glass, packaging, automotive fuel tanks and acrylic fibers.
- VAM is produced by a gas phase acetoxylation of ethylene over a Pd–Au bimetallic silica-supported catalyst promoted with potassium acetate (AcOK) at a reaction temperature of 423–463 K and a total pressure of 600–1000 kPa.

$$CH_3COOH + C_2H_4 + 0.5O_2 \rightarrow CH_3COOCHCH_2 + H_2O$$

Vinyl Acetate Monomer (VAM)

- The combustion of ethylene to CO_2 is a highly undesired secondary reaction since it lowers the yield and complicates the removal of the reaction heat.
- The catalyst plays a crucial role in technology. Previously, catalysts were based on palladium of 1 to 5 wt% impregnated on silica with alkali metal acetates as activators.
- Modern catalysts employ as enhancers noble metals, mostly gold.



Variables in catalyst active surface

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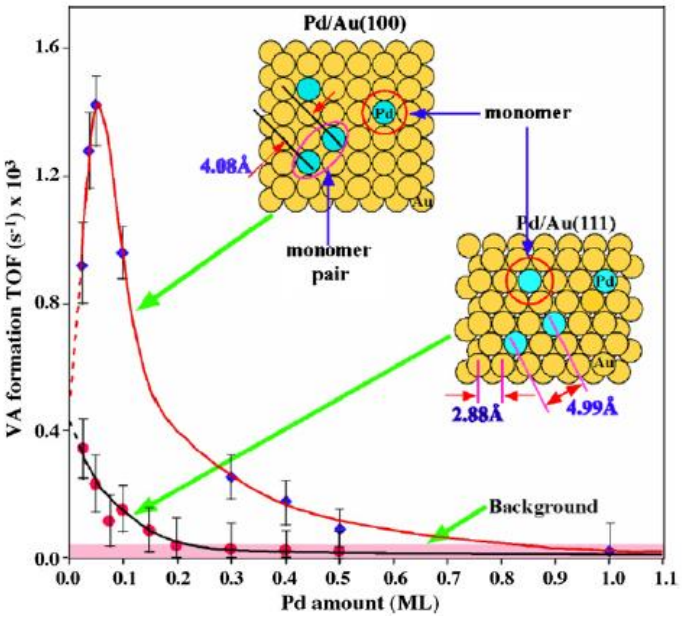
- Reaction mechanism and the nature of the active sites/intermediates in VA synthesis.
- Au–Pd alloys are completely miscible, the reactivity of metal surfaces being a critical function of composition and structure with alloys often showing unique properties compared to the corresponding single component metals.
- Furthermore we have to consider that commercial catalyst is carried on SiO_2 sphere, so we have to count for metals – support interactions.
- Moreover the surface composition of Au–Pd mixtures differs from the respective bulk composition, with the surface being enriched in Au.

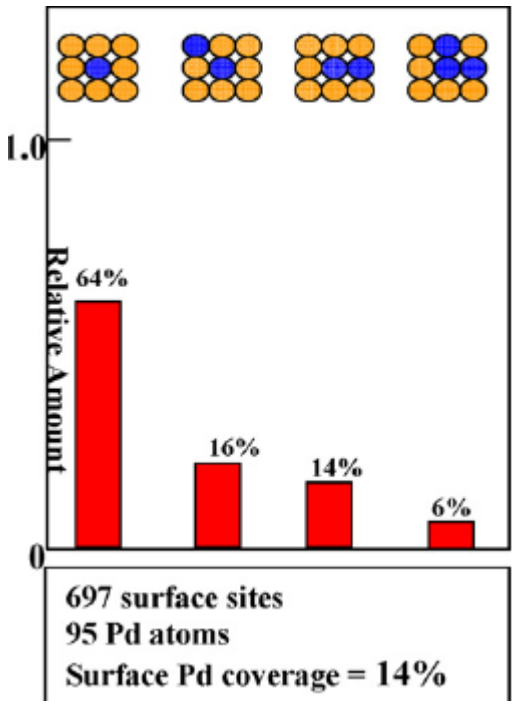
Variables in catalyst active surface (D. Kumar et al. / Catalysis Today 123 (2007) 77–85)

- Pd active sites are formed by Pd was vapor deposited onto two gold substrates, Au(100) and Au(111).
- These Pd/Au(100) and Pd/Au(111) catalysts were used to investigate the rate of formation of VA.
- The reaction rate increased to a maximum at a coverage of 10% of Pd monolayer on Au(100) and decreased with a further increase in the Pd coverage.



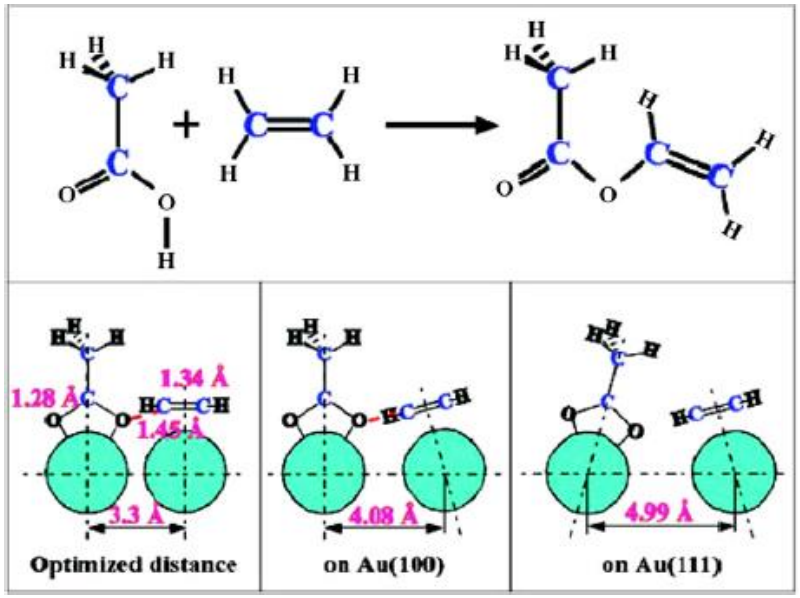
Variables in catalyst active surface

- For the optimum surface of 0.1 ML of Pd, the density of Pd monomers is the highest, consistent with Pd monomers being the active sites for the formation of VA on Pd/Au surfaces.
- There is a strong evidence for isolated Pd atoms (monomers) being the active sites for the reaction.
- A pair of non-contiguous Pd monomer sites, rather than a single isolated site, is required for VA formation (dual site mechanism).



Variables in catalyst active surface

- Considering the bond lengths of adsorbed ethylene and acetate species, the optimized distance between two active sites is 3.3 A ° .
- Au(100) defines the distance between a pair of Pd monomers to be 4.08 A°
- Au(111) defines this distance to be 4.99 A °, a prohibitively long distance for coupling of these two reactive intermediates.



Nobel prize for Chemistry

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The Nobel Prize in Chemistry 2010

Richard F. Heck, Ei-ichi Negishi and Akira Suzuki

"for palladium-catalyzed cross couplings in organic synthesis"

The Nobel Prize in Chemistry 2001

William S. Knowles and Ryoji Noyori

"for their work on chirally catalysed hydrogenation reactions"

The Nobel Prize in Chemistry 1990

Elias James Corey

"for his development of the theory and methodology of organic synthesis"

- Winners of Nobel prize because using precious metals as catalyst or for enantioselective hydrogenation.

Most common PGMs reactivity

- Hydrogenation
- Hydrogenolysis
- Dehydrogenation
- Oxidation
- Isomerization
- Carbon- carbon bond formation