Heterogeneous catalysis and carbon materials: How (why?) are they related?

Fernando Vallejos-Burgos
Universidad de Concepción, Chile
April 2008, Kaneko Labs, Japan

Introduction

- Why we need catalysis?

- Because we need products in an efficient way:
  - Haber process (ammonia)
  - Steam reforming of HC to produce syngas
  - Methanol synthesis
  - Fischer-Tropsch syntesis
  - Hydrog/dehydrog organic compounds
  - Acids production (nitric and sulfuric)
  - Petroleum refining and processing

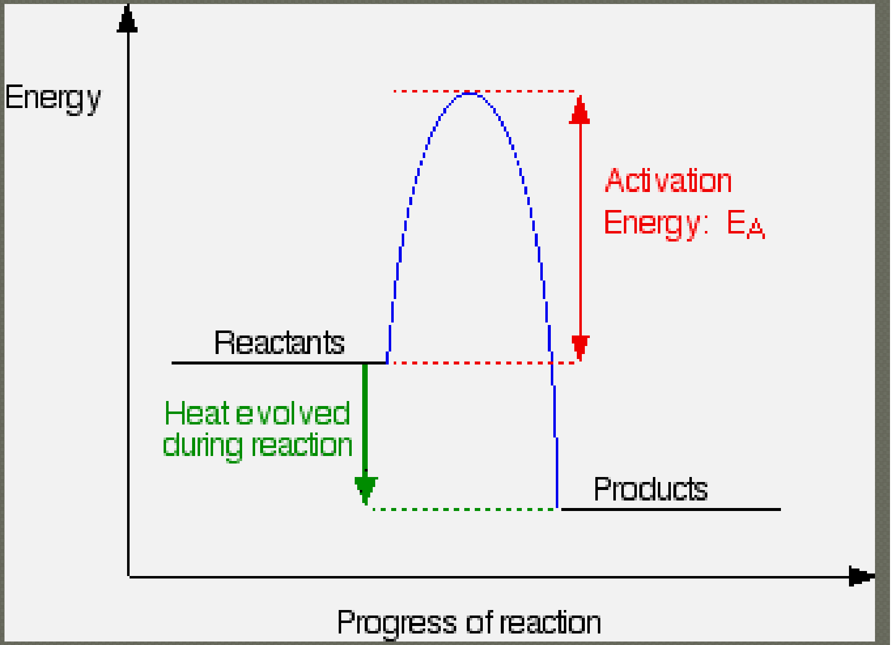
Introduction (2)

- And, of course, for saving our planet

- For example:
  - Abatement of NOx, SO_2, CO, VOC, hydrocarbons
  - Denitrification of drinking water
  - Oxidation of organic pollutants in wastewater

Catalysis: how does it work?

- Activation energy concept



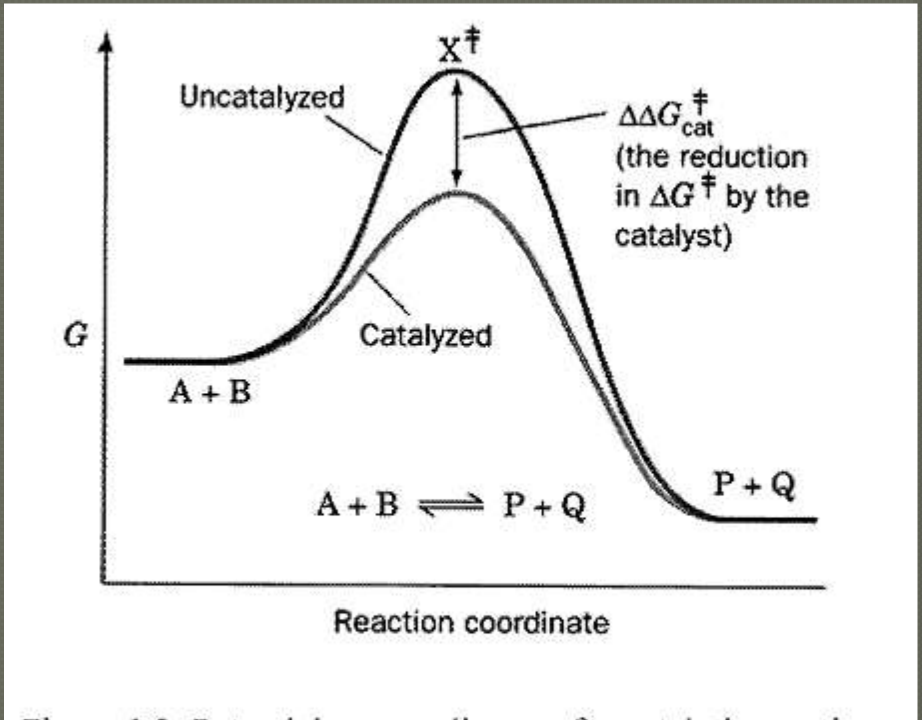
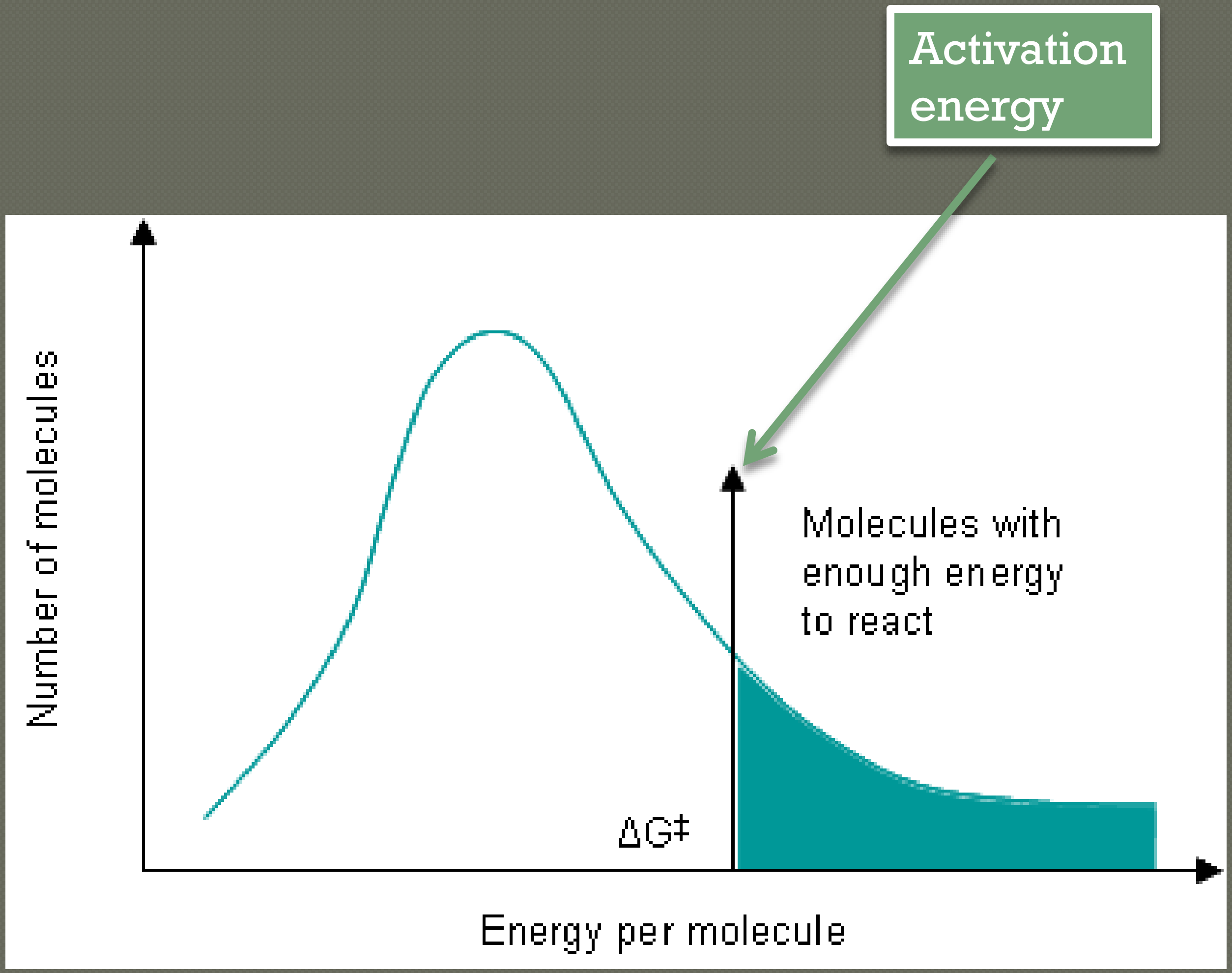


Figure 1.3. Potential energy diagram for catalytic reactions

(Murzin 2005)

- Different paths!

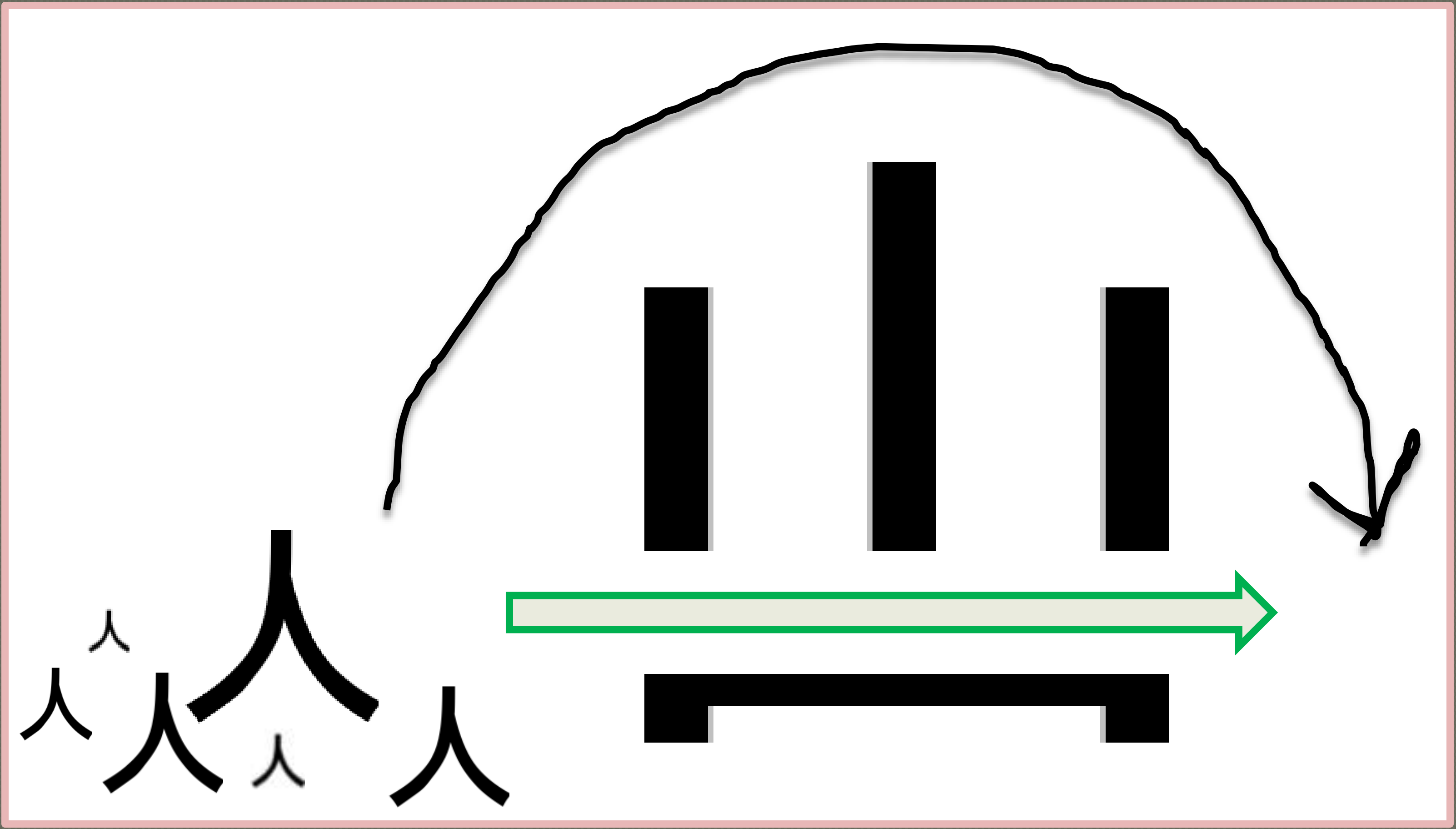
Maxwell-Bolzmann distribution



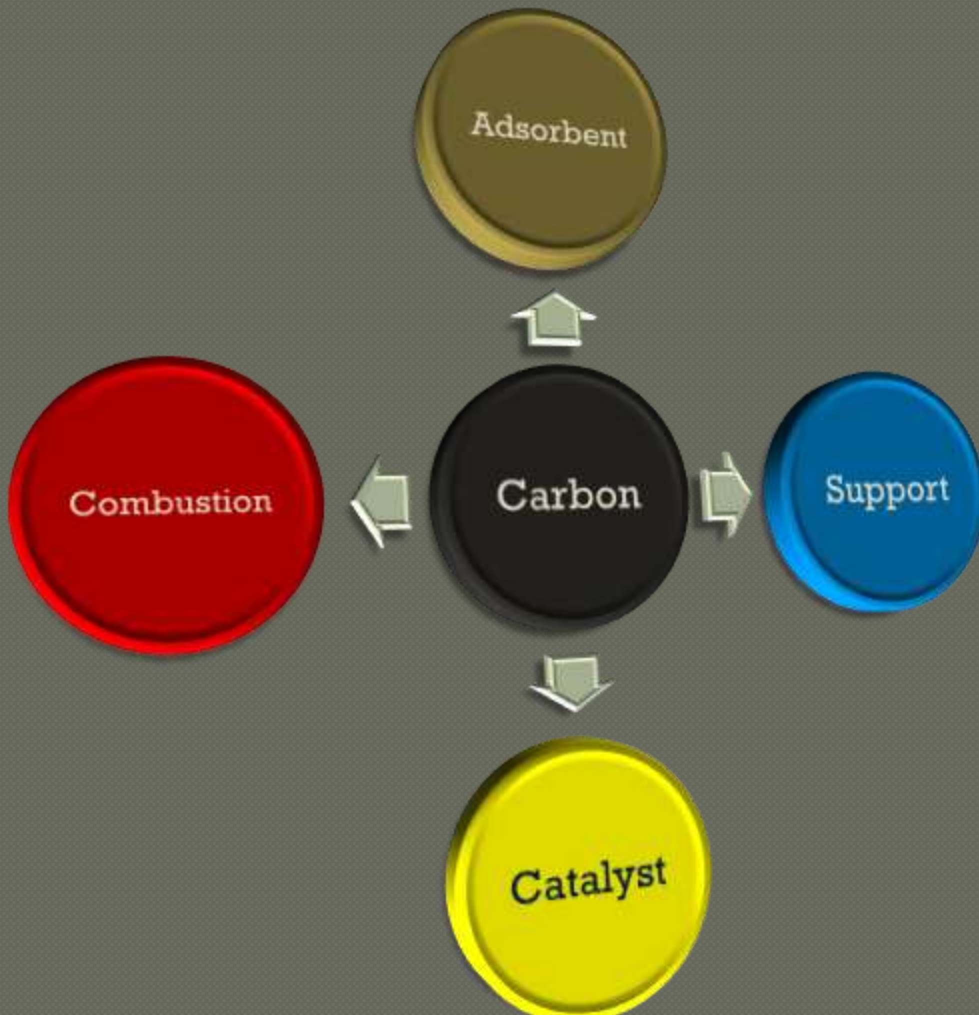
http://www.steve.gb.com/science/kinetics.html

Activation energy 101

- Maxwell-Boltzmann



Uses of carbon materials



…and nanoelectronics, electrodes, etc…

Why using carbon in catalysis?

- Advantages of carbon as catalyst support (Rodríguez-R 1998):
  - Resistant to acidic and basic media
  - Stable at high T°
  - Pore structure [and surface chemistry!] may be tailored
  - Can be prepared in different forms
  - Hidrophobic or hydrophilic
  - Recover of active phase
  - Cheap!

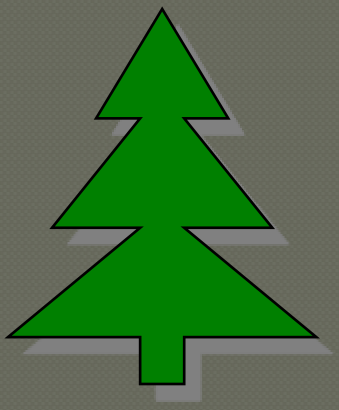
Contents

- Basic concepts on carbon materials
- Surface properties (and chemical structure)
- Changing the carbon
- Reactivity
- Some case examples of carbon as catalyst

Active carbon

Active carbon

- (Rouquerol 1999): ‘There is no precise definition […], but it is generally understood to be a carbonaceous material of high surface area’

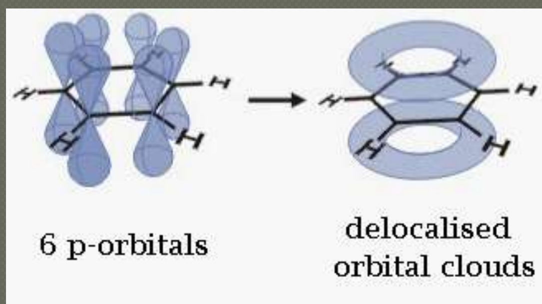


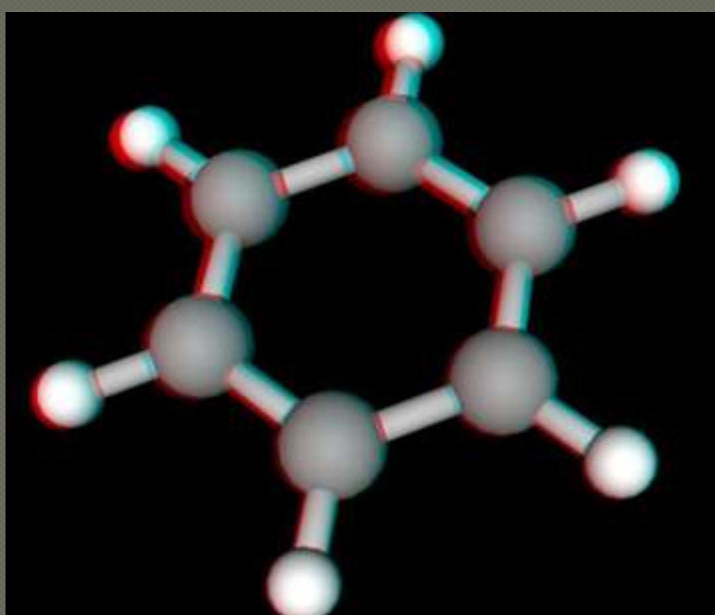
- Where does it come from?

  From any organic source:
  - Wood
  - Coal
  - Biomass
  - Chemicals: polymers

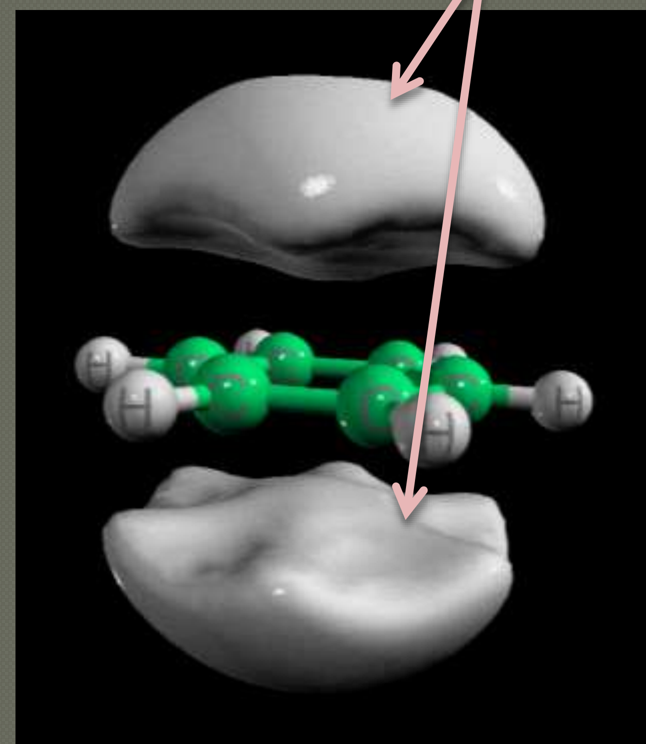
Basic molecule: benzene

- Aromaticity



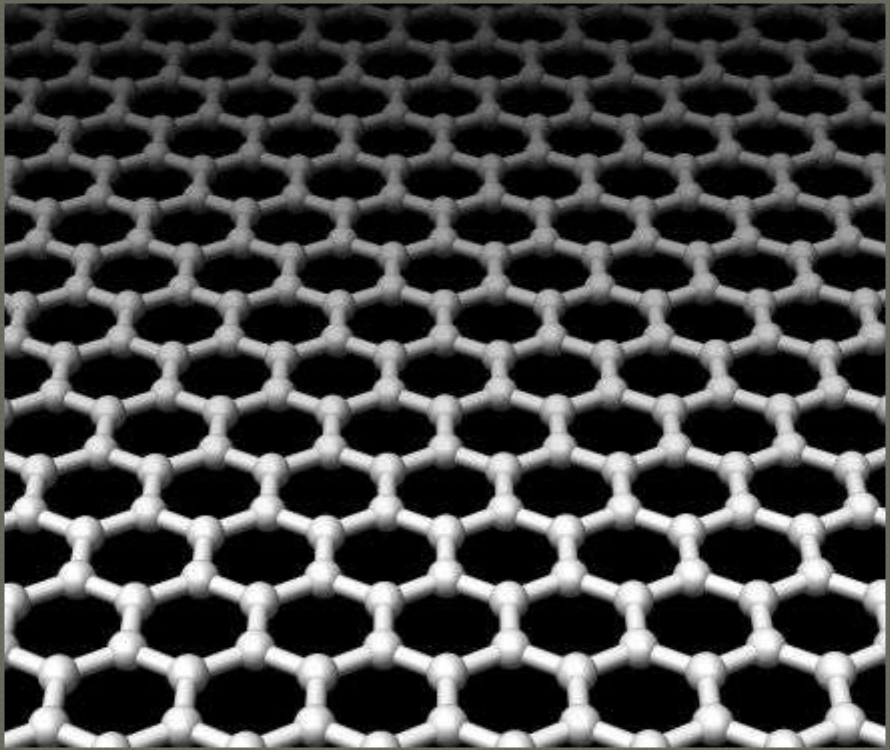


Regions of negative charge: π electrons

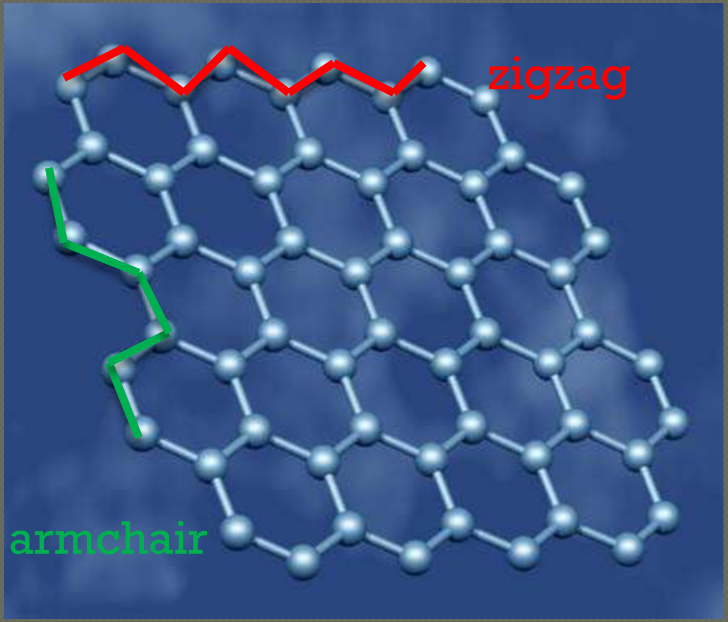


Active carbon: what is it?

- A view from micro to macroscopic

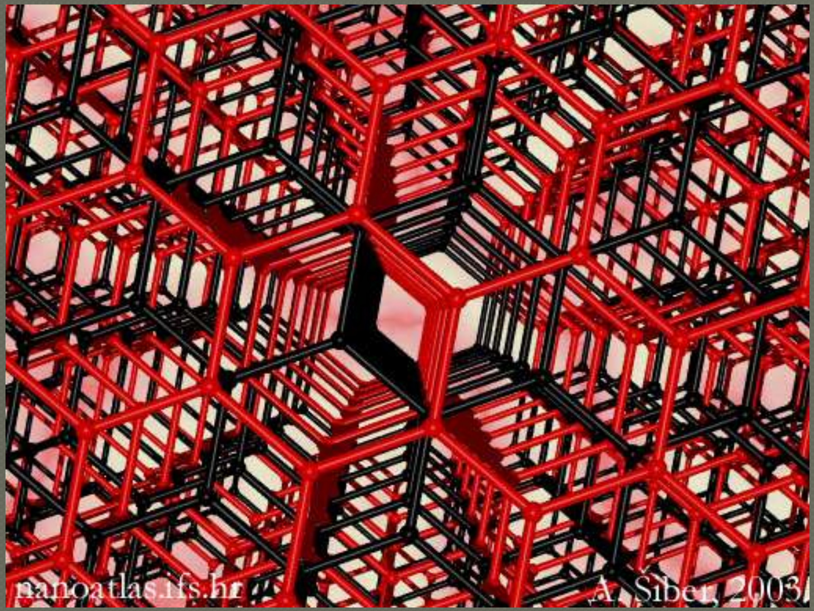


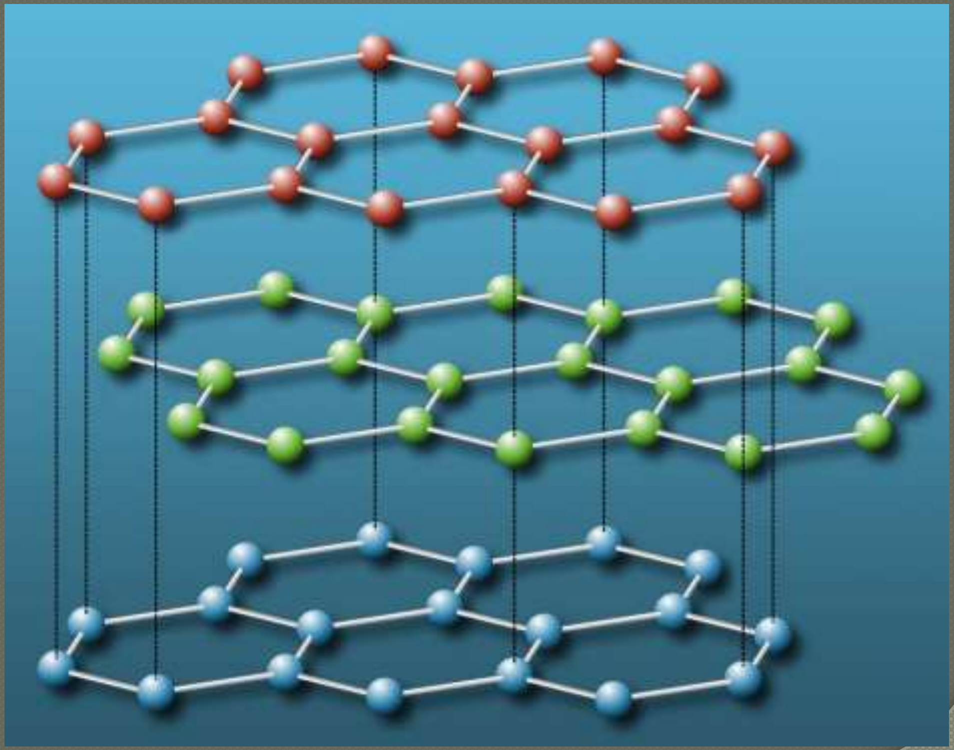
graphene



Active carbon: what is it?

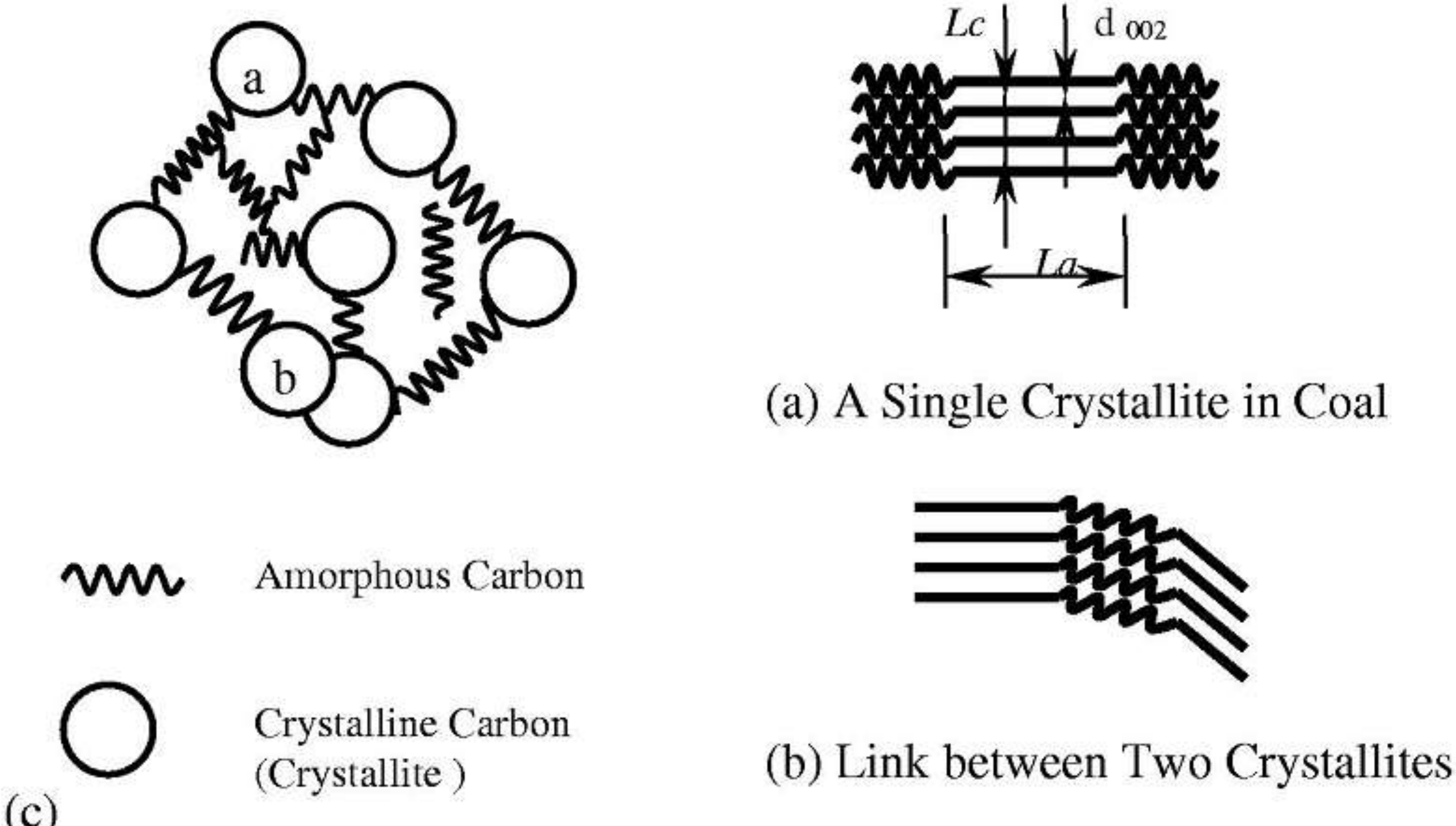
- Many graphene layers → **graphite**





How is porosity generated?

L. Lu et al. / Carbon 39 (2001) 1821–1833

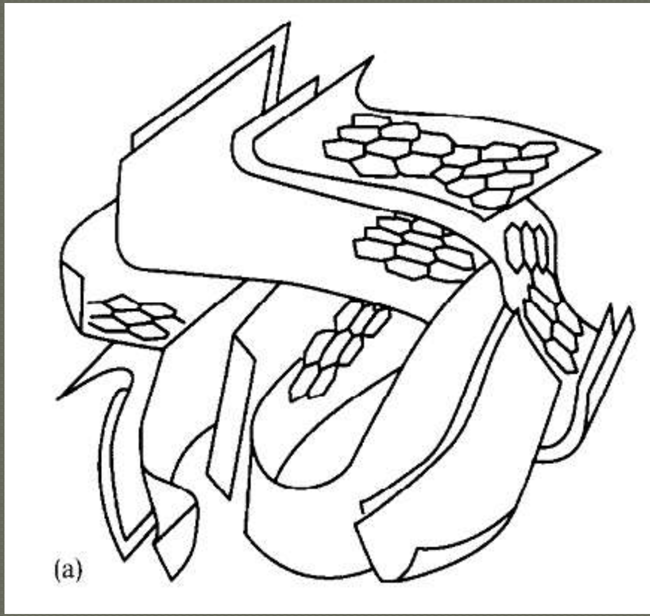


(a) A Single Crystallite in Coal

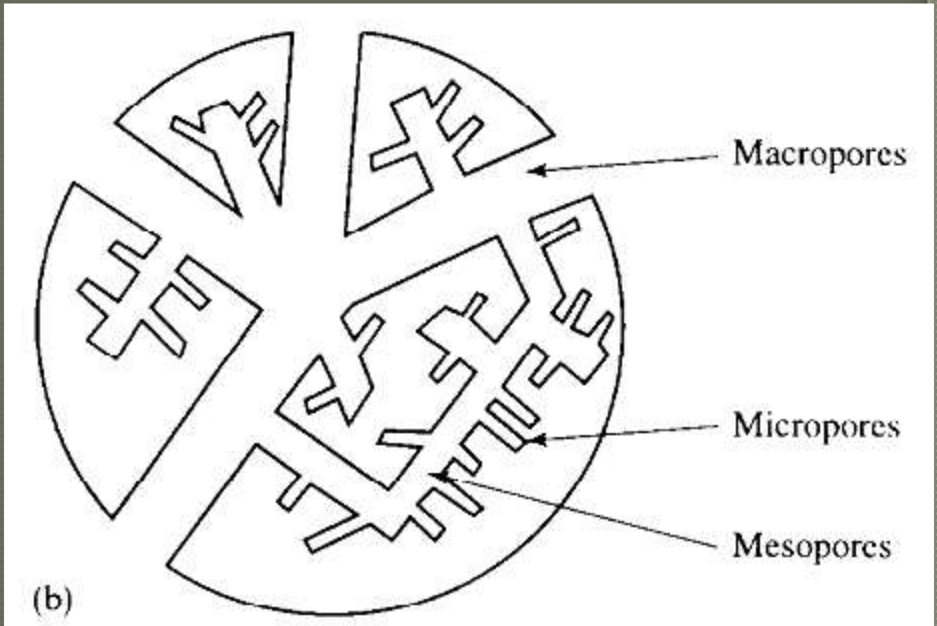
(b) Link between Two Crystallites

Crosslinking

- Graphene crystallites are linked by non-aromatic bonds making the different types of pores



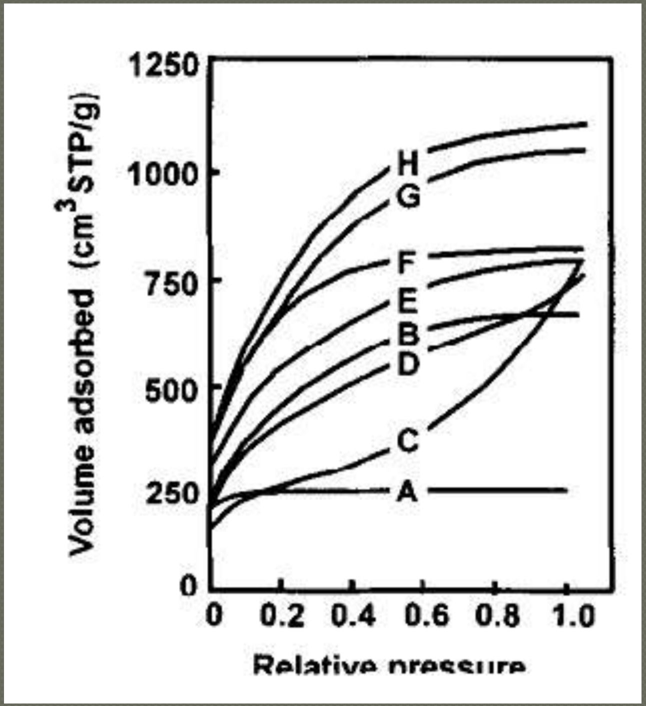
Stoeckli Carbon 1990



Rodriguez-Reinoso Carbon 1998

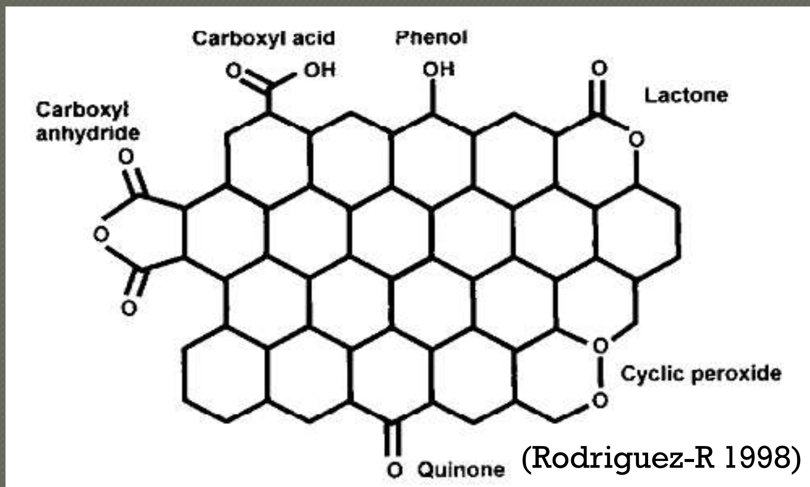
Structure: How can we change it?

- Chemical / physical activation
- Activation conditions (and activating agent) will define the structure of the new carbon

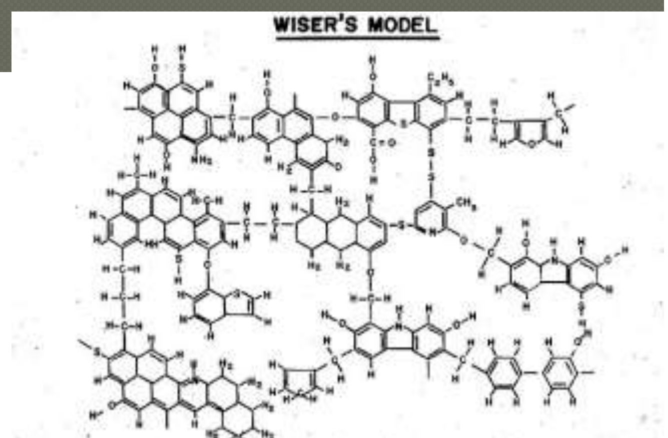


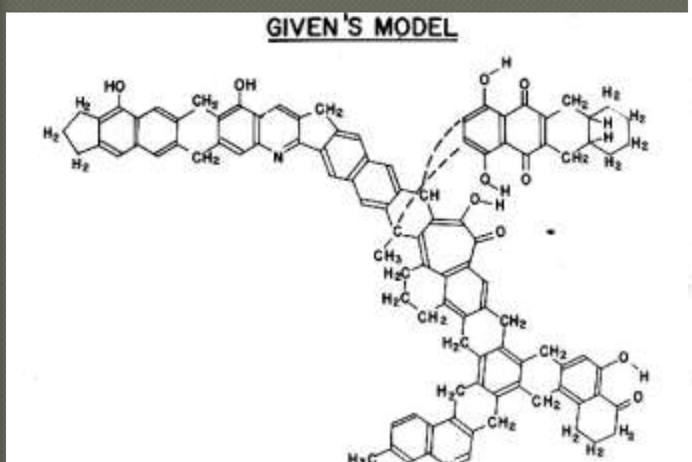
(Rodríguez-Reinoso 1998)

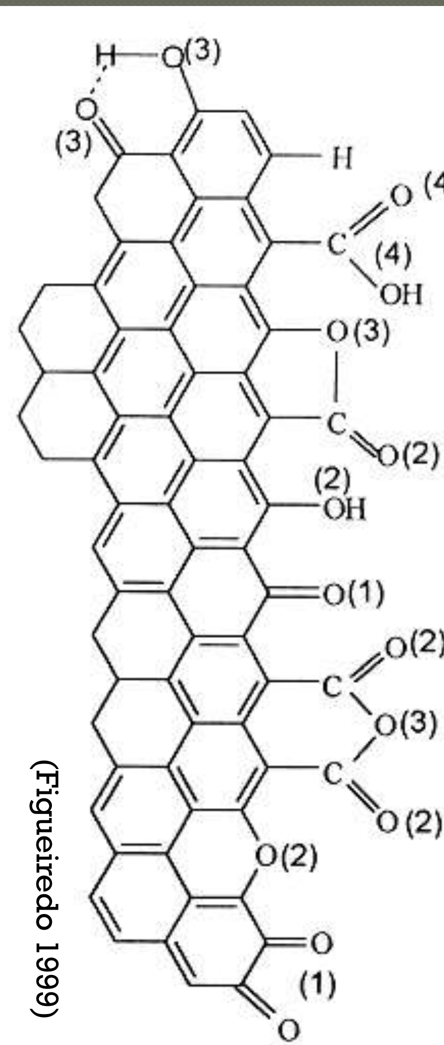
Now the surface chemistry



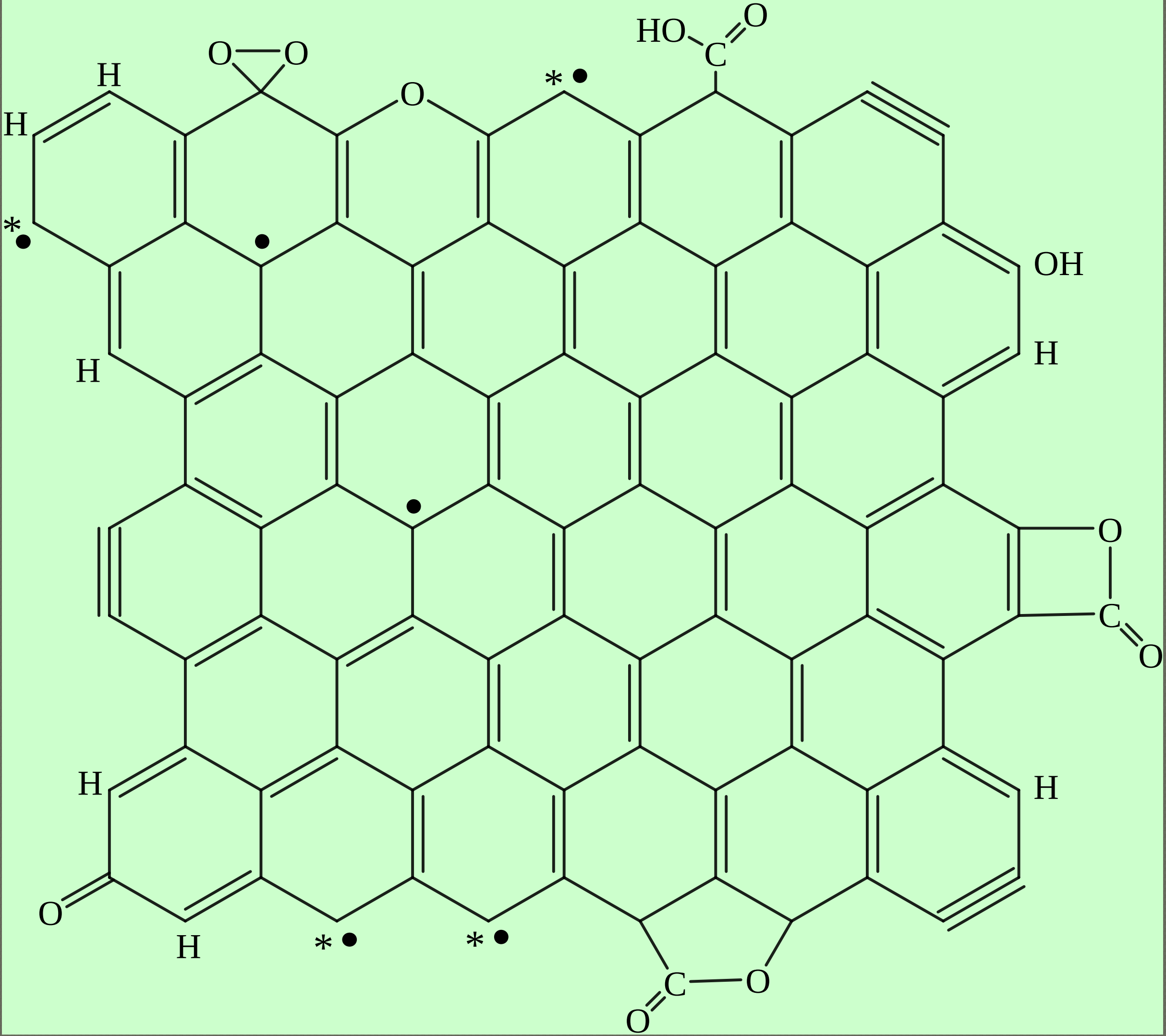
(Rodriguez-R 1998)






(Figueiredo 1999)

Summary of **current** understanding of **main features** of carbon surface chemistry:



Version 3.1

Radovic, L. R. y B. Bockrath (2005). "On the Chemical Nature of Graphene Edges: Origin of Stability and Potential for Magnetism in Carbon Materials." J. Am. Chem. Soc. **127(16): 5917-5927.**

“Conventional” amphoteric solids

$RO^- + H^+ + H_2O = ROH_2^+ + OH^-$

vs.

Unique proton-transfer character of carbons

Origin of the negative charge:

Dissociated acidic functional groups

Origin of the positive charge:

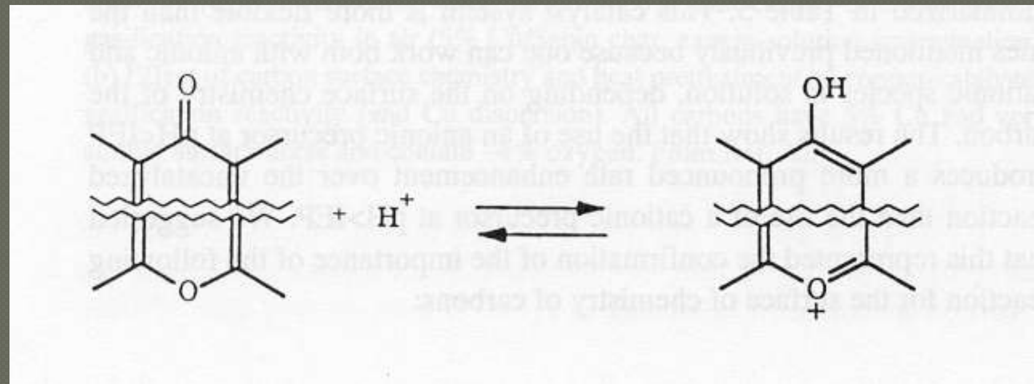
Some functional groups (e.g., pyrones)

Delocalized π electrons (graphene layer)

Carbene sites at graphene edges

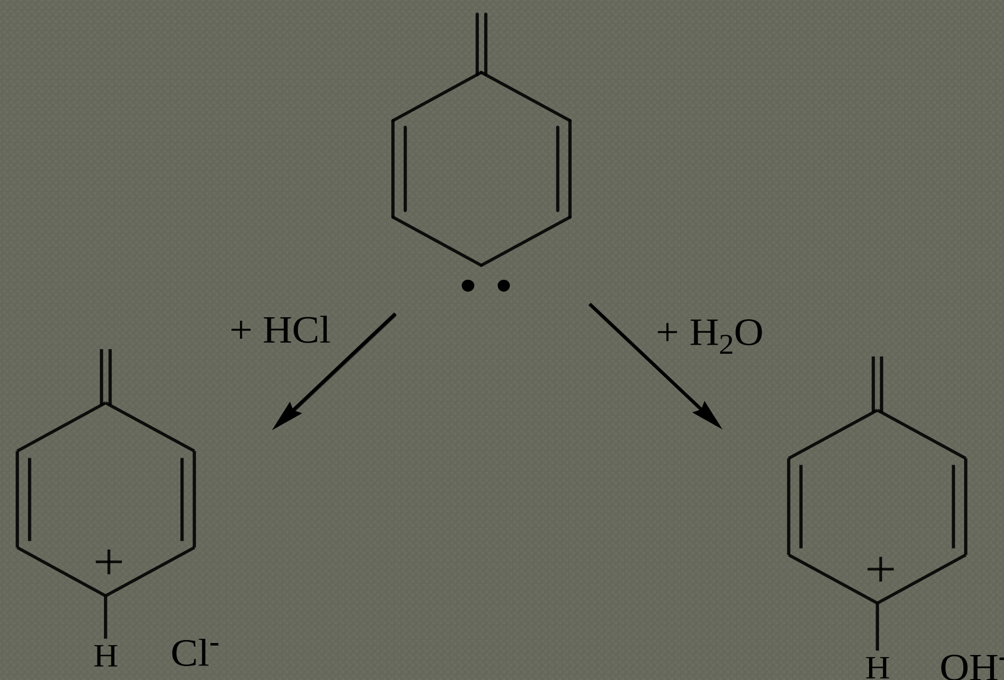
Radovic, L. R. (2007). "Physical Chemistry (or Chemical Physics!?) of Carbon Surfaces: Applications and Fundamentals." The SGL Carbon Award Lecture, Carbon 2007 Seattle, WA, USA

(a)



(b) $C_\pi + 2H_2O = C_\pi\text{--}H_3O^+ + OH^-$

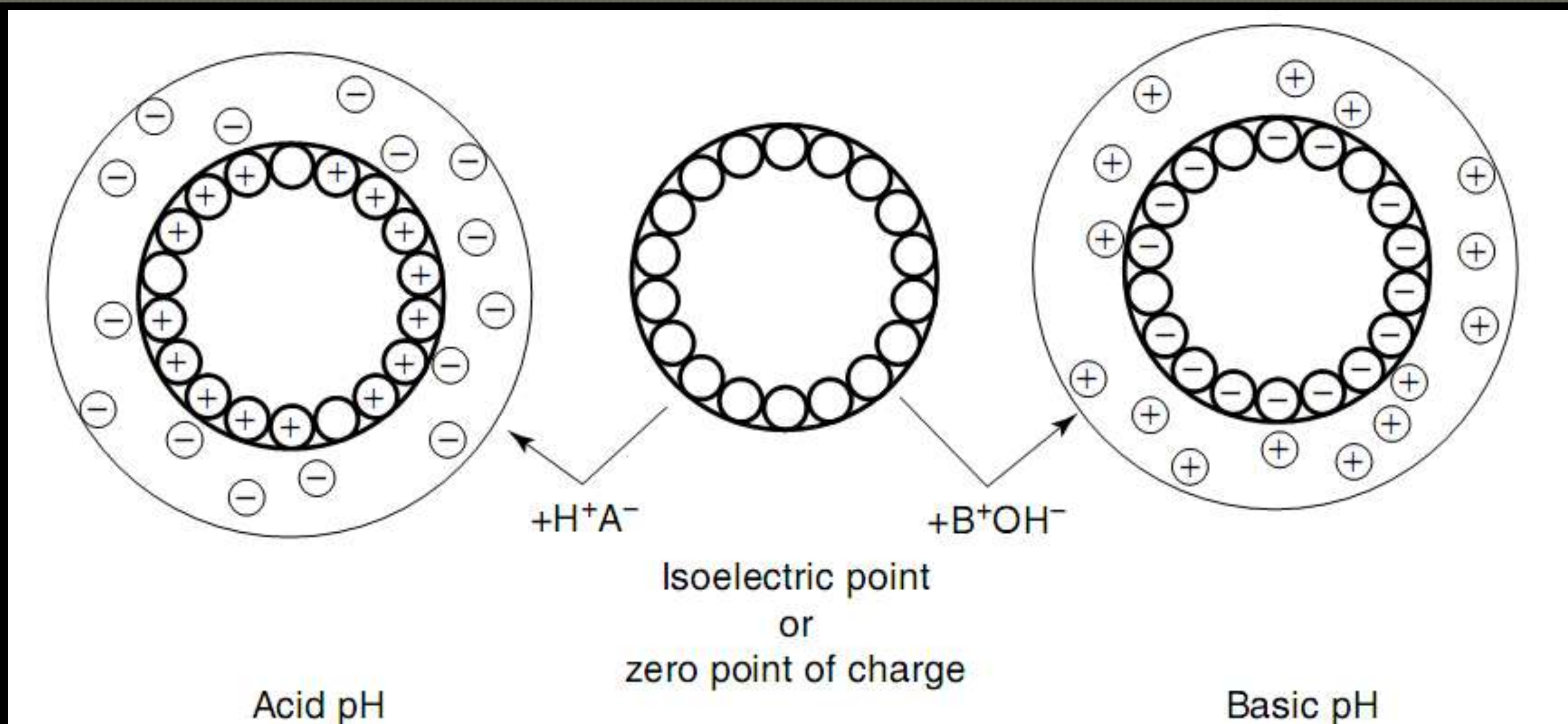
(c)



Radovic, L. R. (2007). "Physical Chemistry (or Chemical Physics!?) of Carbon Surfaces: Applications and Fundamentals." The SGL Carbon Award Lecture, Carbon 2007 Seattle, WA, USA

PZC: Point of Zero Charge

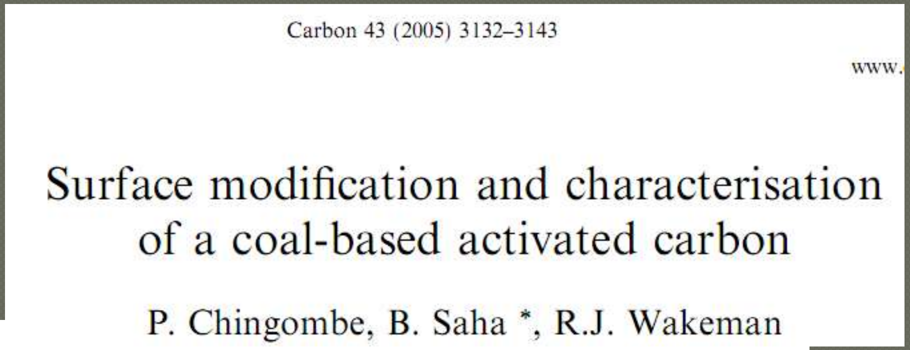
- For ion exchanging



Richards, R. (ed.) (2006). "Surface and Nanomolecular Catalysis." Taylor and Francis

Surface chemistry: How can we change it?

- For example: Nitric acid (HNO_3) treatment


Carbon 43 (2005) 3132–3143

Surface modification and characterisation of a coal-based activated carbon

P. Chingombe, B. Saha *, R.J. Wakeman

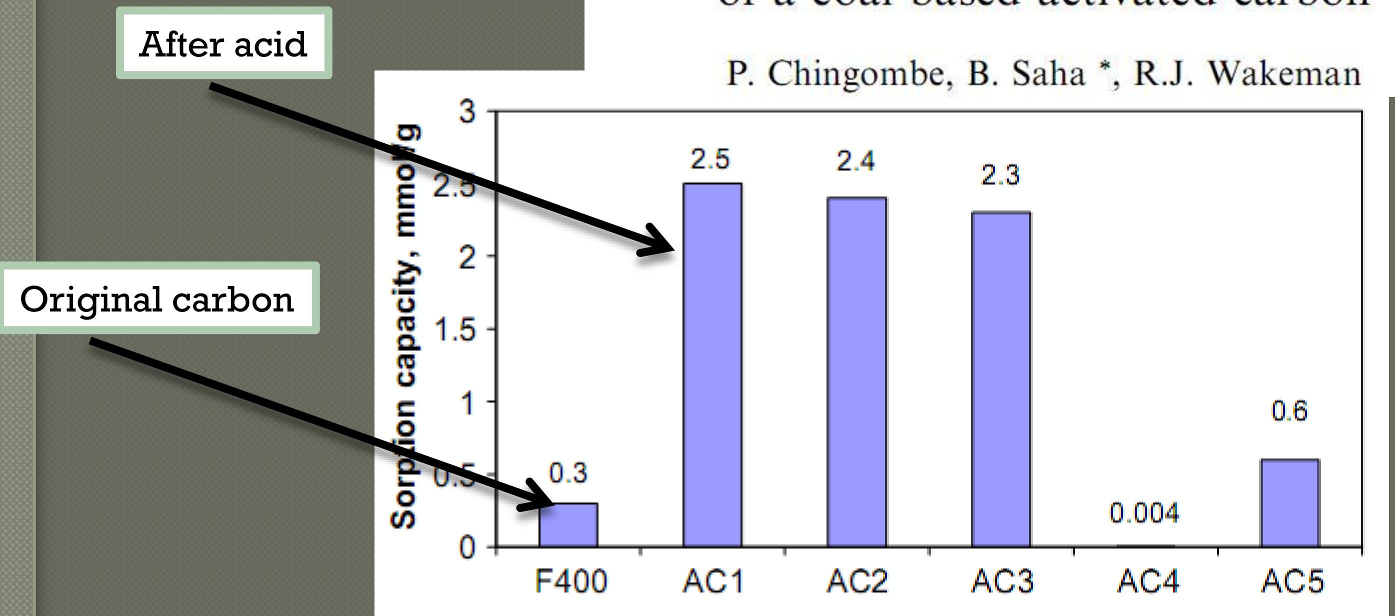


Fig. 7. Sodium capacity values for as-received and modified samples.

And the reactivity?

Carbon Vol. 33, No. 8, pp. 1155–1165, 1995

TOWARDS A UNIFIED THEORY OF REACTIONS OF CARBON WITH OXYGEN-CONTAINING MOLECULES

JACOB A. MOULIJN and FREEK KAPTEIJN
Industrial Catalysis, Department of Chemical Engineering, Delft University of Technology,
Julianalaan 136, 2628 BL Delft, The Netherlands

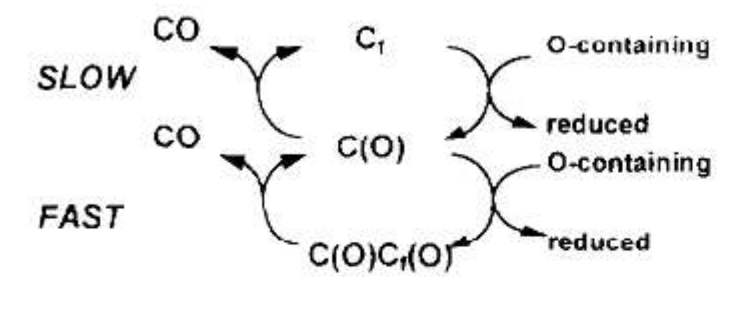
$$2C + O_2 \rightarrow 2CO$$

$$C + H_2O \rightarrow CO + H_2$$

$$C + CO_2 \rightarrow 2CO$$

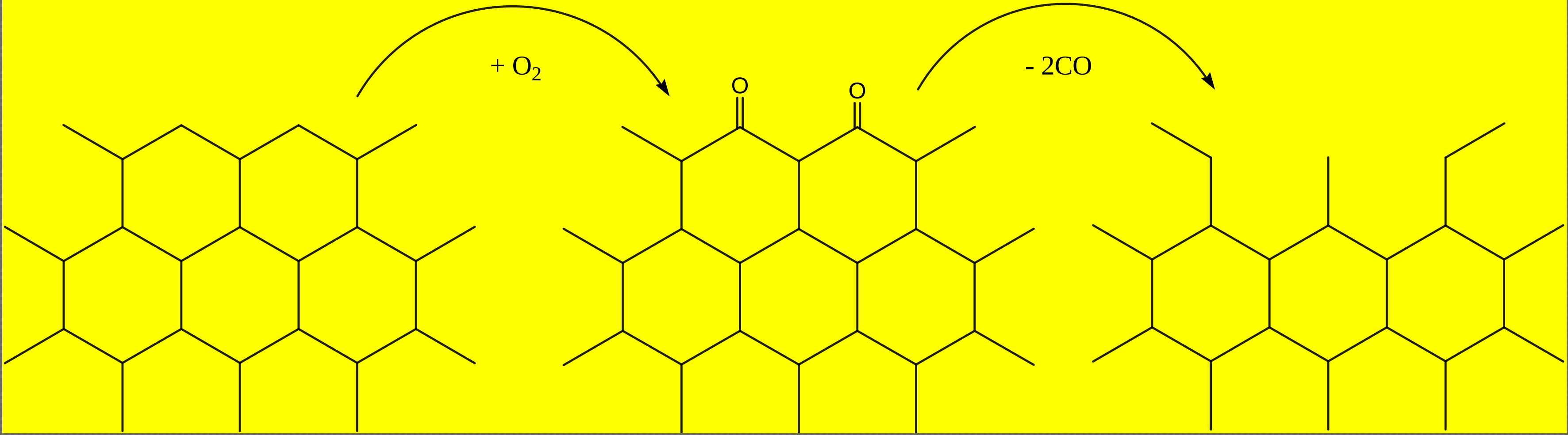
$$C + NO \rightarrow CO + \tfrac{1}{2}N_2$$

$$C + N_2O \rightarrow CO + N_2$$



Unified scheme

Importance of 'nascent' (re)active sites



	Sample	Reactant gas	
		NO (2%)	NO (2%)/O_2 (5%)
NO conversion, %	Cu-char Char	1 1	63 19
C conversion rate, g/g/h	Cu-char Char	0.002 0.002	0.19 0.02
Amount of C(O), mg C/g char	Cu-char Char	0.02 0.02	0.3 0.1
Amount of C-O, mg C/ g char	Cu-char Char	1 2	4 16

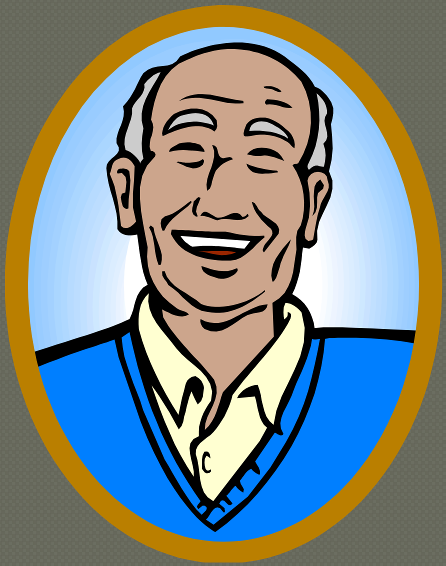
(NO reduction by coal char after 2 h at 573 K: O_2 enhancement)

Radovic, L. R. (2007). "Physical Chemistry (or Chemical Physics!?) of Carbon Surfaces: Applications and Fundamentals." The SGL Carbon Award Lecture, Carbon 2007 Seattle, WA, USA

(Active) carbon roles

AS SUPPORT
AS ADSORBENT

- Old science



AS CATALYST

- Just starting

Some case examples…

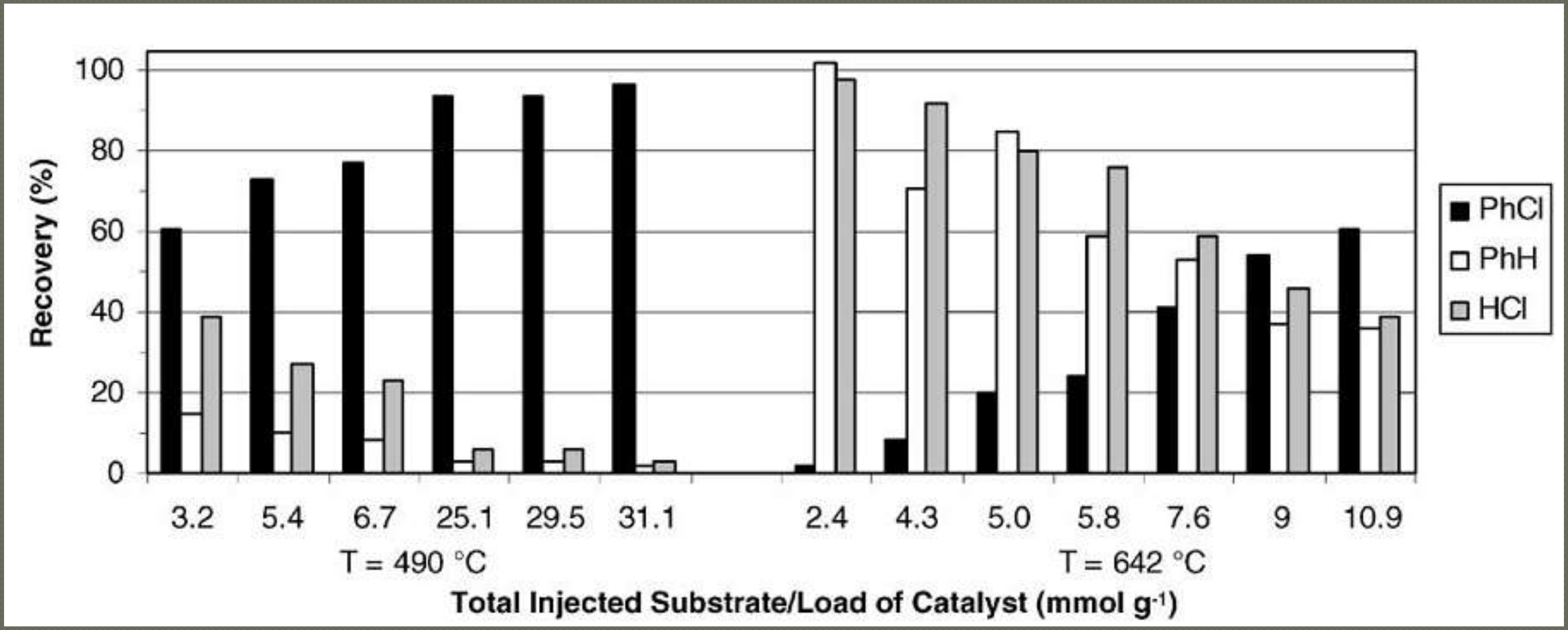
Carbon catalysis: Case 1

- Hydrodehalogenation of chlorobenzene: R-X + H_2 → R-H + H-X (X=halogen)

- Without AC: 800°C
- With AC: 500°C

Santoro, D., V. de Jong, et al. (2003). "Hydrodehalogenation of chlorobenzene on activated carbon and activated carbon supported catalysts." Chemosphere **50(9): 1255-1260.**

Carbon catalysis: Case 1



Santoro, D., V. de Jong, et al. (2003). "Hydrodehalogenation of chlorobenzene on activated carbon and activated carbon supported catalysts." <u>Chemosphere **50(9): 1255-1260.**</u>

Carbon catalysis: Case 2

- Oxidation of hydrogen sulfide:

$$H_2S + O_2 \rightarrow S^0 + H_2O$$

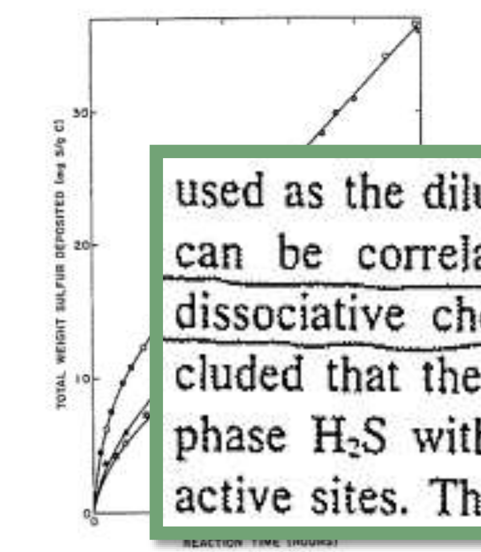
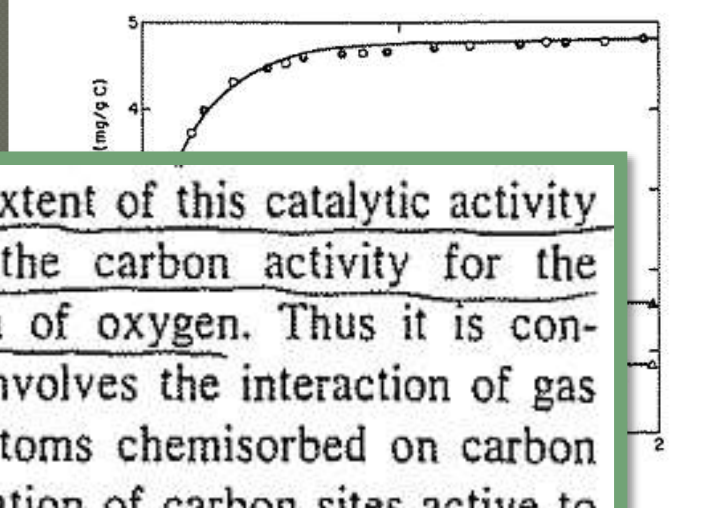


Fig. 2. Runs showing the build-up of sulfur on various carbons as a function of time of oxidation of H_2S at 140°. ■, unactivated and activated in: ●, O_2 (18% B.O.); ○, air (64% B.O.); ▲, CO_2 (60% B.O.); △, CO_2 (20% B.O.).

used as the diluent. The extent of this catalytic activity can be correlated with the carbon activity for the dissociative chemisorption of oxygen. Thus it is concluded that the reaction involves the interaction of gas phase H_2S with oxygen atoms chemisorbed on carbon active sites. The concentration of carbon sites active to



... different carbons exposed for various times to an O_2 pressure of 7·6 Torr at 140°. ■□▽, unactivated carbon of 150 × 250, 65 × 100, and 28 × 48 mesh particle size and carbons activated in: ●, O_2 (18% B.O.); ○, air (64% B.O.); ▲, CO_2 (60% B.O.); △, CO_2 (20% B.O.).

Cariaso, O. C. and P. L. Walker (1975). "Oxidation of hydrogen sulfide over microporous carbons." <u>Carbon **13(3): 233-239.**</u>

Carbon catalysis: Case 3

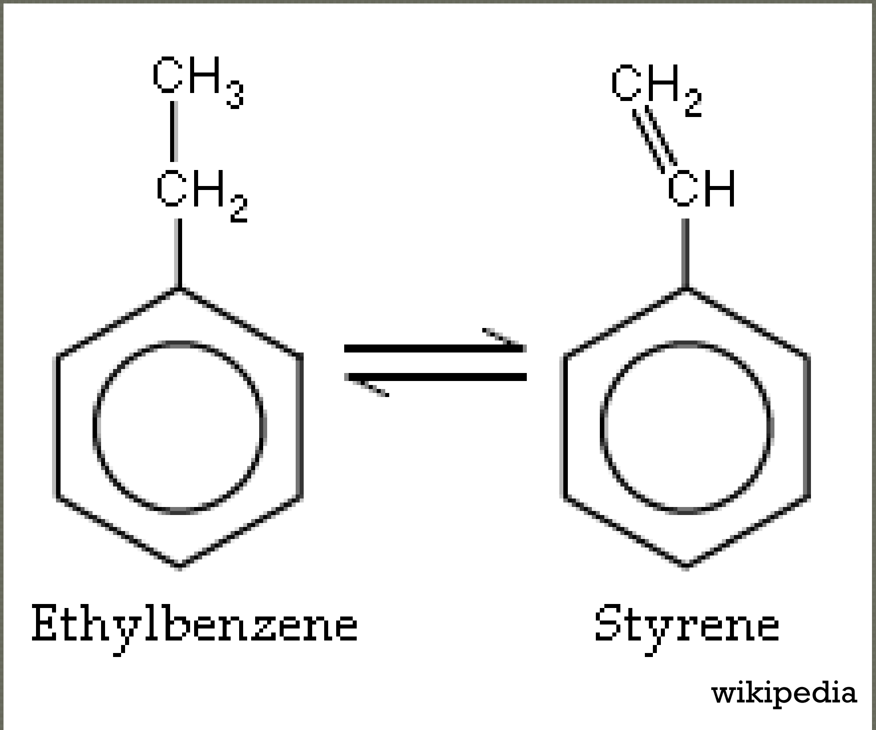
- Chemical decomposition of water giving H_2 (X=halide):

$$H_2O + X_2 \rightarrow HX + HXO$$
$$HXO \rightarrow HX + 1/2\ O_2$$
$$2HXO + C \rightarrow 2HX + CO_2$$
$$2HXO \rightarrow 2HX + O_2$$
$$C + O_2 \rightarrow CO_2$$

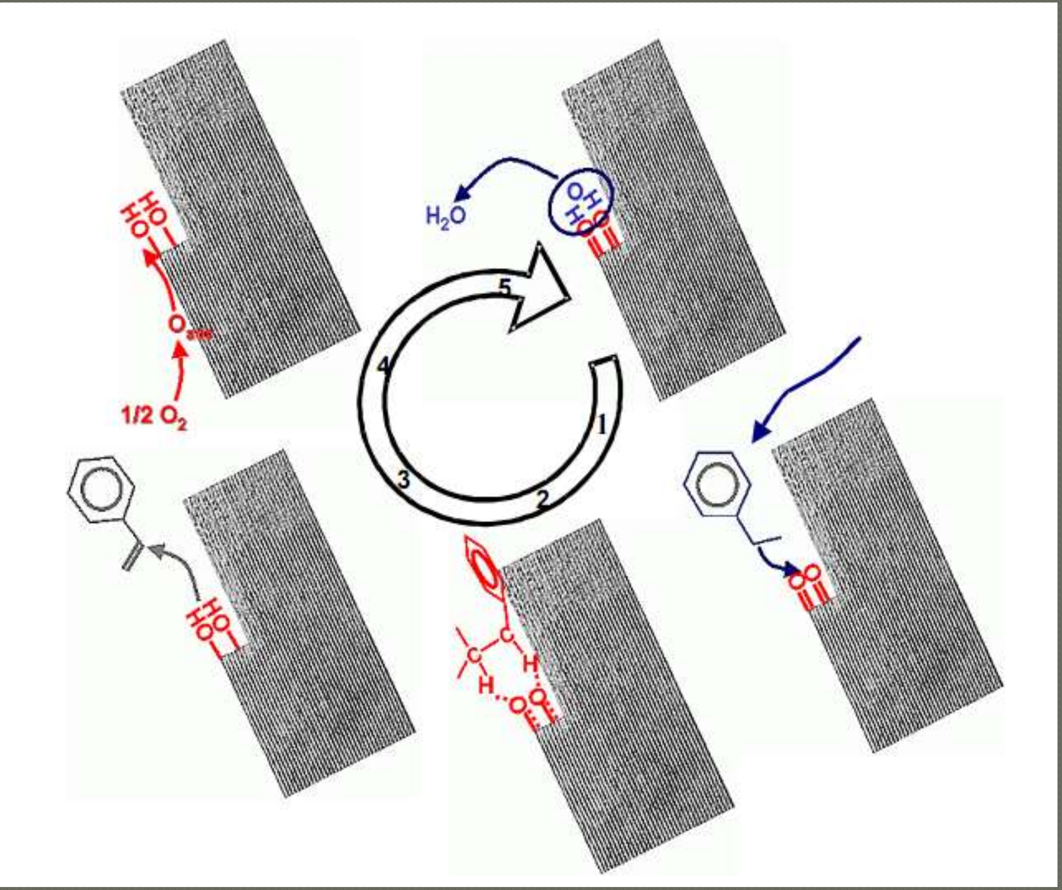
Hibino, K. and K. Tange (1998). Method for decomposing water using an activated carbon catalyst, Toyota Jidosha Kabushiki Kaisha. **Patent 5853690.**

Carbon catalysis: Case 4

- Oxidative dehydrogenation of EB to produce styrene



Carbon catalysis: Case 4



Shekhah, O. (2004). Styrolsynthese: In-situ Charakterisierung und Reaktivitätsmessungen an unpromotierten und Kalium-promotierten Eisenoxid-Modellkatalysatoren. Fachbereich Biologie, Chemie, Pharmazie, Freie Universität Berlin. Berlin. **PhD.**