sticking probability, S

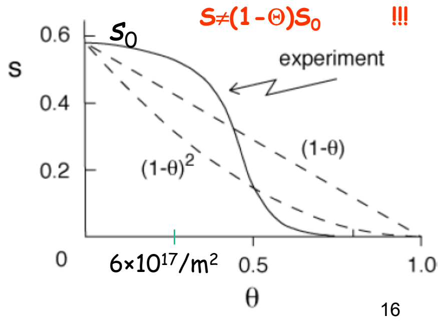
dissipation of the energy of the particle colliding

$$S = \frac{v_{ads}}{\text{frequency of the surface collisions}}$$

v_{ads}: measured, from $p=f(t)$

frequency of the surface collisions: from kinetic gas theory

$$z = \frac{p}{\sqrt{2\pi mkT}}$$



S_0 depends on the potential function

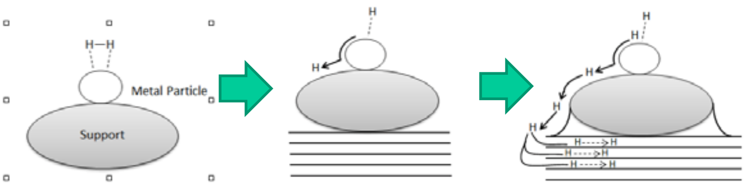
RT

CO/trabónsient metal	0,1-1
N_2/rhenium	<0,01
O_2/silver	0,0001

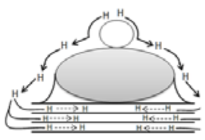
Spillover

transport of a species adsorbed or formed on a surface onto another surface

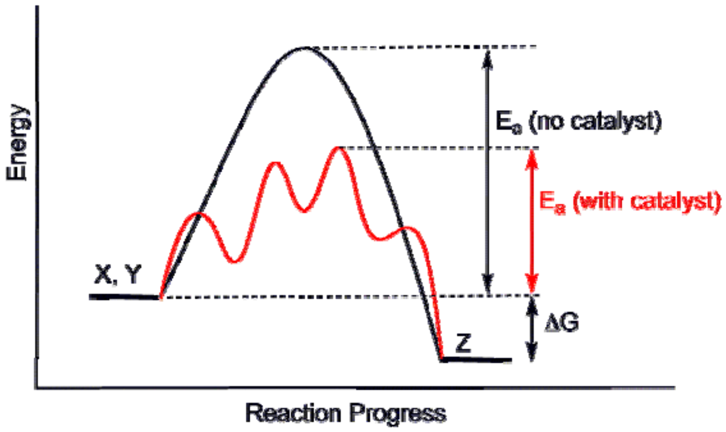
Hydrogen spillover (most common):
1) hydrogen adsorption is most often accompanied with dissociation of molecular hydrogen (H2) to atomic hydrogen (H)
2) Migration of the H atoms from the catalyst to the support
3) Diffusion of the H atoms on the surface of or within the catalyst support



Catalysis: disadvantage
Hydrogen storage: advantage



Heterogeneous catalysis



homogeneous ↔ heterogeneous

Influences only the rate but not the equilibrium:

Reaction path with reduced activation energy

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Important for industry

process	reagents	catalyst	product
Ammonia synth. (Haber-Bosch)	N_2+H_2	Al_2O_3 supported iron oxides	NH_3
Ethylene oxide synth.	C_2H_4+O_2	Al_2O_3 supported silver	C_2H_4O
Desulphurization of mineral oil	H_2+R_2S	Al_2O_3 supported Mo-Co	RH + H_2S
Polymerization of olephines (Ziegler-Natta)	propylene	$MgCl_2$ supported $TiCl_3$	polypropylene

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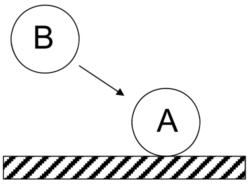
Mechanism of the surface reactions

1. Eley-Rideal



$$A(g) + S(s) \rightleftharpoons AS(s)$$

$$AS(s) + B(g) \rightarrow \text{product}$$

$$v = kp_B \cdot \Theta_A$$

if $\Theta_A = f(p_A)$ Langmuir

$$v = \frac{kKp_Ap_B}{1+Kp_A}$$

1) low p_A: $Kp_A \ll 1$

2) high p_A: $Kp_A \gg 1$ $\quad v \approx kp_B$

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Eley-Rideal mechanism, examples

reagent	catalyst	product
CO_2 + H_2(s)		H_2O + CO
C_2H_2 + H_2(s)	Fe or Ni	C_2H_4
2 NH_3+ ½ O_2(s)	Pt	N_2 + 3 H_2O
C_2H_4 + ½ O_2(s)		H_2COCH_2

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2. Langmuir - Hinshelwood

adsorption to the surface $A(g)+S(s) \rightleftharpoons AS(s)$

diffusion $B(g)+S(s) \rightleftharpoons BS(s)$

reaction

desorption

$$AS(s)+BS(s) \rightarrow product(g)$$

$$\Theta_A + \Theta_B + \Theta_{free} = 1 \qquad v = k \cdot \Theta_A \cdot \Theta_B$$

Langmuir $\Theta_A = \dfrac{K_A p_A}{1+K_A p_A + K_B p_B}$ $\quad \Theta_B = \dfrac{K_B p_B}{1+K_A p_A + K_B p_B}$

$$v = \frac{k K_A p_A K_B p_B}{(1+K_A p_A + K_B p_B)^2}$$

complex T-dependence

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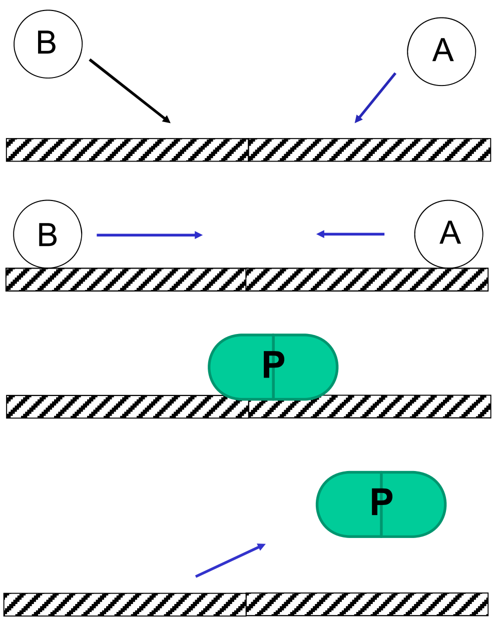
2. Langmuir - Hinshelwood



adsorption to the surface

$$A(g)+S(s) \rightleftharpoons AS(s)$$

$$B(g)+S(s) \rightleftharpoons BS(s)$$

diffusion

reaction

$$AS(s)+BS(s) \rightarrow P(s)$$

desorption

$$P(s) \rightarrow P(g)$$

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$$\Theta_A + \Theta_B + \Theta_{szabad} = 1$$

$$v = k \cdot \Theta_A \cdot \Theta_B$$

Langmuir $\Theta_A = \dfrac{K_A p_A}{1 + K_A p_A + K_B p_B}$

$$\Theta_B = \frac{K_B p_B}{1 + K_A p_A + K_B p_B}$$

$$v = \frac{k K_A p_A K_B p_B}{(1 + K_A p_A + K_B p_B)^2}$$ complex *T*-dependence

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$$v = \frac{k K_A p_A K_B p_B}{(1 + K_A p_A + K_B p_B)^2}$$

a) Both *A* and B adsorb weakly

$$v = k K_A p_A K_B p_B$$

b) B adsorbs weakly

$$v = \frac{k K_A p_A K_B p_B}{(1 + K_A p_A)^2}$$

c) *A* adsorbs very strongly

$$v = \frac{k K_B p_B}{1 + K_A p_A}$$

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Langmuir – Hinshelwood examples

reagents	catalyst	product
$2\ CO + O_2$	platinum	$2CO_2$
$CO + 2H_2$	ZnO	CH_3OH
$C_2H_4 + H_2$	copper	C_2H_6
$N_2O + H_2$	platinum	$N_2 + H_2O$
$C_2H_4 + ½\ O_2$	palladium	CH_3CHO
CO + OH	platinum	$CO_2 + H^+ + e^-$

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TRADITIONAL ADSORBENTS

NO TEXT IS AVAILABLE

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ACTIVATED CARBON

Since BC ~1550

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OUTLINE

Introduction
- forms
- history

Application
- requirements to meet

Synthesis
Characterization
Market
Regeneration
Final message

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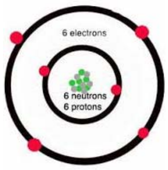
Carbon

6
C
12.011



BBQ

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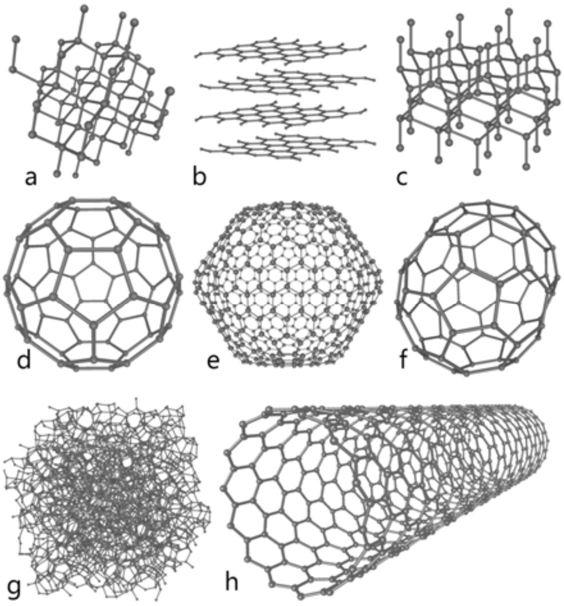
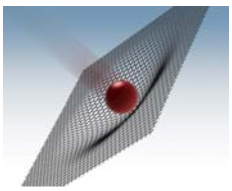
Allotropes



Exotic carbons with unique properties



graphene

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A LITTLE HISTORY…

BC 3750	Egypt, Mesopotamia
1789	element (Lavoisier)
1961	IUPAC (^{12}C atomic mass unit)
1960	W. Libby
1991	S. Iijima CNT (1952 Radushkevich) Nobel nomination
1994	G. Oláh
1996	R. F. Curl Jr. Sir H. W. Kroto R. E. Smalley
2010	A. Geim, K. Novoselov

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http://www.nobelprize.org/

THE WINNER IS….

"**Activated carbon**, characterized by its **exceptional adsorption properties**, has been identified as an **effective solution** for air and water pollution control, which is driving its demand in both mature and emerging markets across the globe. Besides **drinking water treatment** and **air purification**, activated carbon is also actively used in controlling **mercury emissions**, caused by burning of coal in power plants. With growing use in diverse end user industries, such as **mining, food & beverage, pharmaceuticals and chemical & petrochemical**, the global market for activated carbon is expected to post strong growth over the next five years."
(Global Activated Carbon Market Forecast and Opportunities, 2019)

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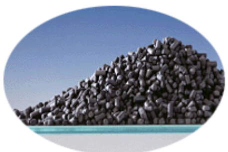
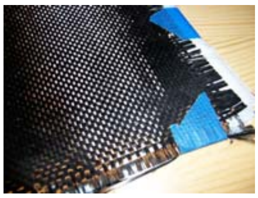
ACTIVATED/ACTIVE CARBON



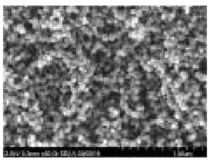
Granular
0.6 - 4.0x10^{-3} m

Powder
15 - 25x10^{-6} m



Carbon fibre/cloth
10 - 30x10^{-6} m

rigid / flexible



Foam/aerogel

5 g porous carbon same area as a soccer field (500-3000 m^2/g)

Applications

Gas phase
Removal of volatile organic compounds (VOC) from air
Regeneration of organic solvents
Reduction of evaporation loss
Adsorption of landfill gas
Air conditioners
Mercury adsorption
Gasmasks
Vehicle outlet gas (SOx, NOx)
Gas storage (natural gas, hydrogen)
Gas separations (molecular sieve)
Energy storage devices (EDLC)

Catalyst support

Liquid phase
(Waste) water treatment
Food industry

Biomedical applications
haemoperfusion
detoxication
prothesis

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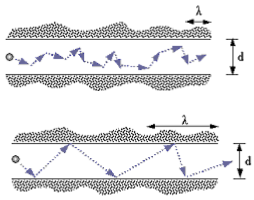
Expectations to be met

- Effective/reversible removal of molecules of different size
- Various conditions (T, conc./pressure)
- Selectivity
- Different chemical environment (humidity, pH, co-s)
- Different dynamics (static, flow)
- Different lifetime
- Regeneration



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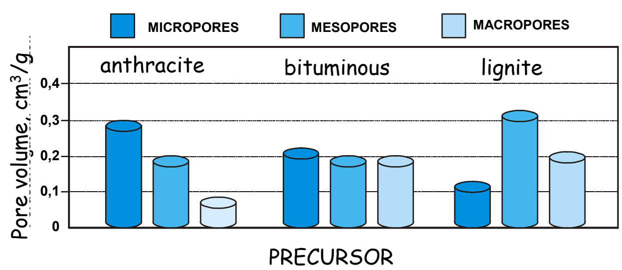
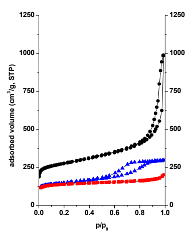
SYNTHESIS

Precursor
Process

TRADITIONAL „MASS" PRECURSORS



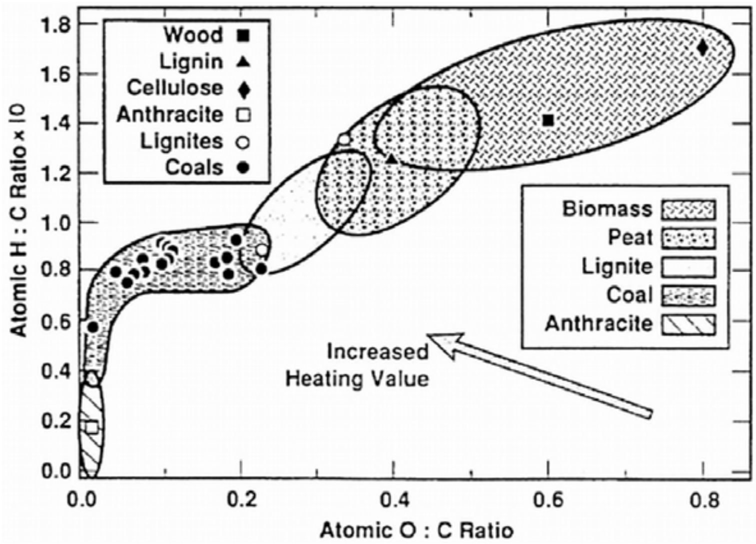


500 000 t/year, ~ 7 %

bituminous $ 80/t (2015)

Precursors predestinate pore size distribution

van Krevelen diagram



https://commons.wikimedia.org/wiki/File:Van_Krevelen_diagram_for_various_solid_fuels.jpg

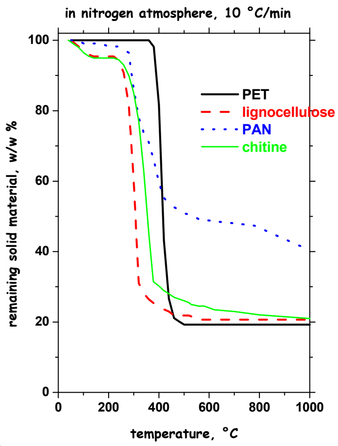
1. Physical activation typically 2 steps

1st step: pyrolysis (inert atmosphere)

2nd step: activation (ash)

Activation agent

- Water vapor
- CO_2
- O_2
- O_3
- Air
- H_2O_2



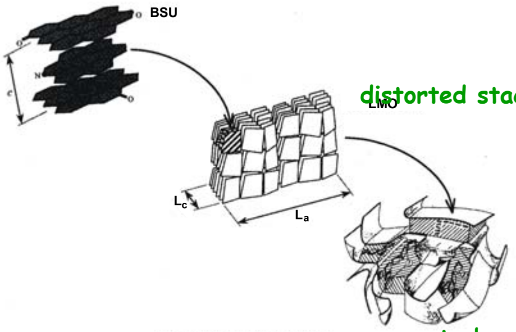
2. Chemical

one-step (H_3PO_4, $ZnCl_2$, NaOH, KOH)

dehydration + prevention of tar formation

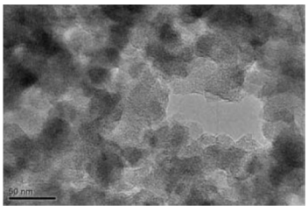
How does the porosity develop during the preparation?

small assembly of polyaromatic rings



distorted stacks

turbostratic structure



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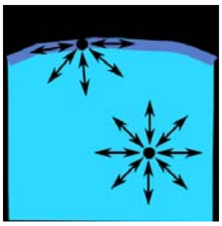
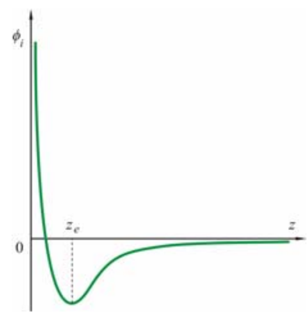
Oberlin, A. *Carbon* 1984

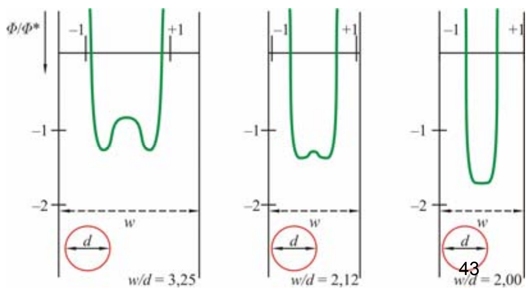
Consequences: high surface area complex porosity



$$\gamma = \left(\frac{\partial G}{\partial A_S}\right)_{p,T}$$

Secondary forces





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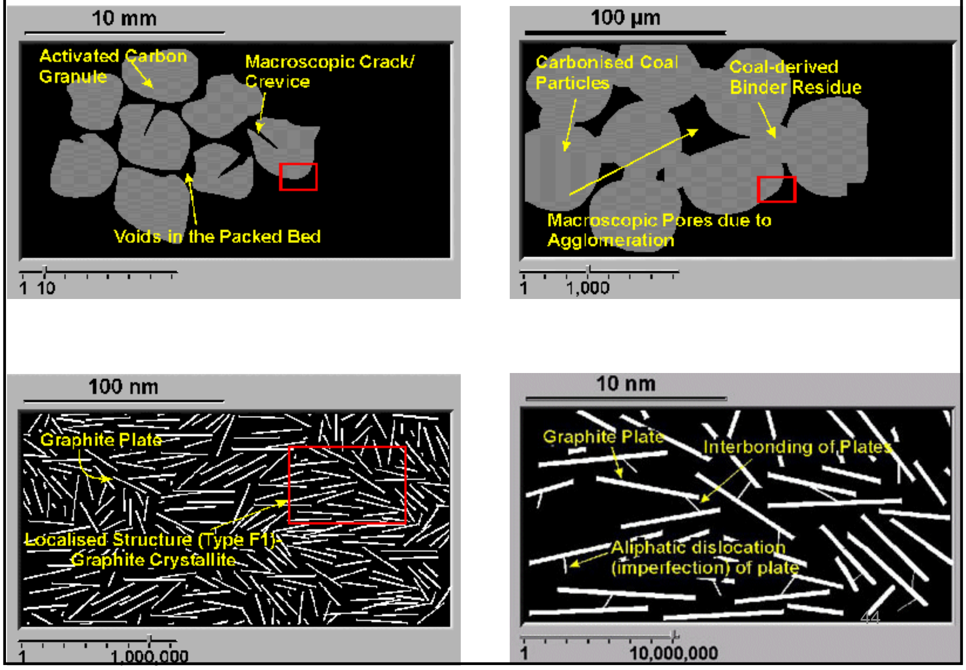
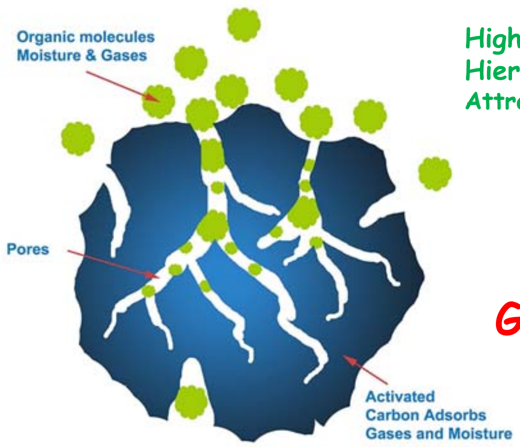
MORHOLOGY





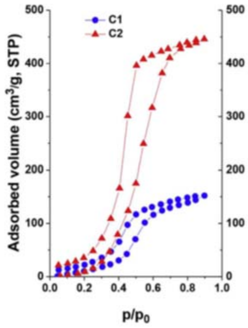
High surface area
Hierarchical pore size distribution
Attraction by secondary forces

General adsorbent

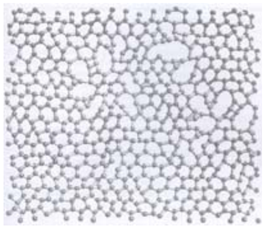
https://www.amazon.co.uk/DRY-PURIFYTM-Dehumidifier-Deodorizer-Charcoal/dp/B01N2G842L 45

SURFACE CHEMISTRY

Hydrophobic



1 Chemical heterogeneity of the graphitic structure



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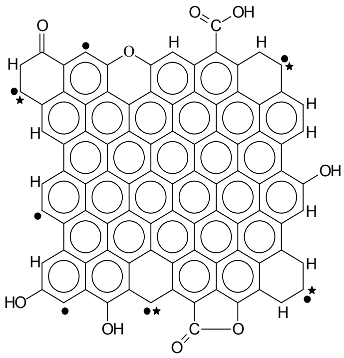
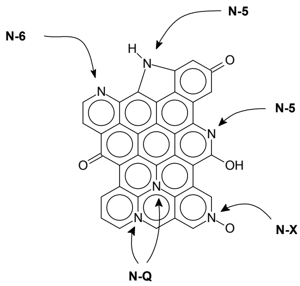
O'Malley, B. *et al*. *Phys Rev* 1998

2 Heteroatoms: H, O, S, N, B, P, Si, Me^{n+}, etc. (ash)

precursor/(chemical) treatment/impregnation/doping





O-containing functional groups at the edges
•:unpaired σ electron
•*: in-plane σ pair
*: localized π electron
Radovic, L. R. in *Surfaces of Nanoparticles and Porous Materials*. Marcel Dekker 1999

N-containing functional groups on carbon surfaces
N-6: pyridinic,
N-5: pyrrolic/pyridone,
N-Q: quaternary,
N-X: N-oxide
Kapteijn, F. *Carbon* 1999

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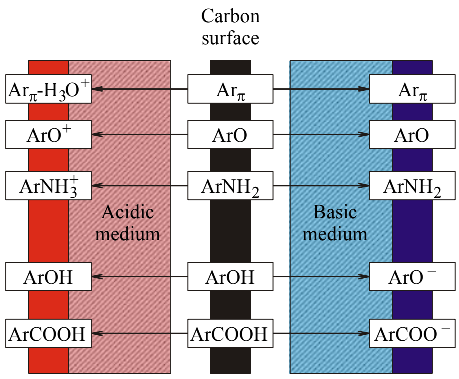
SURFACE CHEMISTRY: AMPHOTERIC CHARACTER



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potential shortages during the application
*sensitivity to erosion
*susceptibility to oxidation
*catalyst
…

B $sp^2 \rightarrow sp^3$
(i) graphitization enhancement,
(ii) boron oxide-oxygen diffusion barrier, site blocking film
(iii) complex disruption of the delocalized π-electrons
and a possible redistribution of the electrons

P **C-P-O** or **C-O-P** at graphene edges → blocking active sites
¿ **P** in the aromatic system?

Si **C-SiO_2** or **SiC** (T > 1400 - 1450 °C)

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Impregnation

Sensitize for a limited number of target chemicals
(vs catalyst support)

iodine
silver
Al, Mn, Zn, Fe, Li, Ca
transient metals: Cu, Mo, etc.

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COMPLEX CHARACTERIZATION IS REQUIRED

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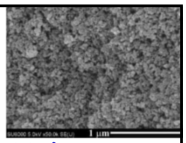
morphology:



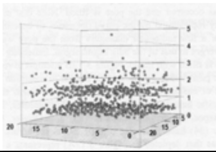
- microscopies
- gas adsorption (N2/Ar, CO2)
- particle size
- small and wide angle scattering (SAXS, SANS, WAXS)
- NMR (cryoporosimetry)

surface chemistry:

- H2O
- „dry” methods (methods and information obtained):
  - elemental analysis, EDX, XPS, FTIR, Raman, IGC, TPD, NMR
- „wet” methods:
  - calorimetry (immersion, flow, etc.),
  - pH, point of zero charge, surface charge
  - titration methods (Böhm, potentiometric titration),
  - adsorption (organics, dyes, ions)

modelling:

- MC, DFT, engineering



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HOW TO SELECT A CARBON?

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Application oriented standardized test methods
AS CLOSE AS POSSIBLE TO APPLICATION CONDITIONS

- BET surface area, PSD
- Iodine number
- Molasses
- Phenol uptake
- Methylene blue
- Dechlorination
- Apparent density
- Hardness/abrasion number
- Ash content
- Carbon tetrachloride activity
- Particle size distribution

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IS IT WORTHWHILE TO WORK IN CARBON DEVELOPMENT?

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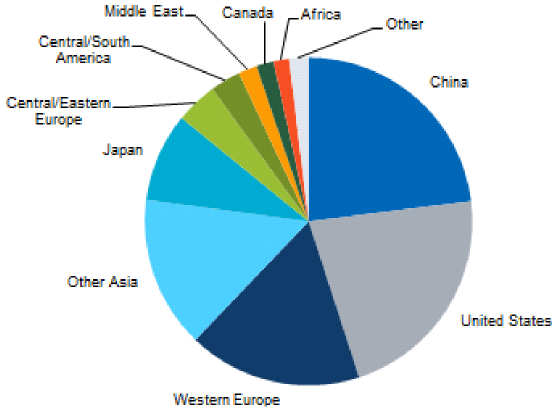
Global activated carbon (AC) consumption 2016



- total world capacity has grown by ~ 400,000 metric tons since 2012
- forecast global average annual growth rate for AC will be ca 3.5% through 2021
- water treatment 41%;
- air and gas purification 30%;
- food processing applications 14%

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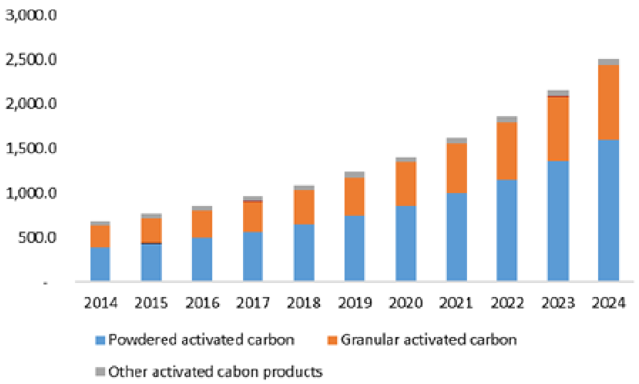
https://ihsmarkit.com/products/activated-carbon-chemical-economics-handbook.html

U.S. activated carbon market revenue by product, 2014 - 2024 (USD Million)



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https://www.grandviewresearch.com/industry-analysis/activated-carbon-market

Regeneration of activated carbon (vs. hazardous waste)

Thermal regeneration
- about 800 °C, controlled atmosphere
- widely used
- disadvantages: high cost
  - energy intensive
  - high carbon losses

Further regeneration techniques
Chemical and solvent regeneration
Microbial regeneration
Electrochemical regeneration
Ultrasonic regeneration
Wet air oxidation

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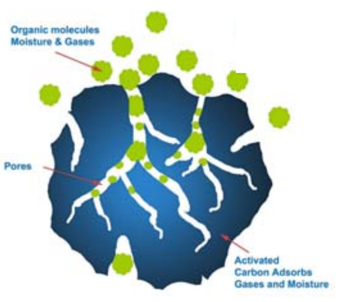
ACTIVATED CARBON: A GENERAL ADSORBENT

The „activity" of activated carbons stems from
- *high surface area 500-3000 m^2/g
- *complex hierarchic porosity
  (micro, meso, macro and beyond)
- *chemical heterogeneity
- *secondary interaction forces



TUNABLE

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METAL OXIDES

Al, Mg, Si — stable, relatively high surface area
(Cr, Ni,) Ti, Fe, Zn — smaller surface area, catalytic activity

Can be
crystalline (TiO2: rutil, anatase)
amorphous (SiO2 silica)

Polar, hydrophilic surface
With water they form hydrates and/or are converted to hydroxils

Typical interactions during adsorption:
- specific (ionic) interactions
- hydrogen bonds
- Lewis electron acceptor – donor exchange

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Porous silica (SiO_2)

Hydrophilic
Typical surface area: 100-200 m^2/g

Main application:

Desiccant

Easy functionalization: with organic groups becomes hydrophobic
e.g., with alcohols:

$$\equiv Si\text{-}OH + R\text{-}CH_2\text{-}OH \rightarrow \equiv Si\text{-}O\text{-}CH_2\text{-}R + H_2O$$

use: Reverse phase liquid chromatography

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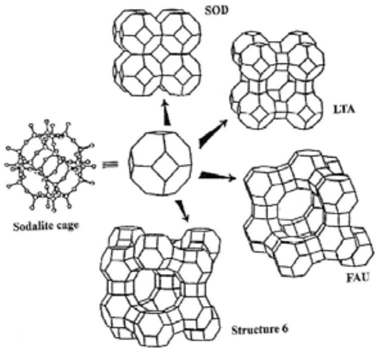
Zeolites

Hydrated aluminum silicates $Na_2Al_2Si_3O_{10}.2H_2O$

natural
synthetic 600-1000 m^2/g

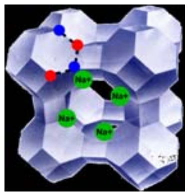
(AlO_4) and (SiO_4) units build up cages with various shape



Good for gas transport

Applications:

- Molecular sieve
- Catalyst
- Ionic exchange in detergents



J. B. Nagy, P. Bodart, I. Hannus, I. Kiricsi: Synthesis, characterization and use of zeolitic Microporous materials. Szeged, 1998

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