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UNDERSTANDING REACTIVE ADSORPTION ON ACTIVATED CARBONS: IMPORTANCE OF SURFACE FEATURES IN NANOREACTORS

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OBJECTIVE

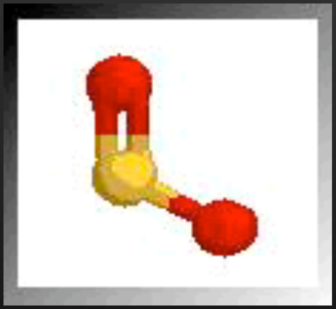
- To remove toxic gases from air
- To provide inexpensive and efficient adsorbents for removal of toxic gases
- To formulate the mechanism of reactive adsorption

- Efficient
    - High capacity
    - Strong adsorption

Examples of species to be removed

Toxic industrial compounds (TICs)

- H_2S (4.3Å)
- SO_2 (4.6Å)
- NH_3 (2.9 Å)
- CH_3SH (4.2Å)
- CH_3SSCH_3 (5.3 Å)
- NO (4.2 Å)
- NO_2 (4.4 Å)
- AsH_3



Common feature: small size → weak dispersive forces at ambient conditions

Physical adsorption forces

- Nonspecific
  - Dispersive interactions (Lennard-Jonnes)
- Specific
  - hydrogen bonding, electrostatic. etc

strength expressed by heat of adsorption < 60-80 kJ/mol

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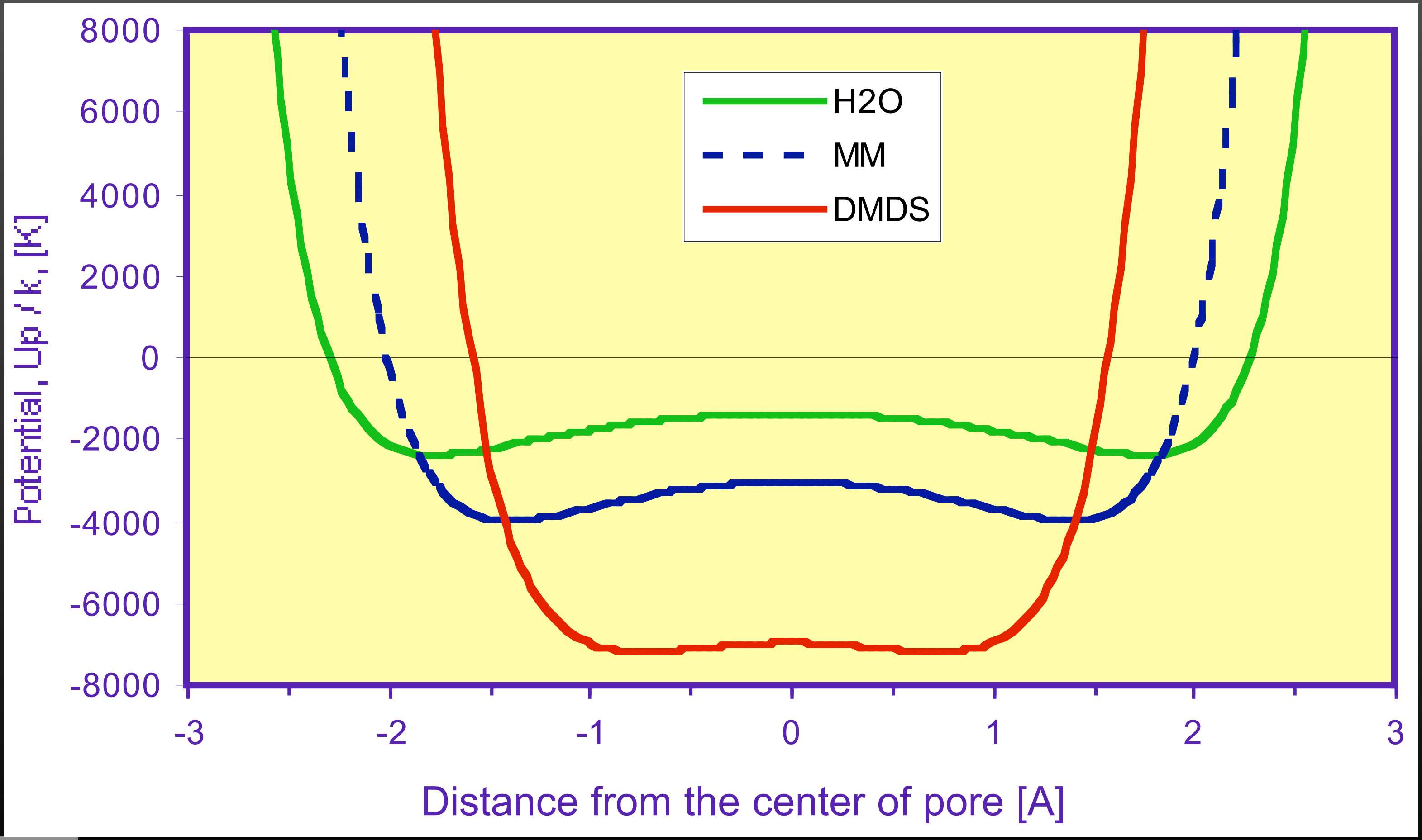
Dispersive interactions

in 7 Å pore



molecular sizes: H_2O: 3.2 Å ; MM 4.2 Å; DMDS: 5.3Å

Heat of adsorpion and Henry constants

Species	Q_{st} [KJ/mol].	K_H
H_2O	19.8	3.83×10^3
MM	33.1	7.81×10^4
DMDS	59.9	4.61×10^{10}

TARGET → Reactive adsorption

- Retention of molecules on the surface enhanced by chemical reaction
  - transformation to non-toxic or strongly adsorbed
  - oxidation and deposition on the surface
  - complexation
  - acid- base reactions
  - photoactivity
  - etc.......

Surface requirements

- (small) pores being able to accommodate the active sites and reagents (water??)
- sufficient volume of large, transport pores
- active sites participating in reactive adsorption
- high dispersion of active sites
- self-regeneration of active sites

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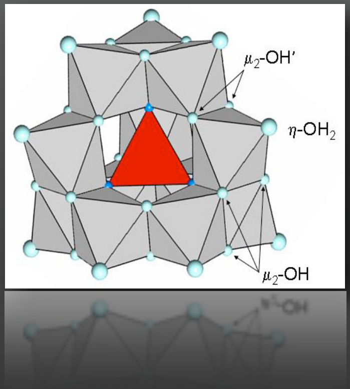
Carbonaceous materials of interest

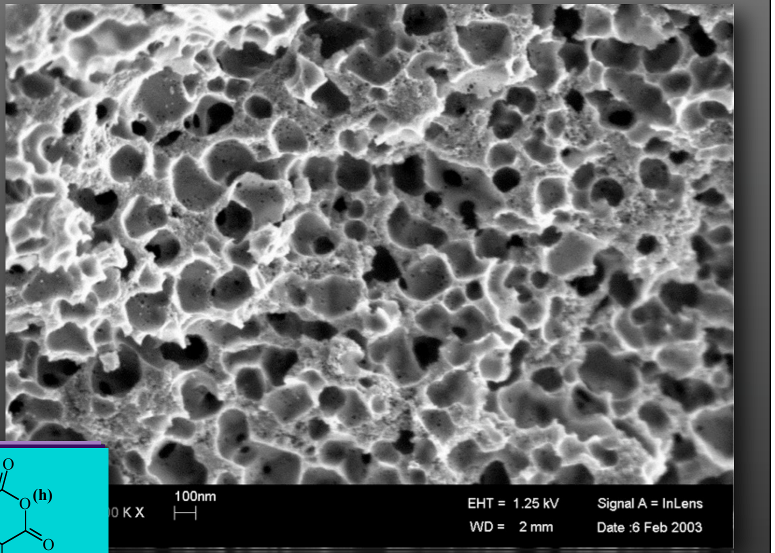
- VIRGIN ACTIVATED CARBONS
- MODIFIED CARBONS
  - impregnated with transition metal salts (Co, Ni, Co, Fe...)
  - impregnated with caustics
  - with Keggin cations deposited on the surface (Al_{13})
  - with HPA (ammonium metatungstate $(NH_4)_6H_2W_{12}O_{40}$)
  - with incorporated nitrogen (quaternary, piridinic..)
  - with incorporated sulfur (sulfonic, thiophenic)
  - composites with metal oxides (CaO, MgO..)

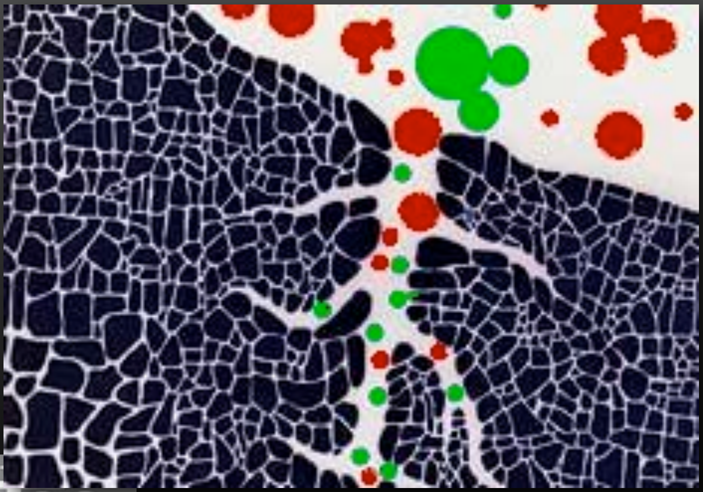


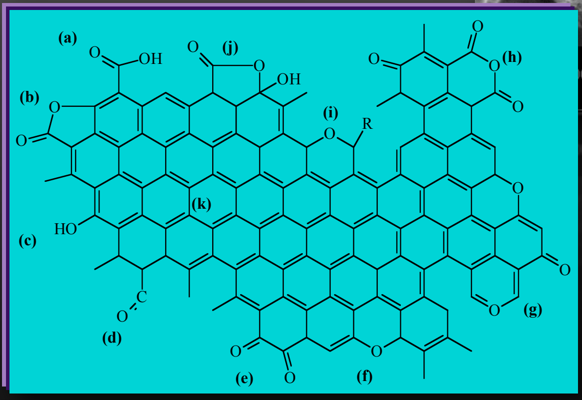
- GRAPHITE OXIDES
  - as received
  - pillared with inorganic/organic species
  - with incorporated nitrogen
  - composites with MOFs and metal hydroxides/ quantum dots

ACTIVATED CARBONS

- high surface area and pore volume (over 1000 m^2/g, 1 cc/g)
- heterogeneous pore structure
- surface functional groups
- relatively easy way of impregnation







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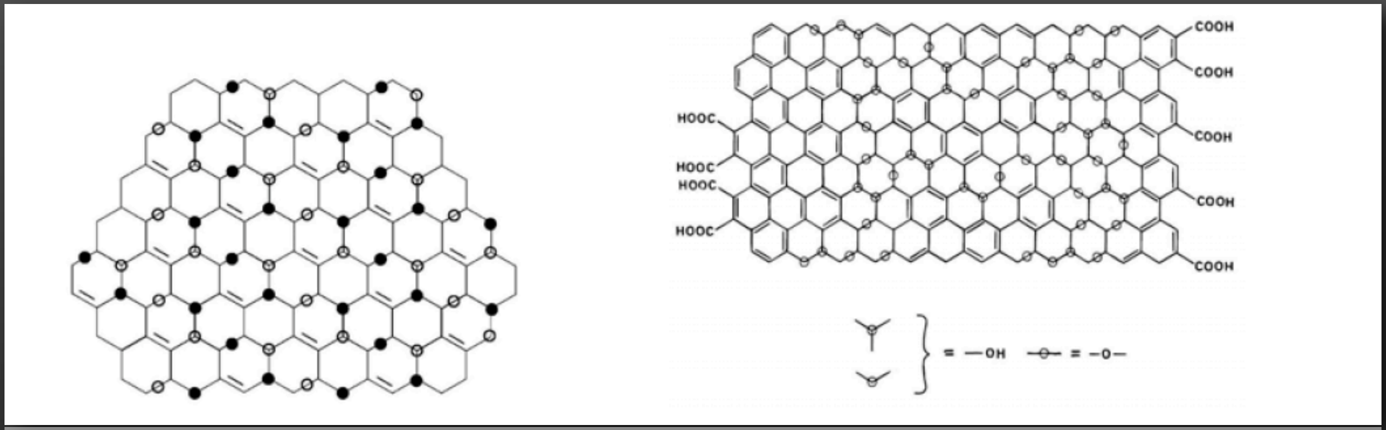
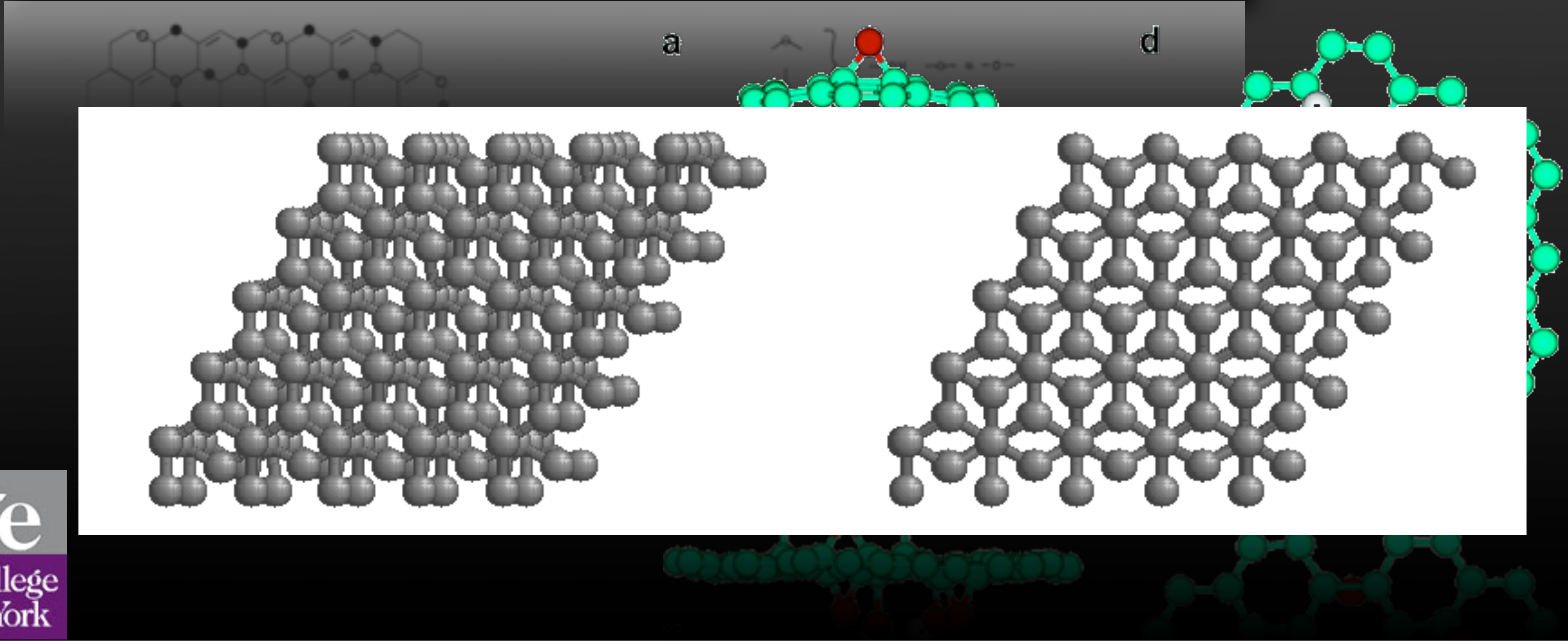
Graphite oxides

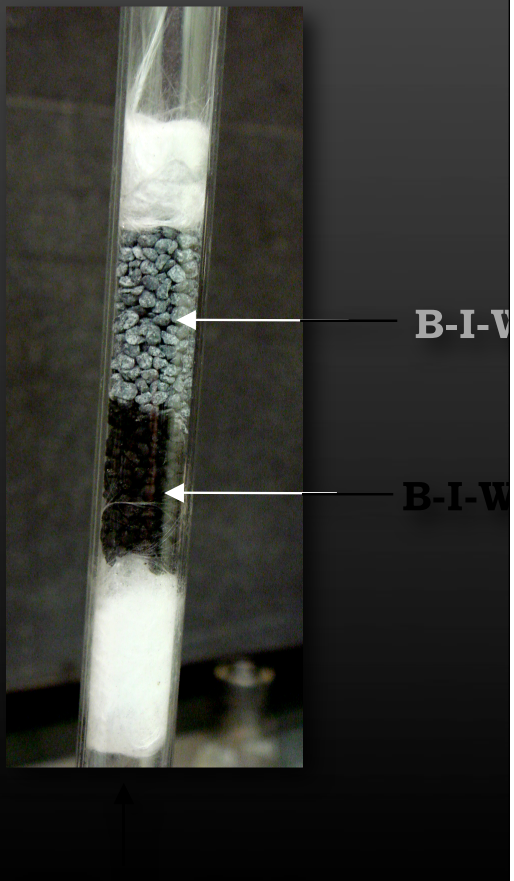


Lerf at al. J. Phys. Chem B 102, 4477 (1998)



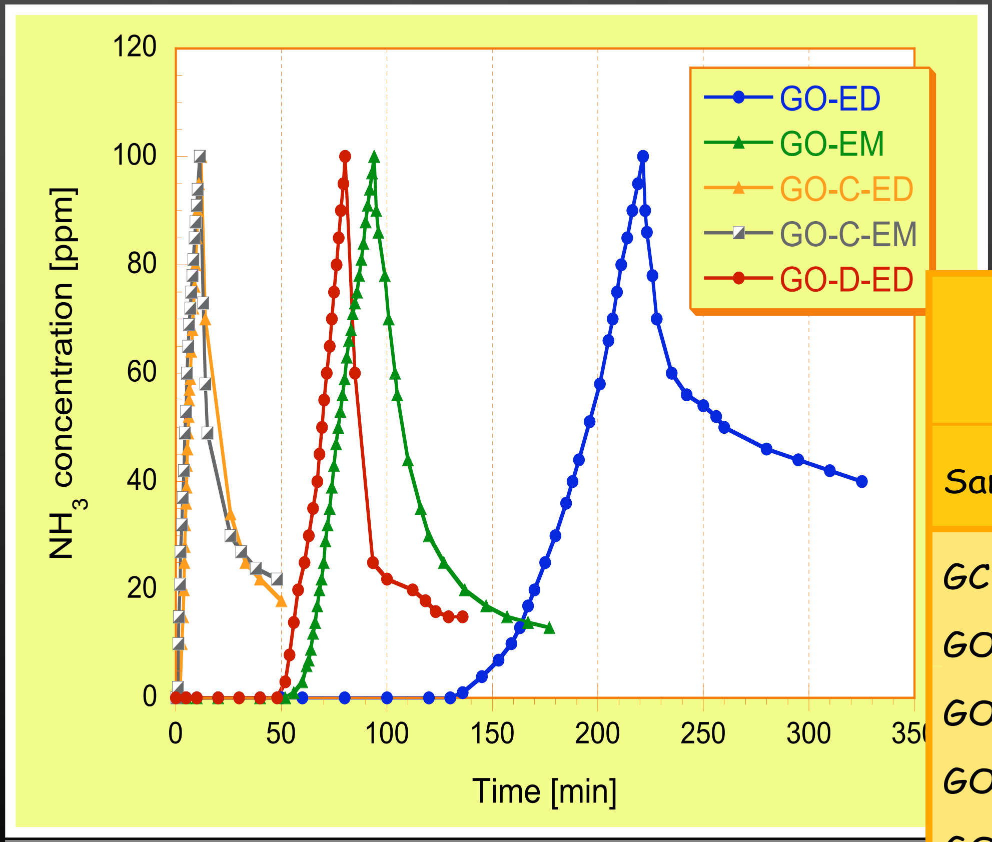
Evaluation of performance

- Breakthrough test- dynamic measurements
  - wet or dry air
  - concentration 1,000-3,000 ppm (accelerated)
  - flow rate (150-400 mL/min)
  - bed size (2-6 cc)



Examples of performance

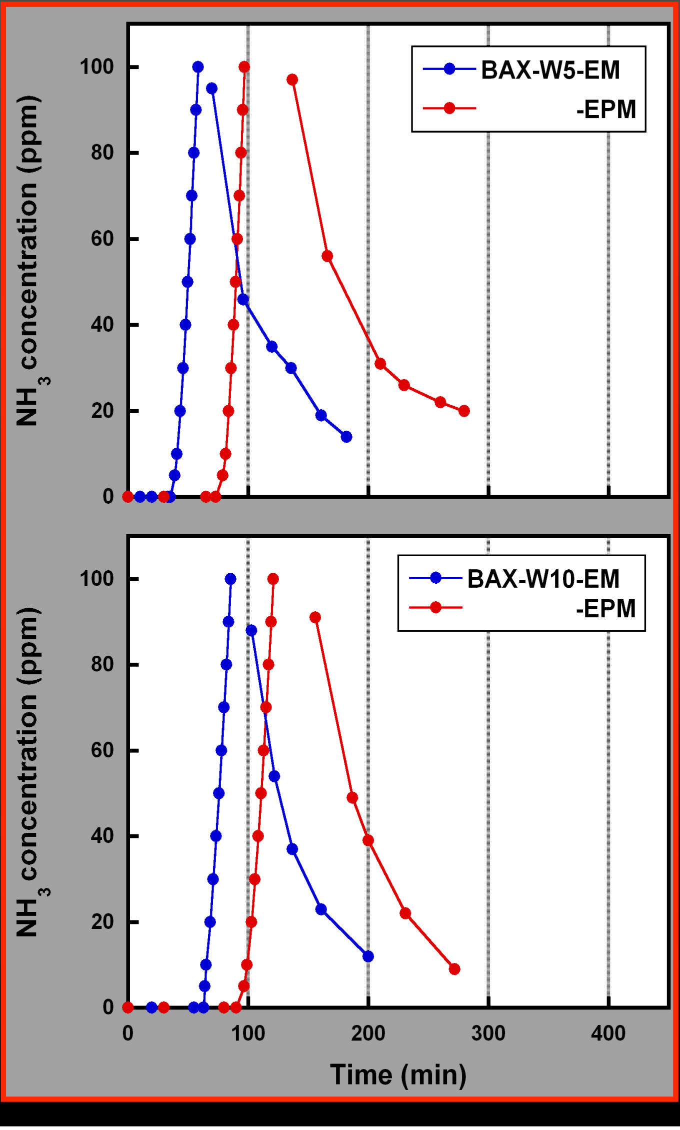
- Ammonia on GO

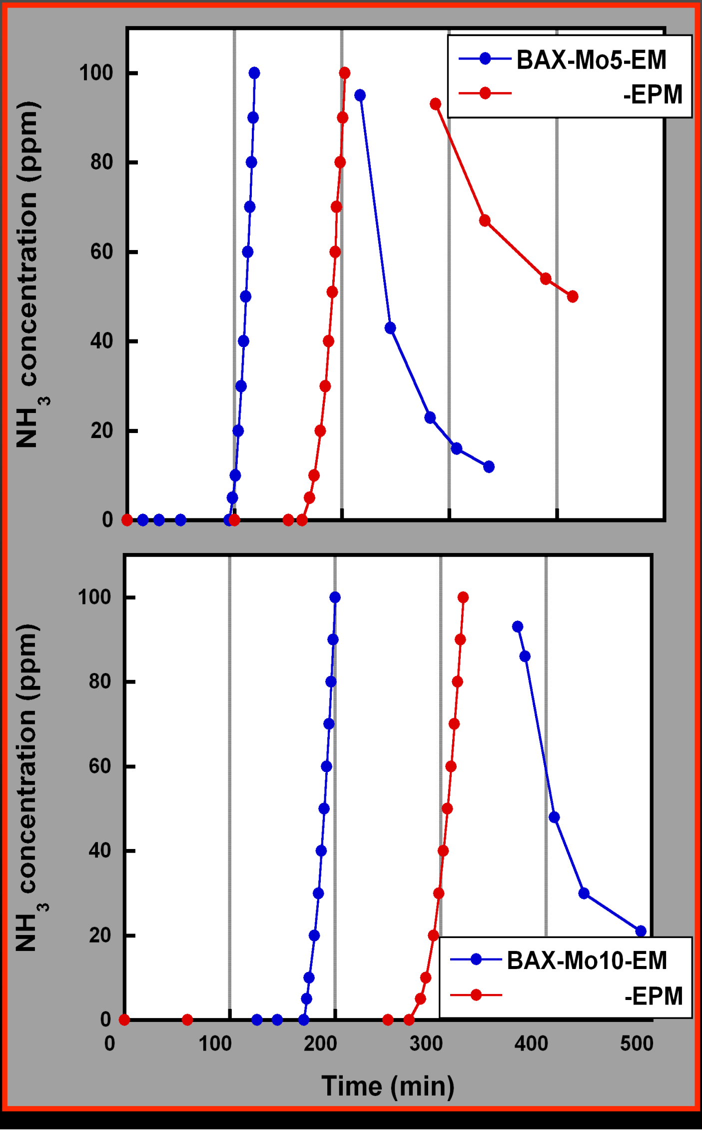


	NH_3 breakthrough capacity		pH	
Sample	[mg/g of ads]	[mg/cm^3 of ads]	Initial	Exhausted
GCB	0.4	0.2	8.66	8.70
GO-D-ED	27.8	12.0	3.40	6.64
GO-ED	61.0	29.9	3.15	7.66
GO-EM	38.4	18.4	3.15	7.40
GO-C-ED	16.8	1.85	6.35	7.45
GO-C-EM	15.5	1.70	6.35	7.20

Ads/Des curves: strength of interactions

Ammonia on WO_3 and MoO_3 modified carbons





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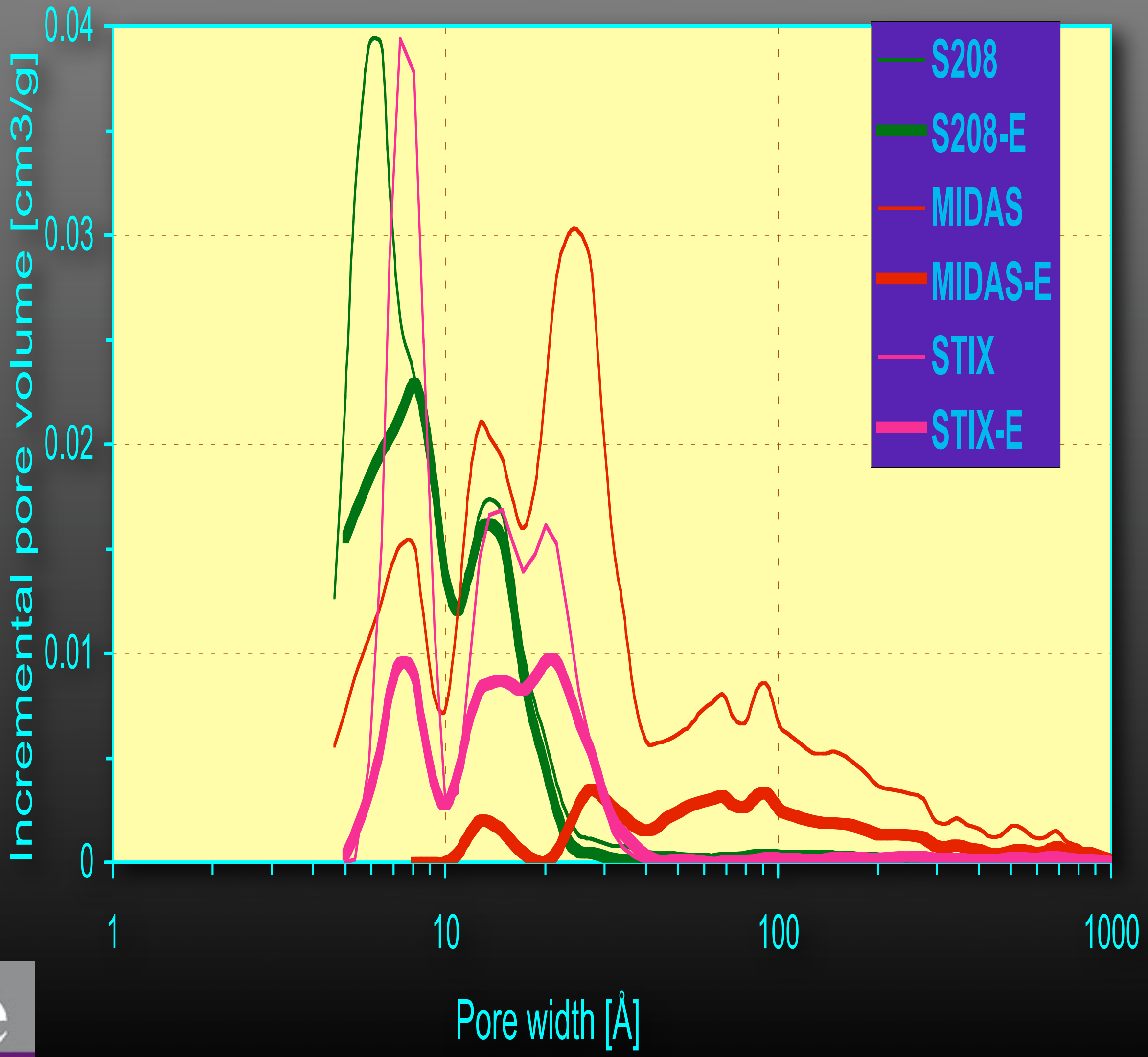
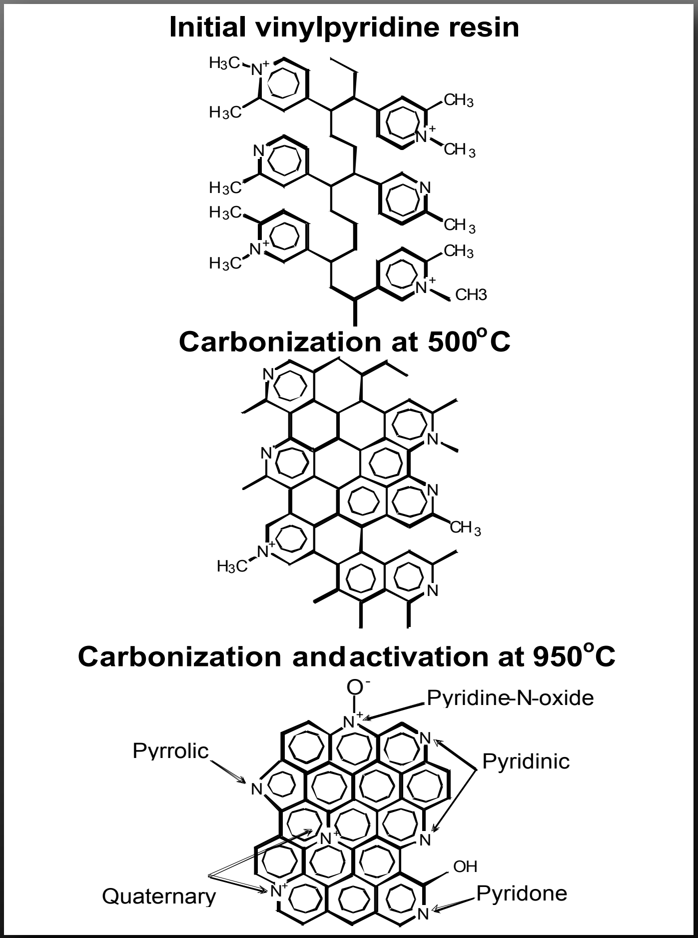
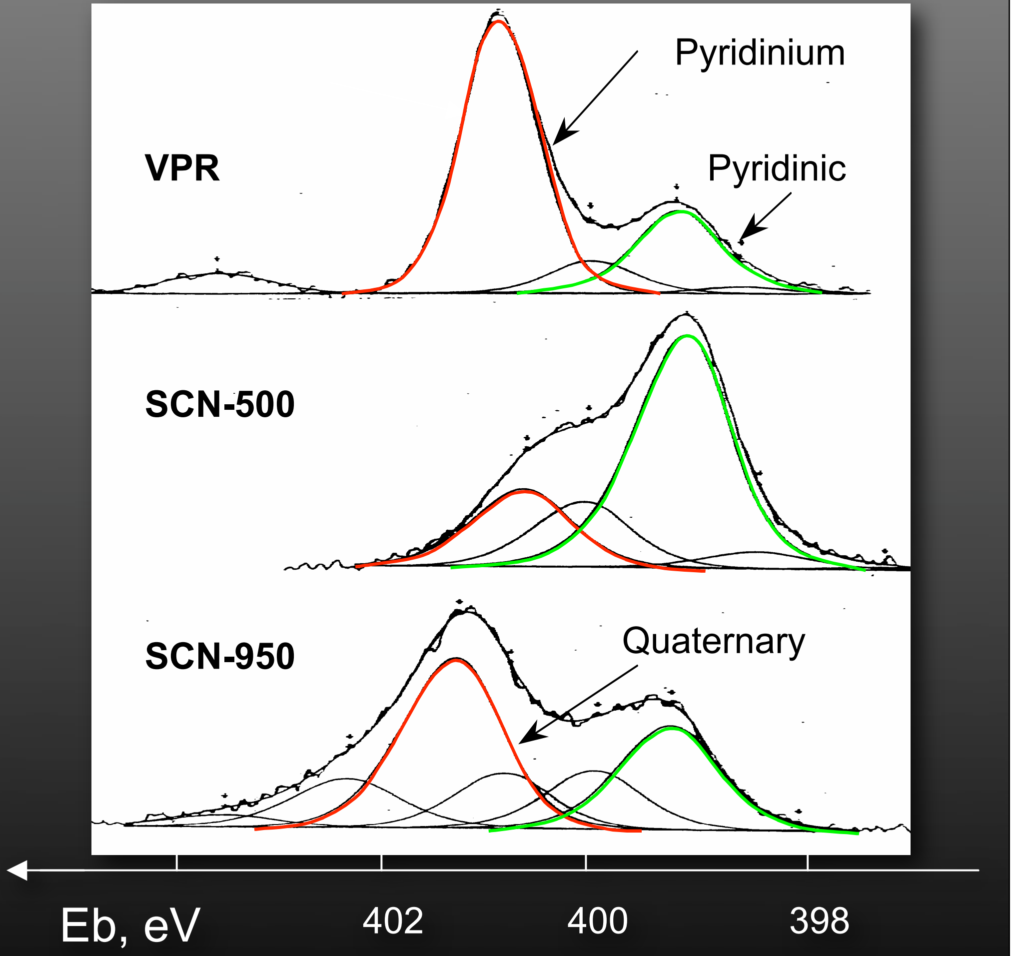
Porosity (before and after H_2S adsorption)



XPS

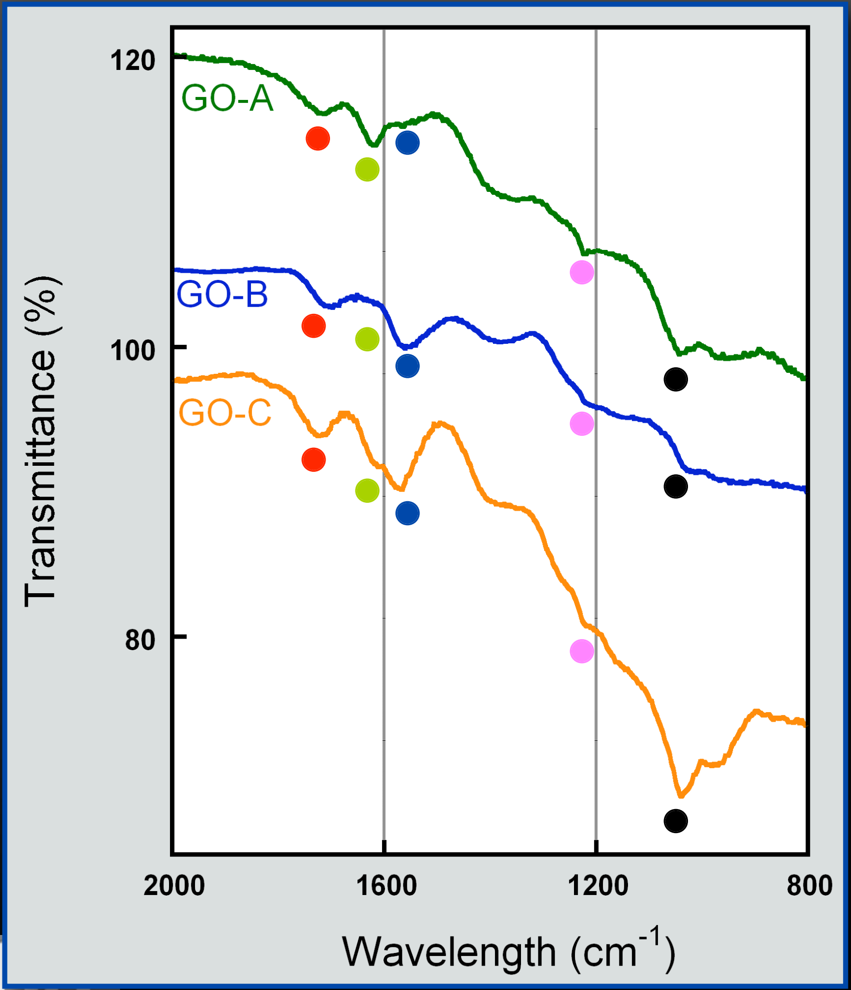


Schematic presentation of the chemical structure of VPR and its derivatives, nitrogen-containing carbons SCN



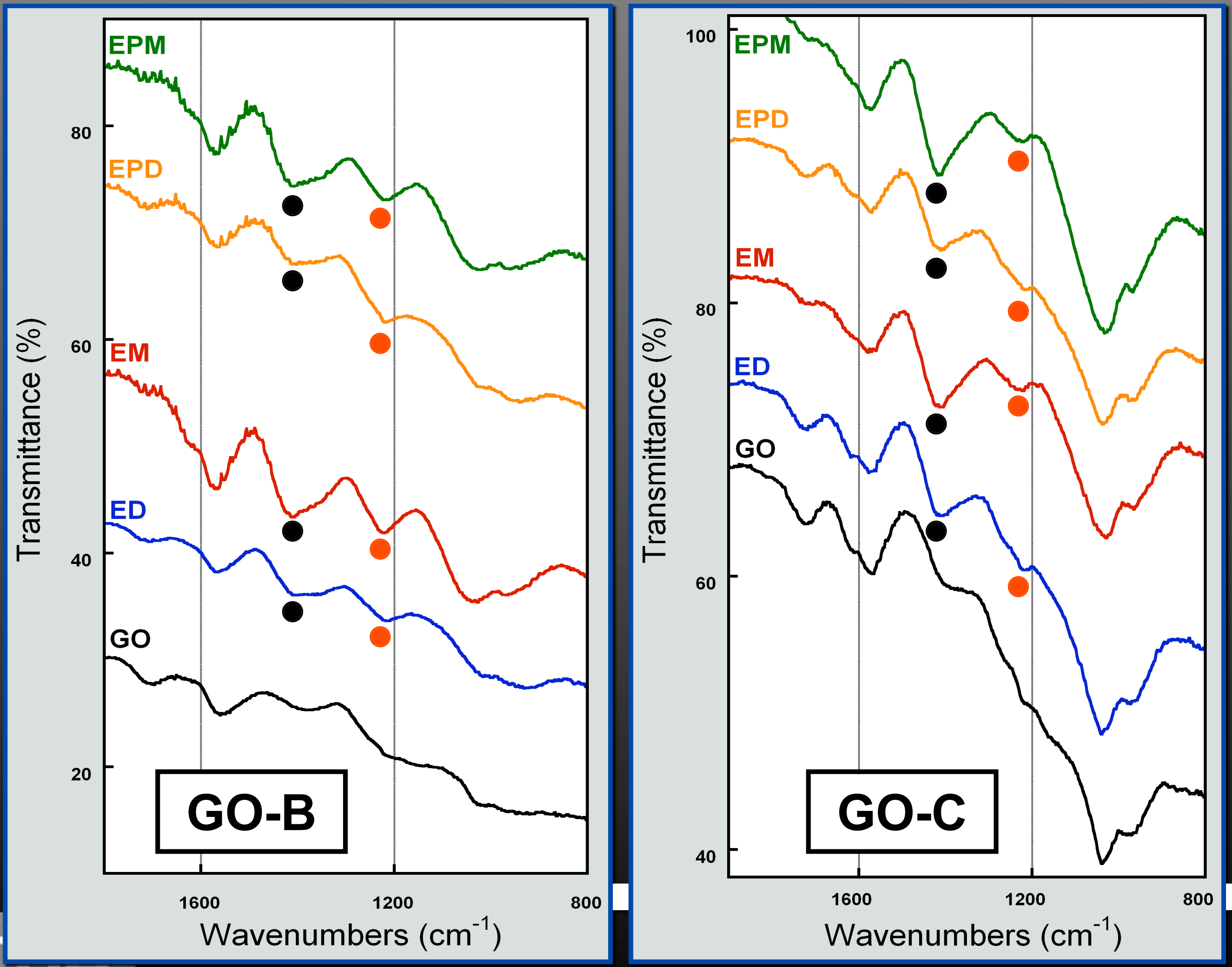
XPS spectra for the initial VPR resin and samples obtained by carbonization at 500 °C and 950 °C

FTIR- GO



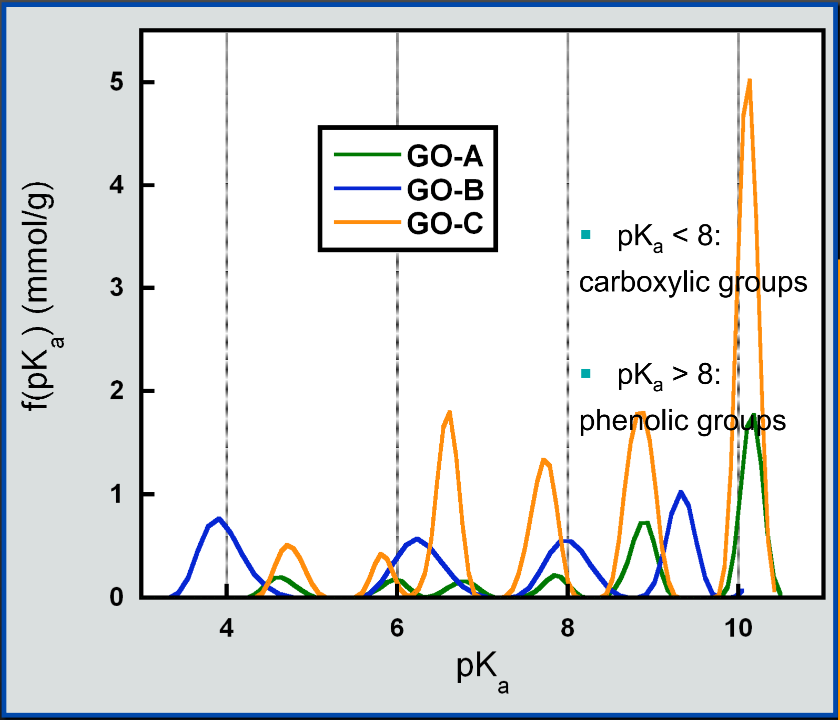
- ● C–O *1045 cm^{-1}*
- ● C=O *1730 cm^{-1}*
- ● Cyclic ether or H_2O *1620 cm^{-1}*
- ● Epoxy groups or C=C *1580 cm^{-1}*
- ● C–O *1220 cm^{-1}*

FTIR- GO exposed to ammonia

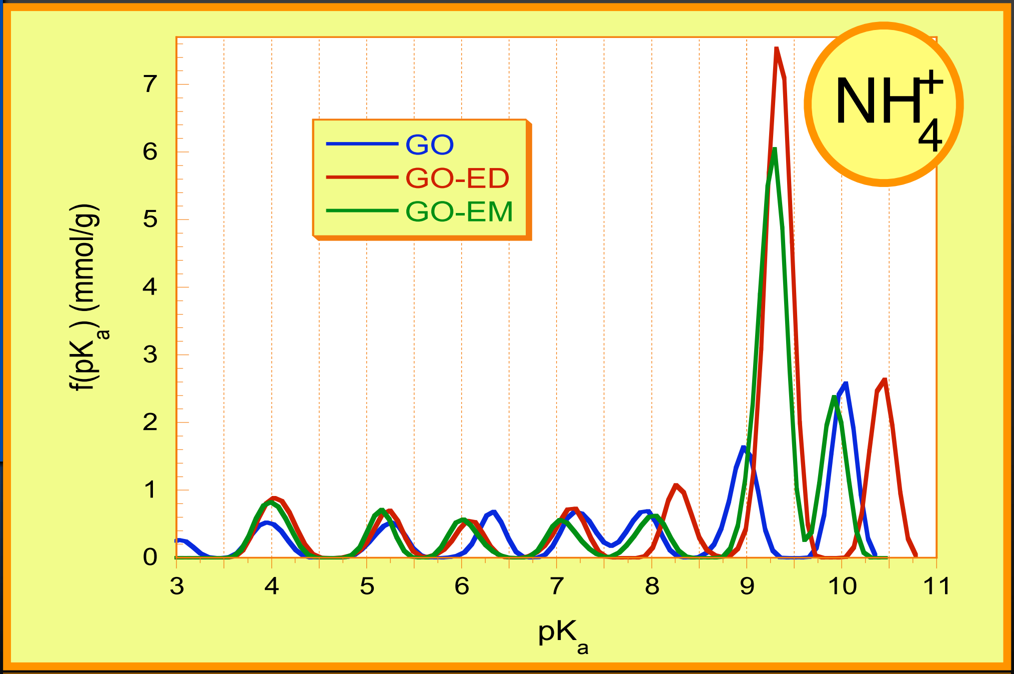


- ● **N–H from NH_4^+** *1420 cm^{-1}*
- ● **C–N from amines** *1220 cm^{-1}*

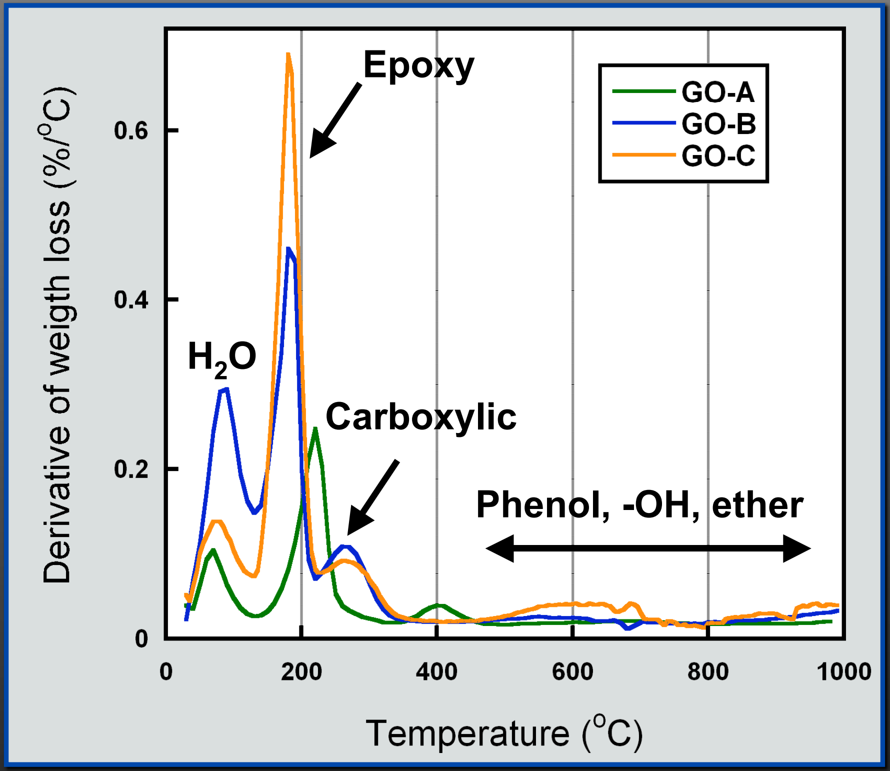
Potentiometic titration

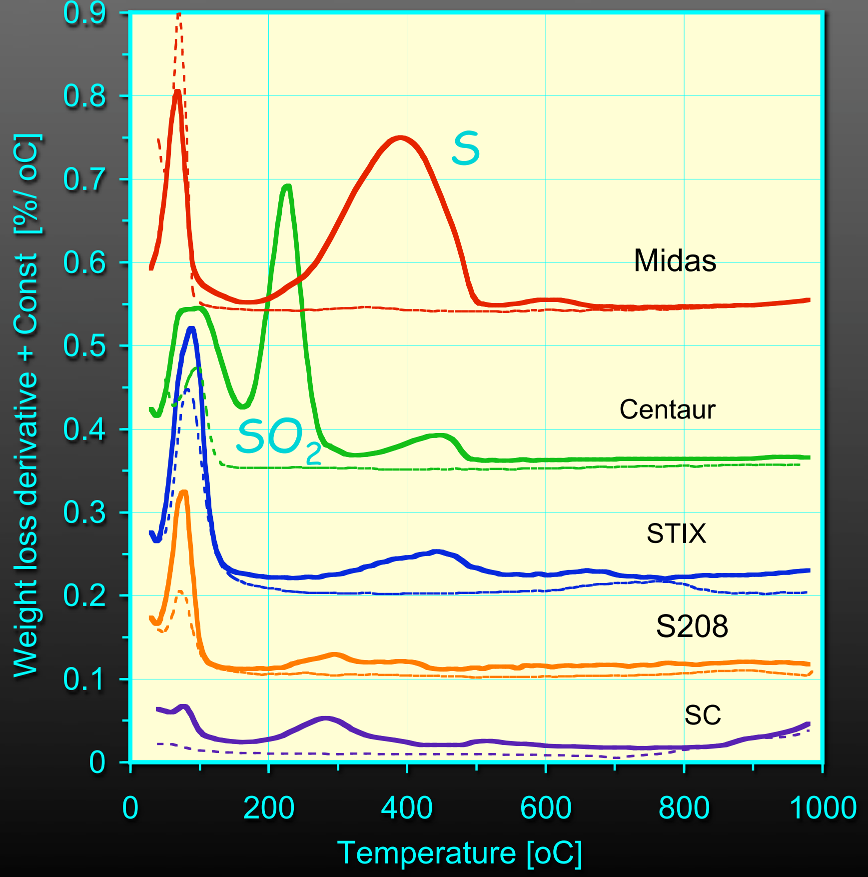


- pK$_a$ < 8: carboxylic groups
- pK$_a$ > 8: phenolic groups



TA analysis





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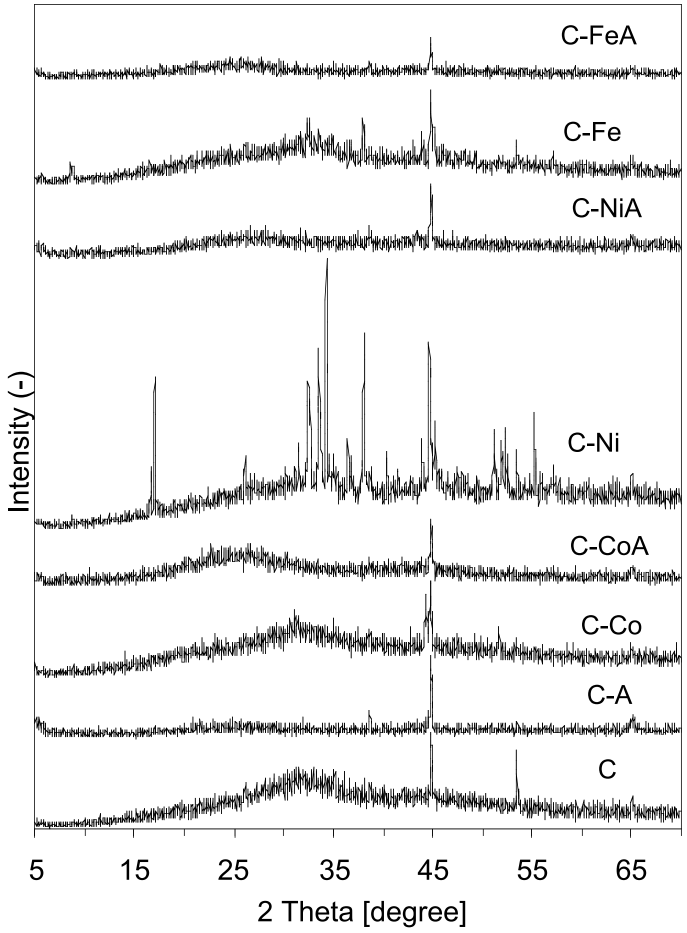
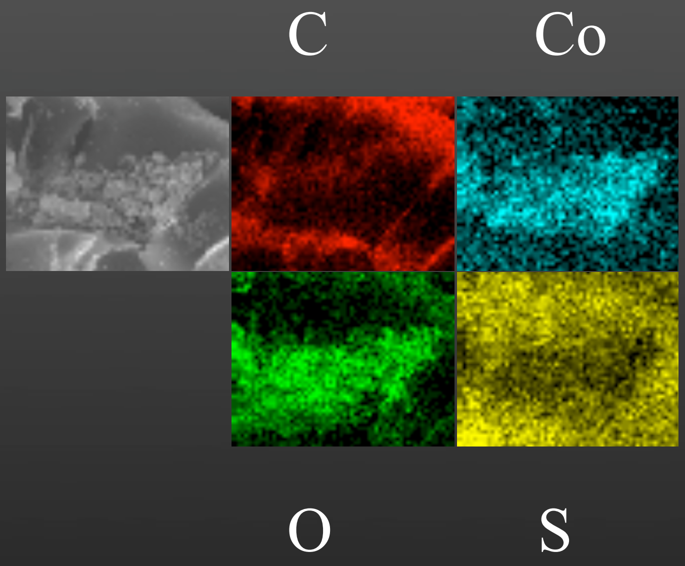
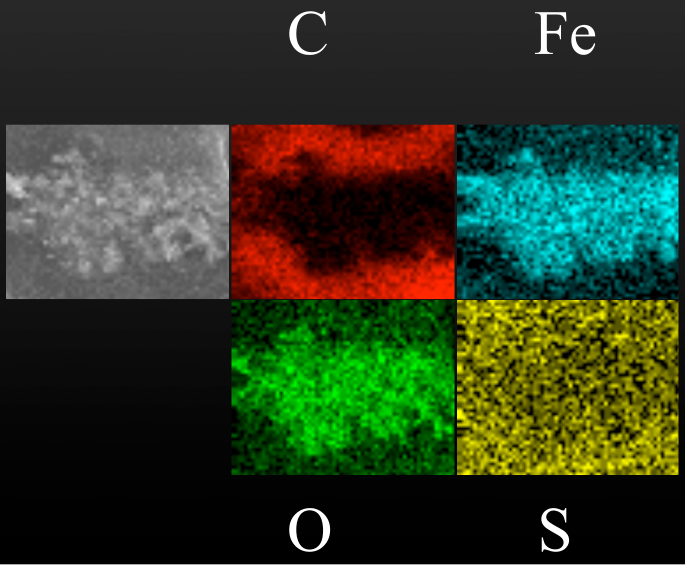
X-ray diffraction

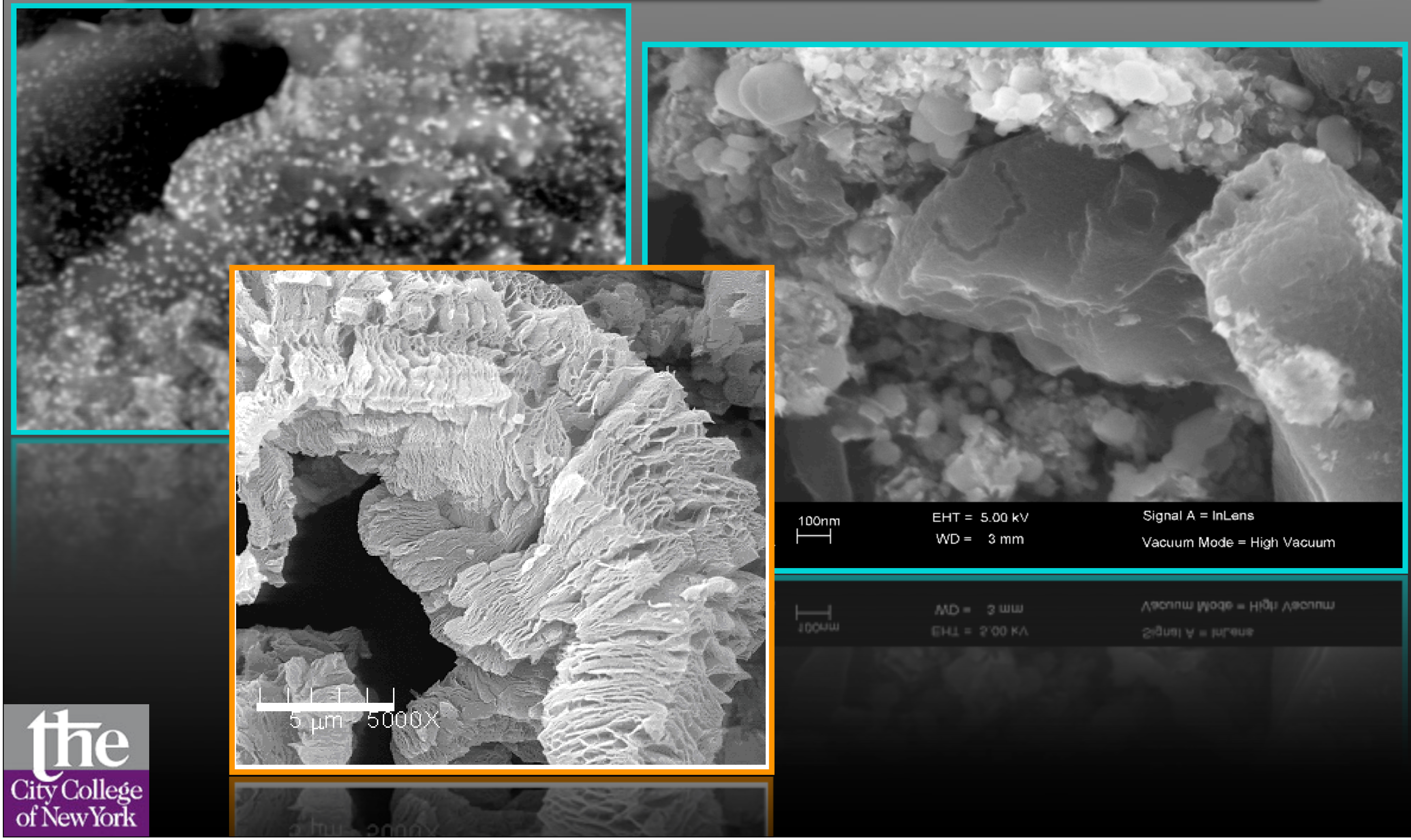


EDAX



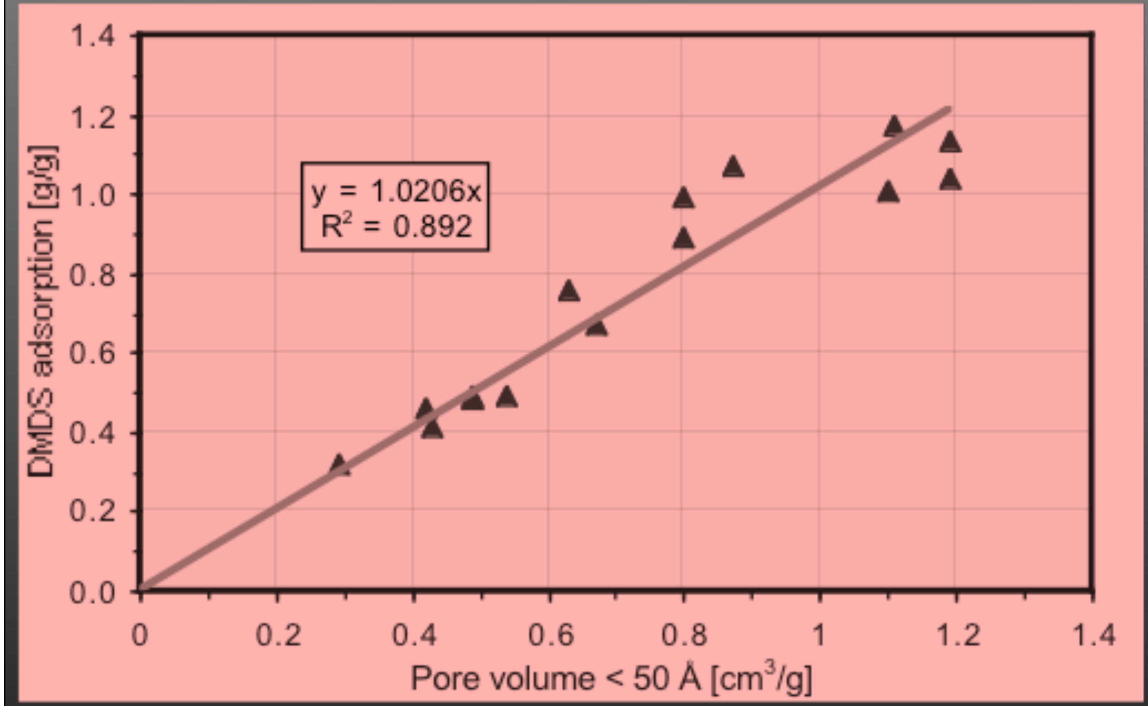


SEM IMAGES

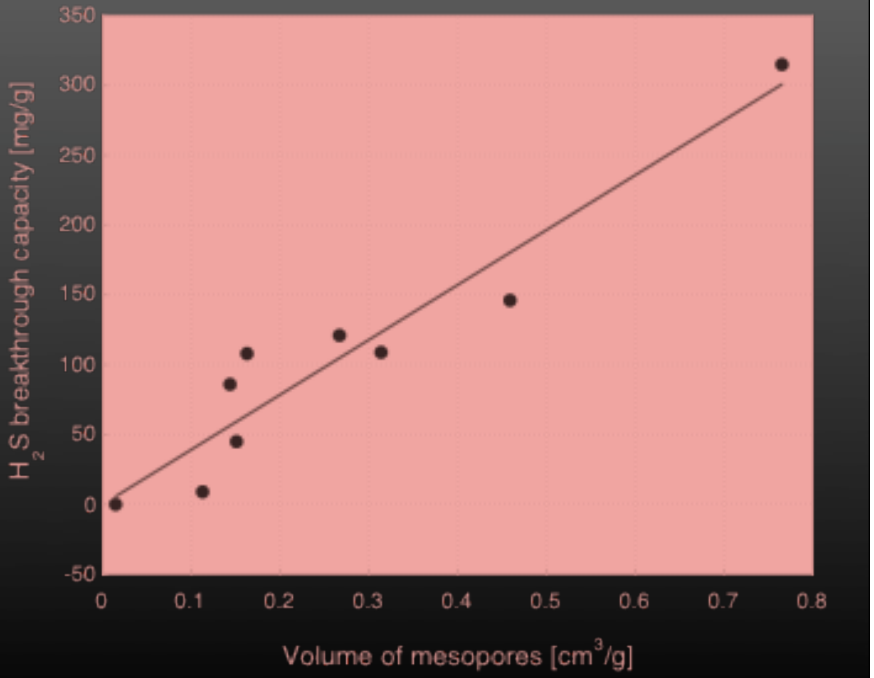

5 µm 5000X
100nm
EHT = 5.00 kV
WD = 3 mm
Signal A = InLens
Vacuum Mode = High Vacuum

Findings: role of porosity

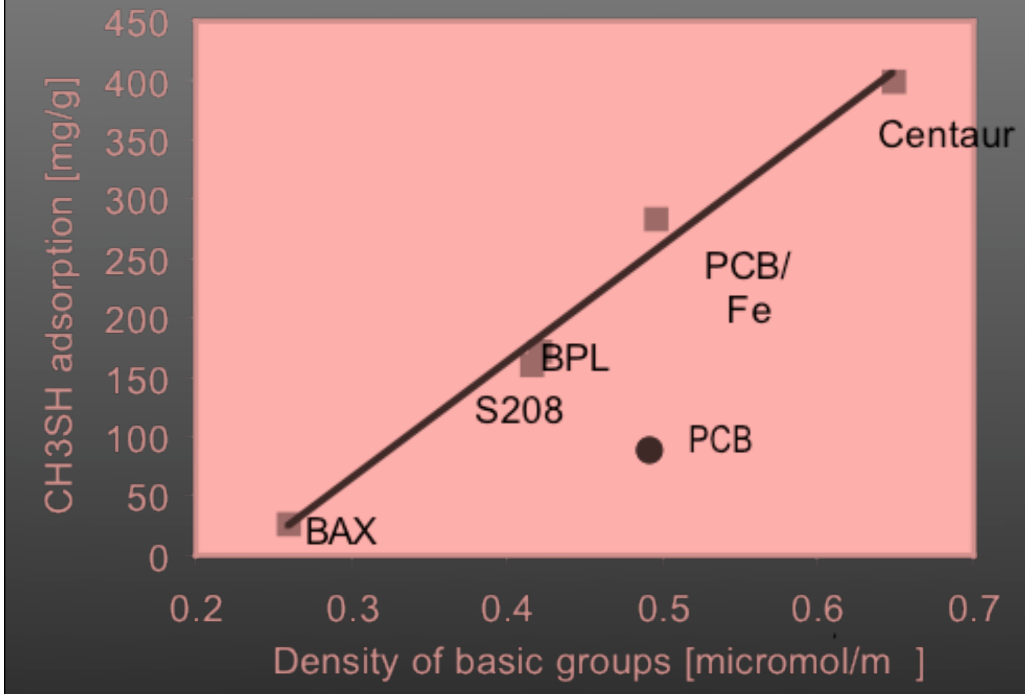
CH_3SSCH_3

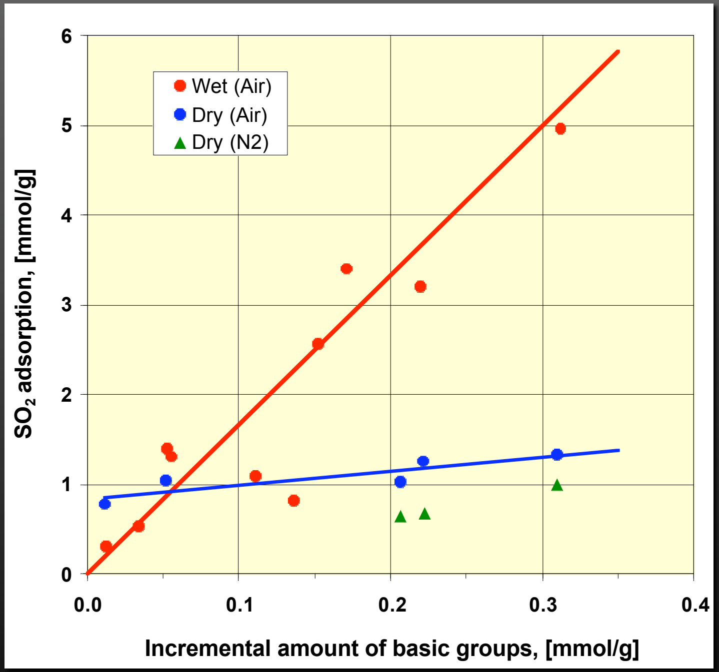


H_2S



Findings: surface chemistry

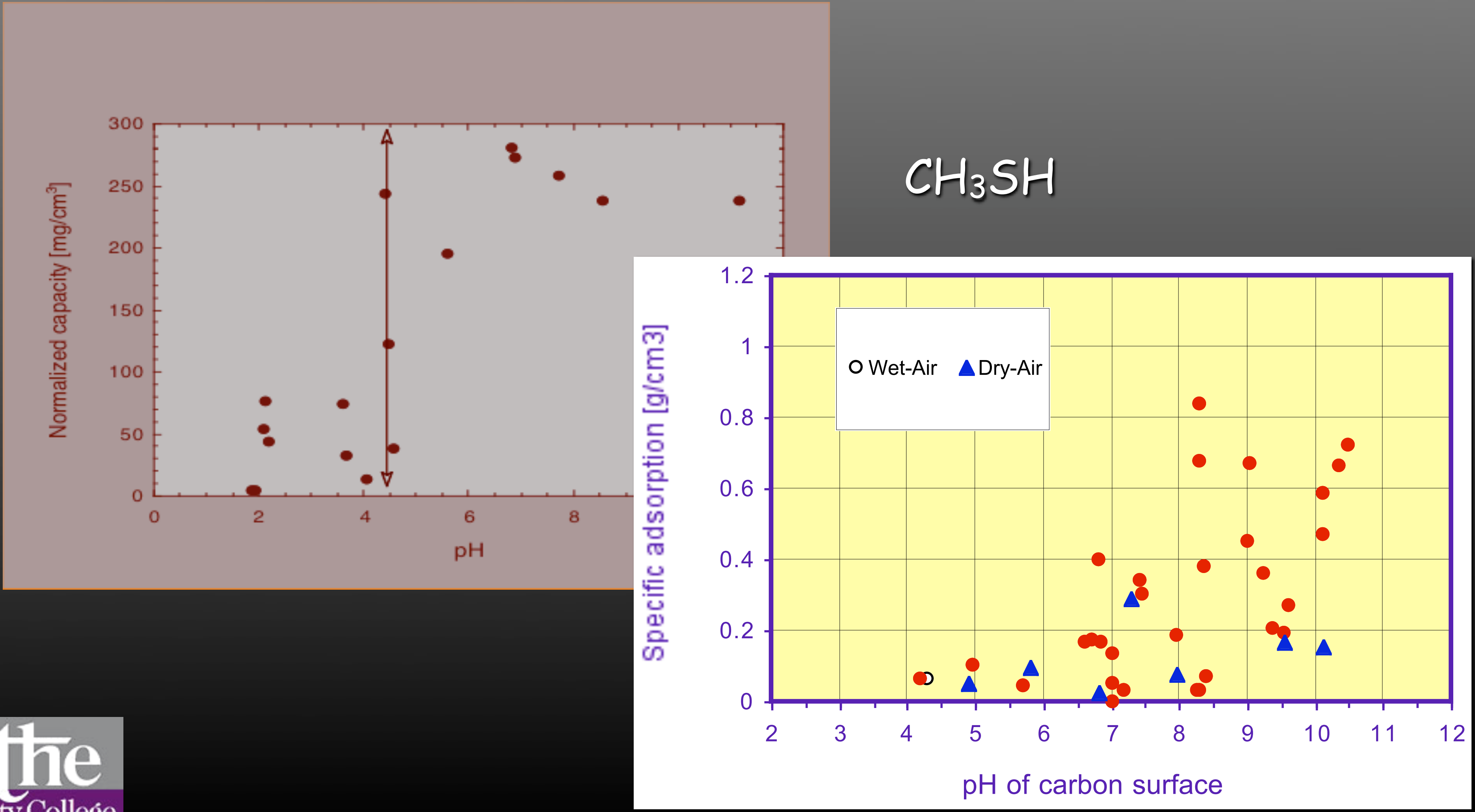




Findings: pH threshold

H_2S

CH_3SH



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Sulfur-direct evidence

H_2S oxidation

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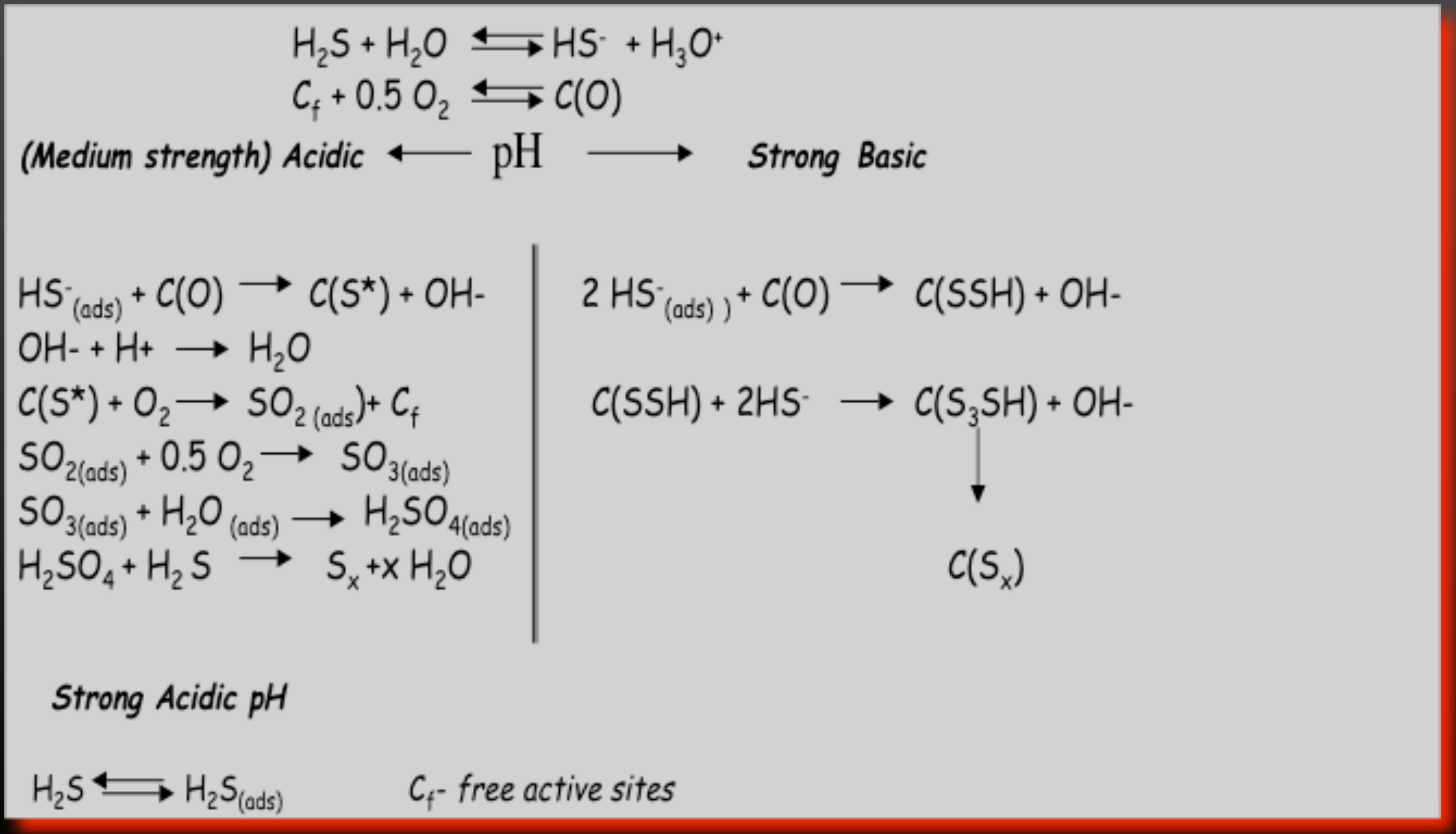
Findings:Catalytic properties

H_2S oxidation



$H_2S + H_2O \rightleftarrows HS^- + H_3O^+$

$C_f + 0.5\,O_2 \rightleftarrows C(O)$

(Medium strength) Acidic ← pH → *Strong Basic*

$HS^-_{(ads)} + C(O) \longrightarrow C(S^*) + OH-$

$OH- + H+ \longrightarrow H_2O$

$C(S^*) + O_2 \longrightarrow SO_{2\,(ads)} + C_f$

$SO_{2(ads)} + 0.5\,O_2 \longrightarrow SO_{3(ads)}$

$SO_{3(ads)} + H_2O_{(ads)} \longrightarrow H_2SO_{4(ads)}$

$H_2SO_4 + H_2S \longrightarrow S_x + x\,H_2O$

$2\,HS^-_{(ads)\,)} + C(O) \longrightarrow C(SSH) + OH-$

$C(SSH) + 2HS^- \longrightarrow C(S_3SH) + OH-$

$\downarrow$

$C(S_x)$

Strong Acidic pH

$H_2S \rightleftarrows H_2S_{(ads)}$

C_f*- free active sites*

Findings:Catalytic properties

H_2S oxidation

ON IRON OXIDES

- $Fe_2O_3 + 3H_2S \dashrightarrow FeS + FeS_2 + 3H_2O$
- $Fe_2O_3 + 3H_2S \dashrightarrow Fe_2S_3 + 3H_2O$
- $2Fe_2S_3 + 3O_2 \dashrightarrow 2Fe_2O_3 + 6S$

ON MAGNESIUM/CALCIUM OXIDES

- Non -reactive
- Very limited solubility
- PROVIDES BASIC pH (CATALYST)

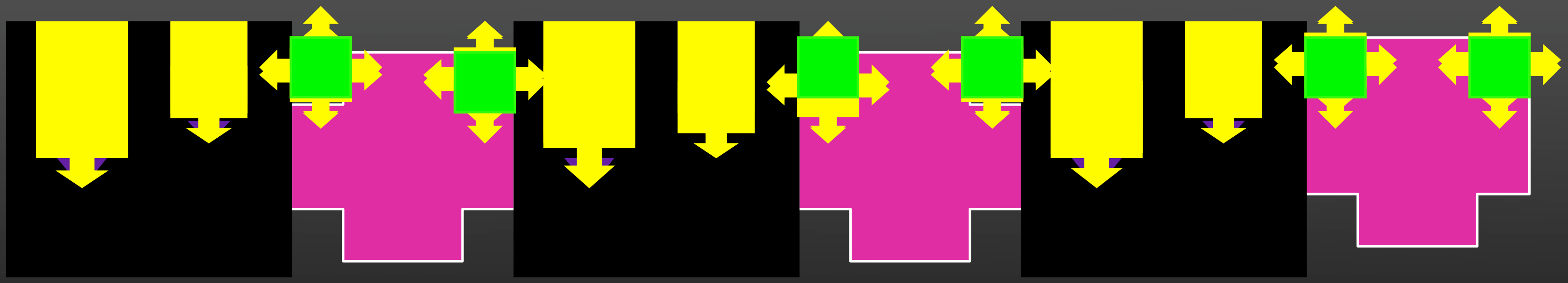
IN THE PRESENCE OF CAUSTICS

- $NaOH + H_2S \dashrightarrow NaHS + H_2O$
- $2NaOH + H_2S \rightarrow Na_2S + H_2O$
- $NaHS + 0.5O_2 \rightarrow S + NaOH$
- $Na_2S + 0.5O_2 + H_2O \rightarrow S + 2\ NaOH$
- $HS^- + H_2O \rightarrow H_2S + OH^-$
- $S^{2-} + H_2O \rightarrow HS^- + OH^-$
- $S + 1.5O_2 + H2O \rightarrow H_2SO_4$
- $2\ NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

PROPOSING MECHANISM

Catalytic H_2S oxidation on basic solid/carbon surface

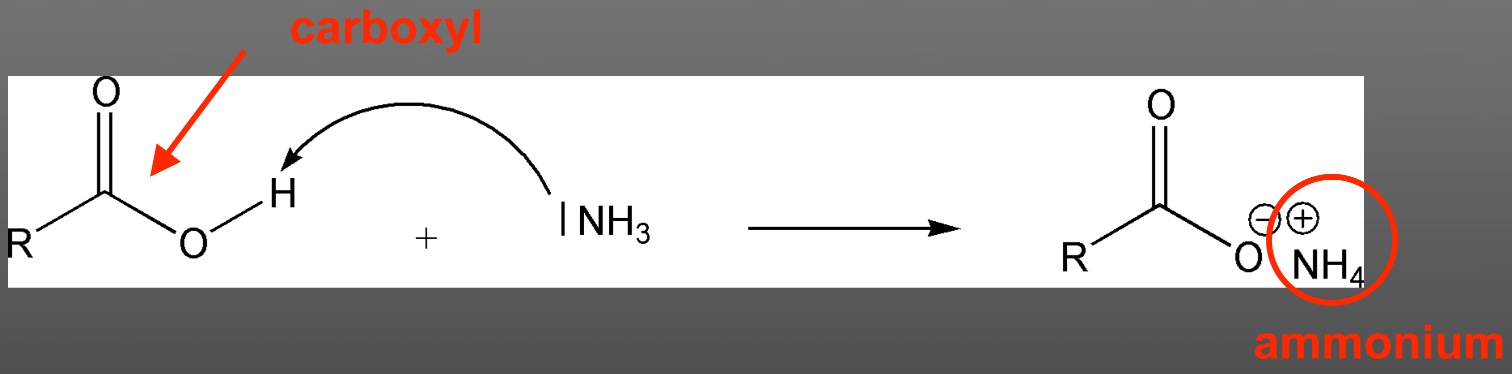
At the presence of air and moisture:

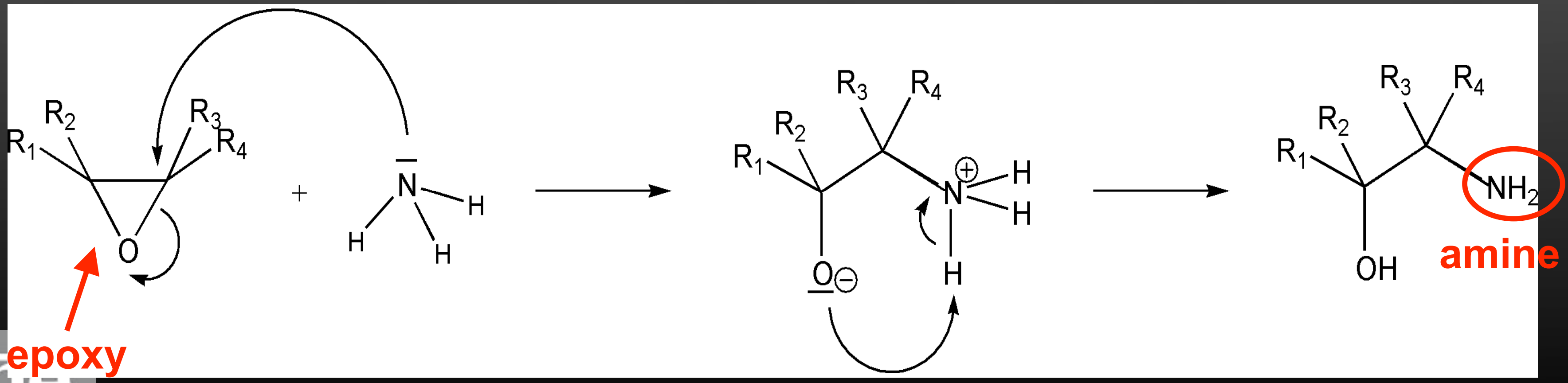


$2xHS^- + x/2O_2 \dashrightarrow S_x + xH_2O$

PROPOSING MECHANISM

Interaction of ammonia with graphite oxides





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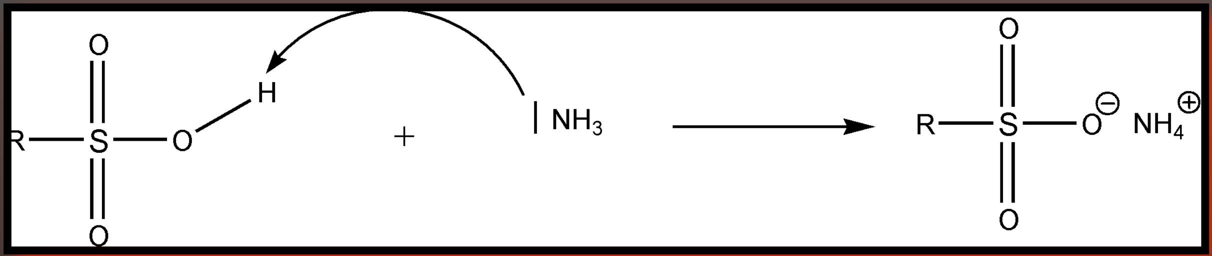
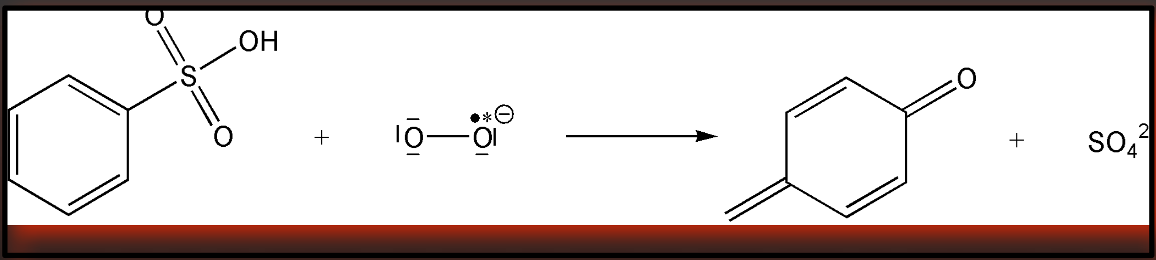
PROPOSING MECHANISM

Enhanced adsorption of NH_3 on GO or carbons containing sulfur





$$2\,NH_4^+ \;+\; SO_4^{2-} \longrightarrow (NH_4)_2SO_4$$

PROPOSING MECHANISM

Interaction of arsine with sulfur containing carbons

Absence of water:

$2AsH_3 + 3O_2^- \longrightarrow As_2O_3 + 3H_2O$

$2AsH_3 + 4O_2^- \longrightarrow As_2O_5 + 3H_2O$

With active oxygen:

$As_2O_3 + O_2^- \longrightarrow As_2O_5$

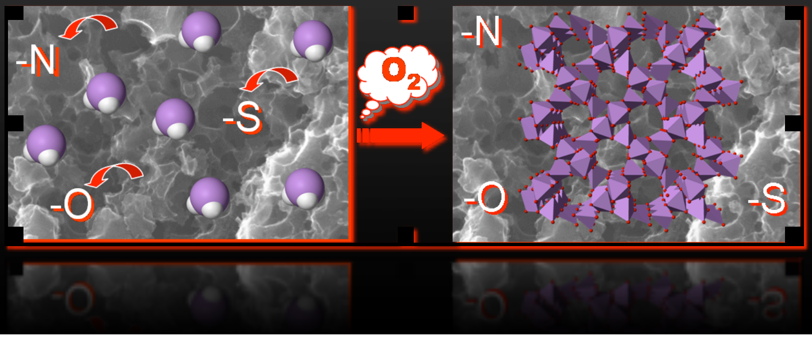
With sulfonic groups:

$AsH_3 + R\text{-}SO_3H \longrightarrow As_xS_y + H_2O$

In moist air, we observe additionally:

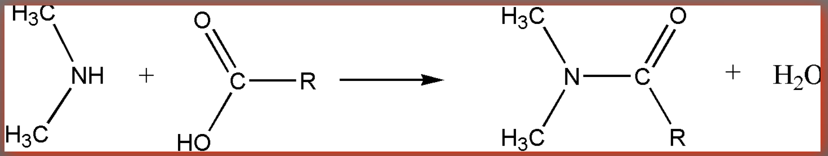
$As_2O_5 + 2H_2O \longrightarrow H_4As_2O_7$

$As_2O_3 + 3H_2O + O_2^- \longrightarrow 2H_3AsO_4$

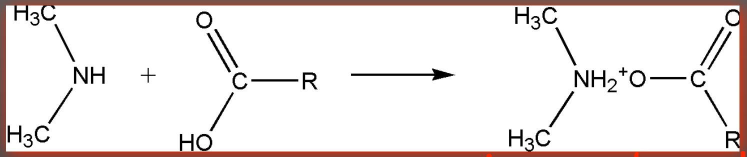


PROPOSING MECHANISM

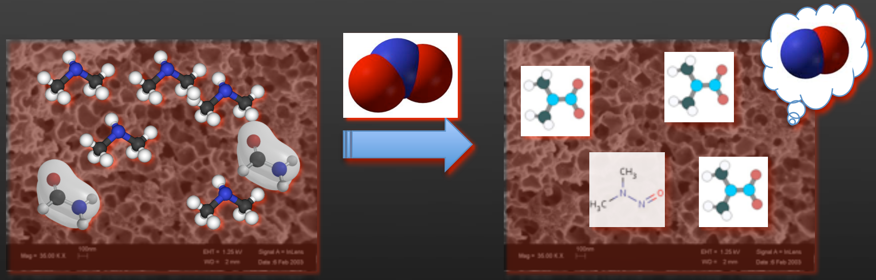
Interactions of NO_x with amine modified carbons carbons

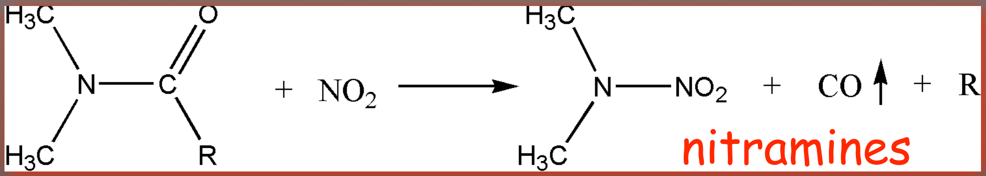


amides

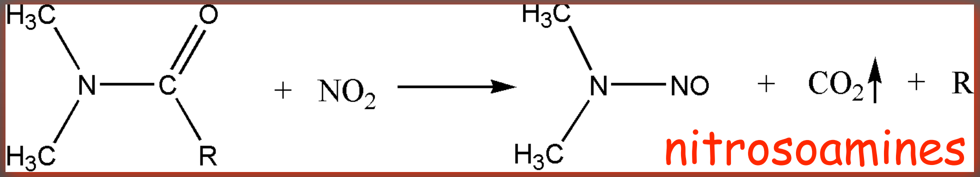


amine carboxylates

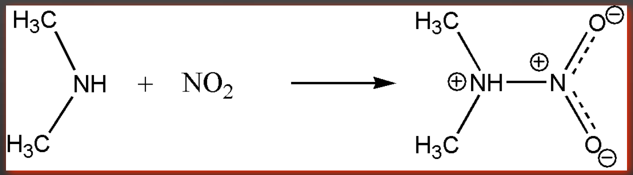


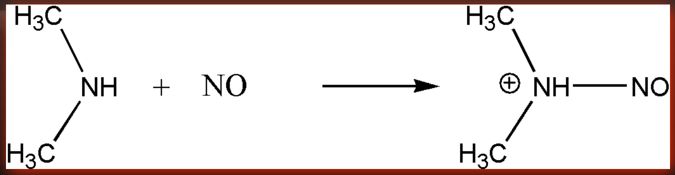


nitramines



nitrosoamines

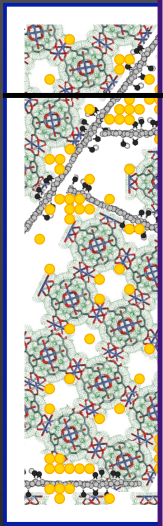




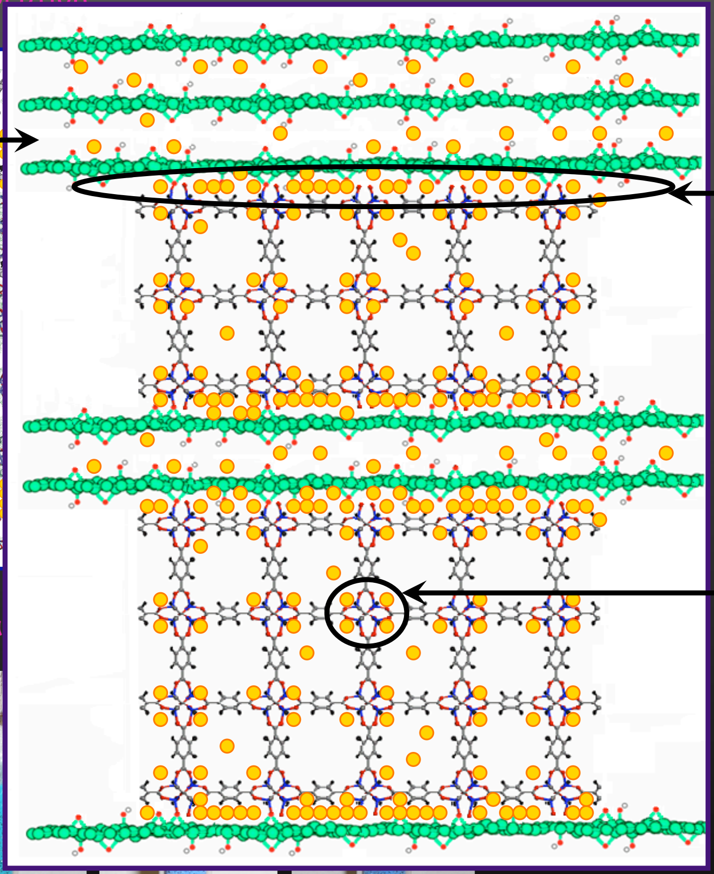
Complex mechanism on GO/MOF composites

- Physisorption
- Coordination to copper
- Reaction with MOF
- Reactions with GO functional groups

Physisorption



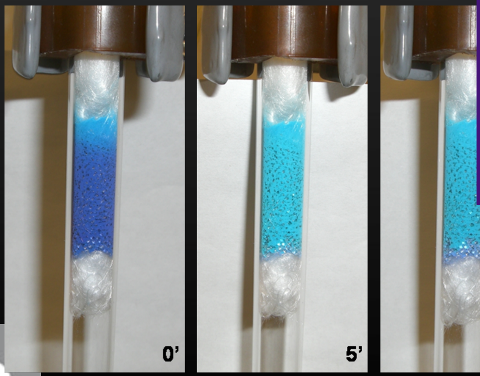
Intercalation between graphene layers

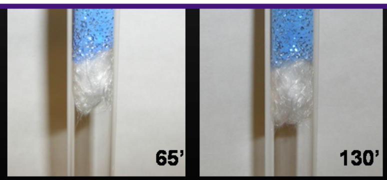


Physical adsorption in new pore space

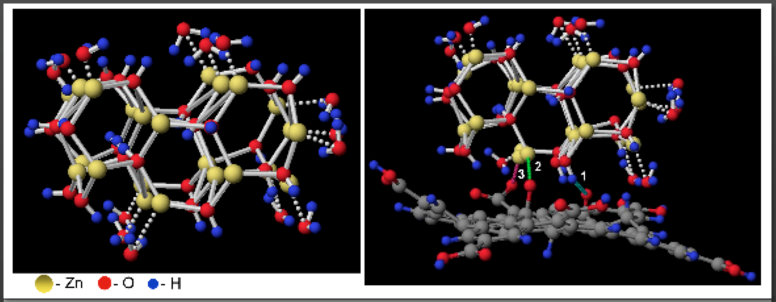
Hydrogen bonding

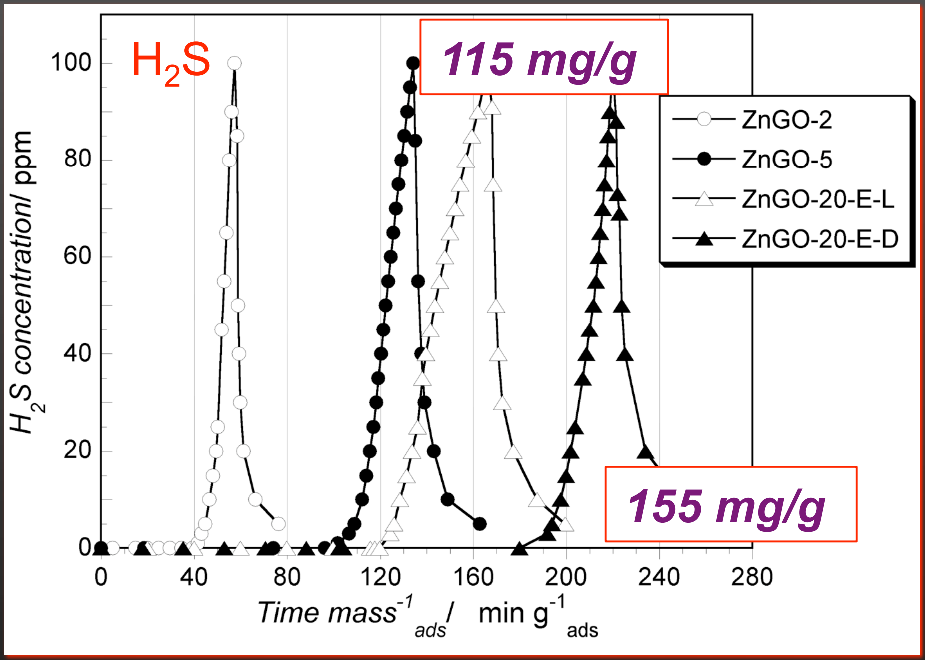
Rea





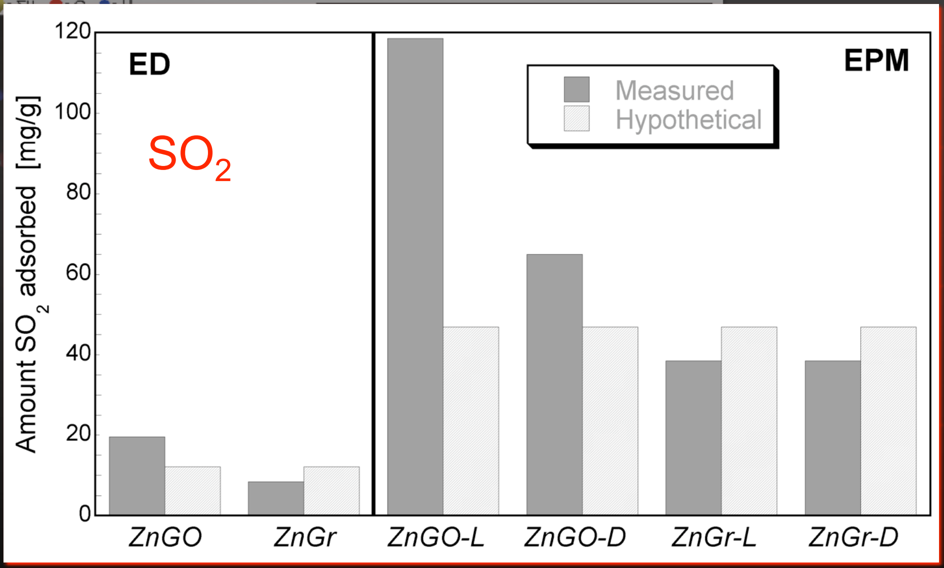
Photoactivity





115 mg/g

155 mg/g



Band gap energy:

$Zn(OH)_2$: 3.02 eV

ZnGO-2: 2.98 eV

ZnGO-5: 2.92 eV

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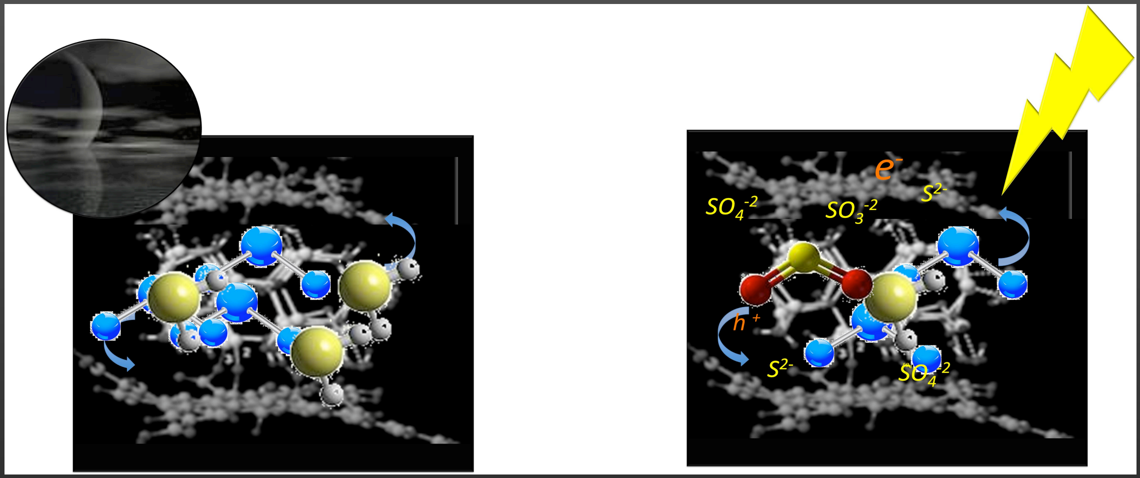
Photoactivity- role of OH



$H_2O + H_2S \longrightarrow HS^- + H_3O^+$

$Zn\text{-}OH + HS^- \longrightarrow Zn\text{-}HS + OH^-$

$ZnOH\text{-}GO + h\nu \longrightarrow e^-(GO) + h^+(Zn\text{-}OH)$

$e^- + O_2 \longrightarrow O_2^{\bullet -}$

$h^+ + OH^- \longrightarrow OH^\bullet$

$O_2^{\bullet -} + H_2O \longrightarrow OH_2^\bullet + OH^-$

$OH_2^\bullet + H_2O \longrightarrow H_2O_2 + OH^\bullet$

$H_2O_2 \longrightarrow 2OH^\bullet$

$H_2O + H_2S \longrightarrow HS^- + H_3O^+$

$Zn\text{-}OH + HS^- \longrightarrow Zn\text{-}HS + OH^-$

$HS^- + OH^\bullet \longrightarrow S^o + H_2O$

$HS^- + OH^\bullet + H_2O \longrightarrow HSO_3^- + H^+$

$Zn\text{-}OH + HSO_3^- \longrightarrow Zn\text{-}HSO_3^- + OH^-$

Photoactivity-role of water

$$ZnO \rightarrow e^- + h^+$$

$$SO_2 + H_2O \rightarrow H_2SO_3$$

$$H_2SO_3 + Zn(OH)_2 \rightarrow ZnSO_3 + 2H_2O$$

$$SO_3^{2-} + H_2O + 2h^+ \rightarrow SO_4^{2-} + 2H^+$$

$$2SO_3^{2-} + 2h^+ \rightarrow S_2O_6^{2-}$$

$$2H^+ + 2e^- \rightarrow H_2$$

$$\boxed{2H_2O + 2e \rightarrow H_2 + 2\,OH^-}$$

$$\boxed{SO_3^{2-} + H_2O + 4h^+ \rightarrow S^{o} + 2O_2 + 2H^+}$$

$$S^{o} + 2e^- \rightarrow S^{2-}$$

$$S^{2-} + Zn(OH)_2 + 2\,H^+ \rightarrow ZnS + 2\,H_2O$$

Conclusions

- To obtain a comprehensive view of the process occurring on the surface of adsorbents during reactive adsorption the results obtained using various methods have to be combined
- The surface should be modified towards expected reactions and properties of the adsorbate

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