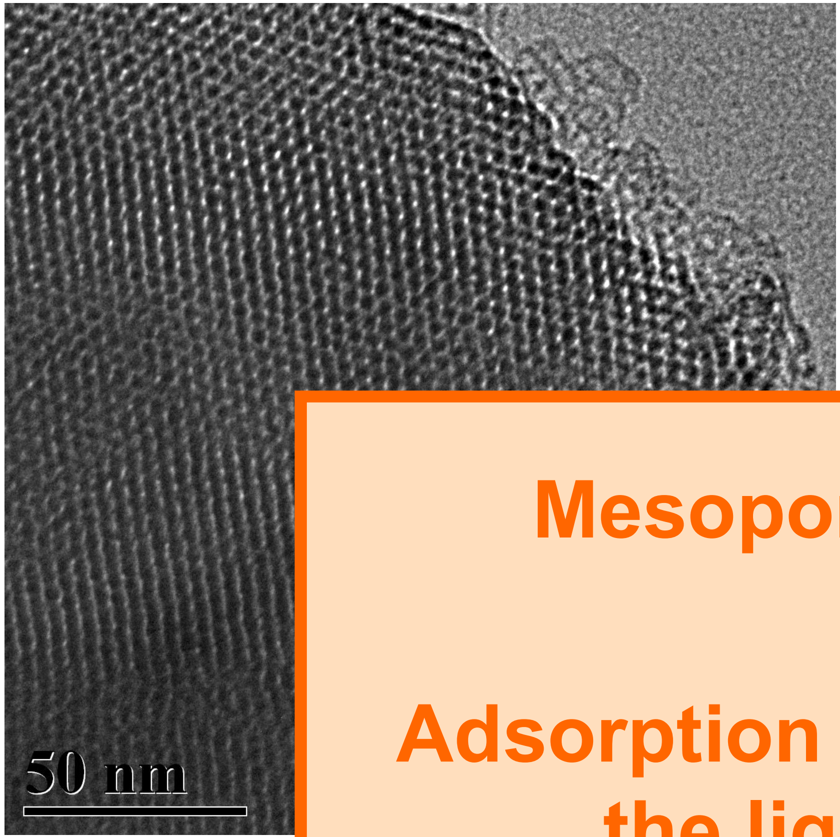
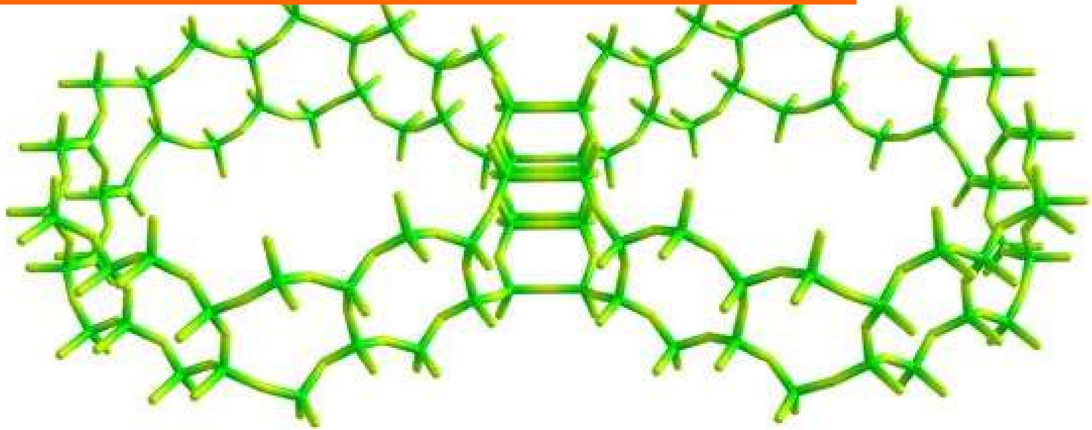


Mesoporous oxides

Adsorption of pollutants in the liquid phase



Adsorption of boron by grafted mesoporous silica

➪ boron (B) capture from aqueous effluents

- 2 main species :

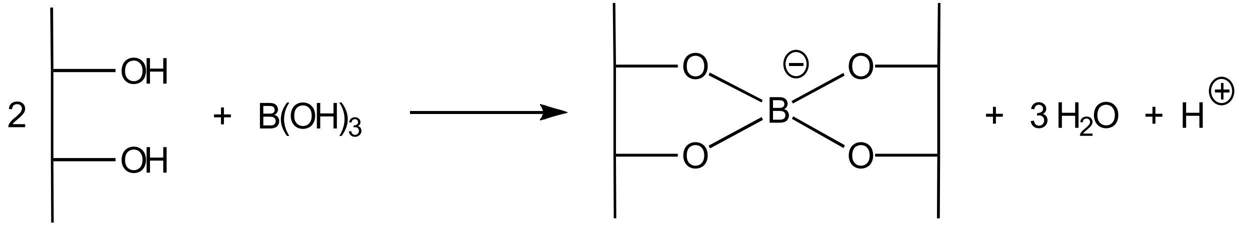
$$H_3\overset{III}{B}O_3 + H_2O \underset{}{\overset{Ka}{\rightleftharpoons}} B(OH)_4^- + H^+ \qquad pKa\ (H_3BO_3 / B(OH)_4^-) = 9.24 \text{ at } 20°C$$

boric acid — borate anions

- element widely used in fertilizers

- WHO (World Health Organisation) standard : $[B] < 0.3\ mg.L^{-1}$ in drinking water

- adsorption mechanism : complexation by polyols



➪ Use of mesoporous solids as solid supports for adsorption

➪ Use of the mesoporosity for the grafting of polyols

Adsorption of boron by grafted mesoporous silica

↳ Mesoporous silica : MCM-41 and SBA-15

Hydrothermal synthesis

- MCM-41 → ionic surfactant

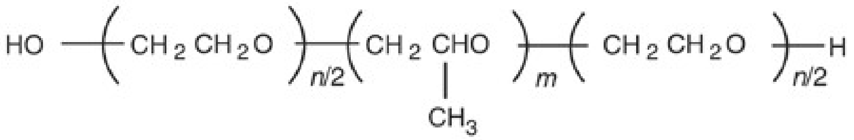
$CTMA^+Br^-$, n = 16, hexadecyltrimethylammonium bromide ($C_{16}H_{31}N(CH_3)_3^+$)

= CetylTrimethyl Ammonium Bromide

- SBA-15 → non-ionic surfactant

Pluronic® : EO-PO-EO tribloc copolymer

(PolyEthylene Oxide - PolyPropylene Oxide - PolyEthylene Oxide)



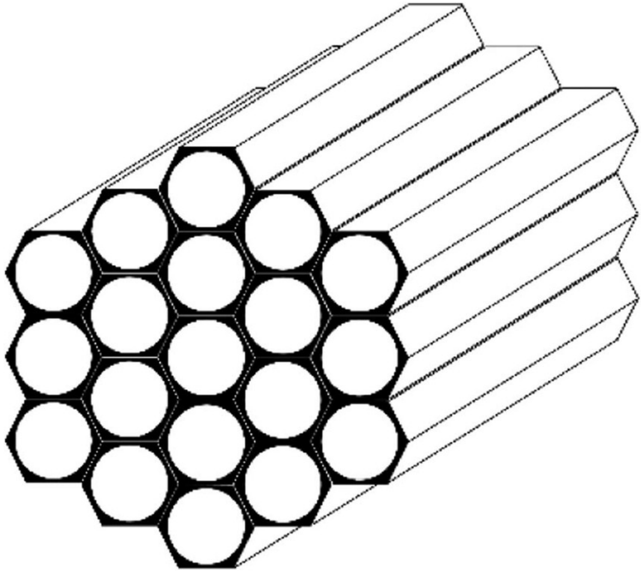
$$\mathrm{HO}-\left(\mathrm{CH_2CH_2O}\right)_{n/2}\left(\mathrm{CH_2}\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CHO}}}\right)_{m}\left(\mathrm{CH_2CH_2O}\right)_{n/2}-\mathrm{H}$$

F127	*n* = 200	*m* = 65	mw = 12 618
L61	*n* = 4.5	*m* = 31	mw = 2018

Poloxamer family
(tri-bloc copolymers)

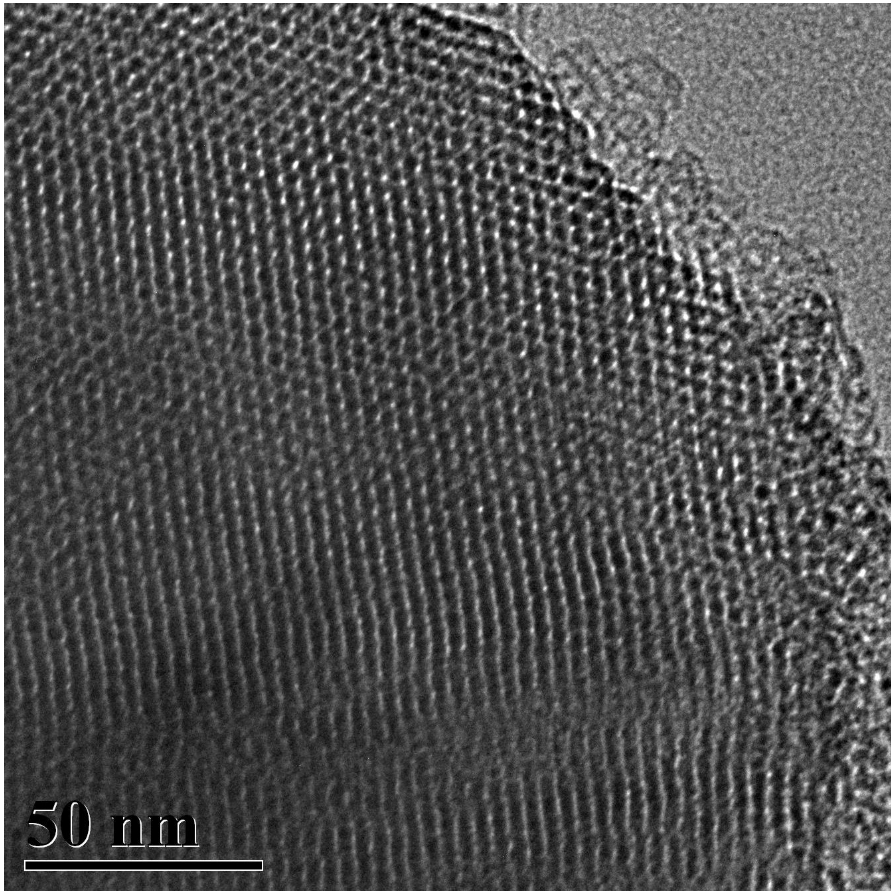
Adsorption of boron by grafted mesoporous silica

↳ Textural properties



Honeycomb porosity

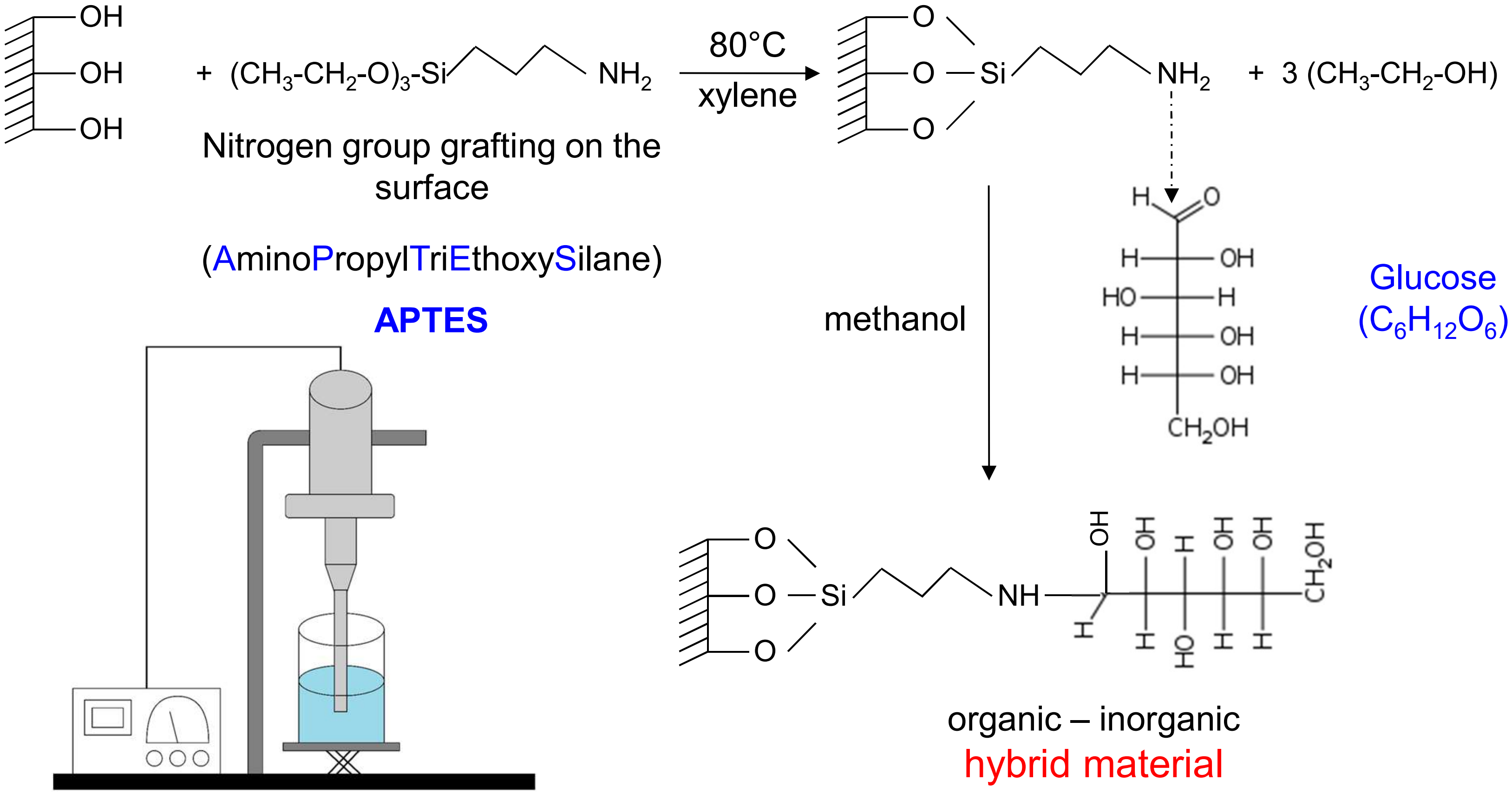
MCM-41



Pore ∅ ~ 5 nm

Adsorption of boron by grafted mesoporous silica

↳ Example : grafting by glucose for –OH groups increasing



Nitrogen group grafting on the surface

(AminoPropylTriEthoxySilane)

APTES

methanol

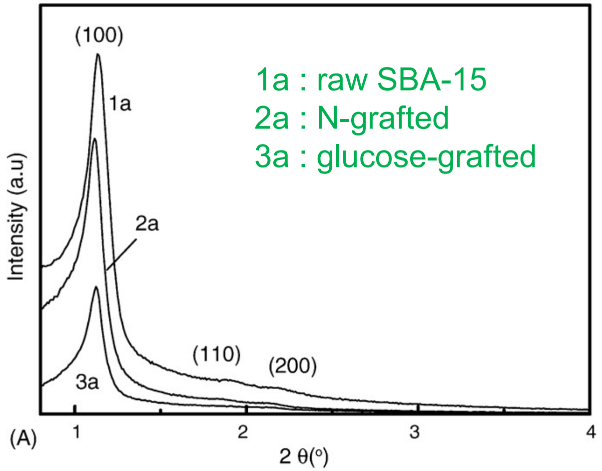
Glucose ($C_6H_{12}O_6$)

organic – inorganic hybrid material

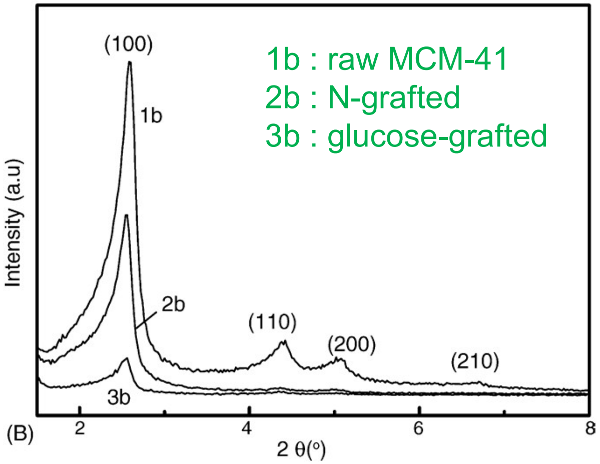
⇒ increase of the number of complexing sites which are fixed on a flexible and mobile chain

Adsorption of boron by grafted mesoporous silica

⇘ X-ray diffraction of MCM-41 and SBA-15 grafted materials



SBA-15



MCM-41

⇨ peaks characteristic of the hexagonal symmetry

⇨ No shift of the peaks position after grafting
↳ the mineral framework is not modified

↘ intensity of the peaks after the first step

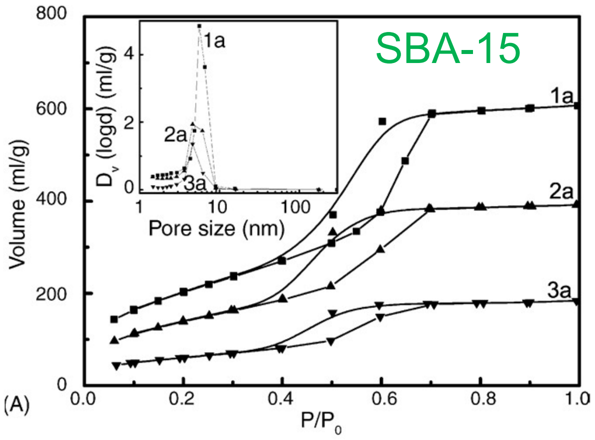
↳ adsorption of X-rays by the organic matter

↳ signature of the presence of the amino group and of the glucose in the porosity

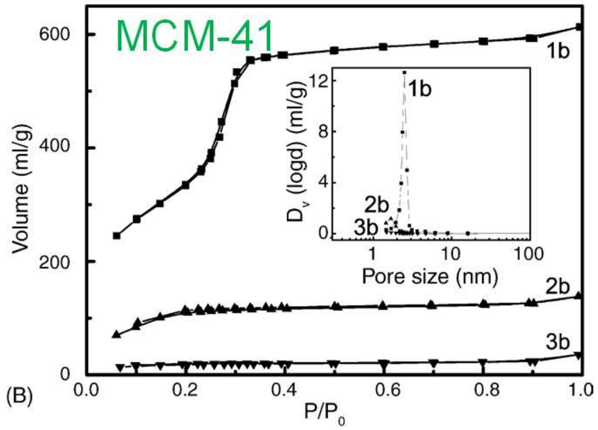
↘ intensity more pronounced for MCM-41 ⇒ greater change in porosity
(to be confirmed by BET surface area measurements)

Adsorption of boron by grafted mesoporous silica

⇨ N_2 adsorption–desorption @77K + pore size distribution (BJH ads.)



1 : raw material
2 : N-grafted
3 : glucose-grafted



type IV, H1 hysteresis ⇒ large mesopores

little hysteresis ⇒ few small mesopores

Sample		S_{BET} ($m^2.g^{-1}$)	V_p ($cm^3.g^{-1}$)	$\varnothing_{pores}$ (nm)
SBA-15	raw	755	0.94	5.6
	N-graf.	524	0.61	4.6
	Gluc-graf.	224	0.29	4.2
MCM-41	raw	1260	0.95	2.5
	N-graf.	457	0.21	1.7
	gluc.-graf.	69	0.056	< 1.5

$\varnothing_{pores}$: SBA-15 > MCM-41

↘ S_{BET} after each grafting step
⇒ clear signature of the presence of the organic matter inside the pores

↘ Much more pronounced for MCM-41
⇒ Confirms XRD observations

↘ Porous volume
~ 70% for SBA-15 / ~ 95% for MCM-41

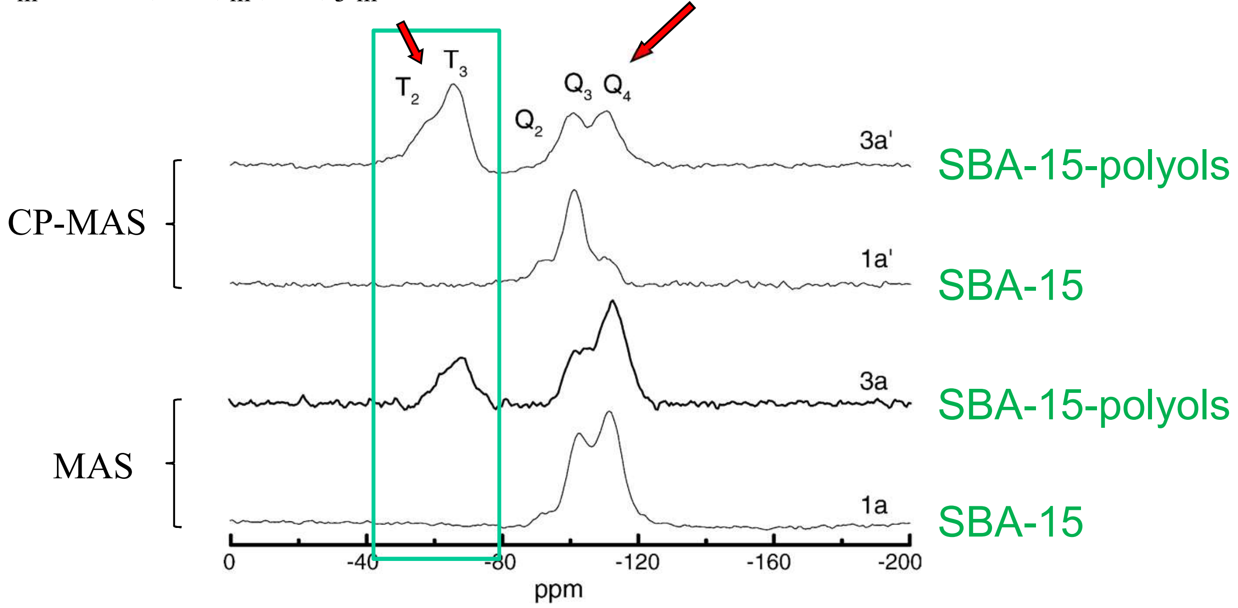
Adsorption of boron by grafted mesoporous silica

➪ ^{29}Si NMR

organosiloxanes

$T_m = RSi(OSi)_m(OH)_{3-m}$, m = 1-3

Si framework $Q_n = Si(OSi)_n(OH)_{4-n}$, n = 2-4



- organosiloxanes ⇨ presence of organic matter **<u>linked</u>** to the mineral framework
- %silanols = $(2Q_2 + Q_3)/(2Q_2 + Q_3 + Q_4)*100$

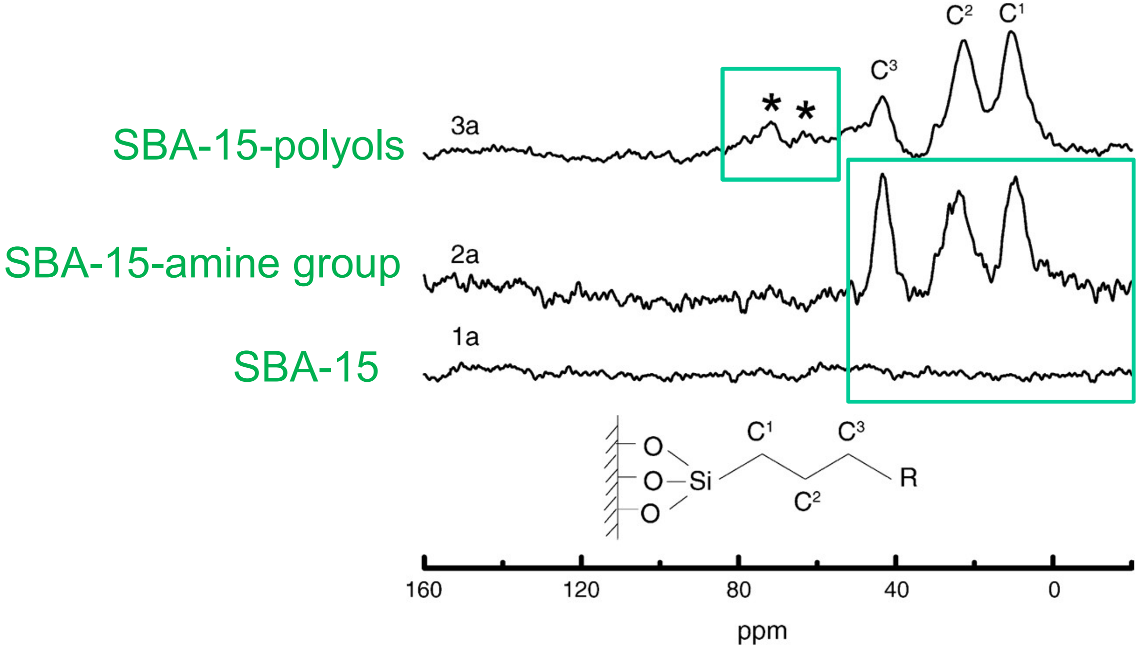
  %silanols ↘ from 42% to 34% after grafting

  ⇒ Incomplete grafting (OH groups difficult to access for glucose)

  ⇒ The material preserves its hydrophilic properties (presence of remaining OH groups)

Adsorption of boron by grafted mesoporous silica

^{13}C NMR



- Before grafting : no signal of the carbon
- After 1st step : 3 peaks characteristic of aminopropyl groups
- After 2nd step : appearance of 2 new peaks attributed to glucose carbon atoms

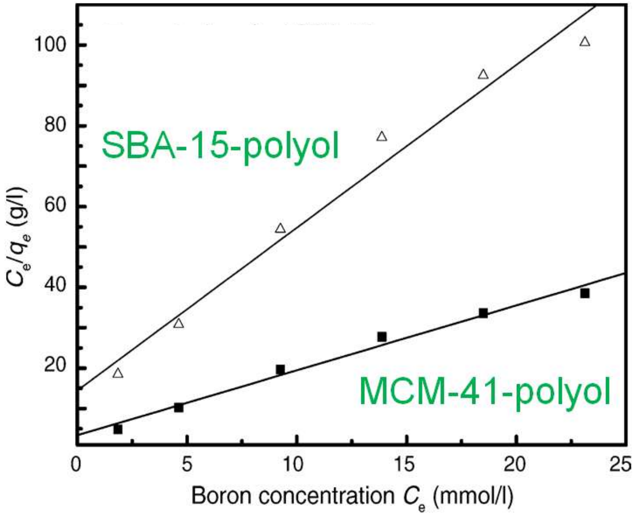
⇒ Presence of glucose confirmed

However, ^{13}C NMR cannot distinguish between chemical grafting and adsorption

Adsorption of boron by grafted mesoporous silica

↳ Adsorption isotherms

0.25 g ads., 10 mL H_3BO_3
20-250 ppm, 30°C, 24h



Langmuir equation
modelling

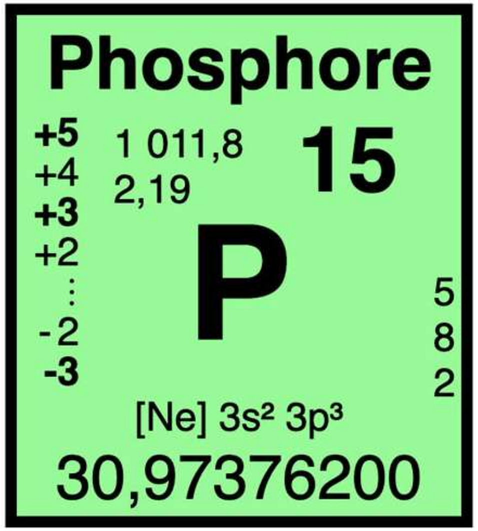
→ Q_{ads} :

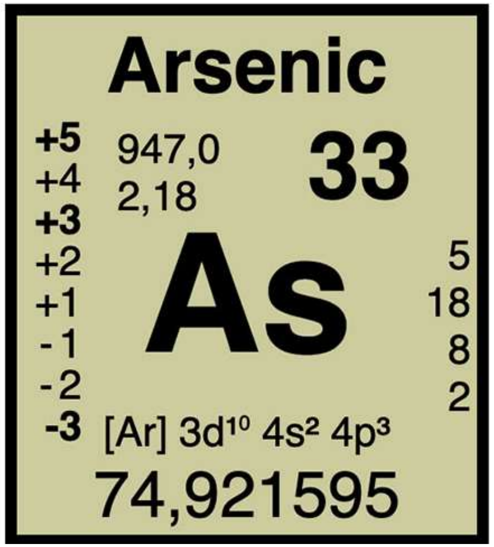
SBA15-polyol ~ 0.6 $mmol.g^{-1}$ > MCM41-polyol ~ 0.3 mmol. g^{-1} > non-grafted silica ~ 0.1 $mmol.g^{-1}$

- porosity MCM41 < SBA-15 ⇒ the clogging of the pores hinders access to adsorption sites
- Other adsorbents : Q_{ads} (vermiculite) ~ 0.04 $mmol.g^{-1}$
  Q_{ads} (polymeric resins) : < 0.9 $mmol.g^{-1}$
- Irreversible adsorption process : complexation = chemisorption

Adsorption of arsenic and phosphorus

cancer

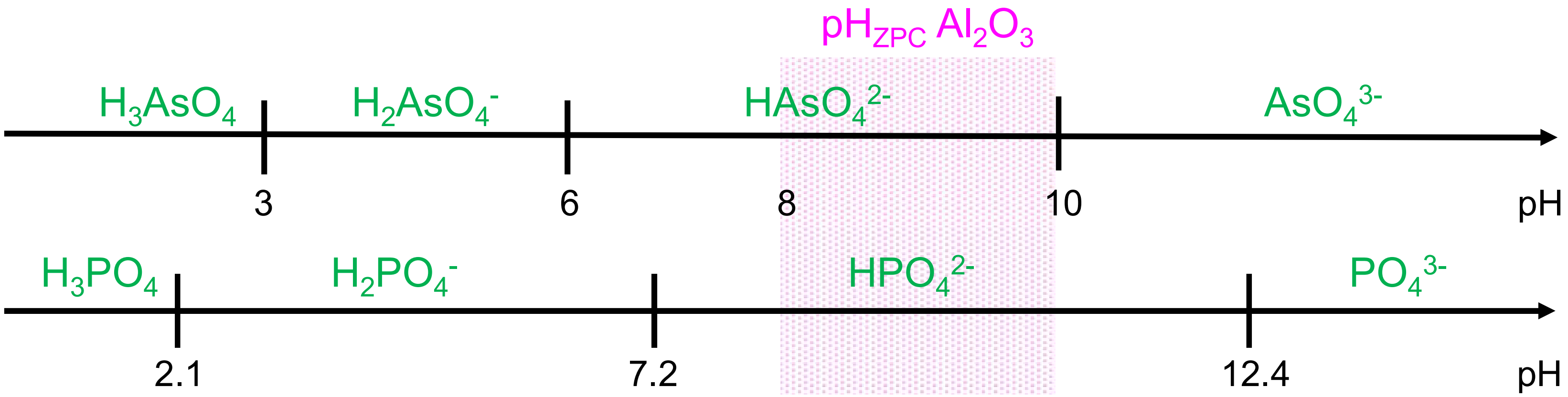




skin lesions

Adsorption of arsenic and phosphorus

- In solution, « As » et « P » are associated to « O » ⇨ formation of anions
- « As » and « P » exist at different valences : +III, +V
- The speciation depends on the pH of the solution (arsenic acid, arsenates, …)



- usual adsorbents
  - → alumina (Al_2O_3)
  - → activated carbons
  - → goethite ($FeO(OH)$)
  - → gibbsite ($Al(OH)_3$)

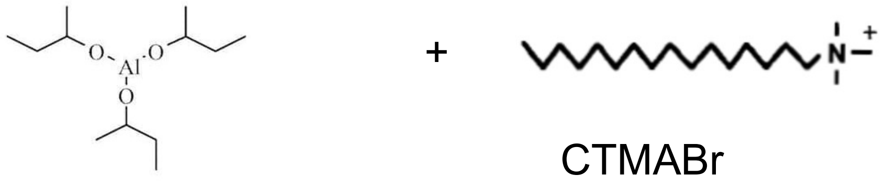
Low adsorption capacities
Slow kinetic rates

- not retained by zeolites, neither clays (negatively charged frameworks)

⇨ Use of a mesoporous alumina (pH_{ZPC} : 8-10)

Adsorption of arsenic and phosphorus

↳ Synthesis of mesoporous Al_2O_3



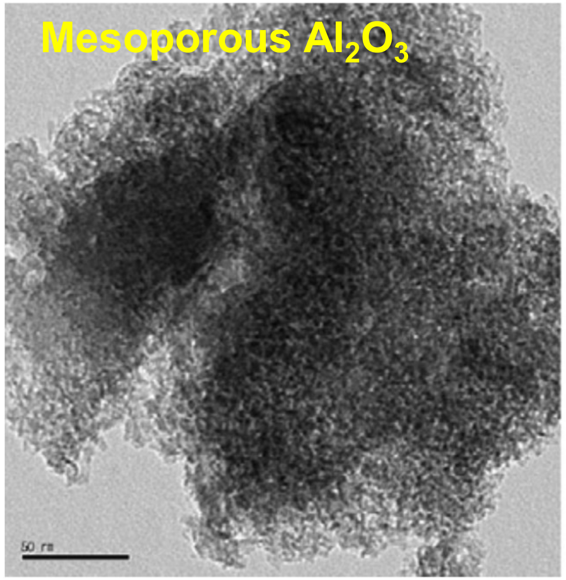
Aluminum Tri-sec-butoxide + CTMABr + H_2O/2-butanol

- Sol-gel route, hydrothermal synthesis (100°C, 24 h) + calcination 500°C, 4 h

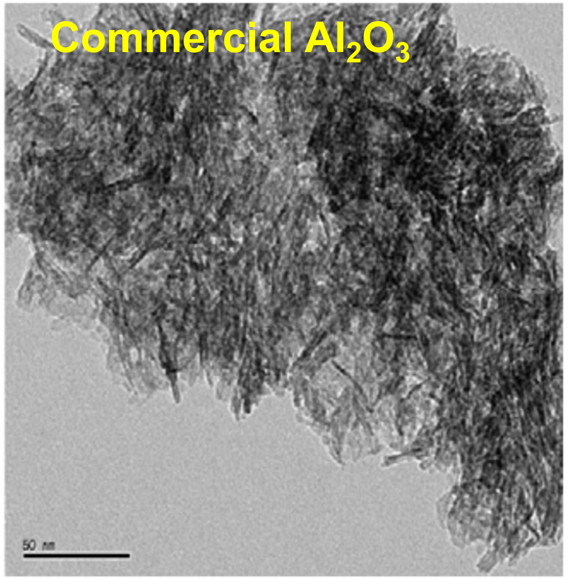
  ⇒ **Activated mesoporous Al_2O_3**

- Comparison of the properties with a **commercial alumina : pseudo boehmite**

TEM



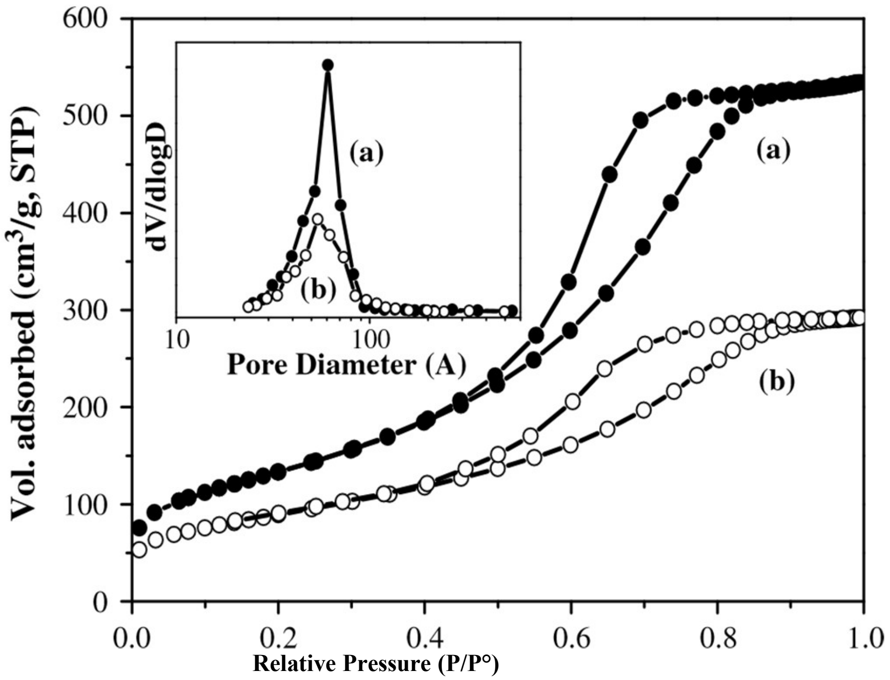
Vermicular texture



Fibrous texture

Adsorption of arsenic and phosphorus

N_2@77K



Al_2O_3 mesoporous

Al_2O_3 commercial

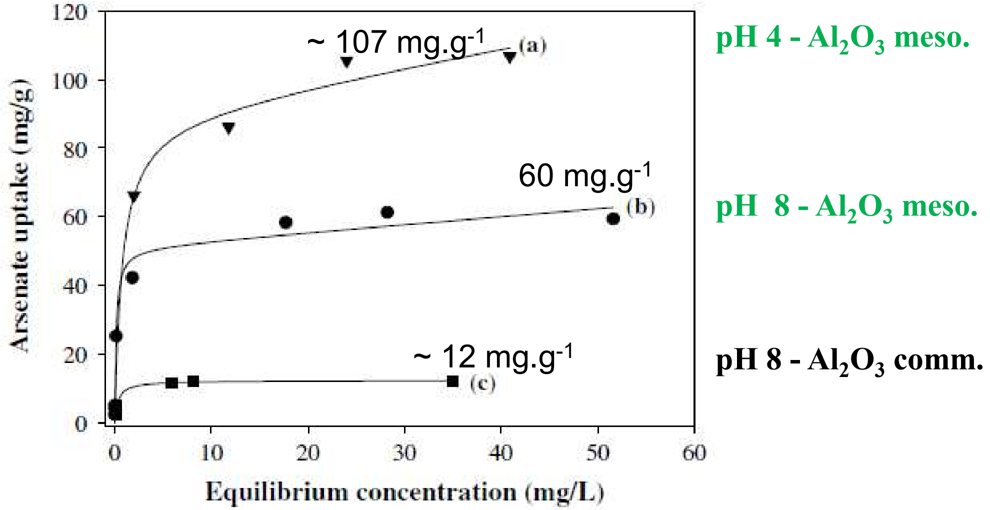
⇨ Type IV isotherm + hysteresis

Adsorbent	S_{BET} (m^2/g)	Vpores (cm^3/g)	∅ Pores (nm, BJH*)
Al_2O_3 meso.	483 ↑ x 1.5	0.82 ↑ x 1.8	4.9
Al_2O_3 comm.	322	0.45	4.5

* Barrett, Joyner, Halenda, 1951

Adsorption of arsenic and phosphorus

⇘ **Adsorption isotherms of arsenic** (C_0 = 10 to 70 mg.L^{-1})



⇨ Al_2O_3 meso : adsorption pH 4 > pH 8 (107 mg.g^{-1} > 60 mg.g^{-1})

At pH 4, substrate/pollutant interactions are favored

→ Surface of the adsorbent : positive : $AlOH^{2+}$, $Al(OH)_2^+$, $Al_{13}O_4(OH)_{24}^{7+}$
→ Charge of the pollutant : negative : $H_2AsO_4^-$

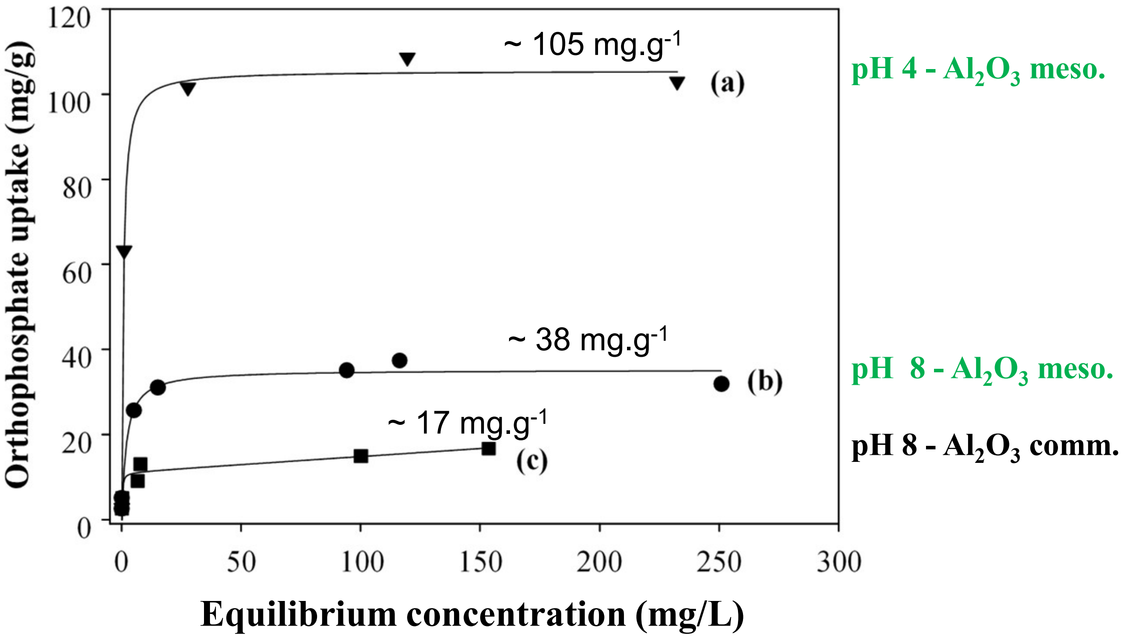
⇨ **Coulombic interactions**

⇨ At pH 8 : $Q_{ads}Al_2O_3$ meso. >>> $Q_{ads}Al_2O_3$ comm. ⇨ $Q_{ads}Al_2O_3$ meso. ~ **5** x $Q_{ads}Al_2O_3$ comm.

⇨ **increased interactions with the pollutant due to larger S_{BET} and V_{pores}**

Adsorption of arsenic and phosphorus

⇘ Adsorption isotherms of arsenic of phosphates (C_0 = 10 to 250 mg.L^{-1})

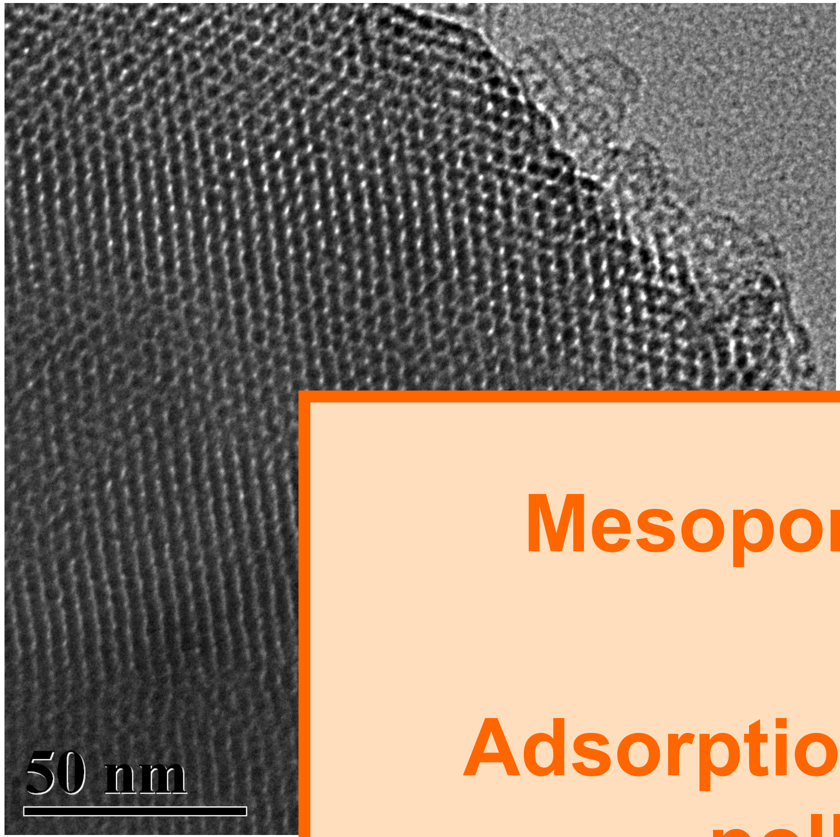


⇨ Al_2O_3 meso. : adsorption pH 4 > pH 8 (105 mg.g^{-1} > 38 mg.g^{-1})

⇒ Coulombic interactions : $AlOH^{2+}$, $Al(OH)_2^{+}$, $Al_{13}O_4(OH)_{24}^{7+}$ / $H_2PO_4^{-}$

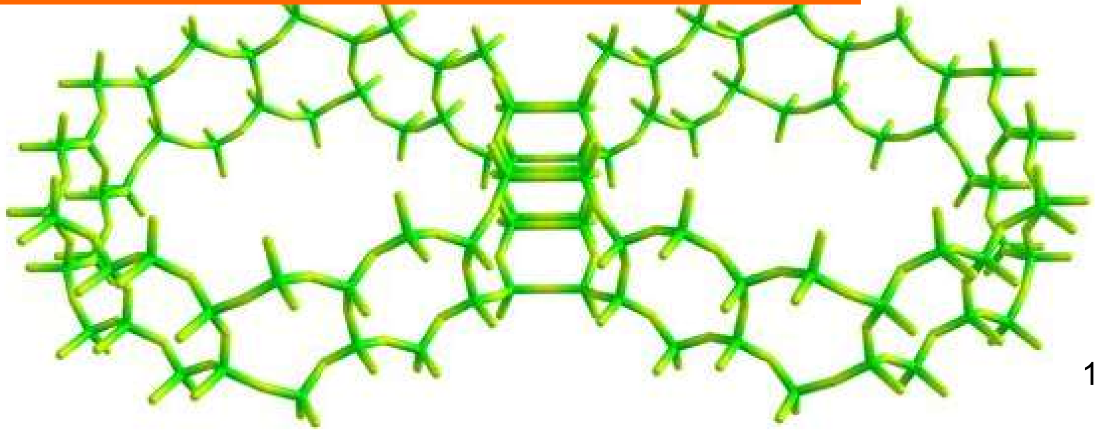
⇨ At pH 8 : $Q_{ads}Al_2O_3$ meso. > $Q_{ads}Al_2O_3$ comm. ⇨ $Q_{ads}Al_2O_3$ meso. ~ **2** x $Q_{ads}Al_2O_3$ comm.

⇨ Good correlation of the values of S_{BET} and V_{pores} with adsorption capacities for both pollutants



Mesoporous oxides

Adsorption of gaseous pollutants



H_2S adsorption on a SiO_2 / ZnO composite

- H_2S → spilled industrial off-gas (steel industry, oil refining plants…)

  → toxic gas (fatal in 30 min if $[H_2S] > 500$ ppm)

  → responsible for pipeline oxidation if concentration is too high

  → generates SO_2 and SO_3 by degradation (responsible for acid rains)

- conventional methods of decontamination : adsorption

  → activated carbons

  → γ-Al_2O_3

  → zeolites

  → Fe-containing clays (FeS precipitation)

⇨ Problems : low mechanical strength, dust generation,
tortuous porosity rapidly inaccessible

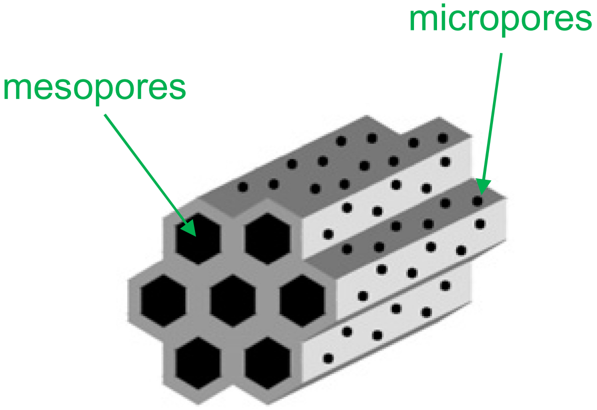
H_2S adsorption on a SiO_2 / ZnO composite

➯ **Development of a micro/meso porous silica (SBA-15)**
+ deposition of ZnO nanoparticles on the surface

Aims → decomposition of H_2S by reaction with ZnO leading to ZnS precipitation

$$ZnO + H_2S \rightarrow ZnS + H_2O$$

- SBA-15 ⇨ internal network of mesoporous channels interconnected by micropores
- Active sites ⇨ nanoparticles of ZnO deposited on the surface of SBA-15



SBA-15

⇒ use of the mesopores to transport the gas towards the active sites

⇒ chemical reactions inside the micropores and mesopore

H_2S adsorption on a SiO_2 / ZnO composite

↳ Synthesis of a SBA-15 / ZnO composite

→ synthesis of SBA-15 by usual sol-gel route (hydrothermal, TEOS, Pluronic®)

→ activation (550°C, 5h)

→ dispersion of the silica into a $Na_2CO_3 + Zn(NO_3)_2$ solution, under ultrasons

→ precipitation and dispersion of the $ZnCO_3$ particles inside the mesoporous framework

$$Na_2CO_3 + Zn(NO_3)_2 \rightarrow ZnCO_3 + 2\ Na^+ + 2\ NO_3^-$$

→ calcination and thermal decomposition of the carbonate (250°C)

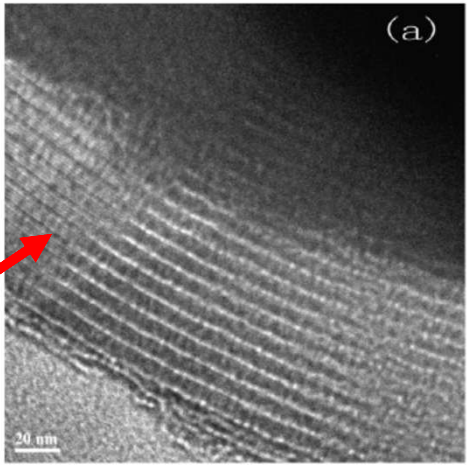
$$ZnCO_3 \rightarrow ZnO + CO_2$$

H_2S adsorption on a SiO_2 / ZnO composite

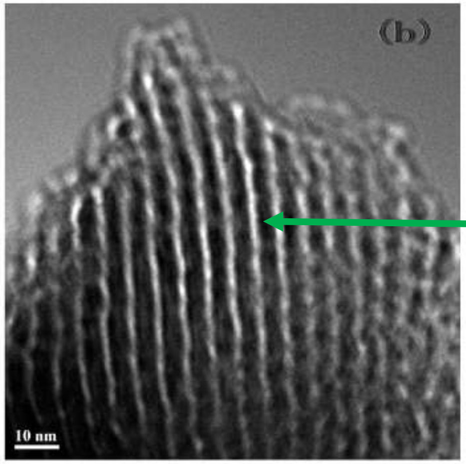
↳ Characterisation of the SBA-15 / ZnO composite

TEM

Honeycomb structure of the silica framework



SBA-15

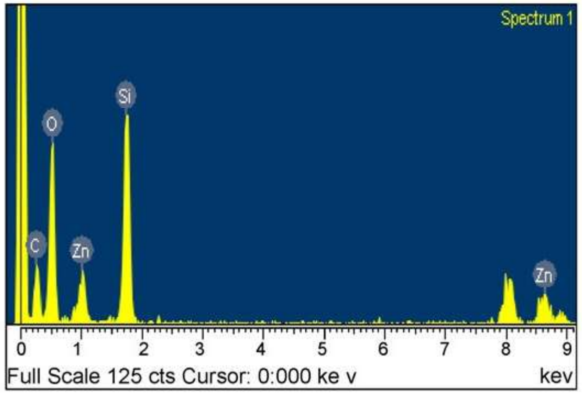


SBA-15 + ZnO

ZnO particles

⇨ Qualitative analysis of the elements

EDS

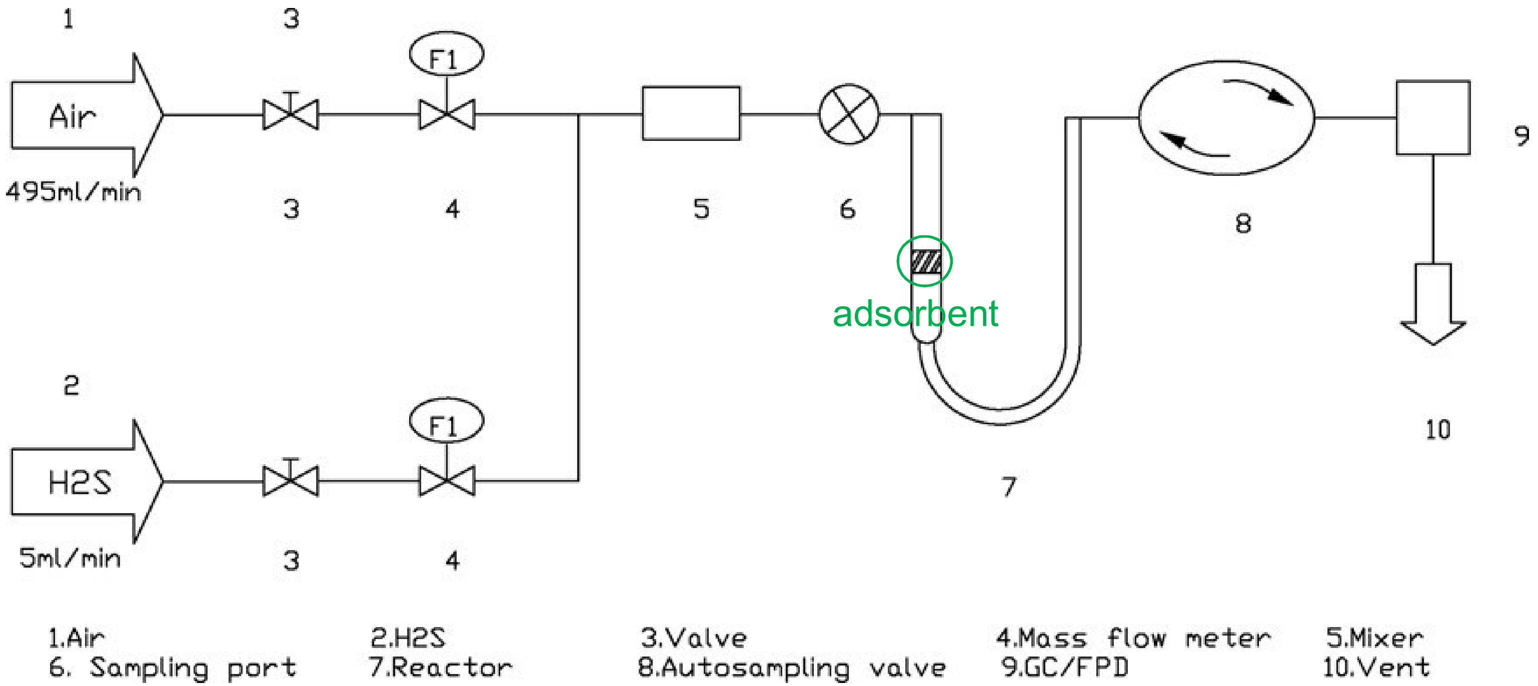


⇨ ZnO is occluded inside the micro and meso porosity

H_2S adsorption on a SiO_2 / ZnO composite

↳ Desulfurisation experiments

298K, 1 atm, air flow/0.1% H_2S (500 $mL.min^{-1}$)



- Measure of the H_2S concentration at the outlet of the column (GC)
- The experiment is stopped when $[H_2S]_{outlet}$ = 50 ppm

H_2S adsorption on a SiO_2 / ZnO composite

↳ Porosity characterisation after desulfurisation

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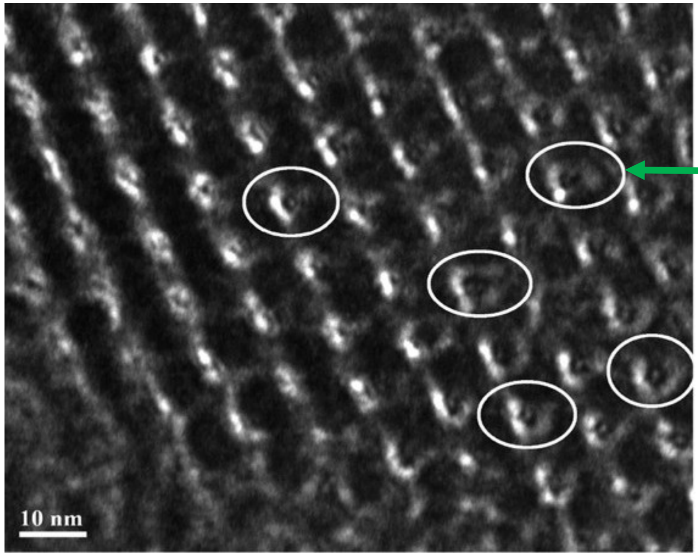
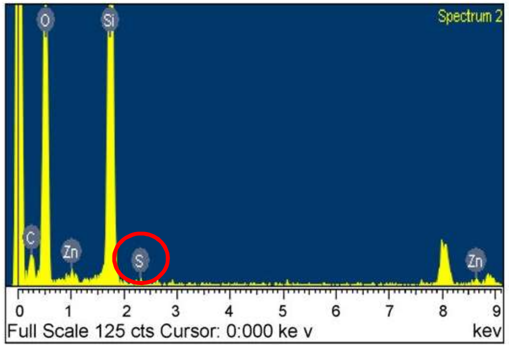


ZnS particules

⇒ The honeycomb structure is preserved

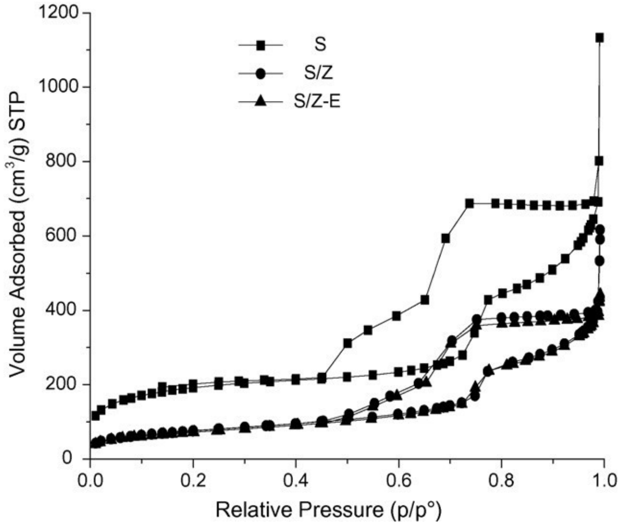
⇒ Presence of nanoparticles (ZnS ?) inside the mesoporosity



H_2S adsorption on a SiO_2 / ZnO composite

⇘ Porosity characterisation before/after desulfurisation

N_2@77K



S : SiO_2
S/Z : SiO_2/ZnO
S/Z-E : SiO_2/ZnO + H_2S

BJH
$V_{meso} >> V_{micro}$

Sample	S_{BET} (m^2/g)	V_{micro} (cm^3/g)	V_{total} (cm^3/g)
SiO_2	690	0.099	1.64
SiO_2/ZnO	270	0.007	0.96
SiO_2/ZnO + H_2S	260	0.007	0.70

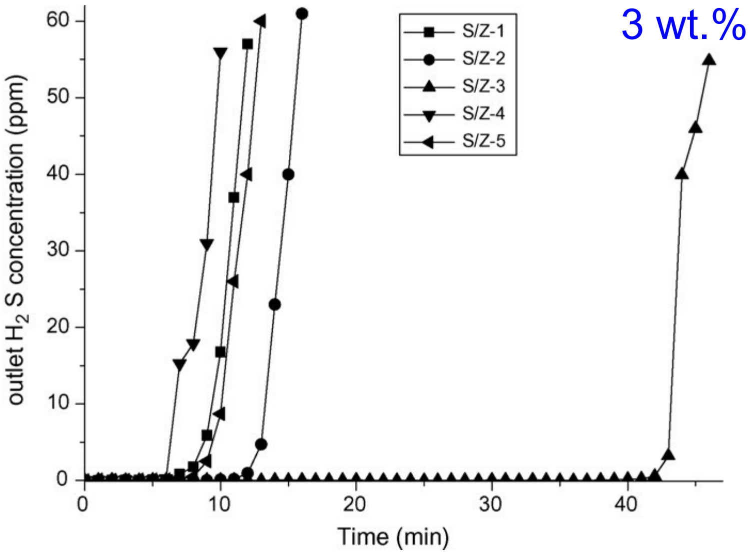
Similar characteristics

- ↘ S_{BET} ⇒ presence of ZnO and ZnS particles inside the micro and macroporosity
- ↘ V_{meso} by 40%
- ↘ V_{micro} by 92%

⇒ Almost complete blockage of micropores

H_2S adsorption on a SiO_2 / ZnO composite

Breakthrough curves



3 wt.% Zn

Sample	Zn (wt. %)	Breakthrough time (min)	Q_{ads} (mgH_2S/g)	pH material
S/Z-1	0.5	6	37	7.9
S/Z-2	1.2	10	95	8.2
S/Z-3	**3**	**40**	**440**	**8.3**
S/Z-4	4.5	7	50	8.4
S/Z-5	9	6	40	8.7

- Q_{ads} ↗ as Zn wt.% ↗ to 3 wt.%
- Above 3 wt.% Zn, Q_{ads} ↘

An excess of ZnO limits the diffusion of H_2S towards the pores (blockage of the porosity)

- Best adsorbent : 3 wt. % Zn (breakthrough in 40 min vs 6-10 min) ⇒ Qads max = 440 mg H_2S/g

- ↗ pH material as Zn wt.% ↗
- Optimal pH ~ 8.3 ⇒ pH which is favorable to the precipitation of ZnS

⇨ If the Zn content is too high ⇒ the porosity is partially blocked ⇒ the active sites are less accessible

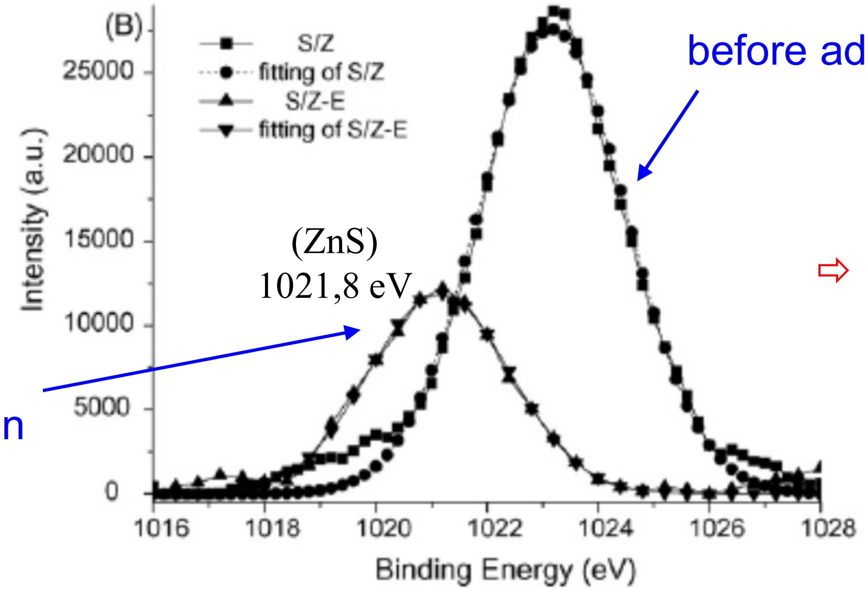
H_2S adsorption on a SiO_2 / ZnO composite

⇘ Adsorption mechanism

XPS reveals a new environment for Zn

XPS

Zn $2p^{3/2}$ (ZnO)
1022,5 eV



(ZnS)
1021,8 eV

before adsorption

after
adsorption

⇨ formation of Zn-S bonds

$ZnO + H_2S \longrightarrow ZnS + H_2O$

Irreversible adsorption : chemisorption