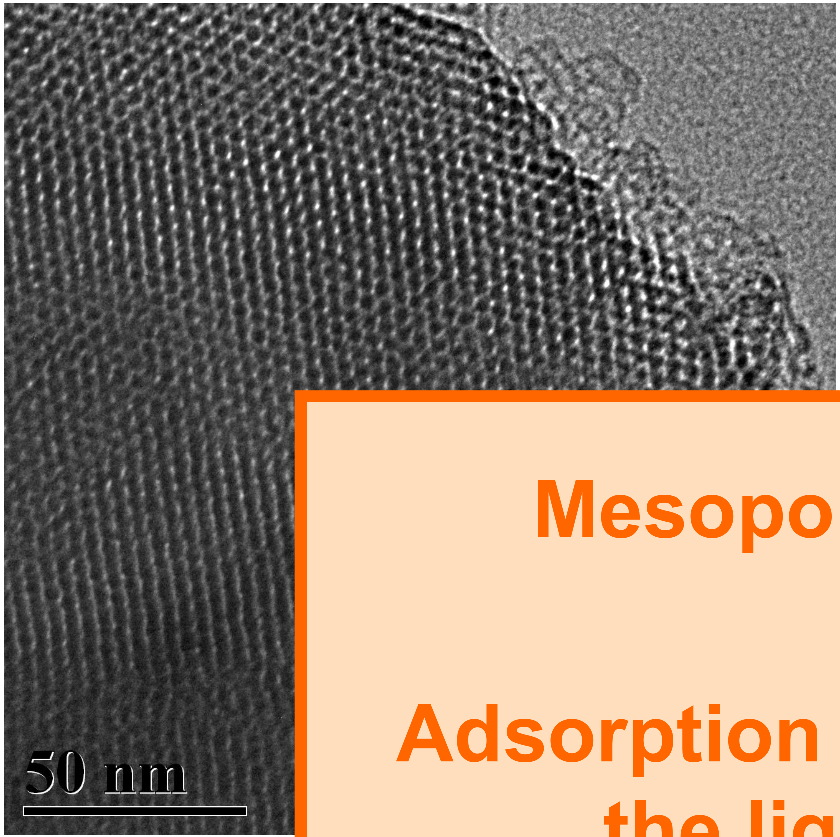
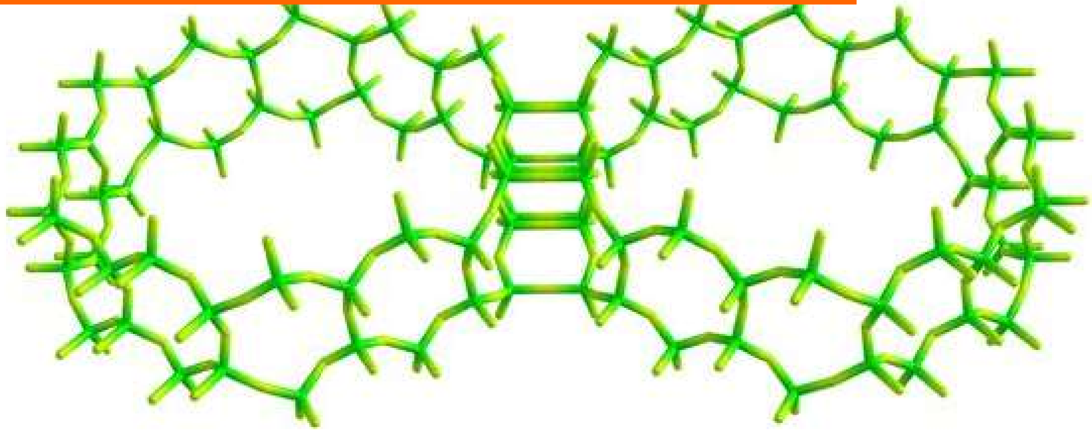


# Mesoporous oxides

# Adsorption of pollutants in the liquid phase



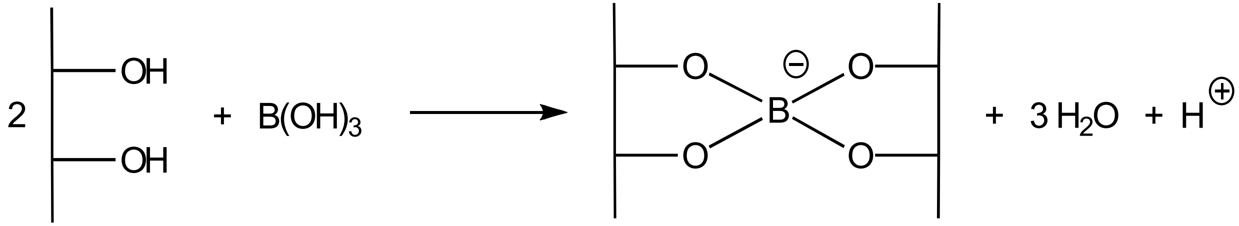
# Adsorption of boron by grafted mesoporous silica

**↳ boron (B) capture from aqueous effluents**

- 2 main species :

$$\underset{\text{boric acid}}{H_3BO_3 + H_2O} \rightleftharpoons \underset{\text{borate anions}}{B(OH)_4^- + H^+} \qquad pKa\ (H_3BO_3\ /\ B(OH)_4^-) = 9.24 \quad \text{at } 20°C$$

- 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

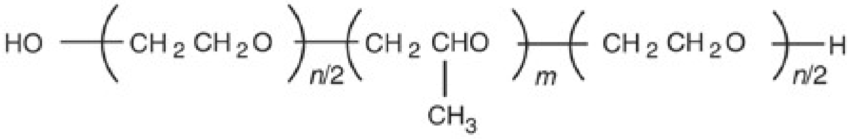
- MCM-41 → ionic surfactant

$CTMA^+Br^-$, 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)



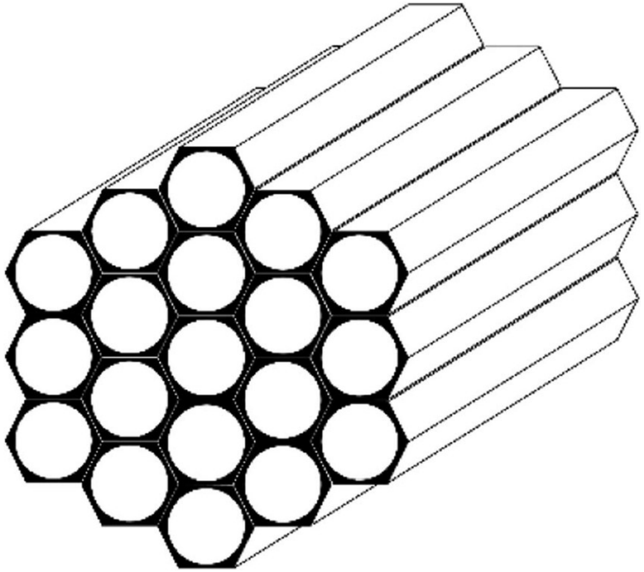
$$HO-(CH_2CH_2O)_{n/2}-(CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HO)_m-(CH_2CH_2O)_{n/2}-H$$

| | | | |
|---|---|---|---|
| F127 | $n = 200$ | $m = 65$ | mw = 12 618 |
| L61 | $n = 4.5$ | $m = 31$ | mw = 2018 |

Poloxamer family
(tri-bloc copolymers)

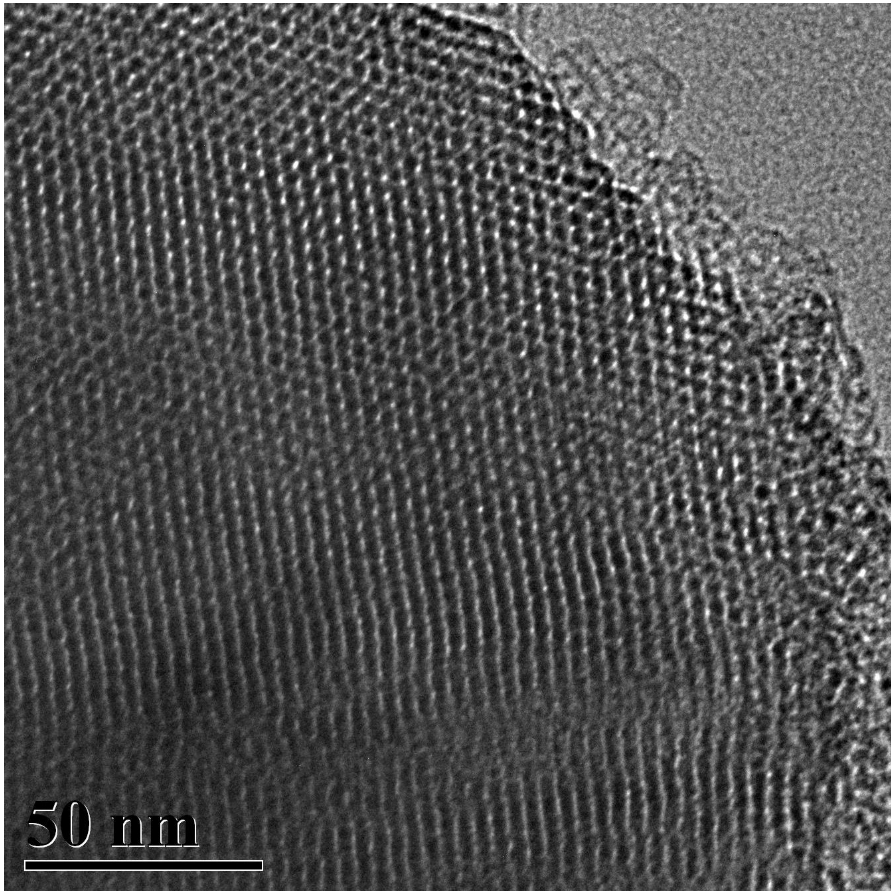
# Adsorption of boron by grafted mesoporous silica

## ↳ Textural properties



Honeycomb porosity

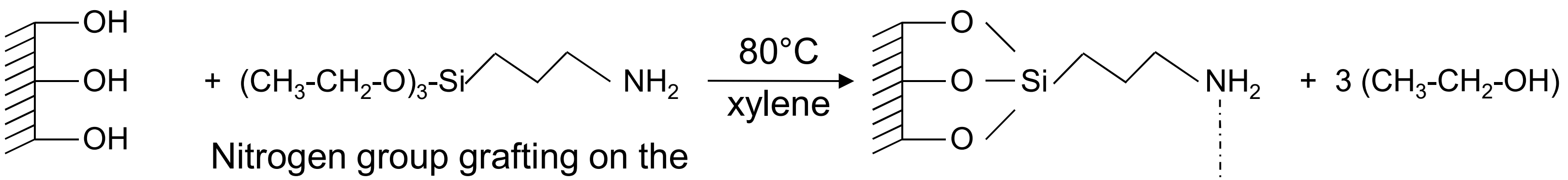
MCM-41



Pore ∅ ~ 5 nm

# Adsorption of boron by grafted mesoporous silica

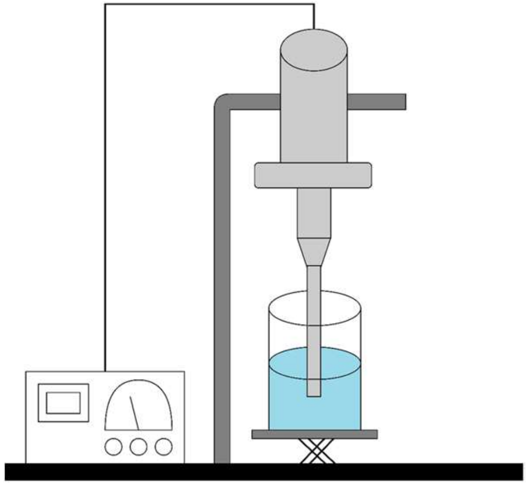
## ➥ Example : grafting by glucose for –OH groups increasing

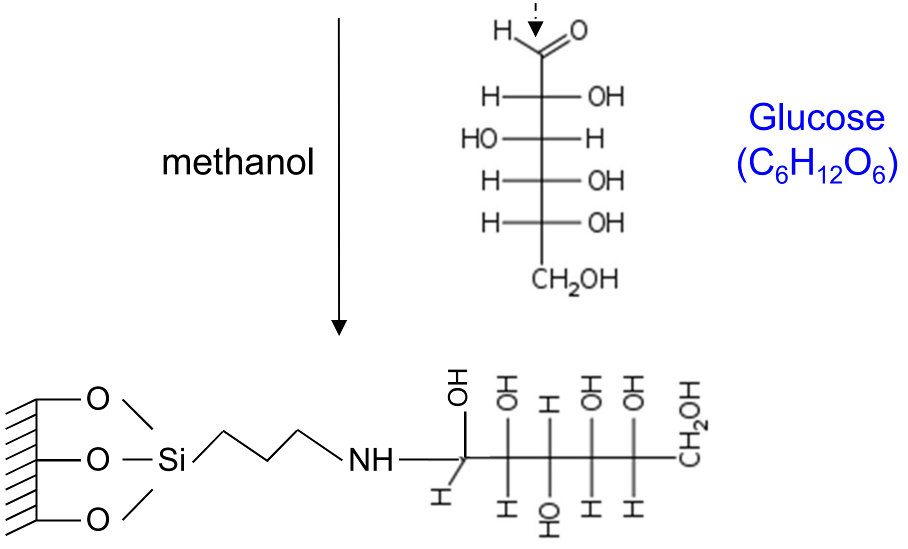


Nitrogen group grafting on the surface

(AminoPropylTriEthoxySilane)

**APTES**





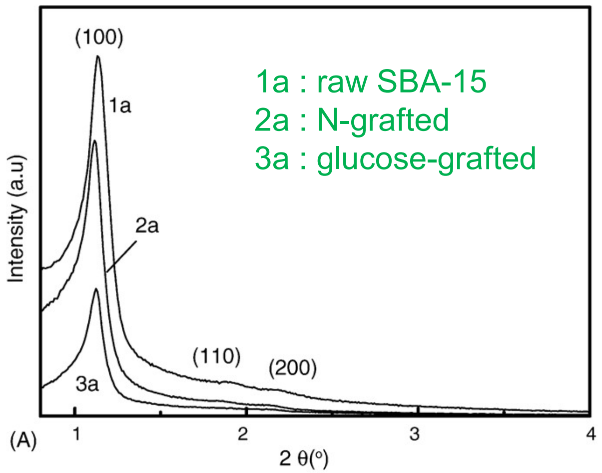
Glucose
$(C_6H_{12}O_6)$

organic – inorganic
hybrid material

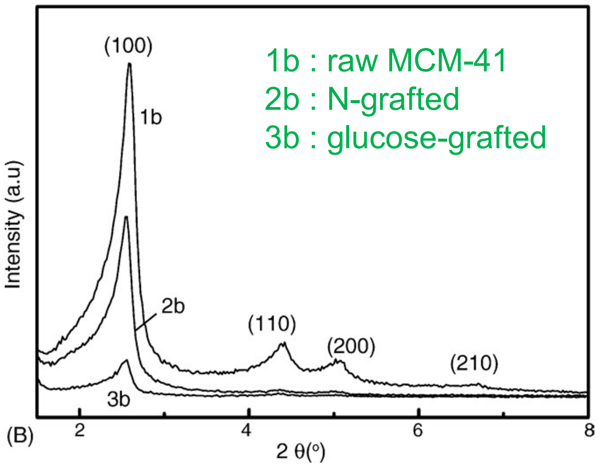
⇒ increase of the number of complexing sites which are fixed on a <u>flexible</u> and <u>mobile</u> chain

# 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

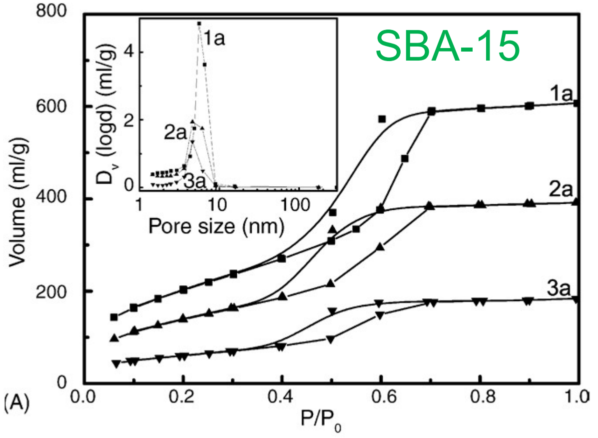
↳ adsorption of X-rays by the organic matter

↳ 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)

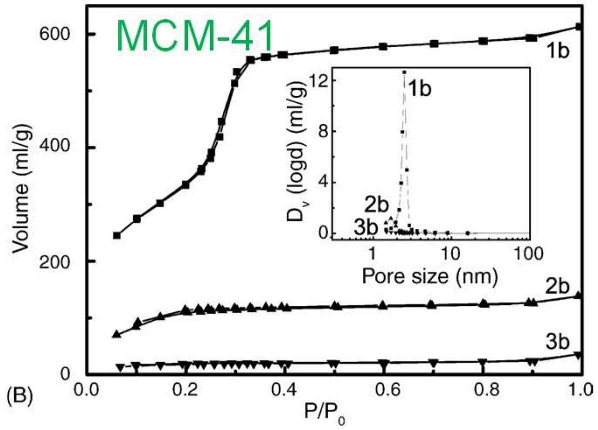
# Adsorption of boron by grafted mesoporous silica

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



type IV, H1 hysteresis ⇒ large mesopores

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



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 |

↘ $S_{BET}$ 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

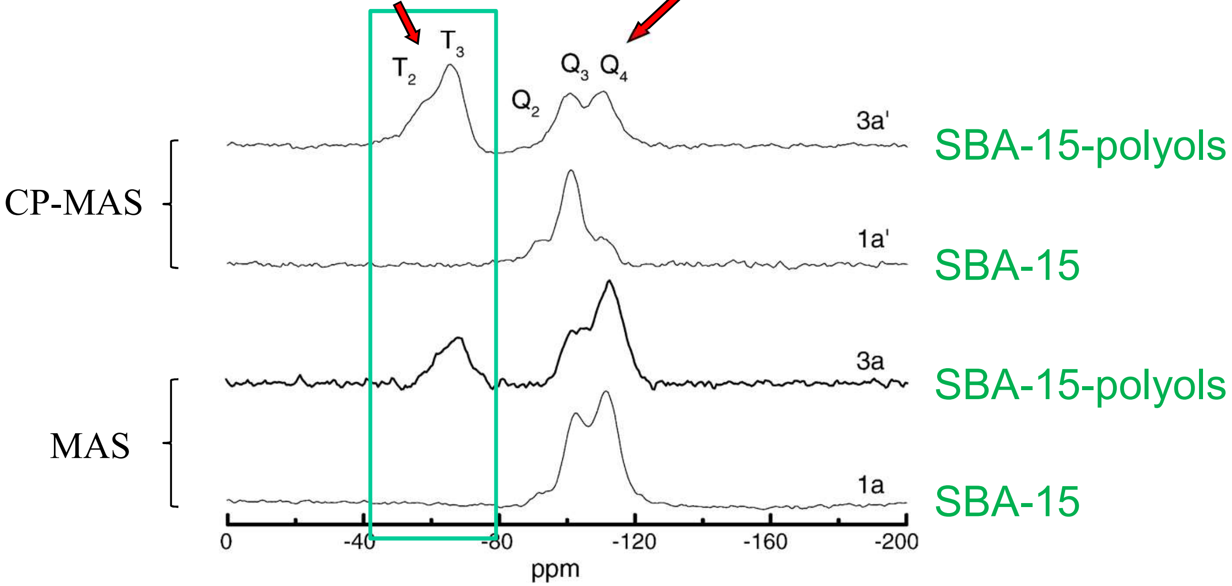
# Adsorption of boron by grafted mesoporous silica

## ⇘ $^{29}$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 **linked** to the mineral framework
- %silanols = $(2Q_2 + Q_3)/(2Q_2 + Q_3 + Q_4)*100$

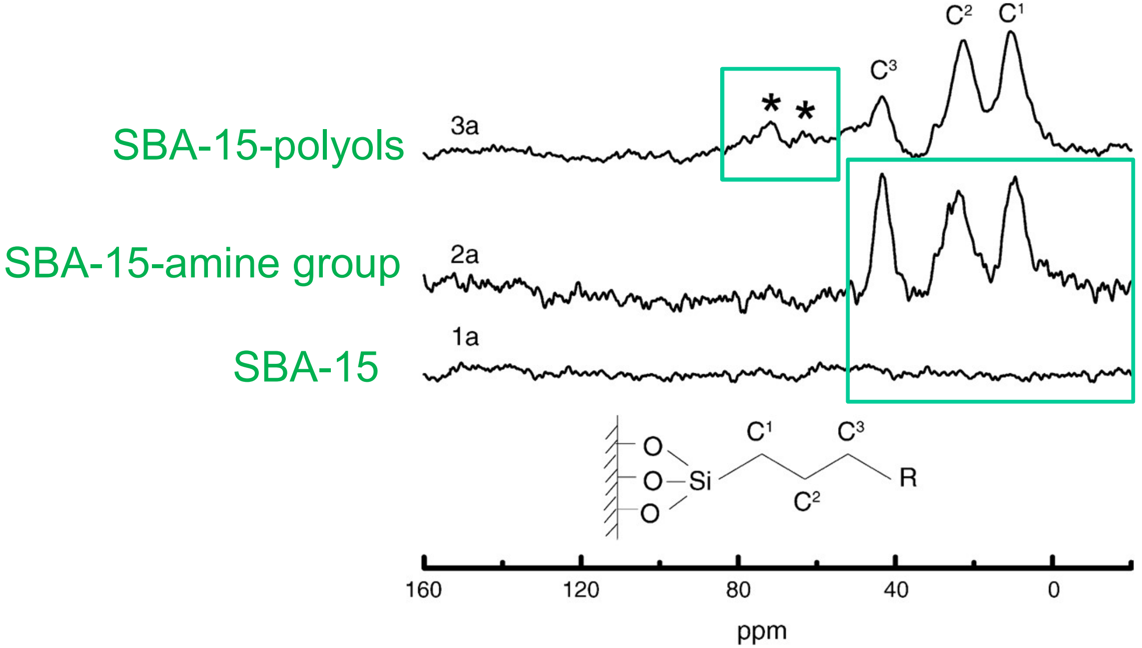
  %silanols ↘ from 42% to 34% after grafting

  ⇒ 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

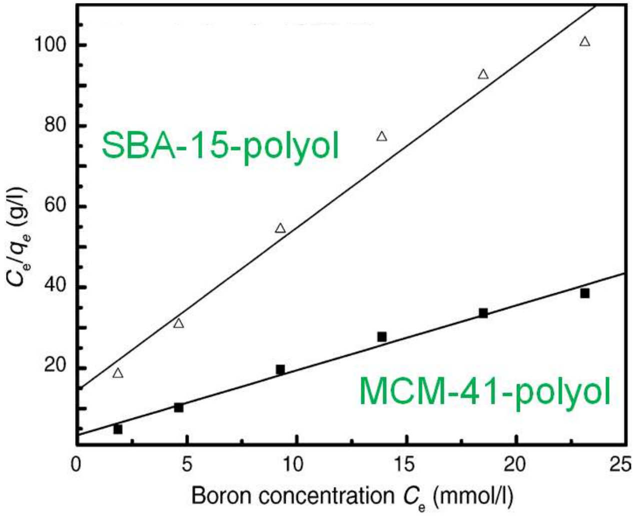
**⇒ Presence of glucose confirmed**

<u>However</u>, $^{13}$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

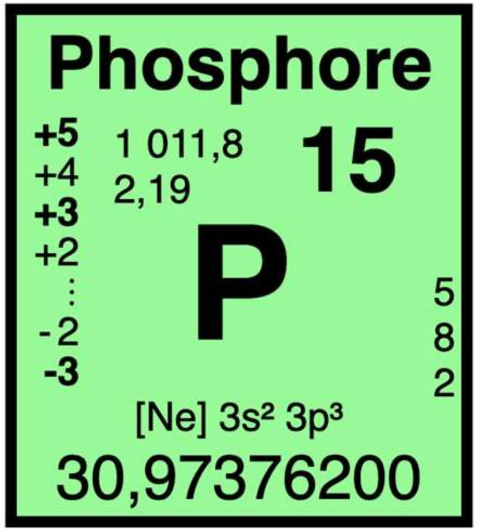
→ **$Q_{ads}$ :**

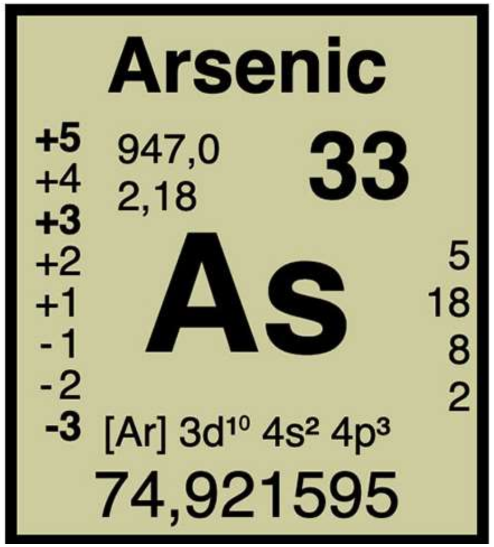
SBA15-polyol ~ 0.6 $mmol.g^{-1}$ > MCM41-polyol ~ 0.3 $mmol.\ g^{-1}$ > non-grafted silica ~ 0.1 $mmol.g^{-1}$

- 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

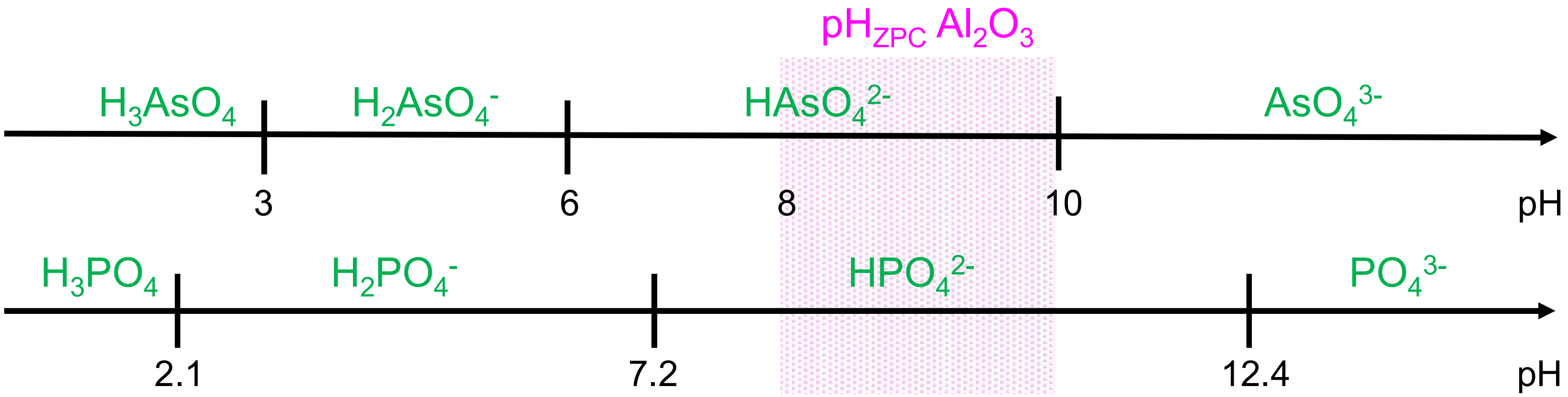




skin lesions

# 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 ($Al(OH)_3$)

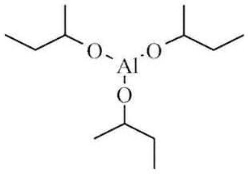
Low adsorption capacities
Slow kinetic rates

- 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

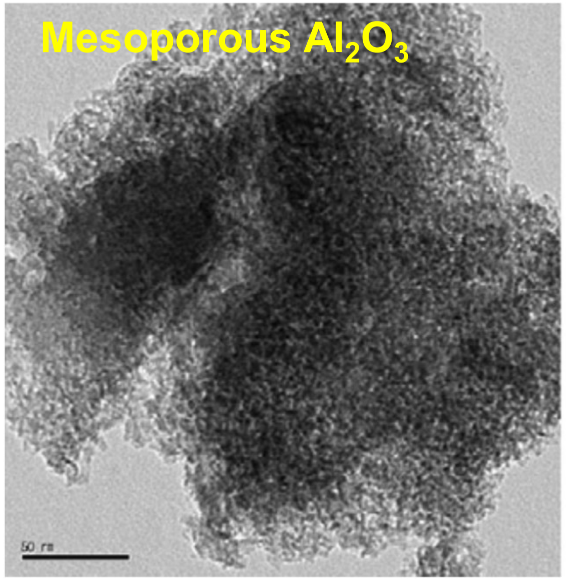
- Sol-gel route, hydrothermal synthesis (100°C, 24 h) + calcination 500°C, 4 h

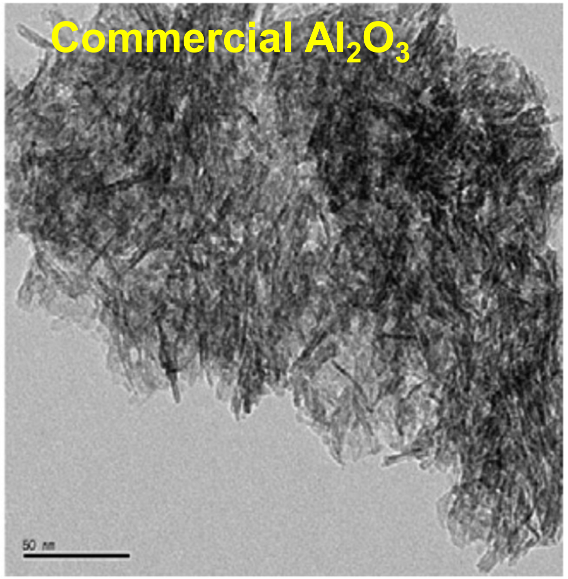
⇒ **Activated mesoporous $Al_2O_3$**

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

**TEM**

Vermicular texture

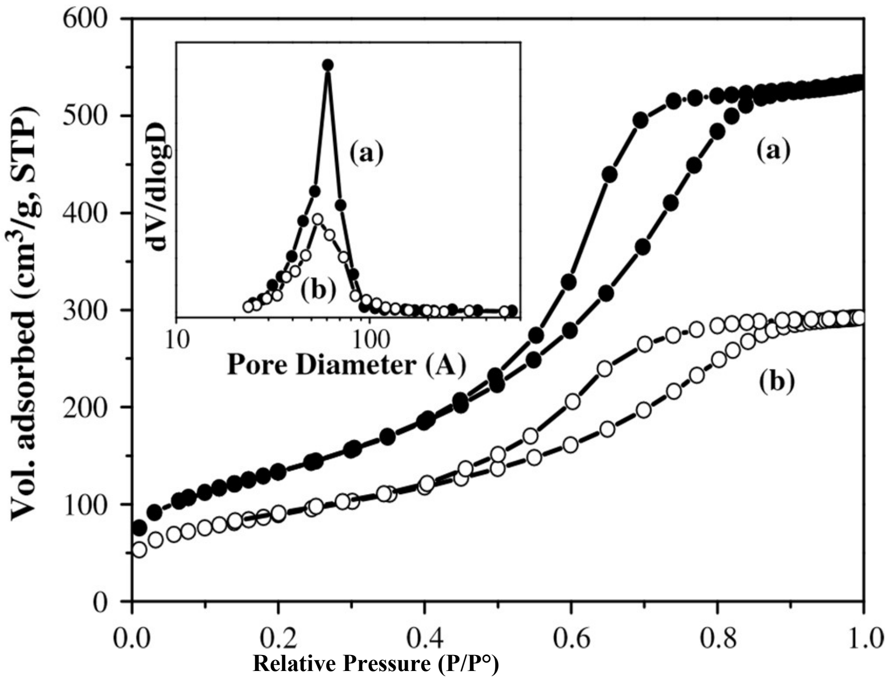




Fibrous texture

# Adsorption of arsenic and phosphorus

$N_2$@77K



**$Al_2O_3$ mesoporous**

**$Al_2O_3$ comercial**

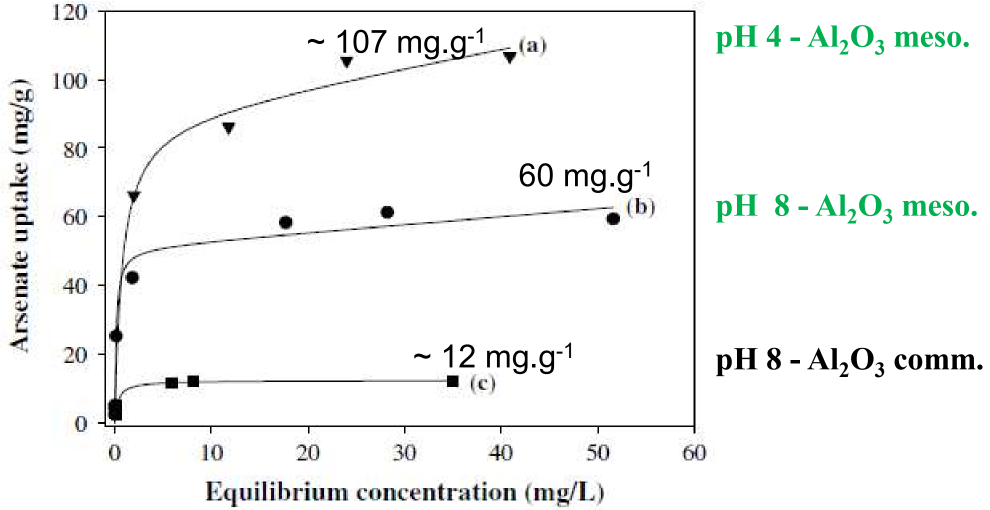
⇨ Type IV isotherm + hysteresis

| 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 : $H_2AsO_4^-$

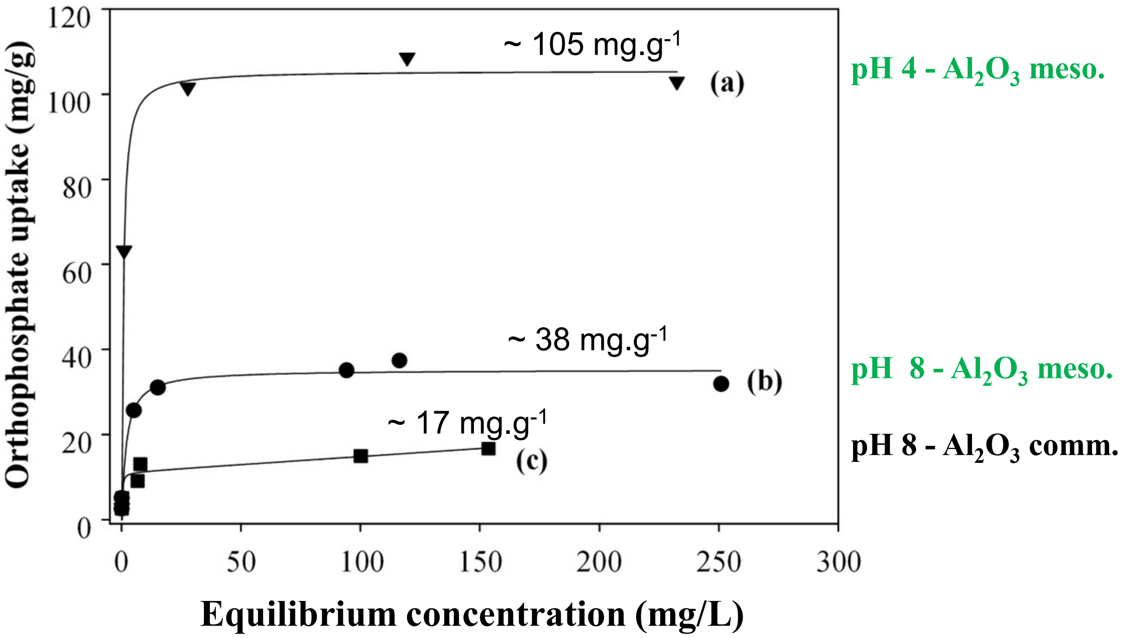
⇨ **Coulombic interactions**

⇨ 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 $mg.L^{-1}$)

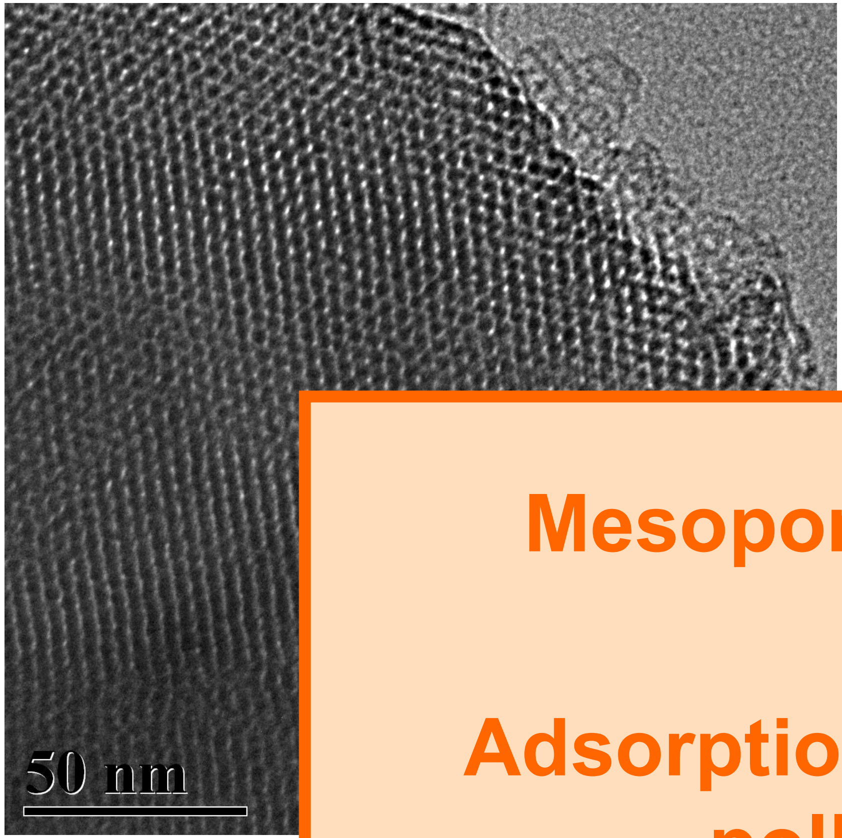


⇨ $Al_2O_3$ meso. : adsorption pH 4 > pH 8 (105 $mg.g^{-1}$ > 38 $mg.g^{-1}$)

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

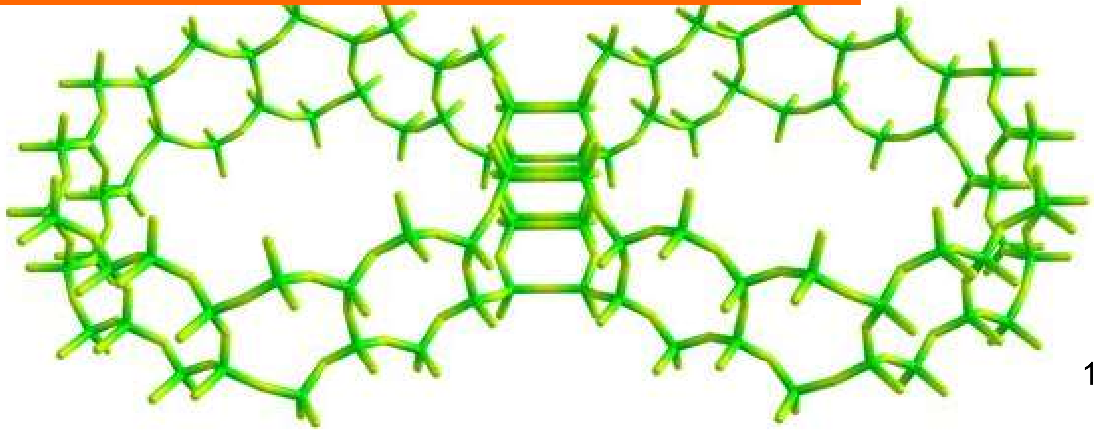
⇨ At pH 8 : $Q_{ads}Al_2O_3$ meso. > $Q_{ads}Al_2O_3$ comm. ⇨ $Q_{ads}Al_2O_3$ meso. ~ **2** x $Q_{ads}Al_2O_3$ comm.

⇨ **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

  → $\gamma$-$Al_2O_3$

  → zeolites

  → Fe-containing clays (FeS precipitation)

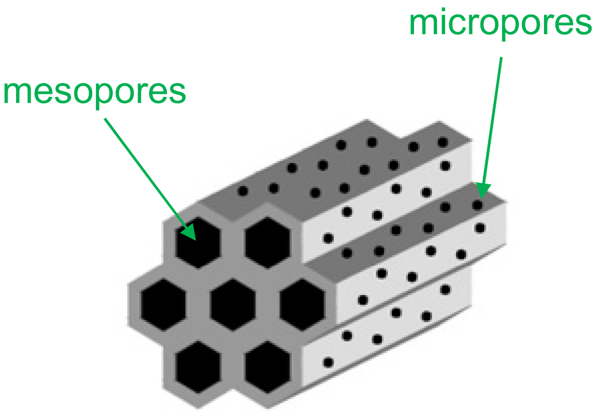
⇨ Problems : low mechanical strength, dust generation,
tortuous porosity rapidly inaccessible

# $H_2S$ 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

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

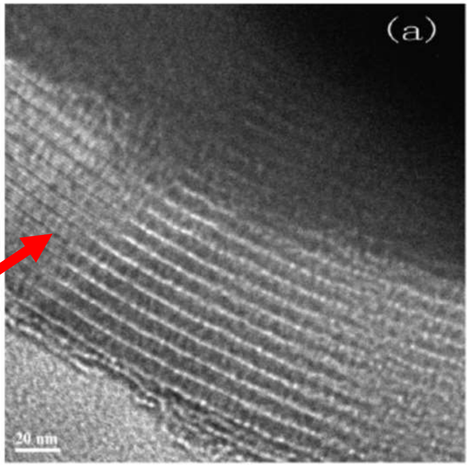
$$ZnCO_3 \rightarrow ZnO + CO_2$$

# $H_2S$ adsorption on a $SiO_2$ / ZnO composite

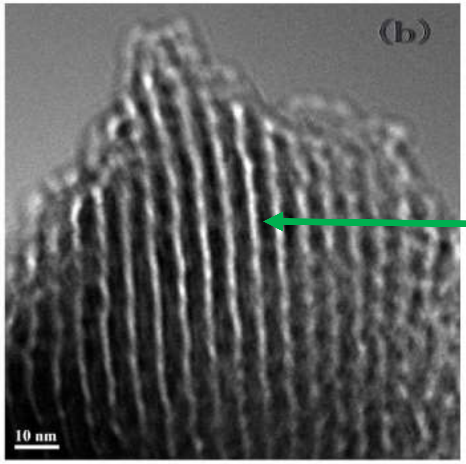
## ↳ Characterisation of the SBA-15 / ZnO composite

**TEM**

Honeycomb
structure of the
silica
framework



SBA-15

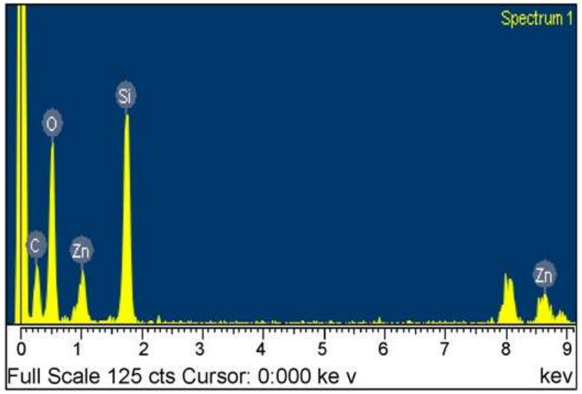


ZnO particles

SBA-15 + ZnO

⇨ ZnO is occluded inside the micro and meso porosity

⇨ Qualitative analysis of the elements

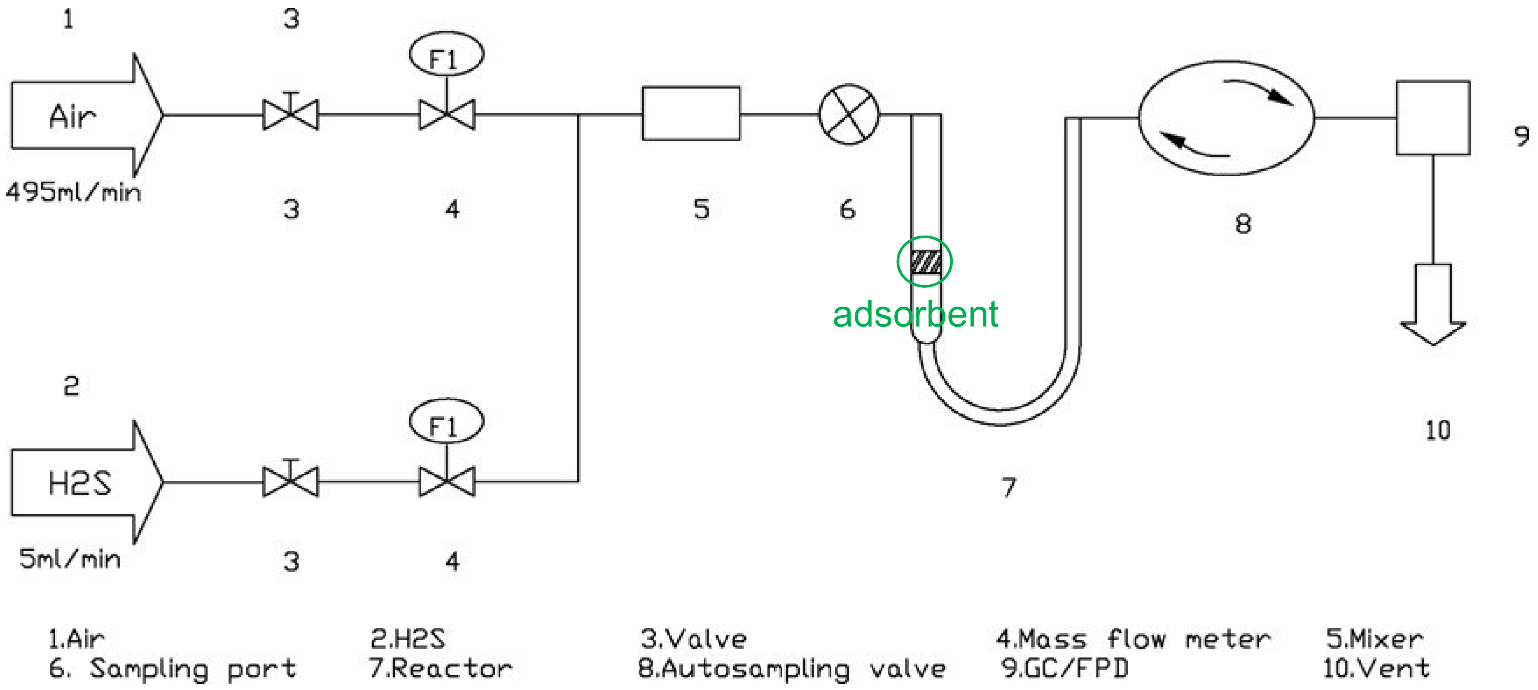


**EDS**

# $H_2S$ adsorption on a $SiO_2$ / ZnO composite

## ⇘ Desulfurisation experiments

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

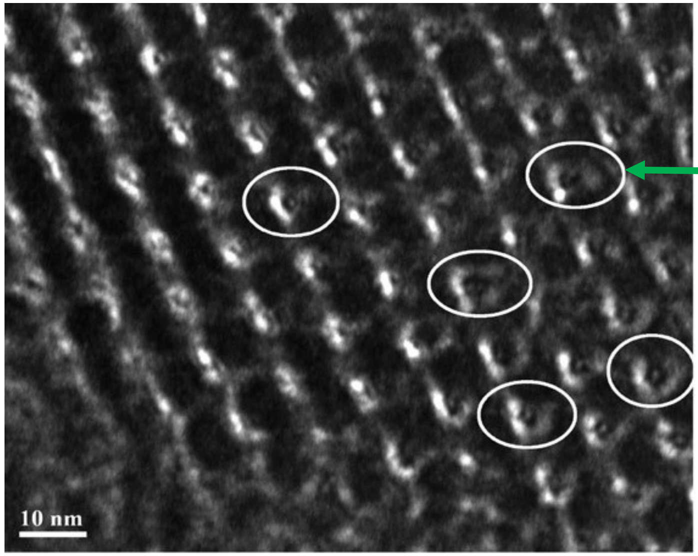


- Measure of the $H_2S$ concentration at the outlet of the column (GC)
- The experiment is stopped when $[H_2S]_{outlet}$ = 50 ppm

# $H_2S$ adsorption on a $SiO_2$ / ZnO composite

## ↳ Porosity characterisation after desulfurisation

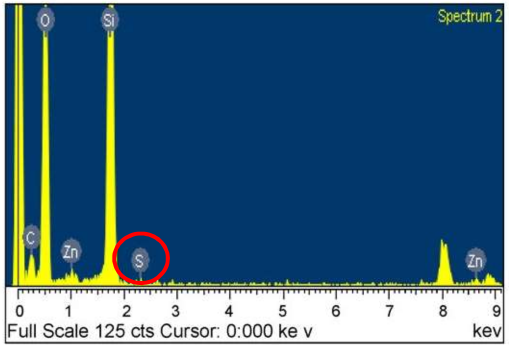
**TEM**



ZnS particules

⇒ The honeycomb structure is preserved

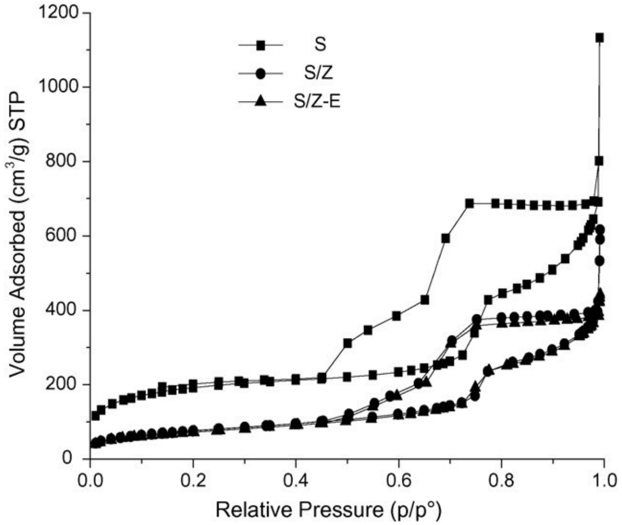
⇒ Presence of nanoparticles (ZnS ?) inside the mesoporosity



# $H_2S$ 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
$V_{meso} >> V_{micro}$

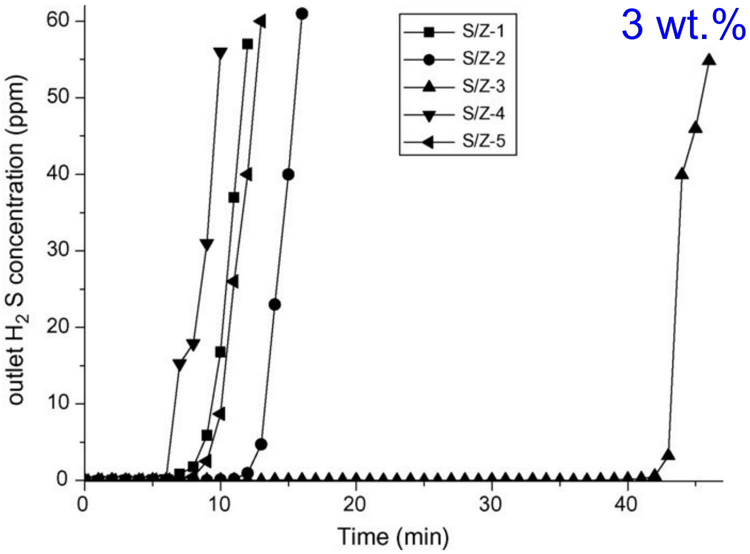
| Sample | $S_{BET}$ (m²/g) | $V_{micro}$ (cm³/g) | $V_{total}$ (cm³/g) |
|---|---|---|---|
| $SiO_2$ | 690 | 0.099 | 1.64 |
| $SiO_2$/ZnO | 270 | 0.007 | 0.96 |
| $SiO_2$/ZnO + $H_2S$ | 260 | 0.007 | 0.70 |

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

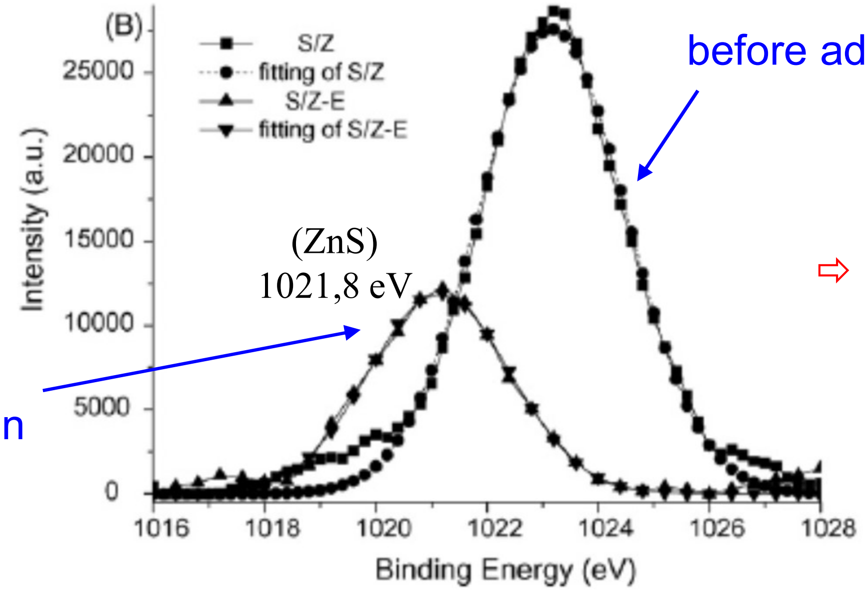
# $H_2S$ adsorption on a $SiO_2$ / ZnO composite

## Adsorption mechanism

XPS reveals a new environment for Zn

**XPS**

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



before adsorption

(ZnS)
1021,8 eV

after adsorption

⇨ formation of Zn-S bonds

$$ZnO + H_2S \longrightarrow ZnS + H_2O$$

Irreversible adsorption : chemisorption