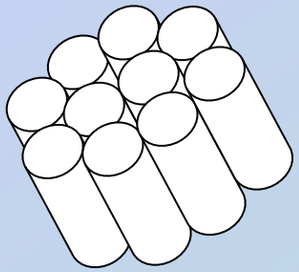
UNIVERSITÉ de Cergy-Pontoise

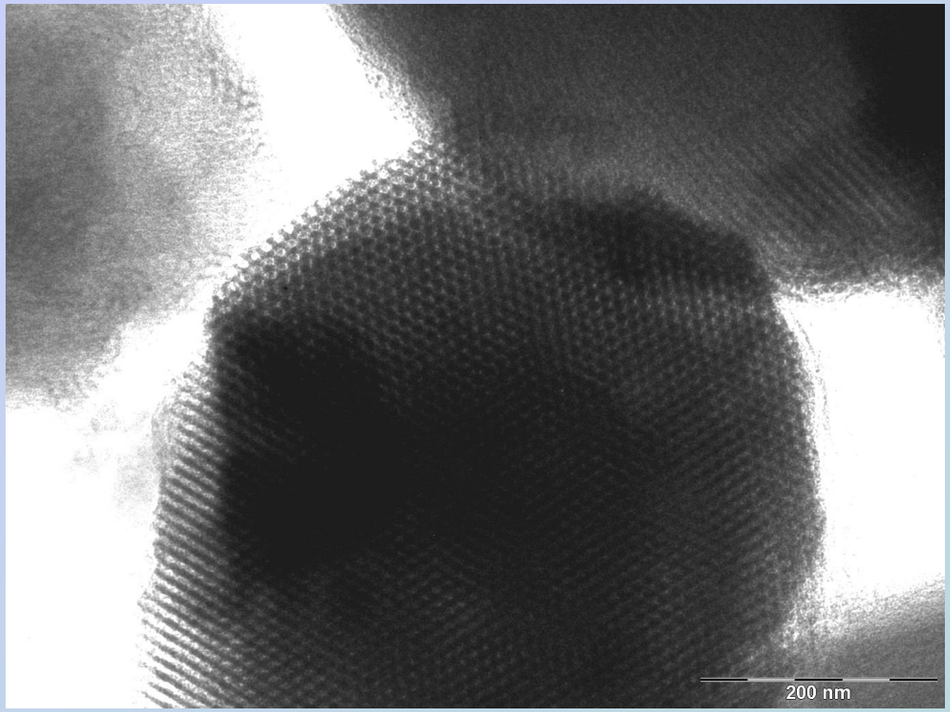
SOSCO Synthèse organique sélective et chimie bioOrganique

EA 4505 - UCP - CNRS

IRAMIS



Confined Water in its role as a Ligand to Cu II



in Hydrophillic and Hydrophobic Nanopores

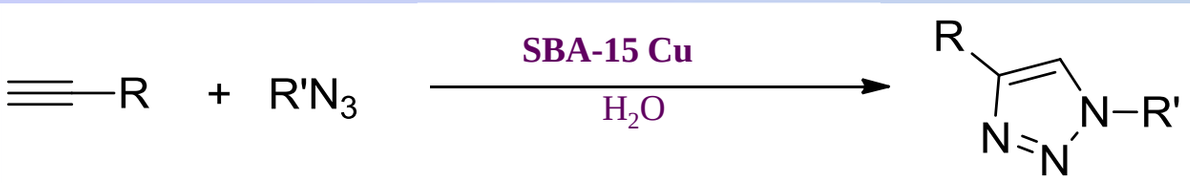
Summary

1. *Why investigate confined water as a Cu II ligand?*
2. *Preliminaries – Porous materials and water as a Cu II ligand*
3. *Cu II loading in hydrophillic pores*
4. *Cu II loading in hydrophobic pores by pressure*
5. *Comparison of the two types of nano pores*
4. *Concluding remarks*

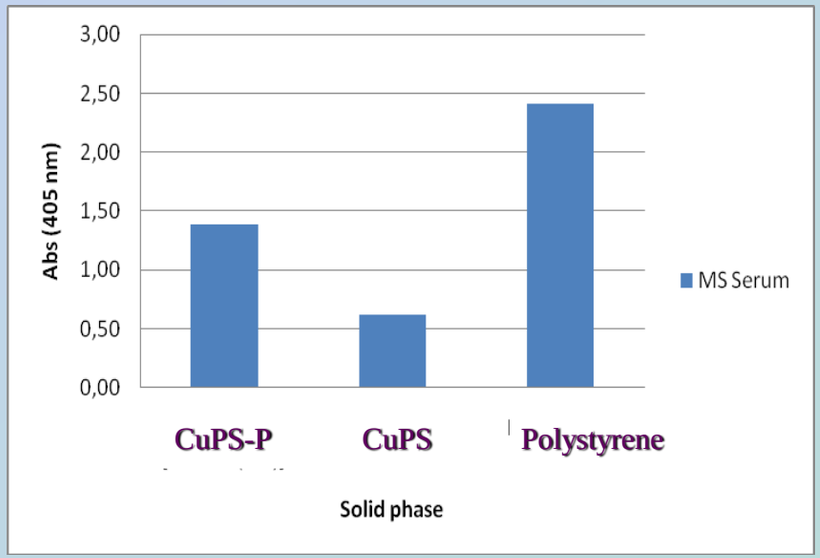
Why investigate confined water as a Cu II ligand?

Water purification – nitrate uptake

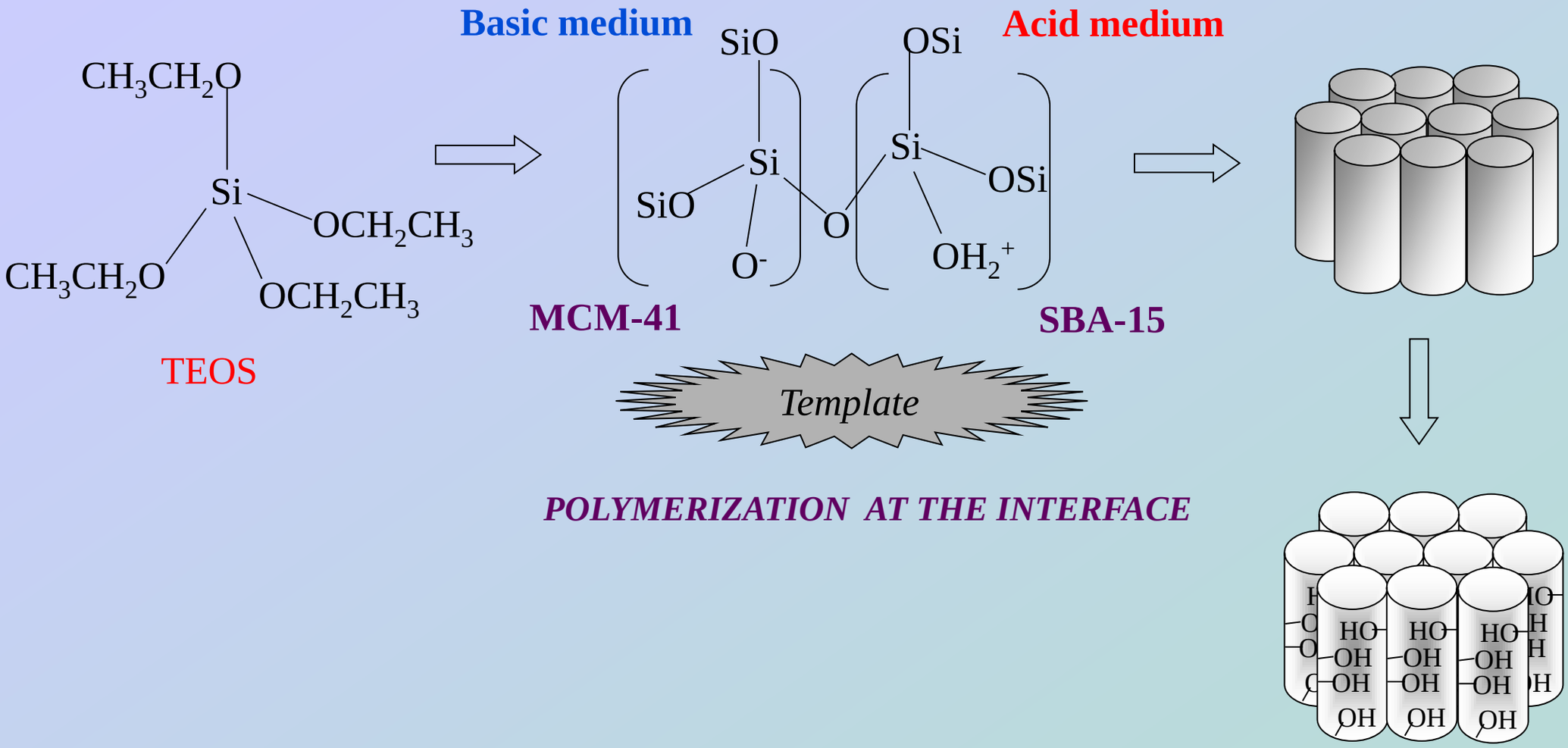
Catalysis in water - green chemistry



Biological interest - Copper modified porous silica (CuPS) surfaces for antibody detection by ELISA techniques

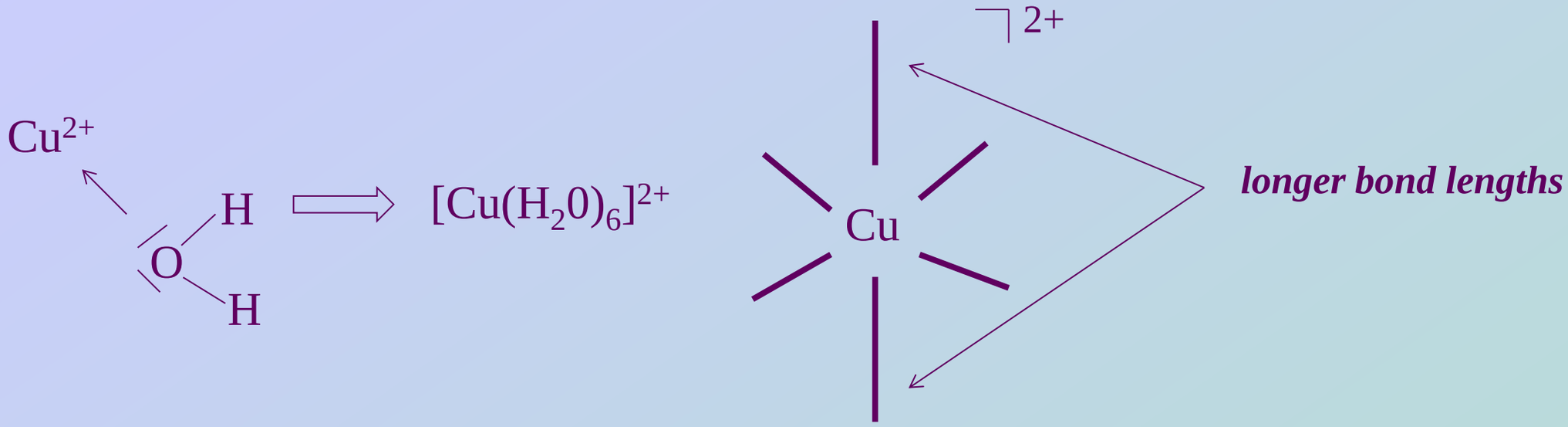


Mesoporous Templated Silicate materials



Water as a Cu II ligand

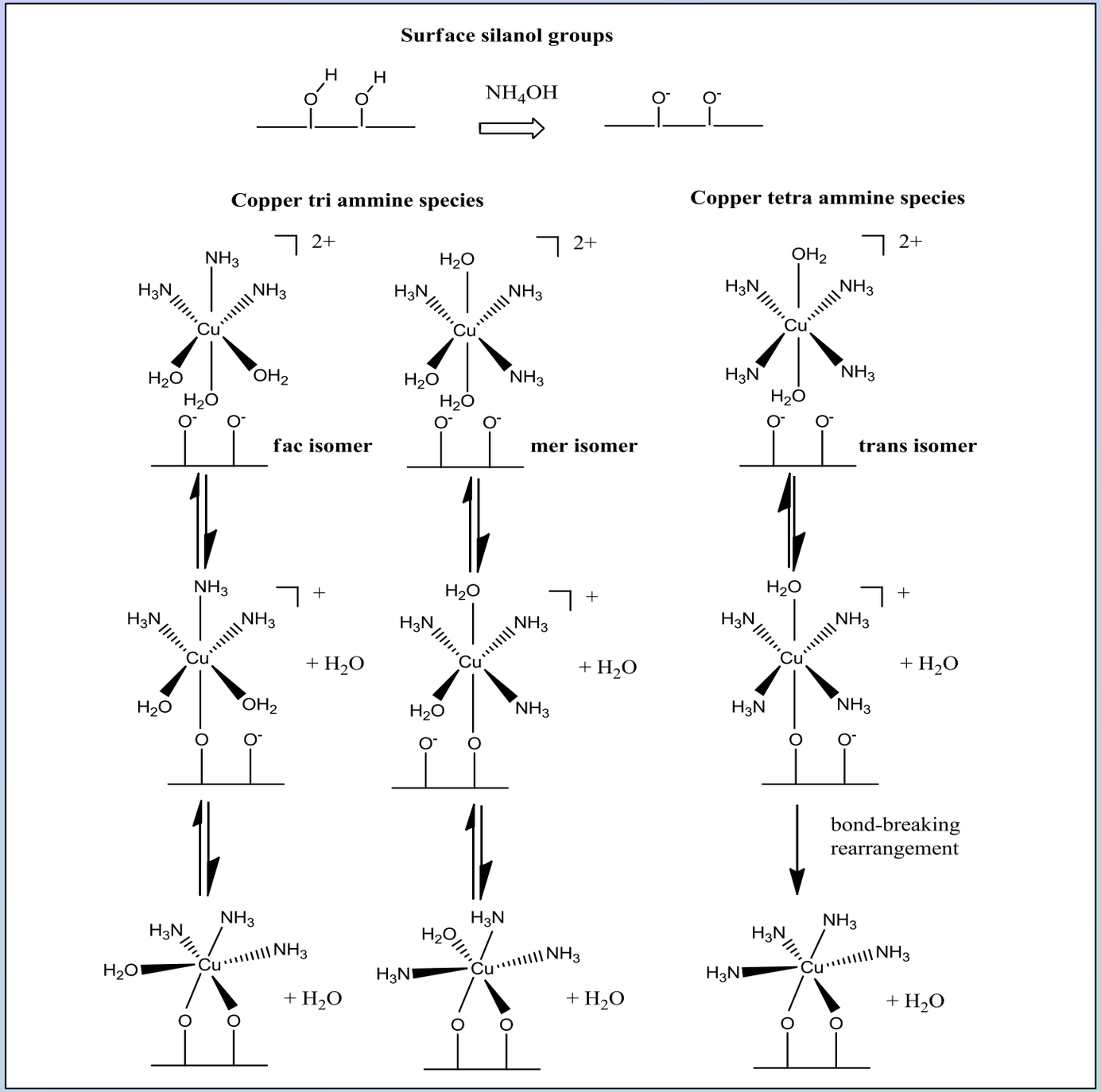
Cu II aqua complexes ***- classed as labile according to Taube's rules***
- water exchange in the 10^6 to 10^8 s^{-1} range



Octahedral Cu II complexes are known to submit to the Jahn-Teller effect!

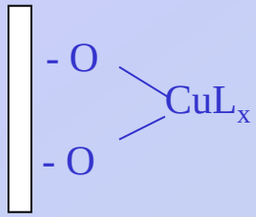
A stretched octahedral structure is expected where 2 out of the 6 bond lengths are longer (weaker bond strengths).

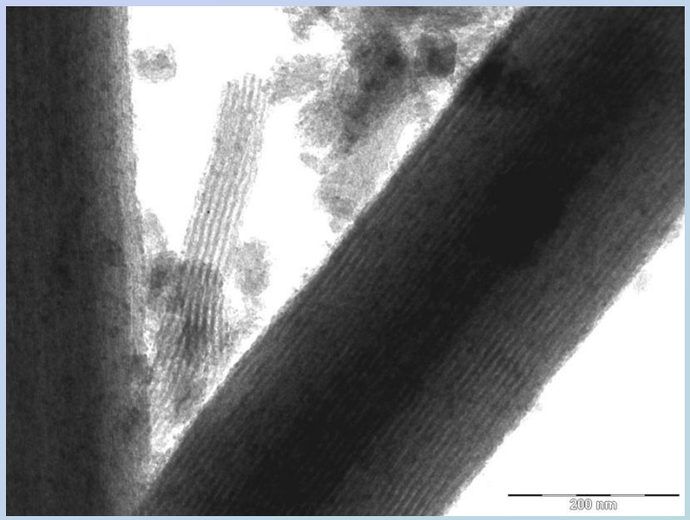
Schematic representation of $[Cu(NH_3)_3(H_2O)_3]^{2+}$ and $[Cu(NH_3)_4(H_2O)_2]^{2+}$ approaching and bonding to the SBA-15 surface.



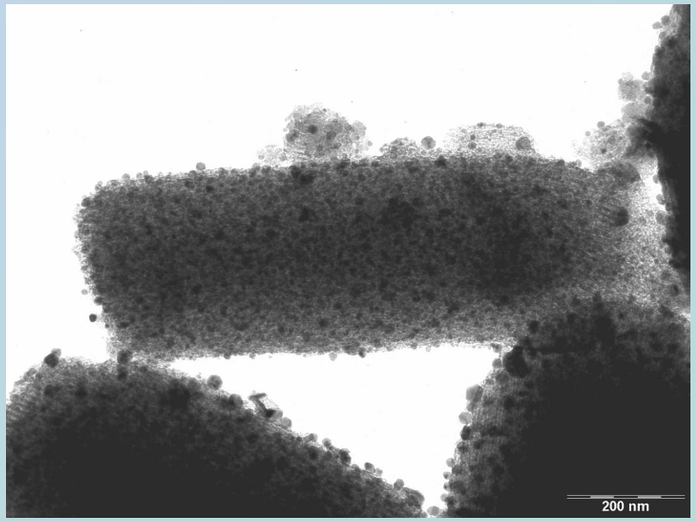
Cu II loading in hydrophilic pores

SBA-15 + Cu II (aq) $\xrightarrow{NH_4OH}$





12% Cu II w/w



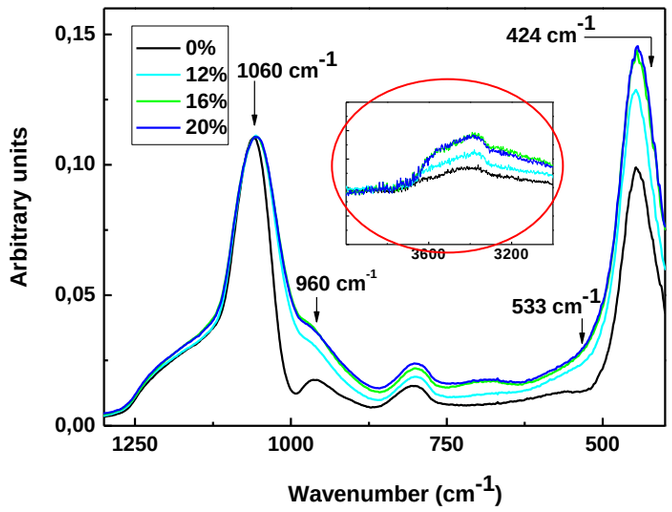
20% Cu II w/w

TEM images

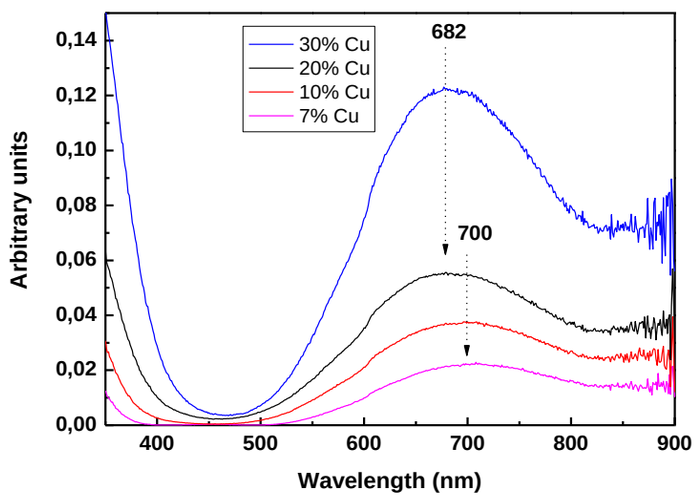
Brodie–Linder, N., Besse, R., Audonnet, F., LeCaer, S., Deschamps, J., Imperor-Clerc, M., Alba–Simionesco, C. Microporous Mesoporous Materials, 132, (2010) 518.

Characterization of SBA-15 Cu

IR spectra



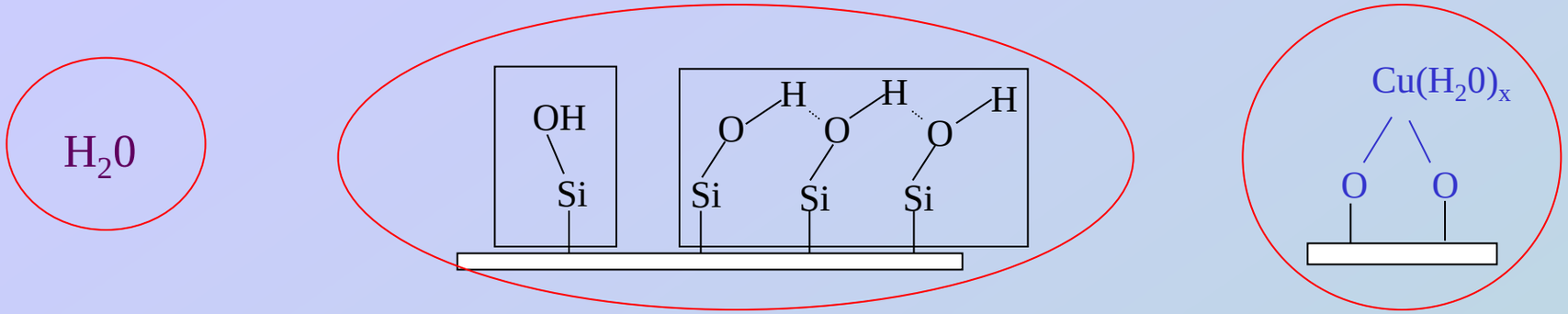
Diffuse reflectance spectra

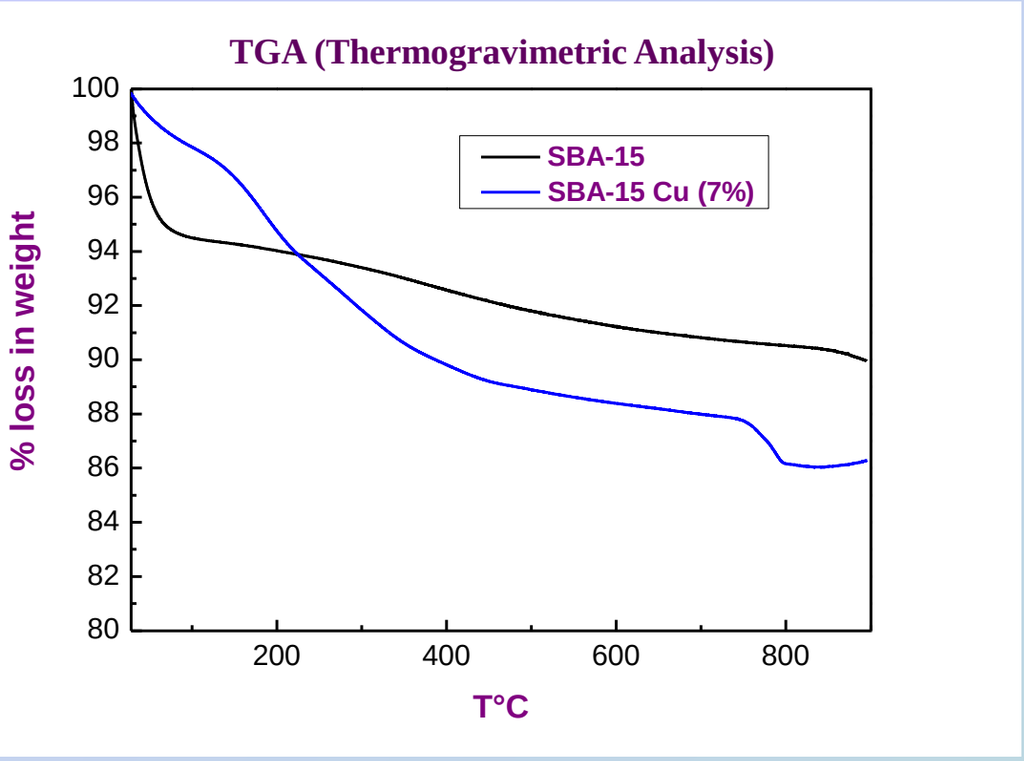


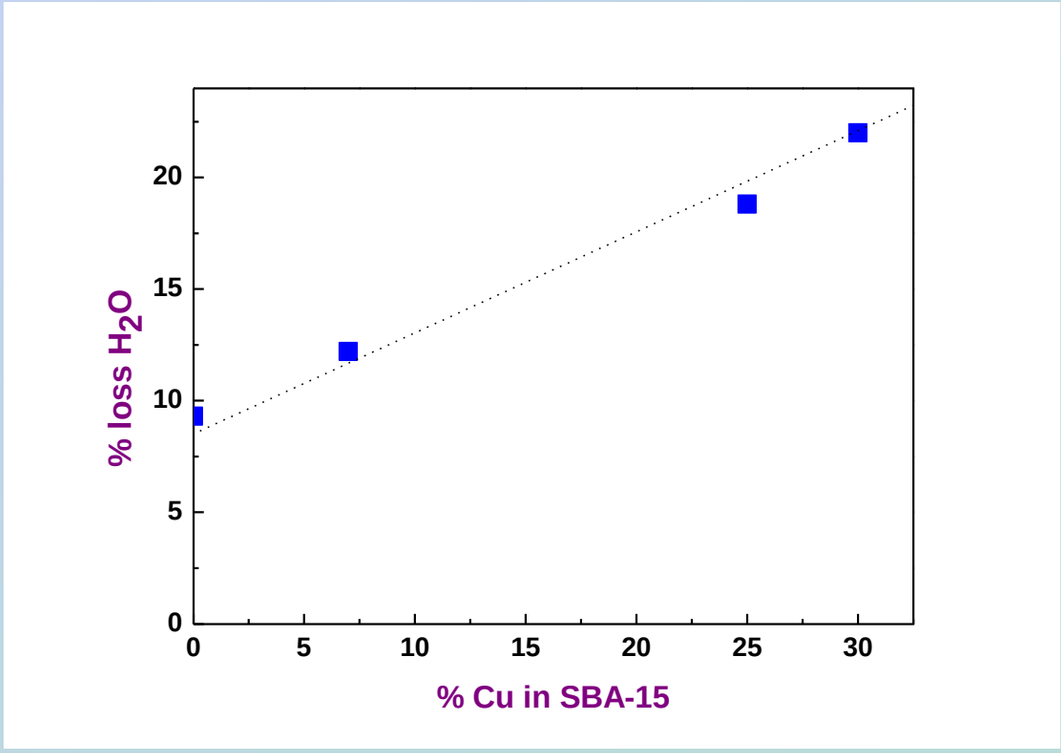
Perkin-Elmer AAnalyst 100 Atomic Absorption Spectrophotometer

Treatment of SBA-15-Cu with 2% HNO_3 to solubilize Cu II atoms by breaking the Cu-O surface bonds.

Loss of H_2O as a function of %Cu II in SBA-15 Cu materials



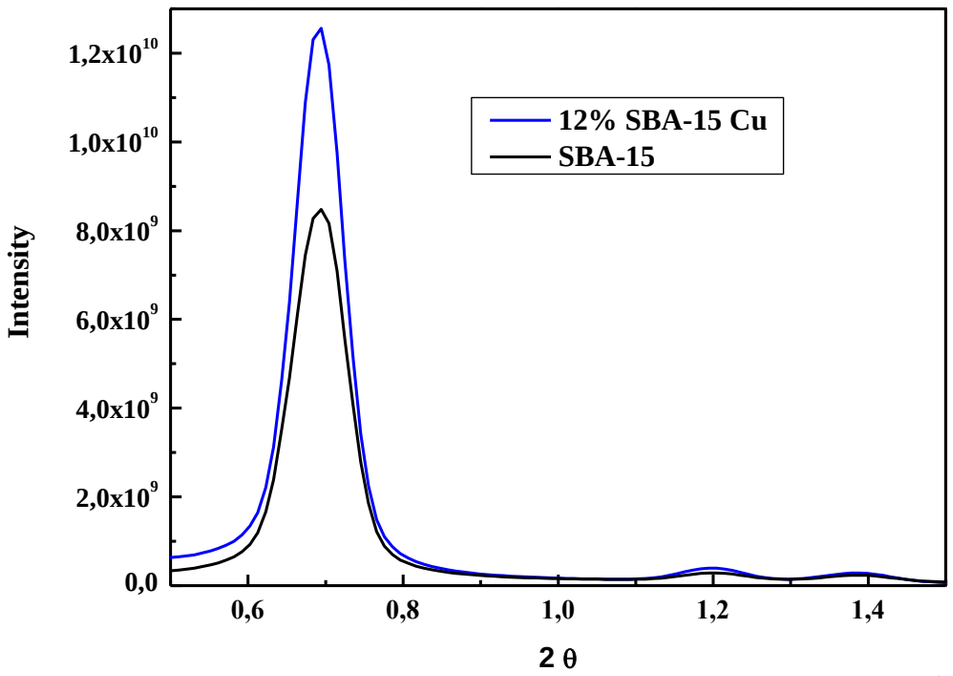




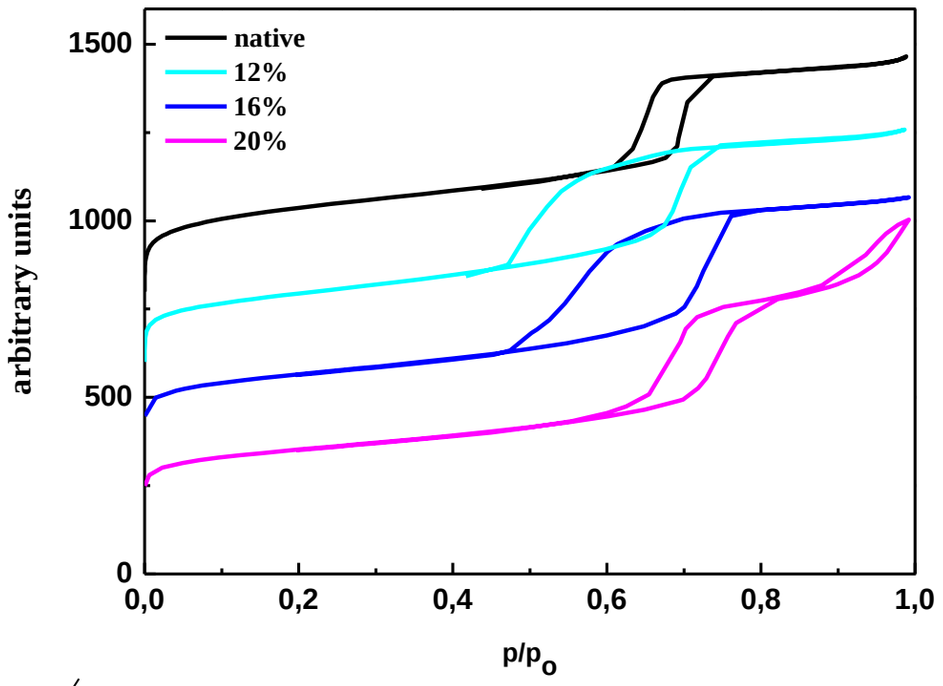
Amount of adsorbed H_2O increases as Cu II loading increases

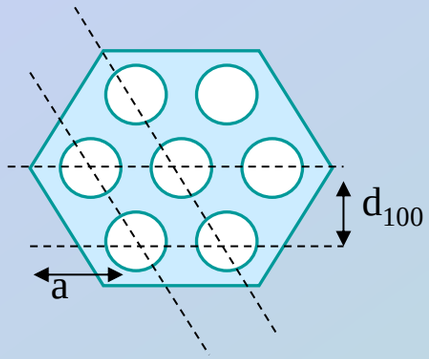
Structural properties

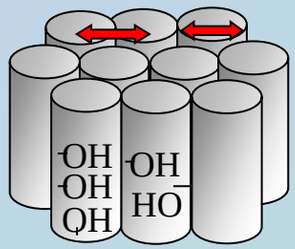
SAX (Small Angle X-ray diffraction)

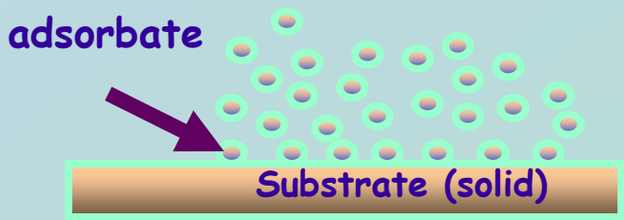


N_2 volumetric adsorption

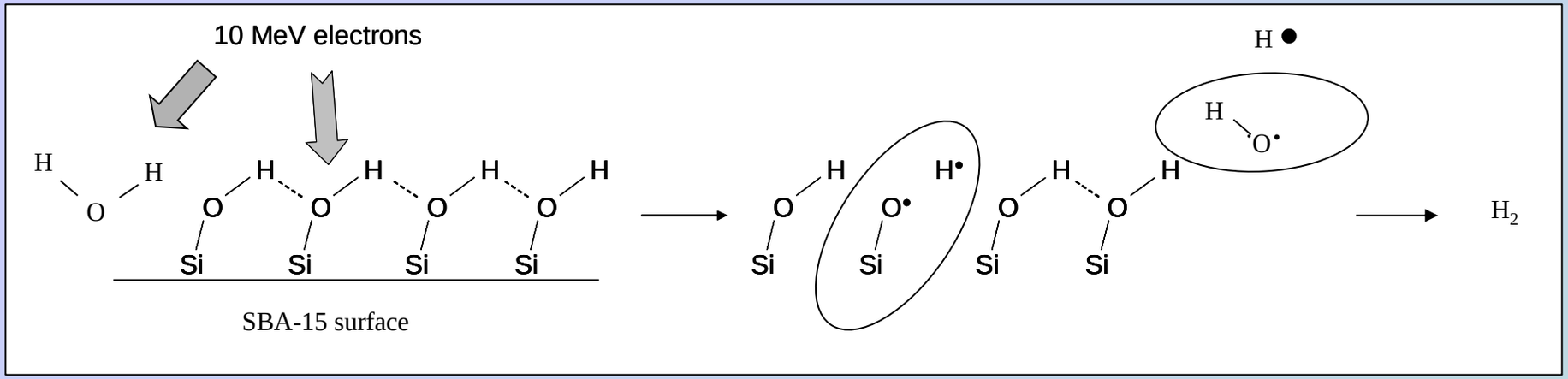


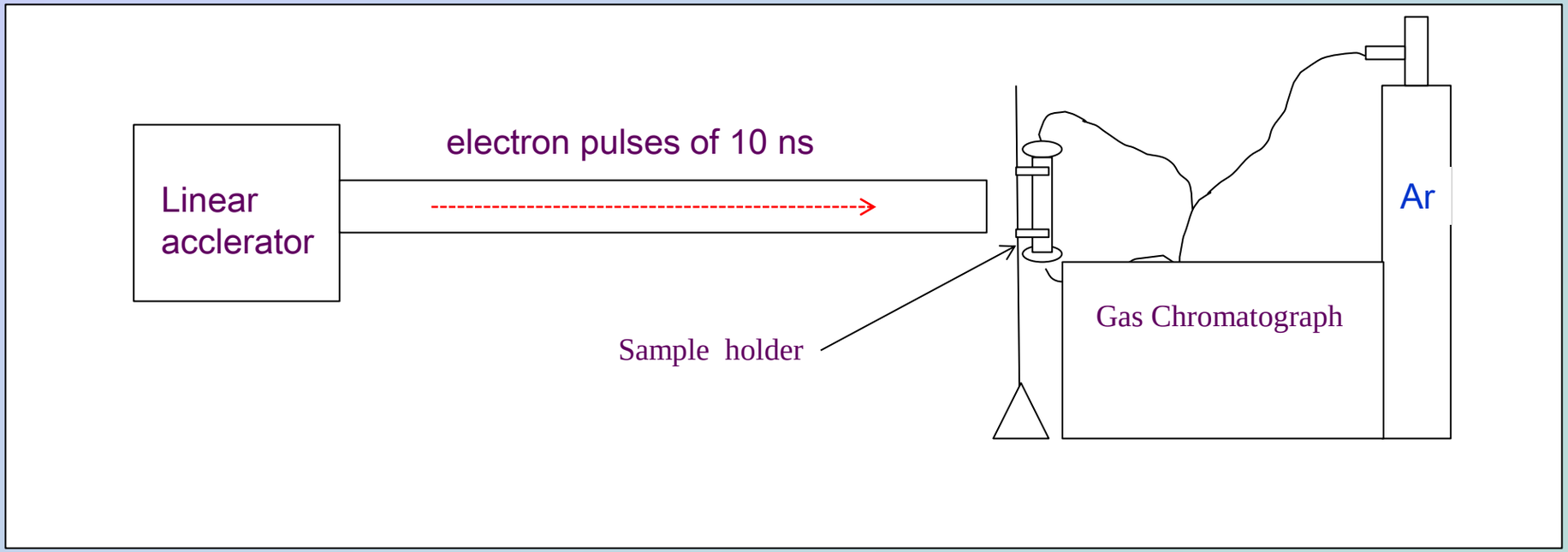




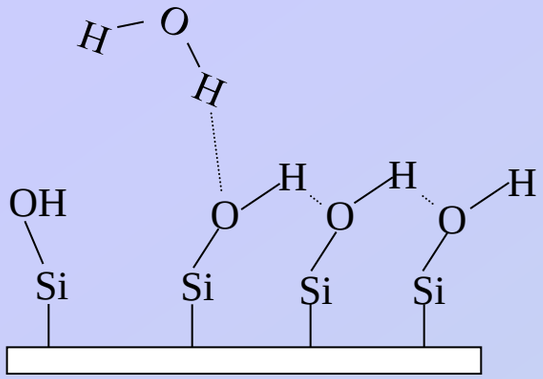


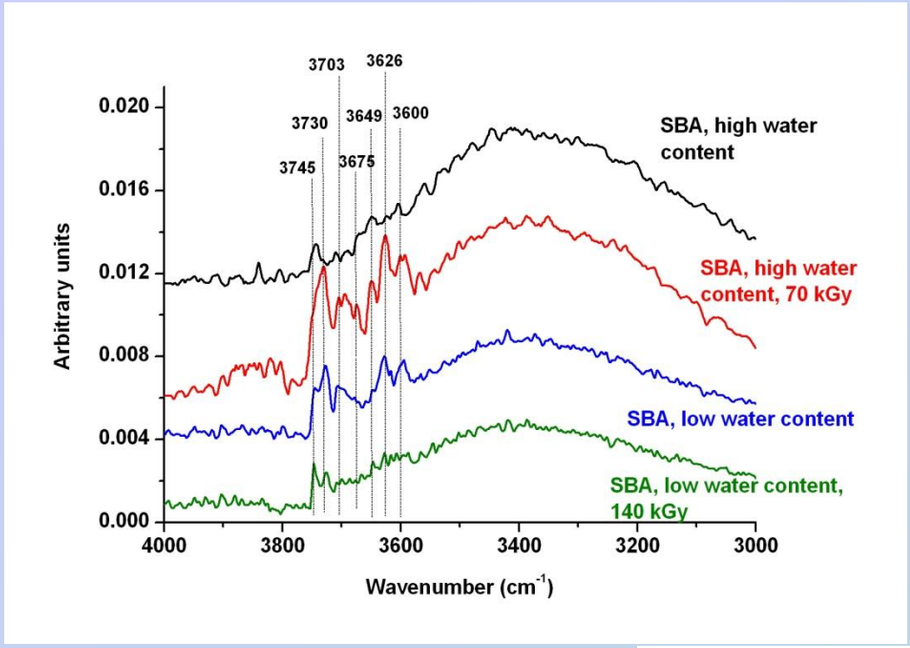
H_2 formation by electron irradiation of SBA-15 Cu materials

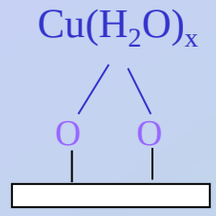


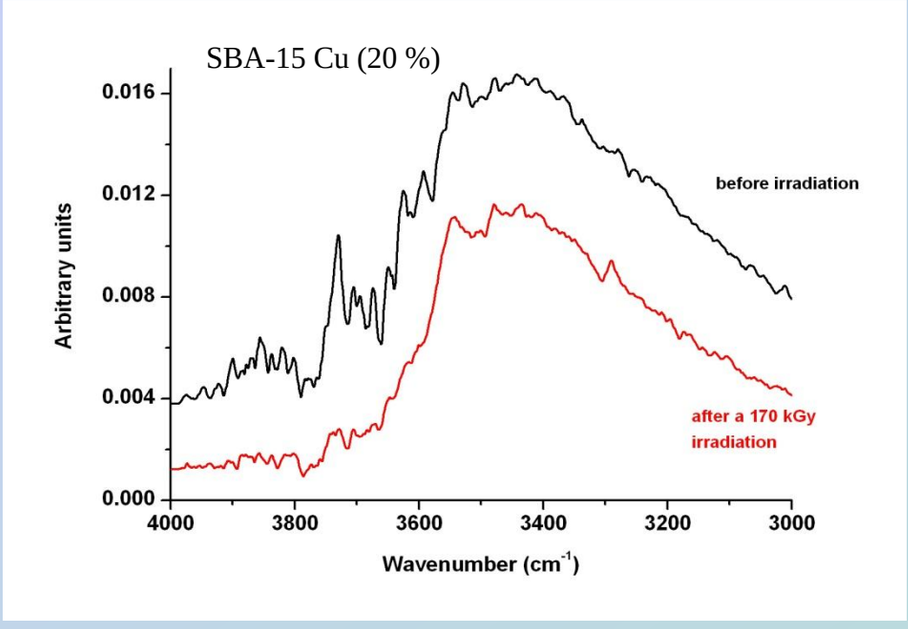


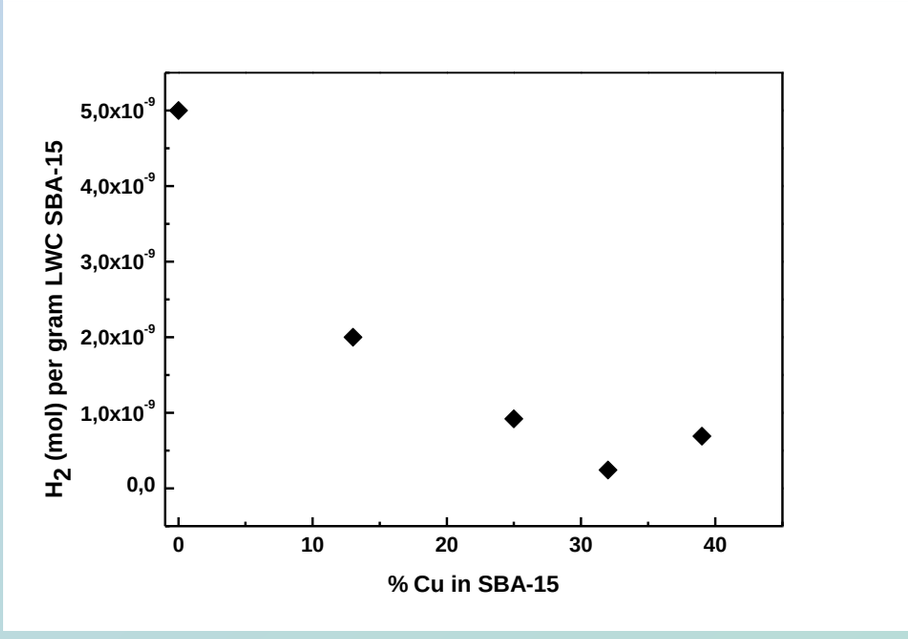
Copper inhibits H_2 formation (water bonded to copper atoms)







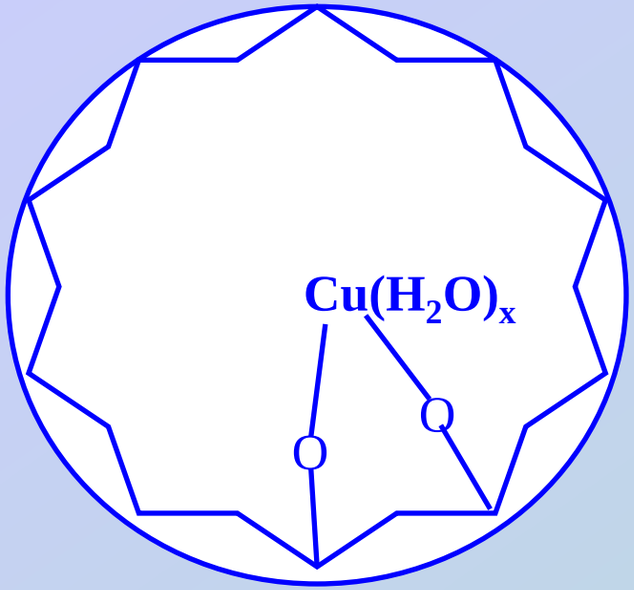




Brodie-Linder N., Le Caër S., Alam M. S.,Renault J.P., Alba-Simionesco C., PCCP, 12 (42), (2010), 14188.

Aqueous Cu II in a Hydrophillic vs a Hydrophobic Nanopore

Hydrophillic Nanopore



Bonded to the surface

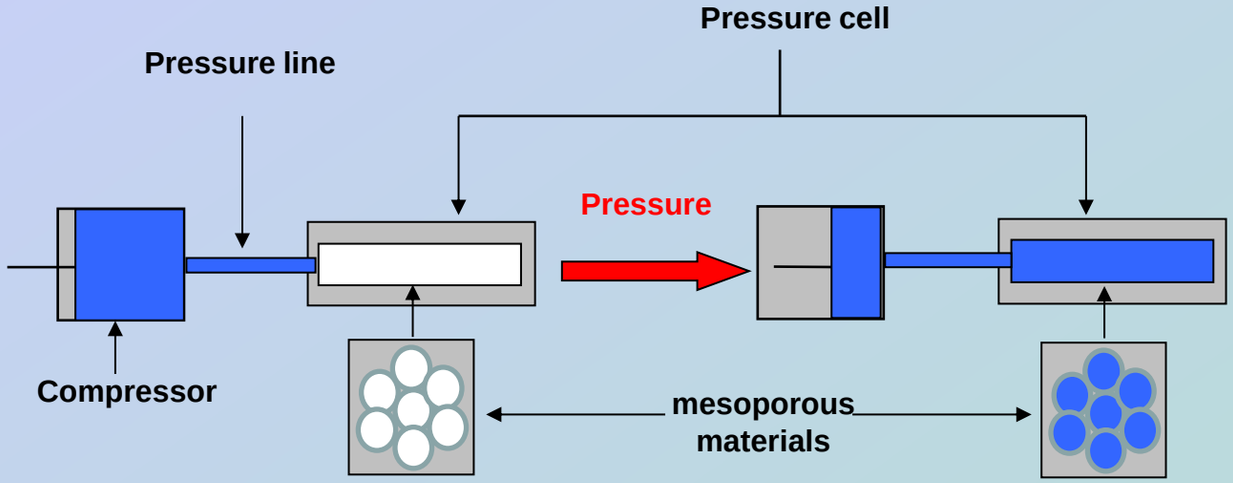
Hydrophobic Nanopore

Free from the surface

Preparation of MCM-41 $OSi(CH_3)_3$-Cu and SBA-15 $OSi(CH_3)_3$-Cu materials

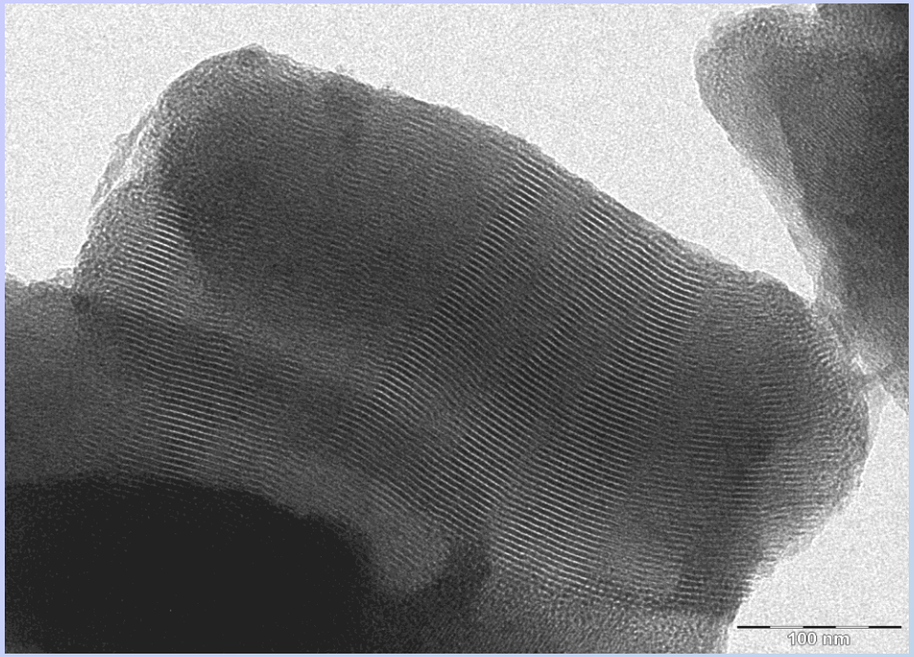
$$\text{MCM-41/ SBA-15} + SiCl(CH_3)_3 \xrightarrow[NEt_3]{CHCl_3} \text{MCM-41 } OSi(CH_3)_3\text{/SBA-15 } OSi(CH_3)_3$$

$$\text{MCM-41 } OSi(CH_3)_3\text{/SBA-15 } OSi(CH_3)_3 + \text{Cu II (aq)} \xrightarrow[4000\ bar]{\text{Under pressure*}} \begin{matrix} - OSi(CH_3)_3 \\ \\ - OSi(CH_3)_3 \end{matrix} \quad CuL_x$$



*Deschamps J., Audonnet F., Brodie-Linder N., Schoeffel M., Alba-Simionesco PCCP, 12, (2010) ,1440.

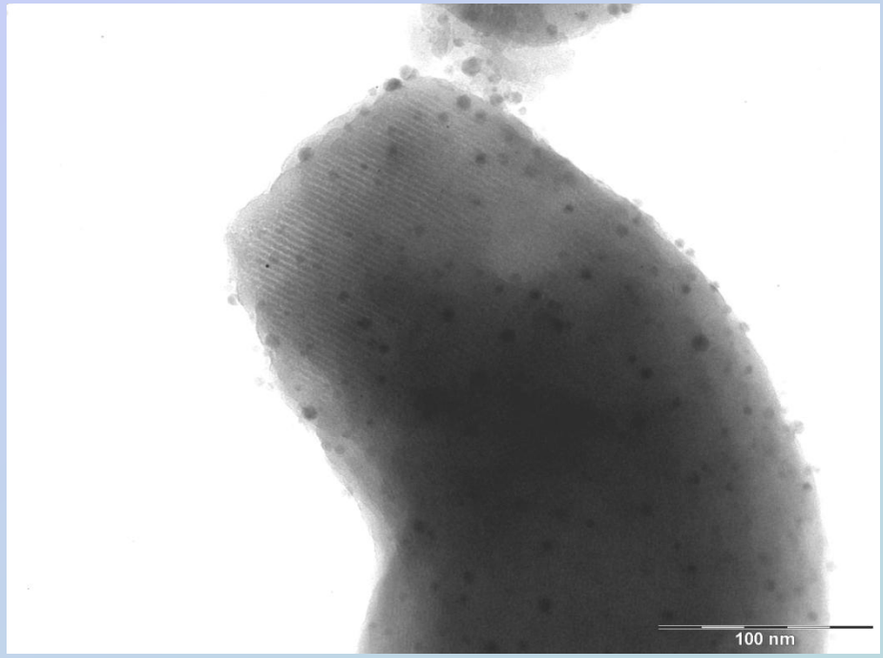
MCM-41- $OSi(CH_3)_3$



4000 bar

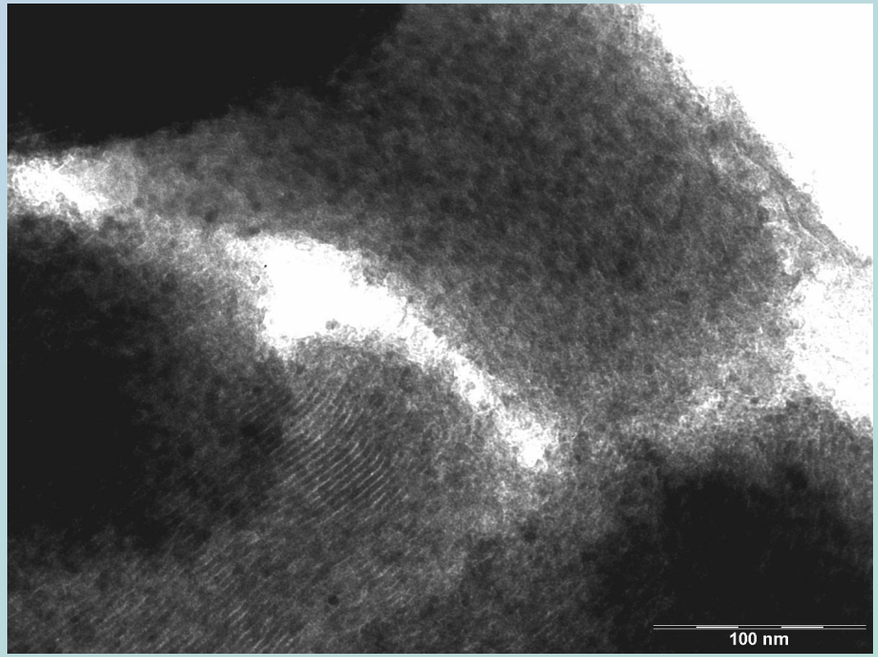
Cu II solution

Without pressure

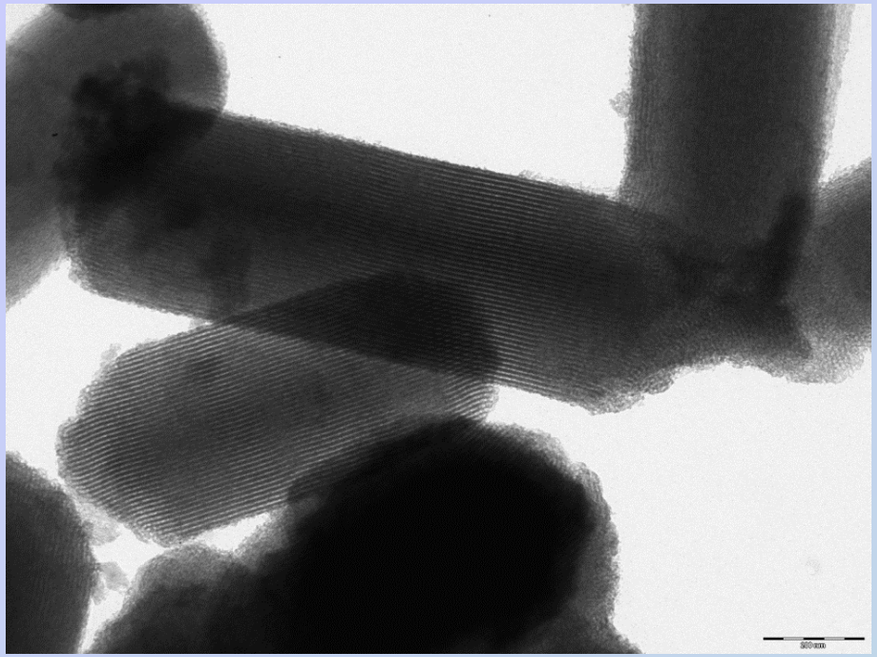


MCM-41- $OSi(CH_3)_3$–Cu II

With pressure



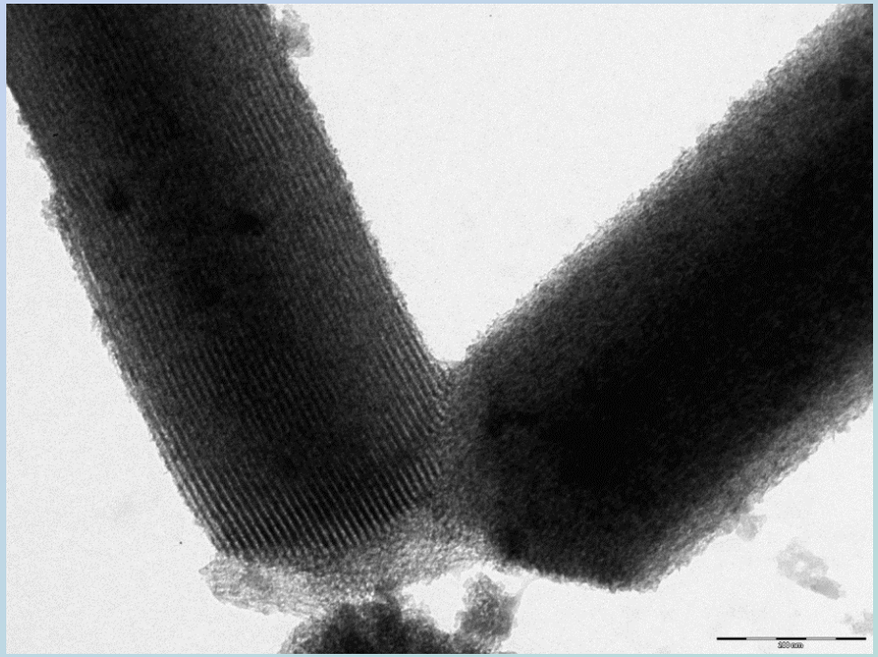
SBA-15-OSi(CH_3)$_3$



4000 bar

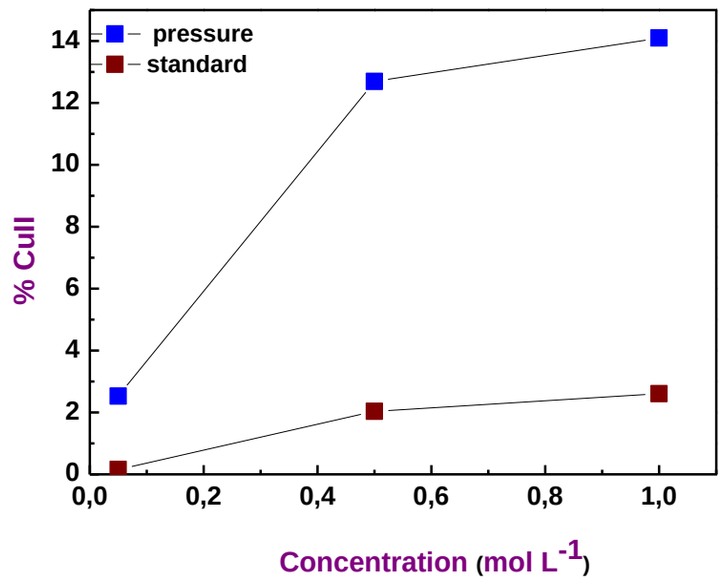
Cu II solution

SBA-15-OSi(CH_3)$_3$-CuII

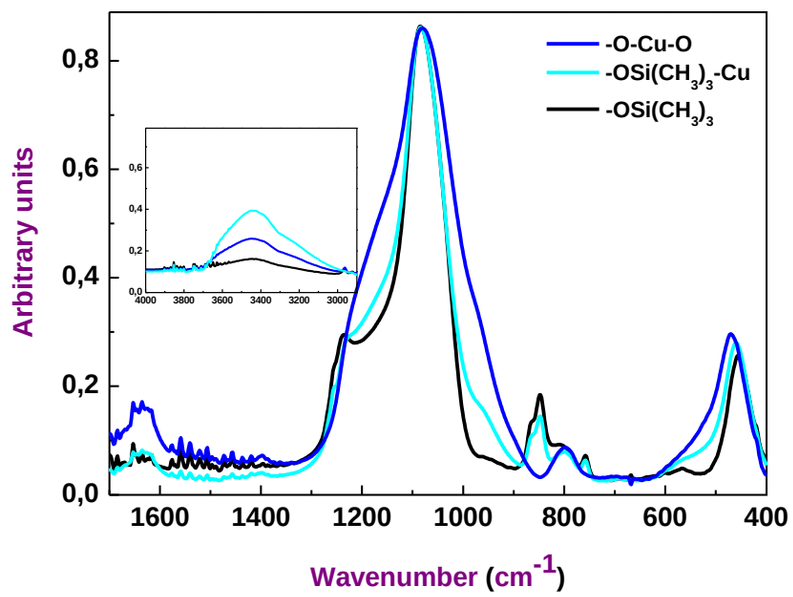


Characterization of MCM-41 C16 materials

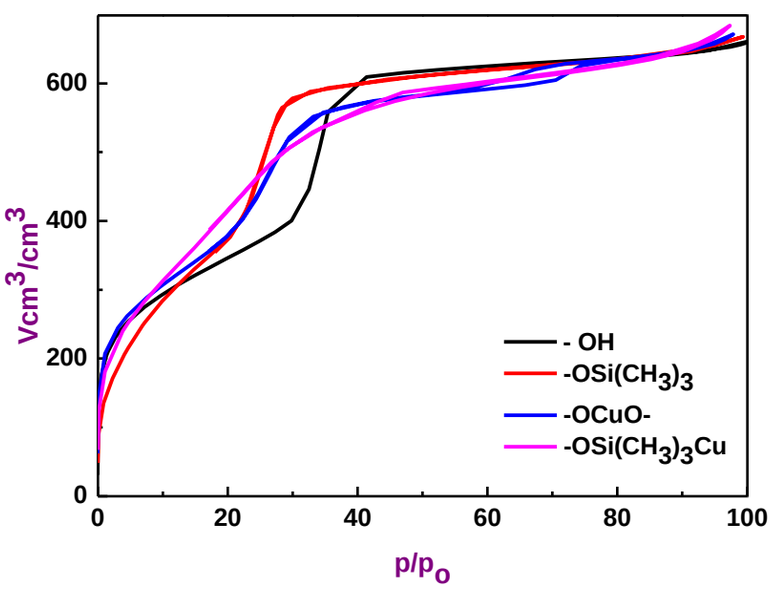
Copper II Loading as a function of Cu II solution



IR spectra

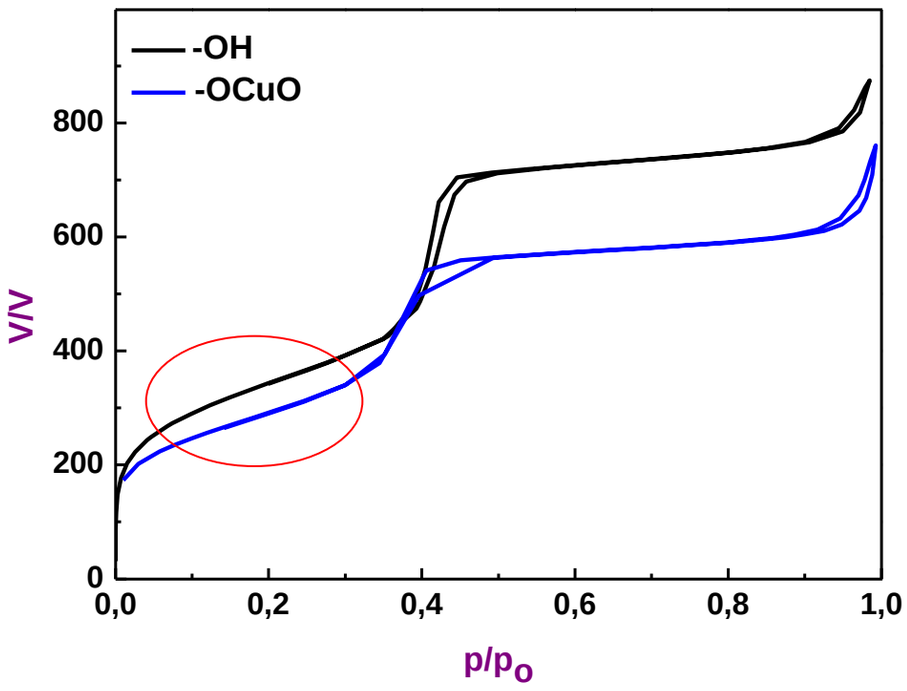


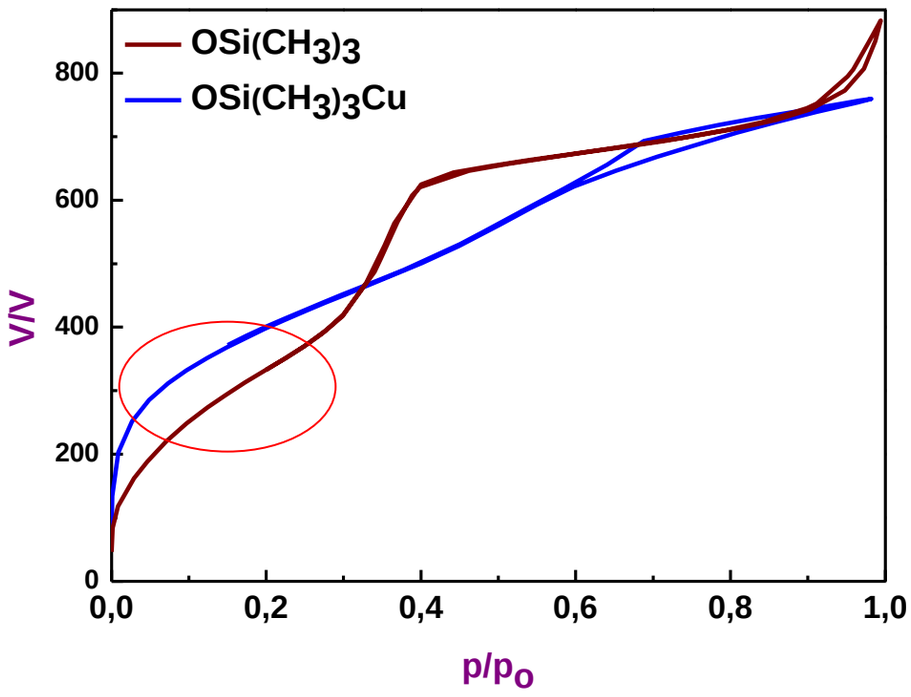
N_2 volumetric adsorption



Effect of Copper II loading in the pores

N_2 adsorption isotherms





Hydrophillic surface ⟷ ***Hydrophobic surface***

MCM-41-OSi(CH$_3$)$_3$Cu

MCM-41-OSi(CH$_3$)$_3$

MCM-41-OH

Concluding remarks

Copper II loading on the surface of mesoporous silicate materials always results in a rise in the amount of confined water.

Water can be confined in hydrophobic pores using Cu II and our pressure method.

Confined Water as a Cu II ligand plays an important role in determining the hydrophillic/hydrophobic nature of MTS materials.

The number of water molecules bonded to the confined Cu II atoms can be modified by dehydration creating a reversible process.

Perspectives: closer look at water in the CuII hydrophobic pores

Collaborators

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Fabrice Audonnet, University Pascal Blaise, Clermond Ferrand
Johnny Deschamps, ENSTA, Paristech
Marcus Schoeffel, Polytechnique, Paristech
Sophie LeCaer, Laboratoire de Radiolyse, Saclay
Jean-Phillip Renault , Laboratoire de Radiolyse, Saclay

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Florian Gallier, SOSCO, University of Cergy Pontoise
Elisa Peroni, SOSCO, University of Cergy Pontoise
Patricia Beaunier, Service de microscopie électronique,
Université Pierre et Marie Curie