Before starting…

- **Julien Schmitt**, postdoc in the Physical Chemistry department

- Internship 2010: Study of the SAXS pattern of *mesoporous materials*

- PhD 2011-2014: Self-assembly mechanism of *mesoporous materials*

- Postdoc 2014-onwards: From *mesoporous materials* towards the formation of an artificial nacre
Mesoporous materials

Julien Schmitt
Physical Chemistry
Outline:

1/ Introduction to porous materials characteristics and applications

2/ Synthesis strategy of porous materials how and why study the formation mechanism

3/ Current research towards the formation of an artificial nacre
Introduction

1/porous materials, characterisation and applications
A huge variety of porous materials!

In nature
Zeolites

naturally occurring crystalline aluminosilicates
Axel Fredric Cronstedt, 1756, stilbite

Synthesized Zeolites
more than 200 structures

Si/Al ratio, cations
pores size and connectivity

Microporosity <2nm

Cristalline walls
**Silica gels**

A silica source:

\[
\text{TEOS} = \text{CH}_2\text{CH}_3\text{O}^- \quad \text{Si}^+ \quad \text{O}^- \quad \text{CH}_2\text{CH}_3
\]

*In water*

**hydrolysis**

\[
\text{Si(OR)}_4 + n\text{H}_2\text{O} \rightarrow \text{Si(OR)}_{4-n} (\text{OH})_n + n\text{ROH}
\]

**condensation**

\[
2\text{Si(OR)}_3\text{OH} \rightarrow \text{Si(OR)}_3 - \text{O} - \text{Si(OR)}_3 + \text{H}_2\text{O}
\]

\[
\text{Si(OR)}_3\text{OH} + \text{Si(OR)}_4 \rightarrow \text{Si(OR)}_3 - \text{O} - \text{Si(OR)}_3 + \text{ROH}
\]

Particles size: 3-10 nm

Pores size: 2-50 nm

Michaux, PhD manuscript

Silica clusters
IUPAC classification

Microporous:  < 2nm
Mesoporous:  2-50nm
Macroporous:  > 50nm

How to ally the properties of a « large » porosity with an organisation of the pores?
Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism

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Mesoporous and mesoporous inorganic solids (with pore diameters of ≤20 Å and ~20–500 Å respectively) have found great utility as catalysts and sorption media because of their large internal surface area. Typical microporous materials are the crystalline framework solids, such as zeolites, but the largest pore dimensions found so far are ~10–12 Å for some metallophosphates and ~14 Å for the mineral cacoxenite. Examples of mesoporous solids include silicas and modified layered materials, but these are invariably amorphous or paracrystalline, with pores that are irregularly spaced and broadly distributed in size. Pore size can be controlled by intercalation of layered silicates with a surfactant species, but the final product retains, in part, the layered nature of the precursor material. Here we report the synthesis of mesoporous solids from the calcination of aluminosilicate gels in the presence of surfactants. The material possesses regular arrays of uniform channels, the dimensions of which can be tailored (in the range 16 Å to 100 Å or more) through the choice of surfactant, auxiliary chemicals and reaction conditions. We propose that the formation of these materials takes place by means of a liquid-crystal 'template' mechanism, in which the silicate material forms inorganic walls between ordered surfactant micelles.

Members of this family of materials, designated MCM-41, were first observed in electron micrographs of products from hydrothermal reactions of aluminosilicate gels in the presence of quaternary ammonium surfactants. We prepared the MCM-41 molecular sieve characterized here as follows: 200 g of a solution containing 26 wt% hexadecyltrimethylammonium, as C16H33(CH3)3N+(OH)−/Cl− (~30% hydroxide) was combined with 40 torr, 49 wt% n-hexane at 40 torr, and 67 wt% benzene at 50 torr. The pore volume of this sample is 0.79 cm³ g⁻¹. The range of pore volumes for MCM-41 samples is 0.7–1.2 cm³ g⁻¹. Figure 3 shows N₂ adsorption isotherms for this material and for an amorphous mesoporous silica. The morphology of MCM-41 depends on synthesis conditions, but it is possible to obtain relatively large (~2 μm) hexagonal prisms of MCM-41, as seen in the scanning electron micrograph in Fig. 4.
Mesoporous materials

- Pores with diameters 2-50 nm
- High surface area ~ 800-1000m²/g
- Ordered or disordered structures (but amorphous)
- Various chemical compositions
- Organic materials function as structure promoters
Huge surface area: 1000 m$^2$/g

How to study the pores organisation and size of these materials?
Small Angle X Ray Scattering

Small angles $\Leftrightarrow$ « big » objects

$$I(q) = A \, P(q) \, S(q)$$

Form factor (type of objects in solution)

Structure factor (interactions)
X-ray diffraction gives fingerprint of the structure
Small angle region!

Bragg’s law

\[ n\lambda = 2d \sin \theta \]

*Bragg’s Law*
Pioneering work (1992-93):

- **M41S - materials**\(^1\)
  - MCM-41 - 2D hexagonal
  - MCM-48 - cubic(Ia3d)
  - MCM-50 - lamellar

- **FSM - materials**\(^2\)
  - 2 D hexagonal
Transmission Electron Microscopy

Transmission electron microscopy gives direct images – structures can be determined.

Figure 4. HREM images and their Fourier diffractograms of the Fe$_3$Al structure ([110] direction) (a) and the FeAl$_3$ structure ([110] direction) (b) and magnified image of white square region in (b) with the schematic drawings of layer A and layer a, (c). The stacking faults make streaks along [111] direction in the Fourier diffractograms as marked with arrows.
Scanning Electron Microscopy

Study the morphology of the grains

Kjellman et al. Chem Mater 2013
Nitrogen sorption gives information on pore geometry, pore size and surface area.
Applications

Heterogenous catalysis: carrier for catalysts

Drug delivery

Nanoparticles synthesis

Argyo et al. Chem Mater 2014

Bleuzen et al. Chem Comm 2010
2/ how and why study the formation mechanism

STRATEGY TO SYNTHESIZE POROUS MATERIALS
How are porous materials “constructed”?

A hint: 
*This image is NOT realistic!*

Astérix, la Serpe d’Or, 1960
Building materials using templates

Put stones around the template
Building completed
-
remove the template
Molecular building

Stones –
“silica molecules”

Templates –
molecules that can be removed
“Cement” – covalent bonds
Pores templated by single molecules

Zeolites

Synthesis in aqueous solution template + silica precursor

Example of templates: cation molecules

Removal of template - porous materials (still microporous!)
Template

Single molecule template

Kresge et al 1992
Inagaki et al 1992
Amphiphiles

Hydrophilic head

Hydrophobic tail
Supramolecular (Micellar aggregates) template

Interfacial (hydrophobic) attraction

Interchain repulsion

Headgroup (hydrophilic) repulsion

Radius $R \leq l_c$

Volume, $v$

Headgroup area, $a_0$

Packing parameter: $g = \frac{v}{a_0 l_c}$
Long range organisations - mesophases

Diagram showing various mesophase structures with labels for different phases such as CMC, L1, L2, H1, H2, V1, V2, and Lα. The diagram also includes a graph with temperature (T/°C) and concentration (c/wt%) on the axes, indicating different phases such as multi phase, hexagonal, cubic, and iso.
1) Cationic (Mobil, Kuroda)

"Classic" MCM-41, MCM-48, MCM-50, FSM-structures

Hydrophilic

\[ \text{Cethyltrimethyl ammonium chloride + TEOS (kanemite) – basic conditions} \]
2.) Non-ionic block copolymer - Pluronic polymer

**SBA-15**

\[(EO)_x-(PO)_y-(EO)_x\]
As-synthesised, composite

Template removed, porous

Silica source in water: hydrolysis/condensation
In presence of surfactant!
SBA-15
SiO$_2$ (amorphous)

2D hexagonal

Mesostructured
Repeat 10nm

Surfactant: P123
(EO)$_{20}$-(PO)$_{70}$-(EO)$_{20}$

Silica source: TEOS

Nonionic Triblock and Star Diblock Copolymer and Oligomeric Surfactant Syntheses of Highly Ordered, Hydrothermally Stable, Mesoporous Silica Structures

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Abstract: A family of highly ordered mesoporous (20–300 Å) silica structures have been synthesized by the use of commercially available nonionic allyl poly(ethylene oxide) (PEO) oligomeric surfactants and poly-(alkylene oxide) block copolymers in acid media. Periodic arrangements of mesosopically ordered pores with cubic, $I4_132$, cubic $I4_1cm$, cubic $I4_1$ (or others), 3-d hexagonal (P6$_3$mcc), 2-d hexagonal (P6$_3$), and lamellar (L$_a$) symmetries have been prepared. Under acidic conditions at room temperature, the nonionic oligomeric surfactants frequently form cubic or 3-d hexagonal mesoporous silica structures, while the nonionic triblock copolymers tend to form hexagonal (P6$_3$) mesoporous silica structures. A cubic mesoporous silica structure (SBA-11) with $Pm3m$ diffraction symmetry has been synthesized in the presence of $C_6H_{12}OC(O)CH_2CH_2OH$ (C$_6$E$_7$OH) surfactant species, while a 3-d hexagonal (P6$_3$mcc) mesoporous silica structure (SBA-12) results when C$_6$E$_7$OH is used. Surfactants with short EO segments tend to form lamellar mesostructured silica at room temperature. Hexagonal mesoporous silica structures with $d(100)$ spacings of 13–27 Å can be synthesized
A simple synthesis

bricks

\[
\text{surfactant solution} + \text{silica precursor} \quad \rightarrow \quad ? \quad \rightarrow \quad \text{Hybrid mesophase formation} \quad \rightarrow \quad \text{Hybrid material (hydrothermal treatment)} \quad \rightarrow \quad \text{Surfactant removal Mesoporous material}
\]

Why are the micelles ordered?
Understand the formation (sequence of events, intermolecular Interactions).

Control properties – rational design.
Micelles are ordered prior to the silica precursor addition?

Possible, «Liquid Crystal Templating» -> monoliths
But! A typical synthesis

Synthesis - 24h (T = RT - 100°C)

Hydrothermal treatment – 24h (T=80 – 200°C)

Calcination (T ≈ 500°C) – removal of the structure director

Mix between a surfactant solution at 2,5 wt% + silica source

MCM41 : Kresge et al, Nature 1992
SBA-15 : Zhao et al, JACS, 1998
A mess!!
Cooperative Templating Mechanism

Surfactant solution + TMOS/TEOS + silica precursor → cooperative mechanism → Hybrid mesophase formation → Hybrid material (hydrothermal treatment) → Surfactant removal Mesoporous material

Final material: sub-micrometric and porous grains
In-situ – experiments to follow the synthesis

SAXS/SAXD
Small angle x-ray scattering/diffraction

USAXS
Ultra small angle x-ray scattering

(Cryo-TEM)
In-situ SAXS/USAXS

Figure 1. Experimental setup for in situ measurements of X-ray scattering and X-ray diffraction.
In-situ SAXS/USAXS
SBA-15 : synthesis

SAXS : SOLEIL – SWING beamline

data modelling via several models

Manet, Schmitt et al, J. Phys Chem B, 2011
SBA-15: mechanism of formation

without TEOS

\( q^{-4} \)

No TEOS  \( t = 1 \) min  \( t = 10 \) min
SBA-15: mechanism of formation

without TEOS

$t = 1$ min

$t = 10$ min

$q^{-4}$

$I (\text{cm}^{-1})$

$q (\text{Å}^{-1})$

$q^{-1}$

$I (\text{cm}^{-1})$

$q (\text{Å}^{-1})$

No TEOS

$t = 1$ min

$t = 10$ min

$t = 18$ min
SBA-15: mechanism of formation

without TEOS

- t = 1 min
- t = 10 min
- t = 18 min
- t = 30 min

No TEOS

- t = 1 min
- t = 10 min
- t = 18 min
- t = 30 min

I (cm⁻¹) vs q (Å⁻¹)
SBA-15: mechanism of formation

without TEOS

I (cm⁻¹)

q (Å⁻¹)

I (cm⁻¹)

q (Å⁻¹)

No TEOS

t = 1 min  t = 10 min

q⁻¹

I (cm⁻¹)

q (Å⁻¹)

No TEOS  t = 1 min  t = 10 min

q⁻¹

I (cm⁻¹)

q (Å⁻¹)

t = 18 min  t = 30 min  t = 45 min  t = 60 min

SBA-15: mechanism of formation
Control the morphology of the grains

SEM

36 °C

40 °C

50 °C

56 °C

TEM

Moulin, Schmitt et al. Soft Matter., 2013
Material in shape of platelets

P104 instead of P123
P104 \((\text{EO})_{27}(\text{PO})_{61}(\text{EO})_{27}\)

D = 1 µm

\(t = 350\) nm
3/ Hierarchical materials

TOWARDS THE FORMATION OF AN ARTIFICIAL NACRE
Creating innovative materials

SBA-15

Hybrid Particle

PNIPAM
Poly(N-isopropylacrylamide)

Thermo-sensitive artificial nacre
The take away messages

• Read Astérix!!

• **Ordered mesoporous materials:** porosity controlled (2-50 nm of pores size, surface area ~ 1000 m²/g)

• Formed using **surfactant as templates** and an **inorganic source**

• Synthesis studied in **SAXS**, powerful tool for **soft matter and material science**