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Synthesis of zeolite LTA under sonohydrothermale condition and investigation of its conversion into sodalite

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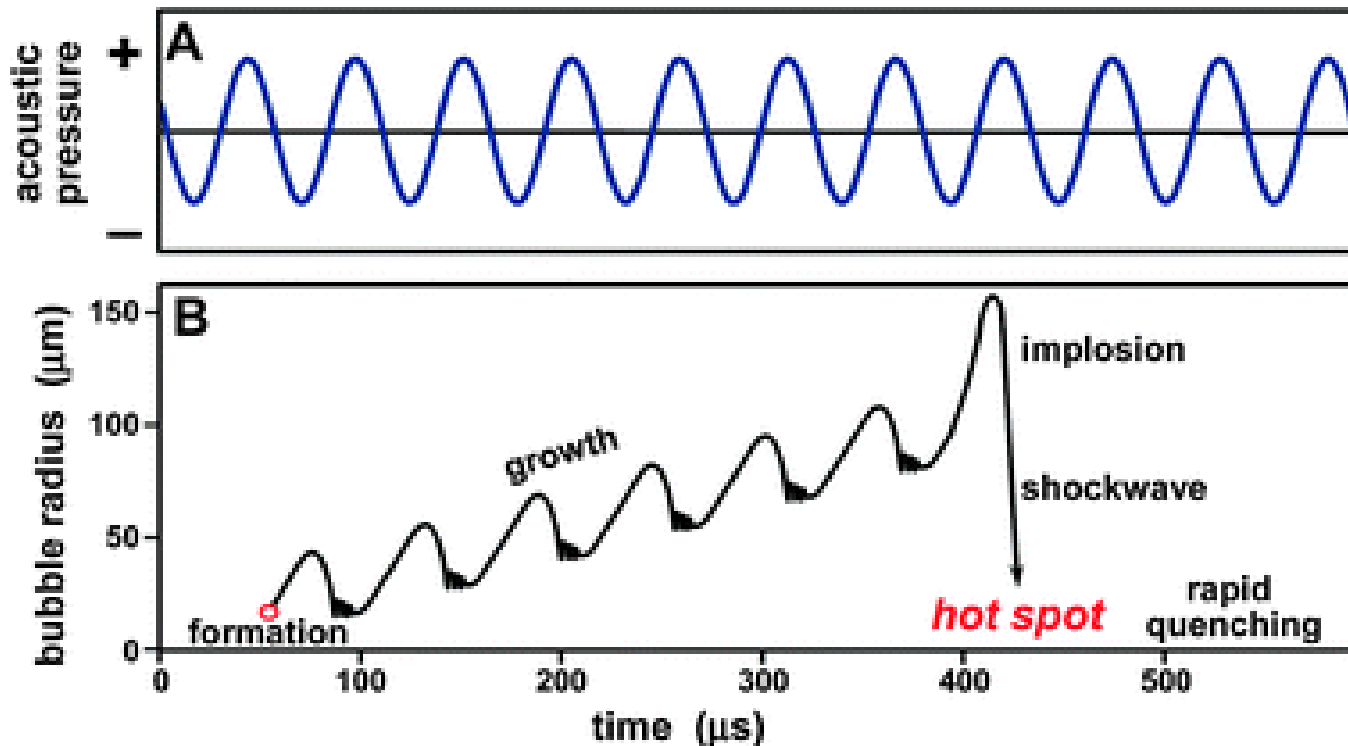


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What is sonochemistry?

Acoustic cavitation

Nucleation > growth > implosive collapse of micro-bubbles



Hot spot model:

$T \sim 5000 \text{ K}$

$P \sim 1000 \text{ bars}$

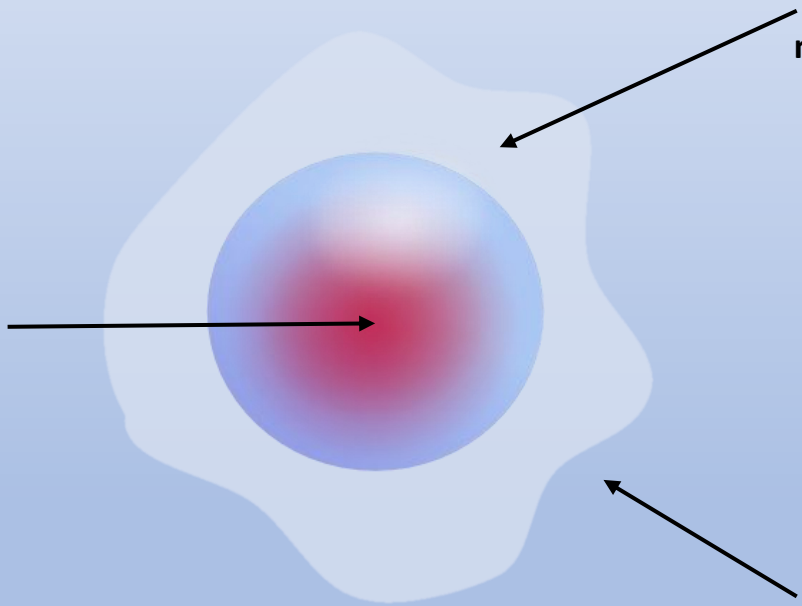
Sonochemistry



chemical effect

Inside the bubble, gas and steam

Radical formation (e.g. HO^\bullet , H^\bullet , CH_3^\bullet),
excited species
(e.g. Xe^* , C_2^* , H_2O^*), ionisation...



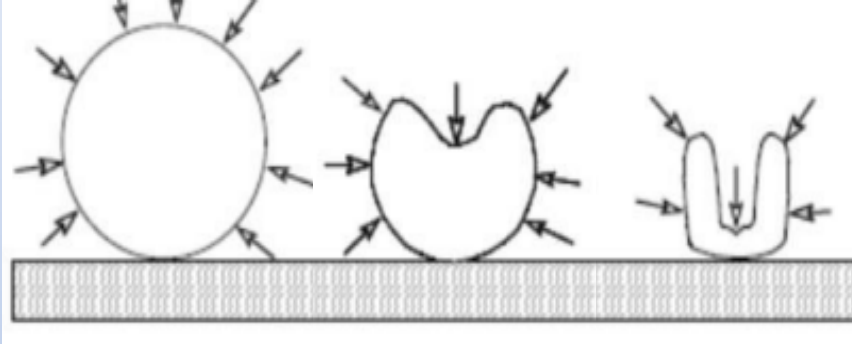
At the interface

Radical trapping, species
thermolysis
non-volatile, hydrothermal
reactions

Bulk

Environmental
conditions: Secondary
reactions

Physical effects



Implosion of a cavitation bubble near an extended surface

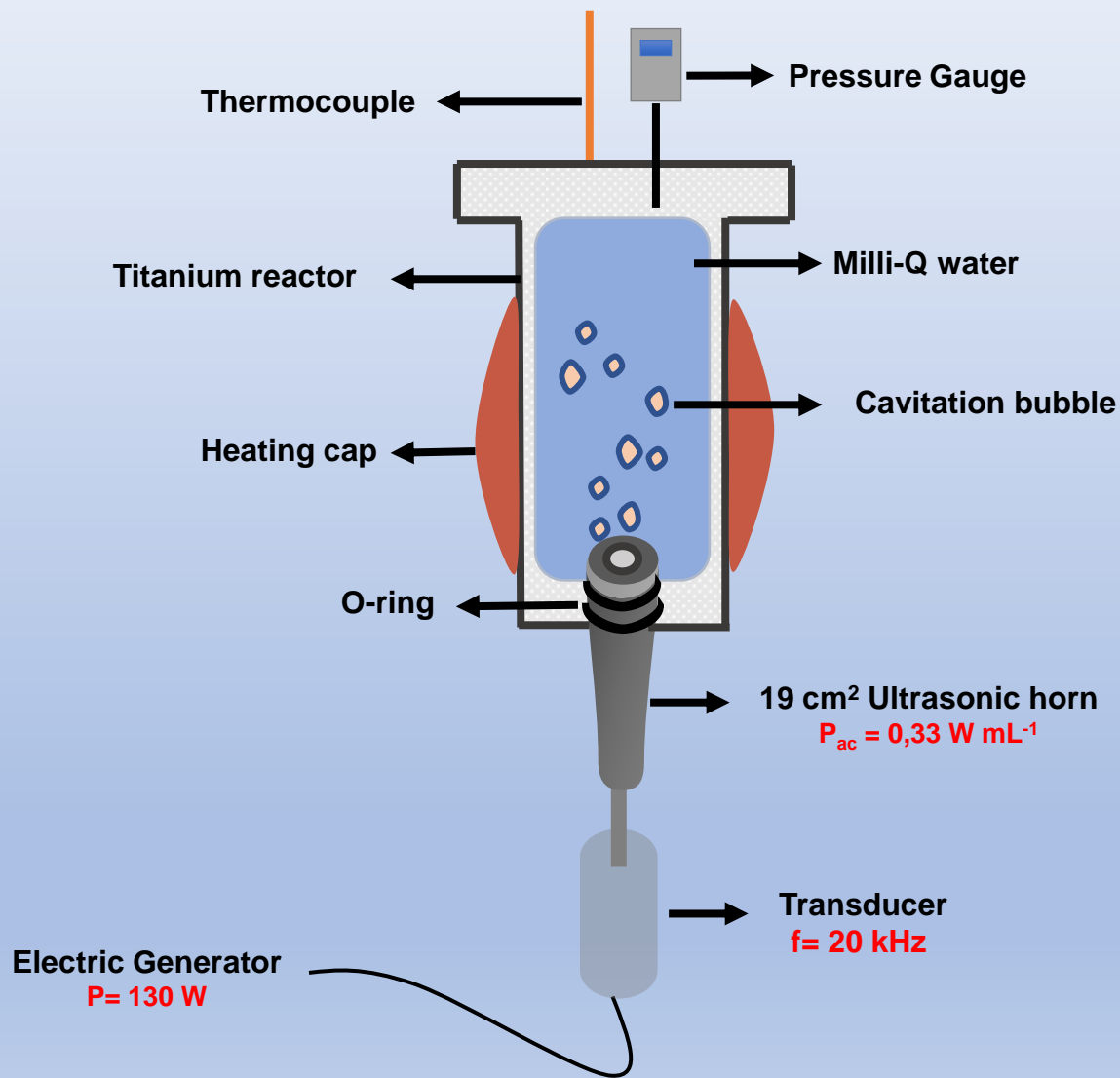


Erosion of a glass surface by micro-jets



Micro-jet: $\sim 150 \text{ m s}^{-1}$ à 20 kHz

Sonohydrothermal Reactor (SHT)

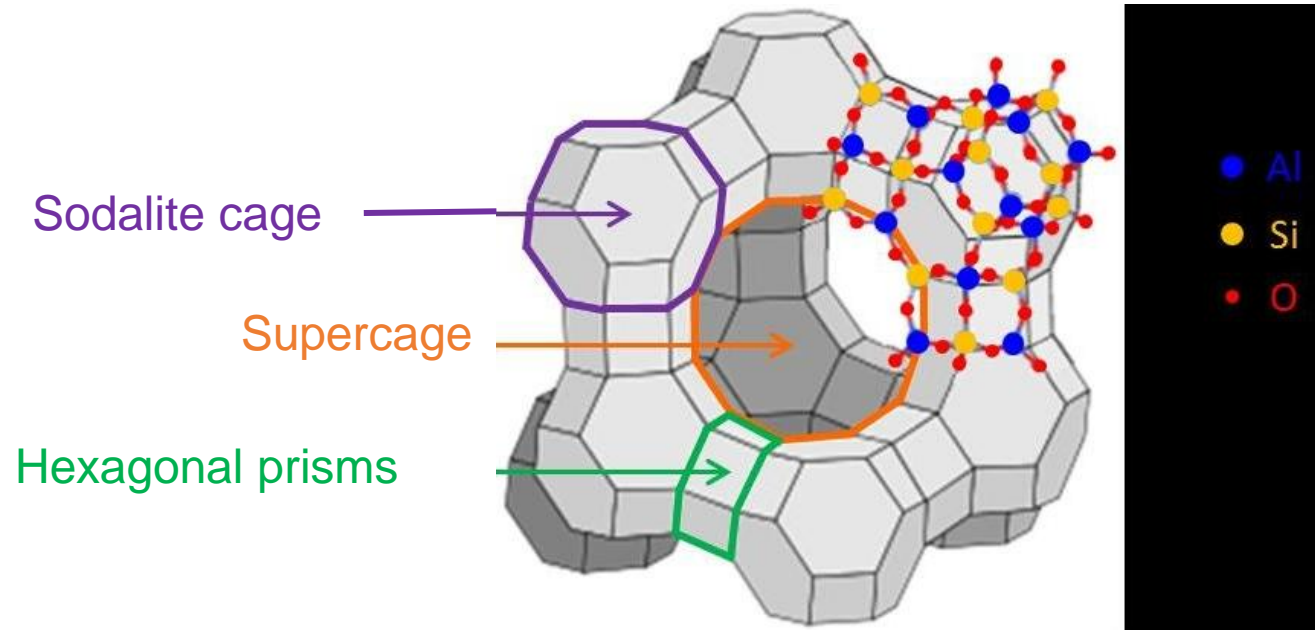


Ultrasonic coupling
and hydrothermal
conditions

C.Cau & al, J phys Chem
C117(44)(2013) 22827-
22833

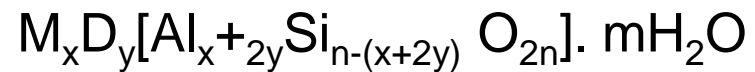
What is a zeolite?

Zeolite is :



1756: discovered by the Swedish mineralogist **Axel Frederik Cronstedt**

General formula of a zeolite :



Eur. J. Mineral. 1998, 10, 1037-1081

The Crystal Chemistry of Zeolithe, E. Paaglia et Richard A. Sheppard

Water waste and air
deppolution

Pétrochemistry

Industrial
applications

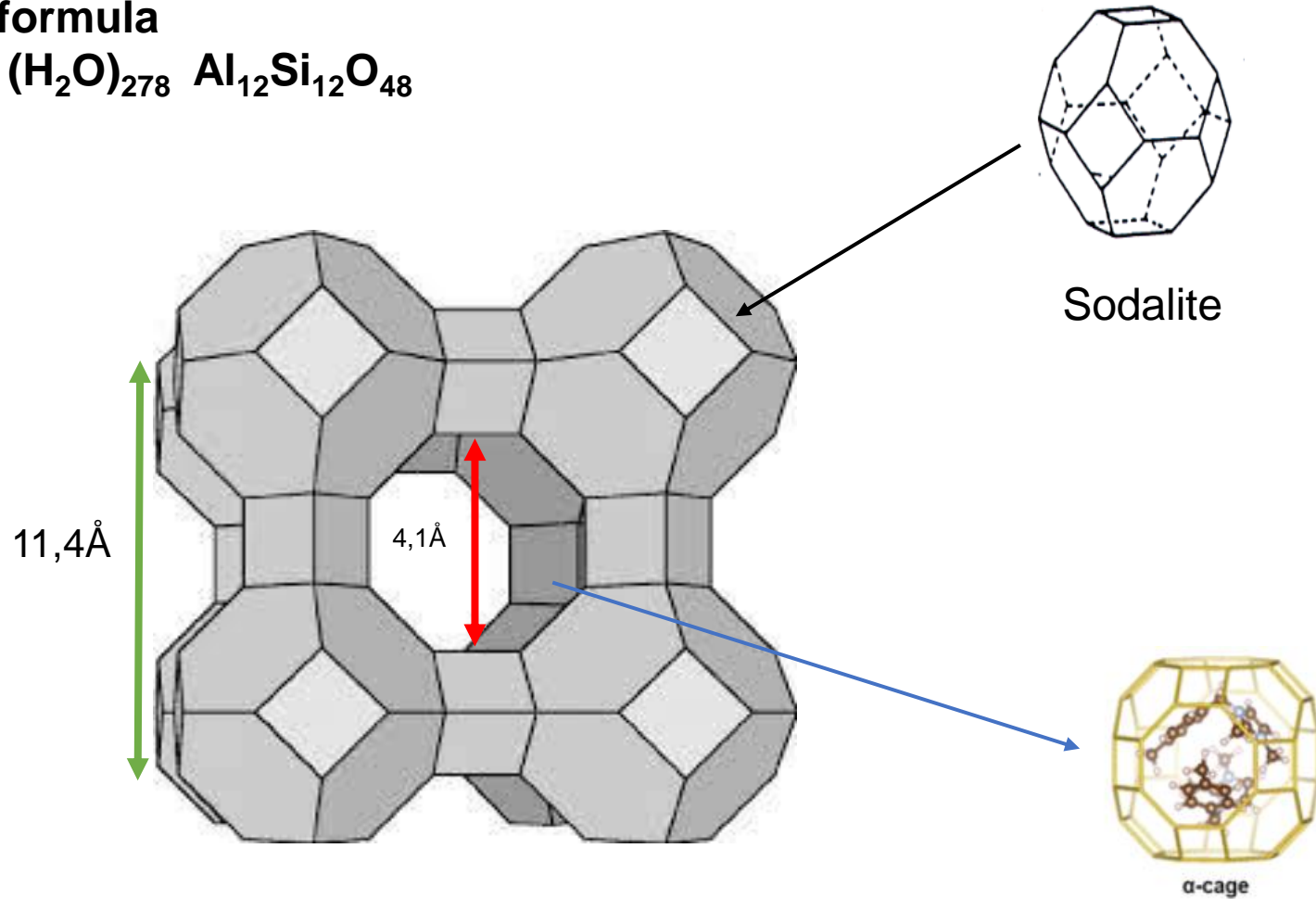
Heterogeneous
catalysis

CO₂ Capture

LTA zeolite

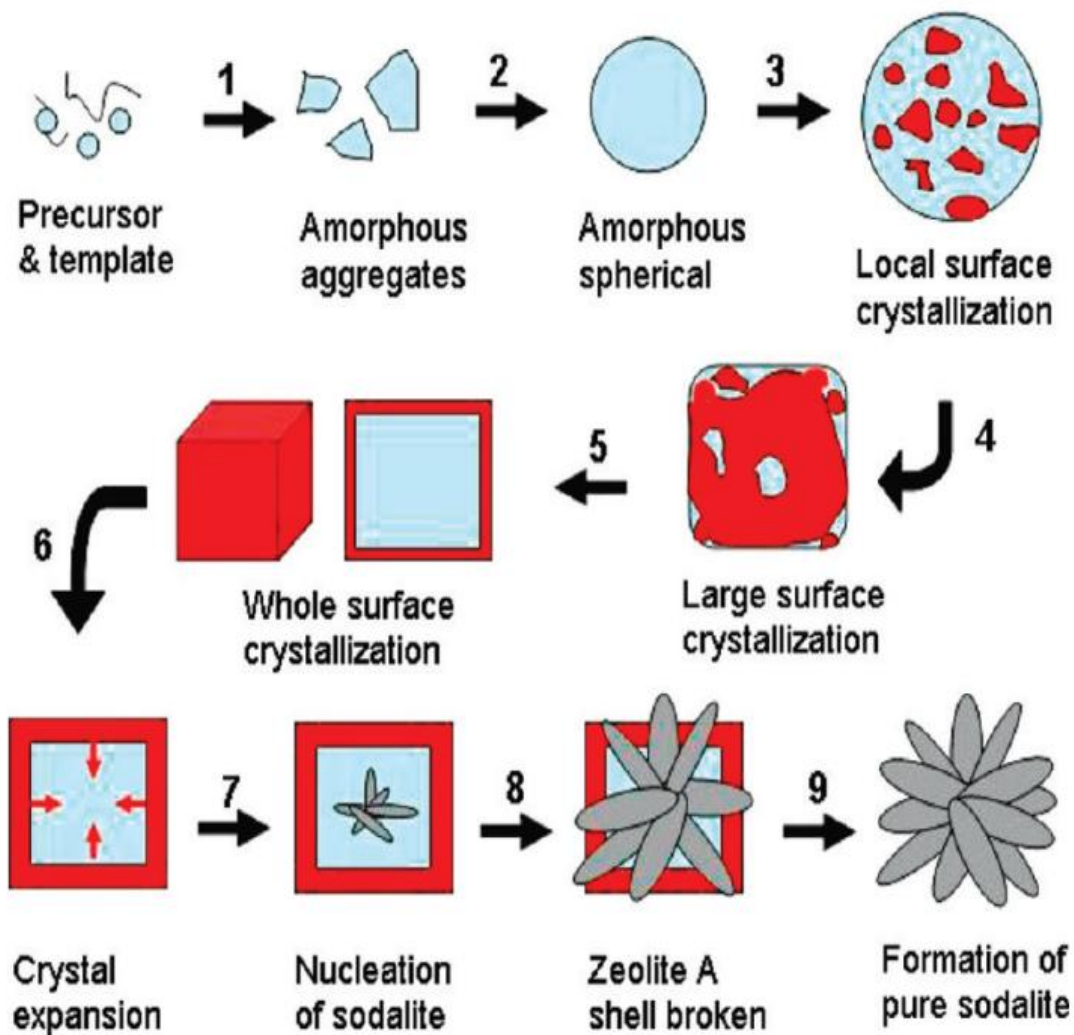


LTA formula



LTA structure

NEW ZEOLITE CRYSTAL GROWTH PATH AND ZEOLITE PHASE TRANSFORMATION



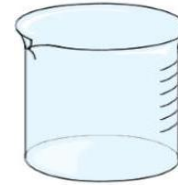
Greer, et al *J. Am. Chem. Soc.* **131**, 17986–17992 (2009).

Experimental section

Zeolite LTA synthesis



+



Silica solution:

- 1.6 g fumed silica
- 21 mL of 3 M sodium hydroxide solution

Aluminium solution

- 4.7 g sodium aluminate
- 27 mL milliQ water

Mechanical shaking 30 minutes (25 °C) or 20 kHz US, 70% amplitude, 30 minutes (70 °C), Pac: 30W



SHT reactor

SHT experimental conditions:

20 KHz , 100 °C
Autogenous pressure (1,4 atm)
50mL gel
Pac: 10W



Hydrothermale

Hydrothermal (Parr reactor)
experimental conditions

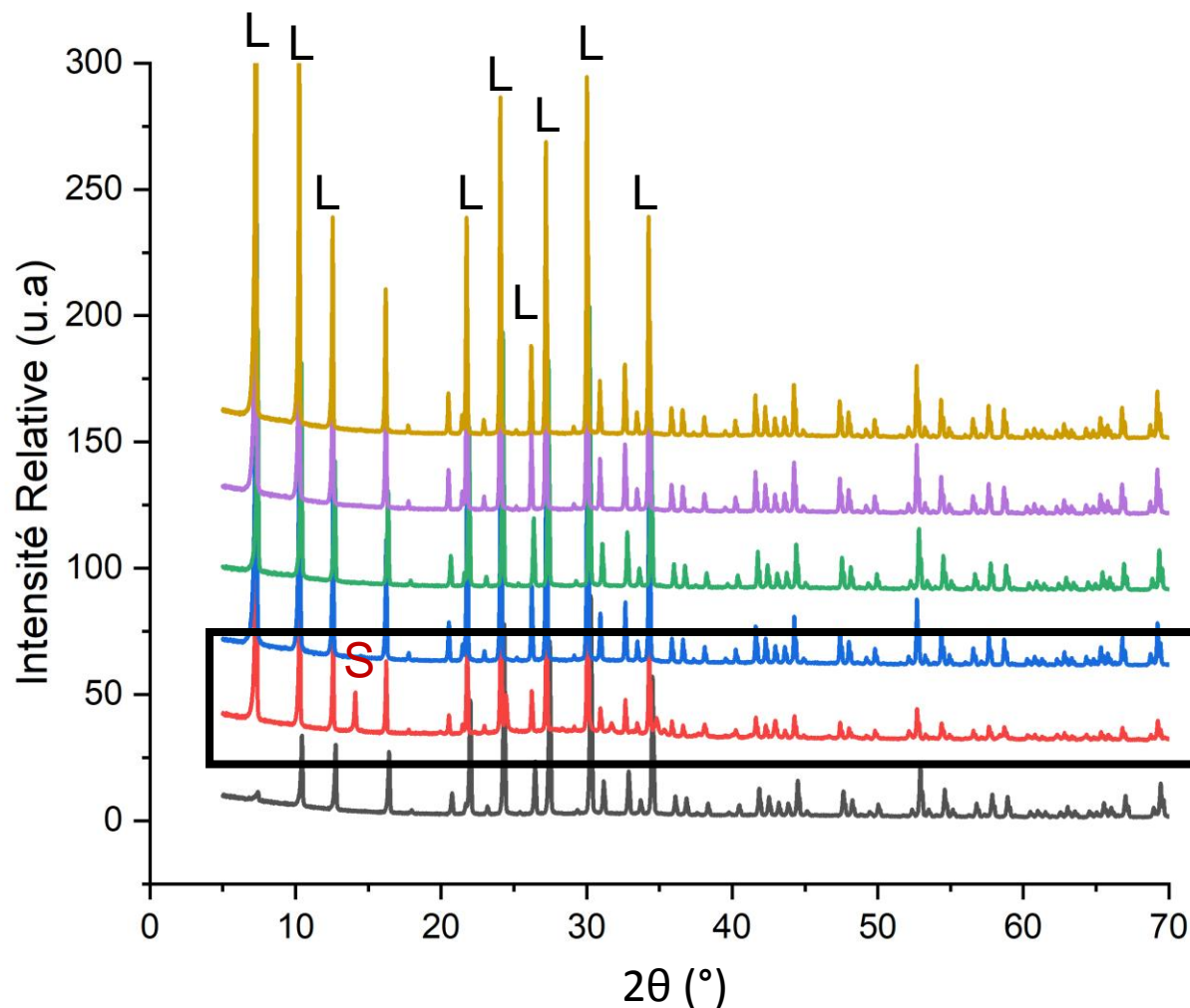
80 °C to 150 °C, 4 h to 12 h

Diffractograms of hydrothermal compounds



L: zéolithe LTA

S: sodalite



LTA9 : Ms30mins_HT(100°C/24h)

LTA8 : Ms30mins_HT(100°C/48h)

LTA7 : Ms30mins_HT(80°C/24h)

LTA6 : Us30mins_HT(80°C/4h)

LTA4 : Ms30mins_HT(150°C/12h)

LTA3 : Ms30mins_HT(80°C/4h)

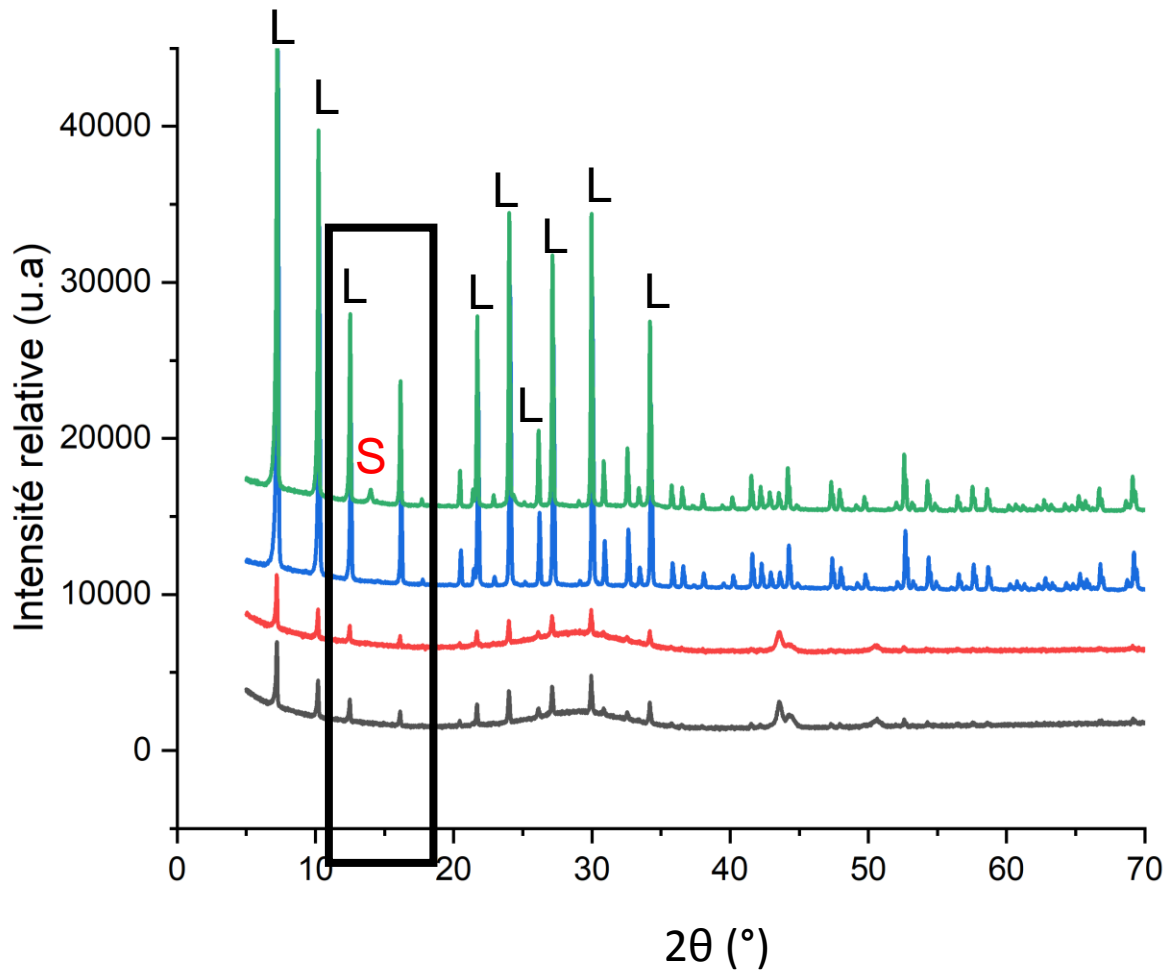
In hydrothermal applications, sodalite forms at high temperatures over long periods of time.

Diffractograms of SHT compounds



L: zéolithe LTA

S: sodalite



24 : Ms30mins_SHT(100°C/30 mins)
23 : Ms30mins_SHT(100°C/25 mins)
46 : Ms30mins_SHT(100°C/20 mins)
47 : Ms30mins_SHT(100°C/15 mins)

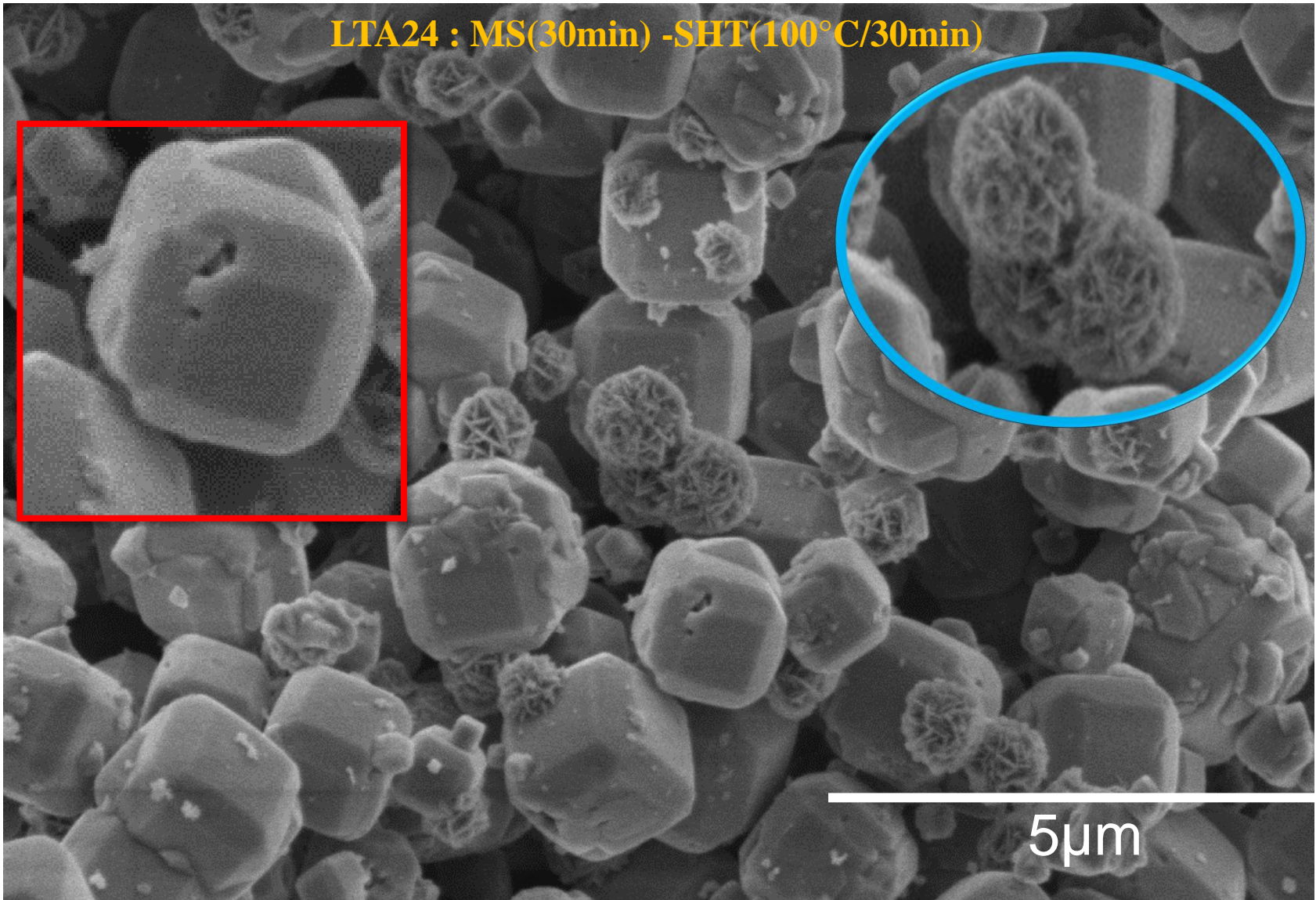
In SHT

- LTA crystallizes well before 15 minutes
- Sodalite forms after 30 minutes

SEM image of compound LTA 24



LTA24 : MS(30min) -SHT(100°C/30min)

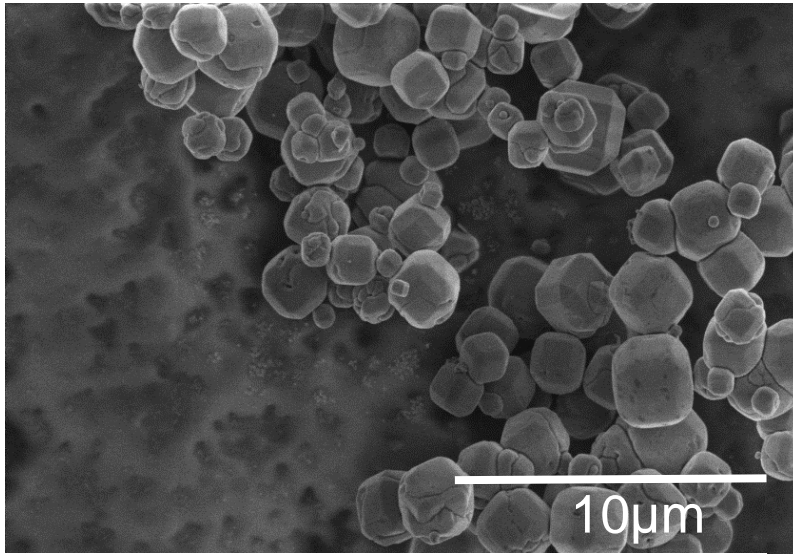


5 μ m

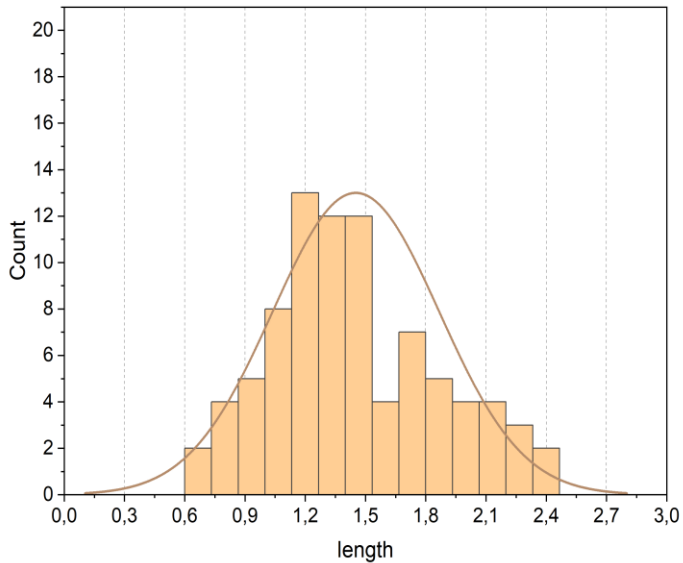
Hydrothermal partical size (μm)



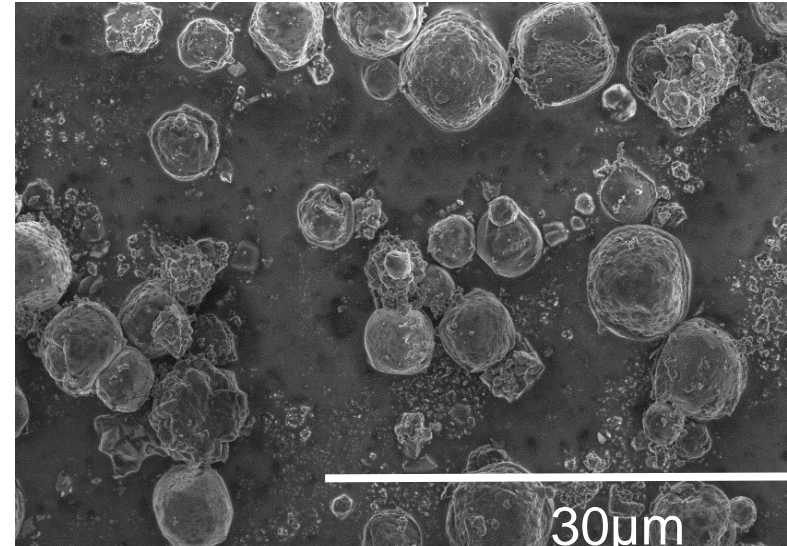
LTA8 : Ms30mins_HT(100°C/48h)



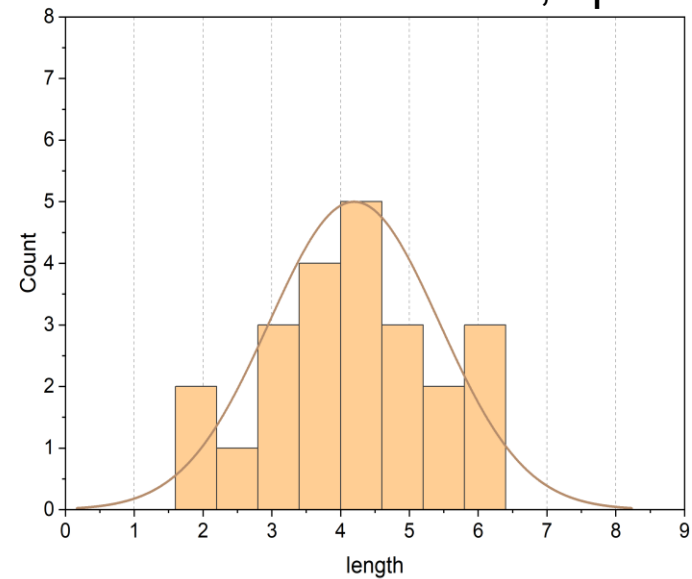
1,45 μm



LTA4 : Ms30mins_HT(150°C/12h)



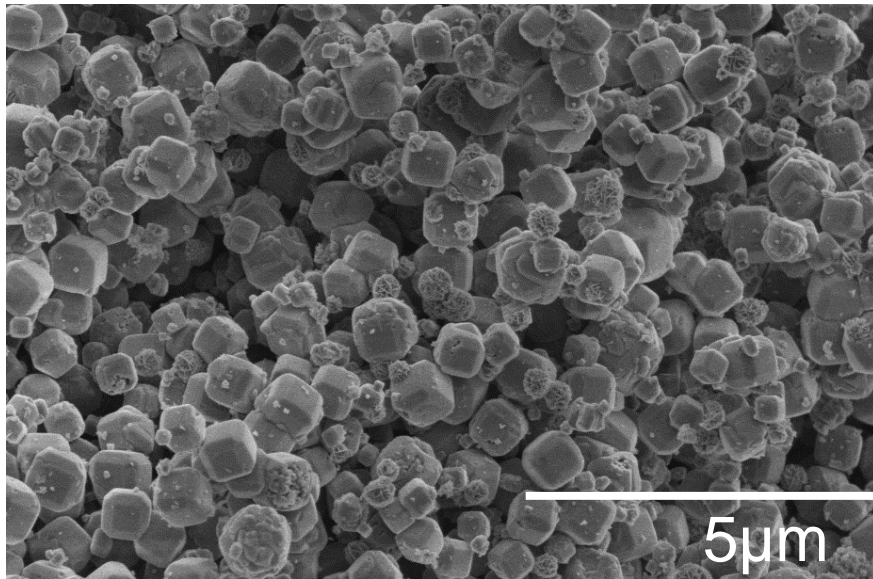
4,2 μm



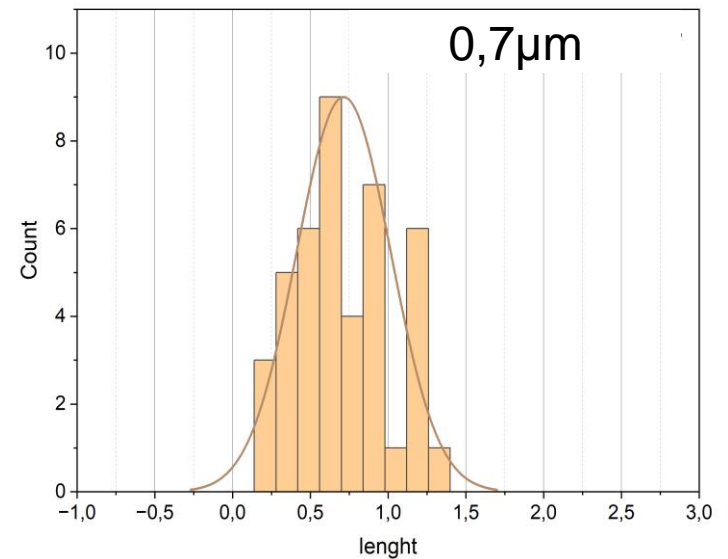
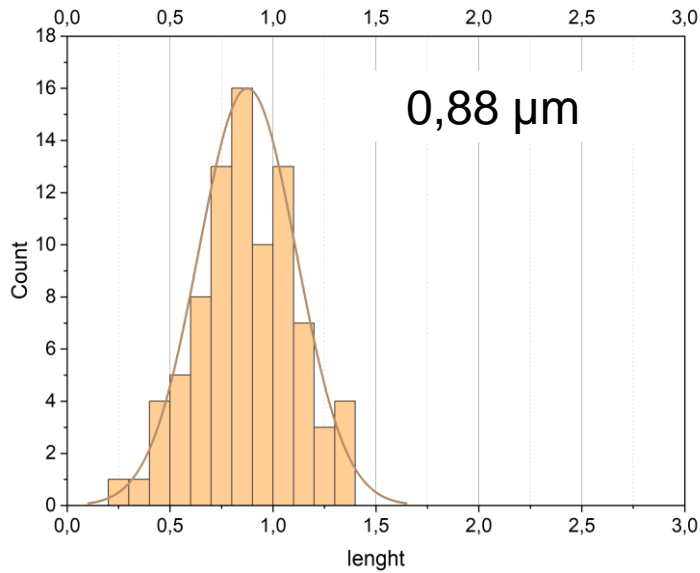
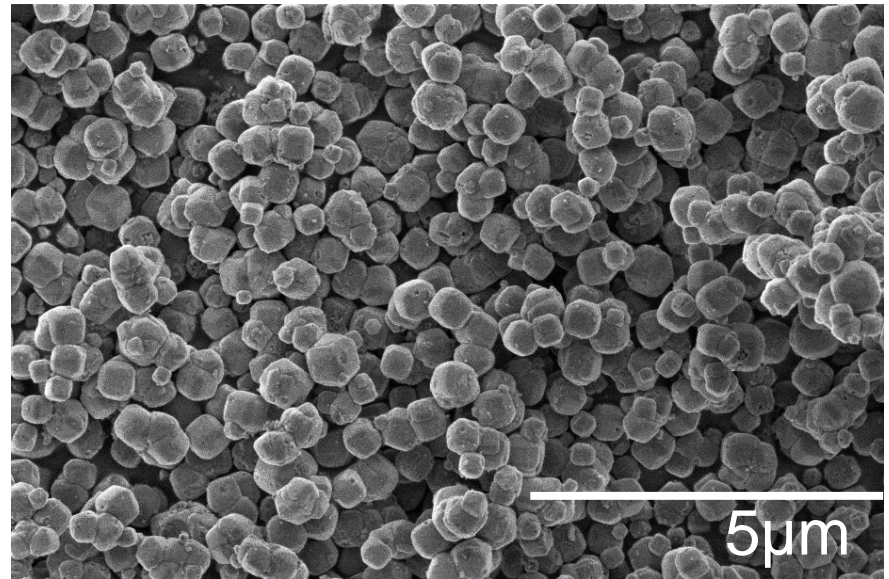
SHT particle size (μm)



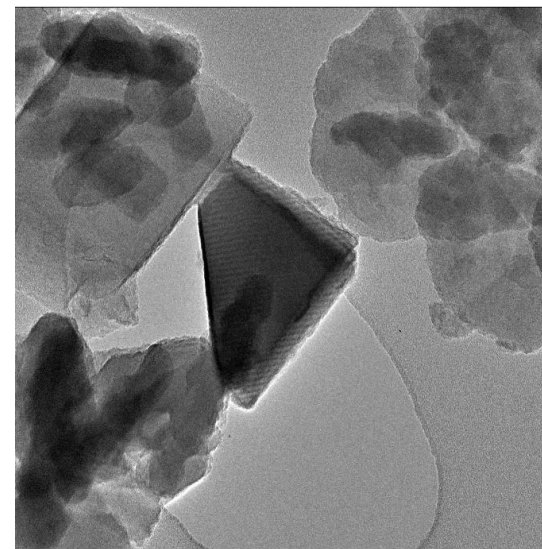
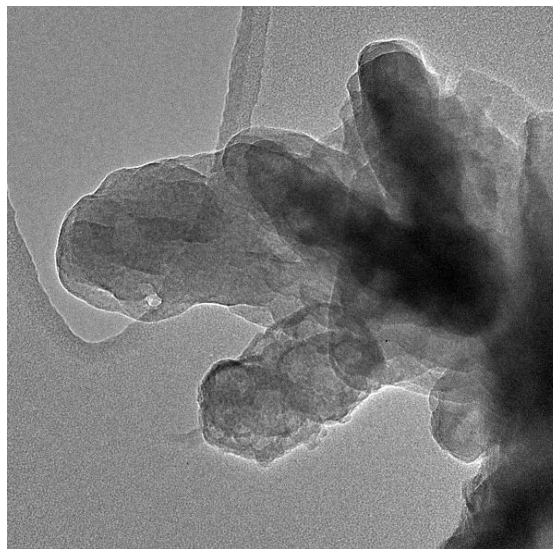
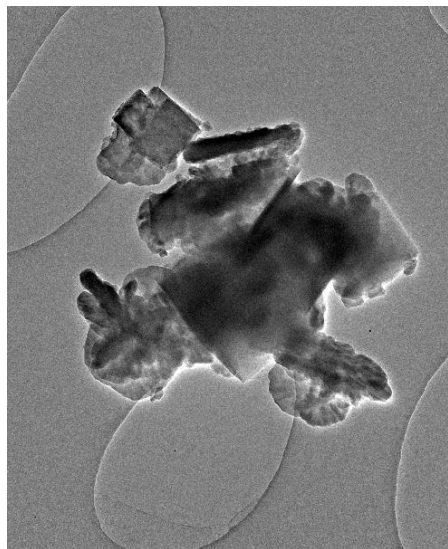
LTA23 : MS(30mins) -SHT(100°C/30mins)



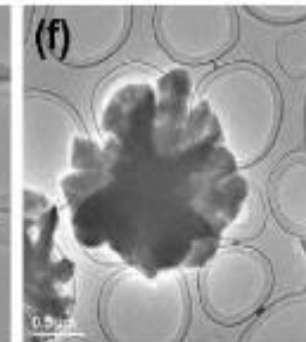
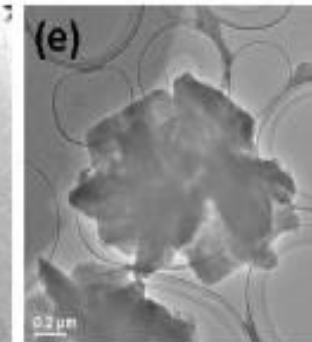
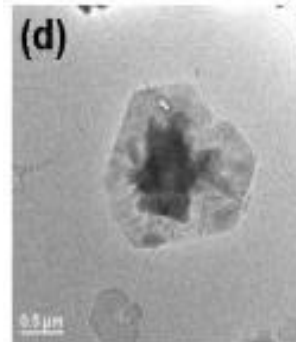
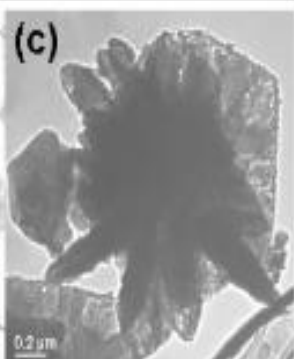
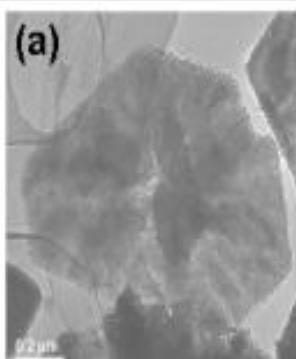
LTA24 : MS(30mins) -SHT(100°C/25mins)



TEM Images



LTA21 : MS(30mins) -SHT(100°C/30mins)



Greer, et al *J. Am. Chem. Soc.* **131**, 17986–17992 (2009).

SHT treatment accelerate the kinetic of LTA conversion into sodalite by factor about 48

Compounds from the SHT reactor are smaller in size



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Influence of acoustic power

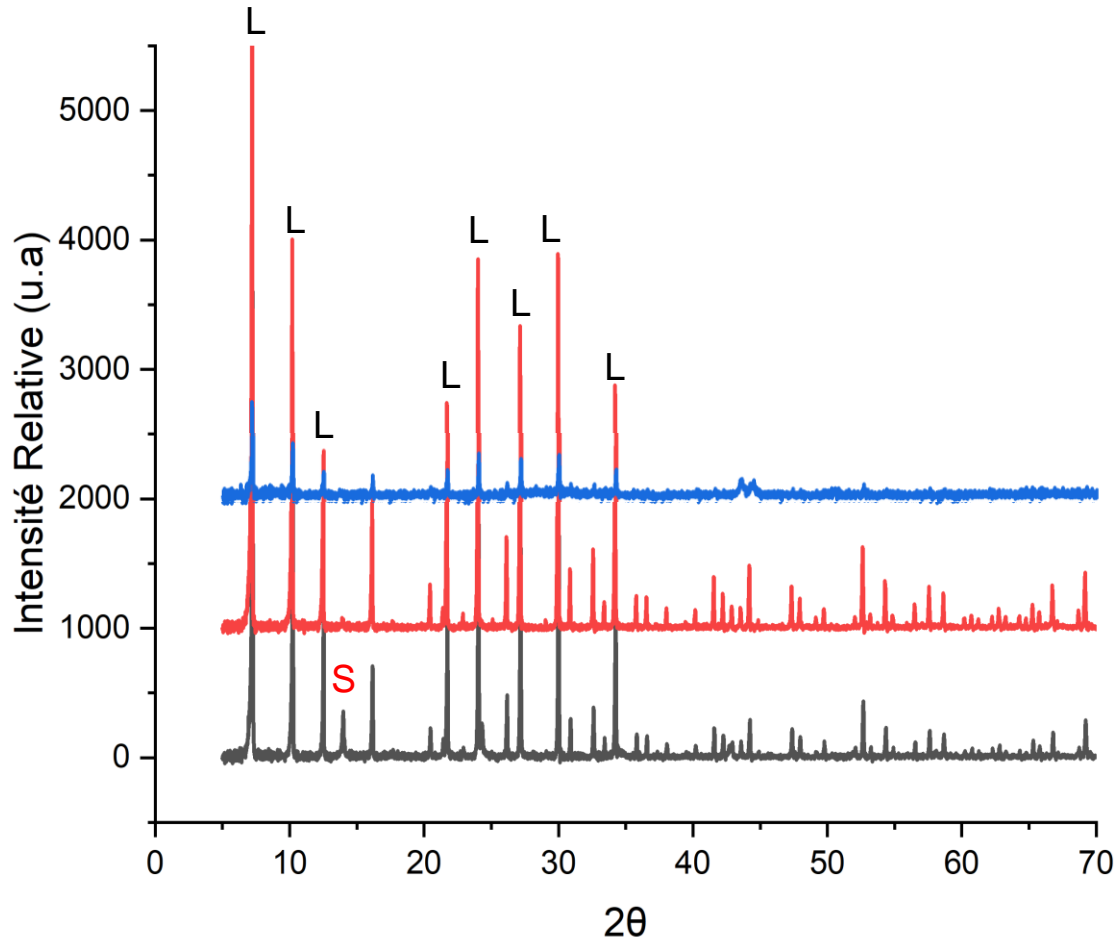
Diffractograms of SHT compounds



SHT 100 °C_1H
Variation in reactor fill rate

L: zéolithe LTA

S: sodalite



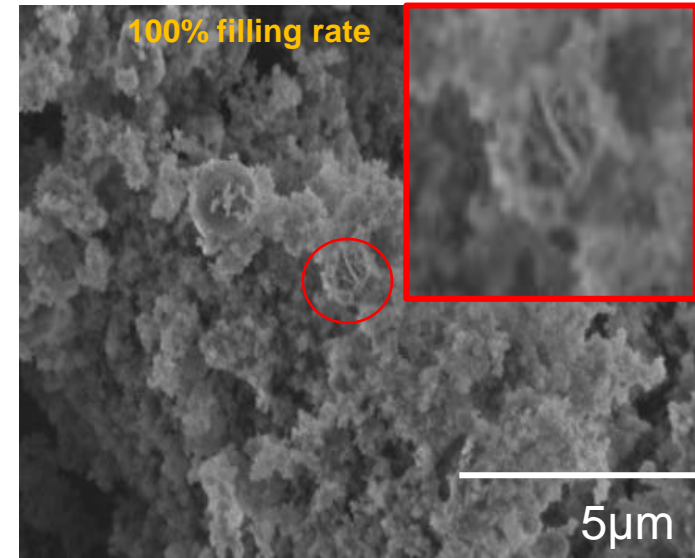
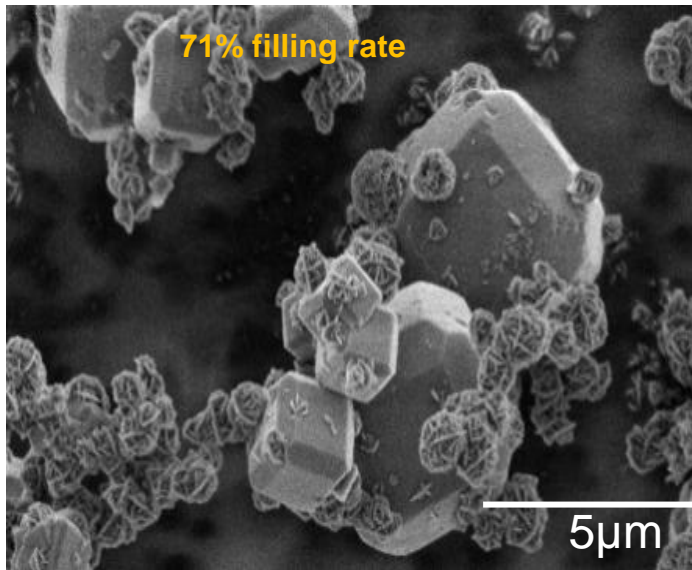
100% filling rate (80mL)

81% filling rate (64mL)

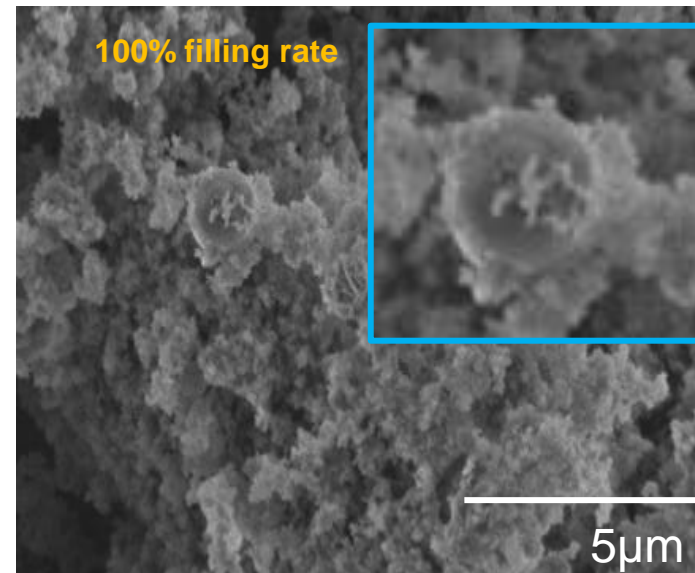
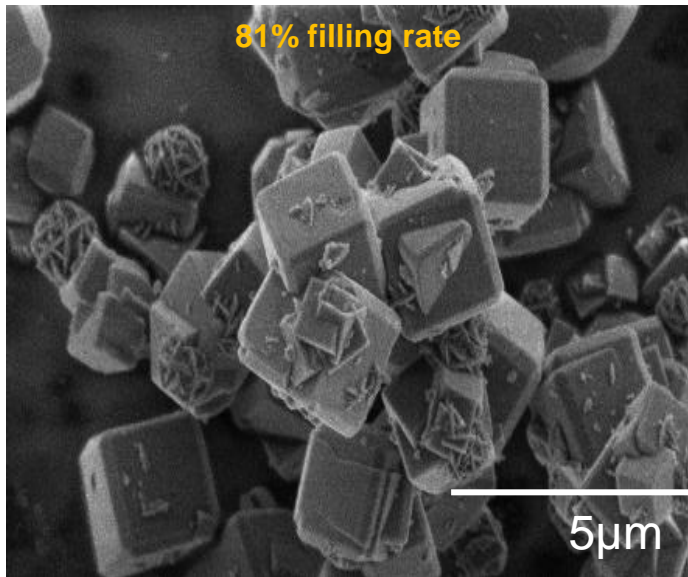
62% filling rate (50mL)

Reduced conversion of amorphous gel to LTA and LTA to sodalite

SEM SHT images 100 °C_1H



SHT 100 °C_1H



Decreasing acoustic power influences the conversion rate of amorphous gel to LTA and of LTA to sodalite



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Le SHT:

- SHT treatment accelerate the kinetic of LTA conversion into sodalite by factor about 48
- SHT treatment has an effect on particle size

Decreasing acoustic power influences the conversion rate of amorphous gel to LTA and of LTA to sodalite



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Merci pour votre attention



Director: Nikitenko Serguei

supervisors:

- Chave tony
- Valange sabine

For SEM image
Lautru Joseph

For TEM image
Le Goff Xavier

William's Nzodom

David-William's.NZODOMDJOZING@cea.fr

Le SHT:

- SHT treatment accelerate the kinetic of LTA conversion into sodalite by factor about 48
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Decreasing acoustic power influences the conversion rate of amorphous gel to LTA and of LTA to sodalite



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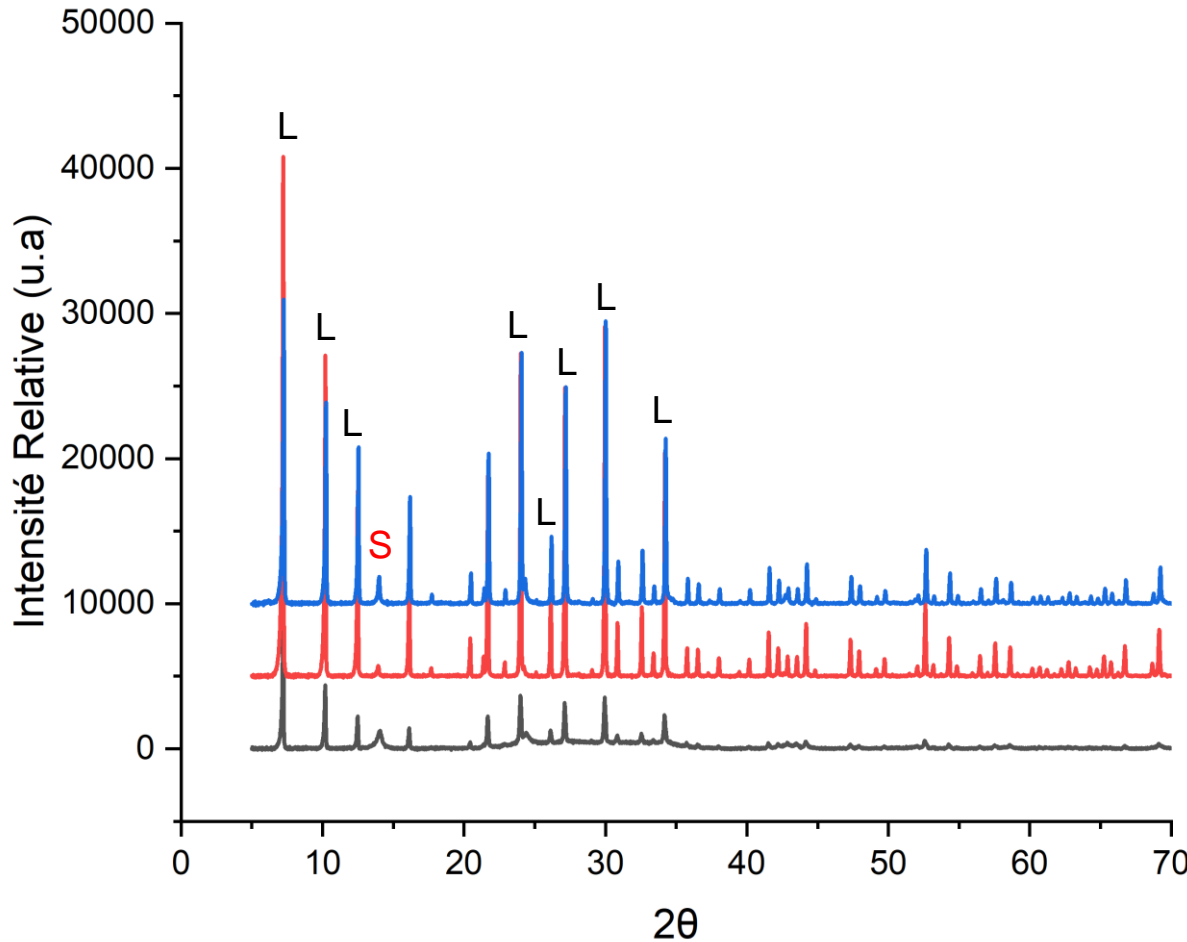
Influence de la densité du gel

Diffractogrammes des composés obtenus en SHT

SHT 100 °C_1H
 Conservation du volume (50mL)
 Variation de la quantité de matière

L: zéolithe LTA

S: sodalite



Forte densité (154 mPa.s)

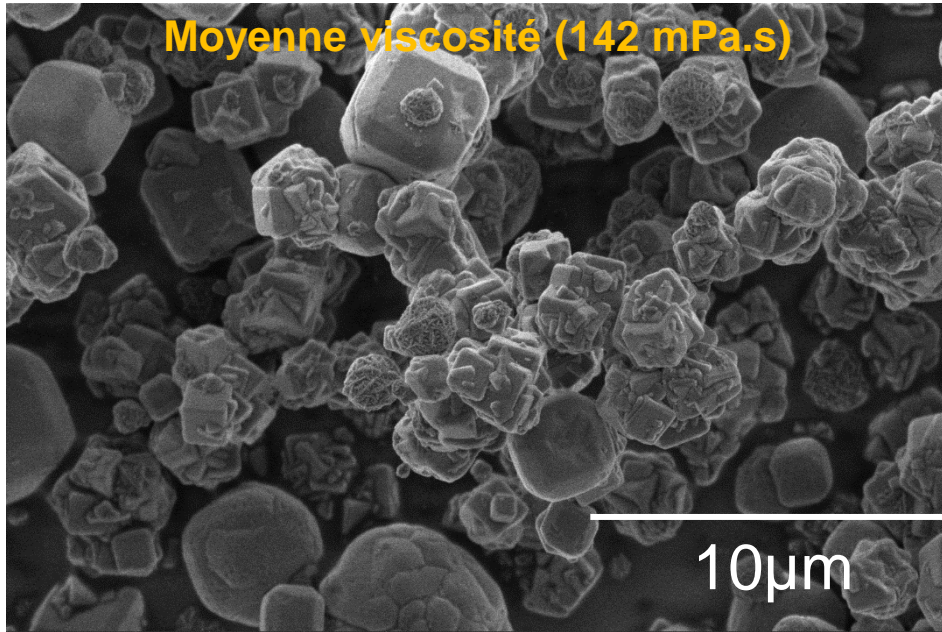
Moyenne densité (142 mPa.s)

Faible densité (93,3 mPa.s)

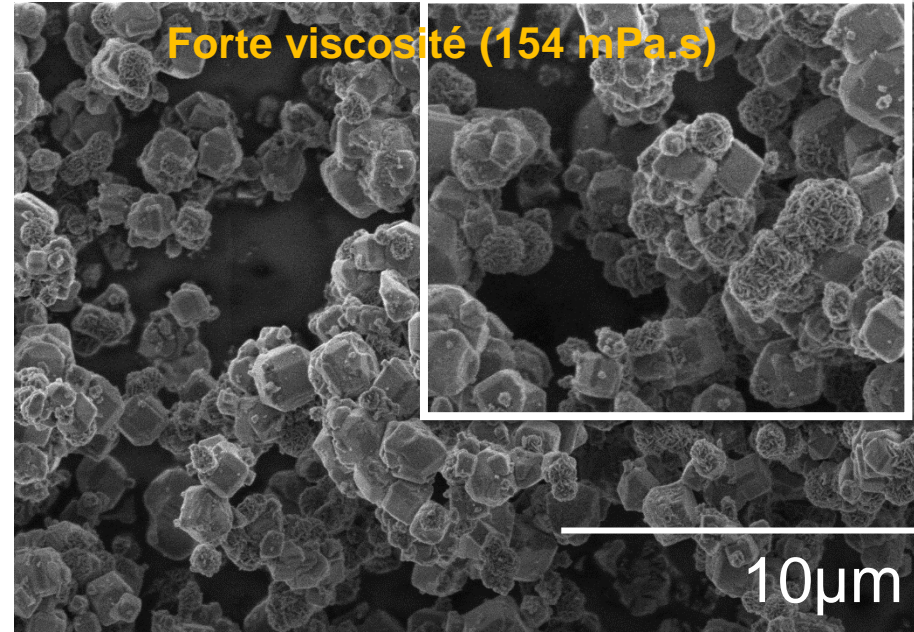
Lorsque la viscosité augmente, le taux de conversion de la LTA en sodalite augmente

SHT 100 °C _1H

Moyenne viscosité (142 mPa.s)



Forte viscosité (154 mPa.s)



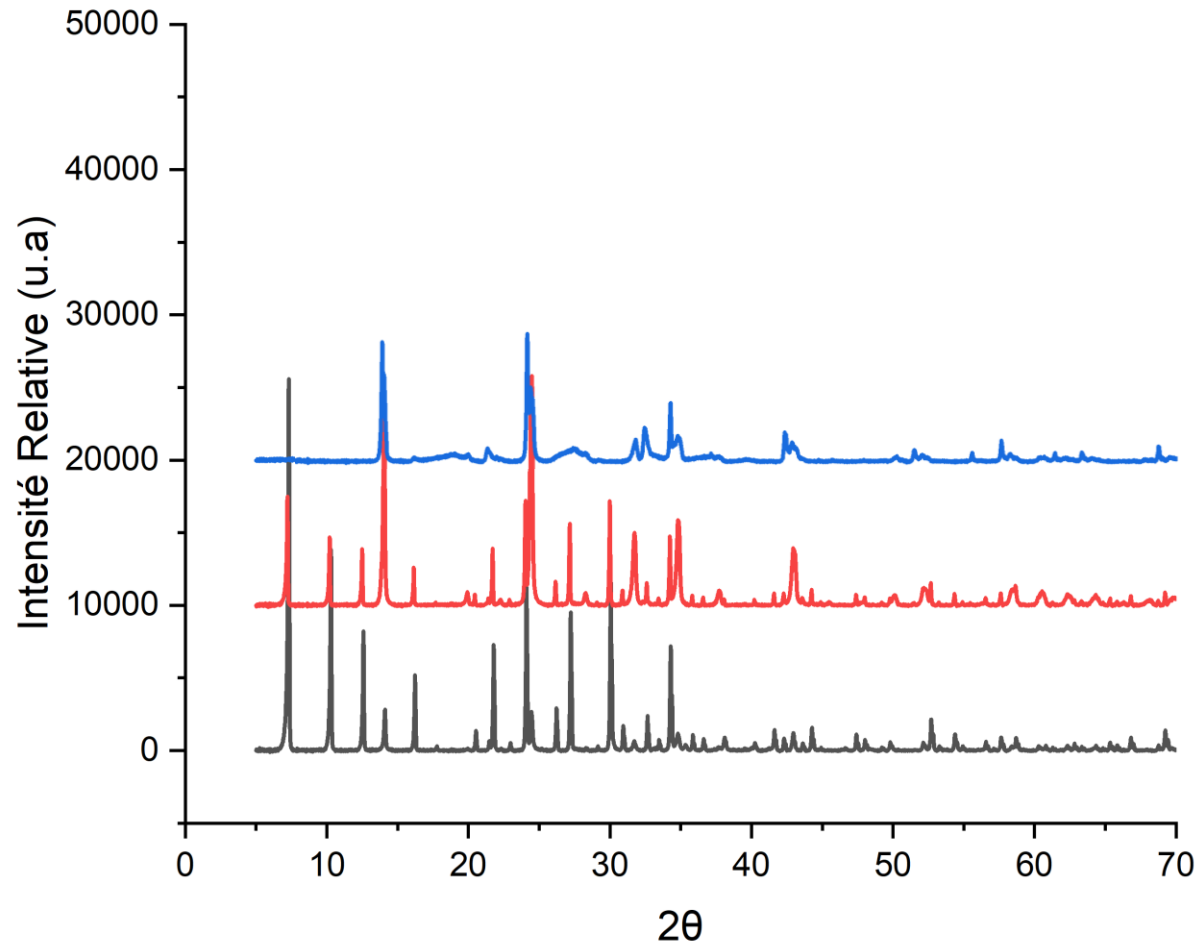
Diffractogrammes des composés obtenus en hydrothermal



HT 150 °C_12H sans agitation
Conservation du volume
Variation de la quantité de matière

L: zéolithe LTA

S: sodalite

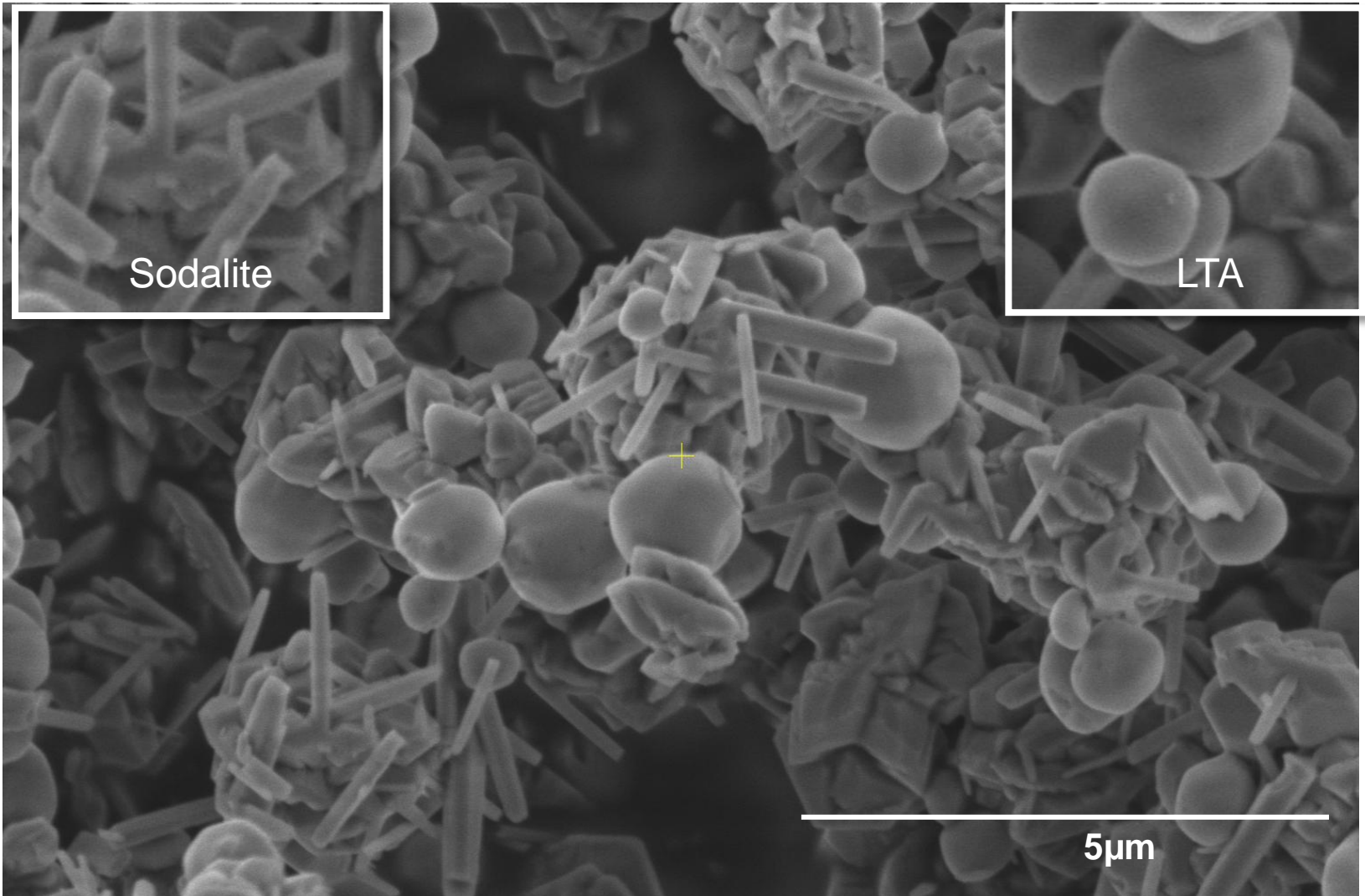


Forte densité (154 mPa.s)

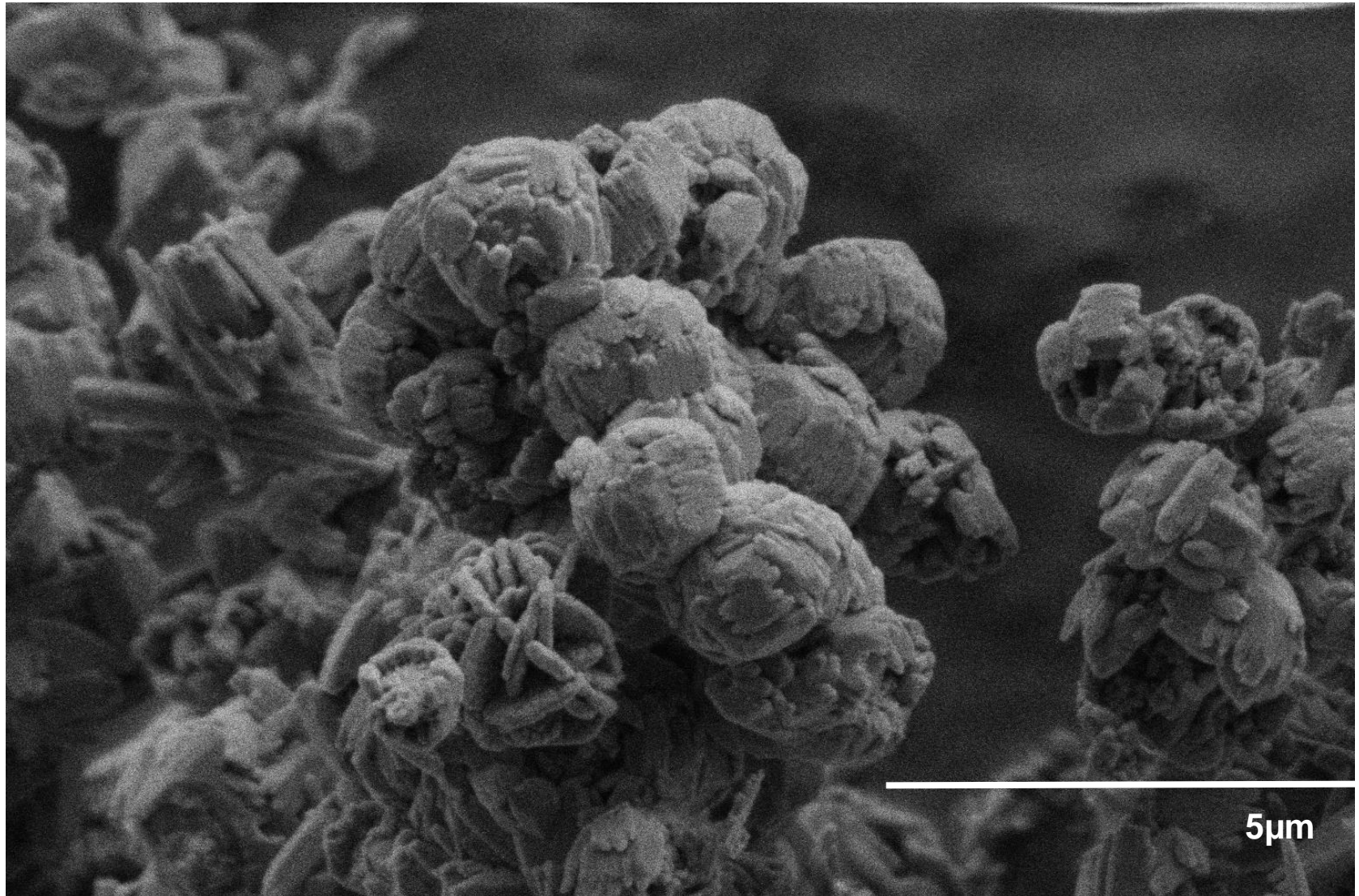
Moyenne densité (142 mPa.s)

Faible densité (93,3 mPa.s)

Lorsque la viscosité est trop importante, la LTA est totalement convertie en sodalite

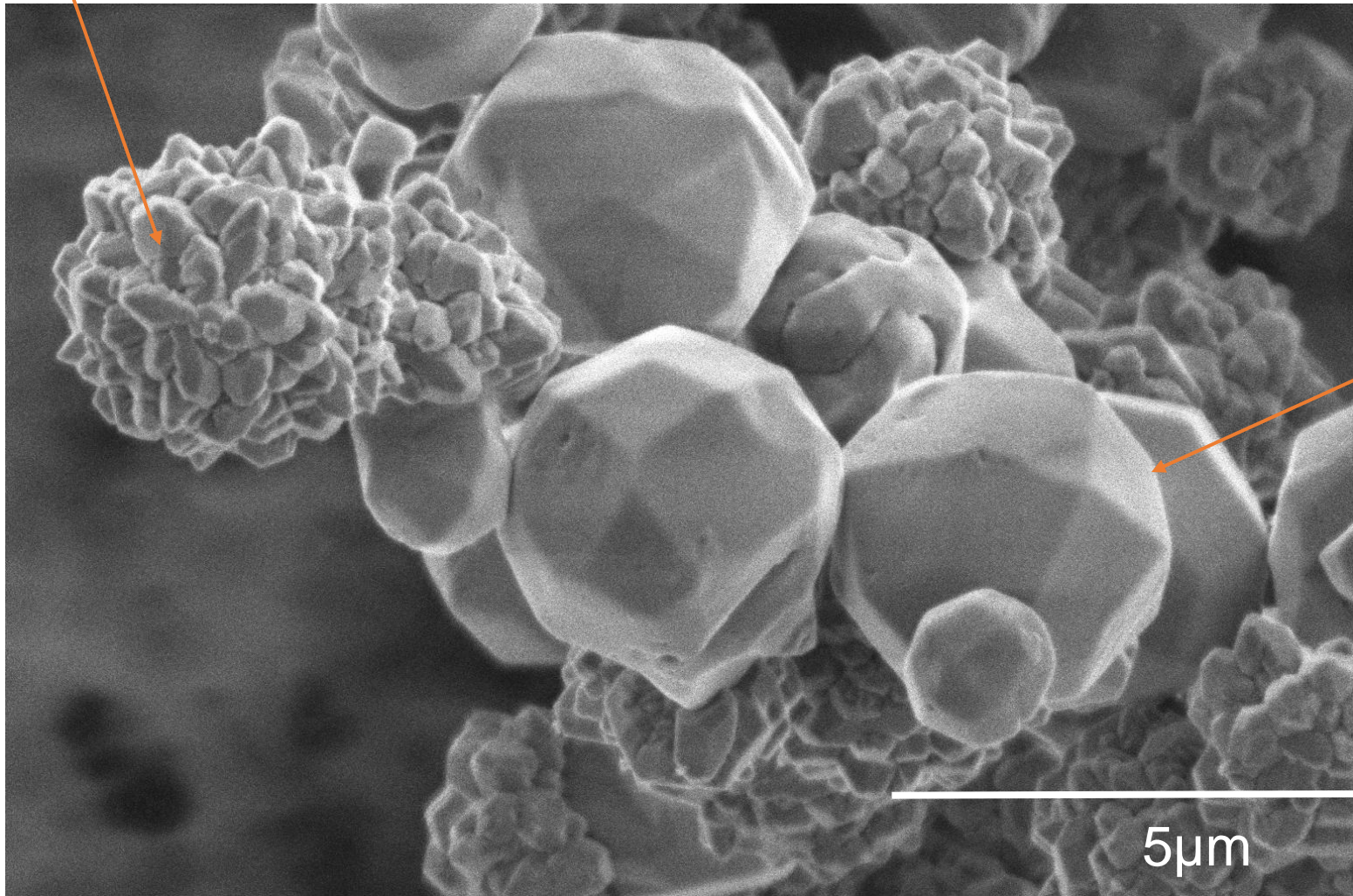


Changement de morphologie de la LTA et de la Sodalite



Sphères creuses de la sodalite

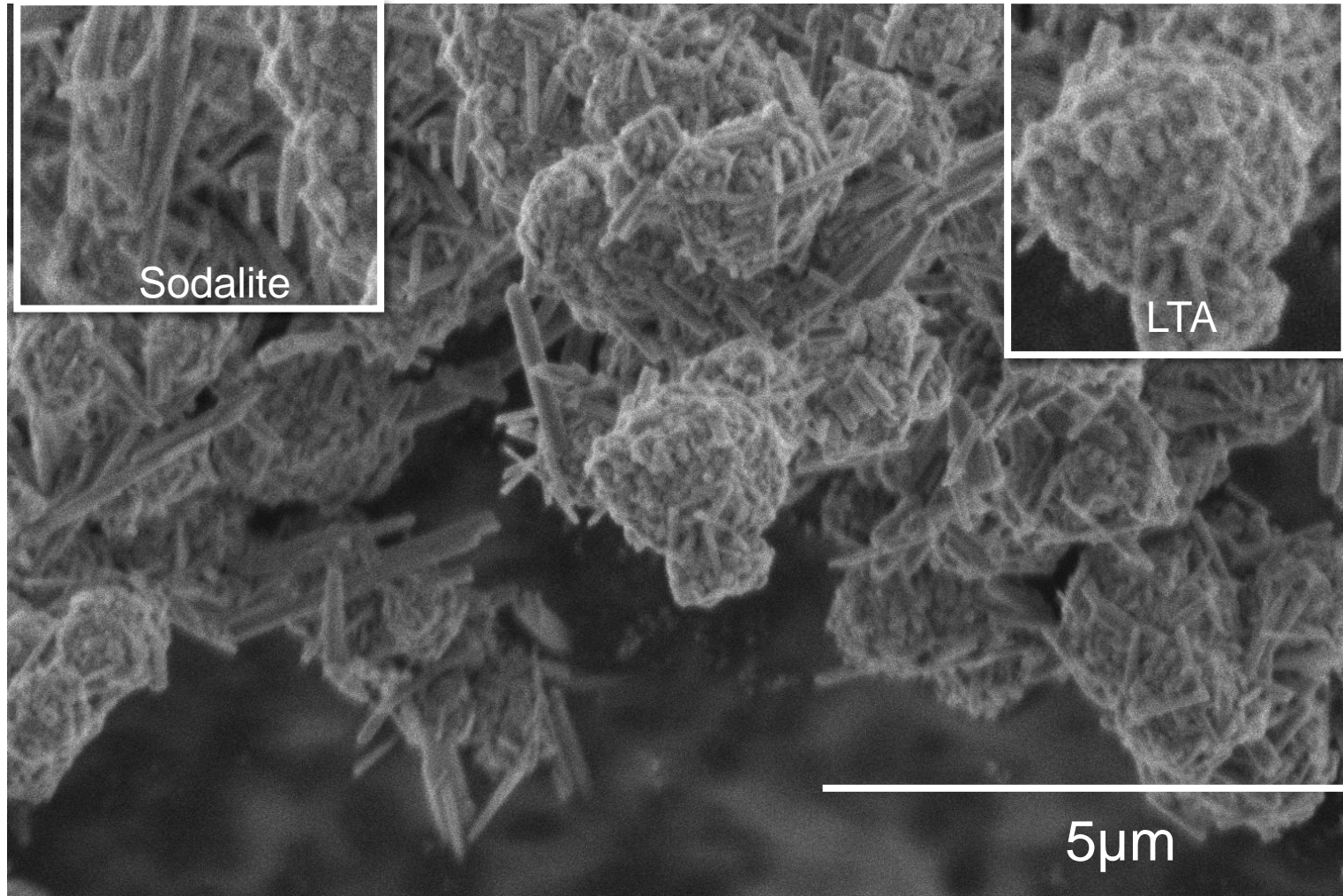
Sodalite

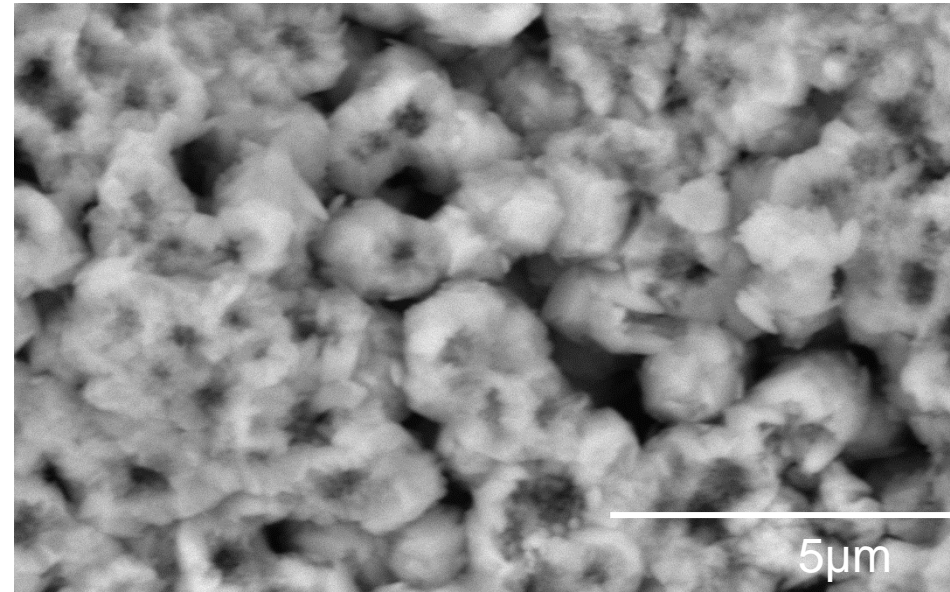
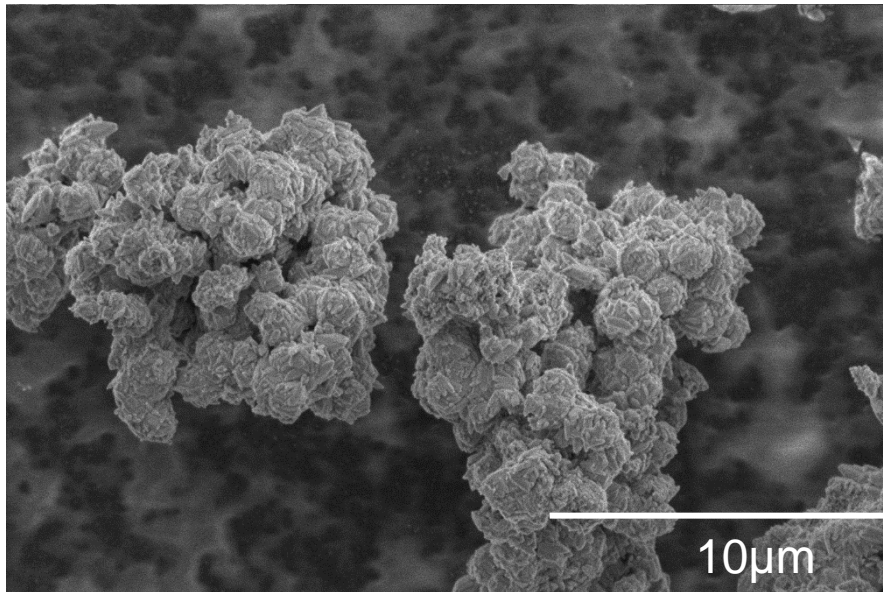


LTA

5µm

Changement de morphologie de la LTA et de la
Sodalite





Mode BSE

Sphère creuse de sodalite

La densité a une influence non négligeable sur la morphologie du composé obtenu en fin de synthèse



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Comment expliquer tous
ces changements?

Nucleation and crystal growth of zeolite A synthesised from hydrogels of different density

Cite this: *CrystEngComm*, 2013, 15, 5784

Ana Palčić,^a Boris Subotić,^a Valentin Valtchev^b and Josip Bronić^{*a}

Various factors affect the process of zeolite formation and thus the characteristics of the ultimate material. The present study is devoted to the influence of the density of the starting aluminosilicate hydrogels, *i.e.* the amount of the solid phase in the system, on the characteristics of the final product. Different density (viscosity) of the five aluminosilicate gels was obtained by changing the ratio SiO₂/H₂O, while the ratios Na₂O/H₂O and SiO₂/Al₂O₃ remained constant. The freshly prepared hydrogels were hydrothermally treated at 80 °C under static conditions. The reaction course was followed by a set of complementary analyses including XRD, chemical analysis, microscopy and thermogravimetry. The linear rate of crystal growth was calculated according to Zhdanov and Samulevich's method. The crystal size distribution curves of the end products were measured and the corresponding curves of nuclei distribution within gel matrix and specific number of crystals were calculated. The observed effect of "local ordered structure" (potential nuclei) formation was commented on from the viewpoint of the autocatalytic nucleation theory.

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www.rsc.org/crystengcomm



Modification du taux de croissance cristalline



Impacter la taille des particule

Scale-up of high performance mordenite membranes for dehydration of water-acetic acid mixtures

Yuqin Li^a, Meihua Zhu^a, Na Hu^a, Fei Zhang^a, Ting Wu^{a,b}, Xiangshu Chen^{a,b,*}, Hidetoshi Kita^b

^a Institute of Advanced Materials (IAM), State-Province Joint Engineering Laboratory of Zeolite Membrane Materials, College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330022, PR China

^b Department of Environmental Science and Engineering, Graduate School Science and Engineering, Yamaguchi University, Tokiwadai 2-16-1, Ube, Yamaguchi 755-8611, Japan



Changement de morphologie de la mordenite lorsque le rapport Si/H₂O diminue



ARTICLE INFO

Keywords:
Mordenite membrane
Scale-up
Reproducibility
Stability
Dehydration

ABSTRACT

Mordenite membranes have been successfully synthesized on 80-cm-long mullite supports by secondary growth method. The morphology and quality of mordenite membrane were greatly affected by fluoride concentration, water content and crystallization mode. Compact and high-flux mordenite membranes were obtained with the addition of NaF in precursor gel, which also exhibited a long-term acid stability for a 90 wt% HAc/H₂O mixture at 75 °C. Typically, 80-cm-long mordenite membrane prepared with transverse crystallization displayed a permeation flux of ca. 0.97 kg m⁻² h⁻¹ and separation factor of ca. 1200 for separating a 90 wt% HAc/H₂O mixture at 75 °C. The pervaporation performance was better than that of membranes prepared with vertical crystallization due to the negligible impact of gravity and temperature gradients. These scaled-up mordenite membranes with high reproducibility showed a promising industrial application for dehydration of water-acetic acid mixtures.



	93,3mPa.S	142mPa.S	154mPa.S
Si/H ₂ O	$9 \cdot 10^{-3}$	0,2	0,4

William's Nzodom

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Le SHT:

- accélération la cinétique de de formation e la LTA ainsi que sa conversion en sodalite
- Réduction de la taille des particules par rapport à la synthèse hydrothermale

La puissance acoustique a un effet sur le taux de conversion du gel amorphe en LTA ainsi que sa conversion en sodalite

La densité du gel influence la morphologie du composé obtenue en synthèse hydrothermale

La variation du rapport $\text{Si}/\text{H}_2\text{O}$ induit une modification de la morphologie des composés obtenus



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