Segmentation and analysis of the porous network of nanomaterials

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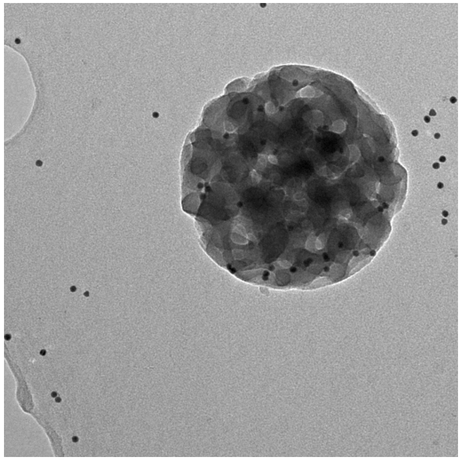
Context

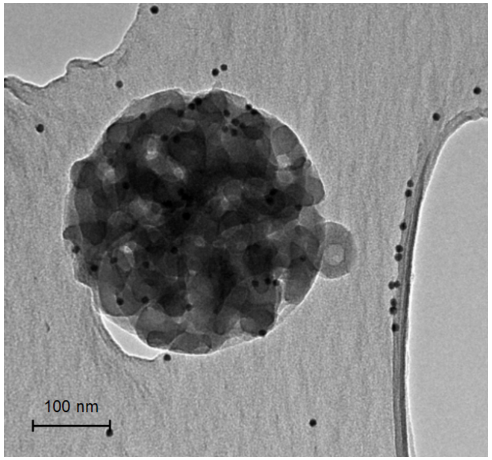
Nowadays, price of barrels rises and quality of oil decreases

More efficient catalytic materials are demanded with higher activities and selectivity
→ precise knowing of the morphology of their texture is required

Context

We focus on macroporous alumino-silicate :
catalytic nano-material used in chemical and petroleum industries





For catalytic cracking of heavy oil, we must be able to predict if a heavy molecule can enter inside the grain of catalysts before cracking

To perform this challenge
→ use of 3D electron tomography and image analysis techniques

Plan

Acquisition

Segmentation

Extraction of the porous volume

Estimation of the macro porosity and of the specific surface area

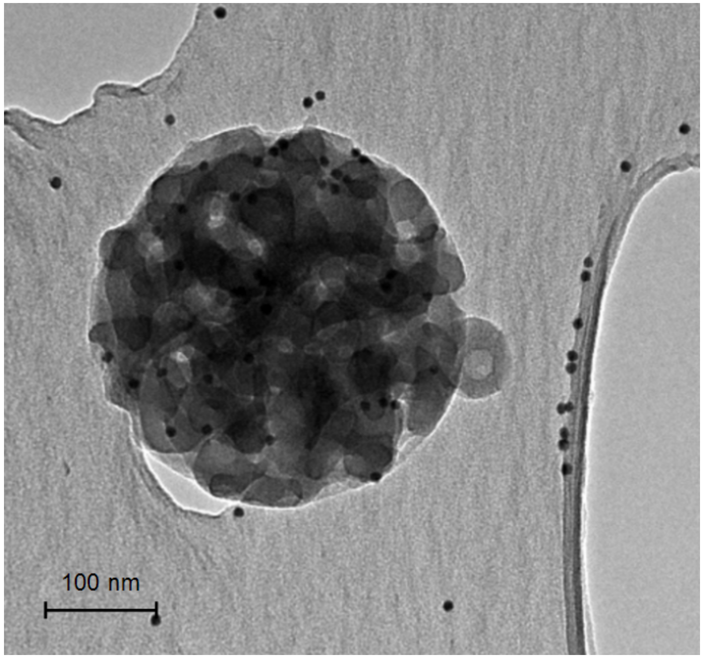
Accessibility to the porous network

Conclusion

Acquisition

Acquisition

Macroporous alumino-silicate catalysts :
aerosol synthesis made of spherical macroporous and mesoporous particles, with microporous alumino-silicate walls *



Diameter: 200 nm to 2 µm

3 samples are studied

* S. Areva, C. Boissière, D. Grosso, T. Asakawa, C. Sanchez, M. Linden, *Chem. Commun.* (2004) 1630-1631

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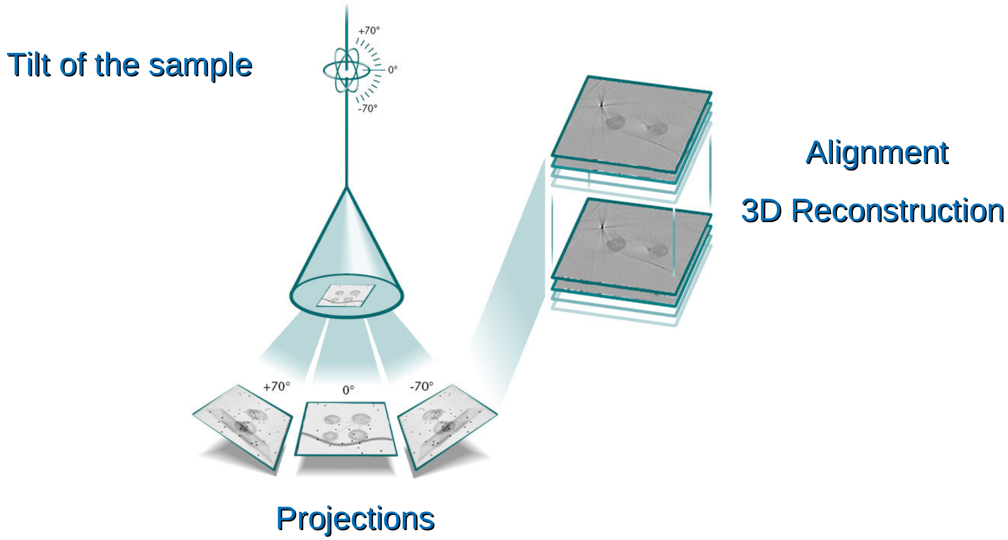
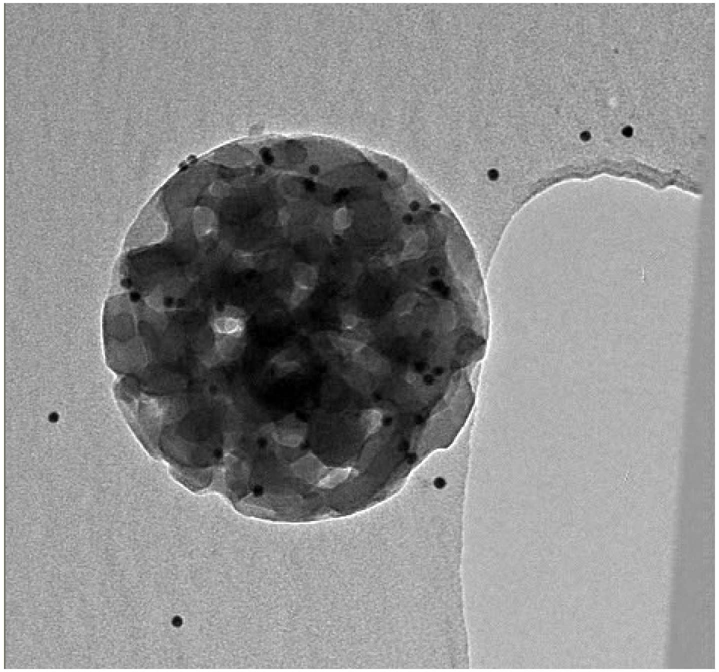
Acquisition

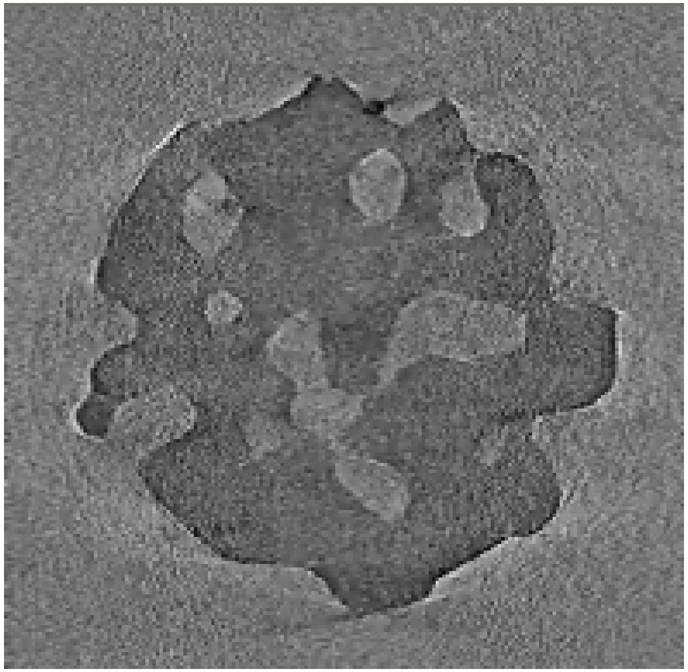
3D-TEM acquisition *:
• automatic TEM bright field images acquisition of series of projections
• semi-automatic alignment of projections by cross-correlation and particles tracking
• tomographic reconstruction by filtered back projection



* Collaboration with C. Crucifix, P. Schultz and O. Ersen from IGBMC and IPCMS Strasbourg France

Acquisition





3D aligned projections

3D reconstructed volume
resolution: 0.5nm/voxel

In the following, for pratical purpose (memory and CPU limitation), sub-sampled volumes are used

Segmentation

Segmentation – pre-filtering

3D images contain noise and reconstruction artifacts due to tomographic reconstruction

Bilateral filter*: non linear and non iterative filter which smooth signal while preserving strong edges

$$O(x) = \frac{1}{k(x)} \sum_{y \in D} f(x-y)\, g(I(x)-I(y))\, I(x) \qquad k(x) = \sum_{y \in D} f(x-y)\, g(I(x)-I(y))$$

$$f(x) = g(x) = \begin{cases} \frac{1}{2}\left[1-\left(\frac{x}{\sigma}\right)^2\right]^2 & |x| \le \sigma \\ 0 & otherwise \end{cases}$$

Tukey's biweight function

Linearization of the filter and use of direct convolution**
→ low memory consuming and fast computation

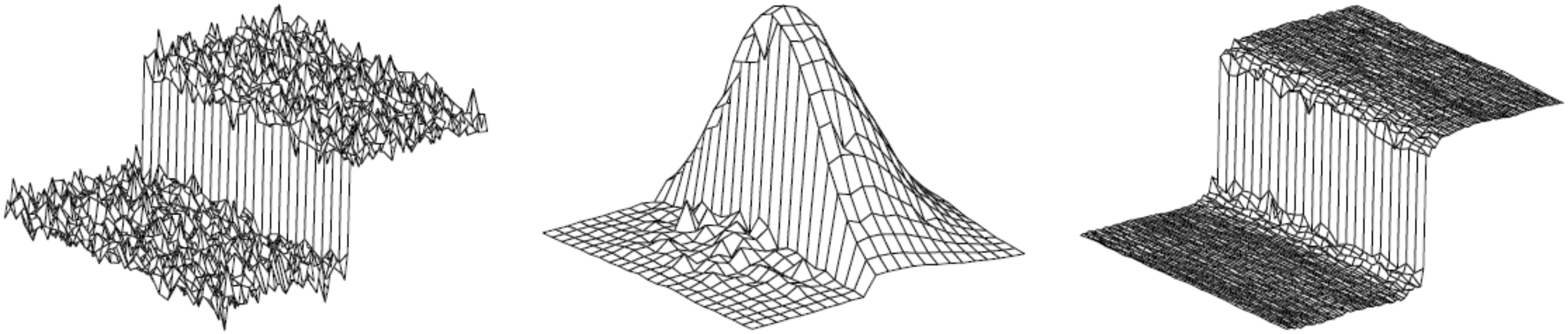
Parameters : σ=2 and 20 for f and g respectively

*C. Tomasi, R. Manduchi, Bilateral filtering for gray and color images, *Proc. of International Conference on Computer Vision, IEEE* (1998), 839-846

**T.Q. Pham, L.J. Van Vliet, Separable bilateral filtering for fast video preprocessing, *International Conference on Multimedia and Expo, IEEE* (2005)

Segmentation – pre-filtering

Bilateral filter : illustration



(a) (b) (c)

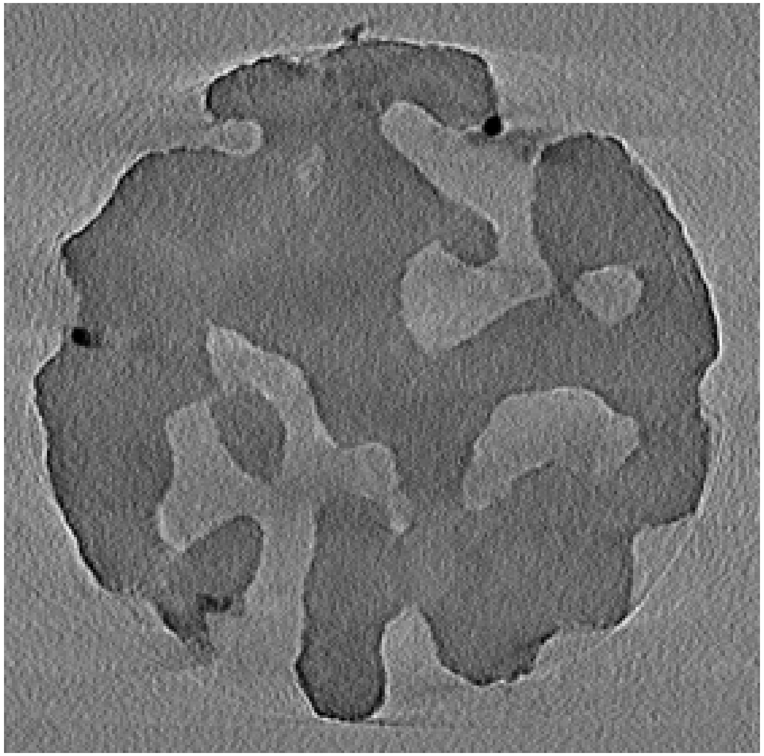
(a) Image 23x23 pixels of transition of 100 grey levels with Gaussian noise with σ=10

(b) Weights combination of f(x,y)g(I(x)-I(y)) for a point x located to the center of the image on the edge. The filter smooths the nearby pixels without these located after the edge

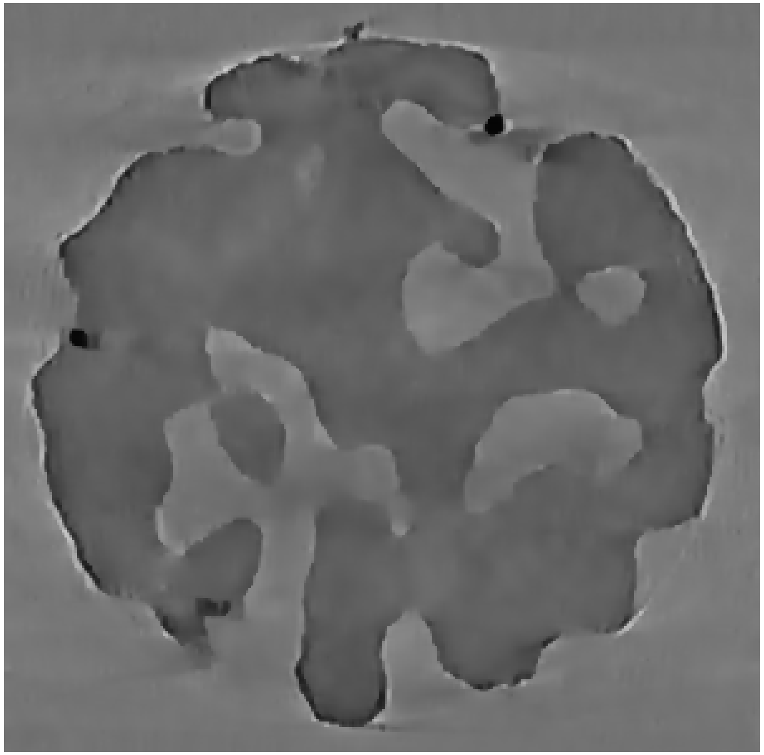
(c) Result with Gaussian function for f and g and with σf=5 and σg=50.

Segmentation – pre-filtering

Results:



initial



bilateral filter

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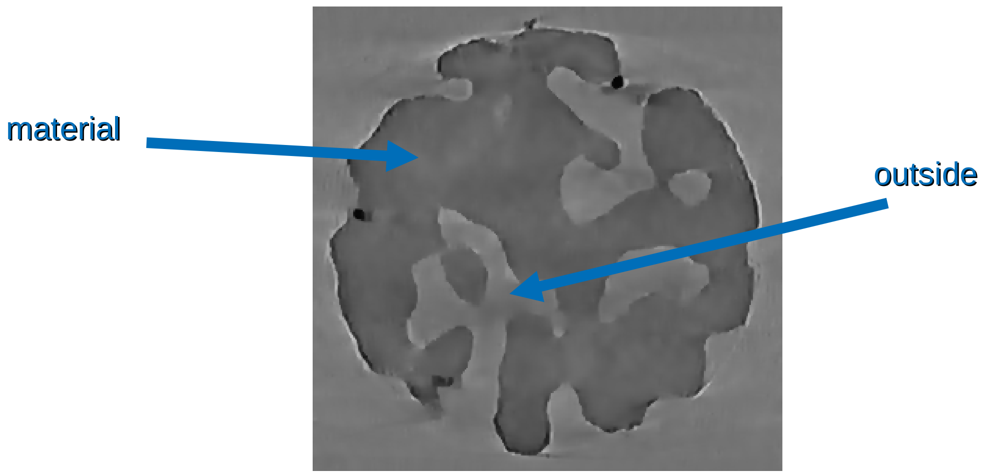
Segmentation

After pre-filtering :
material → dark grey voxels, set not homogenous
outside → light grey voxels, set not homogenous



→ segmentation with two steps:
• analysis of the histogram to determine approximately markers for the two sets
• propagation of these markers by means of watershed operator

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Segmentation - markers

- Detection of flat zone by means of recursive Gaussian filters *

Flat zone = low values of the norm of smooth gradient

- Disconnection of the flat zone (markers with small volume)

- Markers → material, outside or indeterminate.

Classification : voxels values and mean values of the flat zone

Automatic analysis of the histogram

$$M_{in} = \bigcup_{D} p \,\middle|\, I(p) < t_{in}$$

$$t_{in} = \max_{t \in [0,M]} t \left| \sum_{i=0}^{t} h(i) \leq f_{in} . \sum_{j=0}^{t_{MIV}} h(j) \right.$$

$$M_{out} = \bigcup_{D} p \,\middle|\, I(p) > t_{out}$$

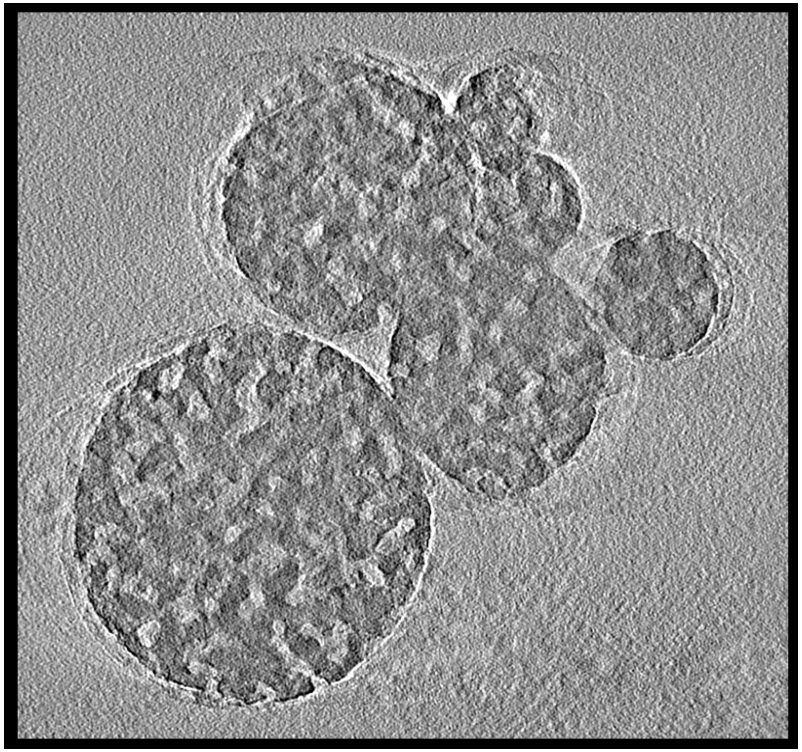
$$t_{out} = \min_{t \in [0,M]} t \left| \sum_{i=0}^{t} h(i) \geq \sum_{j=0}^{M} h(j) - f_{out} . \sum_{k=t_{MIV}}^{M} h(k) \right.$$

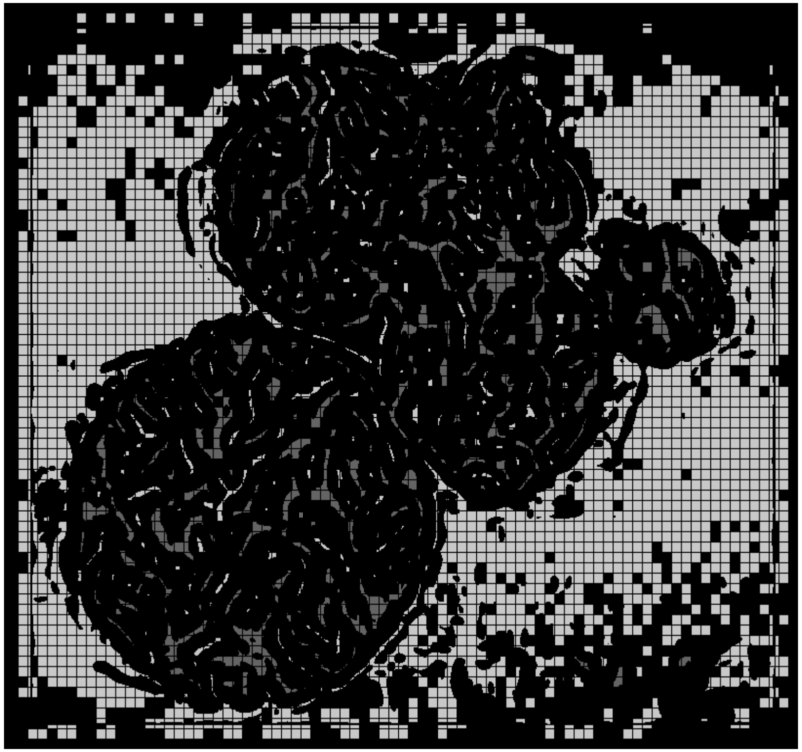
t_{MIV} : automatic threshold by maximization of interclass variance

$f_{in}=f_{out}=0.7$: fraction of voxels that belongs surely to the material and the outside respectively

* R. Deriche, Recursively implementing the Gaussian and its derivatives, *Technical Report 1893, INRIA* (1993).

Segmentation - markers

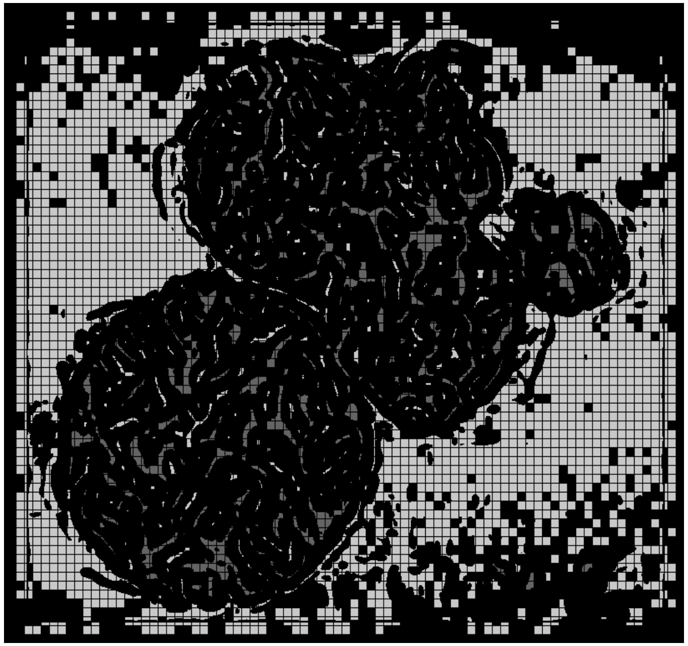


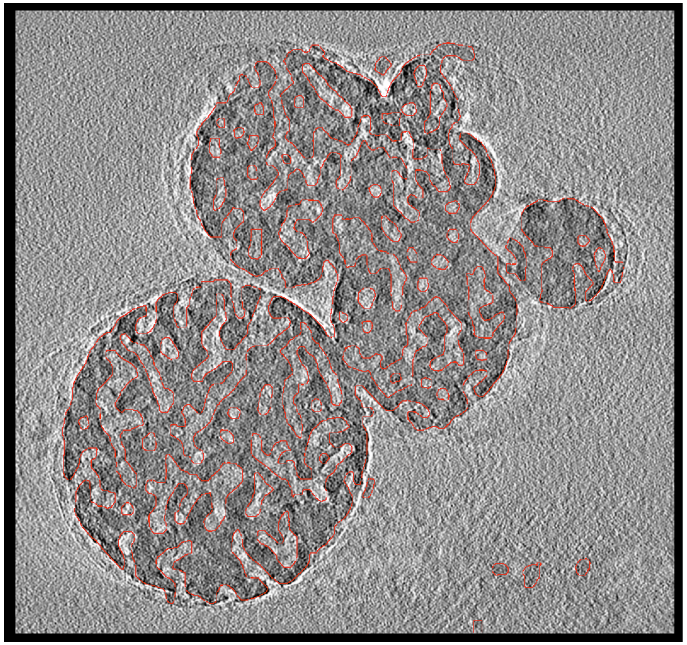


Segmentation - propagation

Markers propogation : marker controlled watershed operator*

Contour function : norm of gradients calculated by recursive derivative Gaussian filter with σ=2**





*S. Beucher, Unbiased Implementation of the Watershed Transformation based on Hierarchical Queues. *CMM Internal note, Paris School of Mines* (2004)

**R. Deriche, Recursively implementing the Gaussian and its derivative, Rapport de recherche n°1893, Programme 4 Robotique, Image et Vision, INRIA, 1993

Extraction of the porous volume

Extraction of the porous volume

→ automatic method using morphological mathematic tools

First step : calculation of the maximum diameter of pores *maxdiam*
→ estimation of the convex envelop by means of morphological close of infinite size

$$ConvEnv = \varphi\infty(SegMat)$$

→ geodesic constrained distance propagated from the material within the outside

$$DistOut = d_{SegMat^c}(SegMat)$$

→ *maxdiam* = maximum of the distance inside the convex envelop

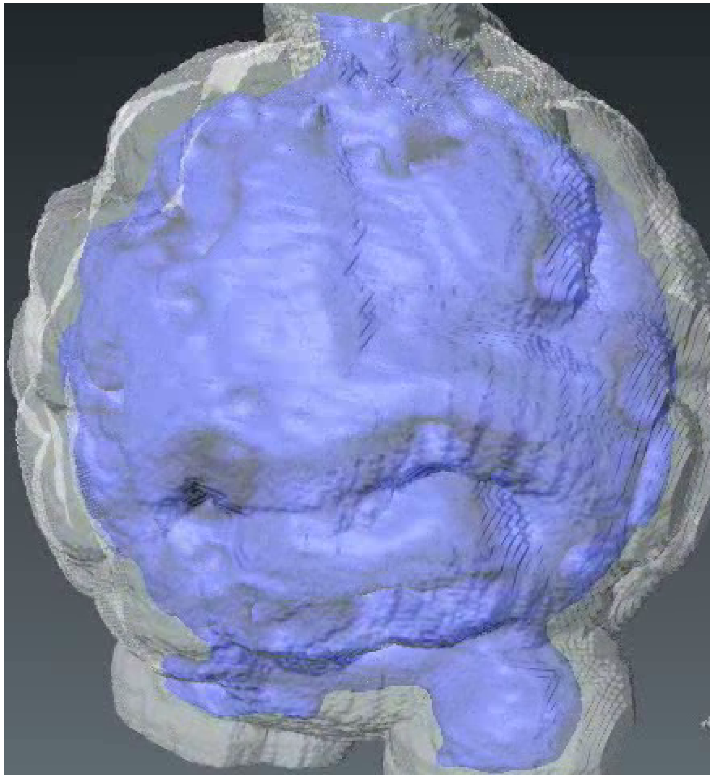
$$maxdiam = max\{DistOut(p) \mid p \in ConvEnv\}$$

Extraction of the porous volume

Second step : extraction of porous volume

→ filling all pores of the material (geodesic dilation of size *maxdiam*)

$$DilSegMat = \delta_{SegMat^C}^{(maxdiam)}(SegMat)$$



Extraction of the porous volume

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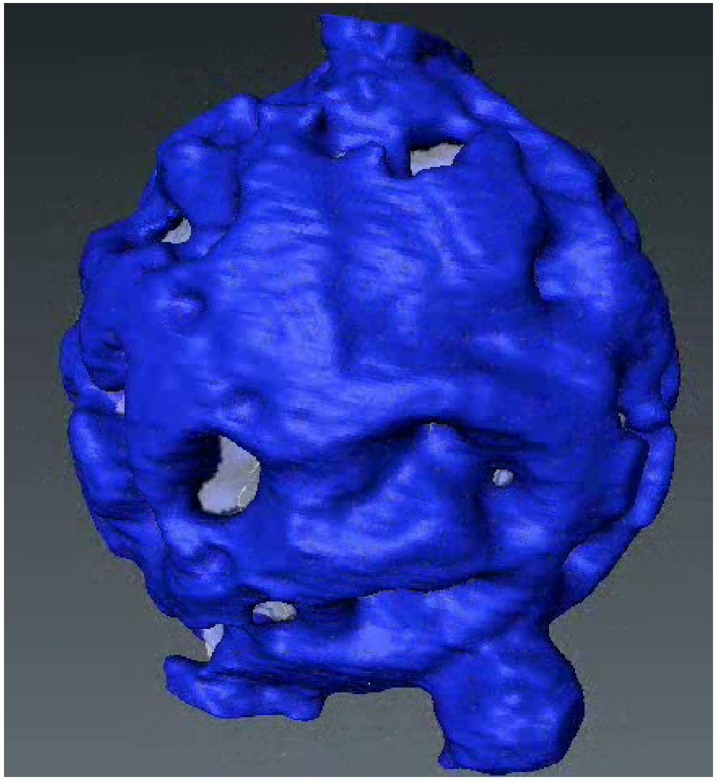
$$DilSegMat = \delta_{SegMat^C}^{(maxdiam)}(SegMat)$$

→ underestimation of the porous volume but restoration of the surface irregularity of the material (geodesic erosion of size k.*maxdiam*)

$$EroDilSegMat = \varepsilon_{SegMat^C}^{(k.maxdiam)}(DilSegMat)$$



Extraction of the porous volume

Second step : extraction of porous volume

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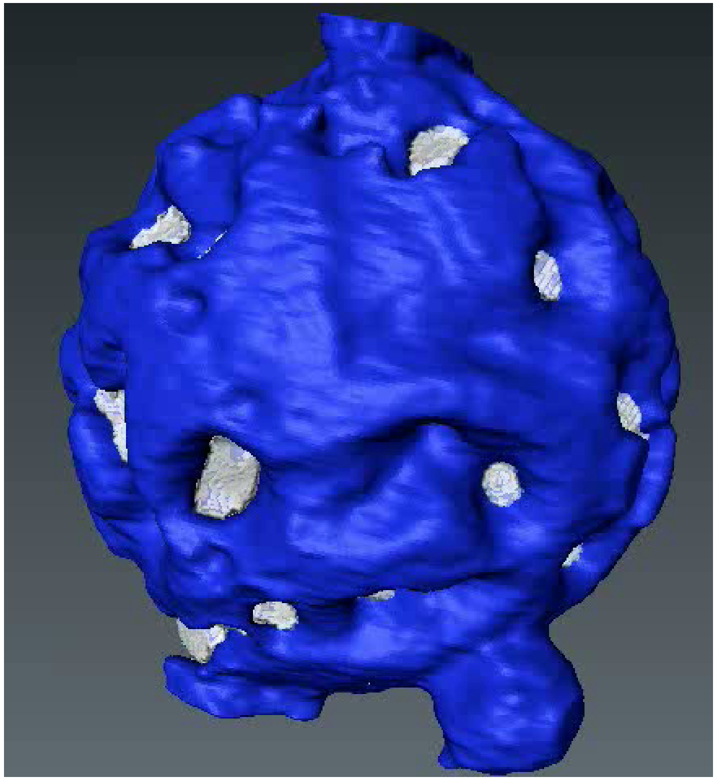
$$DilSegMat = \delta_{SegMat^C}^{(maxdiam)}(SegMat)$$

→ underestimation of the porous volume but restoration of the surface irregularity of the material (geodesic erosion of size k.*maxdiam*)

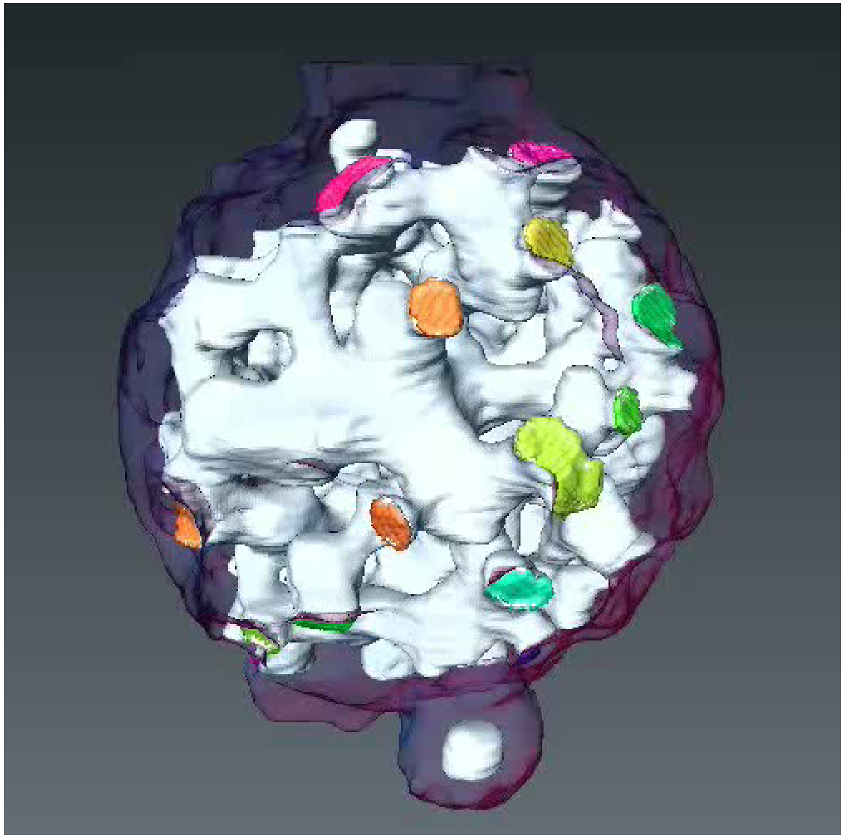
$$EroDilSegMat = \varepsilon_{SegMat^C}^{(k.maxdiam)}(DilSegMat)$$

→ accurate extraction of the porous volume (geodesic dilation of size (k-1).*maxdiam*)

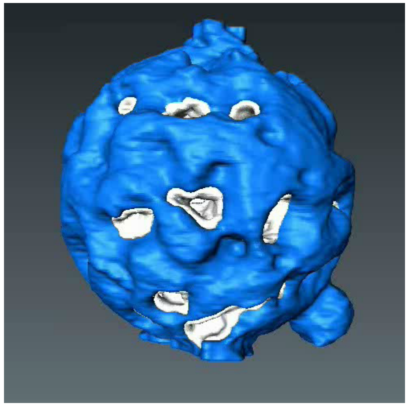
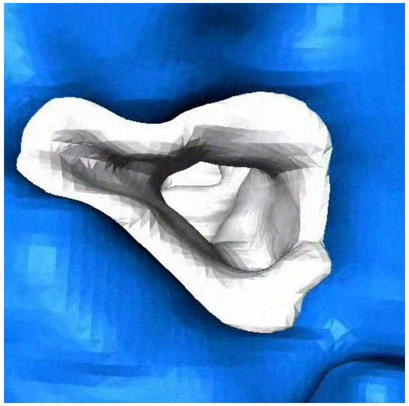
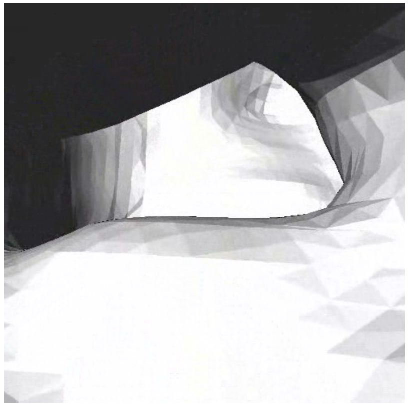
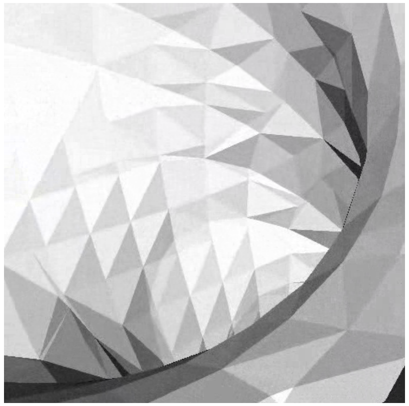
$$PorousVol = \delta_{SegMat^C}^{((k-1).maxdiam)}(EroDilSegMat)$$



Extraction of the porous volume



Extraction of the porous volume

Estimation of the macro porosity and of the specific surface area

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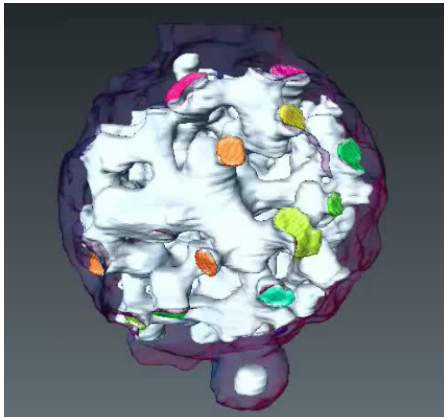
Porosity – specific surface area

Porosity : counting of voxels of the extracted porous volume

Specific surface area : covering of the volume and local estimation*

Sample	Resolution (nm/voxel)	Porosity (cm^3/g)	Specific surface area (m^2/g)
1	2.24	0.299	28.4
2	1.68	0.238	24.4
3	7.18	0.474	37.3
Average		**0.337**	**30**



density : $1.2 g.cm^{-3}$

Results close to classical physical techniques:
Porosity (two methods) : 0.25 – 0.19 cm^3/g
Specific surface area by BET: 31 m^2/g

* Surface area estimation of digitized 3D objects using weighted local configurations, J. Lindblad, Image and Vision Computing 23 (2005) 111-122

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Accessibility to the porous network

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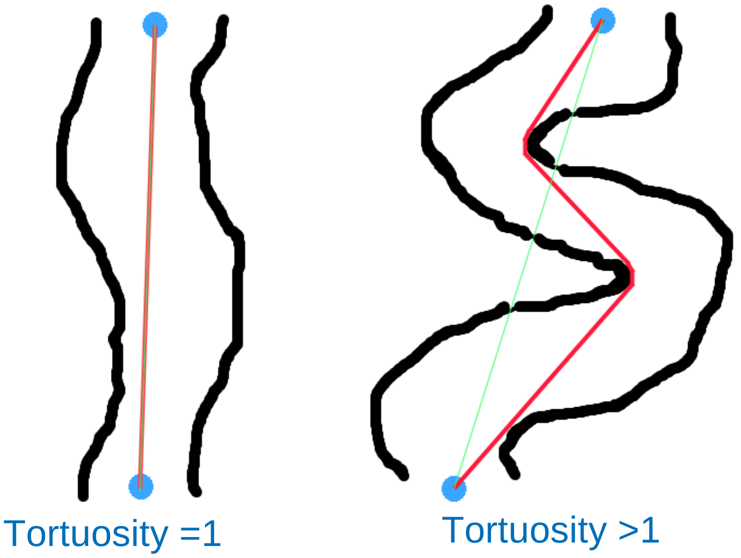
Accessibility - method

Estimation of the accessibility from a pore to one other for a molecule of a known size
→ creation and analysis of a pore-to-pore tortuosity map

$$\text{Tortuosity} = \frac{\text{Geodesic distance}}{\text{Euclidean distance}}$$



Pore-to-pore tortuosity map - construction

Euclidean distance between two pores :
distance between the two barycenters of their emerged surface

Geodesic distance between two pores :
• calculation of 3D skeleton by means of 3D curve thinning method*

$$SkP = \mathrm{3DThinning}(PorousVol)$$

• valuation of the skeleton by the local section of the pores: use of the valuated skeleton by ultimate erosion

$$SkP = \delta^{maxdiam}(\mathrm{UEskeleton}(PorousVol))\Big|\mathrm{p} \in SkP$$

• connection between the skeleton and the external surface of emerged pores

$$SkP = \delta^{maxdiam}_{PorousVol}\left(Surf_{ExtPore}\right) \cup SkP$$

* C. Lohou, G. Bertrand, A 3D 6-subiteration curve thinning algorithm based on P-simple points, *Discrete Applied Mathematics* 151 (2001), 198-228

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Pore-to-pore tortuosity map - construction

• for each pore, propagation of a constrained geodesic distance

$$\text{Dist}_{\text{pi}} = d_{SkP}\left(Surf_{ExtPore}^{pi} \right)$$

• the geodesic distance between two pores is calculated by averaging the distance observed on the emerged surface

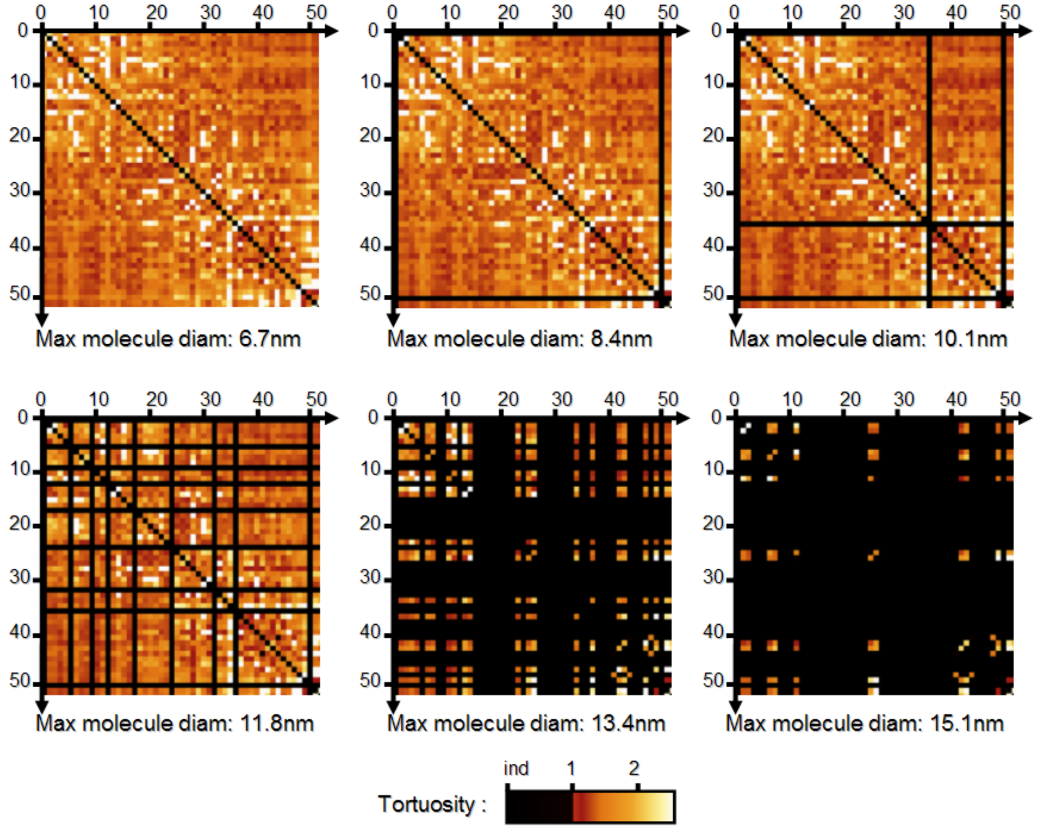
$$\text{distGeo}_{\text{pi-pj}} = \overline{Dist_{pi}(p)} \,\Big|\, p \in Surf_{ExtPore}^{pj}$$

Pore-to-pore tortuosity map : ratio between $\text{distEuc}_{\text{pi-pj}}$ and $\text{distGeo}_{\text{pi-pj}}$ for all possible combinations of pi-pj

Deletion of points p of SkP where SkP(p) = s :
equivalent to fill all the pores with minimum section diameter s
→ obtention of pore-to-pore tortuosity map for molecules with diameter ≥ s

Accessibility - results

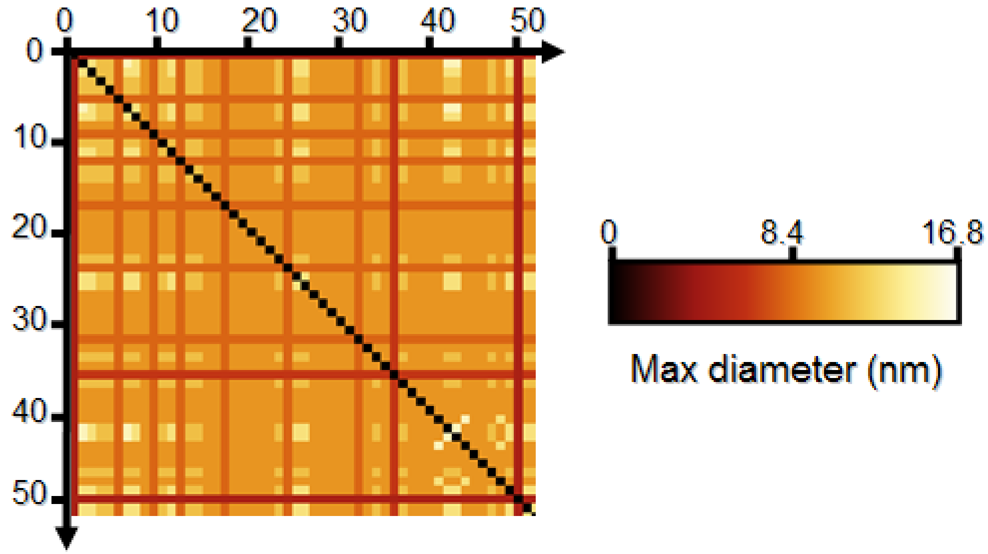
Pore-to-pore tortuosity maps for given sizes of molecules



Sample 2

Accessibility - results

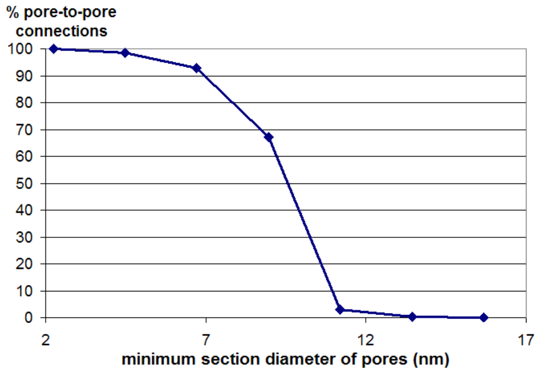
Maximum diameter of molecule before the cutting of a connection
→ pore-to-pore maximum size molecule accessibility map



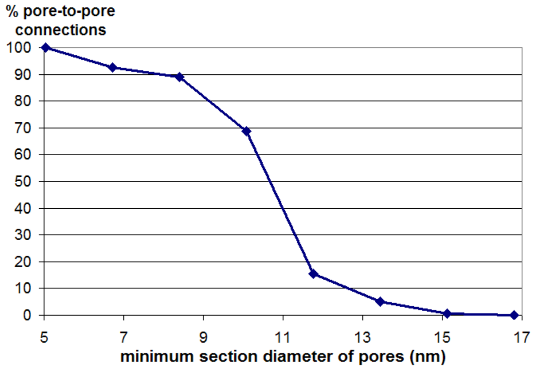
Sample 2

Accessibility - results

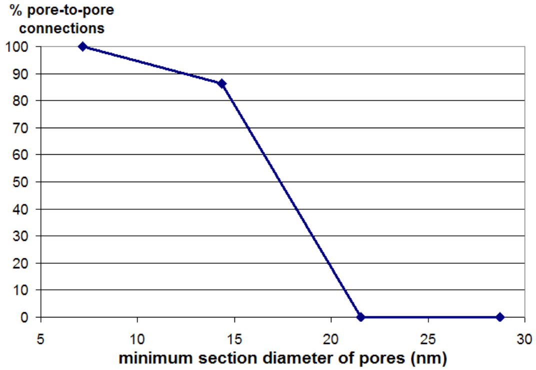
Percentage of interconnections between pores where molecules of a given diameter can go throught the entire material



Sample 1



Sample 2



Sample 3

For the 3 samples :
100% of interconnections can be crossed by molecules with Ø < 5nm like asphaltenes

For the samples 1 and 2 :
50% of interconnections can be still crossed by molecules with Ø <10nm
For the sample 3 :
50% of interconnections can be still crossed by molecules with Ø <17nm

Conclusion

Conclusion

Application of segmentation techniques for 3D-TEM images of macroporous alumino-silicate

Automatic extraction of the porous network keeping intact the surface irregularity

Validation by comparison of measurements of porosity and specific surface area with image analysis and global physical methods

Powerful characterization by means of the analysis of the porous network using a pore-to-pore tortuosity map

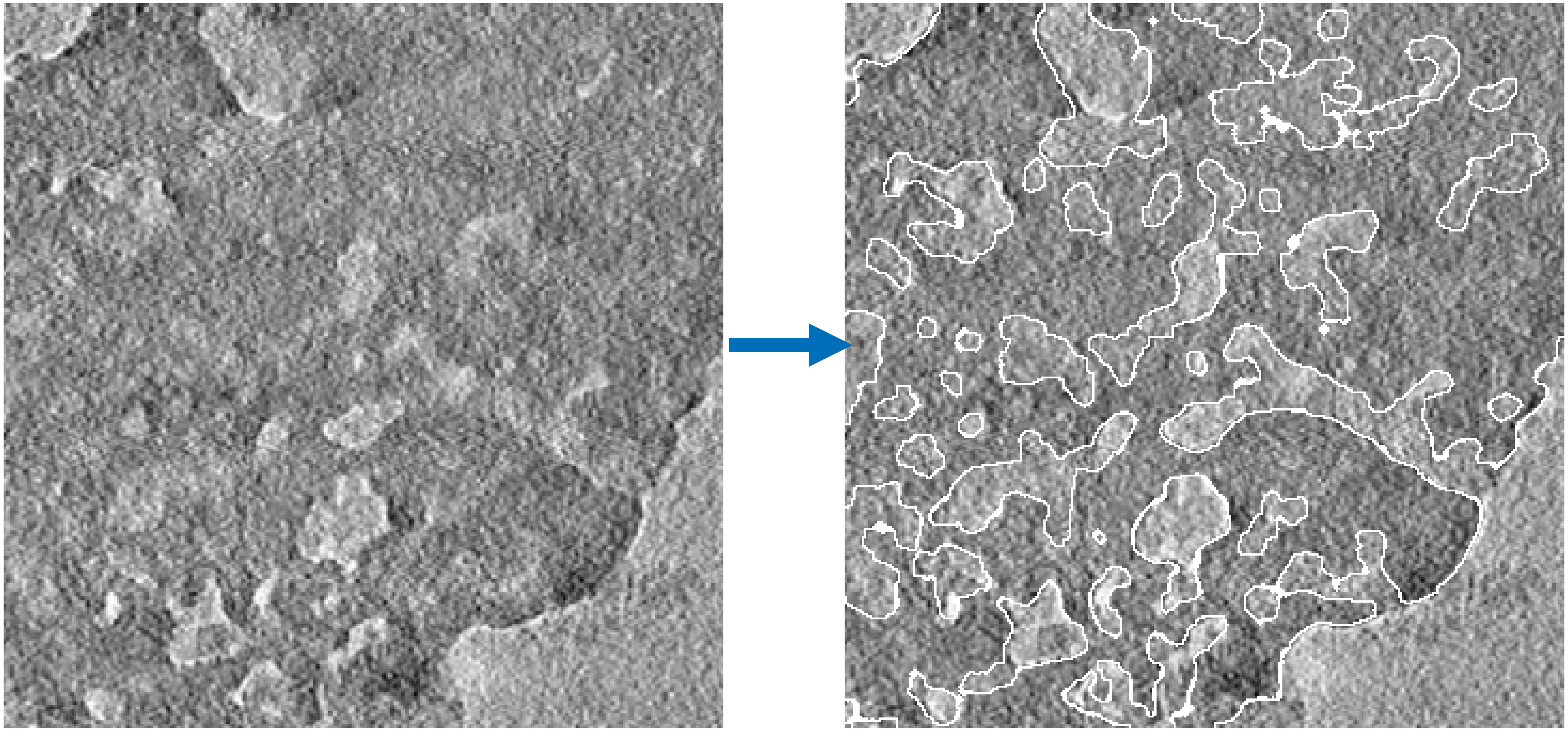
Such analysis are adaptable to other catalyst materials observed by 3D-TEM images (work in progress)

For further details, see:

M. Moreaud et al., Analysis of the Accessibility of Macroporous Alumino-Silicate Using 3D-TEM Images, Materials Science and Technology (MS&T) 2008, October 5-9, 2008, Pittsburgh, Recent Advances in Structural Characterization of Materials.

Conclusion

Other catalyst materials observed by 3D-TEM images (work in progress)



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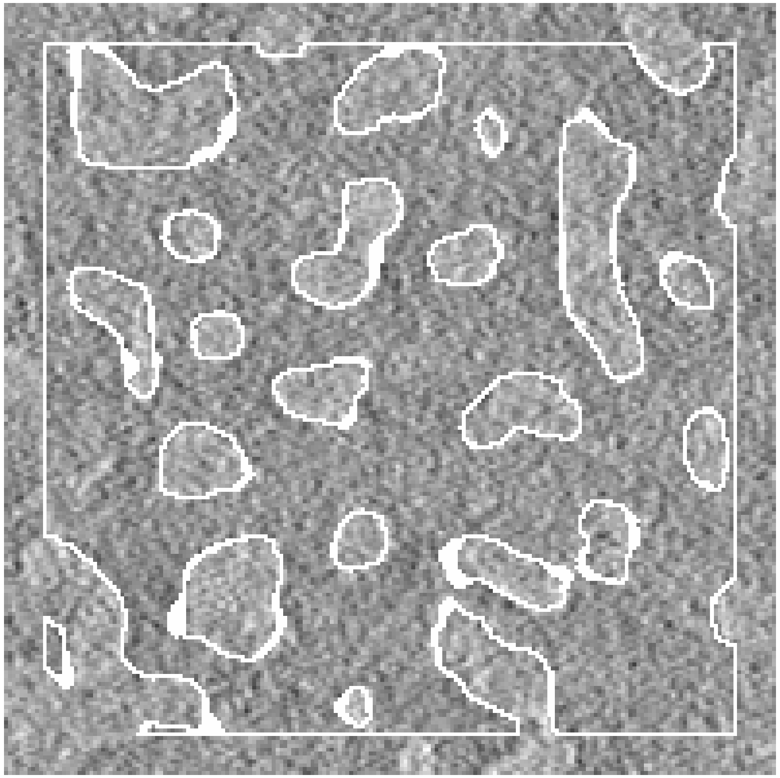

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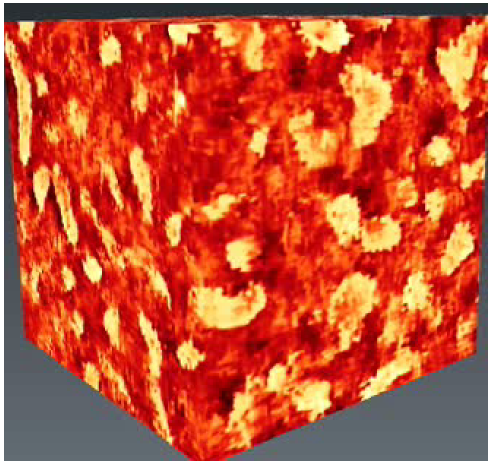

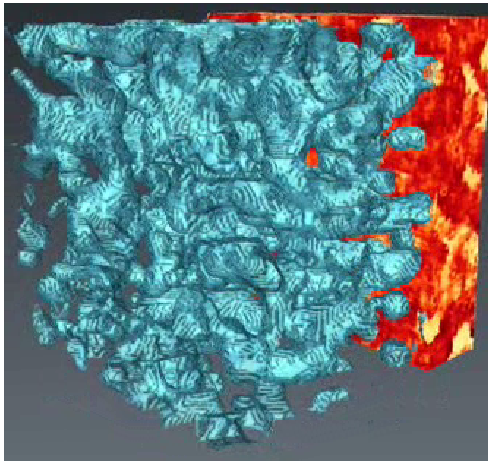

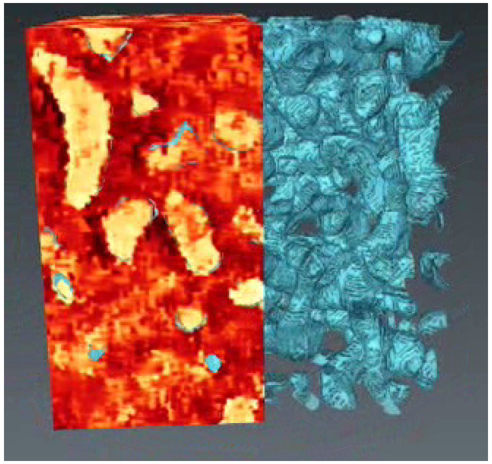

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Thank you for your attention

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