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Special issue: **Focus on SOLEIL for catalysis**

SOLEIL synchrotron is a large scale research infrastructure located on the Plateau de Saclay near Paris, designed to give scientists access to advanced experimental tools using synchrotron radiation, **from infrared to X-rays**. These instruments include multimodal and multiscale structural and spectroscopic methods, with three-dimensional imaging and time-resolved operation down to a picosecond.

Experiments at Synchrotron SOLEIL deal with a wide range of topics and are supported by in-house research that develops the most relevant methods for the users. Building strong collaborative partnerships, such as the one with IFPEN since 2012, is a way for SOLEIL to increase its impact. Starting with a collaboration around **catalysis and X-ray absorption**, this partnership has proven to be exemplary. It has been extended to include new methods and themes, bringing even more benefits to both parties.

This issue takes a look at some key results concerning catalysts stemming from this productive collaboration that has just been renewed. The aim is now to make even more progress in strategic areas central to the energy transition.

Jean Daillant, Director General of SOLEIL

Les brèves

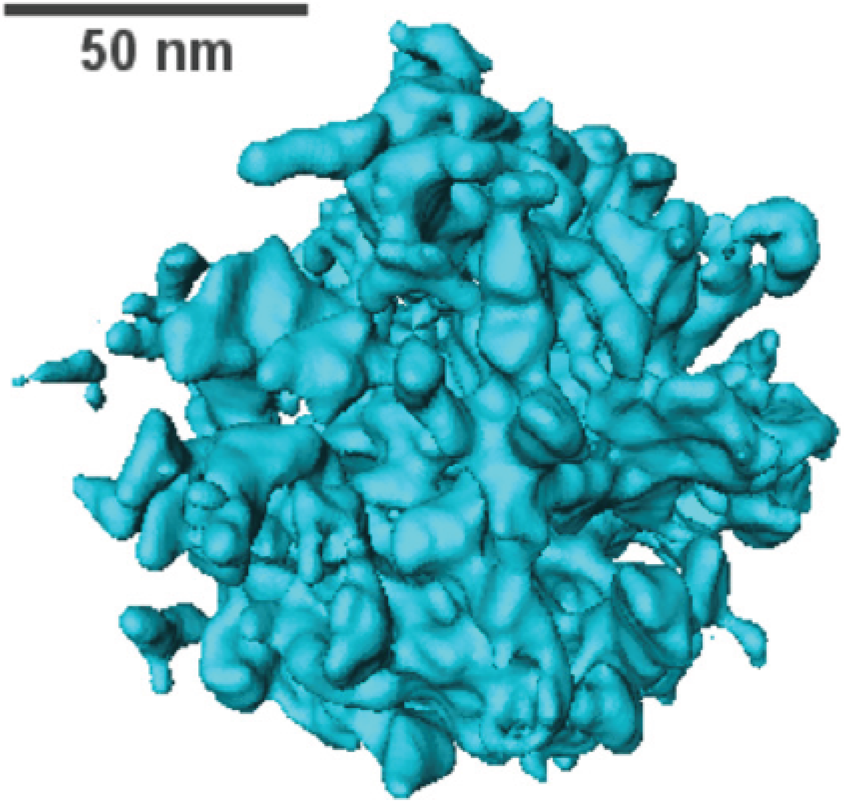
Fischer-Tropsch synthesis is a catalytic process to produce hydrocarbons from a syngas, which could come from biomass. It is therefore **an alternative process to help reduce the share of oil in the energy mix** and **IFPEN is seeking to optimize its performance**, in particular **by improving the catalysts used**.

One of **the main challenges to overcome** is to relate the performance (activity, selectivity) of these catalysts, containing cobalt nanoparticles, to the properties of the metal phase. To achieve this, a good multiscale description of these catalysts is essential.

To this end, **a methodology has been developed** to obtain an original description of cobalt nanoparticles[1]. It **employs two cutting-edge techniques:**

- **electron tomography**, which provides 3D visualization of cobalt aggregates (figure) on a nanometric scale, emphasizes, in particular, their different structures depending on the catalyst's state (oxidized or reduced);

- **anomalous small angle X-ray scattering** (**ASAXS**), performed **on the SWING beamline of the synchrotron SOLEIL**, which enables to characterize the distribution of cobalt, *via* the size distribution of the particles and aggregates. The results obtained have confirmed the observations made by electron tomography, i.e. a better dispersion of cobalt after the reduction step.



3D vizualisation of a (reduced) cobalt aggregate obtained by electron tomography.

This methodology allows **to characterize catalysts at different scales and in all the states encountered during their lifecycle** (oxidized, activated, spent).

The results obtained will **help** provide **a better understanding of**:

- the influence of preparation conditions on the properties of the active phase,

- and the relationship between these morphological properties and catalytic performance.

(1) **S. Humbert, A.-S. Gay, A.-L. Taleb, V. Lefebvre, C. Dalverny, G. Desjouis, A. Berliet, T. Bizien.** *Research pending publication.*

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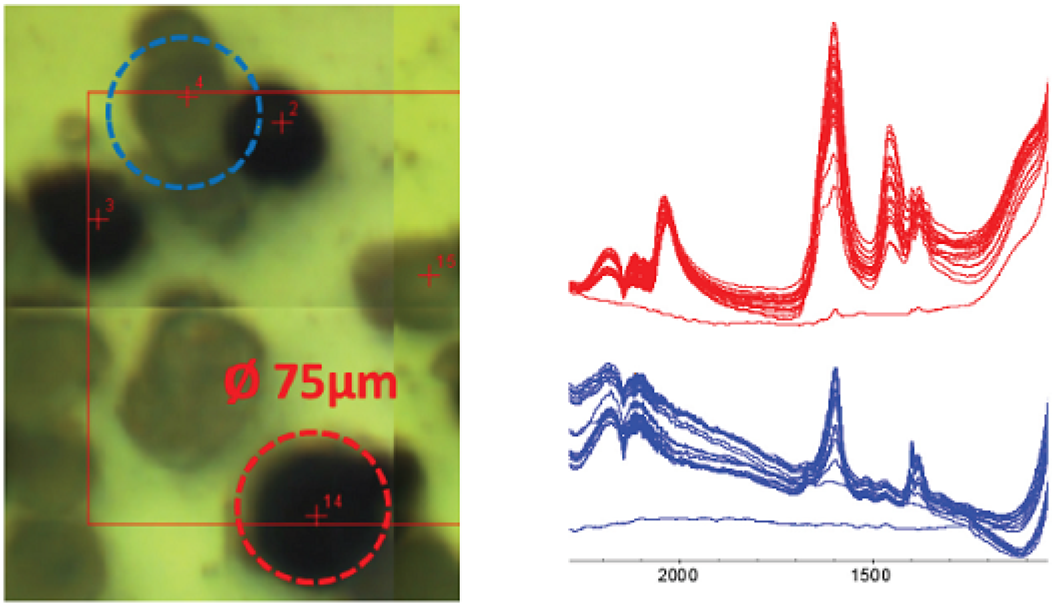
Characterizing catalysts for Fischer-Tropsch: a question of SWING

Improving the reactional performance of a catalytic material (obtained by applying an active phase onto oxide grains) **requires a better understanding of the mechanisms involved in the reaction**. More specifically, **it is necessary to be able to decorrelate the reactions** taking place on the active phase from those occurring on the surface of the oxide supporting it.

This is particularly true in the case of Fischer-Tropsch catalysts, the selectivity of which can be influenced by the support's acid-base surface properties, as well as the heterogeneity of distribution (inter and intra-grain) of the active phase (cobalt). The apparent selectivity can thus vary from one grain to another, depending on the local cobalt content and/or the surface of the support exposed.

An *operando* analysis method using infrared microscopy (µIR) **has been developed in cooperation with teams from the SOLEIL SMIS line** to describe the reactional mechanisms on oxide support grains, impregnated or otherwise with cobalt[1].

The µIR analyses were performed in a reactor at 230°C and at atmospheric pressure, in the presence of CO/H_2 reactive gas mixtures at different ratios. The material studied was composed of a mixture of oxide support grains alone (g_s) or impregnated (g_c).



Optical image and IR spectra of gs (bottom) and gc (top) in reaction conditions.

Comparison of the data, obtained at reactional iso-conditions on the two populations (figure), made it possible to fine-tune the spectral attributions of the surface species generated then chemisorbed (alkane, formiate, carbonyl, carbonate) and to monitor their formation rates.

Monitoring of the reaction kinetics, coupling spatial and temporal resolutions, is an asset specific to the combination of µIR with synchrotron radiation.

Being able to operate in conditions representative of processes **is an additional advantage** for studying and optimizing catalysts.

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(1) ***M. Rivallan, L. Lemaitre, S. Humbert, A. Berliet, S. Maury, C. Sandt, F. Borondics.*** *Research pending publication*

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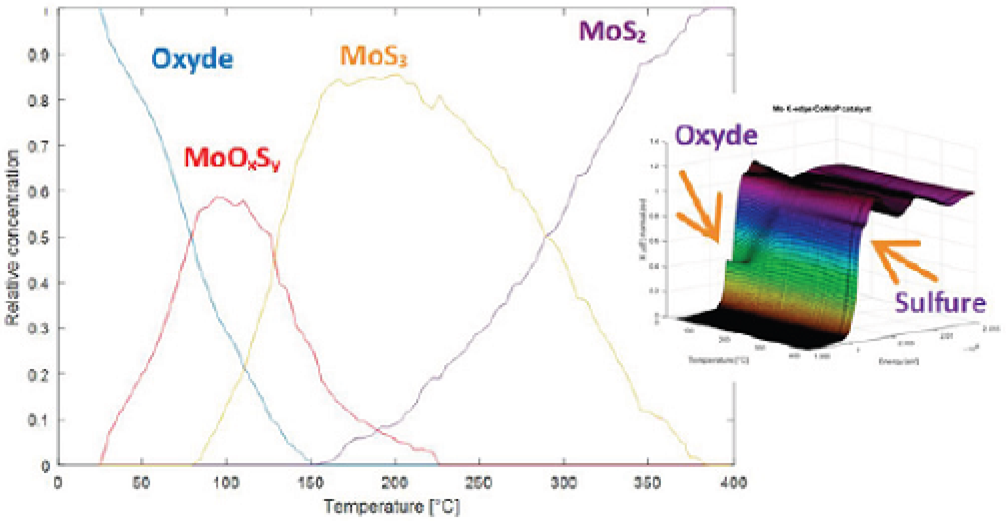
Infrared and SOLEIL: good vibrations under the microscope

The development of **more efficient hydrotreatment catalysts**, based on molybdenum (Mo), requires **advanced characterization methods** that allow materials to be studied in conditions that match those of their real use as closely as possible.

To produce these catalysts, **a crucial activation step is necessary**. This consists of **hot sulfidation of the oxide phase** to form the MoS_2 active phase, generally promoted by cobalt or nickel. Knowing which intermediates are formed and the sulfidation kinetics of the two main players involved in activity — i.e. **Mo and the promoter —** are therefore major advantages when it comes to identifying the principal factors governing catalytic activity.

The SOLEIL synchrotron's Quick-XAS[a] ROCK beamline makes it possible to monitor the almost simultaneous **chemical and structural evolution of Mo and the promotor** in real activation step conditions, **with a temporal resolution of just a few seconds**. Processing the large amount of data generated is also facilitated by the use of chemometric methods, which have recently begun to be used in this context[1].

Analysis of a CoMoP catalyst supported on alumina, has thus demonstrated a multi-step sulfidation process involving Mo (figure), with molybdenum oxysulfide as the first intermediate, followed by the development of an MoS_3 phase, predominant at 200°C, which is then fully converted into MoS_2 at the end of sulfidation at 400°C.



Evolution of XANES spectra and the relative concentration of the four main species as a function of sulfurization temperature.

The IFPEN-SOLEIL collaboration on this line is currently continuing, with the development of a **sulfidation reactor in a gas-liquid medium and under pressure**.

Thanks to this equipment, **continuous XAS analysis of the structural evolution around the molybdenum and cobalt** during the reaction, in conditions representative of industrial processes, will make it possible to make significant advances in our understanding of the mechanisms involved.

[a]- *X-ray absorption spectroscopy with rapid data analysis.*

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(1) A. Rochet, et al., Co-K and Mo-K edges Quick-XAS study of the sulphidation properties of Mo/Al2O3 and CoMo/Al2O3 catalysts, Comptes Rendus Chimie 19 (2016) 1337-1351
>> *DOI: 10.1016/j.crci.2016.01.009*

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ROCK sets the rhythm for catalyst activation

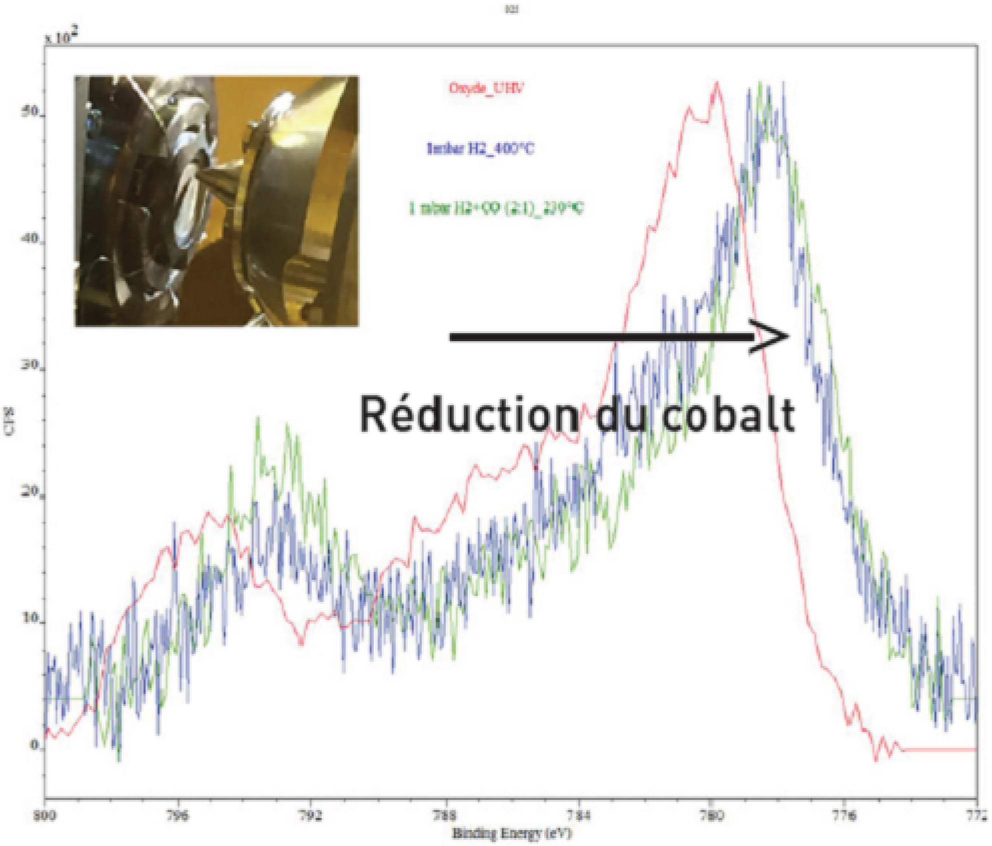
The value of X-ray photoelectron spectroscopy (XPS) resides in **its capacity to supply information on the surface elementary composition** (a few nm) **and the chemical environment of the atoms probed**, something that is **particularly useful for characterizing the active sites of catalysts**.

Until recently, this characterization method was limited to operation under ultra highvacuum conditions, which meant that it was not possible to monitor the surface evolution of the catalysts in reactional medium.

A dedicated system (NAP-XPS[a]) **now allows us to work in environmental mode at pressures of around few millibars**. Combined with the high brillance of a synchrotron radiation, which is energy-adjustable, this system is much more efficient than a laboratory spectrometer. The possibility of introducing gas into the analysis chamber means that it is now possible to monitor the evolution of the species formed under activation or reactive conditions.

In this way, **a model catalyst**, based on cobalt oxide supported on silica, **has been characterized on the TEMPO beamline of the SOLEIL synchrotron**.

Catalyst activation was performed in two stages: first, partial reduction of the cobalt at 400°C under 1 mbar of hydrogen, then introduction of a gas mixture (2 H_2 + CO) at 230°C in order to simulate the reaction conditions of the Fischer-Tropsch process.



Analysis chamber and evolution of the Co 2p oxide spectrum, after reduction under 1 mbar H2 at 400°C and under H2CO (2:1) at 230°C.

Recording of the spectra for cobalt, at an incident energy of 1,100 eV, **demonstrated the evolution at 400°C of the oxide form towards a more reduced form**, characterized by a lower binding energy. **Reduction of the catalyst continues slightly in the presence of the reactional mixture at 230°C**.

These first tests on a catalyst are **promising** and **demonstrated that it is possible to overcome the analytical problems related to the insulating character of the support**, thereby **enabling surface modifications to be monitored in the reactional atmosphere**.

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[a] - *Near Ambient Pressure XPS.*

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Surface characterization at the right TEMPO

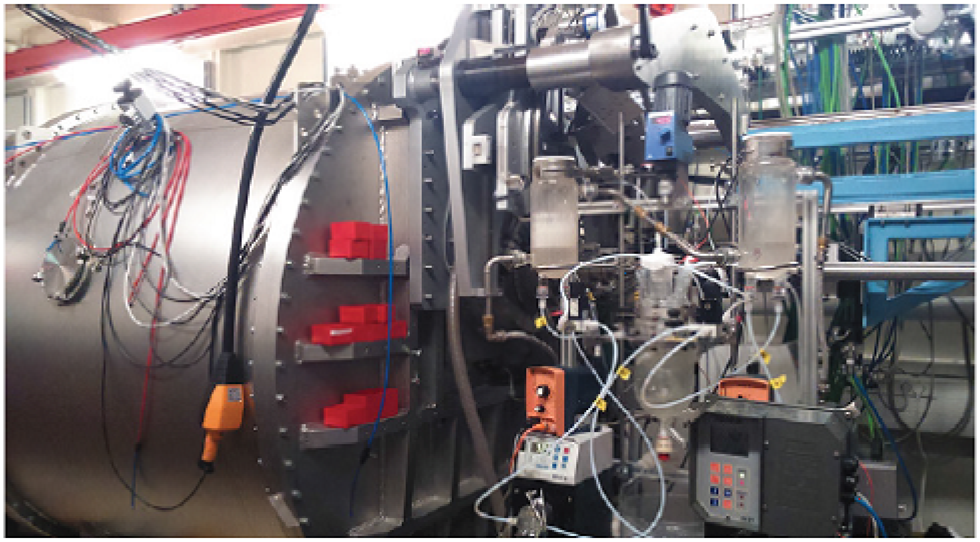
Transition aluminas[a], widely used as catalyst supports, play a key role in numerous refining processes.

Today, the need to develop new and more efficient catalysts demands, among other things, **better understanding and control of all the individual steps involved in the manufacture of this alumina**.

The precipitation of aluminum salts is **a process for the synthesis of boehmite**, the precursor of alumina. The conditions of this synthesis have a direct influence on the textural properties, modifying the arrangement of the elementary particles of boehmite. However, **the correlation between this particle arrangement and the final textural properties of the alumina still needs to be elucidated**.

To make progress in this area, we need to know how to characterize the suspensions on different scales (from particle to agglomerate) **and their evolution during synthesis**.

Studies have therefore been carried out **in collaboration with INP-ENSIACET***, **on the SWING beamline of the synchrotron SOLEIL** in order to monitor by in situ SAXS[b]measurements, the aggregation and agglomeration processes of boehmite crystallites, during synthesis[1].



Installation of the synthesis system on the SWING beamline of the synchrotron SOLEIL.

In particular, these experiments have allowed **to monitor the growth of the aggregates over time during the reagents addition**. A correlation between **supersaturation**[c] at each time of the **synthesis and aggregation mechanisms** has thus been established: a high level of supersaturation generates very compact aggregates, whereas a low level of supersaturation leads to larger and more bulky, open structures.

Thanks to the possibility that it offers to follow continuously and at different scales the processes involved in a synthesis of materials, **the SAXS technique, coupled with synchrotron radiation,** provides an invaluable contribution to the **development of new catalyst supports**.

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[a]- *Aluminas produced by the dehydration of aluminum oxyhydroxide or trihydroxide*
[b]- *Small-Angle X-Ray Scattering*
[c]- *Balance between aluminum salts and boehmite*

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(1) S. Kirchner, S. Teychené, S. Humbert, M. Boualleg, A. Dandeu, C. Frances, B. Biscans, A. Thureau. *Research pending publication.*

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Boehmite rhapsody! Controlled precipitation

Alumina, the archetypal material used for **hydrotreatment catalyst supports, has a porous structure at supramolecular scales,** determining the transport of oil feeds within it. This structure is largely inherited from that of the boehmite pastes from which the supports are made.

These pastes are composed of **a concentrated dispersion of (nano) particles**. Their transformation is achieved via individual operations, such as: **peptization**[a], **extrusion** and **calcination**, the step at which **the boehmite is converted into alumina**.

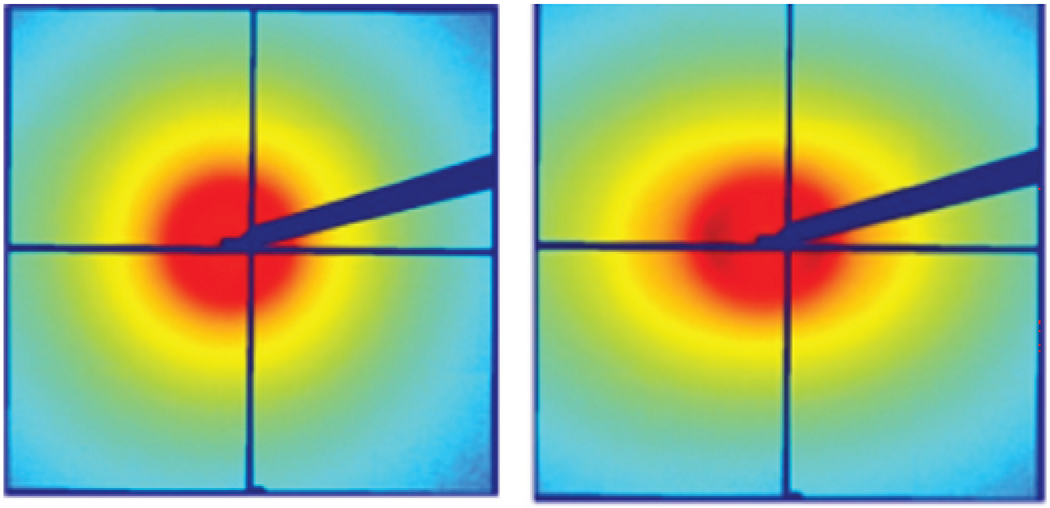
However, the extrusion of boehmite pastes is sometimes difficult — or even impossible — for some dispersions, and it is important to understand why if we want to improve the materials of these supports.

Optical observation under polarized light of boehmite pastes reveals **strong birefringence under flow conditions**, a property that persists at rest. While this observation is a qualitative reflection of a change of organization within the pastes, it cannot adequately describe the latter on a particulate scale.

Boehmite pastes with increasing particle concentrations and controlled salinity were therefore observed in flow conditions **in the SOLEIL synchrotron by small angle X-ray scattering** (SAXS). The flow was imposed by a rheometer, simultaneously enabling precise control of shear conditions and measurement of rheological characteristics[1].

The images taken under the effects of shear (figure) **demonstrate a preferential direction of the particles, which could then be quantified**.

Examination of all the data shows that this direction is primarily controlled by the particle concentration of the pastes. To optimize their extrusion, **more in-depth analysis is required** in order to determine the **relationship between the microscopic structure and the rheology of boehmite pastes**.



SAXS image acquired at rest (left) and under the effects of shear at 3,000 s-1 (right).

[a]- *Disintegration of a powder in liquid phase*

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(1) Camille Morin, « ***Préparation d'alumine à porosité contrôlée : étude de l'interaction de la boehmite dans des solvants et des propriétés fonctionnelles des matériaux résultants*** », UPMC thesis, 2014.

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Extrusion: playing the SAXS for success!
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