

## SLS Symposium on

## Fluids and Soft Matter

Tuesday, September 1<sup>st</sup>, 2015

10:00 to 11:45, WBGB/019

### **CANCELLED** Fluids confined between mica surfaces - an X-ray reflectivity study

*S. Liuzzi, S. Chodankar, R.M. Espinosa Marzal, M. Guizar-Sicairos, A. Diaz, M. Heuberger, and J. Friso van der Veen*

### 10:00 The Role of Metal-Organic Frameworks in Organocatalysis

*Xiaoying Xu, Marco Ranocchiari, Stephan. M. Rummelt, Flavien. L. Morel, Jeroen A. van Bokhoven*

### 10:30 Small-angle scattering tensor tomography: Bridging the gap between nano- and mesoscale

*Marianne Liebi, Marios Georgiadis, Andreas Menzel, Philipp Schneider, Joachim Kohlbrecher, Oliver Bunk and Manuel Guizar-Sicairos*

### 11:00 Coffee

### 11:15 Sub-nanometric gold particles supported on silica: a simple synthesis with a high reward

*A. Beloqui Redondo, M. Ranocchiari, J. A. van Bokhoven*

# The Role of Metal-Organic Frameworks in Organocatalysis

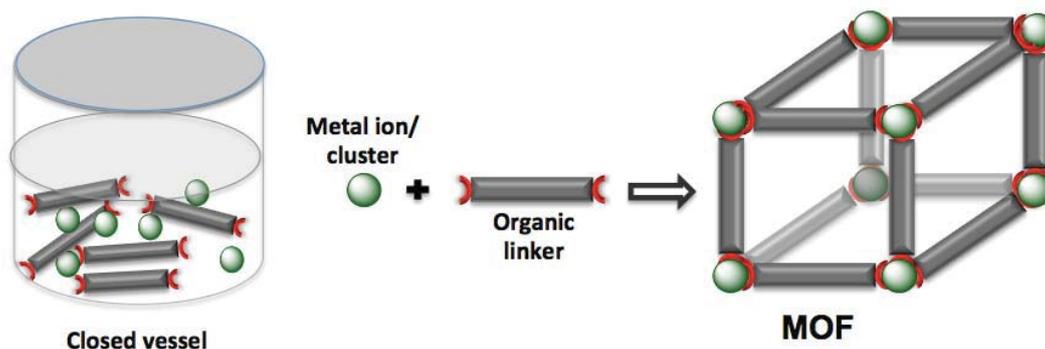
Xiaoying Xu<sup>1,2</sup>, Marco Ranocchiari<sup>2\*</sup>, Stephan. M. Rummelt, Flavien. L. Morel, Jeroen A. van Bokhoven<sup>1,2</sup>

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Metal-organic frameworks (MOFs) are synthesized by self-assembly of metal ions and/or clusters and organic linkers to form one, two and three-dimensional frameworks (Figure 1).[1] Thanks to the high surface area, relatively good thermal stability and large pores, they are appropriate materials for catalysis.[2] The high crystallinity of MOFs compared to other solid materials reduces the complexity of the catalytic system and leads to much more clearer structure-performance relationships in reactions. Organocatalysis uses low-molecular weight compounds as catalysts. Organocatalysts based on MOFs are promising materials for developing chemical efficiency and high value-added chemical synthesis, owing to the advantages: low molecular-weight catalysts (e.g. proline, amines), to be designed for specific reactions, easy separation and efficient recycling. It is feasible to design heterogeneous MOF-based catalysts for application in certain reactions where desired products are favored and by-products are eliminated.



**Figure 1.** Schematic model of the preparation of a MOF.

In our contribution, MOFs with Lewis base sites such as an amino or phosphine group were designed and synthesized for several targeted organocatalysis reactions.[3,4] Tunable pore sizes and local environment allow the activity of such MOFs to be rationalized via analyzing size of substrates and possible intermediates within the MOF cage. Diverse characterization techniques including X-ray diffraction, nuclear magnetic resonance (NMR) spectroscopies, and density functional theory (DFT) calculations facilitated understanding of structure-activity relationship in the MOF-mediated catalysis at an atomic level. The local environment around active sites and reactivity of catalysts was fine-tuned with the aid of confined space, size and density of functional groups in the MOF cage.

[1] H. Li, M. Eddaoudi, M. O’Keeffe, O.M. Yaghi, *Nature* 402 (1999) 276.

[2] M. Ranocchiari, J. A. van Bokhoven, *Phys. Chem. Chem. Phys.* 13 (2011) 6388.

[3] X. Xu, S. M. Rummelt, F. L. Morel, M. Ranocchiari, J. A. van Bokhoven, *Chem. Eur. J.* 20 (2014) 15467.

[4] X. Xu, J. A. van Bokhoven, M. Ranocchiari, *ChemCatChem.* 6 (2014),1887.

## Small-angle scattering tensor tomography: Bridging the gap between nano- and mesoscale

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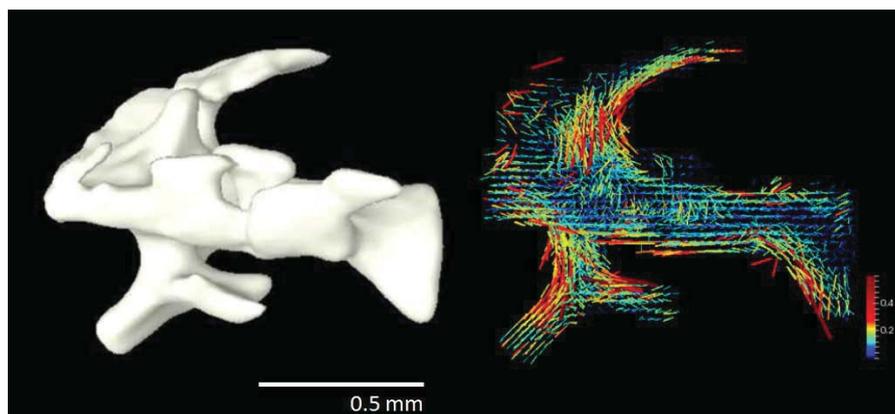
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We have developed a new method, which combines scanning small-angle X-ray scattering (SAXS) with computed tomography (CT) to assess the three-dimensional ultrastructural orientation with 3D spatial resolution.

The sample is moved continuously through a focused X-ray beam while 2D SAXS patterns are recorded at different rotations of the sample. Compared to e.g. absorption-based tomography, for which a single rotation axis is sufficient, for SAXS tensor tomography multiple tilt angles of the tomographic rotation axis are needed, as in each voxel not only a scalar, but a tensor representing the full 3D reciprocal space map needs to be reconstructed.

An iterative reconstruction technique was developed where for each voxel the 3D reciprocal-space map is modeled with a series of spherical harmonics. An optimization algorithm is used to minimize the error between the modeled intensity of all voxels in the beam path projected to the detector plane and the measured intensity for each scanning point under all rotation axes.

The technique is demonstrated on bone, where in each voxel ( $25 \times 25 \times 25 \mu\text{m}^3$ ) the main orientation and degree of orientation of nanoscale mineralized collagen fibrils was reconstructed. Figure 1 shows the CT reconstruction of the X-ray absorption (left) and the result of the SAXS tensor tomography (right) of a human trabecular bone. The orientation of the collagen fibrils are represented by a 3D vector and the degree of orientation by its color and the length.



**Figure 1.** CT reconstruction of human trabecular bone, retrieved from the transmitted X-ray intensity using standard filtered backprojection (left) and orientation of the bone ultrastructure as retrieved from Small-angle X-ray tensor tomography (right).

**References:** Liebi, M. *et al.* “Nanostructure surveys on macroscopic specimens by small-angle scattering tensor tomography.” (submitted)

## Sub-nanometric gold particles supported on silica: a simple synthesis with a high reward

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The formation of hydrogen from formic acid dehydrogenation ( $\text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2$ ) is considered an attractive process to circumvent the use of fossil fuels.[1,2] Selective and stable catalysts are key to reach performance levels that are feasible. Supported gold nanoparticles have long been considered powerful catalysts for this reaction. Keeping the size of the gold clusters small is a determining factor for high activity [3,4]. Using mesoporous SBA-15 as a silica support in catalysis is advantageous due to its high surface area, highly ordered structure, and inertness. However, the synthesis of small gold particles on silica by conventional methods has been challenging until now due to the poor interaction between the gold precursors and the support surface.[5]

A new synthetic route to prepare gold particles with diameters below 1 nm on SBA-15 has been developed. This was done through a combination of modifying the silica surface with amine groups (N-SBA-15) and controlling the solution pH during gold deposition. This procedure yielded highly active and selective catalysts in the dehydrogenation of formic acid. Figure 1a shows the conversion of formic acid over Au/N-SBA-15 and Au/SBA-15 prepared at pH 11. Au/N-SBA-15 catalysts showed improved performance compared to Au/SBA-15 catalysts. Catalysts performing at low temperature were more selective to hydrogen. Figure 1b,c shows transmission electron micrographs of both catalysts, where gold particles can be seen as bright spots. The positive of the developed preparation method on the gold particle size is illustrated.

Multiple gold catalysts were synthesized using different bases and pH conditions and their performance in the dehydrogenation of formic acid was investigated. A strong correlation between performance and particle size was determined. In addition, surface modification increased the thermal and chemical stability of gold clusters.

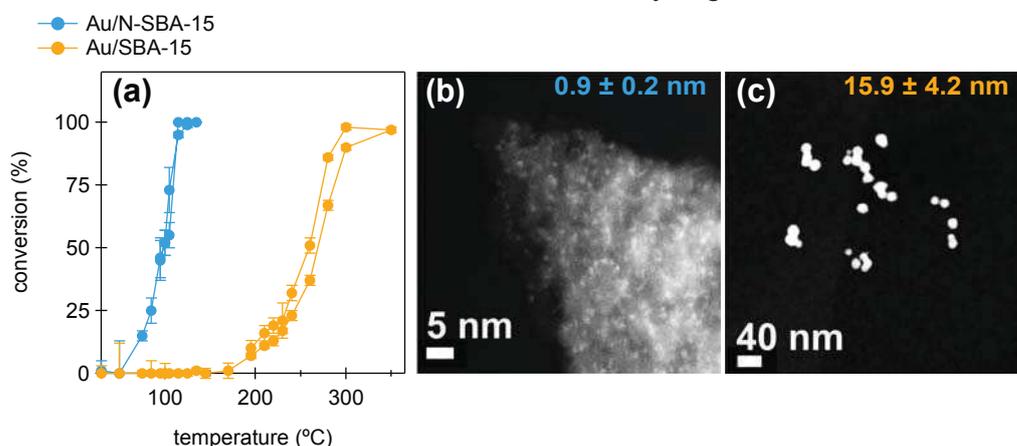


Figure 1. (a) Formic acid conversion over Au/N-SBA-15 and Au/SBA-15 prepared at pH 11 and STEM images of (b) Au/N-SBA and (c) Au/SBA. The average size and standard deviation are indicated on the micrographs.

[1] Loges, B.; Boddien, A.; Junge, H.; Beller, M. *Angewandte Chem. Int. Ed. Engl.* **2008**, *47* (21), 3962.

[2] Joó, F. *ChemSusChem* **2008**, *1*, 805.

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[4] Bi, Q.-Y.; Du, X.-L.; Liu, Y.-M.; Cao, Y.; He, H.-Y.; Fan, K.-N. *J. Am. Chem. Soc.* **2012**, *134*, 8926.

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