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Report **Experiment MA-1175** performed on 4-8 November 2010

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Report: SAXS studies of nanocomposite hydrides for hydrogen storage applications

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Storage of hydrogen in a safe and efficient medium is a major challenge for the introduction of hydrogen as an energy carrier for mobile applications. One of the most promising directions is the use of hydrogen as energy vector for vehicular applications in the form of solid storage material based on nanoscaffold hydrides. When dealing with nanoporous materials small-angle scattering gives invaluable information that can help to develop the most suitable solid material. Recently, we used small-angle X-ray scattering (SAXS) performed at ESRF to characterize nanosized hydrides confined in carbon scaffolds.[1,2] We found that the integration into the scaffold of sodium alanate stabilizes the size of the particles upon heating, while the bulk powders undergoes changes.[1] Nanoscale particles of $Mg(^{11}BD_4)_2$ infiltrated in a activated carbon scaffold (AC1) were also studied by SAXS and their behavior compared with the bulk powders.[2] We observed that upon heating up to 400 ^{o}C the nano-confined particles maintain their size distribution and the decomposition affects only

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[1] Small-angle scattering investigations on nanoconfined sodium alanate for hydrogen storage applications, Sabrina Sartori, K. D. Knudsen, A. Roth, M. Fichtner, and B. C. Hauback, *Nanoscience and Nanotechnology Letters*, *Special Issue: Nanomaterials and Nanoscale phenomena for clean energy applications*, *in press*.

[2] Nanoconfined magnesium borohydride for hydrogen storage applications investigated by SANS and SAXS, Sabrina Sartori, K. D. Knudsen, Z. Zhao-Karger, E. Gil Bardaji, J. Muller, M. Fichtner, B. C. Hauback, *Journal of Physical Chemistry C* **114** (2010), 18785-18789.

the particles surface. On the contrary, the bulk powders showed a significant modification of particle size and surface under the same conditions.

We consider these data useful in the interpretation of the relation between the structural changes during the confinement and the improved hydrogenation properties of the nanocomposite hydrides compared to the bulk powder alone.

During the experiment **MA-1175** we investigated new hydrides and/or new scaffolds. Hydrides as bulks and infiltrated in cmk-3 carbon scaffolds were studied. They were bulk $Mg(BH_4)_2$ in liquid NH_3 and the respectively two infiltrated samples with 70% and 40% hydride loading, respectively. Bulk $Ca(BH_4)_2$ in liquid NH_3 and the respectively two infiltrated samples with 70% and 40% loading were also measured.

In situ SAXS patterns were collected at the beam line (BM26B) at the ESRF in Grenoble, France. The wavelength was 0.954 Å, and the sample was contained in a 0.8 mm boron-silica glass capillary and heated under dynamic vacuum from room temperature (RT) up to 500 ^{o}C or 600 ^{o}C at a constant heating rate of 3 or 5 ^{o}C min^{-1}. Wide angle X-ray scattering (WAXS) was recorded during the SAXS acquisition. The data obtained were integrated and put on a linear scale by means of the Fit2D program.

The hydrides were dissolved in liquid NH_3 and successively infiltrated in carbon scaffolds. Once infiltrated, the release of hydrogen in case of $Mg(BH_4)_2$ infiltrated in cmk-3 reached a maximum at 50 ^{o}C lower temperature compared with the behaviour of the bulk alone. In the case of $Ca(BH_4)_2$ in cmk-3 the behaviour seemed to be the opposite.
When dissolved in NH_3, $Mg(BH_4)_2$ tends to form the complex $Mg(BH_4)_2$ * 6 NH_3, with different characteristics then $Mg(BH_4)_2$ alone. SAXS performed on the bulk powders displayed values of the slope parameter (α) between 3 and 4 in all *q*-ranges as shown in Figure 1. This is consistent with a system with very big particles with rough surfaces.

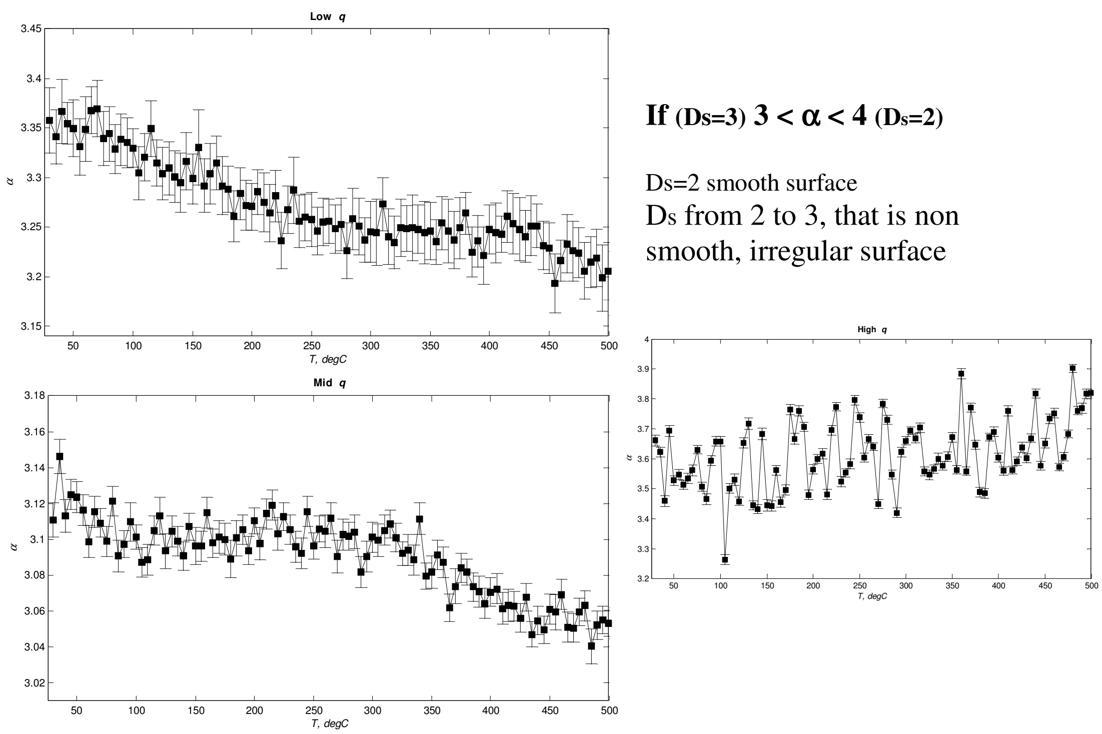

Figure 1: α parameters from SAXS of bulk $Mg(BH_4)_2$ in NH_3.

Once loaded inside the scaffold this hydride shows different decomposition temperatures and a fractal-like behaviour with values of α lower then 3, Figure 2. The loading degree seems to play a role in the fractal behaviour and this aspect has to be deeply investigated, Figure 2 (a) and (b).

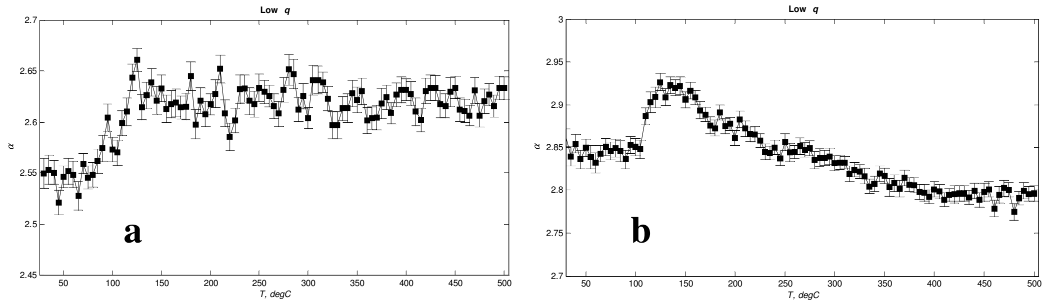

Figure 2: α parameters at low q from SAXS of cmk-3 / $Mg(BH_4)_2$ 70% loading (a) and cmk-3 / $Mg(BH_4)_2$ 40% loading (b).

$Ca(BH_4)_2$ powders follow a complicate desorption behaviour. Preliminary investigations via SAXS indicates very small particles when infiltrated in cmk-3 scaffolds, being the values of α lower then 3 even at high *q*, as shown in Figure 3 in the case of cmk-3 / $Ca(BH_4)_2$ 40% loading.

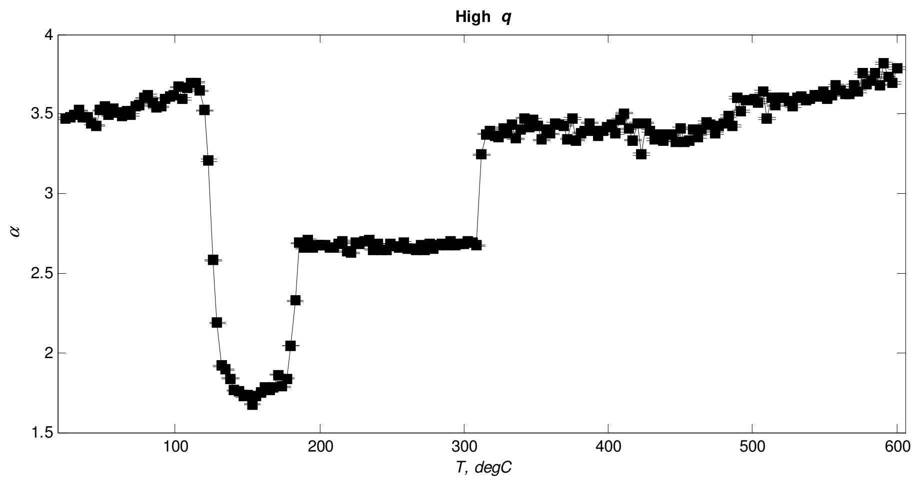

Figure 3: α parameters at high q from SAXS of cmk-3 / $Ca(BH_4)_2$ 40% loading.

A detailed analysis of the collected SAXS and WAXS data will be necessary to understand the decomposition behaviour of the samples and will suggest the suitability of them as materials for hydrogen storage.