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**SAXS studies of hydrides nanocomposites**

Sabrina Sartori

Institute for Energy Technology, P.O. Box 40, NO-2027 Kjeller, Norway
E-mail: sabrinas@ife.no
Tel: +47 63806388
Fax: +47 63810920

With an increasing global demand for energy, the search for new energy sources as substitute to the fossil fuel has moved in the direction of a hydrogen economy. 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. Using small-angle x-ray scattering we observed that when decomposing and releasing hydrogen, the bulk powders are reduced significantly in particle size and also their surface undergoes changes. On the contrary, when integrated into a scaffold, the particles were stabilized upon heating.

*In situ* small-angle x-ray scattering (SAXS) patterns were collected at the beam line (BM26B) at the European Synchrotron Radiation Facility (ESRF) in Grenoble. The wavelength used was 0.95 Å, and the sample was contained in a 0.8 mm boron-silica glass capillary and heated under dynamic vacuum from room temperature (RT) to 290 or 400 $^{o}$C at a constant heating rate of 5 $^{o}$C/min.

Figure 1 shows SAXS data collected on the composite and on the scaffold alone, while in Figure 2 are shown the SAXS data collected on the bulk $NaAlD_4$. In both cases we report

only selected *in-situ* SAXS data where the samples were heated at a rate of 5 $^{o}$C/min from room temperature to 290 $^{o}$C.

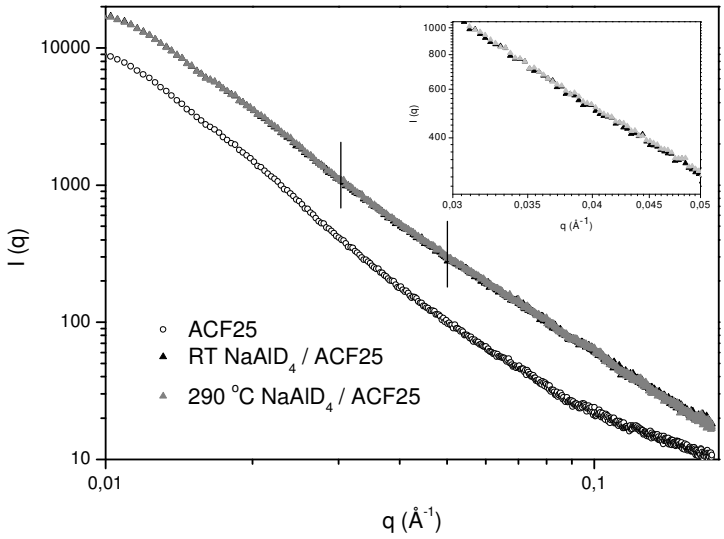


**Figure 1.** SAXS data for the composite at room temperature and at 290 $^{o}$C compared with the scaffold alone at RT. Inset: selected and magnified view of the RT and 290 $^{o}$C curves.

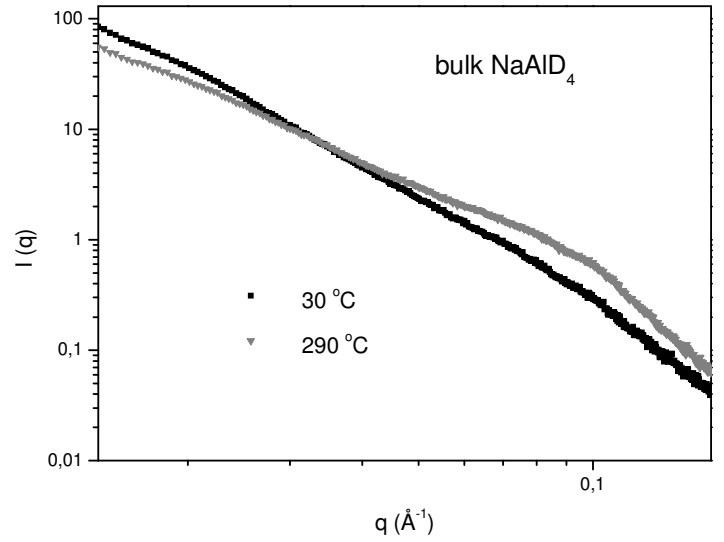


**Figure 2.** *In-situ* SAXS data on bulk $NaAlD_4$ at RT and 290 $^{o}$C.

As can be seeing from the superposition of the curves in Figure 1 and inset, heating seems to have no effect on the composite, at least in the nanosize range which is accessible by

SAXS. This is an important observation since it indicates that the $NaAlD_4$ particles are well stabilized by the integration into the scaffold.

Contrary to what is observed for the composite it is evident that for the bulk there are significant changes taking place in the scattering upon heating (Figure 2). By inspection one can see that upon heating to 290 $^oC$ the scattering intensity is shifted from low *q*-values (large sizes) to high q-values (small sizes). Thus already from visual inspection of the SAXS data one can conclude that the overall effect of heating to 290 $^oC$ is a significant reduction in the particle sizes. The slope of I(*q*) vs *q* can give important information about the nanostructure of the material. In Figure 1 and 2 we identified two distinct regions in the data, below and above $q \sim 0.1$ $Å^{-1}$. These will be named "central *q*" and "high *q*", and correspond respectively to the mass fractal regime (slope parameter between 2 and 3), where we probe the space filling behaviour of the particles, and to the surface fractal regime (slope generally between 3 and 4), where we probe the smallest lengths scales that give us information about the surface roughness. Thus, by following simultaneously changes with temperature in the central and high q regions we are able to probe independently both the space filling characteristics of the $NaAlD_4$ particles and any modification taking place on the surface. The slope parameter in these two regions for selected temperatures shows an interesting difference of behaviour between the bulk and the nanoconfined material (Figure 3). As visually observable from Figure 1, the slope parameter of the composite remains constant during heating at a value of $\alpha \sim 2.35$ at central *q* and ~ 2.26 at high *q*. This result would suggest that the nanoconfined alanate display a different behaviour during decomposition compared to the bulk. It seems that the decomposition do not affect the particle size at this detectable range. It is possible that during the decomposition of the nanoconfined alanate the structural changes occur only at the local atomic range.

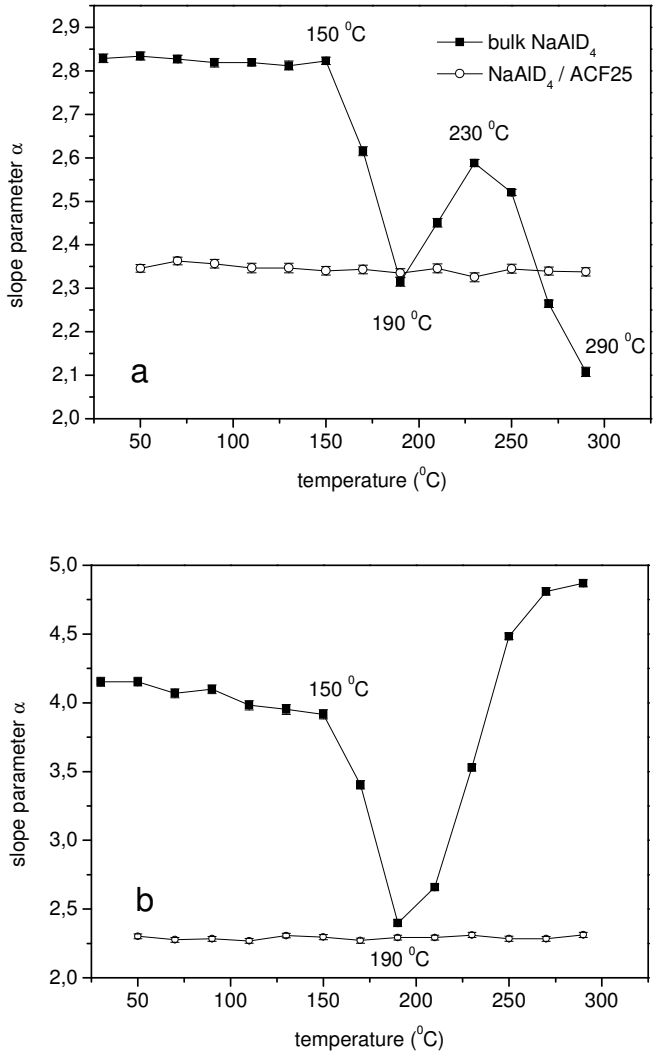


**Figure 3.** Slope parameter at central (a) and high $q$ (b) for bulk $NaAlD_4$ (■) and for the composite (o).

Similar investigations during decomposition of nanoconfined $Mg(BD)_4$, (Figure 4), show a constant slope parameter in the central $q$, that is particle sizes stabilized by the presence of the scaffold, with the only changes localized on the surface and visible at high $q$. Also in this case, the behavior of the bulk powder alone is different (see Figure 5), showing a change in the slope parameter at central and high $q$.

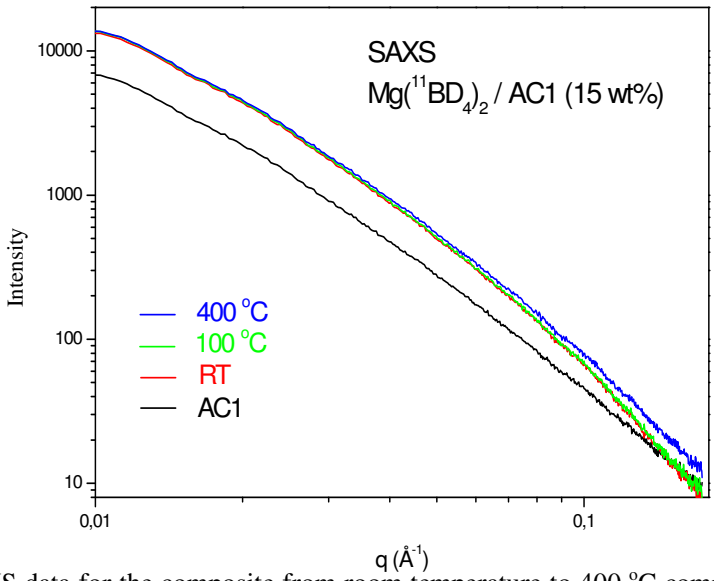


**Figure 4.** SAXS data for the composite from room temperature to 400 °C compared with the scaffold alone at RT.

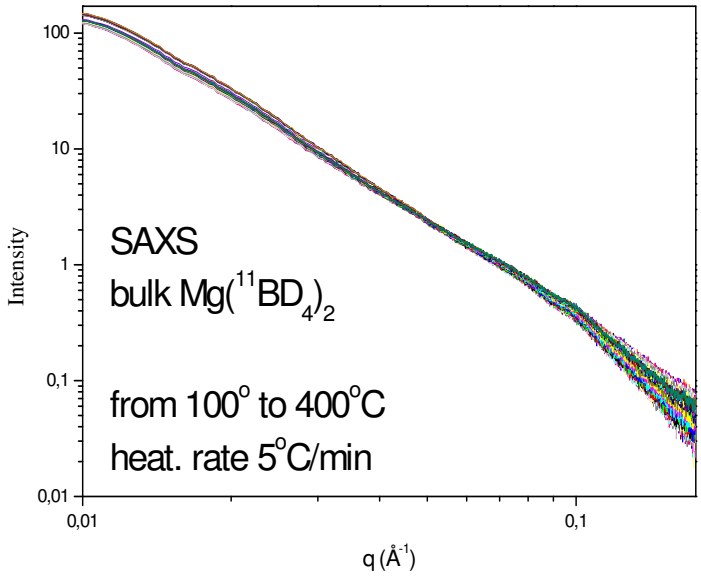


**Figure 5.** *In-situ* SAXS data on bulk $Mg(^{11}BD_4)_2$ from 100 to 400 °C.

In conclusion, the use of small-angle x-ray scattering on nanoconfined hydrides has therefore provided us with important information on the characteristics of this hydride material within the supporting carbon scaffold. This data will be useful in the interpretation of the relation between the structural changes during the confinement and the improved hydrogenation properties of the composite hydrides compared to the bulk powder alone.