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Experiment Report Form

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- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
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(next page)

DUBBLE	**Experiment title:** Probing the role off gel species in the formation off AlPOs synthesized from ionic liquids	**Experiment number**: **26-02-458**
Beamline: BM26 A	**Date(s) of experiment**: From: 8-12-2008 To: 12-06-2008	**Date of report**: 14-11-2009
Shifts: 9	Local contact(s)**: Lucia Fernandez-Ballester**	

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Report: (max. 2 pages)

The original aim for the beam time allocation, was to attempt to understand the pre-crystalline species formed during the synthesis of microporous aluminophosphates (AlPOs) from an ionic liquid (IL) type gel using combined in situ multiple techniques. Such experiments are important as understanding the formation of these porous materials is required if a more rational design approach towards tailored catalytic materials is to be achieved. In particular we wished to examine the effect of the organic template orientation within forming AlPO and observe if particular conformations can also be related to particular structure as we have shown in our previous work on non-IL AlPO synthesis (1).

Unfortunately, the modified hydrothermal capillary cell used was found to be unsuitable for the experiments due to the difficulties in loading the IL gel in a manner that stopped movement during heating and synthesis. It therefore proved impossible during the time period available (after installation of the multiple-technique setup) to obtain any suitable data from the IL synthesis. Nevertheless, the experience has allowed us to understand the problems associated with measuring these IL-type systems and will allow us to modify the setup to cope with these problems in the future.

Despite this problem, we did manage to adapt the setup on-site to measure the standard 'non-IL' AlPO synthesis (as such experiments have to date not been performed) and these have provided us with considerable data as detailed below.

Combined SAXS-WAXS and some Raman data was obtained on gels containing AlPO and a 'substitution' metal (i.e. Co or Zn). In particular considerable changes were observed in the SASX-WAXS data as detailed in Figure 1 (e.g. cobalt system). From this data it can be seen that crystallization toke place after about 25 min of reaction. Figure 1a then shows the transmission ion chamber (It) readings which decreased from the start of the experiment indicating the formation of more absorbing particles. The formation of such WAXS amorphous particles was confirmed in the SAXS where 3 different size species were observed (figure 1b). Interestingly larger species (118 Å) where observed prior to the formation of smaller particles of 95 Å which formed just prior to crystallization. Such double distributions have been observed by us in similar gels. The larger species of 380 Å then most likely represent the formation of the (initially disordered) aggregates that go on to form the final crystalline product. These are also observed just prior to Bragg crystallization and then disappear soon after as the particles continue to grow beyond the range of the SAXS camera. Finally we observed (figure 1c) changes in the 'porod region' of

the SAXS data with the slope changing from 3 to 2 during the early stages of the reaction. Such data should provide us with additional information on the nature of the forming particles such as their 'roughness'..

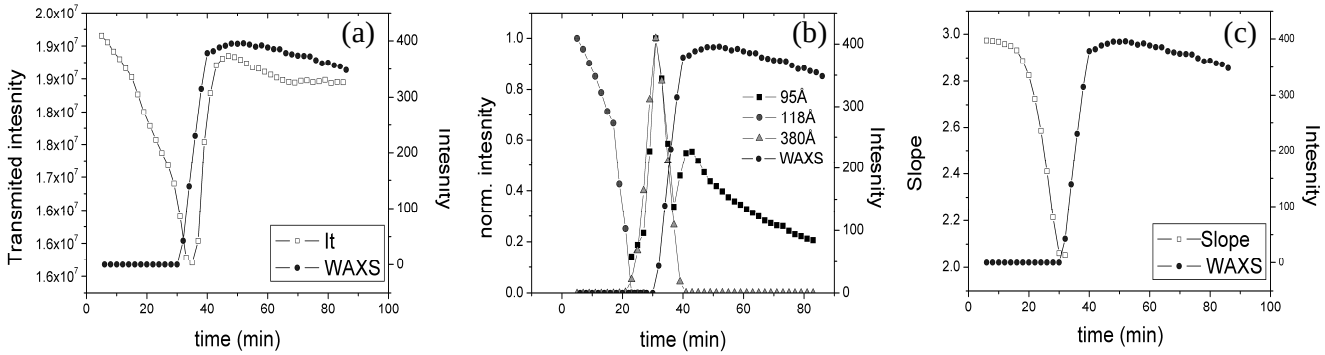

Figure 1: the slope intensity of It (a) the intensity of the particles observed in the SAXS data (b) and the change in slope of the SAXS data (c) compared with the formation of WAXS crystalline particles during the formation of CoAlPO-34.

Conclusions

Whilst, due to technical problems, the work was unable to provide data on the IL-type synthesis the beam time has provided us with invaluable data on the formation of non-IL AlPO formation. This work is to be combined with other in situ and ex situ work from numerous techniques *such as Uv-Vis and NMR) to provide a far more comprehensive picture as to the synthesis of these materials, which should considerably help in the aim of 'rational design' of these materials.

References

1. O'Brien, M. G., Beale, A. M., Catlow, C. R. A., Weckhuysen, B. M. *J. Am. Chem. Soc.*, 128, 11744, **2006.**