EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

.

ESRF	**Experiment title:** Crystal structure of new Ziegler-Natta catalyst supports ($MgCl_2$ ·*n*EtOH with n > 3.33)	**Experiment number**: CH-3371
Beamline: BM01B	**Date of experiment**: from: 06/06/2012 to: 12/06/2012	**Date of report**:
Shifts: 18	**Local contact(s)**: Paula Macarena Abdala	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Prof. Giuseppe Cruciani, Dip. Scienze della Terra Sez. Mineralogia, Petrologia e Geofisica Universita' di Ferrara Via Saragat 1 - blocco B - II piano, 44100 Ferrara Italy

Dr. Federica Malizia, Basell Poliolefine Italia, 'G.Natta' Research Center, Piazzale G.Donegani 12 (cp 113), 44100 Ferrara Italy

Report:

The target of the CH-3371 experiment was the determination of the crystal structure of $MgCl_2 \cdot nC_2H_5OH$ complexes with *n* greater than 3.33. This experiment was a continuation of our previous successful experiment CH-2924 carried out at the ID31 beamline which resulted in the structure determination of three $MgCl_2 \cdot nC_2H_5OH$ adducts with n ≤ 3.33, precisely $2MgCl_2 \cdot 3EtOH$ (*n*=1.5), $5MgCl_2 \cdot 14EtOH$ (*n*=2.8) and $3MgCl_2 \cdot 10EtOH$ (*n*=3.33) [results published in ″The crystal structure of Ziegler-Natta catalyst supports″ *Chem. Eur. J.*, **2011**, *17*, 13892-13897 by F.Malizia, A.Fait, G.Cruciani].

The importance of crystal structure elucidation of $MgCl_2 \cdot nC_2H_5OH$ complexes lies in the fact that these adducts are the building blocks of Ziegler-Natta catalyst supports used in the production of polyolefins, such as polyethylene and polypropylene on a multi-million ton scale world-wide. Therefore, the knowledge of their structure, at the atomic level, will facilitate the better comprehension of the Ziegler-Natta catalysis. This is principally because the catalyst models developed up until now completely neglect the link to the

structure of their $MgCl_2$ precursor: they are only based on the insertion of $TiCl_4$ species and donors on selected cut surfaces of α-$MgCl_2$. Hence, beyond its academic interest, the crystal resolution will also impact industrial aspects. A substantially better understanding of the structure-property relationships of Ziegler-Natta catalyst and supports will establish the foundation of the design and production of new and more active catalysts.

The proposal of studying $MgCl_2 \cdot nC_2H_5OH$ complexes with ethanol content greater than 3.33 was submitted in conjunction with the ongoing industry research at Basell Poliolefine (Ferrara, Italy) which is focusing the attention on the development of new catalysts generated from $MgCl_2 \cdot nC_2H_5OH$ adducts with EtOH/$MgCl_2$ ratios greater than 3.33. These new catalysts can polymerize olefins with enhanced activity and porosity when compared to catalysts prepared with adducts with $n \leq 3.3$. This fact emphasizes the critical role that the structure of $MgCl_2 \cdot nC_2H_5OH$ precursors play in determining the final performances of the catalytic system and justifies our interest in the crystal structure solution of complexes with higher amount of ethanol.

The task of solving the crystal structure of these adducts is more challenging than ever because of the lack of pure phase samples, in fact, all the prepared powder samples included two or more impurity phases due to complexes with different EtOH/$MgCl_2$ ratio.

Notwithstanding this difficulty, due to the high quality of X-ray powder diffraction data acquired at ESFR, we succeeded in the *ab initio* structure solution of $MgCl_2 \cdot 4EtOH$ adduct, that was achieved after scrupulous subtraction of contributions due to the other present crystal phases, whose structure was known from previous experiment.

The crystal resolution of $MgCl_2 \cdot 4EtOH$ adduct is now being refined and it is our intention to describe the crystal elucidation in a scientific article as soon as possible.

From an experimental point of view, the $MgCl_2 \cdot n$EtOH complexes with n greater than 3.33 were prepared following the synthesis route devised at LyondellBasell's Giulio Natta Research and Development Centre in Ferrara, Italy. This procedure encompasses contacting α-$MgCl_2$ and ethanol in the desired stoichiometric ratio in the absence of an inert liquid dispersant. The composition of all the complexes was checked for ethanol content by using GC-FID (Flame Ionisation Detector) technique and by elemental analysis for magnesium and chlorine determination. Due to the hydrophilic nature of these compounds, where ethanol is readily replaced by water molecules, the synthesized samples were immediately transferred and kept in a dry chamber. Several borosilicate glass capillaries were then filled with each of the three compounds and hermetically sealed by welding the open tip. Laboratory powder diffraction patterns were collected on these capillaries at different times after preparation in order to check for sample purity and possible transformation. Placed in borosilicate capillaries of 1.0 mm in diameter, the samples were spun and translated during data collection in order to minimize the preferred orientation and the radiation damage, respectively.

Preliminary powder diffraction data on a large number of sample capillaries were collected at BM01B in order to select the best candidate(s) for data collection with higher counting statistics. This step was required in spite of the laboratory tests because, although sealed in the glass capillary, the $MgCl_2 \cdot n$EtOH adducts may undergo rapid changes due to their metastability and/or adsorption of atmospheric moisture.

Long counting time measurements (the storage ring was operating in the low current 16 bunch mode) were performed at room temperature, in continuous mode across a range of $1 \leq 2\Theta \leq 65°$, with accumulation times increasing with the scattering angle, and rebinned with a step size of 0.002° 2Θ.

Indexing of the synchrotron powder diffraction patterns and space-group determination of $MgCl_2 \cdot n$EtOH (n = 4 and 4.33) were achieved by the Crysfire suite of programs, in particular using ITO. A subsequent cell-constrained profile fitting conducted by the Le Bail method was performed using the GSAS-EXPGUI package. The *ab initio* crystal structure solution of $MgCl_2 \cdot 4EtOH$ phase was carried out using a combination of direct methods and the simulated annealing approach using the EXPO2009 program.

Figure 1 shows the ongoing GSAS-EXPGUI Rietveld fit (anisotropic peak broadening profile model not applied yet) obtained for the $MgCl_2 \cdot$EtOH complex containing three different crystal phases, precisely $MgCl_2 \cdot 6EtOH$, $MgCl_2 \cdot 3.33EtOH$ and the newly resolved $MgCl_2 \cdot 4EtOH$. The crystal packaging of $MgCl_2 \cdot 4EtOH$ is depicted in Figure 2.

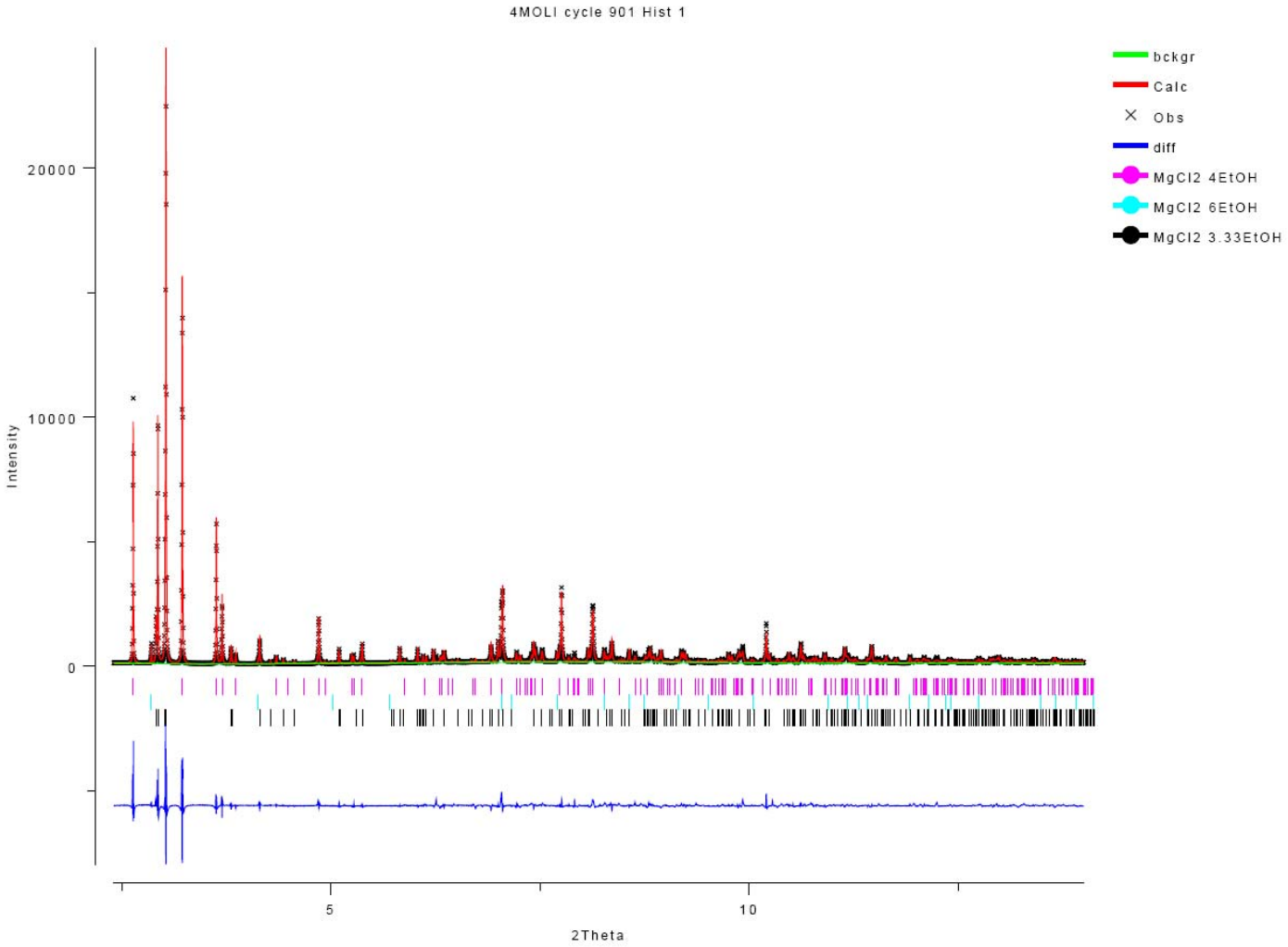

Figure 1. Rietveld fit for the sample containing the newly resolved $MgCl_2$·4EtOH phase (observed green and calculated red patterns, respectively; bottom line: difference curve). Marks refer to Bragg peak positions of phases included in refinement - from the top: a) $MgCl_2$·4EtOH (new structure model from this work); b) $MgCl_2$·6EtOH (structure model from G. Valle, G. Baruzzi, G. Paganetto, G. Depaoli, R. Zannetti, A. Marigo, Inor. Chem. Acta 1989, 156, 157-158) and c) $MgCl_2$·3.33 (structure models from F.Malizia, A.Fait, G.Cruciani *Chem. Eur. J.*, **2011**, *17*, 13892-13897)

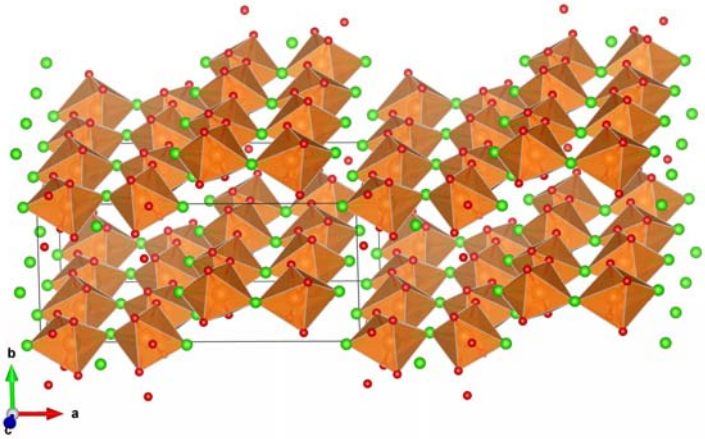

Figure 2. Crystal packaging of the newly solved structure $MgCl_2$·4EtOH (manuscript under preparation).