

PRODEX EXPERIMENT ARRANGEMENT CHANGE NOTICE

Institute: **University of Gent**

PEA No: **4200090364** CN No: 2

Project: **Self-assembly of hierarchical catalysts and absorbent materials from Ordered Liquid Phases (OLPs)**

Title of area affected Funds and Term	Article(s) of the Arrangement: 2 & 3 Initiator of change: ESA
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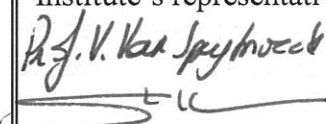
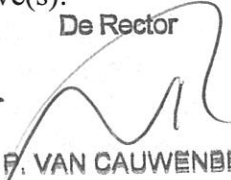
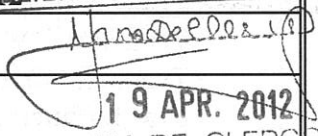
Description of change
Increase of funds and extension of term


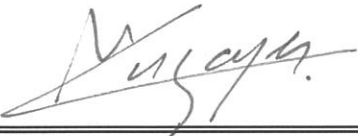
Reason for change
Approval of BELSPO for the continuation of the activities in 2012 with an additional budget (see Work Description and Financial Plan attached)

Funds *in addition to* those stipulated in Article 2.1:
29,400 EUR

Breakdown of Funds in addition to the one stipulated in Article 2.2
See Financial Plan

Effect on other Arrangement provisions N.A.	Commencement of Term 01.01.2012 End of Term 31.12.2012
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Institute	
Institute's representative(s):  De Rector  Prof. F. VAN CAUWENBERGE	Date  19 APR. 2012 YANNICK DE CLERQ REGERINGSCOMMISSARIS 16 APR. 2012

ESA	
PRODEX Office representatives: V. Dowson  M. Lazerges 	Date 21.3.2012

- Title/Acronym: **Self-assembly of hierarchical catalysts and adsorbent materials from Ordered Liquid Phases (OLPs).**
- Abstract (max. 5 lines): This project did and will give further insight into the molecular mechanisms of silica structuring to enable design and synthesis of tailor made materials. Zeolite formation has been discovered to be based on self-organization of nanoscopic precursor species. Shear and convection have strong effect on this self organization process, which only can be studied under microgravity conditions.
- Identification of the overall project selected/endorsed by ESA (AO or none): AO-2004-027: Self-assembly of hierarchical catalysts and adsorbent materials from Ordered Liquid Phases (OLPs); rated Excellent in Peer Evaluation.
- Possible role of the BPI and of each Bco-I in the overall project selected/endorsed by ESA (PI, co-I, other):
 - ⇒ *PI*: C. Kirschhock and J. Martens, COK (Centre for Surface Chemistry and Catalysis), KU Leuven: Overall co-ordination of project. Physico-chemical characterization of OLPs and related development of the necessary hardware. Optimization of flight-sample and post-flight data analysis.
 - ⇒ *co-I*: J. Vermant, CIT (Division of applied rheology and polymer processing, Department of Chemical Engineering), KU Leuven: Rheological characterization of OLPs. Development of a model system for aggregation of sticky ellipsoidal nanoparticles. Development of hardware for combined in-situ DLS and rheological studies. Post-flight data analysis.
 - ⇒ *co-I*: G. Nicolis and P. Gaspard, CENOLI (Centre for nonlinear phenomena and complex systems), ULB: Theoretical description of OLPs.
 - ⇒ *associated co-I (not included in original AO-2004-027 project)*: S. Bals, G. Van Tendeloo, EMAT (Electron Microscopy for Materials Science), University Antwerp: Transmission electron microscopy and tomography to characterize zeolite precursors used for microgravity experiment.
 - ⇒ *associated co-I (not included in original AO-2004-027 project)*: V. Van Speybroeck, M. Waroquier, CMM (Center for Molecular Modeling), University Gent: Molecular Modeling of zeolite precursor aggregation on molecular level.
- Satellite(s) or flight opportunity(ies) (+ date(s)) selected/endorsed by ESA: Foreseen ISS experiment during 2014
- Starting and ending dates of
 - ⇒ the overall project selected/endorsed by ESA: 01/01/2006–TBD
 - ⇒ the requested PEA: 01/01/2012–31/12/2014
 - PEA No. C90229: 01 January 2009 - 31 December 2011; 265.383€

Identification of the BPI.

- Title, surname, name: Professor Christine E.A. Kirschhock and Professor Johan A. Martens
- Institute/University: KU Leuven
- Department/Laboratory: Centre for Surface Chemistry and Catalysis
- Address: Kasteelpark Arenberg 23; B-3001 Leuven
- Tel.: +32 16 321610
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- E-mail: Christine.kirschhock@biw.kuleuven.be
- Website: <http://www.biw.kuleuven.be/m2s/cok/>
- Institute/Department Head, endorsing this Project Proposal: Professor Ivo Vankelekom

Identification of the Bco-I's (if applicable).

- Title, surname, name: Professor Gregoire Nicolis and Professor Pierre Gaspard
 - Institute/University: Université Libre de Bruxelles (ULB)
 - Department/Laboratory: Centre for nonlinear Phenomena and Complex systems
 - Address: Blvd du Triomphe, Campus Plaine CP231, 1050 Bruxelles, Belgium.
 - Tel.: +32-2-650.55.35
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 - E-mail: gnicolis@ulb.ac.be, vbasios@ulb.ac.be
 - Website: : <http://complex.ulb.ac.be>
 - Institute/Department Head, endorsing this Project Proposal: Professor Pierre Gaspard
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- Title, surname, name: Professor Veronique Van Speybroeck and Professor Michel Waroquier
 - Institute/University: University Gent (UG)
 - Department/Laboratory: Center for Molecular Modelling
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 - Tel.: +32-9-264.65.59
 - Fax: +32-9-264.65.60
 - E-mail: Michel.Waroquier@UGent.be, Veronique.VanSpeybroeck@UGent.be
 - Website: <http://molmod.ugent.be/cmm/wiki/>
 - Institute/Department Head, endorsing this Project Proposal: Professor Michel Waroquier.

Project description and motivation.

Crystal nucleation and aggregation phenomena deserve strong experimental and theoretical effort in the fields of soft and condensed matter physics. Zeolites represent a class of materials that are highly relevant for sustainable industrial development. Their large variety of crystal structure makes them both interesting from an application point of view as well as for theoretical research. The interaction of (organic) template-molecules with actual building material (silica) provides a way for chemical nanostructuring which develops through complex self-assembly pathways. This project focuses on the clear-solution synthesis of the fundamental all-silica zeolite Silicalite-1. This system attracts the attention of many research groups around the world. Although a lot of experimental data has already been obtained, certain steps of the process especially those concerned with nucleation still demand further investigation. A full understanding of the synthesis pathway is necessary in order to achieve control of the resulting nano and mesostructure, a crucial step for successful applications.

OBSERVATION HIERARCHICAL SELF-ASSEMBLY

The aqueous synthesis solution contains a template molecule (tetrapropylammonium-hydroxide) and a silica source (tetraethylorthosilicate). Hydrolysis under high pH conditions leads to the formation of precursor units. The strong interaction of these units represents a complex colloidal system, with strong nonlinear kinetics and cooperative effects, potentially exhibiting self-assembled ordering into Ordered Liquid Phases (OLPs) before solidification occurs. After hydrothermal treatment for a surprisingly long time (about 12h at 95°C, depending on the actual composition), the formation of crystallites starts until an equilibrium state between precursor units and colloidal crystalline particles is established. The precursor units can be observed by dynamic light scattering (DLS), small-angle X-ray scattering (SAXS), and via the rheological properties (linear viscoelastic response). Complementary

diagnostics like NMR- and IR-spectroscopy are used to determine the internal structure and connectivity.

MICROGRAVITY RELEVANCE

Under the influence of earth's gravitational field, temperature and density gradients lead to convection in the reaction volume. On one side, this complicates in-situ observation because the emerging flow depends on actual reactor size and shape. Additionally, the established crystal nuclei with their surrounding depletion zones are disturbed. OLPs are thus less likely to be established. Under microgravity conditions, nucleation events and crystal growth are purely driven by the Brownian motion. This yields a unique environment to separate the underlying mechanisms from disturbing influence. Knowledge gained from such experiments will definitely contribute to a refinement of crystallization models, which is necessary to intentionally tailor the nanostructure of functional materials. The proposed project fits well in previous microgravity experiments (MAXUS 4 and 5, Odissea) and is backed up by ongoing ground-based experiments (hypergravity, shear-flow, in-situ diagnostics) as well as advancements in the theoretical understanding (Monte-Carlo, structural, and molecular dynamics simulation).

TASKS

Development of equipment and refinement of experimental procedures

In mid 2011 Phase B of the development of the Zeolite Solution Diagnostics Facility (ZSCDF) was launched. In close collaboration with the industrial consortium (Astrium, QinetiQ, Lambda-X), the design of the breadboard prototype is close to finalization. A significant task in the current proposal is the continuation in supporting the hardware development process and prototype testing. In the ideal case, experiments carried out within this dedicated reactor and diagnostics facility will immediately result in new insights. The ZSCDF represents a unique observation platform for in-situ sample preparation (precisely controlled mixing of reactants), synthesis (pressure and temperature control), and diagnostics (precision DLS, turbidity, and viscosity). Supplemental experiments aim at controlled convection, e.g. by steady and oscillating shear-flow and by colloidal stabilization of OLPs, e.g. by using surfactant additives or external fields. In parallel a number of experimental methods (NMR, SAXS, UV-Raman) will be applied on systems identical to the ones proposed for the microgravity experiments. Cross correlation of these results will allow determining the exact state of the studied system in function of the data obtained by the microgravity hardware.

Complementary to the preparation of the microgravity facility, ground-based experiments at elevated gravity levels up to 20g (maximum for large-diameter-centrifuge LDC at ESTEC) were started and need to be continued. In-situ DLS and sample preparation for offline analysis were demonstrated to yield useful results. Parabolic flights providing zero-g for a timeframe insufficient for complete synthesis, but long enough for analysis (DLS), should be considered as well.

Theoretical understanding and matching to experimental results

A deep theoretical understanding of the nucleation and crystallization processes is necessary for the proper interpretation of obtained results and for drawing the correct conclusions. The Silicalite-1 synthesis seems to exhibit the right degree of complexity to perform numerical analysis by both static and dynamic methods. A first step consists in the development of nonlinear mean-field type models (reactors under sheer, advection-diffusion, external fields). Next, Static Monte-Carlo simulations can provide likely molecular structures, and associated

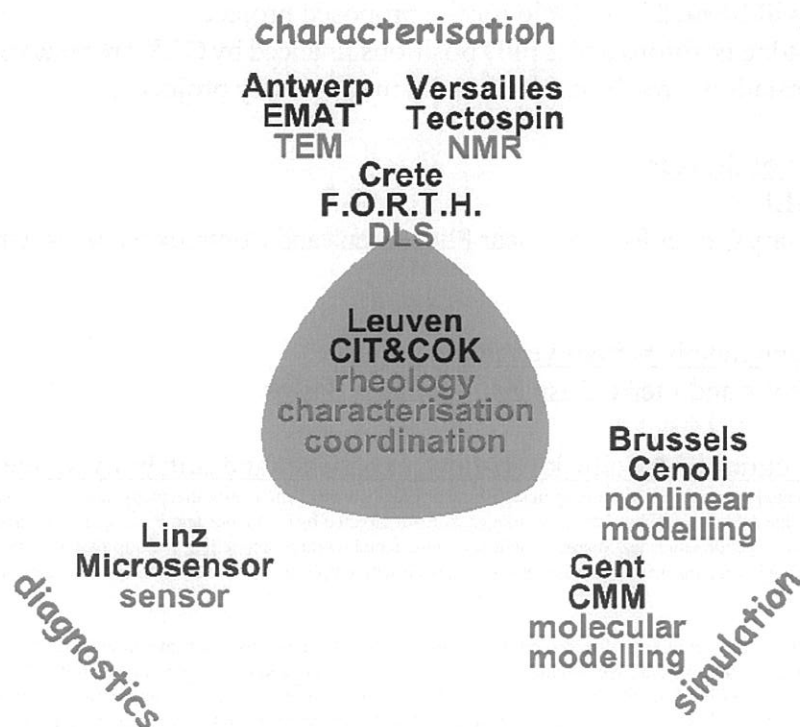
absorption spectra and diffraction patterns. Finally through direct molecular dynamics computations are not yet capable of dealing with the long reaction times observed in the synthesis process, hierarchical (coarse-grained) models suitable for performing Kinetic Monte Carlo simulations might be the proper approach for unravelling the large scale behaviour and are currently being developed. This is of utmost importance in view of limited knowledge of assignment of for example NMR and Raman data obtained in the parallel experimental campaign to unravel zeolite formation on all scales from molecular to macroscopic level.

Interaction with related research fields

Non-standard nucleation and strongly interacting colloids are observed in different fields of science. Proteins, though entirely organic in nature, seem to behave similarly during induction and additive crystal growth. Colloid science, on the other hand, deals with simpler chemical systems (mostly non-reactive) but provides knowledge about collective and self-assembling behaviour and respective ways of observation (e.g. rheological and advanced optical methods). Within this proposal, ties with these fields should be formed and maintained. Especially the aspect of colloidal organisation into supramolecular assemblies will be studied in great detail as this has direct impact on the understanding and interpretation of the data which are to be collected during the microgravity campaign.

Description of the scientific team(s).

The team studying OLPs consists of 8 European research groups. The following scheme indicates the individual function of each team member



Identification of the team

COK - Centre for Surface Chemistry and Catalysis

Department for Microbial and Molecular Systems M²S
Faculty of Bioscience Engineering
Katholieke Universiteit Leuven, KUL
Belgium

List of the team members involved in the project

Project Coordinator: Prof. C. Kirschhock, Prof. J. Martens
3 Postdoc students (2 financed by COK/CIT, 1 financed by Prodex)
2 PhD students (financed by COK /CIT)

Role, contribution and specific know-how, experience and suitability for the assigned activity

Asides the co-ordination of the whole research project the role of the COK is central with regard to the integration of the scientific results of the individual groups. The major role of the COK will be the detailed study of parameters affecting OLPs and the testing and calibration of the sample environments. During the development of the ZSCDF facility with in-situ DLS and viscosity measurements the COK will take over a supportive function ensuring the facility meets the requirements and maximize scientific impact.

In its previous microgravity campaigns the COK was the first group to discover OLPs during the self-organization of nanoscopic zeolite particles. A wide range of expertise in the fields of material synthesis and characterization is available. The COK is leading in the study of zeolite formation from molecular to macroscopic scale and has proven to be able to transfer scientific know-how into the design of functional materials. In close collaboration with team CIT, the effect of forced and spurious convection on assembly at the nanoscale is being investigated.

Funding sources and amounts available outside PRODEX for the requested project

The infrastructure of the COK and international contacts with groups specialized on specific diagnostics will be made available for the proposed project.

Two full Postdoc positions and 2 PhD positions financed by COK are reserved for the analysis of zeolite formation directly supporting the microgravity project.

Identification of the team

Team CeNoLi

Interdisciplinary Center for Nonlinear Phenomena and Complex Systems, Université Libre de Bruxelles

List of the team members involved in the project

Gregoire Nicolis and Pierre Gaspard, Vasileios Basios

Role, contribution and specific know-how, experience and suitability for the assigned activity

The Center is dedicated to research and training in statistical physics, physical chemistry, thermodynamics, stochastic processes, nonlinear science, chaos theory and simulation techniques. A team directed by G. Nicolis and P. Gaspard comprising also V. Basios, P. Grosfils, J. Lutsko and Nelido Gonzalez-Segredo conducts fundamental research, modelling and simulation on nucleation, self-assembly and growth, and related problems arising in microgravity research with emphasis on kinetic aspects, self-organization and nonlinear dynamical behaviours.

The work carried out by the Cenoli team focused on developing mathematical models and computational schemes to account for the non-standard aggregation mechanisms during crystallization in zeolite systems revealed by the experiments of the Leuven group. The models developed explain the experimentally observed induction period and the final apparent equilibrium between nano-particles and zeolite crystals. Furthermore the early stages of self-assembly were analysed with emphasis on the presence of competing pathways, symmetry, size and dimensionality. Our approach is based on a multilevel description involving mean-field analysis, lattice-based stochastic theory and Monte Carlo simulation. The plans for the next three years include:

- (I) The model developed jointly by the Cenoli and Leuven groups will be augmented to include explicitly the nature of intermediates as well as other mechanisms involved in later stages of nucleation, such as Ostwald ripening.
- (II) The model which was so far developed under conditions of a well-stirred reactor, will be further extended to include spectral

degrees of freedom. The resulting nonlinear reaction-diffusion equations will be studied by asymptotic methods and by numerical integration techniques suitable to account for growth.

- (III) A mesoscopic level Kinetic Monte Carlo approach to the growth of zeolite crystals arising from the aggregation of intermediates formed in turn by the combination of nanosize precursors will be developed. The aim is to determine (a) the time evolution of the total amounts of precursors, intermediates and solid crystallites; (b) the structure of the nascent solid and the size distribution of solid particles during different stages of the process; and (c) the role of biases of different kinds and specially those associated to gravity and to advection on the efficiency of the process.

Identification of the team

EMAT , University of Antwerp

List of the team members involved in the project

Prof. Sara Bals, Prof. Gustaaf Van Tendeloo

Role, contribution and specific know-how, experience and suitability for the assigned activity

EMAT is the leading expert in the field of material characterisation by transmission electron microscopy (TEM). This method is indispensable for the ground based investigation of the studied systems. More specifically TEM allows the direct analysis of the degree of order in the materials after aggregation/crystallisation as well as the orientation of the crystal axes in the formed particles. The detailed analysis of these parameters yield important clues on the growth mechanism of zeolites in general and ensures optimum preparation of the microgravity experiments. Due to their complex structure, zeolites are ideally investigated in 3 dimensions. This is particularly challenging since it is often impossible to obtain a large number of high quality images because samples will be damaged when being exposed to the electron beam for too long. Therefore, we will use novel 3D reconstruction algorithms that are able to reduce the number of images for a high quality reconstruction from 100-200 to 10-20.

Identification of the industrial work (if applicable).

The proposed project parallels the ongoing hardware development for microgravity experiments onboard ISS, the Zeolite Solution Crystallization Diagnostics Facility (ZSCDF). The current stage is Phase B, which covers the design and build-up of a laboratory prototype of the actual setup. QinetiQ Space supplies the reactor and process control electronics. Lambda-X provides the optical diagnostics (DLS) facility. Astrium is prime contractor and responsible for system integration, data processing and storage, and additional control electronics. Alenia Space contributes software development. The development of the viscosity sensor electronics is carried out by the Austrian Center for Competence in Mechatronics (ACCM). All of these partners are subject to supply equipment and services that are necessary for scientifically sound ground experiments but not covered by the ESA contract.

Milestones related to continuous activities

M1) Co-ordination of research project and integration of the results from the team members

Teams: COK

Salaries: covered by COK

Travel: **8 k€** spread over 3 years asked from Prodex

M2) Experimental characterisation of molecular building units to be used in OLP

studies

Teams: COK, CIT, EMAT, Tectospin, F.O.R.T.H.

Salaries COK, CIT: 2 PhD position + 1 Postdoc positions over 3 years 100% covered by COK/CIT; 100% **Postdoc** position + 100% **PhD** position over 3 years asked from Prodex
Consumables COK, CIT (high grade chemicals, sample holders, measurement costs for large numbers of sample series synthesised with varying parameters to optimize system): 36 k€ over 3 years: 27 k€ covered by COK, **9 k€** asked from Prodex

Travel COK, CIT: 20 k€ over 3 years: 4 k€ covered by COK; **16 k€** asked from Prodex, including extended stays of students in partner laboratories.

Equipment COK: upgrade of the existing SAXS equipment with a detector with increased resolution in the size range of the studied zeolite nanoparticles. This detector will allow in situ study of crystallization processes to serve as references for the data sets obtained by DLS and viscosity screening (**50 k€**)

Consumables EMAT: **51 k€** over 3 years asked from Prodex: Sample holders, liquid gases, man- and machine time for the TEM analysis of samples related to microgravity project. Sensitivity to electron beam of nanosized samples makes this task extremely demanding and cost intensive. Estimated are 4 samples per month.

Travel EMAT: **9 k€** over 3 years asked from Prodex

M3) Co-operation with research teams in related scientific areas

- Equipment (DLS, rheological methods) already applied for zeolites will be used to study protein crystallization (preliminary experiments already performed).
- Colloidal properties of zeolites will be investigated, and methods to assemble building blocks in the liquid phase will be developed.
- Common methodologies in protein crystallization and in zeolite studies will be further explored.

Teams: COK, CIT, Cenoli

Salaries and travel: see M2, M4

M4) Theoretical study of molecular building units to be used in OLP studies

- Mean field modeling, stochastic analysis and Kinetic Monte Carlo simulation of nucleation of hierarchical self-assembly in zeolite suspensions.

Teams: Cenoli, CMM

Salaries CMM: **50% PhD** over 3 years asked from Prodex

Consumables CMM: **15 k€** over 3 years asked from Prodex, mostly computertime on Flemish supercluster, simulations need to explicitly contain water molecules surrounding the silicate units which is extremely costly in computertime

Travel CMM: **9 k€** over 3 years asked from Prodex

Salaries Cenoli: **50% Postdoc** over 3 years asked from Prodex

Consumables Cenoli: **10.5 k€** over 3 years asked from Prodex

Equipment Cenoli: hardware for multiscale simulation of long range ordering/interaction of silicate units in solution **10 k€** asked from Prodex

Travel Cenoli: **7.5 k€** over 3 years asked from Prodex

M5) Improvement and optimization of rheology sensor

The currently available prototype viscosity sensor will be assessed for further improvement and use beyond viscosity. Among the parameters which could be optimized are surface

roughness and protective coating of the sensor, extension of the monitored frequency range, coupling with a low-frequency resonator and implementation of advanced signal processing

Teams: LINZ,CIT,COK

Travel/salaries: see M2

Equipment CIT/COK: components and small lab items **18 k€** over 3 years asked from Prodex, a laboratory model of the viscosity sensor electronics is asked for, max **70 k€** to cover purchase, installation, and maintenance for 3 years

Milestones directly related to mission preparation (timeline estimation based on unofficial information by ESA)

M6) 0-6months: Phase B hardware development of microgravity equipment

Continuous collaboration with industry partners to guide the design of the space hardware.

Teams: COK, CIT, LINZ

Travel/salaries: see M2

Equipment: components and small lab items **6 k€** asked from Prodex

M7) 6-24 months: Phase C of hardware development

Close collaboration with industry is foreseen to ensure optimum experimental conditions. Test samples and model samples will be prepared and fully characterised to assess performance of breadboards/prototype. Flight samples will be chosen and repeatedly fully characterised using flight prototype and ground based equipment. Sensor implemented in hardware will be calibrated with model and synthesis fluids.

Teams: COK, CIT, LINZ

Travel/salaries: see M2

Equipment: components and small lab items **6 k€** over 2 years asked from Prodex

M8) 24-36 months: Phase D microgravity mission preparation

Close collaboration with industry is foreseen to ensure optimum experimental conditions. Flight samples will be chosen and repeatedly fully characterised using flight prototype and ground based equipment. Sensor implemented in hardware will be calibrated.

Teams: COK, CIT, LINZ

Travel/salaries: see M2

Equipment: components and small lab items **6 k€** asked from Prodex

M9) Microgravity experiments onboard ISS

Teams: COK, CIT

Costs: see M2

M10) Postflight data analysis

Teams: COK, CIT, F.O.R.T.H.

Costs: see M2

Ground based study directly related to microgravity experiments

M11) 0-12 months: Study of shear imposed on zeolite synthesis solutions

Using the available hardware at KULeuven the effect of controlled shear during zeolite formation will be assessed. Samples will also be characterised with the whole range of experimental diagnostics.

Teams: COK, CIT, EMAT Tectospin
Costs: see M2

M12) 0-24 months: Development and characterisation of model system of aggregation behavior of anisotropic, ellipsoidal particles

- Kinetic Monte Carlo simulation of aggregation. Comparison of simulation and experimental results.
- Monodisperse anisotropically shaped particles (ellipsoids and rods) have recently been synthesized and their interactions can be tuned. Their size will be optimised to mimic the situation in zeolite suspension and their behavior will be analysed and simulated in function of convection and shear. The system will allow the development of a model for aggregation of anisotropic particles like nanosized zeolite precursors.

Teams: COK, CIT, Cenoli
Costs: see M2, M4

M13) 12-24 months: Study of dense zeolite suspension using multiple scattering

An experimental setup to analyse and deconvolute light scattering from samples with multiple scattering is available. The setup will allow assessment which information can be extracted from dense zeolite suspensions. Also these samples will be exposed to shear and fully characterised.

Teams: COK, CIT, EMAT Tectospin
Costs: see M2

M14) 0-12 months: Study of increased gravity on zeolite synthesis solutions

An already available DLS setup will be installed inside a centrifuge (ESTEC) to assess the impact of increased g-levels on zeolite formation.

Teams: COK, CIT
Costs: see M2

M15) 12-24 months: Synthesis of experimental and theoretical results to include convection and shear into a model of zeolite formation

While the self-organisation of elemental units into zeolites strongly depends on convection and gravity levels, these effects cannot be explained and predicted. The microgravity results together with the molecular level forces obtained by CMM will allow the development of a model taking flow and convection into account. This model is expected to greatly benefit optimisation of zeolite synthesis in industry.

Teams: COK, CIT, EMAT, CMM, Tectospin, F.O.R.T.H., Cenoli
Salaries, Consumables, Travel: see M2, M4

FINANCIAL PLAN (in Euro)

- Date of this financial plan: 17/12/2011
- Title/Acronym: OLPs
- Name and role (BPI or Bco-I) of the investigator: V.Van Speybroeck (Bco-I)
- Institute/University: CMM - University Ghent
- Starting and ending date of the requested PEA: 01/01/2012 – 31/12/2012

Table 1: Institute Costs.

Post	2012
1. Salaries: – PhD, grant, 50 %	20 000
2. Travel	3 000
3. Small Equipment (< 5 000 € per item)	5 000
4. Overheads (5 %)	1 400
Total	29 400

TOTAL:	29 400
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