PRODEX EXPERIMENT ARRANGEMENT CHANGE NOTICE

Institute: **University of Gent**
PEA No: **4200090364** **CN No**: 3
Project: **Self-assembly of hierarchical catalysts and absorbent materials from Ordered Liquid Phases (OLPs) – Prof Van Speybroek**

Title of area affected **Funds and Term**	Article(s) of the Arrangement: **2 & 3** Initiator of change: **ESA**

Description of change
Increase of funds and extension of term

Reason for change
Approval of BELSPO for the continuation of the activities in 2013 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 **01.01.2013** End of Term **31.12.2013**

Institute

Institute's representative(s):	Date

ESA

PRODEX Office representatives: V. Dowson V Dowson M. Lazerges	Date 8.1.2013

A. Identification of the proposal.

- **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.
- **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 requested PEA: 01/01/2013–31/12/2013
- **Field of research (see annex 1):**
  - ⇨ general (LS&PS/EO/SS): LS&PS
  - ⇨ PRODEX Pole(s) of Expertise (if any): Fluid Dynamics and Surface Tension, Multi-Component Systems; Materials Designed from Fluids

B. 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
- Fax: +32 16 321998

– 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

C. 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
– Fax: +32-2-650.57.67
– 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

– Title, surname, name: Professor Veronique Van Speybroeck and Professor Michel Waroquier
– Institute/University: University Gent (UG)
– Department/Laboratory: Center for Molecular Modelling
– Address: Proeftuinstraat 86, 9000 Gent, Belgium.
– 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

D. Project description and motivation. (max. 2 pages)

SUMMARY

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.

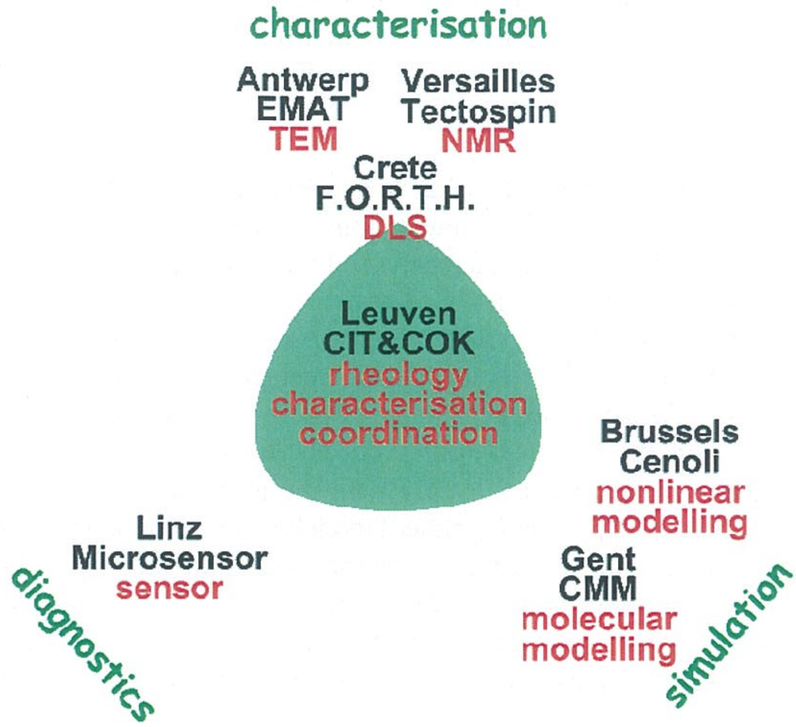
Complementary to the preparation of the microgravity facility, ground-based experiments at elevated gravity levels up to 20g (maximum for large-diameter-centrifuge LDC at ESTEC) were started and need to be continued. In-situ DLS and sample preparation for offline analysis were demonstrated to yield useful 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.

E. Description of the scientific team(s). (max. 2 pages per team)

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
Center for Molecular Modeling (CMM) , Ghent University

List of the team members involved in the project
Prof. Veronique Van Speybroeck, Prof. Michel Waroquier
3 PhD students (2 ½ financed by CMM, ½ financed by Prodex)
1 postdoc financed by FWO

Role, contribution and specific know-how, experience and suitability for the assigned activity
Computational molecular modeling is the core activity of the applicants from Ghent University (CMM). The CMM has already a longstanding experience in modeling porous materials and the catalytic activity of these materials. Determining the active site in these catalysts and elucidating their related reaction mechanism are of paramount importance for the road to the rational design of catalysts and offering prospects of improved formulations of existing catalysts. The COK-CMM team is a unique tandem for an experimental-computational approach of the template mediated formation of porous materials. In this specific topic on zeolite formation both partners have recently published some joint papers and currently two PhD students have started their research activity in this domain under a joint supervision.
Beside zeolites, assembly of precursor particles can also be exploited for the synthesis of microporous-mesoporous hybrid materials. Aggregation on the meso-scale can be obtained

e.g. using surfactants or polymers . Today the situation of microporous-mesoporous hybrid materials is similar to that of zeolites some 20 years ago. In those days the exploration of hypothetical theoretical frameworks in several instances inspired researchers to synthesize new zeolite materials .With the present project the applicants expect to be able to realize a similar breakthrough in zeolite and poly-porous material synthesis.

Mid-term R&D strategy with regard to this project (*i.e.* for the period after the end of the requested project)
Since a couple of years the CMM has built a reputation in developing software packages of general use for a large community of potential users. The development of an extensible GUI-Toolkit with building algorithms for the construction of hierarchical zeolite models can be extended for building any complex molecular system (modeling of initial structures in a solvent, or in an extended periodic environment). The CMM has a special website devoted to all in-house developed software : http://molmod.ugent.be/cmm/wiki/Software .
The development of a new concept for constructing high-level force fields makes an extensive use in a broad area of applications possible. This specific research topic belongs for the moment to the core-business of the CMM with highest priority. It is the intention to gain sufficient expertise to compete with the world for the development of generic force fields for the optimization of large (bio)systems, microporous crystalline silicate materials etc.. This expertise will open a lot of perspectives when transferring the knowledge to other areas of molecular modeling : design of new materials which becomes a new growing topic worldwide. It is a challenge for the CMM to enter the world of the materials science, it opens new perspectives for the various tools developed in house.

F. Identification of the industrial work (if applicable). (max. 1 page)

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.

G. Detailed milestones and related costs. (max. 3 pages)

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 postion + 1Postdoc 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 inofficial 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 mimick 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 aggreation 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: 01/01/2013 – 31/12/2013

Table 1: Institute Costs.

Post	2013
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**