

AO-2004-027 ZEOLITES
INVESTIGATION OF FORMATION OF POROUS SILICATES IN
PRESENCE OF ORGANIC TEMPLATE MOLECULES.

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ABSTRACT

The goal is to improve insight into the molecular mechanisms of structuring of silica with the help of organic templates to enable the design and synthesis of tailor-made materials. The proposed research project will investigate the rheological parameters affecting formation and behaviour of ordered liquid phases (OLPs) and their relation to the structure of the materials obtained from them. As microgravity strongly favours the ordering and aggregation processes within the OLPs, it offers a unique environment where these effects can be studied in detail. Experimental analysis of the OLP will be complemented by theoretical modelling of inter-particle forces concluding in selforganization.

Extract from information available at

http://www.esa.int/SPECIALS/HSF_Research/SEMM32YRA0G_0.html

The team members hereby state that ESA is authorized to post information contained in this report on its website for public information.

Funding of individual team members

Removed

- **Overview of ground based work performed by each team member**

Workpack COK/CIT K.U.Leuven

Workpack F.O.R.T.H.

Workpack Bochum

Members COK/CIT: C. Kirschhock, J. Martens, J. Vermant, L. Follens

Members F.O.R.T.H.: D. Vlassopoulos, B. Loppinet

Members Bochum: H. Gies

The main goal of this project is to improve insight into microscopic mechanisms of structuring of silica in the presence of organic templates to enable the rational design and synthesis of tailor made porous materials. Through the recent discovery under conditions of microgravity that the formation of a particular zeolite (Silicalite-1) relies on self-organization processes, possibly within Ordered Liquid Phases (OLP's) of nanoscopic precursor species, a concise study of the behaviour of these OLPs and the identification of parameters affecting the self-organization was proposed. To reach these objectives, the work was concentrated on two areas: 1) Gaining experience in handling OLPs and 2) Development of experimental environment. On both research areas much progress has been made.

First of all a concise study of the clear solutions, which are the starting point for any synthesis, was made at room temperature. The impact of different parameters like dilution (amount of water and amount of EtOH), pH (amount of TPAOH, TPABr, water, CsOH), amount of template (TPAOH, DTPAOH), on the formation of nanoparticles was studied. In the performed research, dynamic light scattering (DLS) was used as principal technique as it will also be used as probe diagnostic in future microgravity work. Because the studied solutions are highly complex other techniques like SAXS, ^{29}Si NMR, viscosity, pH, RAMAN and TEM were used to complement DLS and avail the interpretation of the results.

A careful analysis of DLS data of the dynamics of the suspensions revealed the occurrence of two distinct diffusive processes. Based on data from the combined SAXS and NMR measurements, a physical interpretation of the two modes was possible. The faster process corresponds to a collective particle diffusion. The slower process corresponds to the particle self-diffusion and is present because of the presence of polydispersity in size, shape and/or surface charge. The self-diffusion coefficient provides a means to estimate the equivalent hydrodynamic radius. On the same samples ^{29}Si NMR data showed the coexistence of silicate oligomers and particles. For the first time, both fractions were analyzed simultaneously, providing a global, quantitative description of the clear solution microstructure. From ^{29}Si NMR patterns particle volume fractions could be deduced. These fractions combined with the SAXS patterns, could also be used to estimate a particle size. Moreover the SAXS data helped us gain insight in the size and structure of the nanoparticles in solution. The observations reveal a complex, polydisperse mixture of particles present at the onset of the Silicalite-1 zeolite formation. Moreover, the role of the effect of particle

size, shape and charge polydispersity should be considered when modeling the zeolite assembly process.

The parametric study revealed some interesting new aspects. It was found that the average connectivity of silicon nuclei in nanoparticles and the size of these particles depend on the composition of the clear solution. Next to these studies at room temperature, the crystallization was followed at elevated temperature for clear solutions with different composition. A turbidity study at elevated temperatures of the same set of samples helped gather information about crystallization times of these clear solutions. *In-situ* SAXS, DLS and liquid ^{29}Si NMR measurements were performed on selected samples. These studies will help us define the most promising experimental conditions for microgravity experiments.

Next to this work, we investigated a clear solution aged for 40 months at room temperature. Aggregates of nano-sized crystalline units of Silicalite-1 zeolite were detected in a detailed TEM analysis of this sample. Inspection of the TEM images reveals the coalescence of these building units into larger crystalline zeolite particles even without heating. The smaller individual units resemble the earlier proposed nanoslab and preferentially stack along a or b crystallographic directions. To further analyze the aggregation sequence, analysis of several clear solutions differing in age and composition with TEM, DLS and liquid state NMR is currently in progress.

The measurements, analysis and interpretations were performed in close collaboration with some other laboratories and research groups. SAXS patterns were recorded at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) on Beamline BM-26B (DUBBLE). These measurements took place in close collaboration with B. Loppinet from F.O.R.T.H. who also helped with the processing and analysis of the obtained data.

The ^{29}Si NMR experiments were carried out at the 'Institut Lavoisier' of the 'Université de Versailles St-Quentin' in close collaboration with M. Haouas and prof. F. Taulelle. This group also made great efforts to help us with a detailed analysis of the obtained spectra. The results from this NMR work are of great importance in the interpretation of the data obtained with SAXS and DLS and for this reason we need to continue this excellent collaboration and include them in the team working on this project (*vide supra*). This work has already led to a publication in *Chem. Mat.* (*vide infra*) and several more manuscripts are currently in preparation..

DLS measurements were performed at the CIT under supervision of Prof. Vermant and at the F.O.R.T.H. institute in Crete with help from B. Loppinet. Both also helped with the analysis of the obtained results. The algorithm to analyze DLS autocorrelation functions (ACFs) with ILT–MEM (Inverse Laplace Transform – Maximum Entropy Regularizer) was developed by Delsuc and co-workers from the Centre de Biochimie Structurale in Montpellier. In collaboration with this group and Prof. Taulelle from the Versailles group, software was developed to analyze the ACFs automatically with the ILT–MEM method, resulting in a decay rate distribution function. The peaks in these decay rate distribution functions are fitted, using Gaussians, to determine the average relaxation rates and associated amplitudes of every peak. This work was also automated in collaboration with the same groups.

TEM images were made at the University of Antwerp thanks to the collaboration with Prof. Van Tendeloo. This work has recently been accepted for publication in *J. Phys. Chem C*. As TEM is a very powerful technique which provides extra information about the solutions under investigation, we need to continue this collaboration in the future to have extra confirmation of the in situ studies of the studied systems. For this reason we propose to add Prof. Van Tendeloo as a team member in this project (*vide infra*).

Asides focusing on the selected study case of Silicalite-1 synthesis, the susceptibility of other porous material syntheses to convection and gravity conditions were explored. Using cyclic template molecules we succeeded to identify the elemental building unit which can lead under different condition to different zeolite topologies. In close collaboration with Prof. Gies (Ruhr University Bochum) this system, besides the silicalite-1 synthesis, serves as model system to develop a new diagnostic method to identify the molecular building units in non-crystalline products. The method relies on extraction of the pair-distribution function from diffraction data recorded over a large q-range. First synchrotron measurements and data analysis indicates this method is a powerful tool to follow the connectivity within molecular building units on their way to solid formation. Research efforts on the further development of this diagnostic tool will continue on an international basis also involving groups in UK and Japan.

In a collaboration with Prof. Steinberg (Queensland University of Technology) the strong effect of low and high gravity condition on the gelation of acid silica sols was analyzed. Currently we hope that this very promising collaboration can be intensified to apply the experience of the Australian group using high-gravity equipment on the zeolite syntheses we currently study. For this reason we propose the group of Prof. Steinberg as new team member.

The second research task was the development of an experimental environment. Construction plans for a shear and flow cell were developed to study the effect of induced shear and flow on OLPs. The actual construction of this cell has been postponed since a similar cell setup is available from colleagues at the Forschungszentrum in Jülich. An agreement was made that we will use their equipment for preliminary measurements on our studied systems to improve our cell designs before continuing with the construction.

In the context of hardware development much effort was invested in the development of a viscosity-sensor in close collaboration with Prof. Jakoby and his team at the University of Linz (*vide infra*). Collaboration with Verhaert space also continued. In the search for materials which can withstand the harshness of our samples some preliminary tests on materials were performed.

Workpack Cenoli ULB

Members: G. Nicolis, P. Gaspard, V. Basios

Model building:

The early steps of self-assembly of the elementary building blocks of nanoparticle materials have been studied, with emphasis on the relative roles of entropic and energetic factors in determining the relative abundance of the final products. To this end a generic mean-field model and a mesoscopic approach in which self-assembly is viewed as an encounter-controlled process on a discrete lattice have been developed. One of the main results of the analysis has been that building

units expected to contribute the most to the formation of the final material exist only as a small fraction when only entropic effects are taken into account. An enhancing mechanism has been proposed, based on the interplay between reversible binding and interparticle interactions. Regarding the relevance of the results in zeolite synthesis, the results so far constitute only a first step of a broader problem. It is now planned to address zeolite synthesis in a more quantitative manner and, in particular, to account for the more mature stages of the process, where ordered liquid phases are formed.

Integration of new experimental data:

In collaboration with members of the Leuven team a mean field model was developed to account for the data available on the kinetics of oligomers, nanoparticles and intermediates during the synthesis of the final solid material. The relative roles of initial conditions, cooperativity and delays related to the formation of aggregates and/or diffusion has been assessed. The full model and simplified versions were run and the simulations reproduce the main qualitative features of the available data. Currently a finer, experiment based tuning of the parameters is being pursued in order to achieve quantitative agreement. Furthermore, work aiming at an analytic insight is in progress.

In order to meet the computational challenges related to the project we finalized the necessary specifications and begun mounting a “PC-Cluster” that will be dedicated to molecular dynamics and the numerical solution of partial differential equations. Concerning the hardware we finalized an appropriate configuration of a High performance computer cluster from “*UniPress.be, HPC - High Performance Computing/Research*”, with a Linux operating system. CPU Pacifica Opteron 8216 2,4 GHz Socket AM2 2x1MB Cache (DUAL CORE), 2Gb of memory (supports extensions up to 128GB), in a UniWide 3U configuration. Concerning software a suite of Finite Element/Finite Difference/AdaptiveMesh algorithms was written in FreeFEM++ language of INRIA (France).

For this work some collaborations were:

- National: Dynamic meteorology and climatology unit of IRM-KMI (Prof. Rouvas-Nicolis) on the development of kinetic models of transitions between states.
- International: Department of Chemistry of DePaul University, Chicago, USA (Prof. J.J. Kozak) and National Research Centre Demokritos, Athens, Greece (Dr. A. Provata) on the mesoscopic approach to self-assembly of nanoparticle materials.

Workpack Linz

Members: B. Jakoby, W. Hilber, E. Reichel, B. Mayrhofer

In the course of this project we aim at devising and investigating a system for the monitoring of structural changes in a liquid medium. In particular we will realize a miniaturized viscosity sensor. Besides the research on and the development of the corresponding hardware we will consider the readout and the interpretation of the sensor signals with respect to the changes in the micro- and nanostructure of the medium under investigation.

Technologies for miniaturized sensors for measurements in colloidal structures are to be devised and evaluated. First piezoelectric thickness shear mode resonators and, alternatively, love-mode sensors and micro machined oscillators are considered. In particular the harsh environmental conditions, due to the high electrical conductivity of the liquid under investigation, have to be

taken into account. A technology and a final design will be selected and will lead to first prototype devices. Furthermore corresponding readout electronics will be designed and fabricated. Measurement of viscosity of Newtonian liquids utilizing quartz crystal resonators operated in thickness shear mode (TSM) are well investigated in the literature. In most of the cases, the sensor is fully immersed in the liquid under test with both electrodes in contact with the liquid. In first experiments carried out during this project, an “of-the-shelf” quartz resonator was used to measure the viscosity of the starting solution of the zeolite synthesis process in cooperation with partners from the Catholic University of Leuven (Belgium; in particular Lana Follens). In these tests, the viscosity of the zeolite starting solution was measured successfully at room temperature utilizing a fully immersed TSM resonator, as shown in Fig. 1. The sensor material could withstand the harsh chemical environment even when heated to the process temperature of 95 °C exposed for 24 hours. No degradation of functionality was observed afterwards. For our partners, the measured indicator for the solution’s viscosity appeared to be a useful indicator to monitor the progress in crystallization.

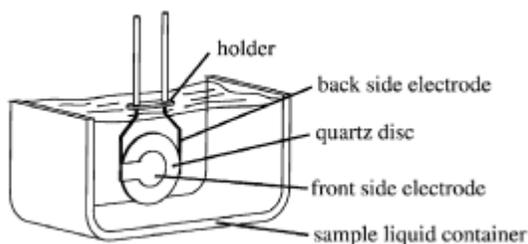


Fig. 1: Schematic of a fully immersed quartz resonator used for viscosity measurement.

At room temperature, the conductivity of the solution is low enough to allow the measurement of the sensor admittance with a highly sensitive impedance analyzer (Agilent 4294A). The electrical equivalent circuit of the immersed resonator is shown in Fig. 2.

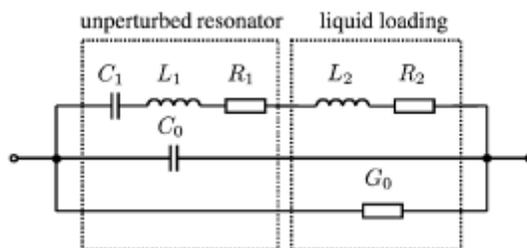


Fig. 2: Electrical equivalent circuit of the immersed resonator. The shunt impedance G_0 leads to measurement difficulties in highly conductive liquids.

During the crystallization process, the solution shows a higher conductivity and some electrochemical effects, which make the use of the fully immersed sensor impractical, though. In the equivalent circuit, this is represented by a spurious shunt conductance G_0 , which can also include a reactive (e.g., inductive) part. Thus a setup is being worked out where the quartz disc is exposed to the liquid only on one side where the other side is sealed off by an O-ring seal. The high alkalinity of the tested zeolite solutions moreover requires proper material selection of the test reactor, especially for the sealing material. To overcome the problem of spurious shunt impedance a packaging of the quartz disc was designed, where only one of the two electrodes is in direct contact with the liquid. A prototype of this packaging consisting of stainless steel housing and a

screw-in sensor element is depicted in Fig. 3. Standard sealing material turned out to degrade during the zeolite synthesis process. The inner resonator electrode is contacted with spring-needle contacts while the outer electrode (exposed to the liquid) is contacted via the metal housing.



Fig. 3: Custom designed stainless steel sensor packaging with sealed quartz disc.

The setup requires a smart design to contact the electrodes, which also minimizes mechanical bias stresses or – alternatively - maintains stress-related effects, which are reproducible. In this context we are currently investigating alternative electrode design aiming at facilitating simple implementation in a setup featuring only one face of the resonator in contact with the liquid (see Fig. 4).

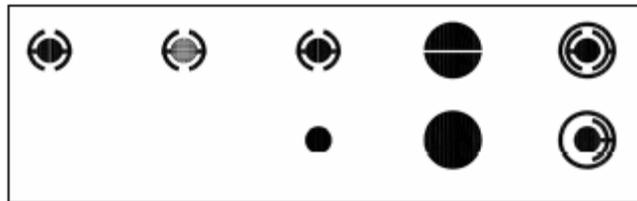


Fig. 4: Alternative electrode layouts under investigation. The shapes show the layouts of the deposited structure on the contacted side (top) and on the liquid side (below, respectively).

All quartz viscosity sensors have to be calibrated with known liquids in order to derive absolute values for the viscosity-density product. Relative changes in viscosity can be tracked without calibration. Especially in the case of the sealed package, additional parameters show a significant influence on the resonant behaviour of the sensor, e.g., the O-ring sealing. In order to reach the desired accuracy level (0.1 mPa.s) it is crucial to calibrate with a known liquid prior to the measurements. Temperature data measured simultaneously can be additionally incorporated to compensate for spurious effects.

The measurement setup currently under development features a quartz disc mounted directly on a printed circuit board, chemical resistant sealings and a PTFE housing for the monitored solution including an online temperature sensor.

For the implementation aboard the ISS a small and robust readout circuit is required, which requires a minimum of electric power during operation. Due to the shunt capacitances and conductances and the high damping due to liquid viscosity, a conventional readout by oscillator circuits is not considered feasible and thus a circuit along the lines we investigated recently is considered. Resonance frequency and damping are both indicators for the viscosity of the liquid. The relation between them can be used to identify non-Newtonian behavior. Fig. 5 and Fig. 6 show a first prototype implementation using an analog front-end actively driving the resonator, where the frequency is adjusted to resonance by a microcontroller circuit. The current prototype draws

about 65 mA out of a +/-5V source. As can be seen in the figures, there is further potential for miniaturization.

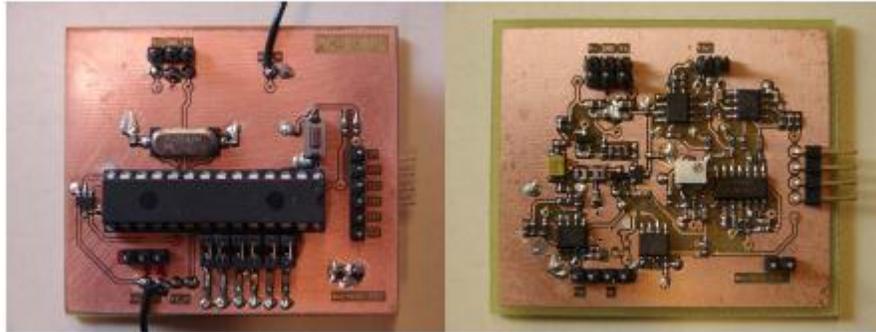


Fig. 5: Prototype implementation of the readout electronics required for TSM resonator sensors: the circuit consists of a microcontroller unit (left) and an analog fronted driving the quartz resonator (right).



Fig. 6: Prototype implementation of the readout electronics required for TSM resonator sensors: the two units (microcontroller unit and analog front-end) are combined in a stacked setup.

First measurements with fully immersed quartz viscosity sensors were performed in June 2006. The viscosity of zeolite starting solutions were measured at room temperature and compared to data measured with laboratory instruments. At that time the sensors were exposed to the solution for 24 hours and more to test for the chemical resistance of the sensor materials.

In October 2006 further measurements were performed using fully immersed quartz sensors. The aim was to track the viscosity development during a full cycle of crystallization process at a temperature of 95 °C. At this temperature the electrical conductivity of the solutions lead to a spurious electrical shunting of the electrodes, which rendered the results useless. The positive result was that the sensor material can withstand the harsh environment even at raised temperatures for more than 24 hours.

The sensor packaging shown in Fig. 3 was characterized with various test liquids in April 2007. To demonstrate the viscosity monitoring capability of the device, the gelation process of a silicone elastomer was measured successfully. The standard sealings used at that time were determined to be not suitable for the zeolite solutions. In the meantime the sealings have been replaced with Viton O-ring seals. Further experiments are required to proof that the recently devised sensor setup is ready for the online measurement of the viscosity during the zeolite crystallization process.

Collaboration between the Institut für Mikroelektronik in Linz and the COK/CIT was optimized with two short stays from a team member from COK/CIT in Linz (June 2006 and October 2006).

During these stays clear solution samples were prepared to test the sensor at room temperature and at elevated temperatures during the crystallization process.

- **Publications and corresponding abstracts**

Refereed Journal Papers

C. L. Pienaar, G. J. A. Chiffolleau, L. R. A. Follens, J. A. Martens, C. E. A. Kirschhock, T. A. Steinberg, Effect of gravity on the gelation of silica sols **2007**, *Chem. Mater.*, 19(4), 660-664.

Abstract: Acid-catalyzed silica polymerization was carried out under gravity conditions varied from 0.01g aboard a reduced gravity aircraft to 70g in a centrifuge. The silicate connectivity of the final xerogels was analyzed using solid state ^{29}Si NMR and the porosity using nitrogen adsorption. Gravity was found to have an important influence on the occurrence of intra- and intermolecular condensation reactions. Under reduced gravity buoyancy driven-free convection is limited and silica polymerization occurs in a diffusion-limited regime. Intramolecular condensations and densifications prevail and extended coils of cages are formed through cyclization reactions in the sol particles. In terrestrial and high-gravity conditions, bimolecular reactions compete more favorably with internal condensations. More open structures composed of chains and rings are formed. These flexible species delay the onset of gelation, leading to an increase in gelation time as the gravity level is increased. During the subsequent drying procedure, pore collapse changes the structure from meso- to microporous. The porosity of the finally obtained xerogels is mostly defined by the drying conditions of the gel, irrespective of the silicate connectivity.

A. Garcia-Cantu and G. Nicolis, Toward a thermodynamic characterization of chemical reaction networks, **2006**, *J. Non-Equilib. Thermodyn.*, 31, 23-46.

Abstract: The relation between the topology of a chemical reaction network and its thermodynamic properties, particularly the energy dissipation patterns, is analyzed. Both regular and complex structures are considered. For networks consisting of linear reactions, this task is analytically accomplished by formulating the network dynamics in terms of the network's connectivity matrix. The thermodynamic effect of nonlinear feedback dynamics on chemical networks is considered in the limits of close to and far away from equilibrium and discussed in connection with the robustness of the response to external disturbances.

V. Basios, Self-organization and nonequilibrium aggregation phenomena in colloidal matter: why microgravity matters, **2006**, *Int. J. of Bifurcation & Chaos*, 16 (6), 1689-1700.

Abstract: The relevance of self-organization, nonlinear phenomena and nonequilibrium behavior in a wide range of problems in space science and microgravity research, calls for a concerted approach using the tools of statistical physics, thermodynamics, nonlinear dynamics, mathematical modeling and numerical simulation, in synergy with experimentally oriented work. The reason behind the ubiquity of such concepts is that in many instances of relevance in space science one witnesses an interplay between molecular and macroscopic-level entities and processes, such as nucleation in phase transitions or aggregation and self-assembly in materials science and biology. These phenomena are fundamentally dynamic in nature. We present two minimal models one dealing with issues of complex behavior at the microscopic level and the second referring to the strong nonlinear nature of macroscopic evolution, relevant to soft-condensed matter under observation both on the ground and in microgravity conditions. These investigations open the way to a whole class of unexpected situations whose proper characterization and control can only be expected in the framework of nonequilibrium physics and complexity theory.

J.J. Kozak, C. Nicolis and G. Nicolis, Modeling the early stages of self-assembling nanophase materials, **2007**, *J. Chem. Phys.*, 126, 154701.

Abstract: The early stages of self-assembly of the elementary building blocks of nanophase materials are studied. The relative roles of entropic and energetic factors in determining the relative abundance of the final products present is analyzed using both a kinetic mean field model and a mesoscopic approach in which self-assembly is viewed as an encounter-controlled process on a discrete lattice. The relevance of the results in zeolite synthesis in connection with the ordered liquid phases recently discovered in these materials is discussed.

G. Nicolis and C. Nicolis, Dynamics of switching in nonlinear kinetics, **2007**, *J. Phys.: Condensed Matter*, 19, 065131.

Abstract: Chemical systems giving rise to multiple steady states and subjected to fluctuations and a variation in time of the parameter controlling the instability are studied, with emphasis on the kinetics of the switching between two states. It is shown that the presence of a ramp in the control parameter in conjunction with the fluctuations considerably affects the switching process as compared to the predictions of the deterministic (mean field) analysis. Furthermore, both these factors have clear-cut signatures at the level of the system's thermodynamic properties, as described by the entropy production.

C. Riesch and B. Jakoby, Novel readout electronics for thickness shear-mode liquid sensors compensating for spurious conductivity and capacitances, **2007**, *IEEE Sensors Journal*, 7(3), 464–469.

Abstract: In this paper, a readout circuit for a thickness shear-mode (TSM) resonator is presented which can be used for sensing applications in liquids such as viscosity sensing. The system features compensation of both spurious capacitances and conductances in parallel to the resonator. This allows measurements even in conductive liquids without the need for an elaborate sealing of the sensor. The influence of the spurious elements is determined by means of two orthogonal synchronous detectors and eliminated by active compensation using voltage-controlled amplifiers (VCAs). Furthermore, the circuit is robust against possible phase errors. The basic concept is discussed in detail, and a readout circuit is developed. A prototype is presented, and sample results are given, demonstrating the feasibility of the approach.

A. Aerts, L.R.A. Follens, M. Haouas, T.P. Caremans, M.A. Delsuc, B. Loppinet, J. Vermant, B. Goderis, F. Taulelle, J.A. Martens, C.E.A. Kirschhock, Combined NMR, SAXS, and DLS study of concentrated clear solutions used in silicalite-1 zeolite synthesis, **2007**, *Chem. Mater.*, 19(14), 3448-3454.

Abstract: Concentrated clear solutions, as used for the preparation of Silicalite-1 zeolite, were synthesized from tetrapropylammonium hydroxide, tetraethylorthosilicate, and water. The solutions were analyzed using three techniques: quantitative ^{29}Si NMR, synchrotron small-angle X-ray scattering (SAXS), and dynamic light scattering (DLS). ^{29}Si NMR showed the coexistence of silicate oligomers and particles. For the first time, both fractions were analyzed simultaneously, providing a global, quantitative description of the clear solution microstructure. The SAXS patterns, typical of interacting particles, could be used together with the ^{29}Si NMR deduced particle volume fraction to estimate a particle size. A careful analysis of DLS data of the dynamics of the suspensions revealed the occurrence of two diffusive processes. The faster process is a collective particle diffusion. The slower process corresponds to the particle selfdiffusion and is present because of the presence of polydispersity in size, shape, and/or surface charge. The self-diffusion coefficient provides a means to estimate the equivalent hydrodynamic radius. The observations hence reveal a complex, polydisperse mixture of particles present at the onset of the Silicalite-1 zeolite formation. Implications on the proposed zeolite formation mechanisms are briefly discussed.

D. Liang, L.R.A. Follens, A. Aerts, J.A. Martens, G. Van Tendeloo and C.E.A. Kirschhock, TEM observation of aggregation steps in room-temperature silicalite-1 zeolite formation, **2007**, *J. Phys. Chem. C*, 111 (39), 14283-14285.

Abstract: Aggregates of nanosized crystalline units of Silicalite-1 zeolite were detected in a detailed TEM analysis of a clear solution aged for 40 months at room temperature. Inspection of the TEM images reveals the aggregation of these building units into larger crystalline zeolite particles even without heating. The smaller individual units resemble the earlier proposed nanoslab and preferentially stack along a or b crystallographic directions.

K. Hayasaka, D. Liang, W. Huybrechts, B.R. De Waele, K.J. Houthoofd, P. Eloy, E.M. Gaigneaux, G. van Tendeloo, J.W. Thybaut, G.B. Marin, J.F.M. Denayer, G.V. Baron, P.A. Jacobs, C.E.A.

Kirschhock, J.A. Martens, Formation of ZSM-22 zeolite catalytic particles by fusion of elementary nanorods, **2007**, *Chem. Eur. J.*, *in press*.

Abstract: A ZSM-22 aluminosilicate zeolite was synthesized using the hydrothermal gel method at 150 C. Products obtained after different synthesis times were characterized using various techniques and catalytic testing. Massive formation of ZSM-22 nanocrystals occurs after only a short synthesis time, appearing as isolated rods with a cross section of 12 ± 4 nm. Nanorods have aluminum enriched at their external surface. Later in the crystallization process nanorods align and fuse sideways, whereby the external surface is systematically converted into an internal micropore surface. The formation of aluminum bearing micropores by the joining of nanorod surfaces is responsible for the enhanced catalytic activity. For this, the zeolite synthesis of nanoscale crystallites is ineffective for enhancing catalytic activity.

Oral Presentation and Refereed Proceedings Abstract

Invited Speaker:

G. Nicolis, Towards a thermodynamics of complex systems, in *International workshop on irreversible thermodynamic*, Rhodes, (September, 2006).

G. Nicolis, Nonlinear dynamics, statistical mechanics and the foundations of complex systems, in *Nanotechnology and Complexity: Building functionalities from multitude*, Paris (December 2006).

V. Basios, A new paradigm for Crystallization: self-organization in complex matter, in *19th Nonlinear Science and Complexity conference & Summer school*, University of Thessaloniki, Thessaloniki, (10th-22nd of July, 2006).

C.E.A. Kirschhock, A. Aerts, L. Follens, J.A. Martens, What has become of the silicalite nanoslab? – Recent insights into key steps of template-directed silicalite-1 formation, keynote lecture in *15th International Zeolite Conference*, Beijing, (12th – 17th of August 2007).

C.E.A. Kirschhock, A. Aerts, L. Follens, J.A. Martens, Catalysts on Demand, in *Post-conference of the 15th International Zeolite Conference*, Changchun, (18th – 21st of August 2007).

Oral Presentation:

T. Caremans, J. Martens, J. Vermant, B. Loppinet, C. Kirschhock, Zeolite Synthesis Through Self-Assembling Building Units, in *Science on European Soyuz missions to the ISS (2001-2005)*, Toledo, (27th-30th June 2006).

C.E.A. Kirschhock, J. Martens, NANOSLAB and ZEOGRID: Microgravity Effect on the Self-Organisation of Zeolite Building Units, in *Science on European Soyuz missions to the ISS (2001-2005)*, Toledo, (27th-30th June 2006).

B. Jakoby, E. Reichel, F. Lucklum, C. Riesch, L. Follens, J. Martens, C. Kirschhock, J. Vermant, Viscosity Sensors for the Monitoring of Phase Transitions and Crystallization Processes, in *Science on European Soyuz missions to the ISS (2001-2005)*, Toledo, (27th-30th June 2006).

V. Basios, Nonstandard Nucleation Mechanism from Combined Structural and Density fluctuations, in *Science on European Soyuz missions to the ISS (2001-2005)*, Toledo, (27th-30th June 2006).

L. Follens, C.E.A. Kirschhock, J. Vermant, J.A. Martens, Microgravity study of the formation of Silicalite-1 from clear solution: past and future, in *Experiments in space and beyond*, Brussels, ULB, (12th – 13th of April 2007).

L. Follens, A. Aerts, M. Haouas, F. Taulelle, J. Vermant, C. Kirschhock, J. Martens, Understanding the formation of Silicalite-1 from clear solution: a combined ²⁹Si NMR, DLS and SAXS study, in *SoftComp Annual Meeting*, Erice, (1st-5th of May 2007).

Poster Presentation

V. Basios, J. Lutsko & G. Nicolis, Nonstandard Nucleation Mechanism from Combined Structural and Density fluctuations, in *Work, Dissipation and Fluctuations in Nonequilibrium Physics*, ULB, Brussels, (22nd –25th of March 2006).

E.K. Reichel, C. Riesch, W. Hilber, L. Follens, C.E.A. Kirschhock and B. Jakoby, Optimized Design of Quartz Disc Viscosity Sensors for the Application in Harsh Chemical Environments, in *International Congress on Ultrasonics*, Vienna, (9th – 13th of April 2007).

L. Follens, T. Caremans, J. Martens, J. Vermant, F. Taulelle, M. Haouas, E. Reichel, B. Jakoby, C. Riesch, B. Loppinet, C. Kirschhock, In-situ investigation of the formation of Silicalite-1 from clear solution, in *15th International Zeolite Conference*, Beijing, (12th – 17th of August 2007).

Organized workshops

Visit of the CECAT by the Japanese microgravity delegation, March 22nd, K.U.Leuven, Leuven

- **Outlook**

Leuven (COK/CIT) / F.O.R.T.H. / Versailles / Antwerp / Australia

Characterization of the clear solutions will continue with DLS, ^{29}Si NMR, TEM and SAXS. This research is mandatory to allow the clear definition of the nature of the involved colloidal particles. With this information a better understanding of the two diffusive modes and a quantitative description of the colloidal processes in solution are hoped to be achieved. Especially the discovery of the two different diffusive modes present in the colloidal synthesis suspension gives rise to a number of questions which we will also address in our future research:

- A flow cell will be used to study and quantify the effect of flow on clear solutions. The respective cell will be built using experience we will collect in collaboration with Forschungszentrum Jülich.

- The effect of acoustic stimuli on the diffusion and aggregation will be studied. The discovered collective diffusive mode is known to be susceptible to local density fluctuation. Imposing such density fluctuations with specific frequencies should therefore affect the mechanism of particle enrichment and –recognition leading to product formation. Together with the department for acoustics of the KULeuven an experimental setup currently is developed. Also first contacts with group of Prof. Schwieger (University of Erlangen) have been made. This group has extensive experience with the use of ultrasound in zeolite systems as diagnostic means.

- The mentioned sensitivity of the collective diffusive mode to convection and the role this mode can play in self-organization prompts a parabolic flight experiment. During this experiment the relative DLS intensities of self-diffusion and collective diffusion will be studied as function of gravity level. Even though the micro- / high-gravity periods during parabolic flights is much too short to follow a zeolite synthesis the effect on the particle diffusion should be observable with DLS. A proposal for such an experiment is in preparation.

- Together with the group of Prof. Steinberg (Queensland University of Technology, QUT) we hope to start analysis of zeolite formations under increased gravity levels. The suitability of the respective equipment available at QUT for the required harsh chemical conditions currently is under investigation.

Under the guidance of ESA the development of flight hardware for experiments aboard the ISS will be continued. This development will occur in close collaboration with other scientific teams with similar experimental requirements.

Linz

We will invest more efforts in developing an optimum packaging being suited to maintain proper operation in the harsh reactor environment. Moreover miniaturized sensors generally probe a different rheological regime than conventional methods (e.g., laboratory viscometers). Therefore the specific rheological regime probed by the selected sensor technology and the impact of the measurement parameters (frequency, shear rate,...) on the measurement results are to be investigated. In particular, the impact of characterizing thin liquid films, which is underlying all viscosity sensors utilizing shear-oscillations, will be considered. Furthermore it shall be investigated to what extent the selected method is non-invasive, i.e. if it does not or if it only marginally interferes with the process to be monitored (in case of the selected pilot application this is a crystallization process). In order to investigate the rheological domain associated with the

sensors, tests with special suspensions and emulsions simulating the character of complex liquids as represented by the zeolite solution will be conducted. These experiments will be performed jointly with the Catholic University of Leuven and the Vienna University of Technology.

The cooperation with the partners of the ESA consortium will be intensified and a meeting is scheduled for ending 2007 in order to synchronize the associated activities.

