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Microgravity effect on the self-organisation of Silicalite-1 nanoslabs.

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ABSTRACT

The effect of microgravity on the kinetics of the formation of Silicalite-1 from clear nanoslab suspensions has been studied. Samples processed on MAXUS4 have been analyzed ex situ and their particle populations have been compared to references obtained under gravity. Microgravity has an unexpected and strong retarding effect on the aggregation of Silicalite-1 nanoslabs.

INTRODUCTION

Zeolites are low-density crystalline silicates, characterized by their microporous nature. Zeolite channels and cavities exchange cations and guest molecules with their environment. This property is extensively exploited in zeolite applications as catalysts, adsorbents and sensors. The ultimate goal is to design and synthesize tailor-made zeolites. Driven by this ambition, fundamental knowledge of the molecular mechanism responsible for formation of zeolite materials has to be explored.

Bulk zeolite Silicalite-1 can be synthesised by aggregation of nanoscopic Silicalite-1 particles (nanoslabs) in suspension. The synthesis of silicalite nanoslabs is based on the structure directing effect of the primary template tetrapropylammonium-cation (TPA+) on the silicon source. Due to the alkaline nature of the reaction medium the formed nanoslabs are negatively charged and therefore stabilised by a protective cover of TPA+. Charge and cover prevent further aggregation in this colloidal suspension at room temperature. The properties of the surrounding liquid medium determines the size of the nanoslabs in the clear solution. At elevated temperatures the aggregation barriers can be overcome and the slabs organize into bulk silicalite. This occurs in a stepwise and organized manner due to the strong anisotropy of the aggregating entities.

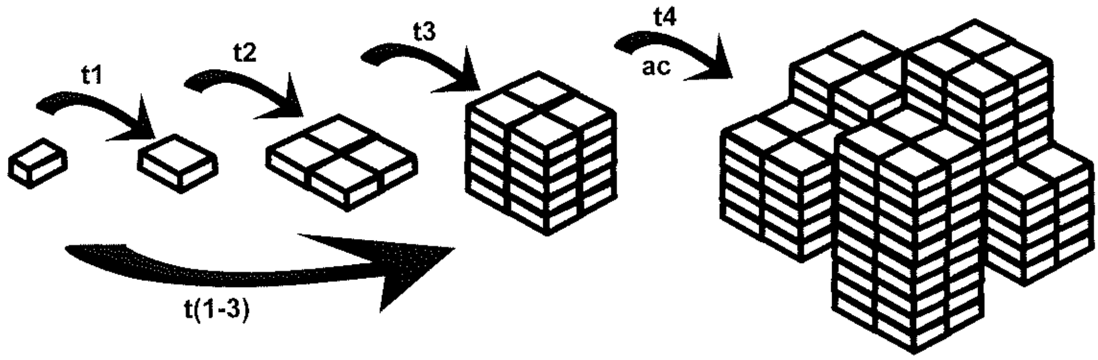


Figure 1:Microgravity experiments to study the aggregation behaviour of those nanoslabs have been carried out on MAXUS4. The objective of this project is the achievement of a full understanding of the involved self-organization and aggregation. Previously, the successive aggregation steps of the colloidal particles have been observed to be sensitive to convection. Therefore several microgravity experiments on MAXUS4 under conditions of minimized convection have been conducted.

EXPERIMENTAL

Experiment strategy

Aggregation of Zeosil nanoslabs occurs at a noticeable rate only at temperatures above 100°C. Therefore clear nanoslab suspensions were pressurized to prevent boiling and heated to the selected reaction temperatures. By quenching the samples at selected times, the particle populations as a function of process time were preserved to obtain kinetic profiles of the formation of Silicalite-1. Each series of samples obtained under microgravity conditions corresponded to a reference series obtained in an identical experimental setup under gravity.

Three series of samples were prepared during the MAXUS4 mission. The reference series were obtained later in a re-assembled experiment module. The following systems were studied:

1) aggregation of concentrated nanoslab suspension at 155 °C
2) aggregation of diluted nanoslab suspension at 155 °C
3) aggregation of diluted nanoslab suspension at 145 °C

The samples (gravity and microgravity experiments) were treated the same way with respect to storage temperatures and times before measurements. However, it turned out that the samples remained stable with time and did neither change with respect to particle size nor with respect to particle concentration. This supports our previous observation that quenched samples can be stored and analyzed at leisure without concern for eventual aging .

Sample analysis

To determine the rate constants of the individual aggregation steps the respective particle populations had to be derived as function of process time. For this X-ray scattering at low angles has been performed in transmission geometry. The liquid samples were sealed in capillaries with outer diameter of 1mm. As X-ray source served a rotating anode with Cu target. The source was equipped with a parabolic mirror to obtain an intense parallel beam. The scattered and diffracted X-ray intensity was recorded with a scintillation detector in steps of 0.02° between 0.3 and 50° 2Θ, corresponding to d-values between 380 and 1.7 Å.

To determine the accurate rate constants, the scattering volumes of each particle population had to be determined from the measured scattering curves. As fitting curves asymmetric peak functions were selected. The asymmetry was adapted to conform to the known scattering functions of the regarding particles. The areas of the obtained curves are equivalent to the scattering intensity of the corresponding particle population. This intensity relates to the total scattering volume of the population multiplied with the scattering properties depending on size and shape of the individual scattering entity. To obtain the volume fractions of the different populations the derived intensities were normalized using the fact that the sum of scattering volumes remained constant. The volume fractions as function of time were fitted with mathematical expressions based on the kinetic model (figure 1)

RESULTS

Already visual inspection of the X-ray scattering curves of gravity and microgravity samples revealed the presence of distinct particle populations, which vary with the progress of aggregation. This observation is in full agreement with the aggregation mechanism of Zeosil nanoslabs, which obviously remains valid under microgravity conditions. Marked differences in scattering intensity were observed, indicating a strong influence of gravity on aggregation speed. To quantify this effect on the individual aggregation steps the X ray scattering curves were analyzed. Up to the size of tablets (figure 1) gravity and microgravity experiments could be fitted with identical sizes of nanoslabs and tablets. The intermediates, however, grow larger under microgravity conditions. Due to the dilution with water in series 2 and 3 most of the small entities like Subnanos and Nanoslabs were converted to tablets already at room temperature. Therefore not all rate constants could be determined from the available data. The derived kinetic parameters are summarized in table 1. The longer the characteristic time of a step the slower is the rate of this step. Rate constants k_i are the reciprocal value of the characteristic times t_i ,listed in table 1. It is immediately obvious that the reduction of convection reduces the aggregation rate. This can even better be observed when inspecting the variation of populations and the fitted reaction curves as function of time (figures 2 and 3):

		t_1/s	t_2/s	t_3/s	$t_{(1-3)}$/s	t_4/s	ac
Series 1	Gravity	96	116	169	188	66	0.85
	Microgravity	576	356	385	375	120	0.83
Series 2	Gravity			74	(74)	64	0.894
	Microgravity		123	252	(252)	118	0.815
Series 3	Gravity			148	(148)	115	0.894
	Microgravity		219	423	(423)	211	0.815

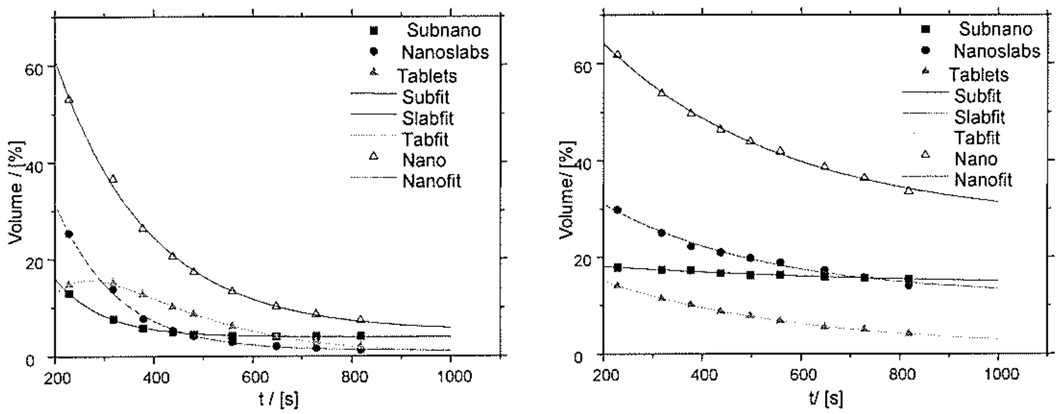


Figure 2: Volume fractions of the individual Nanoparticles (Subnano, Nanoslab, Tablets) and their sum (Nano). Symbols represent measured values, continuous lines are the calculated population evolutions using characteristic times from table 2. The left graph refers to gravity conditions, the right graph shows the corresponding microgravity experiment (sample series 1).

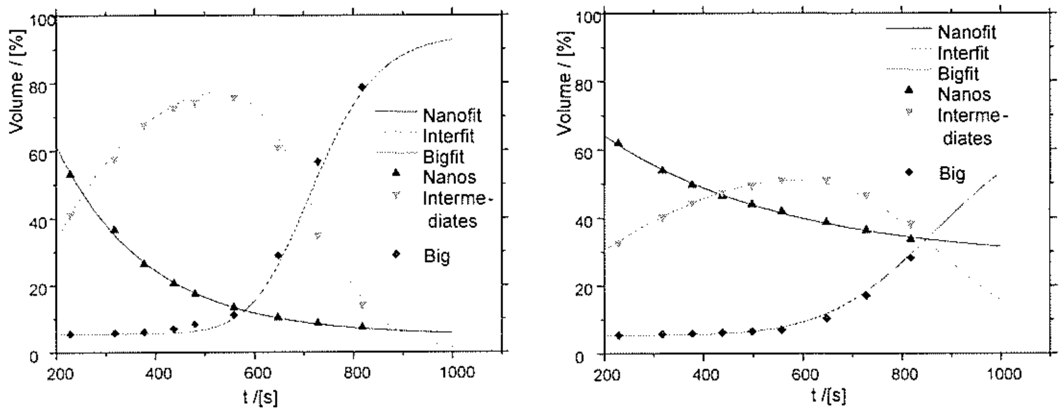
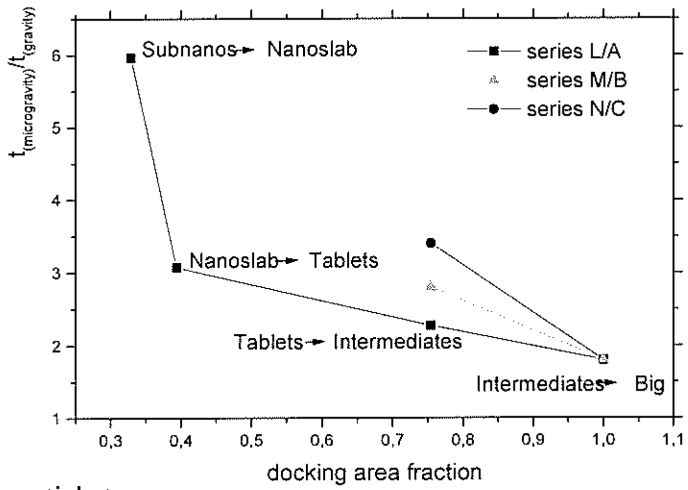


Figure 3: Volume fractions of Nanoparticles (sum of Subnano, Nanoslab, Tablets), Intermediates, and big product particles. Symbols represent measured values, continuous lines are the calculated population evolutions using characteristic times from table 2. The left graph refers to gravity conditions, the right graph shows the corresponding microgravity experiment (sample series 1

DISCUSSION

Considering the size of the aggregating particles their dynamics should entirely be dominated by Brownian motion. Neither flow induced re-orientation nor sedimentation should have any influence on the local environment of the nanoslabs. In contradiction to this expectation a strong retarding microgravity effect has been observed. An explanation can be the existence of colloidal domains (I do not know if this is the right term but structures is too general in my opinion) in which the nanoslabs are oriented in a specific manner, which are sensitive to convection. In those collectives the particles do not readily fuse without an external push, disturbing the internal organization. This necessary disturbance could then be convection induced. Following this working model two conditions have to be met for each individual aggregation:



1) the aggregating species have to be able to approach
2) opposing faces of approaching species have to match

The first step requires sufficient interference in the system to disturb the nanoslab collectives. It was observed that in all aggregation processes the characteristic times are significantly longer under microgravity conditions (Table 1). This leads to the tentative conclusion that the approach (1) of the aggregating species is the rate limiting step under microgravity. It has also been observed that the individual rate constants are affected to different degrees. Alignment of the particles (2) should be related to the available docking areas of each individual particle type.

With the rough assumption that the change of particle orientation is independent of its shape, the time a particle spends with a specific face in one specific direction is proportional to this face area per overall area. Therefore, the bigger the docking area per particle surface, the higher is the probability that the particle is oriented in a favourable way for aggregation. This means the retarding effect under microgravity should be strongest for the particle with the smallest docking area per overall area. This is indeed what is observed (figure4).

CONCLUSIONS AND OUTLOOK

The unexpected strong influence of microgravity on the aggregation behaviour of Zeosil nanoslabs clearly shows that this system can not be treated like a classical crystallization process. Recognition of the aggregation species and their self-organization play major roles in the formation of Silicalite-1 from nanoslabs. Further experiments to clarify the observations and to refine the understanding of this system are called for and will be performed shortly aboard the ISS. In parallel efforts to prove the existence of the postulated nanoslab collectives are taken.