doi:10.2533/chimia.2024.142 Chimia 78 (2024) 142–147

Up-scaling a Sol-Gel Process for the Production of a Multi-Component Xerogel Powder

Barbara Pföss*[a], Jonathan Caldi[b], Sutida Jansod[b], Christophe Allemann[b], Pierre Brodard[b], and Roger Marti*[b]

Abstract: A sol-gel process for the synthesis of a multi-component oxide material from the system SiO_2-ZrO_2-Al_2O_3 underwent optimization and up-scaling. Initially, on a laboratory scale, components including precursors, catalysts, and additives were methodically evaluated to ensure a safe and efficient transition to larger volumes. Subsequently, the equipment for the whole setup of the sol-gel process was strategically selected. Leveraging insights from these optimizations, the process was successfully scaled-up to pilot-scale operation, conducting hydrolysis, condensation reactions, gelation, aging, and drying within a single, integrated conical dryer system for an 80 L batch. A visual test and FTIR spectroscopy were applied for process control and monitoring.

Keywords: Glass ceramic · Sol-gel chemistry · Up-scaling

Dr. Barbara Pföss' special focus lies on oxide materials, especially glasses and her main field of research for the past years has been glass ceramics, sol-gel technology and innovation. In her current position at Straumann she focuses mainly on glass ceramics for dental applications including continuous development of products and working in cooperation with academic partners. She holds a PhD from Aachen University in Germany where she gained expertise and fundamental understanding in glass science and technology and became familiar with experimental setups and analytical methods for glass characterization.

Jonathan Caldi, a Chemical Engineer, earned his Master of Science in Life Science with a specialization in Chemical Development and Production from HES-SO in 2016. His professional focus lies in process analysis, development and scale-up, which he has aptly applied across a wide array of projects spanning diverse fields, including polymer science, ink formulations, organic chemistry, and ceramics.

Dr. Sutida Jansod is an analytical chemist specializing in electrochemistry. She earned her degree from the University of Geneva in 2020. She possesses a deep-seated passion for analytical chemistry, where she combines her expertise with various scientific disciplines such as materials science, biophysical chemistry, and organic chemistry. Her experience covers the utilization of spectroscopy, chromatography, and thermal analysis techniques.

Dr. Christophe Allemann worked 9 years for Syngenta (Switzerland and UK), after postdoctoral work at UCLA (USA) in computational chemistry. In 2013 he joined HEIA Fribourg, where he is currently the head of the Institute of Chemical Technology. He has competences in organic synthesis, catalysis, process chemistry, process intensification and flow chemistry. Finding the right technology and the best sustainable process for scale-up is an important aim of his research.

Dr. Pierre Brodard, Professor of Physical Chemistry at HEIA Fribourg, is an expert in non-destructive characterization as well as in thermal analysis of materials. In particular, he investigates surfaces by Raman spectroscopy and mapping, combined with electron microscopy and energy-dispersive X-ray spectroscopy. Thermal behavior and thermal safety of products and processes are his other research interests. He is the President of the Swiss Society for Thermal Analysis and Calorimetry STK.

Dr. Roger Marti is Full Professor UAS of Organic Chemistry & Process Chemistry at the Institute ChemTech at HEIA Fribourg. His research interest and competences are in synthetic organic chemistry & process chemistry for the synthesis and sustainable production of functional organic molecules and polymers using innovative synthesis technologies.

**Correspondence:* Prof. R. Marti, E-mail: roger.marti@hefr.ch, Dr. B. Pföss, E-mail: barbara.pfoess@straumann.com
[a]Institute Straumann AG, Peter Merian-Weg 12, CH-4052 Basel, Switzerland; [b]Institute of Chemical Technology, Haute école d'Ingénierie et d'Architecture Fribourg, HES-SO University of Applied Sciences and Arts Western Switzerland, Boulevard de Pérolles 80, CH-1700 Fribourg, Switzerland.

1. Introduction

Sol-gel chemistry is a diverse, adaptable and well-established technique in the field of inorganic material synthesis, offering precise control over the composition, structure, and morphology of materials at the nanoscale. The fundamental principle is that three-dimensional networks are formed through controlled hydrolysis and condensation reactions of precursor molecules. Tailoring reaction parameters such as pH, temperature, and precursor choice, which brings possibilities to adjust the chemical and physical properties of the resulting materials, making sol-gel chemistry very attractive for the design of a wide variety of materials, including ceramics, glasses and glass ceramics.

A sol-gel synthesis route using metal alkoxides for the SiO_2-ZrO_2 system and pursuing with the preparation of a glass ceramic material was first described by Nogami[1,2] and shortly afterwards, Yoldas also described copolymerization of ZrO_2 with SiO_2 and hot-press sintering leading to tough ceramic materials.[3] Based on this, an adjusted process was later developed by Persson and Fu.[4,5]

Unlike conventional production methods for glasses, the sol-gel route avoids the problem of high temperatures very elegantly by making use of wet chemistry, *i.e.* by triggering hydrolysis and condensation reactions of suitable Si/Zr-precursors. An amorphous structure is always the starting point for obtaining a glass ceramic material, which then nevertheless demands further heat treatment. The sol-gel process developed by Fu[5] takes place at ambient temperature. After drying and calcination, an amorphous powder is obtained, which is densified in a pressure-assisted sintering process, between 1’000 °C and 1’300 °C. These sintering conditions lead to a simultaneous softening of the glass and initiation of the crystallization of tetragonal ZrO_2 nanocrystals. The *t*-ZrO_2 spheres with a diameter of approximately 30 nm form a network-like structure embedded in a glassy SiO_2 matrix. This material finally shows impressive mechanical properties with bending strengths of up to 1’000 MPa, along with remarkable aesthetics making it a suitable candidate for dental applications.

The up-scaling of sol-gel processes in general is only rarely discussed in scientific literature. However, Heinrichs *et al.* addresses in particular the industrial applications of sol-gel technology for a coating application.[6]

2. Results & Discussion

The initial synthesis described by Fu for the preparation of the xerogel, the amorphous raw powder, was the starting point for scale-up studies presented in this paper.[5,7] First lab tests revealed the challenges such as very slow dosing of fuming aqueous hydrochloric acid to avoid the hydrolysis reaction going too fast and the formation of precipitates, very long time for gelation and aging of the sol-gel (three days at 60 °C), and ‘uncontrolled’ drying of the gel by transferring it to a beaker and keeping it for three days at 120 °C in an oven to obtain the final xerogel powder. First, we worked on the chemistry optimization, such as counterbalancing the reactivity of the Si versus the highly reactive Zr alkoxides by using chelating agents and evaluating different catalysts to control hydrolysis and condensation and so the sol-gel process.[8,9]

The sol-gel route was followed, and the reactor setup optimized, with the aim of developing a robust process that includes process analytics, in order to allow changes in the formulation, eventually leading to an upscaled and validated production method (Fig. 1).

2.1 *Optimization at Lab Scale*

As mentioned, Fu’s laboratory process was the starting point for our studies on the production of different compositions of the SiO_2-ZrO_2-Al_2O_3 system. The ZrO_2 content was between 40 and 60 *wt%* and the Al_2O_3 content between 0 and 5 *wt%*. The addition of a small amount of Al_2O_3 to the composition was found to be beneficial, in particular for the later densification step. Three main challenges of the synthesis were addressed: firstly, the rapid and uncontrolled hydrolysis and the formation of hydroxide precipitates during the reaction, secondly, the very long gelation and aging time and thirdly the reaction in an open glass beaker and open drying in an oven to obtain the final powder. To ensure a smooth and safe scale-up, the mixing and reaction for sol-gel synthesis, aging and then distillation of the solvent and drying of the raw xerogel powder had to be addressed first, keeping in mind the scalability of the equipment and the simplicity of the process. Reports from Ben-Arfa on the use of a laboratory rotary evaporator to distill the solvent to dry the gel and obtain the powder allowed us to simplify and standardize the synthesis protocol for Si/Zr/Al-oxide xerogels on a laboratory scale (up to 1 L).[10] The reaction mixture was stirred with a magnetic stirrer or an overhead stirrer and after aging the solvent was distilled off with a laboratory rotary evaporator.

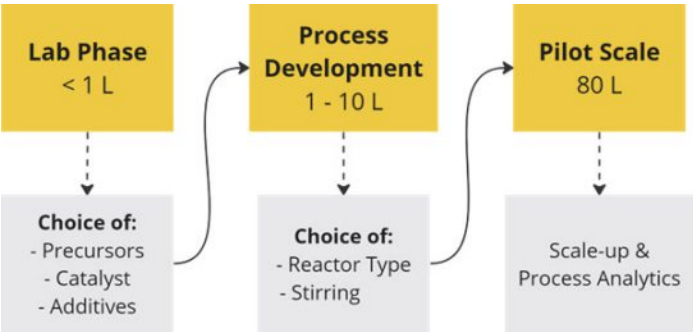

Fig. 1. Focus of optimization on various scales.

For an intermediate scale-up, the sol-gel reaction was directly performed in a 6 L flask on a large-scale rotavapor. All reagents were loaded under mechanical stirring, and once the gelation was finished, typically after 15-20 minutes, the opaque yellowish gel was then kept at 60 °C in an oil bath overnight without stirring. The flask was then mounted on the large-scale rotavapor equipment, the solvent was distilled off at reduced pressure, and the resulting powder was finally dried under vacuum, yielding an orange powder. Upon calcination, this raw powder transformed into a pristine white material. This rotavapor process was further scaled up to a 20 L flask without any problems, in this case, the mixing for the sol-gel reaction was performed in an Hastelloy 20 L reactor, and the reaction mixture was then transferred to the rotavapor flask for gelation and overnight aging at 60 °C.

A reaction calorimeter study found no critical exotherms and accumulation in the sol-gel process and an adiabatic temperature rise of only 10 °C was determined, which was well controllable by running the process under semi-batch conditions.

2.1.1 *Chelating Agent Selection*

When synthesizing a multi-component material, the reactivity of the chosen precursors can vary significantly. This adds complexity to process development. If hydrolysis dominates over condensation, unintended precipitation can result. Chelating agents can be used to mitigate the reactivity of the highly reactive Zr precursors so that they can be mixed with the less reactive Si or Al precursors to obtain a homogeneous multi-component material. Acetylacetonate is known to act as a chelating ligand for the zirconium cation by forming a stable β-diketone complex and thus slowing down the reaction rate.[11] Other additives such as ethanolamine, diethanolamine, or 2-methoxyethanol were also tested but were found to be less efficient than acetylacetone, as precipitation of Zr oxides was observed even when used in large excess to the Zr precursor. Finally, a mixture of 1 mol acetylacetonate per 1 mol Zr precursor was successfully integrated into the synthesis process, consistently yielding gels without any precipitation.

2.1.2 *Catalyst Selection*

The choice between acid and alkaline catalysts in sol-gel synthesis can greatly affect the microstructure of the product, because it influences the reaction pathway or the rate of gelation. Under acidic conditions hydrolysis of the silica species is predominant and condensation reactions are determining the overall reaction rate. On the other hand, for a sol-gel synthesis under alkaline-conditions, condensation reactions are favored and hydrolysis serves as the decisive mechanism governing the rate.[8]

In order to control the sol-gel reaction and also further avoid precipitation, a comprehensive catalyst screening was carried out (Fig. 2). With strong inorganic acids (HCl, H_2SO_4) we observed undesired precipitates. Organic acids, for instance formic acid induced fast precipitation, whereas with acetic acid no precipitates were observed and a homogenous gel was obtained. However, with acetic acid as the catalyst the calcination of the xerogel resulted in a black material, which was identified by Raman spectroscopy as carbon black residues in the xerogel. It is assumed that the structure of the gel synthesized using acetic acid favors the trapping of organic groups, which then upon calcination form these (carbon) black residues. The screening experiments have shown that the best catalyst for this process is aqueous ammonia (25 %), which produces uniform white powders after calcination. Using 25 % aqueous ammonia as catalyst and acetylacetone as chelating agent for the Zr-precursor, an opaque gel formed within 15 minutes without precipitates.

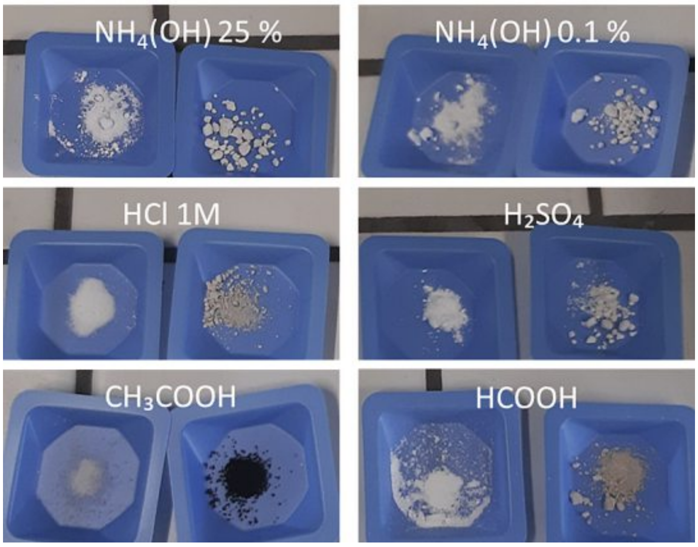

Fig. 2. Material synthesized using various catalysts, before (left side) and after (right side) calcination.

2.1.3 *Process Optimization and Up-scaling*

The initial improvement by changing from open glass beakers for performing the sol-gel reaction to the rotary evaporation process played a crucial role in the implementation of a controlled laboratory process. Nevertheless, there are limitations, especially in terms of mass and heat transfer efficiency at larger volumes. To overcome this challenge, the possibility of stirring during the aging process was further investigated.

Several trials at 1 L scale were performed to test various stirrer types and their effects on the sol-gel reaction as well as on the distillation of the solvent. The results revealed that conventional mixers such as propellers, anchors, viscojet, and half-moon show different performance in the various process steps. The most challenging part was the distillation of the organic solvents from the gel mass: once most of the solvent has been removed, the gel mass became so viscous that it blocked the viscojet, halfmoon and anchor stirrer. After passing this critical phase, a free-flowing powder was obtained and again all stirrers worked well. The aging time to obtain a white powder after calcination of the raw xerogel was around 2.5 to 4 hours for all stirrer types.

To shorten cycle time and facilitate the operations by minimizing transfers, we decided to run the synthesis and distillation steps in a single device. Moreover, the drying step would ideally run in the same device. For that, three commercially available reactor types, namely the IKA conical dryer (*MagicPlant*), the LIST kneader reactor,[12] and the Bolz conical dryer equipped with a screw stirrer were tested, (Table 1).

Table 1. Various setups used on different scales.

DEVICE FOR SYNTHESIS	REACTION VOLUME
Glass flask with propellers, anchors, viscojet, or half-moon stirrer Solvent distilled by Rotavapor	1 L
LIST Kneader reactor Endless screw 2x	2 L
Bolz conical reactor Rotating screw or Helical stirrer	1.6 L
IKA conical reactor (*MagicPlant*) Helical stirrer	1.6 L
IKA conical reactor (CD100) Helical stirrer	80 L

The kneader reactor uses a strong, high shear rate to thoroughly knead the material throughout the volume of the reactor, with the stirrer unit being horizontal. The Bolz reactor uses an endless screw that moves the reaction mass vertically from the bottom of the reactor to the top. The endless screw is mounted on a rotating arm which rotates within the reactor. The helical stirrer of the IKA *MagicPlant* offers an axial agitating movement that stirs the entire batch evenly and continuously. All these configurations demonstrated their effectiveness in enhancing the synthesis and aging process. The continuous stirring of the gelation significantly reduced the ageing time for all reactors tested, from more than 8 hours without stirring to 2.5 hours with stirring.

2.2 *Pilot Scale Trials*

Having decided to pursue the concept of the conical dryer beyond the IKA *MagicPlant* lab equipment, we took the next step to the IKA *CD100* reactor for further scale-up studies. These two devices have the same geometric design and the scale-up is therefore easy to engineer (Fig. 3).

The IKA *MagicPlant* mixer is a heated 2 L steel reactor with a helical stirrer. With this setup, we studied the sol-gel process on a lab scale. By monitoring the torque of the stirrer, the gel formation is monitored after approximately 15 minutes as shown in Fig. 4. The mixing of the gel was very efficient, and we obtained a reproducible aging of the gel after stirring for approximately 4 hours at 60 °C. During distillation of the solvent, we observed an increase in the torque until a free-flowable powder was obtained (Fig. 4).

Fig. 3. Conical dryer used at laboratory scale (left) and conical dryer used at pilot scale (right).

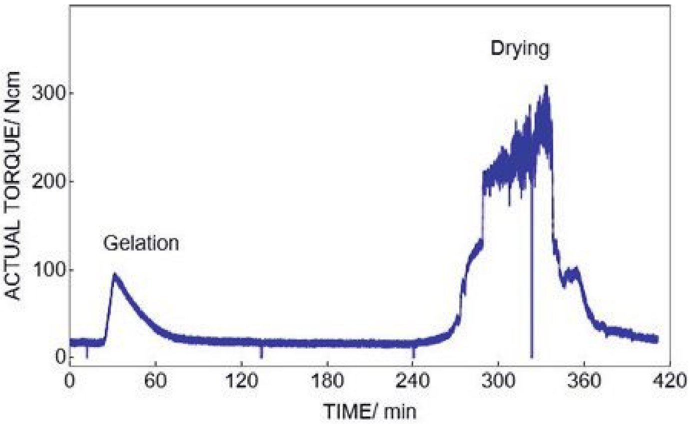

Fig. 4. Typical sol-gel reaction with the gelation after 15 minutes and solvent distillation and drying process between 240 – 360 minutes.

Next, we rented an upscaled IKA system and installed it in our ATEX pilot plant at HEIA Fribourg. The production unit consisted of an IKA *CD100* reactor for sol-gel synthesis, solvent distillation and powder drying. It was connected to a Büchi 100 L reactor, which served as a condenser unit for the distillation of the solvent. The entire plant was also connected to two gas scrubber towers for the neutralization of ammonia (Fig. 5).

After charging ethanol and tetraethoxysilane (TEOS), the 80 L solution was heated to 30 °C. Aqueous ammonia was then added as catalyst to start the sol-gel reaction. A reproducible temperature increase of approximately 10 °C was observed. As soon as the temperature increase was detected, a solution of ethanol, zirconium *n*-propoxide and acetylacetone was charged. The reaction mass was then heated to 60 °C. During this heating phase, an increase in torque was observed, indication that the gel was formed. The newly formed gel has a rigid but wobbly character, similar to a pudding, which when continuously stirred has the appearance of a very viscous paste. After 2.5 hours of aging under continuous stirring, the main amount of solvent was removed by distillation under reduced pressure and in a following second drying step with increased vacuum and increased temperature the final xerogel powder was obtained.

In total, we performed 12 batches in the IKA *CD100* reactor, varying and optimizing the process conditions (time, temperature, vacuum, stirring speed), and producing xerogels of different Si/Zr/Al compositions. Overall, more than 150 kg of xerogel powder was produced, in consistently good quality, highlighting the robustness of the developed process.

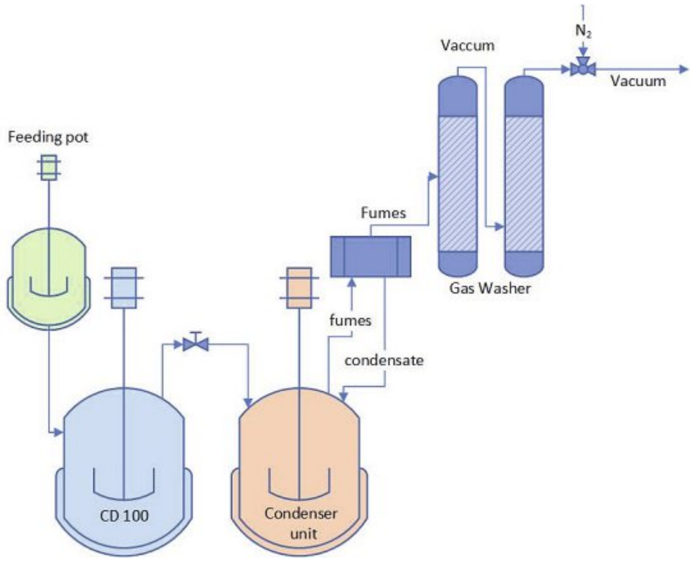

Fig. 5. Setup of the IKA CD100 production unit.

2.3 *Process Control and Monitoring*

Process control focuses on the observations of gelation and aging times, exploring *e.g.* how different configurations regarding the ZrO_2 content and increasing scales affect these crucial characteristics (Fig. 6). Understanding the dynamics of gelation and aging is essential for optimizing the synthesis process for various applications.

2.3.1 *Gelation Time*

The gelation time is predominantly influenced by the reaction rates, which are closely tied to the quantity of inert solvent utilized and the inherent reactivity of the precursors. While a reduced amount of solvent is obviously advantageous for the subsequent drying phase and solvent removal, it is essential to maintain homogeneous reactions. Achieving this requires a balance, as slower and controlled reaction rates are preferable to ensure homogeneity. To achieve a homogeneous structure for a multi component system, the synchronization of reaction rates is also important.

Therefore, the effect of varying composition (different ZrO_2 contents) and the effect of various scales on the gelation time was examined (Fig. 6). In a set-up without stirring the gelation time was approximately 45 minutes regardless of the composition. For process conditions including continuous stirring the gelation time could be reduced to approximately 15 minutes. This is seen as a useful processing window and acceptable reaction rate for a reliable and also time effective process.

2.3.2 *Aging Time*

During aging, the structure of the material continuously evolves. With increasing aging time, cross-linking intensifies and more covalent bonds are formed. The process control includes a careful evaluation of the appearance of the material (visual test) as well as the characterization of the material structure by FT-IR spectroscopy.

For the visual test, small samples from the wet gel were collected at different stages of aging. These samples were then heated to 600 °C for one hour. The optical appearance of the material was assessed after the heat treatment (Fig. 6 and Fig. 7).

For short aging times, after drying for the visual test, the material appears completely black, but it is gradually transforming into a pristine white powder as the aging time extends. A completely white appearance of the material is associated with the minimum necessary aging time. To avoid the appearance of the black color, or even black spots, it is important to carefully evaluate the mini-

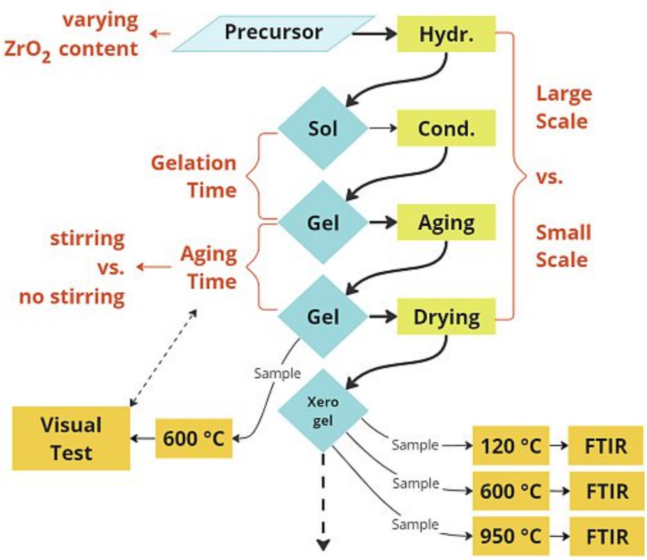

Fig. 6. Process diagram for sol-gel synthesis and sampling for monitoring.

mum necessary aging time while keeping in mind a time efficient process.

Stirring emerged as the dominant factor for influencing the minimum necessary aging time, with a notable distinction observed between the non-stirred rotavap process on various scales and the stirred process employing an IKA *MagicPlant* reactor (2 L), or IKA *CD100* reactor (100 L); see results of visual test in Fig. 7. Indeed, the unstirred process required more than 5 hours of aging to yield a white powder, whereas less than 2.5 hours were required for all stirred processes. This observation underscores the significant impact of stirring on the efficiency of the sol-gel synthesis process. As aging is conducted at elevated temperatures (60 °C), the heat transfer in the gel is the limiting factor and can explain the much longer necessary aging times for larger volumes. Thus, a good heat transfer was required and achieved by stirring. The stirred process demonstrated remarkable efficiency regardless of scale. Actually, the pilot scale IKA *CD100* setup was able to reduce the minimum aging time to approximately 1 hour to produce the desired white material, as seen in Fig. 7.

With increasing temperature, structural changes in the material also occurred, and this was monitored with FTIR spectroscopy. To see the structural evolution, samples of the dried amorphous raw powder were heat treated at different temperatures and their FTIR spectra compared (Fig. 6 and Fig. 8).

Results reveal that organic residues and water remained below 600 °C, the signals at 1'600 cm^{-1} being associated with H-O-H deformation vibration.[1] Clearly an inorganic network is formed *via* the sol-gel synthesis route, as indicated by the broad signal between 800 cm^{-1} and 1'100 cm^{-1}, including symmetric and asymmetric Si-O-Si stretching vibrations, $Si-O^-$ non bridging oxygen, and most likely also mixed Si-O-Zr bonds. Crystalline tetragonal ZrO_2 evolves for temperatures above 900 °C, reported in various studies and confirmed here by the FTIR signal at around 500 cm^{-1}, evolving for the sample heat treated at 900 °C.[1,13] With crystallization FTIR also clearly detected a blue shift towards higher wavenumbers indicating the structural change in the material (Fig. 8). The samples from the 80 L scale setup in the IKA *CD100* reactor show very similar structural evolution to that in the smaller rotavapor setup (Fig. 8).

3. Experimental

As an example, for a batch performed with the IKA *CD100* device the following steps were performed to achieve a final oxide composition of 60 mol% ZrO_2, 36 mol% SiO_2, 4 mol% Al_2O_3.

In the IKA *CD100* reactor under N_2-atmosphre, the Si/Al precursor solution was prepared by mixing 4.7 kg of tetraethoxysilane (> 99 % from Sigma-Aldrich) and 1.6 kg of aluminum acetylacetonate (97 % from ABCR) into 26.8 kg of ethanol A15 (from Thommen Furler). In a separate stainless-steel tank, the Zr precursor solution was prepared by dissolving 16.9 kg of zirconium *n*-propoxide (70 % in propanol from ABCR) and 1.8 kg of acetylacetone (> 99 % from Sigma-Aldrich) in 13.5 kg ethanol A15.

The Si/Al precursor solution was heated to 30 °C and then under strong stirring 5.8 kg of aqueous 25 % ammonia solution (from VWR) was added. After 5 minutes the Zr precursor solution was added within 5 minutes. The resulting opaque mixture was then heated to 60 °C under continuous stirring. The gelation occurred after 20 minutes and was indicated by increase of torque and by visual observation. The viscous reaction mass was stirred for 2.5 h at 60 °C. The solvent was removed by distillation at 60 °C under vacuum (100 mbar) and a total of 56.04 kg distillate was recovered. The material was then finally dried under vacuum (0.8 mbar) at 65 °C. The resulting powder (10.1 kg) was used as recovered.

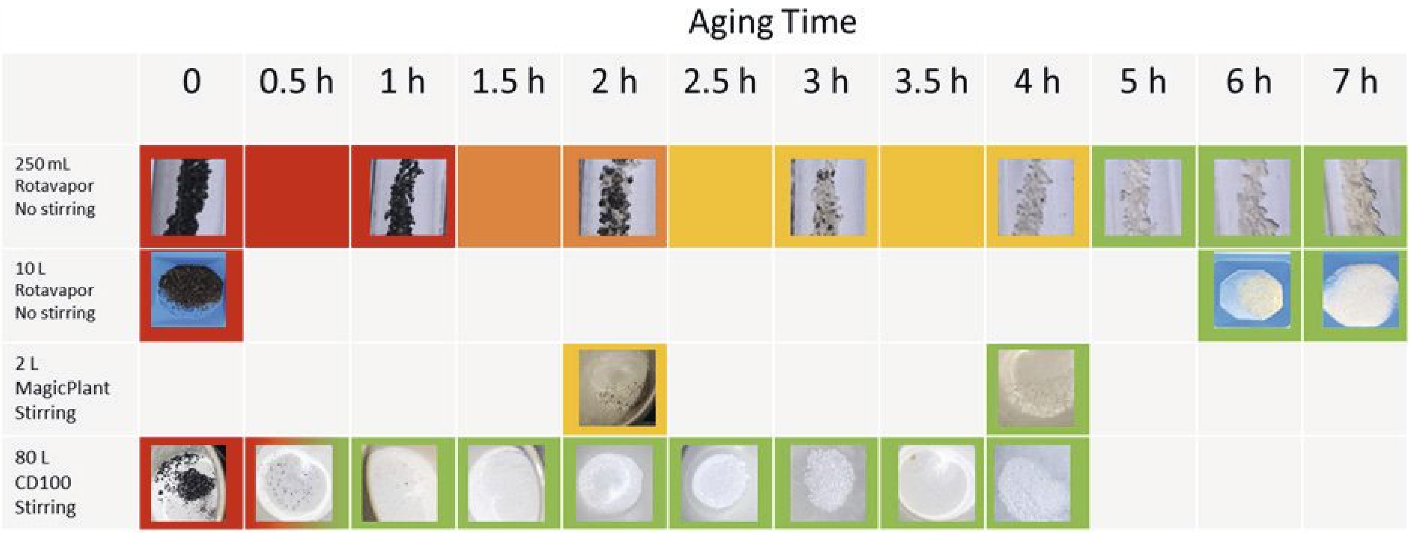

Fig. 7. Visual test showing material after various aging times.

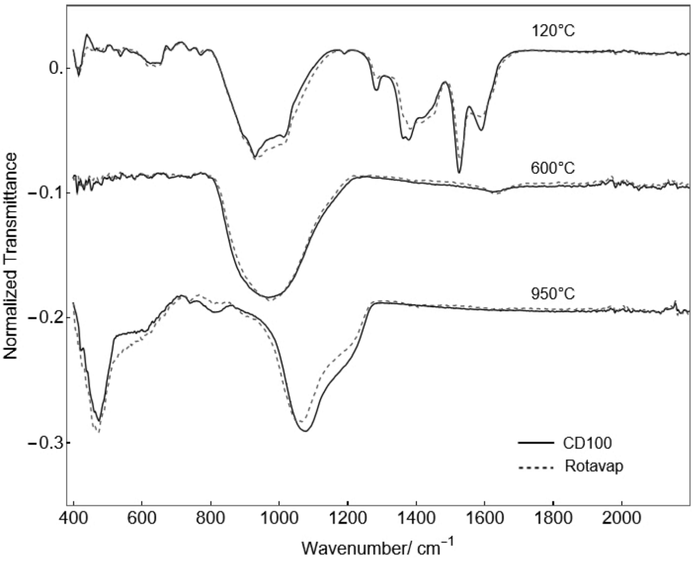

Fig. 8. FTIR spectroscopy for 10 L and 80 L set-up.

4. Conclusions

With well-considered adjustments it was possible to upscale a sol-gel synthesis process for the production of an amorphous powder composed of SiO_2-ZrO_2-Al_2O_3 to multi kilogram scale. The use of aqueous 25 % ammonia solution as catalyst for the hydrolysis and condensation reactions in combination with acetylacetone as a chelating agent for the zirconia precursor provided the most favorable reaction conditions for process development. Agitation with a helical stirrer significantly improved the process by reducing the aging time from an overnight process to less than 2.5 hours and further enabled efficient distillation of the solvent from the reaction mass. To demonstrate the potential for industrial use, an IKA *CD100* conical dryer with a capacity of 100 L was rented and installed in the facility of HEIA Fribourg. A campaign with a total of 12 batches was successfully carried out and a total of 150 kg of xerogel powder was produced. This not only confirmed the scalability and robustness of the developed sol-gel synthesis process, but also underlined its potential for industrial use. These findings offer valuable insights into optimizing a sol-gel synthesis route for diverse uses, including dental applications.

Acknowledgements

This work was generously supported by Innosuisse, who provided invaluable financial assistance throughout the project (Innovation Project 51867.1 IP-ENG).

We would like to thank Dr. Marc Stephan (Institute Straumann) for the significant professional contribution to the project as well as enabling the fruitful cooperation between Straumann and HEIA-FR.

Additionally, we extend our appreciation to our extended project team and project partners, the Fraunhofer IKTS, in particular Dr. Susan Conze and Dipl. Ing. Jan Räthel for their helpful collaboration and expertise for the sintering process and their sincere interest and motivation. Their contributions were instrumental in the success of this work, and we look forward to continuing our valuable partnership in future scientific pursuits.

We would like to thank all the staff of HEIA Fribourg for the engineering, installation and operation of the CD100 reactor, especially Mr. Michel Audriaz, Mr. Eric Clement and Mr. Maurice Dupré for their important work during the installation of the reactor, Mr. Andrea Ramorini for his assistance during the production campaigns, as well as Ms. Cylia Protopapa and Mr. Arnaud Gendre for their help during the process development phase.

Received: December 15, 2023

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