Continuous Zeolite Crystallization in Micro-Batch Segmented Flow

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Abstract

Zeolites are porous aluminosilicates that occur both naturally and synthetically, having numerous applications in catalysis, adsorption and separations. Despite over a half century of characterization and synthetic optimization of hundreds of frameworks, the exact mechanism of synthesis remains highly contested, with crystallization typically occurring under transport-limited regimes. In this work, a microcrystallization reactor working under segmented oscillatory flow has been designed to produce a semi-continuous flow of zeolite A. The fast injection of the reactants in a mixing section forms droplets of aqueous precursors in a stream of paraffin, dispersing microdroplets and avoiding any clog from occurring in the system. The crystallization occurred in the system at atmospheric pressure and isothermal conditions (65°C). This allowed for a rather slow crystallization kinetics which was important to study and highlight the different crystallization mechanisms between flow and batch synthesis. The morphology, size distributions, crystallinity, and porosity were examined by ex-situ characterization of the samples by scanning electron microscopy, X-ray diffraction, Raman spectroscopy, and N₂ Physisorption to support the conclusions drawn. The size distribution of the particles achieved in the flow reactor was conclusively narrower than the distribution achieved in the batch reactor. The average size of the crystals for both synthesis methods is reported as 400 nm and the crystallinity achieved was comparable between the two. However, the morphology was quite different between the two systems, the flow products having a much higher mesoporosity due to the presence of crystal aggregates at high crystallinity when compared to the batch crystals. Finally, extended crystallization
times leads to a decline of the crystallinity of the product, which might be explained by the metastable state of zeolites in solution.
Table of contents

Acknowledgment .................................................................................................................. 2
Abstract ................................................................................................................................. 3
Table of contents .................................................................................................................... 5
List of figures .......................................................................................................................... 7
List of tables ........................................................................................................................... 9
Introduction ............................................................................................................................ 10
I · Background ....................................................................................................................... 11
   A · Crystallization ................................................................................................................ 11
      1 · Nucleation .................................................................................................................. 11
      2 · Growth ...................................................................................................................... 12
      3 · Kinetic model for crystallization: the Avrami-Erofe’ev model ............................ 13
      4 · Crystallization in Oscillatory Flow Reactor .............................................................. 14
   B · Zeolites .......................................................................................................................... 14
      1 · Description + history .................................................................................................. 14
      2 · Important parameters ............................................................................................... 16
         i · Morphology (shape, surface area) ........................................................................ 16
         ii · Structure (MFI, LTA, FAU, etc.) ....................................................................... 16
         iii · Ratio Si/Al ............................................................................................................ 18
         iv · Pore size and topology ......................................................................................... 19
         v · Size (100 nm, 1 um, 10 um, hierarchical) ............................................................ 20
         vi · Organic Structure Directing Agents (OSDA) ...................................................... 20
         vii · Zeolite stability in water ..................................................................................... 21
      3 · Zeolite Synthesis: Tradition and opportunities .......................................................... 21
         i · Classical methods ................................................................................................... 21
         ii · New/emerging methods ......................................................................................... 22
         iii · Core-shell zeolites ............................................................................................... 23
   C · Zeolite A (framework LTA) .......................................................................................... 23
      1 · Structure ................................................................................................................... 23
      2 · Properties .................................................................................................................. 24
      3 · Applications .............................................................................................................. 24
II · Methods and experiments ............................................................................................... 25
   A · Products used ............................................................................................................... 25
B - Batch syntheses ............................................................................................................. 25
  1 - Set up of the system ..................................................................................................... 25
    i - Low Si/Al ratio set: Traditional zeolite A synthesis in batch .................................. 25
    ii – High Si/Al ratio set: Batch LTA to confirm literature kinetic data ....................... 26
C - Flow Syntheses ............................................................................................................. 27
  1 - Design of the oscillatory flow experiment (including data) ....................................... 27
  2 - Mixing section ............................................................................................................ 28
  3 - Experiments conducted in flow .................................................................................. 29
D - Products purification and preparation ......................................................................... 31
E - Analytical ...................................................................................................................... 31
  1 - XRD ............................................................................................................................ 31
  2 - Raman ........................................................................................................................ 32
  3 - SEM ............................................................................................................................ 32
  4 - Adsorption ................................................................................................................. 32
III - Results ......................................................................................................................... 33
A - Crystal morphology ....................................................................................................... 33
B - Batch results ................................................................................................................ 34
  1 – Low Si/Al ratio batch set ............................................................................................ 34
  2 – High Si/Al ratio batch set ........................................................................................... 36
C - Flow results ................................................................................................................ 37
D - Punctual comparison between batch and flow results ................................................. 40
E - Avrami fitting of batch experiment and confirmation of literature example ............... 40
  F - Attempt of fitting on the flow results ......................................................................... 43
  G - Absorption analysis of batch and flow products ......................................................... 44
IV - Discussion .................................................................................................................... 47
A - Decay at long crystallization time ............................................................................... 47
B - Insight on crystallization mechanism ......................................................................... 47
C - Enabling Zeolite Crystallization in Flow ................................................................... 49
D - Impact of Aging on Crystallization Kinetics ............................................................... 50
E - Analysis of Avrami plots ............................................................................................ 51
  F - Discussion on the Adsorption results ....................................................................... 53
  G - Batch and flow systems: fundamental differences ..................................................... 53
    1 - Heat transfer ............................................................................................................ 53
List of figures

Figure 1- Kossel model of crystal surface growth ................................. 12
Figure 2- Typical Avrami plots of crystallization. Y is the advancement of the crystallization and t is the crystallization time. ............................................. 13
Figure 3- Molecular sieves 4Å, Zeolite A.................................................. 16
Figure 4- Different frameworks of zeolite (a) zeolite A, b) zeolite Y, c) zeolite L, d) zeolite ZSM-5 .............................. 16
Figure 5- Ternary plots showing the change of zeolite framework depending on the ratio used, at different temperatures (A- 65 °C, 7 days, B-100 °C, 7 days, C-180 °C, 21 days) .................. 18
Figure 6- Different zeolite structures and micropores associated .................. 19
Figure 7- TetraPropylAmmonium Hydroxyde (TPAOH), common OSDA for zeolite synthesis (ZSM-5 for example) ......................... 20
Figure 8- Batch reactor: the autoclave .................................................... 21
Figure 9- SEM picture of fly ash (source: www.monolithic.org) .................. 22
Figure 10- Zeolite A LTA framework (source: IZA structure website) ........... 23
Figure 11: Schematic of the system used. To ease comprehension, aging section and furnace are decomposed here, but in fact they happened at the same place.

Figure 12: Zoom on a filled reactor.

Figure 13: Filled reactor.

Figure 14: Screen of the oscillation control panel.

Figure 15: Crystal size distribution and morphology comparison between batch and flow results.

Figure 16: A) XRD spectra collected of the low Si/Al ratio batch set products. B) Raman spectra collected of the low Si/Al ratio batch set products.

Figure 17: Raman spectra collected from the auxiliary experiment of the low Si/Al ratio batch set.

Figure 18: Plot of the relative crystallinity against crystallization time, for both Raman and XRD analysis.

Figure 19: XRD spectra collected from the products of the high Si/Al ratio batch set experiments.

Figure 20: Superposition of the composition used in Grizzetti et al. paper on the ternary plot from Maldonado et al.

Figure 21: Stacking of all flow XRD patterns form the flow experiment products.

Figure 22: Raman spectra of the flow results.

Figure 23: Plot of the relative crystallinity against aging time.

Figure 24: Plot of the relative crystallinity against crystallization time.

Figure 25: Avrami plot of the batch experiments and comparison with literature data.

Figure 26: Plot of the batch experiments and comparison with literature data.

Figure 27: Attempt of Avrami plot on flow experiment products and comparison with batch results.

Figure 28: Adsorption curves of batch and flow products.

Figure 29: DFT analysis of pore sized distribution.

Figure 30: Proposed mechanism for zeolite A crystallization in batch and flow.

Figure 31: Superposition of the composition used for the low Si/Al ratio batch set and flow experiments with the work of Maldonado et al.

Figure 32: Superposition of the composition used for the high Si/Al ratio batch set with the work of Maldonado et al.

Figure 33: SEM picture of low Si/Al ratio batch product, 5 min crystallization time. Zoom X2000.

Figure 34: SEM picture of low Si/Al ratio batch product, 5 min crystallization time. Zoom X15000.

Figure 35: SEM picture of low Si/Al ratio batch product, 5 min crystallization time. Zoom X55000.

Figure 36: SEM picture of low Si/Al ratio batch product, 90 min crystallization time. Zoom X2000.

Figure 37: SEM picture of low Si/Al ratio batch product, 90 min crystallization time. Zoom X15000.
Figure 38 - SEM picture of low Si/Al ratio batch product, 90 min crystallization time. Zoom X55000........................................................................................................... 73
Figure 39 - SEM picture of low Si/Al ratio batch product, 12 h crystallization time. Zoom X2000........................................................................................................... 74
Figure 40 - SEM picture of low Si/Al ratio batch product, 12 h crystallization time. Zoom X15000........................................................................................................... 74
Figure 41 - SEM picture of low Si/Al ratio batch product, 12 h crystallization time. Zoom X55000........................................................................................................... 75
Figure 42 - SEM picture of low Si/Al ratio batch product, 24 h crystallization time. Zoom X2000........................................................................................................... 75
Figure 43 - SEM picture of low Si/Al ratio batch product, 24 h crystallization time. Zoom X15000........................................................................................................... 76
Figure 44 - SEM picture of low Si/Al ratio batch product, 24 h crystallization time. Zoom X55000........................................................................................................... 76
Figure 45 - SEM picture of low Si/Al ratio flow product, 90 min crystallization time 45 min aged. Zoom X2000. ................................................................. 77
Figure 46 - SEM picture of low Si/Al ratio flow product, 90 min crystallization time 45 min aged. Zoom X15000. ................................................................. 77
Figure 47 - SEM picture of low Si/Al ratio flow product, 90 min crystallization time 45 min aged. Zoom X55000. ................................................................. 78
Figure 48 - SEM picture of low Si/Al ratio flow product, 90 min crystallization time 12 h aged. Zoom X2000. ................................................................. 78
Figure 49 - SEM picture of low Si/Al ratio flow product, 90 min crystallization time 12 h aged. Zoom X15000. ................................................................. 79
Figure 50 - SEM picture of low Si/Al ratio flow product, 90 min crystallization time 12 h aged. Zoom X55000. ................................................................. 79
Figure 51 - SEM picture of low Si/Al ratio flow product, 90 min crystallization time 24 h aged. Zoom X2000. ................................................................. 80
Figure 52 - SEM picture of low Si/Al ratio flow product, 90 min crystallization time 24 h aged. Zoom X15000. ................................................................. 80
Figure 53 - SEM picture of low Si/Al ratio flow product, 90 min crystallization time 24 h aged. Zoom X55000. ................................................................. 81

List of tables

Table 1 - Parameters extracted from the Avrami plots of the low and high Si/Al ratio batch experiments. .................................................................................. 41
Table 2 - Parameters extracted from the kinetic plots of the low and high Si/Al ratio batch experiments. .................................................................................. 42
Table 3 - Estimation of Avrami equation parameters of flow results................................. 44
Table 4 - BET, DR and BJH analyses of the adsorption curves. ........................................ 45
Table 5 - Interpretation of Avrami exponent ........................................................................ 52
Table 6 - Thermal diffusivities estimated different materials used .................................... 53
**Introduction**

Zeolites are key products in industrial processes needing heterogeneous catalysis. Involved in various reactions, in particular for oil cracking, these materials are widely used. Zeolites are products that are either naturally derived or synthesized artificially. In 2016, the world production of natural zeolites is estimated around 3 million tons and the reserves available are very large.\(^1\) No numbers are available for synthetic zeolites, however, the quantity can be expected to be very large due to their implications is ion-exchanger, heterogeneous catalysis, molecular sieving, desiccants, and detergents amongst others.\(^2\)

Zeolite A, produced in 1950, is one of the first and most common synthetic zeolites, thanks to the various possible applications, such as molecular sieving, shape selective catalysis, purification of gases and, water softening.

The production of zeolites in industry is based on batch crystallizers, leading to discrepancies between lots and various mass and thermal transfer limitations within the reactor. Furthermore, little is known of the kinetics and mechanisms of zeolite crystallization.

This work aims to synthesize zeolite A in flow, using a continuous micro-batch segmented flow reactor. Comparison between batch and flow products has been realized and an extraction of kinetic data has been proposed.
I - Background

A - Crystallization

Crystallization has been studied for decades, as it is one of the most used processes in chemical industries, and well understood models of it have been developed. Mostly realized in batch processes, this process is used in various industries, such as pharmaceutical and food processing, to achieve a high purity of a small amount of product. Crystallization occurs regularly in two steps: nucleation followed by crystal growth.

Crystallization rate is dependent of many factors, such as composition of the media, temperature, pressure, nucleation rate, and growth rate. It is important to notice that the nucleation rate and the growth rate are interdependent.

1 - Nucleation

The nucleation phase, where species aggregate when super saturation is reached in solution, can wear two faces.

One is the homogeneous nucleation, occurring without contact with external surfaces. It is a spontaneous and stochastic event and it requires a high supersaturation of the solution to occur. It is a slow process, which makes it a rare mechanism to encounter. As a matter of fact, homogeneous nucleation is a delicate balance between the free energy provided by the driving force (here supersaturation limit) and the energy needed to create the new interface between the media and the crystal nucleus.

While the other one, the heterogeneous nucleation, occurs in the presence of external surfaces and is much more common to observe. Indeed, in presence of
impurities (such as dust or crystals already present in the media) will significantly decrease the energy needed to create the new interface.\textsuperscript{4}  

A second nucleation can occur, where crystal fragments get torn off the seed crystals, by shocks between crystals and surfaces (walls, stirrer, etc.). They then fall in the solution, which produces crystal dust which, in a supersaturated media, will serve as a new nucleus during the growth phase.\textsuperscript{5}  

\textbf{2 - Growth}  

Crystal growth is a topic widely studied around the world, due to its implications at an industrial level. Growth of the crystal occurs from the outside: flat regions at the crystal surface (terraces) are the place where solute molecule fills kinks or vacancies of its structure. Islands (solute molecules aggregates) can nucleate at the surface of those terraces, and terraces can undergo a dislocation hillock (or axial screw dislocation, where terraces grow as spirals), to enable the growth to continue on other levels. Those occurrences can be observed using Atomic Force Microscopy (AFM).\textsuperscript{6}  

To achieve this growth, multiple processes are at work: first the species is transported from the bulk solution to the crystal surface and bonds to it. Then, the species is transported along the crystal surface to its final attachment location where it will remain. Depending of the media’s nature, more transport barriers can be added, for example in the case of a gel media, transport through solution and then through the gel structure itself will be observed.
3 - Kinetic model for crystallization: the Avrami-Erofe’ev model

Amorphous to crystalline processes have been widely studied, and kinetic models for this crystallization process have been established empirically. The most utilized is the Avrami and Erofe’ev kinetic model which highlights both nucleation and growth phenomena. This model is based on the Johnson-Mehl-Avrami-Erofe’ev-Kolmogorov (JMAEK, sometimes shorten to JMAK) equation:

\[ \alpha = 1 - \exp(-(kt)^n) \]

where \( \alpha \) is the advancement of the crystallization, \( k \) and \( n \) being empirical constants. In order to fit data to this model, this equation is modified to:

\[ \ln(-\ln(1-\alpha)) = n \ln(t) + n \ln(k) \]

where the constants can easily be extracted.8–11

However, other models exist and are used in research, such as the Prout-Tompkins model, the random-scission model, or the Smoluchowski equation amongst others.8–14

A simple kinetic model can also enable an estimation of parameters linked to crystallization, nucleation, and growth phases, using the following type of equation:

\[ \alpha(t_{\text{crystallization}}) = K t^q \]

with \( K \) and \( q \) being constants.
4 - Crystallization in Oscillatory Flow Reactor

In the last four decades, an increasing interest about the Oscillatory Flow Reactor (OFR) has been developed. Its possible applications to continuous crystallization have been studied for various chemicals such as insulin, paracetamol, or salicylic acid. The principle of this technique is to oscillate the flow of a continuous reactor in order to improve the mixing of the chemicals in the bulk. The tubular reactor may contain restrictions to enhance this mixing. One of the challenges of this method is the likely clogging of the system. To get around the issue of clogging, many techniques are experimented (ultrasound and wall coatings, amongst others).

B - Zeolites

1 - Description + history

Zeolites are crystalline alumino-silicates, where the two species AlO$_4$ and SiO$_2$ form tetrahedral structures to form a porous solid. The general, empirical chemical formula of zeolites is the following:

$$\alpha M_{2n}O - 2\alpha Al_2O_3 - SiO_2 - \gamma H_2O$$

where $\alpha$, $\beta$, $\gamma$ are ratio coefficients, and $n$ is the valence of the cation M (M being usually H$^+$, Na$^+$, K$^+$, Ca$^+$, Mg$^{2+}$). Other metallic atoms (such as Co, Fe, Cu for example) can be incorporated in the structure instead of Si or Al atoms during the synthesis or by post-synthesis treatment. Those materials are characterized using different equipment to determine shape (Scanning Electron Microscope (SEM)), crystalline structure and relative crystallinity (X-Ray Diffraction (XRD)) and
Raman spectroscopy), and properties (analysis of absorption experiments), which give a good overview of the characteristics of the material synthesized.

Zeolites were first discovered by the Swedish mineralogist Axel Fredrick Cronstedt, who discovered a mineral (stilbite) which loses water when heated. He named this class of minerals “zeolites” from the classical Greek words “zéō” (= to boil) and “líthos” (= stone). Their application goes back to the third century B.C. where they were used by Romans as an early purification process of the water coming to cities by aqueducts, and entered in the composition of concretes. The different frameworks (discussed later) were first studied before the Second World War, in 1930 by Taylor and Pauling. Research continued after suffering the signature of the war due to no discoveries between 1934 and 1950. Zeolites can be found in natural stone, more precisely in volcanic tuffs, but a vast majority of the frameworks discovered are synthesised artificially.

Zeolites are used worldwide in various applications. As detergents builders, they replaced phosphates which were harmful for the environment; as catalysts, they are used in the Fluid Catalytic Cracking process which represents 95% of catalytic zeolite consumption; they also are used in absorption processes, as molecular sieves for gas separation and ion-exchangers.
2 - Important parameters

i - Morphology (shape, surface area)

Zeolite crystals’ shape can be of various geometry, from the sphere to the hexagonal crystal, including, cubic octahedral, monoclinic, orthorombic, as well as others. The nature of the shape is determined by different factors, such as temperature, mixture composition, mixture aging, pH, and mixing amongst others\textsuperscript{23}. Crystal shape is important from an industrial point of view, as certain geometries will better suit an application than others (the shape needed in membranes is not the same as the one in catalytic beds). Then the product can be compacted in different shapes (spheres, rods, etc.) depending the application desired.

ii - Structure (MFI, LTA, FAU, etc.)

The diversity of industrial applications of zeolites is based on the variety of alumino-silicate frameworks. Each framework corresponds to a specific layout of secondary building units, leading to a unique porous network. All zeolite frameworks discovered so far are organized
into categories represented by a three letters acronym (MFI, LTA, FAU among others). To this date (03/10/2018), 235 frameworks has been approved by the International Zeolite Association (IZA, www.iza-online.org), and about 40 of them can be naturally extracted. But simulations have shown almost a thousand different frameworks possible due to the multiple tetrahedra configuration possible in the crystal lattice.$^5$

Each framework needs specific conditions to be synthesized, dependant on temperature, time, media composition, pH, etc.$^{24}$
The ratio of Silica to Aluminum is one of the most important parameters of the zeolite synthesis. With other parameters fixed, even a slight variation in this ratio can change the framework of the final product synthesized. The work conducted by Miguel Maldonado et al.\textsuperscript{25} shows the phenomena very clearly using tertiary plots, highlighting a region where multiples frameworks can be synthesised at once depending on the Si/Al ratio.

If this ratio is increased (i.e. the content of silica in the zeolite is increased), the thermal and acid resistivities and the hydrophobicity of the product is increased while the hydrophilicity, the acid site density (located on the aluminium sites), and the cation concentration are decreased.
It can be noticed that this ratio also impacts the synthesis itself, as a low ratio (high aluminium species concentration in the media) will tend to increase the nucleation and crystallization time, affecting the crystallization kinetics, but also improving the yield of the final product.

Post treatment synthesis can also modify this ratio and change a zeolite framework to another. For example, the transformation using post treatment modification changes the large pore zeolite Y into the small pore zeolite P, while zeolite X is formed by post treatment dissolution of zeolite A.\textsuperscript{12}

\textit{iv - Pore size and topology}

Zeolites, as being a porous material, have a 3D structure with internal volumes consisting of cages and channels.\textsuperscript{26} Sizes of channels and cages depend on the framework of the zeolite, made of more or less wide rings, producing pore volumes from 0.1 to 0.35 cm\textsuperscript{3}/g.\textsuperscript{27} The pore openings are typically constituted of 8-member rings, leading to pore size of 3.5 to 4.5 Å; 10 members, leading to pore size of 4.5 to 6 Å; and 12 member rings, leading to pore size of 6 to 8 Å.\textsuperscript{28} This pore size is a decisive factor in the application of the zeolite, as it will determine its selectivity,
regarding a specific reaction for example. The size of the cages as well is important, as it can restrict a reaction to a certain pathway by prohibiting certain intermediates to be formed due to their size.

Another class of zeolites exists: the hierarchical zeolites. They present a secondary porosity, added to the base crystal. Two different approaches exist: “top-down” where the crystals produced suffer a post-synthesis treatment (dealumination or desilication usually) which will create mesopores in the structure and lower the Si/Al ratio; and “bottom-top” which generally uses templating agents to create a 3D template of the desired mesopores in the structure, then the zeolite crystals grow in the voids of the structure and the synthesis terminates by the destruction of the template (by combustion for example).29

\textbf{v - Size (100 nm, 1 \mu m, 10 \mu m, hierarchical)}

Zeolite syntheses can achieve very small to large crystal size (20 nm up to roughly 20 \mu m). Large crystals will tend to be used in the case of shape-selective catalysis, while small crystals (high surface area, shorter diffusion path) will have a higher catalysis activity.30

\textbf{vi - Organic Structure Directing Agents (OSDA)}

\textit{Figure 7: TetraPropylAmmonium Hydroxyde (TPAOH), common OSDA for zeolite synthesis (ZSM-5 for example)}

Certain zeolite frameworks cannot be synthesized easily, or in some cases at all, without OSDA. In fact, about 15\% of the frameworks synthesized have been prepared without OSDAs. The OSDA acts as template molecules that will design the zeolite structure and pore size by creating complexes in solution with the
various species in the media. However, to be removed from the product, calcination is necessary, leading to the destruction of the OSDA (which is often an expensive organic salt) and leads to the production of dangerous gases.\textsuperscript{31}

\textbf{vii - Zeolite stability in water}

Zeolite synthesis is subject to a dynamic equilibrium between crystal growth and crystal dissolution. As a metastable state, the zeolite stability in its crystallization media is dependent on its purity.\textsuperscript{32}

As a recovered product, zeolite will tend to dissolve in water. Often used to dry gases in vapour phases, a possible application of zeolites would be as a catalyst in liquid phase, in particular in the biomass to biofuel process. Studying the thermal stability of zeolites, and ways to improve it, are some of the major research areas of zeolites nowadays.\textsuperscript{33–35}

\textbf{3 - Zeolite Synthesis: Tradition and opportunities}

Zeolite synthesis requires both aluminium and silica species to be dissolved in solution. As the crystallization occurs in a strongly alkaline media (pH close to 14), both silica and aluminium species will first be dissolved in a basic solution separately and then mixed together in the crystallization vessel.

\textbf{i - Classical methods}

Zeolite synthesis is traditionally realized in autoclaves (pressure-bombs), where the reactants are placed (usually using a polytetrafluoroethylene (PTFE, or Teflon) liner to prevent reaction with the autoclave wall) and then the vessel is placed in an isothermal oven. This batch hydrothermal synthesis then requires

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{batch-reactor-diagram.png}
\caption{Batch reactor: the autoclave}
\end{figure}
several hours to days of crystallization in the oven to achieve a complete crystalline product. This product is then collected, centrifuged or filtered, and washed several times to remove all reactive species. Finally, the product is dried and sometime calcinated depending on the application.\textsuperscript{25,36,37}

However, this method faces many drawbacks: heat transfer and mass transfer control are very limited, pH control is not possible, sampling is difficult, and there is variation of product quality one batch to another.

Moreover, batch installations in industry are space consuming and need a lot of human interactions for control which does not leave much room for automation.

\textit{\textit{ii - New/emerging methods}}

In recent history, many studies have been made to synthesize zeolite in a continuous way\textsuperscript{38–41}. This synthesis path is studied in order to have a better control of the zeolite synthesis parameters. These parameters include thermal and mass transfer\textsuperscript{42–44}, species mixing\textsuperscript{45}, the possibility of sampling products without having to stop the process. One can even do in-situ analysis and, therefore, have better control on the zeolite crystal produced. Lately, syntheses of membranes\textsuperscript{46} and crystals has been explored.

Another field in development is the synthesis of zeolite using fly ash instead of using traditional sources of Silica and Aluminium (traditionally Sodium Silicate and Sodium Aluminate). Indeed, fly ash being a by-product of coal combustion, are composed of 20
to 60% SiO₂ and 10 to 40% Al₂O₃. Previously released into the atmosphere, their negative environmental impact has been discovered and now they are captured. Right now, they are inefficiently mixed into cements and concrete whereas this new zeolite application might be a clever way for its valorization.⁴⁷,⁴⁸

**iii - Core-shell zeolites**

The synthesis of core-shell zeolites is a field in development working to optimize zeolite catalytic activity. Usually, they are synthesised with a microporous material on the outside to behave like a molecular sieve, and also protects the core, which is made of a microporous material, which enhances the catalytic activity of the particle⁴⁹,⁵₀. Indeed, the molecular sieve will prevent big unwanted molecules from absorbing onto the catalyst and poisoning it, which leads to a substantial increase in the catalyst life expectancy.⁵¹,⁵²

**C - Zeolite A (framework LTA)**

We will focus here on a specific zeolite. Zeolite A, with the structure Linde Type A (which gave the name to the framework category LTA), has been discovered in 1953 by the Linde division of Union Carbide. It is a zeolite only synthesized artificially.

**1 - Structure**

The LTA structure can be described as double 4-member rings units (d4r) linking sodalite cages. The lattice of the crystal has a unit cubic cell parameter of roughly a = 12 Å. The pore’s configuration is a 3D network with channels (4.21...
Å wide) and α-supercages (11.05 Å wide), which has 8-member rings opening at a nanoscale level. 53

2 - Properties

The product of the zeolite A synthesis is a light, white powder, with a crystal density estimated at 1.4142 g/cm³. The void fraction of the material, due to its framework, is 55.51%. The surface area can reach up to 750 m²/g.54

3 - Applications

Zeolite A is used in industry, as it is the most synthesized zeolite. Thanks to the α-supercages, it is widely used in petroleum industries; in n-paraffins and olefins cracking processes (long carbon chains enter the pores and are cracked in smaller chain that will exit the catalyst to return into the media). The supercages have the space for molecules to rearrange and the small pores enhance the selectivity of the catalysis. Zeolite A, due to its fairly low range of Si/Al ratio, is also used in ion-exchange processes.
II - Methods and experiments

A - Products used

Sodium hydroxide (pellets, 97+\% A.C.S. reagent), sodium alumininate (technical, anhydrous), and sodium metasilicate were purchased from Sigma-Aldrich. Paraffin oil (mineral oil, pure) was purchased from Acros Organics. All chemicals have been used as received.

B - Batch syntheses

1 - Set up of the system

For the batch experiments, 22 mL stainless steel autoclaves equipped with PTFE liners have been used, reducing their actual volume to 7.5 mL.

i - Low Si/Al ratio set: Traditional zeolite A synthesis in batch

For this experiment, the following composition was used, from the work of L. Yu et al.\[39\]:

\[ \text{1 SiO}_2 : 1.6 \text{ Al}_2\text{O}_3 : 9.28 \text{ NaOH} : 135.5 \text{ H}_2\text{O} \]

First, 9.14 g of NaOH were dissolved into 60 mL under stirring. This mother solution was then divided in two equal volumes, solution daughter 1 and solution daughter 2. In solution daughter 1, 3.00 g of Na\textsubscript{2}SiO\textsubscript{3} were dissolved under stirring; while in solution daughter 2, 6.44 g of NaAlO\textsubscript{2} were dissolved under stirring. After both solutions turned clear, 2 mL of each solution daughter were loaded into two separate 5 mL syringes and injected at once into the autoclave. Once tightly sealed, the autoclave was left at room temperature for the desired aging time (0, 45 min, 12, 24 h) and afterward set in an isothermal oven during various times (5, 10, 30,
60, 90 min, 12, 24, 36 h) at 65°C. The autoclave was then recovered, briefly cooled down in a water bath, opened, and the product was collected in a centrifugation vial of 50 mL filled with 25 mL of deionized water added before centrifugation and washes.

An auxiliary set of experiments have been realized, where the crystallization time was set at 90 min and aged for various times (0, 45 min, 12, 24 h) was conducted in order to see the effect of aging on batch syntheses.

**ii – High Si/Al ratio set: Batch LTA to confirm literature kinetic data**

In order to validate the model described by Grizetti et al.\textsuperscript{55}, a batch experiment was made to reproduce literature data using a different composition, described below.

For this experiment, the ratio achieved in the mixture was the following one:

\[
1 \text{SiO}_2 : 0.18 \text{Al}_2\text{O}_3 : 8.6 \text{NaOH} : 150 \text{H}_2\text{O}
\]

First, a volume of 60 mL deionized water was divided equally in two beakers. After weighting 7.64 g of NaOH, the amount was divided with a ratio 1/3-2/3. In the solution daughter 1 was dissolved 1/3 of the NaOH was dissolved with 2.71 g of Sodium Silicate; when in solution daughter 2, 2/3 of the NaOH was dissolved with 0.65 g of Sodium Aluminate. Once both solutions were clear, they were injected in the autoclave the same way as in the first set of batch reactions and the following steps remain the same.
**C - Flow Syntheses**

1 - Design of the oscillatory flow experiment (including data)

All tubing used to build the system were made of PerFluoroAlkoxy alkanes (PFA), with an inside diameter of 1.5875 mm and an outside diameter of 3.175 mm.

![Diagram of the system used](image)

*Figure 11: Schematic of the system used. To ease comprehension, aging section and furnace are decomposed here, but in fact they happened at the same place.*

Each aluminium and silica solutions were flowing in different channels until the mixing section. After the first tee, which enabled a tube in tube design downstream, the aluminium flux was flowing through a needle (22 G, 0.72 mm outside diameter, 0.41 mm inside diameter, 102 mm long, Air-Tite sterile). A third line, carrying the paraffin flux, is connected at the second tee intersection: the mixing section. Two piston pumps are used (Standard Infuse/Withdraw PHD Ultra Syringe Pump, Harvard Apparatus), one for the aqueous streams and the other for the paraffin flux only. These pumps were remotely controlled through a program, interface coded for this purpose on LabView. The crystallization reactor used was a 1 m tubing of the same tubing used for the connection channels before, and the isothermal oven set at 65°C used for the experiment was a column oven (LC Column Oven, Scientific Systems Inc.).
2 - Mixing section

The mixing section was conceived in order to solve one of the major risks in continuous zeolite: clogging the system. Indeed, mixing the two solutions of aluminium and silica results immediately into the formation of a gel. This gel is very viscous and adhesive, and forms at the mixing point in a matter of three seconds. This gel solidifies quickly and easily grows onto the needle tip, and from here, clogs the system.

To avoid this event to occurs, many trials have been conducted:

- External shaking of the reactor tubing: using an external device (here, a grinding mill, (Heavy Duty Wig-L-Bug Grinding Mill, 3110-3A, REFLEX Analytical Corporation), the mixing section was held fixed, and the needle was set at various depth into the reactor. But the gel, no matter what frequency of vibration was applied, grew on the needle tip and broke after it length reached about 2 cm, to re-extrude again after. Moreover, due to the shock implied by the external vibration, the tubing material suffered it and was deformed, which facilitated the formation of a clog. This idea was therefore abandoned.

- Sonication: various sonication devices (low, medium and high frequency and power, up to a Sonics Vibracell VC750, high intensity, amplitude about 60 μm), which were placed in various location along the mixing section (before, onto and after the mixing zone of the tee) have been used to prevent the formation of the solid gel, in an attempt to keep the gel as fluid as possible. Unfortunately, it was not possible to prevent the clogging of the system. This idea too was therefore abandoned.
Finally instead of trying to set a very slow flow to do a continuous synthesis, a fast injection at the mixing section enabled the formation of droplets at the liquid state that were carried in the flux of paraffin. To counter balance this fast injection with the rather small reactor used, the flow is stopped when the reactor is filled with droplets to remove the mixing section. Then the reactor was quickly reconnected to the paraffin stream and the oscillation program was launched with the reactor placed in the oven when no aging was needed. When aging was needed, the flux was stopped, and the reactor disconnected. Once the aging time was passed, the reactor was then reconnected to the paraffin stream, oscillated and set into the oven for the length of the crystallization time.

3 - Experiments conducted in flow

The experiment conducted in flow used the same composition as the low Si/Al ratio batch set. The daughter solutions were prepared exactly the same way as for the batch experiments. Once prepared, each solution was loaded into 12 mL syringes which were then placed onto the piston pumps. A syringe of 60 mL was loaded with paraffin and set onto the other piston pump.

![Figure 12: Zoom on a filled reactor.](image)
With respect to droplet formation into the reactor, the paraffin flux was set at 2 mL/min and the aqueous flux was set at 0.6 mL/min (per syringe so the total outlet of this pump was 1.2 mL/min). This flowrate was chosen because it enabled a steady size of the droplets (no merging of the droplets) and prevented any clog to occur. The droplets formed had an average of 1.5 mm length, their volume has been estimated around 3 µL (approximating droplets as cylinders).

For the aging part, the reactor was set at room temperature during various times (0, 45 min, 12, 24 h). The temperature of the room was kept as constant as possible, and therefore the assumption of a constant temperature aging was made.

During crystallization, the reactor was placed in the isothermal oven set at 65°C, and connected to the paraffin flux to oscillate during various times (5, 10, 30, 60, 90 min, 12, 24 h). The oscillation used was the following one: a square function with an amplitude of 4 mL/min, centred on 0. The period used was 22 s, equally shared between the +2 and the -2 mL/min.
The collection of the product was done at the end of the crystallization time, where all the content of the reactor was emptied into separate, identical vials as the one used in the batch synthesis. There were each filled with 25 mL of deionized water to quench the crystallization, prior to the purification of the sample.

**D - Products purification and preparation**

The vials containing the product were centrifuged in order to extract the solid from the oil/water suspension and to prevent any further crystallization. The supernatant was removed, and 30 mL of deionized water was added to wash the solid product. This was repeated two times, after which the supernatant pH was about neutral. The centrifugation device was set at 1500 rpm, for 20 minutes and operated at room temperature each time.

Once the product is collected, the cake is dried overnight in an oven kept at approximately 100°C.

Once analyses were conducted, the sample was kept in a vial and then stored in a desiccator to keep it dry.

**E - Analytical**

**1 - XRD**

X-Ray Diffraction (XRD) patterns of all samples were collected on a Rigaku Geigerflex at 37.5 kV and 25 mA (Cu K-α radiation), using a 2θ range between 6 and 80°. The reference for LTA products was a commercial sample of zeolite A, a molecular sieve 4 Å (beads, 8-12 mesh, Sigma-Aldrich) grinded and then analysed.
2 - Raman

Raman spectra were obtained using a Horiba XploRa Raman microscope operating with a laser set at 785 nm and 50 mW. 60 second scans were realized with an accumulation of 30 scans. An 1800 grating was used with an aperture of 100 and slit width of 300. The laser light was focus on the samples using a 100x magnification Olympus lens.

3 - SEM

Scanning Electron Microscope (SEM) pictures were used to determine the product morphology and coupled with an image analysis, using the software ImageJ, to determine the mean size and distribution on a randomized population of 100 crystals. The SEM analysis was performed on a JSM-7000F SEM instrument, using a LaB6 ion source, the samples mounted on the analysis stage using conductive copper tape. The instrument was set at 10 kV with a working distance (WD) of 10.5 mm.

4 - Adsorption

The adsorption measurement was realized on a Quantichrome Autosorb iQ2. The isotherms, which are 77 K sorption isotherms, were realized using Nitrogen as sorbate. The samples were degassed for eight hours at 623 K before the analyses. Post analyses treatment were realized applying BET, DR, BJH and DFT methods on the isotherms.
III - Results

A - Crystal morphology

First, for both low Si/Al ratio batch and flow products, at low residence times, no crystallization is visible. The material appears amorphous, without any trace of a crystalline structure.

For the batch experiments, the samples collected at the intermediate residence time (90 min), spherical crystals can be observed. With an average size of 200 nm, these crystals seem covered with amorphous materials, which shows a premature stop in the crystallization process, therefore the crystallization is incomplete. For the long residence times (12 h and above), crystals are well defined, with various shapes (spherical, cubic, or orthorhombic). The size distribution is very broad, extended from 100 nm to more than 1 μm, with a mean around 400 nm. Nonetheless, no amorphous phase can be observed at the surface of those crystals, confirming a complete crystallization of the product.

Finally, the flow experiment products seem to follow a different pattern. It has been chosen to analyse the samples with 90 min residence time coupled to various aging times (0, 45 min, 12, 24 h). For any aging time set except 0 min, the
product looks more crystalline, but less defined, as if the crystals were melted together in clusters. No amorphous material is visible on the SEM pictures. For low aging time (45 min), the size distribution is narrow and centred on 200 nm; while for long aging times (12 and 24 h), the size distribution is wider, but much narrower than the batch one, with a mean around 400 nm. This indicates a possibility of control of the crystal size distribution that is not possible to achieve using a batch reactor.

**B - Batch results**

1 – Low Si/Al ratio batch set

The results of the batch experiments show that crystallisation occurs after a minimum of 90 min of crystallization time. The XRD

*Figure 16. A) XRD spectra collected of the low Si/Al ratio batch set products. B) Raman spectra collected of the low Si/Al ratio batch set products.*

*Figure 17. XRD spectra collected from the auxiliary experiment of the low Si/Al ratio batch set.*
pattern of LTA zeolite has reference pics defined at $2\Theta = 7.2^\circ, 10.3^\circ, 12.6^\circ, 16.2^\circ, 21.8^\circ, 24^\circ, 26.2^\circ, 27.2^\circ, 30^\circ, 30.9^\circ, 31.1^\circ, 32.6^\circ, 33.4^\circ$ and $34.3^\circ$ \textsuperscript{56}. It is confirmed on the Raman spectra, with a band appearing around 500 cm$^{-1}$ corresponding to the formation of 4-member rings. With amorphous material, the peak is broad and has a low intensity. When crystalline material appears, the peak gains in intensity and gets sharper. Nonetheless, the presence of the broad peak when the material is not crystalline may indicate the presence in solution of 4-member rings precursor, which then get integrated into the framework, modifying the peak shape. Also, when crystallinity is achieved in the product, peaks form around 340-380 cm$^{-1}$. Those peaks are representative of the presence of 6-member rings, confirming the formation of a structured phase in the sample.\textsuperscript{57}

The auxiliary experiments show an increase in crystallinity as aging time increases. Moreover, it can be observed that a short aging time (45 min) leads to a consequent increase of crystallinity in the product, but further aging does not seem necessary to reach a complete crystallization.

![Figure 18: Plot of relative crystallinity against crystallization time, for both Raman and XRD analysis.](image)

The plot of the relative crystallinity (with the crystallization of the 24 h crystallization time being the reference) vs crystallization time shows, based on the XRD spectra, very well the absence of crystals before 90 min, and after this time a product
showing more and more crystallinity. Nonetheless, a decay seems to appear beyond 24 h crystallization time. On the Raman spectra side, the same trend seems to be followed except for the last point, which instead of decaying is increasing. This might be based on the fact that Raman analyses the surface of a sample, and as the zeolite starts to dissolve, 4-member rings are released in the media, leading to an increase on the surface in 4-member rings detected by the Raman analysis.

2 – High Si/Al ratio batch set

![XRD spectra collected from the products of the high Si/Al ratio batch set experiments.](image)

From a first look, it can be easily determined that the XRD spectra collected after analysis of the high Si/Al ratio batch set do not correspond to the LTA framework XRD pattern. After further investigation, it has been found that this pattern corresponds instead to the XRD pattern of FAU zeolite. To verify this assumption, literature data have been studied to
determine if the conditions used enabled the crystallization of LTA under those conditions. The work done by M. Maldonado et al. highlight the fact that crystallization under those conditions doesn’t seem possible, showing clearly the composition being in the range of FAU zeolite synthesis. Therefore a confirmation of the synthesis kinetics of zeolite A in batch measured in their work was not possible in this work.

\textit{C - Flow results}

\textbf{Figure 21: Stacking of all flow XRD patterns form the flow experiment products.}

The composition here was the same that was used for the batch synthesis of low Si/Al ratio zeolite A, the results of the flow synthesis reactor returned also a LTA framework on the XRD spectra. Crystals appear after 12 h of crystallization
without aging time, but also appears after 60 min of crystallization preceded by 12 h of aging under room conditions of pressure and temperature. It can be observed that before 12 h crystallization time, without aging or with a very short aging (45 min), no crystallization is achieved.

![Figure 22: Raman spectra of the flow results.](image)

The Raman spectroscopy of the flow results confirm the first observations of the XRD plots. No crystallization appears to occur without aging at early crystallization time, and the sharp peak around 500 cm\(^{-1}\) typical of 4-member rings, as well as the peak around 340 cm\(^{-1}\) typical of 6-member rings in the framework, appear.

The plot of relative crystallinity vs aging time of the flow experiment, using the same reference as previously, provide more information. No crystallization occurs at low crystallization time (5, 10, 30 min) even if using any aging time. The results of the 60 and 90 min crystallization time show that at moderate (12 h) and
long (24 h) aging time, crystallization happened, however 100% crystallinity was still not reached. The zeolite crystallization seems to be completed for products from 12 and 24 h crystallization, without distinction of aging time. However, a decay seems present for long aging and crystallization (24 h/24 h).

The plot of relative crystallinity vs crystallization time shows the same trend for each aging time. At low crystallization time no crystallization occurs, then the product shows more crystallinity until it reaches the maximum crystallinity. At further crystallisation time, a decay seems to appear as the one present in the batch results.
**D - Punctual comparison between batch and flow results**

The first observation possible to do on those results is that a comparable crystallization can be obtained in flow synthesis compared to the batch synthesis one. Indeed, by comparing Figure 18 and Figure 24, we can see that taking the same reference for both, a crystallinity of 100% is reached in the flow products. There are huge discrepancies between the flow and the batch crystallization parameters. On the example of 90 min crystallization, with various aging times, it can be observed that at no or low aging time (0, 45 min), no crystallization occurs in flow when it is already happening in batch synthesis.

**E - Avrami fitting of batch experiment and confirmation of literature example**

![Avrami plot of the batch experiments and comparison with literature data.](image)

In order to extract the kinetic data from the experiment conducted in batch, an Avrami plot has been realized. The reference chosen came from the work of R. Grizzetti and G. Artioli\(^5\), which could not be reproduced in this work, where the
synthesis was conducted as described above for the high Si/Al ratio batch experiment. The results of the low Si/Al ratio batch synthesis show a similar slope for the Avrami plot, but the intercept is different.

The equation used here is:

\[
\ln(-\ln(1-\alpha)) = n \ln(t) + n \ln(k)
\]

The slope of the Avrami curve is then the \( n \) parameter and the constant \( k \) can be extracted from the intercept.

Here are the results extracted from this plot:

<table>
<thead>
<tr>
<th></th>
<th>Low Si/Al ratio batch experiment results</th>
<th>High Si/Al ratio experiment (from literature)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n )</td>
<td>1.78</td>
<td>1.8</td>
</tr>
<tr>
<td>( k )</td>
<td>0.0027</td>
<td>0.099</td>
</tr>
</tbody>
</table>

Then, a simple plot \( \alpha \) vs \( t_{\text{crystallization}} \) of isothermal results using the following kinetic equation:

\[
\alpha(t_{\text{crystallization}}) = K t_{\text{crystallization}}^q
\]
may provide more information on the synthesis growth and nucleation mechanisms.

It can be observed that the results obtained are relatively close, or at least in the same order of magnitude.

Table 2: Parameters extracted from the kinetic plots of the low and high Si/Al ratio batch experiments.

<table>
<thead>
<tr>
<th></th>
<th>Low Si/Al ratio batch experiment results</th>
<th>High Si/Al ratio batch experiment results (literature)</th>
</tr>
</thead>
<tbody>
<tr>
<td>q</td>
<td>1.13</td>
<td>1</td>
</tr>
<tr>
<td>K</td>
<td>0.037</td>
<td>0.064</td>
</tr>
</tbody>
</table>

Figure 26: Plot $\alpha$ vs $t_{\text{crystallization}}$ of the low Si/Al ratio batch experiment results.
**F - Attempt of fitting on the flow results**

The attempt of the Avrami plot of the flow results are presented above. Overall, it can be observed that the slope of the curve seems to decrease as the aging time increases, but always remains lower than the one collected in batch. A similar trend seems to be followed by the intercept, and therefore the constant k values will decrease, but stay below the value obtained by the batch experiment.
Table 3: Estimation of Avrami equation parameters of flow results.

<table>
<thead>
<tr>
<th>Aging time [min]</th>
<th>Avrami exponent ‘n’</th>
<th>Constant ‘k’</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.12</td>
<td>0.0017</td>
</tr>
<tr>
<td>45</td>
<td>1.51</td>
<td>0.0036</td>
</tr>
<tr>
<td>720</td>
<td>1.28</td>
<td>0.0050</td>
</tr>
<tr>
<td>1440</td>
<td>0.63</td>
<td>0.0027</td>
</tr>
</tbody>
</table>

**G - Absorption analysis of batch and flow products**

![Adsorption curves of batch and flow products](image)

Adsorption curves of the different product obtained provide various information on the zeolite produced and the difference of the batch and flow products. Multiple analyses have been conducted on these results to collect as much information as possible presented in Table 4.
Table 4: BET, DR and BJH analyses of the adsorption curves.

<table>
<thead>
<tr>
<th></th>
<th>Batch 5 min</th>
<th>Batch 90 min</th>
<th>Batch 12h</th>
<th>Flow 90 min + 45 min aging</th>
<th>Flow 90 min + 12 h aging</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area [m²/g]</td>
<td>92,8</td>
<td>150,8</td>
<td>155,6</td>
<td>139,2</td>
<td>214,6</td>
</tr>
<tr>
<td>BET C constant</td>
<td>59,8</td>
<td>318,3</td>
<td>-791,5</td>
<td>60,8</td>
<td>169,8</td>
</tr>
<tr>
<td>DR surface area [m²/g]</td>
<td>73,2</td>
<td>139,1</td>
<td>153,1</td>
<td>106,0</td>
<td>187,8</td>
</tr>
<tr>
<td>DR correlation coefficient</td>
<td>0,999</td>
<td>0,994</td>
<td>0,977</td>
<td>0,994</td>
<td>0,992</td>
</tr>
<tr>
<td>BJH surface area [m²/g]</td>
<td>66,5</td>
<td>65,9</td>
<td>43,2</td>
<td>67,0</td>
<td>93,5</td>
</tr>
<tr>
<td>BJH pore volume [cc/g]</td>
<td>1,03</td>
<td>0,65</td>
<td>0,12</td>
<td>0,65</td>
<td>0,93</td>
</tr>
<tr>
<td>BJH pore radius [Å]</td>
<td>15,3</td>
<td>15,3</td>
<td>17,0</td>
<td>17,0</td>
<td>17,0</td>
</tr>
</tbody>
</table>

The first observation from Table 4 is the Braunauer-Emmett-Teller (BET) method surface area seems to increase as the crystallinity in the sample increases, and the same observation can be observed on the surface areas extracted from the Dubinin-Radushkevich (DR) method. However, the results obtained after applying the Barrett-Joyner-Helenda (BJH) method decrease as crystallinity increases in the batch results when they increase in the flow case. The BJH method being mesopore focused, a further analysis of the pore size distribution has been realised using the Density Functional Theory (DFT).
Figure 29 provides some insight as to the discrepancy between the BET and BJH methods. It can be observed that at early collection of the product, no small pores are formed as there is no crystallinity. Also, a large majority of the surface area measured by the different methods above comes from a large population of large mesopores. However, as crystallization increases in the batch product, the area coming from the mesopores seems to decrease until it disappears while the one coming from the micropores increases. The flow products show a very different distribution. All things considered, for a similar crystallinity in the sample, the one produced by the flow system shows a higher microporosity, and a wide variety of mesopores. On the contrary to the batch product, the flow samples seem to show a trend of increasing mesoporosity as the crystallinity increases. This might be explained by the crystal morphology when synthesized in flow, which are fused aggregates of crystals. Those aggregates might generate mesopores that do not appear in the crystalline single crystals of the batch products.
IV - Discussion

A - Decay at long crystallization time

A decay in crystallization can be observed in products that spent a long time in the crystallization reactors. It has been observed in the petroleum industry a similar tendency has been observed during stimulation of petroleum reservoirs. However this operation is realized with strong acids when the zeolite synthesis occurs in basic media. In the case of a very alkaline media, zeolites being a metastable state in the synthesis media, a dissolution of the material can occur at long crystallization times, leading to a modification of the framework or the disappearing of the crystalline phase. In both cases, the mechanism appears to be similar. The charged specie of the media adsorbs on the surface of the crystal, leading to a weakening in the bonds Si-O or Al-O in the crystal framework. These bonds are hydrolysed in a catalytic reaction, until the lattice is so degraded that a fragment of the crystal leaves the structure.

B - Insight on crystallization mechanism

The results obtained give some information on the crystallization mechanism:

- First, the aging time plays a key role in the crystallization process, by enhancing the crystallization kinetics. Indeed, from the XRD data (Figure 21) and the Raman plots (Figure 22), it can be observed that aging time, when no crystallization occurs, does not lead to crystal formation, but as it
increases, it eases the crystallization of the product for a fixed crystallization time.

- The Raman analysis of the different sample of both batch and flow system show the presence in solution of 4-member rings prior to the crystal appearing. This leads to the conclusion that 4-member rings are precursor to the formation of crystals, which corroborate with the conclusions of Min Bum Park et al.\textsuperscript{61} work.

- However, the observation of crystal shape from the different synthesis method in Figure 15 seems to show a different crystallization path followed during these two methods. This observation seems to be supported by the Figure 29, where different pore size evolutions along crystallization time seem to occur. On the batch crystallization side, the crystallization seems to happen in the form of growth of single crystals, well defined, by consumption of nutrients at the surface of the crystal as defined in the work of Mintova et al\textsuperscript{62}. On the flow crystallization side, the nuclei seem to grow as small

---


\textit{Figure 30: Proposed mechanism for zeolite A crystallization in batch and flow.}
crystals which then stop growing to form fused aggregates of crystals, leading to particles with micro and mesopores.

**C - Enabling Zeolite Crystallization in Flow**

Zeolite synthesis is traditionally realized in batch systems. This pathway has been chosen for decades for its commodity, but it falls short of continuous flow. However, the transition of one to the other remains complicated due to the nature of the phenomena occurring. Indeed, major challenges are to be faced in continuous zeolite synthesis:

- Mixing is a recurrent problem in continuous syntheses, and many studies have been realised to overcome this challenge. One way to deal with it is to mix both aluminium and silica solutions before injecting them in the system. The advantages are that the mixing is controlled at the origin and it reduces the complexity of the geometry needed in the mixing section. However, as seen earlier, aging time has an influence on the final product crystallinity, and here the mixture is already made when injected, resulting in a difference of product when the sample is collected at the other end of the system. Another way of dealing with this challenge is to design a mixing section that will handle the instantaneous gelation of the mixture. Several designs were made so far, and the design presented in this paper is inspired from the work of K. Robertson and L. Yu et al. This design enables a separation of the aluminium and silica solution until it enters the reactor. Furthermore, the tube in tube design enables a good mixing since the droplet and limits the risks of gel growth on the needle tip by increasing
the shear-able surface available of the gel. The fast injection also helped with this aim in mind.

- Not clogging the system is also a big challenge in flow synthesis, a clog being synonym of shutdown of the system. Depending on the composition chosen for the zeolite synthesis, the mixture can behave as a solid gel as well as a liquid with a density close to that of water. The operation method used in this paper got around this problem by injecting both of the solutions quickly at the mixing points, leaving no time to the gel to form at the needle tip, and using a carrier fluid (here paraffin) to prevent a long contact between the solutions and the needle tip.

- Another challenge would be to sustain a real continuous flow for a bench laboratory. Previous works use very long tubing to achieve it, with systems exceeding one hundred meters. The aim of this work is to create a compact system capable of synthesizing zeolites in flow. In order to do so, it has been based on the contemporaneous field of oscillatory flow. While not able to do a very slow injection to respect the continuous flow, a quick injection with oscillated flow achieved to mimic a steady flow condition close enough to assume flow conditions. Moreover, compared to plug flow reactors, this technology enhances mixing, mass and thermal transfers.

D - Impact of Aging on Crystallization Kinetics

The role of aging time in zeolite crystallization has been explored thoroughly using various analytic methods. Here we can see that it enhances crystallization, if not simply enabling it. Furthermore, a broad peak around 500 cm⁻¹ on the Raman
spectra of non-crystalline species is an evidence of 4-member rings already present in the mixture during the aging, but not structured in a lattice, as the corresponding XRD plots show no crystallinity in the samples. This observation is confirmed in the work of F. Tong et al.\textsuperscript{68} who conducted an InfraRed spectroscopy (IR) follows the same trend of the nucleation phase and shows existing bonds Si-O-Si or Al-O-Si in the mixture within SiO\textsubscript{4} tetrahedral structures. The peak intensity increases as the aging time increases, showing a certain degree of polymerization of tetrahedral structures without forming a crystal lattice.

Nonetheless, time is not the only parameter influencing the aging of a solution, as temperature\textsuperscript{69}, and pressure\textsuperscript{68} amongst other also impact this process.

\textbf{E - Analysis of Avrami plots}

The Avrami equation is widely used to determine kinetic parameters of isothermal crystallization of amorphous solids. However, the exact meaning of each parameters n and k is not well defined. The Avrami exponent, n, represents either the nucleation rate or the growth morphology (1, 2 or 3D growth), while the constant k, depends on the temperature, and both nucleation and growth rates\textsuperscript{70}. The temperature dependence of k comes from the growth rate, which is strongly dependant on the temperature due to the mobility at the crystal surface.

An Avrami exponent value above 4 is synonymous to homogeneous nucleation, and below 4 it corresponds to a heterogeneous nucleation\textsuperscript{71}. However, the interpretation of this exponent in the case of this work gives us a disc-like growth.
But in reality it can be observed from Figure 15 that the crystals grow with a sphere-like shape. This discrepancy from Avrami’s model may be explained by the complex nucleation occurring in the gel mixture. Indeed, zeolite nucleation and growth are driven by the gel nature and structure, and it is a delicate topic in the zeolite research field, where homogeneous and heterogeneous nucleation views conflict.\textsuperscript{72,73}

The gel produced by mixing both aluminium and silica solutions results in an amorphous structure that encapsulates solution in pockets. From the homogeneous nucleation point of view, the nucleation occurs in both solution and gel phases: when the heterogeneous nucleation consists here in a nucleation occurring only in the gel structure. In either case the species present in the solution pockets need to diffuse through the gel to reach the nuclei, which complicates the nucleation mechanism, and therefore the kinetics associated with it.\textsuperscript{74}

The results of those plots seem very different between the batch ones and the flow ones. The result for flow with 24 h aging, being affected possibly by the dissolution of the product at long crystallization time, seems very low nonetheless. However, the Avrami exponent extracted from the flow crystallization remains low compared to what could be expected for 3-D crystal growth. This confirms the difficulty in interpreting the meaning of parameters ‘$n$’ and ‘$k$’ for zeolite crystallization compared to regular crystallization of amorphous materials such as polymers.

<table>
<thead>
<tr>
<th>Avrami exponent</th>
<th>Growth geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 \leq n \leq 2$</td>
<td>1D, rod-like</td>
</tr>
<tr>
<td>$2 \leq n \leq 3$</td>
<td>2D, disc-like</td>
</tr>
<tr>
<td>$3 \leq n \leq 4$</td>
<td>3D, sphere-like</td>
</tr>
</tbody>
</table>

Table 5: Interpretation of Avrami exponent.
**F - Discussion on the Adsorption results**

The information given by the adsorption curves provides interesting material from which to draw conclusions. However, some of the methods used do not fit very well with the results with microporous materials. The BET results can be quantified as realistic or not depending on the value of the C constant it provides. This parameter, to obtain an accurate result in the BET surface area calculation, should be in the range of 20-200, which is not the case for some of the results collected on Table 4\textsuperscript{75}. This can be explained by the fact that LTA zeolites has ultra-micropores, which leads to greater errors in the BET surface area evaluation.\textsuperscript{54} Other methods, such as DR or BJH methods are preferred for this kind of material, as they are more precise with microporous materials than the BET method can achieve by itself.

**G - Batch and flow systems: fundamental differences**

1 - Heat transfer

The characteristic heating time can be estimated for each system using

\[ t_{\text{heat}} = \frac{L_c^2}{\alpha} \]

where alpha is the thermal diffusivity (units of m\(^2/s\)) and L\(_c\) the characteristic length of the system. The respective thermal diffusivities of the different materials have been estimated and the values stored in the following table.

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal diffusivity (m(^2/s))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless steel</td>
<td>(4 \times 10^{-6})</td>
</tr>
<tr>
<td>PFA/PTFA</td>
<td>(0.1 \times 10^{-6})</td>
</tr>
<tr>
<td>Crystallization media</td>
<td>(0.2 \times 10^{-6})</td>
</tr>
</tbody>
</table>
The characteristic length used for each material is its respective layer thickness.

For the batch system, the heating time is estimated to be:

\[
t_{\text{heat}} = t_{SS} + t_{PTFE} + t_{\text{media}} = \frac{(0.0088)^2}{4 \times 10^{-6}} + \frac{(0.0038)^2}{0.1 \times 10^{-6}} + \frac{(0.0082)^2}{0.2 \times 10^{-6}} \\
= 19.4 + 144.4 + 336.2 = 500 s
\]

The time needed to actually heat the center of the batch reactor can be estimated to be approximately 8min 20sec.

For the flow system, the heating time is estimated to be:

\[
t_{\text{heat}} = t_{PFA} + t_{\text{media}} = \frac{(0.0008)^2}{0.1 \times 10^{-6}} + \frac{(0.0008)^2}{0.2 \times 10^{-6}} = 6.4 + 3.2 = 9.6 s
\]

The heating time needed to heat the core of the droplets inside the flow reactor is approximately 50 times faster than it is for the center of the batch system to get up to temperature.

The crystallization occurring is exothermic with an enthalpy for our system close to the one measured in the work of Yang, S et al.\textsuperscript{76} where \(\Delta H_{\text{Crystallization}} \approx -450 \text{ kJ/mol}\). This may cause the center of the reaction system (i.e. the mixture in the autoclave and the droplet respectively for the batch and flow systems) to be at a higher temperature compared to the isothermal one set in the oven.

This will lead to a consequent increase in temperature in the batch system as the temperature diffusion occurs slowly, whereas in the flow system this diffusion occurs quicker and will stabilize the temperature within the droplet.

The adiabatic temperature rise represents the maximum temperature the system will reach if all the reaction heat is transferred to the liquid. It is estimated as following:

\[
Q = mc_p\Delta T
\]
\[
\Delta T = \frac{\Delta H_{\text{rxn}}}{mc_p} = \frac{450 \frac{kJ}{mol\ Si} \cdot n_{Si}}{4.6 \times \frac{1\ mol}{18\ g} \times 4.18 \frac{J}{mol\ K}} = 400K
\]

This heat is transferred quickly and efficiently to the media in the flow system, but will not be transferred as fast in the batch system.

2 - Mass transfer

The mixing time of the media in batch is only due to diffusion, as there is no mixing of the system. It can be estimated using \( t_{\text{mixing}} = \frac{L_c^2}{D} \), where \( L_c \) is a characteristic length of the system and \( D \) is the diffusion coefficient, estimated close to \( 5.10^{-7} \text{ cm}^2/\text{s} \). Therefore:

\[
t_{\text{mixing}} = \frac{0.82^2}{5 \times 10^{-7}} = 1.35 \times 10^6 s = 15.5 \text{ days}
\]

Whereas in flow, the mixing is mainly due to convection created by the flow.

\[
Re = \frac{\rho u L}{\mu} = 1 \times 10^{-2}
\]

\[
Sc = \frac{\mu}{\rho \cdot D} = 4.76 \times 10^8
\]

\[
Sh = 0.664 \cdot Re^{\frac{1}{2}} \cdot Sc^{\frac{1}{3}} = 53.4
\]

\[
\frac{k_l \cdot L_c}{D} = 8.65 \rightarrow k_l = 3.33 \times 10^{-4} \text{ cm/s}
\]

\[
t_{\text{mixing}} = \frac{L_c}{k_l} = 240s = 4 \text{ min}
\]

It can be observed that the mixing time is approximately 3 orders of magnitude faster in the case of the flow system compared to the batch system.

This may indicate a big discrepancy in the availability of nutrients within the media in the batch system, which will cause certain crystals to grow more at the expense of others. Therefore, this will lead to a more broad size distribution: some crystals will grow big when others won’t have access to nutrients and stay
small. The enhanced mixing of the flow system enables a better distribution of the nutrients within the system, which will make the size distribution narrower.

### 3 – Kinetic Limitations

Kinetic limitations can arise from slow crystallization rates relative to the heat or mass transfer. In batch the poor thermal transfer coupled to the high exothermicity of the crystallization process leads to a consequent elevation of the temperature within the batch system. It enhances the kinetics at the expense of crystallization thermodynamics, leading to an earlier appearing of crystallinity in the products, which is consistent with the results measured in this work, compared to those synthesised in flow.

In flow, heat transfer is faster, leading to a much more homogeneous temperature within the droplets. As this temperature is lower than the one expected in batch, the kinetics of crystallization will not be as enhanced, therefore crystallization will appear later compared to batch. Again, this is consistent with the results measured in this work.

To study the effect of mass transfer on the system here, an estimation of the Damköhler number can be done, approximating the reaction term to be first order:

\[
Da_{\text{flow}} = \frac{\text{reaction rate}}{\text{mass transfer rate}} = k \frac{l^2}{D} = 0.002 \times \frac{(0.08)^2}{5 \times 10^{-7}} = 32
\]

\[
Da_{\text{batch}} = 0.0027 \times \frac{(0.82)^2}{5 \times 10^{-7}} = 3631
\]

A Damköhler number value greater than one show a mass transfer limitation in the system. However the value estimated in flow is much closer to 1 compared to the value of the batch system. This leads to the consideration that
the flow system is less limited by mass transfer than the batch one is, which enables an optimized kinetics for a similar set of conditions.
V - Conclusions and Prospects

A - Conclusions

In this study, zeolite A was synthesized in a semi-continuous segmented micro-batch oscillatory flow system. The design of the mixing section of the system prevented the formation of clogs and enabled the formation of regular droplets in the carrying flux of paraffin. Various conditions of aging and crystallization times have been tested, but the low pressure and temperature conditions remained constant through these experiments.

Microscopy imaging analysis enabled a comparison of morphology between batch and flow crystals, with singles crystals formed in batch synthesis and fused aggregates of crystals in flow synthesis. Spectroscopic analysis using XRD and Raman gave more insight on the crystallization kinetics and mechanism, and the relative crystallinity growing under different conditions.

The study of the adsorption results gave some information regarding the internal structure of the crystals and demonstrated the difference between the morphologies of crystals. The batch crystals had their mesoporous structure disappearing as crystallization increases, whereas the opposite was observed for the crystals formed by flow synthesis.

Finally, a crystallization mechanism has been proposed, compiling all the results obtained from the analyses of the products of both batch and flow syntheses.
**B – Prospects**

This work showed the possibility of synthesizing zeolite A crystals using a segmented oscillatory flow system. Further studies of zeolite synthesis using various temperature and pressure conditions would be interesting in order to assess the influence of those parameters on the crystals shape and the framework itself.

Furthermore, core-shell flow synthesis of zeolite using a similar system and mixing section would be interesting and would enable a fast way of synthesizing core-shell zeolites in a continuous process.
References


25. Maldonado, M., Oleksiak, M. D. & Chinta, S. Controlling Crystal


64. Pan, Y., Yao, J., Zhang, L. & Xu, N. Preparation of Ultrafine Zeolite A


65
(2005).


Appendix

I) Appendix 1: Calculations of compositions

Calculation of the composition used in the low Si/Al ratio batch set and the flow experiments, from the work of L. Yu et al.39

- Known: weights of $\text{Al}_2\text{O}_3$, $\text{SiO}_2$, $\text{H}_2\text{O}$ and $\text{NaOH}$
- Unknown: ratio of compositions

$3.00 \text{ g } \text{Na}_2\text{SiO}_3, 60 \text{ mL water, 6.44 g NaAlO}_2, 9.14 \text{ g NaOH}$

1) $\text{SiO}_2$

$$n_{\text{SiO}_2} = 3.00 \text{ g Na}_2\text{SiO}_3 \times \frac{1 \text{ mol } \text{Na}_2\text{SiO}_3}{122.06 \text{ g}} \times \frac{1 \text{ mol } \text{SiO}_2}{1 \text{ mol } \text{Na}_2\text{SiO}_3} = 0.02458 \text{ mol SiO}_2$$

2) $\text{H}_2\text{O}$

$$n_{\text{H}_2\text{O}} = \frac{V_{\text{H}_2\text{O}} \rho_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}} = \frac{(60 \text{ mL})(0.997 \frac{\text{g}}{\text{mL}})}{(18 \frac{\text{g}}{\text{mol}})} = 3.32 \text{ mol H}_2\text{O}$$

$$\frac{n_{\text{H}_2\text{O}}}{n_{\text{SiO}_2}} = \frac{3.32}{0.02458} = 135.1$$

3) $\text{Al}_2\text{O}_3$

$$n_{\text{Al}_2\text{O}_3} = 6.44 \text{ g NaAlO}_2 \times \frac{1 \text{ mol } \text{AlO}_2}{81.97 \text{ g NaAlO}_2} \times \frac{1 \text{ mol } \text{Al}_2\text{O}_3}{2 \text{ mol } \text{AlO}_2} = 0.0393 \text{ mol Al}_2\text{O}_3$$

$$\frac{n_{\text{Al}_2\text{O}_3}}{n_{\text{SiO}_2}} = \frac{0.0393}{0.02458} = 1.60$$

4) NaOH

$$n_{\text{NaOH}} = 9.14 \text{ g NaOH} \times \frac{1 \text{ mol } \text{NaOH}}{39.997 \text{ g NaOH}} = 0.228 \text{ mol NaOH}$$

$$\frac{n_{\text{NaOH}}}{n_{\text{SiO}_2}} = \frac{0.228}{0.02458} = 9.28$$

$\text{SiO}_2$: $\text{Al}_2\text{O}_3$: $\text{NaOH}$: $\text{H}_2\text{O} = 1:1.60:9.28:135.1$
- Comparison with the results of Maldonado et al.\textsuperscript{25}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure31.png}
\caption{Superposition of the composition used for the low Si/Al ratio batch set and flow experiments with the work of Maldonado et al.\textsuperscript{25}}
\end{figure}
Calculation of the amount of product needed for the high Si/Al ratio batch set, based on the work of R. Grizzetti et al.\textsuperscript{55}

- Known: Ratios of composition of the mixture
- Unknown: weights needed for the syntheses

$$SiO_2 - 0.18Al_2O_3 - 8.6NaOH - 150H_2O$$

1) $H_2O$

$$V_{H_2O} = 60 \text{ mL}$$

$$n_{H_2O} = \frac{60 \text{ mL} \times 0.997 \text{ g}}{18 \text{ g/mol}} = 3.32 \text{ mol}$$

2) $SiO_2$

$$n_{SiO_2} = \frac{n_{H_2O}}{150} = \frac{3.32 \text{ mol}}{150} = 0.022 \text{ mol} SiO_2$$

$$m_{Na_2SiO_3} = \frac{n_{Na_2SiO_3}}{M_{Na_2SiO_3}} = 0.022 \text{ mol SiO}_2 \times \frac{1 \text{ mol Na}_2\text{SiO}_3}{1 \text{ mol SiO}_2} \times \frac{122.06 \text{ g}}{\text{ mol Na}_2\text{SiO}_3} = 2.71 \text{ g Na}_2\text{SiO}_3$$

3) $Al_2O_3$

$$n_{Al_2O_3} = \frac{n_{H_2O}}{150/0.18} = \frac{3.32 \text{ mol}}{150/0.18} = 0.003984 \text{ mol Al}_2\text{O}_3$$

$$m_{NaAlO_2} = \frac{n_{NaAlO_2}}{M_{NaAlO_2}} = 0.003984 \text{ mol Al}_2\text{O}_3 \times \frac{2 \text{ mol NaAlO}_2}{1 \text{ mol Al}_2\text{O}_3} \times \frac{81.97 \text{ g}}{\text{ mol NaAlO}_2}$$

$$= 0.6531 \text{ g NaAlO}_2$$

4) $NaOH$

$$Ratio_{NaOH} = 8.6 \Rightarrow n_{NaOH} = 8.6 \times 0.022 \text{ mol} = 0.191 \text{ mol}$$

$$m_{NaOH} = 0.191 \text{ mol} \times \frac{39.997 \text{ g}}{\text{ mol}} = 7.64 \text{ g}$$
Comparison with the results of Maldonado et al.\textsuperscript{25}

\textit{Figure 32: Superposition of the composition used for the high Si/Al ratio batch set with the work of Maldonado et al.\textsuperscript{25}}
II) SEM Images of low Si/Al ratio batch and flow products

Batch product 5 min crystallization time

Figure 33 - SEM picture of low Si/Al ratio batch product, 5 min crystallization time. Zoom X2000.

Figure 34 - SEM picture of low Si/Al ratio batch product, 5 min crystallization time. Zoom X15000.
Figure 35 - SEM picture of low Si/Al ratio batch product, 5 min crystallization time. Zoom X55000.

Batch product 90 min crystallization time

Figure 36 - SEM picture of low Si/Al ratio batch product, 90 min crystallization time. Zoom X2000.
Figure 37 - SEM picture of low Si/Al ratio batch product, 90 min crystallization time. Zoom X15000.

Figure 38 - SEM picture of low Si/Al ratio batch product, 90 min crystallization time. Zoom X55000.
Batch product 12 h crystallization time

Figure 39 - SEM picture of low Si/Al ratio batch product, 12 h crystallization time. Zoom X2000.

Figure 40 - SEM picture of low Si/Al ratio batch product, 12 h crystallization time. Zoom X15000.
Figure 41 - SEM picture of low Si/Al ratio batch product, 12 h crystallization time. Zoom X55000.

Batch product 24 h crystallization time

Figure 42 - SEM picture of low Si/Al ratio batch product, 24 h crystallization time. Zoom X2000.
Figure 43 - SEM picture of low Si/Al ratio batch product, 24 h crystallization time. Zoom X15000.

Figure 44 - SEM picture of low Si/Al ratio batch product, 24 h crystallization time. Zoom X55000.
Flow product 90 min crystallization time 45 min aged

Figure 45 - SEM picture of low Si/Al ratio flow product, 90 min crystallization time 45 min aged. Zoom X2000.

Figure 46 - SEM picture of low Si/Al ratio flow product, 90 min crystallization time 45 min aged. Zoom X15000.
Figure 47 - SEM picture of low Si/Al ratio flow product, 90 min crystallization time 45 min aged. Zoom X55000.

Flow product 90 min crystallization time 12 h aged

Figure 48 - SEM picture of low Si/Al ratio flow product, 90 min crystallization time 12 h aged. Zoom X2000.
Figure 49 - SEM picture of low Si/Al ratio flow product, 90 min crystallization time 12 h aged. Zoom X15000.

Figure 50 - SEM picture of low Si/Al ratio flow product, 90 min crystallization time 12 h aged. Zoom X55000.
Flow product 90 min crystallization time 24 h aged

Figure 51: SEM picture of low Si/Al ratio flow product, 90 min crystallization time 24 h aged. Zoom X2000.

Figure 52: SEM picture of low Si/Al ratio flow product, 90 min crystallization time 24 h aged. Zoom X15000.
Figure 53 - SEM picture of low Si/Al ratio flow product, 90 min crystallization time 24 h aged. Zoom X55000.