Continuous flow synthesis of zeolite FAU in an oscillatory baffled reactor

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Abstract
In this work, we report, for the first time, the continuous flow synthesis of zeolite NaX successfully accomplished in a pilot-scale (up to 100 L/h) continuous oscillatory baffled reactor (COBR). The continuous synthesis was achieved by combining the seed-assisted method, in-line mixing of reactants at high temperature and COBR. The use of a COBR not only allowed the same residence time as the batch system, but also a controlled temperature profile, thanks to the plug flow behavior and effective heat transfer. A stable continuous operation was maintained during 5 hours owing to an effective mixing, preventing any hydrodynamic failure caused by the sedimentation of zeolite crystals. The results showed that zeolite NaX was obtained after 99 minutes and crystals between 0.6 and 0.7 μm were observed by scanning electron microscopy. The effect of frequency and amplitude on crystal properties was assessed. Sampling at three points along the COBR allowed the study of steady states of the zeolite concentration in temporal and spatial domains.

Key words
continuous oscillatory baffled reactor, continuous zeolite synthesis, NaX zeolite, reactive heating crystallization

1 INTRODUCTION

Zeolites are crystalline aluminosilicates composed of AlO4 and SiO4 tetrahedrons to form 3D porous structures.[1] They are conventionally synthesized by hydrothermal treatments, in which a reactive gel composed of a structure-directing agent and sources of aluminum and silica is aged at low temperature (aging stage).[2] Then, the crystallization step takes place at high temperature yielding a crystalline solid.[3] This process is usually carried out in batch reactors from several hours to several days.[4] Yet, continuous flow synthesis has been proposed over the past years as an alternative solution to the manufacturing of products in various industrial areas.[5–7] Advantages as enhanced mass/heat transfer, controllable flow pattern, operational flexibility, and ease of scale-up have been described.[8–10]

Cundy et al.[11,12] reported the first attempt for a continuous zeolite synthesis process. The process consisted of a semi-continuous system in which a stirred tank was used as reactor by continuous feeding of a previously prepared synthesis gel and continuous withdrawing. Though ZSM-5 crystals were successfully prepared, the slow crystallization kinetics and therefore long residence time were the main barriers to develop a complete continuous flow process. Braun et al.[13] tried to overcome the limitation of slow kinetics by using a microwave-heated continuous reactor to synthesize AlPO4-5. They found that heating the reaction mixture to 160°C in 1 minute was key to obtain a pure product. Ju et al.[14] described a
continuous synthesis of zeolite A in a microchannel. They demonstrated that prior aging of the synthesis gel reduced the residence time in the microchannel.

Liu et al.\textsuperscript{[15]} described that the major challenges to switch from a batch to a continuous process are the reaction duration and the formation of solid particles during the synthesis. The hydrothermal synthesis of zeolites is usually very long.\textsuperscript{[4]} The sedimentation of solid particles and fouling caused by the lack of effective mixing and continuous operation can cause hydrodynamic failure (reactor clogging).\textsuperscript{[15]}

More recently, an ultrafast synthesis approach has been proposed by the same group\textsuperscript{[16]} where a tubular reactor is used as reaction vessel for a wide range of industrially important zeolites.\textsuperscript{[17–21]} Besides, they proposed a workflow including a series of key components to achieve an ultrafast synthesis. (a) An effective seeding to avoid aging stage and heterogeneous nucleation, (b) a well-tuned synthesis precursor to enable fast crystal growth, (c) fast heating to avoid decomposition of the organic structure-directing agent, and (d) high temperature to accelerate the crystal growth rate of the target structure.\textsuperscript{[17,22]} Another approach was proposed by the same group\textsuperscript{[23]} using pressurized hot water (370°C) to increase the reaction mixture temperature (240°C–300°C). They demonstrated, for the first time, the crystallization of ZSM-5 zeolite in the order of seconds.

The zeolites synthesized through an ultrafast approach are in the order of nanometers minimizing the possibility of solid precipitation that was beneficial for the stability of the process. However, nanosized zeolites are often submitted to post-synthesis treatment to avoid aggregation between the particles.\textsuperscript{[24]} Moreover, the collecting step is carried out by several cycles of high-speed centrifugation which is not viable from an industrial viewpoint.

In all above-mentioned cases, the synthesis gel was first prepared in a batch reactor and possibly aged in the same vessel, and only then continuously fed into the reactor. In addition, the reactants used to prepare the synthesis gel were fed at low temperature (<40°C). Yet, it is also feasible to mix the reactants in-line at high temperature followed by an immediate feeding into the reactor. To the best of our knowledge, no reports were published of in-line mixing of reactants followed by continuous crystallization of zeolites.

The second challenge to tackle in order to achieve a continuous flow process is related to the formation of solid particles during the synthesis. Continuous flow processes having high solid contents are susceptible to hydrodynamic failures caused by constriction, bridging, and random detachment of solid particles.\textsuperscript{[25]} Liu et al.\textsuperscript{[17,23]} proposed a compressed-air-driven vibrator to minimize precipitation or blockage problems. Continuous oscillatory baffled reactors/crystallizers (COBR/COBC) have been used in processes where a crystallization step is involved.\textsuperscript{[26–28]} This technology offers a consistent mixing environment and enhanced heat/mass transfer for flow processes.\textsuperscript{[29,30]} Crystallization of a pharmaceutical compound was achieved in 12 minutes in a COBC without clogging issues during the operation.\textsuperscript{[31]} Briggs et al.\textsuperscript{[32]} carried out a seeded cooling crystallization of β-L-glutamic acid in a DN15 (15 mm diameter) COBC, producing crystals of a desirable polymorph and purity. Moreover, antisolvent\textsuperscript{[33]} and cocystal crystallization\textsuperscript{[34]} were also assessed in COBC. More recently, Jiang et al.\textsuperscript{[35]} reported for the first time reactive seeded cooling crystallization of paracetamol in a COBR at different seed content, enabling smooth, and encrustation-free runs. These results in the field of crystallization herald that a COBR can potentially benefit the synthesis of zeolite materials from the viewpoint of handling of solid particles.

In this work, synthesis of zeolite NaX (FAU type) was, for the first time, investigated in a COBR under different operating conditions (WO 2018/167414). The effect of mixing intensity on crystal properties was investigated. The steady state of zeolite concentration in both temporal and spatial domains was studied.

2 | MATERIALS AND METHODS

2.1 | Chemicals

The raw materials used for the preparation of zeolite NaX were powder alumina (65.4 wt% Al\textsubscript{2}O\textsubscript{3}, 34.6 wt% H\textsubscript{2}O, Alcoa), sodium silicate (26.34 wt% SiO\textsubscript{2}, 7.74 wt% Na\textsubscript{2}O, 65.92 wt% H\textsubscript{2}O, PQ France), and sodium hydroxide (50 wt% NaOH, 50 wt% H\textsubscript{2}O, Akzo) as sources of aluminum, silica, and alkali, respectively. All chemicals were used as received from the suppliers without any further purification.

2.2 | Description of the continuous system

The reactive crystallization of zeolite NaX was carried out in a horizontally oriented DN43 (43 mm diameter) COBR. The DN43 COBR consisted of 10 jacketed baffled straight tubes and 10 jacketed baffled bends. The total length and the volume of the COBR were 42.4 m and 60 L, respectively. The operating flow rates are comprised between 24 and 100 L/h. Two gear pumps (Tuthill) were used to provide the oscillations at different frequencies (0.1-3 Hz) and amplitudes (10-150 mm). Two
thermostatic baths (Lauda XT8HW) were used to heat and control the temperature of the process. An insulation material was wrapped around the tubes and bends to reduce heat loss.

Gear pumps (PHA 2610-4-1) were used to feed reactants (GA1-GA3) from their respective stirred tanks. Nine thermocouples type K (TC Direct) were employed to record the temperature profiles of the operation along the reactor (TR01-TR09). Two pressure sensors (Vegabar 17, VEGA) were installed at different places on the flow system (PSH01-PSH02) to detect any rise of pressure, indicating blockage. During the process, samples were taken at three points along the reactor at regular times. Sampling points 1, 2, and 3 were located in the middle, end, and exit of the reactor, respectively, to follow the reaction kinetics and confirm the completion of the process. They were situated 18.4, 34.4, and 42.4 m after the entrance of the reactor, respectively. Figure 1 shows a schematic representation of the continuous flow system.

2.3 | Procedures

2.3.1 | Synthesis gel preparation

Zeolite X was synthesized in the sodium form (NaX) through a seeded process. The use of seeds enabled the elimination of the aging stage. The synthesis gel was prepared at 85°C by blending sodium aluminate and sodium silicate solutions with the seeds, using a high shear inline mixer (1 wt% of seeds). The sodium aluminate solution was priorly prepared by dissolving powder alumina in diluted sodium hydroxide at high temperature. The sodium silicate was diluted until get the desired concentration. The seeds are an amorphous gel, previously aged, not crystallized. The final molar composition of the mixture was 4.4 Na₂O:Al₂O₃:3.1 SiO₂:180 H₂O.

2.3.2 | Crystallization

The COBR, initially filled with demineralized water, was degassed to remove all the trapped gas. This gas can be compressed during oscillation preventing consistent oscillation through the system length. Once the reactor was bubble-free, the selected operational oscillation condition was switched on. Then, the sodium aluminate (Tank 1) and sodium silicate (Tank 2) solutions as well as the seeds (Tank 3) were pumped through the in-line mixer and then into the COBR by pumps GA1, GA2, and GA3, respectively. The reaction temperature was previously set to 100°C. The operation was carried out during a maximum of 5 hours. The product of the reaction was collected in a tank (Tank 4). For the process shut-down, the reactant feeds are replaced by water at the same flow rate to continue recovering the product stream. The operating and oscillation conditions tested in this work are summarized in Table 1.

In addition, a sample of the synthesis gel was initially recovered and crystallized in batch to be used as a reference. The gel was transferred to a jacketed tank stirred by a custom-made Archimedes-type screw. The crystallization was carried out during 120 minutes at 95°C.

Commonly, three dimensionless groups determine the mixing performance in a COBR: the oscillatory Reynolds number \( (Re_o) \) which is used to measure the...
oscillation intensity, the Strouhal number \((St)\) which determines the length of eddy propagation, and the net-flow Reynolds number \((Re_n)\) based on the superficial velocity of the imposed net flow\(^{[36,37]}\). The above-mentioned dimensionless numbers are defined by the following equations:

\[
Re_o = \frac{2\pi f x_0 \rho D}{\mu}, \\
St = \frac{D}{4\pi x_0}, \\
Re_n = \frac{\rho u D}{\mu},
\]

where \(f\) is the frequency of oscillations (Hz), \(x_0\) is the center-to-peak oscillation amplitude (m), \(D\) is the inner tube diameter (m), \(\rho\) is the fluid density (kg/m\(^3\)), \(u\) is the fluid velocity (m/s), and \(\mu\) is the fluid viscosity (kg/m s).

Another parameter highly used is the velocity ratio \((\Psi)\) which relates the oscillatory velocity \((Re_o)\) to the net flow velocity \((Re_n)\) and it should be at least greater than 1 to assure the effect of vortex cycle (reverse flow)\(^{[38]}\).

### 2.4 | Characterizations

The sample synthesized in the batch reactor, as well as the samples taken at three different points (Points 1, 2, and 3), was filtered, washed with distilled water until neutral pH was obtained and dried in air at 85°C overnight. X-ray diffraction (XRD) analysis was conducted on a Bruker D8 Advance diffractometer using Cu Kα radiation in the range of 5° to 50° with an angular step size of 0.015° to identify the structural phases present, and to determine the relative crystallinity of the zeolite NaX samples. The degree of crystallinity was calculated based on the ratio of the sum of the peaks surface area to that of the reference sample, prepared in batch\(^{[39]}\).

The morphology of the samples was assessed by scanning electron microscopy (SEM, Zeiss GeminiSEM 500) operating at 2 kV. Before characterization, the samples were suspended in ethanol. Then, they were sprayed and dried on the sample holder without any sample coating.

Particle size distribution (PSD) of solid products was measured by laser diffraction technique (Malvern Mastersizer 3000), using an Hydro LV dispersion unit at 2800 rpm. The particles were suspended in a tetraborate pyrophosphate solution to prevent adhesion of particles to the cell window and to help the dispersion. From the PSD curves obtained, the sizes for which the cumulative percentage undersize is equal to 10%, 50%, and 90% (D10, D50, and D90, respectively) by volume were determined. In addition, the curves were deconvoluted to determine the sizes and relative concentrations of single crystals (0.3-1.0 μm) and agglomerates (1.0-20 μm).

### 2.5 | Determination of steady states

Samples taken at three different points along the reactor at regular times were centrifuged at 5000 rpm during 30 minutes. The supernatant (mother liquor) was discarded and the precipitate (zeolite) was dried in air at 85°C overnight. Then, the dried zeolite was recovered and weighed to determine its concentration.

Solution concentrations measured at different locations along the reactor allow the determination of spatial steady states. Similarly, solution concentrations measured at different times in the same location enable the determination of temporal steady states.

### 3 | RESULTS AND DISCUSSION

#### 3.1 | Synthesis of zeolite NaX

The NaX zeolite crystals were successfully synthesized in the continuous flow system described in Section 2.2. The XRD patterns for samples taken at different points along the COBR during the run 1 are shown in Figure 2A (30 L/h, 1 Hz-64 mm), which demonstrate that the product of the continuous flow system was single phase NaX.
and no other crystalline phases were detected. Likewise, the synthesis gel, crystallized in batch at 95°C, yielded pure zeolite NaX after 100 minutes. The characteristic bipyramidal morphology of FAU-type zeolite was clearly identified by SEM (Figure 2B,C) for both batch and continuous systems. Single crystals between 0.6 and 0.7 μm were observed for both systems. The system employed for the synthesis did not show any influence on the purity of the final product and size of single crystals.

There was an evolution of the initial synthesis gel (Figure 2A). The bump between 20° and 40° indicates the presence of amorphous material, which gradually crystallized, according to the residence time. Nevertheless, thanks to the mixing of reactants at high temperature combined with seeding to avoid aging stage, the characteristic peaks of zeolite NaX were already identified in the synthesis gel. The crystallization started right after the mixing of reactants.

Although zeolite NaX was observed throughout the COBR (Points 1-3), the residence time plays an important role in the quality of the product in a continuous process. This parameter can be tuned by changing the length of the reactor or modifying the operating flow rate. As shown in Figure 3, the crystallinity was lower (92%) at a shorter length (18.4 m) equivalent to 53 minutes residence time. Fully crystalline zeolite was obtained when the residence time was 99 minutes (34.4 m length). This synthesis time was achieved by the combination of the seed-assisted method, in-line mixing of reactants at high temperature, and effective heat transfer provided by the continuous flow process.

The performance in the batch and continuous systems was almost identical in terms of PSD and crystallinity, meaning that the integration of the COBR in the continuous system did not modify the crystal size and reaction kinetics, respectively. The plug flow behavior, characteristic of COBRs,[32] allowed matching the residence time necessary to complete crystallization of the batch system.

The consistent mixing environment provided by the COBR was suitable for the handling of zeolite crystals avoiding sedimentation and preventing blockage. If a blockage occurred, it would be detected by an increase in reactor pressure. However, no significant difference in COBR pressure (PSH02) was observed over the running time (Figure 4A). Both the crystallinity of the zeolite at different points and the pressure log of the system demonstrate that a stable continuous synthesis was achieved in this work. The effective mixing was also beneficial to suppress fouling. After 5 hours of operation, reactor walls were incrustation-free. In addition, the enhanced heat transfer provided by the COBR resulted in a controlled temperature profile along the reactor during the operation (Figure 4B), ensuring a constant and repeatable environment, essential to obtain a good crystallinity and
avoid the co-crystallization of other zeolite phases. The temperature decrease from 250 minutes is due to the injection of water used to recover the product stream and shut down the system.

Concerning the PSD of samples taken at the outlet of the reactor, an example of deconvoluted curve (Figure 5A) showed a bimodal volume distribution. The maximum position of the small peak (first peak) was attributed to the size of single crystals while the maximum position of the bigger one (second peak) corresponded to the size of agglomerates. After reconstruction of deconvoluted curves (Figure 5B), the profile indicated an evolution of the agglomerates size over the time. Although the crystallinity reached a steady state after 123 minutes of running time at Point 3, the agglomerates size continued to evolve up to 240 minutes. This difference may result from an evolution of the reactivity of the seeds employed during the synthesis procedure. An in-line preparation of the seeds overcomes this issue giving a controlled PSD.

### 3.2 Effect of oscillation intensity and flow rate

The effect of different oscillatory Reynolds numbers on PSD was evaluated (Figure 6A). Two populations were observed: one for the single crystals and another for the agglomerates. The size of the single crystals remains...
unchanged, while the size of agglomerates increases over time. Lawton et al.\cite{31} and Jiang et al.\cite{35} reported the formation of smaller particles with stronger oscillation intensity, contrary to our observations where the size of single crystals does not change. The zeolite crystal size is determined by the number and distribution of nuclei in the gel matrix.\cite{40} Since the concentration of seeds, which replace the nuclei, was kept constant, the crystal growth led to similar sizes. Zhang et al.\cite{41} demonstrated that, despite the considerable differences of stirring speed in the synthesis of zeolite A, particulate properties of the crystalline end products were not affected.

The variation of the agglomerates size observed in Figure 6A agrees with the trend observed in Figure 5B, meaning that the evolution of the reactivity of the seeds was present for all the assessed oscillation conditions. Moreover, the average size of agglomerates slightly changed depending on the mixing intensity. High oscillatory Reynolds number (amplitude/frequency) yields smaller agglomerates. The agglomerate size (240 minutes) decreased from 14.5 to about 12.7 μm for \(Re_o\) of 968 and 1452, respectively.

The crystallization of zeolites starts with nuclei formation in the gel matrix, followed by an assembly of the tetrahedral structures at high temperature.\cite{2} Strong mixing intensity could hinder the right organization of primary structures, resulting in noncoordinated structures that assemble randomly, or even heterogeneous nucleation on the surface of already formed particles. The noncoordinated structures will tend to aggregate among them in order to stabilize, like a nanoscale glue, forming agglomerates instead of single crystals.

The intensity of mixing is known to enhance the mass transfer process, reducing the boundary layer thickness between the solid-liquid interface.\cite{28} Together with the disturbance during the assembly of primary structures, an increasing incorporation of solute from the gel into the solid phase, thanks to an enhanced mass transfer, will slightly change the size of agglomerates.

Despite the observed trend for the agglomerates size, the result at \(Re_o\) of 772 showed a smaller size (11.2 μm) compared to the other conditions. This \(Re_o\) corresponds to 1.5 Hz and 34 mm of frequency and amplitude, respectively. This condition of oscillation intensity was identified as optimal to minimize dispersion and obtain a balance between the radial and axial mixing.

The amount of agglomerates (Figure 6B) also increases over the time. However, this seems to be independent from the oscillatory Reynolds number.

In this work, samples were taken at three different sample points (Points 1, 2, and 3) along the COBR. The zeolite concentration profiles as a function of time, for two different flow rates (run 2:30 and run 5:50 L/h), are shown in Figure 7. For both flow rates, the concentration of zeolite increases over time until a stabilization point is reached corresponding to the steady state. Concentration in Point 1 stabilizes first, followed by Point 2 and finally Point 3. Before the stabilization point, the concentration of zeolite increases over time until a stabilization point is reached corresponding to the steady state. Concentration in Point 1 stabilizes first, followed by Point 2 and finally Point 3. Before the stabilization point, the concentration of zeolite is lower resulting from the initial dispersion of the synthesis gel into the demineralized water initially present in the COBR. As previously shown (Figures 2A and 3) there was an evolution on crystallization, from amorphous gel to crystalline zeolite, which influenced also the concentration of solid. Initially, aluminate and
silicate solutions formed a suspension phase followed by the arrangement of structures until solid crystals are achieved. The zeolite yield obtained during the continuous synthesis was close to the theoretical yield (98-100%), which corresponds to 12% of the total suspension mass (120 g zeolite/kg gel). Since the molar composition of the synthesis gel was not changed, the yield for both flow rates was the same after the stabilization point.

Furthermore, an increase of the flow rate results in less dispersion of the synthesis gel and, as a result, the steady state is reached faster. The difference in concentration over different times is very small confirming that the temporal steady state of concentrations was achieved after 160 and 80 minutes for 30 and 50 L/h, respectively. Similarly, the spatial steady state of concentrations was evaluated by the differences between the concentrations at the 3 sampling points (Point 1 and Point 2, Point 1 and Point 3, and Point 2 and Point 3), having also been attained by the constant difference over time. Unfortunately, we were unable to demonstrate the operation of the continuous system at a higher flow rate (>50 L/h) due to a technical limitation. If the flow rate increases, the residence time will be shorter. In order to achieve a good crystallinity, either the length of the reactor must be enlarged to keep the same residence time or the operating temperature must be also increased, accelerating the reaction kinetics to match the new residence time.

In addition to the advantage presented above, a continuous system for zeolite synthesis integrating a COBR is attractive from a productivity point of view. COBR has been reported as an easily scalable technology (linear scale-up). The validation of the system in a pilot-scale (so far up to 50 L/h) provides the potential for reliable scaling up to industrial-sized production. Future work will focus on the demonstration of the continuous system at higher flow rates and temperatures.

4 CONCLUSIONS

We report, for the first time, a continuous flow synthesis of zeolite NaX that was successfully performed in a COBR without hydrodynamic failure. The combination of a seed-assisted method, in-line mixing of the reactants at high temperature, and effective heat transfer allowed a synthesis in 99 minutes similar to the 100 minutes obtained in the batch system. The COBR itself did not change the crystallization kinetics. The continuous process resulted in a zeolite product with the same morphology and particle size as was obtained in the batch process. The effect of oscillation intensity on crystal properties was discussed, and the single crystal size was not affected by oscillation, while agglomerate size decreased with the increase in the Reₜ number. By analyzing the concentrations at three different locations along the COBR, both temporal and spatial steady states in zeolite concentration were achieved. In addition, a high flow rate resulted in less dispersion of the synthesis gel and faster stabilization of the process, which represents an advantage from the viewpoint of productivity.

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CONFLICT OF INTEREST
Dr Lutz is employed by the ARKEMA Company, she is listed as inventor in ARKEMA patents in the field of the COBR.

AUTHOR CONTRIBUTIONS
H.R.M. performed the experimental part and processed the data. The manuscript was compiled and formatted by H.R.M. with support from M.V.L.P. T.G. and C.L. contributed to the final version of the manuscript and supervised the project.

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