

# A continuous flow reactor setup as a tool for rapid synthesis of micron sized NaA zeolite



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## ARTICLE INFO

### Article history:

Received 20 October 2015

Received in revised form

27 November 2015

Accepted 19 December 2015

Available online 30 December 2015

### Keywords:

Multiphase flow

LTA

NaA

Pilot scale

Continuous flow reactor

CFR

High throughput screening

Zeolite synthesis

## ABSTRACT

Slow crystallization kinetics and a limited thermodynamical stability of the target crystal phase are characteristic to zeolite formation, representing some of the key obstructions for fast zeolite synthesis. In this paper, the possibility of accelerating NaA zeolite synthesis in a continuous flow reactor (CFR) is studied. The CFR reduces the thermal lag by increasing surface to volume ratio, expediting heat transfer and mass transfer. The properties of the CFR and the reference batch synthesized particles were similar as confirmed by X-ray diffraction, scanning electron microscopy, particle size measurement using laser scattering and water adsorption equilibria. The reduced residence time and reduction in thermal lag provided an ideal synthesis environment for NaA zeolite, without side products, yielding 160 g/h per liter reactor volume of dry NaA crystals synthesized in 16 min and 2–3 μm particles for a single CFR. In comparison, the batch process produces 33 g/h per liter reactor volume. The effects of diluting with NaOH-solution and temperature were studied in the CFR, allowing to determine the optimal conditions. With the enhanced reaction kinetics gained from the increased temperature and molar composition, NaA synthesis is performed 10 times faster than in the optimal batch synthesis. The optimal conditions for the synthesis of NaA in the CFR were determined as: a gel composition of  $Na_2O:4.75 - SiO_2:1.93 - Al_2O_3:1.0 - H_2O:192$ , at a synthesis temperature of 150 °C during 16 min without, aging of the gel mixture. This paper shows that the bottlenecks in NaA zeolite synthesis can be widened resulting in faster synthesis in a CFR, making it a feasible pathway for more controllable zeolite synthesis at higher mass production rates (160 g/(h l-reactor)) while reducing the risk of blockage in a continuous flow reactor.

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## 1. Introduction

Zeolites are a group of aluminosilicate materials, exhibiting a porous crystal structure with well-defined structural features as cages and pores. Zeolitic structures are micro porous, thus having pores with a diameter of less than <2 nm. Due to these properties, zeolites can be used as molecular sieve. Zeolite NaA, also known as zeolite 4A, is a material having the Linde type A (LTA) topology with a Si/Al ratio of 1 and sodium cations counterbalancing the negatively charged aluminosilicate framework. Zeolites are meta-stable materials, their crystal structure being strongly dependent on system parameters and residence time during synthesis [1–4]. For example, zeolite 4A converges toward sodalite when treated for longer periods of time [5]. Besides, the synthesis gel homogeneity is crucial during the synthesis. Even small differences in

concentration can lead to a different zeolite structure, such as the faujasite (FAU) topology with a Si/Al ratio of 1.5–2.3 (NaX). The synthesis of zeolites is strictly bound to system parameters and homogeneity, even when using the correct stoichiometric quantities [6,7].

Typical synthesis of zeolites is carried out in batch processes [2,7–14]. In recent years the interest in continuous chemical production processes has grown, in the form of continuously stirred tanks in series (CSTR), tubular flow reactors and capillary flow reactors (CCFR). The two latter reactor types have led to zeolite synthesis yielding more homogeneous particles in size, shape and performance, however mostly lacking satisfactory throughput ( $\mu\text{l min}^{-1}$ ) [15,16]. These types of continuous flow reactors have been studied extensively for other applications mainly utilizing their high surface-to-volume ratio, yielding high heat and mass transfer rates [17–24]. These reactors furthermore exhibit a narrow residence time distribution and plug flow behavior, in contrast with CSTRs [25]. These properties make the continuous flow reactor a valuable tool for critical processes such as zeolite synthesis.

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However, the small channel geometries of capillary flow reactors (< 1 mm) lead an increased risk of catastrophic reactor blockage destroying the reactor [26–30].

The main advantage of the CCFR [16,31–33] is its fast heat transfer, resulting in a quasi instantly heating of the gel mixture to the desired temperature, in contrast to batch processes that require a significant time before the gel mixture reaches the desired temperature. This rapid temperature increase causes the crystals to grow instantaneously rather than the classical discrete shift from nucleation to nucleation-growth and finally growth dominated synthesis. So far, the only way to reach similar heating ramps in the entire liquid in batch synthesis is the use of microwaves, which works well to rapidly increase the temperature but lacks the ability to chill the liquid in a similar fashion [1,2,34] and concomitantly stop the reaction after a specific time interval.

Ju et al. have shown that synthesis in a CCFR is feasible for the production of NaA nano particles (300–900 nm) within 10 min for flow rates of 0.20 up to 0.85 ml min<sup>-1</sup> in a stainless steel tube with a 0.7 mm inner diameter. To achieve a successful synthesis, these authors had to age/cure the gel mixture prior to the hydrothermal synthesis in the capillary to avoid blockage. This aging process allows for gel equilibration and selective nucleation at room temperature [2]. An alternative to aging is the use of segmented flow, dividing plugs of synthesis gel with a continuous immiscible phase [15]. This significantly reduces the chance of blockage and increases the homogeneity due to Taylor vortices in the segments inducing self-mixing of the gel mixture. This technique allows for a fast controlled synthesis of zeolites but requires a secondary step to remove the immiscible phase and induces the risk of particle interactions at the liquid–liquid interphase. Another drawback of CCFR is the low throughput (μl/min).

In this paper, NaA zeolite synthesis in a continuous flow reactor (CFR, mm-scale) was studied, aiming at increasing the overall throughput without losing the ability of rapid heat transfer of the entire bulk. The reactor setup was studied for the rapid synthesis of micron sized NaA zeolite crystals at an increased throughput (ml/min for a single reactor) without aging, to synthesize micron sized NaA particles under varying conditions. Doing so, the effect of synthesis conditions (temperature and synthesis mixture composition) has been evaluated to screen the potential of the CFR. To evaluate the performance of the reactor, the quality of the obtained zeolite particles was evaluated using X-ray diffraction (XRD), scanning electron imaging (SEM) and particle size measurements (PSD). The water adsorption capacity of the CFR synthesized particles was measured, allowing a more quantitative insight regarding the yield of the synthesis and the performance gain using a CFR.

## 2. Material and methods

The synthesis gel was prepared according to Thompson et al. [35] (see Appendix 1). The molar ratio of the mixture was ranged in 1:1.93:(3.17–6.33):(128–256) Al<sub>2</sub>O<sub>3</sub>:SiO<sub>2</sub>:Na<sub>2</sub>O:H<sub>2</sub>O with a fixed ratio of 40 H<sub>2</sub>O:Na<sub>2</sub>O. (Further referred to as the dilution factor described in % described in Table 1).

**Table 1**  
Molar ratio for intended dilution factor.

Dilution (%)	Na <sub>2</sub> O	H <sub>2</sub> O	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>
0	3.17	128	1.93	1.0
25	3.96	160	1.93	1.0
50	4.75	192	1.93	1.0
75	5.54	224	1.93	1.0
100	6.33	256	1.93	1.0
200	9.50	384	1.93	1.0

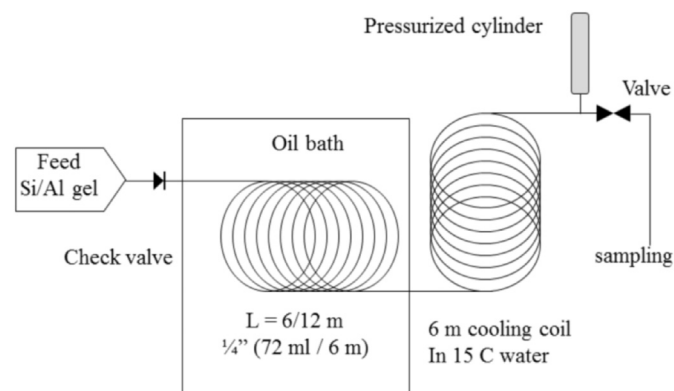
The gel solution was fed to a stainless steel (SS 1/4 inch) reaction tube with a constant-flow pump via perfluoroalkoxy alkane tubing (PFA tubing, 1/4 inch) (see Fig. 1 for reactor setup). The SS tubing, with a length of 12 m, was submerged in the thermostat with circulating oil (Lauda, Germany, thermal oil graded to 250 °C), which was set to the required temperature. Another SS coil was submerged in cold water to cool the fluid/gel to room temperature prior to sampling. The entire reactor was kept at a constant pressure of 5 bar using a pressurized air cylinder. The fluid was cyclically evacuated from the reactor by opening a ball valve at specific time intervals to allow fluid to escape the reactor but keeping the pressure constant without stopping the flow. The flow rate was 11 or 18 ml/min, which corresponds to a residence time of 16 and 7 min respectively, with a pressure drop of 0.5–0.35 bar and autogenic pressure of the gel mixture.

Between each experiment, the reactor was cleaned with deionized water and 10 M NaOH solution prior to feeding a new gel solution, in order to prevent contamination or seeding from the previous experiment in the reactor. The solid particles were recovered from the samples withdrawn from the reactor by filtration over a nylon membrane (Whatman nylon filter 0.45 μm pore size, GE healthcare life sciences, Diegem, Belgium), followed by washing with deionized water until the conductivity (Portavo 907 Multi pH, Knick, Germany) was below 1200 μS/cm<sup>2</sup> and finally dried at 90 °C for 24 h. The obtained particles and their quality were characterized with X-ray diffraction (XRD) and scanning electron micrography (SEM) of which the procedure and description can be found in Appendix 2. The pretreatment procedure for the synthesized particles is described in Appendix 3.

## 3. Results and discussion

The synthesis of zeolites is defined by thermodynamics, kinetics and hydrodynamics with a limited window in which the desired zeolite can be formed. Since an increase in temperature yields faster crystal growth, this was the first parameter to optimize in the CFR to expedite the synthesis process. A temperature increase from 100 °C (reference) to 150 °C was applied. Knowing that the activation energy ( $A_e$ ) for NaA crystallization is 60 kJ/mol, the increase in temperature from 100 °C to 150 °C should yield a 10 times faster synthesis (see Fig. 2) [8].

A temperature profile in an unstirred batch reactor using a SS casing, PTFE liner and thermal capacity and conductivity approximated by that of water using COMSOL 4.3b is shown in Fig. 3(a). Several points are indicated along the axial symmetry (ax symm) showing the temperature evolution over time for these points. The



**Fig. 1.** Flow chart of the CFR setup using SS 1/4 tubing with 12 ml internal volume per meter.

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