

# TRANSFORMATIONS AND SYNTHESIS OF ZEOLITES UPON EXERTING MECHANICAL FORCE AT ELEVATED TEMPERATURE

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## ABSTRACT

The synthesis of zeolite materials, whether in industrial or academic settings, is driven by practical applications necessitating tailored properties. These properties encompass size, morphology, hydrophobicity/hydrophilicity, acidity, additional pore systems, hydrothermal stability, and chemical composition. Exploring new synthesis routes is essential for advancing materials science and unlocking the full potential of zeolites. This pursuit addresses emerging challenges such as enhancing energy efficiency and mitigating environmental impact. Mechanochemistry, including thermomilling treatments combined with *in-situ* monitoring techniques, offers promising avenues for synthesizing zeolites with desired properties. Herein, the examples of thermomilling treatments of clinoptilolite in the presence of various alkali hydroxides reveal insights into phase composition and morphological changes. Furthermore, zeolite A preparation is reported and its morphological features discussed. These findings underscore the potential of mechanochemical methods in zeolite synthesis, paving the way for further advancements in the field.

**Key words:** zeolite, synthesis, mechanochemistry, interzeolite conversion.

## INTRODUCTION

The synthesis of zeolite materials, whether conducted in industrial settings or academic research, is driven by practical applications. Zeolite properties are tailored based on specific requirements dictated by their intended uses and the target features encompass a broad range of characteristics [1, 2]. Firstly, size is a crucial consideration, especially given the increasing demand for nanomaterials, particularly in catalysis and adsorption. Morphology influences surface area, pore volume, as well as accessibility of active sites. Hydrophobicity/hydrophilicity impact the interactions of zeolites with water and other (non)polar molecules. The balance between these characteristics can be finely tuned to suit applications such as adsorption of organic pollutants or separation of water from hydrocarbons. In addition, acidity is a key aspect of zeolite catalysis, whereas the presence of additional pore systems (hierarchical materials) can enhance mass transfer and accessibility of active sites, leading to improved catalytic performance. Further, hydrothermal stability is essential for applications in harsh environments or high-temperature processes. Lastly, chemical composition plays a vital role in determining the overall properties of zeolites and consequently their performance in various industrial processes. Therefore, exploring new routes for zeolites synthesis is essential for advancing the field of materials science, driving innovation and unlocking the full potential of these versatile materials, e.g. discovering novel frameworks [3, 4]. In this pursuit, it is imperative to tackle emerging challenges such as enhancing energy efficiency and mitigating environmental impact. From this perspective, investigating the potential of mechanochemistry in zeolite synthesis emerges as a promising approach. Herein are given several examples of thermomilling treatment of crystalline zeolite materials but also synthesis of zeolites while applying mechanical force at elevated temperature.

## EXPERIMENTAL

Naturally occurring zeolite mineral clinoptilolite (HEU-type; Zlatokop deposit, Vranjska Banja, Serbia) was used as a source material in zeolite thermomilling treatment (InSolido Technologies mixer mill IST636 coupled with a controller unit, a thermocouple, and the heating jacket). Clinoptilolite was milled with sodium hydroxide (NaOH), potassium hydroxide (KOH), cesium hydroxide (CsOH) and tetramethylammonium hydroxide (TMAOH) with a small amount of added water at 110 °C, 30 Hz for 2 h in Teflon lined milling vessels using ZrO<sub>2</sub> ball. The reactions were overseen *in situ* by synchrotron X-ray powder diffraction. The recovered solid phase was washed with distilled water until a neutral pH was attained. The isolated powder products were analyzed by X-ray powder diffraction (XRD), scanning electron microscope (SEM), Fourier-transform infrared spectroscopy (FTIR) and laser light scattering (LLS).

Zeolite A was synthesized using silicagel (Kemika, for chromatography, w(SiO<sub>2</sub>) = 95.415%), sodium aluminate (41 wt.% Na<sub>2</sub>O, 54 wt.% Al<sub>2</sub>O<sub>3</sub>, Riedel-de-Haën), sodium hydroxide (NaOH, Gram-mol, 99%), doubly distilled water produced in our laboratory and zeolite A seeds (Silkem, Si/Al = 1). The needed amount of each chemical was weighted in Teflon liner of the milling jar (milling jar consists of teflon liner and metal jacket), while the molar oxide composition of the reaction mixture prior to the addition of seeds was 1 SiO<sub>2</sub> : 0.32 Al<sub>2</sub>O<sub>3</sub> : 0.57 : Na<sub>2</sub>O : 2.15 H<sub>2</sub>O. The amount of added seeds was 10 wt.% with respect to SiO<sub>2</sub>. The reaction mixture was hydrothermally treated immediately upon mixing of chemicals at 100 °C for 1 h in a vibrating mill operating at 30 Hz in the presence of one ZrO<sub>2</sub> ball. The recovered solid phase was washed with distilled water until a neutral pH was attained. The dried powders were analyzed by XRD, SEM, FTIR and LLS.

## RESULTS AND DISCUSSION

*in-situ* X-ray diffraction synchrotron monitoring of thermomilling clinoptilolite with TMAOH and alkali hydroxides provides insight into the phase composition of the solid phase of the reaction mixture. The obtained materials differ as a function of the employed hydroxide, i.e. cation added to the reaction mixture.

In the presence of TMAOH any change takes place and the starting material remains intact for 90 minutes. Due to experimental issues, the *in-situ* X-ray diffraction monitoring data on RbOH are not utilizable. With NaOH and KOH are observed peaks of the clinoptilolite, but they appear and disappear as the milling proceeds which may be due to unidentified experimental issues. In the milled system using CsOH as mineralizer change occurred promptly yielding ANA after 30 minutes suggesting that the interzeolite conversion process took place [5]. Clearly, this process is more rapid in the presence of CsOH than NaOH, KOH and TMAOH due to differences in the ordering of water and stabilization of small alumo(silicate) precursor species by cations [6].

SEM images (Figure 1) of the samples harvested upon thermomilling treatment of clinoptilolite demonstrate that the intergrown-needles-like morphology of the crystals in the parent HEU-type material remains unaltered in the TMAOH-treated sample, while in NaOH and KOH, besides needles, are observed spherical (composed of intergrown) and sharp-edged (sometimes rod-like) particles, respectively. In terms of morphology, both CsOH and RbOH resulted in particles of uniform size and shape, yet different than the starting clinoptilolite. CsOH yielded small (less than 100 nm), intergrown spherical particles while in RbOH are found ellipsoid rod-like particles.

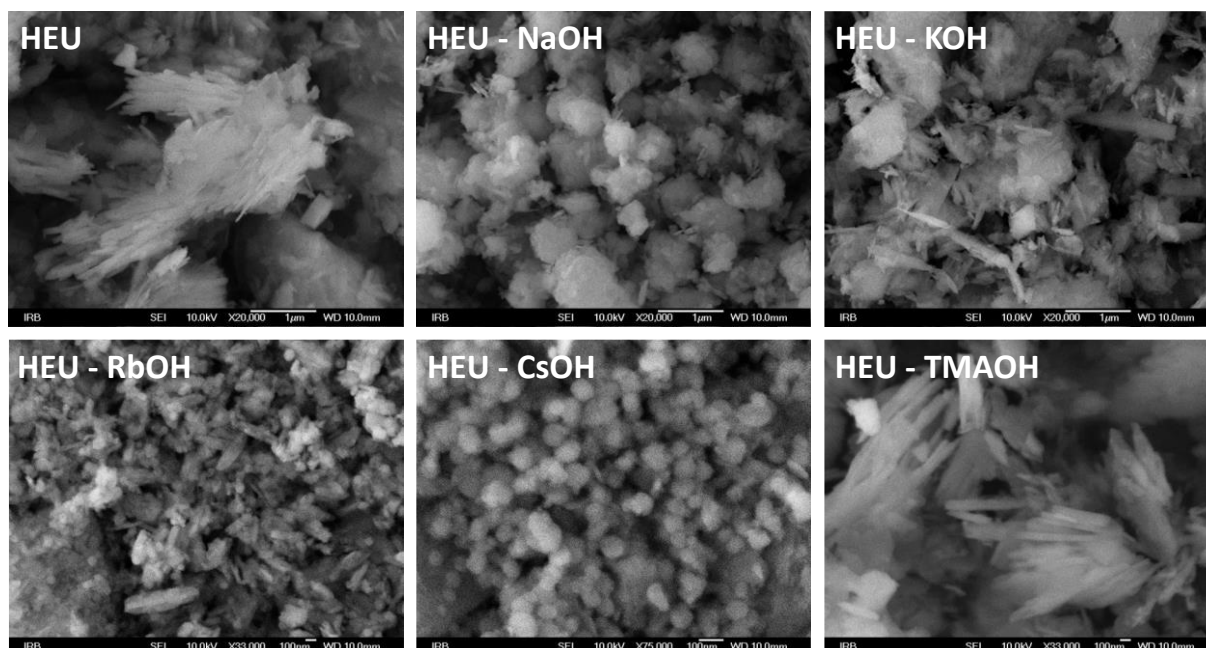


Figure 1. SEM images of the parent clinoptilolite natural zeolite (HEU-type) and the samples harvested upon thermomilling treatment with NaOH, KOH, RbOH, CsOH and TMAOH at 110 °C and 30 Hz for 2 h.

The compiled data indicate that LTA-type material crystallizes readily in less than 1 h at 30 Hz and 100 °C with added 10 wt.% of zeolite A seeds with respect to total SiO<sub>2</sub> content in the synthesis mixture (Figure 2). The first LTA reflexes appear in 20 minutes and upon 1 h thermomilling of the synthesis mixture another, SOD-type material is formed. This material is maintained in the reaction system for the next 2 h, as long as the *in-situ* synchrotron experiment was carried out.

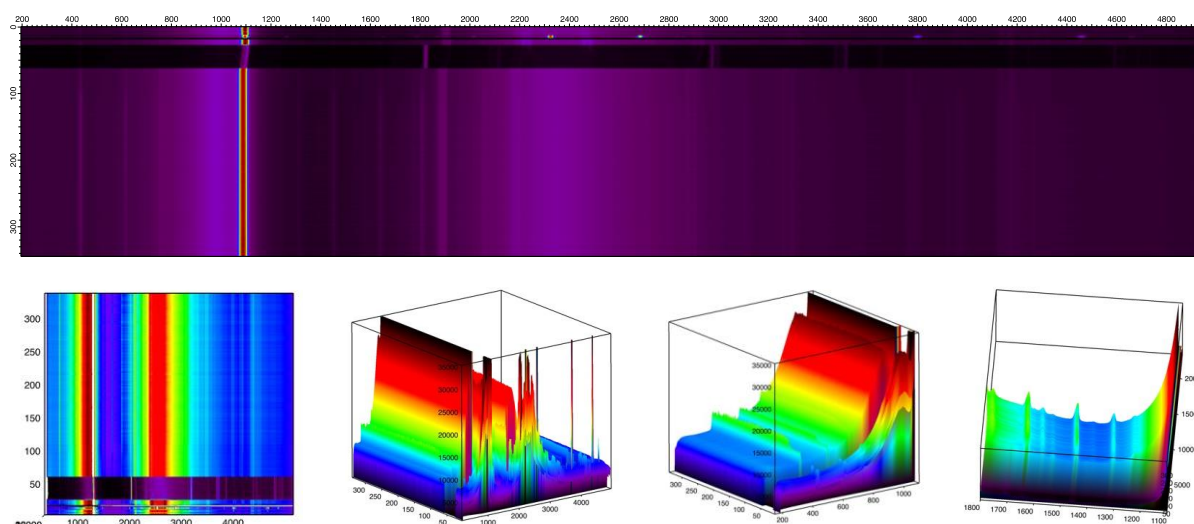


Figure 2. *in-situ* synchrotron X-ray powder diffraction monitoring of zeolite A synthesis mixture at 100 °C and 30 Hz in the presence of 10 wt.% of zeolite A seeds.

The zeolite A sample comprises two distinct kinds of particles in terms of size and morphology. In the SEM images are visible rounded particles smaller than 300 nm. On the other

hand, the second fraction of particles involves particles larger than 1  $\mu\text{m}$ , sometimes even over 10  $\mu\text{m}$ . The large particles too present rounded edges and are composed of intergrown domains.

## CONCLUSION

The collected set of experimental results indicate the interzeolite conversion of natural zeolite clinoptilolite occurs in the presence of CsOH, while TMAOH displays completely opposite behavior – conversion does not take place nor the morphology of the particles in the obtained powder changes. Other employed alkali hydroxides show different behavior and certain variations at the level of phase composition and morphology have been observed. Further, zeolite A has been prepared while thermomilling in the presence of 10wt.% seeds using silicagel, sodium aluminate and sodium hydroxide. It is expected that the findings reported here will provide guidelines for designing and conducting further (thermo) ball milling experiments to achieve even more environment-friendly and energy efficient process of zeolite synthesis that yields materials of required features.

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