

***IN SITU* PXRD MEASUREMENTS OF MECHANOCHEMICALLY INDUCED INTERZEOLITE CONVERSION – ADVANTAGES AND DRAWBACKS**

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ABSTRACT

Synthesis of zeolites is commonly performed by hydrothermal means, be it direct synthesis from a range of silicon and aluminium sources or interzeolite conversion from one zeolite framework type to another. Mechanochemistry, previously utilized only as a pretreatment method in zeolite synthesis, has recently been used for the first successful interzeolite conversion of a FAU-type zeolite to MER, CAN, GIS, ANA and SOD by utilizing the newly developed thermal control of mechanochemical processes. This work aims to expand the knowledge attained in that research by discussing *in situ* PXRD measurements of several analogous thermomechanochemical interzeolite conversion reactions and identifying their benefits and disadvantages.

Keywords: interzeolite conversion, mechanochemistry, *in situ* PXRD

INTRODUCTION

Common methods of zeolite synthesis *via* solution-based methods are well documented.[1] The most common methods of zeolite preparation can be divided into two distinct categories: direct synthesis and interzeolite conversion. Direct synthesis is performed by mixing a source of silicon and aluminium with a mineralizer, usually in water. Interzeolite conversion is used to convert one zeolite type material into another, usually a more porous to a less porous one, by the addition of a mineralizing agent and optionally organic structure directing agent (OSDA).[2]

Hydrothermal synthesis is the most commonly used technique for both synthesis methods. [3]. However, it is rather time-consuming, usually taking up to two weeks to obtain a pure product. Other techniques for zeolite preparation have been studied in an attempt to find faster and more efficient avenues of synthesis, such as sonosynthesis, which has been utilized for the direct synthesis of zeolite A [4] and EMT.[5] This technique of zeolite synthesis requires a completely custom-made apparatus and, as such, is not widely accessible.

Mechanochemistry is an increasingly attractive field in chemistry. It utilizes mechanical energy, such as compression or shearing, to induce chemical change.[6] Mechanochemical reactions are usually faster, more energy efficient and sometimes even enable new intermediates or products to be obtained due to the different reaction pathways compared to classical solution-based synthesis.[7] These reactions use much less solvent (or sometimes none at all), which makes the whole method eco-friendly. However, aside from mechanochemical pretreatment of zeolite reaction mixtures [8] or amorphization [9], no zeolites have been synthesized mechanochemically until very recently. The first successful attempt at the formation of a zeolite material by mechanochemical means was the interzeolite conversion that utilized thermally controlled mechanochemistry [10] and yielded MER-, CAN-, GIS-, ANA- and SOD-type materials from a sodium form of FAU-type zeolite [11].

In an attempt to further the understanding of this new zeolite synthesis technique, *in situ* synchrotron PXRD measurements have been performed on several reactions analogous to the

reported syntheses. This has enabled new insight into mechanochemistry as a viable alternative to classic oven-based synthesis of zeolite materials, but it has also highlighted some drawbacks of the method. This work aims to elucidate the advantages and disadvantages of zeolite synthesis *via* mechanochemistry and *in situ* PXRD as a viable method of analysis of such reactions.

EXPERIMENTAL

In situ synchrotron X-ray diffraction monitoring experiments were performed at the Deutsches Elektronen-Synchrotron (DESY) at the PETRA III, P02.1 beamline equipped with a PerkinElmer XRD1621 detector at 60 keV ($\lambda = 0.207 \text{ \AA}$). 13 ml aluminum jars with PTFE inserts were used. A window cut-out in the aluminium jacket was made to allow the synchrotron radiation to pass through the PTFE inserts during the milling. Synthesis mixtures were prepared by mixing 400 mg of zeolite Y (Zeolyst, CBV 500, ammonium or hydrogen form (calcined CBV500)) with either sodium (60 mg), potassium (168 mg) or cesium hydroxide (268 mg) and 162 mg of water with the addition of 40 mg of CHA or LTA seeds. The molar composition of the mixtures is represented in Table 1. The jars were preheated to 110 °C before the start of the milling. The experiments ran for 120 minutes at 30 Hz with 10 s per frame time resolution. The collected data was integrated with DAWN software and is visually represented by waterfall diagrams without previous background correction for the PTFE insert. To test the reproducibility of the collected data, milling was repeated *ex situ* with the obtained samples washed until pH neutral and dried overnight at 80 °C before PXRD analysis.

RESULTS AND DISCUSSION

Results obtained in the series of *in situ* synchrotron PXRD experiments with their respective molar oxide compositions are represented in Table 1.

Table 1. Molar oxide compositions of the experiments performed *in situ* and identified products with the time they appear ($\text{Al}_2\text{O}_3 = 0.19$). Total milling time for all reactions was 120 minutes, except for reaction systems containing CsOH where the mixture containing the ammonium form of zeolite Y was milled for 60 minutes while the mixture containing the hydrogen form was milled for 30 minutes in total.

Zeolite Y form	Seeds present	SiO ₂	H ₂ O (total)	M ₂ O	Time of product detection (min)	Product phase composition
Na₂O						
NH ₄ ⁺	-	1	4.15	0.2	120	FAU
H ⁺	-	1	4.15	0.2	120	FAU
K₂O						
NH ₄ ⁺	-	1	4.63	0.4	75	MER+CHA
NH ₄ ⁺	10% CHA	1	4.63	0.4	58	CHA
					85	MER+CHA
NH ₄ ⁺	10% LTA	1	4.63	0.4	120	FAU
H ⁺	-	1	4.63	0.4	78	CHA
					88	MER+CHA
Cs₂O						
NH ₄ ⁺	-	1	4.72	0.2	12	FAU+ANA
H ⁺	-	1	4.72	0.2	12.5	ANA

Initially, the results in Table 1 seem to show that obtaining pure products from these reaction systems is possible, but upon further inspection, this may not be the case due to some discrepancies from analogous *ex situ* mechanochemical experiments represented in the Table 2.

Starting with the sodium hydroxide reactions, the *in situ* experiments seem to indicate no change in the reaction mixture. This might be due to the reaction being slower than in other

systems and the new phase is formed after 120 minutes. Unlike in the potassium hydroxide reaction system, no sodium hydroxide reactions with CHA or LTA seeds were performed due to time constraints on the synchrotron beamline.

Table 2. Molar oxide compositions of the analogous experiments performed *ex situ* and identified products.

Zeolite Y form	Seeds present	SiO ₂	H ₂ O (total)	M ₂ O	Product phase composition after 60 min	Product phase composition after 120 min
				K₂O		
NH ₄ ⁺	-	1	4.63	0.4	FAU+CHA+MER+LTA	MER
NH ₄ ⁺	10% CHA	1	4.63	0.4	FAU+CHA+MER	MER+CHA
NH ₄ ⁺	10% LTA	1	4.63	0.4	FAU+LTA	MER
H ⁺	-	1	4.63	0.4	CHA+MER	MER+CHA

Reactions containing potassium hydroxide are much more complex than the sodium hydroxide ones since the simultaneous formation of both MER and CHA phases can be observed at 75 minutes of the reaction where the ammonium form of zeolite Y was used. Additionally, the formation of the product can be affected by the seeds. When CHA seeds were added to the reaction mixture, the pure CHA phase formed at 58 minutes, while the formation of MER was delayed until the 85th minute. However, when LTA seeds were used in an attempt to obtain an LTA phase, no new product was obtained. This again may be a case of a part of the reaction mixture sticking to the side of the jar. The reaction of potassium hydroxide with the hydrogen form of zeolite Y presents a 10-minute window where pure CHA forms before a mixture of CHA and MER is observed (78-88 minutes). However, *ex situ* experiments could not replicate the exact results obtained *in situ*, similar to a study done on ZIF-8 where reproducibility of the products obtained *in situ* was also an issue.[12] The reaction of the ammonium form of zeolite Y without seeds yielded a mixture of FAU, CHA, MER and LTA after 60 minutes, while a pure MER-type material was obtained after 120 minutes. The CHA-seeded reaction yielded a mixture of FAU, CHA and MER after only 60 minutes, putting the result of obtaining pure CHA into doubt. Similarly, the LTA-seeded reaction yielded a mixture of FAU and LTA, while the unseeded hydrogen form reaction yielded a mixture of CHA and MER after 60 minutes. While the same phases were obtained *in situ* and *ex situ*, the discrepancy between the pure phases and mixtures is concerning. This may be due to the *in situ* reactions being measured before the reaction mixture is washed, that is to say before the reaction is effectively stopped. Another possibility is the low crystallinity or low amount of the formed MER phase which is hindered by the intensity of the background peaks (PTFE) in *in situ* measurements.

Finally, reacting the ammonium form of zeolite Y with caesium hydroxide yields a mixture of FAU and ANA after 60 minutes, which is rather surprising since the reaction with the hydrogen form yields pure ANA after only 12.5 minutes (Figure 1). This may be a case of higher stability of the ammonium form of CBV500 compared to the hydrogen form or the bulk of the ANA phase crystallizing on the milling ball so its detection by XRD is delayed.

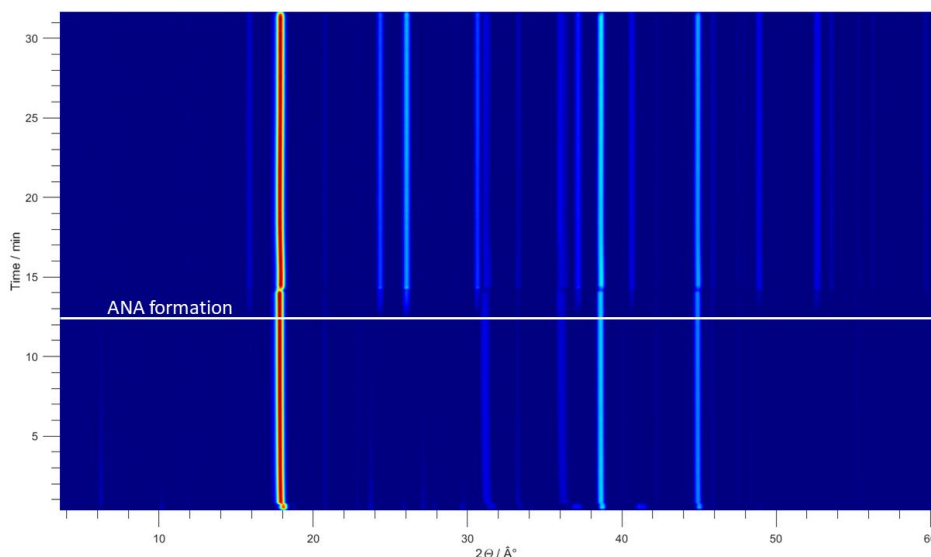


Figure 1. Waterfall diagram of the reaction of the hydrogen form of zeolite Y and cesium hydroxide yielding pure ANA after 13 minutes.

CONCLUSION

The results shown in this paper show how *in situ* synchrotron PXRD measurements can be used for thermomechanicochemical zeolite synthesis. Utilizing this powerful method leads to a better understanding of the reaction and its intermediaries, but it has some drawbacks. While the same phases obtained in *ex situ* experiments are present in the *in situ* measurements, the time at which they appear does not seem to match. Also, the formation of pure phases like CHA observed *in situ* could not be replicated *ex situ*. However, this seems to mostly be a problem for the systems of low crystallinity since the identification of highly crystalline ANA in the cesium hydroxide reaction was trivial. Additionally, the product possibly sticking to the milling ball and obtaining a null result is another problem to contend with. The precision of this method is doubtful for systems containing phases of low crystallinity and should be used in combination with other *in situ* methods (for example Raman spectroscopy) to obtain more precise information on the products and intermediates formed.

REFERENCES

- [1] T. Wakihara, T. Okubo, *Chem. Lett.*, 2004, 34, 276–281.
- [2] K. Zhang, S. Fernandez, M. L. Ostraat, *ChemCatChem*, 2018, 10, 4197–4212.
- [3] T. Wakihara, T. Okubo, *Chem. Lett.*, 2005, 34, 276–281.
- [4] R. M. Dewes, H. Ramirez Mendoza, M. Valdez Lancinha Pereira, C. Lutz, T. Van Gerven, *Ultrason. Sonochem.*, 2022, 82, 105909–105932.
- [5] E.-P. Ng, H. Awala, J.-P. Ghoy, A. Vicente, T. Chuan Ling, Y. Hau Ng, S. Mintova, F. Adam, *Mater. Chem. Phys.*, 2015, 159, 38–45.
- [6] T. Friščić, C. Mottillo, H. M. Titi, *Angew. Chemie Int. Ed.*, 2020, 59, 1018–1029.
- [7] D. Katsenis, A. Puškarić, V. Štrukil, C. Mottillo, P. A. Julien, K. Užarević, M.-H. Pham, T.-O. Do, S. A. J. Kimber, P. Lazić, O. Magdysyuk, R. E. Dinnebier, I. Halasz, T. Friščić, *Nat. Commun.*, 2015, 6, 6662–6670.
- [8] Y. Gu, X. Wang, Z. Qin, S. Mintova, X. Liu, *Microporous and Mesoporous Mater.*, 2020, 306, 110437–110457.
- [9] C. Josanović, J. Bronić, B. Subotić, I. Smit, M. Stubičar, A. Tonejc, T. Yamamoto, *Zeolites*, 1993, 13, 261–281.
- [10] N. Cindro, M. Tireli, B. Karadeniz, T. Mrla, K. Užarević, *ACS Sustainable Chem. Eng.*, 2019, 7, 16301–16309.
- [11] N. Jakupec, K. J. Ardila-Fierro, V. Martinez, I. Halasz, M. Etter, K. Užarević, A. Palčić, *Interzeolite conversion reactions of zeolite Y via thermally controlled mechanochemistry*, 10th International Conference on Mechanochemistry and Mechanical Alloying, 2022, Book of Abstracts, 99.
- [12] A. D. Katsenis, A. Puškarić, V. Štrukil, C. Mottillo, P. A. Julien, K. Užarević, M.-H. Pham, T.-O. Do, S. A. J. Kimber, P. Lazić, O. Magdysyuk, R. E. Dinnebier, I. Halasz, T. Friščić, *Nat. Commun.*, 2015, 6, 6662–6670.