

THE INFLUENCE OF THE PREPARATION METHOD ON THE RATIO OF HETEROATOMS IN THE ZEOLITE BETA STRUCTURE

*Ivana Landripet¹, Andreas Puškarić¹, Josip Bronić¹,
Nataša Zabukovec Logar², Matjaž Mazaj², Massimo Migliori³, Girolamo Giordano³*

¹ Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia

² National Institute of Chemistry, Hajdrihova 19, 1001 Ljubljana, Slovenia

³ Department of Environmental and Chemical Engineering, University of Calabria,
Via Pietro Bucci, 87036 - Arcavacata di Rende (CS), Italy

E-mail: ivana.landripet@irb.hr

ABSTRACT

Beta zeolite is microporous, aluminosilicate characterized by big 12-ring channel systems. It is commonly used as commercial adsorbent and catalyst. Although the pores are exceptionally large there are limitations which decrease efficiency of the catalysts. Such limitations should be avoided by creating mesoporous voids (channels and holes) during catalyst synthesis or by post synthesis treatment of classically prepared microcrystals.

Another important issue in catalysis efficiency is the number of active sites (i.e. Lewis and Brønsted acid sites). It's number can be increased with number of hetero T-atoms within framework by postsynthesis treatment.

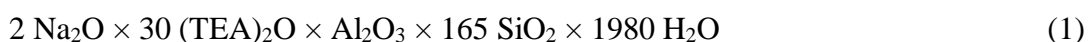
Keywords: mesoporous beta, wet impregnation, mechanochemistry, fluoride postsynthesis treatment.

INTRODUCTION

The BEA framework topology attracts much attention because of the three-dimensional large-pore channel system, large available micropore volume, and the presence of active sites in different concentrations that are useful in a number of acid-catalyzed reactions. Intracrystalline diffusion of the reactants and products within zeolite crystals is limited, and can be avoided reducing the size of the crystals or by introducing mesoporous voids. Efficiency of the catalytic process can be improved by increasing the number of active sites (i.e. Lewis and Brønsted acid sites) and by controlling crystallite size and morphology.

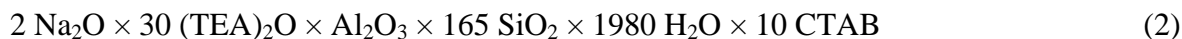
EXPERIMENTAL

Oxide form of the chemical composition of the starting mixture was:



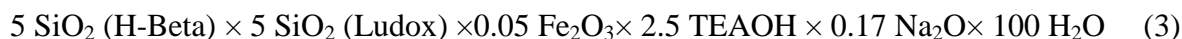
Zeolite beta was prepared by classical hydrothermal synthesis (receipt adopted from ref. 1). The synthesis was made in Teflon-lined autoclaves as one pot synthesis on following way; After addition of aqueous solution of NaOH, redistilled water, 35 wt% aqueous solution of tetraethylammonium hydroxide (TEAOH) and Al(i-OPr)₃, mixture was stirred using magnetic stirrer until complete hydrolysis (about 30 min). Then comes addition of colloidal silica (Ludox HS-40) and stirring for 24 h followed by heating for 5 days at 100 °C and 24 h at 150 °C [1]. Obtained product was washed, dried and slowly calcined at 600 °C in the stream of air. H-form of the samples was obtained by ion-exchange (0.8 M NH₄NO₃) and heating. Postsynthesis treatment to obtain mesoporous (hierarchical structure) was made by dealumination/desilication using 5 M NH₄F solution.

Direct synthesis of hierarchical structure was made using similar procedure. Oxide form of the chemical composition of the starting mixture was:



CTAB was added to the reaction mixture 20 min before beginning of heating to 100 °C. Another part of the postsynthesis treatment was wet impregnation with Cu^{2+} , Zn^{2+} and Fe^{3+} ions and mechanochemical treatment (liquid assisted grinding – LAG) [2] of zeolite with Cu^{2+} and Zn^{2+} . Incorporation of the Fe^{3+} into zeolite was prepared by dry gel conversion (DGC) method (adopted from ref. 3).

Iron nitrate, $\text{Fe}(\text{NO}_3)_3 \times 9\text{H}_2\text{O}$ was used as Fe source. The equimolar amount (Si basis) of mesoporous H-Beta and colloidal silica were used as Si source. Oxide form of the chemical composition of the starting mixture was:



After stirring for 2h at room temperature, the precursor solution was evaporated in order to obtain a dry gel. The obtained dry gel was placed in a Teflon-lined stainless steel autoclave with water separately. It was crystallized at 120 °C for 72 h. The obtained powder was washed with deionized water, dried and then calcined at 550 °C for 5 h in order to remove organic structure-directing agent (OSDA) [3]. H-form of the samples was obtained by ion-exchange (with 0.8 M NH_4NO_3), washed with deionized water and heated in the stream of air.

RESULTS AND DISCUSSION

Obtained zeolite (H-form) is slightly less crystalline which may be result of calcination. After desilication/dealumination treatment, small part of crystal structure is partially destroyed (Figure 1). Wet impregnation with metal cations does not affect the crystal structure and by LAG just a small part of the crystal structure is destroyed (Figure 2). DGC method produces less crystalline material (Figure 2 and Figure 3). LAG with Zn^{2+} ions gives ZnO while diffraction peaks of zeolite beta disappear.

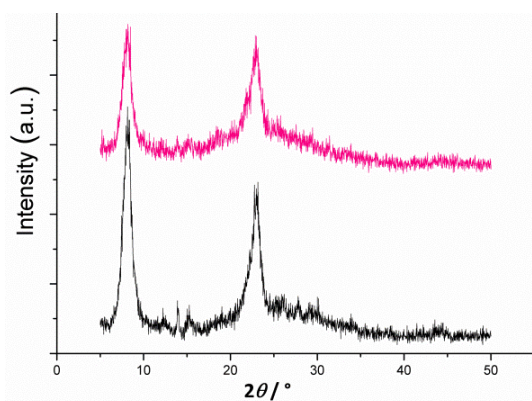


Figure 1. PXRD of the sample before (black) and after (pink) desilication/dealumination.

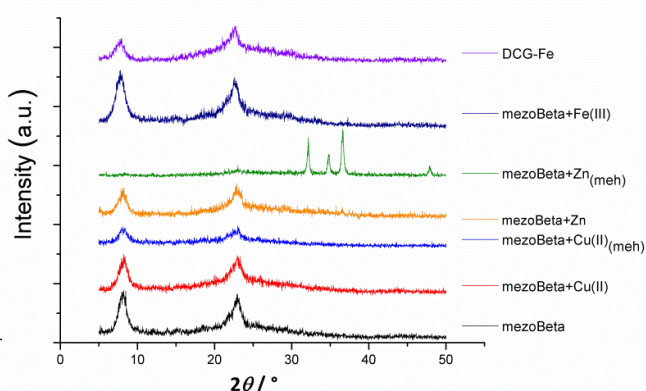


Figure 2. PXRD of the samples after second part of the postsynthesis treatment

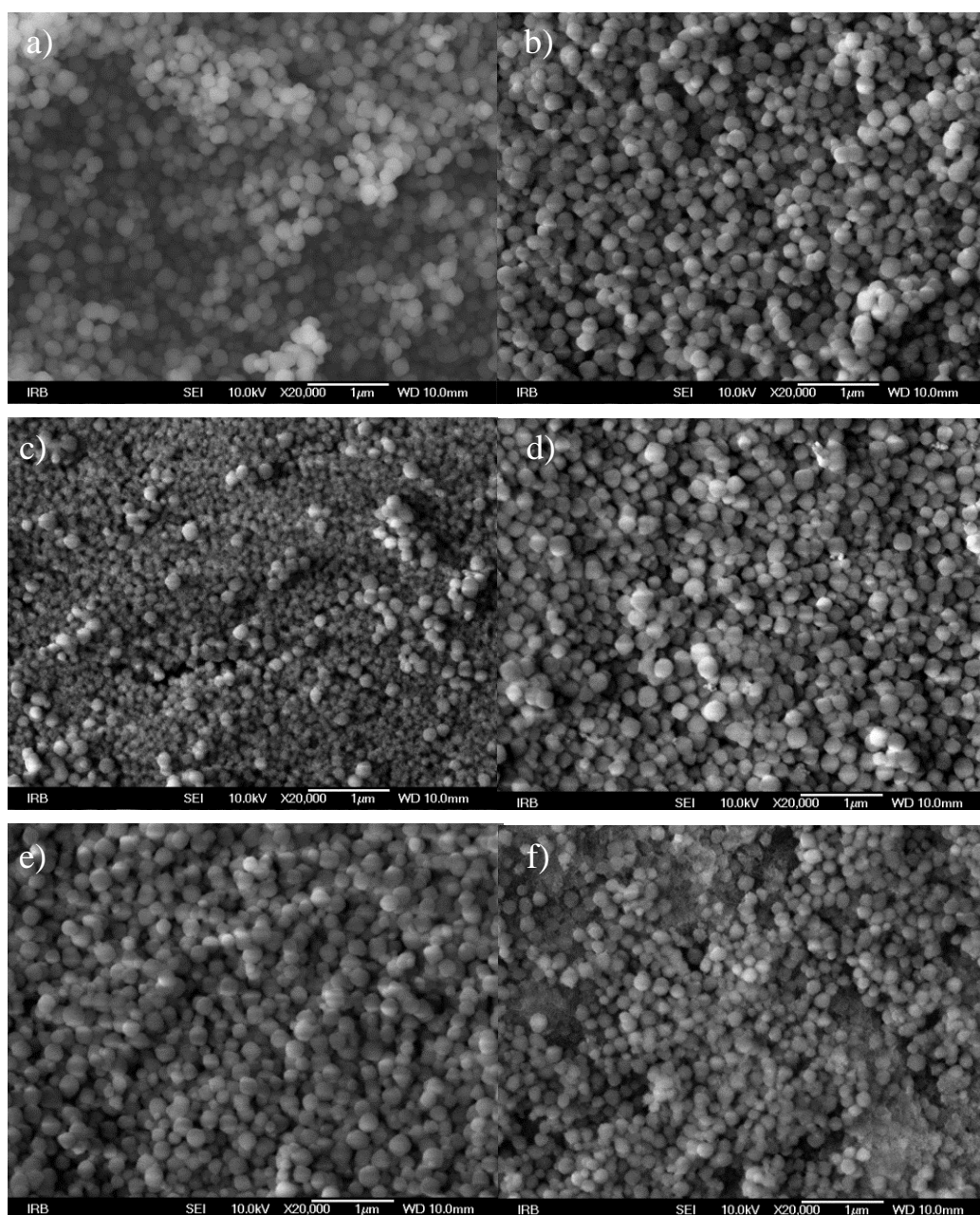


Figure 3. SEM photos of: a) the H-form of the samples after dealumination/desilication (mezoBeta), b) mezoBeta after wet impregnation with Zn^{2+} (mezoBeta+Zn), c) mezoBeta + Cu(II), d) mezoBeta+Cu(II)_(meh), e) mezoBeta + Fe(III) and f) mezoBeta with Fe(III) heteroatoms prepared by (DGC) method.

Second part of the postsynthesis treatment was done using wet impregnation with concentrated salts solutions, with or without weak grinding, followed by thermal treatment, by mechanochemical treatment or, in case of Fe^{3+} incorporating, DGC. The results for all cations that have been embedded show increase of the intensity of lines (vacuum FTIR spectroscopy) characteristic for acid (Brønsted) sites ($3700-3600\text{ cm}^{-1}$). A content of all cations is confirmed by EDS and AAS analysis, and no metallic oxide contamination is present what can be seen at diffractograms, except sample prepared by LAG for Zn^{2+} incorporation.

CONCLUSION

Samples of hierarchical zeolite beta were made by a feasible one-pot (one-step) method, which is suitable for application in industrial production. Introduction of mesoporous voids (hierarchical structure of the crystals) was obtained by postsynthesis treatment with 5 M NH₄F solution or using mesoporous template (CTAB) during catalyst synthesis. That resulted in micro- and mesoporous zeolite beta (hierarchical structure) crystals. Wet impregnation with Cu²⁺, Zn²⁺ and Fe³⁺ ions resulted with incorporation of mentioned cations. Mechanochemical treatment (LAG) of zeolite with Cu²⁺ resulted with incorporation of cation without destroying crystal structure. LAG method with Zn²⁺ resulted in loss of crystallinity of zeolite framework and appearance of ZnO. Incorporation on Fe³⁺ was successful when both wet impregnation and DGC were applied.

ACKNOWLEDGEMENT

This work was supported by Croatian Science Foundation, Project IP-2016-06-2214.

REFERENCES

- [1] S. Mintova, V. Valtchev, T. Onfroy, C. Marichal, H. Knözinger, T. Bein, *Micropor. Mesopor. Mater.*, 2006, **90**, 237-245.
- [2] I. Halasz, A. Puškarić, S.A. Kimber, P.J.Beldon, A.M. Belenguer, F. Adams, V. Honkimäki, R.E. Dinnebier, B. Patel, W. Jones, V. Štrukil, T. Friščić, *Angew. Chem. Int. Ed. Engl.*, 2013, **52**, 11538-11541.
- [3] M. Nakai, K. Miyake, R. Inoue, K. Ono, H. Al Jabri, Y. Hirota, Y. Uchida, M. Miyamoto, N. Nishiyama, *Micropor. Mesopor. Mater.*, 2019, **273**, 189-195.