

ZEOLITE 2018

10th International Conference on the Occurrence,
Properties and Utilization of Natural Zeolites

Book of Abstracts

Edited by Wojciech Franus, Jarosław Madej

24 – 29 June 2018

Cracow, Poland

Title:

ZEOLITE 2018 - 10th International Conference on the Occurrence,
Properties and Utilization of Natural Zeolites (Book of Abstracts)

Editors:

Wojciech Franus, Jarosław Madej

Publisher:

Lublin University of Technology, Nadbystrzycka 40 20-618 Lublin

Copies:

200

Number of pages:

202

The **Book of Abstracts** is available on the conference website:

<http://zeolite2018.org>

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Rector of the AGH University of Science and Technology in Cracow
Prof. dr hab. eng. Tadeusz Słomka
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Adsorptive, catalytic and antimicrobial applications of Serbian natural clinoptilolite

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Clinoptilolite is the most abundant natural zeolite in Serbia, and the Zlatokop deposit (near Vranjska Banja) is the largest deposit. The zeolitic tuff (CT) from Zlatokop contains >70 wt. % clinoptilolite with quartz and feldspar as major mineral impurities. Considering the high clinoptilolite content in the CT, this tuff has been studied in detail as an adsorbent, catalyst carrier and antimicrobial agent. We evaluated the cation-exchange capacity for several toxic metal cations, the sorption efficiency for several anions, the catalytic activity in the processes of valorization of biomass, and the antimicrobial activity of the CT.

Experimental Methods

Sorption experiments were conducted in a batch mode using a solid/liquid ratio of 1/100 at 298-338 K. The particle size of the CT samples used was in the range 0.063-0.1 mm. The rate of sorption of M(II) (M=Mn, Ni, Cu, Zn, Pb) was studied in solutions with initial M(II) concentrations of 50-400 mg dm⁻³. The CT sample modified with Fe(III) according to our published work (Jevtic et al, 2014) was used for sorption studies of nitrate, phosphate and selenate ions present in a concentration range of 50-400 mg dm⁻³.

Samples of CT containing nanoparticles of NiO, ZnO and Cu₂O with an average size of 5-10 nm were prepared by a simple procedure (Rajic et al, 2011) and tested in lignin pyrolysis. The test was performed in a bench-scale fixed-bed reactor under N₂ at 773 K. The resulting gas and liquid products were analyzed by GC and GC/MS. The catalytic activity of CT containing particles of SO₄-SnO₂ was studied in esterification of lavulinic acid with octanol in a batch reactor at 343 K under N₂. The products were analyzed using HP-GC. Ag-, Zn- and Cu-CT samples (with approx. 0.25 mmol of the metal per 1 g of CT) were prepared by an ion-exchange reaction and tested towards *Escherichia coli*, *Staphylococcus aureus* and *Acinetobacter baumannii*. The antibactericidal effect of Ag-containing CT towards *Acinetobacter baumannii* was studied in detail using X-ray near-edge structure (XANES) spectroscopy.

Results and Discussion

Our results show that the CT is quite effective in removing the studied heavy metal cations (HMC). The sorption capacity increased with an increase in initial HMC concentration and with an increase in time and temperature. The sorption mechanism was consistent with an ion-exchange reaction in which Na⁺ from the clinoptilolite structure is replaced by the HMC from aqueous solutions. This was confirmed by X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray analysis (EDXS). XPS showed that all studied HMC did not accumulate at the surface of CT and were uniformly distributed through the entire analyzed depth of samples. EDXS confirmed that the studied HMC mostly replaced the Na⁺ ions from the clinoptilolite structure. The sorption rate followed pseudo-second rate kinetics (Stojakovic et al, 2017), and the sorption efficacy increased in the series Ni < Mn ≈ Zn < Cu < Pb.

Modification of CT with about 18 wt.% Fe(III) increased the specific surface area from 40 to 112 m² g⁻¹. Well crystalline clinoptilolite pseudo-hexagonal sheets covered with flaky amorphous Fe(III)-precipitate were evident at a typical TEM image of Fe(III)-CT (Fig. 1a). Fe(III)-CT effectively removed nitrate, phosphate and selenate ions from water solutions (Pavlovic et al, 2014; Kaplanec et al, 2017; Jevtic et al, 2014). ³¹P solid-state NMR and extended X-ray absorption fine structure (EXAFS) indicated that the adsorption mainly included covalent bonding of the anions to Fe(III). The ³¹P spin-echo mapping NMR spectrum exhibited signals severely shifted due to the strong through-bond hyperfine interactions between the ³¹P nuclear spins and the spins of the unpaired electrons of the paramagnetic Fe³⁺ centers. This suggested that the phosphate

adsorption proceeds *via* formation of P-O-Fe bonds. Moreover, EXAFS showed that selenium is coordinated in the form of oxo-complexes to Fe(III).

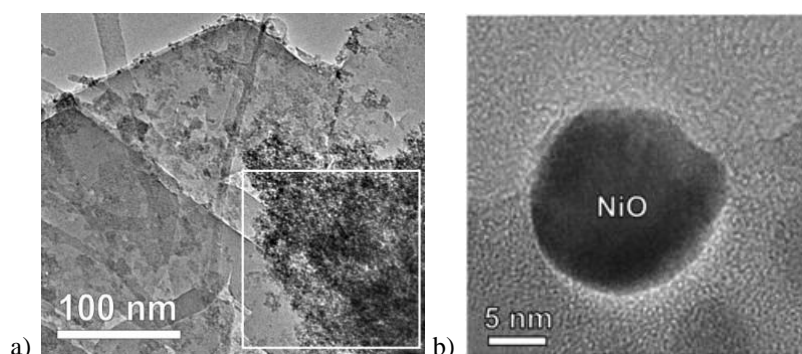


Figure 1. a) TEM image of clinoptilolite crystals covered with Fe(III) precipitate. The selected area electron diffraction (SAED) recorded from the marked area revealed that the precipitate is amorphous; b) A single NiO particle on the TEM image of NiO-containing clinoptilolite. SAED performed over multiple nanocrystals showed diffraction rings with d-values corresponding to cubic NiO.

CT covered with nanoparticles of NiO, ZnO or Cu₂O showed catalytic activity in lignin pyrolysis (Rajic et al, 2013), which was mainly influenced by the type of the nano-oxide. The amount of valuable phenols in the as-produced bio-oil varied from 39 % for ZnO-CT to 50 and 54 % for Cu₂O- and NiO-containing samples, respectively. The highest yield of phenols was obtained in the presence of NiO-CT which was explained by a synergetic interaction of the clinoptilolite structure and nano-NiO particles (Fig 2b). CT modified with SO₄-SnO₂ exhibited a high catalytic activity in the preparation of octyl levulinate by esterification of levulinic acid. The conversion rate was 100 % after 6 hours.

Ag-, Zn- and Cu-CT showed antibacterial activity towards different types of pathogenic Gram-positive and Gram-negative bacteria present in real waters. Measurements of concentration of leached metals after microbiological tests gave concentrations that did not exceed minimal inhibitory concentration (MIC) of the studied metals. This indicated that the antibacterial activity can be ascribed to the metal-containing CT and not to the leached metal cations. The results lead to the conclusion that the studied metal-containing CT are promising materials against pathogenic bacteria present in water media. Finally, the bactericidal effect of Ag-CT against multidrug-resistant pathogenic *A. baumannii* was studied in detail using XANES, which provided insight into the basic molecular mechanism of the antibacterial action of Ag-CT. Our results suggest that Ag ions from CT are responsible for damage of both the DNA and the outer cell membrane of *A. baumannii*.

Acknowledgments

This work was supported by the Serbian Ministry of Science (project no. 172018) and the Croatian Science Foundation (project no. IP-2014-09-5656).

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