Silver-impregnated zeolites for environmental degradation of ozone

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Abstract. The natural zeolites were ultrasonically treated and impregnated with silver nanoparticles. The surface stabilized silver nanoparticles dispersion was obtained using an effective electrochemical reduction method. The phase and elemental composition, structure of the Ag-impregnated zeolites (clinoptilolite and mordenite) was studied by various methods such as powder X-ray diffraction, X-ray fluorescence analyses and Fourier-transform infrared spectroscopy. The Ag-impregnated clinoptilolite and mordenite natural zeolite materials with 1.20 wt %, 0.97 wt %, 0.83 wt % and 1.18 wt % silver content were established by XRF analysis. As initial materials were used three types clinoptilolite from Beli Plast, Most, Golobradovo (Kardzhali, Bulgaria) deposits and mordenite from Lyaskovets deposit in Eastern Rhodopes, Bulgaria. The catalytic ability of Ag-mordenite and Ag-clinoptilolites was investigated in the ecologically important reaction of ozone decomposition. The Ag-loaded mordenite demonstrates the higher conversion degree of ozone more than 40% in comparison with Ag-clinoptilolite materials at room temperature.

Keywords: natural zeolite, clinoptilolite, mordenite, silver nanoparticles, ozone decomposition.

Introduction

Environmental pollution is a problem of humanity. Among the pollutants, ozone is known to be harmful to human health. It is generated in working places and airplane cabins. Ozone causes chronic damage to a lung structure and allergies. The catalytic decomposition of ozone has attracted the attention of researchers due to its advantages such as environmental friendliness, economy, mild reaction conditions, high treatment efficiency, stability and safety (Li et al., 2020).

Natural zeolites are hydrated aluminosilicate minerals. They possess a porous structure with useful physicochemical properties for environmental applications such as cation exchange, sorption, catalysis and molecular sieving (Osmanlioglu, 2006). Among the natural zeolites, clinoptilolite (\((Na,K)\text{Si}_6\text{Al}_6\text{O}_{24}\text{O}_{2}\cdot n\text{H}_2\text{O}\) is one of the most commonly presented predominantly in sedimentary rocks of volcanic origin (Charkhi et al., 2010). Mordenite is a common alteration product of a pyroclastic sediment, sedimentary rock and lava flows. It is an orthorhombic zeolite with a high silica content (\(Na\text{Al}_8\text{Si}_4\text{O}_{12}\cdot 24\text{H}_2\text{O}\)) (Zhou, Boyd, 2014).

The aim of the present study is a preparation of Ag-impregnated mordenite and clinoptilolites. The used initial materials are zeolitized tuffs, containing...
mordenite (from the deposit at the village of Lyaskovets, Bulgaria) and clinoptilolites (from deposits in Beli Plast, Most and Golobradovo, Bulgaria). The structure, phase and elemental composition of the modified natural zeolites are determined using different physicochemical methods. The application of Ag-impregnated natural zeolites as potential catalysts for a decomposition of ozone in environmental systems is studied as well.

Materials and methods

The zeolitized tuffs were milled to particle size below 0.5 mm. The thermal treatment at 300 °C for 4 hours was carried out to remove volatile organic contaminants and moisture. Thereafter, the zeolites were impregnated with a surface stabilized Ag nanoparticles dispersion. Silver nanoparticles (Ag-NPs) were prepared by an electrochemical reduction method with the use of polyvinylpyrrolidone (PVP, K-25, Sigma-Aldrich) as surface stabilizing agent. The impregnation was performed using an ultrasonic treatment (for more effective AgNPs dispersion of zeolite) of 2.1 g zeolite and 30 ml Ag-NPs (average size 20 nm) colloidal dispersion with a total silver concentration of 400 mg/L followed by stirring (600 rpm) for 5 hours at 50 °C using a magnetic stirrer. Then Ag impregnated natural zeolites were filtered, washed several times with distilled water until neutral reaction and dried for 1 hour at 50 °C. The prepared materials were denoted as Ag-mordenite, Ag-clinoptilolite (Beli Plast (BP)), Ag-clinoptilolite (Most (M)) and Ag-clinoptilolite (Golobradovo (GB)).

The obtained materials were analyzed by powder X-ray diffraction (PXRD) performed on an X-ray powder diffractometer “Empyrean” within the range of 2θ values between 5° and 70° using Cu Kα radiation (λ = 0.154060 nm) at 40 kV and 30 mA. Fourier-transform infrared (FTIR) spectra were collected on a Bruker Tensor 37 spectrometer in the region 4000–400 cm⁻¹ by another research group (Lee et al., 2023). The bands situated at 1200–1203 cm⁻¹ can be assigned to the external vibrations between SiO₂ and AlO₄ tetrahedra of the zeolite. The peak at 469 cm⁻¹ associates with the Si–O–Si bending mode. The vibrations in the range 1041–1070 cm⁻¹ and 430 cm⁻¹ are connected to the T–O stretching and bending modes (Aloulou, 2017).

The XRF data are presented in Table 1. The silver content in the Ag-impregnated clinoptilolites and mordenite environmental materials is in the range 0.83–1.20 wt %. The highest Ag amount (1.20 wt %) is registered in Ag-clinoptilolite (BP) than that in the other investigated materials. The Si/Al ratios in the studied natural zeolites are retained after impregnation with silver nanoparticles. The results from XRF and PXRD analyses show that after the impregnation, the zeolite structure is preserved. Similar structure preservation referred to the MWW type zeolites after impregnation with Mo is shown by another research group (Lee et al., 2023). The data obtained from PXRD, XRF and FTIR spectroscopy are in good agreement.

The results about degradation of ozone on the Ag-impregnated mordenite and clinoptilolites are shown in Fig. 1d. The conversion of ozone was determined using the dependence:

\[ O_3 \text{ conversion} = \frac{C_0 - C}{C_0} \times 100\% \]

where \( C_0 \) and \( C \) are inlet and outlet concentrations of ozone, respectively.

The time-conversion degree dependence has been measured during 60 min time interval at room
temperature. The investigated silver-loaded natural zeolites demonstrate catalytic activities in the process of ozone decomposing, following the sequence of Ag-mordenite > Ag-clinoptilolite (BP) > Ag-clinoptilolite (M) > Ag-clinoptilolite (GB). The Ag-mordenite material shows the highest ozone conversion (40%) in comparison with the other tested modified natural zeolites. The ozone conversion degree results reveal the lower activities of Ag-clinoptilolites (BP, M and G) compared to the Ag-mordenite after 60 min. It could be concluded that different silver content affects the catalytic activity of the Ag-impregnated natural zeolites. The investigated natural zeolite supports without silver impregnation do not possess catalytic activity to decompose ozone. The ozone conversion increases during the period of 15 minutes. After that the conversion decreases gradually until the end of the
measurement. The possible reason could be the deactivation of catalyst caused by peroxides (O$_2^–$) accumulation and the formation of silver oxides on the surface of the catalyst (Li et al., 2020).

Conclusions

The natural zeolites – mordenite and clinoptilolites are successfully surface impregnated with silver nanoparticles. The better active surface and adsorption ability of Ag nanoparticles is reached by using highly efficient electrochemical reduction method. The obtained Ag-impregnated mordenite demonstrates the highest catalytic efficiency and leads to the highest conversion degree of ozone in comparison with the Ag-loaded clinoptilolite natural zeolites.

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References


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<th>Mg</th>
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<th>Si</th>
<th>P</th>
<th>K</th>
<th>Ca</th>
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<th>Mn</th>
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<td>–</td>
<td>10.68</td>
<td>9.07</td>
<td>0.30</td>
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<td>0.06</td>
<td>0.11</td>
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