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Preparation and Catalytic Study of Mn-NaX, Cu-NaX and Ag-/AgNPs-NaX Zeolites †

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Abstract: FAU-type zeolite NaX was successfully prepared using hydrothermal synthesis at 90 °C for 6 h. The Mn- and Cu-ion-exchanged NaX zeolites were obtained. After the ion exchange, the zeolite powders were thermally treated at 300 °C. As well as Ag-ion-exchanged zeolite, NaX and zeolite were impregnated with two types of Ag nanoparticle dispersions: citrate surface-stabilized (Cit@Ag NPs) and polymer-stabilized (PVP@Ag) nanoparticles. Silver nanoparticles were synthesized using the electrochemical reduction method. The changes in the phase and chemical composition and structure of the obtained zeolite powders before and after ion exchange or impregnation were investigated by PXRD analysis, FTIR spectroscopy, and XRF analysis. The results show that Mn, Cu-exchanged NaX, and that impregnated with Ag demonstrated catalytic abilities towards ozone decomposition in comparison with pure zeolite (non-catalytic activity).

Keywords: NaX zeolite; ion exchange; silver nanoparticles; ozone decomposition

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1. Introduction

Zeolites are natural crystalline aluminosilicate materials, which possess porous and regular structures formed by three-dimensional frameworks of SiO_4 and AlO_4 tetrahedra [1]. Because of its large pore volume, appropriate ion exchange capabilities, and well-defined structure, NaX zeolite can be used as ion-exchangers, absorbents, and catalysts [2–5].

The hydrothermal method is a liquid-phase technique used to produce high-quality crystal materials, and its effects on reaction parameters have been studied for the preparation of FAU-type zeolites by various research groups [6]. These parameters include the initial sources, the molar Si/Al ratio, temperature, and the crystallization time [1,7–9].

The hydrothermal method was utilized to synthesize the FAU-type zeolite NaX in this paper. The successful Mn-, Cu-, and Ag-ion-exchange of the NaX zeolites was achieved. Additionally, two types of Ag nanoparticle dispersion, namely, the citrate surface-stabilized type (Cit@Ag NPs) and the polymer-stabilized type (PVP@Ag), were used to impregnate the zeolite. Powder X-ray diffraction (PXRD) analysis, Fourier transform infrared spectroscopy (FTIR), and X-ray fluorescence (XRF) analysis were conducted to investigate changes in the crystal phase, chemical composition, and structure of the powders before and after ion exchange or impregnation. The catalytic ability of the produced samples was also examined in the ozone decomposition reaction.

2. Materials and Methods

For the synthesis of the NaX zeolite, the following synthesis steps were carried out. Solution 1 was prepared by dissolving 6.53 g NaOH (Chem-LAB NV, Zedelgem, Belgium) and 3.17 g sodium aluminate (Sigma-Aldrich, Darmstadt, Germany) in 78.5 mL distilled water until a clear solution was obtained. A second solution (Solution 2) was prepared by dissolving 4.3 g NaOH in 39.3 mL distilled water and 0.8 g highly dispersed SiO_2 (Merck, Darmstadt, Germany). A third solution (Solution 3) was prepared by mixing 4.2 g highly dispersed SiO_2 and 62.2 mL of Solution 1. The remainder of Solution 1 was mixed with Solution 2, obtaining a new solution (Solution 4). Solution 3 was transferred into a polypropylene bottle and kept at room temperature for 20 h. Solution 4 was transferred into a polypropylene bottle and placed in an oven at 35 °C for 20 h. After that, Solution 3 and 26 mL distilled water were added to the warm Solution 4 to obtain Solution 5, the resultant molar composition of which was $9.5Na_2O{:}5SiO_2{:}Al_2O_3{:}480H_2O$. The hydrothermal synthesis using Solution 5 was carried out at 90 °C for 6 h in a closed polypropylene vessel. Finally, the polypropylene bottle was cooled to room temperature with tap water, and the precipitate was filtered and washed several times with distilled water until pH~7 was achieved. After drying at 90 °C for 1 h, the precipitate was collected from the filter paper.

The ion-exchanged forms of synthesized NaX zeolite were obtained by the following procedure: 100 mL aqueous solutions of 0.4 M $MnCl_2$ (Valerus Co., Ltd., Sofia, Bulgaria), 0.05 M $CuCl_2$ (Valerus Co., Ltd.), or 0.05 M $AgNO_3$ (Sigma-Aldrich) were added to 2.5g of zeolite. The mixtures were stirred with a magnetic stirrer. The copper- and manganese-ion-exchange processes were performed for 4 h at 40 °C and the silver-ion-exchange process for 5 h at 50 °C. The obtained precipitates were filtered and washed several times with distilled water until a neutral pH was reached. The prepared copper- and manganese-exchanged NaX zeolites (Cu-NaX, Mn-NaX) were dried at 120 °C for 1 h and then activated for 4 h at 300 °C in an ambient atmosphere. The silver-exchanged zeolite (Ag-NaX) was dried at 50 °C for 2 h.

The synthesized NaX zeolite was also impregnated with two types of Ag nanoparticles dispersions: citrate-surface-stabilized (Cit@Ag NPs) and poly(vinyl pyrrolidone)-stabilized (PVP@Ag NPs) nanoparticles. The silver nanoparticles were synthesized using the electrochemical reduction method. The impregnation of the synthesized FAU-type zeolite NaX was performed by stirring 2 g zeolite and 30 mL AgNPs colloidal dispersion (400 ppm) for 5 h at 50 °C using a magnetic stirrer. After that, the Ag-impregnated NaX zeolite was filter-washed several times with distilled water until a neutral reaction occurred and then dried for 2 h at 50 °C.

The prepared samples were characterized using PXRD analysis, FTIR spectroscopy, and XRF analysis. The PXRD analysis was carried out on an X-ray powder diffractometer "Empyrean", with 2θ values in the range between 4° and 70°, using Cu Kα radiation (λ = 0.154060 nm) at 40 kV and 30 mA. FTIR spectra were recorded on a Bruker Tensor 37 spectrometer in the region 4000–400 cm^{-1}, using the KBr pellet technique. Wave-dispersive X-Ray Fluorescence (WDXRF) analyses were performed using a Supermini 200 spectrometer (Rigaku, Osaka, Japan). Data collection was performed by wave-dispersed X-ray fluorescence at 50 kV and 4.0 mA.

The ozone conversion was studied by monitoring the change in the ozone concentration. The experiment was carried out in a tubular glass reactor filled with 0.15 g of catalyst. Ozone was obtained by passing dried oxygen (99.99%) through a 4–9 kV discharge in a self-designed tubular type of ozone generator. An ozone–oxygen mixture with an inlet ozone concentration within 6000 ppm was passed through the reactor at a flow rate of about 6.0 $L \cdot h^{-1}$ at an ambient temperature. The ozone concentrations at the reactor inlet and outlet were measured spectrophotometrically using a BMT model 964 ozone analyzer.

3. Results and Discussion

Powder X-ray diffractograms of the synthesized zeolite samples are shown in Figure 1. The PXRD results determined that, initially, the synthesized zeolite powder is crystalline and all the recorded diffraction positions correspond to the NaX zeolite (Ref. code 00-038-0237), i.e., the initial powder is pure NaX. The powder diffraction data do not indicate significant changes for the registered positions of the diffraction peaks between the pure NaX zeolite, the ion-exchanged Mn-NaX, Ag-NaX, or Cu-NaX, and the Ag-NPs-impregnated zeolite powders. This suggests that the zeolite's structure is preserved after the ion-exchange process and impregnation. On the other hand, a decrease in the intensity of the peaks is observed after the ion-exchange process with Mn^{2+}, Ag^{+}, and Cu^{2+} ions. Similar changes in the intensities of the characteristic peaks of FAU-type zeolites are also registered by [10,11]. The additional reflexes associated with the copper chloride hydrate (Ref. code 01-074-1052) are registered in nonthermally treated Cu-ion-exchanged NaX zeolite. After the activation procedure, the $CuCl_2(H_2O)_2$ phase disappeared.

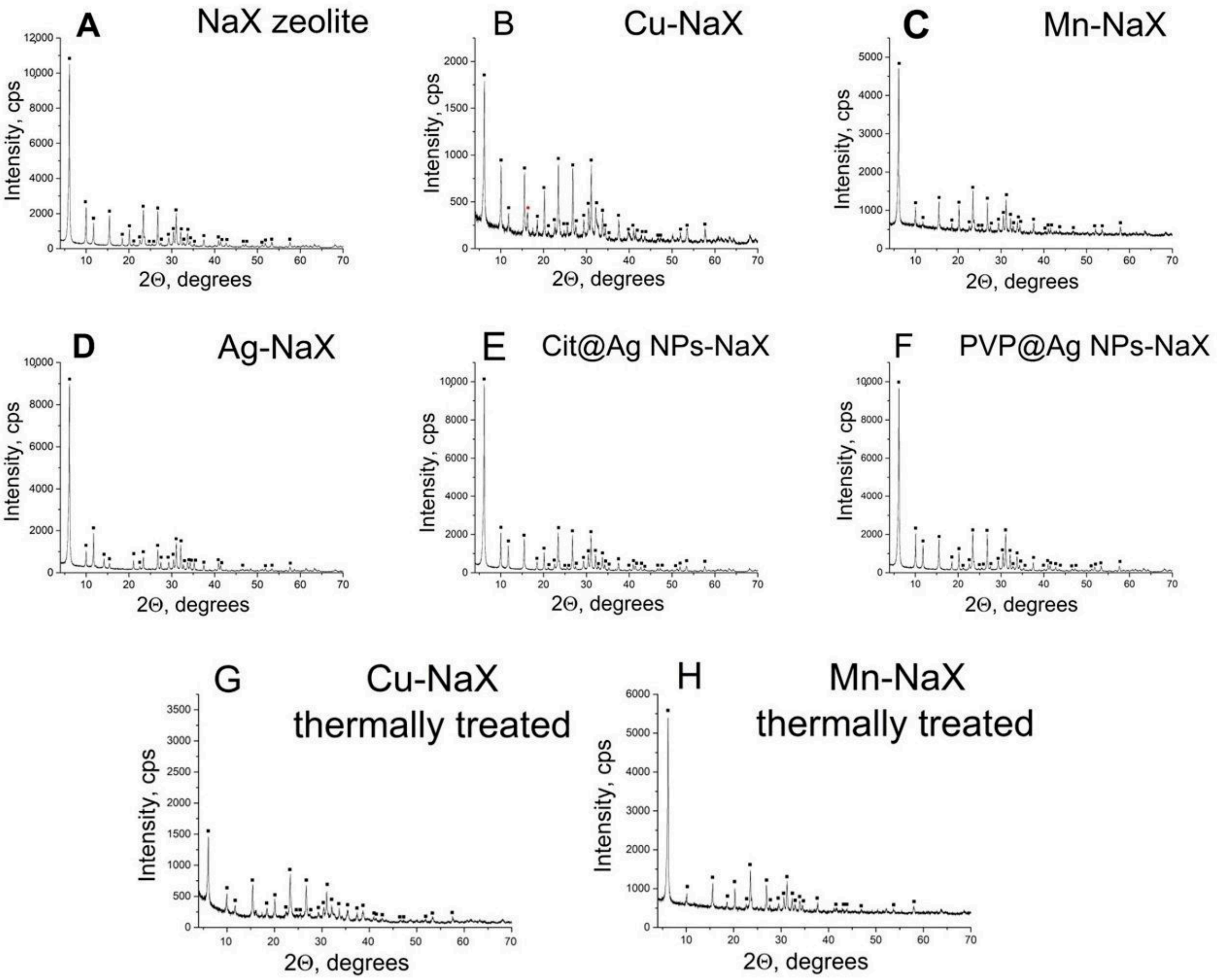

Figure 1. PXRD patterns of (**A**) NaX zeolite; ion-exchanged zeolites: (**B**) Cu-NaX, (**C**) Mn-NaX, (**D**) Ag-NaX, and (**E**) Cit@Ag NPs-NaX. (**F**) PVP@Ag NPs-NaX; thermally treated ion-exchanged zeolites: (**G**) Cu-NaX and (**H**) Mn-NaX zeolites. ■ NaX Ref. code 00-038-0237, ● $CuCl_2$ $(H_2O)_2$ Ref. code 01-074-1052.

The results obtained from the XRF analysis are presented in Table 1. The content of copper, manganese, or silver in the ion-exchanged and impregnated zeolite samples is registered. The Si/Al ratio in the prepared Cu-, Mn-, or Ag-ion-exchanged and Ag-NPs-impregnated samples is similar to that in the synthesized NaX zeolite.

Table 1. Chemical composition of the Cu-, Mn-, or Ag-exchanged NaX zeolites and Ag-impregnated NaX zeolites determined by XRF analysis.

Sample	Si/Al Molar Ratio	Si/Al Mass Ratio	Na Mass %	Al Mass %	Si Mass %	Cu Mass %	Mn Mass %	Ag Mass %
NaX zeolite	1.77	1.84	16.49	29.22	53.91	-	-	-
Cu–NaX	1.41	1.48	5.10	25.39	37.46	29.62	-	-
Mn–NaX	1.55	1.62	2.24	24.80	40.18	-	32.67	-
Ag–NaX	1.53	1.61	11.37	23.67	38.04	-	-	26.85
Cit@Ag NPs-NaX	1.90	1.98	12.44	29.08	57.51	-	-	0.53
PVP@Ag NPs-NaX	1.82	1.89	15.54	28.99	54.66	-	-	0.52

The FTIR spectra of the studied zeolite powders in the range of 4000–400 cm^{-1} are illustrated in Figure 2. The pure NaX zeolite, Mn^{2+}-, Ag^{+}-, or Cu^{2+}-exchanged zeolites, and the Ag-NPs-impregnated zeolite samples show similar FTIR spectra. The absorption bands at wave numbers 3466–3408 cm^{-1} and 1645–1639 cm^{-1} are associated with the stretching vibrations of the physically adsorbed water and bending modes of the OH groups [8]. The peaks located at 1002–983 cm^{-1} and 462–451 cm^{-1} are attributed to the T-O-T stretching vibrations and the T-O bending modes (T assigned to an Si or Al atom), respectively. The symmetric stretching of O-T-O (external tetrahedra) is observed at 757–754 cm^{-1}. The absorption band positioned in the region of 571–559 cm^{-1} is due to the vibrations of double 6 rings (D6R) in FAU-type zeolites [12].

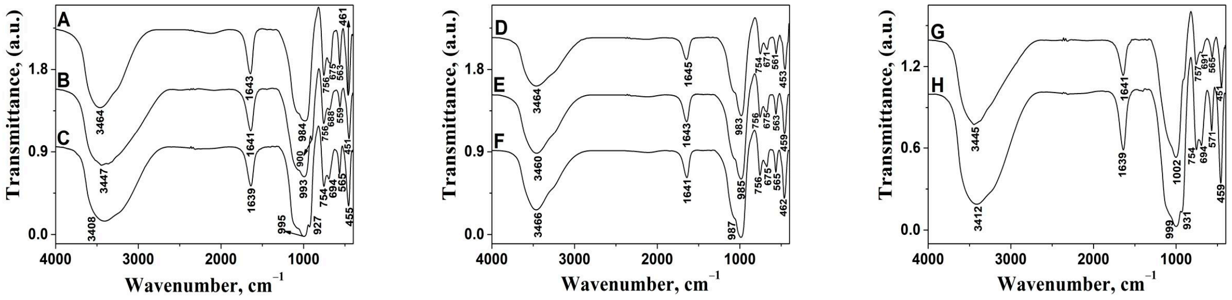

Figure 2. FTIR spectra of (A) NaX zeolite; ion-exchanged zeolites: (B) Cu-NaX, (C) Mn-NaX, (D) Ag-NaX, and (E) Cit@Ag NPs-NaX. (F) PVP@Ag NPs-NaX; thermally treated ion-exchanged zeolites: (G) Cu-NaX and (H) Mn-NaX zeolites.

The data obtained by PXRD and XRF analyses and FTIR spectroscopy are in agreement.

The catalytic efficiency of the obtained samples was tested in decomposing ozone at an ambient temperature. As shown in Figure 3, the time–conversion degree of dependence was measured over the course of 60 min time intervals for the studied samples. The activity of the catalysts was calculated on the basis of the following equation:

$$O_3 conversion = \frac{C_0 - C}{C_0} \times 100\% \qquad (1)$$

where C_0 and C are the inlet and outlet concentrations of ozone, respectively.

The samples exhibit different degrees of activity toward ozone decomposition (17–65%). A conversion degree of about 65% for Mn-NaX zeolite was achieved after 7 min, and then a decrease was observed. It should be noted that the Mn-NaX zeolite catalyst exhibits higher levels of ozone-decomposition activities than the other zeolite catalysts loaded with Ag and Cu. The pure NaX zeolite has no catalytic ability. Similar results concerning the degree of ozone conversion using ion-exchanged natural clinoptilolite zeolite catalysts with Mn and Cu were obtained by Boevski et al. [13]. The citrate-stabilized Cit@AgNPs-

NaX demonstrates higher catalytic activity in comparison with Ag-exchanged NaX and PVP@Ag NPs-NaX zeolites. A possible reason for this relates to the active surface of native silver nanoparticles, which is not partially passivated by the surface coordination of PVP macromolecules.

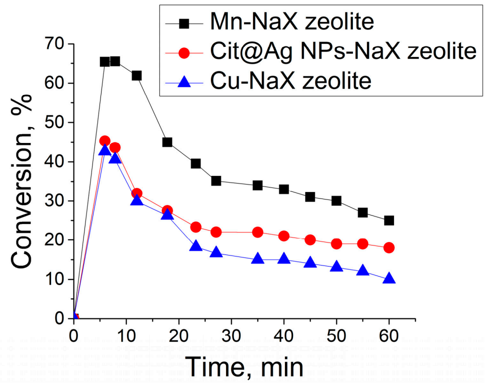

Figure 3. Ozone conversion reaction for Mn- or Cu-exchanged NaX and Cit@Ag NPs-NaX zeolite catalysts.

4. Conclusions

The preparation of Cu-, Mn-, or Ag-ion-exchanged and AgNPs-surface-impregnated hybrids of hydrothermally synthesized NaX zeolites were successfully obtained. The highest conversion degree of ozone was achieved using Mn-loaded NaX zeolite. The best adsorption ability and active surface of Ag NPs was achieved by using the highly effective electrochemical method. The prepared NaX zeolite impregnated with Ag NPs possesses stronger catalytic abilities towards ozone decomposition than the Ag-ion-exchanged zeolite.

Supplementary Materials: The presentation materials can be downloaded at: https://www.mdpi.com/article/10.3390/ECP2023-14649/s1.

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