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Proceeding Paper

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

Borislav Barbov [1,*], Katerina Zaharieva [1], Petya Karakashkova [2], Hristo Penchev [3], Liliya Tsvetanova [1] and Silvia Dimova [3]

[1] Institute of Mineralogy and Crystallography "Akad. I. Kostov", Bulgarian Academy of Sciences, "Akad. G. Bonchev" St., Bl. 107, 1113 Sofia, Bulgaria; zaharieva@imc.bas.bg (K.Z.); lilicvetanova79@abv.bg (L.T.)

[2] Institute of Catalysis, Bulgarian Academy of Sciences, "Acad. G. Bonchev" St., Block 11, 1113 Sofia, Bulgaria; petia.karakashkova@gmail.com

[3] Institute of Polymers, Bulgarian Academy of Sciences, "Akad. G. Bonchev" St., Bl.103A, 1113 Sofia, Bulgaria; hpen4ev@gmail.com (H.P.); dimova@polymer.bas.bg (S.D.)

* Correspondence: barbov@imc.bas.bg

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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 impregnated with two types of Ag nanoparticles dispersions–citrate surface stabilized (Cit@Ag NPs) and polymer-stabilized (PVP@Ag) nanoparticles. Silver nanoparticles were synthesized by electrochemical reduction method. The changes in phase and chemical composition and structure of 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 impregnated with Ag demonstrated catalytic ability towards ozone decomposition in comparison with pure zeolite (non-catalytic activity).

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

1. Introduction

Zeolites are natural crystalline aluminosilicate materials, which possess porous and regular structure formed by three-dimensional frameworks of SiO_4 and AlO_4 tetrahedra [1]. Because of its large pore volume, appropriate ion exchange capability and well-defined structure, the NaX zeolite find applications 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 the reaction parameters have been studied for the preparation of FAU-type zeolites by various researcher groups [6]. These parameters include the initial sources, molar Si/Al ratio, temperature and crystallization time [1,7–9].

The hydrothermal method was utilized to synthesize the FAU-type zeolite NaX in this paper. Successful Mn, Cu, and Ag ion exchange of the NaX zeolites were achieved. Additionally, two types of Ag nanoparticle dispersions, namely citrate surface stabilized (Cit@Ag NPs) and polymer stabilized (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

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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 NaX zeolite the following synthesis steps were carried out. Solution 1 was prepared by dissolving of 6.53 g NaOH (Merck) and 3.17 g sodium aluminate (Sigma Aldrich) in 78.5 mL distilled water until a clear solution was obtained. A second solution (Solution 2) was prepared by dissolving of 4.3 g NaOH in 39.3 mL distilled water and 0.8 g highly dispersed SiO_2 (Merck). A third solution (Solution 3) was prepared by mixing 4.2 g highly dispersed SiO_2 and 62.2 mL of Solution 1. The remaining of Solution 1 is mixed with Solution 2 obtaining a new solution (Solution 4). Solution 3 was transferred into a polypropylene bottle and was 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 with resultant molar composition 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 closed polypropylene vessel. Finally, the polypropylene bottle was cooled with tap water to room temperature, 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), 0.05 M $CuCl_2$ (Valerus Co) or 0.05 M $AgNO_3$ (Sigma-Aldrich) were added to 2.5g zeolite. The mixtures were stirred on a magnetic stirrer. The copper and manganese ion exchange process was performed for 4 h at 40 °C and silver exchange for 5 h at 50 °C. The obtained precipitates were filtered and washed several times with distilled water until neutral pH. 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 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. Silver nanoparticles were synthesized by electrochemical reduction method. The impregnation of 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 Ag impregnated NaX zeolite was filter washed several times with distilled water until neutral reaction and dried for 2 h at 50 °C.

The prepared samples were characterized by PXRD analysis, FTIR spectroscopy and XRF analysis. The PXRD analysis was carried out on a X-ray powder diffractometer "Empyrean" within the range of 2θ values between 4° and 70° using Cu Kα radiation (λ = 0.154060 nm) at 40 kV and 30 mA. FTIR spectra were taken on a Bruker Tensor 37 spectrometer in the region 4000–400 cm^{-1}, using KBr pellet technique. The XRF analyses were performed by Supermini 200 spectrometer-Rigaku, Japan.

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

3. Results and Discussion

Powder X-ray diffractograms of the synthesized zeolite samples are shown on Figure 1. The PXRD results determined that initially synthesized zeolite powder is crystalline and all the recorded diffraction positions correspond to the NaX zeolite (Ref.Code 00-038-0237) e.g., the initial powder is pure NaX. The powder diffraction data do not detect significant changes for registered positions of the diffraction peaks between the pure NaX zeolite, ion exchanged Mn-NaX, Ag-NaX or Cu-NaX and Ag NPs impregnated zeolite powders. This fact suggests that the zeolite structure is preserved after ion-exchange process and impregnation. On the other hand, a decrease in the intensity of peaks after ion exchange process with Mn^{2+}, Ag^{+} and Cu^{2+} ions is observed. Similar changes in intensities of 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) is registered in nonthermally treated Cu ion exchanged NaX zeolite. After activation procedure the $CuCl_2(H_2O)_2$ phase disappeared.

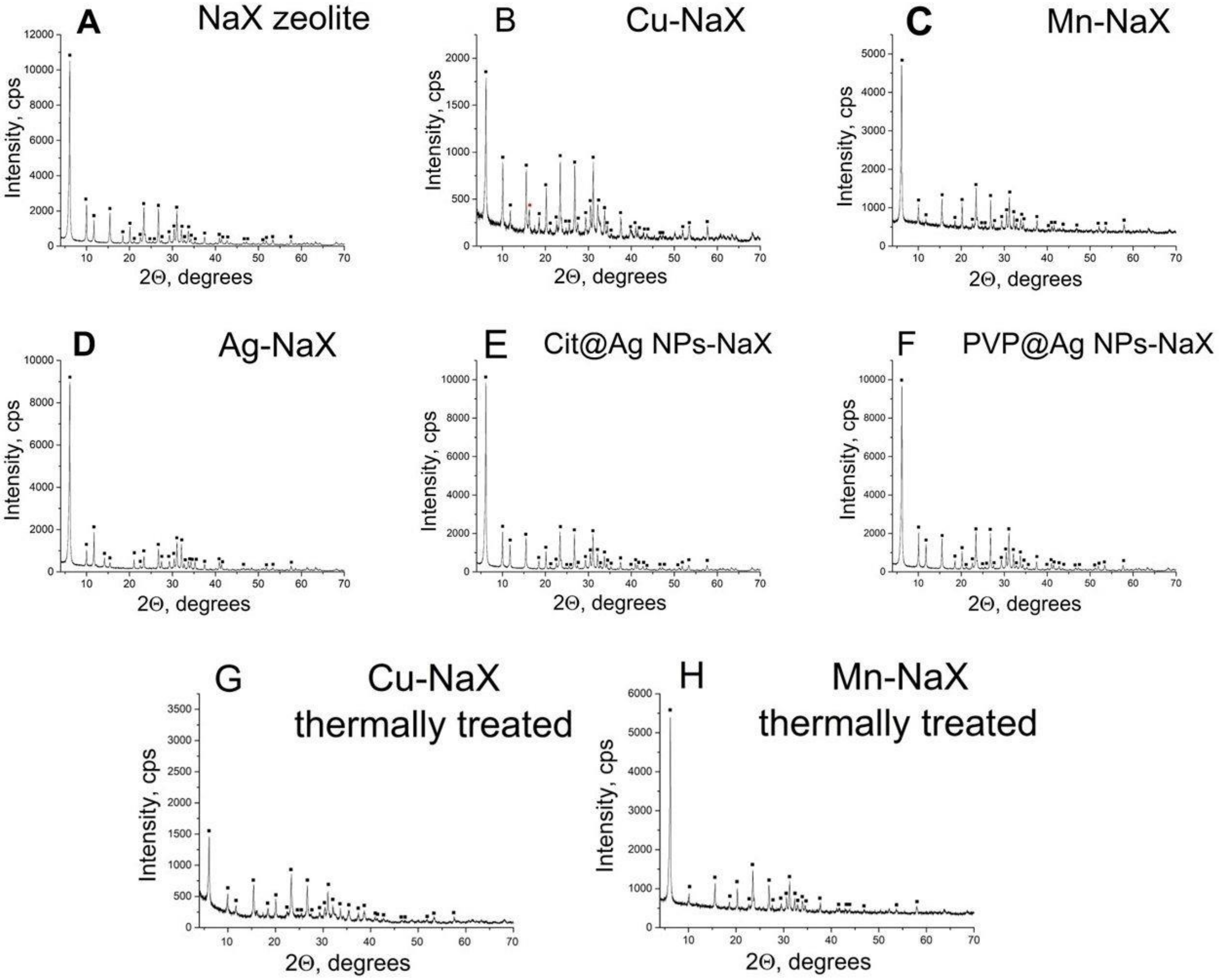

Figure 1. PXRD patterns of (**A**) NaX zeolite; ion-exchanged zeolites: (**B**) Cu-NaX, (**C**) Mn-NaX, (**D**) Ag-NaX and (**E**) Cit@Ag NPs-NaX, (**F**) PVP@Ag NPs-NaX; thermally treated ion-exchanged zeolites: (**G**) Cu-NaX and (**H**) Mn-NaX zeolites. • NaX Ref.Code 00-038-0237, • $CuCl_2$ $(H_2O)_2$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

The results obtained from 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 are similar with 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 4000–400 cm^{-1} are illustrated on the Figure 2. The pure NaX zeolite; Mn^{2+}, Ag^{+} or Cu^{2+} exchanged zeolites and 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 to the stretching vibrations of the physically adsorbed water and bending modes of OH groups [8]. The peaks located at 1002–983 cm^{-1} and 462–451 cm^{-1} attributed to the T-O-T stretching vibrations and T-O bending modes (T assign to Si or Al atom), respectively. The symmetric stretching of O-T-O (external tetrahedra) are observed at 757–754 cm^{-1}. The absorption band positioned in the region 571–559 cm^{-1} due to the vibrations of double six rings (D6R) in FAU type zeolites [12].

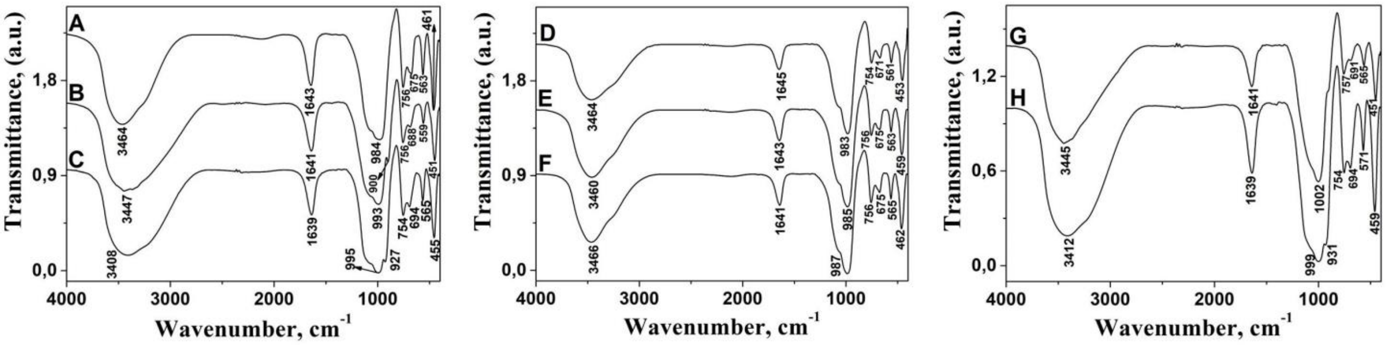

Figure 2. FTIR spectra of (A) NaX zeolite; ion-exchanged zeolites: (B) Cu-NaX, (C) Mn-NaX, (D) Ag-NaX and (E) Cit@Ag NPs-NaX, (F) PVP@Ag NPs-NaX; thermally treated ion-exchanged zeolites: (G) Cu-NaX and (H) Mn-NaX zeolites.

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

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

$$O_3 conversion = \frac{C_0 - C}{C_0} x100\% \quad (1)$$

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

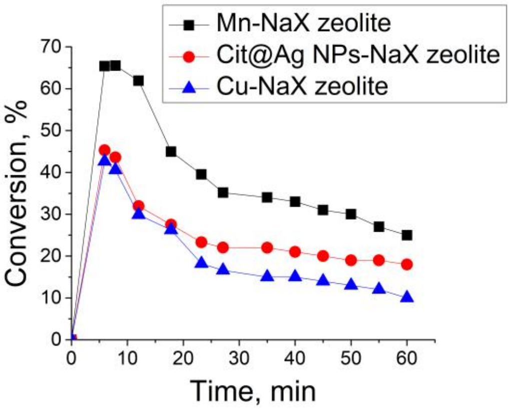

Figure 3. Ozone conversion reaction over Mn or Cu exchanged NaX and Cit@Ag NPs-NaX zeolite catalysts.

The samples exhibit different activities toward ozone decomposition (17–65%). It can be seen that a conversion degree of about 65% over Mn-NaX zeolite was achieved after 7 min, and then decrease was observed. It has to be noted that catalyst Mn-NaX zeolite possesses higher activity in ozone decomposition than the others zeolite catalysts loaded Ag and Cu. The pure NaX zeolite has no catalytic ability. The similar results about ozone conversion degree using ion-exchanged natural clinoptilolite zeolite catalysts with Mn and Cu were determined by Boevski et al. [13]. The citrate stabilized Cit@AgNPs-NaX demonstrates the higher catalytic activity in comparison with Ag exchanged NaX, PVP@Ag NPs-NaX zeolites. The possible reason for this could be the active surface of native silver nanoparticles which is not partially passivated by surface coordination of PVP macromolecules.

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 better adsorption ability and active surface of Ag NPs was achieved by using high effective electrochemical method. The prepared NaX zeolite impregnated with Ag NPs possesses the higher catalytic ability towards ozone decomposition than that of Ag ion-exchanged zeolite.

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