Preparation and catalytic study of Mn-NaX, Cu-NaX and Ag-/AgNPs-NaX zeolites

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AIM

- Synthesis of FAU-type zeolite NaX by hydrothermal method.
- Preparation of Mn, Cu and Ag ion-exchanged NaX zeolites.
- The impregnation of NaX zeolite using two types of Ag nanoparticles dispersions – citrate surface stabilized (Cit@Ag NPs) and polymer stabilized (PVP@Ag NPs) nanoparticles.
- Investigation of phase composition, structure and chemical composition of prepared samples by powder X-ray diffraction (PXRD) analysis, Fourier-transform infrared spectroscopy (FTIR) and X-ray fluorescence (XRF) analysis.
- Study the catalytic ability of obtained zeolite samples in the reaction of ozone decomposition.

SYNTHESIS OF NaX ZEOLITE

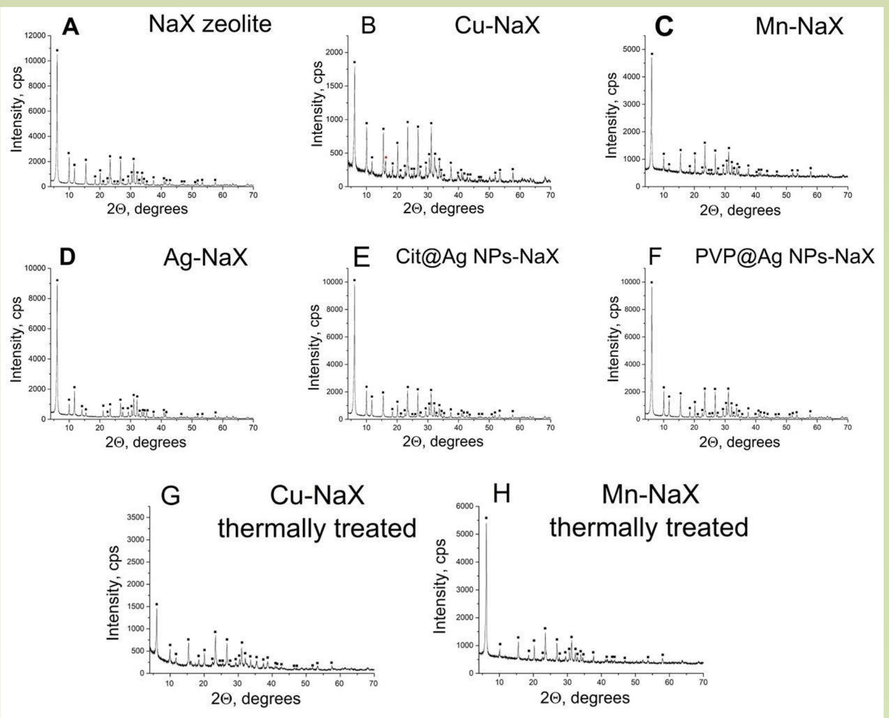
For the synthesis of NaX zeolite the following synthesis steps were carried out. Solution 1 was prepared by dissolving of 6.53g NaOH (Merck) and 3.17g sodium aluminate (Sigma Aldrich) in 78.5ml distilled water until a clear solution was obtained. A second solution (Solution 2) was prepared by dissolving of 4.3g NaOH in 39.3 ml distilled water and 0.8g highly dispersed SiO_2 (Merck). A third solution (Solution 3) was prepared by mixing 4.2g highly dispersed SiO_2 and 62.2ml 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 hours. Solution 4 was transferred into a polypropylene bottle and placed in an oven at 35°C for 20 hours. After that Solution 3 and 26ml 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 hours 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 hour the precipitate was collected from the filter paper.

PREPARATION OF Mn-NaX, Cu-NaX AND Ag-/AgNPs-NaX ZEOLITES

The ion-exchanged forms of synthesized NaX zeolite were obtained by the following procedure: 100ml aqueous solutions of 0.4M $MnCl_2$ (Valerus Co), 0.05M $CuCl_2$ (Valerus Co) or 0.05M $AgNO_3$ (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 hours at 40°C and silver exchange for 5 hours 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 hour and then activated for 4 hours at 300°C in ambient atmosphere. The silver exchanged zeolite (Ag-NaX) was dried at 50°C for 2 hours.

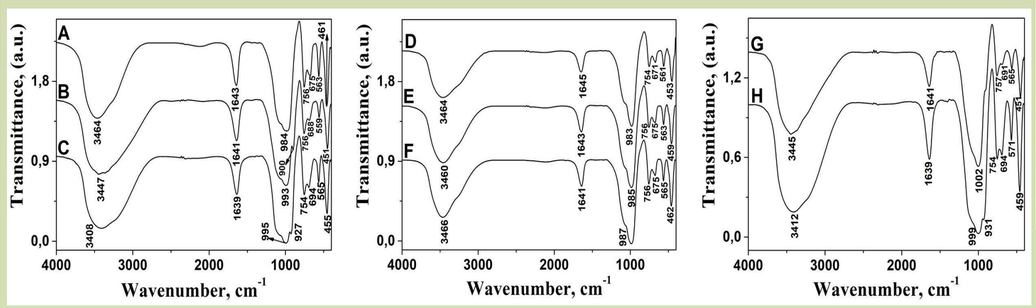
The synthesized NaX zeolite was also impregnated with two types of Ag nanoparticles dispersions – citrate surface stabilized (Cit@Ag NPs) and poly(vinyl pyrrolidone), stabilized (PVP@Ag NPs) nanoparticles. Silver nanoparticles were synthesized by electrochemical reduction method. The impregnation of synthesized FAU-type zeolite NaX was performed by stirring 2g zeolite and 30ml AgNPs colloidal dispersion (400ppm) for 5 hours 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 hours at 50°C.

Characterization



PXRD patterns of prepared zeolite samples.

RESULTS

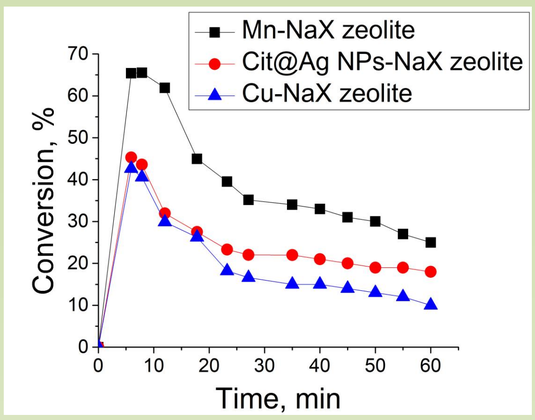


FTIR spectra of A) NaX zeolite; ion exchanged zeolites: B) Cu-NaX, C) Mn-NaX, D) Ag-NaX and E) Cit@Ag NPs-NaX, F) PVP@Ag NPs-NaX; thermally treated ion exchange zeolites: G) Cu-NaX and H) Mn-NaX zeolites.

The results from 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

Ozone decomposition study



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

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.