SYNTHESIS AND CHARACTERIZATION OF BORON MODIFIED ZEOLITE WITH MFI STRUCTURE

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ABSTRACT

In this work MFI type zeolite samples with different amount of boron were prepared. Obtained samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and Fourier transform infrared spectroscopy (FTIR). Results of characterization showed that presence of boron in the reaction mixture influences size and morphology of synthesized zeolite crystals. The amount of boron in the reaction mixture, as well as presence of aluminium, has influence on the extent of boron loss during calcination of the final zeolite product. However, the incorporation of boron into the zeolite structure did not affect the crystallinity - the MFI structure was preserved in all obtained samples.

Key words: boron, borosilicate, MFI type structure, hydrothermal treatment.

INTRODUCTION

Zeolites are porous crystalline aluminosilicates. Because of specific properties related to their structure, zeolites are promising materials for many different applications in industry and everyday life. They are well known as adsorbents, ion exchangers, catalysts, etc.

In the basis of complex zeolite structure are tetrahedra of silicon and aluminium oxide connected through common oxygen atoms [1]. Presence of aluminium brings framework charge which is counterbalanced by different exchangeable cations. If cations are exchanged by proton, Brønsted acid sites of different strength form, which is important for acid catalytic applications. By isomorphous substitution of silicon and/or aluminium atom by other elements (i.e. boron, gallium, germanium, titanium, zinc, iron, etc.), it is possible to modify zeolite porosity and acidity, and in that way, tune zeolite properties for specific applications [2].

Hence, by introduction of boron into zeolite MFI structure, materials with different properties could be obtained. Brønsted acid sites formed are weaker in comparison to the aluminium containing counterpart [3]. Since B-O bonds are shorter than Si-O and Al-O bonds, a size of crystal unit of boron modified zeolites is reduced [3]. Post synthesis treatment of boron containing zeolite can substitute boron by other cations and in that way metallosilicate structures can be obtained which cannot be obtained easily by usual hydrothermal treatment [4]. Additionally, deboronation can also increase number of defects, i.e., silanol nests, H-bonded silanols, in high silica MFI zeolites, which can increase their catalytic activity [5].

In this work, we present preliminary results of our study of boron containing zeolite synthesis with the aim of their possible application in catalysis and adsorption. Therefore, we have hydrothermally synthesized several zeolite samples with different amount of boron in the starting reaction mixture. Obtained samples were characterized by XRD, SEM, EDS and FTIR, to study boron influence on the properties of the final zeolite product.

EXPERIMENTAL

Chemicals used in preparation of the reaction mixtures were boric acid (H_3BO_3, Sigma Aldrich), sodium hydroxide (NaOH, 98%, Kemika), tetrapropyl ammonium bromide (TPABr, 98%, Sigma Aldrich), fumed silica (SiO_2, Sigma Aldrich), aluminium hydroxide ($Al(OH)_3$, Kemika) and deionized water. All chemicals were used as obtained. The molar composition of the reaction mixtures was $60 SiO_2 \cdot 2.5\ Na_2O \cdot x\ B_2O_3 \cdot y\ Al_2O_3 \cdot 8\ TPABr \cdot 800\ H_2O$, where x and y=0 for sample 1; x=1, y=0 for sample 2; x=2 and y=0 for sample 3 and x and y=2 for sample 4. Reaction mixtures were prepared by dissolving appropriate amount of TPABr in water solution of NaOH. Then, fumed silica was added, and white thick gel was obtained. In reaction mixtures, which contained both B and Al, boric acid and aluminium hydroxide were added to the solution of NaOH and TPABr, before adding fumed silica. Four reaction mixtures/gels were prepared. The gels were transferred into Teflon-lined metal autoclaves and heated at 150°C for 5 days. After synthesis, obtained samples were washed with water, dried, and calcined at 550° C for 5 hours. In this way obtained samples were used for further characterization by XRD, SEM, EDS and FTIR.

XRD was done using Rigaku Ultima IV diffractometer in Bragg-Braentano geometry, with Ni filtered CuKα radiation (λ=1.54178 Å). Diffraction data were acquired over the scattering angle 2θ from 2° to 70° with a step of 0.02° and acquisition rate of 1°/min. Elemental analysis was done using EDS (JEOL JSM-6390LV equipped with energy dispersive X-ray spectrometer, Oxford Aztec X-max). The morphology of samples was investigated by scanning electron microscopy (SEM, JEOL JSM-6390LV). Prior to the SEM observations, the powders were coated with gold to minimize charging. FTIR spectra were collected using IRAffinity-1 (SHIMADZU) spectrophotometer; 2 mg of sample was pelletized in 200 mg of KBr (Fisher Scientific); for each spectrum 100 scans were collected with 4 cm^{-1} resolution.

RESULTS AND DISCUSSION

XRD diffractograms in Figure 1 show that all samples are fully crystalline zeolites with MFI type of structure. The peaks of other crystalline phases were not detected in the diffractograms suggesting that boron, when present in the sample, is dispersed in the zeolite structure [6].
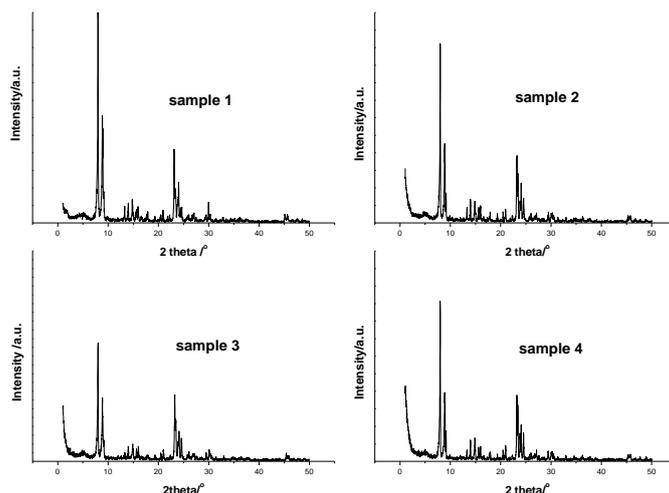

Figure 1. X-ray diffraction patterns of samples 1-4.

SEM micrographs in Figure 2 show the morphology of the obtained samples. In sample 1 (Fig 2a), obtained from the reaction mixture without boron and aluminium present in the reaction mixture, particles have characteristic intergrown structure with crystal size of about 6

μm. By addition of boron into reaction mixture (Si/B=30), in obtained sample 2 (Fig 2b) particles become more rounded, but their sizes remain quite similar. With further increase of the boron amount in the reaction mixture (Si/B=15), particles of obtained sample 3 are large polycrystalline spheres with size of about 17 μm, as visible in the Fig 2c. When both aluminium and boron were present in the reaction mixture (Si/B=15, Si/Al=15) obtained sample 4 has large and rounded particles with size of about 16 μm, with surface morphology (Fig 2d) resembling intergrown structure. It was shown that by simple change of Si/B ratio in the reaction mixture is possible to influence the size and shape of the obtained zeolite particles, which is in agreement with literature data [7].
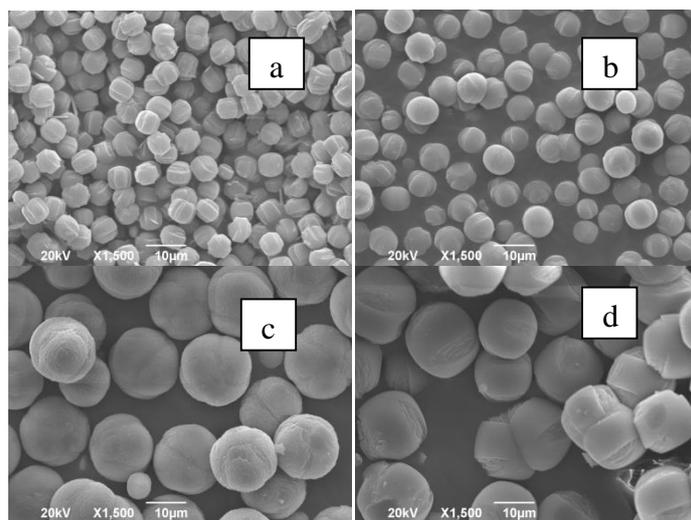

Figure 2. SEM of samples: a) sample 1, b) sample 2, c) sample 3, d) sample 4.

EDS results show that after calcination of the samples the amount of boron in the sample 2, although present in the reaction mixture, is not present in the calcined material. On the other side in the samples 3 and 4, where amount of boron is present in the reaction mixture in double amount, boron is still present also in the calcined samples: 4.73 wt% in sample 3 and 5.37 wt% in sample 4.

FTIR results presented in Figure 3 corroborate EDS results, and in spectra of samples 3 and 4 it is possible to notice bands that suggest presence of boron in the zeolite structure, which are not found in the samples 1 and 2.
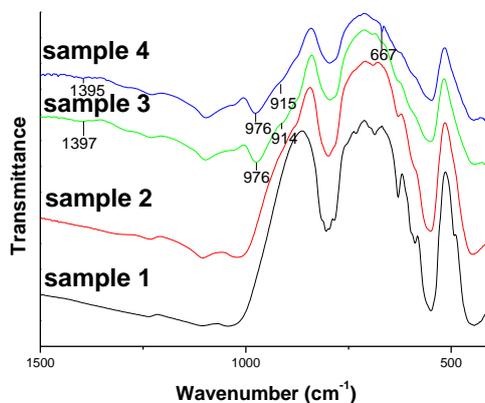

Figure 3. FT-IR spectra of samples 1-4.

The weak shoulder and band at about 660 cm^{-1}, for samples 3 and 4, respectively, are attributed to the bending vibrations of B-O-Si [7]. For the samples 3 and 4, presence of wide

shoulders at about 920 cm^{-1} are connected to symmetric stretching B-O-Si modes and presence of tetracoordinated boron**,** while small shoulders at about 1090 cm^{-1} are due to stretching modes of BO$_4$ units [8]. Bands at about 970 cm^{-1} are connected to Si-OH stretching vibration of bridging hydroxyls but could also be connected to the Si-O-B vibrations [9]. Band at about 1400cm^{-1} is ascribed to asymmetric B-O stretching of the [B(OSi)$_3$] units in calcined samples [10,11]. Its weak intensity in our samples 3and 4 is probably due to the strong interaction of boron in trigonal coordination with water [11].

CONCLUSION

Results obtained in this work showed that incorporation of boron in MFI zeolite structure brings changes of the morphology of zeolite particles, from intergrowth structure of pure MFI structure to polycrystalline spherical particles. Size of borosilicate crystals depend on the Si/B ratio in the reaction mixture. In FTIR spectra of boron modified zeolites, besides characteristic bands for MFI structure, additional bands can be noticed, indicating incorporation of boron atoms in the MFI structure. In calcined samples the amount of boron is lower than expected from reaction mixture composition. This finding could be partly ascribed to the deboronation process during calcination but also to the possible lower incorporation of boron during synthesis. It seems that amount of boron in starting reaction mixture and presence of aluminium has important influence on the range of the abatement.

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