Ceramics-Silikáty 60 (4), 273-277 (2016)
journal webpage: www.ceramics-silikaty.cz doi: 10.13168/cs.2016.0040

THE EFFECT OF NaOH AND KOH ON THE CHARACTERIZATION OF MESOPOROUS AlOOH IN THE SOLVOTHERMAL ROUTE

FARHAD SALIMI*, #MOZAFFAR ABDOLLAHIFAR*, ALI REZA KARAMI**

*Department of Chemical Engineering, College of Science, Kermanshah Branch, Islamic Azad University, Kermanshah 67131, Iran
**Department of Chemistry, College of Science, Shahid Rajaee Teacher Training University, Tehran 13761, Iran

#E-mail: abdollahifar@gmail.com

Submitted March 21, 2016; accepted July 24, 2016

Keywords: Boehmite, Solvothermal, NaOH, KOH, Nanostructure

In this study boehmite nanostructures have been successfully synthesized using solvothermal method at 180° C and at high basic pH (~13.5), when ethanol was as solvent. The effects of NaOH and KOH as pH adjusting regents on the characterization of synthesized samples were investigated in detail. X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and field emission scanning electron microscopy (FESEM), were used to characterize the samples. The specific surface area, pore size distribution and pore structure of the different boehmite structures at different condition were also discussed by the N_2 adsorption/desorption test. According to our experimental results, the FESEM micrographs show that the samples synthesised by NaOH and KOH are nanostructure and nanoparticles, respectively. The obtained boehmite nanostructure from NaOH exhibited large surface area of 144 $m^2 \cdot g^{-1}$ and high total pore volume of 1.28 $cm^3 \cdot g^{-1}$.

INTRODUCTION

Various metal oxyhydroxides nanostructures with different morphologies and characteristics have been extensively synthesized with various methods and received much attention in recent years [1-3]. These nanostructures have great potential in applications in adsorbents, ceramics, and catalysts. On the other side, nanostructure materials also provide large surface areas compared with their micro and macro counterparts. Owing to these, several researches have broadly addressed to develop new methods to prepare oxyhydroxides nanostructures [1-11]. Among these, boehmite (AlOOH) has attracted extensive attention because of their nontoxic and low cost characteristics for many applications [12-17].

Synthesis method has an important effect on properties and characterizations of material products. Conventional processes for synthesizing boehmite nanostructures include sol-gel [18], precipitation [19], hydrothermal [20, 21] and solvothermal [22] and other related routes [23]. Among the reported synthetic routes, solvothermal technique have been broadly employed as the effective method do to the mild synthesis conditions and flexible change of experimental parameters. In this method, the synthesis conditions, such as solvent [24], reaction temperature and time [20], solution pH [25], adding surfactants [26] and pH adjusting regent [10] have great effects on the structure and character of boehmite.

To our best knowledge, the synthesis of boehmite via solvothermal route in different pH adjusting regents have not been reported. In this paper, we present a facile route for the fabrication of high surface area boehmite nanostructures.

EXPERIMENTAL

The starting materials utilized are $Al(NO_3)_3 \cdot 9H_2O$, NaOH, KOH and ethanol 96 %, were purchased from Scharlau, Spain, and used as received without further purification.

In a typical process, 10 g Aluminium nitrate was dissolved in 120 ml of ethanol, and it was stirred for 15 min at room temperature. NaOH or KOH solution (2 Molar) was subsequently added drop by drop to the solution to give lacteous precipitates immediately. At this point, the pH value of the reaction mixture was ~13.5, then transferred into Teflon-lined stainless steel autoclave (200^{cc}), and heated at 180°C for 24 h. These samples were treated by centrifugation, rinsed with ethanol several times, and then dried at 60° C in an oven for 48 h. The boehmite samples prepared by NaOH and KOH were labelled N–B, K–B, respectively.

The crystalline phase of products was identified using X-ray diffraction (B8 ADVANCE, BRUKER X-ray diffractometer) patterns were recorded in step scanning on a by using CuKa radiation (λ = 1.54 Å) and a scan rate of 1.5°·min^{-1}. IR reflection spectroscopy was performed with a RAYLEIGH WQF-510 spectrometer in the range 1000 - 4000 cm^{-1} at room temperature. The morphology and nanostructure were observed using a field emission scanning electron microscope (FESEM, HITACHI S-4160 XL30). The specific surface area of synthesised samples was determined using BEL SORP, MINI II-310 analyser. In this technique the Brunauer-Emmett-Teller (BET) equation was employed to calculate the specific surface area and the mean sizes of pores were calculated using the original Barrett, Joyner, and Halenda (BJH) method.

RESULTS AND DISCUSSION

The phase structure and purity of the products were examined by XRD. Figure 1a shows the XRD patterns of typical samples prepared with different pH adjusting regents. When compared to the standard pattern (JCPDS card no. 001-1283), the reflections of both the products were readily indexed to the orthorhombic boehmite phase, the XRD peaks at 14.39, 28.13, 38.23, 48.93, 51.59, 54.94, 60.03, 63.69, 64.68, 66.76 and 72.03 can be attributed to the (020), (120), (140), (131), (200), (160), (151), (211), (231), (071) and (251) planes of the boehmite structure, respectively. Furthermore, no characteristic peaks from other crystalline impurities were detected by XRD, suggesting that high purity of the boehmite samples. The high peak intensity and narrow peak width indicate the good crystallinity of the both sample, especially boehmite synthesized with NaOH.

The crystallite sizes were calculated the using Scherrer equation:

$$D = (k \cdot \lambda)/(B \cdot \cos\theta) \quad (1)$$

where k is a constant ~ 0.9, λ is the wavelength of the X-rays, B is the full width of diffraction peak at half maximum intensity and θ is the Bragg angle. By using all the diffraction peaks in the XRD pattern, the calculated average crystallite sizes of B–N, B–K samples were 16 and 13 nm, respectively. Comparison of XRD patterns of the prepared samples showed that the extent and percentage of crystallinity of samples do not differ significantly. These results indicated that the NaOH and KOH have a low influence on the crystallite phase of the samples.

Figure 1b exhibits FTIR spectrums of the synthesized boehmite nanostructures. For both sample the FTIR spectra were similar regardless of the difference in intensity peaks. As shown in Figure 2a, for the B–N, five strong bands at 480, 630, 746, 1064, and 1171 cm^{-1} were observed. As can be seen, for both samples, the intensive bands at 3092 and 3300 cm^{-1} belong to the υ_{as}(Al)O–H and υ_{s}(Al)O–H stretching vibrations [21]. The two weak bands at 1970 and 2090 cm^{-1} are the combination bands. The absorption edge of the hydroxyl bands on the surface was found at 1636 cm^{-1}, and this absorbance in the spectra of AlOOH nanoarchitectures are very weak, indicating a very small amount of physically adsorbed water molecules.

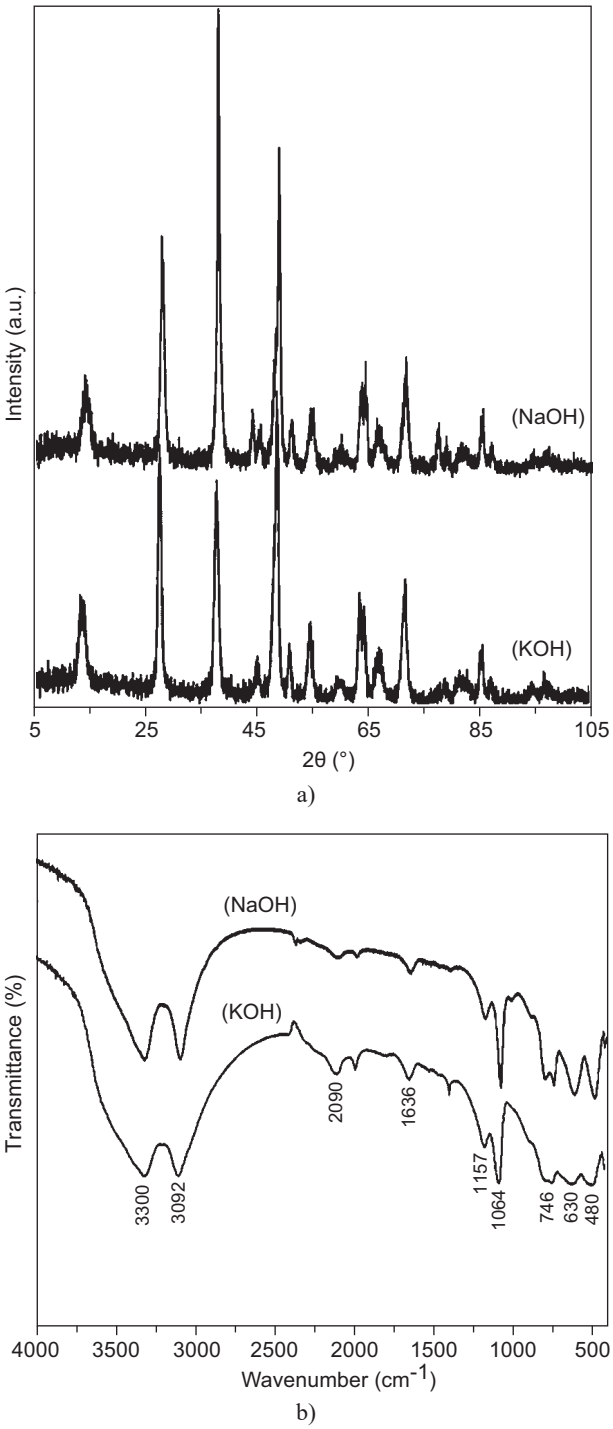
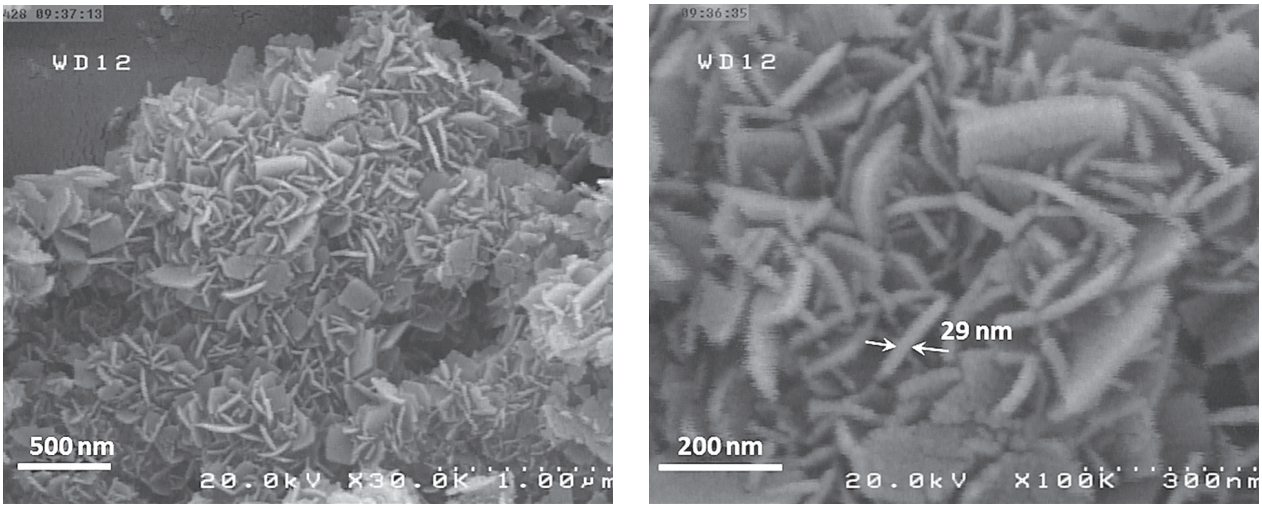


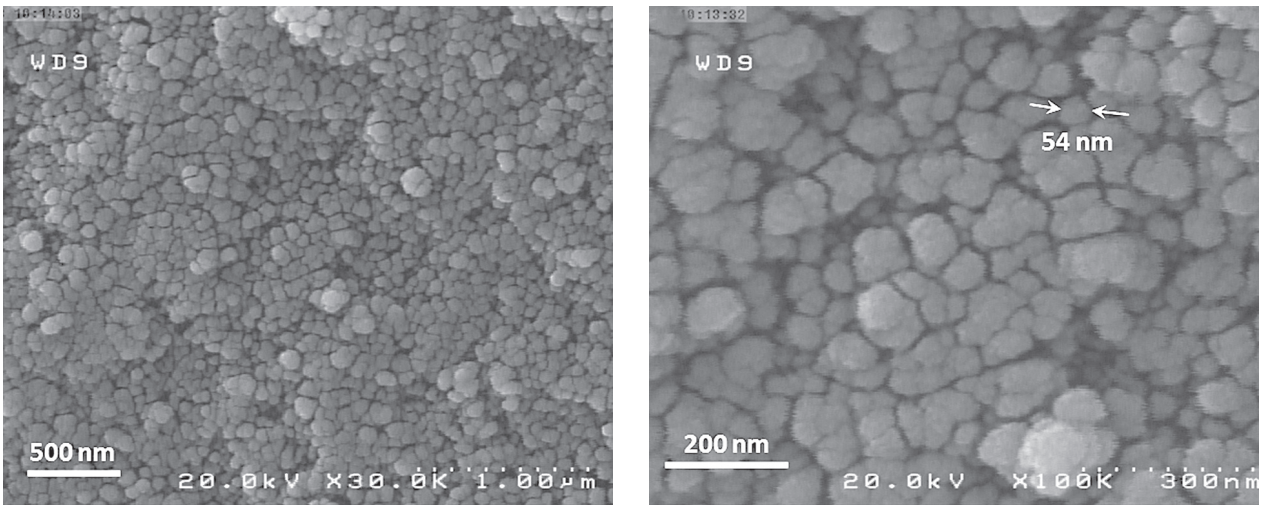
Figure 1. XRD patterns (a) and FTIR spectra (b) of as-synthesized samples.

The morphologies of the as-prepared boehmite samples in this work were examined by using FESEM analysis. Figure 2 shows the representative FESEM images of B–N (a) and B–K (b) samples. However, Figure 2a indicated that hierarchically nanostructures were more densely assembled by platelets and sheets, when NaOH was used for synthesis of boehmite. In this case a typical hierarchically nanostructures were built up by nano-sheets and nano-plates with average thickness of about 35 nm. Generally, changes in pH adjusting regents from NaOH to KOH may favour to the formation process of nanoparticles. It can be found in Figure 2b that there were only irregular nano particles that the size of particles was from 30 to 100 nm, which the average size of the them was about 65 nm.

BET N_2 adsorption-desorption analysis was used to determine the specific surface area and pores size distribution in the boehmite nanostructures at 77 K. As shown in Figure 3a, the typical adsorption-desorption isotherms of the B–N and B–K samples ascertained to be of type IV, according to the International Union of Pure and Applied Chemistry (IUPAC) classification, which is characteristic of mesoporous materials [27]. The adsorption-desorption isotherms of B–N sample have a distinct H3 hysteresis loop in the relative pressure (P/P_0) range of 0.57 - 1.0, which indicates that the pore size distribution is not uniform. The adsorption-desorption isotherms of B–K sample have a distinct H1 hysteresis loop in the relative pressure (P/P_0) range of 0.6 - 0.9, which means that holes have been formed by stacking nano particles. Those results agree with the conclusions we discussed in the structure and morphology characterization section. The specific surface area calculated of the B–N and K–N based on the Brunauer-Emmett-Teller (BET) model are 144 and 55 $m^2 \cdot g^{-1}$ and the pore volume determined by the BJH approaches are 1.23 and 0.18 $cm^3 \cdot g^{-1}$, respectively. Obviously, the specific surface area and pore volume of B–N is extremely larger than the B–K. Figure 3b shows the Barrett-Joyner-Halenda (BJH) calculations for the pore-size



a)



b)

Figure 2. FESEM images of the (a) B–N, (b) B–K samples.

distribution, derived from desorption data, revealed a narrow distribution centred at 4 nm for the B–K and a wide range 2-50 nm for the B–N. The results display that the obtained boehmite products have excellent porous properties.

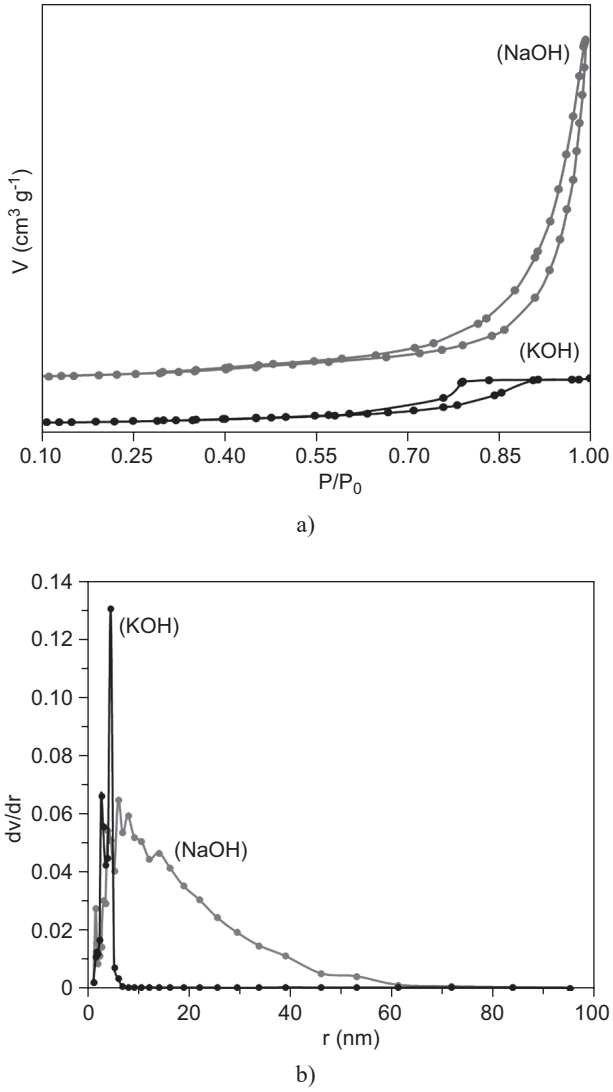


Figure 3. Nitrogen adsorption-desorption isotherm (a) and the corresponding pore size distribution (b) curve for samples.

CONCLUSIONS

In summary, boehmite with nanostructure and nanoparticle morphologies has been successfully synthesized via simple solvothermal route. The effect of NaOH and KOH as pH adjusting agent on the synthesized samples were systematically studied and tested by several techniques. The morphology and texture evolutions of samples were investigated by changing the pH adjusting regents. Our results showed that the boehmite nanostructures with large surface area and higher pore volume were obtained when NaOH as pH adjusting agent was used. Meanwhile, these ordered mesoporous AlOOH nanostructures have potential applications for preparing ceramics, catalysts and adsorbents

Acknowledgements

The authors gratefully acknowledge the supports from Islamic Azad University, Kermanshah Branch.

REFERENCES

1. Abdollahifar M., Zamani R.M., Beiygie E., Nekouei H. (2014): Synthesis of micro-mesopores flowerlike γ-Al_2O_3 nano-architectures. *Journal of the Serbian Chemical Society*, *79*(8), 1007-1017. doi:10.2298/JSC130903007A
2. Prakasam B.A., Lahtinen M., Muruganandham M., Sillanpää M. (2015): Synthesis of self-assembled α-GaOOH microrods and 3D hierarchical architectures with flower like morphology and their conversion to α-Ga_2O_3. *Materials Letters*, *158*, 370-372. doi:10.1016/j.matlet.2015.05.044
3. Wang W., Pan H., Shi Y., Pan Y., Yang W., Liew, K. Song L., Hu Y., (2016): Fabrication of LDH nanosheets on β-FeOOH rods and applications for improving the fire safety of epoxy resin. *Composites Part A: Applied Science and Manufacturing*, *80*, 259-269. doi:10.1016/j.compositesa.2015.10.031
4. Sigg L., Stumm W. (1981): The interaction of anions and weak acids with the hydrous goethite (α-FeOOH) surface. *Colloids and Surfaces*, *2*(2), 101-117. doi:10.1016/0166-6622(81)80001-7
5. Tessier A., Fortin D., Belzile N., DeVitre R., Leppard G. (1996): Metal sorption to diagenetic iron and manganese oxyhydroxides and associated organic matter: narrowing the gap between field and laboratory measurements. *Geochimica et Cosmochimica Acta*, *60*(3), 387-404. doi:10.1016/0016-7037(95)00413-0
6. Zhang Y.C., Wu X., Hu X.Y., Shi Q.F. (2007): A green hydrothermal route to GaOOH nanorods. *Materials Letters*, *61*(7), 1497-1499. doi:10.1016/j.matlet.2006.07.060
7. Li G., Peng C., Li C., Yang P., Hou Z., Fan Y., Cheng Z., Li, J. (2010): Shape-controllable synthesis and morphology-dependent luminescence properties of GaOOH: Dy^{3+} and β-Ga_2O_3: Dy^{3+}. *Inorganic Chemistry*, *49*(4), 1449-1457. doi:10.1021/ic901682x
8. Wang B., Wu H., Yu L., Xu R., Lim T.T. (2012): Template-free Formation of Uniform Urchin like α-FeOOH Hollow Spheres with Superior Capability for Water Treatment. *Advanced Materials*, *24*(8), 1111-1116. doi:10.1002/adma.201104599
9. Abdollahifar M. (2014): Synthesis and characterisation of γ-Al_2O_3 with porous structure and nanorod morphology. *Journal of Chemical Research*, *38*(3), 154-158. doi:10.3184/174751914X13910938972748
10. Haghnazari N., Abdollahifar M., Jahani F. (2014): The Effect of NaOH and KOH on the Characterization of Meso-porous AlOOH Nanostructures in the Hydrothermal Route. *Journal of the Mexican Chemical Society*, *58*(2), 95-98.
11. Rahimi S., Moattari R.M. Rajabi L., Derakhshan A.A., Keyhani M. (2015): Iron oxide/hydroxide (α, γ-FeOOH) nanoparticles as high potential adsorbents for lead remo-

val from polluted aquatic media. *Journal of Industrial and Engineering Chemistry*, *23*, 33-43. doi:10.1016/j.jiec.2014.07.039

12. Abdollahifar M., Haghighi M., Babaluo A.A. (2014): Syngas production via dry reforming of methane over Ni/Al_2O_3–MgO nanocatalyst synthesized using ultrasound energy. *Journal of Industrial and Engineering Chemistry*, *20*(4), 1845-1851. doi:10.1016/j.jiec.2013.08.041
13. Baneshi J., Haghighi M., Jodeiri N., Abdollahifar M., Ajamein H. (2014): Homogeneous precipitation synthesis of $CuO–ZrO_2–CeO_2–Al_2O_3$ nanocatalyst used in hydrogen production via methanol steam reforming for fuel cell applications. *Energy Conversion and Management*, *87*, 928-937. doi:10.1016/j.enconman.2014.07.058
14. Baneshi J., Haghighi M., Jodeiri N., Abdollahifar M., Ajamein H. (2014): Urea–nitrate combustion synthesis of ZrO_2 and CeO_2 doped CuO/Al_2O_3 nanocatalyst used in steam reforming of biomethanol for hydrogen production. *Ceramics International*, *40*(9), 14177-14184. doi:10.1016/j.ceramint.2014.06.005
15. Belhouchet H., Hamidouche M., Bouaouadja N., Garnier V., Fantozzi G. (2009): Elaboration and characterization of mullite–zirconia composites from gibbsite, boehmite and zircon. *Ceramics- Silikaty*, *53*(3), 205-210.
16. Bodišová K., Pach L., Kovar V., (2005): The influence of the preferred orientation of boehmite crystallites on α-Al_2O_3 crystallization. *Ceramics−Silikáty*, *49*(1), 34-39.
17. Yahyavi S.R., Haghighi M., Shafiei S., Abdollahifar M., Rahmani F. (2015): Ultrasound-assisted synthesis and physicochemical characterization of $Ni–Co/Al_2O_3$–MgO nanocatalysts enhanced by different amounts of MgO used for CH_4/CO_2 reforming. *Energy Conversion and Management*, *97*, 273-281. doi:10.1016/j.enconman.2015.03.064
18. Zhang X., Wu Y., Liu G., He S., Yang D. (2008): Investigation on sol–gel boehmite-AlOOH films on Kapton and their erosion resistance to atomic oxygen. *Thin Solid Films*, *516*(15), 5020-5026. doi:10.1016/j.tsf.2008.01.023
19. Hou H., Xie Y., Yang Q., Guo Q., Tan C. (2005): Preparation and characterization of γ-AlOOH nanotubes and nanorods. *Nanotechnology*, *16*(6), 741. doi:10.1088/0957-4484/16/6/019
20. Abdollahifar M., Karami A.R., Haghnazari N., Karami C. (2015): Synthesis of porous boehmite nanostructures: effects of time and temperature in the hydrothermal method. *Ceramics-Silikáty*, *59*(4), 305-310.
21. Ameri E. Abdollahifar M., Zamani M.R., Nekouei H. (2016): The role of urea on the hydrothermal synthesis of boehmite nanoarchitectures. *Ceramics-Silikáty*, *60*(2), 162-168. doi:10.13168/cs.2016.0025
22. Li G., Liu Y., Liu D., Liu L., Liu C. (2010): Synthesis of flower-like Boehmite (AlOOH) via a simple solvothermal process without surfactant. *Materials Research Bulletin*, *45*(10), 1487-1491. doi:10.1016/j.materresbull.2010.06.013
23. Holkova Z., Pach L., Majling J., Kakos J., Kadlecikova M. (2003): Effect of organic additives on crystallization of boehmite gels. *Ceramics- Silikaty*, *47*(4), 149-154.
24. Zhao X., Ji X., Zhang Y., Lu B. (2004): Effect of solvent on the microstructures of nanostructured Bi_2Te_3 prepared by solvothermal synthesis. *Journal of Alloys and Compounds*, *368*(1), 349-352. doi:10.1016/j.jallcom.2003.08.070
25. Chen X.Y., Huh H.S., Lee S.W. (2007): Hydrothermal synthesis of boehmite (γ-AlOOH) nanoplatelets and nanowires: pH-controlled morphologies. *Nanotechnology*, *18*(28), 285608. doi:10.1088/0957-4484/18/28/285608
26. Hicks R.W., Pinnavaia T.J. (2003): Nanoparticle assembly of mesoporous AlOOH (boehmite). *Chemistry of Materials*, *15*(1), 78-82. doi:10.1021/cm020753f
27. Sing K.S.W., Everett D.H., Haul R.A.W. Moscou L., Pierotti R.A., Rouquerol J., Siemieniewska T. (1985): Reporting physisorption data for gas/solid systems – with special reference to the determination of surface area and porosity. *Pure and Applied Chemistry*, *57*(4), 603-619.doi:10.1351/pac198557040603