

SYNTHESIS OF POROUS BOEHMITE NANOSTRUCTURES: EFFECTS OF TIME AND TEMPERATURE IN THE HYDROTHERMAL METHOD

#MOZAFFAR ABDOLLAHIFAR*, ALI REZA KARAMI**, NAHID HAGHNAZARI*, CHANGIZ 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 July 29, 2015; accepted October 19, 2015

Keywords: Boehmite, Nanostructures, Hydrothermal processing, Mesopores, Specific surface area

A hydrothermal approach has been employed for the synthesis of different morphologies of porous γ -AlOOH nanostructures using $Al(NO_3)_3$ and urea as raw materials with urea/nitrate molar ratio of 2. The effect of time and temperature of hydrothermal reaction on the morphologies of synthesized γ -AlOOH were investigated. Samples subjected to different reaction durations from 6 h to 24 h and various temperatures were prepared. The samples were characterized by X-ray diffraction (XRD), transmission electronic microscopy (TEM), field emission scanning electron microscope (FESEM), Fourier transform infrared spectrometry (FTIR) and N_2 adsorption/desorption. X-ray powder diffraction indicated that all samples were single-phase γ -AlOOH. Our results showed that a change in the synthesis conditions may lead to marked differences in the morphology of porous γ -AlOOH. The surface area of samples decreases with increasing of reaction temperature and decreasing time duration in hydrothermal route.

INTRODUCTION

In recent years, much effort has been focused on the preparation of γ -AlOOH (boehmite or aluminium oxyhydroxide) nanomaterials because they can serve as adsorbents and catalysts for chemical processes, coatings on various substrates, membranes, alumina-derived ceramics [1-9], vaccine adjuvant [10] and can be a precursor used to obtain γ - Al_2O_3 [1, 3]. γ - Al_2O_3 is of much importance in areas of catalysts and catalyst supports [2, 6, 7, 9]. Because of these applications, many researchers focused on the relation between the synthesis of γ -AlOOH and its chemical and physical properties. Controlling particle size and morphology is hence of the greatest interest to improve the potentialities of boehmite.

Various γ -AlOOH synthesis procedures have been investigated in the literature in order to control particle size and morphology and porosity of produced powders. A common way is the neutralization of acidic salts, via direct addition of a base [11]. Many parameters have to be considered: pH and temperature of course, nature of salts and bases [3, 12-15] Besides neutralization of aluminium salts, hydrothermal [13], sol-gel [16] and solvothermal [17] techniques can also be used to obtain γ -AlOOH. The complexity of the mechanisms involved

in the formation of precursors leading to different structures of boehmite using various methods explains the long-term research interest in this subject.

In this paper, we compare a simple way for controlling particle morphology of γ -AlOOH nanostructures by studying the effects of time duration and temperature in the case of neutralization of aluminium nitrate by urea with fixed urea/nitrate molar ratio of 2.

EXPERIMENTAL

All the chemical materials used in our experiments are analytical grade without further purification, Aluminium nitrate and urea solutions were prepared with $Al(NO_3)_3 \cdot 9H_2O$ and urea, CH_4N_2O supplied by Scharlau, Spain. Doubly distilled water was used in all the experiments.

According to a procedure described elsewhere [3], 18.75 g of $Al(NO_3)_3 \cdot 9H_2O$ and 6 g of urea, CH_4N_2O with a molar ratio of 1:2 were dissolved into 100 ml and 30 ml of distilled water at room temperature in a beaker and magnetically stirred to obtain a homogeneous solution (A) and (B), respectively. Then solution (B) was added to solution (A), and then the mixed solutions were transferred into a 200 ml Teflon-lined stainless autoclave

and heated at 150 - 200°C for 6 - 24 h under autogenous pressure. After reaching room temperature, the precipitate was filtered, washed three times with distilled water, and finally dried in an oven at 60°C for 24 h in air; the dried samples are γ -AlOOH. Moreover, the effects of growth conditions, such as temperature and reaction durations, on the morphology of γ -AlOOH nanostructures were investigated. The detailed experimental parameters concerning heating temperature and reaction time for corresponding samples are listed in Table 1.

Table 1. Summary of the experimental details for synthesized AlOOH.

Sample name	Time (h)	Temperature (°C)
a	24	150
b	"	175
c	"	200
d	12	"
e	6	"

Fourier transform infrared spectroscopy (FTIR) were performed on a RAYLEIGH WQF-510 spectrometer and X-ray powder diffraction (XRD) analysis on a BRUKER B8 ADVANCE X-ray diffractometer with $\text{CuK}\alpha$ radiation. Typically, a scanning velocity of $1.5^\circ \cdot \text{min}^{-1}$ was used to scan the peaks of the boehmite diffraction pattern in the 2θ range between 5 and 80° . TEM images of the samples were taken using a PHILIPS CM30 transmission electron microscope at an accelerating voltage of 250 kV. FESEM images were obtained using a HITACHI S-4160 field emission scanning electron microscope. The nitrogen adsorption and desorption isotherms at 77 K were measured using a BEL SORP, MINI II-310 adsorption analyzer after degassing the samples in a vacuum at 200°C for 3 h. The Barrett-Joyner-Halenda (BJH) method was applied for the calculation of pore size distributions using the adsorption branch of the isotherms and specific surface areas and pore volume were determined by the Brunauer-Emmett-Teller (BET) and t-plot method.

RESULTS AND DISCUSSIONS

X-ray powder diffraction indicated that all samples were single-phase γ -AlOOH, in accordance with the Powder Diffraction card no. 21-1307 (space group *Amam*, unit-cell parameters, $a = 3.700$, $b = 12.227$, and $c = 2.868$ Å at 25°C). No peaks for other phases such as $\text{Al}(\text{OH})_3$ or Al_2O_3 were observed, indicating its high purity. The main peaks of γ -AlOOH in the XRD pattern are narrowed implying that the γ -AlOOH nanostructures are well crystallized. With increasing reaction time and temperature, samples have a tendency to crystallite

growth (from XRD patterns of these samples as shown in Figure 1). More specifically, it can be observed that the intensity of the peak corresponding to the (020) crystal plane is extraordinarily strong as compared to other peaks. It is known that facets with a slower growth rate will be exposed more on the crystal surface and consequently exhibit relatively stronger diffraction intensity in the corresponding XRD patterns [18]. Therefore, it can be concluded that the (020) facets exhibit a relatively slower growth rate in the boehmite samples. This phenomenon is known from the standard pattern and also indicates the high purity of the samples [18, 19].

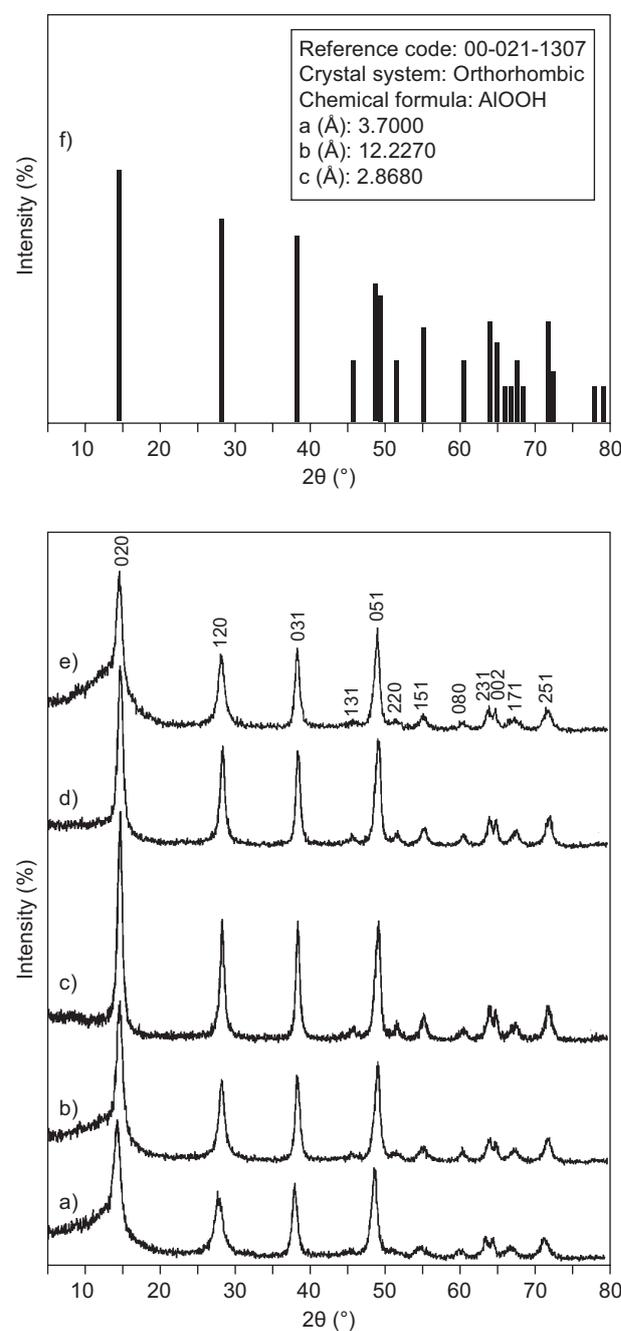


Figure 1. XRD patterns of prepared samples.

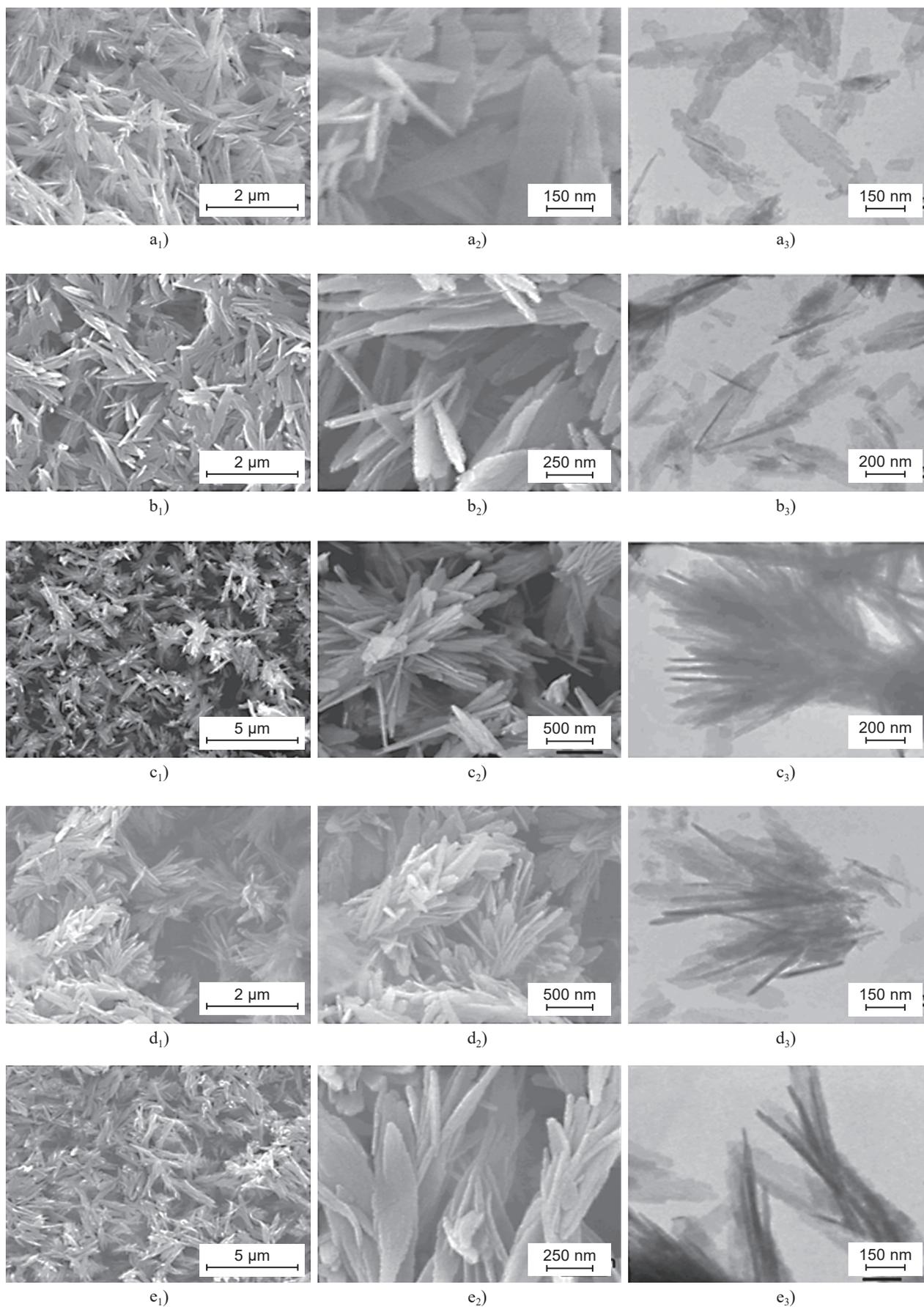


Figure 2. FESEM and TEM images of prepared samples.

In order to further ascertain the chemical compositions of the γ -AIOOH structures, the products were examined by FTIR spectroscopy. As indicated in Figure 3, the absorption bands at around 3410, 3091, 1638, 1069, 748, 612 and 480 cm^{-1} were clearly observed. In detail, the three bands around 748, 612, and 480 cm^{-1} represented the vibration mode of AlO_6 . The band around 1069 cm^{-1} was assigned to the $\delta_s(\text{Al-O-H})$ mode of boehmite, the shoulder around 1638 cm^{-1} to the bending mode of absorbed water, and the intensive bands around 3410 and 3091 cm^{-1} to $\nu_{as}(\text{Al-O-H})$ and $\nu_s(\text{Al-O-H})$ stretching vibrations. The above FTIR

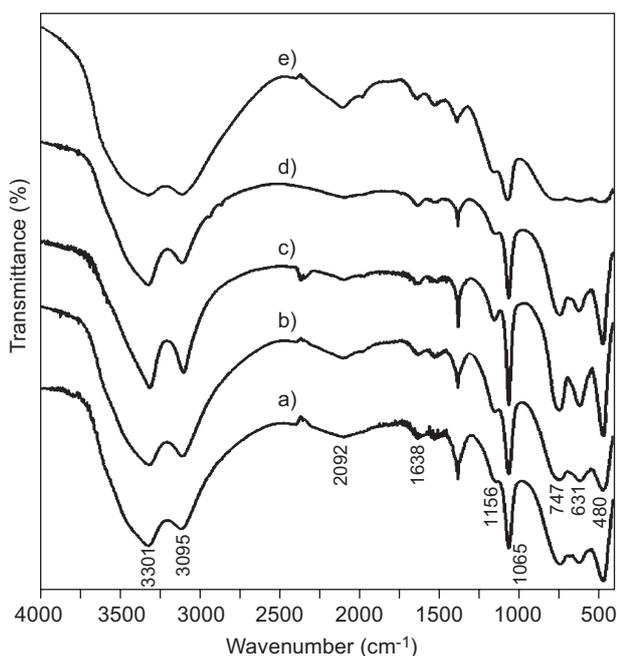


Figure 3. FTIR spectrums of prepared samples.

analysis matches well with the XRD result, confirming that with increasing reaction time and temperature, the peak height were increased and samples have a tendency to crystallite growth. The products are pure phase γ -AIOOH.

The FESEM and TEM images with different magnifications in Figure 2 show the influence of the time and temperature of reaction in the hydrothermal route on the morphology of the synthesized γ -AIOOH samples. As shown in the a and b series of Figure 2 especially the enlarged FESEM images in Figure 2a₂ and b₂, these boehmite samples have uniform lamellar morphology. As can be seen from the micrographs, although the lamellar boehmite products overlapped each other, their boundaries could still be clearly distinguished, thus indicating that each lamellar product has accomplished its morphology evolution process completely in 24 h at 150 (a series) and 175°C (b series). Figure 2c shows the FESEM and TEM images of γ -AIOOH flower-like nanostructures, when time is 24 h and its reaction temperature was 200°C, which is described in another work [3].

When the time of reaction was decreased from 12 h to 6 h (Figure 2d and c, respectively) at a temperature of 200°C, three-dimensional lamellar assemblies were observed with other morphologies, such as irregular agglomerates (see Figure 2d series) and bow tie-like in the Figure 2e, indicating a very high yield of three-dimensional lamellar assemblies.

Table 2 lists the results of textural properties of synthesized AIOOH nanostructures. The total surface areas estimated from the t-plot are consistent with the BET surface areas.

The N_2 sorption isotherms and pore size distribution of the samples synthesized with different time and

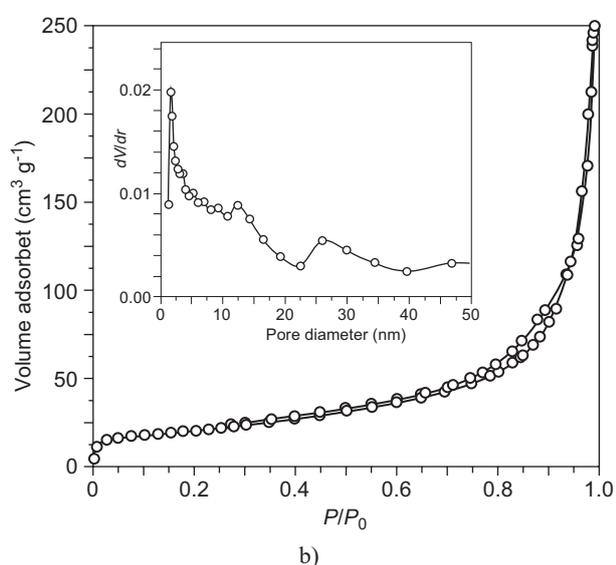
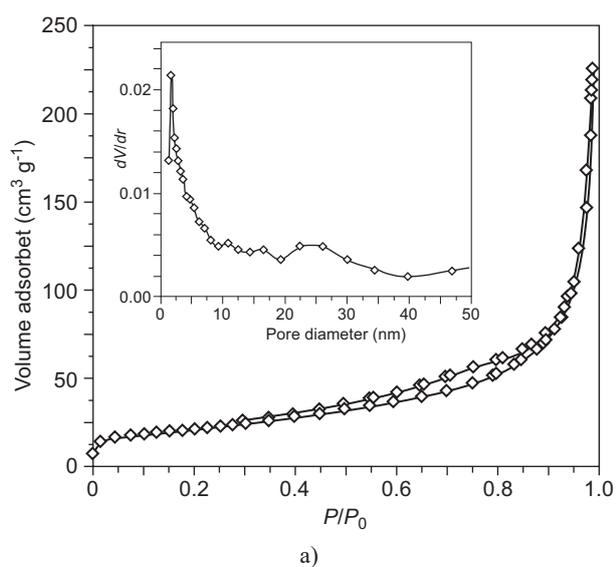
Table 2. Textural properties of synthesized AIOOH.

Sample name	S_{total}^a ($\text{m}^2\cdot\text{g}^{-1}$)	S_{total}^b ($\text{m}^2\cdot\text{g}^{-1}$)	V_p^c ($\text{cm}^3\cdot\text{g}^{-1}$)	V_p^d ($\text{cm}^3\cdot\text{g}^{-1}$)	V_{mic}^e ($\text{cm}^3\cdot\text{g}^{-1}$)	V_{mes}^f ($\text{cm}^3\cdot\text{g}^{-1}$)	D_p^g (nm)
a	74.4	82	0.33	0.32	0.10	0.22	17.7
b	71.5	80	0.37	0.36	0.09	0.27	20.9
c	69.2	75	0.36	0.36	0.09	0.27	21.1
d	68.1	73	0.35	0.35	0.08	0.27	22.0
e	66.1	71	0.33	0.32	0.09	0.23	19.6

^a total surface area from BET method; ^b total surface area from t-plot; ^c total pore volume from BET method; ^d total pore volume from BJH method; ^e microporosity; ^f mesoporosity; ^g average pore diameter.

Table 3. Porosity structures and positions of synthesized AIOOH.

Sample name	Microporosity (%)		Mesoporosity (%)					
	≥ 2 nm		2-5 nm	5-10 nm	10-15 nm	15-25 nm	25-40 nm	40-50 nm
a	31.54		36.41	13.53	6.15	6.11	3.70	2.53
b	26.96		32.98	18.31	9.38	5.27	4.37	2.69
c	26.22		34.26	18.45	9.46	5.44	3.86	2.27
d	23.37		31.02	18.91	11.55	7.12	5.24	2.76
e	27.70		35.65	17.44	7.59	5.29	3.95	2.34



temperature of reaction are illustrated in Figure 4. All the samples exhibit type IV isotherms with clear H3 type hysteresis loops at high relative pressure [20]. This adsorption characteristic was usually attributed to adsorption in mesopores, which were classified by IUPAC [20] as pores of diameter 2 - 50 nm. However, the samples shows a steep increase in adsorption at $P/P_0 = 0.4 - 0.9$. When temperature increased and time of reaction decreased, there were an insignificant decrease in the specific surface area from $74.4 \text{ m}^2 \cdot \text{g}^{-1}$ to $66.1 \text{ m}^2 \cdot \text{g}^{-1}$. As can be seen from the curves of adsorption and desorption is not a reversible phenomenon which leads to the appearance of a hysteresis between the curves of adsorption and desorption. Interestingly, a change in the synthesis conditions may lead to marked differences in the morphology properties (see Figure 4) but not in the specific surface area and pore volume of

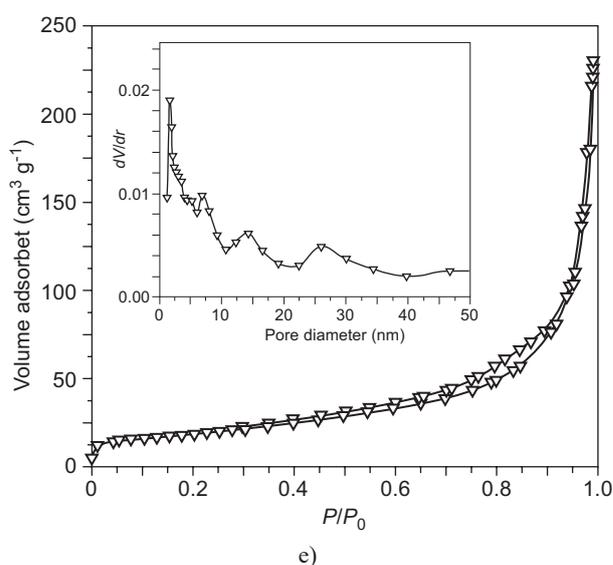
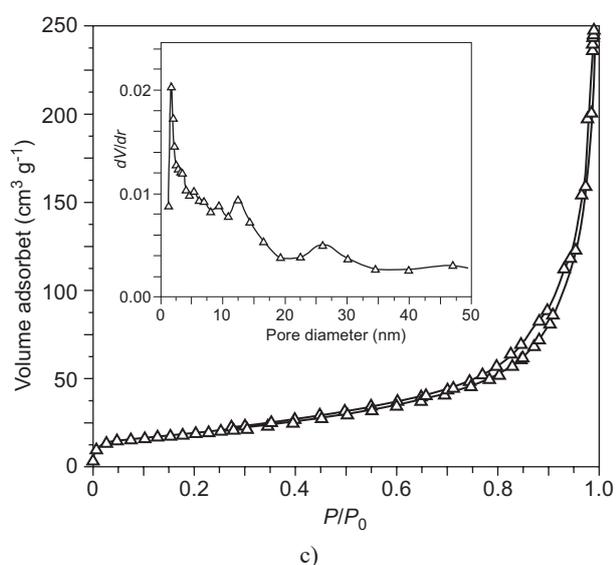
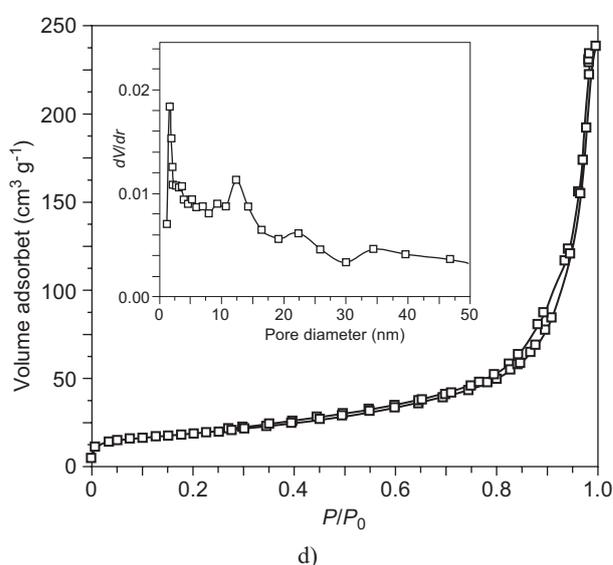


Figure 4. Nitrogen adsorption/desorption isotherms and pore-size distributions of samples prepared at different conditions listed in Table 3.

samples. The pore size distribution curves in this figure for all samples show one narrow and some wide modes which are listed in Table 3. However, the narrow mode at around 2 nm is well-known artefact [21]. It can be seen that the intensity of peaks in the samples changed with different conditions

CONCLUSIONS

Porous γ -AlOOH nanostructures have been successfully synthesized via hydrothermal method using $\text{Al}(\text{NO}_3)_3$ and urea (urea/nitrate = 2) as the starting materials. The time duration and temperature of hydrothermal reaction play important roles in the formation of the various γ -AlOOH morphologies. It has been found that a change in the synthesis conditions may lead to marked differences in the morphology. The surface area of samples decreases with increasing of reaction temperature and decreasing time duration. This study might open an opportunity for synthesis of γ -AlOOH nanostructures with different morphology and broaden their applications in the field of ceramics, adsorbents and catalysts.

Acknowledgements

Supports by Islamic Azad University, Kermanshah Branch are greatly acknowledged.

REFERENCES

1. Abdollahifar M.: *J. Chem. Res.* **38**, 154 (2014)
2. Abdollahifar M., Haghghi M., Babaluo A.A.: *J. Ind. Eng. Chem.* **20**, 1845 (2014)
3. Abdollahifar M., Zamani R.M., Beiygie E., Nekouei H.: *J. Serb. Chem. Soc.* **79**, 1007 (2014)
4. Alemi A., Hosseinpour Z., Dolatyari M., Bakhtiari A.: *Physica Status Solidi B* **249**, 1264 (2012)
5. Arami H., Mazloumi M., Khalifehzadeh R., Sadrnezhad S.: *J. Alloys Compd.* **461**, 551 (2008)
6. Baneshi J., Haghghi M., Jodeiri N., Abdollahifar M., Ajamein H.: *Ceram. Int.* **40**, 14177 (2014)
7. Baneshi J., Haghghi M., Jodeiri N., Abdollahifar M., Ajamein H.: *Energy Convers. Management* **87**, 928 (2014)
8. Kwon M.S., Kim N., Park C.M., Lee J.S., Kang K.Y., Park J.: *Org. Lett.* **7**, 1077 (2005)
9. Shokrani R., Haghghi M., Jodeiri N., Ajamein H., Abdollahifar M.: *Int. J. Hydrogen Energy.* **39**, 13141 (2014)
10. Rimaniol A.-C., Gras G., Verdier F., Capel F., Grigoriev V.B., Porcheray F., Sauzeat E., Fournier J.-G., Clayette P., Siegrist C.-A.: *Vaccine* **22**, 3127 (2004)
11. Karouia F., Boualleg M., Digne M., Alphonse, P.: *Powder Technol.* **237**, 602 (2013)
12. Cai W., Yu J., Mann S.: *Microporous Mesoporous Mater.* **122**, 42 (2009)
13. Haghazari N., Abdollahifar M., Jahani F.: *J. Mex. Chem. Soc.* **58**, 95 (2014)
14. Pania D., Krestou A.: *Powder Technol.* **175**, 163 (2007)
15. Zhang L., Lu W., Yan L., Feng Y., Bao X., Ni J., Shang X., Lv Y.: *Microporous Mesoporous Mater.* **119**, 208 (2009)
16. Zhang J., Liu S., Lin J., Song H., Luo J., Elssfah E., Ammar E., Huang Y., Ding X., Gao J.: *J. Phys. Chem. B* **110**, 14249 (2006)
17. Li G., Liu Y., Liu D., Liu L., Liu C.: *Mater. Res. Bull.* **45**, 1487 (2010)
18. Roh H.-S., Choi G.K., An J.-S., Cho C.M., Kim D.H., Park I.J., Noh T.H., Kim D.-W., Hong K.S.: *Dalton Trans.* **40**, 6901 (2011)
19. Feng Y., Lu W., Zhang L., Bao X., Yue B., Lv Y., Shang X.: *Cryst. Growth Des.* **8**, 1426 (2008)
20. Sing K., Everett D., Haul R., Moscou L., Pierotti R., Rouquerol J., Siemieniowska, T.: *Pure Appl. Chem.* **57**, 603 (1985)
21. Gregg S., Sing, K.: *Adsorption, Surface Area, & Porosity*, 2nd Ed., Academic Press, Inc., New York 1982.