



## A Comparative Study on Characterization of 12-Tungstophosphoric Acid Cesium Salt Depending on Synthesis Methods

ELIF ÖDES AKBAY\* and GÜLBERK DEMİR

Anadolu University, Department of Chemical Engineering, Eskisehir, 26470, Turkey

\*Corresponding author: E-mail: eodes@anadolu.edu.tr

Received: 9 November 2013;

Accepted: 4 April 2014;

Published online: 1 September 2014;

AJC-15854

12-Tungstophosphoric acid cesium salt,  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ , exhibits high catalytic activity for various kinds of acid-catalyzed reactions. This excellent catalytic effect of  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  is attributed to its strong acidity, hydrophobicity, unique pore structure, *etc.* In this study, the methods published in the literature were modified by monitoring the aging, atmospheric drying-vacuum drying and calcination, addition rate of  $\text{Cs}_2\text{CO}_3$  solution to 12-tungstophosphoric acid solution to enhance the surface properties of Cs-12-tungstophosphoric acid such as the surface area and porosity. The characteristic of the synthesized Cs-12-tungstophosphoric acid were obtained by the XRD, FTIR, SEM, TG-DTG, particle distribution and crystallite size and the results were compared with the finding in literature. The each modified methods have different effect on the BET surface area and porosity. The sample coded by 01G50V showed the highest surface area with 4.5 nm pore diameter among synthesized 12-tungstophosphoric acid cesium salt.

**Keywords:** 12-Tungstophosphoric acid, Cesium salt, Impregnation methods.

### INTRODUCTION

Catalysis by heteropoly acids (HPAs) and related polyoxo-metalate compounds is a field of increasing importance and attracting increasing attention worldwide, in which many new and exciting developments are taking place in both research and technology<sup>1</sup>. Heteropoly acids are generally used as catalysts in commercially important process such as hydrocracking, hydrogenation and isomerization. However, heteropoly acid is not preferred as a liquid catalyst in industrial applications, because there will be required additional processes such as purification of the products. Hence, the synthesis of the salt of heteropoly acid catalysts are insoluble in water and in organic solvents are very important<sup>2</sup>.

Heteropoly acids of various heterogeneous catalysts have drawn attention due to their unique features such as well-defined structure, Bronsted acidity, high proton mobility, the ability to exchange electrons<sup>3,4</sup>. As a heteropoly acid, 12-tungstophosphoric acid,  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ , is known as a strong acid and it is considered within the class of super acid<sup>5</sup>. The substitution of protons such as  $\text{Cs}^+$ ,  $\text{K}^+$ ,  $\text{Ag}^+$  and  $\text{NH}_4^+$  can enhance the porosity and surface area as well as the insolubility.

12-Tungstophosphoric acid cesium salt,  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ , has high surface area thus it exhibits high catalytic activities for various kinds of acid-catalyzed reactions<sup>6-8</sup>. This excellent catalytic effect of  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  is attributed to the strong

acidity, hydrophobicity, unique pore structure, *etc.*<sup>9</sup>. It was reported that many reactions were effectively catalyzed by  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  in a solid-liquid reaction system.  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  is an interesting candidate for preference, as a 'water-tolerant' catalyst because of its insolubility in organic and aqueous media, in contrast with  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ <sup>10</sup>.

Therefore there are available studies about this catalyst on a micro-scale synthesis, characterization and catalytic activity in reactions in literature. Among these studies, the study by Okuhara *et al.*<sup>11</sup> is very important to review acidic cesium salt synthesis and its micro-structure. They synthesized the catalyst by impregnation technique at different ratio of cesium and characterized it by NMR, XRD, SEM. They concluded that among cesium salts,  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  ( $x = 1, 2, 2.5$  and  $3$ ),  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  was to be the most effective catalyst because of having highest activity.

In the other study, to evaluate the effects of the content of cesium, the catalyst was prepared having different cesium content,  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  ( $x = 1, 2, 2.5$  and  $3$ ) and characterization was performed using FTIR, XRD and P-MAS NMR. It was shown that the distribution of proton and cesium ion in the salts structures is nearly homogeneous and surface acidity increases sharply as the cesium content increases and it reaches the maximum in  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  salt. On the other hand, it was also shown that  $\text{Cs}^+$  ions are completely settled in  $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$  salt no showing Bronsted acidity<sup>12</sup>.

Therefore,  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  salt called Keggin-type tungstophosphates, possess super acidity and effective in many acid-catalyzed reactions such as alkylation of aromatics<sup>13,14</sup>, skeletal isomerization of *n*-butane<sup>15-17</sup>, hydrolysis of esters in excess water<sup>18</sup>, hydration of olefins in a solid-water reaction system<sup>19</sup>, esterification of palmitic acid and transesterification of tributyrin<sup>20</sup>.

The aim of this study is to determine the best conditions of impregnation method for synthesis of 12-tungstophosphoric acid cesium salt (Cs-TPA). The methods published in the literature were modified by making some change the aging, atmospheric drying-vacuum drying, calcination and addition rate of  $\text{Cs}_2\text{CO}_3$  solution to 12-tungstophosphoric acid solution to enhance the physical properties of salt such as surface area and porosity. The other properties of the synthesized Cs-TPA were also determined by the XRD, FTIR, SEM, TG-DTG, particle distribution and crystallite size and the results were compared with the finding of literature.

## EXPERIMENTAL

The chemicals used in the preparation of catalysts, 12-tungstophosphoric acid hydrate ( $\text{H}_3\text{PW}_{12}\text{O}_{40} \times \text{H}_2\text{O}$ ) and cesium carbonate ( $\text{Cs}_2\text{CO}_3$ ) were purchased from Merck and Alfa Aesar, respectively. Deionized water was used though out in experiments.

**Synthesis of Cs-TPA:** 0.1 M aqueous solution of  $\text{Cs}_2\text{CO}_3$  and 0.08 M aqueous solution of 12-tungstophosphoric acid hydrate were prepared. Then, 20 cm<sup>3</sup> of aqueous solution of  $\text{Cs}_2\text{CO}_3$  was added to 20 cm<sup>3</sup> of aqueous solution of 12-tungstophosphoric acid hydrate with a constant rate of about 1 and 0.1 cm<sup>3</sup>/min at room temperature, under vigorous stirring. The other parameters used at each addition rate of  $\text{Cs}_2\text{CO}_3$  solution is shown in Table-1.

TABLE-1

No.	Sample name	Addition rate (mL/min)	Synthesis method
1	01G50E	0.1	Aging over night drying with drying-oven at 50 °C
	1G50E	1.0	
2	01G50V	0.1	Aging over night drying with vacuum oven at 50 °C
	1G50V	1.0	
3	01G110V	0.1	Aging over night drying with vacuum oven at 110 °C
	1G110V	1.0	
4	01110V	0.1	Drying with vacuum oven at 110 °C
	1110V	1.0	
5	01110V473K	0.1	Drying with vacuum oven at 110 °C calcination at 200 °C
	1110V473K	1.0	

**Characterization of Cs-TPA:** The crystallinity and the phase purity of synthesized samples were analyzed by X-ray diffraction (XRD) patterns using X-ray diffractometer (Rigaku Rind 2000, Japan) and  $\text{CuK}\alpha$  (1.54 Å) radiation (30 kV-40 mA). The scanning was done from  $2\theta = 80^\circ$  to  $2\theta = 5^\circ$  at a rate of  $2^\circ \text{ min}^{-1}$ . FTIR studies of the catalysts were conducted by using a Bruker IFS-66 single channel Fourier transform spectrophotometer, pellet in KBr and a measuring range of 400-4000  $\text{cm}^{-1}$ . Scanning electron microscopy (SEM) results were obtained on the Zeiss Supra 50 VP Microscope with 20 kV accelerating voltage. Thermogravimetry analysis were

performed under dry air, using 80 mg samples and heating rates  $10^\circ \text{C}/\text{min}$ . The studied temperature range  $20\text{-}900^\circ \text{C}$ . The particle size distribution in water was analyzed by laser diffraction method using a Malvern Hydro 2000G analyzer. TG-DTG measurements of sample were carried out using Netzsch Sta 409 PC/PG thermal analyzer. The BET (Brunauer-Emmett-Taller) specific surface area was obtained from  $\text{N}_2$  adsorption-desorption isotherm measured at 77 K in an automatic adsorption apparatus (ASAP2020; micrometric). Prior to measurement, samples were degassed at  $100^\circ \text{C}$  for about 2 h.

## RESULTS AND DISCUSSION

All synthesized Cs-TPA and TPA have been characterized by using XRD patterns due to basic analytical techniques. Diagrams obtained from the analysis is shown in Fig. 1.

Fig. 1 shows that the XRD patterns of all synthesized 12-tungstophosphoric acidsalts is in the  $2\theta$  range of  $5\text{-}80^\circ$  and all Cs-TPAs are identical with each other. The patterns for the Cs-TPA exhibits the characteristic lines of TPA structure and

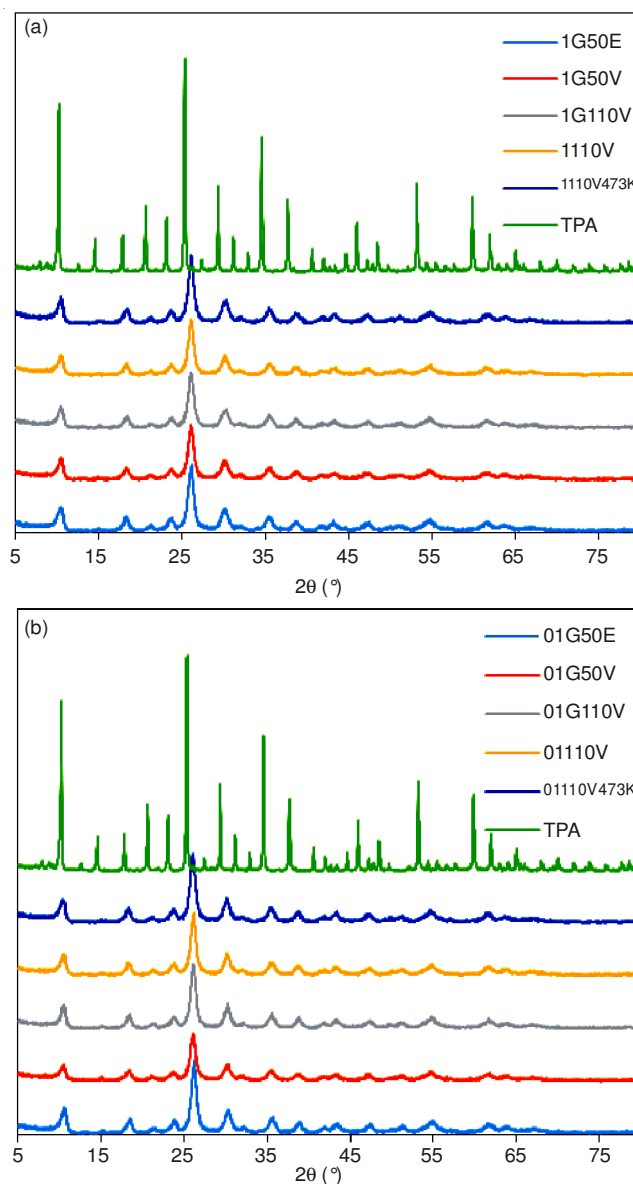


Fig. 1. XRD diagrams for (a) synthesized catalysts with 1 mL/min addition rate (b) synthesized catalysts with 0.1 mL/min addition rate

are in agreement with published data<sup>21,22</sup>. It can be also seen that the location of XRD peaks of Cs-TPA is very similar to that of pure TPA indicating that the Cs salt has similar crystalline structure as the pure TPA. However, the main peaks depicting TPA are shifted towards slightly to higher angles in Cs-TPA<sup>23</sup>.

Fourier transform-infrared spectroscopy analysis (FT-IR) Cs-TPAs was characterized by using FT-IR to investigate structure of catalysts. The results are shown in Fig. 2.

Basic structure of synthesized Cs-TPAs were explained by comparing its absorbance with that of TPA using FT-IR analysis. FT-IR bands of pure TPA (Fig. 3), have six characteristic peaks of Keggin structure observed at 1080 cm<sup>-1</sup> (P-O in central tetrahedral), 990 cm<sup>-1</sup> (W = O<sub>t</sub> terminal oxygen in the Keggin structure), 882 and 804 cm<sup>-1</sup> (W-O<sub>c</sub>-W), 582 and 516 cm<sup>-1</sup>, which coincides with those referred in the literature<sup>22,24-27</sup>. The FT-IR spectrum of Cs-TPA salt exhibits similar characteristic bands compared with that of pure TPA. It was also that all Cs-TPAs have very similar FT-IR bands with each other. However, the typical vibration of the W = O<sub>t</sub> = 990 cm<sup>-1</sup> in TPA is shifted to 985 cm<sup>-1</sup> in Cs-TPA. This shift shows the interaction between Cs<sup>+</sup> and W = O<sup>23</sup>.

**Scanning electron microscopy (SEM):** Because of the similarity of the samples, the surface morphology of Cs-TPA coded by 01G50V and 1G50V are only given in Fig. 3. The other synthesized Cs-TPA have similar SEM images. In the images, it is seen that Cs-TPA are having irregular shape with well-defined crystalline particles. These observations are in accordance with literature<sup>11,28-30</sup>.

**Particle size distribution and crystallite size:** A laser diffraction technique afforded the size of the all synthesized Cs-TPA. The particle size distribution of Cs-TPA dispersed in water is shown in Fig. 4. The particles size varies between 40 to 450 nm. Average particle size for all Cs-TPA are 124 and 112 nm for synthesized catalysts with 0.1 and 1 mL/min addition rate of Cs<sub>2</sub>CO<sub>3</sub> solution to TPA solution, respectively.

The crystallite sizes of all synthesized Cs-TPA were obtained by using Scherrer's equation using XRD data from Fig. 1.  $D = k\lambda/\beta \cos \theta$  where D is crystallite size,  $\lambda$  is the radiation wavelength (1.5406 Å),  $\beta$  is the peak full width at half maximum (FWHM),  $\theta$  is the diffracting angle and  $k = 0.90$  for spherical shape particle. It was found that the average crystallite size of all synthesized Cs-TPA is approximately the same and average value of it is to be 12.54 nm.

**Thermal gravimetric analysis:** The thermal analyses have been carried out on all synthesized Cs-TPA and TPA. The results of these analyses are shown in Fig. 5. The TG and DTG curves of 12-tungstophosphoric acid show a weight loss of about 4 % up to a temperature of 300 °C, indicating loss of free and adsorbed water. The gradual weight loss of about 1 % up to 700 °C corresponds to the mass loss due to the reaction between acidic protons and structural oxygen from 12-tungstophosphoric acid, releasing water, followed by decomposition to WO<sub>3</sub> and PO<sub>x</sub> species<sup>31</sup>. All synthesized Cs-TPA showed a weight loss below 200 °C, indicating loss of free and adsorbed water. Between temperature of 200-900 °C, there is no weight loss of Cs-TPA because of its chemical

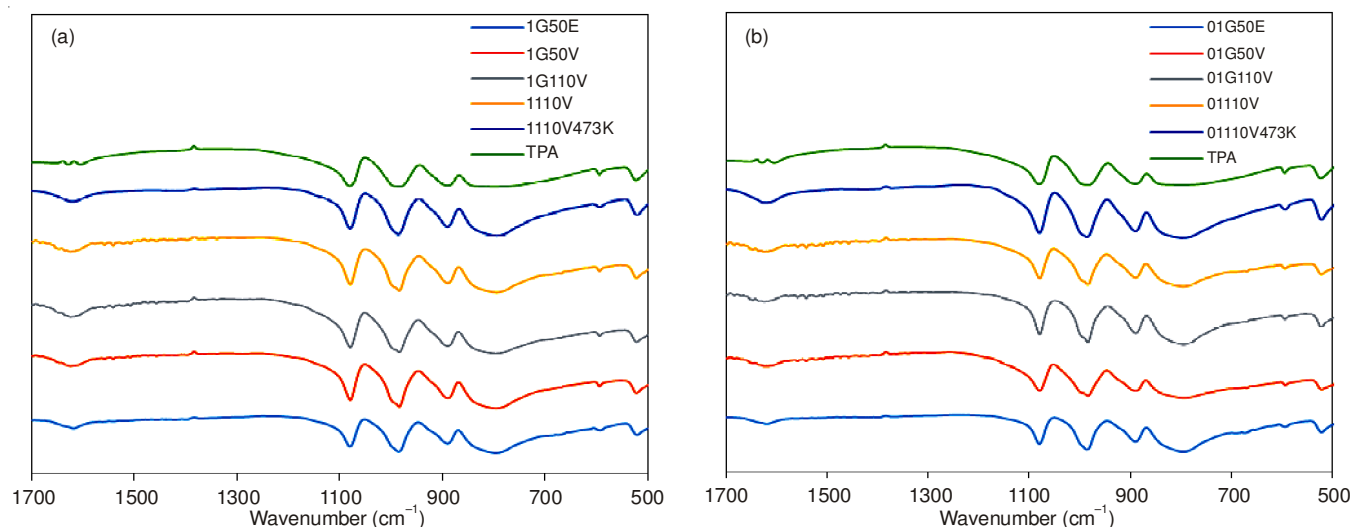


Fig. 2. FT-IR spectrums for (a) synthesized catalysts with 1 mL/min addition rate (b) synthesized catalysts with 0.1 mL/min addition rate

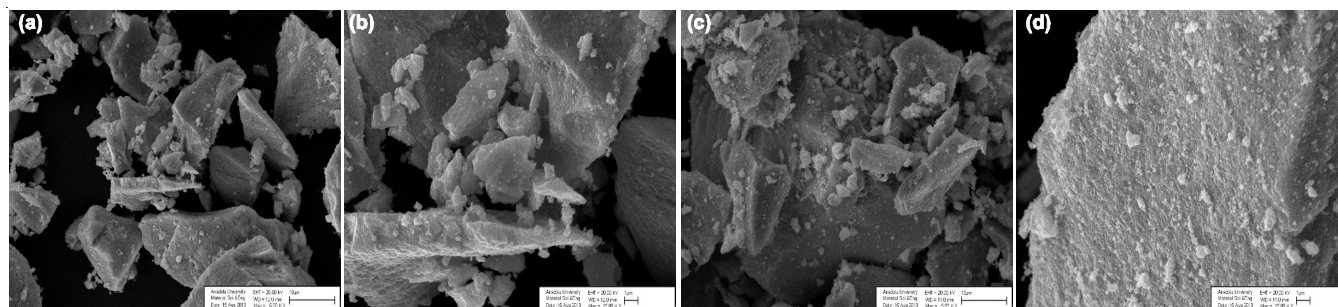


Fig. 3. SEM images of (a) and (b) synthesized catalysts with 1 mL/min addition rate (c) and (d) synthesized catalysts with 0.1 mL/min addition rate at 5 KX and 15 KX, respectively

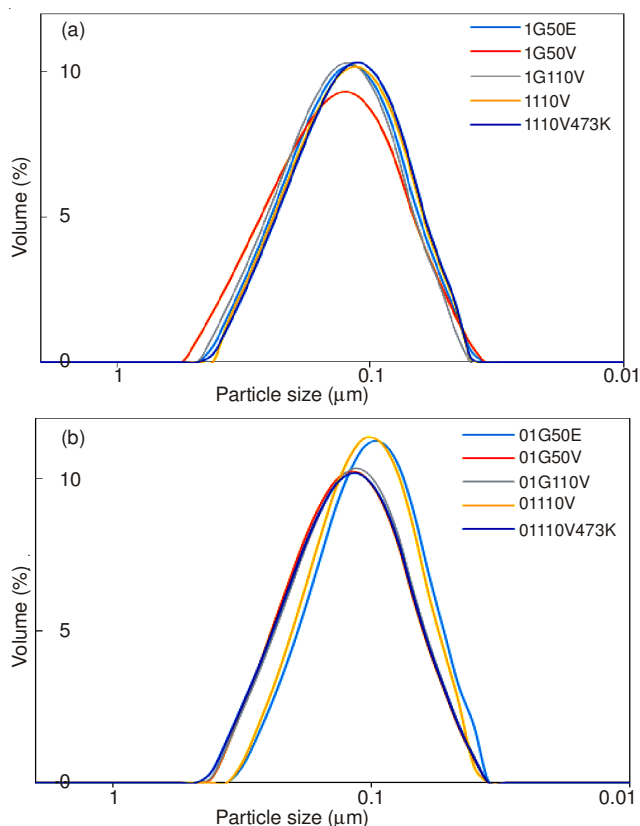


Fig. 4. Particle size distribution for (a) synthesized catalysts with 1 mL/min addition rate (b) synthesized catalysts with 0.1 mL/min addition rate

stability. This chemical stability show that all Cs-TPA was synthesized successfully<sup>23</sup>.

**N<sub>2</sub> adsorption/desorption analysis:** Single and multi-point BET are as, average pore diameters and pore volumes are determined by N<sub>2</sub> adsorption analysis. The results are given in Table-2.

Sample name	Surface area (m <sup>2</sup> /g)			Pore Diameter, d <sub>BH</sub> (Å)	Pore Volume, V <sub>BH</sub> (cm <sup>3</sup> /g)
	BET (multi point)	BET (single point)	S <sub>BH</sub>		
1G50E	88.739	143.399	95.983	40.961	0.09829
01G50E	93.482	140.106	98.523	45.651	0.11244
1G50V	90.644	147.895	94.975	48.307	0.11469
01G50V	96.801	148.538	102.054	40.013	0.10208
1G110V	91.641	147.005	99.964	42.236	0.105552
01G110V	87.850	137.023	93.640	51.998	0.12172
1110V	87.685	145.033	95.307	57.351	0.13665
01110V	85.716	133.344	96.125	39.212	0.09423
1110V473K	86.401	142.792	94.750	42.739	0.10123
01110V473K	91.918	140.328	99.613	39.449	0.09824

It is seen in Table-2 that surface areas, pore volume, average pore diameter of Cs-TPAs obtained by different synthesis conditions have different values. It is concluded that different synthesis conditions such as the aging, atmospheric drying-vacuum drying and calcination, addition rate of Cs<sub>2</sub>CO<sub>3</sub> solution to TPA solution effected the surface area and porosity. Applying vacuum drying in synthesizing of Cs-TPA, BET areas

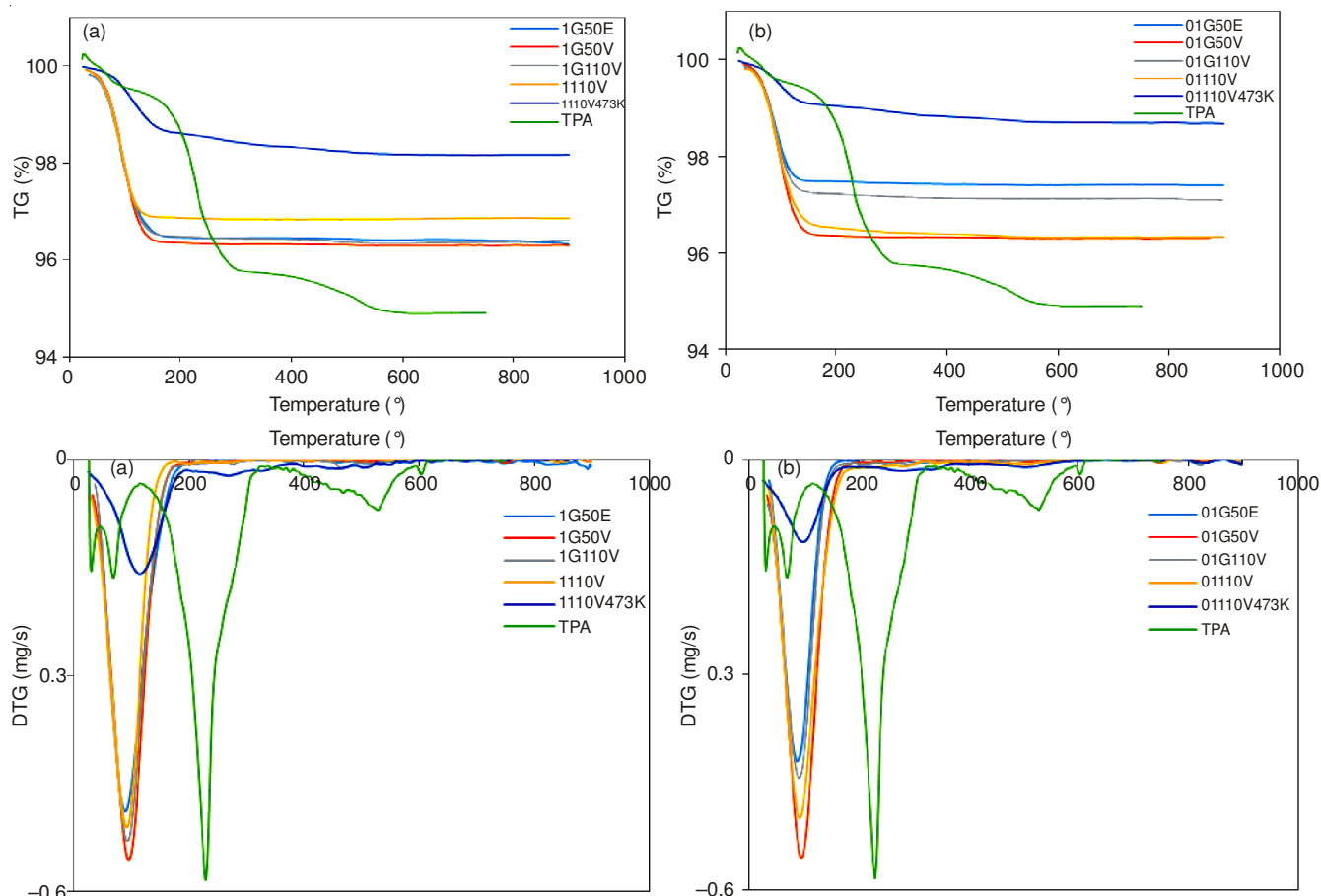


Fig. 5. TG and DTG curves of (a) synthesized catalysts with 1 mL/min addition rate (b) synthesized catalysts with 0.1 mL/min addition rate, respectively

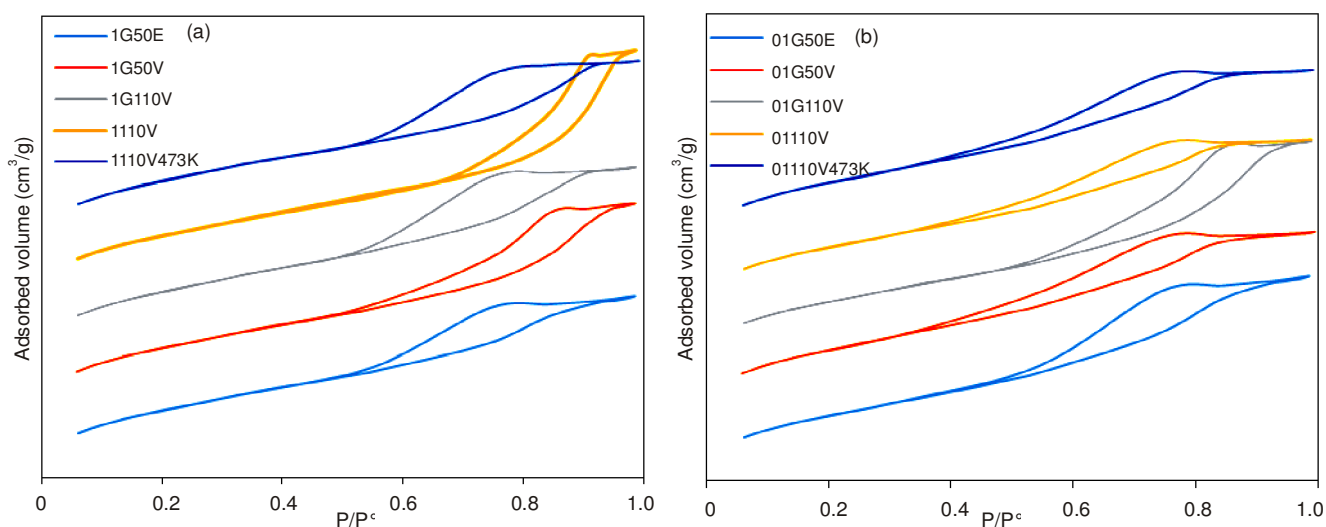


Fig. 6.  $N_2$  adsorption/desorption isotherms of synthesized CS-TPAs (a) synthesized catalysts with 1 mL/min addition rate (b) synthesized catalysts with 0.1 mL/min addition rate

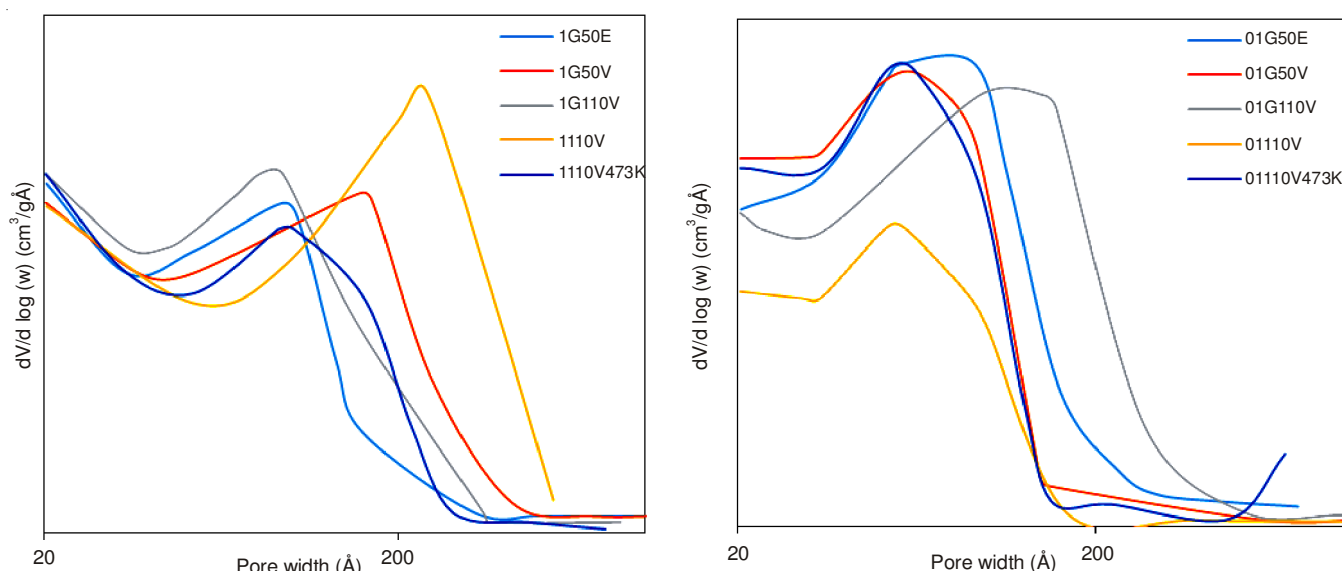


Fig. 7. Pore size distribution plot (a) synthesized catalysts with 1 mL/min addition rate (b) synthesized catalysts with 0.1 mL/min addition rate

and average pore diameters are increased. In the increasing of vacuum drying temperature, BET areas is nearly same but average pore diameters are decreased. The aging, decreases BET areas but increases average pore diameter. Also it is observed that calcination, increases BET areas but decreases average pore diameter. Generally in all methods, increasing the addition rate of  $Cs_2CO_3$  solution to the TPA solution increases BET areas but decreases average pore diameter. The sample coded by 01G50V showed the highest surface area with 4.5 nm pore diameter among all synthesized Cs-TPA.

Effect of each methods on the nitrogen adsorption-desorption isotherms of the all synthesized CS-TPAs are shown in Fig. 6. All synthesized Cs-TPA shows a Type-IV isotherm in which  $H_2$  hysteresis loops was observed<sup>32</sup>. The Type IV isotherm is usually observed for materials having mesopores<sup>9</sup>.

The pore-size distribution curves shown in Fig. 7 exhibits peaks at around 7 nm of pore radius for catalysts obtained at addition rate of 0.1 mL/min and 11 nm for catalysts obtained at addition rate of 1 mL/min. Although pore radius of addition rate of 1 mL/min is higher than that of addition rate of 0.1

mL/min. However micro porosity increases with increasing addition rate.

## Conclusions

In this study, the methods published in the literature were modified by monitoring the aging, atmospheric drying-vacuum drying and calcination to enhance the surface properties such as the surface area and porosity was investigated. The characterization of the synthesized Cs-TPA were examined by the XRD, FTIR, SEM, TG-DTG, particle distribution and crystallite size. The results show that there is no significant difference between synthesis methods of all Cs-TPA's. However,  $N_2$  adsorption/desorption isotherms shows some differences in surface properties of Cs-TPA depending on the synthesizing methods. Generally in each methods, BET surface area is decreasing with the increasing addition rate of the solutions and pore radius is *vice versa*. The sample coded by 01G50V showed the highest surface areawith 4.5 nm pore diameter among the all synthesized Cs-TPA.

## ACKNOWLEDGEMENTS

The authors thank Anadolu University Scientific Research Projects Commission (Project No: 1207F112) for the financial support.

## REFERENCES

1. I.V. Kozhevnikov, *Catal. Rev., Sci. Eng.*, **37**, 311 (1995).
2. E. Papaconstantinou, *Chem. Soc. Rev.*, **18**, 1 (1989).
3. L.E. Briand, G.T. Baronetti and H.J. Thomas, *Appl. Catal. A*, **256**, 37 (2003).
4. I.V. Kozhevnikov, *Chem. Rev.*, **98**, 171 (1998).
5. T. Okuhara, N. Mizuno and M. Misono, *Appl. Catal. A*, **222**, 63 (2001).
6. K. Na, T. Okuhara and M. Misono, *J. Chem. Soc., Faraday Trans.*, **91**, 367 (1995).
7. N. Essayem, G. Coudurier, M. Fournier and J.C. Védrine, *Catal. Lett.*, **34**, 223 (1995).
8. T. Okuhara, T. Nishimura, H. Watanabe and M. Misono, *J. Mol. Catal.*, **74**, 247 (1992).
9. T. Okuhara, T. Nishimura and M. Misono, *Stud. Surf. Sci. Catal.*, **101**, 581 (1996).
10. M. Kimura, T. Nakato and T. Okuhara, *Appl. Catal. A*, **165**, 227 (1997).
11. T. Okuhara, H. Watanabe, T. Nishimura, K. Inumaru and M. Misono, *Chem. Mater.*, **12**, 2230 (2000).
12. J.A. Dias, E. Caliman and S.C. Loureiro Dias, *Micropor. Mesopor. Mater.*, **76**, 221 (2004).
13. T. Okuhara, T. Nishimura, H. Watanabe and M. Misono, *J. Mol. Catal.*, **74**, 247 (1992).
14. T. Nishimura, T. Okuhara and M. Misono, *Appl. Catal.*, **73**, L7 (1991).
15. K. Na, T. Okuhara and M. Misono, *J. Chem. Soc., Faraday Trans. I*, **91**, 367 (1995).
16. N. Essayem, G. Coudurier, M. Fournier and J.C. Védrine, *Catal. Lett.*, **34**, 223 (1995).
17. K. Na, T. Iizaki, T. Okuhara and M. Misono, *J. Mol. Catal. Chem.*, **115**, 449 (1997).
18. M. Kimura, T. Nakato and T. Okuhara, *Appl. Catal. A*, **165**, 227 (1997).
19. T. Okuhara, M. Kimura and T. Nakato, *Chem. Lett.*, 839 (1997).
20. K. Narasimharao, D.R. Brown, A.F. Lee, A.D. Newman, P.F. Siril, S.J. Tavener and K. Wilson, *J. Catal.*, **248**, 226 (2007).
21. G.G. Volkova, L.M. Plyasova, A.N. Salanov, G.N. Kustova, T.M. Yurieva and V.A. Likholobov, *Catal. Lett.*, **80**, 175 (2002).
22. J.A. Dias, E. Caliman and S.C. Loureiro Dias, *Micropor. Mesopor. Mater.*, **76**, 221 (2004).
23. H. Dogan, T.Y. Inan, E. Unveren and M. Kaya, *Int. J. Hydrogen Energy*, **35**, 7784 (2010).
24. S. Choi, Y. Wang, Z. Nie, J. Liu and C.H.F. Peden, *Catal. Today*, **55**, 117 (2000).
25. N. Essayem, A. Holmqvist, P.Y. Gayraud, J.C. Védrine and T.Y. Ben, *J. Catal.*, **197**, 273 (2001).
26. D. Zhao, B.L. Yi, H.M. Zhang, H.M. Yu, L. Wang, Y.W. Ma and D.M. Xing, *J. Power Sources*, **190**, 301 (2009).
27. A. Ghanbari-Siahkali, A. Philippou, J. Dwyer and M.W. Anderson, *Appl. Catal. A*, **19**, 57 (2000).
28. H.Y. Shin, S.H. An, R. Sheikh, Y.H. Park and S.Y. Bae, *Fuel*, **96**, 572 (2012).
29. P. Madhusudhan Rao, M.V. Landau, A. Wolfson, A.M. Shapira-Tchelet and M. Herskowitz, *Micropor. Mesopor. Mater.*, **80**, 43 (2005).
30. S.W. Chuang, S.L.C. Hsu and M.L. Yang, *Eur. Polym. J.*, **44**, 2202 (2008).
31. S.K. Bhorodwaj and D.K. Dutta, *Appl. Catal. A*, **378**, 221 (2010).
32. T. Nakato, Y. Toyoshi, M. Kimura and T. Okuhara, *Catal. Today*, **52**, 23 (1999).