Production of Adipic Acid from Mixtures of Cyclohexanol-Cyclohexanone using Polyoxometalate Catalysts

Aldes Lesbani  
Department of Chemistry, Faculty of Mathematic and Natural Sciences, Universitas Sriwijaya, Indralaya (OI), Sumatera Selatan 30662, Indonesia, aldeslesbani@pps.unsri.ac.id

Sumiati  
Department of Chemistry, Faculty of Mathematic and Natural Sciences, Universitas Sriwijaya, Indralaya (OI), Sumatera Selatan 30662, Indonesia

Mardiyanto  
Department of Pharmacy, Faculty of Mathematic and Natural Sciences, Universitas Sriwijaya, Indralaya (OI), Sumatera Selatan 30662, Indonesia

Najma Annuria Fithri  
Department of Pharmacy, Faculty of Mathematic and Natural Sciences, Universitas Sriwijaya, Indralaya (OI), Sumatera Selatan 30662, Indonesia

Risfidian Mohadi  
Department of Chemistry, Faculty of Mathematic and Natural Sciences, Universitas Sriwijaya, Indralaya (OI), Sumatera Selatan 30662, Indonesia

Follow this and additional works at: https://scholarhub.ui.ac.id/science

Recommended Citation
Lesbani, Aldes; Sumiati; Mardiyanto; Fithri, Najma Annuria; and Mohadi, Risfidian (2015) "Production of Adipic Acid from Mixtures of Cyclohexanol-Cyclohexanone using Polyoxometalate Catalysts," Makara Journal of Science: Vol. 19 : Iss. 2 , Article 6.  
DOI: 10.7454/mss.v19i2.4778  
Available at: https://scholarhub.ui.ac.id/science/vol19/iss2/6

This Article is brought to you for free and open access by the Universitas Indonesia at UI Scholars Hub. It has been accepted for inclusion in Makara Journal of Science by an authorized editor of UI Scholars Hub.
Production of Adipic Acid from Mixtures of Cyclohexanol-Cyclohexanone using Polyoxometalate Catalysts

Cover Page Footnote
The authors thank the Department of Chemistry and the Faculty of Mathematic and Natural Sciences, Universitas Sriwijaya, for the use of laboratory facilities for this research.

This article is available in Makara Journal of Science: https://scholarhub.ui.ac.id/science/vol19/iss2/6
Production of Adipic Acid from Mixtures of Cyclohexanol-Cyclohexanone using Polyoxometalate Catalysts

Aldes Lesbani¹, Sumiati¹, Mardiyanto², Najma Annuria Fithri², and Risfidian Mohadi¹

1. Department of Chemistry, Faculty of Mathematic and Natural Sciences, Universitas Sriwijaya, Indralaya (OI), Sumatera Selatan 30662, Indonesia
2. Department of Pharmacy, Faculty of Mathematic and Natural Sciences, Universitas Sriwijaya, Indralaya (OI), Sumatera Selatan 30662, Indonesia

*E-mail: aldeslesbani@pps.unsri.ac.id

Abstract

Adipic acid production through catalytic conversion of cyclohexanol-cyclohexanone using polyoxometalate \( \text{H}_5[\alpha\text{-BW}_{12}\text{O}_{40}] \) and \( \text{H}_4[\alpha\text{-SiW}_{12}\text{O}_{40}] \) as catalysts was carried out systematically. Polyoxometalates \( \text{H}_5[\alpha\text{-BW}_{12}\text{O}_{40}] \) and \( \text{H}_4[\alpha\text{-SiW}_{12}\text{O}_{40}] \) were synthesized using an inorganic synthesis method and were characterized using Fourier transform infrared spectroscopy (FTIR). Adipic acid was formed from conversion of cyclohexanol-cyclohexanone and was characterized by using melting point measurement, identification of functional group using FTIR spectrophotometer, analysis of gas chromatography-mass spectrometry (GC-MS), and \(^1\text{H}\) and \(^{13}\text{C}\) NMR (nuclear magnetic resonance) spectrophotometer. This research investigated the influence of reaction time and temperature on conversion. The results showed that adipic acid was formed successfully with a yield of 68\% by using \( \text{H}_5[\alpha\text{-BW}_{12}\text{O}_{40}] \) as catalyst at the melting point of 150-152 °C after optimization. In contrast, using \( \text{H}_4[\alpha\text{-SiW}_{12}\text{O}_{40}] \) as catalyst, formation of adipic acid was only 3.7\%. Investigation of time and temperature showed 9 h as the optimum reaction time and 90 °C as the optimum temperature for conversion of up to 68\% adipic acid. Identification using FTIR, \(^1\text{H}\), and \(^{13}\text{C}\) NMR showed that the adipic acid from conversion of cyclohexanol-cyclohexanone was in agreement with the standard adipic acid data in the literatures. GC-MS analysis indicated that several by-products were formed in conversion of cyclohexanol-cyclohexanone using \( \text{H}_5[\alpha\text{-BW}_{12}\text{O}_{40}] \) and \( \text{H}_4[\alpha\text{-SiW}_{12}\text{O}_{40}] \) as catalysts.

Keywords: adipic acid, cyclohexanol-cyclohexanone, polyoxometalate

Introduction

Green synthesis of adipic acid is extremely urgent for environmental reasons. Adipic acid is a precursor for nylon 6,6 and polyurethane plastic synthesis. The main method of synthesizing adipic acid through catalytic methods using nitric acid releases toxic nitrous oxide into the environment [1]. Thus, a catalytic conversion that
forms adipic acid using an eco-friendly catalyst is needed. An approach to synthesizing adipic acid by oxidation of cyclohexanone, cyclohexanol, cyclohexane, or mixtures of these has been developed, using H$_2$O$_2$ as a green oxidant and appropriate catalyst, as shown in Figure 1.

Various catalysts have been tested for adipic acid synthesis, including ionic liquid by two catalytic functions [2], hybrid porous tin (IV) phosphonate [3], manganese catalyst [4], and tungstosilicic acid catalyst [5]. Recently, development of tungstosilicic acid catalyst for adipic acid synthesis has been explored deeply using H$_2$WO$_4$ [6], silica functionalized ammonium tungstate [7], sodium tungstate with stearyl dimethyl benzyl ammonium chloride as surfactant [8], and polyoxometalate compounds. Polyoxometalates are oxygen-metal clusters with various structures and oxidation states and can be used as potential catalyst due to very high acidity and non-toxic solid materials. Polyoxometalates are used intensively as catalyst for oxidation of cyclohexanol-cyclohexanone to adipic acid [9]. Effect of addenda and heteroatoms in polyoxometalate has been studied by Zhu et al. using peroxotungstic acid and peroxomolybdates as catalyst [10]. Common Keggin-type H$_3$PW$_{12}$O$_{40}$ and H$_3$PMo$_{12}$O$_{40}$ with different addenda atoms have been converted into glycine phosphotungstate, and glycine phosphomolybdate acted as catalyst for conversion of cyclohexanol-cyclohexanone with high yield and selectivity [11]. In addition, structure effect has been investigated in the polyoxometalate, which was Anderson type [C(C$_8$H$_{17}$)$_2$N(CH$_3$)$_2$]$_9$Mo$_{12}$O$_{48}$, as catalyst for the conversion of cyclohexane to adipic acid [12].

Herein, we demonstrate the basic structure with different heteroatoms of polyoxometalate H$_3$[α-BW$_{12}$O$_{40}$] and H$_4$[α-SiW$_{12}$O$_{40}$] and with similar addenda atoms (tungsten) but different heteroatoms (boron and silica) used as catalyst for converting a 1:1 mixture of cyclohexanol-cyclohexanone to adipic acid. Based on our knowledge, this is the first report to investigate these polyoxometalate catalysts in conversion of cyclohexanol-cyclohexanone. In addition, several factors affecting formation of adipic acid, such as time and temperature reactions, were investigated in cyclohexanol-cyclohexanone conversion.

Materials and Methods

Materials and instrumentation. Chemicals were supplied from Merck and Sigma Aldrich, including sodium tungstate (Merck), potassium hydrogen carbonate (Merck), potassium carbonate (Merck), sodium metasilicate (Aldrich), ammonium chloride (Merck), potassium chloride (Merck), and disodium hydrogen phosphate dihydrate (Merck). Cyclohexanol and cyclohexanone were obtained from Sigma-Aldrich and used without further purification. FTIR spectrum was recorded using the Shimadzu FTIR 8201PC. Gas Chromatography-Mass Spectrometer Shimadzu 2010QP was used to identify product. $^1$H and $^{13}$C NMR were performed by Jeol 500 MHz and 125 MHz using DMSO and acetone as solvents, respectively.

Synthesis of polyoxometalate H$_3$[α-BW$_{12}$O$_{40}$] and H$_4$[α-SiW$_{12}$O$_{40}$]. Synthesis of polyoxometalate H$_3$[α-BW$_{12}$O$_{40}$] and H$_4$[α-SiW$_{12}$O$_{40}$] was adopted from Lesbani [13] and was characterized using an FTIR spectrophotometer using a KBr disk at room temperature at the range of 400-4000 cm$^{-1}$. Synthesis of H$_3$[α-BW$_{12}$O$_{40}$] was as follows: boric acid (150 g) and sodium tungsten (100 g) were dissolved in 450 mL warm water, and the solution was stirred for 3 h. The solution was cooled and filtered. Boric acid (70 g) was added to the solution with slow stirring for 1 h. The solution was added to 10 mL of hydrochloric acid and stirred for 30 min. The solution was extracted with diethyl ether-hydrochloric acid and the etherate layer was collected and dried by a rotary evaporator to form a white solid of H$_3$[α-BW$_{12}$O$_{40}$].

Synthesis of H$_4$[α-SiW$_{12}$O$_{40}$] was as follows: In a 1 L Beaker glass equipped with magnetic stirring, 11 g of sodium metasilicate was dissolved in 100 mL of water (A). Then, 182 g of sodium tungsten was dissolved in 300 mL of hot water (B). Solution B was added to 165 mL of 4 M hydrochloric acid with vigorous stirring, followed by addition of solution A. The pH of the solution was adjusted to 5–6, and the solution was stirred for 1 h at 100 °C. The solution was cooled at room temperature, and 50 g of potassium chloride was added to obtain solid material. The solid material was dissolved in water, and 100 mL of diethyl ether and 10 mL of hydrochloric acid were added. The solution was extracted, and the bottom layer was collected to obtain a white solid of H$_4$[α-SiW$_{12}$O$_{40}$] after vacuum process using a rotary evaporator.

Catalytic conversion of cyclohexanol-cyclohexanone to adipic acid. Conversion of the mixture of cyclohexanol-cyclohexanone was performed in a 100 mL flask according to the procedure of Zhang et al., with slight modifications, as follows: 10 mL of the cyclohexanol-cyclohexanone mixture (1:1) and 0.1 g of catalyst were added to a flask equipped with a magnetic bar. The mixture was stirred for 15 min, followed by addition of 44 mL of 30% H$_2$O$_2$ with stirring for 10 min. Reaction

![Figure 1. Synthesis of Adipic Acid Via Oxidation of Cyclohexanone](image-url)
mixtures were refluxed for 8 h at 90 °C. After completed reaction, the mixture was cooled in a refrigerator for 12 h at 5 °C. White crystals of adipic acid were formed in the solution, and then the crystal was filtered, washed with cool water, and dried at room temperature [14]. Adipic acid was characterized using an FTIR spectrophotometer and 1H and 13C NMR analysis.

Results and Discussion

Polyoxometalates $H_4[\alpha\text{-BW}_{12}O_{40}]$ and $H_4[\alpha\text{-SiW}_{12}O_{40}]$ with different heteroatoms were characterized using FTIR spectroscopy, as shown in Figure 2.

Polyoxometalates $H_4[\alpha\text{-BW}_{12}O_{40}]$ and $H_4[\alpha\text{-SiW}_{12}O_{40}]$ are Keggin-type heteroatom where M is the heteroatom and X is the addenda atom. In this research, M is B and Si, and X is tungsten. Table 1 shows specific vibrations of these polyoxometalates.

The vibrations in Table 1 are specific to $H_4[\alpha\text{-BW}_{12}O_{40}]$ and $H_4[\alpha\text{-SiW}_{12}O_{40}]$. Vibrations of W-Oc-W and W-Oe-W are similar in wavenumber, from 780–930 cm$^{-1}$, depending on their heteroatom. Vibrations of B-O are 914 cm$^{-1}$ and those of Si-O are 1020 cm$^{-1}$, indicating that the heteroatom oxygen stretches the vibrations. According to these data, polyoxometalates $H_4[\alpha\text{-BW}_{12}O_{40}]$ and $H_4[\alpha\text{-SiW}_{12}O_{40}]$ were synthesized successfully, and their FTIR spectra are in agreement with those in the literature [15].

Polyoxometalates $H_4[\alpha\text{-BW}_{12}O_{40}]$ and $H_4[\alpha\text{-SiW}_{12}O_{40}]$ were used as catalyst for converting the cyclohexanol-cyclohexanone mixture to adipic acid using $H_2O_2$ as an oxidant. Catalysts $H_4[\alpha\text{-BW}_{12}O_{40}]$ and $H_4[\alpha\text{-SiW}_{12}O_{40}]$ activated the $H_2O_2$ to be an active oxidant in this reaction. The first trial of conversion using $H_4[\alpha\text{-BW}_{12}O_{40}]$ and $H_4[\alpha\text{-SiW}_{12}O_{40}]$ as catalysts yielded isolated adipic acid, as shown in Table 2.

The data in Table 2 show that $H_4[\alpha\text{-BW}_{12}O_{40}]$ is more effective for conversion than $H_4[\alpha\text{-SiW}_{12}O_{40}]$. Probably, a Keggin-type heteroatom is key to conversion of cyclohexanol-cyclohexanone into adipic acid. Boron is more acidic than silicon, according to the Lewis acid concept; therefore, activation of $H_2O_2$ needs a more acidic heteroatom [16]. Adipic acid was isolated and characterized using FTIR spectroscopy and then compared with the adipic acid standard, as shown in Figure 3.

![Figure 3](image318x301 to 533x521)

Figure 3 shows that isolated adipic acid (B) is similar to standard adipic acid (A). Vibrations of isolated adipic acid appear at wave number of 2954 cm$^{-1}$ for O-H, 2877 cm$^{-1}$ for aliphatic methylene (CH$_2$), 1697 cm$^{-1}$ for C = O, 1280 cm$^{-1}$ for C-O, and 1195 cm$^{-1}$ for aliphatic C-C. All these vibrations are in agreement with those of standard adipic acid reported in the literature [17]. Characterization of isolated white crystals of adipic acid was conducted using $^1$H, $^{13}$C NMR, and mass spectroscopy. Figure 4 shows the $^1$H NMR spectrum.

### Table 1. Vibration of $H_4[\alpha\text{-BW}_{12}O_{40}]$ and $H_4[\alpha\text{-SiW}_{12}O_{40}]$

| Vibration | $H_4[\alpha\text{-BW}_{12}O_{40}]$ | $H_4[\alpha\text{-SiW}_{12}O_{40}]$ |
|-----------|---------------------------------|---------------------------------|
| B-O       | 914 cm$^{-1}$                   | -                               |
| W-Oc-W    | 810 cm$^{-1}$                   | 786 cm$^{-1}$                   |
| W-Oe-W    | 902 cm$^{-1}$                   | 925 cm$^{-1}$                   |
| W=O       | 960 cm$^{-1}$                   | 979 cm$^{-1}$                   |
| Si-O      | -                               | 1020 cm$^{-1}$                  |

### Table 2. The Yield of Adipic Acid from Conversion of Cyclohexanol-cyclohexanone

| Adipic acid | $H_4[\alpha\text{-BW}_{12}O_{40}]$ | $H_4[\alpha\text{-SiW}_{12}O_{40}]$ |
|-------------|---------------------------------|---------------------------------|
| Yield (Isolated) | 60.7% | < 10% |

Condition: 0.1 g catalyst, 44 mL $H_2O_2$ 30%, 10 mL cyclohexanol-cyclohexanone (1:1), 8 h reaction time, temperature 90 °C.

![Figure 2](image285x301 to 533x521)

Figure 2. FTIR Spectrum of $H_4[\alpha\text{-BW}_{12}O_{40}]$ (A) and $H_4[\alpha\text{-SiW}_{12}O_{40}]$ (B)

![Figure 3](image785x521)

Figure 3. FTIR Spectra of (A) Standard Adipic Acid and (B) Isolated Adipic Acid
The structure of adipic acid having a symmetric molecule can be identified using $^1$H NMR and various deuterated solvents. A peak of DMSO-D$_6$ used as solvent appears at 2.50 ppm. Other peaks related to adipic acid appear at 1.49 ppm (CH$_2$), $\delta$ 2.20 ppm (CH$_2$), and $\delta$ 12.02 ppm (COOH). The isolated adipic acid from this research has high purity compound indicated by no other peaks besides deuterated DMSO and adipic acid peaks were observed. The $^1$H NMR result is supported by the $^{13}$C NMR result, as shown in Figure 5.

Similar to the $^1$H NMR spectrum, the $^{13}$C NMR spectrum for adipic acid detects only three peaks. Acetone D$_6$ was used to measure $^{13}$C NMR of isolated adipic acid. As mentioned earlier, adipic acid can be measured using various solvents, and acetone appeared at 206.4 ppm. Peaks of adipic acid can be observed at 25.2 ppm, 33.9 ppm, and 17 4.7 ppm. Further characterization was conducted using a mass spectrometer (Figure 6).

Adipic acid has a molecular weight of 146 g/mol and a molecular peak of $m/z$ 146. The molecular peak at $m/z$ 146 is not visible clearly in Figure 6. However, other peaks related to molecular fragments at $m/z$ 128, 112, and 100 are obvious, with the highest intensity appearing at $m/z$ 100 (100%) [18]. Figure 7 shows the fragmentation pattern of adipic acid.

Although all characterizations of isolated adipic acid show high purity of the compound, moderately isolated adipic acid obtained from cyclohexanol-cyclohexanone using H$_2$[α-BW$_{12}$O$_{40}$] indicated formation of several by-products and remaining cyclohexanol-cyclohexanone. Figure 8 shows three by-products identified using GC-MS.

On the basis of these results and from comparison with the literature [3,19-20], we propose a plausible mechanism for converting cyclohexanol-cyclohexanone into adipic acid, as shown in Figure 9. Oxygen from peroxide was activated with boric tungsten from polyoxometalate to attack cyclo species from cyclohexanol-cyclohexanone. Intermediate derivative lactone was formed, followed by re-arrangement of lactone to adipic acid and oxygen as a green by-product. This study also investigated reaction time and temperature of conversion. Data are presented in Figures 10 and 11.
According to Alcañiz-Monge et al., conversion of cyclohexene to adipic acid was achieved at 3 h [21]. In this study, the reaction time needed to convert the mixture of cyclohexanone-cyclohexanol was 7-10 h. As shown in Figure 10, at 9 h, up to 61% of cyclohexanol-cyclohexanone can be converted to adipic acid. The yield of adipic acid obtained at 7 h is not significantly different from that obtained at 8 h, 59.5%. By increasing reaction time into 10 h, the yield of adipic acid decreases to 46%. Therefore, the experiment was terminated at the reaction time of 10 h.

Temperature is an important factor in the catalytic conversion of cyclohexanol, cyclohexanone, and cyclohexanol-cyclohexanone mixtures into adipic acid [22]. In this study, temperature was adjusted to 100 °C due to stability of hydrogen peroxide. Figure 11 shows that a temperature of 90 °C yields isolated adipic acid of up to 68%. At lower temperatures, adipic acid formation is about 50-60%. At 100 °C, formation of adipic acid falls to 49%. All results indicated that the 1:1 mixture of cyclohexanol-cyclohexanone could form adipic acid with moderate isolated yield.

**Conclusions**

After optimization of the cyclohexanol-cyclohexanone mixture, adipic acid was synthesized successfully at the yield of 68% at a reaction time of 9 h and a temperature of 90 °C, using H₃[α-BW₁₂O₄₀] as the catalyst and with the melting point of 150-152 °C. Characterization using FTIR spectrophotometer, ¹H, and ¹³C NMR showed that highly pure white crystalline adipic acid was obtained from synthesis.

**Acknowledgments**

The authors thank the Department of Chemistry and the Faculty of Mathematic and Natural Sciences, Universitas
Sriwijaya, for the use of laboratory facilities for this research.

References

[1] Polen, T., Spelberg, M., Bott, M. 2013. Toward biotechnological production of adipic acid and precursors from biorenewables. J. Biotechnol. 167(2): 75-84, doi:10.1016/j.jbiotec.2012.07.008.

[2] Vafaeezadeh, M., Hashemi, M.M. 2013. Dual catalytic function of the task-specific ionic liquid: Green oxidation of cyclohexane to adipic acid using 30% H₂O₂. Chem. Eng. J. 221(1): 254-257, doi:10.1016/j.cej.2013.02.013.

[3] Dutta, A., Pramanik, M., Patra, A.K., Nandi, M., Uyama, H., Bhauimik, A. 2012. Hybrid porous tin(IV) phosphonate: an efficient catalyst for adipic acid synthesis and a very good adsorbent for CO₂ uptake. Chem. Commun. 48(53): 6738-6740, doi:10.1039/C2CC32298F.

[4] Knops-Gerrits, P.P., Thibault-Starzyk, F., Jacobs, P.A. 1994. Adipic acid synthesis via oxidation of cyclohexane over zeolite occluded manganese diimine complexes. Stud. Surf. Sci. Catal. 84(1): 1411-1418, doi:10.1016/S0167-2991(08)63682-4.

[5] Sato, K., Aoki, M., Noyori, R. 1998. A “Green” route to adipic acid: Direct oxidation of cyclohexanes with 30 percent hydrogen peroxide. Science. 281(5383): 1646-1647, doi:10.1126/science.281.5383.1646.

[6] Usui, Y., Sato, K. 2003. A green method of adipic acid synthesis: organic solvent-and halide-free oxidation of cyclohexanes with 30% hydrogen peroxide. Green Chem. 5(4): 373-375, doi: 10.1039/B305847F.

[7] Vafaeezadeh, M., Hashemi, M.M. 2014. Simple and green oxidation of cyclohexane to adipic acid with an efficient and durable silica-functionalized ammonium tungstate catalyst. Catal. Commun. 43(1): 169-172, doi:10.1016/j.catcom.2013.10.001.

[8] Peñate, I.Q., Lesage, G., Cognet, P., Poux, M. 2012. Clean synthesis of adipic acid from cyclohexane in microemulsions with stearyl dimethyl benzyl ammonium chloride as surfactant: From the laboratory to bench scale. Chem. Eng. J. 200-202(1): 357-364, doi:10.1016/jcej.2012.06.041.

[9] Cavani, F., Ferroni, L., Frattini, A., Lucarelli, C., Mazzini, A., Raaboava, K., Alini, S., Accorinti, P., Babini, P. 2011. Evidence for the presence of alternative mechanisms in the oxidation of cyclohexanone to adipic acid with oxygen, catalysed by Keggin polyoxometalates. Appl. Catal. A: General. 391(1-2): 118-124, doi: 10.1016/j.apcata.2010.04.032.

[10] Zhu, W., Li, H., He, X., Zhang, Q., Shu, H., Yan, Y. 2008. Synthesis of adipic acid catalyzed by surfactant-type peroxotungstate and peroxomolybdates. Catal. Commun. 9(4): 551-555, doi:10.1016/j.catcom.2007.07.038.

[11] Ren, S., Xie, Z., Cao, L., Xie, X., Qin, G., Wang, J. 2009. Clean synthesis of adipic acid catalyzed by complexes derived from heteropoly acid and glycine. Catal. Commun. 10(5): 464-467, doi: 10.1016/j.catcom.2008.10.013.

[12] Lù, H., Ren, W., Liu, P., Qi, S., Wang, W., Feng, Y., Sun, F., Wang, Y. 2012. One-step aerobic oxidation of cyclohexane to adipic acid using an Anderson-type catalyst [(C₆H₅)₂N(CH₃)₃]ₓMoₓO₂₄. Appl. Catal. A: General. 441-442(1): 136-141, doi: 10.1016/j.apcata.2012.07.015.

[13] Lesbani, A. 2008. Syntheses of Ionic Crystals of Polyoxometalate-Organometallic Complex and Sorption Properties, Ph.D Dissertation, Department of Applied Chemistry, The University of Tokyo. Japan. pp. 1-120.

[14] Zhang, S-G., Jiang, H., Gong, H., Sun, Z-L. 2003. Green catalytic oxidation of cyclohexanone to adipic acid. Pet. Sci. Technol. 21(1-2): 275-282, doi: 10.1081/LFT-120016948.

[15] Kozhevnikov, I.V. 2002. Catalysts for Fine Chemical Synthesis, Vol 2. John Wiley & Sons Ltd., England. p. 220.

[16] Atkins, P., Overton, T., Rourke, J., Weller, M., Armstrong, F. 2006. Inorganic Chemistry, 4th ed., Oxford University Press, UK. pp. 287-345.

[17] Solomon, T.W.G., Fryhle, C.B. 2008. Organic Chemistry, 9th ed, John Wiley & Sons, USA, pp. 363-364.

[18] Lesbani, A., Firtiliana, Mohadi, R. 2015. Conversion of cyclohexanone to adipic acid catalyzed by heteropoly compounds. Ind. J. Chem. 15(1): 64-69.

[19] Jin, P., Zhao, Z., Dai, Z., Wei, D., Tang, M., Wang, X. 2011. Influence of reaction conditions on product distribution in the green oxidation of cyclohexane to adipic acid with hydrogen peroxide. Catal. Today. 175(1): 619-624, doi:10.1016/j.cattod.2011.04.041.

[20] Blach, P., Bostrom, Z., Frenceschi-Messant, S., Lattes, A., Perez, E., Rico-Lattes, I. 2010. Recyclable process for sustainable adipic acid production in microemulsions. Tetrahedron. 66(35): 7124-7128, doi: 10.1016/j.tet.2010.06.093.

[21] Alcañiz-Monge, J., Trautwein, G., Garcia-Garcia, A. 2014. Influence of peroxometallic intermediaries present on polyoxometalates nanoparticles surface on the adipic acid synthesis. J. Mol. Catal A: Chem. 394(1): 211-216, doi: 10.1016/j.molcata.2014.07.023.

[22] Chavan, S.A., Srinivas, D., Ratnasamy, P. 2002. Oxidation of cyclohexane, cyclohexanone, and cyclohexanol to adipic acid by a non-HNO₃ route over Co/Mn cluster complexes. J. Catal. 212(1): 39-45, doi: 10.1006/jcat.2002.3756.