



Immobilizing Phosphotungstic Acid on Al₂O₃-ZnO Nano Mixed Oxides as a Heterogeneous Catalyst for Biodiesel Production by the Esterification of Free Fatty Acids

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This study investigated the esterification reaction of different carboxylic acids (Acetic acid, Palmitic acid, and Oleic acid) and ethanol by ZnO, Al₂O₃-ZnO mixed oxide, and phosphotungstic acid (10 wt %) immobilized on the Al₂O₃-ZnO mixed oxide. The heterogeneous catalysts were characterized by XRD, BET, FE-SEM, and EDX techniques. Optimum yield was achieved by using 10 % HPW/Al₂O₃-ZnO as the best catalyst, and the effects of the amount of catalyst, molar ratio of acid to alcohol, reaction temperature, and time were investigated to ensure the ideal yield of esterification reaction of acetic acid and ethanol. The results showed that the esterification of acetic acid to its ethyl ester was carried out in 3.5 hours, with an alcohol-to-acid-molar ratio of 2 and a temperature of 80 °C with yield 98 %. Moreover, the 10 % HPW/Al₂O₃-ZnO catalyst showed well activity in biodiesel production by the esterification of palmitic and oleic acids and the reaction yield did not decrease with an increase in alkyl chain length in acid molecules, remarkably.

1. INTRODUCTION

Esters are important substances that are highly applicable to the synthesis of organic industrial materials. For instance, they are used in the chemical, food, cosmetics, and medical industries [1,2].

Moreover, today, the synthesis of biodiesel from transesterification and esterification reactions is interesting to many researchers due to its eco-friendliness and numerous other environmental profits [3]. However, the costs of biodiesel production are primarily calculated by the cost of raw materials. The application of waste oils is a solution to diminishing the expenses of the production process. However, the high content of free fatty acid (FFA) in the mentioned oils cannot be simply transformed to its ester under transesterification reaction by using basic catalysts. This problem could be solved by the pre-esterification of FFAs in the presence of acid catalysts before implementing the transesterification process [4,5].

The process of esterification reaction normally occurs in the presence of heterogeneous and homogenous acidic catalysts. In the past, ester normally was performed over homogenous acidic catalysts [6]. In general, homogenous catalysis leads to faster and higher yields than heterogeneous one. However, it is well known that solid acid catalysts do not have the disadvantages associated with homogeneous ones, such as tedious separation, corrosion, and toxicity, in terms of industry and environment. Therefore, it has been observed that the usage of heterogeneous catalysts in the esterification reaction has rapidly increased over the last decades [2,3].

Among suitable acidic catalysts, phosphotungstic acid (HPW) appears to be a candidate to catalyze the esterification

reaction efficiently. It acts as a very strong Brønsted acid and avoids backward hydrolysis reaction by two properties of hydrophilic and high-water storage. Research and experiments have shown that HPW is a synergic catalyst for esterification and transesterification reaction. However, HPW is soluble in the polar solvents and needs to be immobilized on heterogeneous supports that are capable to perform esterification and transesterification reactions [4,7,8].

Alumina, with a suitable specific surface area and well thermal and mechanical properties, is usually used as a catalyst support for biodiesel synthesis. The physicochemical properties of alumina are related to the synthesis method and treatment conditions. Accordingly, γ -Al₂O₃ is more active and stable than the other phases in the catalytic process [3, 9,10].

On the other hand, zinc oxide (ZnO) is an amphoteric metal oxide that is applied as a catalyst in biodiesel production, effectively. A large number of active sites and the variation of diffusion of ZnO distinct it from other heterogeneous catalysts [11,12].

Besides, the use of mixed-metal oxide can bring in attractive properties, particularly when each part differs extremely from the other. Some metal oxides such as ZnO-La₂O₃ [13], MgO-ZnO [14], TiO₂-MgO [15], CaO/Al₂O₃ [3], and ZnO-Al₂O₃-La₂O₃ [16] are reported as active catalysts for biodiesel production. It appears that the combination of alumina and zinc oxide may establish new acid-based properties.

Here, we report the performance of a series of catalysts including ZnO nanorod, Al₂O₃-ZnO nano-mixed oxides, and HPW immobilized on Al₂O₃-ZnO nano-mixed oxides as heterogeneous catalysts for esterification reaction. The esterification of different carboxylic acids (acetic acid, palmitic acid, and oleic acid) with ethanol into the corresponding ester was chosen as the model reaction. Oleic acid and Palmitic acid are present in significant amounts in

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vegetable oil, and their methyl ester displays great influence on properties of the synthesized biodiesel.

2. MATERIALS AND METHODS

2.1. Materials and instrumentation

All of chemicals such as C_2H_6O , CH_3COOH , $C_{16}H_{32}O_2$, $C_{18}H_{34}O_2$, $Zn(NO_3)_2 \cdot 4H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, and $H_3[P(W_3O_{10})_4 \cdot xH_2O]$ were purchased from Merck company as precursors without any purification step.

The catalysts were characterized by X-ray diffraction (XRD), Unisantix-Xmd 300 instrument, $Cu K\alpha 1$, $\lambda = 1.540598 \text{ \AA}$, and 2θ between 10 to 90° . Field Emission Scanning Electron Microscopy (FE-SEM) was used to provide topographical and elemental information. In addition, specific surface area measurements were carried out using N_2 in a Micrometrics Belsorp mini instrument through the BET and BJH methods. The samples were degassed at $100^\circ C$ for 12 h in nitrogen before measurements. Inductively Coupled Plasma (ICP) analysis is an analytical technique used for detecting trace metals.

2.2. Catalyst preparation

In this study, various catalysts were synthesized by precipitation, co-precipitation, and impregnation methods according to the literature.

The ZnO nanorods were synthesized by the precipitation method. $Zn(NO_3)_2 \cdot 4H_2O$ was dissolved in distilled water and, then, the pH was set to 11 by using 0.1 molar NaOH solution. Filtering and washing were the next steps, followed by drying overnight and calcination at $500^\circ C$ for 5h [17].

Al_2O_3 -ZnO nano-mixed oxide was synthesized by the Co-Precipitation method. Certain amounts of $Zn(NO_3)_2 \cdot 4H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were dissolved in pure and distilled water simultaneously. Oxalic acid was added to the mixture of two solutions quickly, and NH_4 25 % solution was added drop by drop in order to adjust the PH to 7. Then, the washing process was done and it dried at $110^\circ C$ and finally was calcinated at $600^\circ C$ for 2 h [18].

In the following, 10 % HPW/ Al_2O_3 -ZnO was synthesized by the impregnation method. The process began by dissolving phosphotungstic acid in a certain amount of water separately. Al_2O_3 -ZnO mixed oxide mixture was sonicated for 30 minutes. The phosphotungstic acid solution was added to the intensely stirred mixture of Al_2O_3 -ZnO mixed oxide dropwise and, then, stirred for two hours and dried at $100^\circ C$ after completion of the process [19].

2.3. Esterification reactions

Esterification reactions were carried out in a round bottom flask with constant stirring in the oil bath at defined temperatures between 60 - $90^\circ C$, and the cold water was set to cool the condenser. The specific quantities of acetic acid and ethanol by a particular molar ratio along with the catalyst were added to the reactor, and the reactor was dipped in the oil bath. At the end of the reaction, the reactor was cooled, and the catalyst was filtered out from the reaction mixture. Both Auto-titration (Metrohm -model 835 Titrando) and gas chromatography were used to determine the yield and reaction products. The titration was carried out using 0.1 normal sodium hydroxide [20]. GC-MS analysis (Agilent, model Mass 5973N with an MP-5 column from Agilent, 30 mm_0.25

mm_0.25 μm) was used to confirm the chemical composition of products. Each analysis was carried out three times and data showed the average values within $\pm 2\%$ errors.

3. RESULTS AND DISCUSSION

3.1. Characterization of nanocatalysts

XRD analysis was performed for the characterization of ZnO, Al_2O_3 -ZnO and 10 % HPW/ Al_2O_3 -ZnO catalysts (Figure 1). Figure 1 illustrates the XRD patterns of ZnO, which is perfectly in line with the card number (JCPDS No. 00-001-1136) [21]. This sample has a hexagonal crystalline structure with a, b, and c sizes of 3.24, 3.24, and 5.1 angstrom, respectively. This substance is known as zincite mineral.

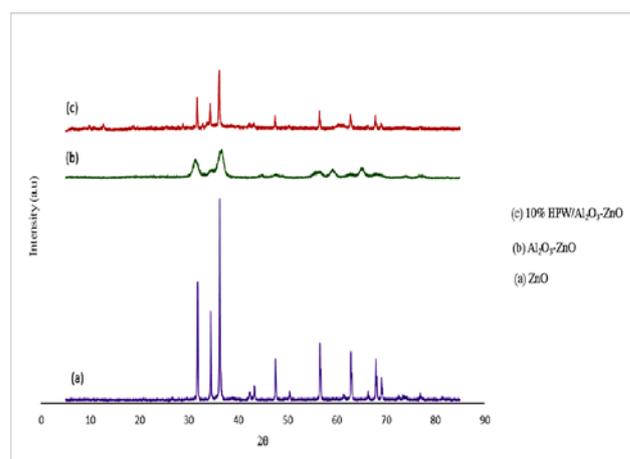


Figure 1. X-ray diffraction patterns of (a) ZnO, (b) Al_2O_3 -ZnO, and (c) 10 % HPW/ Al_2O_3 -ZnO.

XRD patterns with (JCPDS No.00-001-1146) for the sample Al_2O_3 -ZnO are reported in Figure 1. This sample is synthesized by the co-precipitation method using zinc and aluminum salts. As a result of diffraction patterns, a new substance called Gahnite is formed that is essentially beyond the pure zinc oxide and alumina [22]. Finally, the pattern of the sample with immobilized phosphotungstic acid (HPW) was also determined by the XRD technique. It seems that the acidic characters of Keggin-type HPW clusters behave as mineralizing agents and lead to improved crystallinity in 10 % HPW/ Al_2O_3 -ZnO sample [4].

Moreover, in Figure 2(a), the morphological and structural characterization of ZnO is observed. It can be obviously seen that nanorod ZnO structure was formed during the production process. Parts of the nanorods tend to be attached to each other before dispersing in the reaction solution. According to Figure 2(b), Al_2O_3 -ZnO has a spherical morphology, which is obtained by a co-precipitation method and forms a different material.

As shown in Figure 2 (c), it seems that there are many more pores with a greater depth than the ones shown in Figure 2 (a) and (b) due to loading of a keggig structure on the catalyst, which has been brought about by the Phosphotungstic acid.

The elemental compositions of surface on the catalysts were characterized by the EDX detector of SEM (Figure 2).

Moreover, the prepared 10 % HPW/ Al_2O_3 -ZnO catalyst was analyzed by ICP-Mass spectrophotometry to examine the percentage of loaded Phosphotungstic acid. The results show that this catalyst has 7.2 wt % W. The uniform element distribution in this sample is also shown in Figure 3.

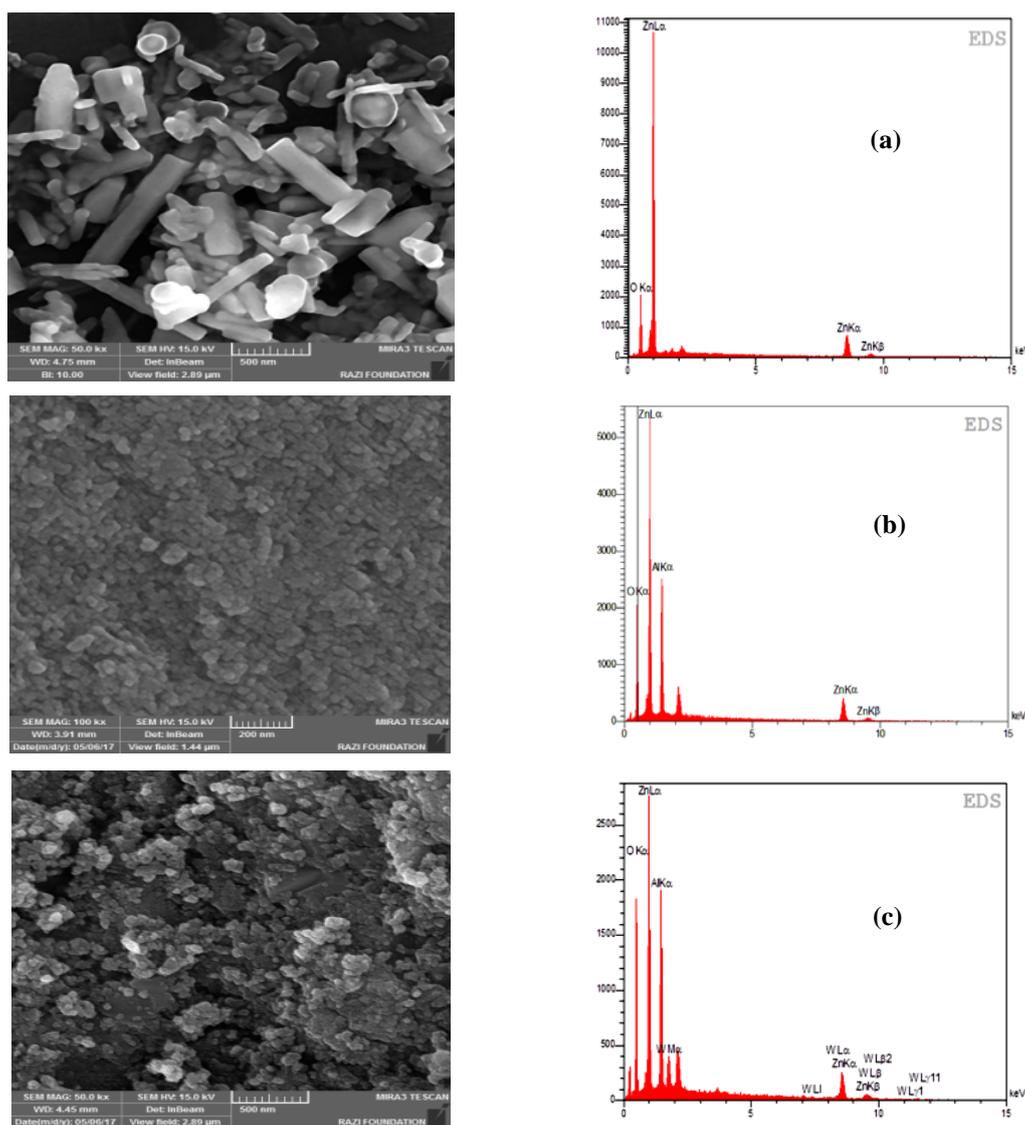


Figure 2. The FESEM image and EDX analysis of (a) ZnO, (b) $\text{Al}_2\text{O}_3\text{-ZnO}$, and (c) 10 % HPW/ $\text{Al}_2\text{O}_3\text{-ZnO}$.

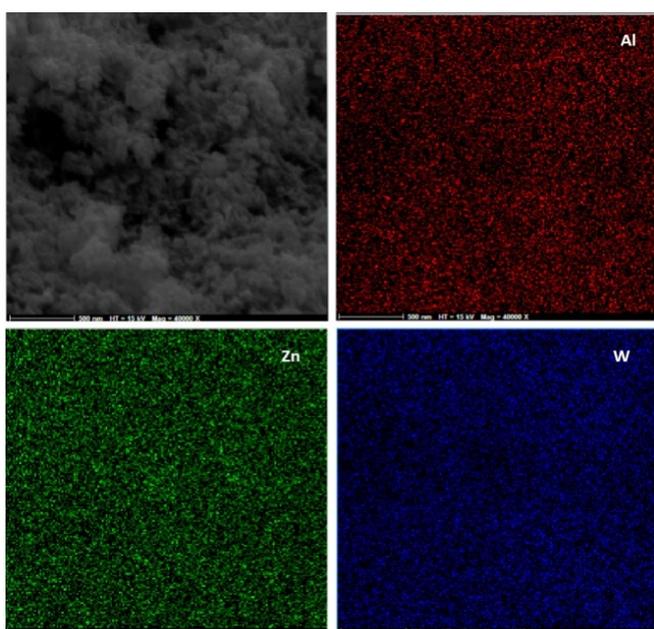


Figure 3. Elemental mapping of 10 % HPW/ $\text{Al}_2\text{O}_3\text{-ZnO}$.

lists the porosity and surface area for the synthesized catalysts. As can be seen, the surface area was enhanced by adding alumina to zinc oxide, because the morphology of ZnO with a rod morphology and lower porosity was changed to a spherical morphology with broadened pores by adding alumina to zinc oxide in the alumina-zinc oxide sample. In addition, Table 1 depicts the role of the HPW present in the structure of the catalysts. The main reason for this is contingently dependent on the creation of a new surface over layer from the HPW, which principally added new pores with a lower average size on the surface of $\text{Al}_2\text{O}_3\text{-ZnO}$ [12]. Therefore, the $\text{Al}_2\text{O}_3\text{-ZnO}$ interacts with HPW, rising the total surface area of the 10 % HPW/ $\text{Al}_2\text{O}_3\text{-ZnO}$ along with decreasing the average pore size.

Table 1. BET results.

Catalysts	Specific surface area (m^2/g)	Average pore size (nm)
ZnO	7.6	2.74
$\text{Al}_2\text{O}_3\text{-ZnO}$	70.2	12.24
10 % HPW/ $\text{ZnO-Al}_2\text{O}_3$	85.5	1.88

The N_2 adsorption-desorption isotherms of ZnO, $\text{Al}_2\text{O}_3\text{-ZnO}$, and 10 % HPW/ $\text{Al}_2\text{O}_3\text{-ZnO}$ are shown in Figure 4. Table 1

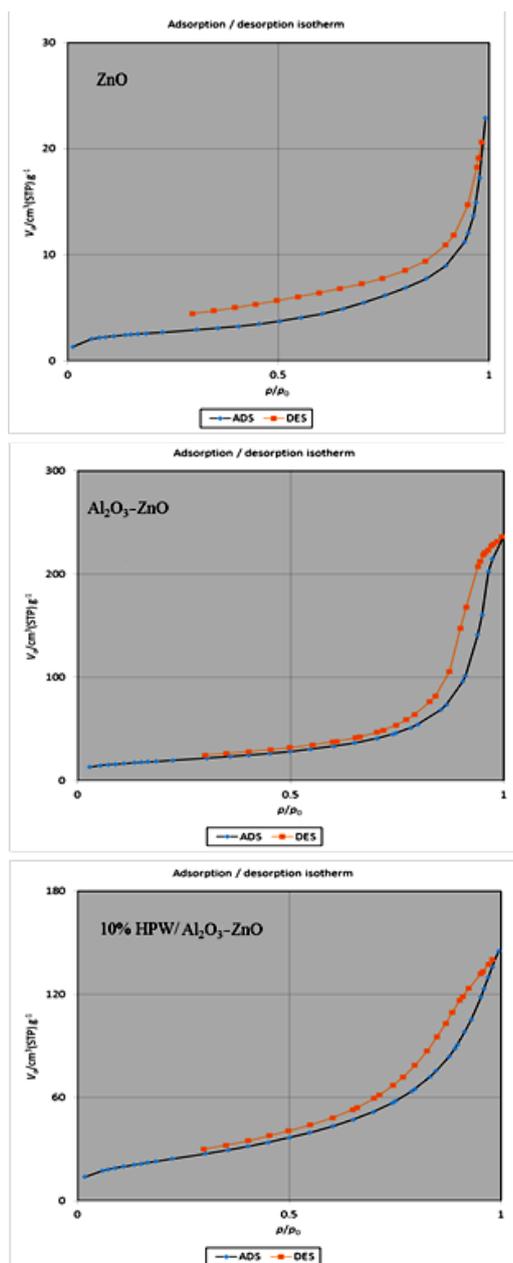


Figure 4. N_2 adsorption-desorption isotherms of ZnO, Al_2O_3 -ZnO, and 10% HPW/ Al_2O_3 -ZnO.

3.2. The Effect of nanocatalysts on esterification reaction

Esterification of acetic acid with ethanol was carried out at 80 °C for 4 h (Figure 5). The molar ratio of ethanol to acetic acid was 2, and 0.3 g of synthesized catalysts (3 wt %) were used. Then, the efficiency was determined by the GC analysis, and the result according to the diagram in Figure 5 was obtained.

Zinc oxide is commonly used as a heterogeneous catalyst in biodiesel production due to its acidic and basic properties. To investigate the effect of alumina on the zinc oxide, alumina was added to zinc oxide by the co-precipitation method. The result showed that the addition of alumina with high acidity and high porosity to zinc oxide had a synergistic effect, which improved the yield percentage [10].

Phosphotungstic acid was added to Al_2O_3 -ZnO due to its high acidity and water absorption abilities and increased the yield rate significantly. As stated before, the most important product of this reaction is water, which advanced the

backward reaction by hydrolysis. Hence, the extremely hydrophilic acid has the ability to absorb water from the reaction medium and prevents the product from returning [23, 24]. Therefore, the best catalyst, as shown in bar chart of Figure 5, is a synthetic material of 10% HPW/ Al_2O_3 -ZnO.

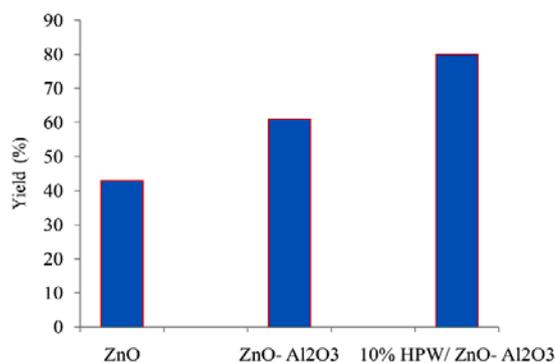


Figure 5. The efficiency of synthesized catalysts in esterification of acetic acid with ethanol.

3.3. Investigation of the effective parameters of the esterification reaction

In the esterification process of acetic acid, a higher yield rate results in an increase in the molar ethanol. The reaction was carried out on the surface of 10% HPW/ Al_2O_3 -ZnO (3 wt %) at 80 °C for 4 h. The reaction efficiency depends strongly on the molar ratio of ethanol to acetic acid parameter. Since the reaction of esterification is an equilibrium reaction, an increase in one of the reactive components prevents the return of equilibrium. Thus, with an increase in ethanol, the equilibrium tends towards producing more ethyl acetate. As shown in Figure 6, efficiency ranged from 53% for a ratio of 1 to 1 of this parameter and to 80% for a ratio of 1 to 2. However, this incremental rate suddenly decreases by increasing the molar ratio to 3 due to the dilution of the reaction solution relative to the catalyst; therefore, the catalyst is distributed in greater volume and, thus, has no significant effect [25].

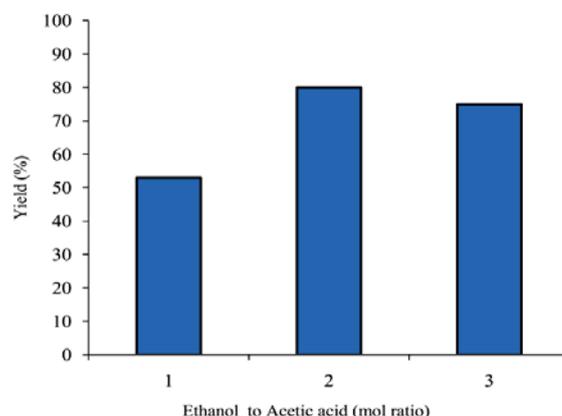


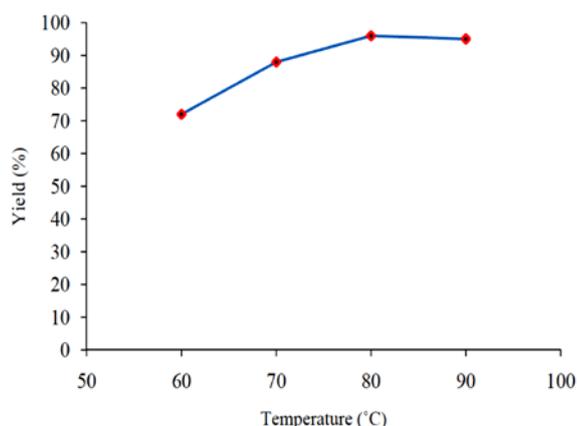
Figure 6. Effect of molar ratio of acetic acid to ethanol in esterification reaction.

As shown in Table 2, the production of ethyl acetate was enhanced with an increase in the amount of catalyst to 5 wt %, because a superior number of acid sites were available with an increase in the quantity of catalyst; however, an additional increase to 7 wt % did not have greater effect on the yield of ethyl acetate [26]. Therefore, the preferred amount of the catalyst was 5 wt % to avoid overuse.

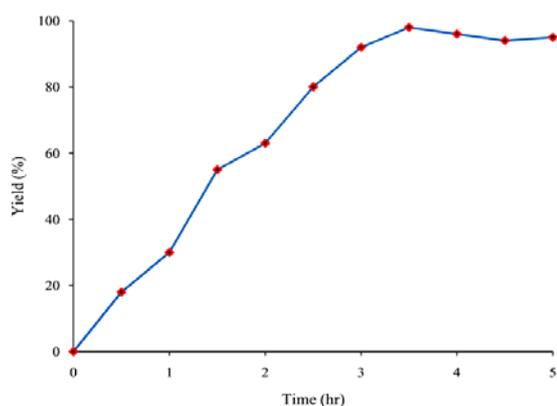
Table 2. Variation of yield by catalyst amounts.

Run	1	2	3	4	5
Catalyst (wt %)	-	1	3	5	7
Yield	3	49	80	96	95

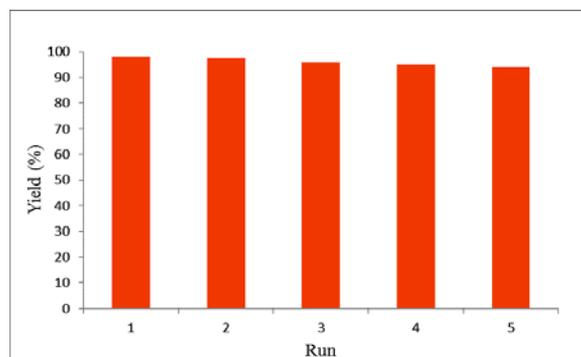
Figure 7 shows the change in yield with increasing temperature. This graph shows that, at upper temperatures, the yield of acetic acid is enhanced. An increase in temperature was clearly an effective parameter and the accelerator of the reaction [27]. It is true that the reaction efficiency increases with increasing temperature; however, the variations in efficiency versus temperature are much less than the other influential parameters so that, even in some sources, the effect of temperature can be ignored.

**Figure 7.** Effect of temperature in the esterification of acetic acid with ethanol.

One important parameter of any catalytic reaction is time. In order to assess the yield of acid acetic as a function of temperature, a series of experiments from 1 to 5 hours were carried out at a reaction temperature of 80 °C for 10 % HPW/ Al₂O₃-ZnO. As observed in Figure 8, a significant uptrend in yield ratio occurred during the first 3.5 hours of reaction, after which the amount of yield stayed approximately constant, implying that the yield was achieved at a near-equilibrium point. By increasing the amount of produced water, the reaction progress decreases subsequently because of competition between the water and acid molecules to react with the active sites on the catalyst [2].

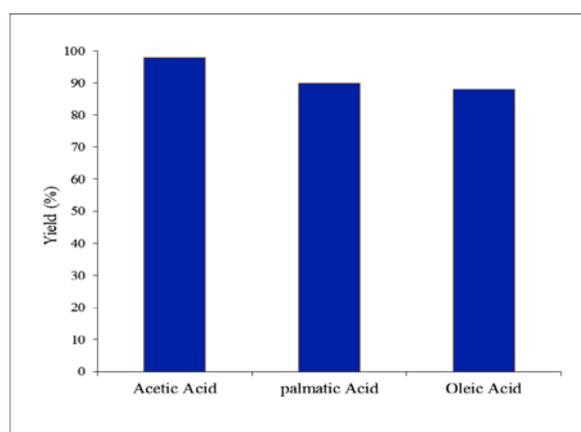
**Figure 8.** Effect of time in esterification of acetic acid with ethanol.

The catalytic stability of the 10 % HPW/ Al₂O₃-ZnO in the esterification of acetic acid is shown in Figure 9. After simply separating the used catalyst from the reaction medium, washing, and drying, it was charged into the reaction medium for a new run under the optimum reaction condition. Since the activity of the catalyst remained almost steady after five runs and a decrease in the yield was negligible, this result indicated that the 10 % HPW/ Al₂O₃-ZnO was recyclable and could be a suitable candidate for esterification reaction.

**Figure 9.** The reusability of the 10 % HPW/ Al₂O₃-ZnO in the esterification of acetic acid with ethanol.

Carbonic acid chain strongly affects the yield. Figure 10 obviously demonstrates that acid with shorter chain carbon can produce better efficiency in a less amount of time; it will soon react at the equilibrium point.

By increasing the length of the carbon chain in carboxylic acid, decreasing the activity in acid will be observed due to induction effect and steric effect [28]. The activation of carboxylic acid decreased with the addition of any component -CH₂ group. The observed trend for the catalytic role in the esterification of acetic acid (C3), palmitic acid (C16), and oleic acid (C18) suggests that increasing the carbon chain increases electrons and the steric effect phenomenon [29,30]. Consequently, in acids with longer carbon traces, alcohol attack on acid occurs at a lower rate.

**Figure 10.** Effect the length of acid chain.

4. CONCLUSIONS

In this paper, the effect of adding alumina and phosphotungstic acid as a Lewis and Bronsted acid on the catalytic activity of zinc oxide in esterification reaction was studied. The 10 % HPW/Al₂O₃-ZnO catalyst showed the highest activity because of strong acid sites, releasing H⁺ and water-resistant properties. The maximum yield of ethyl acetate was 98 % under reaction conditions including ethanol/acetic

acid molar ratio of 2, a reaction temperature of 80 °C, and the time duration of 3.5 h. Moreover, the 10 % HPW/Al₂O₃-ZnO catalyzed esterification of fatty acids (palmitic and oleic acid) to ethyl ester by yield of around 90 % in the optimized reaction condition.

5. ACKNOWLEDGEMENT

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REFERENCES

- Gangadwala, J., Mankar, S., Mahajani, S. and Stein, A.K.E., "Esterification of acetic acid with butanol in the presence of ion-exchange resins as catalysts", *Industrial & Engineering Chemistry Research*, Vol. 43, No. 10, (2003), 2146-2155. (DOI: 10.1021/ie0204989).
- Aghabarari, B., Ghiaci, M., Amini, S.G., Rahimi, E. and Martinez-Huerta, M.V., "Esterification of fatty acids by new ionic liquids as acid catalysts", *Journal of the Taiwan Institute of Chemical Engineers*, Vol. 45, No. 2, (2014), 431-435. (DOI:10.1016/j.jtice.2013.08.003).
- Uprety, B.K., Chaiwong, W., Ewelike, C. and Rakshit, S.K., "Biodiesel production using heterogeneous catalysts including wood ash and the importance of enhancing byproduct glycerol purity", *Energy Conversion and Management*, Vol. 115, (2016), 191-199. (DOI: 10.1016/j.enconman.2016.02.032).
- Alcañiz-Monge, J., El Bakkali, B., Trautwein, G. and Reinoso, S., "Zirconia-supported tungstophosphoric heteropolyacid as heterogeneous acid catalyst for biodiesel production", *Applied Catalysis B: Environmental*, Vol. 224, (2018), 194-203. (DOI: 10.1016/j.apcatb.2017.10.066).
- Soltani, S., Rashid, U., Al-Resayes, S.I. and Nehdi, I.A., "Recent progress in synthesis and surface functionalization of mesoporous acidic heterogeneous catalysts for esterification of free fatty acid feedstocks: A review", *Energy Conversion and Management*, Vol. 141, (2017), 183-205. (DOI: 10.1016/j.enconman.2016.07.042).
- Srilatha, K., Lingaiah, N., Prabhavathi, D.B., Prasad, R.B.N., Venkateswar, S. and Sai Prasad, P.S., "Esterification of free fatty acids for biodiesel production over heteropoly tungstate supported on niobia catalysts", *Applied Catalysis A: General*, Vol. 365, (2009), 28-33. (DOI: 10.1016/j.apcata.2009.05.025).
- Wee, L.H., Bajpe, S.R., Janssens, N., Hermans, I., Houthoofd, K., Kirschhocka, C.E.A. and Martens, J.A., "Convenient synthesis of Cu₃(BTC)₂ encapsulated Keggin heteropolyacid nanomaterial for application in catalysis", *Chemical Communications*, Vol. 46, No. 43, (2010), 8186-8188. (DOI:10.1039/C0CC01447H).
- Manikandan, K. and Cheralathan, K.K., "Heteropoly acid supported on silicalite -I possessing intracrystalline nanovoids prepared using biomass - an efficient and recyclable catalyst for esterification of levulinic acid", *Applied Catalysis A: General*, Vol. 547, (2017), 237-247. (DOI: 10.1016/j.apcata.2017.09.007).
- Ribeiro, J.S., Celante, D., Brondani, L.N., Trojahn, D.O., Silva, C.d. and Castilhos, F.d., "Synthesis of methyl esters and triacetin from macaw oil (*Acrocomia aculeata*) and methyl acetate over γ -alumina", *Industrial Crops & Products*, Vol. 124, (2018), 84-90. (DOI: 10.1016/j.indcrop.2018.07.062).
- Sung, D.M., Kim, Y.H., Park, E.D. and Yie, J.E., "Correlation between acidity and catalytic activity for the methanol dehydration over various aluminum oxides", *Research on Chemical Intermediates*, Vol. 36, (2010), 653-660. (DOI: 10.1007/s11164-010-0201-y).
- Kwong, T. and Yung, K.F., "One-step production of biodiesel through simultaneous esterification and transesterification from highly acidic unrefined feedstock over efficient and recyclable ZnO nanostar catalyst", *Renewable Energy*, Vol. 90, (2016), 450-457. (DOI: 10.1016/j.renene.2016.01.028).
- Anjani, N., Naik, S. and Fernandes, J., "Zinc oxide as a solid acid catalyst for esterification reaction", *Catalysis Communications*, Vol. 65, (2015), 20-23. (DOI: 10.1016/j.catcom.2015.02.009).
- Lee, H.V., Juan, J.C. and Taufiq-Yap, Y.H., "Preparation and application of binary acid- base CaO-La₂O₃ catalyst for biodiesel production", *Renewable Energy*, Vol. 74, (2015), 124-132. (DOI: 10.1016/j.renene.2014.07.017).
- Lee, H.V., Taufiq-Yap, Y.H., Hussein, M.Z. and Yunus, R., "Transesterification of jatropha oil with methanol over Mg-Zn mixed metal oxide catalysts", *Energy*, Vol. 49, (2013), 12-18. (DOI: 10.1016/j.energy.2012.09.053).
- Wen, Z., Yu, X., Tu, S-T., Yan, J. and Dahlquist, E., "Biodiesel production from waste cooking oil catalyzed by TiO₂-MgO mixed oxides", *Bioresource Technology*, Vol. 101, (2010), 9570-9576. (DOI: 10.1016/j.biortech.2010.07.066).
- Carrera, Y., Morales-Mendoza, G., Valverde-Aguilar, G. and Mantilla, A., "ZnO-Al₂O₃-La₂O₃ layered double hydroxides as catalysts precursors for the esterification of oleic acid fatty grass at low temperature", *Catalysis Today*, Vol. 212, (2013), 164-168. (DOI: 10.1016/j.cattod.2012.12.017).
- Chen, C., Liu, P. and Lu, C., "Synthesis and characterization of nano-sized ZnO powders by direct precipitation method", *Chemical Engineering Journal*, Vol. 144, No. 3, (2008), 509-513. (DOI: 10.1016/j.cej.2008.07.047).
- Qi, G., Yang, R.T. and Chang, R., "MnO_x-CeO₂ mixed oxides prepared by co-precipitation for selective catalytic reduction of NO with NH₃ at low temperatures", *Applied Catalysis B: Environmental*, Vol. 51, No. 2, (2004), 93-106. (DOI: 10.1016/j.apcatb.2004.01.023).
- Nie, G., Zou, J.J., Feng, R., Zhang, X. and Wang, L., "HPW/MCM-41 catalyzed isomerization and dimerization of pure pinene and crude turpentine", *Catalysis Today*, Vol. 234, (2014), 271-277. (DOI: 10.1016/j.cattod.2013.12.003).
- Cho, H.T., Salvia-Trujillo, L., Kim, J., Park, Y., Xiao, H. and McClements, D.J., "Droplet size and composition of nutraceutical nanoemulsions influences bioavailability of long chain fatty acids and Coenzyme Q10", *Food Chemistry*, Vol. 156, (2014), 117-122. (DOI: 10.1016/j.foodchem.2014.01.084).
- Pung, S.Y., Ong, C.S., Isha, K.M. and Othman, M.H., "Synthesis and characterization of Cu-doped ZnO nanorods", *Sains Malaysiana*, Vol. 43, No. 2, (2014), 273-281.
- Ullah, R., Zhang, Z., Bai, P., Wu, P., Han, D., Etim, U.J. and Yan, Z., "One-pot cation-anion double hydrolysis derived Ni/ZnO-Al₂O₃ absorbent for reactive adsorption desulfurization", *Industrial & Engineering Chemistry Research*, Vol. 55, No. 13, (2016), 3751-3758. (DOI: 10.1021/acs.iecr.5b04421).
- Oliveira, C.F., "Esterification of oleic acid with ethanol by 12-tungstophosphoric acid supported on zirconia", *Applied Catalysis A: General*, Vol. 372, No. 2, (2010) 153-161. (DOI: 10.1016/j.apcata.2009.10.027).
- Manabe, S., Sun, K. and Kobayashi, X.M., "Dehydration reactions in water. surfactant-type Bronsted acid-catalyzed direct esterification of carboxylic acids with alcohols in an emulsion system", *Journal of the American Chemical Society*, Vol. 123, No. 41, (2001), 10101-10102. (DOI: 10.1021/ja016338q).
- Aghabarari, B. and Dorostkar, N., "Modified bentonite as catalyst for esterification of oleic acid and ethanol", *Journal of the Taiwan Institute of Chemical Engineers*, Vol.45, No. 4, (2014), 1468-1473. (DOI: 10.1016/j.jtice.2014.03.006).
- Borges, M.E. and Díaz, L., "Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reactions: A review", *Renewable and Sustainable Energy Reviews*, Vol. 16, No. 5, (2012), 2839-2849. (DOI: 10.1016/j.rser.2012.01.071).
- Khudsange, C.R. and Wasewar, K.L., "Kinetics, mass transfer, and thermodynamic and statistical modeling study for esterification of valeric acid with n-butanol: Homogeneous and heterogeneous catalysis", *International Journal of Chemical Kinetics*, Vol.50, No. 10, (2018), 710-725. (DOI: 10.1002/kin.21195).
- Newman M.S., *Steric effects in organic chemistry*, London, John Wiley & Sons, (1956).
- Charton, M., "Steric effects In esterification and acid-catalyzed hydrolysis of esters" *Journal of the American Chemical Society*, Vol. 97, No. 6, (1975), 1552-1556. (DOI: 10.1021/ja00839a047).
- Fujita, M.N. and Takayama, T.C., "Nature and composition of Taft-Hancock steric constants", *Journal of Organic Chemistry*, Vol. 38, No. 9, (1973), 1623-1630. (DOI: 10.1021/jo00949a001).