

CHARACTERIZATION OF CHEMICAL STRUCTURE FOR BASE ACTIVE METAL (NaOH) ON PALM OIL INDUSTRIAL WASTE

Article history

Received

26 June 2015

Received in revised form

21 September 2015

Accepted

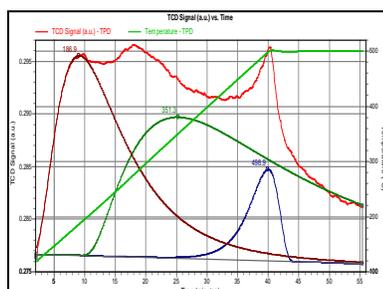
19 December 2015

Noraini Razali*, Marshahida Mat Yashim, Norkamruzita Saadon, Norazah Abdul Rahman

*Corresponding author

Faculty of Chemical Engineering, Universiti Teknologi MARA, Terengganu, Malaysia norainirazali@tganu.uitm.edu.my

Graphical abstract



Abstract

The development of solid catalyst has been investigated by considering the development of the chemical structure. In this study, solid catalyst was produced by using potassium hydroxide (NaOH) as an active metal on three types of support, Magnesium Oxide (MgO), Oil Palm Kernel Shell (OPKS) and Oil Palm Ash (OPA). Catalysts were studied at different temperatures (300 °C, 400 °C, 500 °C) and time (4 and 5 hr) calcination via impregnation process. The catalysts were subjected to characterization analysis using Chemisorption, Thermogravimetric analysis (TGA) and X-Ray Diffractometer (XRD). Chemisorption results showed weaker active sites developed at higher calcination temperatures while TGA results showed higher thermal stability at longer calcination times. In addition, the intensity of the XRD peaks also increased with increasing calcination temperature. The results showed that agricultural waste from the oil palm industry could be tuned as a potential support to produce active catalyst and can be applied in related chemical reactions.

Keywords: Solid catalyst, Characterization, Oil Palm Kernel Shell

© 2016 Penerbit UTM Press. All rights reserved

1.0 INTRODUCTION

Research into catalysis is a major field for the production of most industrial chemicals. Developing solid catalysts have been intensively studied due to the advantages of the catalysts are not consumed or dissolved in the reaction. Hence, the catalyst is easily separated from the products [1, 2]. Solid catalysts produced from agricultural waste are highly suggested due to the environmental aspect. Oil palm kernel shell is an abundantly available throw-away waste from the oil palm industry that has currently emerged to be an ideal solid waste to be utilized as catalyst support. Since, being the largest producer of palm oil in the world, Malaysia has to face the consequences of the huge accumulation (30 million tons per year) of undesired solid waste such as palm fiber, shells, and empty fruit bunches [3]. The characteristics of OPKS

which consists of high carbon but low inorganic contents in oil palm shells make it essential to be used as a raw material to prepare activated carbon [4]. OPKS was used as a raw material in many industrial sectors mostly for floor roofing, water treatment and road-based material [5]. Therefore, the waste from the oil palm industry can be reduced to be used in such industrial sectors. Currently, Malaysia has almost 18 oleochemical plants in operation. According to [6], Malaysia is the largest producer in exporting palm oil and ranked as the fourth contributor to the increasing of income or economy of this country. The utilization of oil palm kernel shell in numerous fields of application is an effective way and overcoming part of the agricultural wastes and problems in Malaysia. Thus, a widespread and great progress in this area can be expected in the future.

A large numbers of heterogeneous catalysts such as alkali metal oxides and derivatives, alkaline earth metal oxides and derivatives, transition metal oxides and derivatives, mixed metal oxides and derivatives [7, 8, 9] and waste material based heterogeneous catalysts are found in literatures in the recent years and their uses in laboratory scale transesterification process. Using wastes as raw materials for catalyst synthesis could eliminate the wastes and simultaneously produced the catalysts with high cost effectiveness. The waste materials used as heterogeneous catalysts studied so far include waste snail shell [10], cocoa pod husk [11], mollusk and eggshell [12]. Besides, the sufficiently active and stable solid catalyst for this application is yet to be discovered in order to develop an effective catalyst with high activity and durability specifically in this study.

Thus, this study focuses on the in-depth understanding of incorporation of alkali metal (NaOH) on the oil palm kernel oil at different calcination temperature (400 to 600 °C) and different calcination period (3 hr to 5 hr). The successful incorporation of alkali metal on waste material has been compared with incorporation of alkali metal on the commercial support (zeolite).

2.0 EXPERIMENTAL

Solid catalyst was prepared by impregnation method. The support (OPKS) and an aqueous solution of sodium hydroxide (NaOH) compounds was impregnated for 24 hr to ensure that NaOH diffused and well dispersed thoroughly on the surface of support. The solid catalyst was calcined at different calcination temperature (400 – 500 °C) and calcination time (4 and 5 hr). Then, the NaOH/OPKS catalysts at different parameter studied were subjected to the Chemisorption, TGA and XRD analysis to analyse active site area and percent metal dispersion.

2.1 Characterization

In principle, the chemisorption system was made of a U-shaped pyrex reactor, equipped with an oven controlled by a PID temperature programmer, mass flowmeter, sampling valve and TC detector. The following standard reduction procedure was applied: the sample (0.1 g) was heated at a linear rate from 473 to 773 K with H₂/He mixture flowing at 10.17 cm³/STP. Then was left for several hours with the constant flowrate of He. The sample was then cooled in He flow to the temperature chosen for oxygen chemisorption.

The powder X-ray diffraction analysis was carried out using a Bruker X-ray diffractometer system (D8 Advance). The diffractometer is equipped with a 2.2 kW Cu anode long fine focus ceramic X-ray tube for

generating a CuK α radiation (1.5405 Å), used as an X-ray source to obtain the XRD patterns. The X-ray source was operated at 40 mA and 40 kV. The XRD patterns were compared to the standards to identify the crystalline phases.

3.0 RESULTS AND DISCUSSION

3.1 Chemisorption Analysis on Effect of Calcination Temperature

The chemisorption analysis of NaOH/OPKS at different temperature 400 °C and 500 °C was performed in this study. In Figure 1 TPD curves for NaOH/OPKS at 400 °C calcined temperature, three peaks were detected. According to [13, 14] these peaks describe consumption of hydrogen, either weakly or strongly linked to catalyst active site respectively.

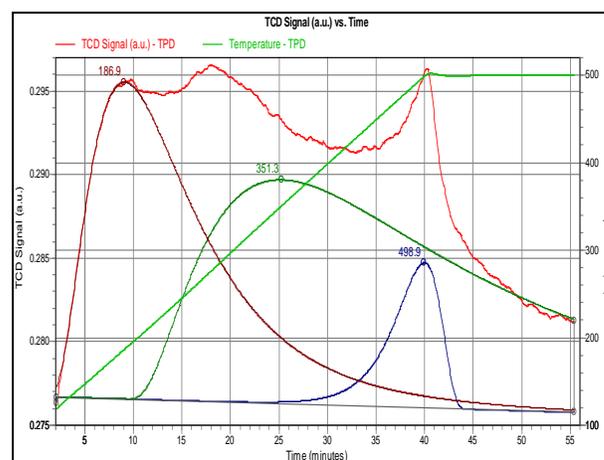


Figure 1 TPD diagram for NaOH/OPKS at calcination temperature of 400 °C

The catalyst has been compared with NaOH impregnated on commercial support, MgO. From Table 1, the area hydrogen absorbed was compared for the 400 and 500 °C of calcined catalyst. The highest area obtained at 400 °C of calcination temperature is at 315.3 °C with 0.41604 and the highest area for 500 °C calcined catalyst is at 346.6 °C with 0.52253. However, at higher detected temperature for both calcined catalyst showed the decreasing of area for hydrogen consumed. The lowest area for NaOH/OPKS catalyst was detected at 500 °C calcined catalyst, with only 0.05167. As contrast, for NaOH/MgO calcined at 600 °C, the area showed lowest at detected temperature of 263.5 °C with only 0.00583. According to [14] at higher temperatures, the pore walls of the support cannot withstand the growing internal stresses leading to pore collapse and the consequent loss of surface area.

Table 1 Chemisorption analysis for NaOH/OPKS catalyst at different calcination temperature

Sample	Calcination Temperature (°C)	Calcination Time (hr)	Detected Temperature (°C)	Area
NaOH/OPKS	400	4	315.3	0.41604
			498.9	0.05539
NaOH/OPKS	500	4	346.6	0.52253
			499.9	0.05167
NaOH/MgO	600	5	263.5	0.00583
			348.9	0.17410

^a NaOH/OPKS and NaOH/MgO catalyst were carried out at same concentration of 1 Molar and 3:1, respectively with vigorous stirring.

3.2 Chemisorption Analysis on Effect of Calcination Time

The chemisorption results of NaOH/OPKS catalyst at 500 °C temperature calcined with different time was illustrated in Table 2. The catalyst has been compared with NaOH impregnated on commercial support, MgO. For NaOH/MgO catalyst, the largest area of absorbed hydrogen obtained at 3 hr of calcination with area 0.29703, while for NaOH/OPKS catalyst, the largest area detected was at 4 hr with area 0.52253. However, the lowest area for absorbing H₂ was shown by NaOH/MgO catalyst for the 5 hr of calcination time

with only 0.00692. From the results, lower detected temperature showed higher absorbing area of hydrogen, which means the area of active site is higher. According to [13], heating the catalyst at high temperature will make the material desorbed both water and hydrogen molecules which result of dehydroxylation which lead to the undeveloped active sites structure. To conclude, the higher the temperature of calcination temperature of NaOH/OPKS catalyst, the weaker active site was developed. In comparison, the suitable calcination temperature for NaOH/OPKS catalyst is at 400 °C.

Table 2 Chemisorption analysis for NaOH/MgO and NaOH/OPKS catalyst at different calcination time

Sample	Calcination Temperature (°C)	Calcination Time (hr)	Detected Temperature (°C)	Area
NaOH/MgO	500	3	255.2	0.29703
			354.9	0.22814
NaOH/MgO	500	5	272.5	0.00692
			353.7	0.16238
NaOH/OPKS	500	4	346.6	0.52253
			499.9	0.05167
NaOH/OPKS	500	5	263.4	0.27436
			500.9	0.26286

^a NaOH/OPKS and NaOH/MgO catalyst were carried out at same concentration of 1 Molar and 3:1, respectively with vigorous stirring.

3.3 TGA Analysis on Effect of Calcination Time

The analysis chemical structure of the catalyst was further investigated by using thermal analysis, TGA in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss). The catalyst calcined at temperature 400 °C, gave total weight loss about 34.5 % while for higher calcination temperature, 500 °C is

27.4 %. The result show that total weight loss at the end point of thermal analysis (Figure 2) decreases by increasing calcinations temperature of catalyst. The lower total weight loss during combustion show the thermal stability catalyst is more stable.

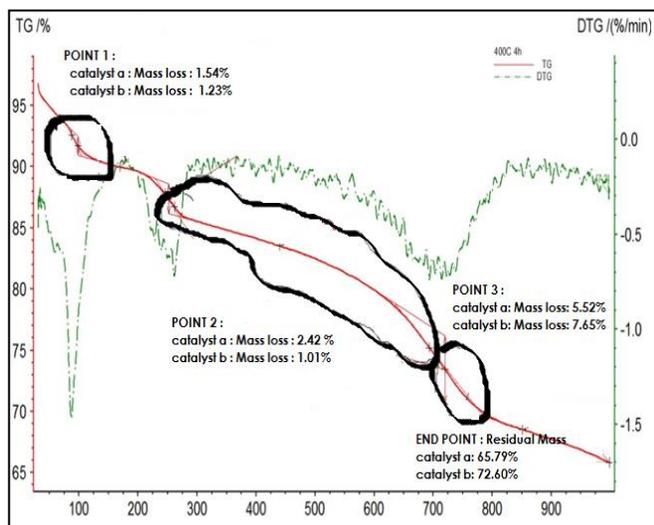


Figure 2 TGA diagram for NaOH/OPKS catalyst with catalyst a: NaOH/OPKS calcined at temperature of 400 °C and catalyst b: NaOH/OPKS calcined at temperature of 500 °C

In Figure 2, point 1 was attributed to the elimination of water absorbed in the pores of carbon at low thermal temperature. The decomposition of material and loss of mass is gradually increasing. The total mass loss in point 2 for catalyst a is 9.48 % while catalyst b is 9.89 %. The losses can be relate to the chemical reaction that take place due to high temperature [15]. The maximum thermal stability of the catalyst calcined at 400 and 500 °C are shown in Figure 2. The catalyst that calcined at 400 °C showed lower residual mass compare with catalyst calcined at 500 °C, with 65.79 and 72.60 %, respectively. To conclude the high thermal stability for a catalyst must have lower decomposition in high temperature and left with higher residue mass at the end of combustion. Hence, in this study, the catalyst calcined at 500 °C showed having more stability compared to 400 °C calcined catalyst.

3.4 XRD Analysis on Effect of Calcination Time

The x-ray diffraction (XRD) patterns has been used to analyse the NaOH supported on oil palm ash catalyst with different calcinations temperature. The X-ray patterns of the catalysts in Figure 3 showed that the intensity of the XRD peaks increased with the increasing of calcinations temperature. The 300 °C of NaOH/OPA Ash, only one diffraction peak of NaOH was detected at angle of $2\theta = 32.3$. Otherwise, 3 additional peaks was observed for the NaOH/OPA at 400 °C of calcination temperature, at angle of $2\theta = 23.5, 35.2, 39.1$ & 44.6 . In addition, for 500 °C of NaOH/OPA, 6 diffraction peak was observed at angle of $2\theta = 23.15, 26.2, 30.1, 35.3, 40.7$ and 43.6 . From the XRD result, the NaOH compound was observed to increase with the increasing of the calcinations temperature. This result was in well agreement with [8] which found that more crystallinity of the NaOH could be detect with the increasing calcination temperature because the

humidity of the catalyst was decreased. Furthermore, NaOH compound was found to have well dispersed on the palm waste support, oil palm ash.

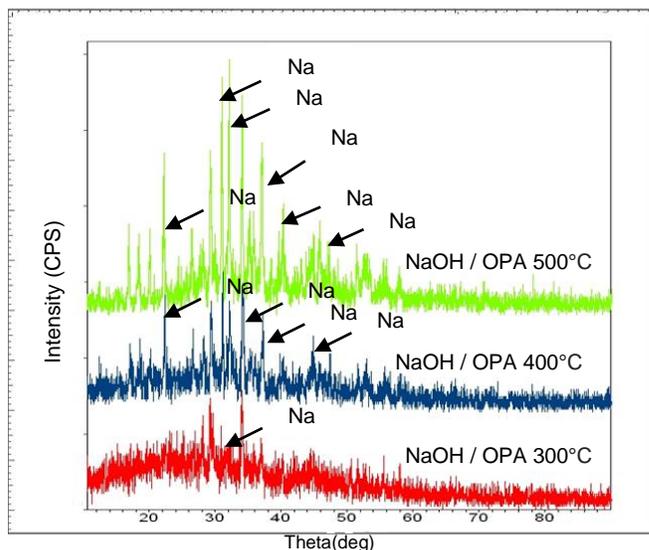


Figure 3 XRD patterns of the NaOH/OPA catalysts: (a) NaOH /OPA at 300 °C (b) NaOH/OPA at 400°C (c) NaOH/OPA at 500°C

4.0 CONCLUSION

Based on the experimental result obtained, it can be conclude that oil palm kernel shell and oil palm ash support could be used as an effective catalyst using NaOH as an active metal. The chemical structure of impregnated NaOH on three types of support shown have high thermal stability at higher calcination time and high intensity and crystallinity at higher calcination temperature. However, future research on this catalyst is still needed to investigate the develop structure via analysis through SEM, TEM and etc. The future study also suggested to cover new possible synthesis parameters such as different active metal, ratio of support and active metal loading, impregnation time and calcinations time to ensure and produce the effective solid catalyst.

Acknowledgement

The authors would like to thank Universiti Teknologi Mara for providing fund via RAGS, reference number: 600-RMI/RAGS 5/3 (82/2013) for this project.

References

- [1] Zabeti, M. W., Wan Daud, M. A., Aroua, M. K. 2009. Activity Of Solid Catalysts For Biodiesel Production: A Review. *Fuel Processing Technology*. 90: 770-777.
- [2] Bartley, J. K., Xu, C., Lloyd, R., Enache, D. I., Knight, D. W. and Hutchings, G. J. 2012. Simple Method To Synthesize High Surface Area Magnesium Oxide And Its Use As A

- Heterogeneous Base Catalyst. *Applied Catalysis B: Environmental*. 128: 31-38. doi:10.1016/j.apcatb.2012.03.036.
- [3] Yang, H., Yan, R., Chen, H., Lee, D. H., Liang, D. T. and Zheng, C. 2006. Pyrolysis Of Palm Oil Wastes For Enhanced Production Of Hydrogen Rich Gases. *Fuel Processing Technology*. 87: 935-942.
- [4] Zariyah, N. 2010. To Produce The Activated Carbon From Matured Palm Kernel Shell. *Universiti Malaysia Pahang*. 12-19.
- [5] Ramin, H. K., Alengaram, U. J., Zamin, M. J., and Hamid, N. 2013. Mix Design For Fly Ash Based Oil Palm Shell Geopolymer Lightweight Concrete. *Construction and Building Materials*. 490-496.
- [6] Puad, E. 2001. The Production Of Palm Kernel Shell Charcoal By The Continuous Kiln Method. *Universiti Putra Malaysia*. 1-25.
- [7] Lo'pez, D. E., Goodwin Jr., J. G., Bruce, D. A. and Lotero, E. 2005. Transesterification Of Triacetin With Methanol On Solid Acid And Base Catalysts. *Applied Catalysis A: Gen.* 295: 97-105.
- [8] Zheng, S. Wang, X. Wang, X. Wang, A., and Wu. 2005. *Material Letter*. 2769-2773.
- [9] Xie, W., Peng, H. and Chen, L. 2006. Transesterification Of Soybean Oil Catalyzed By Potassium Loaded On Alumina As A Solid-Base Catalyst. *Applied Catalysis A, Gen.* 300: 67-74.
- [10] Birla, A., Singh, B., Upadhyay, S. N. and Sharma, Y. C. 2012. Kinetics Studies Of Synthesis Of Biodiesel From Waste Frying Oil Using A Heterogeneous Catalyst Derived From Snail Shell. *Bioresource Technology*. 106: 95-100.
- [11] Ofori-Boateng, C. and Lee, K. T. 2013. The Potential Of Using Cocoa Pod Husks As Green Solid Base Catalysts For The Transesterification Of Soybean Oil Into Biodiesel: Effects Of Biodiesel On Engine Performance. *Chemical Engineering Journal*. 220: 395-401.
- [12] Viriya-empikul, N., Krasae, P., Puttasawat, B., Yoosuk, B., Chollacoop, N. and Faungnawakij, K. 2012. Waste Shells Of Mollusk And Egg As Biodiesel Production Catalysts. *Bioresource Technology*. 106: 95-100.
- [13] Boudjahem, A. G., Monteverdi, S., Mercy, M., Ghanbaja, D. and Bettahar, M. M. 2002. Nickel Nanoparticles Supported On Silica Of Low Surface Area. Hydrogen Chemisorption And TPD And Catalytic Properties. *Catalysis Letters*. 84(1-2): 115-122. Retrieved from ISI:000179179200018.
- [14] Arsalanfar, M., Mirzaei, A. A. and Bozorgzadeh, H. R. 2012. Effect Of Calcination Conditions On The Structure And Catalytic Performance Of Mgo Supported Fe-Co-Mn Catalyst For CO Hydrogenation. *Journal of Natural Gas Science and Engineering*. 6: 1-13. doi:10.1016/j.jngse.2012.01.003.
- [15] Ruiz, H. A, Zambro, M. A, Giraldo, L., Siesra, R. and Moreno-Pirajan, J. C. 2014. Production And Characterization Of Activated Carbon From Oil Palm Kernel Shell For Carboxylic Acid Adsorption. *Oriental Journal of Chemistry*. 31(2): 753-762.