Characterization and Testing of Zeolite Y Dealuminate Catalysts for Glycerol Conversion to Glycerol Mono Laurate

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Characterization and Testing of Zeolite Y Dealuminate Catalysts for Glycerol Conversion to Glycerol Mono Laurate

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This Research has been done to analyze Zeolite Y CBV 712 as a catalyst. Some method used in order to treat the zeolite such as dealumination and X-ray Diffraction to analyze the crystallinity. Zeolite Y CBV 712 was dealuminated by treating it with H_2SO_4 solution, with 3–8 M concentration at 40–60 °C. The dealumination treatment runs for 4 hours. Then, dealuminated zeolite was calcinated with a furnace for 3 hours with temperature range between 500–600 °C. Dealuminated zeolit Y then tested to synthesize Glycerol Mono Laurate (GML). Dealumination affect to increase the ratio of Si/A, caused by removing of aluminium. H_2SO_4 as acid represents the content of free fatty acids produced from the glycerol synthesize and also the main parameters that reflect the catalyst activity. Crystallinity of zeolite was identified by X-ray Diffraction (XRD). The results showed that the increasing crystallinity percentage represents the higher acid conversion. However, the increasing of crystallinity defines decreasing of the GML conversion from 45.17% to 34.98% and decreasing of the conversion Glycerol Di Laurate (GDL) also from 31.68% to 20.32%. On other hand, Glycerol Tri Laurate (GTL) had different results. The more crystallinity caused the increasing conversion to GTL from 9.07% to 20.32%. The results indicated that the increasing of crystallinity of zeolite caused the decreasing of the conversion to GML and GDL, except for GTL.

Keywords: Glycerol, Glycerol Mono Laurate, Zeolite Y, Dealumination.

1. INTRODUCTION

Glycerol is a side product of a biodiesel production using transesterification process and an alcoholic compound that consists of three hydroxyl group. Glycerol (1, 2, 3 propanetriol) is a clear liquid, smell-less and a viscous liquid that tastes sweet. One of the glycerol derivative compounds is Glycerol Monolaurate which used in food additives, surfactant, medicine, cosmetics and others.[1] As a non-ionic surfactant which consists of hydrophilic and hydrophobic group, Glycerol Monolaurate can be used as a nutrition supplement.[2] In the making of Glycerol Monolaurate, catalysts is used to accelerate the reaction and increasing the yield of Glycerol Monolaurate. One of the catalysts that had been used is Zeolite Y.[3] Dealumination is used to increase the acidity of the zeolites[4] Characterizationis used to determine the characteristics of the Zeolit Y that had been dealuminize.[5]

Zeolite Y is a kind of crystalline aluminosilicate with a microscale cavity which has a pore size of about 0.74 nm framework.[6,7] The zeolites have the largest application in catalysis and classified as faujasites.[8] Faujasites is a kind of the zeolite mineral group which is a silicate mineral.[9]

Surface area is important in catalyst applications. The term texture refers to the pore structure covering a surface area, pore size distribution and pore shape. In this case, the total surface area is a crucial criterion for determining the amount of the solid catalyst for catalytic active sites in relation to the activity of the catalyst. Measurement of surface area is using physical adsorption technique with the principle of Van der Waals force. The equilibrium isotherms can be described in which the volume of adsorbed plotted with a *P/Po* (*P*: pressure, *Po*: saturated pressure on temperature measurements). The theoretical method to declare equilibrium in adsorption Brunauer Emmett Teller model is better known as the BET equation.[10]

Characteristic X-ray Diffraction (XRD) is intended to identify a catalyst bulk phase and determine the nature of the crystal or crystallinity of a catalyst. Most of the catalysts that have the form of solids crystalline, such as metal oxides, zeolites and metal.

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XRD is a technique to evaluate the nature of the crystalline phase and the crystal size. In XRD analysis, the catalyst crystals will reflect X-rays sent from the source and received by the detector. Based on the angle of arrival of the X-ray spectrum of specific reflection will deal directly with the lattice spacing of crystals were analyzed. The diffraction patterns were plotted based on the peak intensity stating the crystal lattice parameter maps (Miller index) as a function of 2θ where θ expressed diffraction angles based on Bragg equation. The interpretation of Bragg equation is based on the assumption that the surface of the X-rays reflected by horizontal.

In this study are using three stages of chemical treatment processes dealumination i.e., washing, drying and calcination process. The variables in this dealumination process are temperature and concentration variable of acid (HCl). This research is expected to get the optimum operating conditions of dealumination process on zeolite catalysts.

The process steps are dealumination of zeolite Y using H_2SO_4, drying at 110 °C for 1 hour, and calcination at 500–600 °C for 3 hours. Catalyst characteristics consisted X-ray Diffraction (XRD) to identify the bulk phase and determine the nature of the catalyst crystals or crystalitation of a catalyst. The optimum condition to produce Zeolit Y catalysts is obtained the highest of Glycerol Monolaurate (GML) yield.

2. EXPERIMENTAL DETAILS

Zeolite Y CBV 712 (supplied by Zeolyst International in NH_4 form; mole ratio $SiO_2/Al_2O_3 = 12$; surface area = 730 m^2/g) was dealuminated by treating it with H_2SO_4 solution, with 3–8 M concentration at 40–60 °C. The dealumination treatment was carried out in a three neck flask with stirrer for mixing the sulphuric acid with Zeolite Y, and dealuminated for 4 hours. Then, zeolite that have been dealuminated, calcinated with a furnace for 3 hours with temperature range between 500–600 °C. Dealuminated Zeolite Y then, tested to synthesize glycerol monolaurate using a glycerol weighing 92.24 gr and lauric acid weighing 25 gr. The dealuminated Zeolite Y used for this synthesize is 3.75 gr per sample.

XRD measurements were performed using a Kensa with Cu $K\alpha$ radiation at 30 kV and 30 mA in the range of $2\theta = 2°$ to 90°, a scanning speed of 4° per minute at room temperature. The powder was mounted on a glass side. SEM measurements were performed to inform the surface of the dealuminated Zeolite Y with magnifications 5.000×; 10.000×; 15.000×; 20.000× respectively.

The performance of the catalysts was tested for synthetizing glycerol monolaurate in a stirred reactor. Glycerol with technical grade purity, weighing 92.24 gr and solid phase lauric acid weighing 25 gr and including a dealuminated catalysts weighing 3.75 gr was reacted at atmospheric pressure and temperature of 140 °C for 7 hours. The reaction products were separated using a whatman filter paper. The glycerol monolaurate were analyzed by a gas chromatography-mass spectrometry to know the conversion becoming a glycerol monolaurate.

3. RESULTS AND DISCUSSION

Zeolite Y was dealuminated using a sulphuric acid, basically a strong acid and could possibly damage the framework and also evicted Al from the zeolite framework. Thus, this

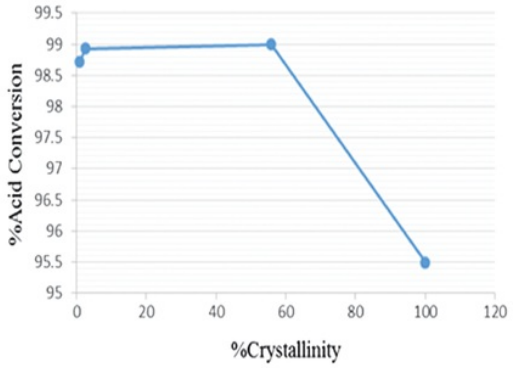

Fig. 1. Effect of catalyst crystallinity on acid conversion.

cause a decreased cristallinity upon the zeolites that have been dealuminated.[11] Dealuminated zeolite also usually change the structure and morphology of the zeolites, causing the changing of surface area, pore diameters and acidic power which disturbed the catalysts balance itself and affect the catalyst selectivity.[12] Dealumination also could affect the amount alumunium framework, by decreasing the amount of framework due to the extraction of alumunium from the zeolitic framework into the acidic solution and the amount of non-framework alumunium for the same reason.[13, 14]

Figure 1 show the change of crystallinity affect in a better acid conversion, rather than using the catalyst that never been dealuminated before. This means that, despite the changes of zeolites framework, the catalysts ability to accelerate the forming of other substrate (glycerol monolaurate) is faster than the using of zeolite Y without dealumination process. Acid conversion represents the content of free fatty acids produced from the glycerol synthesize, and in this case, is considered to be one of the main parameters that reflect the catalyst activity towards its ability to accelerate the forming of glycerol monolaurate.

Based on Figures 2–4, show that the use of dealuminated Zeolite Y, yield higher of glycerol monolaurate rather than the used of non dealuminated zeolite Y. Nevertheless, the selectivity of the dealuminated catalyst to yield another product (glycerol dilaurate and glycerol trilaurate) should be a consideration. However, the result is similar to the findings reported by Machado et al.[5] that the increase in the product yield with the dealumination

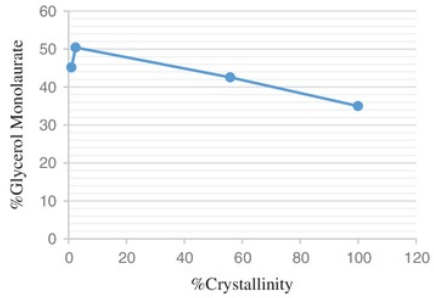

Fig. 2. Effect of catalyst crystallinity on glycerol monolaurate yield.

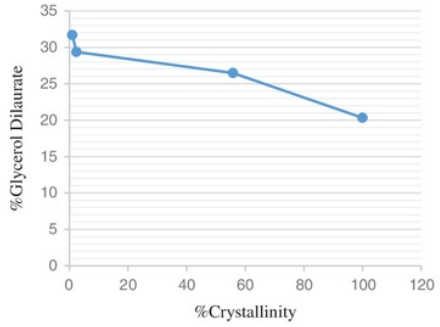

Fig. 3. Effect of catalyst crystallinity on glycerol dilaurate yield.

rate could be related in a first approach to the strength of the acid sites caused by dealumination, since dealumination process increase the Si/Al ratio as the number of framework alumunium diminishes.[15]

Another factor that can influence the catalyst reactivity has to be considered, as the hydrophobicity. Indeed, the catalyst hydrophobicity is expected to increase with the Si/Al ratio, which depressed the affinity of the solid surface for polar molecules such as water and glycerol. Increasing surface area, and the lower concentration of water molecules on the catalyst surface allows to displace the reaction towards the formation of products.

The selectivity of Zeolite Y is primarily towards the glycerol monolaurate, however as the yield increases, monolaurate selectivity falls linearly indicating the monoester is reacting at the external surface of catalyst particles to form the bulkier molecules of dilaurine, which due to their larger size are not formed inside the pores of the zeolite. The formation of glycerol trilaurate could possibly resulted by the long synthesizing time. Thus, further research towards the formation of glycerol trilaurate could be developed.

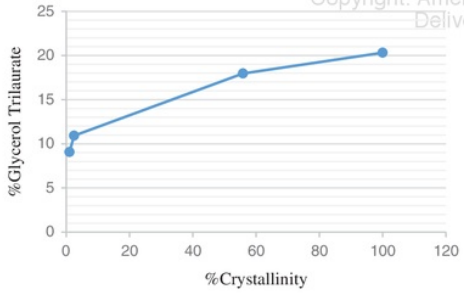

Fig. 4. Effect of catalyst crystallinity on glycerol trilaurate yield.

4. CONCLUSION

The results showed that the increasing crystallinity percentage represents the higher acid conversion. The higher crystallinity defines decreasing the GML yield and GDL yield from 45.17 to 34.98 for Glycerol Monolaurate and 31.68 to 20.32 for Glycerol Dilaurate. The yield of Glycerol Trilaurate had different results. The more crystallinity caused the increasing conversion to GTL from 9.07 to 20.32. The results indicated that the increasing of crystallinity of zeolite caused the decreasing of the conversion to Glycerol Monolaurate and Glycerol Dilaurate, except for Glycerol Trilaurate which equal to the percentage of the crystallinity.

References and Notes

1. T. Y. Wibowo, A. Z. Abdullah, and R. Zakaria, *Appl. Clay Sci.* 50, 280 **(2010)**.
2. R. Nakamura, K. Komura, and Y. Sugi, *Catal. Commun.* 9, 511 **(2008)**.
3. Y. Wang, R. Otomo, T. Tatsumi, and T. Yokoi, *Microporous Mesoporous Mater.* 220, 275 **(2016)**.
4. W. Xu, L. Y. Li, and J. R. Grace, *Chemosphere* 111, 427 **(2014)**.
5. M. D. S. Machado, J. Pérez-Pariente, E. Sastre, D. Cardoso, and A. M. de Guereñu, *Appl. Catal. A* 203, 321 **(2000)**.
6. B. C. Gates, Catalytic Chemistry, John Wiley & Sons, Inc., New York **(1997)**.
7. Y. Chen, B. Wang, L. Zhao, P. Dutta, and W. S. Winston Ho, *J. Membr. Sci.* 495, 415 **(2015)**.
8. C. H. L. Tempelman, X. Zhu, K. Gudun, B. Mezari, B. Shen, and E. J. M. Hensen, *Fuel Process. Technol.* 139, 248 **(2015)**.
9. W. Ratanathavorn, C. Samart, and P. Reubroychareon, *Mater. Lett.* 159, 135 **(2015)**.
10. J. W. Chorkendorff and Niemantsverdriet, Concepts of Modern Catalyst and Kinetics, WILEY-VSH Verlag GmbH & Co. KGaA, Weinheim **(2003)**.
11. J. M. Muller, et al., *Microporous Mesoporous Mater.* 260, 7 **(2014)**.
12. N. A. S. Amin and D. D. Anggoro, *Journal of Natural Gas Chemistry* 11, 79 **(2002)**.
13. X. Jiang, S. Li, G. Xiang, Q. Li, L. Fan, L. He, and K. Gu, *Food Chem.* 212, 585 **(2016)**.
14. M. C. Silaghi, C. Chizallet, and P. Raybaud, *Microporous Mesoporous Mater.* 191, 82 **(2014)**.
15. P. N. R. Vennestrom, T. V. W. Janssens A. Kustov, M. Grill A. Puig-Molina, L. F. Lundegaard, Ramchandra R. Tiruvalam, P. Conception, and A. Corma, *J. Catal.* 309, 477 **(2013)**.

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