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INVESTIGATION OF BIODIESEL-DRIVE GLYCEROL CONVERSION TO POLYGLYCEROL OVER BASIC MODIFIED AlPC CATALYST

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ABSTRACT

Energy, in the form of biofuel production through transesterification of vegetable oils and animal fats is rapidly increasing due to the hasty outgrowth of population and urbanization. Correspondent increase in the production of crude glycerol causes mixed effects. Sustainable biodiesel production requires optimization of its production process and drastic increase in the utilization of glycerol. To ensure high biodiesel yields and low environmental impacts, with respect to needless waste streams. Upgrading of crude glycerol to highly pure glycerol and subsequent utilization in producing value added products are emerging research areas. The production of such value-added chemicals requires new basic heterogeneous catalysts as well as optimization of the conventional catalyst materials. The clay especially mesoporous type clay have great potential as a catalyst. For present study Aluminum pillared clay (AlPC) was prepared by Al_{13} precursors and treated with NaOH to modify as basic which enhance conversion of glycerol to polyglycerol (diglycerol, triglycerol). The modified AlPC samples were well characterized by different latest techniques. The modified ALPC was found stable with high mesoporousity and basicity that enhances etherification reaction. The glycerol conversion and polyglycerol production yield was noted maximum 98% and 80.5% over prepared stable modified AlPC catalysts respectively. Industrially, the findings attained in this study might contribute towards promoting the biodiesel industry through utilization of its by-products.

Keywords: AlPC, lithium, clay, biodiesel, mesoporous.

INTRODUCTION

Energy demand and its resources are increasing day by day due to the rapid outgrowth of population and urbanization. Currently, fuel crisis has globally flounced the economy in every region, especially the oil consuming countries due to its rapidly decreasing available global stock. In view of this serious situation, biodiesel which comes from 100% renewable resources provides an alternative fuel option for future. Approximately 10 pounds of crude glycerol are created for every 100 pounds of biodiesel production. A crude glycerol glut is created due to rapidly expanding biodiesel industry (Ayoub and Abdullah, 2012). The production of biodiesel or value-added chemicals from biodiesel-derived glycerol requires new basic heterogeneous catalysts as well as optimization of the conventional catalyst materials. As mesoporous materials provide a combination of large specific surface area and a certain degree of pore size with shape selectivity, they have one of the greatest potential applications as a heterogeneous catalyst but limited for thermal stability or alkaline loading for basicity due to structure collapse (Ayoub and Abdullah, 2012). The clay minerals have great potential as a catalyst especially for the basic selective reactions to produce fine chemicals. They received substantial attention because of their operational simplicity, low cost, environmental compatibility, high selectivity and, reusability. Intercalated clays have interest as adsorbents, catalysts, and nanoporous materials in potential industrial and environmental applications (Zhou *et al.* 2004). Their applications as sorbents (Barrer; 1989), in fluid separation (Lourdes *et al.* 2006), and in catalysis (Salerno and

Madsen; 1999) have been studied. The development of thermally stable microporous and mesoporous interlayer structures continues to be an important objective in the preparation of cracking catalysts (Reddy *et al.* 2004; Parikh *et al.* 2004).

Pillared clay is mainly composed of oxides of Si and Al. The structure and properties of the pillared fabrications can be modified by varying the chemical components of either the basal layers or the interlayer pillars. One of the most common modifications made to cationic clay minerals to improve their porosity and stability is pillaring, which leads to the formation of a class of material known as pillared clays (Zuo and Zhou, 2006). The increasing mesoporous structure, surface area, pore volume, thermal stability with significant catalytic activity of pillared clays compared to their parent clays, making them highly attractive catalysts, adsorbents and ion exchangers (Ding *et al.* 2001). The most common pillars are metal oxides like aluminum oxide. For pillaring purpose, the pillars can be introduced into the interlayer region of the host clay using ion exchange or generated method. Aluminum oxide pillaring is basically a cation exchange reaction in which the original interlayer cations in the clay are exchanged with polymeric metal ions which fixed in the interlayer region as pillars after calcinations. For increasing basic strength of such pillared calay, first group of periodic table is one of the best choices and lithium is the most attractive due to small in size and high value of alkalinity.

In the present study, aluminum pillared clay (AlPC) was prepared with the help of Al_{13} precursors by ion-exchange method and subsequently it was made basic

with the help of NaOH solution. The prepared basic modified Aluminum pillared clay and parent clay, both were well characterized by different latest techniques to show stability, basicity and high mesoporisity. The prepared modified AlPC was used for etherification of glycerol conversion into polyglycerols. High conversion of glycerol and yield of polyglycerol was observed over this prepared catalyst.

EXPERIMENTAL

Materials

Sodium hydroxide (99%) was purchased from BDH, UK. Montmorillonite K-10 was supplied by Sigma–Aldrich. $AlCl_3.6H_2O$ was purchased from R&M Chemicals, Ltd., Malaysia. All the received chemicals were used without any further purification.

Preparation of the Oligomer for AlPC

The Al-hydroxy oligomer was prepared by gradual addition of 0.2 M NaOH to 0.2 M $AlCl_3.6H_2O$, at the rate of 1 to 3 ml min-1 while stirring vigorously at 25 °C. The resulting Alpolyhydroxy solution was kept at 25 °C for periods of 24 h. To accelerate the aging process of the oligomer, the solution was refluxed at 60 – 90 °C, 6 to 12 h (Kloprogge, 1998). The optimum OH/Al ratio to form the aluminum hydroxy precursor was 1.85.

Prepration of Intercalated AlPC

The prepared oligomer was intercalated on the clay K-10. The clay K-10 was well dispersed in demineralized water for 2 h. The basic clay Na-montmorillonite K-10 was prepared by repeated washings with 1N NaCl until chloride free ($AgNO_3$ test). Intercalation of the Al-hydroxy oligomer on the clay K-10 required its dropwise addition to the suspended clay at a rate of 1 ml/min while stirring vigorously at 25 °C. The newly formed intercalated clay sediment was filtered, washed to chloride-free ($AgNO_3$), air-dried at 50-60 °C, finely ground, and calcined at 550 °C for 4 h and named as AlPC.

Preparation of Basic Modified AlPC

A 250 mL round bottom flask equipped with a reflux condenser was charged with 10 grams of prepared Pillared Clay AlPC, 100 mL deionized water, and an amount of NaOH solution. This mixture was stirred and heated at reflux for 6 hours. The slurry was then allowed to cool to room temperature. The solid were separated from liquid by centrifugation. The liquid portion was decanted and discarded. The solids were washed by resuspending in 500 mL of deionized water and centrifuging. This sequence was repeated two more times to ensure removal of all soluble species. The base modified pillared clay was named as Na-AlPC and calcined in an oven at 550 ºC for 4 hours.

Characterization

The XRD diffraction patterns of the samples were recorded using Cu-Kα radiation and taken in the range of 5-100˚ (2θ) with a step size of 0.01º. Base strengths of the catalysts (H_) were determined using Hammett indicators. About 25 mg of the catalyst sample was shaken with 5.0 ml of a solution of Hammett indicators diluted with methanol, and left to equilibrate for 2 h. After the equilibration, the color on the catalyst was noted. The following Hammett indicators were used: neutral red (H_ = 6.8), bromthymol blue (H_ = 7.2), phenolphthalein (H_ = 9.3), 2,4-dinitroaniline (H_ = 15.0), 4-chloro,2-nitroaniline (H_ = 15.0) and 4-nitroaniline (H_ = 18.4). The N_2 adsorption-desorption isotherms were measured using a Belsorp II system at -196 °C. The samples were degassed at 300 °C for 4 h prior to analysis. The Brunauer-Emmett-Teller (BET) surface area was calculated using adsorption data in a relative pressure ranging from 0.04 to 0.20. The total pore volume was determined from the amount adsorbed at a relative pressure of about 0.99. The pore diameter was calculated from the adsorption branch by using the Barrett-Joyner-Halenda (BJH) method. Scanning electron microscopy (SEM) analysis measurements were performed using a Zeiss Supra 35VP equipment operated at 3.00 kV.

RESULTS AND DISCUSSION

The XRD pattern for clay AlPC and modified Na-AlPC are shown in Figure-1. It can be noticed from the figure that the patterns for both samples are almost identical. In addition, they are both very similar to the pattern of a typical mica and quad showing structure of alumina and silica. This means that modified AlPC was sustained its structure successfully after sodium application. However, there was a clear broadening of the reflections from the modified sample and also found some new peaks which relates to sodium presence. It can also be seen the decrease in peak intensity which might be attributed to the presence of some sodium components after modification.
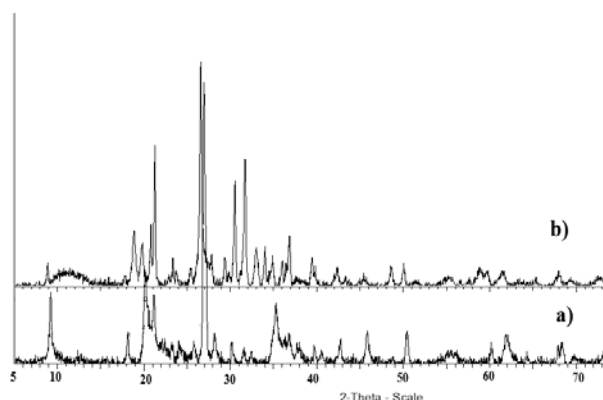

Figure-1. X-ray diffraction patterns and basal spacing of (a) prepared AlPC (b) Na-AlPC.

The SEM images illustrate that there is no change in morphology of both samples but some aggregative and massive appearance was found over AlPC surface after modification with sodium. Figure-2 shows the comparison between scanning electron micrograph images of parent AlPC and Na-AlPC. This figure expose that the majority of the particles in both samples have a lamellar morphology with a composition similar to 2:1 phyllosilicate that correspond with the mica phase (Ayoub and Abdullah, 2013). It can be seen that the intercalated sample has mostly similar morphology to the parent clay consisting mainly of flake-like particles corresponding to a layered structure of Clay K-10. It is also clear that the surface texture of Clay Na-AlPC was different and somewhat rougher than that of the parent pillared clay AlPC. As a conclusion, layered nature seemed to prevail after basic modification over pillared clay AlPC.
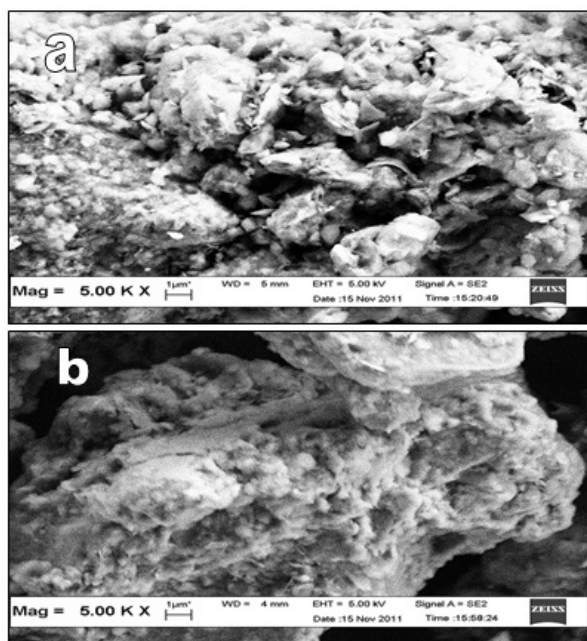

Figure-2. SEM images for (a) prepared AlPC (b) modified Na-AlPC.

The surface properties of parent and modified ALPC was also observed and found some changes in surface area and pore size. In addition, the basic strength of prepared Na-AlPC was highly improved. Table-1 shows the basic strength, BET surface area and pore volume of Clay AlPC and modified clay Na-AlPC after calcination at 550 ºC. As clearly noted, the basic strength of Clay K-10 is normally $H_- < 4.6$ (Ayoub and Abdullah; 2013a) was increased after preparation of AlPC to a value of $4.6 < H_- < 7.2$ and then further increased to a value $7.2 < H_- < 9.3$ after its sodium modified form Na-AlPC. The acidic or basic nature of montmorillonite structure mostly depends on its specific character of having combine water (structurally bound OH form or loosely bound H_2O). It is obvious that the base modification had neutralized most of the acid sites within the clay and replaced them with their conjugate basic sites

(O-) and impregnated the clay with cations (Abdullah *et al.* 2011). It is clear from this table that surface area and mesoporisity of prepared AlPC decreased slightly after modification with sodium. A similar behavior was noted with the pore volume and pore size of prepared AlPC and modified Na-AlPC. The BET surface areas of prepared AlPC and modified Na-AlPC were recorded as 311 and $284 \ m^2 \ g^{-1}$, respectively. It is clear from this table that pore size of AlPC increases with increasing its surface area that is might be due to change in basal spacing after alumina pillaring. On the other hand, after modification with lithium both surface area and pore diameter were found slightly decreasing which might be due to presence of lithium compound in core mesoporous area of prepared material as also claim by some previous researcher (Cseri *et al.* 1995). Actually, the surface area and mesoporisity of modified clay was passed though different processes of preparation and during these processes some portion of layered structure become block or demolish during lithium modification treatment caused decreasing value.

Table-1. The surface properties of clay AlPC and modified Na-AlPC.

Properties	AlPC	Na-AlPC
Surface Area (m²/g)	311	284
Pore Volume (cm³/g)	0.42	0.40
Pore Size (Å)	58	53
Basic Strength (H_)	4.6 <H_ < 7.2	7.2 < H_ < 9.3

The influence of different reaction temperature over reaction time for glycerol conversion and polyglycerol production is shown in the Figure-3. The maximum conversion of glycerol 98% at 260°C was reached after 12 hours of reaction at the amount of 3 wt % of Na-AlPC. The conversion of glycerol was found to be increased with increasing time from 2 to 12 hours. Simultaneously, this conversion was also found to be increased with increasing reaction temperature from 220 to 260°C. Actually, with increasing reaction time, more glycerol molecules got to break up in the form of dehydration or any other form at given condition which cause increasing of glycerol conversion. From Figures-3 it can be seen that the maximum conversion of glycerol 100% was reached at 260°C after 12h in the presence of 3 wt% of catalyst Na-AlPC. The reaction was also conducted at temperature 280°C but glycerol conversion and polyglycerol production was found very low. It may possible that at higher reaction temperature 280°C, the conversion of glycerol speedup in the presence of the strong alkali metal which may lead to the increase some byproduct. This may cause to decrease the polyglycerol production by preceding some new reactions. This behavior also studied by previous researchers and these

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results are in agreement with their results (Charles *et al.* 2003; Ayoub and Abdullah; 2013b).
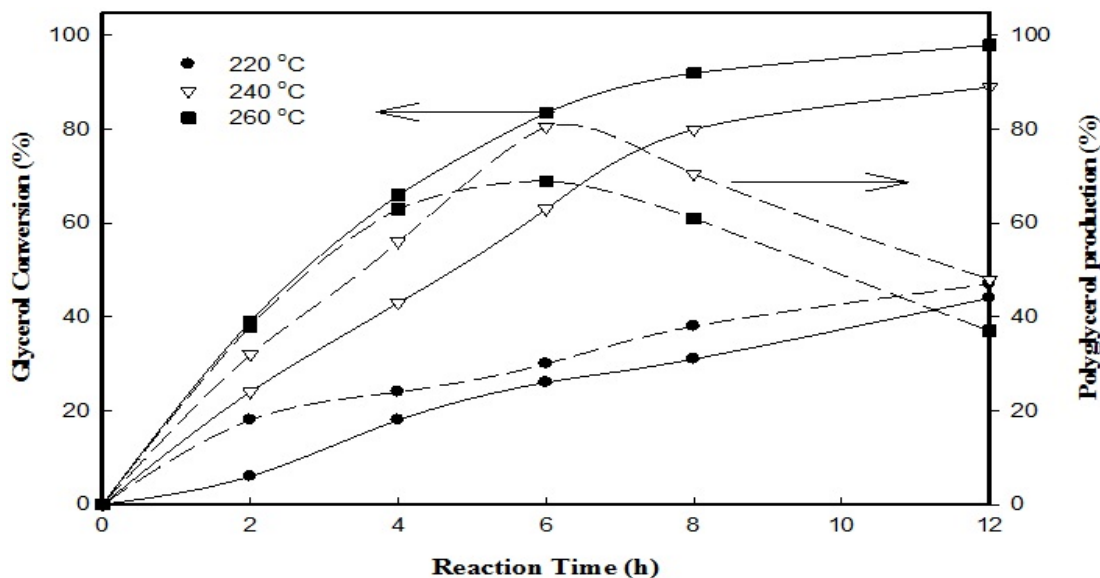

Figure-3. The influence of different reaction temperature over reaction time.

The maximum production of poluglycerol was found 80 % at 240°C after 6 hours at the amount of 3 wt% of catalyst. The productivity of polyglycerol was conversely decreased over passing of this reaction time after 6 hours. Thais production decreasing effect was also noted same over other reaction temperatures at 220 °C and 260 °C. The trend of polyglycerol production was observed first increased during reaction time 2 hours to 6 hours and then further increasing reaction time it was found to be gradually decreased up to 12 hours. Although, the conversion of glycerol was observed increasing after 6 hour to 12 hour at the same reaction conditions while the polyglycerol production was noted decreasing at the same period of time. It might be possible that during conversion of glycerol, the breakup of glycerol molecules may not exactly converted into polyglycerol form but in some other form as a byproduct after 6 hours. These byproducts are not suitable for polymerization etherification reaction and start to conversion of glycerol into some new product like acrolein due to double dehydration of glycerol (Clacens *et al.* 2002). At the same time, newly formed polyglycerol molecules may also convert into some new product. This may happen due to presence of some byproduct which produces during glycerol conversion or weak bounded formation of two polymerize glycerol molecules which may not stable at given reaction conditions. Therefore, the production of polyglycerol was gradually start to decrease after 6 hours of reaction time. It was observed that etherification was slower reaction at the lower reaction temperature, e.g. at 220 °C the maximum conversion of glycerol was very low compared to results at 4 hours and above.

CONCLUSIONS

The clay catalyst AlPC and basic modified AlPC (Na-AlPC) were successfully prepared and well characterized and found to be a stable and basic solid catalyst. This prepared catalyst was determined very active for solvent free etherification of glycerol to polyglycerol at mild reaction conditions. The higher conversion of glycerol (98 %) was observed at 260 °C after 12 hours of reaction. The production of polyglycerol was found maximum (80 %) at 240 °C over 3 wt % Na-AlPC after 6 hours. The basic strength of prepared catalysts was found to be increased after sodium modification which was found helpful for etherification process.

REFERENCES

[1] Abdullah, A. Z., Wibowo, T. Y., Zakaria, R., 2011, Effect of tetramethyl ammonium hydroxide on the activity of LiOH-intercalated montmorillonite catalyst in the transesterification ofmethyl laurate with glycerol. Chemical Engineering Journal, 167, 328–334.

[2] Ayoub, M., Abdullah, A. Z., 2013, LiOH-modified montmorillonite K-10 as catalyst for selective glycerol etherification to diglycerol. Catalysis Communications, 34, 22-25.

[3] Ayoub, M., Abdullah, A. Z., 2013, Diglycerol synthesis via solvent-free selective glycerol etherification process over lithium-modified clay catalyst. Chemical Engineering Journal, 225, 784-789.

[4] Ayoub, M., Abdullah, A. Z., 2012, Critical review on the current scenario and significance of crude glycerol resulting from biodiesel industry towards more sustainable renewable energy industry. Renewable and Sustainable. Energy Review, 16, 2671–2686.

[5] Ayoub, M., and Abdullah, A.Z., 2011. Instability of SBA-15 to strong base: Effects of LiOH impregnation on its surface characteristics and mesoporous structure, Journal of Applied Sciences, 11 (20), 3510-3514.

[6] Barrer, R. M., 1989, Clay minerals as selective and shape-selective sorbents. Pure and Applied Chemical, 61, 1903-1912.

[7] Charles, G., Clacens, J.-M., Pouilloux, Y., Barrault, J., 2003. Preparation of diglycerol and triglycerol via direct polymerisation of glycerol with basic mesoporous catalysators. Oleagineux Corps Gras, Lipides 10, 74–82.

[8] Clacens, J.-M., Pouilloux, Y., Barrault, J., 2002, Selective etherification of glycerol to polyglycerols over impregnated basic MCM-41 type mesoporous catalysts. Applied Catalysis A: General 227, 181–190.

[9] Cseri, T., Bekassy, S., Figueras, F., Cseke, E., de Menorval, L. C., Dutartre, R., 1995, Characterization of clay-based K catalysts and their application in Friedel-Crafts alkylation of aromatics. Applied Catalysis A: General, 132, 141-155.

[10] Ding, Z., Kloprogge, J.T., Frost, R.L., Lu G.Q., and Zhu, H.J., 2001. Porous Clays and Pillared Clays-Based Catalysts. Part 2: A Review of the Catalytic and Molecular Sieve Applications, Journal of Porous Materials, 8 (4), 273-293.

[11] Kloprogge J.T., 1998, Synthesis of smectites and porous pillared clay catalysts: A review, Journal of Porous Materials, 5, 5-41.

[12] Lourdes Chávez-García, M., Liberto de Pablo-Galán, Pilar Saucedo-Ramírez, M., 2006, Synthesis of intercalated Al-hydroxy-montmorillonite. J Mex Chem Soc, 50(1) 36-41.

[13] Parikh, A. N., Navrotsky, A., Li, Q., Yee, Ch. K., Amweg, M.L., Corma, A., 2004, Non-thermal calcination by ultraviolet irradiation in the synthesis of mesoporous materials. Microporos Mesoporous Material, 76, 17-22.

[14] Reddy, C. R., Vijayakumar, B., Iyengar, P., Nagendrappa, G., Prakash, B. S. J., 2004, Synthesis of phenylacetates using aluminium-exchanged montmorillonite clay catalyst Journal of Molecular Catalysis A: Chemical 223, 117-122.

[15] Salerno, P., Mendioroz, S., 2003, Preparation of Al-pillared montmorillonite from concentrated dispersions. Applied Clay Science 22, 115-123.

[16] Zhou, Ch.; Li, X.; Ge, Z.; Li, Q.; Tong, T., 2004, Synthesis and acid catalysis of nanoporous silica/alumina-clay composites. Catalyst Today, 95 (3), 607-613.

[17] Zuo, S., and Zhou, R., 2006. Al-pillared clays supported rare earths and palladium catalysts for deep oxidation of low concentration of benzene. Applied Surface Science 253 (5): 2508–2514