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Heterogeneous catalyst application in biodiesel production: Needs to focus on cost effective and reusable catalysts

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Abstract. Start your abstract here... Uses of heterogeneous catalyst in bio-energy production also refer to as green energy has been in existence and well researched. Majority of recent heterogeneous catalysts produced focus on optimizing yield of biodiesel from a single feedstock without concerted efforts been made to consider the cost of production. They are mostly developed and produced from synthetic chemicals with their attendants high cost of production. The present review summarizes the needs to produce heterogeneous solid catalyst from wastes and natural resources like clay which is available in all parts of the world.

1. Introduction

The uses of heterogeneous catalyst in fatty acid methyl esters (FAME) production was introduced to solve the problems encountered in applying homogeneous catalysts. Some of such problems include: soap formation, difficulty in separation of the final products leading to generation of large waste water, poor recoverability of products etc among others. Heterogeneous catalyst essentially describes processes that involve different phases, solid, liquid and gases. The reactants are mostly liquid or gaseous states while catalyst are solid. Some merits of heterogeneous catalyst that favours its general acceptability in (FAME) production includes: ease separation from the final products, reusability, non-toxic and is environmentally friendly. The process can easily be operated whether batch, continuous or semi-batch mode [1–4]. Helwani et al., [5] asserted that heterogeneous catalyst are mixtures of metallic oxides mostly from non-noble metals. The author said that the catalyst contains both basic and acidic components which are essential properties in converting triglycerides in oil to biodiesel in the presence of alcohol which is similar to those of homogeneous catalyst. [3]. The reaction mechanism also has been reported showing some similarities to those of homogeneous catalyst [6, 7]. Solid acid catalyst is widely employed, if the oil contains high free fatty acid (FFA) and water content. Also, solid acid catalysts require high operating temperature to achieve reasonable conversion to desired products [4–8]. Despite all these advantages of heterogeneous catalyst, mass transfer across interphase boundary remain a major challenge. This is common with most heterogeneous catalyzed process. The reaction rate is reduced resulting in low yield. Hillion et-al.; Mbaraka and Shanks, [8, 9] have suggested a way of overcoming



interphase diffusion limitation in heterogeneous catalysts. These authors suggested the use of promoters or supports which can provide large surface area and pore sizes for active components of the catalyst in order to overcome this limitation and enhance mass transfer conversion. Aluminum oxide, Al_2O_3 (alumina) had been recognized as the suitable promoter for the transesterification reaction without catalyst loss. Heterogeneous catalyst can also be manipulated via understanding of its reaction mechanism to include desired catalyst properties so that the presence of FFA's or water does not adversely affect reaction steps during transesterification. Other advantages of the heterogeneous catalyst include its prolonged lifetime for FAME production and the fact that it is relatively cheap in comparison to homogeneous catalyst [2].

2. Clay as a source of heterogeneous catalyst

Clay is composed of particles of hydrous aluminum silicates and other mixture of metallic oxides and minerals. Clay is available naturally and in modified forms and has several applications as catalytic materials to carry out some typical industrial reactions [10, 11]. Clay minerals are important constituents of the earth crust not only because of their abundance but merely because of their chemical activity. It is found almost everywhere but differs greatly in purity. Clay in its pure condition is comparatively rarely found, the larger portion of the deposit being composed of impure clay. Pure clay is a silicate of aluminum and when found in large quantities it is called Kaolin. Clay material has a wide application for example; it is used in paper, cement and porcelain, sand casting, bricks, dishware, and glass industries and in the removal of heavy metals from waste water and air purification. It is inexpensive, abundant and widely found in every areas and region of the earth crust. [12]. Clay contains several metallic oxides: amongst these is silicon oxide (SiO_2), aluminum oxide, calcium oxide (CaO), iron oxide and so on. The presence of these metallic oxides justifies its usage for biodiesel production. The CaO and Al_2O_3 serve as the basis and acidic component while SiO_2 serves as support for the catalyst which makes it to act like a bi-metallic catalyst.

3. Recent review of some heterogeneous solid catalyst

Ghiaci et al., developed a highly active novel heterogeneous catalyst from biontshell by a tri-step procedure: in complete carbonization- KF impregnation activation and produced biodiesel from rape seed oil [10]. The study revealed that the synthesized catalyst was active for catalyzing transesterification and also recyclable. Transesterification of rape seed oil using 3 wt% of biontshell catalyst, 9: 1 molar ratio of methanol to oil and reaction temperature of 70°C yielded 97.5 % biodiesel within 3 h.

Wei et al. [13], studied waste egg shell as low-cost solid catalyst for biodiesel production from soybean oil and showed high activity. The experimental result showed that transesterification of soybean oil with the waste eggshell catalyst calcined at 1000°C under the reaction condition of 3 wt% catalyst, 9:1 methanol to oil molar ratio at 65°C for 3 h exhibited the best catalytic activity yielding 95% biodiesel. Table 1 below contains some basic heterogeneous solid catalyst for transesterification reaction stating type of catalyst, feedstock used, optimum reaction conditions, biodiesel yield and reference. Also, Table 2 shows the catalyst obtained from naturally occurring and waste materials used for biodiesel production.

Table 1: Some basic heterogeneous solid catalyst used for biodiesel production .

Catalyst	Feedstock	Optimum reaction conditions	Biodiesel FAME yield (%)	Reference
KF/CaO	Chinese tallow seed oil	T= 65°C, t= 2.5h, M:O =12:1	96.8	[14]
KNO ₃ /CaO	Rape oil	T= 65°C, t= 3h M:O=6:1, W = 1 wt.%	98.0	[15]
CaO/ZnO	Ethyl Butyrate	T= 60°C, t= 2h, M:O=12:1,W= 1.3 wt.%	90.0	[16]
Atta pulgite (ATP)/K ₂ CO ₃	Soybean oil	T= 60°C, t= 3h, M:O = 22:1, W = 8 wt.%	93.4	[17]
MnZr/ AlO ₃	Waste cooking oil	T= 150°C, t= 5h, M:O=14:1 W = 2.5 wt.%	93.0	[18]
Fe ₂ O ₃ -MnO-SO ₄ ²⁻ /ZrO ₂ nanoparticle solid catalyst	Waste cooking oil	T= 180°C, t= 5h, M:O = 20:1 W = 3 wt.%	96.5	[19]
Na ₂ ZrO ₃	Ricinus communis oil	T= 65°C, t= 3h, M:O = 15:1 W = 5 wt.%	99.9	[20]
SrO	Palm oil	T= 80°C, t= 3h, M:O = 12:1 W = 5 wt.%	98.2	[21]
KF-Atta-2M-5	Silybum Marianum oil	T= 65°C, t= 5h, M:O = 12:1 , W = 12 wt.%	93.5	[22]
20-CeO ₂ /Li/SBA-15	Cotton seed oil	T= 65°C, t= 4h, M:O = 40:1 W = 10 wt.%	98	[23]
Magnetic Fe ₃ O ₄ /MCM-41 composite-supported sodium silicate	Soybean oil	T= 78°C, t= 8h, M:O = 25:1 W = 3 wt.%	99.2	[24]
MgO/y-Al ₂ O ₃	Soybean oil	T= 60°C, t= 6h, M:O = 6:1 W = 5 wt.%	85.0	[25]
ZnO/y-Al ₂ O ₃	Castor oil	T= 80°C, t= 6h, M:O = 6:1 W = 5 wt.%	97.0	[25]
Calcium glyceroxide	Rape seed oil	T= 60°C, t= 3h, M:O = 8:1 W = 1 wt.%	96.0	[26]

Tungsten (W) supported TiO ₂ /SiO ₂	Waste cooking oil	T= 65°C, t= 4h, M:O = 30:1, W= 5 wt.%	98.0	[27]
K-pumice	Microalgae oil	T= 62°C, t= 10mins, M:O = 12:1 W= 10 wt.%	85.0	[28]

Note: T – reaction temperature; t – reaction time; M:O – methanol to oil; W – catalyst loading

Table 2: Some of the catalyst obtained from naturally occurring and waste materials used for biodiesel production.

Catalytic Materials	Feedstock	Reaction/ Operating condition	Biodiesel yield (%)	Reference
Clamshell	Waste frying oil	C.C. – 3.0% R.T – 60 °C Rt – 180min C.T – 900 °C	89.0	[21]
Waste animal bone	Palm oil	C.C. – 5-25% R.T – 65 °C Rt – NM C.T – 200 – 1000 °C	96.78	[29]
Snail shell	Waste frying oil	C.C. – 1.4% R.T – 50 – 65 °C Rt – 5 – 8 h C.T – 900 °C	87.28	[30]

Note: C.C. – catalyst concentration; RT – reaction temperature; Rt – reaction time; C.T – calcinations temperature; NM-not mentioned

4. General trend in recent catalyst synthesis in biodiesel production

The high performance at the optimum conditions given earlier, is due to relatively high surface area and the net negative charge on the clay [23]. Also the Attapulgite clay used in this work has needlelike shaped silicate with particle size approximately 20 nm in diameter with the length of varying range spanning hundreds of nm to μm [17]. It also contains hydrated magnesium aluminum silicates that contains ribbon of 2:1 phyllosilicate structure. This unique morphology and structure provides reasons for its relatively high yield amidst other operating conditions. Also in the work of high yield recorded by [23] was due to combined effect of Li and Ce in a single catalyst. The bi-metal catalysts possesses greater thermal stability and Li have higher activity. In this work, both metal ions were immobilized over mesoporous silica surface which enhanced its activity. The yield is due to higher surface area from calcined fusion of waste chicken and fish bones catalyst ($34.73\text{m}^2\text{g}^{-1}$) which is better than the uncalcined fusion of waste chicken and fish bone catalyst ($0.87\text{m}^2\text{g}^{-1}$) [29]. Increase in surface area and pore volume of the calcined fusion waste chicken and fish bones after calcination at 1000°C for 4h was responsible for better performance in FAME yield.

In general, majority of recent research in heterogeneous catalysts from wastes and natural resources (clay) for biodiesel production uses interplay of these variables to produce cost effective and reusable catalysts.

5. Conclusion

The synthesis of clay-Bi-Zn composite catalyst for transesterification of waste frying oil is one of the efforts made at producing cost effective and reusable catalyst. Various types of clay supported catalysts can be developed for biodiesel production. In this review, the necessity to focus on wastes and naturally occurring materials to develop heterogeneous catalyst to produce biodiesel from reaction between alcohol and oil (triglycerides) has been emphasized.

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