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Characterization Of Functional Heterogeneous Catalyst Synthesized by Impregnating Calcium Oxide Derived from Periwinkle Shell with Refined Alumina

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***Abstract-** Over the years, functional catalysts have been synthesized from mineral sources, although, this makes them expensive and less economically viable. Based on this, the current work focused on developing a bifunctional heterogeneous catalyst from periwinkle shells and aluminum oxide which possesses basic and acidic properties, and would be useful in catalyzing reactions such as biodiesel production. The catalysts were formulated using incipient wet impregnation at different operating conditions of temperature (600 - 900 oC), time (2 - 5 h), and component mix ratio (CaO:Al2O3, 4:6 - 6:4). The compositions of the catalysts were determined using X-ray diffractometer (XRD), and the surface properties were assessed with Brunauer-Emmett-Teller (BET) analyzer. The results show that the periwinkle shells contained predominantly calcium oxide with 66.08 % and 83.01 % before and after calcination, respectively. The bifunctional heterogeneous catalyst (sample B) had the highest composition of aluminum oxide (42.07 %), and calcium oxide (56.02 %) formulated at a temperature (900 oC) time (5 h) and component mix ratio (CaO:Al2O3) of 6:4. The surface area , pore size and pore volume of sample B catalyst were 11,79 m2/g, (132.23 Å, and (0.00824 cm3/g, respectively. Based on the composition of the formulated bifunctional heterogeneous catalyst (sample), and its properties, it is the best of all the catalysts produced. The bifunctional catalyst produced may help to reduce the cost of biodiesel production, and could be a sustainable strategy for periwinkle shell waste management.**

***Index Terms-** bifunctional heterogeneous catalyst, periwinkle shell, refined alumina, catalyst surface area, calcination.*

I. INTRODUCTION

A catalyst is any substance that can increase the rate of a chemical reaction by lowering the activation energy of the reactant(s) to favour the production of desired product(s) without itself being permanently involved in the reaction. Therefore, a catalyst is capable of creating alternative pathway for the reaction to occur, by modifying the orientation of the reacting molecules for rapid interaction. Secondly, the alternative pathway created by the catalyst allows for the utilization of minimum amount of energy thereby reducing the cost of the process (Robert, 2017). The process of increasing the rate of formation of the desired product, also lowers the formation of the undesired product, and this is called selectivity.

A catalyst can be made of different chemical compounds or elements with specific characteristics that make it unique to catalyze a particular chemical reaction. Most of the catalysts for industrial processes are derived from metallic elements or combination of metals and their oxides; for which transition elements are unique in their catalytic properties; hence widely used in many industrial operations either as single element catalyst or as a promoter for other catalysts. Chemical reactions which involve catalyst are called catalytic reactions. This type of reaction can give rise to the formation of intermediates, which react rapidly with other reactants or another intermediate to produce product(s). Generally, catalysts are categorized into three groups, and each category comprises of sub-groups. Thus, there are biocatalyst (or enzyme), homogeneous and heterogeneous catalysts. Each group functioned efficiently based on the prevailing reaction conditions. The bifunctional heterogeneous catalyst is a type of heterogeneous catalyst that has two active sites of acidic and basic functions; which are generally prepared from oxides of group one to three metals. The three metal oxides group is amphoteric in nature, and always assume acidic properties while the other metal oxides shows basic properties. Thus, it can catalyze chemical reactions which by their chemical nature require acidic and basic catalysts to simultaneously carryout different reactions. Typical bifunctional heterogeneous catalyst models are classified as bimetallic (Pt-Au, Pd-Au, Ca-Zn etc.) and metal-metal oxides catalysts (Pt-ZrO_2, Fe-SiO_2, Ni-MgO, SiO_2-Al_2O_3, CaO-ZnO etc.).

In the case of biodiesel production, which uses oils with high free fatty acid content requires esterification, alongside transesterification. This reaction would effectively require a bifunctional catalyst, in which the catalyst functions as acid to remove the free fatty acids by esterification, and then as base to produce biodiesel by transesterification. In the same vein, reactions involving fuel cells also requires bifunctional catalyst for both oxidation and reduction reactions. Over the years, there has been some efforts to synthesize bifunctional catalyst from mineral and biomass sources for catalyzing reactions. Common mineral sources include limestones, hydrotalcites, zeolites and other mixed oxide sources such as clay. Additionally, biomass sources will include eggshells, rubber seed shells, rice husk, palm tree wastes, molluscas etc. Key precursors from these sources include CaO, Al_2O_3, ZnO, $FeSO_4$. In this study, the Periwinkle shell (which is a Mollusca) was used. It is commonly obtained from fresh water in the African coast. It is one of the most abundant sea creatures with high nutritive value. The two main genera are Tympanotonusfuscatus and Pachymelaniaaurita (Ekop et al, 2022). The Tympanotonusfuscatus are predominant in the Niger Delta region of Nigeria (Bob-Manuel, 2012 and Iboh et al, 2015), and it shells contain a high amount of of calcium oxide (Orji et al, 2017). Before now, the shell were disposed after the removal of the flesh and this has led to environmental pollution, as it causes foul smell at dumb sites and blockages of waterways. But due to its high calcium oxide content, the shells are being used as aggregates for concrete formation for construction works.

Notable reports on bifunctional catalyst formulation or synthesis are presented as follows: Farooq et al (2013), prepared Mo-Mn/y-Al_2O_3-MgO bifunctional catalyst for the transesterification of waste cooking oil which had free fatty of content of 3.37 mg-KOH/g-Oil. The biodiesel yield obtained with the bifunctional catalyst was 91.4 %. The catalyst showed high stability during the reaction, with reusability for eight (8) runs. The stability of catalyst was also attributed to it MgO content which enhanced catalyst basicity. Sulaman et al (2009), developed Cu-Zn/y-Al_2O_3 bifunctional catalyst used for the simultaneous transterification and esterification of a waste cooking oil sample. The effects of calcination temperature and Cu/Zn ratio on catalyst performance were also investigated. The results obtained revealed that Cu/Zn ratio of 10/90 calcined at 800 ºC showed catalyst with particle size distribution of 4 – 6 mm (based on transmission electron micrograph, TEM) and high yield biodiesel production of 88.82 %.

II. MATERIALS AND METHOD

2.1 Materials

The periwinkle (also called Tympanotonusfuscatus specie) shells were collected with the aid of a bucket from a dump site located in Aluu community in Rivers State, Nigeria. The refined bauxite, Al_2O_3 (98 %w/w, Double Bond Chemicals) was purchased from Geochem, Choba, Rivers State.

2.2 Method

This study adopted preliminary treatments for the periwinkle shells such as washing, drying, grinding and sieving, while experimental and analytical methods were used for the synthesis and characterization of the bifunctional catalyst.

2.2.1 Calcination of ground periwinkle shells

The periwinkle shells were thoroughly washed with distilled water to remove soil particles and other impurities, and then dried in oven for 2 h at 100 ºC before been crushed in a grinder. The crushed periwinkle shells were sieved in an electric shaker to obtained a particle size of 75 mμ. This was further subjected to calcination at 800 ºC for 4 h using a calciner (in the form of an electric furnace) in order to decompose the calcium carbonate ($CaCO_3$) content in the periwinkle shells into calcium oxide (CaO). Furthermore, the calcinated and uncalcinated particles of the periwinkle shells were respectively coded as test samples, and were characterized to determine the percentage composition of its metal oxides using X-ray Diffraction method.

2.2.2 X-ray diffraction analysis of particulate uncalcined and calcined periwinkle shells

For the XRD characterization, Mini Flex 600 X -ray diffraction system was used, the sample was placed in a glass plate of 10 –15 mm diameter and approximately 1 mm depth in the sample holder. The XRD patterns were obtained using Cu-Kα radiation (λ = 1.54060 Å), from which the composition was determined using Rietveld refinement technique.

2.2.3 Formulation and Characterization of bifunctional catalysts (CaO/Al_2O_3) obtained from periwinkle shells and refined alumina.

The catalyst formulation was done using the incipient wet impregnation method. Appropriate amounts of CaO (from periwinkle shells) and Al_2O_3 (refined alumina) in specified ratios (Table 1) were weighed using digital balance into different beakers (200 mL capacity each); while deionized water was added to the mixtures to saturation point, amid vigorous agitation for 1 h at 60 ^{o}C using magnetic stirrer to ensure perfect mixing. The mixtures were dried in oven at 120 ^{o}C for 1 h. Thereafter, the dried mixtures were appropriately calcined in an electric furnace at different operating conditions of temperature, mix ratio and time, as generated by Design-Expert software using full factorial design method (Table 1). The formulated catalysts were then stored in appropriately labeled air-tight containers.

Similar to the calcined and uncalcined periwinkle shells, the formulated bifunctional catalyst samples were characterized by BET (Brunauer, Emmett, Teller) analyzer for which the following surface properties of the catalyst were measured as listed: surface area (m^2/g), pore volume (cm^3/g) and pore size (Å). The samples were first prepared by degassing under vacuum pressure for 4 h at 180 ^{o}C, before inserting them into the BET analyzer. The BET analyzer (Nova 800) is software based analyzer, which featured multiple ports and stations for degassing operations, and uses nitrogen adsorption and desorption mechanism onto the catalyst samples for the measurements.

Table 1. Design-Expert Factor combination of operating conditions for the formulation of bifunctional catalyst

Catalyst sample	Temperature (^{o}C)	Time (h)	Component mix ratio ($CaO:Al_2O_3$)
A	900	2	6:4
B	900	5	6:4
C	600	2	6:4
D	600	5	6:4
E	750	3.5	5:5
F	900	2	4:6
G	900	5	4:6
H	600	2	4:6
I	600	5	6:4

III. RESULTS AND DISCUSSION

3.1 Characteristics of calcined and uncalcined periwinkle shells powders

The periwinkle shell powder samples were characterized before and after calcination to ascertain its metal oxide compositions using X-ray Diffractometer. The results obtained are presented in Table 2, and it shows that calcium oxide with 66.08 % was the predominant metal oxide in the periwinkle shell and the least was iron oxide with 0.38 %. Similarly, calcium oxide with 83.01 % was the predominant metal oxide after calcinating the periwinkle shells, and the least was sodium oxide with 0.42 %. Comparing the metal oxide compositions between calcined and uncalcined periwinkle shell powder samples, showed a 16.93 % increase in calcium oxide after calcination of the periwinkle shell powder. This increases, may be attributed to the removal of carbonaceous oxide content of the periwinkle shell powder during calcination. A similar trend of reduction in metal oxide was observed from other metal oxides such as potassium oxide, aluminum oxide, magnesium oxide, sodium oxide and silicon oxide. These results indicated that the periwinkle shell have a high content of calcium oxide, while the calcination process was essentially a calcium oxide enrichment process. Also, the composition of calcium oxide in the calcined periwinkle shell powder for this present study corroborated closely with that the result obtained by Oyawoye et al (2019) which reported a calcium oxide content of 82.4 % in calcined periwinkle, while it was variant to the report of Offiong et al (2017) which had calcium oxide of 46.4 % in calcined periwinkle.

Table 2. Composition of calcined and uncalcined periwinkle shell powder samples

Compound	Composition (%)	
	Uncalcinated	Calcinated
Potassium oxide (K_2O)	5.71	0.668
Aluminum oxide (Al_2O_3)	4.31	2.27
Calcium oxide (CaO)	66.08	83.01
Magnesium oxide (MgO)	0.76	0.49
Sodium oxide (Na_2O)	0.83	0.42
Silicon oxide (SiO_2)	21.07	12.17

3.2 Characteristics of formulated bifunctional heterogeneous catalyst samples

This was conducted to determine the composition of some metal oxides especially the desirable oxide (calcium oxide) in the bifunctional heterogeneous catalysts (samples A - I) formulated from periwinkle shells. The catalyst samples were characterized at various operating conditions of temperature, time and component mix ratio ($CaO:Al_2O_3$) using X-ray diffractometer (XRD). The results obtained from different bifunctional catalyst samples are presented in Figure 1. The results show that bifunctional catalyst (sample C) formulated at temperature of 600 ºC, time of 2 h and component mix ratio ($CaO:Al_2O_3$) of 6:4 had the highest composition of calcium oxide (CaO) of (58.0 %), and bifunctional catalyst (sample G) had the least composition of 36.67 % formulated at a temperature of 900 ºC, time of 5 h) and component mix ratio ($CaO:Al_2O_3$) of 4:6. The disparity in the composition may be attributed to the differences in the operating conditions. For instance, bifunctional catalyst sample G was formulated at a higher temperature (900 ºC, longer time (5 h) and lesser amount of calcium oxide than the bifunctional catalyst sample C. This may have given rise to the decomposition of the calcium oxide in the bifunctional catalyst sample G resulting to a lesser composition of the calcium oxide. Similarly, the lower amount of the calcium oxide in the mix is expected to have a corresponding impact in the final product.

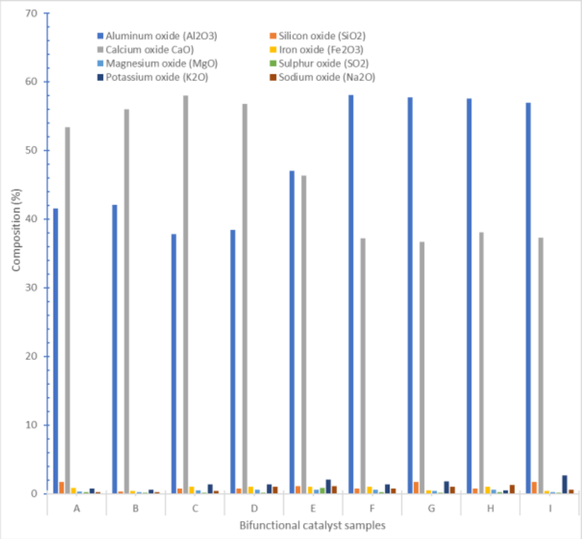

Figure 1. Composition of the bifunctional catalysts (samples A - I) formulated from periwinkle shells at different operating conditions of temperature, time and component mix ratio (calcium oxide:alumina)

3.3 Surface property of formulated bifunctional heterogeneous catalyst from periwinkle shells powders

This was carried out to determine the surface area, pore volume and pore size of the bifunctional heterogeneous catalysts (samples A - I) synthesized from the periwinkle shells, and a commercial calcium oxide. The results obtained are presented in Table 3, and the result show that bifunctional heterogeneous catalyst (sample B) formulated at a temperature (900 ºC) time (5 h) and component mix ratio ($CaO:Al_2O_3$) of 6:4 had the highest surface area (11.79 m^2/g), and the lowest surface area (7.36 m^2/g) was obtained from the bifunctional heterogeneous catalyst (sample F) formulated a temperature (900 ºC) time (2 h) and component mix ratio ($CaO:Al_2O_3$) of 4:6. The disparity in the result could be due to the difference in time and $CaO:Al_2O_3$ since the temperature is the same. Comparing this to the surface area of the commercial calcium oxide (6.02 m^2/g) show that the bifunctional heterogeneous catalyst (sample B) with a surface area of 11.06 m^2/g maybe more effective due to the availability of more active sites for reaction. In addition, the increase in catalyst surface area maybe attributed to a strong interaction and dispersion forces existing between surfaces of Al_2O_3 and CaO. A similar trend of increasing catalyst surface area as a result of material surfaces interactions were reported by Omar et al (2011) and Nizah et al (2014) for which zirconia doped with alkaline metals, and Bi_2O_3 impregnated with La_2O_3 showed increase in their catalyst surface area values respectively. The pore volume and size also showed a direct relationship with the surface area of the catalyst samples.

Table 3. Surface properties of the formulated catalysts

S/N	Catalyst	Surface Area (m^2/g)	Pore Size (Å)	Pore Volume (cm^3/g)
1	A(6:4, 900ºC, 2h)	11.06	131.4	0.0770
2	B (6:4, 900ºC, 5h)	11.79	132.23	0.0824
3	C (6:4, 600ºC, 2h)	9.30	126.05	0.0677
4	D (6:4, 600ºC, 5h)	8.67	117.91	0.0590
5	E (5: 5, 750ºC,3h)	9.02	119.67	0.0680
6	F (4:6, (900ºC, 2h)	7.36	136.07	0.0470
7	G (4:6, 900ºC, 5h)	10.87	141.15	0.0775
8	H (4:6, 600ºC, 2h)	8.23	123.45	0.0323
9	I (4:6, 600ºC, 5h)	8.89	120.55	0.0534
10	CaO	6.02	152.40	0.0628

The pore sizes of the synthesized bifunctional heterogeneous catalysts and that of the commercial calcium oxide are presented in Table 3, The result show that the bifunctional heterogenous catalyst (sample G) formulated at a temperature (900 ºC) time (5 h) and component mix ratio ($CaO:Al_2O_3$) of 4:6 had the highest pore size of 141.15 Å, and the lowest was 117.91 Å obtained from the bifunctional heterogenous catalyst (sample D) at the operating conditions of temperature (600 ºC) time (5 h) and component mix ratio ($CaO:Al_2O_3$) of 6:4. Usually, pore size determines the efficiency of the catalyst by controlling reactant access to the active sites, diffusion rates, and selectively, respectively. Thus, the smaller the pore size, the higher the surface area of the catalyst, but, this limits the diffusion of large molecules. Conversely, the larger the pore size the smaller the surface area, but, there is easier access through the sites by larger molecules. Thus, the bifunctional heterogeneous catalyst (sample B) with a pore size of 132.23 Å had a larger surface area (11.79 m^2/g) than the commercial calcium oxide with a pore size of 152. 40 Å and a smaller surface area of 6.02 m^2/g .

The pore volume like the pore size has strong effect efficiency. It controls the ability of the reactant molecules to assess the active sites of the catalyst, thereby influencing mass transfer, rate of diffusion, and the reaction kinetics. Higher pore volumes of the reactant helps to provide more space for reaction, improve reactant diffusion, and facilitate the releasing of molecules. From Table 3, the highest pore volume of 0.0824 cm^3/g was obtained from the bifunctional heterogeneous catalyst (sample B) formulated at a temperature (900 ºC) time (5 h) and component mix ratio ($CaO:Al_2O_3$) of 6:4. The lowest pore volume of 0.0323 cm^3/g was obtained from the bifunctional heterogeneous catalyst (sample H) which was formulated at a temperature (600 ºC) time (2 h) and component mix ratio ($CaO:Al_2O_3$) of 4:6. The highest pore volume of the sample B shows that this catalyst will promote more mass transfer, high rate of diffusion and reaction kinetic, and more space for the reaction to occur compared to other catalysts (A, C-I). This higher pore volume of sample B will also facilitate the release of product after the reaction might have taking place. Compared to the commercial calcium oxide with a pore volume of 0.0628 cm^3/g and smaller surface area of 6.02 m^2/g, the bifunctional heterogeneous catalyst (sample B) is a more effective catalyst and may show a better performance.

IV. CONCLUSION

The study has demonstrated that periwinkle shell can be a rich source of calcium oxide. The amount of this oxide can be increased through the process of calcination. The high surface area of 11.79 m^2/g, pore size of 132.23 Å and pore volume of 0.0824 cm^3/g of the bifunctional heterogeneous catalyst (sample B) obtained using the incipient wet impregnation method under the operating conditions of temperature (900 ºC), time (5 h) and component mix ratio ($CaO:Al_2O_3$) of 6:4 show that the catalyst may be more efficient in catalyzing reactions such as the transesterification reaction used in the production of biodiesel compared to other bifunctional heterogeneous catalyst formulated including sample A, samples C - D.

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