

Oxidation of Glycerol with Oxygen Molecules as the Oxidant over Activated Clay Material Catalysts

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Abstract-

Interest in glycerol oxidation to more useful products has risen significantly over the years. This has led to the development of several catalysts some of which are scarce, uneconomical and environmentally unfriendly. In this research, two catalysts prepared from red earth - 'A1' (calcined at 500°C) and 'A2' (calcined at 500°C and dealuminated) were characterized using x-ray fluorescence (XRF) and used to oxidize glycerol with O₂ molecules for 240 mins. The XRF results showed that Al₂O₃ (31.3%), SiO₂ (47.9%) and Fe₂O₃ (16.05%) were the predominant components in 'A1' while 'A2' showed a marked significant difference in Al₂O₃ (19.4%), SiO₂ (72.1 %) and Fe₂O₃ (0 %). The selectivities of the oxidation products with A1 were 18.8 % glyceric acid (GLA), 13.1 % lactic acid (LCA), 1.66 % oxalic acid (OXA) and 1.24 % formic acid (FMA), while for A2 they were (20.4%) GLA and (17%) LCA. 88.1% glycerol was converted but selectivity towards any of the products was low.

Key words: Laterite, calcination, dealumination, glycerol, oxidation

1. Introduction

Fossil fuel accounts largely to the global energy production, but with the fast depletion of fossil fuel reserve attention is been shifted to alternative sources of energy one of which is biodiesel. This has generated wide interest over time such that biodiesel production was reported to grow worldwide from 27 million tons in 2012 to 35 million tons in 2017 [1]. The main by-product of biodiesel production is crude glycerol where about 100kg of glycerol is generated in every ton of biodiesel produced [2, 3]. Other methods of glycerol production are: synthesis from propene, fermentation from sugar, hydrogenation of carbon monoxide, photolysis through solar energy and algae [4].

Increase in biodiesel production also translates into proportionate increase in glycerol production, such that glycerol utilization in recent time has become a major challenge. Known areas of glycerol applications are: food industries, drugs, cosmetics, tobacco and as feedstock for other oleo chemical industries amongst others. However, increase in glycerol production led to high percentages of glycerol ending up in landfills, incinerators or ruminant feed [5, 6]. This aroused so much interest such that various works were done to expound the scope of glycerol transformation into more useful end products beyond the limited known areas.

The selective oxidation of glycerol is of particular interest because of the commercial relevance of oxygenated glycerol derivatives [7]. Glycerol oxidation began with the use of stoichiometric



oxidants (chromates, permanganates and hypochlorite) but has now become obsolete since the development of more efficient oxidation technologies [7].

The molecular structure of glycerol gave it a unit nature that depicts the type of products formed during oxidation. It is a polyol with three carbon atoms, each atom is attached to a hydroxyl group that gave it the characteristic name of triol. Oxidation of glycerol takes place at the three oxidizable hydroxyl groups, that is, at the link between the hydroxyl groups and the carbon atoms [7]. The products formed are dependent on whether the primary carbon atom hydroxyl group or the secondary carbon atom hydroxyl group or both are oxidized. Various works done were through catalytic oxidation with most of the works on liquid phase oxidation with oxygen or air over heterogeneous Pt, Pd or Au catalysts [3, 8-11]. Likely products of glycerol oxidation are: glyceric acids, lactic acid, tartronic acid, dihydroxyacetone, glyceraldehyde etc [12, 13].

The applications of these heterogeneous catalysts in glycerol oxidation have their drawbacks. Apart from been expensive [14], they are not easily available; platinum (Pt) and palladium (Pd) are easily poisoned with oxygen and deactivated over time, while Au oxidizes glycerol only in basic medium [3, 15, 16]. The quests therefore to adopt cheaper, easily available and environmentally friendly catalysts for the oxidation of glycerol prompted the adoption of various complex materials as catalysts in the oxidation reaction. Some of these catalysts were: Noyori's catalyst [17], Silica-Alumina catalysts, [18], Grafted mesostructured Silica with TEMPO catalysts [19], CuNiAl catalyst [20].

Based on the foregoing, this work was therefore conceived and developed with the aim of obtaining and enhancing local clay materials for use in glycerol oxidation. Laterite Clay collected from Chelsea field in Ota, Ogun state, Nigeria, was activated by calcination and dealumination. The idea of activation was borne from various works on clay activations for various purposes, especially, zeolite production and the use of zeolite for catalytic cracking of crude petroleum into smaller components [10, 21-26]

2. Methodology

2.1. Materials

Dry clay sample (Laterite) was obtained from Chelsea field, Ota, Ogun state, Nigeria, 98% sulphuric acid (Sigma-Aldrich analysed), sodium hydroxide, (Fisher analysed), glycerol, 99.5% purity (J. T. Baker analysed) Hydrogen Peroxide, 50% aqueous solution (Solvay Interrox), Oxygen gas 99.999% purity (BOC Gases, Nigeria) and distilled water, pH Paper, (BDH, 1 – 14), filter papers, (Whatman, 1-541).

2.2. Equipment/Apparatus.

Electronic Furnace, (Carbonite, HTF 1700,), vacuum pump, (Javac, LT09003), 500 mL stainless steel semi batch reactor (locally fabricated), 50kg Oxygen bottle (BOC Gases), electronic weighing scale, (200g, Ohaus, CS Series), electronic oven, (LDO-201-E, 50 – 320°C), XRF Analyser (UniQuant – Standardless), hot plate magnetic stirrer (20L, IKAMAG, Sigma – Aldrich, 177 x 200), laboratory test sieve, (300Mic, BS410-1-2000), HPLC Analyser [Aminex HPX – 87C (300mm x 7.8mm) Column], 50mL pipette, 500mL conical flask, beakers,

500mL Buckner flask (J – Sil Borosilicate glass), thermometer, 0 – 360°C, (G. H. Zeal), ceramic crucibles (Alsin), Mortar / Pestle (R. G. Wenger), micro wave oven (LDO-201-E, 50 – 320°C)

2.3 Experimental Procedures

The laterite clay was first dried and filtered with a 300 microns sieve to obtain the desired particle size for characterization using the XRF machine. It was then calcined at temperature of 500°C for 6hrs. The calcined product was then dealuminated using the conventional and novel dealumination methods. In both cases 60wt% of H₂SO₄ was first prepared by mixing 85mL of 98wt% H₂SO₄ with 99mL of distilled water. In the conventional method 50g of calcined clay was heated in the acid at 100°C for 5 mins, while in the novel method the clay was soaked in the acid for 1hr, 2hrs, 6hrs, 12hrs, 24hrs and 72hrs respectively. Samples were washed with distilled water and dried by heating at 110°C for 3hrs in a microwave oven. They were then crushed and characterized using XRF method.

Oxidation was done in alkaline medium with oxygen molecules as the oxidant in a semi-batch CSTR. Here, 150ml each of 0.4M glycerol (C₃H₈O₃) and 0.8M sodium hydroxide (NaOH) were first charged into the reactor followed by the addition of 0.5g of the catalyst. The reaction mixtures were then heated to 100°C with continuous stirring and at the stated temperature. Then oxygen at three bar pressure from an oxygen gas cylinder was introduced into the reactor. At different times of 20mins, 40mins, 60mins, 120mins, 180mins and 240mins respectively samples were collected, cooled and analysed with High Performance Liquid Chromatography (HPLC).

Quantitative analysis of the reaction mixture was done with HPLC with 5 mM H₂SO₄ as the eluent and a column temperature of 25°C. The chromatograph (Schimadzu Technologies) was equipped with a Hi-plex column (7.7 mm × 300 mm, Agilent), a refractive index and a UV (190 nm) detector. Three hundred microliters of each sample were diluted with distilled water with a dilution factor of 5/3. An injection volume of 10 µl, a measuring time of 20 min and a flow rate of 0.7 mL min⁻¹ were used.

Known standards of the pure compounds were eluted at the specified conditions and used to obtain the calibration curves. The area of the chromatogram was then obtained. The relationship between the various parameters (area, concentration, retention time, gradient and intercept) of each product is given by equation 1.

$$\text{Area (HPLC)} = \text{Gradient} \times \text{Concentration} + \text{Intercept} \quad (1)$$

$$\text{Concentration} = \frac{\text{Area} - \text{Intercept}}{\text{Gradient}} \quad (2)$$

3. Result and discussions

Results from the High Performance Liquid Chromatography (HPLC) of the various oxidation products are displayed in Figures. 1 (a & b) and 2 (a & b) while Figures. 1 (a) and 2 (a) were obtained using catalyst ‘A1’ at reaction time of 20 and 40 minutes respectively, Figures 1 (b) and 2 (b) were obtained using catalyst ‘A2’ at the same reaction time of 20 and 40 minutes respectively. Except for the intensities of the oxidation products that differ, their elution times were virtually the same. From the chromatogram, Area per retention time was calculated, and

using the calibration curves concentrations, conversion and selectivity of the respective oxidation products were then calculated.

3.1. The Effect of clay treatment on its mineral composition

From Table 1 the XRF results showed that the effects of calcination on the mineral composition of catalyst A1 were not very pronounced compared with the uncalcined clay sample. The silica-alumina ratio that was used to monitor any significant change in the mineral composition was virtually almost constant. From Table 1, the silica – alumina ratio was approximately two (2) for the uncalcined clay and catalyst (A1) samples. The other minerals in the two samples were practically constant as there was no meaningful difference, meaning that mere calcination of the raw laterite (red earth) at 500°C does not affect its mineral compositions.

The results however, revealed that the laterite material, whether raw or calcined, is a complex material composed of about six metallic oxides. From the same table (Table 1), the effect was clearly significant after the dealumination process of the calcined clay sample. It was observed that its silica - alumina ratio increased significantly from about 2 to 4. This was tagged as catalyst A2.

Table 1: XRF Compositions of Raw Clay Material and Catalysts A1 and A2

Components of clay material	% Composition of raw clay material	% Composition of clay calcined at 500°C (Catalyst A1)	De-aluminated Clay Calcined at 500°C (Catalyst A2)
Al ₂ O ₃	30.7	31.3	19.4
SiO ₂	49.8	47.9	72.1
CaO	0.217	0.194	0
TiO ₂	2.41	2.42	3.828
Fe ₂ O ₃	14.84	16.05	0
Ag ₂ O	1.52	1.18	0
MoO ₃	0	0	1.7

Table 2: Conversion, Selectivity and Concentration against Time for Glycerol oxidation with 0.5g Catalyst 'A1' at 100°C

Time (min)	Conversion/ Selectivity (%)					Products Concentration (M)				
	OXA	GLA	GLY	LCA	FMA	OXA	GLA	GLY	LCA	FMA
20	1.54	13	86	4.2	1.1	0.005	0.043	0.056	0.014	0.004
40	1.62	14	86.3	8.7	1.02	0.006	0.048	0.049	0.031	0.004
60	1.24	14	87.5	10.1	1.3	0.004	0.048	0.05	0.035	0.001
120	1.63	14	88	12.4	nd	0.001	0.049	0.048	0.043	nd
180	1.64	19	88	12.8	1.22	0.006	0.064	0.048	0.044	0.004
240	1.66	19	88.1	13.1	1.24	0.006	0.066	0.048	0.046	0.004

'nd' means not detected.

Table 3: Products Conversion, Selectivity and Concentration against Time for Glycerol oxidation with 0.5g Catalyst 'A2' at 100°C

Time (min)	Conversion/ Selectivity (%)					Products Concentration (M)				
	OXA	GLA	GLY	LCA	FMA	OXA	GLA	GLY	LCA	FMA
20	nd	14.1	85.5	8.1	nd	nd	0.048	0.058	0.028	nd
40	nd	15.1	81	10.2	nd	nd	0.05	0.076	0.033	nd
60	1.02	17.8	85.6	13.4	1	0.0035	0.061	0.058	0.046	0.0038
120	nd	17.8	85.8	15.1	nd	nd	0.061	0.057	0.052	nd
180	nd	20.2	86	15.5	nd	nd	0.069	0.057	0.053	nd
240	1.5	20.4	86.5	17	1	0.0051	0.07	0.054	0.058	0.0034

'nd' means not detected.

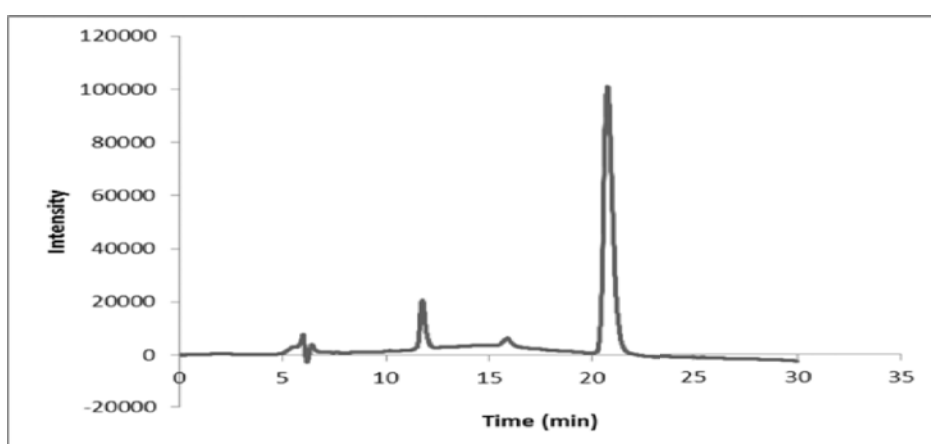


Figure 1: HPLC Chromatograms of glycerol conversion products at 100°C in 20 mins using 'A1' catalyst

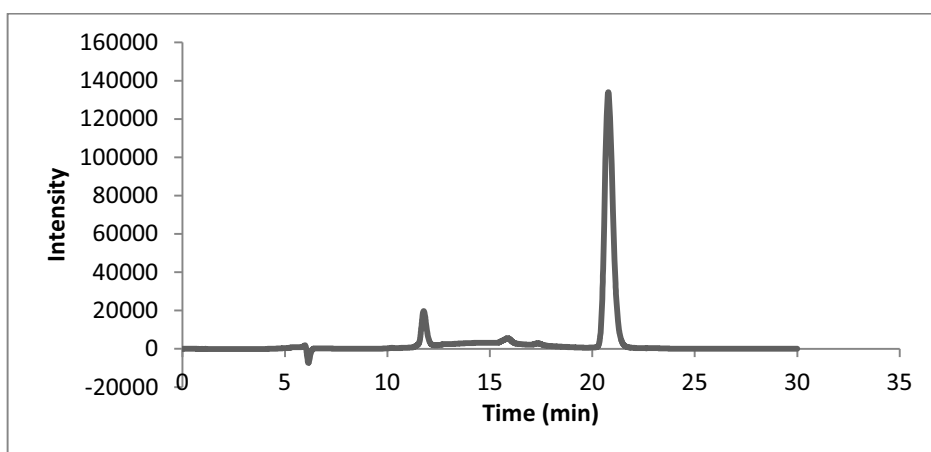


Figure 2: HPLC Chromatograms of glycerol conversion products at 100°C in 20 mins using 'A2' catalyst

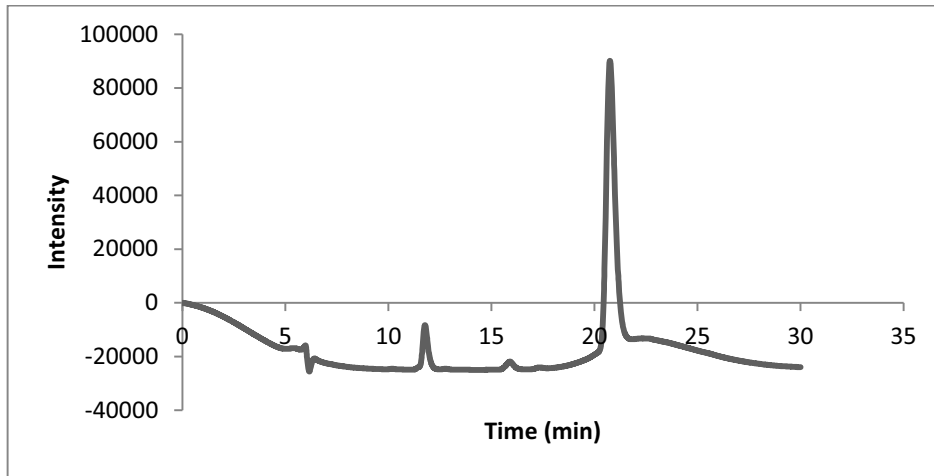


Figure 3: HPLC Chromatograms of glycerol conversion products at 100°C in 40mins using 'A1' catalyst

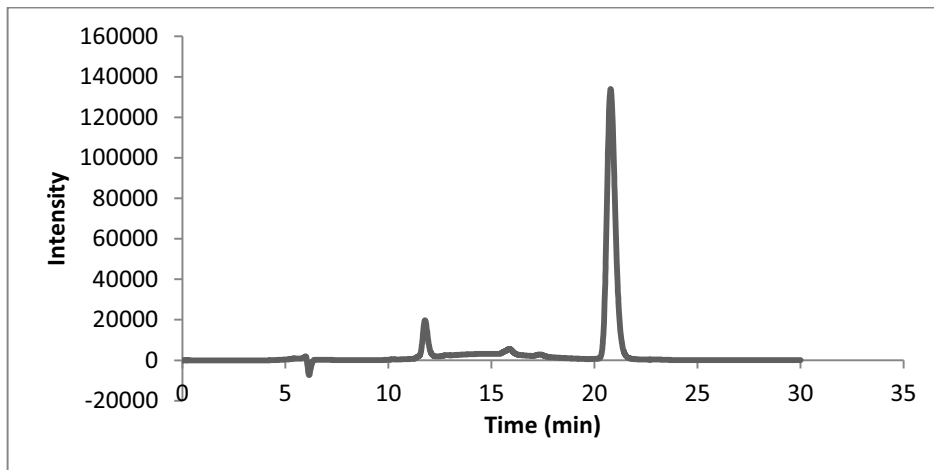


Figure 4: HPLC Chromatograms of glycerol conversion products at 100°C in 40mins Using 'A2' catalyst.

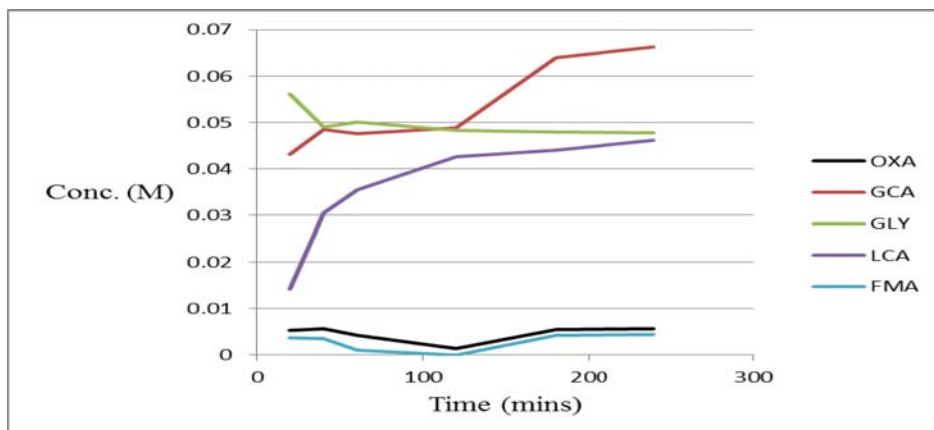


Figure 5: Concentration vs time for the oxidation products over catalyst 'A1'.

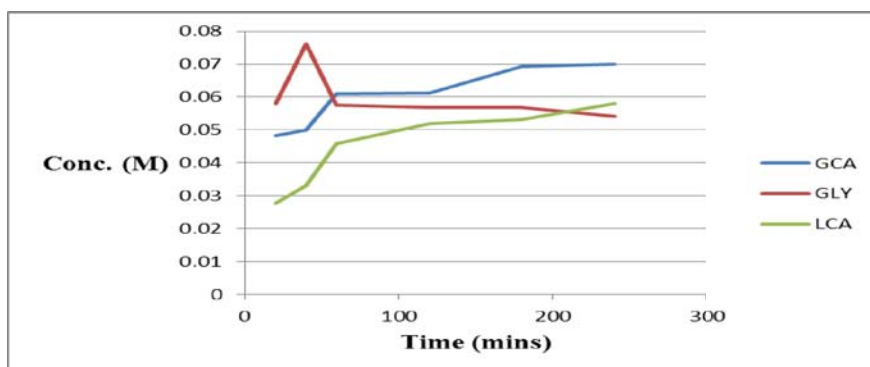


Figure 6: Concentration vs Time for the Oxidation Products Over Catalyst 'A2'.

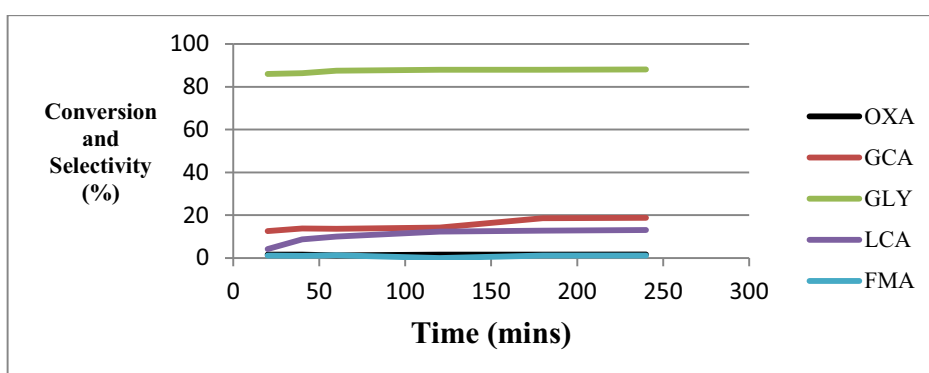


Figure 7: Selectivity/Conversion vs Time for the Oxidation Products over catalyst 'A1'.

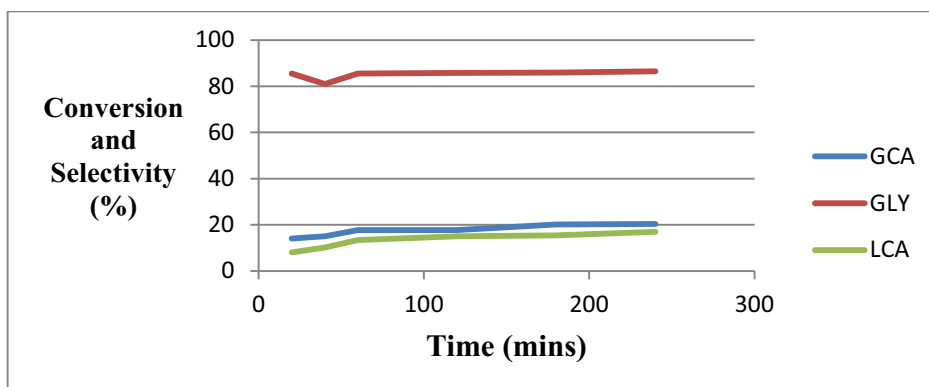


Figure 8: Selectivity/Conversion vs Time for the Oxidation Products over catalyst 'A2'.

3.2. The Effect of Catalysts on the Aqueous Oxidation of Glycerol.

The HPLC analysis of the products of glycerol oxidation using catalyst 'A1' gave the following five products: Glycerol (GLY), Glyceric acid (GLA), Lactic Acid (LCA), Oxalic acid (OXA) and Formic Acid (FMA) at different compositions. However, with 'A2' catalyst, there were only three main products (GLY, GLA and LCA) with both catalysts having selectivity toward Glyceric acid at different percentage compositions, see Tables 2 and 3. The % Glyceric acid obtained using both catalysts increased with time of reaction. At the end of 240 mins, catalyst 'A1' produced GLA (18.8 %); LCA (13.1 %); OXA (1.66 %) and FMA (1.24 %), while, at the same time catalyst 'A2' produced GLA (20.4 %); LCA (17 %); OXA and FMA were in most

of the results not identified, an indication that they were either not produced or too small to be detected. The chromatograms (Figures 1-4) show the effect of catalyst and time on the intensity or amount of oxidation products obtained from the oxidation reactions. It was observed that the intensity or amount of the oxidation products obtained using catalyst A2 was more than those obtained using Catalyst A1 irrespective of the time of reaction. This showed that catalyst A2 was more effective in the conversion of glycerol to glyceric acid (GLA). Comparing Figure 1 (glycerol oxidation using catalyst A1 and 20 minutes reaction time) with Figure 3 (glycerol oxidation using catalyst A1 and 40 minutes reaction time) it was observed that the intensity from the two chromatograms or amount/composition of the oxidation products were essentially the same. The same effect was observed when the two chromatograms, Figure 2 (glycerol oxidation using catalyst A2 and 20 minutes reaction time) and Figure 4 (glycerol oxidation using catalyst A2 and 40 minutes reaction time) were compared. The intensity or amount/composition of oxidation products from the respective chromatogram did not change. The intensity of the oxidation product using catalyst A1, (see Figures 1 and 2), was 100000 while the intensity of the oxidation product using catalyst A2, (Figures 2 and 4), was 120000. Also, the maximum conversion of glycerol was obtained at 240 mins with catalyst A1 achieving 88 % conversion and catalyst A2 86.5 % conversion of glycerol.

The profiles from the plots of concentration against time (see Figures 5 & 6) with both catalysts showed that products concentrations increased with reaction time. From Figures 7 and 8, with 'A1' catalyst – product selectivity of GLA at 20 mins gave a concentration of 0.043 M and at the end of 240 mins concentration increased to 0.069 M. While with 'A2' catalyst, product selectivity of GLA at 20 mins gave a concentration of 0.048 M which increased to 0.069 M at the end of 240mins. However, this was different with GLY concentration that had decrease in concentration from 0.0562 M to 0.0477 M within the time interval of 240 mins. This was expected because as the oxidation of glycerol progressed, its concentration should also progressively decrease with time.

4. Conclusion

Calcination of clay materials has little or no effect on the elemental composition of laterite clay materials. However, this effect became more pronounced after dealumination.

Dealumination clearly shows the depletion in Alumina (Al_2O_3) composition and increase in Silica (SiO_2) composition in the clay materials.

Irrespective of the period of dealumination of the calcined clay at 500°C, Al_2O_3 was not completely depleted.

Results obtained from the oxidation reactions using the two catalysts A1 and A2 showed only slight difference. Using catalyst A1, OXA, GCA, LCA and FMA were identified. While with catalyst A2, only GLA, LCA were identified or produced. Selectivity was towards GLA with both catalysts A1 and A2. Using catalyst A1, 18.8% GLA, 13.1% LCA, 1.66% OXA and 1.24% FMA were obtained at the end of 240mins. While with catalyst A2, only two of the products GLA (20.4%) and 17% LCA (17%) were obtained within the same time interval.

5. Recommendation

Further development of local clay materials and their composites used as catalysts for glycerol oxidation is recommended to enhance product selectivity and specificity.

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