

SODIUM MODIFIED MESOPOROUS GAMMA-ALUMINA FROM KANO
KAOLIN IN METHANOLYSIS OF CORN OIL

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Dedicated to

My mother, **Maryam Murtala**, for her boundless sacrifice and prayer;

My late father, **Abdussalam Bello**, for his support and sacrifice

My wife, **Zahra’u Salisu Abdullahi**, for her support and endurance;

And

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They really help in no small way towards actualizing my dream “doctoral degree”

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ABSTRACT

The developments of cheap and environmentally benign synthetic methods remain the challenges facing scientists. Kaolin is an abundant and non-toxic mineral over the expensive and toxic aluminium alkoxides or inorganic salts used in the synthesis of mesoporous gamma alumina for industrial application. In this study, a novel synthesis of mesoporous γ -Al₂O₃ from Kano kaolin in the presence of non-toxic surfactant, polyoxyethylene (40) stearate (PS), is reported. For comparison alumina is synthesized using PEG-6000. To explore the effect of surfactant mixing mode, PS was added to the boehmite precursor prior and after precipitation. Furthermore, the influence of varying PS concentration and aging time were also studied. The mesoporous γ -Al₂O₃ was modified with NaOH using the wet impregnation method, and tested for the methanolysis of corn oil by batch reaction process. The reaction conditions for the methanolysis are 5% catalyst, 67 °C temperature, 1:15 oil to methanol molar ratio and 3 hours reaction time. The kaolin, alumina and the catalysts were characterized using X-Ray Fluorescence (XRF), Thermogravimetric-Derivative Thermal Analysis (TG-DTA), X-Ray Powder Diffraction (XRD), Fourier Transform Infrared (FTIR), N₂ Adsorption-Desorption, Field Emission Scanning Electron Microscopy (FESEM), Solid State ²⁷Al MAS NMR, Basic Back Titration and Temperature-Programmed Desorption of CO₂ (CO₂-TPD). The product biodiesel was analyzed using Fourier Transform Infrared-Attenuated Total Reflection Analysis (FTIR-ATR), Nuclear Magnetic Resonance spectroscopy (¹H NMR) and Gas Chromatography-Flame Ionization Detector (GC-FID). Structural properties and morphology of the mesoporous γ -Al₂O₃ was found to improve with increasing surfactant amount from 0.45 g to 1.8 g and aging time from 1 to 2 days then dropped beyond that. Mesoporous γ -Al₂O₃ synthesized with 1.8 g PS, mixed after precipitation and age for 2 days possessed a surface area (SA) of 222.7 m²/g, narrow pore size distribution (PSD) of 5.6 nm and pore volume (PV) of 0.45 cm³/g. Whereas higher SA of 319.2 m²/g, PSD of 2.7 nm and PV of 0.42 cm³/g were obtained with mixing prior to precipitation. Although, alumina synthesized with PEG has higher SA of 365.1 m²/g, nevertheless, the one with PS have better thermal stability. Response surface methodology (RSM) was applied for the optimization of methanolysis reaction using four-level factorial Box-Behnken Design (BBD). Up to 98.9% yield was obtained using mesoporous γ -Al₂O₃ modified with 15% NaOH, 6% catalyst loading, 1:15 oil:methanol molar ratio and 2 hours reaction time. From kinetics study, the activation energy, 67.7 kJ mol⁻¹, fall within the range 26-82 kJ mol⁻¹ indicating that the methanolysis was kinetically controlled. The high value of k, 0.03386 min⁻¹, was attributed to the presence of high levels of unsaturated FFA in corn oil. While from the thermodynamics evaluation the positive values of enthalpy and Gibb's free energy implied the methanolysis reaction is endothermic and non-spontaneous, whereas the negative entropy value suggested it is reversible. Result from catalyst reusability tests revealed that the catalyst is relatively stable.

ABSTRAK

Pembangunan kaedah sintetik yang murah dan mesra alam sekitar kekal sebagai cabaran yang dihadapi oleh saintis. Kaolin merupakan mineral yang amat banyak dan bukan toksik dibandingkan dengan alkoksida aluminium yang mahal dan toksik atau garam tak organik yang digunakan bagi mensintesis alumina gama mesoliang untuk kegunaan industri. Dalam kajian ini, sintesis novel γ -Al₂O₃ mesoliang dari Kano kaolin dengan kehadiran surfaktan tak toksik, polioksietilena (40) stearat (PS), adalah dilaporkan. Sebagai perbandingan, alumina telah disintesis menggunakan PEG-6000. Untuk meneroka kesan mod pencampuran surfaktan, PS telah ditambahkan kepada pelopor boehmit sebelum dan selepas pemendakan. Tambahan pula, pengaruh kepekatan PS yang berbeza-beza dan masa penuaan turut dikaji. γ -Al₂O₃ mesoliang diubahsuai dengan NaOH menggunakan kaedah pengisitepuan basah, dan diuji untuk metanolisis minyak jagung menggunakan proses tindak balas kelompok. Keadaan tindak balas metanolisis adalah 5% mangkin, suhu pada 67 °C, nisbah molar minyak kepada metanol 1:15 dan masa tindak balas selama 3 jam. Kaolin, alumina dan mangkin tersebut telah dicirikan menggunakan pendarfluor sinar-X (XRF), analisis terma pembezaan-termogravimetri (TG-DTA), pembelauan sinar-X serbuk (XRD), spektroskopi inframerah transformasi Fourier (FTIR), penjerapan-penyahjerapan N₂, mikroskopi pengimbasan elektron pemancaran medan (FESEM), ²⁷Al MAS NMR keadaan pepejal, pentitratan balik bes dan penyahjerapan CO₂-suhu teraturcara (CO₂-TPD). Produk biodiesel telah dianalisis menggunakan spektroskopi inframerah transformasi Fourier-pantulan keseluruhan dikesilkan (FTIR-ATR), spektroskopi resonans magnet nukleus (¹H NMR) dan kromatografi gas-pengesan pengionan nyalaan (GC-FID). Sifat struktur dan morfologi γ -Al₂O₃ mesoliang didapati bertambah baik dengan peningkatan jumlah surfaktan dari 0.45 g kepada 1.8 g dan masa penuaan dari 1 kepada 2 hari kemudian menjunam selepas itu. γ -Al₂O₃ mesoliang yang disintesis dengan 1.8 g PS, dicampurkan selepas pemendakan dan penuaan selama 2 hari memiliki luas permukaan (SA) 222.7 m²/g, taburan saiz liang sempit (PSD) 5.6 nm dan isipadu liang (PV) 0.45 cm³/g. Manakala SA yang lebih tinggi iaitu 319.2 m²/g, PSD 2.7 nm dan PV 0.42 cm³/g telah diperolehi dengan pencampuran sebelum pemendakan. Walaupun alumina yang disintesis dengan PEG mempunyai SA lebih tinggi iaitu 365.1 m²/g, namun bahan yang mengandungi PS didapati mempunyai kestabilan haba yang lebih baik. Kaedah gerak balas permukaan (RSM) telah digunakan untuk pengoptimuman tindak balas metanolisis menggunakan reka bentuk faktorial empat tahap Box-Behnken (BBD). Sehingga 98.9% penukaran telah diperolehi menggunakan γ -Al₂O₃ mesoliang yang diubahsuai dengan 15% NaOH, 6% muatan mangkin, nisbah molar minyak: metanol 1:15 dan masa tindak balas 2 jam. Daripada kajian kinetik, tenaga pengaktifan adalah 67.7 kJ mol⁻¹, termasuk dalam julat 26-82 kJ mol⁻¹ yang menandakan bahawa metanolisis tersebut terkawal secara kinetik. Nilai k yang tinggi, 0.03386 min⁻¹, adalah disebabkan oleh paras FFA tak tepu yang tinggi dalam minyak jagung. Sementara dari penilaian termodinamik, nilai positif entalpi dan tenaga bebas Gibb menunjukkan bahawa tindak balas metanolisis adalah endotermik dan tak spontan, sedangkan nilai entropi negatif mencadangkan ianya adalah berbalik. Keputusan daripada ujian kebolegunaan semula mangkin mendedahkan bahawa mangkin tersebut relatifnya stabil.

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LIST OF ABBREVIATIONS

¹ HNMR	-	Proton Nuclear Magnetic Resonance
ANOVA	-	Analysis of Variance
AR	-	Analytical Reagent
ASTM	-	American Standard for Testing of Materials
BBD	-	Box Behnken Design
BET	-	Branneur-Emmet-Teller
BJH	-	Barrett–Joiner–Halender
DF	-	Degree of Freedom
DG	-	Diglyceride
DOE	-	Design of Experiment
FAME	-	Fatty Acid Methyl Ester
FESEM	-	Field Emission Scanning Electron Microscopy
FID	-	Flame Ionization Detector
FFA	-	Free Fatty Acid
FT	-	Fischer–Tropsch
FTIR	-	Fourier Transform Infrared
FWHM	-	Full Width at Half Maximum
GC	-	Gas Chromatography
GL	-	Glycerol
ICP	-	Inductively Coupled Plasma
IR	-	Infrared
MG	-	Monoglyceride
MOR	-	Methanol to Oil Ratio
MSDS	-	Material Safety and Data Sheet
NA	-	Nitrogen Adsorption
NMR	-	Nuclear Magnetic Resonance

RMM	-	Relative molecular mass
SEM	-	Scanning Electron Microscopy
SS	-	Sum of Squares
STP	-	Standard Temperature and Pressure
TAG	-	Triacyl Glycerides
TG	-	Triglyceride
XRF	-	X-Ray Fluorescence
XRD	-	X-Ray Diffraction
WCO	-	Waste-Cooking Oil
RSM	-	Response Surface Methodology
TOF	-	Turnover Frequency
HCS	-	Hazard Communication Standard
29 CFR 1910.1200	-	Occupational Safety & Health Administration Code
PS	-	Polyoxyethylene 40 Stearate
PEG	-	Polyethylene Glycol
MCM-41	-	Mobil Composition of Matter
EDX	-	Energy Dispersive X-Ray
TPD	-	Temperature Program Desorption
ATR	-	Attenuated Total Reflection
MAS	-	Magic Angle Spinning
SDBS	-	Sodium Dodecyl Benzene Sulfonate
SDS	-	Sodium Dodecyl Sulphate
CTAB	-	Cetyl Trimethyl Ammonium Bromide
AACH	-	Ammonium Aluminium Carbonate Hydroxide
TX-100	-	Triton X-100
pKa	-	Logarithmic Acid Dissociation Constant
WDXRF	-	Wavelength-Dispersive X-Ray Fluorescence
ED	-	Energy Dispersive
TGA	-	Thermo Gravimetric Analysis
DTG	-	Differential Thermal Analysis
DSC	-	Differential Scanning Calorimetry
BDDT	-	Brunauer, Deming, Deming and Taller
IUPAC	-	International Union of Pure and Applied Chemistry
SBA-15	-	Santa Barbara Amorphous

CCD	-	Central Composite Design
ACT	-	Activation Complex Theory
CMC	-	Critical Micelles Concentration
rpm	-	revolution per minute
JCPDS	-	Joint Committee on Powder Diffraction Standard
ppm	-	Part Per Million
Rel. Int.	-	Relative Intensity
SA	-	Surface Area
PSD	-	Pore Size Distribution
PV	-	Pore Volume

LIST OF SYMBOLS

$\delta +$	-	Partial negative charge
$\delta -$	-	Partial positive charge
$^{\circ}$	-	Degree
%	-	Percent
μ	-	Micro
β	-	Full width at half maximum
β_0	-	Intercept
β_i	-	First order coefficient of the model
β_{ii}	-	Quadratic coefficient of the model
β_{ij}	-	Linear coefficient of the model
θ	-	Angle of measurement
γ	-	Gyromagnetic ratio
l	-	Spin quantum number
λ	-	Wavelength of radiation
ε	-	Experimental error
Σ	-	Summation
ΔG	-	Gibb's free energy
ΔH	-	Enthalpy change
ΔS	-	Entropy change
a	-	Lattice parameter
A	-	Pre-exponential factor
A_1	-	Area of methoxy protons from methyl esters
A_2	-	Area of methylene proton from the esters
d	-	Distance between the scattering planes
E_a	-	Activation energy
f_w	-	Catalyst's active sites

h	-	Plank's constant
$h\nu$	-	Characteristic photon energy of the excitation source
k	-	Rate constant
k_B	-	Boltzmann's constant
K	-	Constant ≈ 1
t	-	Average crystallite size
M	-	Molar mass
m_{cat}	-	Mass of catalysts
n	-	order of the reflection
P	-	Adsorbate equilibrium pressure
P_o	-	Adsorbate saturation pressure
pH	-	Degree of acidity or alkalinity
R	-	Universal gas constant
T	-	Temperature
w	-	Weight
χ	-	Constant related to heat of adsorption of an adsorbate
x	-	Concentration
A	-	First factor
B	-	Second factor
C	-	Third factor
D	-	Fourth factor
Y	-	Response factor
s^{-1}	-	Per second
V_o	-	Volume of adsorbate required for monolayer coverage
V_a	-	Volume at STP of the molecules adsorbed
μm	-	Micrometer
nm	-	Nanometer
\AA	-	Angstrom
ρ	-	Density
I_0	-	Intensity
γ	-	gamma
η	-	eta
θ	-	theta

κ	-	kappa
χ	-	chi
α	-	alpha
δ	-	delta
ϵ	-	epsilon
ρ	-	rho
C	-	BET constant
V	-	Adsorbed gas quantity
V_m	-	Monolayer gas quantity
S	-	Specific surface area
S_{total}	-	Total surface area
N	-	Avogadro's number
P/P ₀	-	Relative pressure
c	-	Velocity of light
H ₀	-	Magnetic field
r	-	Rate law
t	-	Time
R	-	Universal gas constant
K	-	Kelvin

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CHAPTER 1

INTRODUCTION

1.1 Background of the Research

Clays are complex minerals composed of very small particles ($< 2\mu\text{m}$ in diameter) derived from the weathering of silicate rocks by the action of water containing dissolved carbonic acid or other elements (Hornyak *et al.*, 2008). Clays are compounds containing aluminium/magnesium silicates having 1:1 or 1:2 layer structures. They are thermally inert and environmentally friendly. Due to their high aspect ratio and ease of delamination they have many applications such as in processing of active components, binders, catalysts, as ion-exchangers for food processing, additives in detergents and thickening agents in oil drilling operation (Choudhury and Misra, 2011).

Kaolin is a naturally occurring mineral of the clay family comprising largely of one of the kaolin group of minerals; halloysite, dickite, nacrite and kaolinite. Kaolinite is however, the most common kaolin mineral with most versatile and wide industrial applications due to its physical and chemical properties, crystal structure, and surface chemistry (Fitos *et al.*, 2015). Kaolinite is planar hydrous phyllosilicate clay with dioctahedral 1:1 (TO) interlayer structure. The 1:1 structure have structural dimension in the nanometer range with layer thickness of about 0.7 nm (Salahudeen *et al.*, 2015b). Kaolin as a family of clay is an abundant and inexpensive mineral which makes it more economical, over the expensive aluminium alkoxides or inorganic salts, as a precursor for synthesizing mesoporous $\gamma\text{-Al}_2\text{O}_3$. Due to its

excellent properties that includes highly uniform channels, large surface area and narrow pore size distribution it has been extensively used as adsorbents, catalysts supports, ceramics, heat insulating materials, and reinforcements for composite materials (Pan *et al.*, 2013a).

The discovery of M41S type molecular sieves by Mobil Oil Corp. scientists in 1990s open the door for material science to the synthesis of silica and alumina based mesoporous materials. These materials, due to their large surface area ($\sim 1000 \text{ m}^2/\text{g}$) and narrow pore size distribution with long range ordering, have potentiality for various scientific and industrial applications. Some of these applications include; heterogeneous catalysis, separation process, host guest chemistry, adsorbents host for quantum structures, separation of large biological molecules and environmental pollution control (Naik and Ghosh, 2009).

Alumina exist in various meta-stable states including the γ -, η -, σ -, θ -, κ - and χ -phase, as well as the stable α - Al_2O_3 phase. Due to its physical, textural, thermal, and chemical properties, mesoporous γ - Al_2O_3 is an important material used as catalyst substrates in automotive and petroleum industries, structural composites for space crafts, abrasive and thermal wear coatings. It is the most extensively used catalysts support due to its high surface area and relative stability over the temperature range of interest for most catalytic processes. The pore structural properties of mesoporous γ -alumina, high surface area and large pore volume, allow for higher loading of active catalytic phases (Yang *et al.*, 2010; Shi *et al.*, 2016; Xu *et al.*, 2016).

Catalyst is capable of making reaction to occur under the mildest possible conditions which would otherwise be not feasible. Catalyst could be simple or complex, synthetic or natural chemicals. Recently synthetic chemists have developed interest on clays and zeolites derived from soil as one of the important family of catalysts (Nagendrappa, 2002).

Homogeneous catalysts comprising of strong acidic solutions such as hydrochloric acid and sulphuric acid as well as strong basic solutions such as sodium hydroxide, sodium methoxide and potassium hydroxide were traditionally used in the transesterification reaction (Stoytcheva and Montero, 2011). High energy consumption, corrosion and costly separation of homogeneous catalyst from the reaction mixture make the process uneconomical and unsafe. There is also the problem of the formation of soaps through neutralization of FFAs or saponification of triglycerides.

Heterogeneous catalysts are developed in order to overcome the problem encountered with homogeneous catalysts. Heterogeneous catalyst can eliminate the corrosion problem and consequent environmental hazards posed by the homogeneous catalyst (Sivasamy *et al.*, 2009). Solid heterogeneous catalysts have the advantage of reusability which makes continuous fixed-bed operation possible. Such continuous process can reduce costs for biodiesel separation and purification, which will make it cheaper as such can compete with commercial petroleum-based diesel fuel (Stoytcheva and Montero, 2011). Furthermore, heterogeneous catalyst can be designed to give high activity, selectivity and long catalyst life time (Xu and Liu, 2011).

Heterogeneous base catalysts have shorter history than their acids counterparts. They contained Brønsted and/or Lewis basic activity centers that can accept proton from or supply electrons to reactants. Solid base catalysts have higher activity, long catalyst life time (shelf life) and can perform under moderate reaction conditions compared with the solid acid catalysts. Thus base catalyzed transesterification reaction is about 4000 times faster than the acid catalyzed transesterification reaction (Kumar *et al.*, 2012; Atadashi *et al.*, 2013).

Rudolf Diesel proposed vegetable oil as an engine fuel over 100 years ago, (Shay, 1993). However, due to high viscosity its utilization as fuel for diesel engines became unpracticable (Demirbas, 2008). Chemical or physical modifications including pyrolysis, micro-emulsification, dilution, and transesterification have been attempted to improve its properties. Transesterification is the most common method

used to lower the vegetable oils viscosity. The products are collectively called 'biodiesel' because they can be used either neat or blended with the petro-diesel (petroleum diesel) (Lee, 2009).

The developments of environmentally friendly synthetic methods that will not cause long-lasting damage to the environment or disturb the ecological balance are the challenges facing scientists (Nagendrappa, 2002). The greatest advantages of biodiesel are its renewable nature and environmentally benign characteristics. Biodegradability of biodiesel makes it possible to recycle the carbon dioxide emissions, and significantly reduce the emission of green-house gases. Furthermore biodiesel has advantage over traditional petroleum-based diesel fuel due to its higher cetane number, absence of aromatic compounds, very little amount of sulfur, and 10 to 11 percent oxygen by weight. This makes the emission profile of biodiesel and biodiesel-diesel blends to be much cleaner with substantially lower sulfur emissions compared to petroleum-based diesel (Spivey and Dooley, 2011). Additionally, biodiesel blended with petro-diesel fuel in different proportions will have similar energy density and kinematic viscosity to the petro-diesel as such can be used direct in the existing engines without extensive modifications. Due to all these benefits, the development of biodiesel worldwide is rapidly growing annually (Ong *et al.*, 2013).

Polyoxyethylene (40) stearate is a non-ionic surfactant and is considered not hazardous according to OSHA Hazard Communication Standard (HCS) under the toxic and hazardous substances (29 CFR 1910.1200), this gives it advantage over cationic and anionic surfactants that are both toxic. It is used as emulsifier and solubilizer, and due to its non-toxic nature is also used in pharmacy as carrier of solid dispersion to improve the dissolution of griseofulvin and as excipient (Zhu *et al.*, 2009a). For the first time the effect of this surfactant is reported on the synthesis of mesoporous gamma alumina in the present research.

Polyethylene glycol 6000 PEG-6000 is used as an inactive ingredient in the pharmaceutical industry as a solvent, plasticizer, surfactant, ointments and suppository base, as well as tablet and capsule lubricant. PEG-6000 has low toxicity with systemic absorption less than 0.5%. Polyethylene glycol families are widely

used surfactants for the synthesis of mesoporous alumina. Many reports were available on the synthesis of mesoporous alumina using PEG families (Sun *et al.*, 2008a; b; Zhu *et al.*, 2009b; c, 2010; Shi *et al.*, 2014). For this reason PEG-6000 will be used as surfactant in this study to serve as standard for comparison with the novel synthesis using polyoxyethylene (40) stearate.

Nigerian kaolin is reported to have been restricted for the manufacture of bricks, paints, refractories and ceramics, and sold locally or exported to the neighbouring countries, even though it could have promising applications in several clay-based industries, based on its physical and chemical properties (Ekosse, 2010). The uses of kaolin depend on several factors including but not limited to the geological conditions under which the kaolin is formed, the total mineralogical compositions of the kaolin deposits, and its physical and chemical properties (Murray, 2006). Although there are reports on the synthesis of mesoporous alumina from different kaolin, there is none using Kano kaolin. Impact detailed study, characterization and analysis of this kaolin are still limited, hence, the need to evaluate its potentiality for the synthesis alumina.

1.2 Statement of the Problem

The reported common synthesis of mesoporous gamma alumina using aluminium alkoxide or inorganic salts as precursor is hazardous and uneconomical, as they are corrosive and expensive. In the present study, an environmentally friendly and inexpensive process utilizing abundant and non-toxic kaolin is reported. It is first of its kind utilizing Kano kaolin for the synthesis mesoporous γ -alumina. Since there is no report on the use of non-ionic polyoxyethylene (40) stearate (PS) surfactant on the synthesis of mesopotous gamma alumina, the effect of this surfactant on the mesoporous alumina synthesis is unknown. This study is the novel investigation of the effect of polyoxyethylene (40) stearate on the synthesis of mesoporous gamma alumina. The optimization of the synthesis procedure is explored by varaying surfactant mixing mode, surfactant concentration and aging time.

Furthermore, the possible mechanism of interaction between the PS surfactant and alumina precursor is also proposed.

Sodium hydroxide is an excellent catalyst commonly used for transesterification reaction with very good biodiesel yield. But, NaOH suffered from many problems that includes high energy consumption, corrosion and costly separation of catalyst and glycerol associated with homogeneous catalysts. To overcome these problems studies were reported in the literature using alumina as catalyst support for NaOH (Kim *et al.*, 2004; Arzamendi *et al.*, 2007; Taufiq-Yap *et al.*, 2011). However, all these catalysts used commercial alumina as support, as such little is known on the catalytic activities of mesoporous alumina in transesterification reaction. The development of mesoporous gamma alumina with large surface area, large pore volume, narrow pore size distribution and good thermal stability as catalyst support for NaOH is reported in this study. Additionally, the use of NaOH-modified alumina in transesterification of corn oil has not been reported. Also, full evaluation of recyclability, kinetics and thermodynamics of this catalyst are not available in the literature.

The growing increase in the environmental problems caused by excessive usage of fossil fuels, increased in the world energy demand and decreased in fossil fuel supply prompted the need for an alternative energy source (Veljkovic *et al.*, 2009). Renewable energy from biodiesel is one of the most promising substitutions of fossil fuel that help in reducing the emission of greenhouse gases. In the present study the use of corn oil, for biodiesel production, which is generally considered less expensive than other vegetables oil is reported. This will help in reducing the price of biodiesel. Additionally, utilizing corn oil for biodiesel production will not cause the problem of food versus fuel competition since the oil is extracted from the germ of the corn not the corn itself.

1.3 Objectives of the Research

The objectives of this research are;

- i- To synthesize and optimize mesoporous γ -Al₂O₃ from Kano kaolin sample in the presence of polyoxyethylene (40) stearate surfactant and polyethylene glycol 6000 for comparison.
- ii- To modify the mesoporous γ - Al₂O₃ synthesized from polyoxyethylene (40) stearate using sodium hydroxide by wet impregnation method.
- iii- To carry out methanolysis of corn oil and optimization using the as-prepared and modified mesoporous γ -Al₂O₃.
- iv- To study the kinetics, thermodynamics and stability of the synthesized catalyst.

1.4 Scopes of the Research

The scope of this research covered the synthesis, characterization and evaluation of base modified mesoporous gamma alumina for use as stable catalyst in biodiesel production.

The first stage of the research focus on the synthesis of mesoporous gamma alumina from Kano kaolin using novel polyoxyethylene 40 stearate (PS) as surfactant. For comparison another mesoporous γ -alumina was also be synthesized using polyethylene glycol 6000 (PEG-6000) since there are many literature reports on its application for mesoporous alumina synthesis. The effect of varying surfactant mixing mode, surfactant concentration as well as aging time was also explored. The

alumina precursor was leached out from the calcined kaolin using hydrochloric acid at 90 °C, then PS surfactant was added to the AlOOH precursor, followed by calcination to obtain the mesoporous gamma alumina. The synthesized mesoporous γ -Al₂O₃ was modified using sodium hydroxides by wet impregnation method. The instrumentation techniques for characterization of Kano kaolin, mesoporous γ -Al₂O₃ and catalyst include thermogravimetric-derivative thermal gravimetric (TG-DTG), X-Ray powder Diffraction (XRD), Fourier transform Infra-red (FTIR), X-ray fluorescence (XRF), N₂-adsorption desorption (BET), field emission scanning electron microscopy (FESEM-EDX), ²⁷Al-MAS NMR, basic back titration and temperature-programmed desorption of CO₂ (TPD-CO₂).

The second stage was the application of the catalysts for the production of biodiesel through batch transesterification reaction of corn oil with methanol. The conditions for the transesterification are 5% catalyst loading, 1:15 oil to methanol molar ratio, 67 °C reaction temperature and 3 hours reaction time. The methanolysis reaction was also optimized using RSM by Box-Behnken Design with the aid “Design Expert 7.1.6” statistical software. The design factors are NaOH doping (10-20%), catalyst loading (3-6%), oil to methanol molar ratio (1:6-1:15) and reaction time (1-3 hours). Proton nuclear magnetic resonance (¹H NMR), Fourier transform Infra-red (FTIR) and gas chromatography-flame ionisation detector (GC-FID) techniques were used in the analysis of the biodiesel products. Furthermore, the kinetics, thermodynamics and stability of the catalyst were also studied.

1.5 Significance of the Research

Alumina is the most frequently employed catalyst or catalytic support in the chemical industry. The improvement of alumina properties is significant for their catalytic applications. The use of polyoxyethylene (40) stearate (PS) in the synthesis of the alumina is expected to improve the properties of the alumina. Kaolin is a cheap source of aluminium and can serve as a good precursor for the synthesis of mesoporous alumina. Its utilization will reduce the cost of alumina production, and

also make the production environmentally benign as both the kaolin and surfactant are non-toxic. Since the synthesis of mesoporous alumina using PS is novel, PEG-6000, a well established surfactant for mesoporous alumina synthesis will also be used for the sake of comparison.

Biodiesel is an alternative source of energy that will help in reducing emission of greenhouse gases caused by the excessive usage of fossil fuels. The use of corn oil which is generally less expensive than other vegetable oils will help in reducing the price of biodiesel. In some African countries like Nigeria there is large production of corn, but utilization of germ of the corn for oil production is to a very small extent. Using corn oil for biodiesel production will serve as source of income generation at the same time reducing environmental problem.

There are extensive reports in the literature on the kinetics and thermodynamics studies of transesterification reactions under different reaction conditions and methods. However, since each catalyst has its own unique properties there is a need for kinetics and thermodynamics study with introduction of new catalyst. The information derived from the study is expected to be different from the previous ones and will be useful for research development and commercialization. The kinetics study will enable the determination of the reaction rates and catalyst efficiency. Whereas, thermodynamics study will provide information on the energy requirements involved in the methanolysis process.

1.6 Thesis Structure

The thesis is divided into six Chapters based on the research background, literature review, experimental works, discussion of findings and conclusion.

Chapter 1 presents the general background of the research area, problem statement, objectives of the research, scope of the research, significance of the research and the thesis structure.

Chapter 2 presents a comprehensive review on the related literature survey in the area of the present research.

Chapter 3 presents the methodology used for the alumina synthesis, catalysts preparation, methanolysis reaction, optimization, kinetics and thermodynamics analysis as well as characterizations.

Chapter 4 presents the results and discussion on the characterization of Kano kaolin, mesoporous alumina synthesized using polyethylene (40) stearate and polyethylene glycol 6000 surfactant, as well as prepared catalysts.

Chapter 5 presents the results and discussion on the application of catalysts obtained from the synthesized alumina in methanolysis of corn oil, optimization, kinetics and thermodynamics study, as well as catalyst recyclability and leaching test.

Chapter 6 contains the conclusion and recommendations for further works in the research area.

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