CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.0 Introduction

This chapter presents the results obtained in the course of this research study. The results were presented in Parts using publication format, each Part was a manuscript published/reviewed/under review in Tier 1 Web of Science (formally known as ISI) indexed journals except Part One which is an extract of a conference proceeding published in a Scopus indexed journal.

4.0.1 Results and Discussions Overview (RDO)

The first part (based on research objective one) covers the result of the thermodynamic simulation to establish the feasibility of the HDO process of stearic acid (SA) and oleic acid (OA) into paraffinic (C18) biofuel. The results which are detailed in Part One showed that the propensity for the HDO process of the model compounds (MCs) i.e. SA and OA using Aspen Hysys process simulator becomes feasible at a temperature of about 280 °C (although in the liquid phase) and pressure of 200 kPa. Furthermore, the results showed that SA is easily hydrotreated compared to OA due to the double bond in the latter. These operating conditions were validated in series of experimental studies using different catalysts.

In line with the research objective (ii) of this study to screen and establish superior catalytic activities between organometallic and non-organometallic catalysts on the kinetics of HDO process. Two nickel supported on alumina catalyst were synthesized, the first was via incorporation of nickel nitrate into alumina (Ni/Al₂O₃) and the second was via incorporation of nickel oxalate prepared via functionalization of nickel with oxalic acid (OxA) into alumina (NiOx/Al₂O₃). The activities of both
catalysts were tested on the HDO of OA. The result in Figure RDO-1 showed that NiOx/Al₂O₃ has the best HDO activity and in addition it produces isomerized fraction due to the effect of OxA functionalization which increased its acidity. A study on their HDO kinetics showed that the activity of NiOx/Al₂O₃ supersedes that of Ni/Al₂O₃ as shown in Table RDO-1. The details of this study are presented in Part Two.

![Product distribution of the HDO of oleic acid at 360 °C, 20 mg catalyst loading, 20 bar, 100 ml/min (10%) H₂ gas flow and 60 min](image)

**Figure RDO-1** Product distribution of the HDO of oleic acid at 360 °C, 20 mg catalyst loading, 20 bar, 100 ml/min (10%) H₂ gas flow and 60 min

**Table RDO-1** Evaluated kinetic parameter of the HDO of oleic acid using Ni/Al₂O₃ and NiOx/Al₂O₃ at 20 mg catalyst loading, 20 bar, 100 ml/min (10%) H₂ gas flow and 60 min

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>Ni/Al₂O₃</th>
<th>NiOx/Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k₂ (min⁻¹)</td>
<td>k₃ (min⁻¹)</td>
</tr>
<tr>
<td>593</td>
<td>0.198</td>
<td>0.022</td>
</tr>
<tr>
<td>613</td>
<td>0.225</td>
<td>0.026</td>
</tr>
<tr>
<td>633</td>
<td>0.245</td>
<td>0.030</td>
</tr>
</tbody>
</table>
Sequel to this observation and in order to deepen research towards enhancing the isomerization ability of the organometallic catalysts, palladium oxalate (PdOx) precursor prepared from the reaction of palladium salt and oxalic acid was further functionalized with fluoride ion to increase its acidity (Kovacs et al., 2011) prior to incorporation into Zeol support. The activities of the fluoride ion functionalized PdOx catalyst (FPdOx/Zeol) and the non-functionalized PdOx/Zeol catalysts were tested on the HDO of OA and the results are shown in Figure RDO-2. It is very obvious that FPdOx/Zeol possesses both higher HDO and isomerization activities compared to PdOx/Zeol. The enhanced activities of FPdOx/Zeol was ascribed to the increased acidity at the catalyst synthesis stages which improves the solubility of Pd in the support and facilitates the formation of Pd (II) polynuclear complex which in turn guarantee high Pd dispersion in Zeol as well as enhanced textural and morphological properties (Li et al., 2012) as seen in the characterization results detailed in Part Three – Part Four.

![Figure RDO-2 Product distribution of the HDO of oleic acid at 360 C, 20 mg catalyst loading, 20 bar, 10% H₂ gas flow and 60 min.](image-url)
In view of the exceptional invaluable enhanced HDO and isomerization activity of the FPdOx catalyst over PdOx, different metals such as molybdenum, platinum and bi-metallic catalyst using molybdenum to promote nickel were functionalized accordingly. They were supported on zeolite followed by characterization and testing at different operating conditions to satisfy the research objective (iii). Their detailed results are presented in Part Three – Seven. As a follow up to the study on the effect of operating condition to meet the research objective (iv), the HDO of OA process chemistry was studied based on the in-situ analysis of the evolved product FTIR and the results in Part Six showed that OA first undergoes sequential hydrogenation to form saturated SA prior to the O$_2$ molecule removal to form the C18 biofuel. Finally, sequel to research objective (v), the HDO process of OA was optimized for one of the most expensive active metal (platinum) catalyst using D-Optimal design, a form of response surface methods from Design Expert Software Package. The results were detailed in Part Eight. The reusability of all the tested organometallic catalysts was reported in each Part.
PART ONE

4.1 HYDRODEOXYGENATION PROCESS THERMODYNAMIC FEASIBILITY SIMULATION AND PRELIMINARY STUDIES

4.1.1 Aspen Hysys Process Thermodynamic Feasibility Simulation

As previously identified in the literature survey (*Chapter Two*) that oleic acid (OA) and stearic acid (SA) are the most commonly found fatty acids in virtually all known natural occurring triglycerides such as coconut oil, palm kernel oil, palm oil, olive oil, and Shea butter and they usually have the highest percentage especially OA. Consequently, their HDO process was simulated using Aspen Hysys Process simulator based on the overall process chemistry in Equation 4.1 – 4.2 in the Process Flow Diagram (PFD) in Figure 4.1 as earlier described in Section 3.1. The streams parameters are in Appendix A3.

\[ C_{17}H_{33}COOH \text{ (OA)} + 4H_2 \rightarrow C_{18}H_{38} + 2H_2O \]  
\[ C_{17}H_{35}COOH \text{ (SA)} + 3H_2 \rightarrow C_{18}H_{38} + 2H_2O \]

Figure 4.1 Simplified process flow diagram for the hydrodeoxygenation of oleic acid and stearic acid using Aspen Hysys process simulator.
4.1.1.1 Effect of Temperature on Hydrodeoxygenation of Model Compounds

The effect of temperature on the HDO of MCs in Figure 4.2 showed that there is no reaction on the MCs components until about 280 °C which implied that both OA and SA have not received sufficient thermal energy in excess of the activation energy to cause their molecules to interact with the H₂ gas to initiate the HDO process. The result showed that 320 °C is the best minimum temperature for the HDO of the MCs as all reactant were used up at that temperature and the production of the biofuel is not further enhanced with increase in temperature. This is in consonance with the observations of Arend et al., (2011) in a study on the catalytic deoxygenation of OA in continuous gas flow for the production of diesel-like hydrocarbons and Krar et al., (2010) in the hydrotreating of sunflower oil on CoMo/Al₂O₃ catalyst. Interestingly, the shape of the curves for the MCs consumptions and biofuel production is consistent with those reported by Snare et al., (2008) over Ru/C and Santillan-Jimenez et al., (2013) over Ni/C.

![Figure 4.2](image_url)  
**Figure 4.2** Effect of temperature on hydrodeoxygenation of SB, Pressure = 100 kPa, MCs = 10 gmole/h, H₂ = 4 kgmole/h.
4.1.1.2 Effect of hydrogen flow rate on Hydrodeoxygenation of Model Compounds

The results of the effect of H\textsubscript{2} flow rate at 320 °C is shown in Figure 4.3, it can be seen that increase in the H\textsubscript{2} flow rate from 5 to 9.2 kgmole/h enhanced the HDO process as more products are formed, but further increment up to 20 kgmole/h does not seem to have any appreciable enhancement on the biofuel production, although, there is little consumption in the unreacted OA. The amount of unreacted H\textsubscript{2} in the reactor can be seen to progressively increase accordingly from 9.2 kgmole/h which suggested that H\textsubscript{2} is in excess of stoichiometric requirement. The results further showed that SA appears to be first consumed compared to OA. This observation could be ascribed to the fact that OA has a double (C=C) bond (Scheme 4.1) consequently it requires two processing steps, i. e. sequential hydrogenation to saturate the double bond (Equation 4.3) and subsequent deoxygenation to produce the deoxygenated biofuel (Krar et al., 2010; Arend et al., 2011; Kovacs et al., 2011) as compared to the single step of HDO in SA. Other factor that could contribute to the relatively lower HDO rate of OA is its comparatively higher density of 893.4 kg/m\textsuperscript{3} compared to 881.7 kg/m\textsuperscript{3} of SA at STP.

Figure 4.3  Effect of hydrogen flow rate on the HDO of model compound; T = 320 °C, P = 200 kPa, MCs flow rate = 10 kgmole/h.
Scheme 4.1  Structure of oleic (a) and stearic (b) acids

\[ C_{17}H_{33}COOH + H_2 \rightarrow C_{17}H_{35}COOH \]  \hspace{1cm} (4.3)

### 4.1.1.3 Effect of Pressure on Hydrodeoxygenation of Model Compounds

Since at least a gas (H\(_2\)) is involved in the study, the effect of pressure as a thermodynamic state function becomes imperative and also considering the fact of Le Chatelier’s principle. The result of effect of pressure on HDO of MCs in Figure 4.4 showed that the HDO efficiency is comparably lower at a pressure below 200 kPa. This is because according to Equation 4.1- 4.3 it can be seen that the volume of the reactants are larger than the product and this summarily suggests relatively higher pressure would favor the HDO of MCs. The result showed propensity for a pressure range of 180-240 kPa, which is in agreement with previous review (Mortensen et al., 2011) on the catalytic HDO of several bio-oil.
4.1.2 Preliminary Studies on the HDO of Oleic Acid

Prior to the studies on the effect of oxalic acid functionalization on the HDO catalysts to synthesize organometallic catalyst whose activity is to be compared with the conventional metal oxide catalyst, a preliminary blank test was carried out in a semi-continuous reactor based on the results of the simulation studies without catalysts dosage. This study became imperative in view of the reactor and/or its accessories having any possible contributory auto-catalytic effects such as hydrogenation or thermal cracking of the OA feedstock which may tamper with the accuracy of the HDO process kinetics. Though the result actually showed a minuscule conversion of OA, but there was no formation of any C_{18} hydrocarbon except about 3% stearic acid (SA) formation. This suggests that a fraction of OA was marginally hydrogenated to form saturated SA (Equation 4.3) and that cracking of the OA was not imminent at those prevailing operating conditions. It can therefore be concluded that during experimental studies on the activities of the synthesized catalyst there would be only marginal hydrogenation...
contribution for the formation of SA from the reactor and the associated internals made of stainless steel at those prevailing operating conditions. In a previous study (Ayodele et al., 2013a) on the HDO of OA into biofuel using Pd supported on carbon catalyst, the formation of SA as an intermediate compound was also observed.
PART TWO

4.2 EFFECT OF OXALIC ACID FUNCTIONALIZATION ON ALUMINA SUPPORTED NI CATALYST ON THE ISOMERIZATION, KINETICS AND ARRHENIUS PARAMETERS OF OLEIC ACID HYDRODEOXYGENATION INTO BIOFUEL

4.2.1 Characterization Result

4.2.1.1 X-Ray Fluorescence Spectra (XRF)

The XRF spectra results of Al₂O₃, Ni/Al₂O₃ and NiOx/Al₂O₃ samples are shown in Figure 4.5. The spectrum of Al₂O₃ showed its characteristics peaks between 1.48 and 21.4 keV. However, upon the incorporation of Ni (inorganic) precursor into the structure of Al₂O₃, a new and relatively distinct peak at Kα value of 7.47 keV appeared in the Ni/Al₂O₃ spectra. Similarly, sequel to the incorporation of NiOx into Al₂O₃ in the NiOx/Al₂O₃ sample all the characteristics peaks of Al₂O₃ were dwarfed by the brilliant intensity of a peak at Kα value of 7.47 keV and another subordinate peak at Kβ of 8.26 keV. These peaks according to the standard card of peak identification (EDXRF-EPSILON 3 XL, PANalytical) were ascribed to the presence of Ni species. In the NiOx/Al₂O₃ sample, the intense peak at Kα value of 7.47 keV could be ascribed to high dispersion of Ni species due to the formation of Ni-oxalate complex during the OxA functionalization. Similarly, the appearance of two Ni peaks (of varying intensity) is an indication that two different Ni species are present (as would be seen later in the EDX, XRD and Raman spectroscopy results).
4.2.1.2 Elemental Dispersive X-Ray (EDX)

The EDX result of Al$_2$O$_3$, Ni/Al$_2$O$_3$ and NiOx/Al$_2$O$_3$ samples are shown in Figure 4.6. The composition of Al$_2$O$_3$ is basically Al and O$_2$ with some relatively minute quantity of Ca as shown in Table 4.1. Both Figure 4.6 (b) and (c) corroborates the presence of Ni species in Ni/Al$_2$O$_3$ and NiOx/Al$_2$O$_3$ samples. However, as both samples showed Ni peaks at low energy band of 1.9 keV, NiOx/Al$_2$O$_3$ sample showed additional peak at high energy band of 7.5 keV. Furthermore, the Ni peaks in NiOx/Al$_2$O$_3$ sample appeared to be more intense compared to the single peak in Ni/Al$_2$O$_3$. 
Figure 4.6  
EDX spectra of (a) Al\textsubscript{2}O\textsubscript{3}, (b) Ni/Al\textsubscript{2}O\textsubscript{3} and (c) NiOx/Al\textsubscript{2}O\textsubscript{3} samples

Table 4.1  
Elemental composition and textural properties of Al\textsubscript{2}O\textsubscript{3}, Ni/Al\textsubscript{2}O\textsubscript{3} and NiOx/Al\textsubscript{2}O\textsubscript{3}

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental composition (%)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>39.1</td>
<td>43.7</td>
<td>17.2</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Ni/Al\textsubscript{2}O\textsubscript{3}</td>
<td>37.9</td>
<td>41.3</td>
<td>11.54</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>NiOx/Al\textsubscript{2}O\textsubscript{3}</td>
<td>31.03</td>
<td>52.17</td>
<td>5.2</td>
<td>9.3</td>
<td></td>
</tr>
</tbody>
</table>

This observation is not at variance with what was earlier seen in their XRF spectra and it further confirms there is more than one Ni species in the NiOx/Al\textsubscript{2}O\textsubscript{3}
sample. According to the quantification of the EDX spectra in Table 4.1, Ni/Al₂O₃ showed reduction in the O₂ percent composition compared to Al₂O₃ while NiOx/Al₂O₃ showed increment. The reduction in the former was due to the incorporation of Ni while the increment in the latter was due to the presence of oxalate ligand in the incorporated NiOx precursor as a result of the OxA functionalization. There was variation in the amount of Ni from the expected 10% to 8.2% and 9.3% in the Ni/Al₂O₃ and NiOx/Al₂O₃ samples, respectively (obtained from the average of four repeated different points since EDX is more of a point analysis technique). This variation was ascribed to different degree of hydration at the catalysts synthesis stage (Ayodele, 2013). The low variation observed in the NiOx/Al₂O₃ was due to the formation of NiOx complex which is highly insoluble in water due to its organometallic ligand compared to NiO.

4.2.1.3 Scanning Electron Microscopy (SEM)

The morphology of Al₂O₃ shown in Figure 4.7 revealed lumpy and thick flakes with partial uniform particle size distribution and relatively smooth surfaces and edges. After the catalysts synthesis both of Ni/Al₂O₃ and NiOx/Al₂O₃ showed the formation of irregular flaky morphology with random orientation and loss of crystallinity. This observation was due to certain synthesis protocols such as calcination which has been known to remove framework alumina (Ayodele and Hameed, 2013), earlier reports (Panda et al., 2010; Xiaoling et al., 2012) also showed that alumina and aluminosilicates transforms from crystalline into amorphous under thermal treatment. However, the morphological variation appeared to be more pronounced in NiOx/Al₂O₃ due to the acidic effect of the NiOx on the Al₂O₃ support thus removing extra-framework alumina (Xiaoling et al., 2012) and increasing catalytic activity (Li et al., 2012).
4.2.1.4 Nitrogen Adsorption/Desorption Studies (BET Methods)

This loss of crystallinity in the catalyst were seen to have enhanced their textural properties as seen in the reduction of the average particle size which in turn resulted into increase in the specific surface area (Table 4.2) as measured by the N₂ adsorption/desorption studies (BET methods). This textural enhancement is more and clearly evident in NiOx/Al₂O₃ than in Ni/Al₂O₃ due to the effect of acidic NiOx precursor. Generally, organometallic catalyst precursors especially of low pH are known to be structural modifiers, enhancing the mesoporosity of synthesized catalysts (Li et al., 2012; Ayodele and Togunwa, 2014).
Table 4.2  Textural properties of Al₂O₃, Ni/Al₂O₃ and NiOx/Al₂O₃ samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore diameter (nm)</th>
<th>Average Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>64.0</td>
<td>0.21</td>
<td>13.32</td>
<td>4688</td>
</tr>
<tr>
<td>Ni/Al₂O₃</td>
<td>78.3</td>
<td>0.26</td>
<td>13.64</td>
<td>3605</td>
</tr>
<tr>
<td>NiOx/Al₂O₃</td>
<td>120.1</td>
<td>0.38</td>
<td>14.22</td>
<td>2225</td>
</tr>
</tbody>
</table>

The N₂ adsorption/desorption isotherms of Al₂O₃, Ni/Al₂O₃ and NiOx/Al₂O₃ samples are shown in Figure 4.8. Al₂O₃ showed characteristics formation of monolayer isotherm at lower relative pressure as seen in the intermediate flat region which is typical of Type II isotherms and it systematically conformed to the Type IV isotherm typical of mesoporous materials at higher relative pressures. The isotherms of Ni/Al₂O₃ sample did not show much difference from the Al₂O₃, however, NiOx/Al₂O₃ showed characteristics of Type IV over the range of the isotherms signifying enhanced mesoporosity. This was made more evident by the increase in its H3-like hysteresis loop which is typical of inter-particle voids formed by accumulation of plate-like and nano-sized particles having slit-shaped pores (Xue et al., 2012). Similarly, the increase in the amount of N₂ adsorbed in NiOx/Al₂O₃ sample confirmed the enhanced porosity observed in the pore volume (Table 4.2). These modified textural and morphological qualities were due to the incorporation of acidic organometallic NiOx precursor into the Al₂O₃ lattice (Li et al., 2012; Ayodele et al., 2014). Consequently, this well-enhanced mesoporous structure is an indication that the nickel species would be finely dispersed thus forming the amorphous nickel aluminate phase (Ghule et al., 2009; Ghule et al., 2010; Bang et al., 2012; Bang et al., 2013).
Figure 4.8  
Nitrogen adsorption/desorption of Al$_2$O$_3$, Ni/Al$_2$O$_3$ and NiOx/Al$_2$O$_3$ samples

4.2.1.5 X-Ray Diffraction (XRD)

The XRD result of Al$_2$O$_3$, Ni/Al$_2$O$_3$ and NiOx/Al$_2$O$_3$ samples are shown in Figure 4.9. The characteristic peaks at 2θ values of 25.5º, 35.8º, 37.6º, 43.6º, 52.7 º, 57.6 º, 60.6º, 66.4º, 77º and 84.8º typical of γ-Al$_2$O$_3$ are also observed in Ni/Al$_2$O$_3$ and NiOx/Al$_2$O$_3$ hence it is not easy to differentiate the characteristics peaks of Ni. This observation indicates that nickel species were finely dispersed thereby developing an amorphous nickel aluminate phase owing to the effect of proper calcination at the catalyst synthesis stage (Ayodele and Hameed, 2012; Bang et al., 2013). The synthesized catalysts exhibited comparative reduced peaks due to loss of crystallinity earlier observed in the SEM result (section 3.1.3) and it was ascribed to the effect of calcination (Li et al., 2012; Ayodele and Togunwa, 2014). The further reduction in the NiOx/Al$_2$O$_3$ peaks was ascribed to the effect of OxA functionalization at the synthesis stage which also prevented both Ni sintering and collapse of the NiOx/Al$_2$O$_3$ structure
by the well-developed mesopores earlier seen in Figure 4.8. This confirmed that highly dispersed surface type amorphous nickel aluminate phase was prevalent over any possible bulk type (Ghule et al., 2010; Bang et al., 2012; Bang et al., 2013). Furthermore, a close examination revealed that there is shift in the diffraction peaks of the catalyst compared to Al₂O₃, which implied that the Ni species have intimate contact with the γ-Al₂O₃ lattice thus expanding it to form a more nickel-saturated surface nickel aluminate phase (Ghule et al., 2009; Ghule et al., 2010; Bang et al., 2012). This shift in the diffractogram peaks is relatively more visible in the NiOx/Al₂O₃ than in the Ni/Al₂O₃ sample because NiOx complex has comparably larger molecular size.

![XRD patterns of Al₂O₃, Ni/Al₂O₃ and NiOx/Al₂O₃ samples](image)

**Figure 4.9**  XRD patterns of Al₂O₃, Ni/Al₂O₃ and NiOx/Al₂O₃ samples

### 4.2.1.6 Fourier Transform Infrared spectroscopy (FTIR)

Figure 4.10 shows the FTIR spectroscopy of Al₂O₃, Ni/Al₂O₃ and NiOx/Al₂O₃ samples, it can be seen that there is no clear difference between their spectra. This observation is synonymous to XRD result (Figure 4.9) that showed no distinction
between the diffractograms of the Al$_2$O$_3$ and the synthesized catalysts and this was adduced to high Ni dispersion to form surface nickel aluminate spinel (Ghule et al., 2009; Ghule et al., 2010). However, it can be seen that the spectra of all the samples aligned up to about 980 cm$^{-1}$ beyond which the spectrum of Ni/Al$_2$O$_3$ and NiOx/Al$_2$O$_3$ deflected due to the effect of metal incorporation. The deviation is sharp and well pronounced in NiOx/Al$_2$O$_3$ compared to Ni/Al$_2$O$_3$ due to the incorporation of organic NiOx complex precursor. Typically, the presence of metal (transition/noble) incorporation in synthesized catalysts is usually observed in their spectra deviations compared to that of the support at low wavenumbers below 1000 cm$^{-1}$ which is an indication of structural variation (Li et al., 2012). In view of the FTIR spectroscopy limited information about metal-support interaction, Raman spectroscopy was employed to expound more detailed structural variation.

![FTIR spectra of Al$_2$O$_3$, Ni/Al$_2$O$_3$ and NiOx/Al$_2$O$_3$ samples](image)

Figure 4.10 FTIR spectra of Al$_2$O$_3$, Ni/Al$_2$O$_3$ and NiOx/Al$_2$O$_3$ samples
4.2.1.7 Raman Spectroscopy

The Raman spectra of Al₂O₃, Ni/Al₂O₃ and NiOx/Al₂O₃ samples are shown in Figure 4.11. Typical Al₂O₃ bands are seen at 1174, 1085, 1057, 1009, 916, 828, 745, 637, 600, 518, 423 and 377 cm⁻¹, while the strong band at 1300 cm⁻¹ as well as those at 1130 and 1060 cm⁻¹ reflects Al(OH)₃ due to the adsorbed water molecules (Ghule et al., 2009; Ghule et al., 2010). Obviously after catalysts synthesis and calcination those bands drastically reduced in intensity due to dehydroxylation (i.e. 2Al(OH)₃ → Al₂O₃ + 3H₂O) in Ni/Al₂O₃ and NiOx/Al₂O₃. Raman spectroscopic studies have fundamentally established two types of supported metals on Al₂O₃ due to either adsorption or absorption (Ghule et al., 2009; Ghule et al., 2010). Adsorption is typical of metals with high oxidation state and as such cannot be accommodated into the matrix of Al₂O₃ hence they give strong Raman bands at ~1100-900 cm⁻¹. On the other hand, absorption is characteristics of low oxidation state metals that can be absorbed into the surface of the alumina support as Ni²⁺ forming a surface spinel since they can be accommodated and they usually possess Raman bands between ~800 – 300 cm⁻¹. From the Ni/Al₂O₃ spectra, the bands at 510 and 670 cm⁻¹ are characteristics of crystalline NiO adsorbed on the Al₂O₃ surface typical of crystalline NiAl₂O₄ (Ghule et al., 2010). On the other hand, from the spectra of NiOx/Al₂O₃, there are Raman bands in the range of ~1200 – 300 cm⁻¹ which suggests that Ni species are being absorbed and adsorbed probably as NiOx and NiO. This also supports earlier observation in the XRF and EDX result that there are two Ni species in NiOx/Al₂O₃. The NiOx is definitely due to the functionalization with OxA, while the NiO might be from the unreacted Ni salt during the catalyst synthesis stage or possibly thermally decomposed NiOx (i.e. NiC₂O₄ + ½O₂ → NiO + 2CO₂) during calcination. However, the prevalence of the NiOx over NiO in NiOx/Al₂O₃ sample is justified by the absence of bands at 460, 510 and 670 cm⁻¹ which are characteristics of crystalline NiO as well as the low intensity peaks at 375 and 600
$\text{cm}^{-1}$ which are typical of crystalline NiAl$_2$O$_4$ (Ghule et al., 2009; Ghule et al., 2010). These also support the earlier observation in XRD result that the Ni species present in the NiOx/Al$_2$O$_3$ are highly dispersed. It can therefore be concluded that the OxA functionalization was effective, and its presence in the NiOx/Al$_2$O$_3$ is very evident by certain bands of aggressive peaks and the multiple background noise-like vibrations which are typical of the presence of organic functional group (Ghule et al., 2010), the background noise-like vibrations were not present in the inorganic synthesized Ni/Al$_2$O$_3$.

![Raman spectra of Al$_2$O$_3$, Ni/Al$_2$O$_3$ and NiOx/Al$_2$O$_3$ samples](image)

Figure 4.12 Raman spectra of Al$_2$O$_3$, Ni/Al$_2$O$_3$ and NiOx/Al$_2$O$_3$ samples
4.2.2 Catalytic Activities and Kinetics Studies

4.2.2.1 Preliminary Studies on the HDO of Oleic Acid

Prior to the main studies on the catalytic HDO and kinetic of OA into paraffinic biofuel, a blank test was carried out at the previously best observed operating conditions of 360 °C, 20 bar and 100 mL/min gas flow (Ayodele et al., 2014) without the dosage of either of the catalysts. This study became imperative in view of the reactor and/or it accessories having any possible contributory auto-catalytic effect such as hydrogenation or thermal cracking of the OA feed stock which may tamper with the accuracy of the intended kinetics and Arrhenius parameter studies. Though the result actually showed a minuscule conversion of OA, but there was no formation of any C_{18} hydrocarbon except about 3% stearic acid (SA) formation. This suggests that a fraction of OA was marginally hydrogenated to form saturated SA (Equation 4.4) and that cracking of the OA was not imminent at that prevailing operating condition. It can therefore be concluded that there would be only marginal hydrogenation contribution for the formation of SA from the reactor and the associated internals made of stainless steel. In our previous study (Ayodele et al., 2014) on the HDO of OA into C_{18}H_{38} (octadecane) biofuel using acidified zeolite supported fluoropalladium oxalate catalyst we equally observed the formation of SA as an intermediate product (Equation 4.4 – 4.5) from the FTIR of the evolved species.

\[ C_{17}H_{35}COOH + H_2 \rightarrow C_{17}H_{35}COOH \]  \hspace{1cm} (4.4)

\[ C_{17}H_{35}COOH + 3H_2 \rightarrow C_{18}H_{38} + 2H_2O \]  \hspace{1cm} (4.5)
4.2.2.2 Catalytic Activities of Ni/Al₂O₃ and NiOx/Al₂O₃ on HDO of Oleic Acid

The catalytic activities of Ni/Al₂O₃ and NiOx/Al₂O₃ on the HDO of OA at 360 °C, 20 bar, 100 ml/min H₂ gas flow using 20 mg loading of each catalyst showed that NiOx/Al₂O₃ has superior activity producing 67.6% n-C₁₈H₃₈ and 26.4% i-C₁₈H₃₈ compared to 51.2% n-C₁₈H₃₈ and 1.2% i-C₁₈H₃₈ produced when using Ni/Al₂O₃. However, since the amount and intensity of Ni species in NiOx/Al₂O₃ is comparably higher than in the Ni/Al₂O₃ from Table 4.1 and Figure 4.6, respectively, it is relatively difficult to ascribe the superiority of NiOx/Al₂O₃ over Ni/Al₂O₃ directly to either the effect of OxA functionalization or the amount of total Ni species present. Consequently, a repeated HDO of OA was conducted at the same experimental condition but using 22.6 mg of Ni/Al₂O₃, an equivalent of 9.3% Ni of 20 mg NiOx/Al₂O₃. The observed result in Figure 4.13 showed that there is a marginal increase of about 4.3% in n-C₁₈H₃₈ production and no effect on i-C₁₈H₃₈ production.

![Figure 4.13](image-url)  
**Figure 4.13**  Product distribution of the HDO of oleic acid at 360 °C, 20 mg catalyst loading, 20 bar, 100 ml/min H₂ gas flow and 60 min
Thus, this observation confirmed that the superior activity of NiOx/Al2O3 over Ni/Al2O3 can be ascribed to the effect of OxA functionalization which enhances higher Ni dispersion (as seen in the XRD plot) and also ensures the formation of the octahedral Ni species (Li et al., 2012). In addition, the OxA functionalization also engrained in NiOx/Al2O3 the ability to withstand high degree of hydration thereby resulting in comparably higher Ni content and strong Ni spectra as seen in Table 4.1 and Figure 4.6, respectively. Generally, organometallic catalyst with metal-oxalate ligand functionalities have been reported to be acidic and highly reactive as well as having propensity to minimize nefarious side reactions (Li et al., 2012; Tanev and Lange De Oliveira, 2012; Ayodele, 2013). According to the metal-oxalate chemistry, the oxalate ion is quite a versatile ligand because it can act as a mono-, bi-, tri-, and tetradentate ligands as shown in Figure 4.14, thus oxalate ion is capable of forming bridged polynuclear complexes. For example, a nth-positive (Mⁿ⁺) transition metal ion, the corresponding n-chelate product [M³⁺(C₂O₄)₃]ⁿ⁻ is formed (Decurtins et al., 1993). This ability was due to the fact that polynuclear oxalate systems are excellent candidates to deepen our hitherto limited understanding of the way molecules and ions are organized in the solid state to form materials with distinctive physical and chemical properties (Roman et al., 1996). In fact, a recent related catalysis study on the effect of metal source on the catalytic photodegradation of lincomycin and diazepam in sewage treatment plant effluent by photo-Fenton process, Fe-nitrate, Fe-sulphate and Fe-oxalate were tested and the Fe-oxalate was reported to be the most efficient and versatile. The authors (Bautitz and Nogueira, 2010; Dopar et al., 2011) attributed the Fe-oxalate unique and astounding ability to the presence of those certain metal-oxalate ligands that are present in the Fe-oxalate catalyst.
Figure 4.14 Oxalate complexes (Cotton and Wilkinson, 1988)

The presence of i-C\textsubscript{18}H\textsubscript{38} in Figure 4.13 was due to the increase in the NiOx/Al\textsubscript{2}O\textsubscript{3} acidity owing to the OxA functionalization (Ayodele et al., 2014). Previous reports (Kovacs et al., 2011; Ayodele et al., 2014) have shown that the presence of about 20% isomerized components in biofuel can reduce its freezing point by about 12 °C thus enhancing the biofuel cold flow property. There are also instances of decarboxylation/decarbonylation reaction as evident by the presence of C\textsubscript{17}H\textsubscript{36} in the products of Ni/Al\textsubscript{2}O\textsubscript{3} which were not observed in the NiOx/Al\textsubscript{2}O\textsubscript{3} due to the presence of metal-oxalate ligands in the latter. About 29% of non-hydrocarbons comprising unreacted OA, unconverted SA and traces of esters and alcohol functional groups were also conspicuous in Ni/Al\textsubscript{2}O\textsubscript{3} product distribution but were insignificant in NiOx/Al\textsubscript{2}O\textsubscript{3}. The almost total HDO of OA into C\textsubscript{18}H\textsubscript{38} when using NiOx/Al\textsubscript{2}O\textsubscript{3} was similar to the results obtained by Sousa et al., (2012) on the hydrotreatment of sunflower oil using β-Mo\textsubscript{2}C/Al\textsubscript{2}O\textsubscript{3} where all the C\textsubscript{18} acids in the sunflower oil were converted to C\textsubscript{18} biofuel. Similarly, just as no C\textsubscript{17}H\textsubscript{36} was observed when using NiOx/Al\textsubscript{2}O\textsubscript{3}, Sousa et al., (2012) also did not observe decarboxylation /decarbonylation, and they attributed the efficiency and ability of the β-Mo\textsubscript{2}C/Al\textsubscript{2}O\textsubscript{3} catalyst to the expedient organometallic synthesis protocol based on the temperature-programmed carburization (TPC) methodology.
4.2.2.3 Kinetics Studies of Hydrodeoxygenation of Oleic Acid

In order to study the effect of OxA functionalization on alumina supported Ni catalyst on the HDO of OA, the development of a proposed HDO mechanism becomes important for kinetic study. In previous section and our past study (Ayodele et al., 2014), hydrodeoxygenation of OA proceeded via sequential hydrogenation to form the saturated SA followed by oxygen molecule extraction to produce the final biofuel (Equation 4.4 – 4.5). This was also supported by other previous works (Kovacs et al., 2011; Priecel et al., 2011) and it was due to the presence of double bond in the OA structure. In the HDO of OA, SA was observed to be the main intermediate product, although some other species may be present in varying minute quantity. In order to model a mechanism that can be modestly solved, a lumped kinetic model was adopted as shown in Scheme 4.2, where SA represents all the intermediate compounds since its concentration excessively outweighs that of any other possible intermediate products (Ayodele et al., 2013; Zhang et al., 2014). Similarly, since the concentration of OA is far in excess of H$_2$ gas, a pseudo-first-order kinetics was assumed with respect to OA to determine the rate constants (Ayodele et al., 2013; Zhang et al., 2014), $k_i$ ($i = 1, 2, 3$) especially since few preliminary experiments on effect of variation of OA loading at constant catalyst dosage showed that its disappearance conformed to pseudo-first–order kinetics. The kinetic study is also to establish whether the SA formation step or its consumption step is the limiting step.

$$
\begin{align*}
\text{C}_{17}\text{H}_{35}\text{COOH} & \xrightarrow{k_1} \text{C}_{18}\text{H}_{38} + \{\text{H}_2\text{O} + \text{CO} + \text{C}_{17}\text{H}_{36} + \text{CH}_4 + \text{CO}_2\} \\
\text{C}_{17}\text{H}_{35}\text{COOH} & \xrightarrow{k_2} \text{C}_{17}\text{H}_{35}\text{COOH} + \text{H}_2 \\
\text{C}_{17}\text{H}_{35}\text{COOH} & \xrightarrow{k_3} \text{C}_{17}\text{H}_{35}\text{COOH} + 3\text{H}_2
\end{align*}
$$
Scheme 4.2  Simplified proposed mechanism for the HDO kinetics of oleic acid

The following sets of differential Equations (Equation 4.6 – 4.13) were obtained according to the reaction pathway in Scheme 4.2.

**Notation:**  
\[ C_{17}H_{33}COOH \rightarrow OA; C_{17}H_{35}COOH \rightarrow SA; C_{18}H_{38} \rightarrow C_{18} \]

\[ \frac{-dC_{OA}}{dt} = (k_1 + k_2)C_{OA} \quad (4.6) \]

\[ \frac{dC_{SA}}{dt} = k_2C_{OA} - k_3C_{SA} \quad (4.7) \]

From Equation 4.6, \[ C_{OA} = C_{OA_0} \cdot e^{-(k_1+k_2)t} \quad (4.8) \]

As earlier noted that HDO of OA proceeded via sequential hydrogenation to form SA, therefore \( k_1 \) representing the direct formation of the \( C_{18} \) biofuel in Scheme 4.2 can be set to zero, because the rate of direct formation, if at all takes place, will be far too low to be reckoned with.

Therefore Equation 4.8 can be reduced to:

\[ C_{OA} = C_{OA_0} \cdot e^{-(k_2)t} \quad (4.9) \]

Substituting Equation 4.9 into Equation 4.7 gives Equation 4.10, which upon integration with boundary limits: when \( t = 0 \), \( C_{OA} = C_{OA_0} \) and \( C_{SA} = C_{SA_0} = 0 \) gives rise to Equation 4.11.

\[ \frac{-dC_{SA}}{dt} = k_2C_{OA_0} \cdot e^{-(k_2)t} - k_3C_{SA} \quad (4.10) \]

\[ C_{SA} = \frac{k_2C_{OA_0}}{(k_3 - k_2)} \left[ e^{-(k_2)t} - e^{-(k_3)t} \right] \quad (4.11) \]

Consequently, the formation of \( C_{18} \) biofuel can be obtained by substituting Equations (4.9) and (4.11) into Equation 4.12, it is important to note that both n-\( C_{18}H_{38} \) and i-
$C_{18}H_{38}$ formed are summed together as $C_{18}$ since their molecular formula and weight are same.

\[ i.e. \ C_{18} = C_{OA_0} - C_{OA} - C_{SA} \]  \hspace{1cm} (4.12)

\[ C_{18} = C_{OA} - C_{OA_0} \cdot e^{-(k_2)t} - \frac{k_2 C_{OA}}{(k_3 - k_2)} \left[ e^{-(k_2)t} - e^{-(k_3)t} \right] \]  \hspace{1cm} (4.12b)

Rearranging Equation 4.12b gives Equation 4.13 which gives the ratio of $C_{18}$ biofuel production as a function of time with respect to the initial OA concentration.

\[ \frac{C_{18}}{C_{OA_0}} = \frac{1}{(k_3 - k_2)} \left[ k_3 (1 - e^{-(k_2)t}) - k_2 (1 - e^{-(k_3)t}) \right] \]  \hspace{1cm} (4.13)

The experimental data of $C_{18}$ formation for both Ni/Al$_2$O$_3$ and NiOx/Al$_2$O$_3$ at temperature range of 320 – 360 ºC were fitted into Equation 4.13 using MathCAD v13 and plotted in Figure 4.15, where $\frac{C_{SA}}{C_{OA_0}}$ is denoted by $Y(t)$ and represents the developed model, while $C_{18i}$ is the experimental values. The plot fitting showed a high degree of perfect fitting with observed $R^2$ ranges between 0.92 – 0.98. The fitted plots showed that the $C_{18}$ production is enhanced as the HDO temperature is increased from 320 to 360 ºC. For example, when using Ni/Al$_2$O$_3$ the $C_{18}$ production increased from about 70% to 85% when the temperature was increased from 320 to 360 ºC. Similarly, in the same temperature range the $C_{18}$ production of NiOx/Al$_2$O$_3$ increased from 85% to 96%. This clearly indicates that the HDO process of OA irrespective of the catalyst used conforms to the Arrhenius theory of temperature dependent of reaction rates.
This implied that as the temperature was increased the molecules of the OA gained more kinetic energy in excess of activation energy to vigorously interact with the \( \text{H}_2 \) gas at the catalysts active sites. Furthermore, since the viscosity of OA has an inverse relation with temperature, for example according to Aspen Hysys process simulator v7.2, a simulation of the effect of temperature on OA showed that at 320, 340 and 360 °C, the viscosity of OA was 0.4021, 0.3441, 0.2963cp, respectively. Consequently, the reduction in OA viscosity with increased temperature is also considered to have enhanced both the \( \text{H}_2 \) mass transfer into the bulk of OA and its propensity for solubility in the reaction mixture.

A careful look at the fitted plots (Figure 4.15) also revealed that irrespective of the temperature the \( \text{C}_{18} \) production of the \( \text{Ni/Al}_2\text{O}_3 \) is clearly inferior to \( \text{NiOx/Al}_2\text{O}_3 \). For example, at 360 °C the \( \text{C}_{18} \) production of \( \text{Ni/Al}_2\text{O}_3 \) is 85% while \( \text{NiOx/Al}_2\text{O}_3 \) has
96%. This feat was due to the functionalization of the Ni catalyst with OxA, which did not only improve the solubility of Ni salt (Li et al., 2012) but also enhanced its dispersion as earlier observed in the XRF spectra, XRD and Raman spectroscopy results. In addition, according to the EDX result, OxA functionalization increases the ability of the NiOx/Al2O3 to withstand the degree of hydration at the catalyst synthesis stage due to its organometallic functionalities. Consequently, NiOx/Al2O3 has comparably higher Ni species of 9.3% compared to 8.2% observed in Ni/Al2O3, all these contributed to its high catalytic activities. According to the studies of Li et al., (2012) on the synthesis of NiMo/γ-Al2O3 catalyst, they reported that the increase in the catalyst acidity due to functionalization with organic tetr phenylporphyrin increased the metals dispersion, enhanced the morphological and textural qualities which in turn resulted in the formation of octahedral Ni and Mo known to be highly reactive species. Li et al., (2012) findings and another US patent (Tanev and Lange De Oliveira, 2012) supported the high Ni dispersion, enhanced morphological and textural qualities of NiOx/Al2O3 compared to Ni/Al2O3 as earlier seen in their characterization results, hence resulted in its superior HDO and isomerization activity seen in Figure 4.15.

4.2.2.4 Rate Constants and Arrhenius Parameters

The rate constants obtained from Figure 4.15 are shown in Table 4.2. As expected the rate constants when using NiOx/Al2O3 are clearly higher than Ni/Al2O3, which is a confirmation that the former is highly reactive owing to the OxA functionalization as earlier explained. Furthermore, a closer observation showed that k2 > k3 in all cases which implied that sequential hydrogenation of OA into SA is more easily achieved and faster than the O2 extraction stages. This supports and explains why minuscule conversion (about 3%) of OA into SA was the only observation during the preliminary study in the absence of either of the catalysts. The kinetic data in Table 4.2
were fitted into the Arrhenius Equation (Equation 4.14) and plotted as shown in Figure 4.16 to evaluate the pre-exponential factor, $A_0$ (min$^{-1}$) and the activation energy, $E_a$ (kJ/mol K).

$$\ln k = \ln A_0 - \frac{E_a}{RT} \quad (4.14)$$

Table 4.2 Evaluated kinetic parameter of the HDO of oleic acid using Ni/Al$_2$O$_3$ and NiOx/Al$_2$O$_3$

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>Ni/Al$_2$O$_3$</th>
<th>NiOx/Al$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_2$ (min$^{-1}$)</td>
<td>$k_3$ (min$^{-1}$)</td>
</tr>
<tr>
<td>593</td>
<td>0.198</td>
<td>0.022</td>
</tr>
<tr>
<td>613</td>
<td>0.225</td>
<td>0.026</td>
</tr>
<tr>
<td>633</td>
<td>0.245</td>
<td>0.030</td>
</tr>
</tbody>
</table>

Figure 4.16 Arrhenius parameter fitting plot (a) stearic acid formation step, (b) biofuel formation step
From Table 4.3 the values of $A_o$ (which is the total number of collisions per second either leading to a reaction or not) observed for the process showed that SA formation step ($k_2$) has higher values compared to the $C_{18}$ formation step ($k_3$). Similarly, comparing the two catalysts, NiOx/Al$_2$O$_3$ has comparably lower value. According to collision theory (Missen et al., 1999), the higher values observed when Ni/Al$_2$O$_3$ was used could be due to the catalyst’s inability to initiate faster reaction rates to use up the H$_2$ gas, hence the collision rate increases since the H$_2$ flow rate was not reduced and the temperature was elevated. On the other hand, the low $A_o$ observed in NiOx/Al$_2$O$_3$ could imply that the H$_2$ gas was quickly used up since NiOx/Al$_2$O$_3$ has comparable higher reactivity.

Table 4.3 Evaluated Arrhenius parameter of the HDO of oleic acid using Ni/Al$_2$O$_3$ and NiOx/Al$_2$O$_3$

<table>
<thead>
<tr>
<th></th>
<th>Stearic acid formation</th>
<th></th>
<th>$C_{18}$ biofuel formation</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ni/Al$_2$O$_3$</td>
<td>NiOx/Al$_2$O$_3$</td>
<td>Ni/Al$_2$O$_3$</td>
</tr>
<tr>
<td>$A_o$ (s$^{-1}$)</td>
<td>5.01</td>
<td>2.725</td>
<td>2.99</td>
<td>1.21</td>
</tr>
<tr>
<td>Ea (kJ/mole)</td>
<td>158.5</td>
<td>120</td>
<td>242.1</td>
<td>178.5</td>
</tr>
</tbody>
</table>

The lowest Ea of 120 kJ/mole was observed for the SA formation step when using NiOx/Al$_2$O$_3$ while the highest value of 242.1 kJ/mole was observed for the $C_{18}$ formation using Ni/Al$_2$O$_3$ and in both cases the Ea of the SA formation steps is the lowest. This results showed that it is much more easier to overcome the energy barrier in the SA formation step than in the $C_{18}$ formation step and this corroborate the earlier results on the kinetic study and especially the preliminary analysis that showed only marginal conversion of OA into SA without catalyst loadings. In addition, OxA functionalization was able to adequately reduce the activation energy barrier in both the SA formation step and the $C_{18}$ formation step. A more critical analysis of the activation energy revealed that 38.5 kJ/mole (i.e. 158.5 – 120, SA formation step) and 63.6
kJ/mole (i.e. 242.1 – 178.5, C_{18} formation step) would be saved if NiOx/Al_{2}O_{3} is used instead of Ni/Al_{2}O_{3}. The kinetic data adequately supports the earlier observation on the comparison between the catalytic activities of Ni/Al_{2}O_{3} and NiOx/Al_{2}O_{3} on the HDO and isomerization of OA in Figure 4.13 and it is considered a good credit for the process economics.

4.2.2.5 Ni/Al_{2}O_{3} and Niox/Al_{2}O_{3} Reusability Studies

The reusability studies of Ni/Al_{2}O_{3} and NiOx/Al_{2}O_{3} on the HDO of OA was carried out at 360 °C, 20 bar, 20 mg catalyst, 100 mL/min gas flow and 45 min. The results when using NiOx/Al_{2}O_{3} showed consistency with the result in Figure 4.13 for both n-C_{18}H_{38} and iso- C_{18}H_{38} in three consecutive runs after which only iso-C_{18} showed 4% drop after the 4th run. On the other hand, Ni/Al_{2}O_{3} showed a marginal drop of about 2% in the n-C_{18}H_{38} production in the second run, but a drastic reduction of 8% in the third use. The high reusability of NiOx/Al_{2}O_{3} compared to Ni/Al_{2}O_{3} was undoubtedly due to the OxA functionalization which intercalated in it the exceptional high reusability quality of organometallic catalysts (Ayodele and Hameed, 2012). According to previous reports (Li et al., 2012; Tanev and Lange De Oliveira, 2012; Ayodele et al., 2013) organometallic catalysts with metal oxalate ligand complex have been reported to be highly reactive and reaction specific thus minimizing reaction time and prolonging the catalyst life span. Similarly, the presence of the strong M\textsuperscript{+} - oxalate ligand in the NiOx/Al_{2}O_{3} increases the active metal resistance to leaching out of the support which also minimizes the tendencies of multiple side reactions (Tanev and Lange De Oliveira, 2012; Ayodele et al., 2013). The reduction in the iso-C_{18} according to Kovacs et al., (2011) was ascribed to partial loss of the NiOx/Al_{2}O_{3} acidity.
PART THREE

4.3 CATALYTIC UPGRADING OF OLEIC ACID INTO BIOFUEL USING Mo MODIFIED ZEOLITE SUPPORTED Ni OXALATE CATALYST FUNCTIONALIZED WITH FLUORIDE ION

4.3.1 Catalyst Characterization

4.3.1.1 Thermal Gravimetric Analysis (TGA)

In order to study the response of the samples to thermal treatments, TGA analysis was carried out. Figure 4.17 shows the TGA profiles of Zeol, MoOX/Zeol and NiMoFOx/Zeol with three characteristics weight loss regions typical of the alumino-silicates. The first weight loss region is usually ascribed to loosely bonded water molecules and physisorbed water that can be readily removed at a temperature below 200 °C (Ayodele and Hameed, 2012; Ayodele, 2013). The second weight loss region is due to the presence of strongly bonded water molecules that are present in the first coordination sphere and are removable at a temperature between 200-500 °C and in the third region is the structural hydroxyl group that will condense and dehydrate at temperatures above 500 °C (Ayodele and Hameed, 2012; Ayodele, 2013). In the first region MoOx/Zeol sample showed the highest weight loss of about 16% followed by the parent material, Zeol with about 14% weigh loss and finally the NiMoFOx/Zeol sample which showed less than 13%. Similar trend of observation is also seen in the second and third regions. The sudden increment in weight loss of the MoOx/Zeol sample is undoubtedly due to the hydration effects at the catalyst synthesis stage, while the sharp reduction in the NiMoFOx/Zeol is due to the effect of calcinations at 500 °C. However, of importance in the second and third stage is the comparably lower weight loss in the NiMoFOx/Zeol sample compared to MoOx/ Zeol and Zeol samples. This observation was due to sufficient thermal treatment on NiMoFOx/Zeol during
calcination stage which was able to remove the strongly bonded water molecule and any partly occluded material during catalyst synthesis thereby guarantee its chemical stability as well as high metal dispersion. Proper calcination has been reported to guarantee catalyst stability, high metal dispersion and large surface area with enhanced pore volume which in turn increases the number of active sites (Ohtsuka and Tabata, 1999; Ayodele and Hameed, 2012).

![Graph showing thermal gravimetric analysis of Zeol, MoOx/Zeol and NiMoFOx/Zeol](image)

**Figure 4.17** Thermal gravimetric analysis of Zeol, MoOx/Zeol and NiMoFOx/Zeol

### 4.3.1.2 X-Ray Fluorescence (XRF)

The XRF spectrum of Zeol and the calcined NiMoFOx/Zeol samples are shown in Figure 4.18. The successful modification of Zeol support with Mo is seen at Kα value of 17.44 keV, similarly the incorporation of Ni into the matrix of the Zeol is seen in the XRF plot of NiMoFOx/Zeol at 7.47 and 8.26 keV corresponding to Kα and Kβ, respectively. The intensity of the peak at 7.47 keV is excessively stronger than that at 8.26 which suggests that there could be two different species of Ni present in the
NiMoFOx/Zeol. All the peaks are in good agreements with the standard card of peak identification (EDXRF-EPSILON 3 XL, PANalytical).

![X-ray fluorescence spectra of Zeol and NiMoFOx/Zeol samples](image)

**Figure 4.18** X-ray fluorescence of (a) Zeol and (b) NiMoFOx/Zeol samples

### 4.3.1.3 Energy Dispersive X-Ray (EDX)

The elemental composition (EC) and EDX spectra of the Zeol and NiMoFOx/Zeol samples are shown in Table 4.4 and Figure 4.19, respectively. The EC revealed that the Zeol composition comprises of silica and alumina with some oxides of sodium and calcium. The Si/Al ratio of Zeol sample is 1.02 which suggests a Zeolite A type (Yu et. al., 2001), the ratio increased to 2.10 in NiMoFOx/Zeol sample. This increment was ascribed to dealumination of NiMoFOx/Zeol due to the effect of mild acid (oxalic and HF) activation and thermal treatment during NiMoFOx/Zeol synthesis stage and calcinations, respectively. Previous studies (Pal-Borbely, 2007; Xiaoling et. al., 2012; Ayodele, 2013) have shown that extra-framework alumina could be removed by acid treatment and framework alumina could be removed by thermal treatment.
Table 4.4  Elemental composition of Zeol and NiMoFOx/Zeol samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si</th>
<th>Al</th>
<th>O₂</th>
<th>Na</th>
<th>Ca</th>
<th>F</th>
<th>Mo</th>
<th>Ni</th>
<th>Si/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeol</td>
<td>16.88</td>
<td>16.48</td>
<td>49.58</td>
<td>12.41</td>
<td>4.2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.02</td>
</tr>
<tr>
<td>NiMo/FOxZeol</td>
<td>16.28</td>
<td>6.70</td>
<td>51.75</td>
<td>4.74</td>
<td>1.98</td>
<td>4.2</td>
<td>4.89</td>
<td>9.46</td>
<td>2.43</td>
</tr>
</tbody>
</table>

Figure 4.19  Energy dispersive X-ray and Scanning electron microscopy of (a) Zeol, (b) MoOx/Zeol and (c) NiMoFOx/Zeol samples

Similarly, Pal-Borbely (2007) also reported that reduction in the amount of zeolitic water under thermal treatment is usually accompanied by an increase in the Si/Al ratio. The modification of Zeol with MoOx and incorporation of NiFOx earlier
seen in the XRF spectra is further confirmed in Table 4.4. Although the observed quantities of the metals were slightly below the expected value of 5% Mo and 10% Ni which could be due to the high hydration degree at the NiMoFOx/Zeol synthesis stages (Ayodele and Hameed, 2012).

4.3.1.4 Scanning Electron Microscopy (SEM)

The SEM of the Zeol, MoOx/Zeol and NiMoFOx/Zeol samples are shown Figure 4.20, the morphology of Zeol Figure 4.20(a) revealed agglomerates of nano-sized cubical symmetry sharp crystal structure.

Figure 4.20 SEM morphology of (a) Zeol, (b) MoOx/Zeol and (c) NiMoFOx/Zeol samples
There is a high degree of morphological changes due to loss of crystallinity and comparative reduction in the average particle size in the MoOx/Zeol (Figure 4.20b) and NiMoFOx/Zeol (Figure 4.20c) samples when compared to the Zeol parent material. These morphological changes are undoubtedly due to the combined effects of intercalated metals (Ni and Mo) and dealumination at the catalyst synthesis stage which increased the Si/Al ratio from 1.02 to 2.10 owing to the action of acid attack and calcination. Generally, aluminosilicates gradually transforms from crystalline form into amorphous under acid attacks and such transformation is usually accompanied by reduction in particle size (Table 1) which in turn increased the specific surface area (Xiaoling et. al., 2012; Ayodele, 2013). This morphological change is expected to have contributory role on the NiMoFOx/Zeol catalytic activity since catalyst transformation into amorphous has been reported to increase the activity (Xiaoling et. al., 2012; Ayodele, 2013).

4.3.1.5 X-Ray Diffraction (XRD)

The X-ray diffraction pattern for the Zeol, MoOx/Zeol and NiMoFOx/Zeol samples are shown in Figure 4.21. The characteristics peaks of Zeolite A according to the JCPDS card 43-0142 (Yu et al., 2001) were observed in Zeol sample at 2θ value of 7.2, 10.0, 12.4, 16.0, 21.6, 24.0, 27, 30.0 and 34.0°. The Zeol sample is highly crystalline but loss some degree of crystallinity in the MoOx/Zeol while all the characteristics 2θ peak of zeolite A up to 25° were completely removed in the NiMoFOx/Zeol sample. The slight reduction of characteristics peaks in MoOx/Zeol is due to the presence of weak oxalic acid, while the drastic disappearance of the peaks in NiMoFOx/Zeol was due to the functionalization with fluoride ion at the synthesis stage from HF which is a strong acid.
This phenomenon is in accordance with the earlier observation in the EDX and SEM result which showed increase in the Si/Al ratio and morphological transformation from crystalline into amorphous, respectively. Previous reports (Xiaoling et. al., 2012; Ayodele, 2013) have also shown that aluminosilicates undergo morphological transformation from crystalline into amorphous under acid treatments, and such transformation is a function of the acid strength/type, which is also occasioned by increase in the Si/Al ratio. Effect of calcinations could also have contributed to the amorphosization of the NiMoFOx/Zeol which in turn will ensure proper anchoring of the metals (Ghule et al., 2010; Xiaoling et. al., 2012). The peaks at 27.3° and 32.5° reflect the presence of MoO$_3$ (Li-hua et al., 2011; Prieceel et al., 2011), while those at 35.3°, 37.3, 52.3° suggests that nickel oxide is highly dispersed as a surface oxide and it strongly interacts with the zeol support (Ghule et al., 2010; Li-hua et al., 2011; Prieceel et al., 2011; Zhang et al., 2013). In addition, according to Bang et al., (2012) the shift of the diffraction peaks slightly towards the low angle as seen at 25.7°, 43.6° and 68.6° is
an indication of intimate contact between the organo-nickel species i.e. NiOx and the support lattice. The growth of the peaks at 57.6°, 66.5°, 68.8° and 77.1° are reflections of highly dispersed Ni^{2+} from NiOx, while an interesting peak at 43.6° reflects the formation of surface NiMoO_{4} species (Cheng and Huang, 2010; Ghule et al., 2010; Bang et al., 2012).

### 4.3.1.6 Fourier’s Transform Infrared Spectroscopy (FTIR)

The FTIR spectroscopy of the Zeol, MoOx/Zeol and NiMoFOx/Zeol samples are shown in Figure 4.22 with both Zeol and MoOx/Zeol sample showing vibration in the region 3700 - 2900 cm^{-1} with a minimal at 3317 cm^{-1}. This vibration can be assigned to the vibration of the Si–OH and adsorbed water molecules, while the band at 1650 cm^{-1} is due to bending vibration of the adsorbed water molecules (Li et al., 2012). These water molecules vibrations were slightly more in MoOx/Zeol sample relative to the Zeol due to the hydration effect of the MoOx precursor incorporation into the Zeol structure as earlier seen in the TGA results. The water vibrations disappeared in the NiMoFOx/Zeol sample after calcinations. This confirmed that the thermal treatment is adequate to guarantee the Ni and Mo dispersion in the NiMoFOx/Zeol sample since the presence of water molecules has been reported to cause agglomeration of metals in zeolite supercage structure which in turn reduces the catalytic activity (Ohtsuka and Tabata, 1999). Moving from the higher wavenumber towards the lower wavenumber, the slight lag between 1185 - 1060 cm^{-1} for MoOx/Zeol and NiMoFOx/Zeol are attributed to the CO_{3}^{2-} asymmetric stretching modes from oxalic acid (Li et al., 2012). Typically, the presence of exchangeable metal ions are normally observed in the lower wavenumber below 1000 cm^{-1}, as seen, the spectra of both MoOx/Zeol and NiMoFOx/Zeol showed variation from that of Zeol indicating structural change caused
by the presence of Mo and Ni. The slight decrease in the intensity of the band at 880 cm$^{-1}$ for the MoOx/Zeol sample can be ascribed to the Mo=O stretching and Mo$^-$O$^-$Mo asymmetric vibrations (Cheng and Huang, 2010; Li et al., 2012). Similarly, the asymmetric $\nu$Mo=O stretching modes of the MoO$_4^{2-}$ at 985 and 680 cm$^{-1}$ are assigned to polymolybdates species due to the ionic equilibrium between molybdate and polymolybdate species (Equation 4.15) which are present in the MoOx/Zeol solution as Si-O-Mo during support modification stage (Cheng and Huang, 2010; Li et al., 2012; Bang et al., 2012).

![FTIR spectra of the Zeol, MoOx/Zeol and NiMoFOx/Zeol samples](image)

**Figure 4.22** FTIR spectra of the Zeol, MoOx/Zeol and NiMoFOx/Zeol samples

\[
\text{Mo}_7\text{O}_{24}^6^- + 8\text{OH}^- \rightleftharpoons 7\text{MoO}_4^{2-} + 4\text{H}_2\text{O} \tag{4.15}
\]

The variation in the band at 985 cm$^{-1}$ and the decrease in the intensity of the band 680 cm$^{-1}$ as well as the absorption at 576 cm$^{-1}$ are ascribed to the distortion in the
Zeol supercage structure due to the interference of NiOx. Finally, the shift of the band at 556 cm\(^{-1}\) in both Zeol and MoOx/Zeol to 430 cm\(^{-1}\) in NiMoFOx/Zeol confirmed structural change for the surface Si–OH group caused by the presence of NiOx species in MoOx/Zeol, and/or due to evolution of a new band of Si–O–Ni (Li et al., 2012; Bang et al., 2012).

4.3.1.7 Raman Spectroscopy

The spectra in Figure 4.23 (top) compared the characteristic bands of Zeol and MoOx/Zeol based on the modification of Zeol with MoOx, similarly Figure 4.23 (bottom) showed the variations in NiMoFOx/Zeol due to incorporation of NiFOx into MoOx/Zeol matrix and other synthesis effects. The bands 280, 330, 405, 490, 700, 977, 1040 and 1150 cm\(^{-1}\) are typical of zeolite A having 4-, 6- and 8-membered rings (Gannouni et al., 2012). The band at 280 cm\(^{-1}\) in the Zeol sample are signature of the bending mode of higher rings than 4- and 6-membered rings, possibly of the 8 -membered rings of zeolite A since previous studies had shown that smaller rings give bands at higher frequencies and vice versa (Yu et al., 2001). The bands at 330 and 405 cm\(^{-1}\) are due to the bending mode of 6-membered Si-O-Al rings while the strongest band at 490 cm\(^{-1}\) is assigned to the bending mode of 4-membered Si-O-Al rings (Yu et al., 2001). The bands at 977, 1030 and 1100 cm\(^{-1}\) are ascribed to asymmetric T-O stretching motions (Breck 1979; Yu et al., 2001). The effect of MoOx modification on the Zeol was seen to have caused series of multiple stretches of vibrations in MoOx/Zeol which are reflections of the presence of carbonate anion (CO\(_3^{2-}\)) from organics, i.e. oxalate (Ghule et al., 2010; Ray et al., 2006). The free ion of CO\(_3^{2-}\) with D\(_{3h}\) symmetry usually exhibits four normal vibrational modes, viz; a doubly degenerate bending mode (\(\nu_4\)) around 680 cm\(^{-1}\), an out-of-plane bend (\(\nu_2\)) around 879 cm\(^{-1}\), a
symmetric stretching vibration ($\nu_1$) around 1063 cm$^{-1}$ and a doubly degenerate antisymmetric stretch ($\nu_3$) around 1415 cm$^{-1}$ (Ray et al., 2006).

![Raman spectroscopy of Zeol, MoOx/Zeol and NiMoFOX/Zeol samples](image)

Figure 4.23  Raman spectroscopy of Zeol, MoOx/Zeol and NiMoFOX/Zeol samples

After the catalyst synthesis, the bands at 490, 800 and the newly formed 540 and 728 cm$^{-1}$ in MoOx/Zeol disappeared completely probably due to the effect of HF used for fluoride ion functionalization and calcinations. This observation supports the loss of crystallinity earlier observed in the SEM and XRD results. In the Raman spectrum of
NiMoFOx/Zeol, the first three distinctive bands of NiO have vibrational origin and can be assigned accordingly to one-phonon (1P) (TO at ~ 405), two-phonon (2P) (2LO at ~1070 and 1130 cm<sup>-1</sup>) modes, while the last strongest band at 1450 cm<sup>-1</sup> is due to a two-magnon (2M) scattering of NiO, these values were in accordance with earlier report (Mironova-Ulmane et al., 2011). The band at 1290 cm<sup>-1</sup> in the MoOx/Zeol which was due to MoOx modification can be seen to have grown sharply without the trace of the carbonate ion vibration and this corroborate the formation of NiMoO<sub>4</sub> earlier seen in the XRD peak at 43.6°.

4.3.1.8 Nitrogen Adsorption/Desorption Isotherm

The isotherms of Zeol and NiMoFOx/Zeol samples are shown in Figure 4.24; at lower relative pressure both samples exhibited a characteristic formation of monolayer followed by multilayer which is typical of Type II isotherms (Xue et al., 2012). However, towards the high relative pressures, they eventually translated into Type IV isotherm with the steep uptake of N<sub>2</sub> emphasizing the possible presence of inter-particle voids formed by agglomeration of the nano-sized and plate-like particles containing slit-shaped pores which are typical of H3 hysteresis loop (Ghule et al., 2010; Xue et al., 2012). According to the IUPAC classification, this observation is generally observed for mesoporous solids (Ghule et al., 2010). The hysteresis loop of NiMoFOx/Zeol at P/Po = 0.5–0.9 is more obvious than for the parent material indicating increased mesopore formation while increase in the amount of N<sub>2</sub> adsorbed confirmed the increase in the pore volume. This observation was due to the functionalization of the catalyst with FOx from HF and oxalic acid followed by proper calcination at the catalyst synthesis stage which distorted the crystallinity of NiMoFOx/Zeol as earlier observed in the SEM and XRD results. As earlier commented, aluminosilicates generally transforms from
crystalline form into amorphous under acid attacks and such transformation is usually accompanied by reduction in particle size which in turn increased the specific surface area as seen in Table 4.5. The enhanced surface area is considered an advantage for the HDO of OA into biofuel.

![Figure 4.24](image.png)  
**Figure 4.24**  
N\(_2\) adsorption/desorption of Zeol and all Zeol supported catalysts

<table>
<thead>
<tr>
<th>Table 4.5</th>
<th>Textural properties of Zeol and NiMoFOx/Zeol samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>Surface area (m(^2)/g)</td>
</tr>
<tr>
<td>Zeol</td>
<td>202</td>
</tr>
<tr>
<td>NiMo/FOxZeol</td>
<td>426.1</td>
</tr>
</tbody>
</table>
4.3.2 Catalytic Evaluation of NiMoFox/Zeol Catalyst on HDO of Oleic Acid

4.3.2.1 Effect Time of Reaction

The result in Figure 4.25 shows the product distribution profile of effect of HDO time on OA conversion using the NiMoFOx/Zeol catalyst. As the HDO process progresses, the amount of both n-C\textsubscript{18} and i-C\textsubscript{18} which are considered as yield of target fractions (YTF) were observed to increase progressively until a maxima at 60 min with about 67 and 22%. Beyond the maxima, the YTF were observed to reduce due to the prevalence of certain parallel reactions such as cracking and oligomerization which were evidenced by the increase in the amount of gases/vapor fraction up to 90 min and sudden appearance of the >C\textsubscript{18} fraction at 60 min, respectively. The propensity of the latter dominating at 120 min is seen by the slight reduction in amount of gases and further reduction in nC\textsubscript{18} which implied that longer reaction time is capable of oligomerizing the monomer units.

![Figure 4.25](image_url)  
*Effect of time on the HDO of oleic acid into biofuel at 340 °C, 20 bar and 20 mg NiMoFOx/Zeol loading and 100 mL H\textsubscript{2}/min*
At 30 min HDO time, stearic acid (StA) quantity is higher than both nC\textsubscript{18} and iC\textsubscript{18} and this suggests that OA hydrodeoxygenation proceeded via hydrogenation of the unsaturated OA into StA before O\textsubscript{2} extraction (Scheme 4.3). These observations are in accord with some earlier reports (Arend et al., 2011; Kovacs et al., 2011; Mortensena et al., 2011). The relatively high quantity of iC\textsubscript{18} was due to the acidity of the applied catalyst caused by its fluoride content which is favorable for the skeletal isomerization (Kovacs et al., 2011).

\[
\text{OA} + \text{H}_2 \rightarrow \text{SA} + 3\text{H}_2 + 2\text{H}_2\text{O} \\
\text{nC}_{18} \quad \text{iC}_{18}
\]

Scheme 4.3  Mechanism of hydrodeoxygenation of oleic acid via stearic acid into octadecane biofuel

4.3.2.2 Effect of Temperature

The effect of temperature in Figure 4.26 is seen to drastically affect the HDO of OA, for example as the temperature was increased from 320 to 360 °C, there was significant increase in the yield of both n-C\textsubscript{18} and i-C\textsubscript{18} from 41- 72% and 8- 22%, respectively. This implied that the HDO process of OA conforms to the Arrhenius theory of temperature dependence of reaction rates (i.e. \( \Gamma_1 = k(T) \)), such that the molecules of the OA and H\textsubscript{2} gas gained more kinetic energy in excess of activation energy to interact with each other at the NiMoFOx/Zeol active sites. Similarly, since the viscosity of OA decreases with increase in temperature, this would in turn lower the surface tension thereby enhancing the propensity of H\textsubscript{2} to penetrate the bulk of the OA as well as increasing its solubility in the reaction mixture. The combination of Arrhenius theory of temperature dependence and temperature effect on viscosity is the reason for
the enhance YTF especially at 360 °C which is slightly above the boiling point of OA. Beyond 360 °C there was reduction in the YTF from 72 to 68% for the nC\textsubscript{18} and 22 to 20% for the iC\textsubscript{18}. This reduction could be due to cracking of the already deoxygenated biofuel into lighter fractions and this was supported by the increment in the amount of gases that were produced. Arend et al., (2011) also reported similar observation on the deoxygenation of OA using Pd/C catalyst. Similarly, the slight increase in the amount of the lumped unidentified molecules (>C\textsubscript{18}) could be due to secondary reactions such as oligomerization / polymerization and cyclization of the target fractions.

![Figure 4.26](image)

Figure 4.26  Effect of temperature on the HDO of oleic acid into biofuel at 20 bar, 100 ml/min gas flow and 20 mg NiMoFOx/Zeol loading

### 4.3.2.3 Effect of Pressure

Since there is presence of at least a gas (H\textsubscript{2}) in the HDO process, variation in the process pressure will definitely play a significant role as shown in Figure 4.27. Increasing the pressure from 10 – 40 bar showed a maxima at 20 bar representing the experimentally best observed pressure. The lower YTF at 10 bar was ascribed to both
the inability of the reactant molecules to sufficiently react at the catalyst surface before detaching off and reduced partial pressures of hydrogen leading to hydrogen mass transfer limitations to the catalyst surface. Consequently, these promote cracking at the expense of HDO as the amount of gases is slightly higher at 10 bar than at 20 bar. Similarly, the lower YTF observed at pressure above 20 bar was due to the inability of the target fractions to detach from the catalyst surface thereby initiating secondary reaction such as oligomerization (Kovacs et al., 2011) Arend et al., (2011) also observed same phenomenon and proposed that relatively reduced pressure is essential to enhance desorption of reaction products from the catalyst surface in order to prevent deactivation of the catalyst.

![Figure 4.27](image)

Figure 4.27  Effect of pressure on the HDO of oleic acid into biofuel at 360 °C, 20 mg NiMoFOx/Zeol loading and 100 mL H₂/min

4.3.2.4 Effect of NiMoFOx/Zeol Loading

The effect of NiMoFOx/Zeol loading on the YTF of HDO of OA is shown in Figure 4.28. The result showed that increase in the NiMoFOx/Zeol loading from 10 –
30 mg enhanced the YTF especially between 10 – 20 mg because more catalyst active sites were made available for the reaction (Kwon et al., 2011). The sharp increase in the YTF from 61–71% n-C_{18} and 17–21% i-C_{18} between 10 and 20 mg signified that the NiMoFOx/Zeol loading at the latter is essentially too low for the process and this may lead to early catalyst deactivation, however, the soft increase from 71 – 75% between 20 and 30 mg suggested that the NiMoFOx/Zeol loading is gradually approaching a saturation point. This was further corroborated with the result of the YTF of 70% n-C_{18} and 20% i-C_{18} when NiMoFOx/Zeol loading was increased to 40 mg.

![Figure 4.28  Effect of NiMoFOx/Zeol loading on the HDO of oleic acid into biofuel at 360 °C, 20 bar and and 100 mL H_{2}/min](image)

This reduction is however thought to be due to the possibilities of some parallel or secondary reactions such as polymerization due to the increased brisk rate of reaction at the catalyst surface which is unhealthy for the catalyst life span since polymerization reaction has been known to be prominent for coking HDO catalysts (Mortensena et al.,...
A careful study of the effect of NiMoFOx/Zeol loading showed that the ratio of n-\(\text{C}_{18}\)/i-\(\text{C}_{18}\) was not constant but varied from 3.22 – 3.58. It was obvious that the ratio has the lowest value when 40 mg NiMoFOx/Zeol loading was studied, which implied that the rate of isomerization is relatively higher compared to simple HDO. This could also explain why there is more unidentified products (>\(\text{C}_{18}\)) at 40 mg NiMoFOx/Zeol loading earlier ascribed to polymerization since both isomerization and polymerization are considered secondary reactions in HDO process according to previous reports (Kwon et al., 2011; Mortensena et al., 2011). It can therefore be concluded that catalyst overloading increases the propensity of secondary and parallel reactions because there are excess active sites for various reactions. NiMoFOx/Zeol demonstrated better HDO and isomerization abilities compared to the earlier reports (Hancsok et al., 2007; Kubicka et al., 2008; Liu et al., 2009; Arend et al., 2011; Kovacs et al., 2011; Mortensena et al., 2011).

### 4.3.3 Catalyst Reusability

The result of the reusability study on NiMoFOx/Zeol using 360 °C, 30 mg NiMoFOx/Zeol loading and 20 bar using 100 mL H\(_2\)/min showed that there was 99 and 98\% repeatability on the YTF after 2nd and 3rd use. This ability was undoubtedly due to the catalyst synthesis protocol that employed organometallic species, and functionalization with fluoroxalate ligand which belongs to the organofluoride group with the strongest bond in the organic chemistry due to their high thermal and chemical stability (O'Hagan, 2008). The fluoroxalate ligand provides adequate anchor for the active metals on the support thereby minimizing the tendency of metals leaching out of the support. In addition, organometallic catalysts especially metal oxalates have been reported to have high specificity for the primary reactions and minimizing the number
of side reactions which in turn enhance the reaction rates and the life span of the catalyst (Ayodele et al., 2014). Proper calcination of the NiMoFOx/Zeol catalyst (TGA and FTIR plots) at the synthesis stage is also a contributor to the high activity and reusability since proper calcination has been reported to enhance both catalyst activity and stability due to the transformation of the support from crystalline into amorphous (SEM and XRD plots, Figure 4.20 and 4.21) which inhibit the tendency of metal leaching out (Ayodele, 2013). In addition, the zeolite A support has a high thermal stability (Hui et al., 2009).
PART FOUR

4.4 HYDRODEOXYGENATION OF STEARIC ACID INTO NORMAL AND ISO-OCTADECANE BIOFUEL WITH ZEOLITE SUPPORTED PALLADIUM-OXALATE CATALYST

4.4.1 Catalyst Characterization

4.4.1.1 Thermal Gravimetric Analysis (TGA)

The profiles of thermal gravimetric analysis of Zeol and PdOx/Zeol (pre and post calcination) are shown in Figure 4.29 with three characteristics weight loss regions of the alumino-silicates (the post calcination PdOx/Zeol will hence forth be referred to simply as PdOx/Zeol). The first weight loss region is ascribed to loosely held moisture and physisorbed water that can be rapidly removed at a temperature around 150 °C (Pal-Borbely, 2007; Xue et al., 2012). Both Zeol and PdOx/Zeol (pre calcination) samples showed similar weight loss in the first WLR which implied that the drying stage (at 100 °C) during the synthesis of PdOx/Zeol was able to remove the physisorbed and loosely bonded water molecules from the hydration effect of the PdOx precursor incorporation into Zeol during the catalyst synthesis. The second weight loss region between 200-500 °C can be ascribed to the existence of strongly bonded molecules of water that are localized in the first coordination sphere (Ghule et al., 2010; Xue et al., 2012) and also probably due to the partial occlusion of organic matter at the catalyst synthesis stage (Xue et al., 2012). Lastly, in the third region is the structural hydroxyl group that will condense and dehydrate at temperatures above 500 °C (Ayodele and Hameed, 2012; Xue et al., 2012). The profile of the PdOx/Zeol (pre calcination) showed that the amount of the strongly bonded water in the second weight loss region is higher than in the Zeol sample even unto the third weigh loss region. This implied that PdOx/Zeol synthesis procedure was able to guarantee the penetration of the PdOx precursor into the
lattice of Zeol. After calcination at 400 °C, both the strongly bonded water and physisorbed water were seen to have been drastically reduced in the PdOx/Zeol sample leaving behind the PdOx deposit on the support. Proper calcination around 400 °C has been reported to ensure large surface area and pore volume hence increasing the number of active sites (Ghule et al., 2010; Liu et al., 2010), which in turn guarantee a high dispersion of Pd particles since the presence of water molecules leads to its agglomeration which essentially is not very effective in reduction processes such as HDO, although very effective for oxidation processes (Ohtsuka and Tabata, 1999).

![Thermal Gravimetric Analysis of Zeol and PdOx/Zeol](image)

Figure 4.29 Thermal Gravimetric Analysis of Zeol and PdOx/Zeol (before and after calcination)

### 4.4.1.2 X-Ray Fluorescence

Figure 4.30 showed the XRF spectrum of Zeol and the calcined PdOx/Zeol samples, the characteristics peak of Si dominance (Si/Al > 1) in the Zeol sample were
seen at 1.739 keV, the presence of K is also seen at 3.58 keV. The successful intercalation of Pd into the framework of Zeol support is seen in the XRF plot of PdOx/Zeol at Lβ₁ of 3.17 keV which is in accordance with the standard card of peak identification (EDXRF-EPSILON 3 XL, PANalytical). Another growing peak is observed at 21.2 keV which possibly confirm successful dispersion of Pd from PdOx as a result of adequate calcination, since Pd(Kα) is only metal that has such peak at 21.2 keV according to the EDXRF-EPSILON 3 XL, PANalytical standard card.

Figure 4.30 X-ray fluorescence of Zeol and PdOx/Zeol samples

4.4.1.3 Energy Dispersive X-Ray (EDX)

The elemental composition of the Zeol and PdOx/Zeol samples is shown in Table 4.6. Zeol composition comprises of silica and alumina with some oxides of calcium and sodium, its Si/Al ratio was found to be 1.02 which suggests a Zeolite A type. The ratio increased to 2.24 after successful incorporation of acidic PdOx into Zeol and calcination. Pal-Borbely (2007) reported that reduction in the amount of zeolitic water (as seen in the TGA profile) is usually accompanied by an increase in the Si/Al
Consequently, the increment in the Si/Al ratio of the PdOx/Zeol can be ascribed to the effect of proper calcination at 500 °C and the functionalization with OxA which removed framework and extra-framework alumina, respectively. The increment in the amount of O₂ can be ascribed to the presence of oxalate functional group of the PdOx, similarly the incorporation of Pd is seen in Table 4.6 and further corroborated in Figure 4.31 between the peaks 2.2 and 3.8 keV in the EDX spectra. The observed quantity (1.89%) of Pd in Table 4.6 is slightly lower than the calculated 2% and this could be due to the high hydration degree of PdOx/Zeol sample at the synthesis stages (Ayodele and Hameed et al., 2012).

**Table 4.6**  Elemental composition of Zeol and Zeol supported catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si</th>
<th>Al</th>
<th>O₂</th>
<th>Na</th>
<th>Ca</th>
<th>Pd</th>
<th>Si/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeol</td>
<td>16.88</td>
<td>16.48</td>
<td>49.58</td>
<td>12.41</td>
<td>4.2</td>
<td>0</td>
<td>1.02</td>
</tr>
<tr>
<td>PdOx/Zeol</td>
<td>19.78</td>
<td>8.83</td>
<td>56.97</td>
<td>9.72</td>
<td>2.81</td>
<td>1.89</td>
<td>2.04</td>
</tr>
</tbody>
</table>

**Figure 4.31**  Energy dispersive X-ray of Zeol and PdOx/Zeol samples
4.4.1.4 Scanning Electron Microscopy (SEM)

The scanning electron micrographs of the Zeol and PdOx/Zeol samples shown Figure 4.32 revealed some level of morphological variation in PdOx/Zeol which are expected to have a significant role on its catalytic activity. The morphology of Zeol Figure 4.32 (a) revealed agglomerates of micro-sized cubical symmetry sharp crystal structure (Ohtsuka and Tabata, 1999; Pal-Borbely, 2007) which was seen to have reduced in crystallinity in the PdOx/Zeol sample (Figure 4.32 (b)) and it was also occasioned by increase in surface area and reduction in particle size as shown in Table 4.6 (BET analysis). This loss of crystallinity as seen in the reduction of the crystal size can be ascribed to the effect of OxA functionalization and proper calcination at the PdOx/Zeol synthesis stage resulting in dealumination from the lattice structure. Aluminosilicates have been reported to experience loss of crystallinity under acid influence and thermal treatment which is usually accompanied by increase in the specific surface area, and such loss is a function of the acid type / molarity and degree of thermal treatment (Xiaoling et al., 2012).

Figure 4.32  Energy dispersive X-ray and Scanning electron microscopy of Zeol and PdOx/Zeol samples
4.4.1.5 Nitrogen Adsorption/Desorption Isotherm.

As earlier noted in the morphology results (Figure 4.32) that reduction in crystallinity of PdOx/Zeol due to the effect of OxA and proper calcination at the catalyst synthesis stage has effect on its textural properties, it can be seen from Table 4.7 that there is an increase in surface area and pore volume of PdOx/Zeol compared to the parent material (Zeol). The decrease in the average particle size also confirmed the increase in the specific surface area, while increase in the amount of N\textsubscript{2} adsorbed shown in the isotherm of PdOx/Zeol compared to Zeol in Figure 4.33 confirmed the increase in the pore volume.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m\textsuperscript{2}/g)</th>
<th>Pore volume (cm\textsuperscript{3}/g)</th>
<th>Pore diameter (nm)</th>
<th>Average Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeol</td>
<td>202</td>
<td>0.13</td>
<td>10.41</td>
<td>10404</td>
</tr>
<tr>
<td>PdOx/Zeol</td>
<td>371</td>
<td>0.23</td>
<td>14.58</td>
<td>4655</td>
</tr>
</tbody>
</table>

Both samples exhibited Type II isotherms at lower pressure which is a characteristic of the formation of monolayer followed by multilayer (Xue et al., 2012). However, at high relative pressures, they eventually conformed to Type IV isotherm with the steep uptake of N\textsubscript{2} emphasizing the possible presence of inter-particle voids formed by agglomeration of the micro- or nano-sized and plate-like particles containing slit-shaped pores which are typical of H3 hysteresis loop (Xue et al., 2012; Ayodele and Togunwa, 2014). This observation is generally an attribute of solids having mesopores (Ayodele et al., 2013), and this was further corroborated by Figure 4.33 (inset) for PdOx/Zeol showing average pore size of 11.14 nm which falls with the 2-50 nm range for mesoporous materials. This average pore size is considered adequate for this study.
since the SA effective size at the HDO temperature would be less than 46.6 Ångström (4.66 nm) (Moniruzzaman and Sundararajan, 2004) hence SA can have unhindered diffusion through the PdOx/Zeol pores.

Figure 4.33  Nitrogen adsorption/desorption isotherm of the Zeol and PdOx/Zeol samples, inset: pore size distribution of PdOx/Zeol sample

4.4.1.6 X-Ray Diffraction (XRD)

The X-ray diffraction pattern for the Zeol support and PdOx/Zeol catalyst are shown in Figure 4.34. The Zeol support exhibited characteristics peaks at 20 value of 7.2°, 10.0°, 12.4°, 24.0° and 30.0° which according to the JCPDS card 43-0142 are typical of Zeolite A (Hui et al., 2009). The Zeol sample appeared to be highly crystalline but loss some degree of crystallinity in the PdOx/Zeol sample as observed in
the reduced peaks, this is similar to the earlier observation in the samples morphology and it is due to different treatments during catalyst synthesis.

Figure 4.34  X-ray diffraction of the Zeol and PdOx/Zeol samples

This reduction in crystallinity affirms adequate and not excessive thermal treatment during calcination stage (Oh et al., 2007) since excessive calcination temperature leads to increased sharp peaks which indicate increase in the degree of crystallization resulting from crystal growth (Oh et al., 2007). Jia et al., (2012) also reported a linear relationship between increase in calcination temperature and crystal growth (crystallinity) but an inverse correlation with catalytic activity; hence the reduction in the crystallinity of PdOx/Zeol is an indication to excellent catalytic activity via enhanced dispersion of active metal into the matrix of the support (Li et al., 2013). The presence of Pd which is usually seen at around 2θ = 18° and 34° (Pommier and Gelin, 1999; Gannouni and Rozanska, 2012) is not very visible probably because they were not present as bulk PdO and this confirmed that the PdOx species are highly
dispersed in the Zeol due to the OxA functionalization and adequate calcination (Ghule et al., 2010). In addition, since little amount of Pd (about 2%) was employed during synthesis, it is also possible that the PdOx species are partially covered by the Zeol particles, however, the lowering of the diffraction between 2θ of 2.3 and 5.4 was ascribed to expansion of the Zeol lattice structure due to intimate contact of the incorporated PdOx.

4.4.1.7 Fourier’s Transform Infrared Spectroscopy (FTIR)

The FTIR spectrums of the Zeol support and PdOx/Zeol catalyst are shown in Figure 4.35. Zeol sample exhibited vibrations with 3715 - 2970 cm\(^{-1}\) with minimal around 3320 cm\(^{-1}\) which reflect the existence of zeolitic water (Zhang et al., 2014), while the band at 1655 cm\(^{-1}\) is a reflection of water vibration (Xie et al., 2013). Since the presence of water (freely bonded, physisorbed and strongly bonded) in supported Pd catalyst has been reported to cause agglomeration of Pd particles (Ohtsuka and Tabata, 1999) which does not favor HDO process as earlier discussed. The disappearance of these water bands confirmed that the thermal treatment (Figure 4.29) during calcination was adequate in removing all unwanted water molecules thereby guaranteeing high Pd dispersion (Ohtsuka and Tabata, 1999). Generally, the presence of exchangeable cations is normally seen in the lower wavenumber mostly in the region 900 - 600 cm\(^{-1}\) (Breck, 1974), a comparison of the two spectra (neglecting the effect of water vibrations between 3700 - 2900 and 1650 cm\(^{-1}\)) showed a perfect match until around 900 cm\(^{-1}\) beyond which PdOx/Zeol showed a deviation from the Zeol and of importance is the absorption effects at 680 and 639 cm\(^{-1}\). This deviation and absorption are undoubtedly due to the successful intercalation of Pd particles in the Zeol lattice.
Figure 4.35 FTIR spectroscopy of the Zeol and PdOx/Zeol samples

4.4.1.8 Raman Spectroscopy

The spectra in Figure 4.36 show the characteristic bands of Zeol and the variations due to PdOx incorporation and other synthesis effects on the PdOx/Zeol sample. The bands 280, 330, 405, 490, 700, 977, 1040 and 1150 cm\(^{-1}\) are characteristics of zeolite A having 4-, 6- and probably 8-membered rings (Yu et al., 2001). The band at 280 cm\(^{-1}\) in the Zeol sample can be accredited to the bending mode of rings higher than 4- and 6-membered rings, probably of the 8- membered rings of zeolite A more so that earlier study (Elaiopoulos et al., 2010) had shown that higher rings give bands at lower wavenumbers and vice versa. The bands at 330 and 405 cm\(^{-1}\) are reflection to the bending mode of 6-membered Si-O-Al rings and the strongest band at 490 cm\(^{-1}\) is assigned to the bending mode of 4-membered Si-O-Al rings (Elaiopoulos et al., 2010). The bands at 977, 1030 and 1150 cm\(^{-1}\) are ascribed to asymmetric T-O stretching motions (Elaiopoulos et al., 2010; Gannouni and Rozanska, 2012). The effect of the incorporation of PdOx on the Zeol support was first observed by the multiple stretches
of vibrations that appear like background noise which are reflections of the presence of organics, i.e. oxalate (Ghule et al., 2010).

This confirmed that the Pd particles in the PdOx/Zeol retained their oxalate ligand structure even after calcination (Ghule et al., 2010). After the catalyst synthesis, the bands at 490, 1150 and 1457 cm⁻¹ in the Zeol were seen to have slightly denatured and shifted to 480, 1120 and 1440 cm⁻¹, respectively in the PdOx/Zeol, while the band at 800 cm⁻¹ disappeared completely probably due to the loss in crystallinity earlier observed in the SEM and XRD results. The new band at 445 cm⁻¹ and the bands at 650,
740, 928 and 1290 cm\(^{-1}\) confirmed the presence of dispersed palladium particles in the PdOx/Zeol catalyst. Ohtsuka and Tabata (1999) reported 648 cm\(^{-1}\) for the Raman active B\(_{1g}\) vibrational mode of the PdO phase for single crystals or PdO foils and between 626 and 640 cm\(^{-1}\) for oxidized Pd dispersion on alumina or zirconia (Gannouni and Rozanska, 2012). Similarly, Pommier and Gelin (1999) confirmed successful incorporation of palladium particles into zeolite support at 928 cm\(^{-1}\) forming stretching vibrations with the T-O bonds.

### 4.4.2 Hydrodeoxygenation Of Stearic Acid – Effect Of Operational Variables

A systematic approach was adopted for the HDO of SA, first effect of temperature was studied as a thermodynamic state function by conducting the HDO at different temperatures while keeping other variables constant. Secondly, the kinetics of the process was studied by varying the PdOx/Zeol loading over the tested temperature range. Lastly, the effect of pressure and gas flow were investigated at the best temperature and PdOx/Zeol loading, and all studies were conducted within 60 min reaction time.

#### 4.4.2.1 Effect of Temperature and PdOX/Zeol Loading on the Hydrodeoxygenation of Stearic Acid

The profile of effect of temperature on the HDO of SA at different PdOx/Zeol loading is shown in Figure 4.37. The results showed that irrespective of the PdOx/Zeol loading, increment in temperature greatly enhanced the C18 (n- and iso-octadecane), for example, with 25 mg catalyst loading, temperature increment from 300 to 360 °C enhanced the HDO from 53.8 to about 85%. This confirmed that the HDO process of SA conforms to the Arrhenius theory of temperature dependence of reaction rates (i.e.
Γ_i = k(T)), such that the molecules of the SA gained more kinetic energy to react with the \( \text{H}_2 \) gas at the PdOx/Zeol active sites. In addition, the temperature increment is believed to have lowered the viscosity of the SA thereby enhancing the \( \text{H}_2 \) propensity to penetrate the bulk of the SA, which in turn increases the \( \text{H}_2 \) solubility in the reaction mixture. A reduction in the HDO efficiency was observed at 380 °C probably due to cracking of the already deoxygenated paraffin into smaller molecules. Previous studies (Hancsok et al., 2007; Lestari et al., 2008; Bernas et al., 2010; Krár et al., 2010; Arend et al., 2011) have shown that cracking of biofuel molecules occurs at temperatures beyond 360 °C. Another possible cause for this reduction could be what Krar et al., (2010) referred to as secondary reactions such as polymerization, water-gas-shift reaction, methanization and cyclization. Unfortunately the monitoring and quantification of these process was not feasible at the time we conduct this study due to technical limitations.

![Effect of temperature on the HDO of SA at different PdOx/Zeol loading, 100 ml/min carrier gas flow rate (5%H\textsubscript{2}/N\textsubscript{2}) at 40 bar](image)

Figure 4.37  Effect of temperature on the HDO of SA at different PdOx/Zeol loading, 100 ml/min carrier gas flow rate (5%H\textsubscript{2}/N\textsubscript{2}) at 40 bar
The effect of PdOx/Zeol loading at different temperature showed that its increase also increased the HDO efficiency as shown in Figure 4.37 because more Pd active sites are made available for the reaction. Furthermore, the result showed that the effect of PdOx/Zeol increment is not very significant at lower temperature as compared to high temperature. Considering the 20 and 25 mg loadings, for example, it can be seen that there is no appreciable difference between 300 – 320 °C, but a distinctive improvement is seen at 360 °C. This implied that PdOx/Zeol increment cannot enhance the HDO process efficiency beyond the thermodynamically feasible extent in those tested temperatures. Therefore, the result showed that both temperature and catalyst are strong process parameters to be considered in HDO process. PdOx/Zeol seem to show more prospects compared to some earlier reports in the literature on the application of Pd (Simakova et al., 2009; Ping et al., 2010; Na et al., 2012) where higher catalyst loading, temperature and time were required to achieve the HDO of SA and other related feed stocks. For example, Arend et al., (2010) reported a temperature and catalyst loading of 380 °C and 3 g, respectively which are well above the values in this study and they recorded high yield of C\textsubscript{17}H\textsubscript{36} since high temperature according to Kovacs et al., (2011) usually favors decarboxylation process, which is considered unwanted in this present study.

4.4.2.2 Effect of Pressure and Gas Flow on the Deoxygenation of Stearic Acid

The effect of pressure on the HDO of SA at different gas flow rate based on the earlier established best temperature of 360 °C and PdOx/Zeol loading of 25 mg is shown in Figure 4.38. In the three gas flow rates tested, low pressure of 10 bar does not favor the HDO process, but increase to 20 bar showed improvement in the process, however, further increment beyond 20 up to 60 bar does not also favor the HDO
process. For example, at the best observed gas flow rate of 100 ml, C18 production first increased from about 80% at 10 bar to 92% at 20 bar, further increment in pressure from 20 to 60 bar resulted in drastic reduction of C18 production from 92 to about 46%.

![Figure 4.38](image)

**Figure 4.38** Effect of pressure on the HDO of SA at different carrier gas (5%H<sub>2</sub>/N<sub>2</sub>) flow, T = 360 °C, PdOx/Zeol loading = 25 mg

The increment in the efficiency when the pressure was increased from 10 – 20 bar could be ascribed to increase in the H<sub>2</sub> solubility in the reaction mixtures due to its increased partial pressure leading to high impact of H<sub>2</sub> on the SA (Kwon et al., 2011). However, the decrease in C18 production could be due to the inability of the produced C18 to easily desorb from the catalyst sites under high pressure thereby undergoing series of secondary reaction like cracking and WGS reactions earlier discussed. Kovacs et al., (2011) also reported reduction in the C18 production with increase in pressure and attributed it to the formation of intermediate oxygenated compounds, therefore,
moderately reduced pressure is favorable to the desorption of the C18 to avoid the formation of oxygenated compounds that can deactivate the catalyst active site (Lestari et al., 2008). The best observed pressure of 20 bar in this study is same with the works of Kovacas et al.(2011) and is within the range reported in previous studies (Hancsok et al., 2007; Lestari et al., 2008; Bernas et al., 2010; Krár et al., 2010; Arend et al., 2011). However, it is in clear variance with the works of Monniera et al., (2010) that reported high value of 71.5 bar probably due to poor bonding arrangement between the reacting species and their catalyst surface. The effect of gas flow at different pressure is also shown in Figure 4.38 with 100 ml/min having the highest C18 production. It can be concluded that the amount of H₂ present is sufficient for the HDO process and the gas sweeping rate is also adequate. Both 50 and 150 ml/min flow rate showed comparable reduction in the C18 production, the lower C18 production in the former can be attributed to both insufficient H₂ required for the HDO and inadequate product removal rate which can also lead to unwanted secondary reactions. On the other hand, the reduced C18 production at 150 ml/min flow rate is due to shorter reaction time due to quick transportation of premature products from the PdOx/Zeol active sites.

4.4.3 Hydrodeoxygenation of Stearic Acid- Qualitative Study

The three dimension (3D) absorbance of the deoxygenation of SA into C18 biofuel using PdOx/Zeol being monitored on the FTIR spectrums of the evolved products in the range of 4000- 600 cm⁻¹ over the reaction time is shown in Figure 4.39. It can be observed that it took about 10 min for any traces of species to be detected because the molecules of SA has not gained sufficient thermal energy to commence breaking and/or formation of new bonds. This is because the temperature was still ramping up and have not the reached the value where deoxygenation can take place.
The first traces of peaks were seen around 2900, 1779 and 1463 cm\(^{-1}\). For easy identification and interpretation, the 3D absorbance was resolved into two dimension (2D) i.e. wavenumber as a function of reaction time as shown in Figure 4.40.

![Figure 4.39](image)

Figure 4.39 Three dimension (3D) absorbance of HDO process of stearic acid to produce \(\text{C}_{18}\text{H}_{38}\) with reaction time using 2.0 mg of PdOx/Zeol, and 20 ml/min (5%H\(_2/\text{N}_2\)) gas flow rate at 360 °C

Analyzing the spectra in Figure 4.40a from the high wavenumber towards the low wavenumber showed that the peaks at 3820-3731 cm\(^{-1}\) are due to O-H stretching (Wang et al., 2010), while the peak at 3580 cm\(^{-1}\) as well as the band between 3400 and \(~2000\) cm\(^{-1}\) are absolute signature of the O-H stretch of the carboxylic acids because no other functional groups had been reported to have such broad and intense band at high wavenumber (Wu et al., 2004). In fact, the widen band at 3400 and \(~2000\) cm\(^{-1}\) is the major distinguishing factor between SA and other C18 carboxylic acid such oleic acid.
whose broad band span between 3000-2800 cm$^{-1}$ (Lee and Kim, 1998; Wu et al., 2004; Silverstein et al., 2005). Two sharp peaks at 2950 and 2856 cm$^{-1}$ which are superimposed on the O-H stretch are characteristics of asymmetric CH$_2$ stretch and symmetric CH$_2$ stretch, respectively, and the peak at 2377 is due to C=O stretching of CO$_2$ (Wang et al., 2010). The intense peak at 1779 cm$^{-1}$ is due to C=O stretch of carboxylic acid functional group (Wu et al., 2004; Silverstein et al., 2005). Similarly, the band at 1462 cm$^{-1}$ is assigned to O-H in plane band, while the peak corresponding to 1285 cm$^{-1}$ is ascribed to the presence of the C-O stretch (Wang et al., 2010). The so-called progressional bands that arise from the CH wagging and twisting vibrations are seen in the region of 1150–1350 cm$^{-1}$, (Wu et al., 2004) finally, the band at 937 cm$^{-1}$ is assigned to the O-H out-of-plane (Silverstein et al., 2005; Wang et al., 2010).

Figure 4.40a  FTIR spectra of HDO process of stearic acid to produce C$_{18}$H$_{38}$ with reaction time using 2.0 mg of PdOx/Zeol, and 100 ml/min (5%H$_2$/N$_2$) gas flow rate at 360 °C
As the HDO process progresses the characteristics features of the SA begins to diminish, for example, there is reduction in the peak at 3580 cm\(^{-1}\) earlier ascribed to the O-H stretch of carboxylic acids. The broad band which is an attribute of SA drastically narrowed down from its initial 3900 --2000 cm\(^{-1}\) to about 3490-2300 cm\(^{-1}\) within the first 25 min. Similarly, the C=O stretching at 1779 and 2377 cm\(^{-1}\) were seen to be disappearing with time, while another peak in the region of the former at 1680 cm\(^{-1}\) is synonymous to –CH\(_2\) and –CH\(_3\) deformation. The reaction appeared to slow down between 25-45 min as suggested by the superimposition of the spectra in those period, and there is a new peak at 3014 cm\(^{-1}\) on all the spectra in that period which is due to the formation of unsaturation C=H of alkane (Wang et al., 2010; You et al., 2011), this signature disappears with reaction time due to uptake of H\(_2\), an indication that herald the formation of the paraffinic biofuel i.e. octadecane (C\(_{18}\)H\(_{38}\)). After about 45 min of HDO reaction time, virtually all the characteristics of SA has disappeared both at the high and low wavenumber. The product spectrum data after 50 min showed excellent match with the standard spectrum of pure C\(_{18}\)H\(_{38}\) previously reported by You et al., (2011). The products distribution after 60 min is shown in Figure 4.40b. The presence of iso-C\(_{18}\)H\(_{38}\) in the product is definitely due to the functionalization of the synthesized PdOx/Zeol with OxA at the catalyst development stage which increased the acidity. Previous studies (Kubicka et al., 2008; Krar et al., 2010; Kovacs et al., 2011) have shown that acidic catalysts are promising towards the production of iso-paraffins which are known to be good biofuel additive due to their low freezing points. The presence of water confirmed that the O\(_2\) extraction proceeds via HDO process (since CO was not observed) while that of CO\(_2\) is likely due to decarboxylation process which justifies the traces of C\(_{17}\)H\(_{36}\) observed. Part of the CO\(_2\) perhaps had undergone methanization reaction with the H\(_2\) in the carrier gas stream to form the traces of CH\(_4\) observed. However, since no other lower and higher hydrocarbons were observed, it implied that
the operating conditions were not at extremes that could favor cracking and polymerization reactions and also the PdOx/Zeol has the ability to minimize the formation of other side product(s) due to the presence of the metal-oxalate ligands (Ng et al., 1985; Ayodele and Hameed, 2012; Li et al., 2012).

![Diagram](image)

**Figure 4.40b**  Products distribution of the HDO process of stearic acid using 2.0 mg of PdOx/Zeol, and 100 ml/min (5%H2/N2) gas flow rate at 360 °C

In view of the foregoing, a comparison of the PdOx/Zeol activity with other related studies (Hancsok et al., 2007; Lestari et al., 2008; Bernas et al., 2010; Krár et al., 2010; Arend et al., 2011; Kwon et al., 2011; Somnuk et al., 2014; Takase et al., 2014) showed that PdOx/Zeol is comparably highly promising especially considering their feed:catalyst dosage ratio, higher reaction temperature, longer reaction time and product purity. For example, Arend et al., (2011) used 3 g of 2% Pd/C and could only achieve
deoxygenation at 380–450 °C, hence the catalyst suffered deactivation due to carbon deposition. Similarly, Lestari et al., (2008) achieved catalytic deoxygenation of SA over Pd supported on acid modified mesoporous silica SBA15 and MCM-41 with 67% liquid n-pentadecane selectivity after 5h reaction compared to over 90% combined n- and iso-octadecane recorded in this study in 1 h HDO time. In all those studies (Hancsok et al., 2007; Lestari et al., 2008; Bernas et al., 2010; Krár et al., 2010; Arend et al., 2011; Kwon et al., 2011; Somnuk et al., 2014; Takase et al., 2014) the authors did not report any formation of isomerized products which are value added components for biofuel to enhanced its cold flow properties.

4.4.4 Catalyst Reusability

The catalyst reusability was studied at 360 °C, 100 ml/min gas flow rate and 20 bar in 60 min reaction time. After three consecutive experiments the result showed that the HDO efficiency was still consistent. This ability was ascribed to the PdOx/Zeol synthesis protocol that employs the functionalization of palladium with OxA to develop organometallic palladium II oxalate complex catalyst precursor with increased acidity. Generally metal-oxalate catalysts have been reported to be more reactive than the metal oxide catalysts and are highly resistance to leaching of the active metal due to the presence of the strong M\(^{n+}\) - oxalate ligand which also minimizes the tendencies of multiple side reactions (Ng et al., 1985; Ayodele and Hameed, 2012; Tanev and Lange De Oliveira, 2012). However about 2% reduction in isomerization efficiency was observed probably due to slight reduction in the PdOx/Zeol acidity. Kovacs et al., (2011) in their study on hydrotreating of triglycerides using fluorinated NiMo/Al\(_2\)O\(_3\) catalyst also reported some degree of acidity loss which resulted into reduced iso-paraffin production.
4.5 PREPARATION AND CHARACTERIZATION OF ALUMINA SUPPORTED NICKEL-OXALATE CATALYST FOR THE HYDRODEOXYGENATION OF OLEIC ACID INTO NORMAL AND ISO-OCTADECANE BIOFUEL

4.5.1 Characterization Result

4.5.1.1 X-Ray Fluorescence Spectra

The XRF characterization spectra results of Al$_2$O$_3$ and NiOx/Al$_2$O$_3$ are shown in Figure 4.41, the spectrum of the Al$_2$O$_3$ showed its characteristics peaks between 1.48 and 21.4 keV. However, upon the successfully incorporated of NiOx into the structure of Al$_2$O$_3$, all those characteristics peaks were dwarfed by the intensity of a peak at Kα value of 7.47 keV and another subordinate peak at Kβ of 8.26 keV that both reflect the possible presence of two Ni species with different excitation potentials in NiOx/Al$_2$O$_3$ according to the standard card of peak identification (EDXRF-EPSILON 3 XL, PANalytical).

![Figure 4.41 XRF spectra of Al$_2$O$_3$ and NiOx/Al$_2$O$_3$ samples](image-url)
4.5.1.2 Elemental Dispersive X-Ray (EDX)

The EDX result in Figure 4.42 also corroborates the incorporation of NiOx in Al₂O₃ with the presence of Ni peaks at 1.9 and 7.5 keV. Since both the XRF and EDX results reflect Ni with two different peaks each, this suggests that there could be more than one species of Ni. The EDX results and Table 4.8 also showed increase in the amount of O₂ in the NiOx/Al₂O₃ sample which was due to the present of oxalate ligand in the incorporated NiOx precursor as a result of the OxA functionalization. Although the presence of carbon from the oxalate ligand cannot be seen in Table 4.8 because EDXRF analyzer inability to detect and measure Period 2 elements of the Periodic Table except fluorine (and O₂ in most cases) according to the standard card for peak identification (EDXRF-EPSILON 3 XL, PANalytical). However, the presence of the oxalate ligand was established in the Raman spectroscopy result. There was variation in the amount of Ni from the expected 10% to 9.3% obtained from the average of four sets (9.2%, 9.4%, 9.3%, 9.3%) of analysis because EDX is more of a point analysis technique. The observed variation was ascribed to the degree of hydration at the NiOx/Al₂O₃ synthesis stage (Ayodele and Togunwa, 2014).

![EDX spectra and SEM morphology of Al₂O₃ and NiOx/Al₂O₃ samples](image)

Figure 4.42   EDX spectra and SEM morphology of Al₂O₃ and NiOx/Al₂O₃ samples
Table 4.8 Elemental composition of Al₂O₃ and NiOx/Al₂O₃

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al</th>
<th>O₂</th>
<th>Ca</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>39.07</td>
<td>43.73</td>
<td>17.2</td>
<td>0</td>
</tr>
<tr>
<td>NiOx/Al₂O₃</td>
<td>34.16</td>
<td>47.72</td>
<td>8.9</td>
<td>9.3</td>
</tr>
</tbody>
</table>

4.5.1.3 Morphological and textural changes

The morphology of Al₂O₃ shown in Figure 4.43 (a) revealed lumpy and thick flakes with partial uniform particle size distribution and relatively smooth surfaces, while that of NiOx/Al₂O₃ Figure 4.43 (b) showed the formation of irregular flaky morphology with random orientation. This observation was due to the acidity of the successfully incorporated NiOx (Ayodele, 2013), which also caused loss of crystallinity, reduction in average particle size and increase in specific surface area as seen in Table 4.9 measured by the N₂ adsorption/desorption studies using the BET methods. Organometallic catalyst precursors especially of low pH are known to be structural modifiers enhancing mesoporosity of synthesized catalysts (Li et al., 2012).

Figure 4.43 SEM morphology of (a) Al₂O₃ and (b) NiOx/Al₂O₃ samples
Table 4.9  Textural properties of Al\(_2\)O\(_3\) and NiOx/Al\(_2\)O\(_3\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m(^2)/g)</th>
<th>Pore volume (cm(^3)/g)</th>
<th>Pore diameter (nm)</th>
<th>Average Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(_2)O(_3)</td>
<td>64.0</td>
<td>0.21</td>
<td>13.32</td>
<td>4687.53</td>
</tr>
<tr>
<td>NiOx/Al(_2)O(_3)</td>
<td>120.11</td>
<td>0.3817</td>
<td>14.22</td>
<td>725.56</td>
</tr>
</tbody>
</table>

From Figure 4.44, Al\(_2\)O\(_3\) showed characteristics formation of monolayer isotherm at lower relative pressure as seen in the intermediate flat region which is typical of Type II isotherms and it systematically conformed to the Type IV isotherm typical of mesoporous materials at higher relative pressures. However, NiOx/Al\(_2\)O\(_3\) showed characteristics of Type IV over the range of the isotherms signifying enhanced mesoporosity which was made more evident by the increase in its H3-like hysteresis loop which is typical of inter-particle voids formed by accumulation of plate-like and nano-sized particles having slit-shaped pores (Xue et al., 2012).

Figure 4.44  \(\text{N}_2\) adsorption/desorption of Al\(_2\)O\(_3\) and NiOx/Al\(_2\)O\(_3\) samples
Similarly, the increase in the amount of N\textsubscript{2} adsorbed in NiOx/Al\textsubscript{2}O\textsubscript{3} sample confirmed the enhanced porosity observed in the pore volume (Table 4.9). These modified textural and morphological qualities were due to the incorporation of acidic organometallic NiOx precursor into the Al\textsubscript{2}O\textsubscript{3} lattice which will in turn enhances synthesized catalyst activities (Li et al., 2012; Ayodele, 2013). Consequently, it is highly probable that the nickel species were finely dispersed thus forming the amorphous nickel aluminate phase which was made possible by the well-enhanced mesoporous structure (Bang et al., 2012; Bang et al., 2013; Ghule et al., 2009; Ghule et al., 2010).

4.5.1.4 X-ray diffraction of samples

The XRD result of Al\textsubscript{2}O\textsubscript{3} and NiOx/Al\textsubscript{2}O\textsubscript{3} samples is shown in Figure 4.45. The characteristic peaks at 2θ values of 25.5\textdegree, 35.8\textdegree, 37.6\textdegree, 43.6\textdegree, 52.7\textdegree, 57.6\textdegree, 60.6\textdegree, 66.4\textdegree, 77\textdegree and 84.8\textdegree typical of γ-Al\textsubscript{2}O\textsubscript{3} are also observed in NiOx/Al\textsubscript{2}O\textsubscript{3} hence it is difficult to discriminate the characteristics peaks of NiOx. This observation indicated that nickel species were finely dispersed thereby developing an amorphous nickel aluminate phase (Bang et al., 2012; Bang et al., 2013) and it was attributed to effective prevention of metal sintering and collapse of the NiOx/Al\textsubscript{2}O\textsubscript{3} structure by the well-developed mesoporous structure due to the OxA functionalization. The NiOx/Al\textsubscript{2}O\textsubscript{3} diffractograms showed reduction in peaks due to loss of crystallinity already observed in the SEM morphology. This further confirmed that highly dispersed surface type amorphous nickel aluminate phase was prevalent over any possible bulk type (Bang et al., 2013). Previous studies (Xue et al., 2012; Bang et al., 2013; Ayodele and Togunwa, 2014) have reported enhanced textural properties such as increase in the number of mesopores with associated loss of crystallinity in samples that are functionalized with acidic (organic)
agents. Furthermore, a close examination revealed that there is shift in the diffraction peaks of NiOx/Al₂O₃ compared to Al₂O₃ which implied that NiOx complex has an intimate contact with the γ-Al₂O₃ lattice thus expanding it to form a more nickel-saturated surface nickel aluminate phase (Bang et al., 2012; Ghule et al., 2009; Ghule et al., 2010).

![XRD of Al₂O₃ and NiOx/Al₂O₃ samples](image)

**Figure 4.45** XRD of Al₂O₃ and NiOx/Al₂O₃ samples

### 4.5.1.5 FTIR spectroscopy

The FTIR spectroscopy of Al₂O₃ and NiOx/Al₂O₃ samples are shown in Figure 4.46, it can be seen that there is no clear difference between their spectra. This observation is synonymous to XRD result (Figure 4.45) that showed no distinction between the diffractograms of the Al₂O₃ and NiOx/Al₂O₃, a phenomenon that previous reports (Ghule et al., 2009; Ghule et al., 2010) had ascribed to high Ni dispersion to form surface nickel aluminate spinel owing to the OxA functionalization since low
oxidation state of nickel species can be accommodated in Al₂O₃ lattice (Ghule et al., 2010). However, it can be seen that the spectra of the two samples aligned up to around 980 cm⁻¹ beyond which the spectrum of NiOx/Al₂O₃ deflected showing reduction in transmittance due to the effect of metal incorporation. Typically, the presence of metal (transition/noble) incorporation in synthesized catalysts is usually observed by their spectra deviations compared to that of the support at low wavenumbers below 1000 cm⁻¹ which is an indication of structural variation (Li et al., 2012). Since FTIR can only give limited information about metal-support interaction, there is need for Raman spectroscopy to elucidate a more detailed structural variation.

![FTIR of Al₂O₃ and NiOx/Al₂O₃ samples](image)

**Figure 4.46** FTIR of Al₂O₃ and NiOx/Al₂O₃ samples

### 4.5.1.6 Raman spectroscopy

The Raman spectra of Al₂O₃ and NiOx/Al₂O₃ samples are shown in Figure 4.47. Typical Al₂O₃ bands are seen at 1174, 1085, 1057, 1005, 916, 828, 745, 689, 600, 518,
433 and 378 cm\(^{-1}\), while the strong band at 1310 cm\(^{-1}\) reflects Al(OH)\(_3\) due to the adsorbed water molecules (Ghule et al., 2009; Ghule et al., 2010). Obviously after catalyst synthesis and calcination the band at 1310 cm\(^{-1}\) drastically reduced in intensity due to dehydroxylation (i.e. \(2\text{Al(OH)}_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}\)) in NiOx/Al\(_2\)O\(_3\). Generally, Raman spectroscopic studies have revealed two types of supported metals on Al\(_2\)O\(_3\) due to either adsorption or absorption (Ghule et al., 2010).

Adsorption is typical of metals with high oxidation state and they cannot be accommodated in the matrix of Al\(_2\)O\(_3\), hence they give strong Raman bands at ~ 1100-900 cm\(^{-1}\). On the other hand, absorption is characteristics of low oxidation state metals that can be absorbed into the surface of the alumina support as Ni\(^{2+}\) forming a surface spinel because it can be accommodated, and they usually possess Raman bands between

![Figure 4.47 Raman spectra of Al\(_2\)O\(_3\) and NiOx/Al\(_2\)O\(_3\) samples](image-url)
∼800 - 300 cm\(^{-1}\). Since there are Raman bands in the range ∼1200-300 cm\(^{-1}\), this suggested that Ni species are being absorbed and adsorbed in the Al\(_2\)O\(_3\) probably as NiOx and NiO, respectively. This also supports earlier observation in the XRF and EDX result that there are two Ni species. The NiOx is definitely due to the functionalization with OxA, while the NiO might be due to partial thermal decomposion NiOx during calcination (Zhan et al., 2005; Salavati-Niasari et al., 2010) and unreacted Ni salt during the synthesis stage. The prevalence of the NiOx over NiO is justified by the absence of bands at 460 and 510 cm\(^{-1}\) which are characteristics of crystalline NiO as well as the low intensity peaks at 375 and 600 cm\(^{-1}\) which are typical of crystalline NiAl\(_2\)O\(_4\) (Ghule et al., 2010). These also support the earlier observation in XRD result that the Ni species present are highly dispersed. It can therefore be concluded that the OxA functionalization was effective and its presence in the NiOx/Al\(_2\)O\(_3\) is very evident by the multiple background noise-like vibrations which are typical of the presence of organic functional group (Ghule et al., 2009; Ghule et al., 2010).

4.5.2 Catalytic activities

4.5.2.1 Preliminary studies on the catalytic HDO of oleic acid

Prior to the main studies on the catalytic HDO of oleic acid (OA), a blank test was carried out at 360 °C, 20 bar and 100 mL/min gas flow without NiOx/Al\(_2\)O\(_3\) loading to determine if the reactor and/or it accessories has catalytic effect on the reaction. This study became imperative because a new reactor agitator was just installed. Arend et al (2011) had previously proposed a possible auto-catalyzed reaction such as hydrogenation or thermal cracking of the reactant OA. The results actually showed a minuscule conversion of OA, however, there was no formation of any C18 hydrocarbon except about 4% stearic acid formation. This suggests that a fraction of OA was
marginally hydrogenated to form saturated stearic acid and that cracking of the OA was not imminent at that prevailing operating condition. It can therefore be concluded that if pure hydrogen was used as reactant and carrier gas there would be only marginal hydrogenation contribution from the reactor and the associated internals made of stainless steel.

4.5.2.2 Effect of NiOx/Al2O3 Loading on the Catalytic HDO of Oleic Acid

The profile of effect of NiOx/Al2O3 loading on the catalytic HDO of OA is shown in Figure 4.48. It was observed that the product distribution contains both n-C18 and iso-C18 paraffin, the presence of the latter was due to the OxA functionalization which increased the acidity of NiOx/Al2O3 during synthesis stage (Zhan et al., 2005; Kovacs et al., 2011). Generally, iso-paraffin are considered value-added-component in biofuel research because they have low freezing point compared to their straight chain counterpart, and this is advantageous at improving the cold flow properties such as cold filter plugging points of the biofuel (Kovacs et al., 2011). The result shows that as NiOx/Al2O3 loading was increased from 10- 20 mg, n-C18 increase was more favorable increasing by 12% (i.e. 60- 72%) compared to iso-C18 that increased by 5% (i.e. 17-21%). This observation was due to the fact that as the NiOx/Al2O3 loading was increased more Ni active sites were made available for the HDO reaction (Ayodele and Togunwa, 2014), and the comparably lower increase in the iso-C18 fraction was due to the fact that isomerization process is a secondary reaction using the produced n-C18 as its substrate (Kovacs et al., 2011; Kwon et al., 2011). However, further increase to 30 mg resulted in slight reduction of the fraction of n-C18 from 72- 70%, while iso-C18 fraction still enjoys slight increment of about 2%. This implied that NiOx/Al2O3 loading has exceeded favorable limit for HDO process hence proliferating the propensity for
secondary reactions such as oligomerization that scavenges on the already deoxygenated n-C18 molecules as seen in the fraction of >C18 which began to increase at 30 mg loading and beyond. The slight increase in the iso-C18 could be ascribed to the fact that isomerization process as a secondary reaction will require more additional process parameters (Kwon et al., 2011; Mortensen et al., 2011; Ayodele et al., 2014a). A comparison of effect of NiOx/Al2O3 loading on the target fractions plotted as iso-C18/n-C18 showed that increase in the NiOx/Al2O3 loading is favorable for isomerized fraction over the range of study. It can therefore be concluded that superfluous increase in NiOx/Al2O3 loading will introduce excessive active sites which increases the propensity for secondary reactions, and this is further corroborated with the increase in the >C18 fraction at 40 mg loading probably suggesting that oligomerization process is fast coming to the fore.

![Graph](image)

**Figure 4.48** Hydrodeoxygenation of oleic acid at different NiOx/Al2O3 loading using at 20 bar, 360 ºC and 100 mL/min gas flow
4.5.2.3 Effect of Temperature on the Catalytic HDO of Oleic Acid

Figure 4.49 shows the result of the catalytic activity of the NiOx/Al2O3 evaluated on the HDO of OA at different temperatures. It is obvious that as the temperature increases from 320 to 360 °C the yield of n-C18 increased from about 40 to 72%, similarly, iso-C18 yield also increases from about 5 to 21%. It can therefore be inferred that both the HDO and isomerization process of OA into paraffinic biofuel were in accordance with the traditional Arrhenius theory of temperature dependence of reaction rates. This implied that as the temperature was increased the molecules of the OA gained more kinetic energy in excess of activation energy to vigorously interact with the H2 gas at the NiOx/Al2O3 active sites. In addition, since the viscosity of OA has an inverse relation with temperature, increase in temperature will reduces OA viscosity which in turn enhances both the H2 mass transfer into the bulk of OA and its propensity for solubility in the reaction mixture.

![Graph showing yield of target fraction vs. temperature](image_url)

Figure 4.49 Hydrodeoxygenation of oleic acid at different temperature, experimental condition: 20 mg NiOx/Al2O3, 20 bar, 100 mL/min gas flow and 60 min
There is reduction in the yield of n-C18 and iso-C18 at 380 °C, probably due to certain secondary reactions like cracking (Do et al., 2009; Demirbas, 2010; Arend et al., 2011; Kovacs et al., 2011) which was seen to have increased the amount of gases. The continual increase in the iso-C18/n-C18 ratio even beyond 360 °C also confirmed that higher temperature favors secondary reactions since isomerization has been reported to be a secondary reaction. Previous studies (Demirbas, 2010; Arend et al., 2011; Kovacs et al., 2011; Sotelo-Boyás et al., 2011) also reported similar phenomenon.

4.5.3 NiOx/Al2O3 Reusability Studies

The reusability results of NiOx/Al2O3 on the HDO of 40 g OA at 360 °C, 20 bar, 20 mg NiOx/Al2O3, 100 mL/min gas flow and 60 min showed consistency of 72% for n-C18 in five consecutive runs. However iso-C18 showed consistency of 21% for only three consecutive runs and reduced to 20% and 17% after 4th and 5th runs, respectively. The high reusability was undoubtedly due to the functionalization of the organic oxalate which reposed the exceptional high reusability quality of organometallic catalyst in the NiOx/Al2O3 (Ayodele and Hameed, 2013). Generally, organometallic catalysts with metal oxalate ligand complex have been reported to be highly reactive and reaction specific thereby minimizing reaction time and prolonging the catalyst life span (Li et al., 2012; Tanev and Lange De Oliveira, 2012; Ayodele, 2013). The reduction in the iso-C18 can be due to gradual loss of acidity on the NiOx/Al2O3, Kovacs et al., (2011) had also reported similar phenomenon on fluorine acidified NiMo/Al2O3 for the HDO of certain triglycerides.
4.6.1 Catalyst Characterization

4.6.1.1 Thermal gravimetric analysis (TGA)

The result in Figure 4.50 shows TGA of Zeol and FPdOx/Zeol (before and after calcination) with three characteristics regions. For both Zeol and FPdOx/Zeol (before calcination) there exists a rapid weight loss up to 110-170 °C which was undoubtedly due to the release of physisorbed water (Pal-Borbely, 2007; Ayodele, 2013). The value of the physisorbed water appeared higher in the latter than in the former due to the high degree of hydration at the catalyst synthesis stage. The second region is due to the presence of strongly bonded water molecules that are present in the first coordination sphere and requires heat treatment up to about 650 °C for their removal, and finally in the third region was the structural hydroxyl groups that will condense and dehydrate at temperatures above 650 °C (Ayodele, 2013). It can be seen that the catalyst synthesis protocol was able to increase the strongly bonded water even more than the physisorbed water. This implied that the hydrated FPdOx precursor was able to penetrate into the supercage structure of the Zeol support. The effect of calcination showed drastic reduction in both the physisorbed and strongly bonded water as seen in the FPdOx/Zeol (after calcination). Ohtsuka and Tabata (1999) reported that the presence of water in synthesized Pd-catalyst leads to agglomeration of Pd particles while proper calcination guarantees a high dispersion of Pd particles which is a requirement for reduction
processes such as HDO, although agglomerated Pd particles is very active for oxidation processes such as methane combustion (Ohtsuka and Tabata, 1999).

![Thermal Gravimetric Analysis of Zeol and FPdOx/Zeol](image)

Figure 4.50 Thermal Gravimetric Analysis of Zeol and FPdOx/Zeol (before and after calcination)

### 4.6.1.2 X-ray Fluorescence (XRF)

The XRF spectra of both Zeol and calcined FPdOx/Zeol are shown in Figure 4.51. The incorporation of Pd into the matrix of the Zeol is seen in the XRF spectrum of FPdOx/Zeol at Lα1 of 2.99 keV and it is in accordance with the standard card of peak identification (EDXRF-EPSILON 3 XL, PANalytical). Another Pd peak is observed at Lβ1 of 3.20 keV which possibly suggest high dispersion of Pd particles from palladium oxalate (PdOx) due to the effect of proper calcination that reduced the strongly bonded water as seen the TGA profile.
4.6.1.3 Energy dispersive X-ray

The results in Table 4.10 show the elemental composition of Zeol and FPdOx/Zeol samples. The Zeol composition is basically silica and alumina with some amount of sodium and calcium oxides, the Zeol Si/Al ratio is 1.02 typical of Zeolite NaA. After the incorporation of the catalyst precursor and calcination, there is slight increment in the Si/Al ratio to 2.5. This is in consonance with earlier report on zeolite NaA which showed that there is inverse relationship between the amount of zeolitic water and the Si/Al ratio (Pal-Borbely, 2007). As observed in the TGA profile (Figure 4.50), calcination reduced both the physisorbed and the strongly bonded water, and this was further supported by the reduction in the amount of oxygen as shown in Table 4.10. The EDX spectrum shown in Figure 4.52 also corroborated the presence of the Pd particle between 2.4 and 3.8 keV as well as the successful functionalization of fluoride ion.
Table 4.10 Elemental composition of Zeol and FPdOx/Zeol samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si</th>
<th>Al</th>
<th>O₂</th>
<th>Na</th>
<th>F</th>
<th>Cu</th>
<th>Pd</th>
<th>Si/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeol</td>
<td>16.88</td>
<td>16.48</td>
<td>49.58</td>
<td>16.61</td>
<td>0.0</td>
<td>0.45</td>
<td>0.00</td>
<td>1.02</td>
</tr>
<tr>
<td>FPdOx/Zeol</td>
<td>18.73</td>
<td>12.5</td>
<td>46.80</td>
<td>11.72</td>
<td>8.2</td>
<td>0.12</td>
<td>1.86</td>
<td>1.59</td>
</tr>
</tbody>
</table>

Figure 4.52 Energy Dispersive X-ray of (a) Zeol and (b) FPdOx/Zeol samples

4.6.1.4 Scanning Electron Microscopy (SEM)

The changes in the morphology of zeolite and even clays were considered to have significant effects on their catalytic properties (Li et al., 2013). The SEM images in Figure 4.53(a) revealed the morphology of Zeol which consists of agglomerates of micro-sized cubical symmetry crystal structure. The crystalline nature of the Zeol sample was seen to have changed into amorphous-like material in FPdOx/Zeol with considerable reduction in particle size as seen in Table 4.11 (textural properties of the samples as studied by the N2 adsorption/desorption of BET). This denaturation of the crystalline structure can be ascribed to the effect of oxalic acid and probably drops of
HF at the catalyst synthesis stage and the effect of calcination (Ayodele and Togunwa, 2014). Aluminosilicates (zeolites and clays) have been reported to transform from crystalline into amorphous under acid treatments (Ayodele, 2013) and this transformation is always followed by increase in specific surface area (Wang et al., 2012; Ayodele, 2013) as seen in the textural properties of FPdOx/Zeo in Table 4.11.

![Figure 4.53](image)

Figure 4.53  Scanning Electron Microscopy of (a) Zeol and (b) FPdOx/Zeo samples

### 4.6.1.5 Nitrogen Adsorption/Desorption Isotherm (BET)

The textural properties of Zeol and FPdOx/Zeo samples are shown in Table 4.11. As earlier noted that transformation of crystalline material into amorphous is usually associated with increment in specific surface area, the result in Table 4.11 showed that there is increment in the specific surface area and pore volume of FPdOx/Zeo as compared to the parent Zeol, this increment is more evident by the reduction in the average particle size of the FPdOx/Zeo sample probably due to the effect of oxalic acid and calcination at the catalyst synthesis stage as earlier noted. The enhancement in the textural properties can be further corroborated by the N₂
adsorption/desorption isotherm in Figure 4.54 which shows increment in the adsorbed quantities of N\textsubscript{2} at STP from 362 cm\textsuperscript{3} g\textsuperscript{-1} in Zeol to 734 cm\textsuperscript{3} g\textsuperscript{-1} in FPdOx/Zeol. Both samples showed Type IV isotherms which according to the IUPAC classification are generally observed for mesoporous solids (Wang et al., 2012).

Table 4.11 Elemental composition and textural properties of Zeol and FPdOx/Zeol samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Surface area (m(^2)/g)</td>
<td>Pore volume (cm(^3)/g)</td>
</tr>
<tr>
<td>Zeol</td>
<td>202.84</td>
<td>0.13</td>
</tr>
<tr>
<td>FPdOx/Zeol</td>
<td>385.68</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Figure 4.54 Nitrogen adsorption/desorption isotherm of the Zeol and FPdOx/Zeol samples
4.6.1.6 X-ray diffraction (XRD)

X-ray diffraction of the Zeol and FPdOx/Zeol samples are presented in Figure 4.55. The Zeol sample showed characteristics peaks of Zeolite A according to the JCPDS card 43-0142 (Hui et al., 2009). The Zeol sample is seen to be highly crystalline but become amorphous after the FPdOx/Zeol synthesis and this further corroborates the earlier observation on the samples morphology (Figure 4.53). Previous studies have shown that transformation of catalyst sample after thermal and/or chemical treatment from crystalline into amorphous also assures a high dispersion of the active metal into the matrix of the support which inevitably guarantee proper anchoring of the metal onto the support (Li et al., 2013; Ayodele and Togunwa, 2014).

![X-ray diffraction of the Zeol and FPdOx/Zeol samples](image)

Figure 4.55  X-ray diffraction of the Zeol and FPdOx/Zeol samples

The presence of Pd particle is seen at $2\theta = 18^\circ$ and $35.7^\circ$, the latter is close to the $33.9^\circ$ earlier reported by Pommier and Gelin (1999) on H-ZSM-5 zeolite type and $34^\circ$.
reported by Gannouni et al., (2012) others were seen at 38.4°, 42°, 58.7° and 61.8° (Naydenov et al., 2002). The successful incorporation of Pd is also seen to have elevated the base line of the Zeolite A supercage structure in FPdOx/Zeol progressively towards to the low angle after transformation into amorphous material.

4.6.1.7 Fourier’s Transform Infrared Spectroscopy (FTIR)

The FTIR spectroscopy of the Zeol and FPdOx/Zeol samples are shown in Figure 4.56. The vibrations in the region 3700-2900 cm\(^{-1}\) with minimal at 3317 cm\(^{-1}\) in the Zeol sample can be assigned to the presence of zeolitic water (Elaiopoulos et al., 2010), while the band at 1650 cm\(^{-1}\) is due to water vibration. These bands disappeared in the FPdOx/Zeol sample due to the effect of proper calcination. It has been reported that the presence of zeolitic water or other forms of water vibrations causes transformation of dispersed Pd particles into agglomerated Pd which does not favor reduction processes (Ohtsuka and Tabata, 1999) such as HDO of carboxylic acid being considered in this study. The disappearance of these bands indicates the possibility of highly dispersed Pd which is required for the HDO process. Although, Pd siting in zeolite frameworks is not yet properly understood, however, Ohtsuka and Tabata (1999) quoted Bell and co-worker to have proposed models for Pd siting in the form of \(Z^{-}Pd^{2+}(OH)^{-}\) or \(Z^{-}H^{+}(PdO)\), while the standing form takes \(Z^{+}H^{+}(PdO)H^{+}Z^{-}\) for aluminum site of zeolite. The smoothening between the band 1582 and 1306 cm\(^{-1}\) could be due to the presence of the oxalate ligand because it is in close agreement with the spectrum of \(C_{2}O_{4}^{2-}\) (aq) (\(\nu_{C-O}\) at 1569 and \(\nu_{C-O}\) at 1308 cm\(^{-1}\), both asymmetry) reported by Person and Axe (2005) in a study on metal-bonded surface complex. It can be observed that immediately after the 1306 cm\(^{-1}\) band the FPdOx/Zeol spectrum showed a clear deviation and shifting from the spectrum of the Zeol, this is due to the
fact that metals (ions or oxides) presence on aluminosilicates are usually observed in the lower wavenumbers. Hence, the slight shift in 940 cm\(^{-1}\) to \(~918\) cm\(^{-1}\) upon incorporation of the catalyst precursor and calcination can be considered as a good indicator for the presence of Pd oxalate ligands on the zeolite supercage structure which indicated that Pd particle dispersion was sustained after calcination (Pommier and Gelin, 2005). The lowering of band at 675 cm\(^{-1}\) and absorption band at 576 cm\(^{-1}\) could also be ascribed to the interference effect of Pd incorporation.

Figure 4.56  FTIR spectroscopy of the Zeol and FPDox/Zeol samples

4.6.1.8 Raman spectroscopy

Raman spectroscopy bands of different silica mesoporous supports have been well reported such that the \(v_{\text{sym}}(\text{Si-O-Si})\) bands and the \(v_{\text{asym}}(\text{Si-O-Si})\) vibrations have been assigned to the range between 800 - 850 cm\(^{-1}\) and between 1000 - 1200 cm\(^{-1}\), respectively (Pommier and Gelin, 2005; Gannouni et al., 2012). Similarly, the bands
around 550 - 600 cm\(^{-1}\) and 270 - 425 cm\(^{-1}\) have been assigned to \(\nu{(SiO)} + \delta{(OSiO)}\) and \(\delta{(SiOSi)}\), respectively (Gannouni et al., 2012). The characteristic bands of Zeol in Figure 4.57 appears at 280, 330, 405, 490, 700, 977, 1040 and 1150 cm\(^{-1}\) which are typical of zeolite A which contains 4 – and 6 – membered rings (Wang et al., 2009). The strongest band at 490 cm\(^{-1}\) is assigned to the bending mode of 4-membered Si-O-Al rings while the bands at 330 and 405 cm\(^{-1}\) are due to the bending mode of 6-membered Si-O-Al rings (Yu et al., 2001). The bands at 977, 1040 and 1100 cm\(^{-1}\) are ascribed to asymmetric T-O stretching motions (Yu et al., 2001; Gannouni et al., 2012). The Zeol spectrum shows an unusual band at 800 cm\(^{-1}\) which is not a signature of Zeolite A, this band is similar to that found in ZSM-5 and it is ascribed to symmetric stretching (Yu et al., 2001).
It is very remarkable that Zeol exhibits a band at 280 cm\(^{-1}\) which is attributed to the bending mode of higher rings than 4- and 6-membered rings, possibly of the 8-membered rings of zeolite A since previous studies had shown that smaller rings give bands at higher frequencies and vice versa (Yu et al., 2001). The presence of Pd particle on the FPdOx/Zeol is first observed around 640 cm\(^{-1}\) which is close to 648 cm\(^{-1}\) reported by Ohtsuka and Tabata (1999) the band is ascribable to the Raman active B1g vibrational mode of the PdO phase which is commonly seen at 651 cm\(^{-1}\) for single crystals or PdO foils, or between 626 and 640 cm\(^{-1}\) for oxidized Pd deposited on alumina or zirconia (Gannouni et al., 2012). Previous studies has also shown that successful incorporation of Pd particles into zeolite support induces an absorption band around 928 cm\(^{-1}\) as seen in Figure 4.57 and it is attributed to the stretching vibrations of the T-O bonds (Pommier and Gelin, 2005; Gannouni et al., 2012).

4.6.1 Hydrodeoxygenation of Oleic Acid Process Chemistry Using FPdOx/Zeol

Sequel to successful determination of the best observed operating condition from the studies of the factors that influence the HDO of OA, certain studies were undertaken to investigate the HDO process chemistry with reaction time based on the products FTIR using FPdOx/Zeol catalyst. The analysis of the products spectra was done every 7.03 sec at a spectra resolution of 1 cm\(^{-1}\) in the wavenumber range of 4000-600 cm\(^{-1}\).

4.6.1.1 Hydrodeoxygenation Process Chemistry

The 3D absorbance of the evolved products of HDO of OA using FPdOx/Zeol catalyst as monitored with FTIR spectroscopy in the range of 4500-600 cm\(^{-1}\) at different reaction time is shown in Figure 4.58. Similarly, Figure 4.59 shows an insight
into the progress of the HDO process, especially the orthonormalized vector form of the FTIR analysis of the evolved products measured and plotted as a function of time using the Gram Schmidt (GS) process based on the 3D FTIR absorbance in Figure 4.58.

![Figure 4.58 3D absorbance of the evolved products of HDO process of 3.5 g of oleic acid into paraffinic fuel using 2.0 mg FPdOx/Zeol catalyst](image)

It can be seen that as the HDO process progressed from $t = 0$ untill $t = 14$ min, no material loss was observed in both the TGA and the DTA plots (Figure 4.59), this was further corroborated by the GS plot which showed a smooth curve until about 14 min signalling no evolution of reaction products. This phenomenon is also in consonance with the observation on the time scale of Figure 4.58 and it implied that OA was still thermodynamically stable in those time region because the thermal energy gained is not sufficient to initiate breaking and/or formation of new bonds. The FTIR spectra of the evolved species observed in those period is plotted in Figure 4.60 which suggest that water vapor and instrument noise are predominant until around 10-14 min when traces of OA is gradually seen.
Figure 4.59  Progress of the HDO process of OA using 2.0 mg of FPdOx/Zeol catalyst at 370 °C

Figure 4.60  FTIR spectra of evolved products between 0-14 min on the HDO of 3.5 g OA using 2.0 mg of FPdOx/Zeol catalyst at 370 °C
The GS plot showed four regions between 15 and 40 min signifying that there are different stages of intermediate compounds formation until the final product was formed. Between 15 and 19 min which can be considered as initiation stage, only about 2% mass loss was observed as calculated from the TGA plot as the temperature rose to stabilize at 370 °C, this loss could be due to expulsion of moisture and some volatile contents in order to prepare the OA for reaction. The absorbance of the FTIR spectra of the evolved products within this time frame is plotted in Figure 4.61. All the spectra showed distinct characteristics of OA. The band between 3900 and 3500 cm\(^{-1}\) as well as that between 3000 and 2800 cm\(^{-1}\) are absolutely due to the O-H stretch of the carboxylic acid since no other functional group had such broad and intense band at high wavenumber (Wu et al., 2004). Two sharp peaks at 2954 and 2860 cm\(^{-1}\) which are superimposed on the O-H stretch are attributes of asymmetric CH\(_2\) stretch and symmetric CH\(_2\) stretch, respectively (Wu et al., 2004; Silverstein et al., 2005).

![FTIR spectra of evolved products between 15-19 min on the HDO of 3.5 g OA using 20 mg of FPdOx/Zeol catalyst at 370 °C](image)

**Figure 4.61** FTIR spectra of evolved products between 15-19 min on the HDO of 3.5 g OA using 20 mg of FPdOx/Zeol catalyst at 370 °C
The intense peak at 1779 cm\(^{-1}\) is due to the existence of the C=O stretch, and the band at 1462 cm\(^{-1}\) is assigned to CH\(_2\) bending modes, while the peak corresponding to 1285 cm\(^{-1}\) is due to the presence of the C-O stretch (Wu et al., 2004). The observed infrared spectra of OA conform to the OA standard spectrum in NIST Chemistry Webbook. The second region observed in the GS plot is between 20-25 min and the spectra analysis showed that stearic acid was gradually being formed according to the FTIR spectra shown in Figure 4.62. Previous reports (Immer et al., 2010; Arend et al., 2011) have shown that the HDO of unsaturated carboxylic acids such as OA proceeded in two stages; firstly sequential hydrogenation and subsequent deoxygenation. In this case, OA was observed to be first hydrogenated into saturated SA (Equation 4.16), followed by deoxygenation to obtain the paraffinic fuel (Equation 4.17).

\[
\begin{align*}
C_{17}H_{33}COOH + H_2 & \rightarrow C_{17}H_{35}COOH \\
C_{17}H_{35}COOH + 2H_2 & \rightarrow C_{18}H_{38} + H_2O
\end{align*}
\]

Figure 4.62 FTIR spectra of evolved products between 20-25 min on the HDO of 3.5 g OA using 2.0 mg of FPdOx/Zeol catalyst at 370 °C
From Figure 4.62, the drastic reduction of the O-H stretch of the carboxylic acid band between 3900 and 3500 cm\(^{-1}\) earlier observed in the OA spectra and the growth of two peaks around 2370 cm\(^{-1}\) suggest the gradual formation of SA. Similarly, the intense peak seen at 1779 cm\(^{-1}\) which was ascribed to the existence of the C=O stretch in OA is seen to be fast reducing, while another peak in its neighborhood at 1718 cm\(^{-1}\) confirmed the formation of SA in addition to those growing bands between 1463 and 1145 cm\(^{-1}\) which are characteristics of SA according to NIST Chemistry Webbook. According to the same NIST Chemistry Webbook, one important feature that distinguished SA from OA is the increase in the band width for the band between 3000 - 2800 cm\(^{-1}\) in OA to about 3400 – 2400 cm\(^{-1}\) in SA. Finally, there is a formation of a new peak at ~3010 cm\(^{-1}\) at about 23-25 min and it due to the formation of C-H stretch of alkane (You et al., 2011; NIST Chemistry Webbook, 2013) this observation herald the gradual formation of the paraffinic biofuel i.e octadecane (C\(_{18}\)H\(_{38}\)).

Figure 4.63 FTIR spectra of evolved products between 26-34 min on the HDO of 3.5 g OA using 2.0 mg of FPdOx/Zeol catalyst at 370 °C
Successful formation of SA was clearly evident in Figure 4.63 especially between 26-30 min, the fast reducing band between 3900 - 3500 cm\(^{-1}\) earlier observed in the OA spectra (Figure 4.62) has almost completely disappeared except for a little sprout at 3577 cm\(^{-1}\) which is a signature that the SA was formed from OA, since SA does not have such characteristics peak. The intense peak at 1779 cm\(^{-1}\) earlier ascribed to the existence of the C=O stretch of carboxylic acid in OA (Figure 4.61 and 4.62) has also nearly disappeared at 32 min, this and the superimposition of spectrum at 34 min on the spectrum at 32 min confirmed gradual HDO of OA into C\(_{18}\)H\(_{38}\).

![FTIR spectra of biofuel formed from the HDO of 3.5 g OA between 36-44 min using 2.0 mg of FPdOx/Zeol catalyst at 370 °C](image)

The bands between 1463-1145 cm\(^{-1}\) has nearly disappeared after 38 min in Figure 4.64 and the superimposed spectra within 38-44 min showed high degree of correlation with the standard spectrum of pure C\(_{18}\)H\(_{38}\) available at the NIST Chemistry...
Webbook and also the work of You et al., (2011). The superimposing of spectra in that time range also confirmed the thermal stability of the $\text{C}_{18}\text{H}_{38}$ biofuel produced. This implied that the fuel can be conveniently stored without trepidation of deterioration due to any undesirable stray reaction. It is worth noting that saturated alkanes (paraffin) are not very reactive thus stable under storage.
PART SEVEN

4.7 HYDRODEOXYGENATION OF OLEIC ACID INTO N- AND ISO-PARAFFIN BIOFUEL USING ZEOLITE SUPPORTED FLUORO-OXALATE MODIFIED MOLYBDENUM CATALYST: KINETICS STUDY

4.7.1 Catalyst characterization

4.7.1.1 Thermal Gravimetric Analysis (TGA)

Three characteristics weight loss regions (WLR) typical of the alumino-silicates are shown in Figure 4.65 for the Zeol, FMoOX/Zeol (uncalcined) and FMoOX/Zeol TGA profiles. Previous reports on alumino-silicates have shown that the first WLR corresponds to loosely bonded water molecules and physisorbed water that can be readily removed at a temperature below 200 °C (Ayodele and Hameed, 2012; Ayodele, 2013) as seen in the TGA profile of the three samples. Similarly, the second WLR has been ascribed to the presence of strongly bonded water molecules that are usually located in the first coordination sphere and can be removed at a temperature between 200-500 °C. The third WLR is due to the structural hydroxyl group that condenses and dehydrates at temperatures above 500 °C. In the first WLR both the Zeol and uncalcined FMoOX/Zeol samples showed almost same weight loss which implied that the drying stage was able to remove the hydration effect of the FMoOx precursor during the catalyst synthesis stage with some physisorbed and loosely bonded water molecules. However, in the second and even third WLR the uncalcined FMoOX/Zeol profile showed that there is slight increment in the amount of the strongly bonded water molecules which indicates that the catalyst synthesis protocol was able to guarantee the incorporation of the FMoOx precursor into the Zeol support. After calcination at 400 °C, both the physisorbed and strongly bonded water were seen to have drastically
reduced in the FMoOx/Zeol sample leaving behind FMoOx in the Zeol structure. Proper calcination has been reported to ensure large surface area and improved porosity hence guarantee a high active metal dispersion which in turn increases the number of active sites on the catalyst (Liu et al., 2011; Ohtsuka and Tabata, 1999).

![TGA profiles of Zeol, FMoOx/Zeol (uncalcined) and FMoOx/Zeol](image)

**Figure 4.65** TGA profiles of Zeol, FMoOx/Zeol (uncalcined) and FMoOx/Zeol

### 4.7.1.2 Elemental composition and spectra

The elemental composition of Zeol and FMoOx/Zeol samples in Table 4.12 showed that the Zeol composition comprises of silica and alumina with some oxides of sodium and calcium. The Si/Al ratio of Zeol sample is 1.02 which suggests Zeolite A type (Yu et al., 2001), the ratio increased to 2.60 in FMoOx/Zeol sample after the catalyst synthesis. This increment was ascribed to dealumination in FMoOx/Zeol due to the effect of oxalic acid (OxA) and fluoride ion functionalization and thermal treatment.
during FMoOX/Zeol synthesis and calcination stages, respectively. Acid and thermal treatments have been reported to cause dealumination of extra-framework alumina and framework alumina, respectively which eventually resulted into increase in the Si/Al ratio (Panda et al., 2010; Xiaoling et al., 2012; Ayodele, 2013) as shown in Table 4.12.

Table 4.12  Elemental composition of Zeol and FMoOx/Zeol samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si</th>
<th>Al</th>
<th>O₂</th>
<th>Na</th>
<th>F</th>
<th>Mo</th>
<th>Si/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeol</td>
<td>16.88</td>
<td>16.48</td>
<td>49.58</td>
<td>16.61</td>
<td>0.0</td>
<td>0.45</td>
<td>1.02</td>
</tr>
<tr>
<td>FMoOx/Zeol</td>
<td>16.61</td>
<td>6.39</td>
<td>56.74</td>
<td>3.32</td>
<td>7.74</td>
<td>9.21</td>
<td>2.60</td>
</tr>
</tbody>
</table>

The successful incorporation of FMoOx into the structure of Zeol is shown in the XRF spectra (Figure 4.66) which showed the growth of Mo peak at Kα value of 17.44 and at Kβ value of 19.5 keV. The intensity of the peak at the former is stronger than the latter which suggests there could be two different species of Mo present in the FMoOX/Zeol. All the peaks are in good agreements with the standard card of peak identification (EDXRF-EPSILON 3 XL, PANalytical).

Figure 4.66  X-ray florescence spectra of Zeol and FMoOx/Zeol samples
All the observations in Table 4.12 and Figure 4.66 are corroborated by the EDX spectra in Figure 4.67 which also confirmed the successful fluoride ion functionalization; however, the observed 9.21% quantity of the Mo species was slightly below the expected value of 10% Mo probably due to the high hydration degree at the FMoOx/Zeol synthesis stages (Ayodele and Hameed, 2012).

![Energy dispersive X-ray of Zeol and FMoOx/Zeol samples](image)

Figure 4.67  Energy dispersive X-ray of Zeol and FMoOx/Zeol samples

### 4.7.1.3 Morphological and Textural Changes

Figure 4.68 show the morphology of Zeol (a) and FMoOx/Zeol (b), the morphology of Zeol revealed agglomerates of micro-sized cubical symmetry sharp crystal structure, however, there is a huge degree of morphological variation in the FMoOx/Zeol sample owing to loss of crystallinity. The variation in the morphology is due to dealumination of FMoOx/Zeol at the catalyst synthesis stage which in turn increased the Si/Al ratio from 1.02 to 2.60 as a result of the OxA attack, functionalization with fluoride ion, thermal treatment during calcination and incorporation of Mo as earlier observed in the EDX and XRF results. Recent studies
(Panda et al., 2010; Xiaoling et al., 2012; Ayodele and Hameed, 2013) have also reported similar observation of alumino-silicate gradually transformation from crystalline into amorphous form under various degrees of acid attacks and such transformation enhances the catalytic activity of the supported catalyst (Xiaoling et al., 2012).

![Figure 4.68](image)

Figure 4.68 Scanning Electron Micrograph of (a) Zeol and (b) FMoOx/Zeol samples

The loss of crystallinity is also seen to be accompanied by reduction in particle size according to the BET result (Table 4.13) which in turn increased the specific surface area and the amount of $N_2$ adsorbed as seen in the isotherms of Zeol and FMoOx/Zeol samples shown in Figure 4.69. The changes in the textural properties is also in accordance with earlier reports (Panda et al., 2010; Xiaoling et al., 2012; Ayodele, 2013) and it was also ascribed to dealumination and removal of impurities and organic matters that might have blocked the samples pores. The enhanced surface area is considered an advantage for the HDO of OA into biofuel.
Table 4.13  Textural properties of Zeol and FMoOx/Zeol samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore diameter (nm)</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeol</td>
<td>202</td>
<td>0.13</td>
<td>17.27</td>
<td>10404</td>
</tr>
<tr>
<td>FMoOx/Zeol</td>
<td>316</td>
<td>0.19</td>
<td>18.70</td>
<td>2534</td>
</tr>
</tbody>
</table>

Figure 4.69   Nitrogen adsorption isotherms of Zeol and FMoOx/Zeol samples

Both Zeol and FMoOx/Zeol isotherms (Figure 4.69) at lower relative pressure exhibited a characteristic formation of monolayer followed by multilayer typical of Type II isotherm. However, towards the high relative pressures, while Zeol tend to conform with the Type II isotherm, the FMoOx/Zeol systematically conformed to Type IV isotherm with the steep uptake of N₂ emphasizing the possible presence of inter-
particle voids formed by agglomeration of the nano-sized and plate-like particles containing slit-shaped pores which are typical of H3 hysteresis loop (Xue et al., 2012). According to the IUPAC classification, this observation is generally observed for mesoporous solids (Panda et al., 2010; Xue et al., 2012). The variation of hysteresis loop of FMoOX/Zeol at P/Po = 0.4–0.9 is very obvious compared to Zeol which implied increase in mesopore formation and suggest the possible presence of some micro- and macro-porosity (Panda et al., 2010; Xue et al., 2012). This observation also supports the morphology variation earlier observed in the SEM of the FMoOX/Zeol as compared to the parent Zeol sample which was ascribed to the catalyst synthesis protocol.

4.7.1.4 X-Ray Diffraction (XRD)

The X-ray diffraction pattern of Zeol and FMoOx/Zeol samples are shown in Figure 4.70, the characteristics peaks at 2θ value of 7.2°, 10.0°, 12.4°, 16.0°, 21.6°, 24.0°, 27°, 30.0° and 34.0° confirmed that the Zeol support is zeolite A according to the JCPDS card 43-0142 (Hui et al., 2009). The XRD peaks showed that Zeol sample is highly crystalline which also supports the observation in the morphology of the Zeol in Figure 4.68. However, there is intense loss of crystallinity in the FMoOx/Zeol due to the presence of OxA, fluoride ion functionalization and thermal treatment during calcination. This phenomenon is in accordance with the earlier observation in the EDX, BET and SEM result which showed increase in the Si/Al ratio, enhanced textural properties and morphological transformation from crystalline into amorphous, respectively. Other studies (Xiaoling et al., 2012; Ayodele, 2013; Ayodele and Hameed, 2013) also showed varying degree of loss of crystallinity with increase in the Si/Al ratio under various degrees of acid attacks and thermal treatments which in turn ensured
proper anchoring of the active metal. The peaks at 11.7°, and 29.8° in the FMoOx/Zeol catalyst reflect the presence of octahedral polymeric molybdooxalates species of the form \([\text{Mo}_2\text{O}_5(\text{OH})(\text{C}_2\text{O}_4)_2]^{3-}\) due to the effect of protonation from the fluoride ion and the adequate MoOx loading of ~10% on the Zeol (Ng et al., 1985; Cindric et al., 2000; Kitano et al., 2013). Similarly, the peak at 21.4° is ascribed to the presence of bulk MoO\(_3\) in the catalyst probably due to partial decomposition of MoOx during calcination process. Generally, octahedral polymeric molybdates structures are observed for MoOx catalyst synthesized in the pH range 3.75 > pH > 1.25 and they have higher catalytic and isomerization activity compared to both monomeric molybdodioxalate specie of the form \([\text{MoO}_2(\text{OH})_2(\text{C}_2\text{O}_4)_2]^{4+}\) and the simple molybdates which are synthesized at relative higher pH values and are tetrahedral in structure (Ng et al., 1985; Bouchy et al., 2001).

Figure 4.70 X-ray diffraction patterns of Zeol and FMoOx/Zeol samples
4.7.1.5 Fourier’s Transform Infrared Spectroscopy (FTIR)

The FTIR spectroscopy of the Zeol and FMoOX/Zeol samples is shown in Figure 4.71 with Zeol sample showing vibration in the region 3700 - 2900 cm$^{-1}$ with a minimal around 3317 cm$^{-1}$ which can be assigned to the vibration of the Si–OH and adsorbed water molecules. Another band is seen at 1650 cm$^{-1}$ which can be ascribed to the bending vibration of the adsorbed water molecules (Li et al., 2012). The water vibration with a minimal around 3317 cm$^{-1}$ disappeared in the FMoOX/Zeol sample after calcinations implying that the thermal treatment is sufficient to guarantee the Mo ligand dispersion in the FMoOX/Zeol sample since the presence of water molecules usually cause agglomeration of active metals in zeolite supercage structure resulting in loss of catalytic activity (Ohtsuka and Tabata, 1999). Incorporation of transition and noble metals into zeolite and other aluminosilicates structure is typically observed in the lower wavenumber below 1000 cm$^{-1}$ as seen in the spectrum of FMoOX/Zeol which showed significant deviation from the Zeol spectrum indicating structural change caused by the presence of Mo specie (Li et al., 2012).

![FTIR spectra of Zeol and FMoOX/Zeol samples](image)

**Figure 4.71** FTIR spectra of Zeol and FMoOX/Zeol samples
The decrease in the intensity of the band at 880 cm\(^{-1}\) for the FMoOx/Zeol sample can be ascribed to the Mo=O stretching and Mo–O·–Mo asymmetric vibrations, while the asymmetric vMo=O stretching modes of the MoO\(_{4}\)\(^{2-}\) at 985 and 680 cm\(^{-1}\) are assigned to polymolybdates species due to the ionic equilibrium between molybdate and polymolybdate species (Equation 4.18) which are present in the FMoOx/Zeol solution as Si-O-Mo due to protonation (fluoride ion functionalization) during the FMoOx/Zeol synthesis stage (Ng et al., 1985; Cheng and Huang, 2010; Li et al., 2012). Since FTIR spectroscopy is more sensitive to carbon-oxygen and water vibrations and Raman spectroscopy is more sensitive to metal-oxygen (Ng et al., 1985), there is need to validate the Mo presence and structure using Raman spectroscopy.

\[
7\text{MoO}_4^{2-} + 8H^+ \rightleftharpoons \text{Mo}_7\text{O}_{24}^{6-} + 4H_2O \quad (4.18)
\]

### 4.7.1.6 Raman Spectroscopy

The spectra in Figure 4.72 compared the characteristic bands of Zeol and FMoOx/Zeol based on the incorporation of fluoride ion functionalized MoOx into Zeol matrix. Based on previous studies (Hui et al., 2009) the bands at 280, 330, 405, 490, 700, 977, 1030, 1150 and 1457 cm\(^{-1}\) are typical of zeolite A having 4-, 6- and 8-membered rings. Inspecting from the low wavenumber towards the high wavenumber, the band at 280 cm\(^{-1}\) in the Zeol sample can be assigned to the bending mode of rings higher than 4- and 6-membered rings, possibly of the 8 membered rings of zeolite A since previous studies had shown that higher rings give bands at lower wavenumber and vice versa (Yu et al., 2001). Similarly, the bands at 330 and 405 cm\(^{-1}\) are due to the bending mode of 6-membered Si-O-Al rings while the strongest band at 490 cm\(^{-1}\) is assigned to the bending mode of 4-membered Si-O-Al rings (Yu et al., 2001), while those at 977, 1030 and 1150 cm\(^{-1}\) are ascribed to asymmetric T-O stretching motions.
The effect of FMoOx incorporation into the Zeol can be observed to have developed series of multiple stretches of vibrations in FMoOx/Zeol which are reflections of the presence of carbonate anion (CO$_3^{2-}$) from organics, i.e. oxalate. The free ion of CO$_3^{2-}$ with D$_{3h}$ symmetry usually exhibits four normal vibrational modes namely, a symmetric stretching vibration ($\nu_1$) around 1063 cm$^{-1}$, an out-of-plane bend ($\nu_2$) around 879 cm$^{-1}$, a doubly degenerate antisymmetric stretch ($\nu_3$) around 1415 cm$^{-1}$ and lastly doubly degenerate bending mode ($\nu_4$) around 680 cm$^{-1}$ (Ray et al., 2006).

After the FMoOx/Zeol synthesis, the distinctive bands at 490 lost its outstanding peak, while those at 330 and 800 disappeared completely probably due to the effect of fluoride ion functionalization and calcinations. This observation supports the loss of crystallinity earlier observed in the SEM and XRD results. The miniature peak at 660
cm$^{-1}$ can be assigned to symmetric Mo-O-Mo stretches present in the dimeric structure which further confirmed the possibility of MoO$_3$ due to partial decomposition of MoO$_x$ at the calcination stage as earlier observed in the XRD peak at 21.4$^\circ$. The peak at 928 cm$^{-1}$ can be assigned to Mo=O since octahedral polymeric molybdooxalates species of the form [Mo$_2$O$_5$(OH)(C$_2$O$_4$)$_2$]$^{3-}$ are usually found in the stretch region 900- 950 cm$^{-1}$ (Ng et al., 1985; Kitano et al., 2013). The new peak at 1060 cm$^{-1}$ as well as the shift of 1030 and 1150 cm$^{-1}$ peaks in Zeol to 1020 and 1120 cm$^{-1}$, respectively in FMoOx/Zeol confirmed the presence of FMoOx bonding to the lower rings in the Zeol lattice structure. Raman bands observed at 1290 and 1440 cm$^{-1}$ regions correspond to $\nu$(C-O) and $\nu$(C-C) vibration, and $\nu$(C-O) and $\delta$(OCO) vibration of the Mo==oxalate ligand, respectively (Ng et al., 1985).

4.7.2 Catalytic Evaluation of FMoOx/Zeol Catalyst on HDO of Oleic Acid

4.7.2.1 Effect Reaction Time on the Hydrodeoxygenation of Oleic Acid

The product distribution profile of effect of HDO time on OA using the FMoOx/Zeol catalyst is shown in Figure 4.73. It can be observed that as the reaction progresses stearic acid (StA) was formed and reaches its peak of formation at about 30 min but disappeared after 60 min of reaction time. This was in agreement with what had earlier been reported that deoxygenation of unsaturated compound proceed via sequential hydrogenation to saturate the double bond followed by deoxygenation (Immer et al., 2010; Kovacs et al., 2011; Mortensena et al., 2011). The amount of both normal and isomerized octadecane (n-$\text{C}_{18}H_{38}$ and i-$\text{C}_{18}H_{38}$) which are considered as yield of target fractions (YTF) were observed to increase progressively until a maximum at 60 min producing about 59 and 26%, respectively. The presence of the isomerized product was due to the combined effect of OxA and fluoride ion
functionalization at the FMoOx/Zeol synthesis stage which increased it acidity thus making it favorable and active for n-paraffin skeletal isomerization (Kovacs et al., 2011). Generally, isomerized compounds are value added components of biofuel because of their comparably low freezing point which in turn enhances their cold flow properties (cold filter plugging points) (Kovacs et al., 2011). At 90 min of HDO time, the YTF were observed to reduce probably due to the prevalence of certain secondary reactions such as cracking and oligomerization which were evidenced by the increase in the amount of gases/vapor fraction. At 120 min, it became clear that oligomerization reactions is becoming prevalent over any possible cracking process as the fraction of >C<sub>18</sub> which was first observed at 60 min increases from about 3 to 12 % while the fraction of gases decreases.

Figure 4.73  Effect of time on the HDO of oleic acid into biofuel at 340 °C, 20 bar and 20 mg FMoOx/Zeol loading and 100 mL H<sub>2</sub>/min
4.7.2.2 Effect of Temperature on the Hydrodeoxygenation of Oleic Acid

The profile of effects of temperature and FMoOx/Zeol loading over a range of 320-380 °C and 10-30 mg, respectively on the yield of target fractions (YTF) of the HDO of OA at 20 bar and 100 mL H₂/min is shown in Figure 4.74. It can be observed that irrespective of the FMoOx/Zeol loading, temperature increments greatly enhanced the yield of both n-C₁₈H₃₈ and iso-C₁₈H₃₈. For example, considering the effect of temperature at the best observed FMoOx/Zeol loading of 30 mg, about 53% n-C₁₈H₃₈ and 64% n-C₁₈H₃₈ were obtained at 320 and 360 °C, respectively, similar observation was also true for the iso-C₁₈H₃₈ which showed about 19% and 30% at those temperatures. This shows that both the HDO and isomerization process of OA into high grade biofuel were in accordance with the established Arrhenius theory of temperature dependence of reaction rates, which implied that as the temperature was increased the molecules of the OA gained more kinetic energy in excess of activation energy to vigorously interact with the H₂ gas at the FMoOx/Zeol active sites.

Furthermore, since the viscosity of OA has an inverse relation with temperature, as the temperature was increased from 320 – 360 °C, the viscosity of OA decreased from 0.4021 – 0.2963cp (according to Aspen Hysys simulation) as seen in Figure 4.75 which in turn enhances both the H₂ mass transfer into the bulk of OA and its propensity for solubility in the reaction mixture. However, at 380 °C there was reduction in the YTF, this observation has also been reported in previous studies (Krár et al., 2010; Arend et al., 2011; Kovacs et al., 2011) on HDO process and it was ascribed to possible cracking of the already deoxygenated paraffin into smaller molecules. Another possible cause for this reduction could be what Krar et al., (2009) referred to as secondary reactions such as polymerization/ oligomerization, water–gas-shift (WGS) reaction, methanation and cyclization which we could not monitor at the time we conduct this study due to technical limitations.
Figure 4.74  Effect of temperature and FMoOx/Zeol loading on the HDO of oleic acid into biofuel at 20 bar and 100 mL H₂/min

Figure 4.75  Effect of temperature and FMoOx/Zeol loading on the ratio of i-C₁₈/n-C₁₈ biofuel compositions at 20 bar and 100 mL H₂/min. (also showing the effect of temperature on viscosity of oleic acid according to Aspen Hysys simulation)
4.7.2.3 Effect of FMoOx/Zeol Loading on the Hydrodeoxygination of Oleic Acid

The effect of FMoOx/Zeol loading at different temperature showed that its increase also increased the YTF as shown in Figure 4.74 because more FMoOx/Zeol active sites are made available for the reaction. The result showed more obvious increment in the YTF at all temperature as the FMoOx/Zeol loading was increased from 10 to 20 mg compared to the slight increment when increased from 20 to 30 mg. This was because at 10 mg loading the amount of FMoOx/Zeol was far too low for the process while the slight increment between 20 and 30 mg loading is a reflection that the FMoOx/Zeol loading is approaching stoichiometric saturation which implied that further loading may not increase the YTF rather a reduction could be observed due to initiation of some parallel (secondary) reactions (Krár et al., 2010; Kovacs et al., 2011). It is important to point out that at 320 °C the YTF at 20 and 30 mg FMoOx/Zeol loading does not reflect any significant increment, this implied that FMoOx/Zeol increment cannot enhance the HDO process beyond the thermodynamically feasible extent at that temperature.

A careful study of the effect of FMoOx/Zeol loading on the YTF (Figure 4.75) showed that the ratio of i-C_{18}/n-C_{18} was not constant but varied from 0.279 to 0.523 representing 10 mg FMoOx/Zeol loading at 320 °C and 30 mg FMoOx/Zeol loading at 380 °C, respectively. This varied observation implied that increased temperature and catalyst loading is important in order to increase the biofuel isomerized fraction which is an important component due to its low freezing point. This phenomenon can be explained from the stand point that isomerization process just like any other secondary reactions such as oligomerization process will definitely increase the demand of certain process requirements as earlier observed with the formation and increase in >C18 fraction ascribed to oligomerization process due to longer reaction time (Kwon et al., 2011; Mortensen et al., 2011).
4.7.3 Kinetics Studies of Hydrodeoxygenation of Oleic Acid

In view of the new catalyst synthesis protocol via the functionalization of Mo with OxA to develop an organometallic catalyst with considerable high acidity via fluoride ion modification, it is imperative to compare the kinetics and the Arrhenius parameter of FMoOx/Zeol with recent literature report. In the previous section and studies (Krár et al., 2010; Arend et al., 2011; Kovacs et al., 2011; Kwon et al., 2011), hydrodeoxygenation of OA has been observed to proceed via sequential hydrogenation to form saturated SA due to the presence of double bond in the OA structure, followed by oxygen molecule extraction to produce the final biofuel (Equation 4.18 – 4.19).

\[
\begin{align*}
\text{C}_{17}\text{H}_{33}\text{COOH} + \text{H}_2 & \rightarrow \text{C}_{17}\text{H}_{35}\text{COOH} \quad (4.18) \\
\text{C}_{17}\text{H}_{35}\text{COOH} + 3\text{H}_2 & \rightarrow \text{C}_{18}\text{H}_{38} + 2\text{H}_2\text{O} \quad (4.19)
\end{align*}
\]

In order to obtain the kinetic data for the stage-wise formation of the biofuel, a lumped kinetic model shown in Scheme 4.4 was adopted where SA represents all the intermediate compounds since its concentration is in excess of any other possible intermediate products (Ayodele et al., 2012b; Zhang et al., 2014). Similarly, since the concentration of OA is far in excess of H2 gas, a pseudo-first-order kinetics was assumed with respect to OA to determine the rate constants, \( k_i \) (\( i = 1, 2, 3 \)) (Ayodele et al., 2012b; Zhang et al., 2014) and also to verify if the SA formation step or its consumption step is the YTF rate controlling step. Prior to this study, three different agitation speed of 2000, 2500 and 3000 rpm were tested to study if there was any mass transfer limitation and the results showed negligible differences.
Scheme 4.4  Simplified lumped mechanism for the HDO kinetics of oleic acid

As earlier commented that HDO of OA usually proceed via sequential hydrogenation to saturate its double bond thus forming SA which implied that direct formation of the C_{18} biofuel may not be readily feasible. Therefore $k_1$ in Scheme 4.4 can be set to zero, consequently, the following sets of differential equations (Equation 4.20 – 4.26) were obtained.

\[ -\frac{dC_{OA}}{dt} = k_2 C_{OA} \]  \hspace{1cm} (4.20)

\[ \frac{dC_{SA}}{dt} = k_2 C_{OA} - k_3 C_{SA} \]  \hspace{1cm} (4.21)

From Equation 4.20,

\[ C_{OA} = C_{OA_0} e^{-(k_2)t} \]  \hspace{1cm} (4.22)

Substituting Equation 4.22 into Equation 4.21 gives Equation 4.23, which upon integration with boundary limits: when $t = 0$, $C_{OA} = C_{OA_0}$ and $C_{SA} = C_{SA_0} = 0$ gives rise to Equation 4.24.

\[ -\frac{dC_{SA}}{dt} = k_2 C_{OA_0} e^{-(k_2)t} - k_3 C_{SA} \]  \hspace{1cm} (4.23)

\[ C_{SA} = \frac{k_2 C_{OA_0}}{(k_3 - k_2)} [e^{-(k_2)t} - e^{-(k_3)t}] \]  \hspace{1cm} (4.24)
Consequently, the formation of C\textsubscript{18} biofuel can be obtained by substituting Equations (4.22) and (4.24) into Equation 4.25a. It is important to note that for ease of kinetic study both n-C\textsubscript{18}H\textsubscript{38} and i-C\textsubscript{18}H\textsubscript{38} formed are summed together as C\textsubscript{18} since their molecular formula and weight are same.

\[ i.e. \ C_{18} = C_{OA_0} - C_{OA} - C_{SA} \]  
\[ (4.25a) \]

\[ C_{18} = C_{OA} - C_{OA_0} \cdot e^{-(k_2)t} - \frac{k_2 C_{OA_0}}{(k_3 - k_2)} \left[ e^{-(k_2)t} - e^{-(k_3)t} \right] \]  
\[ (4.25b) \]

Rearranging Equation 4.25b gives Equation 4.26 which relates the C\textsubscript{18} biofuel production to the initial OA concentration as a function of reaction time.

\[ \frac{C_{18}}{C_{OA_0}} = \frac{1}{(k_3 - k_2)} \left[ k_3 (1 - e^{-(k_2)t}) - k_2 (1 - e^{-(k_3)t}) \right] \]  
\[ (4.26) \]

The experimental data of C\textsubscript{18} formation using FMoOx/Zeol at temperature range of 320 – 360 ºC were fitted into Equation 4.26 using MathCAD v13 and plotted as shown in Figure. 4.76, where \( \frac{C_{SA}}{C_{OA_0}} \) is denoted by \( Y(t) \) and it represents the developed kinetic model, while C\textsubscript{18}, is the experimental values. The plots showed there is a high degree of correlation between the experimental and the developed model with observed \( R^2 \) of 0.975, 0.963 and 0.955 for 320, 340 and 360 ºC, respectively. As previously observed, there was increase in the production of C\textsubscript{18} biofuel as both reaction time and temperature increased.
Figure 4.76 Experimental data fitting of the HDO of oleic acid at 20 mg catalyst loading, 10% H₂ gas flow and 20 bar
The rate constants obtained from Figure 4.76 are shown in Table 4.14 (after conversion to sec) and the results showed that the effect of temperature on the kinetics of HDO of OA perfectly conformed to the Arrhenius theory of temperature dependence of reaction rates as earlier observed. In addition, it can be observed that the sequential hydrogenation of the OA double bond to form SA is comparably favored and faster than the eventual C\textsubscript{18} formation which implied that the latter step is the reaction controlling step. Generally, the hydrogenation of OA (which is an addition reaction) is expected to be more feasible / spontaneous than deoxygenation at the same temperature especially considering their heat of reactions (H\textsubscript{R}) which is a measure of the amount of energy per mole either released or produced in a reaction. According to Aspen Hysys process simulator v7.2, the H\textsubscript{R} for Equation 4.18 and 4.19 are -1.091*10\textsuperscript{5} and -1.176*10\textsuperscript{5} kJ/mol, respectively using PRSV thermodynamic fluid package. The kinetic data in Table 4.14 were fitted into the Arrhenius equation (Equation 4.27) and plotted as shown in Figure 4.77 to evaluate the pre-exponential factor, A\textsubscript{o} (s\textsuperscript{-1}) and the activation energy, Ea (kJ/mol K).

\[
\ln k = \ln A_o - \frac{E_a}{RT}
\]  

\textbf{(4.27)}

| Table 4.14 | Evaluated rate constants for the hydrodeoxygenation of oleic acid |
|-------------|-----------------|-----------------|-----------------|
| Temperature (ºC) | 320 | 340 | 360 |
| k\textsubscript{2} (sec\textsuperscript{-1}) | 0.15 | 0.2 | 0.28 |
| k\textsubscript{3} (sec\textsuperscript{-1}) | 0.038 | 0.045 | 0.052 |
The $A_0$ values (which is the total number of collisions per second either leading to a reaction or not) evaluated from Figure 4.77 showed that SA formation step ($k_2$) has $22 \times 10^{-3}$ s$^{-1}$ which is higher than $23.1$ s$^{-1}$ obtained for the C$_{18}$ formation step ($k_3$). According to collision theory, the higher the amount of gas (H$_2$) present, the higher the $A_0$ values would be, however, since the H$_2$ gas would have been partly used in the OA sequential hydrogenation for the SA formation, some degree of reduction in the $A_0$ values for C$_{18}$ formation is expected as observed. The Ea for the SA and C$_{18}$ formation steps were 59 and 31.4 kJ/mole, respectively, the latter for the C$_{18}$ formation step is comparably lower than 190.9 kJ/mole recently reported by Kumar et al., (2014). The lower Ea obtained in this study can be ascribed to the effect of OxA functionalization which enhanced the catalytic activity of the FMoOx/Zeol via enhancement of textural properties, development of highly reactive octahedral Mo structure and the presence of the Mo-oxalate ligands (Li et al., 2012; Sousa et al., 2012; Tanev and Lange De Oliveira, 2012; Ayodele et al., 2014b).
4.7.4 Catalyst reusability

The catalyst reusability was tested at 360 °C, 100 ml/min H$_2$ gas flow rate and 20 bar in 60 min reaction time. The result showed that after three consecutive experiments the HDO and the isomerization efficiency were consistent at 64% n-C$_{18}$H$_{38}$ and 30% iso-C$_{18}$H$_{38}$. This is definitely due to the FMoOx/Zeol synthesis protocol that employs Mo-oxalate and functionalization with fluoride ion to form the fluoro-molybdenum-oxalate (FMoOx) complex. Generally supported metal-oxalate catalysts have been reported to me more reactive and highly resistance to leaching of the active metal due to the presence of the strong M$^+$ - oxalate ligand which also minimizes the tendencies of multiple side reactions (Tanev and Lange De Oliveira, 2012; Ayodele 2013). Similarly, fluoro-oxalate which belongs to the family of organofluoride compounds with a carbon–fluorine chemical bond has the strongest bond in organic chemistry with very high thermal and chemical stability (O'Hagan, 2008). These explain why both the HDO and the isomerization ability were consistent even after third experiment making a cumulative of 180 reaction min.
PART EIGHT

4.8 OPTIMIZATION OF CATALYTIC HYDRODEOXYGENATION OF OLEIC ACID INTO BIOFUEL USING FLUOROPLATINUM OXALATE ZEOLITE SUPPORTED CATALYST

4.8.1 Catalyst Characterization

4.8.1.1 Thermal Gravimetric Analysis (TGA)

TGA profiles for the Zeol, FPtOx/Zeol (uncalcined) and FPtOx/Zeol are shown in Figure 4.78 with three characteristics weight loss regions (WLR) which are typical of the alumino-silicates. The first WLR at a temperature slightly below 200 °C corresponds to loosely bonded water molecules and physisorbed water that can be readily removed under comparably mild thermal treatment (Ayodele and Togunwa, 2014). The second WLR at a temperature in the neighborhood of 400 °C is ascribed to the presence of strongly bonded water molecules that are usually domiciled in the first coordination sphere and as such cannot be removed under mild thermal treatment. The third WLR is due to the structural hydroxyl group that condenses and dehydrates at temperatures above 500 °C (Ayodele and Hameed, 2012). In the first WLR around 150 °C, both the Zeol and uncalcined FPtOx/Zeol samples showed almost same weight loss which implied that the drying stage was able to remove only the loosely bonded and physisorbed water molecules. The degree of hydration effect of the FPtOX precursor on the uncalcined FPtOx/Zeol at the catalyst synthesis stage began to show around 180 °C and became conspicuous until 700 °C. This is an indication that the catalyst synthesis protocol was able to guarantee the penetration of the FPtOX precursor into the Zeol matrix. After the calcination, the physisorbed, strongly bonded water and any partially occluded material were seen to have drastically reduced in the FPtOx/Zeol. However,
since the fluoride modified platinum-oxalate complex is thermally stable beyond the calcination temperature of 400 °C (Ghule et al., 2009) due to the fluoro-oxalate bond which belongs to the family of organofluoride compounds known to be the strongest bond in organic chemistry with very high thermal and chemical stability (O’Hagan, 2008). Thus, it can be concluded that the weight loss is not due to thermal decomposition of the Pt-oxalate complex, consequently the FPtOX precursor was successfully incorporated into the Zeol structure after calcination. Furthermore, proper calcination usually leads to removal of framework alumina thus increasing the FPtOx/Zeol surface area and porosity which in turn guarantees high active metal dispersion and increases the number of active sites on the catalyst (Xiaoling et al., 2012).

![Figure 4.78 TGA profiles of Zeol, FPtOx/Zeol (uncalcined) and FPtOx/Zeol](image-url)
4.8.1.2 Energy Dispersive X-ray (EDX)

The elemental composition of Zeol support and FPTOX/Zeol catalyst is shown in Table 4.15, the composition of the former are mainly silica and alumina with Si/Al ratio of 1.02, there are also instances of sodium and calcium which suggests a Zeolite A type (Yu et al., 2001). The Si/Al ratio increased to 2.32 in the FPTOX/Zeol after the catalyst synthesis. This increment was ascribed to dealumination in FPTOX/Zeol due to the combined effects of OxA and fluoride ion functionalization, and the subsequent thermal treatment during FPTOX/Zeol calcination stage. Previous reports (Xiaoling et al., 2012; Ayodele and Togunwa, 2014) have also shown that dealumination of extra-framework alumina and framework alumina can be achieved via acid and thermal treatments, respectively leading to increase in the Si/Al ratio, which in turn enhances synthesized catalyst activity. The successful incorporation of FPTOX into the structure of Zeol matrix seen in Table 4.15 is further validated in the EDX spectra in Figure 4.79 at 2.048 keV and 9.441 keV corresponding to Mα and Lα₁ series emission lines, respectively according to the standard card of peak identification (EDXRF-EPSILON 3 XL, PANalytical). The Pt peaks at 2.048 keV appears more significant than at 9.441 keV and these suggest two different Pt species could be present in FPTOX/Zeol. The observed Pt quantity of 4.71% was slightly below the expected value of 5% probably because of the high hydration degree at the FPTOX/Zeol synthesis stages (Ayodele and Hameed, 2012; Ayodele and Togunwa, 2014).

<table>
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<th>Al</th>
<th>O₂</th>
<th>Na</th>
<th>Ca</th>
<th>F</th>
<th>Pt</th>
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<tr>
<td>FPTOX/Zeol</td>
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<td>6.30</td>
<td>1.73</td>
<td>4.56</td>
<td>4.71</td>
<td>2.32</td>
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</table>
4.8.1.3 Scanning Electron Microscopy (SEM)

Figure 4.80 shows the morphology of Zeol (a) and FPtOx/Zeol (b), the morphology of Zeol suggested agglomerates of micro-sized cubical symmetry sharp crystal structure. However, upon incorporation of the acidic FPtOx precursor and calcination, there is a huge degree of morphological variation in the FPtOx/Zeol sample leading to loss of crystallinity, thus forming an amorphous material compared to Zeol. This change in the morphology is ascribed to the combined effects of OxA attack, functionalization with fluoride ion and calcination during the synthesis stage which resulted into dealumination of FPtOx/Zeol thus leading to increase the Si/Al ratio from 1.02 to 2.32 as earlier observed in the EDX results. This observation is in agreement with earlier works on alumino-silicates transformation from crystalline into amorphous form under varying degrees of acid attacks and thermal treatment leading to removal of extra framework and framework alumina, respectively and such transformation usually improves the activity of the synthesized catalysts (Xiaoling et al., 2012; Ayodele, 2013).
4.8.1.4 Nitrogen Adsorption Isotherms (BET method)

The nitrogen adsorption isotherms of Zeol and FPtOx/Zeol samples are shown in Figure 4.81, both samples exhibited a characteristic monolayer formation at lower relative pressure followed by multilayer typical of Type II isotherm. However, towards the high relative pressures, Zeol sample still tend to conform with the Type II isotherm, but the FPtOx/Zeol systematically conformed to Type IV isotherm with steep uptake of N\textsubscript{2} emphasizing the possible presence of inter-particle voids formed by agglomeration of the nano-sized and plate-like particles containing slit-shaped pores which are typical of H3 hysteresis (Xiaoling et al., 2012; Ayodele, 2013). This observation according to the IUPAC classification is generally observed for mesoporous solids which confirmed that the FPtOx/Zeol synthesis procedure also enhanced textural properties as seen in Table 4.16 (BET result). This is further confirmed by the obvious increment in the hysteresis loop of FPtOx/Zeol at P/P\textsubscript{0} = 0.3–1.0 compared to Zeol which implied increase in mesopore formation.
As previously reported (Xiaoling et al., 2012; Aoydele, 2013), morphological variation leading to amorphization of erstwhile crystalline material (as seen in the SEM morphology, Figure 4.80) usually resulted into enhancement of the textural properties (Table 4.16, BET result) provided the effects of acid and/or thermal treatments are not excessive to destroy the alumino-silicate structural template. The enhanced surface area is considered an advantage for the HDO of OA into biofuel because more effective surface area will be made available for the active metal thus guarantee high Pt dispersion. This will minimize the reacting molecules competition to access the active metals on the amorphous surface of FPtxO/Zeol hence increasing the rate of HDO reaction. In addition, since isomerized product(s) is expected, surface reaction will be more favourable than pore reaction which may hinder the diffusion of branched-chain-products out of the pores.
Table 4.16  Textural properties of Zeol and FPtOx/Zeol samples

<table>
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<tr>
<th>Sample</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore diameter (nm)</th>
<th>Particle size (nm)</th>
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4.8.1.5 X-ray Diffraction (XRD)

The X-ray diffraction pattern of Zeol and FPtOx/Zeol samples are shown in Figure 4.82. The highly crystalline characteristic peaks at 20 value of 7.2, 10.0, 12.4, 16.0, 21.6, 24.0, 27, 30.0 and 34.0° confirmed Zeol support to be zeolite A according to the JCPDS card 43-0142 (Yang et al., 2009). The crystallinity of Zeol peaks are in agreement with the earlier observation in the SEM morphology (Figure 4.80). After the FPtOx/Zeol synthesis, there is loss of crystallinity in those peaks due to the effects of oxalic acid, fluoride ion functionalization and calcination during the synthesis stage as earlier noted. Recent studies (Yang et al., 2009; Horácek et al., 2013) also reported that modification of zeolite with Pt loading above 3.41% in acidified medium resulted into the amorphization of the Pt-modified zeolite, which in turn increased the Si/Al ratio due to combined dealumination in the framework and extra framework positions thus enhancing the hydrogenation and dehydrogenation ability of the catalyst. Furthermore, it can be seen that the peaks of the Zeol and FPtOx/Zeol diffractograms cannot be easily differentiated which indicated that the functionalized Pt particles were finely dispersed. However, a closer examination revealed that there is a marginal shift to the right in the diffraction peaks of FPtOx/Zeol relative to Zeol due to intimate contact of FPtOx with the Zeol lattice structure thus expanding it to form a homogeneous FPtOx/Zeol catalyst after synthesis (Ghule et al., 2009; Bang et al., 2013). This homogeneity is a
confirmation of high Pt particles dispersion thus preventing sintering which is further corroborated by the absence of the usual bulk Pt crystalline peak at 20 value of 39.6° earlier ascribed to Pt sintering (Liu et al., 2012).

![Figure 4.82 X-ray diffraction patterns of Zeol and FPtOx/Zeol samples](image)

4.8.1.6 Fourier’s Transform Infrared Spectroscopy (FTIR)

Figure 4.83 shows the FTIR spectroscopy of the Zeol support and FPtOx/Zeol catalyst, the former reflects the vibration of the Si–OH and adsorbed water molecules in the region 3700 – 2900 cm\(^{-1}\) with a minimal around 3317 cm\(^{-1}\). Another band which can be ascribed to the bending vibration of the adsorbed water molecules is seen at 1650 cm\(^{-1}\) (Ayodele et al., 2014a). The adsorbed water molecules in the region 3700 – 2900 cm\(^{-1}\) and 1650 cm\(^{-1}\) can be seen to have disappeared in FPtOx/Zeol after calcinations which
implied that the thermal treatment during the calcination stage was sufficient. Since the presence of water molecules usually cause agglomeration of active metals in zeolite lattice structure resulting in loss of catalytic activity (Ohtsuka and Tabata, 1999), the disappearance of those water molecule bands further confirmed the high Pt dispersion earlier discussed in the XRD result. Previous studies (Ohtsuka and Tabata, 1999; Li et al., 2012; Ayodele et al., 2014a) also showed that appropriate thermal treatment guarantees high metal dispersion in supported catalysts. According to those reports, the presence of such metals are usually observed towards the lower wavenumber as seen in the spectrum of FPtOx/Zeol which showed significant mismatch from the Zeol spectrum after 1209 cm$^{-1}$ (especially at 680 and 556 cm$^{-1}$) indicating structural modification in FPtOx/Zeol caused by the intercalation of FPtOx specie. No specific Pt – X (X = Al, Si, O) bond was seen in the FPtOx/Zeol spectrum which was quite similar to the earlier observation in the XRD plot due to high metal dispersion, thus there is need for Raman spectroscopy analysis which is more versatile for metal-support interactions.

Figure 4.83   FTIR spectra of Zeol and FPtOx/Zeol samples
4.8.1.7 Raman spectroscopy

The spectra in Figure 4.84 showed the characteristic bands of Zeol and the consequent effect of FPtOx incorporation in the FPtOx/Zeol sample. The bands at 280, 330, 405, 490, 700, 977, 1030 and 1150 cm\(^{-1}\) are typical of zeolite A having 4-, 6- and 8- membered rings (Yu et al., 2001). Previous reports (Yu et al., 2001; Yang et al., 2009) have assigned the band at 280 cm\(^{-1}\) in the Zeol sample to the bending mode of rings higher than 4- and 6-membered rings, possibly of the 8 membered rings of zeolite A since higher rings give bands at lower wavenumber and vice versa. Similarly, the bands at 330 and 405 cm\(^{-1}\) are due to the bending mode of 6-membered Si-O-Al rings while the strongest band at 490 cm\(^{-1}\) is assigned to the bending mode of 4-membered Si-O-Al rings (Yu et al., 2001; Ayodele et al., 2014a). Similarly, the bands at 977, 1030 and 1150 cm\(^{-1}\) are ascribed to asymmetric T-O stretching motions (T = Si or Al) (Yu et al., 2001). After the FPtOx/Zeol synthesis, the distinctive bands at 490 cm\(^{-1}\) lost its uniqueness, while those at 800 and 977 disappeared completely probably due to the dealumination of the extra framework and framework alumina as a result of fluoride ion/OxA functionalization and calcinations, respectively. This observation is in accordance with the loss of crystallinity earlier observed in the SEM and XRD results. Furthermore, there were series of multiple stretches of vibrations in FPtOx/Zeol which are reflections of the presence of organic carbonate anion (CO\(_3^{2-}\)) from oxalate. The oxalate free ion of CO\(_3^{2-}\) with D\(_{3h}\) symmetry usually exhibits four normal vibrational modes viz; doubly degenerate bending mode (\(v_4\)) around 680 cm\(^{-1}\), an out-of-plane bend (\(v_2\)) around 879 cm\(^{-1}\), a symmetric stretching vibration (\(v_1\)) around 1063 cm\(^{-1}\) and lastly a doubly degenerate antisymmetric stretch (\(v_3\)) around 1415 cm\(^{-1}\) (Ray et al., 2006). These observed multiple stretches is similar to the aggressive peaks and multiple background noise-like vibrations which previous report have attributed to the presence of organic functional group (Ghule et al., 2009; Bang et al., 2013).
According to recent studies (Ghule et al., 2009; Ghule et al., 2010; Bang et al., 2013) using Raman spectroscopic techniques, absorption and adsorption mechanisms have been identified as means of active metal incorporation into supports. Absorption is characteristics of low oxidation state metals that can be accommodated into the surface of the support to form a surface spinel and they usually possess Raman bands between \(~300 – 800\) cm\(^{-1}\). Similarly, adsorption is typical of metals with high oxidation state that cannot be accommodated into the matrix of supports and they reflect strong Raman bands at \(~900-1200\) cm\(^{-1}\). From the Raman spectrum of FPtOx/Zeol, the bands at 553, 630, 668, 694 and 754 cm\(^{-1}\) are ascribed to tetrahedral coordinate of plantinum II oxalate (Pt\(^{2+}\)) complex which have been reported to be active catalyst for hydrogenation and hydrogenolysis reactions (Scheeren et al., 2008). The growing bands at 1030 cm\(^{-1}\) and the peaks at 1060, 1120 cm\(^{-1}\) and between 1000-900 cm\(^{-1}\) are ascribed to octahedral
coordinate geometry of Pt$^{4+}$ - oxalate complex (Greenwood and Earnshaw, 1997; Ghule et al., 2009; Ghule et al., 2010; Bang et al., 2013) which according to previous study (Li et al., 2012) was highly active for hydrodemetallation and hydrodeoxygenation processes. Since previous reports (Bernas et al., 2010; Immer et al., 2010; Arend et al., 2011; Kovacs et al., 2011; Lapuerta et al., 2011) have shown that hydrodeoxygenation of oleic acid and other unsaturated feed stocks proceed via sequential hydrogenation and subsequent deoxygenation steps, the presence of Pt$^{2+}$ and Pt$^{4+}$ in the synthesized FPtOx/Zeol is an indication to its potential excellent catalytic activity. The identification of Pt$^{2+}$ and Pt$^{4+}$ in the synthesized FPtOx/Zeol is synonymous to the presence of two different peaks at 2.048 keV and 9.441 keV corresponding to Mα and Lα₁ series emission lines, respectively in the EDX result (Figure 4.79) and can be ascribed to partial thermal decomposition of the platinum oxalate during calcination.

4.8.2 D-Optimal Experimental Design

4.8.2.1 Regression Model Development and Analysis

The result generated from performing experimental runs on the process variables (A, B, C and D) in the varied conditions shown in Table 4.17 are presented in Table 4.18 showing both the experimental and predicted response values. The coefficients of the polynomials, independent variables and their interaction effects on the response function Y (n-C$_{18}$H$_{38}$) and Z (n-C$_{18}$ H$_{38}$) were determined. The corresponding statistical polynomial models obtained by multiple regressions are shown in Equation 4.28 – 4.29.
Table 4.17  Range of selected independent variables

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Table 4.18  Experimental design and response based on experimental runs proposed by D-optimal design

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\[ Y = 71.25 + 5.52A + 4.22B + 3.29C + 7.24 \* D - 17.57A^2 - 14.31B^2 - 8.37C^2 - 16.14D^2 + 5.34AB - 1.99AC + 5.53AD + 1.98BC + 4.93BD + 1.10CD. \] (4.28)

\[ Z = 29.47 + 3.22A + 2.33B + 2.18C + 5.66D - 7.71A^2 - 6.49B^2 - 0.85C^2 - 4.36D^2 + 0.58AB - 0.67AC + 2.70AD + 0.55BC + 0.97BD + 1.94CD \] (4.29)

In order to establish and ascertain a correlation between the model predictions and the experimental responses for both \( Y \) and \( Z \), analysis of variance (ANOVA) was used to test the goodness of fit for the polynomial coefficients in Equation 4.28 and 4.29 and the results are presented in Table 4.19. The values of mean squares were obtained by dividing the sum of squares for each variation by their respective degrees of freedom (DF). Similarly the F-values were calculated by dividing the obtained mean squares with the respective residual mean square (i.e. 9.24 for model \( Y \) and 8.84 for model \( Z \)). The Model F-value is 77.77 and 15.30 for the response function \( Y \) and \( Z \), respectively, and these values implied that the models are significant and there is less than 0.01% probability that Model F-Values this large could occur due to model error or noise, although it may be associated to experimental error (Ayodele et al., 2012b). For model analysis, values of "Prob > F" less than 0.0500 indicate model terms are significant. In the case of HDO process A, B, C, D, \( A^2 \), \( B^2 \), \( C^2 \), \( D^2 \), \( AB \), \( AC \), \( AD \), \( BC \), \( BD \) are significant model terms. However, only A, B, C, D, \( A^2 \), \( B^2 \), \( AD \), \( CD \) are significant model terms for the ISO process. These results showed that all the process parameters studied have individual significance for both the HDO and ISO processes.
Table 4.19   ANOVA test for the response model Y (Hydrodeoxygenation process) and Z (Isomerization process)

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>DF</th>
<th>Mean Square</th>
<th>F Value</th>
<th>Prob &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y (Hydrodeoxygenation process)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Model</td>
<td>10071.27</td>
<td>14</td>
<td>719.37</td>
<td>77.77</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>A</td>
<td>459.62</td>
<td>1</td>
<td>459.62</td>
<td>49.69</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>B</td>
<td>269.59</td>
<td>1</td>
<td>269.59</td>
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</tr>
<tr>
<td>C</td>
<td>158.74</td>
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<td>158.74</td>
<td>17.16</td>
<td>0.0020</td>
</tr>
<tr>
<td>D</td>
<td>656.85</td>
<td>1</td>
<td>656.85</td>
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</tr>
<tr>
<td>A²</td>
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</tr>
<tr>
<td>B²</td>
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<td>456.76</td>
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</tr>
<tr>
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<tr>
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<tr>
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<tr>
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<td>5.239</td>
<td>0.0451</td>
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<tr>
<td>AD</td>
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<td>377.11</td>
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<tr>
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<tr>
<td>BD</td>
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<td>32.26</td>
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<tr>
<td>CD</td>
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<td>1</td>
<td>14.23</td>
<td>1.545</td>
<td>0.2422</td>
</tr>
<tr>
<td>Residual</td>
<td>92.49</td>
<td>10</td>
<td>9.24</td>
<td></td>
<td></td>
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<tr>
<td>Lack of</td>
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<td>5</td>
<td>15.99</td>
<td>6.399</td>
<td>0.0313</td>
</tr>
<tr>
<td>Fit</td>
<td>Pure Error</td>
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<td>5</td>
<td>2.5</td>
<td>4.75</td>
</tr>
<tr>
<td></td>
<td>Error</td>
<td>1813.7</td>
<td>24</td>
<td></td>
<td>1984.5</td>
</tr>
<tr>
<td>Cor</td>
<td>Total</td>
<td>10163.7</td>
<td>24</td>
<td></td>
<td>1984.5</td>
</tr>
</tbody>
</table>
From Table 4.20, the obtained $R^2$ for the HDO and ISO models are 0.9909 and 0.9855, respectively. Similarly, their adjusted regression coefficient, $R^2_{adj}$, that corrects regression coefficient, $R^2$, based on the number of terms in the models and the sample size (Ayodele et al., 2012c) are 0.9782 and 0.9548, respectively. Generally, if a model contains many terms and has small sample size this could result in a much lower $R^2_{adj}$ compared to $R^2$ (Ayodele et al., 2012b; Ayodele et al., 2012c), in these cases the models have high $R^2$ and $R^2_{adj}$ which indicated that the chosen quadratic model for response surface method (RSM) adequately describe the experimental data in the range of the operating parameters. Furthermore, the "Pred R-Squared" of 0.8511 and 0.8325 are in reasonable agreement with the "Adj R-Squared" of 0.9782 and 0.9548 for the HDO and ISO models, respectively. The "Adeq Precision" that measure models signal to noise ratio is 24.440 and 12.185 for the HDO and ISO model, respectively. Generally, an "Adeq Precision" value of 4 implies the signal is desirable (Multifactor RSM Tutorial, 2008), thus the values obtained for the two models are desirable.

<table>
<thead>
<tr>
<th></th>
<th>HDO model</th>
<th>ISO model</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-Squared</td>
<td>0.9909</td>
<td>0.9855</td>
</tr>
<tr>
<td>Adj R-Squared</td>
<td>0.9782</td>
<td>0.9548</td>
</tr>
<tr>
<td>Pred R-Squared</td>
<td>0.8511</td>
<td>0.8325</td>
</tr>
<tr>
<td>Adeq Precision</td>
<td>24.44</td>
<td>12.185</td>
</tr>
</tbody>
</table>

### 4.8.2.2 Regression Model Validation

Typically for model validation to check if there are any deficiencies and/or discrepancies in the model fitting to the experimental data, the plot of run number vs. outlier T points (Figure 4.85a – b) and the plot of internally studentized residuals vs.
normal probability (Figure 4.86a – b) are the most reliable source of information. For example, the plot of run numbers vs. outliers T points had been used to evaluate the assumption of constant variance (Ayodele et al., 2012b). It can be seen from Figure 4.85a – b that the points are structureless and randomly scattered which indicated that all the information are well extracted and the residuals are independent of other variables (Multifactor RSM Tutorial, 2008). In addition, all the points lie within the top outlier (+3.5) and bottom outlier (-3.5) detection limits, which implied that the response transformation is appropriate and successful in capturing the correlation between the four studied parameters influencing both the HDO and ISO of oleic acid into paraffinic biofuel (Multifactor RSM Tutorial, 2008; Ayodele et al., 2012b; Ayodele et al., 2012c).

![Figure 4.85](image)

Figure 4.85   Diagnostics of (a) model Y and (b) model Z based on Internally Outliers T Points

Similarly, the normal probability plot in Figure 4.86a – b shows orchestrated points and points constellation around the diagonal line which is an indication of the homogeneity of the error variances and independent style of the residuals which
confirmed that errors are normally distributed and independent of each other (Multifactor RSM Tutorial, 2008; Ayodele et al., 2012b).

![Figure 4.86 Normal probability of residuals diagnostics of models (a) Y and (b) Z](image)

**4.8.3 Response Surface Plot for the Oleic Acid HDO and ISO Process into Paraffinic Biofuel**

**4.8.3.1 Effect of Reaction Time and FPtOx/Zeol Loading**

The plot of effect of reaction time on the HDO of OA into n-C_{18}H_{38} is shown in Figure 4.87a while Figure 4.87b shows same for the n-paraffin skeletal isomerization (ISO) into iso-C_{18}H_{38}. The presence of iso-C_{18}H_{38} was due to the combined effects of OxA and fluoride ion functionalization during the FPtOx/Zeol syntheses stage which increased its acidity.
Figure 4.87  Effect of time and FPtOx/Zeol loading on the HDO and ISO of oleic acid into paraffinic biofuel at 20 bar, 360 °C and 100 mL H₂/min
Previous reports (Kovacs et al., 2011; Ayodele et al., 2014) on acidified catalysts also reported n-paraffin skeletal isomerization which they referred to as highly invaluable due to its ability to improve the biofuel cold flow properties by reducing its freezing point. The plot showed that irrespective of the FPtOx/Zeol loading increase in time enhances the efficiency of both the HDO and ISO process. However, at a relatively longer reaction time above 60 min, the n-C_{18}H_{38} production reduced irrespective of the FPtOx/Zeol loading, but the iso-C_{18}H_{38} production was seen to be favored even up to 90 min. The increase in the production of both n-C_{18}H_{38} and iso-C_{18}H_{38} was simply because there is more time for the reactions to progress, however, the sudden reduction observed after 60 min for the n-C_{18}H_{38} production could be ascribed to certain parallel secondary reactions such as cracking, isomerization and oligomerization / polymerization reactions (Huber et al., 2007; Bernas et al., 2010; Immer et al., 2010; Arend et al., 2011; Kovacs et al., 2011; Lapuerta et al., 2011). This elucidates why the iso-C_{18}H_{38} production increases up to 90 min especially at higher catalyst loading since iso-C_{18}H_{38} is a product of the secondary reaction of n-paraffin skeletal isomerization process (Kovacs et al., 2011; Ayodele et al., 2014).

Furthermore, it can also be observe that increase in FPtOx/Zeol loading enhanced both the n-C_{18}H_{38} and iso-C_{18}H_{38} productions. However, just as previously observed on the effect time, the n-C_{18}H_{38} production reduced when the FPtOx/Zeol loading exceeded 30 mg (Figure 4.87a), but the reduction is not very pronounced in the iso-C_{18}H_{38} productions. The initial increment in the n-C_{18}H_{38} and iso-C_{18}H_{38} production was due to the fact that as the FPtOx/Zeol loading was increased more Pt active sites were made available for the HDO and ISO reaction (Kovacs et al., 2011; Ayodele et al., 2014). Similarly, the reduction in the n-C_{18}H_{38} production could imply that FPtOx/Zeol has been superfluous increased thus introducing excessive active sites for multiple reactions thereby proliferating the propensity for those secondary reactions that
scavenges on the already hydrodeoxygenated n-C\textsubscript{18}H\textsubscript{38}. The minuscule reduction in the iso-C\textsubscript{18}H\textsubscript{38} production as FPtOx/Zeol loading increases especially at longer reaction time is definitely due to the fact that ISO process is a secondary reaction as earlier opined and previously reported (Huber et al., 2007; Bernas et al., 2010; Immer et al., 2010; Arend et al., 2011; Kovacs et al., 2011; Lapuerta et al., 2011), thus it will need additional process parameter requirements.

4.8.3.2 Effect of Reaction temperature

The effect of temperature on the HDO of OA into n-C\textsubscript{18}H\textsubscript{38} is shown in Figure 4.88a while Figure 4.88b shows same for the n-paraffin skeletal isomerization into iso-C\textsubscript{18}H\textsubscript{38}. The plots clearly showed that as the reaction temperature increases both the HDO and the ISO efficiencies significantly improved. For example, as the temperature was increased from 340 to 360 °C the yield of n-C\textsubscript{18}H\textsubscript{38} increased from about 32 to 65%, similarly, iso-C\textsubscript{18}H\textsubscript{38} yield also increases from about 7 to 28% at 20 bar. At 380 °C, both HDO and ISO efficiencies were seen to have reduced to about 45 and 18 %, respectively. This observation and the RSM plots pattern were similar to the report of Arend et al., (2011) in the study of OA deoxygenation using palladium supported on carbon catalyst. The enhanced efficiencies observed as the temperature was raised can be ascribed to two important phenomena. Firstly, as the temperature was increased the rate of both HDO and ISO reactions increased exponentially in accordance to the Arrhenius theory of reaction rates dependence on temperature (Guzman et al., 2010). Which implied that as the temperature was increased both the OA and the H\textsubscript{2} molecules were able to gain sufficient kinetic energy in excess of activation energy hence colliding more rigorously at faster rate leading to higher rate of product formation.
Figure 4.88  Effect of pressure and temperature on the HDO and ISO of oleic acid into paraffinic biofuel at 20 mg FPtOx/Zeol loading and 90 min
Secondly, in a previous study (Ayodele et al., 2014c) on the upgrading of OA into high grade biofuel using Mo modified zeolite supported Ni oxalate catalyst, it was observed in a transport properties simulation study using Aspen Hysys that increase in temperature of OA has an inverse relation with its viscosity. Consequently, increase in temperature will reduces OA viscosity and lower its surface tension which in turn enhances both the H\textsubscript{2} mass transfer into the bulk of OA and its propensity for solubility in the reaction mixture. The reduction in the yield of n-C\textsubscript{18}H\textsubscript{38} and iso-C\textsubscript{18}H\textsubscript{38} at 380 °C were probably due to certain secondary reactions like cracking and oligomerazation / polymerization reactions (Arend et al., 2011; Kovacs et al., 2011; Ayodele et al., 2014c). This reduction appeared to be more pronounced in the n-C\textsubscript{18}H\textsubscript{38} than iso-C\textsubscript{18}H\textsubscript{38} which confirmed that ISO as a secondary process will still be more comparably favored than the HDO at extremes conditions.

4.8.3.3 Effect of Reaction Pressure

The plot of effect of pressure variation of the HDO and ISO process were also shown in Figure 4.88a and Figure 4.88b, respectively. The parabolic observation on the effect of temperature is also seen in the effect of pressure although with varying degree. Increase in the reaction pressure from 10 to 20 atm at 340 °C enhanced both the n-C\textsubscript{18}H\textsubscript{38} and iso-C\textsubscript{18}H\textsubscript{38} production from 27% to 35% and 8% to 16%, respectively. The increment in the HDO and ISO process could be ascribed to the increase in H\textsubscript{2} partial pressures leading to its enhanced mass transfer into the bulk of the OA at the FPtOx/Zeol surface. In addition, the increase in pressure guarantee sufficient residence time for the reacting molecules to react at the FPtOx/Zeol surface before detaching off into the bulk of the reaction. However, at higher pressure of 30 bar the n-C\textsubscript{18}H\textsubscript{38} and iso-C\textsubscript{18}H\textsubscript{38} production showed reduction probably due to the inability of the hydrodeoxyxygenated fractions to detach from the FPtOx/Zeol surface thereby initiating
secondary reaction such as oligomerization (Kovacs et al., 2011; Ayodele et al., 2014c).
In view of this observation, Arend et al., (2011) recently proposed relatively reduced pressure for the HDO process in order to enhance quick desorption of reaction products from the catalyst surface to prevent catalyst deactivation.

4.8.4 Optimization (Desirability Plot) and Validation of Results

The four process parameters were optimized by setting their outcome values to minimum and the response functions \( Y \) and \( Z \) to maximum. The desirability plot in Figure 4.89(a-d) showed that about 58 min, 27.8 mg FPtOx/Zeol loading, 18 bar and 364 °C is sufficient to produce 28.39% iso-\( \text{C}_{18}\text{H}_{38} \) and 68.93% n-\( \text{C}_{18}\text{H}_{38} \). These results were validated in repeated experiments and the average values (of the 3 runs) were plotted in Figure 4.90. It is interesting to observe that the 26% of iso-\( \text{C}_{18}\text{H}_{38} \) production obtained was lower than the 28.39% predicted in the desirability plot. Similarly, the 70% obtained for n-\( \text{C}_{18}\text{H}_{38} \) was slightly higher than the 68.93% predicted in the desirability plot. These variations cannot be ascribed to inadequacy of the quadratic models \( (Y \) and \( Z \)) because they have been adequately validated as shown in Figure 4.85 – 4.86. Consequently, we ascribed these variations to the fact that the desirability plot predicted comparably lower FPtOx/Zeol loading and time, however, as earlier reported (Arend et al., 2011; Kovacs et al., 2011; Ayodele et al., 2014c) isomerization process is a secondary reaction which will undoubtedly require slightly stringent or increased process parameters. This explains why the n-\( \text{C}_{18}\text{H}_{38} \) production was higher than the predicted since the process condition was not stringent enough to favor more n-paraffin isomerization. The presence of marginal >C18 product(s) and gases could be ascribed to the relatively higher reaction temperature and slightly reduced pressure (compared to those conditions in Figure 4.87 – 4.88) which subsequently favors partial cracking and oligomerization of the already hydrodeoxygenated paraffin.
Figure 4.89  Desirability plot
FPtOx/Zeol Reusability Studies

The reusability study of FPtOx/Zeol was conducted at the process condition obtained from the desirability study (58 min, 27.8 mg FPtOx/Zeol loading, 18 bar and 364 °C). The result showed that FPtOx/Zeol activity was consistent in three separate runs producing 28 ± 0.7% iso-C_{18}H_{38} and ~69% n-C_{18}H_{38}. This ability is undoubtedly due to the effect of OxA and fluoride ion functionalization and proper calcination. Previous study (Ayodele, 2013) have successfully established that metal-oxalate ligands are highly resistant to leaching, in addition, fluoro-oxalate complex which belongs to the organo-fluoride compounds having a carbon–fluorine chemical bond are strongest bond in organic chemistry with very high thermal and chemical stability (O’Hagan, 2008). According to a previous US patents (Tanev and Lange De Oliveira, 2012), the ability of oxalate organometallic catalysts to minimized the formation of side reaction...
could also be responsible for high reusability of FPtOx/Zeol since the reaction load on it would be minimized which will in turn prevent the formation of catalyst poisoning intermediate species.

4.9 Comparative Summary of the Hydrodeoxygenation Process

The simulation results established a range of the thermodynamic feasible operating conditions for the reaction temperature, stoichiometry ratio and pressure for the hydrodeoxygenation (HDO) process of oleic acid (OA) and stearic acid (SA) into paraffinic biofuel. Although there are variations in the simulation and experimental results as expected, but the simulation results served as a veritable template and guide for the catalytic hydrodeoxygenation of OA and SA. In order to validate the simulation results in experimental study, two different sets of supported catalysts were synthesized. The first set of catalysts were two nickel based catalysts supported on alumina, the first catalyst was nickel on alumina (Ni/Al₂O₃) prepared via incorporation of inorganic Ni precursor from nickel nitrate into Al₂O₃. The second was an organometallic catalyst of nickel oxalate supported on alumina (NiOx/Al₂O₃) and it was synthesized via the incorporation nickel oxalate (NiOx) precursor prepared by functionalization of Ni with oxalic acid (OxA).

Both catalysts were characterized for physical and chemical properties and the results showed that Ni species present in Ni/Al₂O₃ was 8.2% while 9.3% was observed for NiOx/Al₂O₃ according to the energy dispersive X-ray (EDX) result. Although the Ni content of both samples were below the expected value 10% due to the degree of hydration at their synthesis stage, the comparably higher value of the NiOx/Al₂O₃ was due to the OxA functionalization because NiOx is highly insoluble in water. Furthermore, X-ray fluorescence, X-ray diffraction, Fourier transform infrared and
Raman spectroscopy results showed that Ni species in NiOx/Al₂O₃ was highly dispersed due to the OxA functionalization which also modified the textural and morphological properties as seen in the N₂ adsorption/desorption and scanning electron microscopy results, respectively. The activities of both Ni/Al₂O₃ and NiOx/Al₂O₃ were validated on the HDO of OA based on the range of values from the simulation study. NiOx/Al₂O₃ did not only showed the best catalytic and reusability abilities, but it also possesses isomerization ability as a result of the OxA functionalization which increased its acidity. The NiOx/Al₂O₃ also has the highest rate constants evaluated using pseudo-first-order kinetics, but the lowest overall activation energies. A more critical analysis of the activation energy revealed that 38.5 kJ/mole and 63.6 kJ/mole would be saved if NiOx/Al₂O₃ is used instead of Ni/Al₂O₃.

In view of the enhanced HDO activity and the additional isomerization ability of the organometallic catalyst (NiOx/Al₂O₃) due to the increased acidity, fluoropalladium oxalate supported on zeolite catalyst (FPdOx/Zeol) was synthesized via functionalization of palladium oxalate with fluoride ion to further enhance its acidity and ensure formation of Pd²⁺ complexes. Both FPdOx/Zeol and the non-fluoro palladium oxalate (PdOx/Zeol) were characterized and their activities were tested on OA. According to the SEM, XRD and EDX characterization results, both catalysts showed loss of crystallinity with increase in the Si/Al ratio due to effect of OxA functionalization and calcination which removed the extra framework and framework alumina, respectively. However, the loss of crystallinity appears to be more intense in the FPdOx/Zeol catalyst due to the fluoride ion functionalization which was also verified by the presence of fluoride in the EDX result (Table 4.21). In addition, both Raman spectroscopy and XRD results showed that Pd particles are more highly dispersed in FPdOx/Zeol than in PdOx/Zeol catalyst. Furthermore, the increased acidity due to fluoride ion functionalization enhanced the textural properties of FPdOx/Zeol
compared to PdOx/Zeol which increases its surface area and porosity according BET result. Their catalytic activities showed that both FPdOx/Zeol and PdOx/Zeol have almost same HDO products, but FPdOx/Zeol possesses higher isomerization activities producing 28% iso-C_{18}H_{38} compared to 11% produced by PdOx/Zeol (Figure 4.91).

Table 4.21  Elemental composition of alumina, Zeol and all supported catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si</th>
<th>Al</th>
<th>O_2</th>
<th>Na</th>
<th>Ca</th>
<th>F</th>
<th>Mo</th>
<th>Ni</th>
<th>Pd</th>
<th>Pt</th>
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<td>0</td>
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<tr>
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</tr>
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<td>NiOx/Al_2O_3</td>
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<td>FMoOx/Zeol</td>
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<td>6.39</td>
<td>56.74</td>
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<td>2.60</td>
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</tr>
<tr>
<td>FPtOx/Zeol</td>
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<td>NiMoFOx/Zeol</td>
<td>16.28</td>
<td>6.70</td>
<td>51.75</td>
<td>4.74</td>
<td>1.98</td>
<td>4.20</td>
<td>4.89</td>
<td>9.46</td>
<td>0</td>
<td>0</td>
<td>2.43</td>
</tr>
</tbody>
</table>

*: Determine by Elemental Dispersive X-ray.

Sequel to the enhanced physical and chemical properties and catalytic activity of FPdOx/Zeol, molybdenum and platinum were equally functionalized with fluoride ion and oxalic acid, in addition, a bimetallic catalyst of Ni and Mo was also functionalized and all the catalysts were supported on zeolite and characterized. Their best observed hydrodeoxygenation of OA results are summarized in Figure 4.91. It is obvious that NiMoFOx/Zeol has the highest HDO product while FMoOx/Zeol has the best isomerization ability. As previously discussed, the best HDO ability displayed by
NiMoFOx/Zeol can be ascribed to the combined synergy of Ni and Mo metals having high dispersions owing to influence of the OxA and fluoride ion functionalization. Similarly, the highest isomerization ability of the FMoOx/Zeol was ascribed to its high acidity due to its high fluoride content as seen in Table 4.21.

Figure 4.91  Summary of hydrodeoxygenation process of oleic acid using synthesized catalysts at the best experimental conditions

A comparison of Ni/Al₂O₃ and NiOx/Al₂O₃ in Figure 4.91 showed that the latter has both superior HDO and isomerization abilities due to the OxA functionalization which also explained why Ni/Al₂O₃ has the lowest HDO product and parsimonious isomerization ability even among all the synthesized and tested catalyst. The HDO product of 63% n-C₁₈H₃₈ observed in NiOx/Al₂O₃ seem close to the 65% n-C₁₈H₃₈ of
FMoOx/Zeol, but a closer study showed that since FMoOx/Zeol has higher iso-C$_{18}$H$_{38}$ of 26% compared to about 16.5% in NiOx/Al$_2$O$_3$. It can be still concluded that FMoOx/Zeol has a better prospect towards industrial application considering the fact that isomerization process is a secondary reaction using already produced n-paraffin as the substrate. Furthermore, it is worth noting that the active metal loading in FMoOx/Zeol is essentially lower than in NiOx/Al$_2$O$_3$ (though they are different metal species) i.e. Mo and Ni loading on FMoOx/Zeol and NiOx/Al$_2$O$_3$ are 9.21% and 9.3%, respectively, although the catalysts different supports could also have certain contributory effects which are not studied in this report. This conclusively confirmed that FMoOx/Zeol is more promising, though comparison based on costing is not yet considered.

Similarly, both PdOx/Zeol and FPdOx/Zeol showed almost same n-C$_{18}$H$_{38}$ quantity, but the fact that the latter has a superior isomerization ability confirmed that it is more prospective for industrial application since it is known that part of the n-C$_{18}$H$_{38}$ produced has been isomerized into iso-C$_{18}$H$_{38}$. A comparison of the Pd supported on Zeol catalyst with other Zeol supported catalysts based on the percent active metal loading in Table 4.21 showed that Pd is comparably more effective for both HDO and isomerization process since its loading in the two catalyst are 1.89 and 1.86%, respectively, while for example, Mo and Pt loading are 9.21 and 4.71%, respectively in FMoOx/Zeol and FPtOx/Zeol. However, based on cost as shown in Table 4.22 with respect to their observed HDO and isomerization abilities (as well as in view of process kinetics, design and product purification), the organometallic catalysts cost effectiveness ($\Sigma$C$_{18}$H$_{38}$ produced/cost per g of catalyst precursor) was of the order NiMoFOx/Zeol, NiOx/Al$_2$O$_3$, FMoOx/Zeol, FPdOx/Zeol, PdOx/Zeol and FPtOx/Zeol. In addition, NiMoFOx/Zeol reusability results (Part Three) are also superior to others strictly owing to its preparation procedure that first employed Mo to modify the Zeol
support prior to Ni precursor incorporation. This observation is supported by previous reports (Simacek et al., 2009; Prieceł et al., 2011; Sotelo-Boyás et al., 2011; Li et al., 2012), and perhaps explains why a good number of reports (Liu et al., 2009; Krár et al., 2010; Li et al., 2012; Gril et al., 2014) have employed bimetallic Ni and Mo supported catalyst in the biofuel research.

Table 4.22 Catalyst precursor unit cost

<table>
<thead>
<tr>
<th>Metal</th>
<th>Precursor</th>
<th>cost of precursor</th>
<th>quantity of precursor (g)</th>
<th>cost per g of precursor (RM/g)</th>
<th>cost per 100 g of precursor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>Nickel nitrate</td>
<td>161</td>
<td>250</td>
<td>0.644</td>
<td>64.4</td>
</tr>
<tr>
<td>Pd</td>
<td>Dihidrogen palladium hexahydrate</td>
<td>580</td>
<td>2</td>
<td>290</td>
<td>29000</td>
</tr>
<tr>
<td>Mo</td>
<td>bis(acetylacetonato)dioxo-molybdenum(VI)</td>
<td>657</td>
<td>50</td>
<td>13.14</td>
<td>1314</td>
</tr>
<tr>
<td>Pt</td>
<td>Potassium hexachloroplatinate</td>
<td>454</td>
<td>1</td>
<td>454</td>
<td>45400</td>
</tr>
</tbody>
</table>

*Based on the Purchase Order of the chemicals from suppliers