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Author: O.B. Ayodele Hamisu U. Farouk Jibril Mohammed Yoshimitsu Uemura W.M.A.W. Daud



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Effect of precursor acidity on Zeolite supported Pdcatalyst properties and hydrodeoxygenation activity for the production of biofuel

O. B. Ayodele^{1,2*}, Hamisu U. Farouk^{1,3}, Jibril Mohammed⁴, YoshimitsuUemura², W. M. A. W. Daud^{1,*}

¹ Department of Chemical Engineering, Faculty of Engineering, University of Malaya, Kuala Lumpur, Malaysia

²Centre for Biofuel and Biochemical Research, Department of Chemical Engineering, UniversitiTeknologi PETRONAS, Tronoh, Perak, Malaysia.

³Department of Pure and Industrial Chemistry, Faculty of Science, Bayero University Kano, P.M.B. 3011, Kano state, Nigeria.

⁴Department of Chemical Engineering, Abubakar Tafawa Balewa University, P.M.B 0248, Bauchi, Bauchi State, Nigeria.

Graphical abstract

Effect of Pd precursor acidity on ZeoliteA properties and activity for the production of biofuel

O. B. Ayodele^{*}, Wan MohdAshri Wan Daud

Department of Chemical Engineering, University of Malaya, Kuala Lumpur, Malaysia

*Corresponding author: Tel +60164955453; E-mail address: ayodele_olumide@yahoo.com

Graphical Abstract



Highlights

- Synthesis of two different palladium precursors of varying acidity.
- Incorporation of the two palladium precursors into zeolite support.
- Characterization of synthesized zeolite supported palladium catalyst.
- Catalytic hydrodeoxygenation of oleic acid with the synthesized catalysts.

Abstract

In this study, two different zeolite supported palladium catalysts (Pd/Zs) of varying acidity were synthesized, characterized and tested for biofuel production. The first Pd/Z was synthesized via the incorporation of palladium oxalate complex (PdOxC) prepared from the functionalization of H₂PdCl₄with oxalic acid at pH 5.3 into ZLT. The PdOxC was further modified with drops of HF until pH 3.7 and incorporated into ZLT to synthesize zeolite supported fluoride ion modified PdOxC catalyst (FPd/Z). Their characterization results showed that there is considerable crystallinity loss in Pd/Z, while FPd/Z showed drastic crystallinity loss according to the SEM and XRD results. In addition, the specific surface area and porosity of ZLT increased from 202 m²/g and 0.13 cm³/g to 371 m²/g and 0.23 cm³/g in Pd/Z, and $427m^2/g$ and 0.29 cm³/g in FPd/Z catalysts, respectively. Pd/Z catalyst produces

56% n-C₁₈H₃₈and 11% iso-C₁₈H₃₈, while FPd/Z produces 58% n-C₁₈H₃₈and 28% iso-C₁₈H₃₈in the hydrodeoxygenation (HDO) and isomerization (ISO) steps, respectively. The enhancements in the catalysts properties are due to the acidic effect of OxA via the incorporation of PdOxC, while the additional enhancements in the properties and the ISO activity of FPd/Z was ascribed to the acidic effect of fluoride ion modification. It is obvious that OxA functionalization and subsequent fluoride ion modification are highly invaluable towards biofuel production.

Keywords: Biofuel; Palladium Catalyst; Hydrodeoxygenation; Isomerization; Oleic Acid

1. Introduction

Aluminosilicates have been widely applied over the decades in various areas such as adsorption in water purification and treatments [1-4], catalysis for different operations such as production of chemicals, pharmaceuticals and fuel, as well as in environmental air pollution abatement [5,6]. Clays and zeolites are two typical aluminosilicates that have received tremendous attention. Kaolinites, bentonite and montmorillonite seem to be the most studied clay minerals for various research and industrial processes [6-9], on the other hand, there are over 200 known types of zeolites of different categories and classifications such as the MCM, Y – types, Z – types, Beta zeolites, N – types, etc used for different applications. Recently, the application of zeolites is gaining more attention that clays minerals in virtually every field where aluminosilicates are employed, and as such zeolites are presently being rapidly synthesized from different clay minerals especially kaolinite [1,2,6,7]. Their selectivity is one of their excellent qualities that made them interesting material for catalyst support especially in petroleum and petrochemical industries. Naturally occurring zeolites are usually impure and contaminated at varying degrees by other materials such as metals, quartz, or other zeolites types. Consequently, naturally occurring zeolites are not good

candidates for many important commercial applications especially where uniformity and purity are essential, and this explains their recent massive synthetic productions[10].

Zeolite A is one of the zeolite types which hitherto has not been frequently used perhaps due to its susceptibility to dissolution under severe acid attack and because it is rarely found pure in nature. It has high thermal and structural stabilities, uniform pore structure, large surface area and possesses excellent adsorption, screening and ion exchange performance [11,12]. Although the synthesis technique of zeolite A is very mature, the exploration for more economic and effective raw materials is still the focus of attentions [12]. Recently, Hui et al. [11] reported a novel and cheap route of zeolite A production with improved structural stability from coal fly ash (CFA) which hitherto is a waste product of combustion of coal in coal-fired power stations with about 800 million tons per annum. Similarly, as an improvement to the existing zeolite A production from kaolinite via the two steps procedure of thermal treatment to transform kaolinite into metakaolinte and alkali treatment, Wang et al. [2] reported the hydrothermal synthesis of high purity zeolite A from natural kaolin without the thermal treatment step to reduce the cost of production. These and many another studies [1,2,13-15] have made the production and application of zeolite Aattractive, however, in all these studies, zeolite A was applied mostly for adsorption and other related environmental problem. Information regarding its application as catalyst support for biofuel production is rarely found up till now [14,15], unlike other zeolite types such as HY and HZSM-5 zeolites[16], NaX zeolite[17], Al-MCM-41 [18]that have been extensively studied and reported for different feed stocks. Therefore in this study, zeolite A is expediently modified with two different types of metal-organic frameworkcatalyst precursors. Firstly with palladium oxalate (PdOxC) freshly prepared via the functionalization of palladium salt with oxalic acid, and the second, with fluoride ion enhanced PdOxC to study the effect of PdOxC

acidity on the synthesized catalysts properties and hydrodeoxygenation and isomerization activity for the production of high grade biofuel from oleic acid.

2. EXPERIMENTAL

2.1 Materials

Analytical grade zeolite A and hydrofluoric acid (68%) were purchased from F.S. Chemicals, while dihydridopalladium(IV) chlorideand anhydrous oxalic acid are from Sigma-Aldrich. All materials were used without any pretreatment.

2.2 Catalyst Development

Two types of catalysts with varying acidity were synthesized. The first was zeolite supported palladium catalyst (Pd/Z) synthesized via functionalization of 9.44 mmolof H₂PdCl₄ with equimolaraqueous oxalic acid (OxA) and was aged for 60 min to guarantee the formation of the polynuclear palladium (II) oxalate complexes (PdOxC) in an aluminum foil wrapped 500 ml conical flask because of the metal-oxalate complex photo-sensitivity [19]. The PdOxC was subsequently added gradually to 50 g zeolite (ZLT) dispersion under stirring for 4 h at 50 °C for the incorporation of PdOxC particles into the ZLT support, the pH was observed to stabilized at 5.3 ± 0.3 (usingEcoScan SC11-4115, Exatech Enterprise pH meter) as the stirring progressed. The second catalyst was synthesized following the same protocol except that the PdOxC was modified with drops of 1.5 M hydrofluoric acid until the pH of the fluoride ion modified complex (FPdOxC) was stabilized at 3.7 ± 0.2 . The Pd/Z and the obtained fluoride ion modified zeolite supported palladium catalyst (FPd/Z) wasfiltered and washed to remove the chloride ions followed by drying at 100 °C for 12 h and calcined at 400 °C for 3 h based on some few preliminary studies.

2.3 Catalyst Characterization

2.3.1 Thermal gravimetric analysis (TGA)

TGA was carried out with a SHIMADZU DTG-60/60H instrument to determine the heat treatment required during calcination. 2 g of each sample was heated in a silica crucible at a constant heating rate of 10 $^{\circ}$ C/min operating in a stream of N₂ atmosphere with a flow rate of 40 mL/min from 30 to 700 $^{\circ}$ C and the weight loss per time, weight loss per temperature increment and temperature increment versus time were recorded.

2.3.2 X-ray fluorescence (XRF)

XRF analysis of the samples were done using a μ Xay μ EDX 100 Schmadzu, NY and X-ray tube of rhodium anode and scintillation detector operating on a 40 mA current and 40 mV voltage to determine the chemical composition of the sample. High-energy X-rays were used to bombard the samples pressed into circular discs to cause ionization of their component atoms.. The detected spectra were amplified and recorded using the computer program installed on the XRF analyzer.

2.3.3 Energy dispersive X-ray (EDX)

EDX was performed to determine the elemental composition variation in the synthesized catalysts compared to the ZLT using EDX microanalysis system (Oxford INCA 400, Germany) connected to the FESEM machine. The EDX analysis used Mn-K α as the energy source operated at 15 kV of accelerating voltage, 155 eV resolutions and 22.4° take off angle.

2.3.4 Scanning electron microscopy (SEM)

SEM was used to study the surface morphology of all the samples. The analysis was carried out using a scanning electron microscope (Model EMJEOL- JSM6301-F) with an Oxford INCA/ENERGY-350 microanalysis system. The samples were evenly distributed on a black double sided carbon tape attached to the aluminum stub and vacuumed for about 10 min prior to analysis.

2.3.5 Nitrogen adsorption-desorption measurements (BET method)

 N_2 adsorption-desorption measurements were performed at liquid N_2 temperature (-196 °C) with an autosorb BET apparatus, Micromeritics ASAP 2020 to determine the surface area, pore size and structure, and the pore volume. Before each measurement, the samples were first degassed at 350 °C for 2 h and thereafter kept at liquid nitrogen temperature to adsorb nitrogen.

2.3.6 X-ray diffraction (XRD)

XRD patterns of the samples were measured with Philip PW 1820 diffractometer to determine the crystal phase and structure of the samples. Diffraction patterns were recorded in the range of $5-90^{\circ}$ (2 theta) with a scanning rate of 2° /min and a step size of 0.01° with Cu K α radiation. The X-ray tube was operated at 40 kV and 120 mA.

2.3.7 Fourier transformed infrared (FTIR) spectroscopy

FTIR analyses were performed on the samples to determine the functional groups present in order to understand the chemistry of the synthesized catalyst with respect to the support. The instrument used is Perkin-Elmer Spectrum GX Infrared Spectrometer with resolution of 4 cm^{-1} operating in the range of 4000-400 cm⁻¹.

2.3.8 Raman spectroscopy

The Raman spectra of all the samples were obtained with a SpexTriplemate spectrograph coupled to a Tracor Northern 1024 large area intensified diode array detector. The excitation source was a 488-nm line (Lexel Model No. 95 Ar^+) laser with a grating monochromator used to reject any spurious lines and background from the laser before the radiation entered the spectrometer. The spectra were taken with 1 cm⁻¹ resolution.

2.4 Oleic acid hydrodeoxygenation experiments

Oleic acid (OA) was hydrodeoxygenated in a 100 mL high pressure semi-batch reactor. The catalysts activities on the HDO process were tested at the previously [20] best observed reaction conditions of 360 °C, 20 bar and 100 ml/min for temperature, pressure and gas flow rate, respectively. The flow of carrier gas and reaction pressure inlet and outlet were controlled by a flow (Brooks 58505 S) and a pressure controller (Brooks 5866), respectively. In a typical experiment,40 g (~45 ml) of OA was added to the reactor followed by a known amount of catalyst (depending on the type of catalysts to be studied) and the catalyst was reduced in situ under flowing H₂ at 200 °C for 1 h prior to use after which the reactor was purged with He. The operating temperature was established and monitored by a type-K Omega thermocouple placed inside the reactor. Before the reaction started, 100 ml/min of 90 vol% N₂ and 10 vol% H₂ was passed through the reactor until the desired reaction pressure was reached and the reaction commences by turning on the stirrer at an earlier predetermined speed of 2000 rpm. Based on preliminary studies, all experiments were performed under 60 min and the reactor set up was cooled by forced air before dismantled for product analysis. Liquid samples withdrawn from the reactor were dissolved in pyridine and thereafter silylated with (100 wt% excess of) N,O-bis(trimethyl)-trifluoroacetamide, BSTFA in an oven at 60 °C for 1 h prior to GC analysis. The internal standard eicosane, C₂₀H₄₂ was added for quantitative calculations. The withdrawn samples were analyzed with a gas chromatograph

(GC, HP 6890) equipped with DB-5 column (60m x 0.32mm x 0.5 mm) and a flame ionization detector. 1 μ l sample was injected into the GC with split ratio of 50:1 and helium was used as the carrier gas. The chromatographic program was well-adjusted to achieve satisfactory separation of the desired product and the product identification was validated with a gas chromatograph–mass spectrometer (GC–MS). Since there was technical limitation in online analysis of the evolved gases (Mgas) during the study, they were calculated according to Eq. 1, and the product distribution was evaluated using Eq. 2.

$$Mgas = [M_b + M_{H2} - M_a]$$
(1)

$$\omega_{i}(\%) = \frac{n_{i}}{\sum_{i=1}^{j} n_{i}} * 100$$
⁽²⁾

Where M_b is the mass of reactor with the OA and catalyst before reaction, M_{H2} is the mass of total H_2 gas required during the experiment evaluated from the H_2 flow rate and its density and M_a is the mass of the reactor with the liquid product and used catalyst after the reaction. Similarly, $\omega_i(\%)$ is the mass fraction of the components in the liquid product.

3. **RESULTS AND DISCUSSION**

3.1 Catalyst characterization

3.1.1 X-Ray Fluorescence

The XRF spectra of ZLT, Pd/Z and FPd/Z are shown in Fig.1, the spectrum of ZLT showed its characteristics peaks between 0.51 and 23 keV. The successful intercalation of PdOxC into the framework of ZLT support is seen in the XRF plot of Pd/Z at L β_1 of 3.20keV and another growing peak is observed at 21.2 keV which possibly confirmed successful dispersion of Pd from PdOxC since Pd(K α) is only metal that has such peak at 21.2 keV

according to the EDXRF-EPSILON 3 XL, PANalytical standard card. However, in contrast with the two Pd peaks observed in the Pd/Z catalyst, FPd/Z catalyst showed three Pd peaks at L α_1 of 2.99 keV, L β_1 of 3.20 and 21.2 keV, in addition, the Pd peaks in the FPd/Z catalyst appeared to be comparably more intense than those in the Pd/Z catalyst. These suggest that the effect of fluoride ion functionalization is effective at guaranteeing higher Pd particle dispersion and probably minimizes the degree of hydration effect on the active metal during the catalyst synthesis stage as seen in Table 1.



Fig.1 XRF spectra of ZLT, Pd/Z and FPd/Z samples

3.1.2 Energy Dispersive X-Ray (EDX)

The elemental composition of the ZLT, Pd/Z and FPd/Z samples in Table 1 showed that silica and alumina are the main components of ZLT with some oxides of calcium and sodium, its Si/Al ratio was found to be ~1.02 which is typical of zeolite A. After successful incorporation of acidic PdOxC and FPdOxC catalyst precursors into ZLT and calcination, the Si/Al ratio increased to 2.2 and 3.45, respectively in Pd/Zand FPd/Z catalysts(Table 1) due to the reduction in framework and extra-framework aluminum.Typically, reduction/removal of framework and extra-framework alumina has been ascribed to effect of thermal treatment and protonation from acid attacks, respectively [19]. However, since both catalysts were subjected to same thermal treatments, the comparably higher Si/Al ratio of FPd/Z compared to Pd/Z was ascribed to the effect of fluoride ion functionalization at the synthesis stage.

	Elemental composition (%)							
Sample	Si	Al	O ₂	Na	Ca	F	Pd	- Si/Al
ZLT	16.88	16.48	49.58	12.41	4.65	0.00	0	1.02
Pd/Z	21.11	9.59	55.90	8.70	2.81	0.00	1.89	2.20
FPd/Z	22.37	6.44	54.81	4.51	1.71	8.30	1.86	3.45

Table 1 Elemental composition of ZLT, Pd/Z and FPd/Zsamples

Both Pd/Z and FPd/Z catalysts showed increment in the amount of O₂ which can be ascribed to the presence of oxalate functional group of the PdOxC and FPdOxC precursors. Similarly the incorporation of Pdearlier seen in Fig. 1 and Table 1can be further corroborated in Fig.2(b,c)between the 2.0 and 3.8 keV in the EDX spectra which also showed the presence of fluoride ion in the FPd/Z catalyst (Fig.2c). From Table 1, the observed quantity of Pd(average of three runs) in Pd/Z and FPd/Z catalysts is1.89% and 1.86% which is slightly

lower than the calculated 2% and this probably could be due to the effect of degree of hydration at the catalyst synthesis stages [8].



Fig.2 EDXand SEM of ZLT, Pd/Z and FPd/Z samples

3.1.3 Scanning Electron Microscopy (SEM)

The SEM morphology of the ZLT, Pd/Z and FPd/Z samples shown inFig.2 (inset)revealed conspicuous degree of morphological variations in Pd/Zand FPd/Z catalysts which are expected to have a substantial contributory effect on their catalytic activities. The morphology of ZLT inFig.2a (inset)depictsagglomerates of sharp micro-sized cubical symmetry crystal structure [12,20,21] which can be seen to have loss considerable crystallinity in Pd/Z (Fig.2b (inset)) and become apparent amorphous in FPd/Z (Fig.2c (inset)) after the catalyst synthesis. The loss of crystallinity in both catalystscan be seen to have considerably reduced their particles sizes with attendant increase in surface area compared to the ZLT supportas shown in Table 2 (BET analysis). As earlier mentioned, aluminosilicatesusually experience loss of crystallinity under acid influence and thermal treatment which is usually accompanied by increase in the specific surface area, and such lossof crystallinity is a function of the acid type and concentration as well as the degree of thermal treatment [22]. The considerable loss of crystallinity in Pd/Z can be ascribed to the combined effect of OxA functionalization and proper calcination at the Pd/Z synthesis stage resulting in dealumination from the lattice structure, while the apparent amorphous observed in FPd/Z can be ascribed to the additional crystallinity loss due to intense dealumination effect from fluoride ion. This result further corroborates earlier observation in Table 1.

3.1.4 Nitrogen Adsorption/Desorption Isotherm

As earlier observed in the catalysts morphology micrographs that the effects of OxAfunctionalization and thermal treatment resulted into loss of crystallinity which is more severe in the FPd/Z catalyst due to the fluoride ion modification, the textural properties results of the samples in Table 2 showed that there is reduction in the average particle sizes (APS) of Pd/Z and FPd/Z compared to the ZLT. As expected, the reduction in the APS can be seen to have increased the specific surface area and porosityof both Pd/Z and FPd/Z, as usual,

these enhancements are more pronounced in the FPd/Z catalyst due to the additional effect of fluoride ion modification. From the isotherms of the samples shown in Fig. 3, ZLT sample exhibited Type II isotherms at lower relative pressures which is a characteristic of the formation of monolayer followed by multilayer [23]. However, after catalyst synthesis, both Pd/Z andFPd/Z eventually conformed to Type IV isotherm with the steep uptake of N₂owing to the development 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 [3,7,23]. This observation is typical of solids having considerable degree ofmesopores[19]. Theincrease in the amount of N₂ adsorbed in the Pd/Zand FPd/Zcompared to ZLTalso supports the data in Table 2 which is in accordance with previous reports that loss of crystallinity usually leads to increase in the pore volume and specific surface area [19-23]. As expected, the FPd/Z showed more N₂ uptake and wider hysteresis loop than Pd/Zdue to the effect of the fluoride ion modification.

Table 2Textural properties of ZLT,Pd/Z andFPd/Z samples

Sample	Surface area	Pore volume	Pore diameter	Average Particle
	(m^2/g)	(cm^3/g)	(nm)	size (nm)
ZLT	202	0.13	10.41	10404
Pd/Z	371	0.23	14.58	4655
FPd/Z	427	0.29	20.11	2534



Fig. 3 Nitrogen adsorption/desorption isotherm of the ZLT,Pd/Z and FPd/Z samples

3.1.5 X-Ray Diffraction (XRD)

The XRD pattern for the ZLT support and the synthesizedPd/Z and FPd/Z catalysts are shown in Fig. 4. According to the JCPDS card 43-0142, the characteristics peaks at $2\theta = 7.2^{\circ}$, 10.0°, 12.4°, 16.06°, 21.64°, 24.0°, 27.10°, 30.0°, 34.16°, 43.6° and 52.3° in the ZLT support are typical of highly crystalline Zeolite A [11,12]. After the catalyst synthesis, Pd/Z showed considerable crystallinity loss while FPd/Z reflects almost complete amorphous structure. These observations corroborate the earlier results seen in the samples SEM morphology and it was ascribed to the varying intensities of acid attack and also the thermal treatment that removes extra framework and framework aluminum, respectively leading to increase in their Si/Al ratios (Table 1).



Fig. 4 X-ray diffraction of the ZLT, Pd/Z and FPd/Z samples

Typically, loss of crystallinity has been ascribed to proper calcination which in turn improves the catalytic activity of the synthesized catalysts, in fact Jiaet al.,[24]reported a linear relationship between excessive thermal treatments and crystallinity (i.e. crystal growth) but an inverse correlation with catalytic activity. Consequently, the loss of crystallinity in the Pd/Z and FPd/Z catalysts indicates high Pddispersion in the matrix of ZLT support which is a pointer to excellent catalytic activity [21]. In addition, the absence of bulk Pd peaks that are usually seen around $2\theta = 18^{\circ}$ and 34° [18,25] further confirmed that the Pd particles are highly disperseddue to increase in thecatalysts acidity at synthesis stage [21,26], i.e. OxA functionalization in both catalysts and additional fluoride ion modification on FPd/Z.Furthermore, in view of the minuscule quantity of Pd used during the synthesis (Table 1) there is speculation that the Pd particles might also have been partly covered by the ZLT particles. However, the lowering of the diffraction between 2θ of 2.3° and 5.4° in Pd/Z owing to the expansion of the ZLTlattice structure due to intimate contact of the incorporated

PdOxC [21], and the presence of the miniature peaks at 38.4°, 44.6° and 58.7° in FPd/Z further confirmed the successful incorporation of Pd particles into the matrix of the ZLT support.

3.1.6 Thermal Gravimetric Analysis (TGA)

The TGA profiles of ZLT, Pd/Z and FPd/Z as well as that of the uncalcinedPd/Z and FPd/Z are shown in Fig.5a-b.All the samples showedthree characteristics weight loss regions (WLR) typical of the aluminosilicates. Thefirst WLRis due to loosely held moisture and physisorbed water that can be rapidly removed at a temperature around 150 °C[4,9]. The second WLRwhich is usually observe between 200-500 °Cwas ascribed to the existence of strongly bonded water molecules that are domiciled in the first coordination sphere and also probably due to partial occlusion of organic matter [3,19]. The thirdWLR comprises of thestructural hydroxyl groups that will condense and dehydrateat temperaturesabove 500 °C [9,19].A careful study of Fig. 5 shows that the uncalcined catalysts showed increase in weight loss compared ZLT due to the hydration effect of the catalyst precursors(PdOxC and FPdOxC)incorporation into ZLTat the catalysts synthesis stages. Although the weight loss is not very pronounced in the first weight loss region ostensibly due to the effect of drying at 100 °C for 12 h, which implied that the drying stage was able to reduce considerable amount of physissorbed and freely bounded water molecules [19].



Fig.5 Thermal Gravimetric Analysis of (a) ZLT and Pd/Z, (b) ZLT and FPd/Z.

Furthermore, it can be observed that there is a marginal increase in the weight loss of the uncalcined Pd/Z, but the weight loss in the uncalcinedFPd/Z is very conspicuous due to the effect of protonation from the fluoride ion modification at the FPd/Z synthesis stage that increased the surface area and the amount of amorphous silica (BET, EDX and SEM results),

thereby increasing the amount of adsorbed and strongly bonded water. This observation is also consistent with previous study where phosphoric acid was employed [19]. The observed increase in the weight loss of the uncalcined catalysts even after drying is an indication that their synthesis protocol was able to guarantee the penetration of aqueous catalyst precursor into the lattice structure of ZLT. After calcination at 400 °C, both Pd/Z and FPd/Z showed reduction in weight loss, which suggests that the thermal treatment during the calcination step was adequate to expel both the physisorbed, strongly bonded water moleculesand any occluded organic matter thus leaving behind only the PdOxCand FPdOxC particles, respectively on the ZLT support. Previous works have shown that adequate calcination around 400 °C increases catalyst surface area and pore volume which in turn increases the number of active sites thereby guaranteeing a high active metal dispersion [4,21].

3.1.6 Fourier's Transform Infrared Spectroscopy (FTIR)

The FTIR spectrums of the ZLT support, Pd/Z and FPd/Zare presented in Fig.6. The ZLTsample reflects the existence of strongly bondedzeolitic water in the region 3665 - 2980 cm⁻¹ with a minimal around 3366 cm⁻¹ and another band at 1655 cm⁻¹ which is attributed to physisorbed water molecules vibration [3,4]. Previous reports [18,27] have shown that the presence of these water molecules is detrimental to the activities of HDO catalysts due to agglomeration of active metal. According to the authors, proper calcination has been highly invaluable to reduce or completely remove the water molecules thus guarantee proper active metal dispersion. From Fig. 6, it is obvious that the thermal treatment during the calcination step is adequate as the water molecule bands at 3665 - 2980 cm⁻¹ and at 1655 cm⁻¹ had completely disappeared in both Pd/Z and FPd/Z, and this observation corroborates the result in the samples TGA profile in Fig. 5.



Fig.6 FTIR spectra of ZLT, Pd/Zand FPd/Z samples

According to Li et al.[26], the presence of exchangeable cations and incorporated active metals in aluminosilicates are usually seen in the lower wavenumber below 1000 cm⁻¹ especially in the region 900 - 600 cm⁻¹. A carefully analysis of the three spectrums (excluding the reflections of water molecules) shows that there is a good match until around 1200 cm⁻¹ and the mismatch became obvious below 1000 cm⁻¹ especially with the relocation of the strong absorption at 940 cm⁻¹ in ZLT support to 1050 cm⁻¹ in Pd/Z and FPd/Z. Similarly, the moderate absorption band at 675 cm⁻¹ in the ZLT support also relocated to 753 cm⁻¹ with reduced intensities in both Pd/Z and FPd/Z, and it almost disappeared in the latter probably to the fluoride ion modification. These observations are indications of successful formation of Si-O-Pd bond due to the incorporation of Pd into the ZLT matrix [4]. In addition, the appearance of a new miniature band at 576 cm⁻¹ can be ascribed to the formation of another bond between Pd particles and Si–Al structure of the support [25].

4.4.1.8 Raman Spectroscopy

The Raman spectrums in Fig.7showed thecharacteristic bands of ZLT, Pd/Zand FPd/Z samples.Characteristics distinctive peaks of Zeolite A are observed in the spectrum of ZLT at 280, 330, 400, 490, 700, 977, 1030, 1150 and 1457 cm⁻¹. Previous work [28] on Raman spectroscopy characterization of zeolite A has shown that it possesses 4-, 6- and 8-membered rings, and smaller rings give bands at higher frequency. Consequently, the band at 280 cm⁻¹ in the ZLT sample can be assigned to the bending mode of the 8 membered rings. Similarly, the bands at 330 and 410 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[28]. Typically, Raman bands in the region of 600 – 900cm⁻¹ are assigned to symmetric T–O stretching modes, on the other hand, the bands at 977, 1030 and 1150 cm⁻¹ are ascribed to asymmetric T–O stretching motions. A clearly distinctive band at 800 cm⁻¹ which obviously is not a characteristic of zeolite A can be seen in spectrum of ZLT which possibly signifies the presence certain impurities since Raman peak at 800 cm⁻¹ is typical of 5-membered ring of zeolite ZSM-5.

The effect of the catalysts precursors (i.e. PdOxC and FPdOxC) incorporation into the ZLTcan be observed to have developed series of multiple stretches of background noise-like vibrations (BNV) in the Pd/Zand FPd/Z catalysts. These BNV according to Ghule et al., [21] reflects presence of carbonate anion (CO_3^{2-}) from organics (i.e. oxalate) with D_{3h} symmetry usually exhibiting four normal vibrational modes which consist of a symmetric stretching vibration (v₁) around 1063 cm⁻¹, an out-of-plane bend (v₂) around 879 cm⁻¹, a doubly degenerate antisymmetric stretch (v₃) around 1415 cm⁻¹ and lastly doubly degenerate bending mode (v₄) around 680 cm⁻¹[29]. The presence of these BNV even after calcination implied that the Pd particles in the Pd/Zand FPd/Z retained their oxalate ligand structure [21]. After the catalyst synthesis, earlier bands seen at 490 and 1150 cm⁻¹ in the ZLT were seen to

have slightly denatured and shifted to 480 and 1120 cm⁻¹, respectively in both the Pd/Z and FPd/Z, while the band at 800 cm⁻¹ disappearedcompletely probably due to the acidic effect of oxalic acid functionalization and calcination that resulted into loss of crystallinity earlier observed in the SEM and XRD results (Fig. 2(inset) and Fig. 4). The comparably severe loss of crystallinity in the FPd/Z catalyst compared toPd/Z earlier observed in the SEM and XRD results which gave rise to its comparably higher Si/Al ratio (Table 1) also explains why certain peaks such as at 443, 480, 575, 740, 1040 and 1120 cm⁻¹ are less intense in the FPd/Z catalyst. The new band at 443 cm⁻¹ and the bands at 648, 740 and 928 cm⁻¹ confirmed the presence of dispersed palladium particles in the Pd/Z and FPd/Z catalyst [18,25,27].



Fig.7 Raman spectra of ZLT, Pd/Zand FPd/Z samples

3.2 Catalytic activities of Pd/Z and FPd/Z on the hydrodeoxygenation and isomerization of oleic acid into biofuel

Recently in attempt to gain thorough insight into the hydrodeoxygenation (HDO) process of different feed stocks, studies onreaction variablessuch as effects of reaction pressure and temperature, H₂ gas flow rate, catalyst loading and even types of reactors and mode of operations have been well studied and reported[20,30-34]. However, since existing hydrotreating units of conventional crude oil refineries can be adapted for the HDO process of biofuel production, studies on expedient synthesis of suitable catalysts such as types of the support and metals [34], systematic catalyst preparation procedure [20,26,35]and additives such as sulfur [36]and phosphorus [31]are currently receiving attention.In this direction, we recently, functionalized nickel with oxalic acid and supported on alumina for the hydrodeoxygenation of oleic acid into high grade biofuel [18]. At the best operational conditions of 20 bar, 360 °C and 100 ml/min of gas flow, the catalystshowed superior activities to other alumina supported Ni catalysts in literature. In addition, the catalyst was able to achieve skeletal isomerization of already hydrodeoxygenated n-paraffin due to the effect of the oxalic acid functionalization.

As a step further, in this work we modified palladium oxalate catalyst with fluoride ion and compared its activities with unmodified palladium oxalate catalyst at the earlier best observed operation condition for the HDO of oleic acid and the result is shown in Fig. 8. It is very obvious that FPd/Z possesses both higher HDO and isomerization activities compared to Pd/Z. Even thoughPd/Z and FPd/Z showed almost same n- $C_{18}H_{38}quantity$, but the fact that the latter has superior isomerization ability confirmed that it is more prospective for industrial application since it is well known that n- $C_{18}H_{38}$ produced in the HDO step is the substrate for the isomerization step to produce the iso- $C_{18}H_{38}$. The enhanced HDO activity of FPd/Z compared to Pd/Z was ascribed to its increased acidity at the synthesis stages which improves the solubility ofPd in the support and facilitates the formation of Pd (II) polynuclear complex which in turn guarantees high Pd dispersion as seen in the XRD result (Fig. 4). In

addition, its increased acidity also modified its morphology from crystalline into amorphous (Fig. 2 (insets)) and enhanced its textural properties (Table 2) which in turn increases the N₂ adsorption/desorption isotherm hysteresis loop as shown in Fig. 3. This observation is in agreement with the works of Li et al. [26] on the functionalization of NiMo/ γ -Al₂O₃ catalysts with varying quantities of urea. They reported that the urea functionalization greatly enhances the textural properties and the solubility of Mo and Ni particles in the support as well as facilitates the formation for molybdate and polymolybdate species due to increased acidity.



Fig. 8 Product distribution of the HDO of oleic acid at 360 °C, 20 mg catalyst loading, 20 bar, 10% H₂ gas flow and 60 min.

Generally, aluminosilicates gradually transform from crystalline form into amorphous under acid attacks [19,37] thus leading to increase in Si/Al ratio as seen in Table 1. Such

transformation is usually accompanied with reduction in particle size which in turn increased the specific surface area and porosity as observed in Table 2.Such morphological and textural properties variation has been reported to increase catalyst activities by ensuring well dispersed activemental particles [22,26]. Therefore, the enhanced textural properties of FPd/Z compared to Pd/Z will equally provide additional and sufficient surface area for active metal incorporation and also guarantee unrestricted access for the reacting molecules owing to enhanced porosity[19,22]. Furthermore, both catalysts were seen to produce isomerized products, while FPd/Z produces about 28% iso-C₁₈H₃₈, Pd/Z produces only 11%. The presence of the iso-C₁₈H₃₈ was due to FPd/Z increased acidity.Previous studies [32,35]have shown that catalysts with increased acidity are highly favorable forparaffinskeletal isomerization. Typically, the presence of isomerized product is considered an advantage due to the ability of iso-paraffin fractions to lower the biofuel freezing point by about 20 °C since n-paraffin (C_{16} - C_{18}) has comparable high freezing point (between 18 °C and 28 °C) which is a disadvantage to their cold flow properties such as cold filter plugging point [32,38]. The increased iso-C₁₈H₃₈content in FPd/Z compared to Pd/Z was unarguably due to the fluoride ion functionalization which further increased the acidity of FPd/Z. The presence of $C_{17}H_{36}in$ Fig. 8 when using Pd/Z confirmed instances of decarboxylation or decarbonylation, and this is further corroborated by the increase in the amount of gases (such as CO₂/CO). Unfortunately, as earlier commented (Section 2.4)the online identification and quantification of these gases were not technically feasible during this study, hence determination of the gas species was not possible. The amount of the lumped unidentified products such as unreacted oleic acid, oligomerized products and other functional group is also higher in Pd/Z showing that its activity and selectivity is comparably inferior to FPd/Z. It is obvious that effect of fluoride ion functionalization is highly invaluablesince only the iso-paraffin content of FPd/Z fall within the range (20 - 40%) reported by Šimác ek et al. [39] that could significantly improve the cold flow properties (CFPP, pour point, cloud point, etc.) of biofuel.

4. Conclusion

Two different zeolite supported catalysts were synthesized from palladium functionalized with oxalic acid, one was further modified with fluoride ion to increse its acidity. The fluoride ion modified palladium oxalate zeolite supported catalyst (FPd/Z) showed considerable enhancement in textural properties and loss of crystallinity compared to the palladium oxalate zeolite supported catalyst (Pd/Z) due to the effect of the fluoride ion. In addition, the FPd/Z also showed relatively stronger Pd intensity according to the EDX results as well as higher Pd dispersion. Their catalytic activity tested at 20 bar, 360 °C, 100 ml/min of H₂gas flow and 20 mg of each catalyst loading showed that both Pd/Zand FPd/Z shared similar hydrodeoxygenation activities producing 56% n-C₁₈H₃₈ and 58% n-C₁₈H₃₈, respectively, but FPd/Z has superior isomerization ability producing 28% iso-C₁₈H₃₈while Pd/Z produces 11% iso-C₁₈H₃₈. Finally, the results showed that with expedient synthesis protocol, cheap zeolite A can be successfully used as biofuel hydrodeoxygenation and isomerization catalyst support to cut down production cost and make the process economically attractive.

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