Catalytic Degradation of Polyethylene to Gas Oil using Synthesized Clay Based Copper Modified Catalyst

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Abstract
In this study local clay was pretreated, characterized, modified and used as catalyst for the degradation of low density polyethylene (LDPE). The raw clay was thermally treated at 800 °C for 4 h in a furnace which was later modified by incorporating copper into it through impregnation method. The functionalities of the catalyst were determined based on their characterization. X-ray diffraction, Fourier transform infrared, Scanning electron microscope, X-Ray Florescence and surface area determination were done for both the raw clay and modified catalysts. Characterization of the catalysts revealed that the interaction between CuO/clay formed a synergetic mixed oxides and this is an important factor to its catalytic activity. The product obtained was analyzed using Gas Chromatography-Mass Spectrometry and the product was mainly composed of hydrocarbons in the carbon range of $C_{16} - C_{25}$ which is the hydrocarbon range of gas oil (diesel) fraction. Also, the data obtained showed that at catalyst loading of 1.0 g, 5.0 g of polyethylene feedstock and reaction temperature of 250 °C, the yield of gas oil was 50.22%.The catalyst easily separates from the product mixture.

Keywords: Degradation, Polyethylene, Impregnation, Characterization, Gas oil.

Introduction

Polymers are widely used throughout the world due to their low price, high capacity of production and simple processing techniques. These qualities of plastic materials confer on them great potentials in many industrial applications, for example, polyethylene itself has a production of 80 million metric tons/year, which gives an insight into the extent of the plastics market (Gorka*et al.*,2007).However, a great drawback is brought about by the widespread use of these materials. It causes environmental pollution. Plastic materials are generally non-biodegradable, in other words, it is incapable of decomposing biologically in nature. This disability brings the problem of accumulation of plastics with an increasing trend and uncontrollable environmental pollution. Some temporary and ineffective solutions to the problem are presently being applied. Land filling is one of the previously used solutions, which is highly temporary due to consumption of available, limited land filling spaces throughout the world. Another partially effective solution is incineration. This technique is not only temporary, but at the same time dangerous and harmful, because of high emission of toxic organic chemicals resulting from the burning reactions (Bhaskar *et al.*,2003).These toxic by-products are extremely dangerous to the health of all living things. Therefore alternative methods are being

researched and developed for safe and effective removal of waste plastics that liter our environment (Aguado *et al.*, 2007).Much workhas been carried out on the recycling of plastic materials using pyrolysis method. However, there exists a problem of high energy consumption of pyrolysis reaction. A temperature range of 450 - 600 °C is generally sufficient for decomposition to occur in a typical pyrolysis reaction (Bockhorn, 2006). Also, the distribution of the products has a wide range of carbon numbers, which is undesirable due to the fact that the desired products are in a specific range. Therefore, in an attempt to overcome difficulties,catalysts are synthesized insuch a way to overcome the aforementioned drawbacks. By the use of catalysts, reaction temperature and residence time can be lowered sufficiently, providing considerable energy savings andshorter residence time. Also, high quality, stable and narrowly distributed products with higher market values may be obtained.

Experimental procedure

LDPE(low density polyethylene) was obtained from Futmin ventures Minna Nigeria, the clay was obtained from an ant hill in Gidan Kwano campus, Minna (between latitude 8°22'N and 11°30'N and longitude 3°30'E and 7°20'E), Nigeria. Copper sulphatepenta hydrate ($CuSO_4.5H_2O$), potassium hydroxide(Aldrich) and deionized water were the other reagents used in the preparation of clay based catalyst. The clay was pre-treated by grinding, sun-dried and sieved to obtain a particle size of 75 μm (called A-raw). The fine powder(A-raw) was oven-dried at 110 °C so as to remove all the water content and then calcined (B-calcined as referred to in this work except otherwise stated) in a furnace at temperature of 800 °C for 4 h.(Folorunso*et al.*,2012)Thereafter, copper was incorporated into sample A-raw by impregnation method. Copper sulphate penta hydrate was used as Cu source, a basis of 10 g catalyst modification was chosen. In this method, 10 g of sample A raw was dispersed into 50 mL of deionized water and continuously stirred on the hot plate with magnetic stirrer at a temperature of 60 °C for 5 h. According to the desired Cu to Clay molar ratio, predetermined amount of $CuSO_4$ (10 g) was dissol· ed in 50 mL of 2 M KOH solution. Then as the clay mixture was being stirred, copper source was added drop wise to the solution and the mixture was stirred for another 5 h. Finally, the mixture was evaporated and the resulting solid product was placed in the oven at 110 °C for 16 h, the resultant solid product was crushed using mortar and pestle and later calcined in a furnace at 800°C for 4 h (sample C).

Activity test for the treated clay

The activity of the synthesized catalyst was tested on the polyethylene (feed) in a stainless steel batch reactor consisting of a stirrer and thermometer. The catalyst was weighed and charged in with the liquefied polyethylene (PE). The liquid PE was made to react with the solid catalyst at atmospheric pressure at the start of the reaction. Mixing commenced immediately after reactants were charged into the reactor to ensure contact between the PE and catalyst. To establish the extent of conversion of the reaction

from the start (t = 0) to the target temperature, separate batches of experiments were run at various time intervals and corresponding yield were calculated. The stirrer speed was adjusted to 360 rpm to avoid mass transfer limitations and this was sufficient to keep the system uniform in temperature and suspension The amount of catalyst used varied from 1.0□4.0g with constant weight PE feedstock (5.0 g). At the end of the experiment, the heater was switched off and the reactor was cooled to a temperature of 60 °C. The gas was collected in di-ethyl ether for analysis using GC-MS.

Characterization of catalyst

The compositions of the A- raw and B-calcined samples were determined using X-ray florescence (XRF) Machine. The morphologies of the samples were studied using Quanta FEG450 model scanning electron microscope (SEM), while the elemental composition were studied using an energy dispersive X-ray (EDX) mounted on the microscope. The crystal structures of the catalyst were determined by X-ray diffraction (XRD) which was carried out on a model Philip PW 1710 with Cu K α radiation. Fourier transform infrared (FTIR) spectrophotometer was used to identify the surface functional groups of the catalyst. The spectra were recorded over the range of 4500 – 500 cm^{-1}.The Gas chromatography (GC-MS) machine was used to analyze the gas obtained during degradation process. The specific surface areas (SSA) of the prepared sample were obtained using methylene blue (MB) adsorption method. The procedure for the determination of the specific surface area of the clay samples was done according to Santamarina *et al.*, (2002). MB solution was prepared by mixing 0.75 g of dry powder of MB into 150 mL of deionized water. 10 g of each clay samples (A,B and C) was mixed with 30 mL of deionized water. Then the MB solution was added into the clay suspension with 0.5 mL increment. After each of 0.5 mL addition of MB, then a small drop was removed from the solution and placed on to Whatman filter paper. If the unabsorbed MB forms a permanent blue halo around the clay aggregate spot on the filter paper, it means that MB has replaced the cation in the double layer and coated the entire surface. Specific surface area (SSA) was therefore determined from the MB amount that required reaching the end point from the following equation.

$$\frac{0.75}{319\,87}\quad\frac{0.75}{150}\quad 0.5N\ A_v\ A_{MB}\quad\frac{1}{10}$$

Where N is number of MB increment added to the suspension solution, A_v is the Avogadro's constant (6.02 $*10^{23}$/ mol), A_{MB} is the area covered by one MB molecule (typically assumed to be 130 $Å^2$).

Results and Discussion

The XRF result is as shown on Table 1.The composition of the clay employed as catalyst in this study showed that it contained iron rich source with relatively high SiO_2 and Al_2O_3 but with low wt. % of TiO_2 and MnO. The SEM images for the as-synthesized catalyst are shown in Figure 1 while the XRD patterns are shown in Figure 2.The SEM images of modified and B-calcined catalyst reveal that both have

rough surfaces and well separated pores which might have increased the catalyst activity due to presence of active sites(Olutoye and Hameed,2009). The XRD pattern of the as-synthesized catalyst showed basically characteristic peaks of SiO_2, TiO_2, and CuO.The peaks observed in A-raw were significantly reduced in B-calcined and sample C due to the structural decomposition of the crystal layer structure of the clay during thermal treatment. The thermal treatment at 800 °C altered the structural arrangement to a new phase as observed by the work of Readmal et al, (2005). The XRD pattern of sample C shows the transformation into four crystallographic forms namely: Tenorite, Quartz, Ankerite and Lisetite which are all crystalline in nature as a result of high temperature used (800 °C) during calcination.This observation is supported by the work of El-Badry and Miner (2011), which revealed that high calcination temperature resulted in the formation of crystalline compound containing Cu and Fe elements. The compound formed by sample C, Cu modified catalyst at the calcination temperature of 800 °C for 4 h has a synergetic nature (better interaction). This is a factor for possible usage in PE degradation where high activity could be obtained (Olutoye and Hameed, 2009).

Table 1: XRF analysis of the A- raw and B-calcined

Samples	Chemical composition										
	SiO_2	P_2O_5	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	V_2O_5	K_2O	MnO	Traces
A-raw	10.88	0.2	10.32	68.20	0.31	5.14	3.18	0.697	0.3	0.51	0.263
B-calcined	10.69	0.185	10.78	68.27	0.28	5.07	3.15	0.642	0.22	0.48	0.228
Cu-modified	10.67	0.184	10.80	68.29	0.26	5.04	3.14	0.640	0.20	0.46	0.316

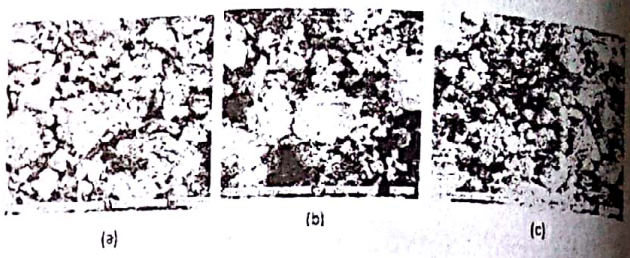

Figure 1: SEM images of as-synthesized catalyst (a) A-raw(Mag=50.00 KX), (b)B-Calcined (Mag=50.00KX) and (c)Sample C (Mag=50.00KX).

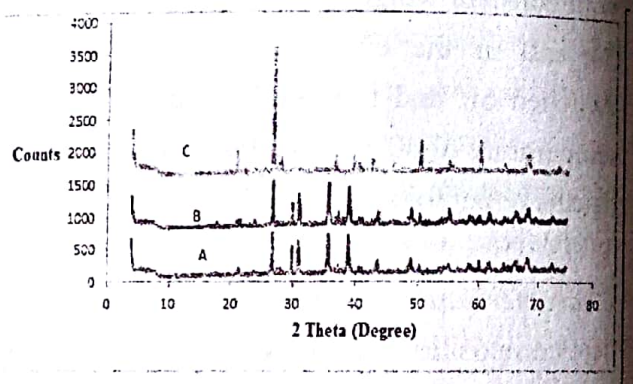

Figure 2: XRD pattern of as-synthesized catalyst (A) A-raw (B) B-calcined © Cu-modified

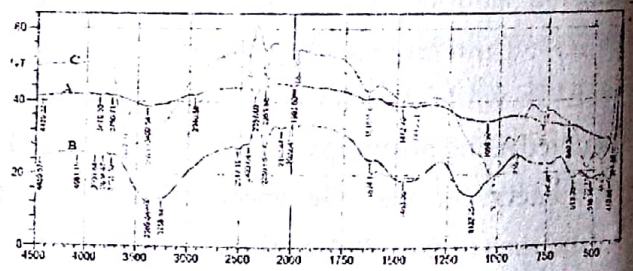

Figure 3: Fourier Transform Infrared (FTIR) spectra of the synthesized catalyst.

The elemental composition of the synthesized catalyst used in this work was also analysed byusing Energy dispersive X-ray detector(EDX) and the result revealed that sample A-raw contained 29.4 wt.% Si, 10.3 wt.% Al, 12.5 wt.% Fe, 3.1 wt.% K, 1.1 wt.% Ca, and 43.6 wt.% O. Sample B- calcined contained 33.7 wt.% Si, 12.0 wt.% Al, 4.1 wt.% Fe, 47.1 wt.% O, 1.9 wt.% K and 1.2 wt.%

Ti. Sample C, Cu - modified catalyst contained 25.1 wt.% K, 21.3 wt.% Si, 16.6 wt.% Cu, 26.8 wt.% O, 7.5 wt.% Al, and 2.7 wt.% Fe. These results were in good agreement with X-ray diffraction (XRD) pattern. The FTIR spectra of sample A raw, B – calcined and sample C, Cu–modified catalyst displayed some bands (as shown in Figure 3). The distinctive broad bands 3390 cm^{-1} for the three samples corresponds to the O–H stretching vibrations and water molecules indicative of the high amount of water physisorbed on the catalyst surface. Similar results were reported by Hasheminejad *et al.*, (2011). The broad appearance at 3400 cm^{-1} corresponding to O–H stretching mode of adsorbed water shifted to relatively lower wave number of 3200 cm^{-1} in sample B and C . The band at 3754 cm^{-1} is a weak absorption and 3830 cm^{-1} is a strong band and both of them are assigned to out of plane stretching vibration and phases symmetric stretching respectively according to Fierro et al.,(2005) The sample A raw clay shows a series of band in the bending region mode with corresponding peak at 2422 cm^{-1}, 771 cm-1 and 516 cm^{-1} and can be respectively assigned to the Al–Al–OH, Al–Mg–OH and Si–OH–Al vibration of clay sheet. Similarly peaks are observed at 2423 cm^{-1}, 752 cm^{-1} and 613 cm^{-1}.These peaks are quite intense and they are attributed to bending vibration mode of adsorbing water on the surface of free silica. Also for sample C, Cu modified peaks are 2527 cm^{-1}, 826 cm^{-1} and 681 cm^{-1}. These peaks are due to thepresence of Cu-O vibrations in the compound. The thermal treatment of the A raw sample could also be responsible for the reduced Aluminium and Magnesium content seen on the XRF result (Table 1). The significant peak decreases in the range of 774 cm^{-1} to 613.4 cm^{-1} are identified as the Iron metal polyoxocations link with Al–O in the alumina tetrahedral sheet and Si–O in the silica octahedral plate. The observed functions in this catalyst are also supported by the work of Fierro et al., (2005). A large surface area of a catalyst is known to favour reactivity and is directly proportional to it as reported by Olutoye and Hameed (2009). Thus, large surface area will enhance the catalyst activity. From Table 2 the surface area determination of the samples showed that A- raw exhibited a surface area of 2.4 m^2/g, B-calcined has 1.8 $m^2/$ and Cu modified sample C has 4.10 m^2/g. According to Tseng and Wang (2011), large surface area of catalyst materials would enhance mass transfer and overcome diffusion resistance. Also large surface areas facilitate good contact between the active sites of catalyst and reactant. (Yukselen and Kaya, (2006). Therefore, the large surface area of Cu modified sample suggest that there will be a good contact between the active sites of the catalyst and the reactant (PE). Hence, Cu modified sample will be a good catalyst for polyethylene degradation when compared to other samples.

Table 2: Specific surface area (SSA), equivalent pore area and pore volume of the synthesized catalyst.

Sample	Specific Surface Area (m^2/g)	Equivalent pore Area (m^2)	Equivalent pore Volume (m^3/g)
A-Raw	2.40	0.0078	0.004
B-Calcined	1.80	0.31	0.034
C, Cu – modified	4.10	0.44	1.76

Performance of the synthesized Copper modified catalyst on polyethylene Degradation

The liquid products obtained from catalytic degradation.of LDPE were characterized using GC-MS analysis which produced chromatogram that contain about 26 peaks and each of these peaks represent an identified compound. The percentage yields of each of the identified compounds were calculated by measuring the area (cm^2) of the line under which they appear as a percentage of the total area of the peaks. The percentage abundance of the identified compounds is shown on Tables 3.

Table 3: Hydrocarbons and their relative abundance in the liquid product

Hydrocarbon	Weight %	Suggested petroleum faction
C_8–C_9	6.46	petrol (gasoline)
C_{10}–C_{15}	32.62	kerosene
C_{16}–C_{25}	60.92	diesel (gas oil)

The GC-MS analysis result was used to characterize the liquid product of catalytic degradation by peaks in the chromatogram and these peaks were assigned to paraffinic and olefin hydrocarbons in the carbon number range C_8—C_{24}. More paraffinics were produced than olefinics and were mostly straight chain. Also, the most abundant compounds are those in the C_{16}—C_{25} range which correspond to gas oil (diesel) fraction. These observations were confirmed by the result of Ortega et al., (2006) which revealed that the liquidhydrocarbon products are classified as gasoline (C_5—C_{12}), kerosene (C_{15}—C_{17}) gas oil (C_{18}—C_{28}), and fuel oil (C_{29}—C_{44}) yet in another report, products in the C_9—C_{25} range obtained were analyzed into fractions and conclusion was made that the products conform to the hydrocarbon products from refineries which include, petrol, C_4—C_{12}, kerosene C_{10}—C_{18}, diesel C_{15}—C_{25}, fuel oils C_{20}—C_{50} (Low et al., 2001). Therefore, it can be inferred that the GC- MS analysis showed that the liquid products obtained in this work also represent those in the main hydrocarbon corresponding to gas oil (C_{16}—C_{25}) boiling point range 20—175°C (Van-Grieken et al., 2001)

Effect of Various Parameters studied during LDPE Degradation Reaction

In order to monitor the performance of the prepared sample C, Cu modified catalyst on the yield of gas oil; several factors were studied such as the effect of catalyst loading, the temperature of reaction and time of reaction.

Effect of Temperature

The effect of the reaction temperature during the degradation reaction was studied with the Cu modified clay catalyst over the ranges of 220–250 °C. Figure 4 shows the effect of time on gas oil yield using catalyst loading of 1.0 g and 5.0 g of PE (feed) at 250 °C in 1 h reaction time, the yield of gas oil increased steadily from 220 to 250 °C, as the temperature increases the yield of gas oil increased to 50.12%. Based on the data generated from GC-MS an increase in reaction temperature increases the liquid products yield. This reaction emphasizes the importance of operating parameter such as temperature on the quality of product yield. Percentage yield of gas product obtained in the presence of Cu modified catalyst are given in Figure 4. Although complete degradation was not achieved but using a basis of 80 wt.% yield of product at T=220 °C,230 °C,240 °C and 250 °C, the yield

obtained is Y_1, Y_2, Y_3 and Y_4 respectively. where T=Temperature (°C) and Y=Gas oil yield (%).

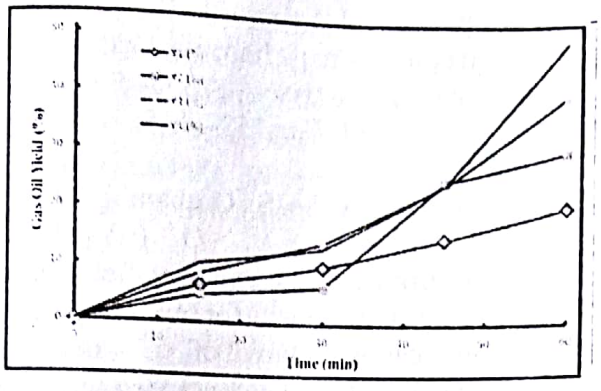

Figure 4: Percentage yield of gas oil (C_{16}—C_{25}) versus time at various operating temperatures of 220-250 °C.

Effect of catalyst loading

The effects of catalyst loading were studied by varying the amount of catalyst loading into the reactor with respect to the mass of the feed (PE) used in the reaction. Within the range of 1 –4 g, the conversion of the feed to gas oil at a temperature 250 °C in 1 h fixed reaction time at different weight is shown in Figure 5. These experiments showed that the yield increases with the catalyst loading up to a maximum of 3 g and then decreases as the loading increased. The loading of 4 g caused the formation of more viscous phase (emulsion) which limited the mass transfer of components to the catalyst active surface causing a phenomenon that can be referred to as saturation and diffusional problems during the reaction. This effect decreased the yield of gas oil as observed with higher catalyst loading.

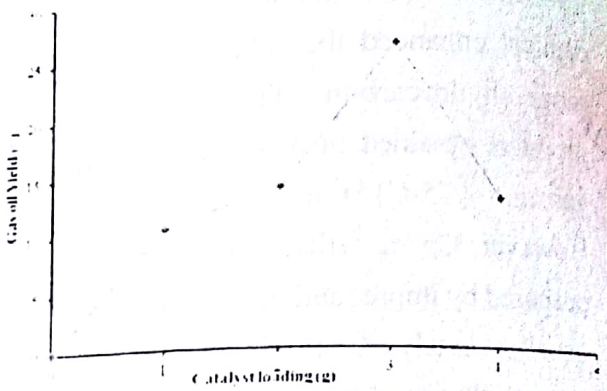

Figure 5: Percentage yield of gas oil versus catalyst loadings

Conclusion

Clay modified with Cu catalysts were successfully synthesized. The synthesized catalyst was used in catalytic degradation of LDPE. Characterization techniques were effective in understanding the structural properties of the synthesized catalyst. XRD analysis of the synthesized catalyst showed that the regularly ordered structures of the clay catalysts were not distorted with incorporation of Cu into the structure. For Cu-modified sample, it was observed that the incorporation was more efficient. SEM images of the synthesized samples revealed regularly ordered honeycomb pore structures especially in Cu-modified sample which is an important factor to its high catalytic performance in the degradation of PE (Olutoye *et al.*, 2009). Also the synthesized catalysts were crystalline which makes it good catalyst for PE degradation. The products obtained were gas and liquid hydrocarbons. The GC-MS analysis of products showed that C_{16}- C_{25} range which corresponds to gas oil (diesel) fraction were predominant and gasoline which is in the range

C5-C15 were also obtained, that is Cu modified catalyst enhanced the production of gasoline range hydrocarbon. Therefore the useful products obtained in this research work were gasoline (C5-C15) and gas oil (C16-C25). However, Cu modified catalyst which was prepared by impregnation method showed to be excellent catalyst for the degradation of PE with several advantages such as high yield of the products, short reaction time, inexpensive and environmental friendly procedure. The catalyst activity was found to increase the yield of gas oil to 50.22% at catalyst loading of 1.0 g and temperature of 250 °C in 1 h.

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