



Aromatic fuel oils produced from the pyrolysis-catalysis of polyethylene plastic with metal-impregnated zeolite catalysts



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ARTICLE INFO

Article history:

Received 5 June 2017

Received in revised form

10 October 2017

Accepted 10 October 2017

Available online 19 October 2017

Keywords:

Pyrolysis

Catalysts

Plastics

Fuel

Chemicals

ABSTRACT

Pyrolysis-catalysis of high density polyethylene (HDPE) was carried out in a fixed bed, two stage reactor for the production of upgraded aromatic pyrolysis oils. The catalysts investigated were Y-zeolite impregnated with transition metal promoters with 1 wt% and 5 wt% metal loading of Ni, Fe, Mo, Ga, Ru and Co to determine the influence on aromatic fuel composition. Pyrolysis of the HDPE took place at 600 °C in the first stage of the reactor system and the evolved pyrolysis gases were passed to the second stage catalytic reactor, which had been pre-heated to 600 °C. Loading of metals on the Y-zeolite catalyst led to a higher production of aromatic hydrocarbons in the product oil with greater concentration of single ring aromatic hydrocarbons produced. The single ring aromatic compounds consisted of mainly toluene, ethylbenzene and xylenes, while the 2-ring hydrocarbons were mainly naphthalene and their alkylated derivatives. There was a reduction in the production of multiple ring aromatic compounds such as, phenanthrene and pyrene. The addition of the promoter metals appeared to have only a small influence on aromatic oil content, but increased the hydrogen yield from the HDPE. However, there was significant carbon deposition on the catalysts in the range 14–22 wt% for the 1% metal-Y-zeolite catalysts and increased to 18–26 wt% for the 5 wt% metal-Y-zeolite catalysts.

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1. Introduction

The plastics contained in municipal solid waste consist of about 50–70% of packaging materials comprising polyethylene (high and low density polyethylene (HDPE & LDPE)), polypropylene (PP), polyethylene terephthalate (PET), polystyrene (PS) and polyvinyl chloride (PVC). Of the plastic waste generated, ~70% is ascribed to polyethylene [1]. With the increasing concerns around waste plastics in the environment, there is current great interest in developing new recycling technologies. Waste plastics recycling processes include mechanical/reprocessing of the waste plastic to form new products, however, this route tends to be based around the production of low quality goods. Incineration of municipal solid waste which contains ~10 wt% plastic is an option which disposes of the plastic to recover energy, but results in loss of the resource. An alternative process, is thermal recycling via pyrolysis/gasification techniques which produce gases, liquid and solid products that can be used as fuels and chemicals [1–6]. Additionally, catalysts may be incorporated into the pyrolysis process to enhance the quality of the end-product liquid and gaseous fuels or the production of higher value chemicals [2,6]. Catalytic degradation of polyolefins, particularly polyethylene, for the production of fuels and chemicals has been studied by several researchers [7–13]. Silica-alumina and zeolite catalysts have been used for catalytic degradation of polyolefins to produce lower molecular weight distribution fuels and chemicals such as benzene, toluene and xylenes [6–15].

Incorporation of metals into the catalyst can enhance the production of upgraded fuels and chemicals in the product stream. Metals incorporated on several catalyst support materials such as zeolite, activated carbon and silica-alumina for pyrolysis-catalysis of plastic waste for the production of fuel and chemicals have been conducted [9,16,17]. For example, Uemichi et al. [9] impregnated Pt, Fe, Mo, Zn, Co, Ni and Cu on activated carbon for the catalytic pyrolysis of polyethylene to produce aromatic hydrocarbons which resulted in the higher production of aromatic hydrocarbons compared with that of the metal free catalyst. Nishino et al. [17] used a Ga-ZSM-5 catalyst for the catalytic

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pyrolysis of industrial plastic waste and reported a liquid product yield of >50% consisting of >80% aromatic compounds which were mostly single ring benzene, toluene, o-xylene, m-xylene, and p-xylene.

There is value in further exploring the influence of incorporating metals into different types of zeolite catalysts to determine their influence on the production of higher grade fuels and chemicals. In this work, the incorporation of transition metals impregnated on Y-zeolite for the pyrolysis-catalysis of high density polyethylene in a two stage reactor for the production of fuels and chemicals has been investigated. The transition metals used were nickel (Ni), iron (Fe), molybdenum (Mo), gallium (Ga), ruthenium (Ru) and cobalt (Co). The Y type zeolite (faujasite) consists of a cage like structure with pores comprised of 12- membered rings.

2. Materials and methods

2.1. Materials

The plastics sample used as feedstock for the experiments was virgin high density polyethylene (HPDE) of ~5 mm diameter particle size in the form of pellets and was obtained from BP chemicals, Grangemouth, UK. The Y-zeolite was obtained from Nankai University Catalyst Co. Ltd, Tianjin, PR China. The transition metals were impregnated on the Y-zeolite at 1 wt% and 5 wt% metal concentrations. The procedure for the preparation of the catalysts involved; aqueous solutions of the metal were prepared from $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, $\text{Ga}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$, RuO_2 , and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ via dissolution in 20 ml deionised water with heating and stirring, at a temperature of 45 °C. The Y-zeolite support was added and then heated to 90 °C and was left to mix for about 1hr until it formed a semi-solid slurry. The slurry was dried overnight in an oven at 105 °C, calcined at 500 °C for 3 h and then sieved to obtain a uniform catalyst size of about 5 mm.

2.2. Pyrolysis-catalysis reactor

The two stage fixed bed reactor (Fig. 1) consisted of pyrolysis and catalytic sections made of stainless steel of total length 50 cm and 2 cm internal diameter. The first section involved pyrolysis where the plastic sample (2 g), held in place by a stainless steel crucible, was thermally heated to a temperature of 600 °C at a heating rate of 10 °C min^{-1} and held at 600 °C for 30 min. The evolved volatiles from pyrolysis of the plastic passed directly to a second stage catalytic bed containing 4 g of catalysts which had been previously heated and maintained at a temperature of 600 °C. Nitrogen was used as the carrier gas to purge product gases from the reactor. Two thermocouples were used to measure the temperature in each reactor. The three condensers cooled in dry-ice (solid CO_2) were used to collect the liquid produced while the non-condensable gases were collected in a 25 L Tedlar™ gas sample bag.

2.3. Gas analysis

The non-condensable gases were analysed immediately after each experiment using packed column gas chromatography (GC). Hydrocarbon gases from C_1 to C_4 were analysed by a Varian CP 3380 GC with a flame ionisation detector (FID), 2 m × 2mm GC column, 80–100 mesh size HayeSep packed column and N_2 carrier gas. Permanent gases, H_2 , CO , N_2 and O_2 were analysed using a second Varian CP 3330 GC with a thermal conductivity detector (TCD), 2 m × 2mm GC column, 60–80 mesh molecular sieve size HayeSep packed column and Ar

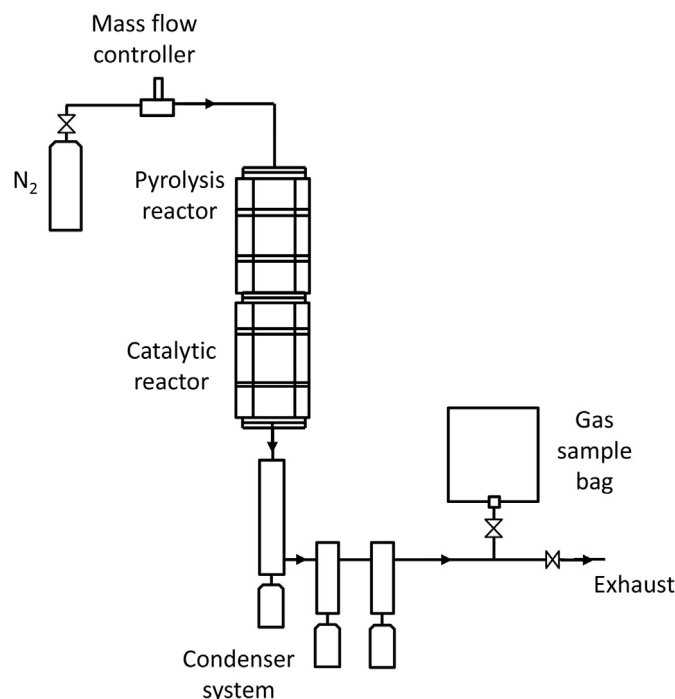


Fig. 1. Schematic diagram of the two-stage pyrolysis-catalysis fixed bed reactor system.

carrier gas. CO₂ was analysed with a 3rd Varian CP 3330 GC with TCD and 2 m long x 2 mm diameter GC column, 60–80 mesh molecular sieve size and Ar as the carrier gas.

2.4. Oil analysis

The oil produced was analysed using a Varian 430 liquid gas GC with FID, equipped with a split/split-less injection port having injection volume of 2 μ L. Hydrogen was used as the carrier gas with a constant flow rate of 1 ml min⁻¹. The analysis was performed on a ZB-1 capillary column 30 m long \times 0.53 mm i.d. and 0.5 μ m solid phase thickness. The GC column was programmed with temperature from 40 to 310 °C at a heating rate of 5 °C min⁻¹. The GC system was calibrated with aromatic and polycyclic aromatic hydrocarbon (PAH) standards. In order to confirm the presence of aromatic components in the oil, relative retention indices and a GC/mass spectrometry (GC/MS) were employed for compound identification. The GC/MS was a Varian CP-3800 GC/Varian Saturn 2200 MS instrument equipped with DB-5 capillary column of 30 m long \times 0.53 mm i.d. and 0.25 μ m solid phase thickness.

2.5. Characterisation of catalysts

Brunauer Emmet and Teller (BET) nitrogen adsorption analysis was used for the determination of surface area, pore size and pore volume of the fresh catalysts using a NOVA 2200e instrument. The catalyst samples were degassed for 3 h at 200 °C under a nitrogen atmosphere and the experiment was then carried out under liquid nitrogen to obtain the adsorption and desorption isotherms at a constant temperature.

Controlled oxidation of the carbon deposited on the used catalysts after reaction was carried out to determine the amount and type of carbon deposited. The used catalysts were analysed by temperature programmed oxidation (TPO) using a Shimadzu 50 thermogravimetric instrument. A sample weight of 25–30 mg of the reacted catalyst was heated from room temperature to 800 °C at a heating rate of 15 °C min⁻¹. Air was used as the oxidising agent. The catalysts recovered from the reactor after pyrolysis-catalysis were also examined using scanning electron microscopy (SEM) using a Hitachi SU8230 SEM instrument.

3. Results and discussion

3.1. Product yield and gas composition in relation to Y-zeolite metal

Table 1 shows the surface area and porosity of the prepared metal Y-zeolite catalysts. The Y-zeolite catalyst had a BET surface area of 421 m² g⁻¹, and impregnation with the metals produced, in most cases, a small decrease in surface area. Pierella et al. [18], also reported a small decrease in the surface of ZSM-5 zeolite catalyst when metal promoters, including Mo and Zn, were incorporated into the catalyst.

The product yield obtained from pyrolysis-catalysis of high density polyethylene over the Y-zeolite catalyst and the Y-zeolite catalyst impregnated with Ni, Mo, Fe, Ga, Ru and Co metals are shown in Table 2. The product yield include gases, liquid, and carbon deposited on the catalyst; no pyrolysis residue or char was produced in these experiments. Pyrolysis of the HDPE without a catalyst, but with a substitute of quartz sand of similar particle size, produced a mainly liquid product of ~70 wt% and a gas yield of 21 wt%. Introduction of the Y-zeolite catalyst into the second stage produced a significant increase in gas yield to 36 wt% and a corresponding decrease in oil yield. In addition, there was deposition of carbon on the catalyst. Addition of the metal promoter to the Y-zeolite showed only a small difference in oil and gas yield compared to the non-metal containing Y-zeolite, however, there was a marked increase in the deposition of carbon on the metal-Y-zeolite catalyst. Uemichi et al. [9] also reported an increase in carbon deposits on metal catalysts compared to metal free catalysts for the thermal degradation of polyethylene. In addition, Guisnet et al. [10] reported the deactivation of catalyst occurred faster with the introduction of Pt metal on zeolite catalyst due to the formation of carbon deposits on the metal catalyst compared to metal free catalyst.

Table 2 also shows the composition of the gas product (as vol%) derived from the pyrolysis-catalysis of the HDPE with the metal impregnated Y-zeolite catalysts. The main gases produced in the absence of catalyst were methane, ethane, ethene, propane and propene together with lower concentrations of C₄ hydrocarbons. However, in the presence of the Y-zeolite, there was significantly higher concentrations of hydrogen produced and lower C₂ – C₄ hydrocarbon concentration. The influence of metal addition to the Y-zeolite was to further enhance the concentration of hydrogen in the product gas and higher concentrations of metal addition further increasing hydrogen concentration in the product gas. For example, the Ni-Y-zeolite produced a product gas with 52 vol% hydrogen content at a metal loading of 1 wt %, which further increased to 66 vol% of hydrogen as the metal concentration was increased to 5 wt% Ni. Similarly, the Co-Y-zeolite catalyst produced a hydrogen content in the gas product of 47 vol% at 1 wt% metal loading and increased to 68 vol% hydrogen at a 5 wt% cobalt loading. The order of the metal impregnated catalysts in terms of hydrogen vol% in the product gas at 5 wt% metal loading was Co > Ni > Mo > Ga > Fe > Ru. The increased hydrogen content of the product gases produced a consequent decrease in C₁-C₄ hydrocarbons.

Table 1
BET surface area and porosity of prepared metal-Y-zeolite catalysts.

Catalysts	BET surface area (m ² g ⁻¹)		Pore volume (cm ³ g ⁻¹)		Pore size (nm)	
Y-zeolite (no-metal) (Y-Zeo)	421		0.26		1.81	
Metal content (wt%)	1%	5%	1%	5%	1%	5%
Ni-Y-zeolite (NiYZ)	357	311	0.23	0.19	2.02	2.19
Fe-Y-zeolite (FeYZ)	340	293	0.22	0.20	1.99	2.37
Mo-Y-zeolite (MoYZ)	422	376	0.26	0.25	1.71	2.02
Ga-Y-zeolite (GaYZ)	424	396	0.27	0.25	1.86	1.84
Ru-Y-zeolite (RuYZ)	405	418	0.25	0.27	1.72	2.13
Co-Y-zeolite (Co-YZ)	431	383	0.27	0.25	1.74	2.01

Table 2
Product yield from the pyrolysis-catalysis of high density polyethylene with Y-zeolite and metal-Y-zeolite.

	Pyrolysis	Y-zeolite	Ni-Y-zeolite		Mo-Y-zeolite		Fe-Y-zeolite		Ga-Y-zeolite		Ru-Y-zeolite		Co-Y-Zeolite	
			1 wt%	5 wt%	1 wt%	5 wt%	1 wt%	5 wt%	1 wt%	5 wt%	1 wt%	5 wt%	1 wt%	5 wt%
Gas yield (wt.%)	21	36	36	36	38	36	33	38	37	37	42	31	36	40
Oil yield (wt.%)	69	45	36	43	31	35	40	30	36	29	34	43	36	30
Carbon (wt.%)	–	10	22	18	24	20	14	22	18	24	18	20	22	26
Gas composition (vol%)														
Hydrogen	5	33	52	66	48	60	36	45	38	54	31	39	47	68
Methane	19	24	18	28	18	12	25	18	23	16	26	8	18	12
C ₂ hydrocarbons	47	18	11	1	13	10	18	12	17	11	18	21	12	5
C ₃ hydrocarbons	23	22	16	3	18	12	17	17	20	15	21	27	19	9
C ₄ hydrocarbons	6	3	3	3	4	5	4	7	3	4	3	4	4	6

3.2. Oil composition

Figs. 2 and 3 show the aliphatic and aromatic hydrocarbon content of the product oils produced from the pyrolysis-catalysis of high density polyethylene over the prepared metal-Y-zeolite catalysts in relation to metal loading concentrations of 1 wt% and 5 wt%. Compared to the non-catalysed pyrolysis, there was a marked change in product oil chemistry with the introduction of the catalyst. Non-catalytic pyrolysis produced a mainly aliphatic product oil of >99% product oil composition. Therefore, the yield of oil which was 69 wt% was almost entirely aliphatic in composition (Table 2). However, introduction of the Y-zeolite to the pyrolysis-catalysis process, although reducing oil yield to 45 wt% (Table 2), produced an oil product with an aromatic hydrocarbon content of ~80% (Fig. 2). Also, the addition of a 1 wt% metal concentration to the Y-zeolite produced a decrease in the product oil yield, but an increase in aromatic hydrocarbon content of the product oil and a consequent decrease in aliphatic hydrocarbon content. For some particular metals, the aromatic content increased markedly. For example, the aromatic content of the product oil for the 1 wt% Ga-Y-zeolite was 93.1%, for the 1 wt% Fe-Y-zeolite it was 93.5%, for the 1 wt% Ru-Y-zeolite the aromatic content reached 94.4% (percentages calculated as GC peak area). The addition of 5 wt% of cobalt to the Y-zeolite produced no effect on the aromatic hydrocarbon content of the product oil compared to the non-metal zeolite catalyst. It should also be noted that the Co-Y-zeolite also produced the highest deposition of carbon on the catalyst during reaction.

Serrano et al. [19] have reviewed different types of solid acid catalysts (e.g. zeolites) and their influence on the process of catalytic pyrolysis of waste plastics (polyolefin plastics) for the production of fuels and chemicals. They also suggested a mechanism for the catalytic pyrolysis process through a carbocation catalytic cracking mechanism to produce carbenium ions via Lewis acid site reactions or carbonium ions via protonation of hydrocarbons on Bronsted acid sites. Subsequent isomerisation, oligomerization, cyclization, aromatisation and cracking reactions occur on the catalyst to produce an aromatic-rich product oil. This is in contrast to non-catalytic pyrolysis where the polymer degradation process produces a mainly aliphatic hydrocarbon product slate consisting of alkanes, alkenes and alkadienes [20,21]. The mechanism involves initial random scission of the C – C bonds in the linear polymer structure to produce hydrocarbon fragments which stabilise to produce alkanes and alkenes through carbon-carbon double bond stabilisation [19–21].

Other researchers have reported the increase in aromatic content through the use of catalytic pyrolysis. For example, Auxilio et al. [22] used a two-stage pyrolysis-catalyst reactor system with continuous feeding of the plastic for the processing of virgin plastics and mixed plastic waste. The catalysts used were five different zeolite catalysts and clay-based catalysts in powder or pellet form. They reported that a high acidity clay-based catalyst in pellet form produced the highest yield of gasoline range (C₅ – C₁₁) oil product with 22 wt% aromatic content for the processing of high density polyethylene. Silva et al. [23] developed a novel HZSM-12 zeolite catalyst for the catalytic pyrolysis of high density polyethylene. The non-catalytic pyrolysis of the plastic produced a heavy molecular weight range hydrocarbon product mainly consisting of C₈ – C₂₂ hydrocarbons whereas catalytic pyrolysis produced mainly C₃ – C₇ hydrocarbons. Almstapha et al. [24] investigated a sulphated zirconia catalyst for the catalytic pyrolysis of high density polyethylene in a fixed bed reactor. The product oil contained hydrocarbons with a molecular weight range of C₇ – C₁₂ hydrocarbons with an aromatic content of 58 wt%.

It has been shown that the zeolite supporting material in addition to the presence of metals influences the production of aromatic hydrocarbons. For example, Huang et al. [25], described the application of transition metals supported on zeolite or silica-alumina catalyst as bifunctional catalysts with two functions, whereby the acidic support provides the cracking and isomerisation function while the metals provide the hydrogenation or aromatisation function. Fricke et al. [26] have suggested that introduction of a transition metal (gallium) into zeolites favours dehydrogenation activity and increases selectivity of aromatic hydrocarbons in the processing of hydrocarbons. Chang et al. [27] studied the reactions of hexane over Ga-ZSM-5 zeolite and reported that gallium provides the active site for cracking, oligomerization and cyclization of aliphatic hydrocarbon while the major factor influencing the performance of Ga-supported catalysts is the dispersion of gallium rather than its oxidation state [27]. Other researchers have investigated metal impregnated catalysts on different support materials such as activated carbon, silica-alumina, and zeolites for the thermal degradation of polyethylene for the production of aromatic hydrocarbons [25,28]. Scott et al. [28] investigated iron impregnated on charcoal for the fast pyrolysis-catalysis of polyethylene and other plastics and found high yields of aromatic compounds were produced. Uemichi et al. [9] also studied the use of transition metals as catalysts for the degradation of polyethylene over different support material such as activated carbon, Al₂O₃ and SiO₂-Al₂O₃. They reported that activated carbon gave the highest yield of aromatic hydrocarbons compared to Al₂O₃ and SiO₂-Al₂O₃ over the transition metals Pt, Fe, Mo, Zn, Co, Ni and Cu, with Pt, Fe, and Mo reported to be the most effective. Later work by the same group [16] showed that for catalytic pyrolysis of polypropylene, Pt produced more aromatic hydrocarbon yield than Fe on activated carbon as the catalyst support [16]. The literature suggests that the increased yields of aromatic compounds with certain transition metal-Y-zeolite catalysts used in this work is due to the dual activity of the Y-zeolite which induces cracking and isomerisation and that the metals enhance dehydrogenation and aromatisation reactions.

The addition of increased metal content at 5 wt% in the Y-zeolite catalysts produced a decrease in aromatic hydrocarbon concentration in the product oil (Fig. 3). The decrease in aromatic content was small for the Ni-, Fe- and Ru-Y-zeolite catalysts, but was more significant for the

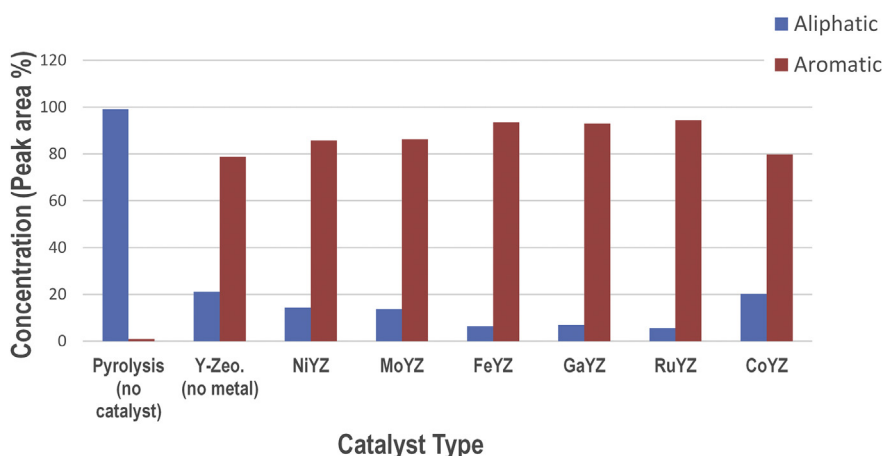


Fig. 2. Hydrocarbon composition of oil produced from pyrolysis-catalysis of HDPE, over Y-zeolite catalyst and with 1 wt% metal-Y-zeolite catalysts.

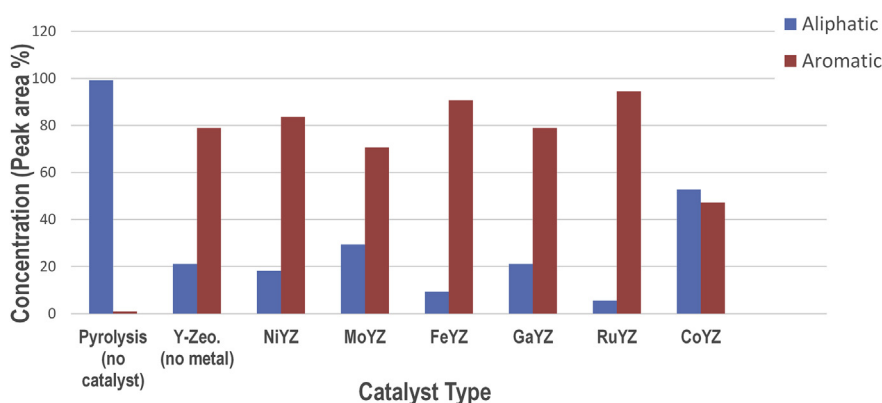


Fig. 3. Hydrocarbon composition of oil produced from pyrolysis-catalysis of HDPE, over Y-zeolite catalyst and with 5 wt% metal-Y-zeolite catalysts.

Mo-, Ga- and Co-Y-zeolites. For example, the 5 wt% Mo-Y-zeolite catalyst showed a reduction in aromatic hydrocarbon content from 86.3% for the 1 wt% catalyst to 70.6% at 5 wt% metal content. Also, for the cobalt Y-zeolite catalyst at 5 wt% addition, the aromatic hydrocarbon content of the product oil fell to only 47.3 wt%. The 5 wt% Co-Y-zeolite catalyst also produced the lowest oil yield and the highest deposition of carbon onto the catalyst at 26 wt% (Table 2).

Table 3 shows the single and 2-ring aromatic hydrocarbons and larger polycyclic aromatic compounds distribution of the aromatic hydrocarbons of the product oil. The results show that most of the aromatic hydrocarbons are single and 2-ring aromatic hydrocarbons. The Y-zeolite with no metal addition produced a product oil with 95.3% 1–2 ring aromatic hydrocarbon content and with the addition of the metal promoters this increased to 97–99% 1–2 ring aromatic content. The single ring aromatic hydrocarbons were mostly toluene, ethylbenzene and xylene and the 2-ring aromatic hydrocarbons were naphthalene and alkylated naphthalenes. The higher molecular weight >3-ring polycyclic aromatic hydrocarbons were mostly 3-ring phenanthrene and 4-ring pyrene and alkylated derivatives. Increasing the metal content to 5 wt% resulted in only a small decrease of ~1% in 1–2 ring aromatic hydrocarbon content. Matsui et al. [29] in their investigation of the reactions of polycyclic aromatic hydrocarbons over nickel-zeolite reported an increased yield of single and two ring aromatic hydrocarbons.

3.3. Carbon deposited on the catalyst

Thermogravimetric analysis-temperature programmed oxidation (TGA-TPO) was used for the determination of the amount of carbon deposited on the reacted metal-Y-zeolite catalysts. The pyrolysis-catalysis processes can form carbon deposits on the catalyst, the TGA-

Table 3

Aromatic ring distribution of oil produced from pyrolysis of HDPE, over Y-zeolite and 1 and 5 wt% metals/Y-zeolite catalysts, (peak area %).

	Y-Zeolite (no metal)	Ni-Y-Zeolite	Mo-Y-Zeolite	Fe-Y-Zeolite	Ga-Y-Zeolite	Ru-Y-Zeolite	Co-Y-Zeolite
1 wt% metal							
1-2 ring aromatics	95.3	98.6	98.7	96.8	98.9	98.0	98.3
Multiple ring aromatics	4.7	1.4	1.3	3.2	1.1	2.0	1.7
5 wt% metal							
1-2 ring aromatics	95.3	96.2	97.7	97.3	96.3	96.9	97.0
Multiple ring aromatics	4.7	3.8	2.3	2.7	3.7	3.2	3.0

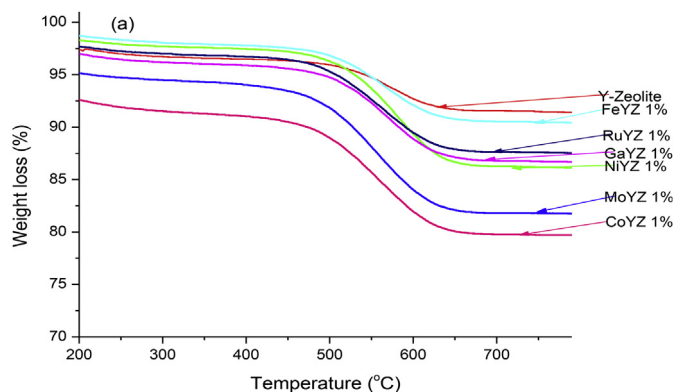


Fig. 4. TGA-TPO thermograms for the used 1 wt% metal loaded Y-zeolite catalysts after pyrolysis-catalysis of the HDPE.

TPO process oxidizes the carbon in relation to the temperature of oxidation. Fig. 4 shows the TGA-TPO thermograms for the used 1 wt% metal loaded Y-zeolite catalysts and Fig. 5 shows the TGA-TPO thermograms for the 5 wt% metal catalysts after pyrolysis-catalysis of the HDPE. The TGA-TPO weight loss data showed that between 14 and 22 wt% carbon was deposited on the 1% metal-Y-zeolite catalyst while for the 5 wt% metal-Y-zeolite catalysts the range of carbon deposition was between 18 and 26 wt% (data also shown in Table 2). This indicates that as the percentage metal loading on the catalyst was increased from 1 wt% to 5 wt%, the more carbon was deposited on the catalyst. The oxidation of the carbon occurred over a temperature range of 400–650 °C. It has been reported that carbon oxidation occurring in the lower temperature range of 450–550 °C is mainly ascribed to amorphous type carbon and oxidation in the temperature range of 550–650 °C is ascribed to filamentous type carbon [30]. The amorphous type carbons are more problematic for catalyst activity in that they encapsulate the metal particles, reducing catalyst activity. Filamentous carbons grow away from the catalyst surface and have lesser of an effect on catalyst activity.

The deposition of carbon onto the Y-zeolite catalysts will have significant impact on the efficiency of the pyrolysis-catalytic processing of the plastic. The carbon will block the pores of the Y-zeolite and also cover the acidic active sites of the Y-zeolite and the metal active sites of the added promoter metals. Thereby, the reactions of the pyrolysis gases produced from the pyrolysis of the plastic over the catalyst will be reduced, leading to lower content of aromatic hydrocarbons in the product oil. For example, the Co-Y-zeolite with the highest carbon deposition on the catalyst produced an oil with a lower aromatic hydrocarbon content. Scanning electron microscopy (SEM) imaging was used to characterise the reacted metal-Y-zeolite catalysts. These images give an identification to the types of carbon deposited on the reacted catalyst. Fig. 6 show the SEM images of the Y-zeolite and the Co-Y-zeolite at 1 wt% and 5 wt% loading. Noticeable on the SEM micrographs were the filamentous type deposits of carbon on the catalyst surface, particularly at the 5 wt% metal loading.

The process of two-stage pyrolysis-catalysis of high density polyethylene for the production of a high aromatic content feedstock for the production fuels or chemicals has been demonstrated. However, further investigation is required to advance the process. There is particular interest in developing different types of catalyst for example, hierarchical catalysts [19] or staged catalysis [31] where the large polymer hydrocarbon fragments from pyrolysis can be firstly cracked to smaller molecules which can then enter smaller pores to enhance the yield of aromatic hydrocarbons [19]. Minimisation of catalyst deactivation through coke formation on the catalyst, which blocks active catalytic sites, is also an area for catalyst development. For real-world waste plastics there is also the issue of contamination of the plastics and the potential release of sulphur and halogenated species which may poison the catalyst. Scale-up of the technology to a continuous system would also be required for larger scale plants. The two-stage system would require a continuous first stage such as a rotary kiln or screw kiln pyrolysis unit followed by the catalytic stage, where the catalyst could be quickly regenerated, such as a circulating fluidised bed, similar to a petroleum refinery catalytic cracking unit. Testing the product oil either for its potential as a substitute refinery ready feedstock for further processing, direct application as a fuel for use as a boiler/furnace fuel or use in engines should also be assessed [6].

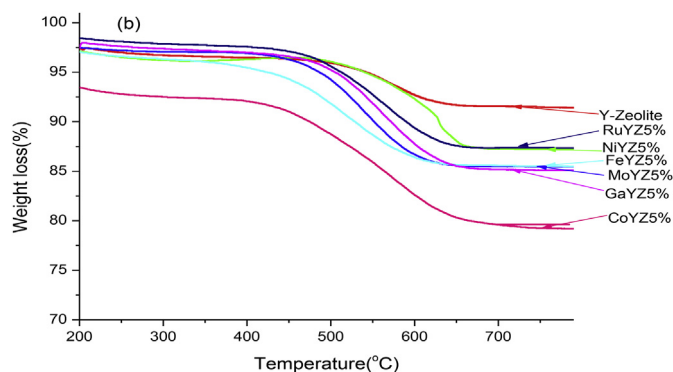


Fig. 5. TGA-TPO thermograms for the used 5 wt% metal loaded Y-zeolite catalysts after pyrolysis-catalysis of the HDPE.

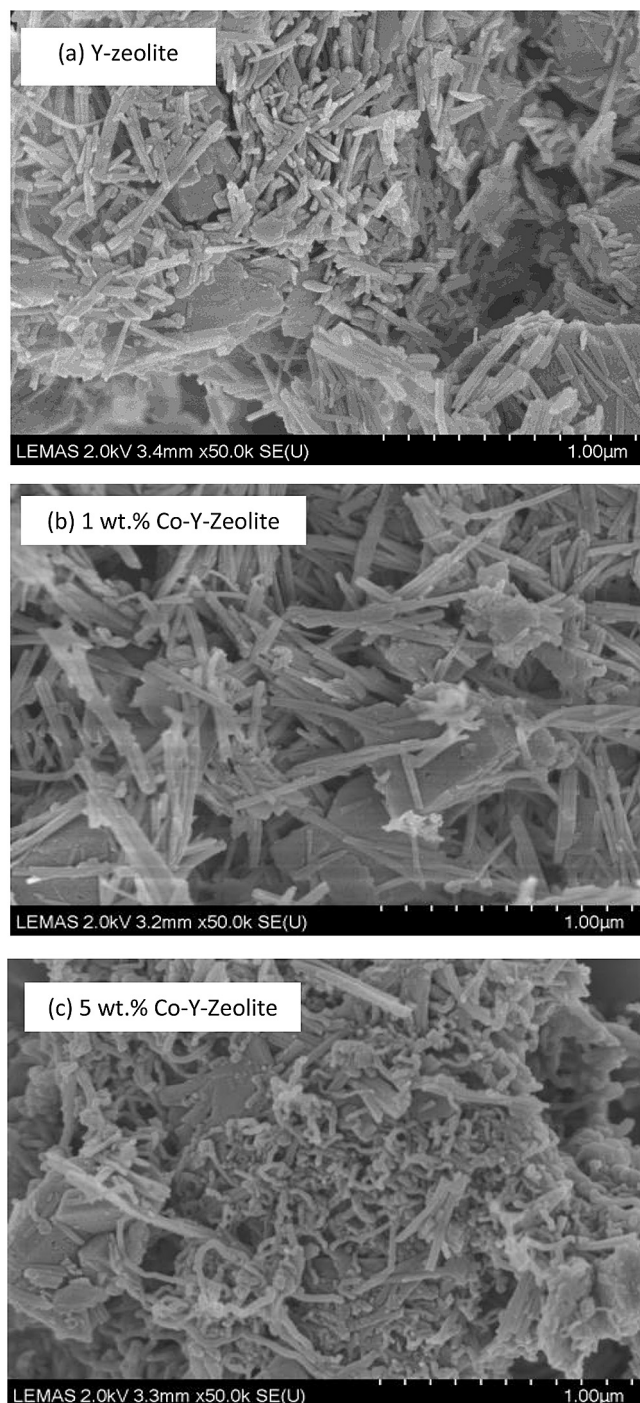


Fig. 6. Scanning electron microscope images of (a) the Y-zeolite and (b) the 1 wt% Co-Y-zeolite and (c) the 5 wt% Co-Y-zeolite after pyrolysis-catalysis of the high density polyethylene.

4. Conclusions

High density polyethylene (HDPE) has been pyrolysed in a fixed bed two stage pyrolysis-catalysis reactor at a catalyst temperature of 600 °C. The non-catalytic pyrolysis of the HDPE produced a high oil yield (~70 wt%) comprising of almost 100% aliphatic hydrocarbon content. Introduction of the Y-zeolite catalyst produced a reduction of oil yield, but the composition of the oil was mostly aromatic hydrocarbons (~79%). Loading transition metals which included nickel, iron, molybdenum, gallium, ruthenium and cobalt on the Y-zeolite catalyst promoted the formation of aromatic hydrocarbons (80–95%) in the product oil and increased hydrogen gas production. The aromatic hydrocarbons in the product oil using the metal-promoted Y-zeolite catalysts showed that the oil was composed of between 97 and 99% 1–2 ring aromatic compounds. The aromatic hydrocarbons in the oil were mostly toluene, ethylbenzene and xylene and the 2-ring aromatic hydrocarbons were naphthalene and alkylated naphthalenes. However, the introduction of the metal promoters to the Y-zeolite at

1 wt% addition resulted in high carbon deposition onto the catalysts of between 14 and 26 wt% of catalyst and at the higher metal loading of 5 wt% producing even higher carbon deposition. The carbon deposits were identified as mostly filamentous type carbon.

Acknowledgements

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 643322 (FLEXI-PYROCAT). Financial support from the Petroleum Technology Development Fund (PTDF) of Nigeria for a scholarship for K.A is also acknowledged.

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