MODIFICATION OF A SULPHATED ZIRCONIA CATALYST USING CALCIUM CARBIDE FOR CONVERSION OF PLASTIC WASTE INTO NON-AROMATIC LIQUID HYDROCARBONS

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ABSTRACT

Plastic consumption has increased 8% annually since the 1950 reaching an estimated 300 million tonnes in 2014, where more than 50% was discarded after single-use. Many recycling methods have been proposed to manage this growing waste, but most have practical, environmental and economic limitations. Catalytic conversion, a chemical recycling method using a suitable catalyst, has been suggested as a viable option since it can return plastic to a chemical feedstock, which is the aim of this work. Four potential catalysts, namely sulphated zirconia SZ, calcium carbide CC, molybdenum carbide MC and zirconium oxide ZO were tested for HDPE conversion, which was selected from five different polymer samples due to its high thermal resistance. It was found that only calcined SZ and calcined CC showed some impact HDPE conversion. However, SZ was marked with high coke yield while calcined CC had low conversion with virtually no coke. Therefore a hybrid catalyst was considered, where the SZ and the CC were mixed together on equal weight bases forming the hybrid catalyst SZ1CC1. Fixed bed pyrolysis showed an excellent HDPE conversion of virtually 100wt% using the hybrid catalyst at 410°C with 66.0wt% liquid yield against a 98.0wt% conversion with only 39.0% liquid yield for the pure SZ and no conversion in the case of HDPE only. The hydrocarbon composition of the liquid fraction obtained changed significantly from 58% aromatic and 16% paraffinic for the SZ to 74% olefinic and 23% naphthenic for the SZ1CC1. The improvement in liquid yield and selectivity to non-aromatic liquid was strongly linked to a modification in the acidic strength of the hybrid catalyst SZ1CC1. The moderation in acidity and textural properties, such as surface area and porosity were found to suppress excessive cracking and limiting secondary cracking reactions, that promotes high gas yield and aromatisation in the SZ. Overall, it is concluded that the SZ on its own, which had high acidic strength and large surface area, promoted secondary reactions during HDPE cracking that yielded aromatics. However, the hybrid catalyst SZ1CC1, which had moderate acid strength and low surface area halted any secondary reaction and terminated the cracking reaction at stages that produced only olefinic and naphthenic hydrocarbons.
DEDICATION

This work is dedicated to my beloved parents Alhaji Mustapha Dallatu and Hajiya Sa’adatu Mustapha and to the memory of cousin brother Late Alhaji Bello Mu’azu.
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NOMENCLATURE

BET        Brunauer-Emmett-Teller
CC         Calcium carbide
CHP        Combined Heat and Power
ECD        Electron Capture Detector
EDX        Energy-dispersive X-ray spectroscopy
ESA        External surface area
FCC        Fluid catalytic cracking
FID        flame ionisation detector
FIT-RHI    Feed-in tariffs and the renewable heat incentive
FPD        Flame Photometric Detector
GC         Gas Chromatography
HDPE       High Density Polyethylene
LDPE       Linear density polyethylene
LLDPE      Linear low density polyethylene
MCM-41     Mobil Composition of Matter No. 41
MOR        Mordenite
MS         mass spectrometry
MSW        Municipal solid waste
PAH        Polycyclic aromatic hydrocarbon
PS         Polystyrene
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
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<tbody>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>PVC</td>
<td>Polyvinylchloride</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning Transmission Electron Microscopy</td>
</tr>
<tr>
<td>SZ</td>
<td>Sulphated zirconia</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermal gravimetric analysis</td>
</tr>
<tr>
<td>TPD</td>
<td>temperature programmed desorption</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>Zeolite Socony Mobil–5</td>
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Hague, The Netherlands on April 21-25, 2013


Chapter 1 – INTRODUCTION AND GENERAL OVERVIEW

1.1 Background

Plastic is touted as “one of the greatest innovations of the 20\textsuperscript{th} century” due to its durability, low cost, safe usage and light weight (Panda et al., 2010). These properties coupled with its energy efficient production and design flexibility has made plastic a vital part of most aspects of human activities (Singhabhandhu and Tezuka, 2010, Zadgaonkar, 2004). As a result, the worlds’ plastic consumption increased from around 2 million tonnes per year in the 1950s to about 245 million tonnes per year in 2010 with a projection of reaching 300 million tonnes by 2015 (Singhabhandhu and Tezuka, 2010, Panda et al., 2010, Reddy et al., 2013). Since more than 50\% of the plastic is discarded after just a single-use, this has resulted in great environmental problems due to a sharp increase in the amount of post-consumer plastic waste (Singhabhandhu and Tezuka, 2010, Hopewell et al., 2009). Plastic waste resists natural degradation, and this makes landfill an unattractive option for plastic waste management (Miskolczi et al., 2009, Shent et al., 1999, Shah et al., 2010a, Huang et al., 2010, Lin et al., 1998, Lin and Yen, 2005, Zadgaonkar, 2004, Keane, 2009). Further, incineration may release harmful emissions into the environment and thus is difficult to implement due to local resistance (Singhabhandhu and Tezuka, 2010). Hence, there is a great opportunity to recycle plastic waste back into chemicals and/or fuels.

Thermal conversion of plastic waste to liquid hydrocarbon has a great potential as a chemical recycling method (Miskolczi et al., 2009, Al-Salem et al., 2009, Panda et al., 2010, Aguado et al., 2008, Walendziewski and Steininger, 2001, Wei et al., 2010, Coelho et al., 2010, Haig et al., 2013, Miskolczi et al., 2006, Miskolczi et al., 2004a). However, thermal conversion typically results in non-selectivity towards liquid product and requires high temperatures of over 500°C (Lin et al., 2007, Shah et al., 2010a). In view of this, catalytic conversion for improved selectivity and reduced conversion temperature has been suggested as a promising method to convert plastic waste to liquid hydrocarbon products that could be used as fuels and raw materials for the chemical industry (Lin et al., 1998, Shah et al., 2010a, Keane, 2009). Moreover, this method requires less energy and could be highly selective towards desired products, such as high liquid yields with a low aromatic content (Lin et al., 1998, Shah et al., 2010a, Jan et al., 2010).
Research in the area of catalytic conversion of plastic waste has received significant interest, where a range of studies using different types of polymers and plastic wastes as well as different catalysts have been published (Jan et al., 2010, Hussain et al., 2010, Shah et al., 2005, Lin et al., 1998, Lin et al., 2010, Lin, 2009, López et al., 2011). The catalysts reported were mainly zeolites based systems, such as ZSM-5, HUSY, BETA and HMOR (Arandes et al., 2007, Serrano et al., 2000a, Gobin and Manos, 2004, Serrano et al., 2007a, Lin and Yen, 2005, Tarrio-Saavedra et al., 2011). In addition, Al-MCM-41, silica-alumina, and FCC catalysts have also been reported (Huang et al., 2010, Saha et al., 2008, Shah et al., 2010a). However, most of these catalysts are very expensive and associated with low conversion, high gaseous product yield and low liquid yield with a high content of aromatic compounds (Saha et al., 2008). This has been associated with high acidity of the catalysts, which may result in secondary cracking of the liquid range hydrocarbons from the primary cracking to yield gaseous products. Hence, a tailored catalyst with moderate acidity, such as a doped super acid sulphated zirconia catalyst, might be suitable for a high conversion of plastic waste with high liquid yield (Saha et al., 2008, Akpanudoh et al., 2005). Little is known about the catalytic conversion of polyolefin plastic waste using sulphated zirconia, particularly HDPE based polymers, which accounts for 60-70% of the total plastic waste in municipal solid waste (Lin and Yen, 2005, Aboulkas et al., 2008a, Serrano et al., 2000b). However, sulphated zirconia catalyst has been reported as an excellent catalyst for oil refining processes, such as isomerisation, hydrocracking, alkylation, condensation, esterification, acylation and oligomerisation as well as for hydrocracking of waste plastic after modified with platinum and nickel (Clark, 2002, Reddy et al., 2005, Venkatesh et al., 1996).

In this work, a ‘super’ acid catalyst, sulphated zirconia (SZ) and its modified versions (SZCC) formed after series of modification were used as catalysts to converts polyolefin polymers into fuel-like hydrocarbons. Sulphated zirconia was selected as the main catalyst matrix for this work because it has been reported to have excellent catalytic properties, such as acidity, mesoporosity coupled with excellent stability, which makes it an exceptional catalyst for catalytic cracking (Yadav and Nair, 1999, Clark, 2002, Arata et al., 2003, Hino et al., 2006, Ahmed et al., 2008). However, sulphated zirconia on its own is known to promote aromatisation of long chain unsaturated hydrocarbon after cracking of the polymer structure. Also it deactivates quickly at high temperature as a result of coke formation on its surface, probably due to
its high acidity (Yadav and Nair, 1999, Clark, 2002). In view of this, the sulphated zirconia catalyst was modified by doping with other catalysts to modify the acidic and the textural properties of the resultant catalytic system. The modification may strengthen the catalyst against deactivation and improve its liquid product yield. The properties of the resultant hybrid catalyst may as well promote excellent performance towards plastic waste conversion and selectivity towards high-valued hydrocarbon products. Thus, the product could be used as a fuel substitute or as feedstock for the chemical industries.

1.2 Aims and objectives of the research

1.2.1 Research aim

This research work was aimed at developing a catalyst for efficient chemical conversion of polyolefin-based plastic wastes (LDPE, HDPE and PP) into fuels and feed-stocks for chemical industry. The research work is specifically aimed at modifying sulphated zirconia, a commercial catalyst by regulating its properties. Thus, the resultant catalyst could be cost-effect and thermally and mechanical stable at operational conditions. Emphasis was given to low temperature conversion aiming at high liquid yields with a low aromatic content. This will provide an option for sustainable and cost-effective recycling of plastic waste into non-aromatic liquid hydrocarbon, with the overall aim to promote the redirect waste polyethylene from landfill into fuels and recyclable materials.

1.2.2 Research objectives

The main research objectives were:

1. Modification of a sulphated zirconia catalyst to improve its thermal performance for improved conversion with low coke yield of plastic waste into liquid hydrocarbon (Chapter 4).
2. Test catalytic conversion using the modified sulphated zirconia thermally on a range of polymers and study the kinetics of the polymer degradation (Chapter 4).
3. To characterise the physicochemical, surface and bulk properties as well as the acidic and textural properties of the catalysts using a wide range of catalyst characterisation techniques (Chapter 5).

4. To pilot the catalysts for plastic waste conversion using a fixed-bed reactor and optimise the reaction conditions towards optimal liquid yields (Chapter 6).

5. To analyse the liquid and gaseous fraction for their hydrocarbon composition and carbon number distribution for possible usage to complement fossil fuels (Chapter 7).
Chapter 2 – LITERATURE REVIEW

2.1 Overview of global plastic production, consumption and waste generation

2.1.1 Global plastic production and consumption

The world’s plastic production has significantly increased from around 2 million tonnes in 1950 to around 245 million tonnes in 2010 due to high demand from different sectors of the economy (PlasticEurope, 2013, Almustapha and Andrésen, 2012, Butler et al., 2011, Panda et al., 2010). Figure 2.1 shows the world’s plastic production in 2012, where China was the largest producer with 23.9% followed by the whole of Europe with 20.4%. Western Europe alone generated 22 million tonnes with UK producing about 4.7 million tonnes (Aguado et al., 2008). Other Asian countries produced 15.8% of the world production which was about 50 million tonnes. As production keeps increasing, a significant amount of waste is generated in regions with strong per capita plastic consumption and where necessary action has not been taken to mitigate the growing waste from this plastic consumption.

Figure 2.1 World plastic production in 2012 (PlasticEurope, 2013).
Figure 2.2 compares the global per capita plastic consumption from 1980 to 2010 (Panda et al., 2010). United State of America has the highest per capita consumption of plastic of 150 kg/year followed by Western Europe with 120 kg/year and Japan with 100 kg/year. Since the consumption increases about 20-25% every ten years for US and Western Europe, this indicates that by 2020 the per capita of plastic consumption for the US and Western Europe alone will rise to about 200 Kg/year and 160 Kg/year, respectively (Al-Salem et al., 2009, Murata et al., 2009, Mutha et al., 2006, Singhabhandhu and Tezuka, 2010). More importantly, with the emerging Indian and Chinese markets, their average plastic per capita consumption of 10-40 kg/year in 2010 may increase to over 100-200 kg/year by 2030. The expected increase in plastic consumption will result in a significant generation of plastic waste which can have serious environmental consequences if not recycled (Miskolczi et al., 2004b, Coelho et al., 2010) This is highly likely due to the extensive use of plastic products, such as packaging, building & construction, automobile, electronics, health, and household with increased prosperity.

![Figure 2.2 Per capita plastic consumption in some countries and regions of the world (Panda et al., 2010).](image-url)
Figure 2.3 compares the plastic demand by different sectors of the economy in Europe. Plastic consumption in 2012 was 45.9 million tonnes, where packaging sector constituted the largest portion with 18.1 million tonnes followed by the building and construction sector with 9.3 million tonnes. The packaging industry, which uses mainly thermoplastic polymers, accounts for more than 1/3 of the plastic used in Europe and the whole world by extension (Shah et al., 2008). The subsequent increase in plastic consumption has resulted in a significant increase in plastic waste within EU and several studies have looked at the handling of municipal solid waste (MSW) that is generated (Miskolczi et al., 2004b, Coelho et al., 2010).

![Diagram showing plastic demand by different sectors](PlasticEurope2013.png)

**Figure 2.3 The European plastic demand by different sectors (PlasticEurope, 2013).**

### 2.1.2 Plastic waste generation

Currently, European plastic waste constituted about 15-25% of their total municipal solid waste (Achilias et al., 2007, Miskolczi et al., 2004b, Miskolczi et al., 2004a, Aguado et al., 2008). Current studies published by the Scottish Government showed that Scotland produced up to 305,000 tonnes in 2009 and this is expected to
increase to 500,000 tonnes per annum in 2015 (Haig et al., 2013). Less than half is being recycled, since plastic waste is increasingly becoming a very significant part of municipal solid waste where separation into traditional recyclable plastic is difficult. For example, in 1988, plastic waste was only 8% of all United States municipal solid waste, which rose to 11% in 2002 and 12.1% in 2007 and yet only 1/12 was recycled (Al-Salem et al., 2009, Encinar and Gonzalez, 2008, USEPA, 2011). Thus, large amounts of plastic waste are being generated and its accumulation has become a global environmental problem, particularly in developing countries, where state-of-the-art techniques to process solid municipal domestic wastes have not been properly put in place (Okonko and Eboatu, 1999). In Nigeria for instance, all Federal and States agencies are yet to ascertain the total per capita generation of plastic waste (Okonko and Eboatu, 1999). However, in main cities like Lagos, Kano and Ibadan, littering of plastic waste from food packaging is very common (Okonko and Eboatu, 1999). This is why the international environmental regulations and European legislations are promoting alternatives to land filling and incineration (Encinar and Gonzalez, 2008, Panda et al., 2010, Briassoulis et al., 2012, Haig et al., 2013, Serrano et al., 2000b). One of such alternatives is catalytic conversion of plastic waste into chemicals as studied here if the type of plastics facilitates this.

### 2.1.3 Types of plastic waste generated

Figure 2.4 compares the types of post-consumer plastic wastes generated globally from different sectors of the economy. It shows that the packaging sector has the largest share of all plastic wastes sources, where plastic waste from thermoplastic polymers mainly polyethylene and polypropylene, is the largest constituent accounting for over 80% of the total plastic waste (Al-Salem et al., 2009, Ahmad, 2011). In the UK, more than 20% of plastics produced goes to packaging (Singhabhandhu and Tezuka, 2010). The plastic waste from polyolefin polymers, high density polyethylene (HDPE), in particular accounts for about 60-70% of the total plastic waste in MSW (Lin and Yen, 2005, Aboulkas et al., 2008a, Serrano et al., 2000b). Correspondingly, HDPE is the world’s third largest commodity material, which is used for making plastic for numerous applications, including packaging (carrier bags, milk and water jugs), automobile (vehicle fuel tanks) and construction (plastic tents, storage sheds). Also, due to its strong resistance to many chemicals, HDPE it widely used in making chemical containers, chemical-resistance piping system, heat-resistant fireworks display mortars,
geothermal heat transfer piping system, natural gas distribution pipe systems and water pipes, just to mentioned a few (Kumar et al., 2011). These types of plastic products are usually discarded after single use and, thus, bring about large volumes of solid domestic waste (Ahmad, 2011). Hence, the packaging industry has been identified as a key waste generator, where about 30% of all MSW is derived from packaging leading to issues in landfills (Shah et al., 2008, Al-Salem et al., 2009).

![Figure 2.4 Types of post-consumer plastic waste globally (Ahmad, 2011).](image)

Table 2.1 compares the natural degradability of some materials known to be found in MSW. Organic and paper wastes take less than three weeks to degrade, while cotton cloth degrades within 8 to 20 weeks. The wastes from wood and wooden items take up to fifteen years to naturally degrade, while those of metallic take between one hundred to five hundred years. However, wastes from plastic could take more than five hundred years to degrade naturally (Zadgaonkar, 2004, Keane, 2009). This shows that plastic is the most difficult to decompose within waste. The problem associated with plastic waste disposal is colossal and in 2004 it was estimated globally to cost about two billions US dollars annually and without any value addition afterward (Zadgaonkar, 2004). Thus, there is an urgent need to find an immediate waste management solution to the problem of plastic wastes.
Table 2.1 Comparison of natural degradability of different waste materials (Zadgaonkar, 2004).

<table>
<thead>
<tr>
<th>Type of waste</th>
<th>Time taken to degrade</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic wastes</td>
<td>1 - 2 weeks</td>
</tr>
<tr>
<td>Paper</td>
<td>1 - 3 weeks</td>
</tr>
<tr>
<td>Cotton Cloth</td>
<td>8 - 20 weeks</td>
</tr>
<tr>
<td>Wood</td>
<td>10 - 15 years</td>
</tr>
<tr>
<td>Wooden Items</td>
<td>&gt;10 years</td>
</tr>
<tr>
<td>Tin, aluminium, and other metals</td>
<td>100 – 500 years</td>
</tr>
<tr>
<td>Plastics</td>
<td>&gt; 500 years</td>
</tr>
</tbody>
</table>

2.2 Current plastic waste management strategies

Figure 2.5 shows the different management options adopted in Western Europe for treatment of plastic waste in 2005. Land filling, unfortunately, was the main treatment method used, which accounted for 53% followed by energy recovery, or incineration with 29%, while feedstock recycling being the lowest with only 2% (Aguado et al., 2008). However, land filling and incineration may not be viable options in the future (Panda et al., 2010, Huang et al., 2010, Wei et al., 2010). For instance, non-availability of land in some countries, risk of ground water contamination and non-degradability of the plastic waste (see Table 2.1), make land filling unsustainable. Moreover, most of the landfills in many countries are approaching their full capacity (Panda et al., 2010, Huang et al., 2010, Wei et al., 2010). Energy recovery, on the other hand, may release harmful complex gaseous compounds, such as carbon monoxide, dioxin, furan derivatives, heavy metals, and carcinogenic PAH compounds, which may cause serious environmental problems that are more severe than the plastic waste itself (Miskolczi et al., 2009, Shent et al., 1999, Shah et al., 2010a, Serrano et al., 2000b). Landfilling and energy recovery methods are increasingly becoming unpopular due to resistance by the general public, who protest against possible airborne pollution that may be caused by the release of the harmful gaseous mixtures (Singhabhandhu and Tezuka, 2010). Also, landfilling and energy recovery methods do not add much value to the waste itself but are still in use, since plastic waste has been identified as the most difficult to handle among all the MSW components (Encinar and Gonzalez, 2008, Huang et al., 2010, Lin et al., 1998, Panda et al., 2010, Zadgaonkar, 2004, Keane,
2009). In view of this, various recycling methods, such as mechanical, biological and other chemical recycling have proposed (Panda et al., 2010, Shent et al., 1999).

![Figure 2.5 Plastic waste recycling options adopted in Western Europe in 2005 (Aguado et al., 2008).](image)

2.2.1 Basic methods of recycling plastic waste

Figure 2.6 lists the different municipal solid waste (MSW) management strategies for recycling waste. These include mechanical (primary and secondary recycling methods), biological recycling method and thermo chemical (tertiary and quaternary recycling methods).
Figure 2.6 Different ways of managing plastic wastes (Panda et al., 2010).

Mechanical recycling aims at converting the waste to similar applications as the original products through segregated (primary) or mixed plastics (secondary) methods (Hopewell et al., 2009, Panda et al., 2010). Primary mechanical recycling involves the conversion of plastic waste and other scraps to products with comparable characteristics with the original products, but can only use clean plastic waste (Al-Salem et al., 2009). Secondary mechanical recycling involves the conversion of the plastic wastes into products that are of different characteristics and can still be used as plastics. Mechanical recycling companies recover a number of plastic wastes to be used for injection and rotational moulding, vacuum forming, sheet extrusion and supply it to other industries which make products that could be used for construction and packaging. Mechanical recycling method is a good approach to deal with plastic waste as it reduces large volume of the plastic waste that otherwise could go to incineration or landfill and also conserve much of the fossils fuel that would be used in producing more plastics (Shah et al., 2010a, Shent et al., 1999). However, the plastic obtained from mechanically recycled plastic is often of low quality (Serrano et al., 2007b). Furthermore, the cycle involved in mechanical recycling is limited because in the end the plastic waste has to eventually be disposed through landfill or incineration and end up in the waste stream or go back to chemical recycling (Garforth et al., 2004, Al-Salem et al., 2009). Also, in
some cases, due to the processes involved, the products obtained from mechanical recycling are even more expensive than the original virgin plastic. Hence, the method is only economically viable on a selected subsection of plastic waste (Garforth et al., 2004, Panda et al., 2010).

Biological recycling involves an additional stage during the production of plastic such as blending with starch, to make the plastic biodegradable (Shah et al., 2008). The idea was developed to produce alternative plastics that can be degraded easily after usage through mechanisms such as biodegradation by microorganisms or photodegradation by exposure to sunlight (Shah et al., 2008). Although the method proved useful to some extent, the main problem associate with biodegradable plastic is the handling of the waste, as it is difficult to separate from non-biodegradable when mixed. Also the degradable plastics do only degrade in certain natural conditions, where photodegradable polymers will not degrade without sunlight if buried in landfills (Shah et al., 2008). Biodegradable polymers may also encourage people towards littering due their assumption that the waste will degrade easily and naturally. In addition, the methane gas release during the biodegradation process may increase the greenhouse effect (Panda et al., 2010).

Thermo-chemical recycling is a method that involves chemical bond breaking and formation of new compounds and comprises of two major approaches, namely quaternary recycling and tertiary recycling. The quaternary recycling involves the recovery of energy content of the waste. One of the advantages of this method is the use for plastic waste for energy generation through incineration, where hydrocarbon gases with high calorific values are obtained (Panda et al., 2010, Kumar et al., 2011). However, this method faces serious resistance from people because it is being associated with numerous environmental issues. Tertiary recycling on the other hand is a process dealing with the conversion of plastics either back to their original monomers or into different chemicals and fuels through a chemical process. The products obtained from this process have a wide range of applications including the use as feedstock to chemical and petrochemical industries as well as transport fuels (Al-Salem et al., 2009). This method has perhaps the most potential for dealing with the problem of plastic waste, because it is the only method which converts plastic back into chemical and fuel for further utilisation (Walendziewski and Steininger, 2001, Panda et al., 2010, Miskolczi et al., 2006, Al-Salem et al., 2009, Aguado et al., 2006, Wei et al., 2010).
Table 2.2 gives some of the common terms and their equivalents that are commonly used to describe these methods (Hopewell et al., 2009). Tertiary recycling with HDPE polymer was chosen in this study for catalytic conversion to fuel and/or chemical feedstock for chemical industries, where catalytic pyrolysis can become a waste management method by recycling plastic back to a feedstock (Lin et al., 1998, Shah et al., 2010).

Table 2.2 Different terminologies used for plastic waste recycling process (Hopewell et al., 2011).

<table>
<thead>
<tr>
<th>ASTM D5033 definitions</th>
<th>Equivalent ISO 15270 (draft) definitions</th>
<th>Other equivalent terms</th>
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<tbody>
<tr>
<td>Primary recycling</td>
<td>Mechanical recycling</td>
<td>Closed-loop recycling</td>
</tr>
<tr>
<td>Secondary recycling</td>
<td>Mechanical recycling</td>
<td>Downgrading</td>
</tr>
<tr>
<td>Quaternary recycling</td>
<td>Energy recovery</td>
<td>Valorisation</td>
</tr>
<tr>
<td>Tertiary recycling method</td>
<td>Chemical recycling</td>
<td>Feedstock recycling</td>
</tr>
</tbody>
</table>

2.2.2 Tertiary recycling method (Feedstock recycling)

The tertiary recycling method is divided into thermal and catalytic conversion of plastic waste to different products. Thermal conversion without catalyst results in ‘unguided’ decomposition of the feedstock coupled with non-selectivity of the products of interest and it requires high temperatures to be accomplished (Lin, 2009, Lin et al., 2010). Thus, catalytic conversion using an appropriate catalyst to obtain useful products might be appropriate as a tertiary recycling method (Al-Salem et al., 2009, Lin, 2009, Lin et al., 2010, Miskolczi et al., 2006).

Table 2.3 summarises the three basic processes used for tertiary recycling, namely depolymerisation/chemolysis, partial oxidation/gasification and cracking/pyrolysis (Panda et al., 2010, Kumar et al., 2011). Depolymerisation is a reversible thermal process that is mainly applicable to condensation polymers. In this process, the condensation polymers are converted back to their original monomers with heat and sometimes steam. Chemolysis involves the use a chemical agent to completely depolymerise the polymer through processes such as alcoholyis, hydrolysis and glycolysis. The partial oxidation/gasification method involves direct reaction of plastic wastes with air or steam to produce synthesis gas which can be used in a fuel cell or to
produce hydrocarbons and other chemicals. Cracking/pyrolysis involves conversion of polymeric material in an oxygen free environment leading to formation of lower molecular weight compounds that can be used as a fuel and chemical feedstock. This method does not reverts plastic waste back to its original monomer, but instead converts it to liquid and gaseous products that can be used as fuels and chemicals. Hence, it is highly applicable to polyolefin polymers (Keane, 2009). Of the three tertiary recycling methods cracking/pyrolysis appeared to be the most advantageous method since, it is applicable to addition polymers such as HDPE, which constituted about 60-70% of municipal solid waste plastics. Also, it turns the waste into useful products, such as fuel and chemical feedstock for industrial use. Thus, it can serve as a source of clean and high calorific value fuel, which can be used as fuel oil and for boilers or for electricity generation and gas engines without the need for further upgrade if the cracking process is properly guided.
Table 2.3 Brief classifications of methods involved in tertiary recycling method (Garforth et al., 2004, Panda et al., 2010).

<table>
<thead>
<tr>
<th>Type of Feedstock recycling method</th>
<th>Suitable polymers</th>
<th>End products</th>
<th>Drawbacks /Benefit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depolymerisation/Chemolysis</td>
<td>Condensation polymers such as polyamides, polyesters, nylon etc. Eg. polyester $HO[-R - COO - R^1 - COO -]_nH$</td>
<td>Monomers such as amines, diols, diamines, diacids etc.</td>
<td>Not applicable to addition polymers such as polyolefins which accounts for 60-70% of municipal solid plastic waste</td>
</tr>
<tr>
<td>Partial oxidation/Gasification</td>
<td>Both addition and condensation polymers</td>
<td>Synthesis gas (CO and H$_2$)</td>
<td>Noxious materials such light hydrocarbons, NOx, dioxins and sulphur oxides which are released during the process makes it harmful to the environment</td>
</tr>
<tr>
<td>Cracking/pyrolysis</td>
<td>Addition polymers, eg. Polyethylene (PE), polypropylene (PP), polymethyl pentane (PMP) and polybutane-1 (PB-1)</td>
<td>Smaller molecules in form of liquid and gases.</td>
<td>Product could be used directly as transport fuel of as a precursor for many chemicals. Minimal pollutants and applicable for thermoplastic polymers</td>
</tr>
</tbody>
</table>

2.3 Types of polymers

Polymers are classified thermoplastic and thermosets polymers (Nicholson, 1997). Thermoplastic polymers are polymers which when heated, melts and regain its properties after cooling and constitute mainly linear and lightly branched polymer molecules. Thermoplastic polymers include polyamide (nylon), polyvinylchloride (PVC), polymethyl methacrylates (Acrylic), high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP) and polystyrene to mention but few.
On the other hand, thermosets are polymers that do not melt when heated but decomposed through irreversible chemical reaction at high temperature and they mainly compose of cross-linked polymers with three dimensional network of covalent bonding (Nicholson, 1997). Thermosets polymers include polyester, phenolic polyurethane, urea and epoxy.

The second broad classification which is based on chemical reaction involved during polymerisation, generally classified polymers into two classes, namely condensation and addition polymers. Condensation polymers are formed as a result of condensation reaction where two molecules react to form one large molecule by losing small molecule such as water as by product. Polyester and nylon are good examples of condensation polymers and Equation 2.1 show the polyester formation (Nicholson, 1997).

\[
n\text{HO-R-OH} + n\text{HOOC-R}^1\text{-COOH} \rightarrow \text{HO} \left[ -\text{R-COO-R}^1\text{-COO} - \right]_n \text{H} + (n-1)\text{H}_2\text{O} \quad 2.1
\]

Addition polymers, on the other hand, are polymers formed by addition reaction of unsaturated monomers, which is not accompanied by the loss of any small molecule. These polymers are grouped as polyolefin polymers. Typical examples of addition polymers include polyvinylchloride, polyethylene, and polypropylene.

2.3.1 Polyolefin polymers

Polyolefin polymers constitute large block of thermoplastic or addition polymers and are the most commercially important polymers (Nicholson, 1997). These polymers include polyethylene (PE), polypropylene (PP), polymethylpentane (PMP) and polybutane-1 (PB-1). However, the most prominent are polyethylene (PE) and polypropylene (PP) and these polymers formed the basis of this research.

2.3.1.1 Polyethylene polymers

Polyethylene polymers are polymers that belong to the thermoplastic polymer group, which are produced mainly through catalytic polymerisation of ethylene (Equation 2.2). Polyethylene polymers were first produced for commercial purposes in 1939 and today represent the largest plastic commodity globally with sales volume of
about 6 million tonnes (Nicholson, 1997, Paabo and Levin, 1987). The average melting points for polymers with different densities ranges from 120 to 180°C

\[ n(CH_2=CH_2)_\text{Catalyst} \rightarrow [-CH_2-CH_2-]_n \]  

This group of polymer constitutes of high density polyethylene (HDPE), low density polyethylene (LDPE) and linear low density polyethylene (LLDPE). Their structures, densities and molecular weight distribution differ depending on the different conditions employed during manufacturing process (Paabo and Levin, 1987). They have the same molecular structure with long chain hydrocarbon that possesses hydrogen to carbon ratio of about 2. All the polymers in this group have a common chemical structure, \([-\text{CH}_2\cdot\text{CH}_2\cdot]_n\), where \(n\) stands for repetitive unit of the monomer. But LDPE, LLDPE and HDPE differ by their extent of branching, which result in their densities differing significantly. Figure 2.7 shows the structures of HDPE, LLDPE and LDPE, where all the three structures contain repetitive unit of \(-\text{CH}_2\cdot\text{CH}_2\cdot\) but only differ by the number of branches. HDPE is linear and has little or no branches while LLDPE is liner with short branches and LDPE is equally linear but with long branches.

![Figure 2.7 Structures of different polyethylene polymers differs by their degree of branching.](image)

2.3.1.2 Polypropylene

Polypropylene is another member of thermoplastic polymers with a molecular structure containing methyl group as a branch\([-\text{CH}_2 \cdot CH(CH_3) \cdot]_n\). Figure 2.8 shows the structure of polypropylene, which contained \(CH_3\) branches. Polypropylene is isotactic and share many properties with polyethylene with the exceptions of few important ones which made it unique. Polypropylene polymer has a lower density compared to polypropylene and exhibit higher softening point which makes it
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susceptible to higher temperature applications such as used in making kettles, jugs to mentioned but few. Unfortunately it does not withstand environmental stress cracking because can be easily oxidized due to the presence of tertiary C-H bond within its molecular structure (Nicholson, 1997).

2.4 Cracking

Cracking is a thermochemical process which involves bond breaking and formation of new compounds, such as conversion of long polymer chains to lower molecular weight compounds that can be used as a chemical feedstock or fuel precursor (Garforth et al., 2004). Cracking is normally conducted under oxygen-free conditions called pyrolysis (Al-Salem et al., 2009, Panda et al., 2010). It tends to form gaseous and liquid fractions with different components, such as paraffins, olefins, naphthenes and aromatics, as well as a solid char, where the yields differ depending on the polymer type (Panda et al., 2010, Wei et al., 2010, Keane, 2009). There are three known cracking processes, namely hydrocracking, if hydrogen is used, thermal cracking, if heat only aids the process and thermo-catalytic cracking, if, in addition to heat, a catalyst is used.

2.4.1 Hydrocracking

Hydrocracking of plastic wastes involves the thermochemical reaction of plastic under a hydrogen atmosphere over a hydrogenation catalyst (Garforth et al., 2004, Panda et al., 2010). The hydrogenation catalyst enables external hydrogen to react with any free radicals formed during the cracking to form high quality hydrocarbon liquids from the plastic wastes. The reaction is usually carried out in a stirred batch reactor at 150 to 400°C, a pressure of 3-10 MPa hydrogen and using a hydrogenation metal catalyst on an acidic support (Garforth et al., 2004, Panda et al., 2010). Depolymerisation-liquefaction of different polymers using four superacid catalysts, $\text{SO}_4^{2-} / \text{Fe}_2\text{O}_3$, $\text{SO}_4^{2-} / \text{ZrO}_2$, $\text{SO}_4^{2-} / \text{Al}_2\text{O}_3$ and Pt-modified $\text{SO}_4^{2-} / \text{ZrO}_2$, was reported to have a yield of over 90 wt% of branched paraffin within the gasoline range (Shabtai et al., 1997). Platinum and nickel promoted $\text{SO}_4$ and $\text{WO}_3$ modified zirconium oxide catalysts were also reported for hydrocracking of HDPE at 375 °C, where a 98wt% conversion
was achieved with a 35wt% gaseous fraction and a 65wt% gasoline range liquid containing mainly isoalkanes (Venkatesh et al., 1996). Superacid catalysts are catalysts that have acidic strength stronger than that of 100% H$_2$SO$_4$ (Hall and Conant, 1927). Some of the super acid catalysts also showed high resistance to sintering and coking due to metal doping (Venkatesh et al., 1996). In addition, the hydrocracking of n-hexadecane using Pt-modified $\text{SO}_4^{2-}/\text{ZrO}_2$ was reported at 130-170°C with 300 psig initial hydrogen pressure and 15-75 min reaction time, where a 65wt% conversion was achieved with over 90% selectivity towards isoparaffins (Wen et al., 1990). A bimetallic NiMo carbide catalyst was reported as an efficient, stable and very active catalyst in hydrocracking of n-octane with a conversion of about 90wt% after 3 hours reaction time, where the carbide exhibited very interesting properties towards coke reduction (Reyes et al., 2004). Hydrocracking is technically a preferred method, where the desired product is used as transport fuel without any need for modification. However, the method requires hydrogen, which is costly thus making it too expensive as a general waste treatment option. In addition, the process is conducted at very high pressure making the safety of the process an issue of great concern. Thus the method is currently of little industrial use, and thermal cracking without hydrogen appears more viable.

### 2.4.2 Thermal cracking

There are basically two forms of thermal cracking adopted for plastic waste recycling, thermolysis and thermo catalytic pyrolysis, depending on whether a catalyst is added or not.

#### 2.4.2.1 Thermolysis

Thermolysis is a thermal process of degrading plastic waste at high temperature ranging from 400 to 800°C (Aguado et al., 2008). Many studies have been reported on the thermal conversion of plastic wastes to different products. For instance, Miskolzci et al. (2004a) carried out the degradation of municipal plastic wastes in a horizontal tube reactor over a range of temperature from 490 to 550°C. Their finding showed an overall conversion of less than 35wt% with only a 22wt% liquid yield composed of some C7-C18 paraffins and mostly aromatic hydrocarbons. To avoid the formation of aromatics, the use of solvent during thermal degradation of different type of polymers has been proposed. For instance, Aguado et al. (2007) carried out thermal degradation of HDPE
using different HDPE/decalin ratio in an autoclave reactor pressurised at 20bar at 400°C under nitrogen. Their finding showed that the presence of decalin had improved the liquid range hydrocarbon, particularly C5 to C35, which are mainly naphthens and olefins. Similarly, Serrano et al., (2007b) conducted thermal conversion of HDPE using four different solvents, namely tetraline, 9,10-dihydroanthracene, decalin and 1-methylnaphthalene with the aim of increasing the C5 – C33 \( \alpha \)-olefin yield. They found that solvents with poor hydrogen-donating ability promoted high yield of C5–C32 hydrocarbons. Different studies also were reported on the applicability of hydrocarbon products obtained from thermal degradation of plastic wastes to fuels indicating that low conversion is the problem during thermolysis (Demirbaş, 2005, Walendziewski, 2002, Singhabhandhu and Tezuka, 2010, Miskolczi et al., 2004a, Aguado et al., 2007). Thermolysis appears to be promoting low liquid yield with carbon number distribution higher than the gasoline range and is generally non-selective and requires high temperature due to the difficulties in controlling the mechanisms involved and thus catalytic degradation may be advantageous (Walendziewski and Steininger, 2001, Hernandez et al., 2006, Zhibo et al., 1996).

### 2.4.2.2 Mechanisms of thermal degradation (thermolysis) of polymers

The mechanism of thermal degradation of polymers has been proposed to follow four general routes depending on the polymer type (Panda et al., 2010, Buekens and Huang, 1998, Paabo and Levin, 1987, Chauhan et al., 2012). The mechanisms involved during thermal degradation of polymers are very complex chemical processes, which involve different reactions routes (Panda et al., 2010). Many studies have been conducted to ascertain the actual reaction mechanism of the polymer degradation and different reports have been published (Buekens and Huang, 1998). Different thermosetting and thermoplastic polymers have been reported to follow different reaction routes during the degradation. These routes include (i) End-chain scission or unzipping (depolymerisation), where the polymer is sequentially broken down from end groups to monomers as shown by Equations 2.3 and 2.2, (ii) Random-chain scission/fragmentation, in which the polymer chain is broken at random to unequal parts as illustrated by Equation 2.5, (iii) Chain-stripping, this involves elimination of side chains from the main polymer chain, which lead to the release of cracking products, and (iv) Cross-linking, which results in the formation of a chain network and normally occur only when thermosetting polymers are heated to high temperature which led to
formation of a high molecular aromatic compounds, mainly char (Panda et al., 2010, Singh and Sharma, 2008).

\[ M_n^* \rightarrow M_{n-1}^* + M \]  
\[ M_{n-1}^* \rightarrow M_{n-2}^* + M \]  
\[ M_n \rightarrow M_x + M_y \]

Table 2.4 summarises some of the established mechanisms believed to be involved during the thermal degradations of different types of polymers. Polyethylene and polypropylene polymers mainly follow a random chain rupture type of mechanism during thermal degradation yielding mostly waxes, olefins and paraffins at low temperature and gases and liquid oil at high temperature. The thermal degradation of polyvinylchloride involves chain-stripping and yields HCl and benzene at low temperature and toluene at high temperature. Polystyrene, polymethyl methacrylate, polyamide 6 and Polytetrafluoro ethylene involve unzipping and chain rapture producing their oligomers and monomers. The thermal degradation of polyethylene terephthalate polymers involve β-hydrogen transfer, rearrangement and decarboxylation and produce mainly benzoic acid and vinyl terephthalate.

It is clear that the principal problem with thermolysis is random scission, which has been reported as the main mechanism involved during degradation of polyolefin polymers, particularly polyethylene (Simha and Wall, 1952, Wall et al., 1954, Grimbley and Lehrle, 1995). Some researchers reported the degradation to follow chain-end scission (Kiran and Gillham, 1976). However, Murata et al. (2002) reported that the degradation of polyolefin polymers involves two mechanisms simultaneously. Random scission initially causes molecular weight reduction of the virgin polymer and the chain-end scission of carbon to carbon single bond taken place at gas-liquid interface and results in volatile liquid yields as in Equations 2.1 and 2.2, respectively. Thus, in more general term, a radical-chain mechanism is a widely acceptable reaction model for polyolefin polymer degradation (Murata et al., 2002, Ceamanos et al., 2002, Bockhorn et al., 1999a, Bockhorn et al., 1999b, Shah et al., 2010a). In the radical-chain mechanism, polymer degradation simply follow three normal pattern of initiation, where the polymer is first cracked to unstable free radicals at high temperature, then propagation in which the free radicals will either undergo chain rearrangement or fission.
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of C-C bond at β position and the finally termination where intermediate radicals will undergo self-propagation mechanism and ends by recombination the free radicals (Shah et al., 2010a, Panda et al., 2010). Thus, catalytic pyrolysis which promotes initial scission and leads to chain rearrangement into olefins that stops chain-end scission could produce aromatic liquid and support gas formation.
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Mode of thermal decomposition</th>
<th>Low temperature products</th>
<th>High Temperature products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>Random chain rupture (involves random fragmentation of polymers and oligomers)</td>
<td>Waxes, paraffin oil, ( \alpha )-olefins</td>
<td>Gases and liquid oils</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>Random chain rupture</td>
<td>Vaseline, olefins</td>
<td>Gases and light oils</td>
</tr>
<tr>
<td>Polyvinylchloride</td>
<td>Chain-stripping (side chain reactions involving substitutes on side groups (HCl) on the polymer chain, chain dehydrogenation and cyclization)</td>
<td>HCl (&lt;300°C), benzene</td>
<td>Toluene (&gt;300°C)</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>Combination of unzipping and chain rupture, forming oligomers</td>
<td>Styrene and its oligomers</td>
<td>Styrene and its oligomers</td>
</tr>
<tr>
<td>Polymethyl methacrylate</td>
<td>Unzipping (Cracking is first targeted at chain end then successively down to polymeric length and monomer formation)</td>
<td>Monomer methyl methacralate</td>
<td>Less Methyl methacralate, more decomposition</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>Unzipping</td>
<td>Monomer tetrafluoro ethylene</td>
<td></td>
</tr>
<tr>
<td>Polyethylene terephthalate</td>
<td>( \beta )-Hydrogen transfer, rearrangement and decarboxylation</td>
<td>Benzoic acid and vinyl terephthalate</td>
<td></td>
</tr>
<tr>
<td>Polyamide 6</td>
<td>Unzipping</td>
<td>Caprolactum</td>
<td></td>
</tr>
</tbody>
</table>
2.4.2.3 Thermo-catalytic pyrolysis

Catalytic cracking/pyrolysis has been argued as the best method for managing plastic waste if it can be used to control the random chain-rapture mechanisms. Catalysts used in petroleum refining and petrochemical industries, including different zeolites and FCC, are widely used for catalytic conversion of PP, PE plastic waste (Buekens and Huang, 1998). Many studies have been focussing on catalytic systems applicable for converting the plastic waste to different valuable products. Some of these catalysts include BaCO$_3$, ZnO, MgO, CaC$_2$, PbS and Al-Zn composite catalyst for both cracking and dechlorination of PVC polymers (Tange et al., 2003, Jan et al., 2010, Shah et al., 2010a, Shah et al., 2005). This process is advantageous over the thermal process because the presence of a catalyst allow the polymer degradation to occur at low temperatures and with higher selectivity towards the desired products (Aguado et al., 2008, Singh and Sharma, 2008). Nonetheless, the selectivity of the product depends not only on the catalysts, but the entire system, which include reactor type, catalyst type, and reaction conditions that promote certain degradation mechanisms.

2.5 Catalytic cracking

A catalyst is a chemical substance which, when added in the reaction medium, accelerates the chemical reaction but remains unchanged at the end of the process. The catalyst does accelerates the chemical reaction by forming bond with reacting species, and by allowing the species to react and form products that are detached and leave the catalyst unchanged, such that it become available for the subsequent reaction (Chorkendorff and Niemantsverdriet, 2007). A catalyst, depending on its properties, does not only affects the rate of the reaction, but can also offer alternative path to the reaction, which is apparently complex, but energetically favourable, as exemplified in Section 2.4.2.3. A catalyst does change the reaction kinetics, but not thermodynamics, because the overall change in free energy remains the same regardless of the presence of catalyst or not. The presence of catalyst only affects the equilibrium constant of a reaction and thus cannot change thermodynamically unfavourably reaction. The presence of a catalyst basically lowered the activation energy ($\Delta$Ea) compared to uncatalysed reaction resulting in a faster reaction using the same condition of temperature and reactant concentrations.
The catalytic process can offer an alternative route during a chemical process, often with significant energy and cost reductions. For instance, unlike pure thermal degradation which involves high temperatures from 500 to 900°C, catalytic conversion takes place around 350 to 450°C (Lin et al., 2010, Panda et al., 2010). Many reports on polymer degradations showed that the presence of a catalyst considerably lowered the reaction temperature and residence time and significantly increased the conversion rate (Ohkita et al., 1993, Panda et al., 2010). Hence, the use of catalyst narrows provides control over the hydrocarbon distribution during polymer degradation which may lead to a promotion of a value-added products (Panda et al., 2010).

### 2.5.1 Reaction kinetics

Reaction kinetics also known as chemical kinetics provides bases for describing the rate at which a chemical reaction occur and also relates to a reaction mechanism (Chorkendorff and Niemantsverdriet, 2007). Chemical kinetics deals with how different experimental conditions affect the rate of reaction. Rates of reaction usually increase with increasing temperature, although this may not be the case in the presence of a catalyst. Hence, the rate of chemical reaction related to temperature is often given by the Arrhenius Equation given in Equation 2.6, where T is the temperature in kelvin, R the gas constant, A is the preexponential factor (in s\(^{-1}\) for 1st order reaction) and Ea the activation energy (in kJ/mole). According to Arrhenius Equation, activation energy is an energy barrier that has to be overcome for the reaction to complete. Pre-exponential factor is a measure of frequency of collisions between reactants molecules occur regardless of their potential energy where the rate of successful collisions is determine by multiplying A and the exponential factor, \(e^{-\frac{E_a}{RT}}\) (Atkins and de Paula, 2006). So, the rate of reaction with low activation energy will be faster than that with large activation energy. The function of catalyst is to lower this energy barrier so that the reaction rate is faster than the uncatalysed reaction.

\[
k(T) = Ae^{-\frac{E_a}{RT}}
\]

#### 2.5.2 Mechanism of catalytic cracking of polymers

The thermal cracking of a polymer is generally believed to be initiated by an uncontrolled radical-chain mechanism (Murata et al., 2002, Ceamanos et al., 2002, Bockhorn et al., 1999b, Shah et al., 2010a, Kumar et al., 2011). Hence, the main role of
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a catalyst is to speed up the rate of catalytic cracking by lowering the activation energy (Kumar et al., 2011). During catalytic cracking, it is widely believed that polymer cracking first involves carbenium ion formation, where the catalyst acid sites plays a major role in the chemistry, involving H-transfer, chain/β-scission, isomerisation and aromatisation (Panda et al., 2010, Kumar et al., 2011, Park et al., 1999). The carbenium ion is formed either by abstraction of a hydride ion from the polymer by a Lewis acid site of the catalyst or addition of a proton to the polymer C-C bonds due to a Brønsted acid site (Kumar et al., 2011, Park et al., 1999). Brønsted acidity is reported to favour the cracking towards olefinic compounds (Panda et al., 2010).

According to Bueken et al. (1998) and Panda et al. (2010), the mechanism of catalytic degradation of polyolefin polymer could be described as in the following stages.

**Initiation stage:** At this stage the polymer chain undergoes some defect resulting in the formation of an on-chain carbenium ion either by proton addition by the catalyst or via random hydride-ion abstraction by low molecular-weight:

$$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 - + X^+ \rightarrow -\text{CH}_2\text{CH}_2^+\text{CHCH}_2\text{CH}_2\text{CH}_2 - + \text{HX} \quad 2.7$$

The polymer chain may be broken up via β-scission:

$$-\text{CH}_2\text{CH}_2^+\text{CHCH}_2\text{CH}_2\text{R}_1 \rightarrow -\text{CH}_2\text{CH}_2\text{CH} = \text{CH}_2 + \text{CH}_2\text{CH}_2\text{R}_1 \quad 2.8$$

**Depropagation stage:** At this stage, the acid sites of the catalyst together with carbonium ions present will attack the main polymer chain causing it to cleave and form oligomers. Moreover, the oligomers formed may be further fragmented due to direct β-scission of chain-end carbenium ion yielding gas and liquid products.

$$\text{R}_1-\text{CH}_2^+\text{CH}_2 \xrightarrow{X^+} \text{R}_2-\text{CH}_2^+\text{CH}_2 + \text{CH}_2 = \text{CH}_2 \quad 2.9$$

**Isomerisation stage:** At this stage, the carbenium ion may undergo rearrangement as a result of hydrogen or carbon atom shift:

$$\text{CH}_2 = \text{CH} - \text{CH}_2-\text{CH}_2-\text{CH}_3 \xrightarrow{\text{H}^+} -\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3 \xrightarrow{\text{H}^+}$$

$$\text{CH}_3-\text{CH}_2-\text{CH} = \text{CH} - \text{CH}_3 \quad 2.10$$
This is an example of a double-bond isomerisation of an olefin that may occur during the depropagation process stage of polymer catalytic cracking.

**Aromatisation stage:** At this stage, aromatic compounds are formed through cyclization of some carbenium ion intermediates. A very good example is the formation of olefinic carbenium ion through the hydride-ion abstraction on the olefin:

\[
R_1^+ + R_2-CH = CH-CH_2-CH_2-CH_2-CH_3 \Leftrightarrow R_1H + R_2CH = CH-CH_2-CH_2-CH_3 + 2H_2
\]  

\[2.11\]

Subsequently, the olefinic carbenium ion undergoes intramolecular attack on the double bond and forms aromatic compounds:

\[\text{The hydrogen produced during aromatisation is normally consumed during depropagation to form paraffin rather than olefins. Hence, this forms a light hydrocarbon fraction and an aromatic fraction with little industrial value. Selecting a catalyst that supress the aromatisation stage will leave an olefin rich liquid and, thus, it is important to look at different activities of the catalysts for degradation of polymers.}\]

**2.5.3 Catalysts for cracking of plastic wastes and polymers**

For catalytic cracking of plastic wastes to be a successful approach in dealing with the problems associated with plastic wastes, it is important to find a suitable catalytic system that will promote excellent polymer conversion with high liquid yields. Different catalysts have been tested in literature for efficient conversions and selectivity and normally these catalysts were chosen based on their applications in petroleum refining processes as reviewed below.
2.5.3.1 Solid acid catalysts

Liu and Meuzelaar (1996) used a high-pressure thermogravimetry (TG) with a rapid on-line gas GC/MS to test different catalysts for the catalytic conversion of comingle plastic wastes composed of mainly HDPE and a mixture of coal and plastic waste. Catalysts tested included solid acid catalysts, namely Fe$_2$O$_3$/SO$_4^{2-}$, Al$_2$O$_3$/SO$_4^{2-}$ promoted with 0.5wt%Pt, sulphated zirconia (ZrO$_2$/SO$_4^{2-}$), SiO$_2$AlO$_3$, NiMo/Al$_2$O$_3$ mixed with SiO$_2$/Al$_2$O$_3$ at 1:1 ratio and a zeolite catalyst HZSM5. This work was among the many earlier studies that open up the research interests in the area of catalytic conversion of plastic waste and polymers with a view to obtain valuable products and, thus, could provide a safe, sustainable and cost effective recycling method for plastic waste. It is interesting to note that of all the catalysts tested, the sulphated zirconia catalyst was reported to have the highest cracking activities towards plastic waste degradation with about 86% conversion within the first 30 min residence at 420°C. The result further revealed that with increasing acidity, the catalyst was more likely to give lower hydrocarbon compounds and branched aromatics. For example, it was found that the cracking products obtained using the highly acidic catalysts HZSM-2 and SiO$_2$/Al$_2$O$_3$ contained more short chain aliphatic and aromatic hydrocarbons with carbon number distribution ranging from C4-C11. The drive then shifted to identify catalysts and reaction conditions that retain conversion but gave better product compositions using modified solid acid systems.

2.5.3.2 Solid acid zeolite catalysts

Serrano et al. (2000) conducted catalytic conversion of polyolefin mixtures over different solid acid zeolite catalysts at 400°C in a pyrex batch reactor under a continues stream of nitrogen gas. Their results indicated a conversion of 84wt% using a n-HZSM to only 20wt% using a standard HZSM-5 zeolite catalyst. The product selectivity of n-HZSM toward gaseous products was nearly 50wt%. In addition, Park et al. (2000) conducted catalytic conversions of a high density polyethylene (HDPE) polymer over some zeolite catalysts, namely HNSM-5 zeolite, natural zeolite (HNY), HY zeolite and silica-alumina. These catalysts were tested at varying temperature ranging from 450 to 500°C using a fixed bed reactor, where a gas chromatography/mass spectroscopy (GC/MS) was used to analyse the liquid products. Their results indicated gaseous fraction over 60wt% for all the catalysts except HNZ catalyst, which had only 35% gas.
Although there was high conversion with carbon number distribution of C$_5$-C$_{13}$, almost all the catalysts tested appeared to have promoted aromatic compounds with HZMS-5 having highest aromatic constituent of 50-75wt%. The high aromatic content is of concern if the liquid fuel is to be used as transport fuel (Serrano et al., 2000b). Further to this, another research comparing the catalytic activities of zeolite (HZSM-5, HUSY and HMOR) and non-zeolite (SAHA and MCM-41) on conversion of propylene polymer was reported using a fluidized bed as a reactor under a constant nitrogen flow (Lin and Yen, 2005). In addition to the effect of the catalyst on the degradation and products yield and composition, the study looked at the influence of certain reaction conditions. The work established that both zeolite and non-zeolite catalysts showed reasonable conversions, but regardless of varying reaction conditions, the amount of gaseous products remain extremely high with no more than 15 wt.% liquid. This was more evident in the case of acidic zeolites. The work reported by Huang et al. (2010) and Wei et al. (2010) compared the activity of different zeolites on the catalytic degradation of a mixture of post-consumer plastic waste using a fluidised bed reactor. Similar to other works reported using acidic zeolite catalysts, about 85w% conversion was achieved within 20 min but all the catalysts tested promoted high yields of gaseous products despite varying reaction conditions, such as reaction temperatures between 290 and 420$^\circ$C, varying catalysts to polymer ratios and different fluidizing rates. Similarly, Lin Y-H, (2009) and Lin et al. (2010) reported catalytic pyrolysis of mixtures of post-consumer hospital wastes plastic which comprises of polyethylene, polystyrene, polypropylene and polyvinyl chloride (PE, PS, PP and PVC) using different zeolite catalysts, FCC-R1, SAHA, ZSM-5 and a non-zeolite catalyst, HUSY. The process was optimised at different reaction conditions using a fluidized-bed reactor. None of the zeolite catalysts tested had a liquid fraction of more than 10wt% despite optimising the reaction conditions, such as reaction temperature, plastic waste to catalyst ratio and rate of fluidising gas. Their overall result indicated that the zeolite catalysts promoted gaseous product compared to their non-zeolite counterparts.

2.5.3.3 Non-zeolite catalysts

In an attempt to test some low-cost and non-zeolite catalysts, Shah et al. (2010) compared the catalytic activities of some non-zeolite acidic and basic catalysts, namely silica, alumina, calcium carbide, magnesium oxide, zinc oxide and mixture of alumina and silica for conversion of LDPE plastic waste. The conversion was conducted at
different reaction conditions using a Pyrex glass tube reactor to get the optimal yield of volatile products. At the optimal conditions, CaC\textsubscript{2} and SiO\textsubscript{2} reported the best results for plastic waste conversion. The CaC\textsubscript{2} promoted high conversion within short residence time of 90 min with selectivity towards aliphatic hydrocarbon in the liquid fraction. The SiO\textsubscript{2} on the other hand had highest conversion at the optimal conditions of 400°C, 90 min residence time and 3:1 LDPE to catalyst ratio. Their overall results showed that with the exception of CaC\textsubscript{2}, the compositions of liquid fraction obtained using all the catalysts contained significant amount of aromatic and polar compounds ranging from 25 to 50wt%, which made the liquids unattractive in terms of usage as transport fuel. By contrast the catalytic activity shown by the CaC\textsubscript{2} promoted high liquid yield with high aliphatic content at lower temperature. Hence, CaC\textsubscript{2} was chosen to be tested alone and in a mixture with sulphated zirconia catalyst, which could result in catalyst system with modified acid strength that may improve the conversion and the selectivity towards less aromatic compounds. In principle, acid strength be modified with basic catalyst.

2.5.3.4 Basic catalyst

Jan et al. (2010) reported a catalytic conversion of high density polyethylene (HDPE) municipal waste to fuel using a basic catalyst (BaCO\textsubscript{3}) at different reaction conditions. At 450°C, 1 hour and a 1:10 catalyst to LDPE ratio they obtained a total conversion of 80wt% with liquid and gaseous fractions of 30 and 25wt%, respectively. Wax and residue constituted 25 and 20wt%, respectively. When residence time was increased to 2 hours, a high conversion of about 96wt% was achieved. This indicates that the role played by catalyst type and also optimising the reaction conditions, particularly residence time, which enable the attainment of optimal conversion and improve products yields by reducing the amount of unconverted feed. However, the use of basic catalysts, such as BaCO\textsubscript{3} appeared not attractive, because it require high temperature and longer residence time, otherwise large portion of plastic waste only turn to wax or remain unconverted. So, the acidic properties of the catalyst need to be enhanced to improve its activities towards polymer conversion.

2.5.4 Influence of catalyst acidity on polymer cracking

Acidity strength was found in Section 2.5.3.1 to be one of the major determining factors responsible for the catalytic activity and to product selectivity by a particular
catalyst (Park et al., 1999, Serrano et al., 2000b, Liu and Meuzelaar, 1996). Solid acid catalysts with strong acid strength have been reported to promote high polymer cracking leading to high gaseous fraction yield, because high acidity normally cause subsequent cracking of liquid or waxy product into gaseous compounds. In a work reported by Serrano et al., (2000), different solid acid catalysts with different acidity strength and textural properties were used for conversion of a polyolefin mixture. In this work, the zeolite catalyst n-HZSM-5 with the highest acidity gave highest gaseous yield and this led them to conclude that high acidity promotes higher gaseous yield. Nonetheless, high acidity may not necessarily give the highest conversion (Singh and Sharma, 2008, Arandes et al., 2007, Aguado et al., 2006). For instance, Arandes et al. (2007) reported similar results in their work, where the activities of three catalysts with different total acidities were compared for catalytic conversion of polyolefin under FCC conditions. The catalysts tested are CAT-1, a catalyst used in a fluid catalytic cracking (FCC) unit, which has lower acidity compared to two hybrid catalysts, CAT-H11 and CAT-H12 formed by mechanical mixing of CAT1 at 75wt% with HZSM-5 zeolite that contains different proportions of SiO$_2$/Al$_2$O$_3$. Their findings showed that CAT-1, despite having lower total acidity gave higher conversion than the hybrid catalysts. Therefore, to find a cost-effective catalyst with excellent catalytic activity in this work, a hybrid catalyst was synthesised through mechanical mixing of sulphated zirconia, which is highly acidic with different moderators, including calcium carbide and molybdenum carbide. The resultant hybrid catalyst may possess moderate acidity for effective conversion of polyolefin polymers and could promote high liquid yield with minimum aromatic component. Due to the environmental concern a minimum aromatic content of not more than 3% is required for a transport fuel (Arandes et al., 2007, Serrano et al., 2000b). It has also been reported that most of the highly acidic catalysts used for polyethylene conversions gave more gaseous than liquid yields with most liquid containing large proportion of aromatics (López et al., 2011, Marcilla et al., 2009). This is why high acidity is strongly linked to high gaseous yield and low acidity may promote olefinic formation (Saha et al., 2008). However, catalysts selectivity is believed also to be controlled by its textural properties (Aguado et al., 2009).

### 2.5.5 Influence of textural properties on the catalyst performance and selectivity

The textural properties of a catalyst are believed to play a significant role in its selectivity towards a particular compound as described by Aguado et al., (2009). They
argue that catalysts with high surface area may offer less diffusional hindrance and support easy access to internal acid site located within the pores and promote secondary reaction, such as aromatisation. The diffusional hindrance caused the low surface area may then impedes secondary reactions, which lead to the production of aromatic compounds (Sharratt et al., 1997, Serrano et al., 2007a, Marcilla et al., 2007a) . Further, Lopez et al. (2011) linked catalyst selectivity to its acidity type and was supported by Marcillah et al. (2009), who suggested that particularly a high number of Lewis acid sites might favours aromatisation during HDPE degradation. Other factors, such as reactor type and reaction conditions may play a significant role as well. Hence, limiting access to pore sites and reduced Lewis acid sites might be suitable modifications of acidic non-zeolite catalysts, such as sulphated zirconia catalyst.

2.5.6 Sulphated zirconia catalyst

Sulphated zirconia catalyst is a zirconium oxide that has been modified with a sulphate ion. The sulphate ion modification is meant to strengthen its acidity and become “super” acidic depending on the treatment (Yadav and Nair, 1999). Zirconium oxide (ZrO$_2$), which is the precursor for sulphated zirconia, on its own has an amphoteric character. The introduction of SO$_4^{2-}$ ion promotes its acidity to “super” acidity. This is because of the inductive effect of the S=O group from SO$_4^{2-}$, which creates electronic deficiencies that promotes the Lewis acidity of the Zr cation (Comelli et al., 1995). Sulphated zirconia was first reported in 1979 for its excellent activity for isomerisation of straight chain alkane, particularly n-butane isomerisation at lower temperature (Stichert et al., 2001, Stichert and Schüth, 1998, Chen et al., 2001, Hino et al., 2006, Clark et al., 2000).

Sulphated zirconia is normally produced through a wet impregnation method, where a chemical precursor, zirconyl chloride (ZrOCl$_2$.8H$_2$O) is hydrolysed with aqueous ammonia and treated with sulphuric acid (H$_2$SO$_4$) and this has been a widely reported method (Chen et al., 1993, Wang and Mou, 2008, Reddy et al., 2005, Zmierczak et al., 1994, Larsen et al., 1995, Wen et al., 1990, Stichert and Schüth, 1998, Bedilo and Klabunde, 1998). This method of preparation has been reported in detail in the work of Chen et al. (1993) and a similar method is used industrially as the sulphated zirconia catalyst precursors used in this work. Here 0.5M solution of zirconyl chloride was initially prepared by dissolving 64.4g zirconyl chloride (ZrOCl$_2$.8H$_2$O) in 500ml of
water at room temperature. To the freshly prepared zirconyl chloride solution, drops of 28wt% aqueous ammonia (NH₄OH) solution was added with continuous agitation until the pH level reached 8.4. The mixture was then filtered, washed with excess water to remove all chloride ions and the dried overnight for 24 hours at 120°C. Sulphuric acid solution was then added to the dried filtrate and allowed to react for 20min at room temperature, then filtered without washing and dried at 120°C for 24 hours. The resultant sulphated zirconia was calcined under static air at required temperature of 400°C and 800°C for 3 hours. Since this is an established method that many recommended, albeit not universal it has not been research in this work.

Sulphated zirconia catalyst is a promising catalyst that has in recent time gained much interest in heterogeneous catalysis due to its super acidity, non-toxicity and efficient activity even at low temperatures (Rathod et al., 2011, Clark, 2002, Reddy et al., 2005, Wang and Mou, 2008, Stichert and Schüth, 1998, Clark et al., 2000). It has been studied for many years and reported to be a very effective catalyst used in catalysing many processes in the oil refining and petrochemical industries (Reddy et al., 2005, Zhao et al., 2008). Apart from alkane isomerisation, sulphated zirconia is a very efficient catalyst for many important processes, namely hydrocracking, alkylation, condensation, esterification, acylation, oligomerisation and a range of organic synthesis reactions (Manoli et al., 1998, Hamada et al., 2009, Wen et al., 1990, Shabtai et al., 1997, Clark, 2002, Wang and Mou, 2008, Arata et al., 2003, Clark et al., 2000). Sulphated zirconia has been reported to have exceptional catalytic properties that can promote conversions of hydrocarbons to highly branched alkanes, where its catalytic structure and activity can be tailored by calcination (Ahmed et al., 2008).

### 2.5.6.1 Effect of calcination on sulphated zirconia catalyst

Calcination plays an important role in forming the structure, acidic strength and catalytic activity of sulphated zirconia. Sulphated zirconia catalyst when freshly prepared is normally orthorhombic and inactive, but upon calcination at 450 to 600°C, it transforms into a tetragonal phase and at high temperature around 800°C it changes to a monoclinic system, which is less active (Stichert and Schüth, 1998, Stichert et al., 2001). Ahmed et al. (2008) studied the structural characterisation of sulphated zirconia and found that sulphated zirconia upon calcination in air at 500°C was predominantly tetragonal that was believed to be stabilised by its SO₄²⁻ groups, with a few percentage
monoclinic. When the calcination temperature was increased to 700°C, the tetragonal phase decreased and the monoclinic phase dominated.

It was also reported that calcination affects the surface area and sulphate loading of the sulphated zirconia, where both tended to decrease with increasing calcination temperature above 600°C (Yadav and Nair, 1999, Tran et al., 1998). Tran et al. (1998) studied the effect of calcination on the acidic and catalytic properties of sulphated zirconia where the sulphur content of sulphated zirconia was found to decreases with increasing calcination temperature from 500 to 600°C, while the BET surface area remain nearly constant over this temperature range. Similar work was reported, where the sulphur content and surface area decreased with increasing calcination temperature above 600°C (Chen et al., 1993). This is also in agreement with another work reported, where a calcination temperature of 480°C gave a sulphate (SO$_4^{2-}$) content of 5.7 % and surface area of 117 m$^2$/g but after increasing the calcination temperature to 620°C, the sulphate (SO$_4^{2-}$) content and surface area dropped to 3.0% and 104 m$^2$ g$^{-1}$, respectively (Comelli et al., 1995). This shows that calcination at 550°C will retain the active tetragonal phase.

The acidic property of a catalyst is thought to be dependent on the starting material and the various preparatory methods employed during the synthesis of the catalyst (see Section 2.5.6). The Equations 2.13 and 2.14 represent a simple mechanism for the creation of the acid site on the surface of sulphated zirconia as proposed by Chen et al. (1993). Reaction in Equation 2.13 is believed to occur during the impregnation with sulphate and Equation 2.14 during calcination. Some of the sulphated zirconia properties observed by removing H$_2$O include resistance to sintering, stable tetragonal phase and smaller crystallite sizes are evidence backing up the mechanism (Chen et al., 1993, Yadav and Nair, 1999).

\[
\text{Zr(OH)}_{4n} + x\text{H}_2\text{SO}_4 \leftrightarrow \text{Zr}_n(\text{OH})_{4n-2x}(\text{SO})_4 \quad 2.13
\]

\[
\text{Zr}_n(\text{OH})_{4n-2x}(\text{SO})_4 \rightarrow \text{Zr}_n\text{O}_{2n-x}(\text{SO}_4)_x + (2n-x)\text{H}_2\text{O} \quad 2.14
\]

In view of this, it is important to select suitable preparation methods particularly calcination temperature, that will result in excellent performance by the catalyst. Equations 2.13 and 2.14 indicate that other elements can be introduced during
calcination. Thus, in this work, calcination temperature of 550°C has been proposed, as described in Chapter 3, to retain surface structure and acid sites.

### 2.5.6.2 Surface structure and nature of acid sites of sulphated zirconia

Sulphated zirconia has been described by many as a super acid catalyst due to its high acidic strength, where Arata et al. (2003) ranked it as second among thirteen solid acid catalysts with an acid strength, $H_0$ of -16.1. The $H_0$ acid strengths were estimated by colour change using a Hammett indicator. However, whether its active sites are Lewis, Brönsted or combined is still an issue of intense debate (Yadav and Mehta, 1994, Bedilo and Klabunde, 1998). Many studies were reported by different researchers using various techniques on the nature of the acid sites of the sulphated zirconia catalyst. Figure 2.9 depicts a Lewis acid (a) and a Brönsted acid (b) site structure contained within a pentavalent sulphur structure as proposed by White et al. (1995). The structure may explain most of the acidic properties attributed to sulphated zirconia. The Lewis acid site (a) structure may be formed through insertion of planar $\text{SO}_3$ molecule into the tetragonal $\text{ZrO}_2$ crystals, where the lone pair of oxygen in the oxide has a strong affinity to an electron pair. For the Brönsted acid (b) site, there is a $\text{H}^+$ available for donation.

![Figure 2.9 Proposed sulphated zirconia structures containing pentavalent sulphur with (a) Lewis ($\star$) and (b) Brönsted ($\bigcirc$) acid site structures (White et al., 1995).](image)

Hino et al. (2006) conducted thermal analyses and spectroscopic studies, XPS and infrared (IR) on sulphated zirconia to study its surface structure. Figure 2.10 shows their proposed surface structure of sulphated zirconia, where $\text{SO}_4$ combined with Zr element in the bridging bidentate state. In this case, they showed that in the sulphate
complex the nature of S=O double bond is more robust than that of simple metal sulphur. Thus, the Lewis acid strength of Zr$^{4+}$ increase significantly due to inductive effect of S=O within the complex as indicated by the arrows, where the Lewis acid sites (★) are converted to Brønsted acid sites (○) in the presence of water through proton transfer as shown in Figure 2.11. Hino et al. (2006) also reported that the active site in the sulphated zirconia is the polysulphate species, which contain three or four S atoms that are combined with other atoms through ionic bonds (S-O-Zr) and covalent bonds (S=O) and linked to Zr. Thus, the Lewis acid sites on the sulphur atoms were regarded as active sites. Similarly, Clark et al. (2000) studied the acidic nature of sulphated zirconia using FTIR spectroscopic and titration with pyridine. The outcome of their findings showed that sulphated zirconia calcined between 500-550°C exhibited mainly Lewis acid sites as widely speculated, but due to quick absorption of atmospheric water at Lewis acid centres during cooling, its acid sites transformed to nearly 100% Brønsted acid sites. The Lewis acid fails to appear in an IR cell even after drying at 300°C. Thus, at normal condition, activated sulphated zirconia may be considered as a Brönsted acid. But some researchers are of the view that sulphated zirconia contain a mixture of both Brønsted and Lewis types of acid sites (Katada et al., 2000).

![Figure 2.10 Proposed surface structure for sulphated zirconia suggesting Lewis acid site (★) on sulphur atoms being the active sites (Hino et al., 2006).](image1)

![Figure 2.11 Surface structure for sulphated zirconia showing transformation of Lewis acid site (★) to Brønsted acid sites (○) due to water absorption (Hino et al., 2006).](image2)
The properties of sulphated zirconia, such as high acidity, mesoporosity and its excellent stability makes it an exceptional catalyst for reaction involving alkylation of aromatic compounds from long chain unsaturated hydrocarbons, which can be easily polymerised (Clark, 2002). Despite its several excellent properties, sulphated zirconia has also been associated with some short comings. It deactivates quickly at high temperature as a result of coke formation, where some studies have applied transition metals, such as platinum, to prevent this (Yadav and Nair, 1999). This work is aimed at introducing a modifier, such as calcium carbide, into sulphated zirconia to modify its acidity and activity as well as strengthening the catalyst against deactivation. In addition, the introduction of calcium carbide may result in the formation of a hybrid catalyst with a reduced pore size distribution that may give excellent selectivity towards primary cracking products. This may improve the selectivity towards low-aromatic hydrocarbon molecules product within the gasoline range.

Gasoline range hydrocarbon can be describe as room temperature liquid compounds, such as paraffins, olefins, naphthenes and aromatics, whose carbon atoms distribution range from C5 to C12 which gives the required volatility when combusted (Buekens and Huang, 1998, Harris et al., 1999, Abrams et al., 2009). Although other carbon atom ranges, such as C5-C9 and C5-C15 were reported as the gasoline range, C5-C12 has been the most widely agreed range in the literature (Abrams et al., 2009, Park et al., 1999, Shabtai et al., 1997, Miskolczi et al., 2009, Buekens and Huang, 1998, Harris et al., 1999) In view of this, compounds with C5-C12 carbon atom range will be regarded as gasoline range compounds in this research and modifying SZ with CC may promote this.

2.5.6.3 Possible chemical reactions involving sulphated zirconia SZ and calcium carbide CC

When sulphated zirconia and calcium carbide are mixed and calcined, a number of chemical reactions are expected to occur, which may lead to the formation of new compounds. One of the most probable reaction that will occur during calcination of a mixture of the two solid catalysts is a deoxidation reaction, which is a reaction between the metal oxide and the calcium carbide to give calcium oxide and a free metal (Krasicka-Cydzik et al., 2001). In the case of sulphated zirconia and calcium carbide, it expected that calcium carbide will reacts with and reduce zirconium oxide from
sulphated zirconia to yield zirconium metal and calcium oxide as shown in Equation 2.15.

\[
\text{ZrO}_2 + 2\text{CaC}_2 \rightarrow 2\text{CaO} + \text{Zr} + 4\text{C} \tag{2.15}
\]

Another possible reaction route is the sintering of zirconium oxide (\(\text{ZrO}_2\)) by the calcium oxide, which may results in the formation of calcium zirconium oxide (\(\text{CaZrO}_3\)) as shown in Equation 2.16 (Kalinkin et al., 2012). For calcium carbide and sulphated zirconia, this reaction could be between the CaO generated either from deoxidation or through decomposition of calcium carbide during sintering in air as shown in Equation 2.17.

\[
\text{CaO} + \text{ZrO}_2 \rightarrow \text{CaZrO}_3 \tag{2.16}
\]

\[
2\text{CaC}_2 + 5\text{O}_2 \rightarrow 2\text{CaO} + 4\text{CO}_2 \tag{2.17}
\]

Calcination thus, transfers \(\text{CaC}_2\) to a safer compound for used in a hybrid with SZ. Catalysts acidity may not be the only factor that influences the catalytic cracking of polymer and product selectivity, since reaction conditions also can be important. Some of these conditions are briefly discussed here, including, but not limited to, reactor type, catalyst type and size, polymer catalyst ratio and optimized reaction conditions, such as retention time and temperature.

### 2.6 Influence of reactor types and reaction conditions on catalytic cracking of plastic waste and polymers

#### 2.6.1 Types of reactors

A wide range of reactors have been used for the conversion of plastic waste and polymers, including fixed-bed reactor, fluidized bed reactor, batch-reactor, semi-batch reactor, continues flow reactor and other laboratory-scale set up reactors. The choice of a particular reactor set-up primarily depends on how effectively it can achieve the mass-heat transfer and catalyst polymer contact needed and how efficiently it will provide an even temperature distribution and favour a targeted product distribution. Polymer properties, such as low thermal conductivity and high viscosity, could hinder the effective mass and heat transfer. Hence, a reactor system that would promote mass and heat transfer has traditionally been explored and used (Aguado et al., 2008).
2.6.1.1 **Fixed-bed reactor**

Fixed-bed is the simplest reactor for catalytic conversion of plastic wastes and polymers. It is simply designed such that polymer and catalyst at appropriate ratios are contacted directly and introduced into the reactor and held stationary without moving. This simplicity in design and handling was what informed the choice of this reactor in this research. It is also believe that if the catalyst developed from this research works with this simple reactor, it will certainly work even better using the most advanced reactors. However, fixed-bed reactor has been reported to be associated with some drawbacks, which include pressure drop, blockage, and poor polymer catalyst contact resulting in large residue formation (Aguado et al., 2008, Huang et al., 2010). One attempt to avoid this is shown in Figure 2.12, which is an example of a fixed-bed reactor used for the catalytic conversion of plastic waste, such as LDPE, HDPE and PP, as reported by Achilas et al. (2007). Here the reactor was designed vertically with two separate compartments, reactor tube and a piston. The reactor was filled with the catalyst and the piston with the polymer and the feed and catalyst were mixed together in to the vertical bed reactor. This help in minimizing the pressure drop and reduced the possibility of blockages. However, physical mixing prior to heating is currently the best way to use a fixed-bed reactor.

![Fixed-bed reactor](image)

*Figure 2.12 Fixed-bed reactor for catalytic degradation of plastic wastes (Achilias, et al., 2007)*
2.6.1.2 Fluidized bed reactor

Figure 2.13 is an example of a fluidized bed reactor used for the catalytic conversion of post-consumer plastic wastes as reported by Huang et al. (2010). It shows how the plastic waste is continuously fed into the reactor, where the catalyst is fluidized up using a gas at a certain temperature. Several fluidized bed reactors have been proposed, including continuous flow reactors, (Lee et al., 1995, Lin et al., 2010, Guo et al., 2010, Hernandez et al., 2006, Ji et al., 2001, Lin and Yen, 2005, Lin, 2009, Wei et al., 2010). Using fluidized bed may provide an efficient heat and mass transfer characteristics, which will result in uniform temperature distribution within the reactor that gives excellent yield and product distribution (Aguado et al., 2008, Huang et al., 2010). However, introducing the plastic waste feed into the already heated fluidized bed may be somehow difficult. This is because of the possibility that the plastic will melt in continues polymer feed before it reaches the bed of the reactor. The melting point of plastic, HDPE in particular, is 130°C and the reaction temperature is normally between 380-500°C. Other problems associated with fluidized bed reactors include longer residence time, low liquid yields due to excessive cracking, high catalyst to feed ratio required, hard to scale-up and bed defluidisation (Panda et al., 2010, Arandes et al., 2007).

![Figure 2.13 Fluidized-bed reactor used for catalytic conversion of post-consumer plastic waste (Huang et al., 2010).](image-url)
2.6.1.3 Batch reactors

Batch and semi-batch reactors, ranging from laboratory to industrial scale have been reported for catalytic conversion of plastic wastes, where Miskolczi et al. (2006) used batch reactor for the catalytic conversion of polyethylene and polystyrene wastes over different cracking and zeolites catalysts. Liquid and gas products were obtained at different proportion depending on the catalyst and operating conditions used. Many other works were equally reported using batch reactor for plastic waste conversion (Shah et al., 2010a, Jan et al., 2010, Shah et al., 2010b, Aguado et al., 2009). The semi-batch was also used by some workers and reported in the literatures (Tang et al., 2003, Akpanudoh et al., 2005, Park et al., 1999). Semi-batch reactor might be used to tackle the problem of polymer catalyst contact, as the polymer and catalyst are being heated separately in semi-batch reactors. However, batch reactor systems are generally disadvantageous, because the process takes longer time and the effective function of the catalyst is low (Panda et al., 2010).

2.6.1.4 Continuous stirred tank reactor

Figure 2.14 shows a continuous stirred tank reactor used for plastic waste conversion as reported by Murata et al. (2009). They reported different options of arranging the catalyst and polymer. Firstly, the catalyst was placed in a cage and the cage was placed in the melted polymer at a steady temperature of 420°C. Secondly, the cage containing the catalyst was placed above the melted polymer after reaching 420°C. Third option, the catalyst and polymer were mixed together without the use of any cage and stirrer. The third option appeared the most efficient and gave the highest conversion. This is interesting, because in this research, similar method of mixing catalyst and polymer was adopted as already suggested in Section 2.6.1.1 and detailed in Section 3.4.2 for HDPE conversion using a fixed-bed reactor. Continuous stirred reactor system has also been reported for polymer conversion by other researchers (Zhibo et al., 1996, Miskolczi et al., 2009).
2.6.2 Reaction temperature

Reaction temperature is an important variable that plays a very vital role during catalytic conversion of plastic waste. Depending on the catalytic system, different operating temperatures give rise to different product distributions. For instance, in the work of Jan et al. (2010), HDPE plastic waste was degraded using a basic catalyst, \(\text{BaCO}_3\) and it was observed that increasing the temperature from 250 to 450°C significantly affect the polymer conversion from no conversion at 350°C, low conversion to only gaseous products at 400°C with about 95wt% conversion with maximum liquid yield at 450°C. This showed that in the presence of a basic catalyst, increasing the temperature above 400°C favoured high conversion and promoted high liquid yield. However, it is different when acidic catalysts are used, where high temperature favours high yield of gaseous products (Lin and Yen, 2005, Huang et al., 2010, Lin et al., 2010). For example, Lin and Yen (2005) studied the conversion of PP using an acidic catalyst and showed that the liquid yield decreased while the gaseous fraction increased with increasing temperatures from 290 to 430°C. The effect of temperature on the selectivity of hydrocarbon compounds has also been investigated by Lin, (2009), which revealed that olefinic compounds decreased with increasing temperature from 330 to 430°C as paraffinic and aromatic compounds increased at 450°C. It was also reported that branched hydrocarbons decreased with increasing
temperature, from 390 to 460°C and could lead to a high carbon number distribution (Miskolczi et al., 2004b, Lin et al., 2010). In view of this, optimisation of reaction temperature during catalytic degradation is recommended for this research work.

2.6.3 Retention time

Retention time is another important parameter that play a crucial role for a complete catalytic conversion (Jan et al., 2010). Depending on the catalyst and reactor used, residence time always affect the yield and the composition of the final products. For instance, if the process is carried out at longer retention time, there is an increasing possibility of getting secondary products, such as coke and tar, as a result of primary products cracking, though little has been done to ascertain this effect (Panda et al., 2010, Lin et al., 2010, Buekens and Huang, 1998, Hernandez et al., 2006, Marcilla et al., 2007b). For example, Hernandez et al. (2006) studied the influence of resident time on the products obtained from HDPE conversions with and without catalyst. They established that catalysts are more effective at lower residence time and affirmed that longer residence time could lead to secondary cracking reactions, which could promote high gaseous yield. Also, longer residence time was reported to affect the structure of the hydrocarbons, as a result of a further degradation of the liquid product (Park et al., 1999, Miskolczi et al., 2004a). However, when a basic catalyst was used for HDPE degradation by Jan et al. (2010) using BaCO$_3$, it was showed that an increase in the resident time from 0.5 to 2hrs favoured high liquid yield.

2.6.4 Polymer to catalyst ratio

The polymer to catalyst ratio is another important parameter concerning the catalytic conversion of plastic waste. It is usually optimised to ascertain the ratio that favours optimum yield and product distribution. Different ratios used during catalytic degradation of different polymers have been studied and their effects have also been reported. For instance, Jan et al. (2010) reported that 1:10 was the optimum ratio for effective polymer conversion using CaCO$_3$. Depending on the reactor type used, high polymer catalyst ratio may promote more unconverted polymer material, because material that may stick on the wall of the reactor as a result of poor catalyst polymer contact (Lin et al., 2010, Huang et al., 2010).
2.6.5 Catalyst type

The choice of a particular catalyst type for catalytic conversion of plastics is equally very important. Different types of catalysts have been reported for catalytic conversion of different types of plastics, where different composition of products were obtained (Walendziewski, 2002, Walendziewski and Steininger, 2001, Hesse and White, 2004, Miskolczi et al., 2006, Miskolczi et al., 2009, Baraniec-Mazurek and Mianowski, 2010a, Baraniec-Mazurek and Mianowski, 2010b). These catalysts include zeolite base such as ZSM-5, PtHZSM-41 and PtHY, silica-alumina, NiMo, Cobalt molybdenum, BaCO$_3$, Al-Zn composite ZnO, MgO, CaC$_2$, SiO$_2$, Al$_2$O and mixture of SiO$_2$ and Al$_2$O$_3$ as detailed in Section 2.5.3.

2.7 Summary of the catalytic degradation of plastic wastes and polymers

Table 2.4 summarises some of the published works on catalytic conversion of polyolefin plastics and polymers using different catalysts, reactors and different reaction conditions. Total conversion achieved and liquid and gaseous fractions obtained were compared. A catalytic conversion of LDPE was reported by Aguado et al. (2009) using zeolite mordenite catalyst at 420$^\circ$C for 30 minutes, where the highest conversion of only 57.1 wt% was achieved with 31.3 and 25.8 wt% liquid and gaseous fractions, respectively. In another work reported by Park et al. (1999), HDPE was catalytically converted using four solid acid catalysts at 450$^\circ$C in 60 minutes. A total conversion of 91 to 100 wt% was achieved depending on the catalyst used. In the presence of a HY5.5 zeolite catalyst, liquid and gaseous fractions of 14.9 and 75.8 wt%, respectively were obtained. But in the presence of HZM-5, liquid and gaseous fractions of 10.9 and 88.4 wt%, respectively, were obtained, whereas HNZ/Ni catalyst, gave 64.3 and 35.1 wt% gaseous and liquid fractions, respectively. In related work, a catalytic conversion of hospital plastic waste (LDPE/HDPE/PP/PS) was reported by Huang et al. (2010), where a total conversion of 91 to 96 wt% was achieved at 360$^\circ$C in 20 minutes with a 2:3 waste/catalyst ratio. In the presence of a USY catalyst, liquid and gaseous fractions of 3.7 and 87.5 wt%, respectively, were obtained and 3.3 and 93.1 wt%, respectively, in the presence of HZM-5. While, using MCM-41, 5.6 and 87.3 wt% were obtained as liquid and gaseous fractions, respectively. Similarly, Serrano et al. (2000) reported on catalytic conversion of polyolefin mixture (LDPE/HDPE/PP) at 400$^\circ$C using different solid acid catalyst at a 1:1 ratio. In the presence of a n-HZSM-5 catalyst,
a total conversion of 84wt% with 34 and 50wt% liquid and gaseous fractions, respectively, were achieved, but using HBeta, a 68wt% conversion with 33 and 35wt% liquid and gaseous fractions, respectively, were obtained. However, using the HY catalyst, less than 10wt% conversion with non-traceable liquid or gases was achieved. Jan et al. (2010) reported the catalytic conversion of HDPE waste at 450°C in the presence of a basic catalyst, BaCO₃, where a total conversion of 84wt% with 37, 29 and 28wt% as liquid, wax and gaseous fractions, respectively, were obtained. Finally, Liu and Meuzelaar, (1996) reported a HDPE conversion of 86wt% in the presence of a 10% sulphated zirconia in a TGA setup, where no products yield was analysed. Overall, this shows that achieving efficient conversion does not only depends on reactor and catalyst types, but the temperature at which the conversion take place. Most of the work reported did not approach 100wt% conversion with more gaseous that liquid fractions, particularly acidic catalysts, which appeared to promote more gaseous fraction with increasing temperature.

In view of this, catalyst modification and reaction conditions, particularly temperature, will be optimised in this work to find the condition that would promote optimal liquid product with less aromatic component. This would make the liquid product obtained suitable for as transport fuel, which is one of major aims of the research.
Table 2.4 Summary of the previous works on catalytic degradation of plastic wastes and polymers.

<table>
<thead>
<tr>
<th>Plastic</th>
<th>Temperature (°C)</th>
<th>Res. time (Min.)</th>
<th>Catalyst/Polymers</th>
<th>Reactor Type</th>
<th>Conversion (%)</th>
<th>Liquid (wt%)</th>
<th>Gas (wt%)</th>
<th>Aromatics</th>
<th>Paraffins+ olefins</th>
<th>Researchers</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE</td>
<td>420</td>
<td>120</td>
<td>1:5</td>
<td>Batch</td>
<td>57.1</td>
<td>31.3</td>
<td>25.8</td>
<td>25</td>
<td>75</td>
<td>Aguado et al., 2009</td>
</tr>
<tr>
<td>HDPE</td>
<td>450</td>
<td>60</td>
<td>NR</td>
<td>Fixed-bed</td>
<td>91</td>
<td>14.9</td>
<td>75.8</td>
<td>29.4</td>
<td>70</td>
<td>Park et al., 1999</td>
</tr>
<tr>
<td>HDPE</td>
<td>450</td>
<td>60</td>
<td>NR</td>
<td>Fixed-bed</td>
<td>99</td>
<td>10.9</td>
<td>88.4</td>
<td>26.6</td>
<td>73.5</td>
<td>Park et al., 1999</td>
</tr>
<tr>
<td>HDPE</td>
<td>450</td>
<td>60</td>
<td>NR</td>
<td>Fixed-bed</td>
<td>100</td>
<td>65.1</td>
<td>34.9</td>
<td>34.9</td>
<td>65.2</td>
<td>Park et al., 1999</td>
</tr>
<tr>
<td>Hospital waste (LDPE/HDPE/PP/PS)</td>
<td>450</td>
<td>60</td>
<td>2:3</td>
<td>Fluidised-bed</td>
<td>100</td>
<td>34.9</td>
<td>65.1</td>
<td>34.3</td>
<td>65.7</td>
<td>Park et al., 1999</td>
</tr>
<tr>
<td>Hospital waste (LDPE/HDPE/PP/PS)</td>
<td>360</td>
<td>20</td>
<td>2:3</td>
<td>Fluidised-bed</td>
<td>91</td>
<td>3.7</td>
<td>87.5</td>
<td>NR</td>
<td>NR</td>
<td>Huang et al., 2010</td>
</tr>
<tr>
<td>Hospital waste (LDPE/HDPE/PP/PS)</td>
<td>360</td>
<td>20</td>
<td>2:3</td>
<td>Fluidised-bed</td>
<td>96</td>
<td>3.3</td>
<td>93.1</td>
<td>NR</td>
<td>NR</td>
<td>Huang et al., 2010</td>
</tr>
<tr>
<td>polyolefin mixture (LDPE/HDPE/PP)</td>
<td>400</td>
<td>30</td>
<td>1:1</td>
<td>Pyrex batch</td>
<td>84</td>
<td>50</td>
<td>50</td>
<td>NR</td>
<td>NR</td>
<td>Serrano et al., 2000</td>
</tr>
<tr>
<td>polyolefin mixture (LDPE/HDPE/PP)</td>
<td>400</td>
<td>30</td>
<td>1:1</td>
<td>Pyrex batch</td>
<td>68</td>
<td>60</td>
<td>35</td>
<td>NR</td>
<td>NR</td>
<td>Serrano et al., 2000</td>
</tr>
<tr>
<td>polyolefin mixture (LDPE/HDPE/PP)</td>
<td>400</td>
<td>30</td>
<td>1:1</td>
<td>Pyrex batch</td>
<td>&lt;10</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>Serrano et al., 2000</td>
</tr>
<tr>
<td>HDPE WASTE</td>
<td>450</td>
<td>60</td>
<td>1:1</td>
<td>Fixed-bed</td>
<td>84</td>
<td>37+29</td>
<td>28</td>
<td>NR</td>
<td>NR</td>
<td>Jan et al., 2010</td>
</tr>
<tr>
<td>HDPE</td>
<td>420</td>
<td>30</td>
<td>1:9</td>
<td>TGA</td>
<td>86</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>Liu and Meuzelaar, 1996</td>
</tr>
</tbody>
</table>
2.8 Review of the instrumental analysis

This section briefly reviews the basic principles of the analytical instruments used for analyses in this research work, namely Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM/EDX), X-ray diffraction (XRD), Gas Chromatography (GC), surface adsorption analysis (BET) and NH₃ Temperature Programmed Desorption (TPD).

2.8.1 Thermogravimetric analysis (TGA)

Thermogravimetric analysis, which is often called thermal gravimetric analysis (TGA), is analytical measurement equipment used for material characterisation. It is specifically design to study the thermal analysis and primary reactions during decomposition of organic solids, such as polyolefin polymers (Quan et al., 2009, Gobin and Manos, 2004, Navarro et al., 2003). During thermogravimetric analysis, the alteration in the mass of the solid sample due to an increase in the temperature is captured by the sensitive microbalance and recorded continuously as a function of temperature or time. The result is usually displayed on a thermogram or thermal decomposition curve, which shows mass or mass percentage as a function of temperature or time. The TGA data provides physico-chemical properties of a particular solid material by measuring the changes in mass as a function of temperature or time at constant heating rate (Coats and Redfern, 1963, Cai et al., 2008). Physico-chemical information provided by TGA include, the thermal stability of material at high temperature, compositions of the materials, kinetic data such reaction order and kinetic energy (Seo et al., 2010, Quan et al., 2009, Aboulkas et al., 2008b). Figure 2.15 shows a typical TGA thermogram and DTG curve illustrating how thermal information can be obtains from calculations of a catalyst precursor. With increasing temperature in an inert gas environment, three different weight loses occur, which are, water (100°C), carbon monoxide (400°C) and carbon dioxide (650°C) that are clearly shown on the thermogram.
Figure 2.15 TGA thermogram showing decomposition of calcium oxalate monohydrate (Fröberg, 2015).

Figure 2.16 shows a schematic diagram of thermobalance with its basic components (A-F) produced by Mettler-Toledo. Components, A, B and C are the balance beam, sample cup/holder and a counterweight, respectively. D is the lamp and photodiodes, E and F are the magnetic coil and permanent magnet, respectively. Components G, H, and I are the computer data-acquisition, data-processing, and control, respectively. Component J is the printer and display unit (Skoog et al., 2007b). As B is heated, the system will measure the change in weight.

Figure 2.17 Schematic representation of a thermobalance (Skoog et al., 2007a).

Figure 2.17 shows the TG and DTG curves of HDPE degradation at different heating rates as conducted by Aboulkas et al. (2010), where the non-isothermal TGA data was used to analyse the activation energy and reaction model of the HDPE degradation. The DTG curves showed that the HDPE degradation was a one step
process as evidenced by only one peak, which also determined the temperature of maximum degradation. In the work reported by Navarro et al. (2003), TGA analysis was used to study the thermal decomposition of recycled polypropylene containing elastomers. They used the TGA data in dynamic and isothermal modes to develop a kinetic model, which was used to analyse the apparent kinetic parameters. In another work reported by Gobin and Manos (2004), a TGA analysis was used to study the catalytic degradation of polyolefin polymers, namely HDPE, LDPE, LLDPE and PP. In this work, the TGA analyses was carried out to study the thermal behaviour of all the polymer samples and conduct the preliminary testing of the potential catalysts on the polymer degradations as well as using the data to obtain some kinetic parameters. Several other research works have been reported using TGA as a tool for studying the physico-chemical properties of different organic solids, particularly for studying the decomposition reaction, kinetics and reaction mechanisms of organic solids, such as different types of plastic and polymer wastes, coal and biomasses (Quan et al., 2009, Aboulkas et al., 2008b, Aboulkas et al., 2008a, Aboulkas et al., 2010, Park et al., 2012, Seo et al., 2010, Seo et al., 2011, Cai et al., 2008, Zhou et al., 2006, Ren et al., 2009, Leroy et al., 2010, Murty et al., 1998).

![TGA and DTG curves for HDPE degradation](image)

**Figure 2.17 TGA and DTG curves for HDPE degradation (Aboulkas et al., 2010).**

### 2.8.2 Scanning Electron Microscopy (SEM)

Figure 2.18 is a schematic diagram of an electron microscopy showing how different signals are obtained when a beam of electron strikes a sample. In electron microscopy, interaction between the electron beam and the sample provides structural information, such as morphology, chemical composition and crystallography (Chorkendorff and Niemantsverdriet, 2007). For this method, electrons are used rather
than photons to study the solid materials. When the electron beam strikes a sample, most pass through without loss of energy, but some are diffracted by the sample particles, which are used to get crystallographic information. Equally, some electrons collide with sample atoms and back-scatter depending on the mass of the atom. The intensity of the back scattering provides information on the atoms. Electron microscopy is a powerful technique used to analyse particle size and shape analysis (Chorkendorff and Niemantsverdriet, 2007). It is generally classified based on the imaging principles (Kogure, 2013). It encompasses of different microscopic technologies, namely Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Scanning Transmission Electron Microscopy (STEM). Scanning Electron Microscopy (SEM), as used in this study, is commonly used for catalyst characterisation.

![A schematic diagram of an electron microscopy showing resultant signals due to interaction between the electron beam and sample (Chorkendorff and Niemantsverdriet, 2007).](image)

Figure 2.18 A schematic diagram of an electron microscopy showing resultant signals due to interaction between the electron beam and sample (Chorkendorff and Niemantsverdriet, 2007).

Figure 2.19 shows a typical scanning electron microscopy setup (Kogure, 2013). An electron beam at high voltage up to 40 keV is directed towards the specimen chamber where the sample under study is placed. The beam generated using electron gun consisting of a cathode with filament made from tungsten or lanthanum hexaboride (LaB6) due to their ability of emitting electron at low pressure. The electrons beam that passes from the cathode towards anode, where some are allowed to pass through condenser lens, scanning coil, objective lens before striking on surface of the sample (Kogure, 2013). The scanning coil allows the SEM to generate magnified images of the
sample surface. The detectors shown on Figure 2.19 (B) detect the signals generated after the electron beam strikes the sample (Kogure, 2013, Chorkendorff and Niemantsverdriet, 2007). Backscattering electron and x-rays are the two main signals that provide information on morphology and chemical composition of the solid sample. The backscattering electrons are detected by an electron detector and provide high resolution images and sample surface topography. The X-rays emitted has the characteristics of the element and are detected by an energy-dispersive X–ray (EDX) detector and generate information on the chemical composition of the sample (Chorkendorff and Niemantsverdriet, 2007, Bogner et al., 2007).

Figure 2.19 Schematic diagram of (A) a scanning electron microscope (SEM) with (B) different detectors (Kogure, 2013).

Figure 2.20 shows SEM micrograph and a corresponding EDX plot from the work reported by Miskolczi et al. (2009) where the surface morphology and chemical compositions of a catalyst were analysed. The SEM micrograph shows the particle size of the catalyst while the EDX plot gives the elemental composition of the catalyst. Scanning electron microscopy (SEM) is widely used for characterisation of solid catalyst to analyse its microstructure and morphology (Zhou et al., 2007, Angyal et al., 2009). Many works have used SEM/EDX to study surface morphology of different catalysts (Miskolczi et al., 2004b, Angyal et al., 2009, Miskolczi et al., 2009, Rathod et al., 2010, López et al., 2011, Chen et al., 2001). For instance, Chen et al. (2001) reported the use of SEM to study the morphological and particle size of sulphated
zirconia over MCM-41 catalyst. Further to this, Angyal, et al. (2009) reported the use of scanning electron microscopy (SEM) coupled with energy-dispersed X-ray analysis (EDX) technique to study the textural properties and deactivation of FCC catalyst by following the change in the surface morphology.

![Figure 2.20 SEM and EDX micrographs of polyethylene over a ZSM-5 catalyst (Miskolczi et al., 2009).](image)

**2.8.3 X-ray diffraction (XRD)**

X-ray diffraction (XRD) is a powerful tool used for investigating structural and chemical characterisations of a material (Cullity, 1978, Ingham and Toney, 2014, Chorkendorff and Niemantsverdriet, 2007). Powdered x-ray diffraction was developed in 1916 by the Dutch physicist, P. Debye and Swiss physicist P. Scherrer (Ingham and Toney, 2014). Powder X-ray diffraction (XRD) involves beaming monochromatic X-rays (a strong K characteristic component) at a powdered sample and monitor the diffraction caused by the structural characteristics of the sample (Cullity, 1978, Ingham and Toney, 2014).

Powdered X-ray diffraction is used for various applications including identification of unknown components, measurement of sample purity, material phase identification and determination of crystalline size of the material. For identification of unknown components, a scattering intensity is plotted against the scattering angle (2θ) and the peaks width, shapes, intensities, and positions will provide information about the structure of the unknown component. The identification is carried out by comparing the data obtained with that of the Joint Committee on Powder Diffraction Standards
(JCPDS) file which has data of thousands of crystalline substances (Cullity, 1978). Phase identification is a common application of x-ray diffraction due to its sensitivity to crystal structure, lattice parameters, symmetry and atomic co-ordinates within the unit cell (Ingham and Toney, 2014). There are different data bases for diffraction patterns for identification of unknown substances, where the most intense peaks are matched (Ingham and Toney, 2014). The current diffraction patterns data base includes, International Centre for Diffraction Data (ICDD), the Cambridge Crystallographic Data Centre (CCDC), the Fachinformationszentrum (FIZ; Karlsruhe, Germany) and the US National Institute of Standards and Technology (NIST)).

Figure 2.21 is an illustration of the diffraction phenomena as explained by Bragg’s law, that forms the bases for Bragg’s Equation (Equation 2.15) (Ingham and Toney, 2014). According to Bragg’s law, d is the distance between the two parallel diffracting planes, λ is the wavelength of the X-ray, n is an integer, usually called the order of reflection and θ is the half of the scattering angle, 2θ. An X-ray diffraction (XRD) analysis can thus be used for determination of the crystallite size from the x-ray diffraction peaks using the Scherrer equation (Equation 2.18) (Ingham and Toney, 2014, Burton et al., 2009). Where, 2θ is the scattering angle in radian, FWHM is the Full Width at Half Maximum of the peak defined in Equation 2.19; b is dimensionless constant with a value ranges between 0.89 and 0.94, depending on the actual shape of the crystallite, D is the mean size of the crystallite.

\[
\frac{n\lambda}{2d} \sin \theta = 2
\]

\[
FWHM \ (2\theta) = \frac{b\lambda}{D \cos \theta}
\]

Figure 2.21 Diffraction of x-rays by a crystal (Ingham and Toney, 2014).
Figure 2.22 is a typical example of an X-ray diffraction (XRD) pattern of a sulphated zirconia reported by Angeles-Beltrán et al. (2006). The peaks marked with the green lines were identified as zirconium oxide compound and the diffraction pattern corresponds to a sulphated zirconia with a tetragonal phase (see Section 2.5.6). This shows that X-rays diffraction analysis can be used for both phase identification and chemical analysis. Manoli et al. (1998) characterised sulphated zirconia doped with platinum using XRD to compare the physicochemical properties of fresh and calcined catalysts. The Pt and ZrO\textsubscript{2} were identified and compared on both fresh and calcined catalysts, where the information obtained was used to make conclusions on the crystallinity of the catalyst and also how calcination can affected it (Manoli et al., 1998). Similarly, elemental analysis is another application of X-ray diffraction analysis, as reported by (Wu et al., 2014). In their work, the catalytic reduction of carbon monoxide using a Cu-Ni alloy at different temperatures was monitored by in-situ XRD, where reflections observed were used to assign for changes in Cu, Ni metals and Ni-Cu alloys.

![XRD pattern of a sulphated zirconia (Angeles-Beltrán et al., 2006).](image)

2.8.4 Gas chromatography (GC)

Figure 2.23 sketch the gas chromatographic operations showing the separation of a mixture of two components A and B. Gas chromatography is a technique that basically separates mixture of chemical components based on the partitioning behaviour between its mobile and stationary phases, where the mobile phase could be gas or liquid and stationary phase may be liquid film or a solid surface (Braithwaite and Smith,
In gas chromatography (GC), the mobile phase composition is continuously monitored by selected detectors. The level of the detector signal denotes the amount of the component as it passes through the detector and the peak area is proportional to the overall amount of components in the eluted band and their molecular structure. At the end, an electronic integrator processes the signal by plotting it against time and form a chromatogram. This can be used to calculate the exact retention time, peak area, height and width, which are used to identify and quantify the components (Braithwaite and Smith, 1996). Gas chromatography is basically carried out in three different modes, namely gas-liquid chromatography, (GLC), capillary column GC and gas-solid chromatography (GSC) and in all cases it is the gaseous mobile phase that transports components over a stationary phase. However, GLC is most commonly used particularly for separation of gas components. Flame ionisation detector (FID), thermal conductivity detector (TCD) and electron capture detector (ECD), flame photometric detector (FPD) are some of the detectors usually coupled with GC depending on the nature of the solute to be analysed. The GC is calibrated by running various dilutions of the compounds of interest, where their retention time and peak area is used to analyse the concentration of sample components by comparison on calibration curve. A calibration curve is normally produced by plotting the response time of the various sample compounds against their concentrations, where no two compounds will have exactly the same calibration curve. Calibration is usually repeated at regular intervals.

Figure 2.23 Summary sketch of a gas chromatogram (GC) showing the separation the mixture of two components (Watson and Sparkman, 2008).

Figure 2.24 shows a GC chromatogram of a gaseous hydrocarbon mixture obtained from catalytic conversion of HDPE waste over FCC catalyst as reported by
Miskolczi et al. (2004b). The peaks on the chromatogram represent gaseous hydrocarbon compounds with their corresponding isomers (Miskolczi et al., 2004a, Fernández-Varela et al., 2009, Lin et al., 2007, Williams and Slaney, 2007). The use of Gas Chromatography coupled with Flame Ionisation Detector (GC/FID) have been reported widely for hydrocarbon gaseous analysis due its sensitivity to organic compounds and non-interference with common carrier gases, such as He (Fernández-Varela et al., 2009, Miskolczi and Bartha, 2008, Williams and Slaney, 2007, Colón and Baird, 2004).

![Figure 2.24 A typical GC chromatogram showing gaseous hydrocarbon compounds analysed from the gaseous fraction from HDPE waste conversion using a FCC catalyst (Miskolczi et al., 2004b).](image)

2.8.4.1 Gas Chromatography/Mass Spectrometry (GC/MS)

Figure 2.25 shows a schematic diagram of a total ion chromatogram of a GC/MS analysis of a liquid alcohol containing different compounds as presented by Braithwaite and Smith (1996). The spectrum at the bottom is a GC chromatogram, where different alcoholic compounds were separated based on their retention time while the top one represents a mass spectrometer (MS), which identifies the compound base on its m/z spectrum, toluene in this case. As already stated, GC is mainly a separation technique so, the role of detectors is limited to monitoring of the quantity as compounds emerge from the column but not to identify the components (Braithwaite and Smith, 1996). The technique of a mass spectrometer (MS) attached to the GC is efficient for analyses and identification of components from complex mixture, such as crude oil, biofuel and liquid from plastic conversion (Watson and Sparkman, 2008, de Hoffmann and Stroobant, 2007).
Figure 2.25 Schematic diagram of the total ion chromatogram (TIC) of GC/MS analysis of a liquid alcohol containing different alcoholic compounds (Braithwaite and Smith, 1996).

Figure 2.26 shows a GC/MS chromatogram of a liquid product obtained from the catalytic hydrocracking of HDPE showing the distribution of hydrocarbon compounds (C11-C32) as reported in the work of Shabtai et al. (1997). The use of GC/MS is instrumental in analyses of different liquid containing complex mixtures (Watson and Sparkman, 2008). Quite a number of research works has been published where GC/MS has been used for liquid fuel analyses (Reddy and Quinn, 1999, Williams and Slaney, 2007, Fernández-Varela et al., 2009, Seo and Shin, 2002, Jan et al., 2010, Lim and Andrésen, 2011, Lee, 2008). For instance, Reddy and Quinn, (1999) used GS/MS to analyse the North Cape oil spill by analysing the total petroleum hydrocarbons and polycyclic aromatics in seawater samples. Another classical example of GC/MS applications is for analysis of bio oils as used in work of Lim and Andrésen (2011) where different components in the oil, namely phenolic, methoxy phenolic, cyclic, O-ring, benzenes derivatives and saccharides were identified. So in this research work, GC/MS was selected for liquid products analyses. This is to identify and quantify the hydrocarbon compounds in the liquid products and also to understand the selectivity of the sulphated zirconia and hybrid catalysts.
2.8.5 Brunauer-Emmet-Teller (BET) surface adsorption

The Brunauer, Emmett, and Teller (BET) surface adsorption theory is an extension of the Langmuir theory, which is based on monolayer adsorptions that assume all surfaces to have the same adsorption energy (Brunauer et al., 1938). The Langmuir theory which is was the bases of adsorption science relates the monolayer adsorption of gas molecule upon a solid surface to the gas pressure above the solid surface (Langmuir, 1918). However the BET surface adsorption theory is based on multilayer adsorption which set to addressed some flaws in the Langmuir theory such as monolayer adsorptions assumption (Barron, 2014, Brunauer et al., 1938, Brunauer et al., 1940). The BET theory was based on three basic assumptions, namely (i) Gas molecules will physically adsorb on a solid in layers infinitely, (ii) there is no interaction among the adsorption layers and (iii) the theory is applicable to each adsorption layer (Brunauer et al., 1938, Barron, 2014). In BET surface analyses nitrogen is commonly used due to its purity, availability and its strong adhesion ability on most of solid surface. After the nitrogen gas adsorption, a partial vacuum is achieved with relative pressure less than 1atm and then adsorption layers formed. The solid sample after heated released the adsorbed nitrogen which is quantified and the Bet isotherm is plotted as amount of gas adsorbed verses relative pressure (Barron, 2014). Nitrogen adsorption isotherm has been widely reported method of analysing the textural properties of solid catalysts (López et al., 2011, Sing, 2001, Tahir and Amin, 2013, Zhao et al., 2008).
Figure 2.27 shows five absorption isotherms believed to describe most gas and solid interactions (Brunauer et al., 1940, Storck et al., 1998). Each adsorption isotherms gives specific information about the pore and surface characteristics of the solid sample under investigation (Brunauer et al., 1940, Donohue and Aranovich, 1999, Barron, 2014, Sing, 1998, Sing, 2001, Storck et al., 1998). Type I is a pseudo-Langmuir isotherm showing a unimolecular layer adsorption, which is usually characteristics of microporous material with pore diameter of less than 2nm. Type II isotherm is an isotherm for samples that have monolayer-multilayer adsorption and isotherm and capillary condensation. It is typical of multi-adsorbents with strong affinity. Type III isotherm indicates multilayer adsorption and is typically for macroporous adsorbent with weak affinity. Type IV isotherm is typically associated with capillary condensation which occurs in mesopores. The shape of Type IV isotherm is generally associated with mesoporous adsorbent with strong affinity which are materials with typical pore diameter between 2-50nm. Type V isotherm is characteristics for mesoporous adsorbents with weak affinity.

![Figure 2.27 Types of adsorption isotherms (Storck et al., 1998).](image-url)
The data derived from an adsorption isotherm is used in the BET equation (Equation 2.20) to determine the surface area of a particular solid sample. Where \( w \), is the weight of nitrogen adsorbed at a particular relative pressure \( (P/P_\theta) \), \( P \) and \( P_\theta \) are the equilibrium and saturation pressure on adsorbates, respectively, and \( w_m \) is the amount of gas adsorbed by monolayer at STP. The BET constant \( C \), which is related exponentially to the enthalpy change (heat) of adsorption in the first adsorbed layer and is given by Equation 2.21, where \( E_1 \) and \( E_2 \) represent heat of adsorption of first layer and heat of liquefaction, respectively.

\[
\frac{P}{w(P_\theta-P)} = \frac{1}{w_mC} + \frac{C-1}{w_mC} \left( \frac{P}{P_\theta} \right) \quad 2.20
\]

\[
C = \exp \left( \frac{E_1-E_L}{RT} \right) \quad 2.21
\]

For multi-point BET, three to five data points within the \( P/P_\theta \) range of 0.025 to 0.3 are used to analyse the BET surface area using the BET equation (Barron, 2014). External surface area, micropore volume and micropore area can be calculated using t-plot method, which is considered to be a plot of \( V_{ads} \) vs \( t \) (Storck et al., 1998, Leofanti et al., 1998). Figure 2.28 (a and b) shows an example of t-plots that can be used to predict the presence of a type of porosity in solid materials. The micropore volume is estimated form a straight line extrapolated to a positive intercept on the ordinate. For quantitative determination of micropore volume, Equation 2.22 is used, which on the choice of reference isotherm (either Halsey or Harkin-Jura, see Equation 2.23 and 2.24).

\[
V_p = \frac{(V_f/22414)M}{pl} \quad 2.22.
\]

\[
t = 3.54(5/\ln(p_o/p_s))^{1/3} \quad (\text{Hasley}) \quad 2.23
\]

\[
t = \frac{(13.99/(0.034 - \log(p_o)))^{1/2}} \quad (\text{Harkins-Jura}) \quad 2.24
\]

Where, \( V_p \) is the micropore volume and \( V_f \) is the volume of nitrogen to fill the pore.
2.8.6 Temperature Programmed Desorption (TPD)

Temperature Programmed Desorption (TPD) is a method widely used to measure the acidic properties of a catalyst (Niwa and Katada, 1997, Katada et al., 1997). Ammonia TPD in particular is used to determine the acidic strength of acid sites as well as the acid site classification (Katada and Niwa, 2004, Niwa and Katada, 2013, Zhao et al., 2008). The ammonia desorbed at a particular temperature range determines the concentration of acid sites and the temperature where maximum desorption occurs determines the acid sites strengths. Typically, NH$_3$-TPD spectra are classified into $L$-peaks representing weak and strong acid sites, respectively due to the nature of how ammonia molecule is held by the catalyst surface. L-peaks are normally found at low temperatures, 200-350°C while peaks representing strong acid sites (H-peak) are found at 350-550 and above 550°C corresponding to very strong acid sites (López et al., 2011, Zhao et al., 2008, Katada et al., 1997, Hwang and Mou, 2009). According to Yadav and Murkute (2004), desorption peaks can be divided into three acid sites based on the temperature of maximum desorption. Intermediate or medium acid sites in the range of 100 to 200°C, Strong acid sites at 200 to 400°C and very strong acid site above 400°C. However, peaks observed at low temperature below 150°C were not considered, since they are normally due to physisorbed ammonia. It was also reported that L and H acid sites may be corresponding to relative Lewis and Brønsted acid sites, respectively (López et al., 2011, Katada et al., 1997, Shi and Li, 2013).
Chapter 3 EXPERIMENTALS

3.1 Introduction

This chapter provides detailed descriptions of all the methods used in this research work. Section 3.2 describes the procurement and preparations of the catalysts and polymer samples, including the plastic waste. The Section 3.3 describes the detailed methodology of the techniques used during catalyst characterisation. Section 3.4 describes the methodology for polymer conversion using TGA and fixed-bed reactor. The Sections 3.5 and 3.6 discuss the analytical methods used for product analyses and the methodology for kinetic analysis, respectively.

3.2 Procurement and preparation of samples

3.2.1 Virgin polymer samples

Table 3.1 lists the densities and average molecular weight for the five virgin polyolefin polymers studied, namely high density polyethylene (HDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE) and polypropylene (PP). All the virgin polymer samples were purchased from Sigma-Aldrich, UK (>99%) in pellets form of about 3mm in diameter.

<table>
<thead>
<tr>
<th>Plastic sample</th>
<th>Density</th>
<th>Average MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>0.952 g/mL</td>
<td>na</td>
</tr>
<tr>
<td>LDPE</td>
<td>0.925 g/mL</td>
<td>na</td>
</tr>
<tr>
<td>LLDPE</td>
<td>0.918 g/mL</td>
<td>na</td>
</tr>
<tr>
<td>PP1</td>
<td>0.90 g/mL</td>
<td>~190,000</td>
</tr>
<tr>
<td>PP2</td>
<td>0.90 g/mL</td>
<td>~250,000</td>
</tr>
</tbody>
</table>

3.2.2 Preparations of virgin polymers

Prior to experiments, the polymers were grounded to < 0.5mm using a SM2000 Retsch Milling Machine consisting of a rotor with a 2.2 kW power drive with a speed of 1.500 min\(^{-1}\) with both stationary and moving blades. The polymer size reduction was carried out to increase the surface area of the polymer, which enhances the surface contact with the catalyst for subsequent use in the TGA and the experimental reactor.
The size reduction took place by cutting and shearing forces, where the polymer sample was pulverize between the blades and the stationary double acting cutting bars. About 100g of the polymer sample was introduced into the SM2000 Retsch Milling machine feed hoper before starting the rotor. The polymer sample was then slowly moved into the cutting chamber using screw feeder. After about two minutes in the cutting chamber, the ground polymer sample started coming through the opening of the cutting chamber. An 0.5mm sieve was attached to the discharge point of the cutting chamber. No melting or colour change was observed during the size reduction. The process continued and the sample grounded to a size below 0.5mm continued passing through the sieve and collected in the receptacle until the entire sample with not more than 0.5mm particle size was collected. The remaining sample sizes more than 0.5 mm was collected after removing the sieve and kept for the future used. About 10g was collected as left over after the 10 minutes process. The cutting chamber of the machine was then opened and cleans thoroughly using a specially designed vacuum cleaner before introduction of the next polymer sample. The shredded samples were transferred into a clean and dry container and stored for further use.

3.2.3 Plastic waste

Trident recycling company based in Glasgow, kindly provided the plastic waste for research purposes only. The plastic waste was a postconsumer waste comprising of 85-90% HDPE and about 10-15% LDPE and PP, as described by the Trident recycling company. The plastic waste was derived from crushed recycle bins, buckets, pipes, pallets sheets, trays, bottle caps and similar plastic wastes. Figure 3.1 shows the stages the company followed to obtain representative samples of the plastic waste. Trident first screened the plastic waste, where the > 5mm fraction can be sold since it meets commercial standards. The < 5mm fraction is about 10-20% of the weight and has to be landfilled due to non-compliance. About 2kg of plastic waste sample was obtained from the supplier and 23g was collected from different locations within the sample. Since it was a heterogeneous mixture of variable sizes, it was mixed thoroughly to get a homogeneous mixture. A representative sample was then sieved into four particle sizes fractions; <1mm, 1-3mm, 3-5mm and >5mm and Table 3.2 lists the mass distribution based on the particle size. This showed that portion of the plastic waste with particle size range 3-5 mm comprises of larges share of nearly 42%.
3.2.4 Potential catalyst precursors

Four different solid chemicals, namely calcium carbide (CaC\textsubscript{2}, 80% purity), molybdenum carbide (Mo\textsubscript{2}C, 99.5% purity), zirconium oxide (ZrO\textsubscript{2}, 99% purity) and sulphated zirconia (SZ), were chosen to be used as potential catalysts precursors for polymer conversion in the preliminary investigation using thermogravimetric analysis (TGA). Calcium carbide, molybdenum carbide and zirconium oxide were purchased from Sigma Aldrich, UK. A commercial catalyst sulphated zirconia (ZrO\textsubscript{2}/SO\textsubscript{4}\textsuperscript{2+} [7Mol.% SO\textsubscript{4}\textsuperscript{2-}]) was kindly provided by MEL Chemicals, UK. Molybdenum carbide
(Mo$_2$C), zirconium oxide (ZrO$_2$) and sulphated zirconia were supplied in powdered form with particle sizes ranging from 100-150µm while the calcium carbide was in the form of pebbles with a particle size of about 10mm. Due to its high risk of releasing flammable gases when exposed to moisture, the container of the CaC$_2$ sample was always kept tightly and stored in dried, cool, and well-ventilated area and away from sources of ignition before calcination.

3.2.4.1 Preparations of potential catalysts

Dry calcium carbide, which was obtained as pebbles with particle size of 10 mm, was grounded to 100-120 µm using a TEMA mill Pulveriser. About 20g of the calcium carbide was charged into the TEMA Mill chamber and pulverised to powder for a period of about 3 minutes. The powdered sample was transferred to a wire mesh sieve of 120 µm size to screen out the larger particles. The sample with large particles was transferred back to the TEMA Mill and pulverised for about 2 minutes and then sieved to get the required sizes of <120 µm. The powdered calcium carbide sample and three other potential catalyst precursors were transferred into clean and dry containers and labelled. The powdered samples, namely calcium carbide (CaC$_2$), molybdenum carbide (Mo$_2$C), zirconium oxide (ZrO$_2$) and sulphated zirconia, were then calcined at 550ºC for four hours in air using muffle furnace to activate them as highlighted in Section 2.5.6.1. However, molybdenum carbide decomposes during calcination, so it was decided to use it as obtained. The calcined catalyst precursors were stored in clean and dry containers and kept in a desiccator for future use. Prior to any analysis, the potential catalysts were dried for one hour at 200ºC to remove any moisture content and used immediately.

3.2.4.2 Preparation of hybrid catalysts

Figure 3.2 shows a sketch describing the steps followed during preparation of the hybrid catalysts from sulphated zirconia and calcium carbide and Table 3.3 gives their ratios and corresponding codes representing each of the hybrid catalysts. Seven hybrid catalysts were synthesised through mechanical mixing and calcination of sulphated zirconia (SZ) and calcium carbide (CC) at different compositional ratios described in Table 3.3. Mechanical mixing was chosen due to the hygroscopic nature of calcium carbide when in contact with water or any moisture. The first hybrid catalyst (SZ4CC1) was produce by mixing 8g of sulphated zirconia and 2g calcium carbide, i.e.
a ratio of 4:1. Sulphated zirconia (SZ) and calcium carbide (CC), which are white and dark grey in colour, respectively, were mechanically mixed thoroughly and shaken for five minutes until a homogeneous mixture with a light grey colour was obtained. The mixture was immediately transferred to an alumina crucible and placed in a muffle furnace for calcination. The calcination was carried out using a heating rate of \(20°C/min^{-1}\) in air to 550°C and kept at 550°C for four hours. The temperature 550°C was used based on the recommendation of the catalyst supplier that temperature above 600°C will result in sulphate lost. The same method was used to prepare the remaining six hybrid catalysts (SZ7CC3 to SZ1CC4) by varying the mixing ratios. The calcined hybrid catalyst were transferred into separate dry, clean and labelled containers and kept in a desiccator for future use. Prior to use, each hybrid catalyst was heated to 200°C for one hour to eliminate any possible moisture. The catalysts sulphated zirconia SZ, calcium carbide CC and the hybrid catalysts (SZ4CC1 to SZ1CC4) were then taken for characterisation.

**Figure 3.2 Steps involved in preparation of hybrid catalysts containing different weight percent composition of sulphated zirconia (SZ) and calcium carbide (CC).**
### Table 3.3 Ratios of sulphated zirconia (SZ) and calcium carbide (CC) for preparing the hybrid catalysts.

<table>
<thead>
<tr>
<th>Hybrid catalysts</th>
<th>Sulphated zirconia (wt%)</th>
<th>Calcium carbide (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SZ4CC1</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>SZ7CC3</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>SZ3CC2</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>SZ1CC1</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>SZ1CC3</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>SZ3CC7</td>
<td>30</td>
<td>70</td>
</tr>
<tr>
<td>SZ1CC4</td>
<td>20</td>
<td>80</td>
</tr>
</tbody>
</table>

### 3.3 Catalyst characterisation

This section provides the detailed description of various techniques used for characterisation of the potential catalysts prepared. The techniques involved were scanning electron microscopy (SEM/EDX), Section 3.3.1, powder X-ray diffraction (XRD), Section 3.3.2, Surface adsorption analyses (BET) Section 3.3.3, and Temperature Programmed desorption (TPD), Section 3.3.4. The catalyst characterisation was carried out to examine the morphology and elemental and oxide composition of the catalysts together with their surface and bulk properties.

#### 3.3.1 Scanning electron microscopy with energy dispersive X-ray (SEM/EDX)

In this work, the SEM/EDX analyses were carried out using an FEI QUANTA 600F, version 2.4, which was coupled to an EDAX Genesis spectrum version 5.21 EDX machine. All the catalyst samples were oven dried in air at 110°C for three hours to eliminate any possible moisture content. The powdered catalyst sample was then deposited at the edge of a conductive double-sided sticky conductive carbon pad attached to an aluminium stub. Dried air was used to blow the sample onto the surface of the tab so as to have a single layer for SEM observation. The samples prepared were labelled with sample numbers at the bottom of the stub and then stored in a desiccator. For efficient conductivity during morphological analysis, gold was sprayed onto the catalyst. However, gold was not sprayed during chemical analysis. Prior to analysis, the EDX energy level of only minor variation less than 10eV was calibrated. A 5 kV high energy electron beam generated by a tungsten filament was used for SEM images collected for morphological analysis while 15 kV was used for the EDS analyses used.
Chapter 3 – Experimental

for chemical analyses. The SEM images were collected at three different locations on the sample at a magnification of 40,000x at high vacuum mode. For chemical composition analyses, the sample was scanned at specific area on the sample of the catalyst at a magnification of 1300x at low vacuum mode and spectra were collected with the EDS. The identification of element and oxides were carried out using an Oxford-INCA EDS software package.

3.3.2 Powdered X-ray diffraction (XRD) analyses

In this research, powder X-ray diffraction (XRD) analyses were carried out using a 3kW Hiltonbrooks DG 3 model with a step motor drive operating at 40kV, 20mA using a Philips PW 1050 goniometer with a proportional detector and monochromatic Cu K$_\beta$ radiation ($\lambda = 1.54$ Å). The scanning was carried out at scan speed of $2^\circ$ (2$\theta$) min$^{-1}$ across a 5-65 degree range with a step size of 0.05$^\circ$. Prior to analysis, the powdered catalyst sample was oven dried at 110$^\circ$C overnight. The dried powdered catalyst sample of about 100µm particle sizes was transferred into a sample holder made up of a rectangular aluminium cavity, which was covered with a clean transparent glass. The sample in the sample cavity holder was gently pressed making the sample packed compactly within the cavity, then labelled with sample number and used for the XRD analysis.

3.3.3 Surface adsorption analyses

In this work, a Micrometrics Gemini VII 2390 V3.03 surface area/porosity analyser was used to analyse the textural properties of the catalyst. Total surface area (BET), external surface area, micropore volume and micropore area were all calculated using the software supplied with the Micrometrics Gemini VII 2390 V3.03 surface area/porosity analyser. The catalyst samples were initially degassed overnight at 200$^\circ$C under continues nitrogen flow. Sample evacuation was conducted at the rate of 760.9 mmHg/min and equilibrated for 5 min. The BET surface area was analysed on the adsorption isotherm using three to five data points within the $P/P_o$ range of 0.025 to 0.3. External surface area, micropore volume and micropore was calculated using method of t-plot theory, where $V_{ads}$ is plotted against t (see Figure 2.28 (a and b) in Section 2.8.5). The micropore volume was estimated from a straight line extrapolated to a positive intercept on the ordinate. The quantitative micropore volume was calculated using
Equation 2.22 in Section 2.8.5 used by choosing a reference isotherm (either Halsey or Harkin-Jura, see Equation 2.23 and 2.24).

### 3.3.4 Temperature Programmed desorption (TPD)

In this work, ammonia Temperature Programmed Desorption (TPD) measurement was carried out to determine the acidity the catalysts. The analysis was carried out using a Quantachrome ChemBET TPR/TPD instrument, which was fitted with a TPRWin version 3.5 for data analysis. Approximately 0.5g of the catalyst sample was weighed and placed into a pre-weighed quartz sample cell with internal diameter of about 4mm. Prior to the TPD analysis, the catalyst sample was degassed at 250°C using a heating rate of 20°C/min under a continuous flow (30 mL/min) of pure helium for 30 minutes. The catalyst sample was then cool down at 30°C/min to 80°C under continuous helium flow. Subsequently, the gas flow was switched to ammonia gas at a flow rate of 20 mL/min for ten minutes. The gas flow was switched back to pure helium for 30 minutes to purge the physisorbed ammonia from the catalyst sample. Finally, the TPD analysis was conducted by increasing the analysis temperature from 80°C to 600°C with a heating rate of 10°C/min until the end of the analysis. The TPD spectrum was obtained from continues monitoring the amount of ammonia in the exit gas stream by the TCD detector as the temperature was changed. The temperature of desorption peaks were used to analysed the acidic strength of the catalyst. However peaks observed at low temperature below 150°C were not considered, since they are normally due to physisorbed ammonia.

### 3.4 Polymer conversion procedures

#### 3.4.1 Thermal Gravimetric Analysis (TGA)

In this work, the TGA analysis was carried out using a Perkin-Elmer Pyris1 thermogravimetric analyser (TGA1). About 30mg of each sample was placed in a quartz crucible and the actual weight of the samples was automatically measured by the autosampler. The analysis was performed under a nitrogen gas atmosphere with flow rate of 20 ml/min to purge all the volatile materials formed during the process. The analysis temperature was set from 35 to 900°C with isothermal temperature accuracy of ±2°C at constant heating rate of 10°C/min. For testing the potential catalysts, a ratio of 1:9 catalyst to HDPE was used, where exactly 10mg catalyst and 90mg HDPE were
mixed thoroughly and about 30mg was taken for TGA analysis. This gives the composition of the catalysts in the mixture as 10wt%.

Figure 3.3 shows the PerkinElmer Pyris1 thermogravimetric analysis (TGA) instrument used for thermogravimetric analysis (TGA) of the polymer samples. Pyris1 TGA consists of four basic components, namely, (1) a highly sensitive microbalance (thermobalance), (2) a quick response furnace, (3) an autosampler and (4) computer control system for data acquisition and analysis. The thermobalance in Pyris1 TGA is design to handle a sample weight ranging from 1 to 1300 mg with precision of 0.001%.

Figure 3.3 Pyris 1 Thermogravimetric analysis (TGA) instrument by PerkinElmer.

3.4.2 Fixed-bed reactor set-up

Figure 3.4 is a schematic diagram of the fixed-bed reactor designed and used for the catalytic degradation of the HDPE polymer in this study. The reactor was made up of a horizontal stainless steel tube of 2.23cm internal diameter and 46cm length. A stationary crucible containing a mixture of equal amount by weight of HDPE and catalyst at 1:1 ratio was placed inside the reactor tube, which was connected to a programmable temperature controller furnace, which provided a uniform heat transfer across the tube. The inlet of the tube was connected to a nitrogen gas source with flow
of 30cl/min and the outlet connected to specially design cooling traps made up of three conical flasks immersed in an ice bath.

Before an experiment was conducted, the empty crucible boat, the condensers and the connector between the tube and the condensers were weighed. Equal amount (w/w) of 2g each of HDPE and a catalyst were weighed, mixed and transferred to the crucible boot, which was then placed in the reactor tube. The reactor was purged with nitrogen gas for about 20-30 minutes in order to establish an oxygen-free atmosphere throughout the reactor. The conversion was carried out using a heating rate of 20°C/min to reach temperatures between 370 and 430°C and held at that temperature for 30min. The volatile products were purged by continues nitrogen gas with flow rate of 30cl/min. The condensable liquids were collected through the cooling traps where gaseous product was passing through the exhaust trap and sample was collected using gas bags. The liquid and gaseous products were analysed offline using GC/MS and GC/FID/TCD, respectively. The percentage products yield were calculated as the mass of a particular product obtained divided by the initial mass of the polymer sample multiply by 100. Any coke residue was calculated by dividing the mass of unconverted polymer (minus the catalyst weight) by the original HDPE weight (Miskolczi et al., 2009). The nitrogen flow of 30cl/min, HDPE to polymer ratio of 1:1 and residence time of 30min were kept constant for all the HDPE conversion at different temperatures.
Figure 3.4 Schematic diagram of fixed bed reactor set-up for used in this study.
3.5 Analytical analysis

3.5.1 Elemental Analysis (EA)

Figure 3.5 shows a schematic diagram of a CHNS elemental analyser (EA) indicating its various components (Thompson, 2008). Elemental analysis (EA) is an analytical tool specifically designed to simultaneously analyse and quantify the amount of Carbon, Hydrogen, Nitrogen and sulphur (CHNS) in organic and related materials (Thompson, 2008). There are different types of elemental analysers manufactured by different companies with different configurations, which include CHN, CHNS and CNS depending on the elements it is intended to analyse. During the EA analysis the sample is combusted to about 1000°C under a constant flow of oxygen. In this process, carbon is converted to carbon IV oxide, nitrogen to nitrogen gas, hydrogen to water and sulphur to sulphur IV oxide. These gases are then separated by gas chromatogram and detected by a detector as shown on Figure 3.5.

![Figure 3.5 Schematic diagram of a CHNS Elemental Analyser (EA) (Thompson, 2008).](image)

In this work, the elemental analysis of the polymer samples was performed using a Thermo Scientific Flash Elemental Analyser (Flash EA, 1112 series) connected to a MAS 220 R autosampler controlled by an Eager Xperience software. Approximately 3mg of sample was weighed and wrapped in a tin capsule. The capsule was then introduced into the combustion chamber using an auto sampler, which also injected the appropriate amount of oxygen for the combustion. Helium gas was used as a carrier gas to purge the combusted gaseous product to the gas chromatography (GC) column. A
thermal conductivity detector (TCD) was used where the percentage weight fraction of each element was determined.

### 3.5.2 Gas Chromatography Flame Ionization Detector Thermal Conductivity Detector (GC/FID/TCD)

In this work, a Perkin Elmer Clarus 580 Gas Chromatograph (GC) which was fitted with a Flame Ionization Detector (FID) and Thermal Conductivity Detector both operating at 200°C was used. About 5 µl of gas sample was injected using helium as the carrier gas at 50mL min⁻¹ at constant pressure of 10psi. The oven temperature was set to 60°C for 13 minutes and then increased to 160°C at a heating rate of 10°C min⁻¹ and held for another 13 minutes. The flame ionisation detector (FID) detected hydrocarbon compounds, which are the main compounds in the gaseous product. The thermal conductivity detector (TCD) detected non-hydrocarbon compounds, mainly nitrogen and hydrogen. A packed column was prepared by passing by passing the carrier gas overnight through the column. The packed column injector, which consists of a septum cap, needle guide, quartz injector liner and the injector body was used with 1/8-inch inch glass packed columns.

### 3.5.3 Gas Chromatography/Mass Spectrometry (GC/MS) analysis

In this work, a Varian CP-3800 Gas Chromatography interfaced to a 1200 Quadrupole mass spectrometer (ionising energy 70 eV, source temperature 280°C) was used to analyse the hydrocarbon compositions of the liquid product. The separation was performed by a VF-1MS fused silica capillary column (50 m x 0.32 mm i.d.) coated with a BPX5 phase (0.25 µm thickness). Helium was employed as the carrier gas, and a programme temperature was set at 50°C for 2 min and then increased to 300°C using a heating rate of 5°C/min and held for 30 minutes at 300°C. Approximately 1µl of the liquid sample was dissolved in about 10µl dichloromethane (DCM). The diluted sample was transferred into a 10µl vial and placed in an auto sample tray of the GC/MS, which then injected the sample automatically. The eluted components were monitored in both full scan mode and selected ion monitoring. Each peak was identified based on the available Variant MS software library.
3.6 Kinetic analysis of TGA Data

Apparent kinetic parameters generally give information on overall reaction kinetics rather than individual reactions involved (Yang et al., 2001, Aboulkas et al., 2008a). The apparent kinetic parameters were studied in this work because thermal decomposition of plastics in complex and involves numerous parallel reactions. Thus, obtaining the kinetic parameters of each reaction is nearly impossible. Hence, the apparent kinetic parameters, which are mainly describing the general behaviour of the plastic decomposition and representing the overall weight loss behaviour of plastics as a function of temperature, are adopted in this work to compare the thermal behaviour of the polymers samples and compare the functions of the potential catalysts. The integral method which uses the Arrhenius Equation to fit the weight loss data is the most widely reported method for kinetic analysis of using TGA data obtained from solid polymer materials conversion (Liu et al., 2004, Cai et al., 2008, Conesa et al., 1996, Guo and Lua, 2001, Yang et al., 2001). In this method the rate of thermal decomposition of polymers is generally expressed as in Equation 3.1 to 3.4.

\[
r = \frac{dx}{dt} = k(1 - \alpha)^n \tag{3.1}
\]

\[
k = A e^{(-\frac{E_a}{RT})} \tag{3.2}
\]

\[
\alpha = \frac{M_o - M_i}{M_o - M_f} \tag{3.3}
\]

\[
\frac{da}{dt} = A e^{(-\frac{E_a}{RT})} (1 - \alpha)^n \tag{3.4}
\]

Where \( k \) is the rate constant as defined in the Arrhenius equation (Equation 3.2) and \( \alpha \) is the extent of conversion or weight loss at a particular temperature or time, (Equation 3.3), \( A \) is frequency or pre-exponential factor of the degradation process, \( E_a \) is the activation energy, \( R \) is the universal gas constant, \( T \) is the absolute temperature, \( M_o \) is the initial weight at the commencement of degradation, \( M_i \) is the actual weight at any particular point of interest on curve and \( M_f \) is the final weight of polymer at the end of degradation. Equation 3.5 combines Equations 3.1 and 3.2.

Since heating rate (\( \beta \)) is defined as, \( \beta = \frac{dT}{dt} \), Equation 3.4 now becomes Equation. 3.5
Chapter 3 – Experimental

\[
\frac{da}{dt} = \frac{A}{\beta} e^{-(\frac{E_a}{RT})(1 - \alpha)^n}
\]

Integrating Equation 3.5 gives simplified expression in Equation 3.6 and since polymer degradation was assume to be first order (n=1), Equation 3.7 emerged from Equation 3.6 (Guo and Lua, 2001, Cai et al., 2008, Liu et al., 2004). Since

\[
\ln \left[ \frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} \right] = \ln \left[ \frac{AR}{\beta E_a} \right] - \frac{E_a}{RT}
\]

\[
\ln \left[ -\frac{\ln(1-\alpha)}{T^2} \right] = \ln \left[ \frac{AR}{\beta E_a} \right] - \frac{E_a}{RT}
\]

Thus, plotting \( \ln \left[ -\frac{\ln(1-\alpha)}{T^2} \right] \) against \( \frac{1}{T} \) will give straight line, where \( \frac{E_a}{R} \) as slope can be used to obtain activation energy (Ea) and pre-exponential factor (A) from the intercept. In this work, the same approach was used to obtain the apparent kinetic parameters, namely activation energy, Ea and the pre-exponential factor, A by taken 1 as the order of reaction.

3.7 Loss on ignition (LoI) test

Loss on Ignition (LoI) analysis is a simple method used to determine the mass loss of an organic solid when heated under controlled conditions of temperature, time, and atmosphere. In this research work, the LoI test was conducted using the ASTM D7348 method, where about 1g of sample was placed in a crucible and heated to 750°C using a heating rate of 10°C/min in a continuous flow of air and held at 750°C for 2 hours until a complete combustion. The sample was then cooled and weight was measured immediately.
Chapter 4 – POLYMER SELECTION AND CATALYST TESTING

4.1 Introduction

This chapter presents the results of the thermogravimetric analysis (TGA) of the five virgin polymers selected for this research, namely high density polyethylene (HDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE) and polypropylene (PP1 and PP2). The most challenging polymer will be selected to be tested with the four potential catalysts, namely sulphated zirconia, zirconium oxide, molybdenum oxide and calcium carbide.

4.2 Thermogravimetric analysis (TGA) of virgin polymers

4.2.1 Comparison of virgin polymers TGA profile

Figure 4.1 compares the TGA profile of the five polyolefin polymers, namely LLDPE, HDPE, LDPE, PP1 and PP2 on their own under nitrogen flow using a linear heating rate of 10°C min⁻¹. The red cycle on Figure 4.1 indicates the initial weight loss (Tᵢ) for the polymers. Low density polyethylene (LDPE) had the lowest at 266°C followed by the polypropylenes, PP1 at 299°C, PP2 at 307°C, and high density polyethylene (HDPE) at 337°C and, lastly, linear low density polyethylene (LLDPE) at 389°C. Both LLDPE and LDPE have similar structures but differ in their degree of branching. LLDPE has a substantial number of short-chain branching, whereas LDPE has a uniform long chain branching and narrower molecular weight distribution (Kumar et al., 2011). In comparison, HDPE has a linear structure with little or no branching. These differences in terms of branching made the polymers to respond differently to thermal stress, since polymers without or with shorter branching are expected to have stronger intermolecular forces and tensile strength that make their bonds harder to break (Kumar et al., 2011, Coelho et al., 2010). For instance, the high temperatures of initial weight loss of 337°C and 389°C observed for linear low density polyethylene (LLDPE) and high density polyethylene (HDPE), respectively, might be due to their shorter branching. This compares to 266°C and 299°C for LDPE and polypropylene, respectively, which have non-linear and long-chain branching.

Figure 4.1 also indicates that all the polymers have a single step weight loss which occurs within the temperature range of 400-550°C. This corresponds to the organic matter decomposition that is believed to be due to a radical-chain mechanism as
discussed in Section 2.4.2.2 (Bockhorn et al., 1999b, Bockhorn et al., 1999a, Murata et al., 2002, Murata et al., 2009, Ceamanos et al., 2002, Shah et al., 2010a, Park et al., 1999). All the polymers had similar decomposition characteristics and appear to follow a first-order kinetics as also reported by other researchers (Conesa et al., 1996, Aboulkas et al., 2008b, Aboulkas et al., 2010, Ahmaruzzaman and Sharma, 2007, Navarro et al., 2003, Guo and Lua, 2001). Based on this finding first-order kinetics was used to analyse the kinetic parameters for polymer conversion as described in Section 3.6. The kinetics might also be affected by the temperature of initial weight loss, where early propagation might promote volatile hydrocarbons (Murata et al., 2002, Bockhorn et al., 1999b, Bockhorn et al., 1999a). As the temperature increases, the radicals from the propagation stage within the bulk polymer chain lead to a strong intermolecular hydrogen transfer and results in increased volatiles. This was observed in Figure 4.1, where there was a rapid weight loss between 400-550°C for all the polymers. This gives an opportunity to test the potential catalysts around 400°C, where the onset is.

It was further indicated in Figure 4.1 that all the polymer samples had their temperature of final weight loss above 490°C indicating that condensation reaction might not occur. The polypropylenes, PP1 and PP2 had the lowest temperature of final weight loss (T_f) of 494 and 492°C, respectively. Low density polyethylene (LDPE) followed at 501°C, while linear low density polyethylene (LLDPE) and high density polyethylene (HDPE) followed at 510°C and 511°C, respectively. This indicates that HDPE is highly resistant to thermal cracking and could be a good candidate for further studies. A constant weight residue was found for all the polymers after their T_f up to 700°C. LLDPE had the highest residue of 7wt% followed by the propylene, PP1 and high density polyethylene (HDPE) both with 4wt%, polypropylene, PP2, with 2wt% and linear density polyethylene (LDPE) with only 1wt%. A loss on ignition (LoI) test carried out on the samples at 750°C (see Section 3.7) indicated that all the virgin polymers had < 0.1wt% ash. Thus, the constant weight residue remaining at the end of the pyrolytic volatilisation process leaves behind an unconverted solid carbon residue or char. For a catalytic conversion char deposit is unwanted because it shield the catalyst active sites leading to catalyst deactivation. Hence, there is a need for a catalyst that promotes maximum conversion with virtually no char deposit. Catalyst with moderate acidity might work better, as catalysts with high acidity may cause excessive cracking and be associated with high char formation (see Section 2.5.4).
Figure 4.1 TGA curves for LDPE, LLDPE, HDPE, PP1 and PP2 degradation under N2 flow of 30ml/min using a linear heating rate of 10°C/min. The circle in red indicates where difference occurred in terms of initial temperature of degradation.
4.2.2 Comparison of the DTG curves for the five virgin polymers.

Figure 4.2 compares the DTG curves for the five polyolefin polymers, namely LLDPE, HDPE, LDPE, PP1 and PP2. The linear low density polyethylene (LLDPE) and high density polyethylene (HDPE) appeared to reach their maximum rate of degradation (T_m) at the relative high temperatures of 492 and 494°C, respectively. This compares to the T_m for low density polyethylene (LDPE) of 477°C, and the polypropylenes PP2 at 472°C and PP1 at 476°C. This was aligned with the TGA results (Section 4.2.1), where the T_i and T_f for both HDPE and LDPE were the highest followed by the polypropylenes and then LDPE. This can be used to describe the thermal stability of the polymers, the T_m is used as a common measure for the nature of their weight loss (Hujuri et al., 2008). The DTG curves indicated that all the polymers have comparably similar shapes but different thermal behaviours, which could be attributed to their chemical bonds and the differences in terms of their branching (Cai et al., 2008, Aboulkas et al., 2010, Kumar et al., 2011). The LLDPE and HDPE, whose structures have short-chain or virtually no branching, showed high thermal stability compared to PP1, PP2 and LDPE with a uniform long chain branching and narrower molecular weight distribution.
Figure 4.2 DTG traces for LDPE, LLDPE, HDPE, PP1 and PP2 thermal degradations under N₂ flow of 30cl/min using a linear heating rate of 10°C/min.
Table 4.1 summarises the thermal behaviours of all the five polymers and ranks the polymers according to their thermal stability based on temperatures of initial ($T_i$), final ($T_f$) and maximum rate of degradation ($T_m$). In terms of temperature of initial weight loss ($T_i$), linear low density (LDPE) had the lowest temperature (266°C) followed by the two propylenes, P1 and P2 with 299 and 307°C, respectively. HDPE and LLDPE have the highest temperatures of 337 and 389°C, respectively. Propylenes, P1 and P2 and LDPE had the lowest $T_m$ temperatures of 476, 472 and 477°C with highest weight loss of 72, 68 and 67wt%, respectively. This is compared to HDPE and LLDPE, which had $T_m$ of 494 and 492°C with a weight loss of 65 and 63wt%, respectively. For the temperature of final weight loss ($T_f$) and char deposit, PP1 and PP2 had the lowest temperature of 494 and 492°C with char deposits of 4 and 2wt%, respectively. LDPE followed with 501°C and char deposit of 1wt%. Again, HDPE and LLDPE have the highest $T_f$ of 511 and 510°C with char deposits of 4 and 7wt%, respectively. This indicates that LLDPE and HDPE are more stable to thermal stress than the rest of the polymers.

The rank of polymers in order of their overall thermal stability was LDPE < PP1 < PP2 < HDPE < LLDPE as evidence by their $T_i$. But in terms of $T_m$ and $T_f$ their thermal stability appeared to be similar. The thermal instability of the polypropylenes, P1 and P2, and LDPE, which appeared low compared to LLDPE and HDPE is again attributed to the presence of branches in their structures, which make the attack on their bonds easier and, hence, results in faster degradation (Gobin and Manos, 2004, Kumar et al., 2011). In the same way, the high thermal stability shown by both HDPE and LLDPE was again attributed to the presence of fewer branches in their structures, which makes attacks on their bonds difficult and thus harder to degrade. The results further suggest that the molecular weight differences of the polymers might not play a significant role during polymer degradation. This is evident for PP1 and PP2, which have different average molecular weight of 190,000 and 250,000, respectively, but have similar, initial ($T_i$) and final ($T_f$) temperatures of weight loss as well as temperatures of maximum weight loss ($T_m$).
### Table 4.1 Comparison of thermal degradations of LDPE, LLDPE, HDPE, PP1 and PP2 and ranking in order of thermal stability based on temperatures of initial weight loss ($T_i$), maximum weight loss ($T_m$) and final weight loss ($T_f$) carried out under $N_2$ flow of 30cl/min using a linear heating rate of 10°C/min.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_i$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>%W loss @ $T_m$</th>
<th>$T_f$ (°C)</th>
<th>Char remaining (wt %) @$T_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE</td>
<td>266</td>
<td>477</td>
<td>67</td>
<td>501</td>
<td>&lt; 1.0</td>
</tr>
<tr>
<td>PP1</td>
<td>299</td>
<td>476</td>
<td>72</td>
<td>494</td>
<td>4.0</td>
</tr>
<tr>
<td>PP2</td>
<td>307</td>
<td>472</td>
<td>68</td>
<td>492</td>
<td>2.0</td>
</tr>
<tr>
<td>HDPE</td>
<td>337</td>
<td>494</td>
<td>65</td>
<td>511</td>
<td>4.0</td>
</tr>
<tr>
<td>LLDPE</td>
<td>389</td>
<td>492</td>
<td>63</td>
<td>510</td>
<td>7.0</td>
</tr>
</tbody>
</table>

### 4.3 Kinetic study of the polymer samples using TGA data

A kinetic study was carried out on the TGA data according to Section 3.6 to investigate the rate at which each polymer degrades within a particular temperature range. This will be used to further assess and compare the thermal stability of the individual polymer samples. The study of apparent kinetic parameters here is only to be use for purpose of understanding the thermal stability of potential polymers, where particularly activation energy, will be used to compare the activities of the potential catalysts. The apparent kinetic parameters to be analysed were activation energy ($E_a$), and pre-exponential factors ($A$). Also, the kinetic data, Comparison of apparent kinetic energy and frequency factors for the polymer samples.

Table 4.2 compares the apparent kinetic parameters for the thermal degradation of the HDPE, LLDPE, LDPE and propylenes (PP1 and PP2) polymers. The apparent kinetic parameters were analyses at a temperature range within the temperatures of initial weight loss and maximum degradation of each polymer as shown in Table 4.2. Linear low density polyethylene (LLDPE) as expected had the highest activation energy and frequency factor of 315 kJ/mole and 2.94E+19s$^{-1}$, respectively. This is followed by the HDPE with activation energy of 216 kJ/mole and frequency factor of 7.19E+11s$^{-1}$. Polypropylenes (PP1 and PP2) were then followed with activation energies of 100 and 113 kJ/mole and frequency factors of 6.07E+06s$^{-1}$ and 7.81E+04s$^{-1}$, respectively. Low density polyethylene (LDPE) had the lowest activation energy of 78kJ/mole and lowest frequency factor of 1.49E+04s$^{-1}$. This showed that for effective degradation of LLDPE and HDPE, energy barriers of 315kJ/mole and 216kJ/mole must be to be overcome by...
collision of molecule at a rate of 2.94E+19s\(^{-1}\) and 7.19E+11s\(^{-1}\), respectively. This showed that the energy barrier required to overcome for LLDPE is nearly two times that of HDPE, three times that of PPs and four times LDPE. Therefore, the potential polymers can be arranged in order of their thermal stability in the following sequence, LLDPE > HDPE > PP2 ≥ PP > LDPE. This is in agreement with the results already highlighted in Section 4.2, where LLDPE followed HDPE appeared to have the highest onset temperature than the rest of the polymers, which is a feature attributed to the presence of no or few branches in their structures.

### Table 4.2 Comparison of the apparent kinetic parameters from TGA data for LDPE, LLDPE, HDPE, PP1 and PP2 carried out under \(N_2\) flow of 30ml/ min using a linear heating rate of 10\(^o\)C/min.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation energy, (E_a) (kJ/mole)</th>
<th>Frequency Factor, (A) (s(^{-1}))</th>
<th>Correlation Coefficient ((R^2))</th>
<th>Temperature Range ((^o)C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLDPE</td>
<td>315</td>
<td>2.94E+19</td>
<td>0.999</td>
<td>400-500</td>
</tr>
<tr>
<td>HDPE</td>
<td>216</td>
<td>7.19E+11</td>
<td>0.994</td>
<td>350-500</td>
</tr>
<tr>
<td>PP1</td>
<td>100</td>
<td>6.07E+06</td>
<td>0.998</td>
<td>300-450</td>
</tr>
<tr>
<td>PP2</td>
<td>113</td>
<td>7.81E+04</td>
<td>0.998</td>
<td>300-450</td>
</tr>
<tr>
<td>LDPE</td>
<td>78</td>
<td>1.49E+04</td>
<td>0.999</td>
<td>300-450</td>
</tr>
</tbody>
</table>

4.3.1 **Comparison of apparent kinetic data obtained from this work with literature.**

The kinetics of the thermal degradation of polyolefin polymers has been widely researched and different methods have been established (see Section 3.6). Table 4.3 compares the apparent activation energy of the polymers tested in this work using integral method with that reported in published works that used different methods. The activation energy of HDPE in this work is the same as reported by Ceamanos, et al. (2002) and close to that of what Yang et al. (2001) and Aboulkas et al. (2010) reported using curve fitting and Mean activation methods, respectively. Similarly, the activation energies of PP1 and PP2 in this work is virtutally the same as what Yang et al. (2001) using a curve fitting method reported. Also, all the the literature reported the activation energy of the LDPE to be less that that HDPE and LLDPE. However, the activation energies of some polymers, particularly LDPE, were relatively lower than those reported in literature. The reason for the wide variation may be linked to the fact that the activation energy for this work was calculated only at one point mainly where
maximum degradation occurred, and this results in limitation for this (Park et al., 2000). However, the method could still be used for the bases of comparison among the polymers and also to study the activities of the potential catalysts towards polymer conversion by comparing their activation energy.

Table 4.3 Comparison of apparent activation energies from literature with this work obtained from TGA data of LDPE, LLDPE, HDPE, PP1 and PP2 carried out under N2 flow of 30ml/min using linear heating rate of 10°C/min.

<table>
<thead>
<tr>
<th>Polymer samples</th>
<th>This work φ</th>
<th>(Ceamanos et al., 2002)ψ</th>
<th>(Yang et al., 2001)§</th>
<th>(Aboulkas et al., 2010)*</th>
<th>(Park et al., 2000)¥</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLDPE</td>
<td>315</td>
<td>NR</td>
<td>NR</td>
<td>227</td>
<td></td>
</tr>
<tr>
<td>HDPE</td>
<td>216</td>
<td>171</td>
<td>240</td>
<td>238±5</td>
<td>338</td>
</tr>
<tr>
<td>PP1</td>
<td>100</td>
<td>171</td>
<td>126</td>
<td>179±6</td>
<td>NR</td>
</tr>
<tr>
<td>PP2</td>
<td>113</td>
<td>NR</td>
<td>222</td>
<td>215±3</td>
<td>196</td>
</tr>
<tr>
<td>LDPE</td>
<td>78</td>
<td>NR</td>
<td>222</td>
<td>215±3</td>
<td>196</td>
</tr>
</tbody>
</table>

φIntegral method
ψDifferential and isconversional method at 12°C/min heating rate covering temperature up to ≤ 430°C
§Curve fitting method
*Mean activation energy calculated at different conversion level from 0.1-0.9 using Friedman method.
¥Dynamic Model method
NR: Not reported

Based on the data in Table 4.1 and the kinetic results in Table 4.2 and Table 4.3, where LLDPE and HDPE appeared the most thermally stable polymers, HDPE was selected to be used throughout this research work. Although, LLDPE showed the highest thermal stability, there is a practical reason for selecting HDPE for further studies apart from its resilience towards thermal degradation. The HDPE polymer is the world’s third largest plastic material used for numerous applications, including packaging (carrier bags, milk and water jugs), automobile (vehicle fuel tanks) and construction (plastic tents, storage sheds). Also, due to its strong resistance to many chemicals, HDPE also is widely used in making chemical containers, chemical-resistance piping system, heat-resistant fireworks display mortars, geothermal heat transfer piping system, natural gas distribution pipe systems and water pipes (Kumar et al., 2011). Hence, HDPE plastic waste accounts for about 60-70% of the world plastic wastes (Kaminsky et al., 2004, Lin and Yen, 2005). So, catalytic recycling of the waste from this type of polymer back to chemicals would make a significant contribution to waste management of plastics. HDPE will first be used to test the potential catalysts for
lowering the cracking temperatures, particularly the temperatures of initial and maximum weight losses using TGA.

### 4.4 Thermogravimetric analysis (TGA) of HDPE with potential catalysts

This section presents results of testing the catalytic activities of the potential catalysts on HDPE conversion using TGA. The results in the presence of these catalysts were compared with that of HDPE on its own to establish which of the potential catalyst show primarily catalytic activity towards HDPE conversion.

#### 4.4.1 Comparison of the TGA profiles of HDPE alone and HDPE mixed with potential catalysts

Figure 4.3 compares the thermal degradation profiles of HDPE on its own and HDPE mixed with 10wt% each of the four potential catalysts, namely sulphated zirconia (SZ), zirconium oxide (ZO), molybdenum carbide (MC) and calcium carbide (CC). The mixing was explained in Section 3.4.1. Since no weight loss was observed for the potential catalysts < 600°C, only the polymer fraction is shown in Figure 4.3 for clarity. The result suggests that the presence of the potential catalysts each had significant impact on the HDPE conversions when compared with HDPE alone. As can be seen in Figure 4.3, the presence of 10wt% sulphated zirconia (SZ) has significantly reduced the temperatures of initial weight loss ($T_i$) to 187°C and that of the final weight loss shifted to 477°C with a 5wt% char. In the presence of 10wt% calcined CC, the temperatures of initial ($T_i$) and final ($T_f$) weight loss were reduced to 292°C and 524°C, respectively, with only 2wt% char. A shift was observed, as shown by the blue arrows in Figure 4.3, indicating that the calcined CC lowered the temperature of maximum weight loss ($T_m$). In the presence of 10wt% each of zirconium oxide and molybdenum carbide, the temperatures of initial ($T_i$) and final weight loss were at 359°C, 539°C, and 371, 542°C, respectively. This showed that the presence of zirconium oxide and molybdenum carbide have only resulted in a negative impact on HDPE degradation, where all the temperatures of weight loss were rather higher than that of HDPE only as shown by the red arrow in Figure 4.3.

Overall, the results here indicated that the SZ has the most significant catalytic activity as evidence by its excellent performance in reducing the $T_i$, and $T_f$ compared to HDPE alone but increased the char yield. Calcined CC also appeared to have
appreciable catalytic activity, where it reduces the temperature of initial weight loss and more significantly lowered the char content to only 2wt%. This shows that out of the four potential catalysts tested, only the SZ and the calcined CC showed catalytic activities towards HDPE degradations.
Figure 4.3 Comparison of the TGA curves for HDPE alone and mixed with 10wt% each of the potential catalysts, namely calcium carbide (CC), molybdenum carbide (MC), zirconium oxide (ZO), and sulphated zirconia (SZ) under 30cl/min nitrogen flow using heating rate of 10°C/min.
4.4.2 Comparison of the DTG traces for the thermal degradation of HDPE alone and with 10wt% of each of potential catalyst

Figure 4.4 compares the DTG curves for the thermal degradation of HDPE alone and HDPE mixed with 10wt% each of the four potential catalysts, namely sulphated zirconia (SZ), zirconium oxide (ZO), molybdenum carbide (MC) and calcium carbide (CC). Sulphated zirconia (SZ) had the lowest temperature of maximum weight loss of 422°C followed by calcined CC at 451°C as compared to 494°C for HDPE alone. Although the SZ showed the most excellent activity, the ability of calcined CC to reduce the temperature of maximum degradation is also encouraging and showed that it may be an excellent catalyst if studied further. Molybdenum carbide and zirconium oxide appeared to have the highest temperature of maximum weight loss at 502°C and 510°C, respectively, which are even higher than that of HDPE alone with 494°C. This showed that MC and ZO do not show the desired catalytic activity needed for HDPE conversion and was not taken further.
Figure 4.4 Comparison of the DTG traces for HDPE polymer alone and mixed with 10wt% of each of the potential catalysts, calcium carbide (CC), molybdenum carbide (MC), zirconium oxide (ZO), and sulphated zirconia (SZ) potential catalysts under nitrogen flow of 30ml/min using heating rate of 10°C/min.
4.4.3 Ranking of potential catalysts based on their TGA performance towards HDPE degradation

Table 4.4 summarises the result of the HDPE degradation in the presence of 10wt% each of the potential catalysts, namely calcium carbide (CC), molybdenum carbide (MC), zirconium oxide (ZO) and sulphated zirconia (SZ). The potential catalysts were ranked based on their catalytic activities according to their temperature of initial weight loss. Both the SZ and the calcined CC have significantly reduced the temperatures of initial weight loss as well as temperatures of maximum and final weight loss to below that of HDPE alone. For instance, in the presence of sulphated zirconia, all the temperatures of initial (187°C), maximum (419°C) and final (477°C) weight losses were less than those of HDPE alone. Calcined CC followed closely by reducing the temperatures of initial (292°C) and maximum (475°C) weight loss, even though the temperature of the final (524°C) increased slightly. Calcined CC however, reduced the char deposit to 2wt% compared to 4 and 5wt% for HDPE alone and in the presence of sulphated zirconia, respectively. Molybdenum carbide and zirconium oxide on the other hand showed poor catalytic activities by somehow increasing all the temperatures of initial, final and maximum weight loss to even above that of HDPE alone as evidenced in Figures 4.3 and 4.4. In term of their catalytic activities on HDPE degradation, the potential catalysts tested were ranked is in the following sequence SZ > CC > ZO > MC. This indicates that sulphated zirconia showed the best catalytic activity followed by the calcined CC while molybdenum carbide and zirconium oxide may not have any catalytic potential towards HDPE conversion and hence were not pursued further. Hence, only the SZ and the calcined CC were used for further research toward HDPE conversion.

Table 4.4 Ranking of the thermal degradations of HDPE by the potential catalysts

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_i$(°C)</th>
<th>$T_m$(°C)</th>
<th>$T_f$(°C)</th>
<th>Char (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE+SZ</td>
<td>187</td>
<td>419</td>
<td>477</td>
<td>5.0</td>
</tr>
<tr>
<td>HDPE+CC</td>
<td>292</td>
<td>475</td>
<td>524</td>
<td>2.0</td>
</tr>
<tr>
<td>HDPE Only</td>
<td>337</td>
<td>494</td>
<td>516</td>
<td>4.0</td>
</tr>
<tr>
<td>HDPE+ZO</td>
<td>359</td>
<td>502</td>
<td>539</td>
<td>2.0</td>
</tr>
<tr>
<td>HDPE+MC</td>
<td>371</td>
<td>510</td>
<td>542</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Sulphated zirconia catalyst, which has been widely reported as an excellent catalyst for many processes, has not been reported for plastic waste conversion based on
the literature surveyed (Yadav and Nair, 1999, Clark, 2002, Arata et al., 2003, Hino et al., 2006, Ahmed et al., 2008). However, nickel, platinum and palladium doped versions have been reported for catalytic hydroisomerisation and hydrocracking of a long-chain alkanes and polyolefins (Venkatesh et al., 1996, Larsen et al., 1995, Wen et al., 1990). Sulphated zirconia is a solid acid catalyst and, depending on the method of preparation, it has been reported to have a Hammett acid strength of no less than \( H_0 = -16.1 \) when calcined between 500-600°C, (see Section 2.5.6) (Arata et al., 2003, Yadav and Nair, 1999). It is also highly mesoporous and has high thermal stability (Clark, 2002). These properties make it an excellent cracking catalyst, but may make it susceptible to excessive cracking and secondary reaction that will promote high gaseous product and formation of aromatic compounds and, consequently char during the polymer conversion. This has been suggested here from the 5wt% char in the presence of sulphated zirconia at temperature of final weight loss \( T_f \) of 445°C compared to 4wt% for HDPE alone. This shows that sulphated zirconia could be a good catalyst in terms of initiating the polymer cracking at lower temperature as seen here, but may promote other reactions that lead to some unwanted products at high temperature. Calcined CC also showed excellent activities by lowering the temperatures of initial and maximum weight loss. It also shows no evidence of promoting other reactions by reducing the char to only 2wt%. Moreover, it has been reported in the literature as an active catalyst for plastic polymer degradation with high selectivity to aliphatic components, but only showed a low conversion at low temperatures (Shah et al., 2010a).

Two main observations were made from Table 4.4. Sulphated zirconia SZ showed excellent activity on HDPE degradation at much lower temperature possibly due its highly acidic properties, which perhaps resulted in high char. In comparison, the calcined CC showed lower activity towards HDPE degradation than sulphated zirconia, but much higher than that for HDPE alone and produced much lower char probably due to its low acidity. Thus, if the two potential catalysts are mixed together, a new hybrid catalyst could emerge with new excellent catalytic activity due to the synergetic effect of both catalysts. The new catalytic properties could include moderate acidity, which may reduce the excessive cracking and char yield and promote high liquid yield. This could improve the HDPE conversion at low temperature with high liquid yield and promotes selectivity towards valuable hydrocarbon compounds. Therefore, it is suggested that the SZ and the calcined CC as well as the new suggested hybrid catalyst be tested for HDPE conversion and compare their catalytic activities.
4.5 Testing the catalytic activity of the hybrid catalyst

4.5.1 Comparison of the TGA profile of HDPE alone and HDPE mixed with 10wt% of the sulphated zirconia SZ, the calcined CC and the hybrid catalyst SZ1CC

Figure 4.5 compares the thermal degradation (TGA) profiles of HDPE alone and HDPE mixed with 10wt% each of the sulphated zirconia SZ, the calcined CC and hybrid catalyst SZ1CC1. The detailed methodology for preparing the hybrid catalyst is given in Section 3.2.4.2. In the presence of the hybrid catalyst SZ1CC1, the temperature of initial weight loss was reduced to 220°C compared to 337°C for HDPE alone and 292°C in presence of only the calcined CC, but was still slightly higher than 187°C for sulphated zirconia SZ only. The temperature of final weight loss was equally reduced to 469°C compared to 516, 524 and 477°C for HDPE only, in the presence of calcined CC and the SZ only, respectively. The new hybrid catalyst showed excellent activity by reducing the char deposit to less than 0.5wt% compared to 4, 5 and 2wt% for HDPE only in the presence of SZ and the calcined CC, respectively. This indicates that mixing sulphated zirconia and calcium carbide had resulted in a new catalyst with new improved properties. The addition of calcium carbide has significantly modified the SZ by moderating some of its properties that reduced the char as evidence with virtually no char produced by the hybrid catalyst SZ1CC1.
Figure 4.5 TGA curves comparing the degradation of HDPE alone with HDPE mixed with 10wt% each of the SZ, the calcined CC and the hybrid catalyst SZ1CC1 using a heating rate of 10°/min under nitrogen flow of 30cl/min.
4.5.2 Comparison of the DTG traces for HDPE only and HDPE alone mixed with 10wt% each of the SZ, the calcined CC and the hybrid catalyst SZ1CC1

Figure 4.6 compares the DTG curves for the thermal degradation of HDPE alone and thermocatalytic degradation of HDPE mixed with 10wt% of the sulphated zirconia SZ, the calcined CC and the hybrid catalyst SZ1CC1. In the presence of the hybrid catalyst SZ1CC1, the temperature of maximum weight loss was 451°C, which is less than that of HDPE alone (494°C) and the calcined CC (475°C) but still higher than that of the SZ (422°C). The combined TGA and DTG results indicated that the mixture of sulphated zirconia and calcium carbide has some synergetic effects that resulted in a great enhanced activity. For instance, the new hybrid catalyst SZ1CC1 showed better catalytic activity than that of the calcined CC by lowering all the three temperatures of weight loss. It also showed some improvements over that of sulphated zirconia alone by lowering the temperature of final weight loss and char deposit to less than 1wt%. Possibly the presence of the calcined CC in the mixture has modified the acidic strength and some textural properties of the hybrid catalyst and halted excessive cracking that results in high char as observed from the TGA results in Figure 4.3. The new properties of the new hybrid catalyst could promote HDPE conversion with high liquid yield and tailor the selectivity towards more aliphatic hydrocarbons rather than aromatic. A catalyst with a moderate acidity may solve the problem of excessive cracking at high temperatures, which promotes high gas yield as well lead to the formations of aromatic hydrocarbons (Saha et al., 2008).
Figure 4.6 DTG traces comparing the degradation of HDPE only of HDPE alone with HDPE mixed with 10wt% each of the sulphated zirconia SZ, the calcined CC and the hybrid catalyst SZ1CC1 using a heating rate of 10°C/min under nitrogen flow of 30cl/min.
4.5.3   **Ranking of degradation of HDPE alone and HDPE mixed with 10wt% of the calcined CC, the sulphated zirconia SZ and the hybrid catalyst SZ1CC1**

Table 4.5 compares the overall degradation of HDPE alone and HDPE mixed with 10wt% each of the calcined CC, the SZ and the hybrid catalyst SZ1CC1. The catalysts were ranked in order of their activities towards reducing the char deposits. The hybrid catalyst SZ1CC1 showed an excellent activity with less than 1wt% char at 469°C, a temperature lower than achieved by all other potential catalysts tested here. This was followed by calcined CC with 2wt% char and then HDPE only, which had 4wt% char. The sulphated zirconia SZ appeared to have promoted the highest char deposit of 5wt%, probably due its high acidity. The ranking of the catalysts tested, which is based on their ability to reduce char deposit, was in the following sequence hybrid catalyst SZ1CC1 > calcined CC > HDPE alone > SZ. The SZ appeared to have least activity in terms of char deposit despite having the lowest temperature of weight loss. This showed that mixing of calcium carbide with sulphated zirconia has resulted in a new potential catalyst that has combined properties of both, i.e. high conversion at low temperature with low coke yield. The addition of calcium carbide has greatly reduced the tendency of the new catalyst to coke as evidence with virtually no char.

<table>
<thead>
<tr>
<th>Samples</th>
<th>T&lt;sub&gt;i&lt;/sub&gt; (°C)</th>
<th>T&lt;sub&gt;m&lt;/sub&gt; (°C)</th>
<th>T&lt;sub&gt;f&lt;/sub&gt; (°C)</th>
<th>Char wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE+SZ1CC1</td>
<td>220</td>
<td>451</td>
<td>469</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>HDPE+CC</td>
<td>292</td>
<td>475</td>
<td>524</td>
<td>2.0</td>
</tr>
<tr>
<td>HDPE Only</td>
<td>337</td>
<td>494</td>
<td>516</td>
<td>4.0</td>
</tr>
<tr>
<td>HDPE+SZ</td>
<td>187</td>
<td>422</td>
<td>477</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Overall, its evidence that the SZ showed the best catalytic activities based on the temperatures of initial weight loss, but in terms of promoting low char deposits the hybrid catalyst SZ1CC1 showed the most promising activity followed by the calcined CC. The apparent kinetic data for HDPE alone and that in the presence of these catalysts could shed further information on their catalytic activities towards HDPE conversion.
4.5.4 **Comparison of apparent activation energy of thermal degradations of HDPE alone and HDPE mixed with 10wt% SZ, calcined CC and the hybrid catalyst SZ1CC1**

Table 4.6 compares the apparent activation energy ($E_a$) and frequency factor ($A$) derived from the TGA data for HDPE alone and HDPE mixed with 10wt% each of the SZ, the calcined CC and the hybrid catalyst SZ1CC1. The kinetic data was obtained within the temperature range where maximum weight loss occurred. Apparent activation energy for HDPE alone was 181 kJ/mol, a value that is close to what have been reported elsewhere using different methods as shown in Section 4.3.1 (Yang et al., 2001, Aboulkas et al., 2010). The detailed of the method used to calculate the kinetic data is given in Section 3.6. In the presence of 10wt% each of the sulphated zirconia SZ, the hybrid catalyst SZ1CC1 and the calcined CC, the activation energies significantly reduced to 104, 131 and 135 kJ/mole, respectively. The frequency factor ($A$) decreased significantly from 7.19E+11 for HDPE alone to 1.42E+05, 3.48E+07 and 3.08E+07 in the presence of SZ, calcined CC and the hybrid catalyst SZ1CC1, respectively. This indicates that the SZ, calcined CC and hybrid catalyst SZ1CC1 all enhanced the HDPE degradation rate when compared to HDPE only. However, the SZ showed the most significant impact on the HDPE degradation rate, where the activation energy reduced by more than 60%. The CC and the hybrid catalyst showed low impact, where activation energy only reduced by about 40%.

Table 4.6 **Comparison of the apparent kinetic energy from TGA data of HDPE alone and mixed with 10wt% SZ, CC and the hybrid catalyst SZ1CC1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation Energy, $E_a$ (kJmol$^{-1}$)</th>
<th>Frequency Factor, $A$ (s$^{-1}$)</th>
<th>Correlation Coefficient ($R^2$)</th>
<th>Temperature Range ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE only</td>
<td>216</td>
<td>7.19E+11</td>
<td>0.993</td>
<td>350-450</td>
</tr>
<tr>
<td>HDPE + SZ</td>
<td>104</td>
<td>1.42E+05</td>
<td>0.999</td>
<td>300-430</td>
</tr>
<tr>
<td>HDPE + CC</td>
<td>135</td>
<td>3.48E+07</td>
<td>0.997</td>
<td>300-430</td>
</tr>
<tr>
<td>HDPE + SZ1CC1</td>
<td>131</td>
<td>3.08E+07</td>
<td>0.999</td>
<td>300-430</td>
</tr>
</tbody>
</table>

4.5.5 **Summary of the polymer selection and catalysts testing**

Five virgin polymers, namely high density polyethylene (HDPE), linear low density polyethylene (LLDPE), low density polyethylene (LDPE) and two polypropylene (PP1 and PP2), were preliminary investigated using thermogravimetric
analysis (TGA) to analyse and compare their thermal behaviour. The results of the TGA analysis showed that all the five polymers had similar thermal decomposition behaviour. However, LLDPE and HDPE showed more resistance to degradation with higher temperatures of initial, final and maximum of degradation. Further, the TGA data was used and calculated the apparent kinetic data, namely activation energy (Ea) and frequency factor (A). Equally, HDPE and LLDPE appeared to have higher activation energies and lower frequency factors, which still indicated their high thermal stability compared to the rest of the polymer samples. In view of this, HDPE was chosen for detailed investigation not only for its high resistance to degradation and high thermal stability, but also because it constitutes 60-70% of all plastic waste generated.

HDPE was thermocatalytically degraded using TGA in the presence of 10wt% of each potential catalyst, namely sulphated zirconia (SZ), molybdenum carbide (MC), calcium carbide (CC) and zirconium oxide (ZO). This was to ascertain the catalytic activities of the potential catalysts towards HDPE degradation. The TGA results indicated that only the SZ and the calcined CC showed promising activity towards HDPE conversion. The SZ shifted significantly the onset of HDPE degradation to a much lower temperature than of HDPE alone or with the calcined CC. However, the SZ had a high char deposit of 5wt% compared to only 2wt% for the calcined SZ. Similarly, the kinetic parameters calculated from the TGA data showed that the SZ and the calcined CC had significantly reduced activation energy compared to the rest of the potential catalysts and HDPE alone. Thus, the two catalysts were chosen to further study the HDPE degradation. Equally, to reduce the char formation observed in the presence of the SZ, the two catalysts, the SZ and the calcined CC were mixed at equal weight by weight (w/w) and calcined at 550°C to generate a hybrid catalyst SZ1CC1. The hybrid catalyst SZ1CC1 was tested for HDPE degradation and the result obtained showed the most promising activity, as it reduced the char to less than 1.0wt% and the conversion was achieved at temperature much lower than that of the HDPE alone or in the presence of the calcined CC only. The kinetic energy was also less compared to HDPE alone and in the presence of the CC alone.

Based on the TGA results in Table 4.5 and the kinetic data in Table 4.6, the SZ, calcined CC and the hybrid catalyst SZ1CC1 were chosen for HDPE conversion using a fixed-bed reactor to further understand the catalytic performance of each catalyst. However, to better understand the catalytic behaviour of the hybrid catalyst a
comprehensive characterisation studies about the interaction between the SZ and CC during calcination was suggested.
Chapter 5 - CATALYSTS CHARACTERISATIONS

5.1 Introduction

This chapter presents the results of characterisation of the sulphated zirconia SZ, the calcined CC and the seven hybrid catalysts (SZ4CC1 to SZ1CC4) from the mixtures of the SZ and the CC. Physicochemical, bulk and surface properties of the potential catalysts were examined using different analytical techniques, namely scanning electron microscopy/Energy-dispersive X-ray spectroscopy (SEM/EDX), powder X-ray diffraction (XRD), NH$_3$-temperature programmed desorption, chemisorption and N$_2$-adsorption isotherms. The mixtures were characterised to study the impact of the CC addition on the SZ, such as acidity and textural properties, as discussed in Sections 2.5.4 and 2.5.5. It was established in Chapter 4 that when SZ and CC were calcined together, coking was reduced during HDPE conversion which may be related to the resultant acidity of the hybrid catalyst (Akpanudoh et al., 2005). Thus, analysing the detailed characterisation of this range of hybrid catalysts could explain which components make the positive impacts. This will help in understanding the best mixing ratio that will promote the plastic waste conversion towards high liquid yield and promote low-aromatic product.

5.2 Bulk elemental and oxide compositions

5.2.1 Comparison of bulk elemental compositions of calcium, carbon and calcium to carbon ratio of CC and the hybrid catalysts SZ4CC1 to SZ1CC4

Figure 5.1 compares the overall bulk elemental composition of calcium, carbon, sulphur, oxygen and zirconium contents of the SZ, CC and the seven hybrid catalysts SZ4CC1 to SZ1CC4. The results here are from a single point analysis and may not be representative of the whole sample, since the SZ and CC were only mixed mechanically and may not be 100% homogeneous. The amount of elemental calcium and carbon in SZ was < 0.1At% (below detection limit) and also zirconium and sulphur on CC were all < 0.1At% and are presented as zero.

In terms of elemental calcium, after addition of 20 and 30wt% CC to SZ (SZ4CC1 and SZ7CC3), the elemental calcium was 11.2At% and 15.0At%. With increasing CC additions to 40wt% (SZ3CC2), the elemental calcium decreased to 13.6At%, which then increased to 19.0At% and remains somewhat constant within the
confidence range of ±2At% after increasing the CC addition to 50wt% to 80wt% (SZ1CC1 to SZ1CC4). The CC on its own had the elemental calcium of 22.6At%. For elemental carbon, after additions of 20 and 30wt% CC to SZ the hybrid catalysts SZ4CC1 and SZ7CC3 had 14.5 and 14.8At%, respectively. With further increase in CC additions to 40 to 70wt% (SZ2CC3 to SZ3CC7) the elemental carbon increases to 19.7At% and remained constant within the confidence limit of ±1At%. But after increasing the CC addition to 80wt% (SZ1CC4) the elemental carbon significantly decreased to 15.7At% and a calcined CC on its own had 19At% elemental carbon. Overall, this showed that the composition of elemental carbon reached its maximum when CC was between 40 and 70wt%, where it remains nearly constant within confidence range of ±1At% and this also a range where calcium reached its maximum. Overall, both calcium and carbon do not show any consistent changes with increasing CC addition. For zirconium and sulphur, the pure SZ on its own had 26.1 and 1.7At%, respectively. After the additions of 20wt% (SZ4CC1), the zirconium content reduced sharply to 10.6At% while the sulphur content increased to 3.0At%. With further increase in the CC addition to 30 and 40wt%) both the zirconium and sulphur content decreased to 8.0 and 6.2At% and 2.4 and 1.6At%, respectively. However, when the CC addition was increased to 50 and 60wt%, the zirconium content slightly increased to 6.5% and decreased 3.7At% while the sulphur content decreased to 1.1At% and remained unchanged. With subsequent CC additions to 70 and 80wt%, both zirconium and sulphur decrease to 2.3 and 1.7At% and 0.8 and 0.7At%, respectively, and calcined CC on its own had no zirconium or sulphur. Overall, the composition of zirconium and sulphur content decreased with increasing the CC addition except for hybrid catalysts SZ1CC1 and SZ1CC4, where zirconium increased slightly to 6.5At% and sulphur to 3.0At%, respectively. For elemental oxygen the pure SZ had 72At%, which was the highest as expected. After the addition of 20, 30 and 40wt% CC (SZ4CC1 to SZ3CC2), the oxygen decreased to 60.7, 60.0 and 59.0At%, respectively, which remain within the confidence range of ±1At% as shown by the green line in Figure 5.1. It is also interesting to note that calcined CC on its own had 58 At% elemental oxygen, which indicates that significant surface oxidation have taken place during calcination. However, when the composition of both SZ and CC were equal (SZ1CC1), the elemental oxygen was at its lowest of 52At%. The changes observed in terms of elemental oxygen in the catalysts after the CC addition indicates the possibility of some chemical interactions among different compounds in the CC and SZ mixture during
calcination. These multiple reactions might have resulted in modified properties in the hybrid catalysts especially towards interaction with sulphated zirconia. Based on this the amount of possible metallic oxides obtained from EDS were compared in the next Section 5.2.2.

![Comparison of bulk elemental compositions of calcium, carbon, sulphur, oxygen and zirconium content of the SZ, CC and hybrid catalysts SZ4CC1 to SZ1CC4.](image)

**Figure 5.1 Comparison of bulk elemental compositions of calcium, carbon, sulphur, oxygen and zirconium content of the SZ, CC and hybrid catalysts SZ4CC1 to SZ1CC4.**

**5.2.2 Comparison of calcium oxide, zirconium oxide and SO$_4^{2-}$ contents in the sulphated zirconia SZ, calcined CC and the hybrid catalysts SZ4CC1 to SZ1CC4**

Figure 5.2 compares calcium oxide, zirconium oxide and sulphate content of the SZ, the calcined CC and the hybrid catalysts (SZ4CC1 to SZ1CC4). The CaO content in SZ was < 0.1A% (below detection limit) thus the ZrO$_2$ and SO$_4^{2-}$ content in the CC as expected were zero. The composition of CaO in the SZ was < 0.1Mol% as expected. After the additions of 20 and 30wt% CC (SZ4CC1 and SZ7CC) the CaO content was 28.5 and 37.5Mol%, respectively. But with further increase in the CC addition to 40 and 50 wt% (SZ3CC2 and SZ1CC1) the CaO content decreases to 33.3 and 27.7Mol%,
respectively. After subsequent increase in the CC additions to 60, 70 and 80wt% (SZ2CC3 to SZ1CC4) the CaO content increased again to 42.0, 56.6 and 52.0Mol%, respectively. Calcined CC on its own had 53.0Mol% CaO, which again indicating significant oxidation during calcination (Section 2.5.6.3). The results indicate that the 1:1 hybrid catalyst SZ1CC1 had the least amount of calcium oxide of 27.0Mol%, which suggests probable interaction with zirconium oxide. For ZrO\textsubscript{2} the content in the SZ was 94Mol%, which is as expected the highest composition of all the catalyst samples. After addition of 20, 30 and 40wt% calcium carbide (SZ4CC1 to SZ3CC2) the ZrO\textsubscript{2} content decreased significantly to 27.4, 20.1 and 15.3Mol%, respectively. But with further increase in CC addition to 50wt% the ZrO\textsubscript{2} content increased significantly to 25.5Mol%. With subsequent increase in CC addition to 60 to 80wt% (SZ2CC3 to SZ1CC4) the ZrO\textsubscript{2} composition decreases to 8.7, 5.9 and 4.6Mol%, respectively. As expected, the ZrO\textsubscript{2} content in CC on its own was <0.1Mol%.

The change in compositions of CaO and ZrO\textsubscript{2} with increasing calcium carbide addition in the hybrid catalysts indicates a strong interaction between the two oxides. This might be associated with the available elements that took part in the formation of the oxides (see Section 2.5.6.3). The hybrid catalyst SZ1CC1, which has the lowest oxygen (see Figure 5.1), coincidentally had the lowest CaO with a corresponding increase in the ZrO\textsubscript{2} (Figure 5.2). This shows that the hybrid catalysts SZ1CC1 may have some special features. Figure 5.2 also indicates that most of the chemical interactions that occurred between calcium carbide and zirconium oxide took place when the composition of calcium carbide was in the range of 30 to 70wt%. For instance, when 20wt% calcium carbide was added to sulphated zirconia, there was a significant change in terms of surface calcium oxide and zirconium oxide. While zirconium oxide significantly reduced from 93.4 to 27.4 Mol%, calcium oxide increases from < 0.1 to 28.5Mol%. But with increasing calcium carbide, the surface calcium oxide only slightly increased and then decreased while zirconium oxide decreases slightly and then increased as well until both have equal composition (SZ1CC1). However, immediately after increasing the calcium carbide in mixture to 60wt% (SZ2CC3) the CaO content increases while the ZrO\textsubscript{2} decreases. This range (SZ3CC7 to SZ7CC3) is considered as the transition point where both calcium carbide and sulphated zirconia compete for dominance as shown by blue circle. The reason for the fluctuation between surface zirconium oxide and calcium oxide may be due to certain reactions, such as deoxidation reaction, which may involve a reaction between the calcium carbide (CaC\textsubscript{2}) and the
zirconium oxide (ZrO\textsubscript{2}) as described in Section 2.5.6.3. In the hybrid catalyst SZ1CC4, the amount of zirconium oxide is more than enough to converts the 20wt\% calcium carbide to calcium oxide. But, as the calcium carbide additions increases, it will perhaps interact more with ZrO\textsubscript{2} and produce proportionally more CaO. This may be why ZrO\textsubscript{2} decreases with increasing CaO. However between SZ7CC3 and SZ3CC7 no significant changes were observed probably due to competition between the CaO and the ZrO\textsubscript{2}.

The SO\textsubscript{4}\textsuperscript{2-} content of the pure SZ was 6.5Mol\% which increased to 7.6Mol\% after the addition of 20wt\% CC (SZ4CC1). With further CC addition of 30 to 80wt\% the SO\textsubscript{4}\textsuperscript{2-} content continuously decreased to 6.0Mol\% showing a strong correlation with increasing CC addition. This showed that an increase in the CC addition continuously reduced the SO\textsubscript{4}\textsuperscript{2-} content, which perhaps decreased the acidity of the hybrid catalyst. In Figures 4.3 and 4.4 of Section 4.4, it was established that zirconium oxide on its own only delayed the onset of weight loss during HDPE conversion. So, the presence of SO\textsubscript{4}\textsuperscript{2-} doped in the sulphated zirconia was responsible for its enhanced acidity that resulted in the improved catalytic performance towards HDPE (Zhao et al., 2008). However, the presence of calcium carbide in the mixture may cause acidity moderation which could affect the products yield, its composition and compound selectivity (Serrano et al., 2007a, Akpanudoh et al., 2005, Saha et al., 2008, Almustapha and Andrésen, 2012). Hence, moderation of the acidic and textural properties by reducing the SO\textsubscript{4}\textsuperscript{2-} content, the surface area and porosity through the calcium carbide addition may improve the liquid yield and change the product selectivity towards low aromatic compounds. Hence, tailoring the hybrid with calcium carbide can avoid high acidity and high surface area that promotes excessive cracking, which gives high gas yield and also results in secondary reactions that favours the formation of aromatic hydrocarbons in the liquid product as described in Sections 2.5.4 and 2.5.5 (Saha et al., 2008, Akpanudoh et al., 2005, Miskolczi et al., 2004b, Miskolczi et al., 2009, López et al., 2011, Aguado et al., 2009). In view of this, studying the acidity, textural properties and morphology of the principal catalysts and hybrid catalysts will help to explain the level of chemical interactions between the principal components, the overall changes in properties of the new hybrid catalysts and the possible impact on their catalytic conversions and selectivity.
5.3 \textit{NH}_3 Temperature-Programmed Desorption (TPD)

Figure 5.3 compare the exact \textit{NH}_3 TPD curves of the SZ, the calcined CC and the seven hybrid catalysts (SZ4CC1 to SZ1CC4). The broad desorption spectra showed by all the potential catalysts within 150 and 700\textdegree C indicate a wide range of acid sites of different strength (Zhao et al., 2008, Hwang and Mou, 2009). The SZ showed two main desorption peaks at 200-350\textdegree C and 350-550\textdegree C and a shoulder above 600\textdegree C indicating the presence of moderate, strong and very strong acidic strengths similar to what has been reported in literature (Zhao et al., 2008, Barthos et al., 2001, Oh et al., 2011). However, after additions of the calcium carbide (SZ4CC1 and SZ1CC4) the peak above 600\textdegree C, which indicates very strong acid strength completely diminished and shifted to a region within 350 to 550\textdegree C in addition to the peaks at 200 to 350\textdegree C. This indicates a reduction in the acid strength after calcium carbide addition. Also the intensity of desorption peak at 300 to 550\textdegree C increased steadily with increasing calcium carbide addition. The calcined CC on its own showed only one major desorption peaks at 350 to 550\textdegree C. This shows that the increase in the intensity of desorption peak at 350-550\textdegree C
could due to ammonia adsorption by CaO in the calcium carbide, which increase with increasing calcium carbide additions (see Section 5.2.2). Thus, this adsorption may not exclusively account for only strong acid strength as desorption peak in between 350 and 550°C was reported to be due to ammonia desorption by CaO (Yang et al., 2012).
Figure 5.3 Comparison of NH₃ Temperature-programmed Desorption (TPD) curve-fitted spectra of the SZ, the calcined CC and the hybrid catalysts (SZCC1 to SZ1CC4)
Table 5.1 summarises the data from the curve-fitted NH$_3$-TPD spectra for each of the potential catalysts. The curve were fitted based on four temperature regions, namely, <200°C, 200-350°C (a), 350-550°C (b) and above 550°C (c). The adsorption at <200°C was discounted as it is mainly due to physisorption. The three desorption peaks considered were based on range of temperatures where maximum ammonia desorption occurred, which are also representing moderate, strong and very strong acid sites as described in Section 2.8.6 (Katada et al., 1997, Zhao et al., 2008, López et al., 2011, Elordi et al., 2009, Shi and Li, 2013). The SZ appeared to have the highest ammonia desorption of 337.0µmolNH$_3$/g which reduced to 150.0µmolNH$_3$/g after the addition of 20wt% calcium carbide SZ4CC1. With further calcium carbide additions to 30, 40 and 50wt% (SZ7CC3 to SZ1CC1) the ammonia desorption decreased with increasing the CC addition steadily to 49.7, 11.0 and 23.4µmmolNH$_3$/g, respectively. However, subsequent increase in the CC additions to 60, 70 and 80wt% (SZ2CC3 to SZ1CC4) showed a dramatic increase in ammonia desorption to 39.2, 97.5, and 64.4µmolNH$_3$/g. The calcined CC on its own had ammonia desorption of 45.923.4µmmolNH$_3$/g. The increased ammonia desorption observed at 350-550°C with increasing addition of calcium carbide is attributed largely to ammonia adsorbed by CaO as reported by Yang et al. (2012). This literally showed that as the calcium carbide additions increased, the acidity strength of the catalysts decrease and hybrid catalysts SZ2CC3 to SZ1CC4 that showed large ammonia desorption were strongly linked with contribution from adsorption due to CaO from the CC added.

It has also been reported in literature that area of desorption peaks of different strength, which in this case peaks at 200-350 and 350-550°C could represent relative concentration of Lewis and Bronsted acid sites (Si et al., 2010, López et al., 2011). It is however not possible to assign these peaks to Lewis and Bronsted acid sites as large adsorption by CaO was observed. Thus, pyridine TPD and FT-IR analysis is recommended to determine amount of Lewis and Bronsted acidities of each potential catalysts and study the impact of CC addition on each. Owing to the large contribution of ammonia desorbed by CaO in the hybrid catalysts, particularly SZ3CC7, the SO$_4^{2-}$ content, which is directly linked with catalyst acidity, was compared with the total ammonia desorbed across the catalyst in the next Section with increasing CC addition.
Table 5.1 Comparison of the acidic strength and total ammonia desorption from curve-fitted NH$_3$-TPD spectra of the SZ, the calcined CC and the seven hybrid catalysts (SZ4CC1 to SZ1CC4)

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>NH$_3$ desorbed (µmolNH$_3$/g)</th>
<th>&lt;200$</th>
<th>200-300</th>
<th>300-550</th>
<th>&gt;550</th>
<th>Total NH$_3$ desorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>SZ</td>
<td>15.8</td>
<td>142.0</td>
<td>158.5</td>
<td>37.1</td>
<td>337.6</td>
<td></td>
</tr>
<tr>
<td>SZ4CC1</td>
<td>10.7</td>
<td>58.0</td>
<td>91.8</td>
<td>0</td>
<td>149.8</td>
<td></td>
</tr>
<tr>
<td>SZ7CC3</td>
<td>2.4</td>
<td>12.3</td>
<td>37.5</td>
<td>0</td>
<td>49.8</td>
<td></td>
</tr>
<tr>
<td>SZ3CC2</td>
<td>0.2</td>
<td>2.0</td>
<td>9.0</td>
<td>0</td>
<td>11.0</td>
<td></td>
</tr>
<tr>
<td>SZ1CC1</td>
<td>0.1</td>
<td>2.8</td>
<td>20.6</td>
<td>0</td>
<td>23.4</td>
<td></td>
</tr>
<tr>
<td>SZ2CC3</td>
<td>0.5</td>
<td>1.9</td>
<td>*37.3</td>
<td>0</td>
<td>39.2</td>
<td></td>
</tr>
<tr>
<td>SZ3CC7</td>
<td>2.6</td>
<td>5.5</td>
<td>*92.0</td>
<td>0</td>
<td>97.5</td>
<td></td>
</tr>
<tr>
<td>SZ1CC4</td>
<td>0.2</td>
<td>2.3</td>
<td>*62.1</td>
<td>0</td>
<td>64.3</td>
<td></td>
</tr>
<tr>
<td>CC</td>
<td>0.2</td>
<td>1.4</td>
<td>44.4</td>
<td>0</td>
<td>45.8</td>
<td></td>
</tr>
</tbody>
</table>

$May be due to physisorption, so discounted

*Desorption increased due to ammonia adsorption by CaO

5.3.1 Comparison of the bulk SO$_4^{2-}$ content and total ammonia desorption with increasing the CC addition

Figure 5.4 compares the bulk SO$_4^{2-}$ content with the total ammonia desorbed by the SZ, the hybrid catalysts (SZ4CC1 to SZ1CC4) and the calcined CC. The SZ with SO$_4^{2-}$ content of 6.5Mol% had the highest total ammonia desorption of 337.0µmolNH$_3$/g. After addition of 20wt% calcium carbide (SZ4CC1) the SO$_4^{2-}$ content increased slightly to 7.6Mol% while the total ammonia desorption decreased to 150.0µmolNH$_3$/g. With further calcium carbide additions to 30 to 50wt% (SZ7CC3 to SZ1CC1) both the SO$_4^{2-}$ content and the total ammonia desorption continued decreasing where the hybrid catalysts SZ3CC2 and SZ1CC1 had the lowest total ammonia desorption of 23.4 and 39.2µmolNH$_3$/g, respectively. Subsequent additions of calcium carbide to 60wt% (SZ2CC3) showed slight increase in both the SO$_4^{2-}$ content and the total ammonia desorption to 2.7Mol% and 97.2µmolNH$_3$/g, respectively. However, after increasing the calcium carbide additions to 70 and 80wt%, the SO$_4^{2-}$ content decreased continuously while total ammonia desorption increased significantly. Overall, this shows that as the calcium carbide addition increases, the SO$_4^{2-}$ content and the total ammonia desorption decreased simultaneously with the exception of the hybrid catalysts SZ2CC3 to SZ1CC4. The increase in total ammonia desorption observed for
the hybrid catalysts SZ2CC3 to SZ1CC4 despite a decrease in the \( \text{SO}_4^{2-} \) contents was attributed to contribution of the ammonia desorbed by CaO, which increased with increasing the calcium carbide addition (see Table 5.1). This showed that decrease in \( \text{SO}_4^{2-} \) content due to calcium carbide addition resulted in reducing the catalyst acidity as evidenced by the reduction in total ammonia desorption. This further supported a suggestion made in Section 5.2, where \( \text{SO}_4^{2-} \) content was believed to be responsible for catalysts acidity. Therefore addition of calcium carbide into the sulphated zirconia, which reduces its \( \text{SO}_4^{2-} \) content, is another way of moderating its acidity to provide suitable properties for plastic waste conversions, since moderate acidity is needed for improvement in the liquid yield and to prevent coke and deactivation.

![Figure 5.4 Comparison of the \( \text{SO}_4^{2-} \) content and total ammonia desorption of the SZ, calcined CC and the hybrid catalysts (SZCC1 to SZ1CC4).](image)

**Figure 5.4** Comparison of the \( \text{SO}_4^{2-} \) content and total ammonia desorption of the SZ, calcined CC and the hybrid catalysts (SZCC1 to SZ1CC4).

### 5.4 Surface morphology of the potential catalysts with increasing CC addition

Figure 5.5 compares the SEM micrographs of the two principal catalysts, the SZ, the calcined CC and the six hybrid catalysts SZCC1 to SZ1CC4 with different
compositions of the SZ and the calcined CC. The SEM micrographs of the two principal catalysts showed that they exhibited a similar particle sizes ranging from 100 to 200nm. However, the particles in the calcined CC appeared more aggregated than that of the SZ. Also, for the SZ, there are several open pores (Circle A), which are not visible on the surface of the calcined CC (Circle H). This indicates that the calcined CC may possess much lower pore volume than that of the SZ. Thus, the surface area and porosity of the SZ could also be much higher than that of the calcium carbide. After the addition of 20wt% calcium carbide, the particles in the hybrid catalyst become more aggregated and with subsequent additions from 30 to 80wt% (SZ4CC1 to SZ1CC4), the particles appeared increasingly more aggregated with increasing calcium carbide additions. This indicates a good solid-solid interaction between the SZ and the calcined CC as evidence by the nature of how the particles of both are integrated well with one another during calcination at 550°C.

Visual observation also showed that the open pores in the SZ as indicated by circle A, were possibly filled after the calcium carbide additions. Circles B-G on the hybrid catalysts SZ4CC1 to SZ1CC4 are typical examples showing how the calcium carbide has been integrated within the sulphated zirconia possibly by blocking the open pores of the SZ. This perhaps led to a reduction in pore volume of the hybrid catalysts with increasing calcium carbide addition, which may subsequently lower its surface area and porosity. This may alter the catalytic functioning of the new hybrid catalysts, particularly the coke formation and selectivity. This is because reducing the pore volume, which subsequently reduces the porosity, may halt the possible secondary reactions that promote aromatic production (Sharratt et al., 1997, Serrano et al., 2007a, Marcilla et al., 2009, Aguado et al., 2009). Hence, there is a need to analyse the structure of both the principal catalysts and the hybrid catalysts to see if changing their composition due calcium carbide addition may form mixed oxide between calcium and zirconium.
Figure 5.5 Comparison of SEM micrographs of the SZ, the calcined CC and the six hybrid catalysts (SZ4CC1 to SZ1CC4)
5.5 X-ray diffraction (XRD)

5.5.1 Comparison of XRD pattern of the SZ before and after calcination

Figure 5.6 compares the powder X-ray diffraction pattern of the SZ before (BC) and after (AC) calcination. Figure 5.6 shows that the crystal phase of sulphated zirconia both before and after calcination contained exclusively tetragonal ZrO$_2$ (JCPD no. 50-1089), where the four peaks in the diffractograms were observed at $2\theta = 30.41$ (relative intensity is 100) as well as 35.25 (20), 50.71 (52) and 60.28 (31). This is similar to what was previously reported in the literature (Reddy et al., 2005, Zhao et al., 2008, Yamamoto et al., 1999, Mishra et al., 2003, Wang and Mou, 2008, Chen et al., 1993). However, the sulphated zirconia before calcination was poorly crystalline. After calcination the peaks became sharper indicating that calcination also has improved its crystallinity (Iranmahboob et al., 2001).
Figure 5.6 Comparison of powder XRD diffraction pattern of the pure SZ before (BC) and after (AC) calcination at 550°C, where (●) represents characteristic lines due to tetragonal ZrO$_2$.

5.5.2 Comparison of XRD pattern of the CC before and after calcination

Figure 5.7 compares the powder X-ray diffraction pattern of the calcium carbide CC before (BC) and after (AC) calcinations. The phases of the compounds obtained before calcination are indexed as CaC$_2$ (JCPD no. 65-2656), CaO (JCPD no. 37-1497), Ca(OH)$_2$ (JCPD no. 04-0733), but after calcination phases of compounds obtained are
CaC\(_2\) (JCPD no. 51-1167), CaO (JCPD no. 48-1467), Ca(OH)\(_2\) (JCPD No. 44-1481) and CaCO\(_3\) (JCPD No. 44-1481). The XRD diffractogram peaks indexed for CaC\(_2\) (■) had five reflections observed at \(2\theta = 26.55, 28.10, 32.30, 42.60\) and 48.90 where after calcination three peaks with reflections observed at \(2\theta = 28.10, 32.30\) and 48.90 disappeared. Similarly, the peaks indexed for CaCO\(_3\) ($) were not observed before calcinations, but after calcinations at 550\(^\circ\)C five new peaks were observed at \(2\theta = 23.20, 29.80, 36.00, 39.85\) and 48.90 indicating the emergence of a new phase due to calcination. The XRD diffractogram peaks indexed for Ca(OH)\(_2\) (♦) and CaO (♣) had five peaks observed at \(2\theta = 18.20, 28.60, 34.10, 47.10\) and 51.20, and two peaks observed at \(2\theta = 36.90\) and 54.20, respectively where no peak emerged or lost from both compounds after calcination. The sharpness of all peaks increased significantly after calcination which just as for sulphated zirconia indicates that the crystallinity of the sample had increased. However, unlike the SZ the intensities of some peaks had significantly were affected by calcination significantly. For instance, the intensity of each of the four peaks representing calcium hydroxide increased about fivefold, so also in the case of CaC\(_2\), where the intensities of the two peaks showed negligible change while two other peaks peak disappeared after calcination indicating possible conversion to CaCO\(_3\). Similarly, five new peaks representing calcium carbonate (CaCO\(_3\)) emerged after calcination. However, the intensities of the peaks representing calcium oxide (CaO) showed negligible change after calcination. From the XRD results, it is apparent that a series of chemical reaction occurred during calcinations of calcium carbide on its own. In particular, the disappearance of peaks representing CaC\(_2\) and emergence of new peaks representing CaCO\(_3\) indicating a shift from CaC\(_2\) to CaCO\(_3\). The change of intensities of most of the XRD peaks representing some components is a clear demonstration of the occurrence of the chemical reactions during the calcination. For instance, in Section 5.2, the SEM/EDS results revealed the presence of calcium oxide and calcium carbonate in the calcined calcium carbide and the XRD results here confirmed their presence.
The shift in diffraction pattern in Figure 5.7 may reflect the reactions as shown in Equations 5.1 to 5.4. Calcium carbide is hygroscopic in nature and undergoes self-hydration even after a brief exposure to atmosphere and produce acetylene and calcium hydroxide. So, a precautionary measure was taken in handling it by keeping it always in a dry and air-tight container and kept away from any source of heat and moisture. At high temperature, the calcium hydroxide may decompose to calcium oxide and water as
illustrated in Equations 5.1 and 5.2 (Zhang et al., 2014). The acetylene released during hydration of calcium carbide oxidised and release CO\(_2\) (see Equation 5.3). The CO\(_2\) may reacts with calcium hydroxide (Ca(OH)\(_2\)) and forms calcium carbonate through a carbonation reaction (see Equation 5.4), as carbonation of calcium oxide has been proved possible even at lower temperature of 60 to 90°C (Haghnegahdar et al., 2011, Shih et al., 1999). So, the appearance of peaks representing calcium carbonate after calcination might be due to carbonation of calcium hydroxide or due part of the calcium carbide that was involved in the self-hydration as two peaks representing calcium carbide disappeared after calcination. By comparing the two principal catalysts, it is evident that they have different chemical compositions as already highlighted in Section 5.2.

\[
\begin{align*}
2\text{Ca(OH)}_2 & \rightarrow 2\text{CaO} + 2\text{H}_2\text{O} & \text{(5.1)} \\
\text{CaC}_2 + 2\text{H}_2\text{O} & \rightarrow \text{C}_2\text{H}_2 + \text{Ca(OH)}_2 & \text{(5.2)} \\
2\text{C}_2\text{H}_2 + 5\text{O}_2 & \rightarrow 4\text{CO}_2 + 2\text{H}_2\text{O} & \text{(5.3)} \\
2\text{Ca(OH)}_2 + \text{CO}_2 & \rightarrow \text{CaCO}_3 + 2\text{H}_2\text{O} & \text{(5.4)}
\end{align*}
\]

5.5.3 **Comparison of XRD pattern of the SZ with the seven hybrid catalysts (SZ4CC1 to SZ1CC4)**

Figure 5.8 compares the powder X-ray diffraction pattern of the pure SZ with the seven hybrid catalysts ranging from SZ4CC1 to SZ1CC4. The spectra indicate that the peaks in the diffractograms of tetragonal ZrO\(_2\) were observed at 2\(\theta\) = 30.41, 35.25, 50.71 and 60.28 in the SZ have all emerged in the hybrid catalyst. This is a good development as catalytic activities of sulphated zirconia and its equivalents depends largely on its tetragonal phase (Zhao et al., 2008). But with increasing calcium carbide addition, particularly after addition of 60wt% (SZ2CC3) the intensities of some of the tetragonal ZrO\(_2\) decreased. This shows the important phase of ZrO\(_2\) remain active until after addition of 60wt% calcium carbide. However, a new phase of compound indexed CaZrO\(_3\) (JCPD no. 48-0904) emerged in all the hybrid catalysts SZ4CC1 to SZ1CC4, which increased with increasing calcium addition. This shows that the calcium carbide addition affected the chemical compositions of the hybrid catalysts, which perhaps resulted in a chemical reaction between the main compounds, zirconium oxide and
calcium oxide in the precursors as indicated in Section 2.5.6.3. Although it has not been quantified, visual observations showed that the intensity of the peak representing the CaZrO$_3$ increased with increasing CC addition. This further support the hypothesis in Section 5.2.2 in Figure 5.2, where it was observed that despite an increase in the CC addition, ZrO$_2$ remained unchanged particularly between hybrid catalysts SZ7CC3 and SZ2CC3 which was aligned with the XRD results in Figure 5.8. This strongly suggests that the calcium oxide from the calcium carbide reacted with ZrO$_2$ to produce calcium zirconium oxide as described in Section 2.5.6.3. The increase deposit of CaZrO$_3$ with increasing calcium addition could be responsible for the continues blockage of open pores of the sulphated zirconia which could results in pore volume and pore size reduction and subsequently lower porosity. Hence, analysing the adoption properties of sulphated zirconia and the hybrid catalysts will very important in understanding the effect of calcium carbide addition on the textural properties of the catalysts.
Figure 5.8 Comparison of the powder XRD diffraction pattern of the SZ and the hybrid catalysts SZ4CC1 to SZ1CC4, where (●) represents characteristic lines due to tetragonal ZrO$_2$ and (◊) due to CaZrO$_3$. 
5.5.4 Contrast of crystallite size with increasing calcium carbide addition

Figure 5.9 compares the average crystallite size calculated from the broadening of the (111) ZrO$_2$ at 2$\theta$ = 30.41 (relative intensity is 100) as well as 35.25 (20), 50.71 (52) and 60.28 (31) of the SZ and the hybrid catalysts SZ4CC1 to SZ1CC4 as calculated using the Scherrer Equation (see Section 2.8.3). The average crystallite size increased with increasing the CC addition. The SZ had the lowest crystallite size of 3.8nm. After the addition of 20wt% CC (SZ4CC1) the crystallite size increased to 5.8nm. Further CC additions to 30 to 60wt% (SZ7CC3 to SZ2CC3) increased the crystallite size to 6.3nm and remained within the average of 6.2nm. With subsequent additions of the CC to 70 and 80wt%, the crystallite size increased to 7.0 and 12.6nm, respectively, where the calcium carbide on its own had a 14.0nm crystallite size. It appeared that the SZ and the hybrid catalyst SZ4CC1 had the lowest crystallite sizes (see purple arrow), while the hybrid catalysts (SZ7CC3 to SZ2CC3) had intermediary average crystallite sizes (see orange circle). However, as the CC addition increases above 60wt% (SZ3CC7 and SZ1CC4), the average crystallites sizes of the hybrid catalysts increased significantly (see blue arrow). This indicates that with increasing CC in the mixture, the average crystallite sizes of the resulting catalysts are increasingly becoming large. Thus, the increase in the average crystallite size will ultimately increase the particle size and results in surface area and porosity reduction. This is largely in agreement with that observation made, when comparing the surface morphology of the catalysts in Section 5.4, where the particles became more clustered with increasing calcium carbide addition whose particles were found embedded within the open pores of sulphated zirconia. This might have resulted in an increase in the crystallites sizes as the CC addition increases, as observed in Figure 5.9. This suggests that the addition of the CC might have result in reduced pore volume of the hybrid catalysts due to the interaction of CaZrO$_3$ into the open pores of SZ. This may ultimately reduce the surface area and porosity of the new hybrid catalysts as the calcium oxide content increases. So, in views of this, a detailed analysis of the catalysts adsorptive properties was studied to analyse the impact of CC additions on the textural properties of the catalysts.
Figure 5.9 Comparison of catalyst average crystallite size of the sulphated zirconia SZ, the hybrid catalysts SZ4CC1 to SZ1CC4 and calcium carbide CC calculated using Scherrer's equation from the XRD data.

5.6 Adsorption isotherm, surface area and porosity analysis

5.6.1 Adsorption isotherm

Figure 5.10 compares the N₂-adsorption isotherms of the SZ, the hybrid catalysts (SZ4CC1 to SZ1CC4) and the calcined calcium carbide, CC. The N₂-adsorption isotherms in Figure 5.10 showed characteristic of type II and type IV adsorption isotherms with step capillary condensation over the relative pressure range of 0.4 to 0.9 (see Section 3.3.3) (Storck et al., 1998). With increasing relative pressure, capillary condensation occurred which is a typical feature of mesoporous material (Donohue and Aranovich, 1999, López et al., 2011, Gao et al., 2015, Tahir and Amin, 2013, Mishra et al., 2003, Serrano et al., 2007a). Recently, Gao et al. (2015) reported similar isotherms for microcellular foam catalysts (MFC) as typical type IV isotherms, which confirmed the existence of mesoporous material in all the catalysts. The monolayer-multilayer adsorption on the internal surface of the catalyst occurred at initial part of the isotherm with low relative pressure (\(P/P^o < 0.1\)) while capillary condensation commenced by the
steep adsorption at high relative pressure (Tahir and Amin, 2013). Although both the SZ, the hybrid catalysts SZ4CC1 to SZ1CC4 and the CC all showed the same type of isotherm, the nitrogen absorption was more prominent in the SZ and the hybrid catalysts SZ4CC1 and SZ3CC7, which indicated higher adsorption capacity than the rest of the hybrid catalysts. The characteristics of the isotherms also show a uniform size distribution that filled spontaneously due to capillary condensation (Yadav and Murkute, 2004). The SZ appeared to have the highest nitrogen adsorption of about 1.10mmol/g at low relative pressure (P/P^o <0.1) than the remaining hybrid catalysts indicating the possibility of micropores (Schneider, 1995, Serrano et al., 2007a). With the addition of 20wt% calcium carbide SZ4CC1 the nitrogen adsorptions at low relative pressure (P/P^o <0.1) reduced to 0.9mmol/g. Further increases in the calcium carbide additions to 30 and 80wt% (SZ3CC7 to SZ1CC4) showed that the nitrogen adsorptions at low relative pressure (P/P^o <0.1) continuously decreasing with the hybrid catalyst SZ1CC4 having about 0.12mmol/g. Calcined CC on its own had the lowest nitrogen adsorption at low relative pressure (P/P^o <0.1) of only 0.10mmol/g indicating nearly an absence of any possibility of micropores (Serrano et al., 2007a). However, a steep jump between hybrid catalyst SZ7CC3, which had 0.60mmol/g, and the rest of the hybrid catalysts that showed adsorption of below 0.30mmole/g at low relative pressure (P/P^o <0.1). This suggests that a uniform reduction in pore size and pore volume had occurred with increasing CC additions, which could lead to a reduction in surface area (Yadav and Murkute, 2004). This coincided with what was observed for the crystallite size of the catalysts in Section 5.5.4, where an increase in the CC addition leads to an increase in the crystallites sizes.

Overall, the N\textsubscript{2}-isotherm of the catalysts showed that the nitrogen adsorption capacity decreased with increasing the CC additions. This showed that increase in calcium carbide lead to a decrease in surface area and pore volume. This again correlated with the SEM results in Section 5.4, where the particles became more clustered with increasing calcium carbide additions. Furthermore, the XRD results also showed that the crystallites size of the catalysts increases with increasing the calcium carbide additions, indicating reduction in particle sizes and pore volume. As the N\textsubscript{2}-adsorption isotherms shown on Figure 5.10 do not have desorption isotherms due to limitation from the analyser, which does not show hysteresis, therefore to confirm the actual porosity of the catalyst, pore size distribution using Barrett-Joyner-Halenda (BJH) analysis would be on great importance.
Figure 5.10 Comparison of N\textsubscript{2}-adsorption isotherms of the SZ, the CC and the hybrid catalysts SZ4CC1 to SZ1CC4.

5.6.2 Surface area and porosity analysis

Figure 5.11 compare the pore size distribution of the SZ, the hybrid catalysts (SZ4CC1 to SZ1CC4) and the calcined CC. The pore size distribution on Figure 5.11 showed that there is broad distribution in all the samples ranging from 2 to 12nm. This also indicates that all the samples have mesoporous structure, as particles are largely distributed between 2 to 12nm. This confirmed the existence of mesoporous materials in all the samples as suggested by the nitrogen adsorption isotherm in Figure 5.10 (Rezaei et al., 2006, Mishra et al., 2003).
Table 5.2 summarises the textural properties of the SZ, hybrid catalysts SZ4CC1 to SZ1CC4 and the calcined CC. The SZ on its own had a BET surface area and an external surface area (ESA) of 116 and 112 m$^2$/g, respectively. After addition of 20 wt% CC (SZ4CC1), the BET and ESA reduced to 100.7 and 99.6 m$^2$/g, respectively. With further increase in the CC additions to 30 to 80 wt% (SZ3CC7 to SZ1CC4), both the BET and the ESA decrease continuously with the hybrid catalyst SZ1CC4 having 15.1 and 14.0 m$^2$/g, respectively. The calcined CC on its own had the lowest BET and ESA of 10.2 and 8.7 m$^2$/g, respectively. This showed that addition of the CC significantly affected the total surface area of the catalysts. It also indicates that virtually all the surface area is external for the hybrid catalysts. The decrease in surface area with increasing the CC addition supported the results in Section 5.6.3, where adsorption at low relative pressure decreased with increasing calcium carbide addition which is aligned with the general observation where the surface area of a material determines its sorption capacity (Carmody et al., 2007). The BET surface area reported here for SZ is comparable to that reported by Mishra et al. (2003), where sulphated zirconia calcined at 600°C had a surface area of 116 m$^2$/g.

Figure 5.11 Pore size distributions of the SZ, the CC and the hybrid catalysts SZ4CC1 to SZ1CC4 using BJH method.
Table 5.2 shows that the SZ had a pore volume of 0.21 mL/g. After the addition of 20 wt% CC (SZ4CC1), the pore volume reduced to 0.17 mL/g. With increasing the CC additions to 30 wt% (SZ7CC3), the pore volume decreases to 0.13 mL/g and with further increase in CC addition to 40 and 80 wt% (SZ2CC3 to SZ1CC4), the pore volume decreases continuously, where the hybrid catalyst SZ1CC4 had the lowest pore volume of 0.02 mL/g. The sulphated zirconia had a pore width and BJH mean pore diameter of 10.80 nm and 3.22 nm, respectively. After addition of 20 wt% CC (SZ4CC1), the pore width and the mean pore diameter reduced to 10.78 and 3.18 nm, respectively. With increasing CC additions to 30 wt% (SZ7CC3), the pore width slightly increased to 11.70 nm and mean pore diameter decrease to 3.1 nm. With further increase in the CC addition between 40 and 60 wt% (SZ3CC2 to SZ2CC3), the pore width and the mean pore diameter decreased continuously, where the hybrid catalyst SZ2CC3 had the pore width of 8.6 and 2.89 nm, respectively. However, after increasing the CC addition to 70 and 80 wt% (SZ3CC7), the pore width decreased to 7.9 and 6.4 nm while the mean pore diameter increased slightly to 3.1 and 3.2 nm, respectively. The calcined CC had pore width of 5.0 nm and the mean pore diameter of 3.2 nm. The decrease pore volume with the increase in the CC can be correlated to a decrease in the surface area as stated earlier, where a surface area of material determines its sorption capacity (Matsuhashi et al., 2009, Carmody et al., 2007).

The reduction in surface area and subsequent pore volume could be related to the increase in the amount of large particle from CaZrO₃ which may block some open pores of the SZ leading to reduction in surface area and pore volume (Yadav and Murkute, 2004). Furthermore, the mean pore diameter of SZ calculated by the Barrett Joyner Halenda (BJH) method reduced slightly as CC addition increased to 30 wt% and then increased slightly. Also, the median pore width showed a marked decrease with from 10.8 nm for the SZ to 5.0 nm for the CC. The decrease in the particle sizes due to the CC addition could be linked to increase in crystallite size as observed in section 5.5.4, which might have resulted in reduction of particle sizes (Tahir and Amin, 2013). The BJH mean pore diameter above 2 nm for SZ and all the hybrid catalysts, including CC may suggest the possibility of mixture of mesoporous materials in all the catalysts (Storck et al., 1998). For the micropore volume and micropore area, the SZ had 0.0013 mL/g and 3.90 m²/g, respectively. This indicates the presence of rather low internal micro porosity in SZ, which is possible for mesoporous materials (Carmody et al., 2007, López et al., 2011, Storck et al., 1998, Schneider, 1995). However, after addition of the
20 to 80wt% CC (SZ4CC1 to SZ4CC1) the micropore volume and micropore area were below the detection levels indicating disappearance of microporosity. This was already observed by the low adsorption at low relative pressure \((p/p_0)\) below 0.1 in Section 5.6.1.

Table 5.2 Summary of the adsorption properties of the SZ, CC and the hybrid catalysts (SZ4CC1 to SZ1CC4)

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>SZ</th>
<th>SZ4 CC1</th>
<th>SZ7 CC3</th>
<th>SZ3 CC2</th>
<th>SZ1 CC1</th>
<th>SZ2 CC3</th>
<th>SZ3 CC7</th>
<th>SZ1 CC4</th>
<th>CC</th>
</tr>
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<tr>
<td>BET total surface area (m²/g)</td>
<td>116.0</td>
<td>100.7</td>
<td>71.6</td>
<td>25.6</td>
<td>23.1</td>
<td>19.1</td>
<td>17.1</td>
<td>15.1</td>
<td>10.2</td>
</tr>
<tr>
<td>External surface area (m²/g)</td>
<td>112.0</td>
<td>99.6</td>
<td>71.1</td>
<td>24.5</td>
<td>22.2</td>
<td>19.0</td>
<td>16.7</td>
<td>14.0</td>
<td>8.7</td>
</tr>
<tr>
<td>Pore volume (mL/g)</td>
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<td>0.17</td>
<td>0.13</td>
<td>0.04</td>
<td>0.03</td>
<td>0.03</td>
<td>0.02</td>
<td>0.012</td>
<td></td>
</tr>
<tr>
<td>Median pore width (nm)</td>
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<td>10.8</td>
<td>11.7</td>
<td>9.4</td>
<td>8.2</td>
<td>8.6</td>
<td>7.9</td>
<td>6.5</td>
<td>5.0</td>
</tr>
<tr>
<td>Mean pore diameter (nm)</td>
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<td>3.18</td>
<td>3.10</td>
<td>3.10</td>
<td>2.98</td>
<td>2.89</td>
<td>3.0</td>
<td>3.10</td>
<td>3.20</td>
</tr>
<tr>
<td>Micropore vol. (mL/g)</td>
<td>0.00</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
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<td>nd</td>
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<tr>
<td>Micropore area (m²/g)</td>
<td>3.90</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
</tr>
</tbody>
</table>

*Measure from adsorption isotherm (relative pressure of 0.05 to 0.3)
*Measured by application of t-plot
*Measured using H-K method at \(p/p_0 = 0.95\)
*Measured by the nitrogen adsorption isotherm using BJH method

5.6.3 Comparison of BET surface area

Figure 5.12 compares the total surface area (BET) of the sulphated zirconia SZ, the hybrid catalysts (SZ4CC1 to SZ1CC4) and the calcium carbide CC. The SZ had the highest total surface area of 116m²/g. After addition of 20 and 30wt% CC (SZ4CC1 to SZ2CC3) the total surface area decreased down to 71.6m²/g following a linear trend as shown by the blue arrow in Figure 5.12. A further increase in the CC addition to 40 to 60wt% (SZ3CC2 to SZ2CC3) showed a further marked drop in the surface area, where the hybrid catalyst SZ1CC1 had a total surface area nearly the same as the hybrid catalyst SZ3CC2 as shown by the orange circle in Figure 5.12. With a further increase
in the CC additions to 60 to 80wt% (SZ3CC2 to SZ1CC4), the total surface area decreases steadily with increasing CC following a linear relationship as shown by the purple arrow. These two linear relationships between surface area and increase in CC addition could be due to the dominance of either of the principal compounds, ZrO$_2$ and CaO, which are used in the formation of CaZrO$_3$. However, the nonlinear relationship between the increase in sulphated zirconia and surface area observed during the calcium carbide addition of 40 to 60wt% may possibly be a transition point, where each of the principal compounds was trying to have dominance as shown by the orange circle. A similar region has been identified as the critical point for elements (Ca, O, C and S) and oxides (SO$_4^{2-}$, CaO and ZrO$_2$) as shown in Figures 5.1 and 5.2 in Section 5.2 and Figure 5.9 in Section 5.5.4. This suggests that the hybrid catalysts in this region are the ones that undergo most of the solid-solid interactions during their formation.

The BET surface area correlation in Figure 5.12 is also agreement with that observed by SEM in Section 5.4, which showed that the particles of calcium carbide are more clustered and less porous than that of SZ. It also agrees with the TPD results in Section 5.3, where total ammonia desorption decreased with increasing CC addition that lead to surface area reduction. These changes in the textural properties and particularly surface area due to CC additions may modify the catalyst performance and product
selectivity of the new hybrid catalyst by averting secondary reaction as described in Section 2.5.5.

5.7 Summary of catalyst characterisation

The overall results of the catalysts characterisation have shown a possible of series of chemical interactions during the formations of the hybrid catalysts leading to formation of new compounds. The bulk composition of elemental and oxide of the hybrid catalysts were found to have different composition of elements and oxides as the CC addition increases. For instance, carbon, calcium and CaO increased while oxygen, sulphur, SO$_4^{2-}$ and ZrO$_2$ decreased with increasing calcium carbide addition. This was anticipated as changes in the bulk elements and oxides were as a result of the change in the composition of their precursors in the mixture. It was also observed that the SO$_4^{2-}$ content decreased with increasing CC addition and, subsequent to that, the acidic strength of the catalysts were reduced. This was confirmed by NH$_3$ temperature programmed desorption (TPD), where the total ammonia desorbed due to strong acid sites decreased with increasing CC Addition. Also the total ammonia desorbed reduced linearly with SO$_4^{2-}$ content as the CC increased. However, the compositional changes observed on the hybrid catalysts with increasing calcium carbide addition between 40 to 60wt% were not linear.

The SEM results showed that the particles in all the catalysts were homogenous but tend to be more clustered with increasing CC addition. In the hybrid catalysts, the calcium carbide was found to be well integrated within the SZ by embedding within its open pores. This was found to reduce the pore volume of the hybrid catalysts as the CC addition increased. Also, the crystallite size increase with increasing calcium carbide addition. The BET total surface area and crystallite size showed a similar trend with that observed in the case of surface elements and oxides, where the relationship appeared nonlinear when calcium carbide composition was between 40 to 60wt%. Overall, these are believed to be transition points for both precursor components. In view of this, in Figures 5.1, 5.2, 5.3 and 5.12, most of the chemical interactions between the two principal catalysts are believed to have occurred among the hybrid catalysts SZ3CC2, SZ1CC1 and SZ2CC3. Thus, with SZ1CC1 falling in between the three hybrid catalysts, it may be likely to have the best composition for HDPE conversions. Hence, the principal catalysts, namely sulphated zirconia SZ and calcium carbide CC, as well as
five hybrid catalysts were selected for HDPE conversions using a fixed bed reactor to compare their catalytic activities and select the catalyst that promotes maximum HDPE conversion and highest liquid yield.
Chapter 6 – HDPE CATALYTIC CONVERSIONS AND TEMPERATURE OPTIMISATION

6.1 Introduction

In this chapter, the sulphated zirconia SZ, the calcium carbide CC and the five hybrid potential catalysts SZ4CC1 to SZ1CC4 were initially used for HDPE conversions to liquid and gaseous hydrocarbon products. The catalytic activities of the principal catalysts and the five hybrid catalysts are compared in relation to conversions, liquid and gaseous yields. Since the TGA result in Section 4.5 showed that the temperature of maximum weight loss \( T_m \) of HDPE was in the range of 420 to 470°C for all the catalysts, the HDPE conversions were therefore carried out just below the onset at 400°C. A 30min residence time and 1:1 HDPE to catalyst ratio with 30cl/min nitrogen flow was used as operation condition. The residence time of 30min was estimate to cover 6-8 minutes for melting, 8-10 minutes for complete conversion and 8-12 minutes for evacuation of products and reactor stabilisation (see Section 3.4.2).

6.2 Catalytic conversion and product yield

This section presents the results of HDPE conversion carried out according to Section 3.4.2 using a fixed bed reactor at constant reaction conditions of 400°C, 30 min residence time and 1:1 HDPE to catalyst ratio under a nitrogen stream of 30cl/min. The HDPE conversions were carried out using each of the potential catalysts, namely the sulphated zirconia SZ, the calcium carbide CC and the five hybrid catalysts SZ4CC1 to SZ1CC4. The main aim was is to compare their catalytic activities in terms of maximum conversion and liquid yield.

6.2.1 Comparison of HDPE conversions with catalysts \( \text{SO}_4^{2-} \) content and total ammonia desorbed due to strong acid strength in the presence of SZ, CC and the hybrid potential catalysts SZ1CC4 to SZ4CC1

Figure 6.2 compares the total HDPE conversions achieved in the presence of the SZ, the CC and the five hybrid catalysts SZ1CC4 to SZ4CC1. Also, the \( \text{SO}_4^{2-} \) content and total ammonia desorbed due to strong acid strength with increasing calcium carbide additions are plotted for comparison. In terms of HDPE conversion, the sulphated zirconia SZ on its own showed a conversion of 98.5wt%. This excellent conversion was increased to 99 and 100% with increasing calcium carbide additions from 20 to 60wt%.
(SZ4CC1 to SZ2CC3). However, the HDPE conversion suddenly dropped to only 22wt% after increasing the addition of calcium carbide to 80wt% (SZ1CC4). The calcium carbide CC on its own did not show any appreciable catalytic activity at 400°C, as only 19wt% conversion was achieved at the end of 30 min residence time. Attempts to convert HDPE only at 400°C using the same method described in Section 3.4.2 was not successful, as the polymer only melted and no reduction in mass was recorded after 30 min residence time. This shows that both the sulphated zirconia SZ and the hybrid catalysts (SZ4CC1 to SZ2CC3) have excellent catalytic activities when compared to some other catalysts used at similar reaction conditions (Park et al., 1999, Miskolczi et al., 2006). For instance, Park et al. (1999) reported HDPE conversion using silica alumina (SA), ZSM-5, HY, Y-zeolite and normal zeolite (NZ) catalysts at 400°C for 1h, but a conversion of only less than 30wt% was achieved. Even when the temperature was raised to 450°C the HY catalyst still only had a 91wt% conversion. Likewise, the work of Miskolczi et al. (2006), where cracking catalysts namely, FCC, ZSM-5 and a clinophillolite used for conversion of HDPE plastic waste at 430°C, showed that none of these catalysts gave a conversion of more than 70wt%. Even after improving the surface area of the catalysts, the highest conversion achieved using ZSM-5 was only about 90wt%. This reconfirmed that the catalysts produced in this work have excellent activities towards HDPE conversion, which was achieved at temperature as low as 400°C and within only 30min residence time.
Chapter 6 – HDPE Catalytic Conversions and Temperature Optimisation

In terms of the impact of catalyst acidity on HDPE conversion, the $\text{SO}_4^{2-}$ content and the total ammonia desorbed due to strong acid strength using the values from Table 5.1, Section 5.3 were compared with HDPE conversion as the calcium carbide addition increased. The SZ on its own which had the $\text{SO}_4^{2-}$ content of 6.6Mol% and the highest ammonia desorption of 337.6µmolNH$_3$/g had a conversion of 98.5wt%. With the addition of 20wt% CC (SZ4CC1) the HDPE conversion increased to 99wt%, where the $\text{SO}_4^{2-}$ content increased slightly to 7.6Mol% and total ammonia desorbed decreased to 149.8µmolNH$_3$/g. With increasing calcium carbide addition to 30, 40 and 50wt% (SZ7CC3 to SZ1CC1), the HDPE conversion increased to 100wt%, while the $\text{SO}_4^{2-}$ content and ammonia desorbed decreased continuously to 6.0, 3.9 and 2.5Mol% and 49.8, 11.0 and 23.4µmolNH$_3$/g, respectively. With further calcium carbide addition to 60wt% (SZ2CC3), the conversion and the $\text{SO}_4^{2-}$ content remains nearly unchanged, while the ammonia desorbed increased to 39.20µmolNH$_3$/g. When the calcium carbide addition was raised to 80wt% (SZ1CC4), the $\text{SO}_4^{2-}$ content decreased to 1.8Mol% and the total ammonia desorbed decreased to 64.3µmolNH$_3$/g, but the HDPE conversion significantly decreased to only 22wt%. The calcined CC, which had the lowest $\text{SO}_4^{2-}$ content (< 0.1Mol%) and ammonia adsorption of 45.8µmolNH$_3$/g had only 18.5wt%
HDPE conversion. This shows a good correlation between the catalysts acidity and HDPE conversion up to hybrid catalyst SZ2CC3, where the HDPE conversion remained excellent despite reduction in total ammonia desorption. The steep decrease in terms of HDPE conversion observed, when the calcium carbide addition was raised to 80wt%, may be due to a decrease in acidic strength of the catalyst, since it was observed that the large ammonia desorption observed was due to CaO which increased with increasing CC addition (see Section 5.3). This was evidenced for the calcium carbide itself, which had ammonia desorption of 45.8µmolNH$_3$/g but had conversion of only 18.0wt (see Table 5.1 in Section 5.3). It was also observed that the increased in ammonia desorption after increasing calcium carbide addition to 60 and 80wt% was due to contribution due to CaO which increased with increasing CC addition (see Figure 5.4), where on its own does not promotes polymer cracking as evident from Figure 6.1.

Figure 6.1 confirms that the SO$_4^{2-}$ is determinant of catalyst acid strength, which probably promoted high HDPE conversion observed by the sulphated zirconia SZ and particularly, the hybrid catalysts SZ4CC1 to and SZ1CC1 which gave outstanding HDPE conversions of nearly 100wt%. However, a poor HDPE conversion of only 18.5wt% was observed from the hybrid catalyst SZ1CC4 with very low SO$_4^{2-}$ content despite large ammonia desorption of 64.3µmolNH$_3$/g. This indicates that SO$_4^{2-}$ content is a key for the catalyst acidity and is responsible it’s cracking ability. None the less, the SZ and the other hybrid catalysts that have high SO$_4^{2-}$ content and high ammonia desorption due strong acid strength may promote excessive cracking and subsequently low liquid yield (Saha et al., 2008, Akpanudoh et al., 2005, Miskolczi et al., 2004b, Miskolczi et al., 2009, López et al., 2011, Zhao et al., 2008, Hernandez et al., 2006). Thus, there is a need to analyse the products yield obtained from each catalysts to ascertain the impact the acidity moderation and changes in their properties have on the liquid yield and compositions as a function of calcium carbide addition.

6.2.2 Comparison of the products yield from HDPE conversion in the presence of the calcined CC, the SZ and the hybrid catalysts SZ1CC4 to SZ4CC1

Figure 6.2 compares the hydrocarbon product yields obtained using the sulphated zirconia SZ, calcined CC and the hybrid catalysts SZ4CC1 to SZ1CC4 for HDPE conversion at 400°C and 30 min residence time and 1:1 catalyst to HDPE ratio. In the presence of the sulphated SZ and after addition of 20wt% CC, the liquid yields
were 34.3 and 33.0wt%, respectively. With increasing the CC addition to 40 to 60wt% (SZ3CC2 to SZ2CC3) the liquid yields increased until it reaches a peak of 54.0wt% each for the hybrid catalysts, SZ1CC1 and SZ2CC3. With further calcium carbide addition to 80wt%, the liquid yield significantly reduced to only 5.0wt%. The CC on its own had only 18.5wt% liquid yield. In terms of the gaseous product yields, the SZ and the hybrid catalyst SZ4CC1 appeared to have the highest yield of 64.2wt% and 66.0wt%, respectively. The hybrid catalyst SZ3CC2 followed with 59.0wt% and then SZ1CC1 and SZ2CC3 with 46.0wt% each. The hybrid catalyst SZ1CC4 and the CC had 16.8wt% and 6.2wt%, respectively, but appeared to have the highest residue content of 82 and 78wt%, respectively. The SZ and the hybrid catalyst SZ4CC1 had residue of 1.5 and 1.0wt%, respectively. The remaining hybrid catalysts (SZ3CC2, SZ1CC1 and SZ2CC3) showed the lowest residue of less than 0.2wt% each (detection limit).

The excellent performance shown by the two hybrid catalysts SZ1CC1 and SZ2CC3 showed that addition of calcium carbide had improved their activities towards HDPE conversions by increasing their liquid yields and promoting virtually no coke formation. This is clear indication that addition of the calcium carbide, which reduced the acidic strength of the resultant mixture, has tremendously lead to the improvement of liquid yield. This was a huge improvement compared to the SZ, which even though showed an excellent performance with 98.5wt% conversion, had a liquid yield of only 34.3wt% and 1.5wt% residue. The 1.5wt% residue is somehow lower than the TGA results, where 5w% residue was obtained, when using 10wt% SZ (see Section 4.4). The 1:1 catalyst to HDPE ratio used might be responsible.
Figure 6.2 Comparison of the product yield obtained from HDPE conversions in the presence of the SZ, CC and the hybrid catalysts SZ1CC4 to SZ4CC1 at 400°C, 30min residence time and 1:1 catalyst to HDPE ratio.

6.2.3 Comparison of liquid yields from HDPE degradation with the changes in bulk compositions of CaO, ZrO$_2$ with total ammonia desorbed due to strong acid strength and SO$_4^{2-}$ with increasing calcium carbide addition

One of the aims of this research is to improve the liquid yield, which is currently the most economic important hydrocarbon component. This section will examine the bulk chemical compositions that promote high liquid yields. The catalysts with such composition will be taken further for more detailed research. In that regard, Figure 6.3 compares the liquid yields with the changes in bulk compositions of CaO, ZrO$_2$ with the total ammonia desorbed due to strong acid strength and SO$_4^{2-}$ as CC addition increased. The liquid yield was 34.3wt% in the presence of the sulphated zirconia SZ, which had the highest total ammonia desorbed of 206.0µmNH$_3$/g, ZrO$_2$ content of 93.4Mol%, SO$_4^{2-}$ content of 6.6Mol% and CaO content of < 0.1Mol%. With the addition of 20wt% calcium carbide SZ4CC1, the liquid yield slightly decreased to 33.0wt% as the total ammonia desorbed and ZrO$_2$ decreased to 130.0µmNH$_3$/g and 27.4Mol%, respectively.
while CaO and SO$_4^{2-}$ content increased to 28.5 and 7.6Mol%, respectively. With further calcium carbide addition to 40 to 50wt% (SZ3CC2 to SZ1CC1), the liquid yield increased and reached a peak of 54.0wt%, where the total ammonia desorbed, SO$_4^{2-}$ contents and ZrO$_2$ decreased to 19.4µmNH$_3$/g, 2.4Mol% and 8.7Mol%, respectively while CaO increased to 42.1Mol%. With further increase in calcium carbide addition to 80wt% SZ1CC4, the liquid yield suddenly dropped to its lowest level around 5.0wt% as the CaO and total ammonia desorbed increased to 52.1Mol% and 81.4µmNH$_3$/g while ZrO$_2$ and SO$_4^{2-}$ decreases to < 0.1 and 1.8Mol%, respectively. In the presence of the CC1 which had a total desorbed of 133.0µmNH$_3$/g, ZrO$_2$ and SO$_4^{2-}$ of < 0.1Mol% and CaO of 53.1Mol%, the liquid yield was only 12.3wt% but with the lowest HDPE conversion of less than 20wt%. This shows that the liquid yields increased with decreasing ZrO$_2$, SO$_4^{2-}$ contents and total ammonia desorbed as CaO content increased until a maximum liquid yield was obtained (see green circle). This coincides with where total ammonia desorbed, SO$_4^{2-}$, CaO and ZrO$_2$ showed nonlinear trend. Overall, there is clear correlation between liquid yield increase and reduction in acidic strength shown by the decreased in total ammonia desorbed and SO$_4^{2-}$ content up to the hybrid catalyst SZ1CC1, which obviously had moderate acidity. After which the liquid yield decreases while the SO$_4^{2-}$ content decreased but total ammonia desorbed increased again, which was linked to adsorption due to CaO.
Figure 6.3 Comparison of liquid yields obtained from HDPE conversations in relation to the changes in the surface and bulk compositions of all the catalysts tested.

It is worth noting here that the hybrid catalysts SZ1CC1 and SZ2CC3, which gave the highest liquid yields happened to be in the range where major shifts in terms of bulk composition occurred as shown on Figure 6.3. Correspondingly, a new compound phased indexed calcium zirconium oxide was identified on XRD spectra of these hybrid catalysts, which is believed to have been formed due to interaction between ZrO$_2$ and CaO (see Section 5.5.3), where in particular SZ1CC1 may contained significant proportion of the new compound (see blue circle on Figure 5.2 in Section 5.2.2). The new compound could possibly play a significant role in promoting the high liquid yield observed and may as well helped in redirecting the selectivity of the new hybrid catalyst towards a hydrocarbon composition required for a liquid to be used as transport fuel and chemicals for industrial use. It is not mere coincidences that high liquid yields were obtained in the presence of hybrid catalysts SZ2CC3 and SZ1CC1 but something that had already been hypothesised by findings in the preceding chapters, where addition of calcium carbide was shown to have moderated the acidity of the new hybrid catalysts by changing the liquid to gas ratio.
The hybrid catalysts SZ1CC1 and SZ2CC3 have shown the best compositions with high conversion, maximum liquid yields and minimal residue content at 400°C. The sulphated zirconia SZ and hybrid catalysts SZ4CC1 and SZ3CC2 also showed good catalytic performance, but appeared to be promoting high gas yield. The CC and the hybrid catalyst SZ1CC4 did not show sign of good performance, since significant amount of polymer remains unconverted when they were used. The sudden sharp increase in the liquid yield in the presence of hybrid catalysts SZ1CC1 and SZ2CC3 as well subsequent increase in gas yield in the presence of the hybrid catalysts SZ3CC2 and SZ4CC1 and the sulphated zirconia SZ could also be linked with other physical and chemical changes in the composition of the catalysts, particularly acidic strength, which occurred as the calcium carbide addition increased (see Section 5.7).

6.2.4 Ranking of all the catalysts based on high liquid yield obtained from HDPE conversion.

Table 6.1 summarises the catalytic conversion of the HDPE polymer using the two principal catalysts, the sulphated zirconia SZ and the calcium carbide CC and the five of the hybrid catalysts SZ4CC1 to SZ1CC4. The performance of the catalysts towards HDPE conversion was used to rank them based on their ability to promote high liquid yields and low char residue. In terms of the liquid product yields, which is considered to be the most important component, hybrid catalysts SZ2CC3 and SZ1CC1 gave the highest yields of 54.0wt% and thus were ranked the best among all the catalysts tested. This was followed by the hybrid catalyst SZ3CC2 with 41.0wt%, then sulphated zirconia SZ and SZ4CC1 with 34.0wt% and 33.0wt%, respectively. The calcined CC and the hybrid catalyst SZ1CC4 were ranked the lowest with liquid yields of only 12.0wt% and 5.0wt%, respectively. The ranking of the sulphated zirconia SZ, calcined CC and the five hybrid catalysts SZ4CC1 to SZ1CC4 is simplified in the following sequence, SZ2CC3 and SZ1CC (54wt%) > SZ3CC2 (41wt%) > SZ (34.0wt%) > SZ4CC1 (33.0wt%) > CC (12.0wt%) > SZ1CC4 (5.0wt%). However, the calcined CC was ranked the lowest due to its poor conversion ability and having the highest unconverted residue of nearly 82.0wt%.

It is evident that addition of calcium carbide from 20 to 60wt% increased the liquid yields, whereas further calcium carbide additions above 60wt% leads to the lowest liquid yield and HDPE conversion. Low $SO_4^{2-}$ content in both CC and SZ1CC4
is believed to be responsible for the low conversions. Low liquid yield observed by hybrid catalysts SZ3CC2 and SZ4CC1 and the sulphated zirconia SZ, despite recording excellent conversion, is believed to be due their large acid strength and SO$_4^{2-}$, which possibly caused excessive cracking leading to low liquid yields. This is evidenced as the liquid yield increased with decreasing the total ammonia desorbed, except for the calcined CC and hybrid catalyst SZ1CC4, whose sudden increase in ammonia desorption were believe to be due to ammonia adsorption CaO. Hence possessed very weak acidic strength shown by their very low SO$_4^{2-}$ content, which was not enough to execute the efficient HDPE cracking (see Section 4.5). The high activity and lower L/G ratio associated with the sulphated zirconia SZ and the hybrid catalyst SZ4CC1 is a typical example of catalysts with very strong acidic strength. The acidic strength of the these catalysts perhaps led to excessive cracking during the HDPE conversion, which gave rise to light hydrocarbon and thus low liquid yields (Miskolczi et al., 2009, Aguado et al., 2009). Although, calcined CC on its own did not give much appreciable conversion, its mixture with the sulphated zirconia SZ improved the activity towards high liquid yields probably by moderating the overall acidity of the mixture.

Table 6.1 Ranking of the catalysts based on the liquid yield each produced and their catalytic activities during the catalytic conversion of HDPE at 400°C, 30 min residence time and 1:1 HDPE to catalyst ratio.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Liquid yield (wt%)</th>
<th>Gas yield (wt%)</th>
<th>Conversion (wt%)</th>
<th>Residue (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SZ1CC1</td>
<td>54.0</td>
<td>46.0</td>
<td>99.9</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>SZ2CC3</td>
<td>54.0</td>
<td>46.0</td>
<td>99.9</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>SZ3CC2</td>
<td>41.0</td>
<td>59.0</td>
<td>99.9</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>SZ</td>
<td>34.2</td>
<td>64.3</td>
<td>98.5</td>
<td>1.5</td>
</tr>
<tr>
<td>SZ4CC1</td>
<td>33.0</td>
<td>66.0</td>
<td>99.0</td>
<td>1.0</td>
</tr>
<tr>
<td>SZ1CC4</td>
<td>12.3</td>
<td>6.2.0</td>
<td>18.5</td>
<td>81.5</td>
</tr>
<tr>
<td>CC</td>
<td>5.0</td>
<td>16.82</td>
<td>21.8</td>
<td>78.2</td>
</tr>
</tbody>
</table>

The hybrid catalyst SZ1CC1 appeared as the best catalyst for plastic waste conversion going by its excellent HDPE conversion of nearly 100 wt%, which was achieved at only 400°C in just 30 min residence time. It also demonstrated excellent performance by promoting higher liquid yields. In view of this, the hybrid catalyst SZ1CC1 was taken further to find the best reaction conditions that will promote more
Chapter 6 – HDPE Catalytic Conversions and Temperature Optimisation

liquid yield and direct the selectivity towards hydrocarbon compounds of interest and compare its performance with the sulphated zirconia.

### 6.3 Optimisation of reaction temperature during HDPE conversion in the presence of the SZ and the hybrid catalyst SZ1CC1

The study of temperature optimisations were carried out for HDPE conversions using the SZ and the hybrid catalyst SZ1CC1 due to their excellent performance at 400°C in Section 6.2, in particular the high liquid yield of 54.0wt% obtained in the presence of the hybrid catalyst SZ1CC1. The optimisation was carried out to study the effect of temperature on the catalytic performances and the liquid yields of the two catalysts. The conversions of HDPE were optimised at temperatures ranging from 370 to 430°C in the presence of the sulphated zirconia SZ and the hybrid catalyst SZ1CC1, where all other conditions were kept constant as described in Section 3.4.2.

#### 6.3.1 The SZ temperature dependence on the HDPE conversion and resultant product yields

Figure 6.4 compares the average hydrocarbon product yields from HDPE conversion in the presence of the sulphated zirconia SZ over temperature range from 370 to 430°C. The liquid fraction yield was 35.0wt% at 370°C, but as the temperature increased to 380°C the liquid yield increased to 39.0wt%. With further temperature increase to 390°C and 430°C, the liquid yields decreased with increasing temperature, where lowest liquid yield of 32.0wt% was obtained at 430°C. The gaseous fractions were 63.0wt% and 59.0wt% at 370 and 380°C, respectively, but increased as the temperature increased from 400°C to 430°C, where the highest gas yield of 68.0wt% was obtained. This is in line with what was expected from the catalysts with high acidity as discussed in Section 2.5.4. The fraction of solid residue was 2.0wt% at 370, 380 and 390°C, but decreases as the temperature increased to 400°C and 430°C, where it finally decreased to < 0.1wt% at 430°C. This shows that in terms of liquid yields, 380°C and 390°C may be the best temperatures for HDPE degradation using sulphated zirconia catalyst. Hence, 380°C being the temperature with the highest liquid and lowest gas yield may be regarded as the best temperature despite having 2.0wt% residue. Thus, 380°C is regarded as optimal temperature for HDPE degradation using the sulphated zirconia SZ. This additionally showed that the sulphated zirconia SZ has an excellent
catalytic activity and was able to convert up to 98% of HDPE to volatile hydrocarbon at temperature as low as 380°C with up to 39wt% liquid.

Figure 6.4 Comparison of products yield from HDPE conversions at 370-430°C using the sulphated zirconia SZ under 30cl/min N₂ flow, 30 min residence time and 1:1 HDPE to catalyst ratio.

6.3.2 The hybrid catalyst SZ1CC1 temperature dependence on the product yields

Figure 6.5 compares the average hydrocarbon product yields from HDPE conversion in the presence of the hybrid catalyst SZ1CC1 over the temperature range 370 to 430°C. The liquid fraction yield was initially 23.0wt% at 370°C, but as the temperature increased to 380°C to 410°C, the liquid yields increased and reached the highest yield of 66.0wt% at 410°C and then decrease slightly with increasing temperature down to 58.0wt% at 430°C. The gas fraction yield was 65.0wt% at 370°C, but decreases as the temperature increased to 380°C to 410°C, where the yield was lowest at 34.0wt% at 410°C. With further increase in temperature to 420°C and 430°C the yield then increased slightly to 36 and 42wt%, respectively. The solid residue was considerable at 370°C with a value of 12.0wt%, but decreased to 5.0 and 4.0 as the temperature increased to 380 and 390, respectively. With further increase in temperature
to 400, 410 and 430°C, the solid residue significantly decreased down to less than 0.1 wt%. This showed that in the presence of hybrid catalyst (SZ1CC1), the liquid yield increase was promoted by the increase in temperature. This is against what was obtained using the acidic SZ, where the liquid yield decrease with increasing temperature. The acidity moderation by calcium carbide addition probably played a major role in improving the liquid yield and conversion rate as well reducing the char residue to zero.

Based on this, 410°C appeared the optimal temperature for HDPE conversion using the hybrid catalyst SZ1CC1, where the highest liquid yield of 66.0 wt%, zero char residue and 100% conversion were achieved. The optimal temperature of 410°C was found to be low compared to the temperatures reported elsewhere in similar works using other catalysts (Wei et al., 2010, Huang et al., 2010, López et al., 2011, Park et al., 1999)

![Figure 6.5 Comparison of products yield from HDPE conversions at 370-430°C using hybrid catalyst SZ1CC1 under 30cl/min N2 flow, 30 min residence time and 1:1 HDPE to catalyst ratio.](image)
6.3.3 *Comparison of the effect of temperature variation on the liquid yields in the presence of the sulphated zirconia SZ and the hybrid catalyst SZ1CC1*

Figure 6.6 compares the liquid yields from HDPE conversions in the presence of the SZ and the hybrid catalyst SZ1CC1 across the temperature range from 370 to 430°C. In the presence of the SZ, the liquid yield at 370°C was 35.0wt%, which increased to its highest yield of 39.0wt% after increasing the temperature to 380°C, and then decreased down to its lowest yield of 32.0wt% with increasing temperature to 430°C. However, in the case of the hybrid catalyst SZ1CC1, the liquid yield at 370°C was only 23.0wt%, but increased to the highest yield of 66.0wt% with increasing temperature to 410°C. The liquid yield then decrease with increasing temperature to 430°C. This shows that, the highest liquid yield of 39wt% was achieved in the presence of the SZ after increasing temperature from 370 to 380°C and then decreases continuously with increasing temperature up to 430°C. But in the presence of the hybrid catalyst SZ1CC1, the liquid yield continue increasing with increasing temperature from 370 until 410, where the highest yield of 66.0wt% was obtained and then decrease slightly with increasing temperature. In comparing the effect of temperature variation, it is obvious that the two catalysts responded differently in terms of liquid yields. In the presence of the hybrid catalyst SZ1CC1, increase in temperature from 370 to 410°C significantly favoured liquid yields increase. With further increase in the temperature from 420 and 430°C the hybrid catalyst SZ1CC1 showed slight increase in gaseous product yields, but sulphated zirconia showed continued significant increase in gaseous yields over liquid. There was a similar slope at the temperature of optimal liquid yields for both catalyst, but for the hybrid catalyst SZ1CC1 the presence of calcium carbide delayed the gasification until at high temperature above 420°C. The high gas yield property associated with the SZ with increasing temperature may not be unconnected with its strong acidity, which on its own promote high gas yield. The hybrid catalyst SZ1CC1 on the other hand showed excellent performance with high liquid yield despite temperature increase. This could however be due to moderation of its acidity by calcium carbide addition, which is major cause of high gas yields as discussed in Section 2.5.4 (López et al., 2011, Angyal et al., 2009, Miskolczi et al., 2004b).
Chapter 6 – HDPE Catalytic Conversions and Temperature Optimisation

6.4 Summary

The HDPE was converted using a fixed-bed reactor in the presence of the SZ, the calcium carbide CC and the five hybrid catalysts SZ1CC4 to SZ4CC1 to choose the best catalysts with a high performance towards HDPE conversion. The hybrid catalyst SZ1CC1 showed the best performance in terms of HDPE conversion and liquid yield. Thus, sulphated zirconia SZ, which is one of the two principal catalysts, and the hybrid catalyst SZ1CC1 were selected for further study through temperature optimisations in the range of 370 to 430°C. This was to ascertain the influence of the temperature variation on the HDPE conversion and liquid yields. Based on the temperature optimisations results in Figures 6.4 to 6.6, 380 and 410°C were considered the temperatures of optimal liquid yields for the SZ and the hybrid catalyst SZ1CC1, respectively. However, the hybrid catalyst SZ1CC1 proved better than the SZ in terms of promoting high liquid yield and total conversion. It is believed that the moderate acidity of the hybrid catalyst SZ1CC1 was responsible for its excellent performance, which was moderated by the addition of appropriate amount of the CC to the SZ.
Therefore, analyses of the hydrocarbon composition of the liquid and gaseous fractions obtained at these temperatures of optimal liquid yields were carried out to further understand the catalytic effect of both catalysts on the hydrocarbon compositions and their selectivity.
Chapter 7 – PRODUCTS COMPOSITIONAL ANALYSES

7.1 Introduction

This chapter presents the results of the hydrocarbon compositional analysis of the liquid and gaseous products obtained from the HDPE conversions using the sulphated zirconia SZ1CC1 at 380°C and the hybrid catalyst SZ1CC1 at 410°C, as identified in Chapter 6 as the temperatures where each catalyst has its maximum liquid yield. The hydrocarbon compositions of the gaseous and the liquid fractions obtained at the temperature of optimal liquid yields were analysed using GC/FID/TCD and GC/MS, respectively, to study the selectivity of the two catalysts towards different hydrocarbon compounds. Catalyst deactivation and regeneration were also investigated. All the results of products composition discussed here are qualitative due to the difficulty faced in obtaining the pure reference compounds to be used for calibration of instrument during the analysis. This is why in comparing the compounds selectivity and yields all products peak areas were presented as only relative amount of the compounds, which is merely qualitative.

7.2 Compositional analysis of the gaseous product obtained in the presence of the sulphated zirconia SZ at 380°C and the hybrid catalyst SZ1CC1 at 410°C.

Figure 7.1 compares the GC/FID/TCD chromatograms of the gaseous products obtained from thermal conversion of HDPE in the presence of the SZ at 380°C with hydrocarbon compounds identified by FID (A) and non-hydrocarbons by TCD (B). Seventeen peaks representing various hydrocarbon compounds were identified in the FID chromatogram (A) labelled with peak numbers 1 to 17. There was a distribution of peak heights as expected for an acidic catalyst (see Section 2.8.4). Two peaks representing hydrogen and nitrogen gases were detected in the TCD (B) chromatogram and labelled with peak numbers 18 and 19. The line right before Peak 19 representing the carrier gas N₂ was one point baseline error by the FID detector.
Figure 7.1 GC/FID/TCD Chromatograms of the gaseous product obtained from thermal conversion of HDPE in the presence of the SZ at 380°C for hydrocarbon using FID (A) and non-hydrocarbon using TCD (B).

Figure 7.2 compares the GC/FID/TCD chromatograms of the gaseous products obtained from thermal conversion of HDPE in the presence of the hybrid catalyst SZ1CC1 at 410°C, where the hydrocarbon compounds were identified by FID (A) and non-hydrocarbons by TCD (B). Seventeen peaks representing various hydrocarbon compounds were identified in FID chromatogram labelled with peak numbers 1 to 17. Two peaks representing hydrogen and nitrogen gases were detected in the TCD chromatogram and labelled with peak numbers 18 and 19. Comparing Figures 7.1 and 7.2, it is obvious that Peaks 1 to 4, 6 and 12 are more pronounced in Figure 7.1 than in Figure 7.2. On the other hand, in Figure 7.2, Peaks 8, 9, 11, 14 to 17 are more...
pronounced than in Figure 7.1, while no marked difference were observed among the rest of the peaks from Figure 7.1 and Figure 7.2. The compounds were qualitatively identified and the amount of each was quantified by dividing the percentage area of each peak by the total peak area of all the peaks times the total gas percentage in wt%.

Table 7.1 lists the detailed description of all the peaks identified in Figures 7.1 and 7.2, including their names and corresponding volume percentages. Table 7.1 shows that the gaseous products obtained using both the SZ and the hybrid catalyst SZ1CC1 contain a broad mixture of hydrocarbon compounds (C1 to C5). The gaseous fraction obtained in the presence of sulphated zirconia SZ, contained 59.9 wt% of C1 to C4.
hydrocarbon, which was slightly higher than 54.9 wt% of the gases obtained using the hybrid catalyst SZ1CC1. However, the C5 gaseous fraction was larger for the hybrid catalyst SZ1CC1 with 44.5 wt% compared to that obtained using the SZ with 39.7 wt%. The high composition of gases with lower carbon atoms in the gas obtained when using the SZ could be linked to high acidic strength associated with its large \( \text{SO}_4^{2-} \) content (see Section 6.2), which may promote excessive cracking. For the light hydrocarbon compounds C1 and C2 very low level were detected. The amount of the C1 and C2 compounds appeared particularly low in the presence of the hybrid catalyst SZ1CC1 with only 0.21wt%. Even though, the time in between the sample collections and analysis was very short, usually around 15 to 20 minutes, it is very possible that some portion of the lighter components were lost during the process as it was not online analysis. Gaseous products from both catalysts showed increasing order of hydrocarbon compounds distribution in order of increasing carbon atom number in the following order, C1 < C2 < C3 < C4 < C5. Hydrogen was also detected using both catalysts with 0.44 wt% in the presence of the SZ and 0.56 wt% for the hybrid catalyst SZ1CC1. What is interesting was the marked difference between the alkanes and alkenes as discussed in the next section.
Table 7.1 Comparisons of the compositions of hydrocarbon and non-hydrocarbon compounds in the gaseous products obtained from the thermal conversions of HDPE using the SZ and the hybrid catalyst SZ1CC1.

<table>
<thead>
<tr>
<th>Peak Label</th>
<th>Retention time</th>
<th>Carbon No.</th>
<th>Compound names</th>
<th>SZ (wt %)</th>
<th>SZ1CC1 (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.11</td>
<td>H2</td>
<td>Hydrogen</td>
<td>0.44</td>
<td>0.56</td>
</tr>
<tr>
<td>2</td>
<td>2.109</td>
<td>C1</td>
<td>Methane</td>
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<tr>
<td>3</td>
<td>2.556</td>
<td>C2</td>
<td>Ethane</td>
<td>0.22</td>
<td>0.06</td>
</tr>
<tr>
<td>4</td>
<td>3.07</td>
<td>C2</td>
<td>Ethene</td>
<td>0.42</td>
<td>0.10</td>
</tr>
<tr>
<td>5</td>
<td>4.565</td>
<td>C3</td>
<td>Propane</td>
<td>2.25</td>
<td>0.62</td>
</tr>
<tr>
<td>6</td>
<td>8.51</td>
<td>C3</td>
<td>Propene</td>
<td>9.48</td>
<td>11.58</td>
</tr>
<tr>
<td>7</td>
<td>12.45</td>
<td>C4</td>
<td>Iso-butane</td>
<td>24.62</td>
<td>4.19</td>
</tr>
<tr>
<td>8</td>
<td>14.19</td>
<td>C4</td>
<td>n-Butane</td>
<td>1.63</td>
<td>0.70</td>
</tr>
<tr>
<td>9</td>
<td>18.91</td>
<td>C4</td>
<td>Trans-2-butene</td>
<td>5.33</td>
<td>7.97</td>
</tr>
<tr>
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<td>C4</td>
<td>1-Butene</td>
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<tr>
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<td>C4</td>
<td>Iso-butene</td>
<td>9.19</td>
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<td>C4</td>
<td>Cis-2-butene</td>
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<td>5.81</td>
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<td>Cyclopentane</td>
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<td>3.19</td>
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<td>n-Pentane</td>
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<td>0.96</td>
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<tr>
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<td>C5</td>
<td>Trans-2-Pentene</td>
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<td>7.95</td>
</tr>
<tr>
<td>16</td>
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<td>3-Methyl-1-Butene</td>
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<td>17</td>
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<td>1-Pentene</td>
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<tr>
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<td>24.31</td>
<td>C5</td>
<td>Cis-2-Pentene</td>
<td>1.66</td>
<td>5.22</td>
</tr>
</tbody>
</table>

7.2.1 Comparison of selectivity towards saturated or unsaturated hydrocarbons in the gaseous products obtained in the presence of the SZ and the hybrid catalyst SZ1CC1.

Figure 7.3 compares the catalyst selectivity towards saturated (alkanes) and unsaturated (alkenes) hydrocarbons for the gaseous products obtained in the presence of the SZ and the hybrid catalyst SZ1CC1. In the presence of the SZ the composition of hydrocarbons in the gaseous fraction appeared to contain nearly the same amount of alkane of 49.9wt% and alkene 50.1wt% compounds. However, in the presence of hybrid catalyst SZ1CC1 the composition of hydrocarbons in the gaseous fraction had a higher amount of alkenes of 89.7wt% than alkanes of only 9.7wt%. This is expected as the SZ
had high acidity and has been associated with excessive cracking of the polymer chain and volatile products, which results in high gaseous products that may contain large amount of alkanes (see Section 2.5.4). It might be possible that this formation is associated with the formation of aromatics and excess hydrogen through secondary reactions. The hydrogen, was then perhaps used to form more saturated hydrocarbon compounds in the gas as also evidenced by the low amount of hydrogen (0.44wt%) in the gaseous fraction (Uemichi et al., 1984). The gas composition when using the hybrid catalyst SZ1CC1 showed that alkenes were dominant in the gaseous fractions. The results indicated that a different mechanism has taken place, probably as a result of primary $\beta$-scission (see Equation 2.5 Section 2.5.2). This may be the reason the coke fraction obtained in the presence of hybrid catalyst SZ1CC1 was < 0.01wt% (see Section 4.5). Overall, the hybrid catalyst SZ1CC1 appeared to have more selectivity towards heavier alkene hydrocarbon than the SZ indicating a low aromatic content in their corresponding liquids.

![Figure 7.3 Comparison of the catalysts selectivity towards either saturated or unsaturated hydrocarbons in the gaseous products obtained from the thermal conversion of HDPE using the SZ at 380°C and the hybrid catalyst SZ1CC1 at 410°C.](image)

*Figure 7.3 Comparison of the catalysts selectivity towards either saturated or unsaturated hydrocarbons in the gaseous products obtained from the thermal conversion of HDPE using the SZ at 380°C and the hybrid catalyst SZ1CC1 at 410°C.*
7.3 Hydrocarbon compositional analyses of the liquid products obtained at 380°C for the sulphated zirconia SZ and 410°C for hybrid catalyst SZ1CC1.

This section presents the detailed results of the hydrocarbon compositional analyses of the liquid fractions obtained using the SZ at 380°C and the hybrid catalyst SZ1CC1 at 410°C, where optimal liquid yields were obtained (see Section 6.3). The liquid products at the optimal temperatures have been selected as representative samples for detailed analysis to compare the selectivity of the two catalysts.

7.3.1 Hydrocarbon compositional analysis of the liquid product obtained in presence of the sulphated zirconia SZ at 380°C

Figure 7.4 shows the GC/MS chromatogram of the liquid fraction obtained from the catalytic conversion of HDPE at 380°C in the presence of the sulphated zirconia SZ. Fifty prominent peaks labelled 1-50, accounting for about 85% of the total peak area, were identified and named using the available GC/MS library. The peak areas were used to quantitatively determine the relative amount of each compound and its carbon number distribution in the liquid. The relative amounts were calculated based on the weight% of the liquid fraction with respect to the amount of HDPE converted. The peaks representing the most abundant compounds were found between 7 and 22 minutes retention time, while the least predominant compounds appeared between 23 and 29 minutes. The detailed analytical methodology has been described in Section 3.5.3.
Figure 7.4 The GC/MS chromatogram of the liquid fraction obtained at 380°C using the SZ within 30 min residence time under 30cl/min N₂ using 1:1 HDPE catalyst ratio. A total of 50 peaks labeled 1-50 were identified.
Table 7.2 gives the detailed summary of the fifty most abundant peaks identified from the GC/MS chromatogram of the liquid product obtained at 380°C where the optimal liquid yield was obtained in the presence of the SZ. Each of the fifty peaks was identified by its retention time, peak area, molecular formula and the name of the compounds it represented. The compounds identified comprise all the four main groups of hydrocarbon compounds, namely paraffin, olefins, naphthens and aromatics, in different proportions. This shows that the sulphated zirconia SZ had mainly promoted paraffinic and aromatic hydrocarbon compounds, whose carbon atoms distribution range was between C8 to C13, which are within the gasoline range (see Section 2.5.6.2). Hence, the SZ appeared to have promoted the conversion of HDPE to liquid fraction with hydrocarbon compounds composed of carbon atoms largely within the gasoline range. However, the high selectivity towards aromatic compounds could explain the tendency to form coke (see Section 4.4) and could be detrimental for its reuse.
Table 7.2 Detailed peak analyses of the fifty peaks identified from the GC/MS chromatogram of the liquid product obtained in the presence of the SZ at 380°C, 30 min residence time and 1:1 HDPE to catalyst ratio.

<table>
<thead>
<tr>
<th>Peak No</th>
<th>Retention time</th>
<th>Peak Area</th>
<th>Molecular Formula</th>
<th>Compounds Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.732</td>
<td>5.36E+03</td>
<td>C7H14</td>
<td>3-Heptene</td>
</tr>
<tr>
<td>2</td>
<td>6.773</td>
<td>3.48E+06</td>
<td>C8H16</td>
<td>3-Ethyl-2-methylpent-2-ene</td>
</tr>
<tr>
<td>3</td>
<td>7.001</td>
<td>9.41E+06</td>
<td>C8H18</td>
<td>2-Methylheptane</td>
</tr>
<tr>
<td>4</td>
<td>7.18</td>
<td>6.95E+06</td>
<td>C8H18</td>
<td>2-Methylheptane</td>
</tr>
<tr>
<td>5</td>
<td>7.468</td>
<td>4.55E+06</td>
<td>C8H16</td>
<td>6-methylhept-2-ene</td>
</tr>
<tr>
<td>6</td>
<td>7.611</td>
<td>4.43E+06</td>
<td>C8H16</td>
<td>3-Ethylhex-2-ene</td>
</tr>
<tr>
<td>7</td>
<td>7.839</td>
<td>8.99E+06</td>
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</tr>
<tr>
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<td>3,5-Dimethylhex-2-ene</td>
</tr>
<tr>
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<td>8.445</td>
<td>5.07E+06</td>
<td>C8H18</td>
<td>3-Ethylhexane</td>
</tr>
<tr>
<td>10</td>
<td>8.779</td>
<td>1.35E+07</td>
<td>C9H20</td>
<td>3,5-Dimethylheptane</td>
</tr>
<tr>
<td>11</td>
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<td>C9H18</td>
<td>4-Ethylhept-3-ene</td>
</tr>
<tr>
<td>12</td>
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<td>C9H18</td>
<td>4-Ethylhept-3-ene</td>
</tr>
<tr>
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<td>1,2,3-trimethylcyclohexane</td>
</tr>
<tr>
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<td>C8H10</td>
<td>p-xylene</td>
</tr>
<tr>
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<tr>
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<td>cis-4-Nonene</td>
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<tr>
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</tr>
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</tr>
<tr>
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</tr>
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<tr>
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</table>
Table 7.2 Continuation.

<table>
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<tr>
<th>Peak No</th>
<th>Retention time</th>
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<th>Compounds Name</th>
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<tbody>
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<td>C11H22</td>
<td>1-Pentyl-2-propylcylopropane</td>
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<td>1,2,3,4-Tetramethylbenzene</td>
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<tr>
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<td>C11H16</td>
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</tr>
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7.3.2 Hydrocarbon compositional analysis of the liquid product obtained in the presence of the hybrid catalyst SZ1CC1 at 410°C

Figure 7.5 is a GC/MS chromatogram of the liquid products obtained from the catalytic conversion of HDPE in the presence of the hybrid catalyst SZ1CC1 at 410°C, where optimal liquid yield was obtained. Eighty two peaks, labelled 1-82, accounting for about 95% of the total peak area were identified and named using the available GC/MS library. The peak areas were used to quantitatively determine the relative amount of each compound in the liquid. The relative amounts were calculated based on the weight% of the liquid fraction with respect to the amount of HDPE converted. The peaks representing the most abundant compounds were shifted from 7 to 22 minutes for sulphated zirconia to 5- 20 minutes retention time for the hybrid catalyst SZ1CC1. The least predominant compounds were found at 21-24 minutes for the hybrid catalyst SZ1CC1 compared to 23-29 minutes for the SZ. All the peaks were identified and their carbon member distributions were found to be between C7 and C14.
Figure 7.5 The GC/MS chromatogram of the liquid product obtained in the presence of the hybrid catalysts SZ1CC1 catalyst at 410°C where an optimum liquid yield was obtained during the conversion of HDPE. A total of 82 peaks labeled (peak 1-82) were identified.
Table 7.3 give the detailed summary of the eighty two most abundant peaks identified from the GC/MS chromatogram of the liquid fraction obtained in the presence of hybrid catalyst SZ1CC1 at 410°C, where the optimal liquid yield was obtained. Each of the eighty two peaks was identified by its retention time, peak area, molecular formula and the name of the compound it represents. The compounds identified composed of only three of the four main group hydrocarbons, namely, paraffins, olefins, and naphthens in different proportions. Unlike in the presence of the sulphated zirconia SZ, no aromatic hydrocarbon was identified using the hybrid catalyst SZ1CC1. For carbon number distributions of the hydrocarbon compounds in the liquid fraction, all the compounds identified from the 82 peaks have their carbon atoms between C7 and C14, where compounds with carbon atoms, C8 to C12 constituted the largest number of compounds, which accounted for 85% of all the compounds in the liquid fraction. The remaining compounds with carbon number, C7, C13 and C14 accounted for the only 15% of the liquid fraction. This shows that the hybrid catalyst SZ1CC1 had mainly promoted the formation of olefinic and some naphthenic hydrocarbon compounds, whose carbon atoms distribution range was mainly C7 to C12 that are again within the gasoline range (see Section 2.5.6.2). Hence, the hybrid catalyst SZ1CC1 appeared to have promoted the conversion of HDPE to liquid fraction with hydrocarbon compounds composed of non-aromatic hydrocarbons within the gasoline range and with a high selectivity towards olefinic and naphthenic compounds.
Table 7.3 Detailed peak analyses of the eighty two peaks identified from the GC/MS chromatogram of the liquid product obtained at 410°C in the presence of the hybrid catalyst SZ1CCI at 30 min residence time, 1:1 HDPE to catalyst ratio.

<table>
<thead>
<tr>
<th>Peak No</th>
<th>Retention time</th>
<th>Molecular Formula</th>
<th>Peak Area</th>
<th>Compounds Name</th>
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<tr>
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</table>
7.4 **Comparison of the liquid products obtained using the SZ at 380 and hybrid catalyst SZ1CC1 at 410°C.**

This Section compares the colour appearance, the trend of each of the hydrocarbons, namely paraffins, olefins, naphthens and aromatics and their carbon number distributions in the liquid fractions to study the selectivity of the two catalysts and ascertain the applicability of the liquid products as fuel or chemical precursors.

7.4.1 **Colour comparison of the liquid products obtained in the presence of the SZ at 380°C and the hybrid catalyst SZ1CC1 at 410°C.**

Figure 7.6 compares the colour appearance of the liquids obtained in the presence of the SZ and hybrid catalyst SZ1CC1. Visual observation showed that the liquid obtained in the presence of the SZ is a dark yellow colour, whereas the one obtained in the presence of the hybrid catalyst SZ1CC1 appeared as a very pale yellow colour liquid. The colour difference suggests that the compositions of the liquids differ significantly. This supported the results in Sections 7.2 and 7.3, which showed that the liquids obtained using the SZ was mainly aromatic, that normally gives a dark yellow or brown coloured liquid probably due to the presence of chromophores in some aromatic compounds.
Figure 7.6 Comparison of the physical appearance of the liquid products obtained in the presence of the hybrid catalyst SZ1CC1 at 410°C and the SZ at 380°C where the optimal liquid yields were obtained.

### 7.4.2 Comparison of hydrocarbon compositions of the liquid products obtained using the SZ and the hybrid catalyst SZ1CC1

Figure 7.7 compares the hydrocarbon compositions of the liquid fractions obtained in the presence of the SZ at 380°C and hybrid catalyst SZ1CC1 at 410°C with respect to initial weight of converted HDPE. The liquid products were compared based on their paraffinic, olefinic, naphthenic and aromatic proportions. The compositions of each of the hydrocarbon group in the liquid fraction using the SZ were 6wt% paraffins, 8wt% olefins, 2wt% naphthenes and 22wt% aromatics. Aromatic compounds appeared to have the highest composition of 22wt%, which accounts for 58% of the entire liquid fraction followed by olefins and paraffins with 6 and 8wt% accounting for 16 and 21% of the liquid fraction, respectively. Naphthenes composition was 2wt%, which was the lowest and accounted for only 5% of the liquid fraction. The hydrocarbon composition of the liquid fraction using the hybrid catalyst SZ1CC1 were 3% paraffins, 74% olefins,
23% naphthenes and <0.1% aromatics. Olefinic and naphthenic compounds appeared to constitute the highest compositions accounting for 97% of the entire compounds in the liquid fraction. The same hydrocarbon compounds were reported elsewhere using other catalysts, such as, fluid catalytic cracking (FCC), BaCO$_3$ HZSM-5, Ga-ZSM-5, HNZ, clinoptilolite and silica-alumina (Jan et al., 2010, Miskolczi and Bartha, 2008, Nishino et al., 2008, Miskolczi et al., 2009, Park et al., 1999, López et al., 2011). However, the temperature reported in this work is lower than the temperatures reported elsewhere which were mainly between 430 to 500°C (Park et al., 1999, Miskolczi et al., 2009, Miskolczi and Bartha, 2008, López et al., 2011). The composition of the liquid obtained in the presence of the sulphated zirconia SZ appears to contain all the four main hydrocarbon compounds in different proportion. The relative amount of the paraffinic compounds in the liquid fraction obtained in the presence of the sulphated zirconia SZ was 6wt% compared to only 2wt% in the presence of the hybrid catalyst SZ1CC1, which indicates a hydrogen transfer reactions as identified in Section 7.2.1. In terms of the olefinic compounds, the relative amount in the presence of the SZ was only 8wt% compared to 49wt% for hybrid catalyst SZ1CC1. This again indicates a β-scission mechanism for the hybrid catalyst SZ1CC1. The relative amount of naphthenic compounds was only 2wt% in the presence of the SZ compared to 15wt% for the hybrid catalyst SZ1CC1 indicating that ring closing was a main mechanism for the hybrid catalyst SZ1CC1. Finally, the relative amount of aromatic compounds was 22wt% for the SZ compared to less than 0.1wt% for the hybrid catalysts SZ1CC1, which again supported the secondary cracking reaction assumption for the SZ.

Overall, this showed that the hydrocarbon compositions of the liquid fractions obtained in the presence of the two catalysts were significantly different. While the SZ promoted the formation of mainly aromatic and some paraffinic compounds, which accounted for 74% of all hydrocarbons, the hybrid catalyst SZ1CC1 facilitated the formation of mainly olefinic and some naphthenic compounds, which accounted for 97% with virtually no aromatics. This confirmed that the two catalysts had different selectivity towards different groups of hydrocarbon compounds. The physical appearance of the liquids from the two catalysts suggested this difference also (see Section 7.4.1). The SZ, which promoted large amount aromatic compounds showed comparable result with other catalysts reported elsewhere that produced large proportion of aromatic compounds, such as HZSM-5 (75.6%), HY (29.4%), HNZ (50.7%) and Ga-ZSM-5 (>80%) (Nishino et al., 2008, Park et al., 1999). The SZ catalyst possibly
promoted the production of aromatic compounds through secondary reactions during cracking of the HDPE chain possibly due to its strong acidic strength shown by the presence of a peak above 550°C, which represent very strong acidic strength, the large total ammonia desorption of 337.0µmolNH₃/g and high surface of 116.0m²/g,. However, the hybrid catalyst SZ1CC1 had moderate acidity shown by the absence of any desorption peak above 550°C, the low total ammonia desorption and low surface area of 23.4µmolNH₃/g and 23.1m²/g, respectively. This had promoted mainly branched olefinic and naphthenic compounds with aromatics below 0.1wt%. The distinction between the two catalysts could be linked to the change in properties, such as bulk compositions, morphology and acidity. Particularly, the textural property could be important, as catalyst with high total surface area and porosity is believed to promote secondary reactions that result in saturated and aromatic compounds as in Section 2.5.5 (Sharratt et al., 1997, Serrano et al., 2007a, Marcilla et al., 2009, Aguado et al., 2009).

![Figure 7.7](image_url)

*Figure 7.7 Comparison of the hydrocarbon composition of the liquid fractions obtained using the SZ at 380 and the hybrid catalyst SZ1CC1 at 410°C.*
7.4.3 Comparison of the carbon number distributions in the liquid fractions obtained in the presence of the sulphated zirconia SZ and the hybrid catalyst SZ1CC1

Figure 7.8 compares the carbon number distributions of the compounds in the liquid fractions obtained in the presence of the sulphated zirconia SZ and hybrid catalyst SZ1CC1 for HDPE conversion at 380 and 410°C, respectively. The liquid obtained in the presence of the sulphated zirconia SZ had carbon atoms ranging from C8 to C13, where C8 to C11 constituted the largest amount of 35wt%. The remaining compounds with carbon atoms C12 and C13 constituted only 4wt%. However, in the presence of the hybrid catalyst SZ1CC1 the distribution of carbon atoms of compounds in the liquid fraction was between C7 to C14, where C8 to C12 had the largest amount of 56wt%. The remaining compounds with carbon atoms, C7, C13 and C14 constituted of only 11wt%. This shows that the relative amounts of compounds with carbon atoms C7-C12, which is within the gasoline range (see Section 2.5.6.2), constituted the largest portion in both cases which indicates identical distribution that may suggest similar reaction pathways by both catalysts. For instance, the liquid obtained in the presence of the SZ had 35wt% of C7-C12, which constituted 96% of all the compounds, whereas, for the liquid fraction obtained in the presence of the hybrid catalyst SZ1CC1 the C7-C12 compounds was 59wt% and accounts for 90% of all compounds in the liquid. Hence, the liquid products obtained using both catalysts appeared as potential transport fuels due their significant amount of gasoline range hydrocarbon compounds (Miskolczi et al., 2009). The shift towards longer chained hydrocarbon for the hybrid catalyst SZ1CC1 also indicates that fewer secondary reactions have taken place. Also, it suggests that at 410°C the pure thermal cracking plays not a significant role which might change with increasing temperatures.
In this section, the hydrocarbon compositions of liquid products obtained across the temperatures (380 to 430°C) were analysed and compared to assess the impact of increasing conversion temperature on the liquid compositions. Ten major peaks representing different compounds at different residence times were selected from the GC/MS chromatogram of the all the liquid across the temperature range in the presence of both the SZ and the hybrid catalyst SZ1CC1. The composition of the liquid fractions at 370°C was not analysed due to poor conversion at that temperature, particular in the presence of the hybrid catalyst SZ1CC1 (see Figure 6.5 in Section 6.3)
7.5.1 Hydrocarbon compositional analysis of the liquid fraction obtained in the presence of the SZ from 380 to 430°C

Figures 7.9 compares the GC/MS chromatograms of the liquid products obtained from HDPE conversions in the presence of the SZ across the temperature range from 380 to 430°C. Ten major peaks (labelled 1-10) representing different hydrocarbon components were identified and named using the available GC/MS library. The peak areas of the ten peaks were used to quantitatively compare the relative amount of each hydrocarbon compound and their carbon number distribution across the temperature range 380-430°C. The ten peaks selected were between 10 to 28 minutes residence time since visual observations of the peaks on all the chromatogram showed that the most prominent peaks were situated between 8 and 26 minutes residence time. The peaks at the same resident time were selected for comparison purpose. For instance, peak one and two were selected at residence time 10.9 and 12.7 minutes for all the chromatograms of different temperature. Compounds identified for each peak and their peak areas were compared to find the impact of temperature change.
Figure 7.9 GC/MS chromatograms of the liquid fractions obtained at 380 to 430°C using the hybrid catalyst SZ1CC1 using 30 minutes residence time under 30cl/min N₂, 1:1 HDPE to catalyst ratio. The ten prominent peaks are labelled 1-10.
Table 7.4 summarises the detailed analysis of the ten peaks identified from each of the GC/MS chromatograms of the liquid fractions obtained in the presence of the SZ across the temperature range of 380 to 430°C. For each of the chromatograms, the retention time, peak area, molecular formula and the name of the compounds for each peak were analysed and listed in Table 7.4. After comparing the types of hydrocarbons identified from the ten major peaks, it was found that all the compounds identified were aromatics of different isomers. In terms of carbon number distribution, Peak1 was identified as C9 while Peak 2 to 5, Peak 6 and 8, Peak 7 and 9 and Peak 10 as C10, C11, C12 and C13, respectively. This shows that the SZ regardless of reaction temperature, promoted mainly aromatic compounds whose carbon number distribution was between C9 to C13. This is in line with the detailed results in Section 7.3, where the SZ appeared to promote mainly aromatic compounds with carbon atoms ranging from C8 to C13.

As the temperature increases from 380 to 430°C, there were little evidences of compositional changes among the hydrocarbon compounds across the temperatures range. For instance, Peak 1 found at 10.9 minute which represents C9H12 was identified as trimethyl benzene and remained the same in the liquid fractions at all the temperatures. This shows that mechanism of the hybrid catalyst SZ remains the same towards selectivity of hydrocarbon compounds across the temperature range. Therefore, apart from given the highest liquid yield, qualitatively this can justify the choice of only gaseous and liquid fractions at 380°C for detailed analysis made in Sections 7.2.1 and 7.3.1. However, to also assess impact of temperature changes quantitatively, compounds with same carbon atoms in each liquid fraction obtained across 380 and 430°C, were quantitatively analysed and compared.
Table 7.4 Comparison of hydrocarbon compounds for the ten selected peaks from the GC/MS chromatograms of the liquid fractions obtained over temperature range of 380 to 430°C using the SZ at 30 min residence time and a 1:1 HDPE to catalyst ratio.

<table>
<thead>
<tr>
<th>Peak label</th>
<th>Ret. Time</th>
<th>Mol. formula</th>
<th>380°C</th>
<th>390°C</th>
<th>400°C</th>
<th>410°C</th>
<th>420°C</th>
<th>430°C</th>
</tr>
</thead>
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<td>Compound’s name</td>
<td>Compound’s name</td>
<td>Compound’s name</td>
<td>Compound’s name</td>
</tr>
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<td>1,3,5-trimethyl benzene (6)</td>
<td>1,3,5-trimethyl benzene (7)</td>
<td>1,2,4-trimethyl benzene (7)</td>
<td>1,3,5-trimethyl benzene (8)</td>
<td>1,3,5-trimethyl benzene (8)</td>
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<td>12.7</td>
<td>C10H14</td>
<td>1-ethyl-3,5-dimethyl benzene (9)</td>
<td>1-ethyl-2,4-dimethyl benzene (10)</td>
<td>1-ethyl-2,4-dimethyl benzene (11)</td>
<td>1-ethyl-3,5-dimethyl benzene (9)</td>
<td>2-ethyl-1,4-dimethyl benzene (9)</td>
<td>1-ethyl-2,4-dimethyl benzene (10)</td>
</tr>
<tr>
<td>3</td>
<td>13.5</td>
<td>C10H14</td>
<td>1,2,3,4-tetramethyl benzene (7)</td>
<td>1-methyl-4-(1-methylethyl) benzene (6)</td>
<td>1-methyl-3-(1-methylethyl) benzene (6)</td>
<td>1-methyl-4-(1-methylethyl) benzene (6)</td>
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<td>1,2,3,5-tetramethyl benzene (6)</td>
</tr>
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<td>1-ethyl-2,3-dimethyl benzene (7)</td>
<td>1-ethyl-2,3-dimethyl benzene (6)</td>
<td>1-ethyl-2,3-dimethyl benzene (7)</td>
<td>1,2,3,4-tetramethyl benzene (7)</td>
<td>1,2,3,4-tetramethyl benzene (6)</td>
</tr>
<tr>
<td>7</td>
<td>17.6</td>
<td>C12H18</td>
<td>1,3,5-trimethyl-2-propylbenzene (8)</td>
<td>2,4-dimethyl-1-(1-methylethyl) benzene (7)</td>
<td>2,4-dimethyl-1-(1-methylethyl) benzene (6)</td>
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<tr>
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<td>22.7</td>
<td>C12H12</td>
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</tbody>
</table>

*The numbers in parenthesis represents peak areas
7.5.2 Comparison of the relative amounts of the hydrocarbon compounds in the liquid products obtained across the temperatures ranging from 380 to 430°C in the presence of the SZ

Figure 7.10 compares the relative amounts of the compounds represented by the ten prominent peaks selected from the GC/MS chromatograms of the liquid fraction obtained from 380 to 430°C in the presence of the sulphated zirconia SZ. As the temperature changes from 380 to 430°C there is slight evidence of increase in the relative amount of the lower hydrocarbon compounds of C9 and C10. This corresponds with a decrease in the relative amounts of C12, which changes from 20% at 380°C to 15% at 430°C due to a lowering in the number of alkyl substituents attached to benzene and naphthalene compounds. The slight increase in the relative amount of C9 and C10 compounds and a decrease in C12 could be due to large number of alkyl substituents in the C12 compounds which might have been dealkylated as the temperature increases. It is well known that the ease of dealkylation increases with temperature. The increase in the amount of gaseous hydrocarbon with increasing temperature in the presence of the sulphated zirconia SZ as showcased in Section 6.3.1 is strong evidence suggesting the occurrence of dealkylation reactions. This shows that in the presence of sulphated zirconia SZ, increasing the temperature does not only favour high gas fraction yield, it does also affect the compositions of the hydrocarbon compounds in liquid. However, the choice of liquid and gas fractions at 380°C as representative samples for detailed analysis in Sections 7.2.1 and 7.3.1 was based on fact that optimal liquid yield was obtained at that temperature.
Figure 7.10 Comparison of relative amounts of hydrocarbon compounds in the liquid fractions from 380 to 430°C in the presence of the sulphated zirconia SZ.

7.5.3 Hydrocarbon compositional analysis of the liquid fraction obtained in the presence of the hybrid catalyst SZ1CC1 from 380 to 430°C.

Figure 7.11 shows the GC/MS chromatograms of the liquid fraction obtained from HDPE conversions in the presence of the hybrid catalyst SZ1CC1 across the temperature range of 380 to 430°C. Ten major peaks labelled 1-10 representing different hydrocarbon components were identified and named using the available GC/MS library. The peak areas of the ten peaks were used to quantitatively compare the relative amount of each hydrocarbon compound and their carbon number distribution across the temperatures range of 380-430°C. The ten peaks selected were between 10 to 17 minutes residence time since visual observations of the peaks on all the chromatograms showed that, the most prominent peaks were situated between 8 and 26 minutes residence time.
Figure 7.11 GC/MS chromatograms of the liquid products obtained from 380 to 430°C using the hybrid catalysts SZ1CC1 within 30 min residence time under 30cl/min N2 using a 1:1 HDPE to catalyst ratio. Ten prominent peaks are labelled 1-10.
Table 7.5 summarises the detailed analysis of the ten peaks identified from each of the GC/MS chromatograms of the liquid fractions obtained in the presence of the hybrid catalyst SZ1CC1 across the temperature range of 380 to 430°C. For each chromatogram, the retention time, peak area, molecular formula and the name of the compound each peak represents were analysed and listed in Table 7.5. After comparing the types of hydrocarbons identified from the ten major peaks, it was found that all the compounds identified were mainly olefinic and some naphthenic compounds. In terms of carbon number distributions, Peak1 was identified as C9 while Peak 2 to 5, Peak 6 and 8, Peak 7 and 9 and Peak 10 as C10, C11, C12 and C13, respectively. This shows that hybrid catalyst SZ1CC1 had strong selectivity towards olefinic and naphthenic hydrocarbon compounds whose carbon atom range was between C9-C13.

As the temperature increases from 380 to 430°C, there were little evidences of structural changes among the hydrocarbon compounds across the temperatures range. For instance, Peak 1 found at 8.2 min in all the ten chromatogram, which represents a C9 identified as 3-nonene remained the same at all temperatures except 400°C, where it changed to 4-Ethylhept-3-ene and 420°C to 4-nonene. This show evidences of only minor structural changes among the hydrocarbon compounds across the temperature, which might be due to structural isomerism. The changes are not systematic across the temperature and therefore may not be due to overall effect of temperature change and may reflect GC/MS library fits. Therefore, apart from given the highest liquid yield, qualitatively this may justify the choice of only gaseous and liquid fractions at 410°C for detailed analysis in Sections 7.2.1 and 7.3.2. However, to assess whether there were any quantitative changes due to temperature each liquid fraction obtained across 380 and 430°C, were quantitatively analysed and compounds with same carbon atoms were group together and compared.
*Table 7.5 Comparison of hydrocarbon compounds for the ten selected peaks from the GC/MS chromatograms of the liquid fractions obtained over temperature range of 380 to 430°C using the hybrid catalyst SZ1CC1 at 30 min residence time and a 1:1 HDPE to catalyst ratio.

<table>
<thead>
<tr>
<th>Peak label</th>
<th>Ret. Time</th>
<th>Mol. formula</th>
<th>Compound’s name</th>
<th>Compound’s name</th>
<th>Compound’s name</th>
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</tr>
</thead>
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<td>2,6-Dimethylcyclopropane (7)</td>
</tr>
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</tbody>
</table>

*The numbers in parenthesis represents peak areas*
7.5.4 Comparison of the relative amount of the hydrocarbon compounds in the liquid products obtained from 380 to 430°C in the presence of the hybrid catalyst SZ1CC1

Figure 7.11 compares the relative amount of the compounds represented by the ten prominent peaks selected from the GC/MS chromatograms of the liquid fraction obtained from 380 and 430°C in the presence of the hybrid catalyst SZ1CC1. As the temperature changes from 380 to 430°C there is evidence of an increase in the relative amount of light weight hydrocarbons of C9 and C10. Correspondingly, the relative amount of heavier hydrocarbons C11 and C12 decreased with increasing temperature. The increase in the relative amount of C9 and C10 compounds appears to be temperature dependant, where at 390 to 400°C it is about 34% and after 410°C it increases sharply to 42%. This indicates that thermal cracking is taking place above 420°C, which corresponds to increased gas production described in Section 6.3.2. The decrease in the relative amount of heavier hydrocarbons C11 and C12, especially above 410°C, might again be due the large number of alkyl substituents attached to the long straight chain for those compounds, which make them susceptible to cleavage. The increase in liquid yield in the presence of the hybrid catalyst SZ1CC1 as the temperature increased up to 410°C, as shown in Section 6.3.2, is a further evidence of how moderate acidity can halt excessive cracking at low temperature. This shows that in the presence of the hybrid catalyst SZ1CC1, increase in temperature does affect the compositions of the hydrocarbons and also favoured high liquid yield up to 410°C. However, the choice of liquid and gas fractions at 410°C as representative samples for detailed analysis in sections 7.2.1 and 7.3.2 was based on observation that the optimal liquid yield was obtained at that temperature where an improved liquid yield was one of the aims of this research.
Comparing the activities of the two catalysts towards HDPE conversion, it is noted that despite having similar carbon number distribution of C9 to C13, each of the catalysts promoted different hydrocarbon compounds of similar carbon number distribution. This is the first indication that the sulphated zirconia SZ and the hybrid catalyst SZ1CC1 have different selectivity towards different hydrocarbon compounds. Also, the results in Tables 7.3 and 7.4 showed evidences of occasional changes among the hydrocarbon compounds as the temperature increases from 380 to 430°C in the presence of both catalysts. However, it was also evident that the two catalysts have different selectivity towards hydrocarbon compounds, where regardless of reaction temperatures, the liquid fraction in the presence of the SZ appeared to contain mainly aromatic compounds, while the hybrid catalyst SZ1CC1 promoted mainly olefinic and naphthenic compounds. The differences in terms of their selectivity could be linked to their different chemical compositions and textural properties as highlighted in Sections 5.2 to 5.6. Overall, it was found that the change in temperature from 380 to 430°C for HDPE conversion in the presence of both the SZ and the hybrid catalyst SZ1CC1 showed systematic structural changes to lighter compounds among the hydrocarbon compounds with increasing temperatures. However, regardless of what temperature
used, a significant difference in terms of hydrocarbon composition was observed in the liquids obtained from the two catalysts. Of special concern was the aromatic content of the SZ, which could promote quick catalyst deactivation.

### 7.6 Catalysts deactivation and regeneration

#### 7.6.1 Introduction

This section presents the results of a study to test the deactivation cycles of both the SZ and the hybrid catalyst SZ1CC1 used for HDPE conversions up to six times. The HDPE conversions were carried out at 380 and 410°C, which are temperature of maximum liquid yields in presence of the SZ and the hybrid catalyst SZ1CC1, respectively, as established in Section 6.3. The results here are only for HDPE conversions and no product yields are presented.

#### 7.6.2 Catalysts deactivation

Figure 7.12 shows the results of HDPE conversions observed with the aim of studying the catalysts deactivation resistance. Both the SZ and the hybrid catalyst SZ1CC1 were recycled six times for HDPE conversions. It is remarkable to note that the hybrid catalyst SZ1CC1 maintained a conversion of about 100wt% for four runs, whereas the sulphated zirconia SZ reduced to 98% after first run. At the fifth run, the conversion rate reduced to 97 and 80wt% in the presence of the hybrid catalyst SZ1CC1 and the SZ, respectively. In the presence of the SZ, the HDPE conversion started to decline just after first run, which indicates a build-up of coke. In the presence of the hybrid catalyst SZ1CC1 it started declining only after fourth run, where, after the fifth run, the amount of unconverted residue started to build up. This showed that the new hybrid catalyst SZ1CC1 tackled the problem of quick deactivation and coke deposit compared with the SZ (Yadav and Nair, 1999, Clark, 2002). Both catalysts were regenerated after the sixth run by heating in air at 600°C for two hours for deactivation test. Figure 7.12 shows the results of HDPE conversion in the presence of the SZ and the hybrid catalyst SZ1CC1 after regeneration. The results showed that the HDPE conversion in the presence of the regenerated SZ and the hybrid catalysts SZ1CC1 rise again to about 98 and 99%, respectively. This again showed that both catalysts regained their catalytic performance after the regenerations. However, as the product compositions were not analysed, it is not known if their selectivity still remains as for fresh catalysts. Although both catalysts...
show excellent performance after regenerations, the hybrid catalyst SZ1CC1 again showed the most commendable activity in terms of HDPE conversion.

![Comparison of HDPE conversion rates](image)

**Figure 7.12** Comparison of HDPE conversion rates at 380°C in the presence of SZ and hybrid catalyst SZ1CC1 at 410°C for six consecutive runs to test the catalyst deactivation and regeneration.

### 7.7 Influence of particle size on plastic waste conversion

In this section an actual plastic waste, as described in Section 3.2.3, which contained different particle sizes, was used to test the effect of particle size distribution on conversion rate using the hybrid catalysts SZ1CC1 only at 410°C. The plastic waste was divided into four categories of different size, ranging from 1mm to >5mm as described in Section 3.2.3. The plastic waste samples were converted separately in a fixed-bed reactor using the same method described in Section 3.4.2 and the outcome of the conversion were compared.

Figure 7.13 compares the conversion rates achieved for plastic waste of different particle sizes in the presence of the hybrid catalysts SZ1CC1. It was observed that the
conversion rate decreased with increasing particles sizes. A conversion rate of 98wt% was achieved for plastic waste with particle size of less than 1mm, which reduced to 93wt% for sample with particle sizes of 1-3mm. Subsequent increase in the sizes of plastic waste to 3-5mm and >5mm resulted in reduction of conversion rate to 91 and 43wt%, respectively. This showed that particle size of the plastic waste samples played a very important role in achieving high conversion rate. This was evidenced by only 43wt% conversion achieved when the plastic waste particle sizes were above 5mm. This indicates that pyro-catalytic conversion can be a valuable process for recycling where plastic waste with particles >5mm can be directly reused while <5mm can be converted back to liquid hydrocarbon.

![Conversion rates of plastic wastes of different particle sizes](image)

**Figure 7.13** Comparison of conversion rates of plastic wastes of different particle sizes using the hybrid catalyst SZ1CC1 at 410°C.

7.8 Summary of compositional analyses of gaseous and liquid fractions obtained in the presence of the SZ and the hybrid catalyst SZ1CC1

7.8.1 Product compositional analyses

The compositional analyses of the liquid fractions obtained from 380 to 430°C in the presence of both the SZ and hybrid catalysts SZ1CC1 was carried out using a
GC/MS to ascertain if temperature changes have any significant effect on the hydrocarbon composition of the liquid fractions both qualitatively and quantitatively. The overall results revealed that there were evidences of only minor change in the hydrocarbon compositions of the liquid fractions obtained across, 380 and 430°C.

The results of the gaseous products analysis revealed that the gaseous product obtained in the presence of the SZ contained more alkane hydrocarbon than in the presence of hybrid catalyst SZ1CC1, which promoted mainly alkenes. This is coherent with the liquid product composition using these catalysts where the SZ promoted mainly aromatic and paraffinic compounds and the hybrid catalysts SZ1CC1 gave mainly olefinic and naphthenic compounds. The SZ catalyst possibly promoted the production of aromatic compounds through secondary reactions and leading to dehydrocyclisation and aromatisation during cracking of HDPE chain. The liquid obtained in the presence of the SZ appeared to contain all the four main hydrocarbon compound classes with aromatic having the largest constituent of 58% followed by 21% olefins, 16% paraffins and 5% naphthens. The high selectivity towards aromatics might have possibly occurred due to its high acidity and total surface area compared to the hybrid catalyst which give insignificant amount of aromatic compounds. It was reported that most of the highly acidic catalysts promote high gas yields during polyethylene conversions and correspondingly low liquid yield and most had large aromatic content, where textural properties play a significant role (see Sections 2.5.4 and 2.5.5). The hybrid catalyst SZ1CC1 on the other hand gave high liquid yield, and promoted mainly olefinic and naphthenic hydrocarbons. The liquid fraction in the presence of the hybrid catalyst SZ1CC1 had only three main hydrocarbon classes, where olefins constituted the largest portion of 75% followed by 23% naphthens, and 3% paraffins. The selectivity towards olefins may be due to absence of secondary reactions as a result of the change in its acidic and textural properties due to the addition of calcium carbide, since moderate acidity mainly promotes high liquid yields and supports selectivity towards olefinic compounds (Aguado et al., 2009, Saha et al., 2008). As demonstrated in Section 5.3, the surface acidity of the sulphated zirconia was lowered by the addition of calcium carbide. This gave the hybrid catalyst SZ1CC1 a moderate acidity, which possibly supported the formation of olefinic rather than aromatic compounds. The hybrid catalyst SZ1CC1 also exhibit low BET and external surface areas and pore volume as highlighted in Section 5.6. This perhaps played a significant role in changing the
selectivity of the new hybrid catalyst SZ1CC1 towards olefinic and naphthenic compounds.

Both the SZ and the hybrid catalyst SZ1CC1 had features that are of important for industrial applications. The high aromatic content in the liquid obtained using the SZ is a very important component for a very high quality gasoline which improves its octane rating. However, the amount is far above the 3% recommended for gasoline in line with the global environmental regulations to lower the aromatic hydrocarbons in gasoline (Serrano et al., 2000b). The SZ also deactivates quickly. For the hybrid catalyst SZ1CC1 the high amount of olefinic and naphthenic compounds, particularly the branched ones, with low carbon number distribution are good components of gasoline in the liquid and they also makes the liquid an excellent feedstock for the petrochemical industries. The high olefinic compounds promoted by the hybrid catalyst SZ1CC1 also made the liquid excellent precursor for many chemicals. This is because olefinic compounds are used as intermediaries of many valuable and expensive chemicals and, hence, industrially more attractive than the pure saturated compounds (Buekens and Huang, 1998). Also the low aromatic content of <0.1% is in agreement with global environmental regulations of less than 3%. The 15% naphthenic compounds may take care of the octane rating requirement for renewable gasoline additives. Overall, the high liquid yield promoted by the hybrid catalyst SZ1CC1 and its selectivity towards olefinic compounds makes it an excellent catalyst for HDPE conversation when compared to the sulphated zirconia SZ1CC1. This is because promotion of excellent conversion with high liquid yields and selectivity towards desired hydrocarbon compounds at lower temperature are properties required by any catalyst used for plastic conversion. Liquid product obtained could be used straight away as chemical precursor in chemical industries or may be used to transport fuel to supplement the current conventional and renewable energy sources. Thus, the SZ and the hybrid catalyst SZ1CC1 can be used for catalytic conversion of plastic wastes. Using these catalysts for this purpose does not only promote environmental cleanness, but add value to the waste by converting it to products that are of commercial and industrial benefits.
7.8.2 Catalytic performance and selectivity of the SZ and the hybrid catalyst SZ1CC1 during HDPE conversions

Figure 7.14 summarises the catalytic activities of the SZ and the hybrid catalyst SZ1CC1 during HDPE conversions. The scheme also describes a proposed scenario on why the two catalysts promoted different hydrocarbons. The HDPE interaction with the SZ resulted in low liquid yield, which contains mainly aromatic compounds. It is believed that when HDPE was heated together with the catalyst, part of the bulky HDPE chain interacted with the acid sites on the catalyst surface, cracked and yielded light hydrocarbon gases and some long chain compounds in the liquid range. Subsequently, part of the HDPE vapour and part of the long chain hydrocarbons formed diffused through the large pores of the SZ, access the internal acid sites and underwent secondary reactions that yielded different hydrocarbons ranging from methane gas to liquid aromatic and paraffinic compounds (see Sections 2.5.2 and 2.5.4). The properties of the SZ, which include high acid strength, large BET and external surface areas as well as large pore volume and smaller crystallite particles, make it susceptible to this scenario. High acid strength allows the catalyst to promote excessive cracking, which promotes high gas yield and lower liquid yield. Its textural properties, namely large BET and external surface area, large pore volume made the catalyst easily accessible by the bulky HDPE chain to undergo secondary reactions, which lead to aromatisation and hence yield more aromatics (see Section 2.5.5).

On the other hand, the HDPE interaction with the hybrid catalyst SZ1CC1 during the HDPE conversions resulted in low gas yield and a significant amount of liquid containing mainly olefinic compounds. Possibly, when the HDPE was heated together with the hybrid catalyst SZ1CC1, it melted and was converted on the surface of the catalyst. The melted HDPE interacted with the reactive surface of the catalyst leading to β-scission of the long chain HDPE and, subsequently, yielded olefinic components. The properties of the hybrid catalyst SZ1CC1, which include moderate acidity, low BET and external surface areas and small pore volume and large crystallite particles, are believed to be responsible for the products yield and selectivity observed. Its moderate acidity promotes low gas yield and high liquid yield and its modified textural properties, which might have caused diffusional hindrance that possibly halted any secondary reactions, promoted mainly olefinic and naphthenic compounds instead of aromatics and hence changed the selectivity. This indicates that the hybrid catalyst
SZ1CC1 could be a highly effective and economical catalyst used for plastic waste conversion.

*Figure 7.14 Summary of the catalytic activities and selectivity of the SZ and the hybrid catalyst SZ1CC1 during HDPE conversions.*
8.1 Summary Conclusions

This research was specifically aimed at modifying a highly acidic commercial sulphated zirconia catalyst by regulating its acidic and textural properties through mechanical mixing with a different oxide or carbide and calcination. Two carbides metal oxide, namely calcium carbide, molybdenum carbide and zirconium oxide and were tested as moderators for sulphated zirconia. A number of hybrid catalysts were produced and their activities towards polymer conversion were tested. Initially five polyolefin-based virgin polymers, namely HDPE, LDPE, LLDPE and two PP were tested in this study, as virtually all plastics that generate wastes are made from these polymers, where HDPE in itself accounts for 60-70% of the total plastic waste generated.

Thermogravimetric analysis (TGA) was used to analyse the thermal behaviour of the polymer samples and tests the impact of the potential catalysts. The TGA results indicated that all the polymer samples had a single step weight loss albeit at different temperatures. The LDPE, PP1 & PP2 samples had temperature of initial weight loss, \( T_i \) at 266, 299 and 309\(^\circ\)C and temperature of maximum weight loss \( T_m \) at 477, 476, 472\(^\circ\)C, respectively. The LLDPE and HDPE, on the other hand showed more resistance to degradation with \( T_i \) at 389 and 337\(^\circ\)C and \( T_m \) at 492 and 494\(^\circ\)C, respectively. This was attributed to the lack of tertiary carbons in their structures, which make their cracking very difficult. In view of this, and the fact that polyethylene polymers accounts for 38% of all plastics and HDPE is the most common of the PE, HDPE was chosen to represent plastic waste to test the potential catalysts for recycling back in to liquids.

Of all the four carbides and oxides initially tested on the HDPE, only the sulphated zirconia (SZ) and calcium carbide (CC) showed some impact towards HDPE conversions. In the presence of SZ, the \( T_i \), \( T_m \) and \( T_f \) all significantly reduced form 337, 494 and 510\(^\circ\)C for HDPE alone to 187, 419 and 477\(^\circ\)C, respectively. In the presence of the CC, the \( T_i \) and \( T_m \) reduced from 337 and 494\(^\circ\)C to 292\(^\circ\)C and 475\(^\circ\)C, respectively. The results suggested that CC could moderate the properties of sulphated zirconia, especially towards preventing high char yield. Hence, a hybrid catalyst SZ1CC1, with equal proportion of SZ and CC was first tested for HDPE conversion using TGA. The
result showed that the temperature of initial weight lost \( T_i \) was lowered to 220\(^\circ\)C compared to 337\(^\circ\)C for HDPE alone and 187 and 292\(^\circ\)C for SZ and CC, respectively. The temperature of maximum weight lost \( T_m \) was also lowered to 451\(^\circ\)C compared to 494\(^\circ\)C for HDPE alone and 422 and 475\(^\circ\)C in the presence of SZ and CC, respectively. The kinetic studies also indicated the dramatic decrease of activation energy from 181kJ/mole for HDPE alone to 104, 131 and 135kJ/mole in the presence of SZ, SZ1CC1 and CC, respectively. In view of this, seven hybrid catalysts with compositions from 80wt%SZ and 20wt% CC to 20wt% SZ and 80wt% CC were produced. The SZ, CC and all the seven hybrid catalysts (SZ4CC1 to SZ1CC4) were characterized for their acidity, physicochemical and textural properties. SZ appeared to have the highest surface acid strength with ammonia desorption of 337.6\(\mu\)molNH\(_3\)/g and \(\text{SO}_4^{2-}\) content of 6.5Mol\%, which decreased with increasing calcium carbide addition, where the hybrid catalyst SZ1CC1 had moderate acidity with ammonia desorption and \(\text{SO}_4^{2-}\) content of 23.4\(\mu\)molNH\(_3\)/g and 2.5Mol\%, respectively. The calcined CC on its does not show any evidence of acidity as it has no \(\text{SO}_4^{2-}\) even though it had ammonia desorption of 45.8\(\mu\)molNH\(_3\)/g, which happened to be due to CaO adsorption. Overall, SZ had the largest acidic strength, highest ammonia desorption and \(\text{SO}_4^{2-}\) content, while calcined CC does not show any acidic strength and hybrid catalyst SZ1CC1 had moderate acidic strength with moderate ammonia desorption. Physicochemical analyses results revealed the occurrence of a series of chemical interactions after calcining mixture of SZ and CC. This was evidence by the emergence of a new compound, calcium zirconium oxide (\(\text{CaZrO}_3\)). The new compound, \(\text{CaZrO}_3\) appeared in all the XRD pattern of the seven hybrid catalysts and the intensity of the peak indexed for the compound increased with increasing calcium carbide addition. The compound was confirmed to be formed as a result of sintering of \(\text{ZrO}_2\) with CaO. The XRD results also indicated the effect of calcination on the catalysts, where both SZ and CC had their crystallinity improved after calcination. The composition of calcium carbide has also changed drastically after calcinations where peaks indexed for CC nearly disappeared and those of calcium \(\text{CaCO}_3\) that were not there before calcination appeared and.

SEM analysis suggested that all the catalysts were homogenous with similar particle sizes ranging from 100 to 200nm. However, the particles became more clustered with increasing calcium carbide in the mixture as Ca-complexes were found to integrate within the open pore structure of sulphated zirconia. This was believed to cause a reduction in surface area and pore volume of the hybrid catalysts as the CC
addition increased. SZ had the highest pore volume, micropore area, BET and external surface areas of 0.21 cm$^3$/g, 3.9 m$^2$/g, 116 m$^2$/g and 112 m$^2$/g, respectively, which systematically reduced with increasing CC addition. The hybrid catalyst SZ1CC1 had pore volume, micropore area, BET and external surface areas of 0.036 cm$^3$/g, < 0.1 m$^2$/g, 23.1 m$^2$/g and 22.2 m$^2$/g, while calcined CC own had 0.012 cm$^3$/g, < 0.1 m$^2$/g, 10.2 m$^2$/g and 8.7 m$^2$/g, respectively. The shape of N$_2$-adsorption isotherm of the SZ, CC and all the hybrid catalysts showed characteristics of a Type IV isotherm indicating a typical mesoporous materials, which was confirmed by the BJH pore size distribution ranging from 2 to 11 nm and average pore diameter of > 2 nm for all the catalysts. However, the SZ showed some adsorptions at low relative pressure (P/P$_o$ < 0.1) that indicated some microporosity, which diminished after CC addition. A marked jump was observed between the hybrid catalyst SZ7CC3, which had 0.60 mmol/g, and the remaining hybrid catalysts with adsorption less than 0.30 mmol/g at low relative pressure (P/P$_o$ < 0.1). This point coincided with what was regarded as a transition point where major changes occurred. Overall, this indicated that the reduction of surface area and porosity was function CC addition and hybrid catalysts between SZ3CC2 to SZ2CC3 may have the best catalytic performance towards HDPE conversion.

The HDPE conversion in the presence of the SZ and the five hybrid catalysts SZ4CC1 to SZ1CC4 was carried out at 400$^\circ$C using HDPE to catalyst ratio of 1:1. The results obtained showed that only the SZ and the hybrid catalysts SZ4CC1 to SZ2CC3 gave excellent conversions of not less than 98.5%. However, the hybrid catalyst SZ1CC1 gave an excellent performance with virtually 100% conversion and high liquid yields of 53 wt%. Thus, the hybrid catalyst SZ1CC1 and the SZ were selected to test temperature optimisations in the range of 370 to 430$^\circ$C and select find the temperature that support high liquid yield. It was found that 380 and 410$^\circ$C gave the peak liquid yields for the SZ and the hybrid catalyst SZ1CC1, respectively. These Hydrocarbon products obtained at these optimum temperatures were then used for detailed analysis. The carbon number distribution of the liquids from both catalysts was within the gasoline range of C7 – C12, indicating a possible usage of the liquid fraction as a transportation fuel. Some changes in the hydrocarbon compositions of the liquids were observed across the temperature range for both catalysts. The composition of the gaseous fraction in the presence of the SZ had nearly the same amount of 49.9 wt% alkane and 49.5 wt% alkene compounds and 0.44 wt% H$_2$ indicating an increase in cracking. But the composition in the presence of the hybrid catalyst SZ1CC1
significantly changed with more amount of alkene (89.7 wt%) than the 9.7 wt% alkane with 0.56 wt% H\textsubscript{2}. The liquid fraction in the presence of the SZ had 58% aromatic, 16% paraffinic, 21% olefinic and only 5% naphthenic and compounds. However, in the presence of the hybrid catalyst SZ1CC1 the liquid fraction contained 74% olefinic, 23% naphthenic compounds and only 3% paraffinic compounds with virtually zero aromatics.

Overall, this showed that the addition of the calcium carbide has modified the properties and catalytic performance of the SZ, which lead to the improvement the liquid fraction yield and changed its selectivity towards olefinic and naphthenic rather than aromatic and aliphatic hydrocarbons. The improvement in liquid yield was strongly linked with the moderation of the acidic strength from very strong acidic strength and high ammonia desorption of 337.6 µmol NH\textsubscript{3}/g for SZ to moderate acidic strength and low ammonia desorption of 23.4 µmol NH\textsubscript{3}/g for SZ1CC1. Since catalyst with very strong acidic strength is known to promote excessive cracking that results in production of low molecular weight gaseous hydrocarbons with very low liquid yields. Also, the change in the liquid composition was due to the changes in the textural properties of the new catalyst in particular surface area reduction linked with increasing deposit of CaZrO\textsubscript{3} complex formation, which caused diffusional hindrance and limits the access to internal acid sites that promotes secondary reaction leading to aromatisation. Therefore, the excellent performance of the hybrid catalyst was generally linked with the new properties exhibited due to CC addition.

This showed that catalytic conversion of plastic waste using the newly developed hybrid catalyst SZ1CC1 will be energy efficient, sustainable, cost-effective and economically viable. In general, it can be concluded that addition of calcium carbide in the SZ had resulted into a new hybrid catalyst SZ1CC1 with excellent properties, which significantly changed its catalytic performance towards HDPE conversion. The acidity has changed from strong acidity to moderate acidity which resulted in huge increase in liquid yield and the new textural properties have also changed the selectivity of the catalyst from aromatic and paraffinic dominance to olefinic and naphthenic hydrocarbon dominance. The new catalyst formed had also significantly reduced the coke formation on its surface hence its life span is enhanced. Overall, the main part of this research aims have been achieved by the new hybrid catalyst.
8.2 Recommendations

After successfully developing a new catalyst that showed excellent activities towards HDPE conversion, the following issues should also be tackled to strengthening the research work.

1. Optimisation of other reaction conditions, such as retention time, carrier gas flow and ratio of catalyst to HDPE as only temperature was optimised.
2. Test the catalyst using well design reactor with high capacity that will allow the industrial scale assessment of the catalyst for conversion of plastic waste.
3. Due difficulty in acid site classification as a result of ammonia adsorption due to CaO that caused huge desorption with calcium carbide addition, its recommended that a pyridine titration using Hammett indicators and IR analysis is conducted to support the ammonia TPD test.
4. Fuel tests, such as density, specific gravity, viscosity, flash point, pour point, and ignition tests should be conducted on the liquid fraction to reaffirm its applicability as transport fuel.
5. An extensive energy balance and economic analysis should be conducted to establish the cost-effectiveness and sustainability of the recycling method that would adopts the catalysts for plastic waste recycling.
### APPENDICES

**Appendix 1 Surface elemental composition of the principal catalysts, sulphated zirconia (SZ), calcium carbide (CC), and the hybrid catalysts (SZ4CC1 to SZ1CC4) obtained from SEM/EDX.**

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>C (At%)</th>
<th>O (At%)</th>
<th>Zr (At%)</th>
<th>S (At%)</th>
<th>Ca (At%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SZ</td>
<td>&lt; 0.1</td>
<td>72.3</td>
<td>26.1</td>
<td>1.7</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>SZ4CC1</td>
<td>14.5</td>
<td>60.7</td>
<td>10.6</td>
<td>3.0</td>
<td>11.2</td>
</tr>
<tr>
<td>SZ7CC3</td>
<td>14.8</td>
<td>60.0</td>
<td>8.0</td>
<td>2.4</td>
<td>15.0</td>
</tr>
<tr>
<td>SZ3CC2</td>
<td>19.7</td>
<td>59.0</td>
<td>6.2</td>
<td>1.6</td>
<td>13.6</td>
</tr>
<tr>
<td>SZ1CC1</td>
<td>20.7</td>
<td>52.8</td>
<td>6.5</td>
<td>1.1</td>
<td>19.0</td>
</tr>
<tr>
<td>SZ2CC3</td>
<td>19.5</td>
<td>58.5</td>
<td>3.7</td>
<td>1.1</td>
<td>17.4</td>
</tr>
<tr>
<td>SZ3CC7</td>
<td>21.5</td>
<td>62.1</td>
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<td>0.8</td>
<td>21.5</td>
</tr>
<tr>
<td>SZ1CC4</td>
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<td>62.2</td>
<td>1.7</td>
<td>0.7</td>
<td>19.7</td>
</tr>
<tr>
<td>CC</td>
<td>19.0</td>
<td>58.3</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>22.6</td>
</tr>
</tbody>
</table>

**Appendix 2 Surface oxides composition of the principal catalysts, sulphated zirconia (SZ), calcium carbide (CC), and the hybrid catalysts (SZ4CC1 to SZ1CC4) obtained from SEM/EDX.**

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>ZrO$_2$ (Mol. %)</th>
<th>CaO (Mol. %)</th>
<th>SO$_4^{2-}$ (Mol. %)</th>
<th>CaCO$_3$ (Mol. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SZ</td>
<td>93.4</td>
<td>&lt;0.1</td>
<td>6.6</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>SZ4CC1</td>
<td>27.4</td>
<td>28.5</td>
<td>7.6</td>
<td>36.5</td>
</tr>
<tr>
<td>SZ7CC3</td>
<td>20.1</td>
<td>37.5</td>
<td>6.0</td>
<td>36.4</td>
</tr>
<tr>
<td>SZ3CC2</td>
<td>15.3</td>
<td>33.3</td>
<td>3.9</td>
<td>47.5</td>
</tr>
<tr>
<td>SZ1CC1</td>
<td>25.5</td>
<td>27.7</td>
<td>2.5</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>5.9</td>
<td>56.6</td>
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</tr>
<tr>
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<td>53.1</td>
<td>&lt;0.1</td>
<td>46.9</td>
</tr>
</tbody>
</table>
Appendix 3 HDPE only

Appendix 4 LLDPE only
Appendices

Appendix 5 PP1 only

\[ y = -11.962x + 7.4916 \]
\[ R^2 = 0.998 \]

Appendix 6 PP2 only

\[ y = -13.541x + 3.0145 \]
\[ R^2 = 0.9979 \]
Appendices

Appendix 7  LDPE only

\[ y = -9.2111x - 1.7413 \]
\[ R^2 = 0.9992 \]

Appendix 8 HDPE + SZ

\[ y = -12.474x + 3.6974 \]
\[ R^2 = 0.9989 \]
Appendices

Appendix 9 HDPE + SZ1CC1

\[ y = -15.837x + 8.8337 \]
\[ R^2 = 0.9993 \]

Appendix 10 HDPE + CC

\[ y = -16.256x + 8.9301 \]
\[ R^2 = 0.9971 \]
<table>
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<th>Catalysts</th>
<th>Scaling</th>
<th>Ratio</th>
<th>&lt;200 °C</th>
<th>200-300 °C</th>
<th>300-550 °C</th>
<th>&gt;550 °C</th>
<th>Area</th>
<th>&lt;200 °C</th>
<th>200-300 °C</th>
<th>300-550 °C</th>
<th>&gt;550 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SZ</td>
<td>35</td>
<td>50%</td>
<td>345</td>
<td>3083</td>
<td>3453</td>
<td>808</td>
<td>3845</td>
<td>4.5%</td>
<td>40.1%</td>
<td>44.9%</td>
<td>10.5%</td>
</tr>
<tr>
<td>SZ4CC1</td>
<td>25</td>
<td>36%</td>
<td>612</td>
<td>3309</td>
<td>5242</td>
<td>0</td>
<td>3273</td>
<td>5.7%</td>
<td>30.7%</td>
<td>36.1%</td>
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</tr>
<tr>
<td>SZ7CC3</td>
<td>25</td>
<td>36%</td>
<td>269</td>
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<td>4240</td>
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<td>12.9%</td>
<td>27.1%</td>
<td>0.0%</td>
</tr>
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<td>14</td>
<td>20%</td>
<td>69</td>
<td>669</td>
<td>2935</td>
<td>0</td>
<td>735</td>
<td>0.4%</td>
<td>3.5%</td>
<td>9.3%</td>
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</tr>
<tr>
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<td>43%</td>
<td>10</td>
<td>441</td>
<td>3211</td>
<td>0</td>
<td>1569</td>
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<td>SZ2CC3</td>
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<td>SZ3CC7</td>
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Appendix II TPD curve fitting data
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